



# A review of the structural architecture of tellurium oxycompounds

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## ABSTRACT

Relative to its extremely low abundance in the Earth's crust, tellurium is the most mineralogically diverse chemical element, with over 160 mineral species known that contain essential Te, many of them with unique crystal structures. We review the crystal structures of 703 tellurium oxysalts for which good refinements exist, including 55 that are known to occur as minerals. The dataset is restricted to compounds where oxygen is the only ligand that is strongly bound to Te, but most of the Periodic Table is represented in the compounds that are reviewed. The dataset contains 375 structures that contain only  $\text{Te}^{4+}$  cations and 302 with only  $\text{Te}^{6+}$ , with 26 of the compounds containing Te in both valence states.  $\text{Te}^{6+}$  was almost exclusively in rather regular octahedral coordination by oxygen ligands, with only two instances each of 4- and 5-coordination. Conversely, the lone-pair cation  $\text{Te}^{4+}$  displayed irregular coordination, with a broad range of coordination numbers and bond distances. A threshold was applied for  $\text{Te}^{4+}$ –O links of  $\sim 2.45$  Å or 0.3 valence units with some flexibility, as a criterion to define strongly bound Te–O polymers and larger structural units. Using this criterion,  $\text{Te}^{4+}$  cations display one-sided 3-, 4- or 5-coordination by oxygen (with rare examples of coordination numbers 2 and 6). For both valence states of Te, examples are known of  $\text{Te}_m\text{O}_n$  complexes which are monomeric ( $m = 1$ ; neso), noncyclic finite oligomers (soro), rings (cyclo), infinite chains (ino), layers (phyllo) and frameworks (tecto tellurates). There is a clear analogy to the polymerization classes that are known for silicate anions, but the behaviour of Te is much richer than that of Si for several reasons: (1) the existence of two cationic valence states for Te; (2) the occurrence of multiple coordination numbers; (3) the possibility of edge-sharing by  $\text{TeO}_n$  polyhedra; (4) the possibility for oxygen ligands to be 3-coordinated by Te; and (5) the occurrence of  $\text{Te}_m\text{O}_n$  polymers that are cationic, as well as neutral or anionic. While most compounds contain only one or two symmetrically distinct types of Te atom, Pauling's Fifth Rule is frequently violated, and stoichiometrically simple compounds such as  $\text{CaTeO}_3$  can have polymorphs with up to 18 distinct Te sites. There is a tendency for local symmetry features such as the threefold axis of a  $\text{TeO}_6$  octahedron or the acentric symmetry of a  $\text{Te}^{4+}\text{O}_n$  polyhedron to be inherited by the host structure; the latter in particular can lead to useful physical properties such as nonlinear optical behaviour. We develop for the first time a hierarchical taxonomy of Te-oxysalt structures, based upon (1) valence state of Te; (2) polymerization state of  $\text{Te}_m\text{O}_n$  complexes; (3) polymerization state of larger strongly-bound structural units that include non-Te cations. Structures are readily located and compared within this classification.

**KEYWORDS:** tellurium, oxysalt, crystal chemistry, polymerization, crystal structure, structural hierarchy.

## Introduction

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TELLURIUM (Te) is an unusual element in that its cosmic abundance is greater than that of any other

element with an atomic number >40, as measured by relative number of atoms in C1 chondrite (Anders and Ebihara, 1982). Nevertheless, Te is one of the rarest elements in the Earth's crust (0.4–10 ppb; Parker, 1967; Levinson, 1974; Govett, 1983; McDonough and Sun, 1995; Reimann and de Caritat, 1998) and also in seawater (up to 0.0009 ppb; Andreae, 1984; Lee and Edmond, 1985). It is thus 3 to 5 orders of magnitude less abundant than other even-number elements that are nearby in the periodic table, such as tin and barium, and is in fact rarer than platinum or gold.

The extreme depletion of Te in the Earth's crust is probably due to its strongly siderophile character at high pressure, which resulted in much primeval Te being sequestered in the core, and the small amounts of Te in the outer layers of the Earth arriving after core formation in a "late veneer" (Wang and Becker, 2013). The extreme scarcity of Te makes it all the more remarkable that there are ~160 Te minerals described from Nature: ~3% of all known species. Christy (2016) showed that most chemical elements show a power-law dependence between their abundance in the Earth's crust and the number of mineral species in which they are essential constituents. Other elements that are major constituents of 150–200 species are much more abundant, such as Ce and Ni, present in the crust at 33 and 105 ppm, respectively, according to Taylor and McLennan (1985). Conversely, if Te followed the typical trend, there would be only seven Te minerals. Tellurium is, in fact, the most extreme example of an element that forms an anomalously large number of distinct species in the Earth's crust. Telluride minerals, containing Te as an anion, are probably best known, and are well studied due to their association with gold in epithermal Au–Te deposits (cf. Cook and Ciobanu, 2005; Ciobanu *et al.*, 2006), often related to alkaline magmatism (e.g. Jensen and Barton, 2000). Rare sulfosalts are also known in which cationic  $\text{Te}^{4+}$  plays a role analogous to  $\text{As}^{3+}$ , such as the tetrahedrite-group mineral goldfieldite, ideally  $\text{Cu}_{10}\square_2(\text{TeS}_3)_4\text{S}$  (Trudu and Knittel, 1998). Hence, Te can adopt either anionic or cationic roles as a chalcophile element, like As and Sb. Also, like those elements, it oxidizes readily to form secondary oxycompounds under near-surface conditions. About half of the known Te minerals are such tellurites and tellurates.

The recent explosion of new secondary mineral species, particularly from Otto Mountain, California, has seen publication of descriptions for 14 new Te minerals from 2010 up to September, 2015 (Kampf *et al.*, 2010a; Back *et al.*, 2011;

Housley *et al.*, 2011; Pekov *et al.*, 2010; Christy *et al.*, 2016). This represents the greatest flurry of activity in the study of Te secondary minerals since the 1970s. The majority of these new minerals are also compounds new to inorganic chemistry, and possess new crystal-structure types. Crystal structures are now known for 55 of the ~80 Te oxyminerals. It is of particular interest that the Te oxyanions show a wide range of polymerization, somewhat analogous to silicates: examples range from isolated  $[\text{Te}^{4+}\text{O}_3]^{2-}$  and  $[\text{Te}^{6+}\text{O}_6]^{6-}$  anions to complex three-dimensional frameworks. The analogy to rock-forming silicates is strengthened by the observation that, in a locality with an unusually large number of tellurate species, there appears to be a correlation between polymerization state and both the early or late position of a mineral in the local paragenetic sequence, and the abundance of 'network-modifying' species such as  $\text{Cu}^{2+}$  (Christy *et al.*, 2016).

A search of the Inorganic Crystal Structure Database (ICSD) and recent literature has found good-quality crystal structures for 703 compounds, in all. The number of structures referenced per year for the present study suggests that the rate of synthesis and structure refinement has been increasing through time, and that 40 new compounds and structures per year may now be typical (Fig. 1). Thus, the current interest in both synthetic and natural Te oxycompounds, along with the anomalously large number of the latter, justifies a review of their structural chemistry. It should be noted that new compounds appear in the literature constantly, but we had to stop updating our working list in mid-2015, in order to avoid repeated shuffling of the database and the associated risk of introducing errors.

Examination of the known structures of Te oxycompounds reveals extraordinary diversity due to a combination of factors, namely: (1) Te may occur as  $\text{Te}^{4+}$  or  $\text{Te}^{6+}$ , which are of comparable stability under atmospheric conditions, so compounds also occur with both oxidation states coexisting. (2)  $\text{Te}^{6+}$  is almost invariably octahedrally coordinated by oxygen (Christy and Mills, 2013). The  $\text{Te}^{6+}\text{O}_6$  group is strongly bound, in that the average Te–O bond valence is unity. In contrast,  $\text{Te}^{4+}$  has a stereoactive lone electron pair, and may adopt a wide range of coordination geometries. Usually, three to four oxygens are strongly bound to form an asymmetric coordination polyhedron, but there may also be several other neighbours at longer distances (Christy and Mills, 2013). (3) As noted above,  $\text{TeO}_n$  polyhedra polymerize readily to form

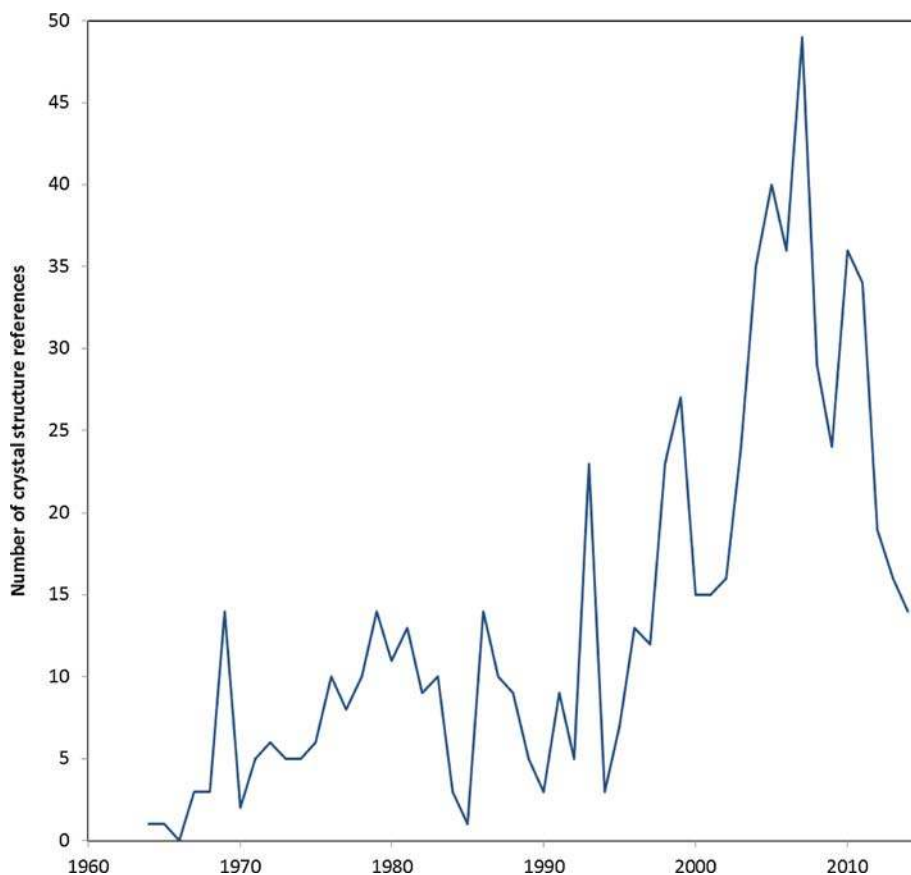


FIG. 1. Number of crystal structure references cited per year for the current study.

oligomers, chains, layers and frameworks. These units also link readily to other strongly-bonding cations to form heteropoly structural building units. (4) The geometries of  $\text{TeO}_n$  polymers are even more flexible than those of silicates, in that the polymers may contain Te with various coordination numbers, and may carry not just negative or zero net charge, but may also be positively charged in Te 'salts'. For example, a  $[\text{Te}_2^{4+}\text{O}_3\text{OH}]^+$  infinite layer cation can be identified in  $(\text{Te}_2\text{O}_3\text{OH})(\text{NO}_3)$  (Anderson *et al.*, 1980), while the  $[\text{Te}^{4+}(\text{OH})_3]^+$  ion has been recently identified in the structure of  $\text{Na}_{11}\text{H}[\text{Te}(\text{OH})_3]_8[\text{SO}_4]_{10}(\text{H}_2\text{O})_{13}$  by Mills *et al.* (2016). (5) Te polyhedra readily share edges, as well as corners, in contrast to  $\text{SiO}_4$  tetrahedra. (6) Oxygen may be coordinated by three  $\text{Te}^{4+}$ , as in winstanleyite,  $\text{TiTe}_3\text{O}_8$  (Bindi and Cipriani, 2003). This possibility does not arise in conventional silicates because the short Si–O distance causes strong Si $\cdots$ Si

repulsion, although edge-sharing of non-silicon tetrahedra and 3-coordination of oxygen atoms are seen in beryllosilicates and zincosilicates, where the lower cation valence decreases repulsion, and gives a small effective non-bonded radius relative to bond distances (O'Keeffe and Hyde, 1981). The longer bond distances make such geometries possible for Te–O polyhedra as well.

A structural hierarchy for silicates (Bragg, 1930; Zoltai, 1960; Liebau, 1985) is used widely to organize classic textbooks such as Deer *et al.* (1966). More recent schemes, such as those for borate (Hawthorne *et al.*, 1996) and sulfate minerals (Hawthorne *et al.*, 2000), render intelligible the diversity of these large, complex classes, highlight structure-composition-property relationships and facilitate comparison between species, and also aid in applying group nomenclature (Mills *et al.*, 2009b). A major objective of the present study is to

create such a structural hierarchy for Te oxycompounds.

In NMR spectroscopy, a concise ‘Q notation’ to describe polymerization states of silicate species, in which ‘Q<sup>n</sup>’ ( $n = 0-4$ ) designates silicate tetrahedra with  $n$  bridging oxygen atoms and, by implication,  $4-n$  non-bridging oxygen atoms (cf. Lippmaa *et al.*, 1980). It would be convenient to use a similar notation in the present study for TeO<sub>n</sub> polyhedra. However, the original symbology makes the assumptions that (1) the coordination of Si is always 4; (2) the coordination of O by Si is either 1 (non-bridging) or 2 (bridging) and, concomitantly; (3) the number of non-bridging oxygen atoms is the same as the number of next-nearest neighbour Si atoms. For Te, all three of these assumptions are invalid, as they are violated as a result of variable Te coordination number (CN), plus the possibilities of edge-sharing and CN3 oxygen. More information is needed to fully specify the polymerization state of a Te cation, including the numbers of oxygen ligands connected to 1, 2 or 3 Te cations, and the number of edges (i.e. 4-rings, Te–O–Te–O) shared between Te polyhedra. An extended notation Q<sup>abcz</sup> can do this using four single-digit integers:  $a$  = number of CN1 oxygen atoms,  $b$  = number of CN2 oxygen atoms,  $c$  = number of CN3 oxygen atoms and  $z$  = number of shared edges. The total Te CN =  $a + b + c$ , the corresponding number of oxygen ligands per Te is  $a + \frac{1}{2}b + \frac{1}{3}c$ , and the number of next-nearest Te atoms is  $b + 2c - z$ . The original silicate Q<sup>n</sup> would be written Q<sup>(4-n)000</sup> in the extended notation (Q<sup>0</sup>  $\equiv$  Q<sup>4000</sup>, Q<sup>1</sup>  $\equiv$  Q<sup>3100</sup>... Q<sup>4</sup>  $\equiv$  Q<sup>0400</sup>). Note that  $0 \leq z \leq \frac{1}{2}p(p-1)$ , where  $p = b + c$ .

A very large number of different Q<sup>abcz</sup> states can occur. For 4-coordinate Te alone, there are 80 possibilities, and 17 of these are found in the structures of the present study. In order to illustrate the value of the notation, the corresponding topologies are shown very diagrammatically in Fig. 2.

### Te–O bond length and polyhedral geometry

‘Bond valence’ is a parameter that expresses the strength of a chemical bond between a cation and an anion in terms of the effective number of electron pairs involved in bonding. It is thus a generalization of the concept of ‘bond order’, well entrenched in organic chemistry (IUPAC, 1997), and of the “electrostatic bond strength” of Pauling (1929). The bond-valence model relates bond distance,  $r$ , to bond valence,  $s$ , for a given cation–anion pair via a

smoothly varying function of two parameters. The equation most often used is  $r = r_0 - b \ln s$ , where:  $r_0$  is the distance at unit bond valence, and  $b$ , a ‘softness’ parameter (Brown and Altermatt, 1985; Brese and O’Keeffe, 1991; Brown, 2002). Bond valences and their sums on a central atom are powerful crystallographic tools for distinguishing species of similar scattering factor, but different valence, and for identifying species such as O<sup>2-</sup>, OH<sup>-</sup> and H<sub>2</sub>O and hydrogen bonds when H cannot be located in structure refinements.

While a universal softness value  $b = 0.37$  Å is often assumed (e.g. Brown and Altermatt, 1985; Brese and O’Keeffe, 1991), it has become apparent that this does not model the bonding behaviour well for many heavier atoms. Several alternative parametrizations for particular species have been published in recent years [e.g. for Pb<sup>2+</sup> by Krivovichev and Brown (2001); U<sup>6+</sup> by Burns *et al.* (1997); Tl<sup>1+</sup> by Locock and Burns (2004); and Sb<sup>3+</sup> and Sb<sup>5+</sup> by Palenik *et al.* (2005), Sidey *et al.* (2009) and Mills *et al.* (2009a)], and we examined the available structural data for Te<sup>4+</sup>–O, Te<sup>4+</sup>–Cl and Te<sup>6+</sup>–O bonds in a recent paper (Mills and Christy, 2013). For Te<sup>4+</sup>–O, we obtained the parameters  $r_0 = 1.9605$  Å and  $b = 0.41$  Å, while for Te<sup>6+</sup>–O, we obtained the parameters  $r_0 = 1.921$  Å and  $b = 0.56$  Å. We considered all Te–O distances out to 3.5 Å as at least weakly bonded. Conversely, Te<sup>4+</sup> showed a broad distribution of coordination numbers from 3 to 12, with two modes at CN6 and CN8 (fig. 1 in Mills and Christy, 2013). The distribution of Te<sup>4+</sup>–O bond distances is also bimodal (Fig. 3). Thus, the oxygen neighbours of Te<sup>4+</sup> separate into two groups: strongly-bound ligands on the opposite side of the Te from its stereoactive lone electron pair, with bond valences typically 0.3–1.3 valence units (vu) (corresponding to a distance of 1.85–2.45 Å), and more distant ligands, with bond valences usually <0.15 vu (2.74 Å). When three short Te<sup>4+</sup>–O bonds are present, the Te<sup>4+</sup>O<sub>3</sub> geometry is invariably a rather symmetrical trigonal pyramid, with oxygen atoms at three of the four corners of a tetrahedron, and the lone pair of the Te directed towards the fourth vertex (Fig. 4a); any more distant oxygen atoms are on the same side of the Te as the lone pair. An apparently unique alternative to this geometry for 3-coordination is seen in Nd[Te<sub>2</sub>O<sub>5</sub>]Br, where the three Te–O bonds are coplanar, forming a ‘T’-shape (Tarasov *et al.*, 1996; described as structure #285 below). Te<sup>4+</sup>O<sub>4</sub> may be either square pyramidal, with four O–Te–O angles approximately equal (Fig. 4b), or have the oxygen atoms at the apices and two

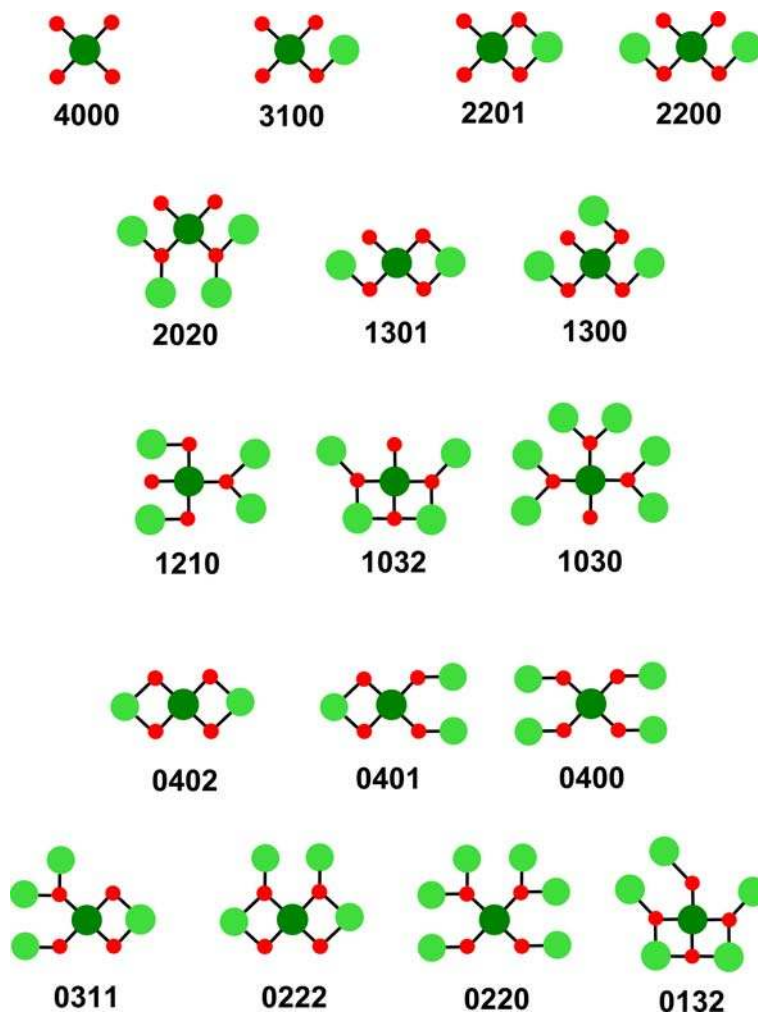


FIG. 2. The 17 distinct  $Q^{abcz}$  states that are observed for 4-coordinate Te in this study. The central Te atom is dark green, next-nearest neighbour Te atoms are light green and oxygen atoms are red. Examples of all of these in real structures will be depicted in later figures. In some cases, the topology corresponding to the Q number is not unique: for example, there is a different  $Q^{0132}$  configuration to that shown in which an edge is shared between a CN2 oxygen atom and one of the CN3 oxygen atoms.

equatorial positions of a trigonal bipyramid, with the lone pair replacing the missing ligand (Fig. 4c). The rarer examples of  $\text{Te}^{4+}\text{O}_5$  approximate octahedra with the lone pair replacing one ligand (Fig. 4d).

Subsequent investigation of the  $\text{Te}^{4+}\text{O}_6$  subset of these data by Christy and Mills (2013) showed that, although the Te–O distances within a given polyhedron could show a large variance, the oxygen atoms of a  $\text{Te}^{4+}\text{O}_6$  polyhedron (including long bonds) generally fall very nearly on the surface of a sphere, not centred on the Te, but on a point

$\sim 1 \text{ \AA}$  away from the Te atom, which is consistent with the centre of lone-pair electron density. However, the Te–O distances within a given polyhedron could show a large variance, and the radius of the sphere of oxygen atoms increased linearly with the tellurium lone-pair distance (Christy and Mills, 2013). The volume of the  $\text{Te}^{4+}\text{O}_6$  polyhedron varied, depending on both the sphere radius and the uniformity of the distribution of oxygen atoms over the sphere's surface. The polyhedra ranged in volume from nearly twice that

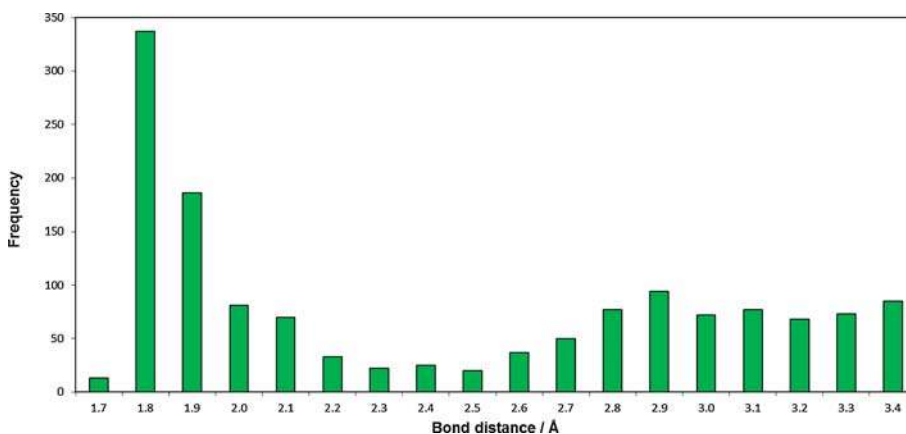


FIG. 3. Overall distribution of Te<sup>4+</sup>-O bond distances for the data of Mills and Christy (2013).

predicted for a regular Te<sup>4+</sup>O<sub>6</sub> octahedron, when the oxygen atoms are uniformly distributed and the lone pair is highly stereoactive, to 20% less than that of a regular octahedra, when the oxygen atoms are crowded on one side of the sphere. Extreme flexibility in the volume of coordination polyhedron is, thus, another feature of lone-pair cations, such as Te<sup>4+</sup>, which can contribute to their accommodation in a wide range of crystal structures.

A further unusual feature, occasionally noted, is that bonding interactions of lone-pair cations are not limited to those of the conventional cation-anion type. Christy and Mills (2013) found that the most compressed Te<sup>4+</sup>O<sub>6</sub> polyhedra also showed short distances between the lone pair and large cations, such as K or Ba and/or other Te<sup>4+</sup> cations, suggesting that weak monopole-dipole (K,Ba)-lone-pair and dipole-dipole Te<sup>4+</sup>-lone-pair interactions also help to stabilize the relevant structures. These non-classical 'bonds' complicate the application of the bond-valence model to structures containing stereoactive lone pairs.

Mills and Christy (2013) verified the strong preference of Te<sup>6+</sup> for octahedral geometry: that dataset included 100 examples of Te<sup>6+</sup>O<sub>6</sub> octahedra, plus another five where six additional oxygen atoms lay near the cut-off distance, but only 13 examples of other coordinations. Examples of polyhedra with CN4-6 are shown in Fig. 4e-g.

### The chemical and structural diversity of Te oxycompounds

In the current study, we examine the 703 Te oxycompounds for which good structure

refinements are available. Where multiple refinements were available for a compound, one of the better ones was selected. Structures with obvious errors or that were of solid-solution variants of a pure end-member were usually rejected. The dataset includes 55 mineral species, about two-thirds of those described to date.

### Chemical constituents

The frequency of occurrence of specific elements as essential constituents in these 703 compounds is shown on periodic tables in Fig. 5. Apart from Te and O, the most common constituents in the mineral species are Cu and Pb (22 out of 55), H (21), Cl (9), Fe (8) and Zn (6). While H, Cu, Cl and Pb are also important in the dataset as a whole, including synthetic compounds (223, 70, 68 and 42 compounds respectively out of 703), many of the latter also include Mo (77), Na (73), K (65), N (49), Ba (48) and P (38). The alkali metals Na and K are common as counteranions in many laboratory-crystallized Te oxysalts; while the number of N compounds is boosted by the analogous use of the ammonium ion, NH<sub>4</sub><sup>+</sup>. The anomalously large number of Mo compounds is due to the large number of salts of the tellurohexamolybdate anion, [Te<sup>6+</sup>Mo<sub>6</sub><sup>6+</sup>O<sub>24</sub>]<sup>6-</sup>, that have been prepared, while the majority of P compounds are hydrogen-bonded adducts of Te(OH)<sub>6</sub> with alkalis and various phosphate anions.

The large proportion of Cu, Pb and H minerals is consistent with these elements, like Te, showing unusually high mineral diversity (Christy, 2015), and the common association of primary telluride minerals with sulfides of Cu and Pb. It is surprising



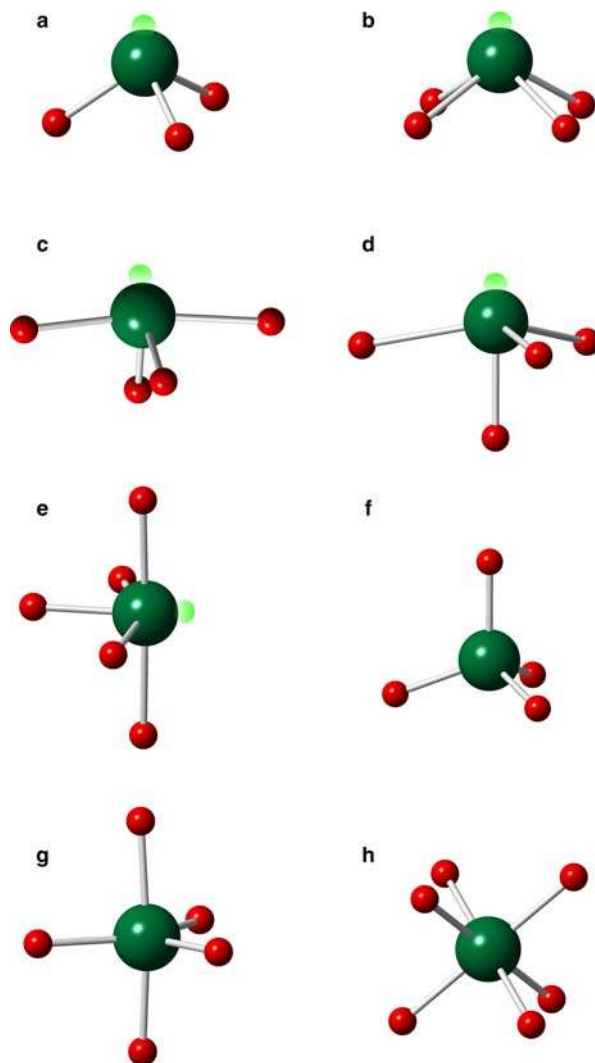


FIG. 4. Monomeric  $\text{TeO}_n$  anions. Lone-pair electron concentrations on  $\text{Te}^{4+}$  cations are depicted by small light-green spheres, reflecting their stereochemical role as ‘pseudo-anions’. (a)  $[\text{Te}^{4+}\text{O}_3]^{2-}$  in teinite,  $\text{CuTeO}_3 \cdot 2\text{H}_2\text{O}$  (Effenberger, 1977); (b) square pyramidal  $[\text{Te}^{4+}\text{O}_4]^{4-}$  in nabokoite,  $\text{K}[\text{Cu}_7(\text{TeO}_4)(\text{SO}_4)_5]\text{Cl}$  (Pertlik and Zemmann, 1988); (c) ‘trigonal prism-1’ coordinated  $[\text{Te}^{4+}\text{O}_4]^{4-}$  in tellurite,  $\text{TeO}_2$  (Kholodkovskaya *et al.*, 1995); (d) Capped trigonal pyramid  $[\text{Te}^{4+}\text{O}_4]^{4-}$  deduced to be a component of a layer anion in  $\text{BiTe}_2\text{O}_5\text{Cl}$  (Berdonosov *et al.*, 2007); (e) ‘octahedron-1’ coordinated  $[\text{Te}^{4+}\text{O}_5]^{6-}$  in  $\text{Ba}_2\text{Te}(\text{PO}_4)_2\text{O}$  (Kim *et al.*, 2010); (f) Tetrahedral  $[\text{Te}^{6+}\text{O}_4]^{2-}$  in  $\text{Cs}_2\text{TeO}_4$  (Weller *et al.*, 1999); (g) trigonal bipyramidal  $[\text{Te}^{6+}\text{O}_5]^{4-}$  in  $\text{Cs}_2\text{K}_2\text{TeO}_5$  (Untenecker and Hoppe, 1986a); and (h) octahedral  $[\text{Te}^{6+}\text{O}_6]^{6-}$  in mc Alpineite,  $\text{Cu}_3\text{TeO}_6$  (Falck *et al.*, 1978a).

that so few secondary Te minerals containing As, Sb and Bi are known, as these are also mineralogically diverse chalcophile elements. Syntheses of many Cu and Pb tellurates were probably attempted because of the importance of such phases as minerals.

#### Definition of $\text{Te}^{4+}$ coordination and structural unit

Mills and Christy (2013) chose 3.5 Å as a cutoff distance for inclusion of weak bonds to oxygen in the  $\text{Te}^{4+}$  coordination sphere. The corresponding

a

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	57- 71*	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	89- 103 **	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Fl	115 Uup	116 Lv	117 Uus	118 Uuo

6*	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
7**	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

Occurs in % of mineral species				
0	< 5%	5–10%	10–20%	20–50%

b

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	57- 71*	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	89- 103 **	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Fl	115 Uup	116 Lv	117 Uus	118 Uuo

6*	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
7**	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

Occurs in % of all compounds					
0	< 2%	2–5%	5–10%	10–20%	20–50%

FIG. 5. Periodic table of elements, colour-coded according to the frequency of specific elements as essential constituents in all the crystal structures of this study (above) and in mineral species only (below). All structures include Te and O (black).



bond valence is  $\sim 0.023$  vu. In contrast, the current study is concerned primarily with the strongest bonds of a structure, which define structural building units. For this study, we divide the 'primary' and 'secondary'  $\text{Te}^{4+}$ -O bonds at the minimum in the probability distribution between the two modes of Fig. 2. The threshold bond distance is thus 2.40–2.45 Å, corresponding to a bond valence of 0.34–0.30 vu, using the bond-valence parameters of Mills and Christy (2013). Note that this division is consistent with Hawthorne (2014) and references cited therein, who use a bond balance of  $\sim 0.30$  vu to differentiate, in crystal structures, between the more strongly bound 'structural unit' and weakly bound 'interstitial complex'. The bond-valence threshold identifying bonds that form the structural unit is employed with some flexibility. The smaller divalent octahedral cations Mg, Zn,  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$ , with bond-valence close to 0.33 vu, are part of the structural unit if they bond to tellurate oxygen atoms. However, for  $\text{Cu}^{2+}\text{O}_{4+2}$  octahedra, elongated due to Jahn-Teller distortion, it was usually the case that only the four shortest bonds were strong enough to be included. Weaker bonds to these small cations were sometimes included, if needed to preserve the integrity of a well-defined coordination polyhedron. Conversely, the larger divalent cations Ca, Sr, Ba and Cd typically occurred with  $\text{CN} > 6$  or a mixture of sixfold and higher coordination numbers, and were not generally included, unless they occurred on sites that were occupied by small cations in isostructural compounds. Other large cations with  $\text{CN} \geq 7$  (e.g.  $\text{REE}^{3+}$ ,  $\text{Zr}^{4+}$  and  $\text{Th}^{4+}$ ) or highly irregular coordination ( $\text{Pb}^{2+}$  or  $\text{Bi}^{3+}$ ) were similarly excluded from the structural unit, except for  $\text{U}^{6+}\text{O}_n$  polyhedra ( $n = 6$ –8). The dimensionality of the heteropoly structural unit was often higher than that of the Te oxyanion alone, as is apparent below.

When long bonds are excluded, the ranges of coordination numbers for the Te–O bonds included in the present study were between 2 and 6 for  $\text{Te}^{4+}$  and between 4 and 6 for  $\text{Te}^{6+}$ . The '2-coordinate'  $\text{Te}^{4+}$  of  $\text{Bi}_2(\text{TeO}_3)_2\text{O}$  has additional ligands at just over 2.5 Å (Mercurio *et al.*, 1998), while the 6-coordinate examples have the pyrochlore structure type, with  $\text{Te}^{4+}$  in octahedral coordination (Loopstra and Goubitz, 1986; Weber and Schleid, 2000). The other polyhedra are all of the types shown in Fig. 3 above. For 428 symmetrically distinct  $\text{Te}^{6+}\text{O}_n$  polyhedra, frequencies were 2, 2 and 424 for  $n = 4, 5$  and 6, respectively. For 846 symmetrically distinct  $\text{Te}^{4+}\text{O}_n$  polyhedra, frequencies were 1, 535, 271, 37 and 2 for  $n = 2, 3, 4, 5$  and 6, respectively,

although it should be noted that, while the distribution is little changed for  $\text{Te}^{4+}$ -only compounds (for which the numbers are, respectively, 1, 530, 257, 24, 1), the small sample of mixed-valence compounds show a much greater preference for 4- and 5-coordination (frequencies for  $\text{CN} = 2, 3, 4, 5$  and 6 are 0, 5, 14, 13 and 1, respectively).

We have classified the diverse Te-bearing moieties using a set of nested criteria, as follows: (1) Structures are separated into three oxidation-state taxa: those that contain only  $\text{Te}^{4+}$  as an essential major constituent, those that contain only  $\text{Te}^{6+}$ , and those that necessarily contain both  $\text{Te}^{4+}$  and  $\text{Te}^{6+}$ . (2) Within each oxidation-state taxon, we consider only the Te and its strongly-bound oxygen atoms. The next level of subdivision is on the basis of dimensionality of the  $\text{Te}_m\text{O}_n$  species. By analogy with the silicates (e.g. Deer *et al.*, 1966), we use the categories (dimensionality taxa): neso ( $m = 1$ ), soro (non-cyclic finite groups with  $m > 1$ ), cyclo (finite groups containing a ring of at least 3 Te), ino (infinite chains), phyllo (infinite layers) and tecto (infinite frameworks). When more than one distinct type of  $\text{Te}_m\text{O}_n$  group is present, the highest-dimensional group with largest  $m$  and  $n$  determines the classification. (3) Within each dimensionality taxon, species are arranged in an order that facilitates further subdivision, if justified. Cyclo-, ino- and phyllo-tellurates are first separated depending on whether there is a single or multiple ring/chain/layer. They, along with neso/soro/tecto cases, are then ordered according to the number of Te and anions in the finite complex or, for infinite polymers, the translational repeat unit. (4) Finally, we consider linkage to non-tellurium cations to make larger heteropolymeric 'structural units'.

Note that consistent focus on Te oxyanions sometimes leads to rather counterintuitive divisions between the 'Te oxyanion' and the 'rest of the structural unit'. For example, on the basis of highest-valence bonds, the structure of mroseite,  $\text{Ca}_2\text{Te}_2^{4+}\text{O}_4(\text{CO}_3)_2$ , can be divided into two weakly-bonding  $\text{Ca}^{2+}$  cations, two carbonate groups and a neutral  $[\text{Te}_2\text{O}_4]^0$  residual complex that consists of a pair of edge-sharing  $\text{TeO}_3$  pyramids (cf. Fischer *et al.*, 1975). The formula as written above emphasizes this analysis. However, one oxygen atom of each carbonate triangle also links to a Te via a bond that is strong enough to fall within the bond-valence threshold, to make a larger structural unit that is a finite carbonatotellurite cluster  $[\text{Te}_2\text{C}_2\text{O}_{10}]^{4-}$ . This can be written hierarchically so as to emphasize the carbonate groups, while not showing the full Te coordination, as  $[(\text{Te}_2\text{O}_4)$

$(\text{CO}_3)_2]^{4-}$ , or alternatively, so as to show the Te coordination, but breaking up the carbonate groups,  $[(\text{CO}_2)_2(\text{Te}_2\text{O}_6)]^{4-}$ . In the Tables below, mroseite is classified as having an edge-sharing  $[\text{Te}_2\text{O}_6]^{4-}$  dimer, but both versions of the structural formula are used in the tables and text below, depending on context. Other compounds, in which oxygen atoms are shared by Te and other high bond-valence cations, are treated similarly, that is, with more intuitive or compact versions of formulae alongside structural formulae that emphasize Te environments.

Because the C–O links in mroseite have very high bond valence ( $\sim 1.33$  vu), in order to avoid overbonding of the oxygen, the bond from Te to the carbonate oxygen atom is longer and weaker than the other Te–O bonds:  $2.313 \text{ \AA} = 0.42$  vu using the parameters of Mills and Christy (2013), as opposed to  $0.80\text{--}1.32$  vu for the other Te–O bonds. Similar weak bonding is observed when Te shares an oxygen atom with other high bond-valence cations, and the need to reduce bond valence can increase the Te coordination number. Out of the 24 examples of  $\text{TeO}_5$  polyhedra in  $\text{Te}^{4+}$ -only compounds, 16 (67%) have  $\text{Te}^{4+}\text{--O--P}^{5+}$ ,  $\text{Te}^{4+}\text{--O--As}^{5+}$  or  $\text{Te}^{4+}\text{--O--Se}^{4+}$  links, where the non-Te cation makes a bond of  $1.25\text{--}1.33$  vu. Interestingly,  $\text{Te}^{4+}$  compounds with  $\text{S}^{6+}$  and  $\text{V}^{5+}$  do not show the same trend, because they tend instead to have very strongly bonded CN1 oxygen atoms on the non-Te cation, thus reducing the valence of the bond to the bridging oxygen atom.

### Crystal structure symmetry and complexity

The Te oxysalts in the present study show a nearly even split between Te valences: the dataset contains 375 structures with  $\text{Te}^{4+}$  only, 302 with  $\text{Te}^{6+}$  only, and 26 with Te in both valence states. Interestingly, the distribution of structures between different crystal systems is quite distinct for the different valence states. As shown in Fig. 6, structures with only  $\text{Te}^{4+}$  are significantly more likely than average to be monoclinic or orthorhombic, and less likely to be trigonal, while the converse is true for structures that have only  $\text{Te}^{6+}$ . Structures that include both valences are particularly likely to be orthorhombic, while having surprisingly few triclinic examples. These differences suggest that, to a degree, the symmetry of the overall structure inherits (or at least is influenced by) the point symmetry of the Te oxyanion. The low symmetry of coordination polyhedra such as those of Figs 4*c–d* may make low-symmetry  $\text{Te}^{4+}$  structures more numerous, while  $\text{TeO}_6$  octahedra (Fig. 4*h*) are likely to have

at least one threefold rotation axis, which enhances the number of trigonal and cubic  $\text{Te}^{6+}$  phases.

The polarity due to lone-pair stereoactivity in  $\text{Te}^{4+}$ , in combination with the capacity for local symmetry inheritance by the structure, suggested that there might be a dependence of centrosymmetry on Te valence. However, the percentages of  $\text{Te}^{4+}$  and  $\text{Te}^{6+}$  structures lacking a centre of inversion were, respectively, 18.9% (71 out of 375) and 17.5% (53 out of 302), not significantly different from each other or the overall average of 18.6%. A higher proportion of acentric structures did occur for the mixed-valence structures (7 out of 26 = 26.9%), but this is also insignificant, given the small sample size. Further subdivision of the dataset by Te polymerization and coordination number did reveal two small groups with significantly high proportions of acentric structures. This was the case for eight out of 24 of the structures with isolated  $\text{Te}^{4+}\text{O}_{4-5}$  polyhedra and five out of nine structures with mixed-valence layer anions, suggesting that there is a slight tendency to inheritance of polarity.

The structures in the present study markedly violate ‘Pauling’s Fifth Rule’ that “the number of essentially different kinds of constituents in a crystal tends to be small” (Pauling, 1929), although Burdett and McLarnan (1984) noted that there is no *a priori* reason for such parsimony, except as an indirect corollary of some of Pauling’s other rules. For both  $\text{Te}^{4+}$  and  $\text{Te}^{6+}$ , the average number of symmetrically distinct polyhedra per structure is greater than unity, there being a total of  $846 + 428 = 1274$  distinct polyhedra for the 703 structures. Fig. 7 shows the percentages of the 375  $\text{Te}^{4+}$ -only, 302  $\text{Te}^{6+}$ -only and 26 mixed-valence structures that have different numbers of symmetrically distinct Te sites. Structures with larger numbers of distinct sites are generally less numerous, although a quarter of  $\text{Te}^{4+}$ -only compounds still have between 3 and 5 distinct Te sites. The  $\text{Te}^{4+}$ -only compounds also include one example each of structures with 9, 10 and 18 distinct Te sites. The last of these is a polymorph of  $\text{CaTeO}_3$  (Stöger *et al.*, 2009), dramatically demonstrating that simplicity of formula does not imply simplicity of structure.

### Detailed tabulation and descriptions of Te oxysalt structures

#### Te–O complexes

The diversity of  $\text{Te}_m\text{O}_n$  polymers is summarized in Tables 1 through 7, which order the different Te–O

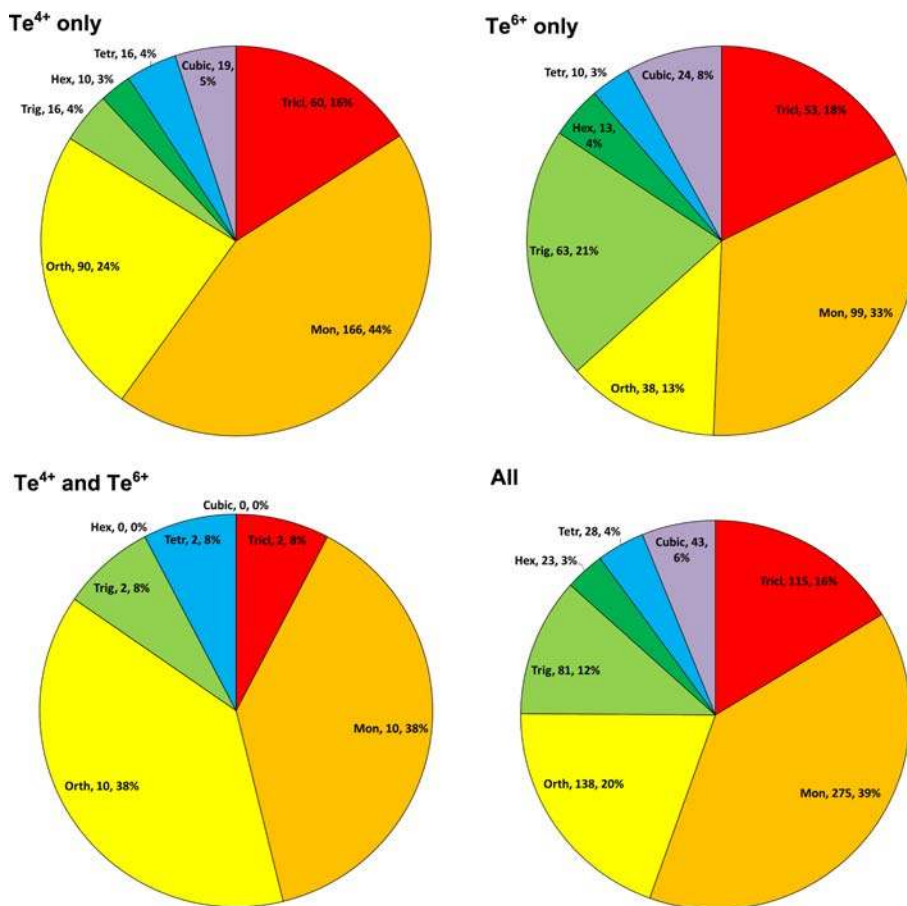


FIG. 6. Distribution of crystal structures among crystal systems for structures with  $\text{Te}^{4+}$  only,  $\text{Te}^{6+}$  only, both valences and all structures. Key: Hex = hexagonal; Tetr = tetragonal; Trig = trigonal; Tricl = triclinic; Mon = monoclinic; Orth = orthorhombic.

topologies according to the hierarchical principles given above. These tables serve, additionally, as an index for the listings of individual structures that follow in Tables 8–26. These tables have been deposited with the Principal Editor of *Mineralogical Magazine* and are available from [www.minersoc.org/pages/e\\_journals/dep\\_mat\\_mm.html](http://www.minersoc.org/pages/e_journals/dep_mat_mm.html). Note that the tables separate  $\text{Te}^{6+}\text{X}_6$  monomers into two groups: compounds that contain anionic  $[\text{TeO}_{6-x}(\text{OH})_x]^{(6-x)-}$  groups and those that contain neutral  $\text{Te}(\text{OH})_6$  molecules which form hydrogen-bonded structures with cations, anions,  $\text{H}_2\text{O}$  and polar organic molecules. For conciseness, specific structures are referenced below by the unique ordinal number that they are assigned in Tables 8–26 (deposited), where the corresponding literature reference is cited. These structure numbers will be prefixed with '#' and highlighted in **boldface**.

The finite oligomeric (soro and cyclo)  $\text{Te}^{4+}$  oxyanions of Table 1 have the topologies shown in Fig. 8. The numbers of Te atoms in these complexes range from 2 to 8, although the structure number ranges of Table 1 make it clear that some configurations are strongly preferred: we have 20 examples of the trimer  $\text{Te}_3\text{X}_8$  (Fig. 8g), 16 of the simple dimer  $\text{Te}_2\text{X}_5$  (Fig. 8a) and 14 of  $\text{Te}_4\text{X}_{11}$  (Fig. 8k). All of these groups are finite linear chains of corner-sharing  $\text{TeO}_n$  polyhedra, but while the dimer has Te in only 3-coordination, the other common anions show a tendency to alternate between 3-coordinated and 4-coordinated Te, which is also widespread among the less usual polymers (cf. Figs 8c,g,j,k,m,o). Tellurium in five-fold coordination is rare, and seems to be a characteristic of compounds that contain other highly electronegative cations such as P, As and Se (Figs 8e, f,i). Corner-linkage of  $\text{TeO}_n$  polyhedra through a

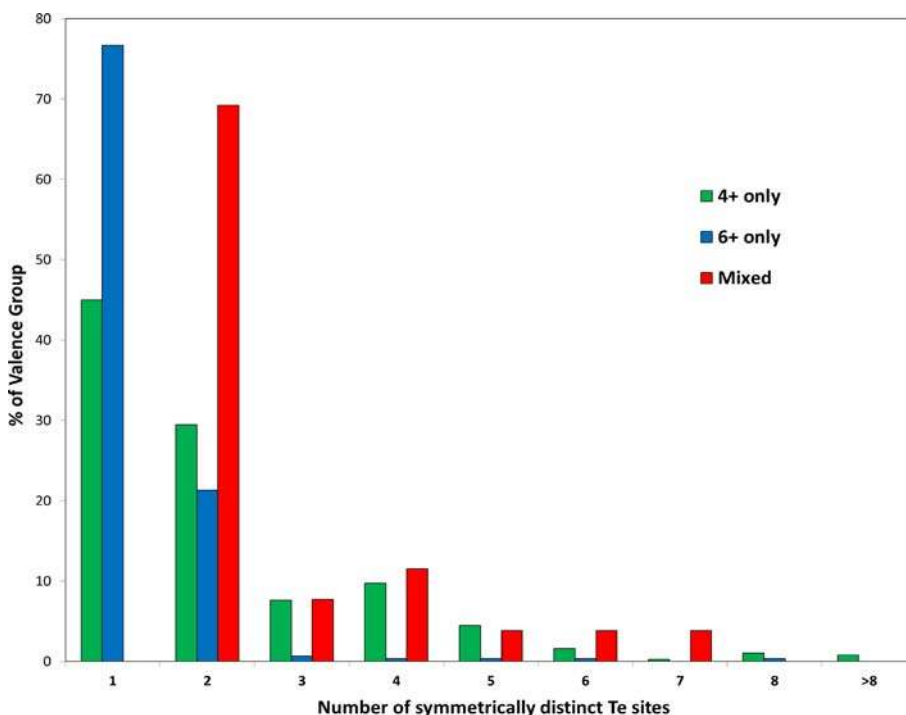


FIG. 7. Frequencies of structures with different numbers of distinct Te sites for  $\text{Te}^{4+}$ -only,  $\text{Te}^{6+}$ -only and mixed-valence compounds.

2-coordinate bridging oxygen atom is by far the most common polymerization mechanism, but there are also examples of edge-sharing through two such oxygen atoms (Figs 8*b,e,j,o*) and linkage through 3-coordinate oxygen atoms (Fig. 8*h*). The wide range of possibilities available allows formation of isomers with the same composition, but different topologies – Figs 8*b* and 8*c* provide an example. Most of the polymers are unbranched *soro* chains, although Fig. 8*l* shows an open-branched pentamer, Fig. 8*n* is a cyclo 6-ring, and Fig. 8*i* defies classification in the scheme of Liebau (1985), because its three CN5 Te atoms are  $\text{Q}^{3111}$  in our extended Q notation, joined through a mutually shared CN3 oxygen atom, as well as through additional bridging oxygen atoms of the conventional CN2 type.

The increased diversity of  $\text{Te}_m\text{X}_n$  polymer topologies relative to silicates is further evidenced by the chain structures collected in the present study. Single-chain topologies are listed in Table 2 and depicted in Fig. 9. Note that although the first entry in Table 2 appears to be a simple *einer* chain  $\text{TeX}_3$  in the terminology of Liebau (1985), with all Te atoms translationally equivalent (#281), the

bridging oxygen atom is split between two half-occupied positions, suggesting that the crystal structure as published shows an average of disordered *zweier* chains  $\text{Te}_2\text{X}_6$ . The stoichiometrically simplest chain type that occurs is a *zweier* edge-sharing chain of CN4 Te,  $\text{Te}_2\text{X}_4$ . Note that if all cations are  $\text{Te}^{4+}$  and all X are  $\text{O}^{2-}$ , then this is a neutral complex  $[\text{Te}_2\text{O}_4]^0$  rather than a chain anion, as is the case in the example  $\text{Ag}(\text{TeO}_2)(\text{NO}_3)$  of Fig. 2*a* (#282). The mineral telluroperite,  $\text{Pb}_3\text{TeO}_4\text{Cl}_2 = \text{Pb}_2(\text{PbTeO}_4)\text{Cl}_2$ , contains topologically similar chains in which the cations  $\text{Pb}^{2+}$  and  $\text{Te}^{4+}$  are disordered in a 1 : 1 ratio to give an anionic chain  $[\text{PbTeO}_4]^-$  (#283).

The most common coordination of Te in the chains is 4. However, CN3 also occurs in Figs 7*b,e,g,h,j,k,m,o* and CN5 in Figs 9*d,j,m,n*. Although polymerization is usually achieved through CN2 bridging oxygen atoms, the chains of Figs 9*f* and 9*l* also feature edge-sharing. The repeat unit along the chain backbone is most often 2 (*zweier*), although the chain of Fig. 9*h* is *dreier*, and others are *vierer* (Figs 9*e,f,j,m,n*) or *sechser* (Figs 9*k,l,o*). The chains in Figs 9*i,m,n,o* have open branches, which attach

TABLE 1.  $\text{Te}_m\text{O}_n$  monomers and finite polymers with  $\text{Te}^{4+}$  only, found in the current study, classified by the most complex Te anion if more than one type is present.

Class	Stoichiometry	Descriptive notes	Fig. #	Structural unit heteropolymerization	Structure #
neso	$\text{TeX}_3$	(trigonal pyramid)	4a	none, clusters, chains, layers, frameworks	1–171
	$\text{TeX}_4$	(square pyramid)	4b	none, layers	172
	$\text{TeX}_4$	(trigonal bipyramid -1 ligand)	4c	clusters, chains, layers, frameworks	173–193
	$\text{TeX}_5$	(octahedron -1 ligand)	4d	framework	194
soro	$\text{Te}_2\text{X}_5$	( $\Delta-\Delta$ )	8a	chains, layers, frameworks	195–206
	$\text{Te}_2\text{X}_6$	( $\Delta-\diamond$ )	8b	none, chains, layers, frameworks	207–213
	$\text{Te}_2\text{X}_6$	( $\diamond=\diamond$ )	8c	clusters, chains, layers, frameworks	214–223
	$\text{Te}_2\text{X}_7$	( $\diamond-\diamond$ )	8d	layer	224
	$\text{Te}_2\text{X}_8$	( $\square=\square$ )	8e	chains	225–226
	$\text{Te}_2\text{X}_9$	( $\square-\square$ )	8f	framework	227
	$\text{Te}_3\text{X}_8$	( $\Delta-\diamond-\diamond$ )	8g	none, chains, layers, frameworks	228–247
	$\text{Te}_3\text{X}_9$	( $\Delta-\diamond-\diamond$ )	8h	none	248
	$\text{Te}_3\text{X}_{11}$	3 $\square$ , CN2 and CN3 bridging O	8i	layer	249
	$\text{Te}_4\text{X}_{10}$	( $\Delta-\diamond=\diamond-\Delta$ )	8j	none, layers, frameworks	250–255
	$\text{Te}_4\text{X}_{11}$	( $\Delta-\diamond-\diamond-\Delta$ )	8k	none, layers	256–273
	$\text{Te}_5\text{X}_{12}$	$\diamond(-\Delta)_4$	8l	framework	274
	$\text{Te}_5\text{X}_{13}$	( $\Delta-\diamond-\Delta-\diamond-\Delta$ )	8n	none	275–278
	$\text{Te}_{10}\text{X}_{26}$	open-branched decamer	8o	framework	279
	$\text{Te}_6\text{X}_{12}$	[ $-\Delta-\Delta-\Delta-\Delta-\Delta-$ ]	8n	layer	280
cyclo					

'X' = (O,OH); other symbols are ' $\Delta$ ' =  $\text{TeO}_3$ , ' $\diamond$ ' =  $\text{TeO}_4$ , ' $\square$ ' =  $\text{TeO}_5$ , ' $\circ$ ' =  $\text{TeO}_6$ , ' $\cdot$ ' = corner-sharing, ' $\cdot$ ' = edge-sharing, ' $[\dots]$ ' = entities forming closed ring.

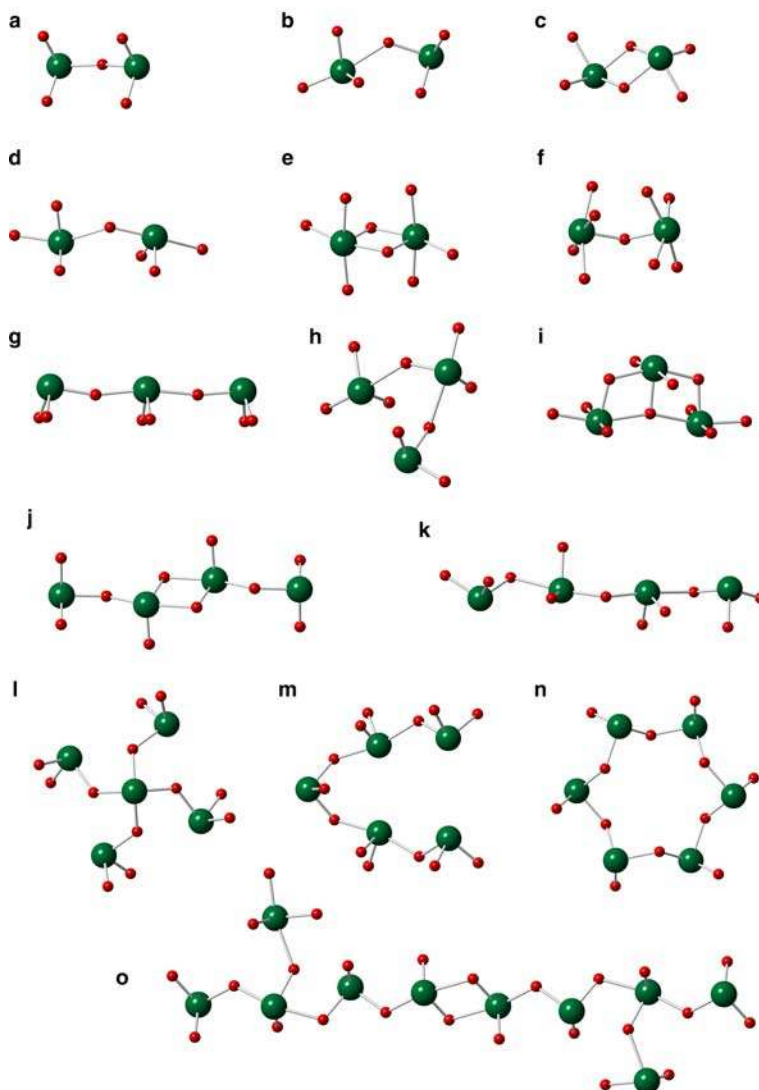


FIG. 8. Finite oxycomplexes containing only  $\text{Te}^{4+}$ . (a)  $\text{Te}_2\text{X}_5$  ( $\text{Q}^{2100}$  Te) in  $\text{Cs}_2\text{Te}_2\text{O}_5$  (#195); (b) mixed-coordination corner-sharing  $\text{Te}_2\text{X}_6$  in poughite,  $\text{Fe}_2(\text{Te}_2\text{O}_6)(\text{SO}_4) \cdot 3\text{H}_2\text{O}$  (#211); (c) four-coordinate edge-sharing  $\text{Te}_2\text{X}_6$  ( $\text{Q}^{2201}$ ) in  $\text{Pb}_3(\text{Te}_2\text{O}_6)\text{Br}_2$  (#215); (d)  $\text{Te}_2\text{X}_7$  ( $\text{Q}^{3100}$ ) in  $\text{BaMo}_2(\text{Te}_2\text{O}_7)\text{O}_4 \cdot \text{H}_2\text{O}$  (#224); (e) edge-sharing five-coordinate  $\text{Te}_2\text{X}_8$  ( $\text{Q}^{3201}$ ) in one polymorph of  $\text{Te}(\text{AsO}_3\text{OH})\text{O}$  (#226); (f) corner-sharing five-coordinate  $\text{Te}_2\text{X}_9$  ( $\text{Q}^{4100}$ ) in  $\text{Te}_2(\text{PO}_4)_2\text{O}$  (#227); (g)  $\text{Te}_3\text{X}_8$  in  $\text{Sr}_4(\text{Te}_3\text{O}_8)\text{Cl}_4$  (#228); (h)  $\text{Te}_3\text{X}_9$  in  $\text{Dy}_4(\text{Te}_3\text{O}_9)(\text{TeO}_3)_3$  (#248) (i)  $\text{Te}_3\text{X}_{11}$  trimer linked through two CN2 and one CN3 bridging oxygen atoms in  $\text{Te}_3(\text{AsO}_4)_2\text{O}_3$  (#254). The outer Te are  $\text{Q}^{3111}$  and the central one is  $\text{Q}^{2212}$ ; (j)  $\text{Te}_4\text{X}_{10}$  in  $\text{Na}_2(\text{Te}_2\text{O}_5) \cdot 2\text{H}_2\text{O}$  (#255); (k)  $\text{Te}_4\text{X}_{11}$  in  $\text{Yb}_2(\text{Te}_4\text{O}_{11})$  (#268); (l)  $\text{Te}_5\text{X}_{12}$  open-branched pentamer in  $\text{Cu}_4(\text{Te}_5\text{O}_{12})\text{Cl}_4$  (#274); (m)  $\text{Te}_5\text{X}_{13}$  in  $\text{Nd}_5(\text{Te}_5\text{O}_{13})(\text{TeO}_3)_2(\text{MoO}_4)\text{Cl}_3$  (#275); (n) cyclo  $\text{Te}_6\text{X}_{12}$  in  $(\text{NH}_4)_6[\text{Mo}_6(\text{Te}_6\text{O}_{12})(\text{TeO}_3)_2\text{O}_{18}][\text{Mo}_2\text{O}_7] \cdot \text{H}_2\text{O}$  (#280); (o)  $\text{Te}_{10}\text{X}_{26}$  in  $\text{Nb}_8[\text{Te}_{10}\text{O}_{26}](\text{TeO}_3)_6\text{O}_8$  (#279).

to a Te cation of the chain backbone through CN2 oxygen in most cases, but via a CN3 bridging oxygen for the chain of Fig. 9*i*. Figure 9*j* shows a loop-branched chain, in which a succession of

4-membered rings are united through common vertices.

Overall, the most common chain configurations are corner-sharing types with alternating CN3 and



TABLE 2.  $\text{Te}_m\text{O}_n$  single chains with  $\text{Te}^{4+}$  only (not tellurites), found in the current study.

Stoichiometry	Descriptive notes	Fig. #	Structural unit heteropolymerization	Structure #
$\text{TeX}_3$	see text	—	framework	281
$\text{Te}_2\text{X}_4$	$(\dots = \diamond = \diamond = \dots)$	9a	none	282–283
$\text{Te}_2\text{X}_5$	$(\dots - \Delta - \diamond - \dots)$	9b	none, frameworks	284–289
$\text{Te}_2\text{X}_6$	$(\dots - \diamond - \diamond - \dots)$	9c	chains, layers	290–298
$\text{Te}_2\text{X}_8$	$(\dots - \square - \square - \dots)$	9d	frameworks	299–301
$\text{Te}_4\text{X}_{10}$	$(\dots - \Delta - \diamond - \Delta - \diamond - \dots)$	9e	none, chains, layers	302–306
$\text{Te}_4\text{X}_{10}$	$(\dots - \diamond - \diamond - \Delta - \Delta - \dots)$	9f	none	307
$\text{Te}_4\text{X}_{10}$	$(\dots - \diamond = \diamond = \diamond = \diamond - \dots)$	9g	frameworks	308–311
$\text{Te}_4\text{X}_{10}$	$(\dots - (\diamond - \Delta) - (\diamond - \Delta) - \dots)$	9h	none	312
$\text{Te}_4\text{X}_{10}$	$(\dots - (\diamond - \Delta) - \diamond - \Delta - \dots)$	9i	chain	313
$\text{Te}_4\text{X}_{12}$	$(\dots - \diamond - \diamond - \dots)$ with branches on CN3 oxygen atoms	9j	layer	314
$\text{Te}_6\text{X}_{14}$	loop-branched <i>vièrer</i> chain with Te CN = 3 and 5	9k	framework	315
$\text{Te}_6\text{X}_{16}$	$(\dots - \Delta - \diamond - \diamond - \Delta - \diamond - \dots)$	9l	none	316
$\text{Te}_6\text{X}_{16}$	$(\dots - \diamond - \diamond = \diamond - \diamond - \diamond = \diamond - \dots)$	9m	frameworks	317–322
$\text{Te}_6\text{X}_{18}$	$(\dots - \diamond - (\Delta - \square) - \diamond - (\Delta - \square) - \dots)$	9n	framework	323
$\text{Te}_6\text{X}_{22}$	$(\dots - (\square - \square) - \diamond - (\square - \square) - \diamond - \dots)$	9o	framework	324
$\text{Te}_8\text{X}_{22}$	$(\dots - (\diamond - \Delta) - \diamond - (\diamond - \Delta) - \diamond - \dots)$	9p	none	325

Symbols as for Table 1, plus ‘ $(\dots \# \# \# \dots)$ ’ =  $\# \# \#$  forming infinite chain, ‘ $(\dots \# \# (\#) \# \# \dots)$ ’ chain with side branch inside additional parentheses.

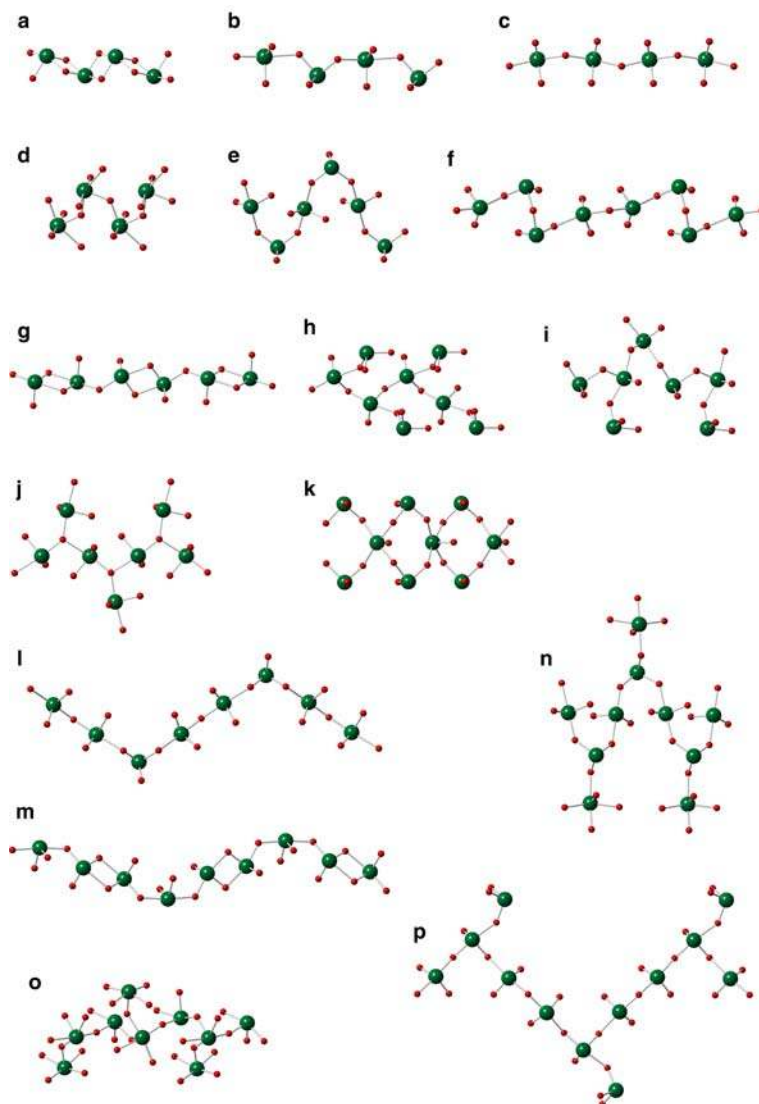


FIG. 9. Single-chain Te–O complexes containing only  $\text{Te}^{4+}$ . Chains all extend horizontally. The terms *zweier*, *dreier*, *vierer*, *sechser* imply chain backbone repeats of 2, 3, 4 and 6 Te atoms, respectively. The Q state is indicated where it is the same for all Te. More complex structures are discussed in the text. (a) Edge-sharing *zweier*  $\text{Te}_2\text{X}_4$  ( $\text{Q}^{0402}$ ) neutral complex in  $\text{Ag}(\text{TeO}_2)(\text{NO}_3)$  (#282); (b) mixed-coordination corner-sharing *zweier*  $\text{Te}_2\text{X}_5$  anion in *rajite*,  $\text{Cu}(\text{Te}_2\text{O}_5)$  (#284); (c) four-coordinate corner-sharing *zweier*  $\text{Te}_2\text{X}_6$  ( $\text{Q}^{2200}$ ) in *schmitterite*,  $(\text{UO}_2)(\text{TeO}_3)$  (#292); (d) five-coordinate *zweier*  $\text{Te}_2\text{X}_8$  ( $\text{Q}^{3200}$ ) in one of the  $\text{TeSeO}_4$  dimorphs (#300); (e) corner-sharing *vierer*  $\text{Te}_4\text{X}_{10}$  in *chekhovichite*,  $\text{Bi}_2(\text{Te}_2\text{O}_5)(\text{TeO}_3)_2$  (#302); (f) different order of CN3 and CN4 Te sharing corners in  $\text{Te}_4\text{X}_{10}$  of  $\text{Ho}_2(\text{Te}_2\text{O}_5)\text{Cl}$  (#307); (g) corner- and edge-sharing *vierer*  $\text{Te}_4\text{X}_{10}$  ( $\text{Q}^{1301}$ ) in *denningite*,  $\text{MnMn}(\text{Te}_4\text{O}_{10})$  (#310); (h) open-branched *zweier*  $\text{Te}_4\text{X}_{10}$  in  $\text{K}_2(\text{Te}_2\text{O}_5)$  (#312); (i) Open-branched *dreier*  $\text{Te}_4\text{X}_{10}$  in  $\text{Ba}_2\text{V}^{5+}(\text{Te}_4\text{O}_9\text{OH})\text{O}_3$  (#313); (j) open-branched *zweier*  $\text{Te}_4\text{X}_{12}$  with branches attached to CN3 bridging oxygen atoms in  $(\text{NH}_4)_2\text{W}(\text{Te}_2\text{O}_6)\text{O}_2$  (#314); (k) loop-branched *vierer*  $\text{Te}_6\text{X}_{14}$  in  $\text{Ni}_2(\text{Te}_3\text{O}_7)(\text{TeO}_3)$  (#315); (l) mixed-coordination *sechser*  $\text{Te}_6\text{X}_{16}$  in  $\text{Pb}_2\text{Te}_3\text{O}_8$  (#316); (m) corner- and edge-sharing *sechser*  $\text{Te}_6\text{X}_{16}$  in *spiroffite*,  $\text{Mn}_2\text{Te}_3\text{O}_8$  (#318); (n) open-branched *vierer*  $\text{Te}_6\text{X}_{18}$  in  $\text{Fe}^{2+}\text{Fe}^{3+}(\text{Te}_3\text{O}_9)(\text{TeO}_3)$  (#323); (o) open-branched *vierer*  $\text{Te}_6\text{X}_{22}$  in  $\text{Te}_3(\text{PO}_4)_2\text{O}_3$  (#324); (p) open-branched *sechser*  $\text{Te}_8\text{X}_{22}$  in  $\text{Ca}_4(\text{Te}_4\text{O}_{11})(\text{TeO}_3)$  (#325).

TABLE 3.  $\text{Te}_n\text{O}_n$  multiple chains with  $\text{Te}^{4+}$  only (inotellurites), found in the current study.

Stoichiometry	Descriptive notes	Fig. #	Structural unit heteropolymerization	Structure #
Double chains				
$\text{Te}_2\text{X}_4$	<i>einer</i> with CN3 bridging oxygen atoms	10a	none	326
$\text{Te}_3\text{X}_{12}$	<i>zweier</i> with one CN3 oxygen and one chain loop-branched	10b	none	327
$\text{Te}_6\text{X}_{14}$	<i>zweier</i> open-branched chains	10c		328–329
$\text{Te}_6\text{X}_{14}$	<i>zweier</i> chains linked through $(-\diamond = \diamond -)$ pair	10d	none	330
$\text{Te}_6\text{X}_{16}$	<i>dreier</i> chains	10e	framework	331
$\text{Te}_8\text{X}_{18}$	<i>zweier</i> chains linked through $\text{Te}_4$ double-triangle	10f	none	332
Triple chains				
$\text{Te}_8\text{X}_{24}$	<i>zweier</i> chains; outer two are open-branched	10g	layer	333
Quadruple chains				
$\text{Te}_{12}\text{X}_{26}$	outer chains are <i>zweier</i> , inner pair are <i>dreier</i> and share edges to make $\text{Te}_4$ double-triangles; CN3 oxygen atoms link extra Te to outer chains	10h	none	334

CN4 (eight instances of the *zweier* chain of Fig. 9b, four of the *vierer* chain of Fig. 9e) and CN4 chains with regularly-spaced edge-sharing links (four examples of the denningite-type *vierer* chain of Fig. 9f and six of the spiroffite-type *sechser* chain of Fig. 9l). Topographic isomers are common: the four different configurations Figs 9e–h all have the same  $\text{Te}_4\text{X}_{10}$  stoichiometry.

A chain is defined as multiple if it is possible to selectively remove some Te–O links so as to break it into two or more subchains that themselves remain continuous. The dataset of this study contains several types of double chain, as well as a triple chain and even a quadruple chain. These are listed in Table 3, and depicted in Fig. 10.

The simplest double chain found in this study is the uncharged *einer* double chain  $\text{Te}_2\text{O}_4$  of  $\text{Bi}_3(\text{Te}_2\text{O}_4)(\text{TeO}_3)_2\text{Cl}_5$  (#326). The bridging oxygen atoms of each subchain make a third Te–O bond, linking the two subchains together (Fig. 10a), to make a chain of  $\text{Q}^{1032}$  Te polyhedra that is almost an infinitely extended homologue of the finite trimer in Fig. 8i. All but one of the other multiple chains have *zweier* periodicity along the chain length, but show a remarkable range of complexity in the connection patterns between chains. One of the two inequivalent subchains of Fig. 10b can be regarded as loop-branched: backbone Te are  $\text{Q}^{1300}$ , but connect to additional  $\text{Q}^{2110}$  Te, making 3-rings, which, in turn, link to the unbranched subchain of  $\text{Q}^{2110}$  Te via the CN3 bridging oxygen. The zigzag pattern of 6-rings in Fig. 10c can be formed through conventional corner-linkage of open-branched subchains. This is also the case for the isomeric chain of Fig. 10d, except that the branches there do not link directly to the other subchain, but instead share edges to form a (Te = Te) pair that is not part of either backbone. The only *dreier* double chain (Fig. 10e) has unbranched subchains that corner-link directly to form a ribbon of 5-rings, reminiscent of the 6-rings of Fig. 10c. Both of these structures occur for Fe tellurates. The most complex double chain occurs for the chemically simple compound  $\text{Na}_2\text{Te}_4\text{O}_9$  (#332; Fig. 10f). Each *zweier* subchain backbone can be regarded as loop-branched, so that the subchains are each made of linked 5-rings. However, the loops of the subchains join via a shared edge and two corner-linkages to form a cluster  $\text{Te}_4\text{O}_n$  in which two 3-rings are united at a common shared edge. An isolated cluster with the same topology occurs for  $\text{Te}^{6+}$  (Fig. 13d). It will be seen below that this ‘double-triangle’ moiety appears to be unusually stable, recurring as part of

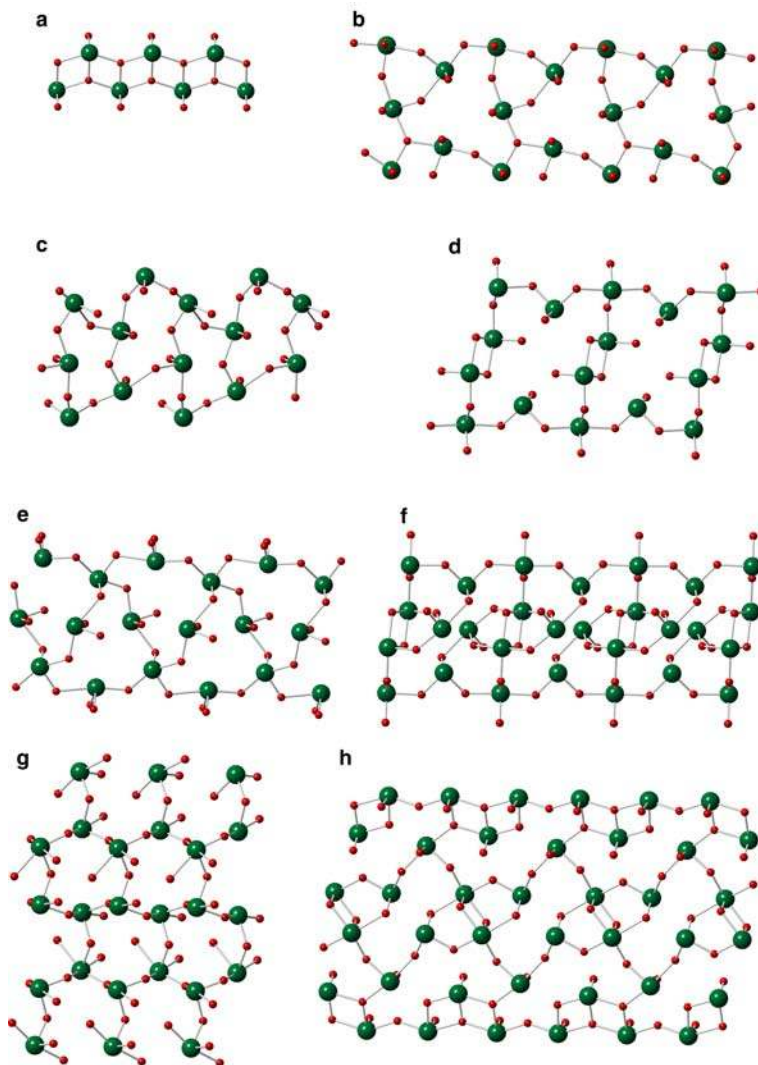


FIG. 10. Multiple-chain Te–O complexes containing only  $\text{Te}^{4+}$ . Chains all extend horizontally. (a) Four-coordinate Te make an *einer*  $\text{Te}_2\text{X}_4$  neutral complex with CN3 bridging oxygen atoms in  $\text{Bi}_3(\text{Te}_2\text{O}_4)(\text{TeO}_3)_2\text{Cl}_5$  (#326); (b) loop-branched and unbranched subchains join to make a *zweier*  $\text{Te}_5\text{X}_{12}$  double-chain anion in  $\text{Cd}_7(\text{Te}_5\text{O}_{12})(\text{Te}_2\text{O}_5)\text{Cl}_8$  (#327); (c) open-branched subchains link to make *zweier*  $\text{Te}_6\text{X}_{14}$  with zigzag 6-rings in  $\text{Fe}^{3+}(\text{Te}_3\text{O}_7)\text{Cl}$  (#328); (d) branches of subchains share edges to make isomeric *zweier*  $\text{Te}_6\text{X}_{14}$  in  $\text{Tl}_2(\text{Te}_3\text{O}_7)$  (#330); (e) unbranched subchains link to form *dreier*  $\text{Te}_6\text{X}_{16}$  with ribbon of 5-rings in  $\text{Fe}_4^{3+}(\text{Te}_6\text{O}_{16})(\text{Te}_2\text{O}_6)$  (#331); (f) loop-branched *zweier* subchains link to form  $\text{Te}_8\text{X}_{18}$  double chain with  $\text{Te}_4\text{X}_{12}$  ‘double triangle’ clusters between chain backbones in  $\text{Na}_2(\text{Te}_4\text{O}_9)$  (#332); (g) open-branched *zweier* triple chain  $\text{Te}_8\text{X}_{24}$  in  $\text{Te}_4(\text{PO}_4)_2\text{O}_5$  (#333); (h) quadruple chain  $\text{Te}_{12}\text{X}_{26}$  with *zweier* and *dreier* subchains, CN3 bridging oxygen atoms and double-triangle clusters  $\text{Te}_4\text{X}_{10}$  where central subchains link in  $\text{Cd}_4(\text{Te}_6\text{O}_{13})\text{Cl}_6$  (#334).

several larger polymers. The topology of the *zweier* triple chain of Fig. 10g is similar to that found in silicates for jimthompsonite and related ‘biopyr-iboles’ (Veblen and Burnham, 1978), but with additional side branches. Finally, Fig. 10h shows a

quadruple chain which exhibits almost every complexity known in Te oxyanions. It contains Te with CN3, 4 and 5. While the two outer chains are *zweier*, the two central chains are *dreier*. Furthermore, the central chains join to each other

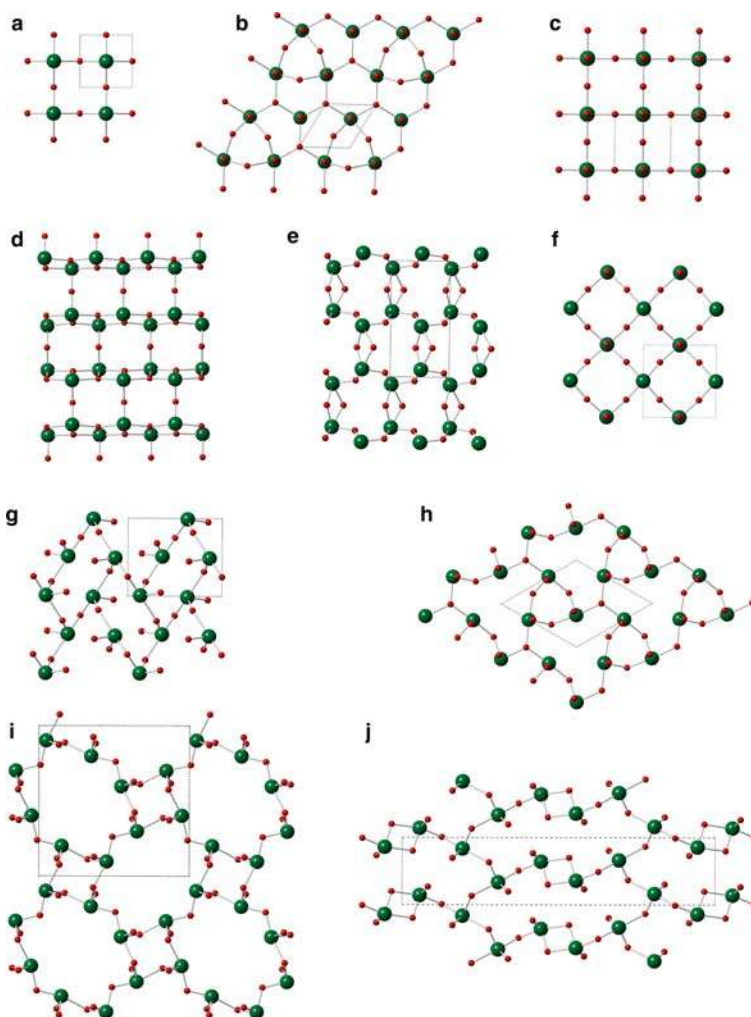


FIG. 11. Single-layer Te–O complexes containing only  $\text{Te}^{4+}$ . Unit-cell outlines are shown dashed when the projection direction is down a principal axis of the cell. The number of Te in the  $\text{Te}_m\text{X}_n$  formula unit corresponds to the translational repeat unit for the topology in its most symmetrical configuration; the repeat unit of the actual structure may be larger. (a)  $\text{TeX}_2$  layer of square pyramids ( $Q^{0400}$  Te) in  $\text{Nd}(\text{Te}_2\text{O}_4)\text{OCl}$  (#335); (b) most symmetrical local configuration for  $\text{TeX}_{2.5}$  in the disordered structure of  $\text{Bi}(\text{Te}_2\text{O}_5)\text{Cl}$  (#337); (c)  $\text{TeX}_3$  with CN5 Te ( $Q^{1400}$ ) in  $\text{Bi}_2(\text{TeO}_3)(\text{TeO}_2)\text{OBr}_2$  (#338); (d) cationic  $(\text{Te,Sb})_2\text{X}_3$  layer ( $Q^{0132}$  Te) with 1 : 1 ratio of disordered  $\text{Te}^{4+}$  and  $\text{Sb}^{3+}$  in  $\text{Cu}^{1+}(\text{SbTeO}_3)^{1+}\text{Cl}_2$  (#339); (e) cationic  $\text{Te}_2\text{X}_4$  layer ( $Q^{0401}$ ) in  $(\text{Te}_2\text{O}_3\text{OH})(\text{NO}_3)$  (#340); (f)  $\text{Te}_2\text{X}_5$  layer with ordered CN4 and CN5 Te in  $\text{Bi}_4(\text{Te}_2\text{O}_5)\text{O}_4\text{Br}_2$  (#342); (g) CN4 Te ( $Q^{1300}$ ) forming  $\text{Te}_2\text{X}_5$  layer with 6-rings in  $\text{Mg}(\text{Te}_2\text{O}_5)$  (#346); (h)  $\text{Te}_3\text{X}_7$  layer in which 3-rings are linked via CN3 bridging oxygen atoms ( $Q^{1210}$  Te) in  $\text{La}_2(\text{Te}_3\text{O}_7)_2(\text{WO}_4)$  (#349); (i)  $\text{Te}_4\text{X}_{10}$  layer of  $Q^{1300}$  Te, with 4- and 8-rings in mackayite,  $\text{Fe}^{3+}(\text{Te}_2\text{O}_5)\text{OH}$  (#350); (j)  $\text{Te}_4\text{X}_{10}$  layer of CN4 Te with 10-rings, edge-sharing pairs of Te having two rather than three bridging oxygen atoms, in one dimorph of  $\text{Li}_2(\text{Te}_2\text{O}_5)$  (#351); (k)  $\text{Te}_4\text{X}_{10}$  layer of CN4 Te with 10-rings, edge-sharing pairs of Te having three bridging oxygen atoms, in  $\text{Ti}_2(\text{Te}_2\text{O}_5)$  (#352); (l)  $\text{Te}_8\text{X}_{18}$  layer with 6-rings containing one or two CN3 Te, in  $(\text{NH}_4)_2(\text{Te}_4\text{O}_9)$  (#355); (m)  $\text{Te}_8\text{X}_{18}$  layer with 6-rings containing zero or two CN3 Te, in  $\text{K}_2(\text{Te}_4\text{O}_9) \cdot 3.2\text{H}_2\text{O}$  (#356); (n) convoluted  $\text{Te}_{16}\text{X}_{36}$  layer with edge-sharing pairs of CN5 Te and corner-sharing CN3/CN4 Te, making 3-, 4- and 12-rings, in  $(\text{NH}_4)\text{Rb}(\text{Te}_4\text{O}_9) \cdot 2\text{H}_2\text{O}$  (#357); (o) loop-branched  $\text{Te}_{40}\text{X}_{100}$  layer in which tubes with 4-, 7- and 8-rings, running vertically on the page, are connected via sparser tubes with 9- and 10-rings, in  $\text{Ba}_6(\text{Te}_{10}\text{O}_{25})\text{Br}_2$  (#359).



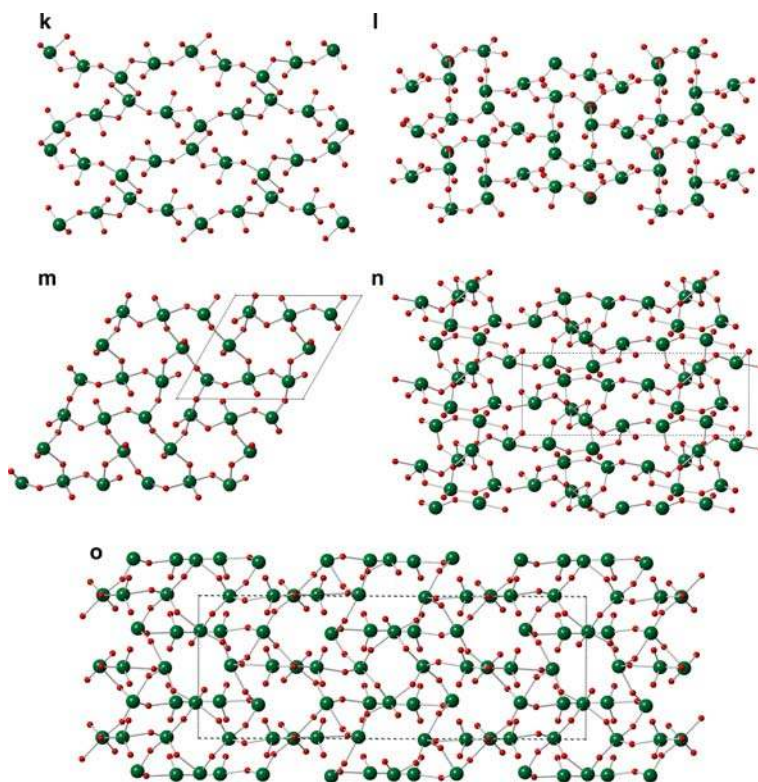


FIG. 11. Continued.

through Te–O polyhedra sharing edges and corners, to form again the ‘double-triangle’ cluster seen in Fig. 10*f*. Conversely, the central chains join to the outer chains less conventionally, via oxygen atoms which are CN3, as they also join to additional Te cations, so that the outer chains can be regarded as sequences of trimeric clusters resembling those of Fig. 8*i*.

Polyhedra  $\text{Te}^{4+}X_n$  polymerize further to form layers, which may attain considerable complexity. The simplest single layers have  $\text{TeX}_4$  square pyramids that link via corners to form a sheet  $\text{TeX}_2$  (Fig. 11*a*), in which all Te are equivalent. All or half of these polyhedra may be capped by an additional ligand to form sheets with either  $\text{TeX}_3$  (Fig. 11*c*) or  $\text{Te}_2X_5$  (Fig. 11*f*) stoichiometry. A very different type of layer with  $\text{Te}:X = 2:5$  is seen in Fig. 11*b*. This compound, ideally  $\text{Bi}(\text{Te}_2\text{O}_5)\text{Cl}$  shows considerable structural disorder, and has all Te equivalent in its average structure. The Te shows short distances to one capping ligand (O1), three ~75%-occupied CN3 oxygen atoms (O2) and six

~25%-occupied CN2 oxygen atoms (O3). Short distances mean that O2 cannot be occupied simultaneously with its three nearest O3 sites, and O3 cannot be occupied simultaneously with its nearest O2 or its two nearest O3 sites. Figure 11*b* shows the most symmetrical way of satisfying these short-range order constraints, with  $\frac{3}{4}$  of the Te in distorted 5-coordination ( $Q^{1220}$ ) and  $\frac{1}{4}$  in the capped pyramidal coordination of Fig. 3*d* ( $Q^{1030}$ ). Figure 11*d* shows a  $(\text{Te}_{0.5}\text{Sb}_{0.5})_2X_3$  sheet in which double chains of the type shown in Fig. 10*a*, featuring CN3 oxygen atoms, are connected through additional Te–O–Te links to produce a sheet with  $Q^{0132}$  cations  $[(\text{SbTe})\text{O}_3]^+$  that is positively charged, rather than anionic. The layer in Fig. 11*e* has  $\text{Te}_2X_4$  stoichiometry. All Te are CN4 and all  $X$  are CN2, but each  $\text{TeX}_4$  polyhedron shares one edge, so that it links to only three others ( $Q^{0401}$  configuration). Figure 11*e* shows the  $[\text{Te}_2\text{O}_3\text{OH}]^+$  complex from  $(\text{Te}_2\text{O}_3\text{OH})(\text{NO}_3)$ , which again is cationic rather than anionic. However, the neutral sheet  $[\text{Te}_2\text{O}_4]^0$  of tellurite,  $\text{TeO}_2$  (#341) has the



TABLE 4.  $\text{Te}_m\text{O}_n$  single layers with  $\text{Te}^{4+}$  only (phyllosilicates), found in the current study. The formula unit is the smallest possible translational repeat unit for the topology.

Stoichiometry	Descriptive notes	Fig. #	Structural unit heteropolymerization	Structure #
$\text{TeX}_2$	CN4 Te corner-linked to make 4-rings	11a	none	335–336
$\text{TeX}_{2.5}$	disordered CN4 and CN5 Te making 3-rings via CN2 and CN3 oxygen atoms	11b	none	337
$\text{TeX}_3$	CN5 Te corner-linked to make 4-rings	11c	none	338
$(\text{Te}_2\text{M})_2\text{X}_3$	CN4 Te linked via CN3 oxygen atoms into double chains and then via CN2 oxygen atoms into layer	11d	none	339
$\text{Te}_2\text{X}_4$	$(>\diamond = \diamond<)$ pairs share corners to make 6-rings	11e	none	340–341
$\text{Te}_2\text{X}_5$	$[-\diamond-\diamond-\diamond-\diamond-] 4\text{-rings}$	11f	none	342
$\text{Te}_2\text{X}_5$	$(-\diamond-)$ making 6-rings	11g	none, layer, frameworks	343–348
$\text{Te}_3\text{X}_7$	CN4 Te 3-rings linked via CN3 oxygen atoms to make 6-rings	11h	none	349
$\text{Te}_4\text{X}_{10}$	$(\diamond-\diamond)$ making 8- and 4-rings	11i	framework	350
$\text{Te}_4\text{X}_{10}$	$(-\diamond = \diamond-)$ link via $(-\diamond-\diamond-\diamond-)$ to make 10-rings; each $(-\diamond = \diamond-)$ pair shared by two rings	11j	none	351
$\text{Te}_4\text{X}_{10}$	$(>\diamond = \diamond<)$ link via $(-\diamond-\diamond-\diamond-)$ to make 10-rings; each $(>\diamond = \diamond<)$ pair shared by four rings	11k	none	352–353
$\text{Te}_8\text{X}_{18}$	$[-\diamond-\diamond-\diamond-\diamond-\diamond-]$ and $[-\diamond-\diamond-\diamond-\diamond-\diamond-]$ 6-rings	11l	none	354–355
$\text{Te}_8\text{X}_{18}$	$[-\diamond-\diamond-\diamond-\diamond-\diamond-]$ and $[-\diamond-\diamond-\diamond-\diamond-\diamond-]$ 6-rings	11m	none	356
$\text{Te}_{16}\text{X}_{36}$	$(-\diamond-\diamond-\diamond-\diamond-\diamond-)$ chains linked through $(\square = \square)$ pairs to make 3-, 4- and 12-rings	11n	none	357–358
$\text{Te}_{40}\text{X}_{100}$	tubes with 4- 7- and 8-rings or 9- and 10-rings linked into looped sheet	11o	none	359

TABLE 5.  $\text{Te}_m\text{O}_n$  with  $\text{Te}^{4+}$  only in double layers (phyllosilicates) and frameworks (tectotellurites), found in the current study.

Stoichiometry	Descriptive notes	Fig. #	Structural unit heteropolymerization	Structure #
double layers (phyllo)				
$\text{Te}_6\text{X}_{13}$	$[-\diamond-\diamond-\diamond-\diamond-]$ 3-rings linked through CN3 oxygen to upper or lower Te of $(\diamond = \diamond)$ , to make 12-rings in each sublayer	12a	frameworks	360–362
$\text{Te}_6\text{X}_{14}$	$[-\square-\square-\square-\square-\square-\square-]$ 8-rings in sublayers, $[-\square-\square-\square-\square-]$ and $[-\square-\square-\square-\square-\square-\square-]$ bridging layers	12b	layer	363
frameworks (tecto)				
$\text{TeX}_2$	cristobalite type (CN4, $\text{Q}^4$ )	12c	none	364–365
$\text{TeX}_3$	pyrochlore type (CN6, $\text{Q}^6$ )	12d	none	366
$\text{TeX}_7$	Te links to four oxygen atoms with CN 1,2,2,3	12e	framework	367
$\text{TeX}_7$	Te links to four oxygen atoms with CN 1,2,2,3	12f	framework	368
$\text{TeX}_8$	Te links to four oxygen atoms with CN 1,1,3,3	12g	framework	369–373
$\text{TeX}_9$	4-rings $[-\diamond-\diamond-\diamond-\diamond-]$ linked through pairs of $\text{Q}^2-\diamond$	12h	none	374
$\text{TeX}_{11}$	$(\diamond = \diamond = \diamond = \diamond)$ linked through $\diamond$ and CN3 oxygen to make chains of 6-rings, cross-linked by perpendicular chains $(-\diamond-\diamond-\diamond-)$ making 8- and 10-rings.	12i	none	375

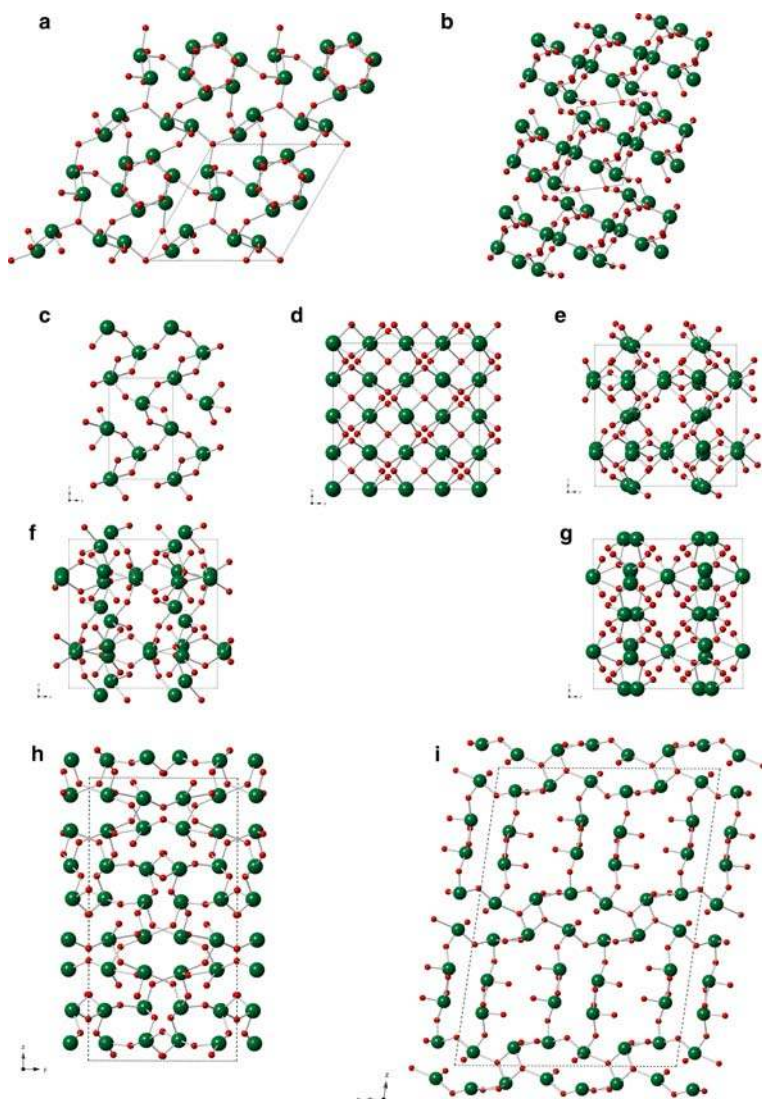


FIG. 12. Double-layer and framework Te–O complexes containing only  $\text{Te}^{4+}$ . Unit-cell outlines are shown dashed for the frameworks. (a)  $\text{Te}_6\text{X}_{13}$  double layer in  $\text{Zn}(\text{Te}_6\text{O}_{13})$  (#360); (b)  $\text{Te}_6\text{X}_{14}$  double layer in  $\text{Te}_3(\text{SeO}_3)\text{O}_5$  (#363); (c)  $\text{TeX}_2$  framework ( $\text{Q}^{0400}$ ) of the paratellurite polymorph of  $\text{TeO}_2$  (#364); (d) pyrochlore framework  $\text{TeX}_3$  ( $\text{Q}^{0600}$ ) in  $\text{Pr}_2(\text{Te}_2\text{O}_6)\text{O}$  (#366); (e)  $\text{Te}_3\text{X}_7$  framework in  $\text{KGa}(\text{Te}_6\text{O}_{14})$  (#367); (f)  $\text{Te}_3\text{X}_7$  framework in cliffordite,  $(\text{UO}_2)(\text{Te}_3\text{O}_7)$  (#368); (g)  $\text{Te}_3\text{X}_8$  framework of winstanleyite,  $\text{Ti}(\text{Te}_3\text{O}_8)$  (#372); (h)  $\text{Te}_4\text{X}_9$  framework of  $\text{Cs}_2(\text{Te}_4\text{O}_9)$  (#374); (i)  $\text{Te}_5\text{X}_{11}$  framework of  $\text{Pb}(\text{Te}_5\text{O}_{11})$  (#375).

same topology, but is much more deeply corrugated. When  $\text{TeX}_4$  polyhedra share three corners only ( $\text{Q}^{1300}$ ) to form 6-rings, a  $\text{Te}_2\text{X}_5$  sheet such as Fig. 11g is obtained, topologically similar to the silicate sheet of micas, but less regular geometrically. As is the case for phyllosilicates, the non-bridging oxygens can be distinguished between

those that point ‘up’ and those that point ‘down’ relative to the overall plane of the layer, and different up/down ordering patterns of apical oxygen atoms may occur. In the present study, most examples (including that of Fig. 11g) show alternation of pairs of ‘up’ and pairs of ‘down’ polyhedral apices. However, one of the dimorphs of

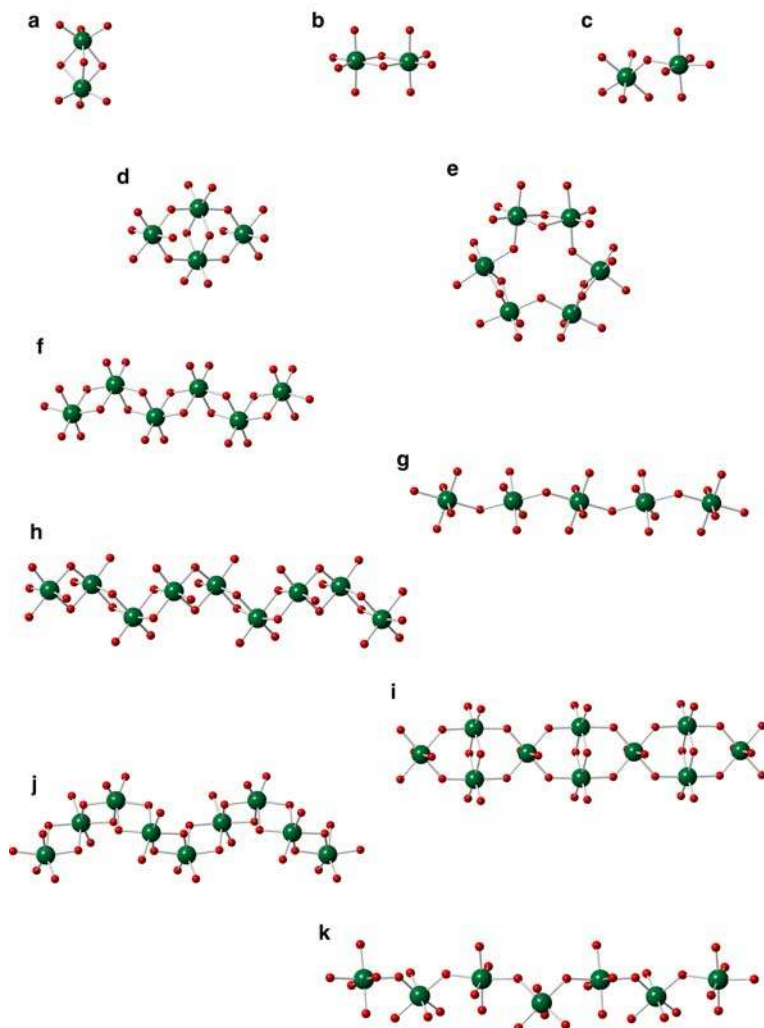


FIG. 13. Finite oligomers and chains containing only  $\text{Te}^{6+}$ . (a) Face-sharing dimer  $\text{Te}_2\text{X}_9$  in  $\text{Ba}_3(\text{Te}_2\text{O}_9)$  (#619); (b) edge-sharing  $\text{Te}_2\text{X}_{10}$  in eckhardite,  $\text{Ca}_2\text{Cu}_2(\text{Te}_2\text{O}_{10}) \cdot 2\text{H}_2\text{O}$  (#639); (c) corner-sharing  $\text{Te}_2\text{X}_{11}$  in schiefelinite,  $\text{Pb}_{10}(\text{Te}_2\text{O}_8(\text{OH})_3)_2(\text{TeO}_2(\text{OH})_4)_2(\text{SO}_4) \cdot 5\text{H}_2\text{O}$  (#642); (d) 'double-triangle' tetramer  $\text{Te}_4\text{X}_{18}$  of  $\text{K}_2(\text{Te}_4\text{O}_8(\text{OH})_{10})$  (#644); (e) cyclo 6-ring  $\text{Te}_6\text{X}_{27}$ , with alternation of edge- and corner-sharing in  $\text{K}_{8.5}(\text{H}_3\text{O})_{0.5}(\text{Te}_6\text{O}_{18}(\text{OH})_9) \cdot 17\text{H}_2\text{O}$  (#645); (f) edge-sharing *zweier* chain  $\text{Te}_2\text{X}_8$  in  $\text{CaTeO}_4$  (#648); (g) corner-sharing *zweier* chain  $\text{Te}_2\text{X}_{10}$  in ottoite,  $\text{Pb}_2(\text{Te}_2\text{O}_{10})$  (#655); (h) helical edge-sharing *dreier* chain  $\text{Te}_3\text{X}_{12}$  in  $\text{Ag}_3(\text{TeO}_4)\text{I}$  (#657); (i) loop-branched *zweier* chain of 'double-triangle' clusters  $\text{Te}_3\text{X}_{12}$  in  $\text{K}_2(\text{Te}_3\text{O}_8(\text{OH})_4)$  (#658); (j) helical edge-sharing *vierer* chain  $\text{Te}_4\text{X}_{16}$  in  $\text{Li}_2(\text{TeO}_4)$  (#662); (k) corner-sharing *vierer* chain  $\text{Te}_4\text{X}_{20}$  in housleyite,  $\text{Pb}_6\text{Cu}(\text{Te}_4\text{O}_{18}(\text{OH})_2)$  (#663).

$\text{Li}_2\text{Te}_2\text{O}_5$  (#351) has all apices oriented in the same direction, similar to the micas.

The trigonal  $\text{Te}_3\text{X}_7$  sheet of Fig. 11h has CN2 oxygen atoms linking Te into 3-rings and additional CN3 oxygen atoms forming 6-rings ( $\text{Q}^{1210}$  configuration); note that the hybrid double chain of Fig. 10b is actually a slice of this structure.

Figure 11i shows a  $\text{Te}_4\text{X}_{10}$  sheet with 4- and 8-rings, which again is strongly analogous to a well-known silicate structure, apophyllite (Colville *et al.*, 1971). The isomeric  $\text{Te}_4\text{X}_{10}$  structures of Figs 11j and 11k both have all Te 4-coordinated, but in 10-rings only, which requires some Te to link to only two others rather than three, and hence, for

some edges to be shared. In Fig. 11*j*, the edge-sharing Te are  $Q^{1301}$  and the others  $Q^{1300}$ , while in Fig. 11*k*, the edges are shared by  $Q^{0401}$  polyhedra and the others are  $Q^{2200}$ . The isomeric pair of  $Te_8X_{18}$  alkali tellurite sheets in Figs 11*l* and 11*m* have no shared edges, but both have  $\frac{1}{4}$  of the Te in CN3 rather than CN4. The Te form 6-rings which contain one or two CN3 cations in Fig. 11*l*, but zero or two CN3 cations in the pseudohexagonal sheet of Fig. 11*m*. The much more complex and highly convoluted  $Te_{16}X_{36}$  sheet of Fig. 11*n* has Te in 3-, 4- and 5-coordination, making 3-, 4- and 12-rings. The CN5 Te occur in edge-sharing pairs. Finally, Fig. 11*o* shows an extraordinarily complex sheet made by  $Q^{2200}$  Te cross-linking elliptical tubes which have 4-, 7- and 8-rings of CN4 Te.

Analogously to the case for chains, a phyllo-tellurate has a double layer if deletion of selected Te–O bonds can separate it into two distinct sublayers which themselves remain continuous. Our dataset contains two types of double layer, as seen in Table 5 and Fig. 12. The  $Te_6X_{13}$  double layer of Fig. 12*a* has all Te CN = 4, but half of them are  $Q^{1300}$ , sharing corners to form 3-rings, while the other half of the Te are branches off these rings, which share edges ( $Q^{0311}$ ) to link the two sublayers. Oxygen atoms with CN3 link the edge-sharing dimers to complete each of the sublayers. Conversely, the  $Te_6X_{14}$  double layer of Fig. 12*b* has no edge-sharing or CN3 oxygen atoms, but has Te in three different coordination states ( $Q^{0300}$ ,  $Q^{1300}$  and  $Q^{1400}$  configurations). Like many Te–O polymers containing CN5 Te, this thick double layer is braced by additional polyhedra containing other high-charge, low-CN cations ( $Se^{4+}O_3$  in this case).

$Te^{4+}O_n$  polyhedra also form a range of infinite three-dimensional frameworks. Figure 12*c* shows the electrically neutral tetragonal framework of paratellurite,  $TeO_2$ , and its metastable orthorhombic distorted variant  $\gamma$ - $TeO_2$ ; these are polymorphs of tellurite, which has a layered structure of the type seen in Fig. 11*e*. The paratellurite framework is of interest in that it is isopuntal with the low-cristobalite form of  $SiO_2$  (Dollase, 1965), and yet can also be derived from the structure of rutile (and the dense stishovite form of silica) by deformation of coordination octahedra  $TeO_6 \rightarrow TeO_{4+2} \rightarrow TeO_4$ . Note that the  $Q^{0400}$  Te polyhedra are much less symmetrical than  $SiO_4$  tetrahedra. The paratellurite structure is thus a shared hettotype structure that could act as a transition state for diffusionless phase transformations between the low-density/high-temperature structure of high-cristobalite on the

one hand, and the high-pressure stishovite structure on the other, analogous to the transformation mechanisms described in Christy (1993).

Figure 10*d* shows a rare example of  $Te^{4+}$  in  $Q^{0600}$  polyhedra that are nearly regular octahedra, with no lone-pair stereoactivity, and which link to form the pyrochlore framework. The frameworks of Figs 12*e–g* are all closely related, and like that of Fig. 12*d*, have cubic unit cells with  $a \approx 10$  Å; all can ultimately be derived from  $2 \times 2 \times 2$  superstructures of the fluorite type. The  $Te_3X_7$  framework of  $KGa(Te_6O_{14})$  (Fig. 10*e*) is formed when  $\frac{1}{4}$  of the ‘fluorite’ cations are replaced by non-Te species and  $\frac{1}{6}$  of the anions omitted, to make a framework in which Te are in a  $Q^{1210}$  configuration, linked through  $2 \times$  CN2 oxygen atoms and one CN3 oxygen atom. The isomeric cliffordite framework (Fig. 12*f*) has a similar range of oxygen CN and the same  $Pa\bar{3}$  space-group symmetry, but the topology of linkage of the CN2 and CN3 oxygen atoms is different. The structure of the winstanleyite group,  $M^{4+}(Te_3O_8)$ , is a slightly distorted fluorite superstructure in which the Te framework has  $Q^{2020}$  Te linked through two CN3 oxygen atoms only; it can thus be represented as a 3-connected net with CN3 oxygen at the nodes and  $(TeO_2)$  groups decorating the links (Fig. 12*g*).

Figure 12*h* shows a more open tetragonal  $Te_4X_9$  framework in which half the Te cations are  $Q^{0400}$ , forming  $Te_4O_{12}$  rings which are arranged on a  $D$  lattice complex (Fischer and Koch, 2006), analogous to the Ti atoms in anatase ( $TiO_2$ ; Howard *et al.*, 1991) or Ca in scheelite ( $CaWO_4$ ; Zalkin and Templeton, 1964). These Te atoms are linked to form a framework through pairs of  $Q^{2200}$  Te atoms, making additional 4-rings. The  $Te_5X_{11}$  framework of  $Pb(Te_5X_{11})$  is even more open (Fig. 12*i*). This structure has five distinct types of Te, all CN4, but in four distinct Q states. Te1 ( $Q^{0222}$ ) and Te3 ( $Q^{0401}$ ) form edge-sharing tetramers  $Te3 = Te1 = Te1 = Te3$ , while  $Q^{1210}$  Te2 links to Te3 of one tetramer and through CN3 oxygen to both Te1 of the next, so that Te1, Te2 and Te3 form continuous chains of 6-rings which run  $\parallel x$  and lie in layers  $\parallel (001)$ . Between these layers and cross-connecting them are corner-sharing chains running  $\parallel y$  of  $Q^{1300}$  Te4 and Te5, where the chain backbones  $-Te4-O-Te5-O-$  have an asymmetrical crankshaft geometry, very similar to that of the Pb–O chains in massicot (Hill, 1985). Connections are so sparse that the smallest rings to include Te4 or Te5 have eight and ten members.

As noted above, the stereochemistry of  $Te^{6+}$  is much less diverse than that of  $Te^{4+}$ , so the range of

TABLE 6.  $\text{Te}_n\text{O}_n$  complexes with  $\text{Te}^{6+}$  only, found in the current study. ' $M$ ' = another CN6 cation in solid solution with Te.

Class	Stoichiometry	Descriptive notes	Figure #	Structural unit heteropolymerization	Structure #
neso	$\text{TeX}_4$	tetrahedral	4e	none	432, 434
	$\text{TeX}_5$	trigonal bipyramidal	4f	none	433–434
	$\text{TeX}_6$	octahedral	4g	none, clusters, chains, layers, frameworks	375–431 ( $\text{Te}(\text{OH})_6$ adducts) 435–618 ( $\text{TeX}_6$ anions)
soro	$\text{Te}_2\text{X}_6$	( $\text{O} \equiv \text{O}$ )	13a	none	619–620
	$\text{Te}_2\text{X}_{10}$	( $\text{O} = \text{O}$ )	13b	none, chains, layers, frameworks	621–641
	$\text{Te}_2\text{X}_{11}$	( $\text{O}-\text{O}$ )	13c	none	642–643
cyclo	$\text{Te}_4\text{X}_{18}$	'double triangle'	13d	none	644
	$\text{Te}_6\text{X}_{27}$	6-ring with alternating corner- and edge-sharing	13e	none	645
ino	$\text{Te}_2\text{X}_8$	edge-sharing	13f	none	646–652
	$\text{Te}_2\text{X}_{10}$	corner-sharing	13g	none, framework	653–656
	$\text{Te}_3\text{X}_{12}$	edge-sharing	13h	none	657
	$\text{Te}_3\text{X}_{12}$	loop-branched zweier	13i	none, layers	658–661
	$\text{Te}_4\text{X}_{16}$	edge-sharing	13j	none	662
	$\text{Te}_4\text{X}_{20}$	corner-sharing	13k	none	663
phylo	$(\text{Te}_2M)\text{X}_3$	edge-sharing, 6-rings (cation CN octahedral)	14a	layers	664–666
	$(\text{Te}_2M)\text{X}_3$	edge-sharing, 6-rings (cation CN trigonal prismatic)	14b	layers	667
tecto	$\text{TeX}_4$	corner-sharing, 4-rings	14c	none, framework	668–670
	$\text{TeX}_{14}$	corner-sharing, 8-rings	14d	none	671
	$(\text{Te}_2M)\text{X}_2$	distorted rutile ( $\text{VO}_2$ ) type	14e	none	672–673
	$\text{TeX}_3$	distorted $\text{ReO}_3$ ( $\text{FeF}_3$ ) type	14f	none	674
	$\text{TeX}_7$	weberite type	14g	none	675–676
	$(\text{Te}_2M)_4\text{X}_{12}$	edge- and corner-sharing	14h	none	677



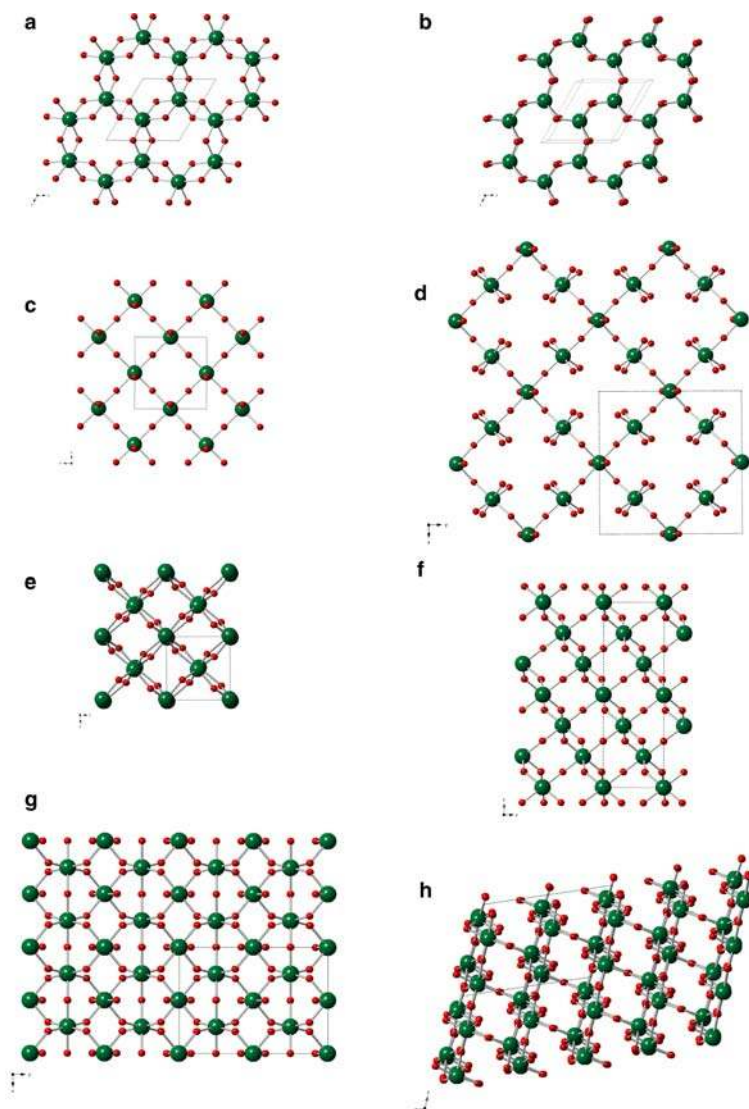


FIG. 14. Layers and frameworks containing only  $\text{Te}^{6+}$ . (a) Edge-sharing octahedral  $(\text{Te,Fe})\text{X}_3$  layer in burckhardtite,  $\text{Pb}_3(\text{Fe}^{3+}\text{Te}^{6+}\text{O}_6)(\text{AlSi}_3\text{O}_8)$  (#666); (b) edge-sharing trigonal prismatic  $(\text{Te,Mn})\text{X}_3$  layer in  $\text{Sr}(\text{Mn}^{4+}\text{Te}^{6+}\text{O}_6)$  (#667); (c) corner-sharing  $\text{TeX}_4$  layer in  $\text{Bi}_2(\text{TeO}_4)\text{O}_2$  (#669); (d) chiolite-type layer  $\text{Te}_3\text{X}_{14}$  of  $\text{Ca}_5(\text{Te}_3\text{O}_{14})$  (#671); (e) distorted rutile framework  $(\text{Te,Ni})\text{X}_2$  of  $(\text{Ni}^{2+}\text{Te}^{6+})\text{O}_4$  (#673); (f)  $\text{FeF}_3$  (collapsed  $\text{ReO}_3$  type) framework of  $\text{TeO}_3$  (#674); (g) weberite-type framework  $\text{Te}_2\text{X}_7$  of  $\text{Na}_2(\text{Te}_2\text{O}_7)$  (#675); (h) strongly layered  $(\text{Te,Fe})_4\text{X}_{12}$  framework with edge-sharing in  $\text{Pb}_3(\text{Fe}_2^{3+}\text{Te}_2^{6+}\text{O}_4)$  (#677).

polymeric complexes is also more restricted. Table 6 shows that the tetrahedral  $\text{TeO}_4^{2-}$  anion (Fig. 4e) and bipyramidal  $\text{TeO}_5^{4-}$  (Fig. 4f) occur in only three structures altogether, one of which contains both of them. Conversely, octahedral complexes  $\text{TeX}_6$  (Fig. 4h) are extremely common. The neutral ‘orthotelluric acid’ molecule  $\text{Te}(\text{OH})_6$ ,

with its ability to make a profusion of hydrogen bonds, is the defining Te species in 59 structures, while no less than 182 have less protonated octahedral anions as their most complex Te complex. Thus, isolated  $\text{TeX}_6$  octahedra are the most complex Te complex in about one third of the total database. Only five types of finite oligomer are

TABLE 7.  $\text{Te}_m\text{O}_n$  monomers and finite polymers with mixed  $\text{Te}^{4+}$  and  $\text{Te}^{6+}$  found in the current study, classified by the most complex Te anion type.

Class	Stoichiometry	Descriptive notes	Fig.#	Structural unit heteropolymerization	Structure #
neso	$\text{Te}^{6+}\text{X}_6$	+ separate $\text{Te}^{4+}\text{X}_3$		framework	678
ino	$(\text{MTe}^{4+})\text{Te}^{6+}\text{X}_8$	loop-branched <i>zweier</i> (double triangles)	15a	none	679
	$\text{Te}^{4+}\text{Te}_2^{6+}\text{X}_{11}$	loop-branched <i>zweier</i> (3-rings)	15b	none	680
	$\text{Te}_2^{4+}\text{Te}_2^{6+}\text{X}_{12}$	loop-branched <i>zweier</i> (3-rings)	15c	none	681
phyllo	$\text{Te}^{4+}\text{Te}^{6+}\text{X}_6$	corner-sharing, 3-rings and 4-rings	15d	none	682–684
	$\text{Te}^{4+}\text{Te}_2^{6+}\text{X}_6$	corner-sharing, 3-rings and 5-rings	15e	none	685
	$\text{Te}^{4+}\text{Te}^{6+}\text{X}_6$	double triangles, 8-rings	15f	none	686
	$\text{Te}^{4+}\text{Te}_2^{6+}\text{X}_6$	double triangles, 4-rings	15g	none	687
	$\text{Te}^{4+}\text{Te}^{6+}\text{X}_7$	6-rings	15h	layers, frameworks	688–694
	$\text{Te}_3^{4+}\text{Te}^{6+}\text{X}_9$	3-, 4- and 6-rings	15i	none	695
	$\text{Te}^{4+}\text{Te}^{6+}\text{X}_5$		16a	none	696
tecto	$\text{Te}_2^{4+}\text{Te}^{6+}\text{X}_8$	$\text{Te}^{6+}$ linked by edge-sharing dimers of $\text{Te}^{4+}$	16b	none	697
	$\text{Te}_2^{4+}\text{Te}^{6+}\text{X}_8$	cross-linked chains of double triangles	16c	none	698
	$\text{Te}_2^{4+}\text{Te}_2^{6+}\text{X}_{11}$	kagome $\text{Te}^{6+} + \text{Te}^{4+}$ layers cross-linked by edge-sharing dimers of $\text{Te}^{4+}$	16d	none	699
	$\text{Te}_3^{4+}\text{Te}^{6+}\text{X}_{12}$	ordered pyrochlore framework	16e	none	700
	$\text{Te}_3^{4+}\text{Te}^{6+}\text{X}_{12}$	modified pyrochlore framework	16f	none	701
	$\text{Te}_2^{4+}\text{Te}_3^{6+}\text{X}_{14}$	kagome $\text{Te}^{6+}$ layers cross-linked by edge-sharing dimers of $\text{Te}^{4+}$	16g	none	702
	$\text{Te}_3^{4+}\text{Te}_5^{6+}\text{X}_{23}$	modified pyrochlore framework	16h	none	703

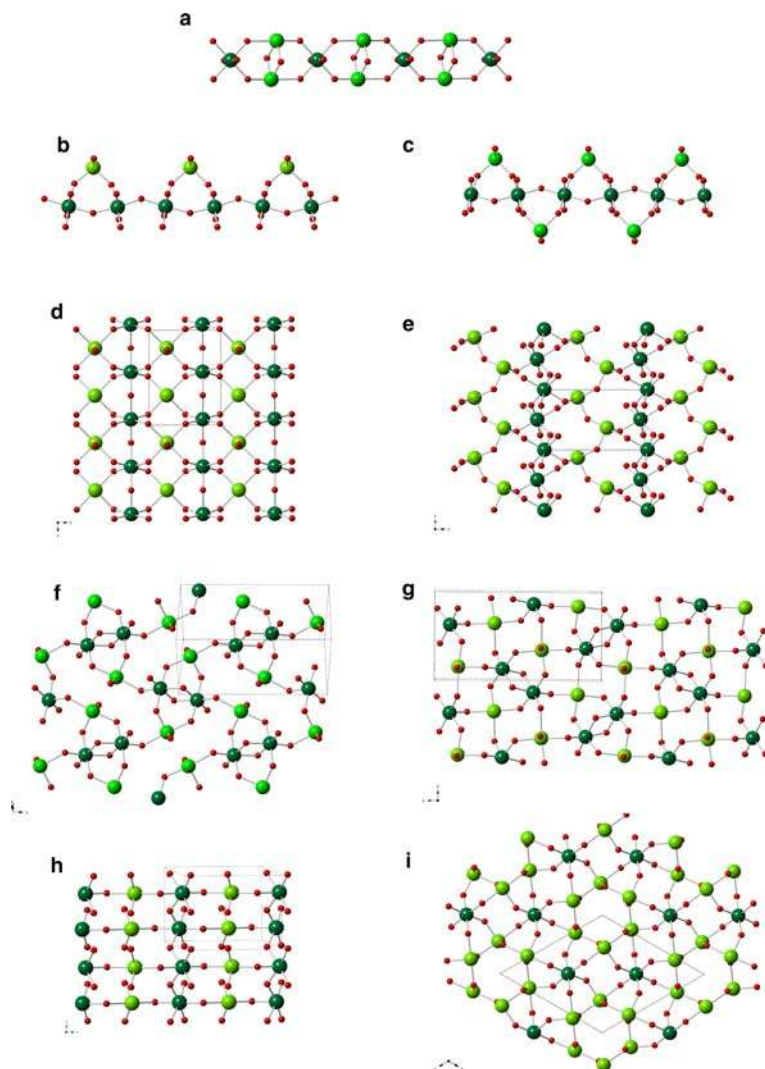


FIG. 15. Te–O chain and layer complexes containing both  $\text{Te}^{4+}$  (light green) and  $\text{Te}^{6+}$  (dark green). (a) Loop-branched *zweier* chain  $(\text{Te}^{4+}, \text{Bi}^{3+})_2\text{Te}^{6+}\text{X}_8$  containing ‘double triangle’ motifs in  $\text{Bi}[(\text{Bi}^{3+}\text{Te}^{4+})\text{Te}^{6+}\text{O}_8]$  (#679); (b) loop-branched *zweier* chain with 3-rings  $\text{Te}^{4+}\text{Te}_2^{6+}\text{X}_{11}$  in  $\text{Cd}_2\text{Te}^{4+}\text{Te}^{6+}\text{O}_7 = \text{Cd}_4(\text{Te}^{4+}\text{Te}_2^{6+}\text{O}_{11})(\text{Te}^{4+}\text{O}_3)$  (#680); (c) loop-branched *zweier* chain with 3-rings  $\text{Te}_2^{4+}\text{Te}_2^{6+}\text{X}_{12}$  in  $\text{Cd}_4(\text{Te}_2^{4+}\text{Te}_2^{6+}\text{O}_{12})(\text{Te}^{4+}\text{O}_3)_2$  (#681); (d) layer with 3- and 4-rings in  $(\text{NH}_4)(\text{Te}^{4+}\text{Te}^{6+}\text{O}_5(\text{OH}))$  (#682); (e) layer  $\text{Te}^{4+}\text{Te}^{6+}\text{X}_6$  with  $\text{Te}^{4+}$  and  $\text{Te}^{6+}$  making 3- and 5-rings in  $\text{Te}^{4+}\text{Te}^{6+}\text{O}_4(\text{OH})_2$  (#685); (f) layer  $\text{Te}^{4+}\text{Te}^{6+}\text{X}_6$  with double-triangle clusters and 8-rings in  $\text{Ag}_2(\text{Te}^{4+}\text{Te}^{6+}\text{O}_6)\text{-I}$  (#686); (g) layer  $\text{Te}^{4+}\text{Te}^{6+}\text{X}_6$  with double-triangle clusters and 4-rings in  $\text{Ag}_2(\text{Te}^{4+}\text{Te}^{6+}\text{O}_6)\text{-III}$  (#687); (h) strongly corrugated layer  $\text{Te}^{4+}\text{Te}^{6+}\text{X}_7$  of 6-rings in  $\text{SrCu}(\text{Te}^{4+}\text{Te}^{6+}\text{O}_7)$  (#688); (i) 6-rings of  $\text{Te}^{4+}$  sharing corners through  $\text{Te}^{6+}$  in  $\text{Te}_3^{4+}\text{Te}^{6+}\text{O}_9$  (#695).

documented. Octahedral dimers may share faces ( $\text{Q}^{3303}\text{Te}_2\text{X}_9$ , Fig. 13a), edges ( $\text{Q}^{4202}\text{Te}_2\text{X}_{10}$ , Fig. 13b) or corners ( $\text{Q}^{5101}\text{Te}_2\text{X}_{11}$ , Fig. 13c). The only larger oligomers are a bicyclic ‘double triangle’ tetramer  $\text{Te}_4\text{X}_{18}$  (Fig. 13d), which is a  $\text{Te}^{6+}$  analogue of the  $\text{Te}^{4+}$  clusters that occur as parts

of more complex polymers in Figs 10f and 10h, and a 6-ring  $\text{Te}_6\text{X}_{27}$  with alternating corner-sharing and edge-sharing of octahedra (Fig. 13e).

Table 6 shows that the variety of infinite  $\text{Te}^{6+}$  chains is similarly limited. Only single chains are known. *Zweier* chains may be edge-sharing  $\text{Te}_2\text{X}_8$

(Fig. 13*f*) or corner-sharing  $\text{Te}_2\text{X}_{10}$  (Fig. 13*g*). Edge-sharing *dreier* chains  $\text{Te}_3\text{X}_{12}$  occur (Fig. 13*h*), as do edge-sharing *vierer*  $\text{Te}_4\text{X}_{16}$  (Fig. 13*j*) and corner-sharing  $\text{Te}_4\text{X}_{20}$  (Fig. 13*k*). Note that the *vierer* periodicity of the latter is determined by having alternation of  $\text{Q}^{2400}$  octahedra with *cis* and *trans* bridging oxygen atoms, a type of variability that does not occur with coordination numbers below 5. Note that all the corner-sharing *zweier* chains of this study have *trans* bridging oxygen atoms. The most complex chain is a loop-branched *dreier*  $\text{Te}_3\text{X}_{12}$  isomer (Fig. 13*i*), which is made by polymerization of the ‘double triangle’ cluster of Fig. 13*d*.

The  $\text{Te}^{6+}$  polyhedra also link to form layers and frameworks, but again, the range of polymer types is restricted relative to that seen for  $\text{Te}^{4+}$ .  $\text{Q}^{0603}$  octahedra share edges to form  $\text{TeX}_3$  sheets with the same topology as those of the  $\text{Al}(\text{OH})_3$  polymorphs, such as gibbsite (Saalfeld and Wedde, 1974; Fig. 14*a*). However, the Te in these octahedra appears always to be in solid solution with another cation of lower valence ( $\text{Fe}^{3+}$ ,  $\text{Ti}^{4+}$ ,  $\text{Mn}^{4+}$  or  $\text{Ge}^{4+}$ ), which gives the layer an overall negative charge. The same is true for the single case where a sheet is formed through edge-sharing of trigonal prisms, rather than octahedra (Fig. 14*b*). Such charge reduction is not necessary when  $\text{Q}^{2400}$  octahedra share corners to form  $\text{TeX}_4$  sheets with 4-rings (Fig. 14*c*). The most complex tellurate layer type has corner-sharing of  $\text{Q}^{2400}$  and  $\text{Q}^{4200}$  octahedra to form a layer with overall stoichiometry  $\text{Te}_3\text{X}_{14}$  (Fig. 14*d*), with the same topology as that seen in chiolite,  $\text{Na}_5(\text{Al}_3\text{F}_{14})$  (Jacoboni *et al.*, 1981).

Long-range disorder is shown by  $\text{Te}^{6+}$  with lower-valence cations again in  $\text{MTeO}_4$  tellurates with a monoclinically distorted  $(\text{Te},\text{M})\text{X}_2$  rutile framework, containing  $\text{Q}^{0062}$  octahedra (Fig. 14*e*). Here, disordered substitution with low-valence cations results in electroneutrality of the framework. Further analogies between Te–O and Al–F frameworks are provided by the rhombohedrally distorted  $\text{ReO}_3$  structure of  $\text{TeO}_3$  itself (Fig. 14*f*), collapsed so that the oxygen atoms approximate hexagonal close packing, which is shared with a polymorph of  $\text{AlF}_3$  (Daniel *et al.*, 1990), and the  $\text{Te}_2\text{X}_7$  framework of Fig. 14*g*, which is that of weberite,  $\text{Na}_2(\text{MgAlF}_7)$  (Knop *et al.*, 1982). The weberite framework contains many 3- and 6-rings, similar to the pyrochlore framework of Fig. 12*d*, but half of the octahedra are not  $\text{Q}^{0600}$ , but are instead partly depolymerized to  $\text{Q}^{2400}$ , which allows extra anions to be included. The unique  $\text{Te}_4\text{X}_{12}$  framework of Fig. 14*h* also contains many 3- and 6-rings (as well as 4- and 8-rings), but there is also some

edge-sharing: half the octahedra are  $\text{Q}^{0601}$  and the other half  $\text{Q}^{0602}$ . In this framework, dense zigzag columns  $\parallel z$  share polyhedral edges in the *y* direction to define layers, which in turn are linked into a framework via relatively sparse Te–O–Te bridges. Again, this particular structure has Te mixed with another cation ( $\text{Fe}^{3+}$ ) on all the octahedral sites, in order to give it an overall negative charge.

Last, we consider the 26 structures of the present study which contain both  $\text{Te}^{4+}$  and  $\text{Te}^{6+}$ . Only one of these structures (#675) has separate  $\text{Te}^{4+}$  and  $\text{Te}^{6+}$  polyhedra which are not linked by strong bonds. In all the rest, ino, phyllo or tecto polymers contain Te in both valence states. Given their different stereochemical preferences,  $\text{Te}^{4+}$  and  $\text{Te}^{6+}$  are always ordered on distinct sites. The three types of chains are all only *zweier* in backbone periodicity, but nevertheless, display other complexities. In Fig. 15*a*,  $\text{Te}^{4+}$  and  $\text{Bi}^{3+}$  are disordered in pairs of edge-sharing  $\text{Q}^{0401}$  polyhedra, which are linked through  $\text{Q}^{2400}$   $\text{Te}^{6+}$  to make a chain of ‘double triangles’. Figures 15*b* and *c* show chains in which  $\text{Q}^{2400}$   $\text{Te}^{6+}$  backbones are decorated by  $\text{Q}^{2200}$   $\text{Te}^{4+}$  to make 3-rings. Again, Cd demonstrates a tendency to be associated with structurally complex anions (cf. Fig. 10*b* and *h*). Figure 15*d* shows a relatively common type of  $\text{Te}^{4+}\text{Te}^{6+}\text{X}_6$  layer (four examples known) in which  $\text{Q}^{1400}$   $\text{Te}^{4+}$  and  $\text{Q}^{0600}$   $\text{Te}^{6+}$  share corners to 3- and 4-rings. Other isomeric layers with the same stoichiometry are seen in Figs 13*e–g*. The layer of Fig. 15*e* features *zweier* chains of  $\text{Q}^{2400}$   $\text{Te}^{6+}\text{O}_6$ . Unlike the *zweier*  $\text{Te}^{6+}$  chains of Fig. 13*g*, these strongly zigzag chains are *cis*-bridged. They are linked through massicot-like chains (cf. Hill, 1985) of  $\text{Q}^{0400}$   $\text{Te}^{4+}\text{O}_4$ , to form 3- and 5-rings; the 3-rings on the  $\text{Te}^{6+}$  backbone form a loop-branched chain resembling that of Fig. 15*c*. The topologies of Figs 15*f* and 15*g* both feature edge-sharing between  $\text{Te}^{6+}$  octahedra to produce ‘double triangle’ clusters, but differ in coordination number of  $\text{Te}^{4+}$ , numbers of non-bridging oxygen atoms on  $\text{Te}^{6+}$ , and ring sizes in the layers. Note that the positions of  $\text{Te}^{6+}$  and  $\text{Te}^{4+}$  in the ‘double triangles’ are reversed here, relative to the chain of Fig. 15*a*. Figure 15*f* has  $\text{Q}^{1300}$   $\text{Te}^{4+}$  and  $\text{Q}^{1501}$   $\text{Te}^{6+}$  with 8-rings between the clusters, while Fig. 15*g* has  $\text{Q}^{1400}$   $\text{Te}^{4+}$ ,  $\text{Q}^{0601}$   $\text{Te}^{6+}$  and 4-rings. One compound,  $\text{Ag}_2(\text{Te}^{4+}\text{Te}^{6+}\text{O}_6)$ , has three polymorphs ‘I’, ‘II’ and ‘III’, displaying, respectively, the topologies of Fig. 15*f*, *d* and *g* (#686, 684 and 687). The most popular type of mixed-valence layer, with seven examples, is the  $\text{Te}^{4+}\text{Te}^{6+}\text{X}_7$  topology of Fig. 15*h*. Here again, zigzag *cis*-bridged chains of  $\text{Te}^{6+}$  ( $\text{Q}^{2400}$ ) are

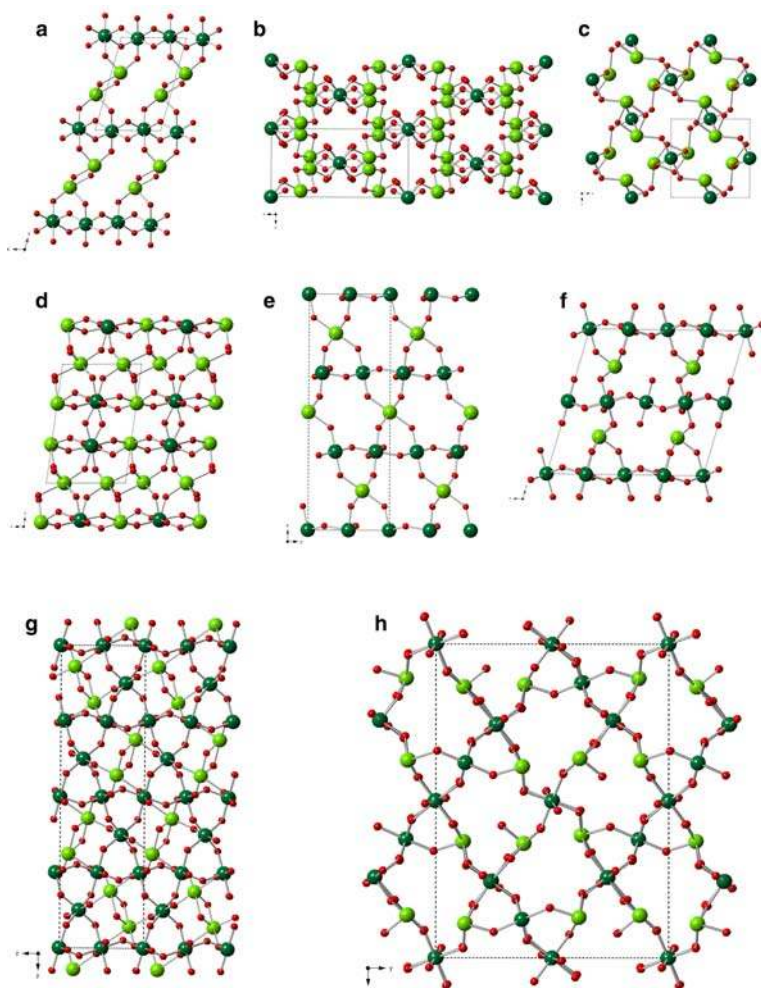


FIG. 16. Te–O frameworks containing both  $\text{Te}^{4+}$  and  $\text{Te}^{6+}$ . (a) Framework of  $\text{Te}^{4+}\text{Te}^{6+}\text{O}_5$  (#696). (b)  $\text{Te}_2^{4+}\text{Te}^{6+}\text{X}_8$  in carlfriesite,  $\text{Ca}(\text{Te}_2^{4+}\text{Te}^{6+}\text{O}_8)$  (#697); (c)  $\text{Te}_2^{4+}\text{Te}^{6+}\text{X}_8$  in  $\text{Sr}(\text{Te}_2^{4+}\text{Te}^{6+}\text{O}_8)$ , viewed down chains of double triangles (#698); (d)  $\text{Te}_2^{4+}\text{Te}^{6+}\text{X}_{11}$  in  $\text{Ag}_2(\text{Te}_2^{4+}\text{Te}^{6+}\text{O}_{11})$  (#699); (e) ordered pyrochlore framework  $\text{Te}_3^{4+}\text{Te}^{6+}\text{X}_{12}$  in  $\text{Cs}_2(\text{Te}^{4+}\text{Te}^{6+}\text{O}_{12})$  (#700); (f) sheared and depolymerized pyrochlore framework  $\text{Te}_3^{4+}\text{Te}^{6+}\text{X}_{12}$  in  $\text{K}_2(\text{Te}^{4+}\text{Te}^{6+}\text{O}_{12})$  (#701); (g)  $\text{Te}_2^{4+}\text{Te}^{6+}\text{X}_{14}$  framework in  $(\text{Na}_{1.6}\text{Ag}_{0.4})(\text{Te}_2^{4+}\text{Te}^{6+}\text{O}_{14})$ , emphasizing kagome layers (#702); (h) modified pyrochlore framework  $\text{Te}_3^{4+}\text{Te}^{6+}\text{X}_{23}$  of  $\text{Rb}_4(\text{Te}_3^{4+}\text{Te}^{6+}\text{O}_{23})$  (#703).

connected through  $\text{Te}^{4+}$  ( $\text{Q}^{2200}$ ), but the two non-bridging ligands on both types of cation give a greater  $X/\text{Te}$  ratio. The strong nonplanarity of the layer and small O–Te–O angles allow four 6-rings to meet at each  $\text{Te}^{6+}$ , in contrast to the three 6-rings meeting at each node in the more familiar mica-type layer (Fig. 11g). In Fig. 15i, a layer of stoichiometry  $\text{Te}_3^{4+}\text{Te}^{6+}\text{X}_9$  is formed by 6-rings of  $\text{Q}^{0400}$   $\text{Te}^{4+}$  linked through  $\text{Q}^{0600}$   $\text{Te}^{6+}$  to make a sheet with additional 3- and 4-rings.

All the mixed-valence framework compounds have unique structures, although some of them are closely related to one another. In particular, most of them contain component layers with the well-known ‘hexagonal tungsten bronze’ or ‘kagome’ topology (O’Keeffe and Hyde, 1996), where 3- and 6-rings alternate around each node of the net in the order 3.6.3.6. Figure 16a shows the framework of  $\text{Te}^{4+}\text{Te}^{6+}\text{O}_5$ , in which corner-sharing layers (similar to Fig. 14c) of  $\text{Q}^{0600}$   $\text{Te}^{6+}$  are cross-linked via



corner-sharing massicot-like chains of  $Q^{0400} Te^{4+}$ ; cross-linkage produces 3-rings, as so often is seen in tellurate polymers. In carlfriesite,  $Ca(Te_2^{4+}Te^{6+}O_8)$ ,  $Q^{2400} Te^{6+}$  are cross-linked through edge-sharing dimers of  $Q^{0401} Te^{4+}$  to make a trellis-like, nanoporous framework (Fig. 16b). The isomeric framework of  $Sr(Te_2^{4+}Te^{6+}O_8)$  is also zeolite-like, but is formed by cross-linkage of chains similar to those of Fig. 15a, made from 'double-triangle' clusters containing  $Q^{0600} Te^{6+}$  and edge-sharing dimers of  $Q^{0501} Te^{4+}$  (Fig. 15c). Figure 16d shows another rather open framework of stoichiometry  $Te_2^{4+}Te_2^{6+}X_{11}$ , in which  $Q^{0500} Te^{4+}$  and  $Q^{0600} Te^{6+}$  define layers with a pseudohexagonal kagome net.  $Te^{6+}-O-Te^{6+}$  bridges link pairs of such layers, producing ladder-like double chains of  $Te^{6+}$ . Layer pairs are, in turn, linked into a framework through pairs of edge-sharing  $Q^{0501}$  polyhedra. Kagome layers are also found in the  $Te_3^{4+}Te_6^{6+}X_{12}$  framework of Fig. 16e, which is that of pyrochlore and, thus, contains kagome nets in four different orientations. The framework, ideally cubic in symmetry, is rhombohedrally distorted as a result of  $Te^{4+}-Te^{6+}$  ordering. Like Fig. 12d, this is a rare example of  $Te^{4+}$  in octahedral coordination, with no evidence of a stereoactive lone pair: all Te cations are  $Q^{0600}$ . The K analogue of the Cs compound of Fig. 16e has the modified pyrochlore framework shown in Fig. 16f. Monoclinic shear of the structure is accompanied by breaking of some  $Te^{4+}-O-Te^{6+}$  links, so that  $Te^{4+}$  is now  $Q^{0500}$  (with a stereoactive lone pair) and one-sixth of the  $Te^{6+}$  are  $Q^{2400}$ . Kagome nets are also a major feature of the  $Te_2^{4+}Te_3^{6+}X_{14}$  framework in Fig. 14g, where the  $Q^{0600} Te^{6+}$  form such layers, which are cross-linked via pairs of edge-sharing  $Q^{5001} Te^{4+}$ . As for the framework of Fig. 16d, the cross-linkage produces additional 3- and 4-rings. The orthorhombic  $Te_3^{4+}Te_5^{6+}X_{23}$  framework is yet another modification of the pyrochlore type, in which the lone pairs of  $Te^{4+}$  are accommodated by breaking some  $Te^{4+}-O-Te^{4+}$  links, with complete elimination of  $1/24$  of the oxygens. The ordering pattern of  $Te^{4+}$  and  $Te^{6+}$  is quite different from those of Figs 16d and 16e. Kagome layers are preserved in two orientations, but are not exclusively  $Q^{0600} Te^{6+}$ : alternate layers have  $1/6$  or  $1/3$  of their cations  $Q^{0500} Te^{4+}$ .

## Descriptions of individual structures

### Finite $Te^{4+}-O$ complexes

Our descriptions of individual structures begin with those that contain finite  $Te^{4+}-O$  complexes (neso,

soro and cyclo tellurites), **#1–280**. The various topologies that occur are summarized in Table 1 and depicted in Figs 4 and 8.

### Structures with monomeric $Te^{4+}O_3$ , no larger structural unit, and no other anions or water

Structures **#1–24** are listed in Table 8 (deposited), along with their full references. In  $Li_2[TeO_3]$  (**#1**), helical columns of edge-sharing  $LiO_4$  tetrahedra  $\parallel x$  are cross-linked into layers  $\parallel (002)$ , with  $TeO_3$  pyramids bracing the layers. Layers are held together only through weak  $Te \cdots O$  interactions across the interlayer.

$Na_2[TeO_3]$  and  $Ag_2[TeO_3]$  (**#2–3**) have a monoclinic  $\sqrt{2} \times 3 \sqrt{2} \times 1$  superstructure of the rocksalt type, with the Te coordination environment distorted to give only three close neighbours.  $Tl_2[TeO_3]$  (**#4**) has an orthorhombic  $3 \times 2 \times 1$  superstructure of rocksalt with a different cation ordering pattern. Short bonds form  $-Te-O-Tl-O-Tl-O-$  chains  $\parallel x$ , with a crankshaft shape reminiscent of the Pb–O chains in the massicot form of PbO; such chains recur frequently in the structures of the present study, as noted above. Both Tl and Te have stereoactive lone pairs and only three close oxygen neighbours, making the structure strongly layered  $\parallel (020)$ .  $AgTl[TeO_3]$  (**#5**) has similar cell dimensions but a different cation ordering pattern and space group. Again, the structure is layered, but this time  $\parallel (200)$ .

$K_2[TeO_3]$  and  $Cs_2[TeO_3]$  (**#6–7**) have nearly-identical structures that are both oxygen-stuffed derivatives of the  $Ni_2In$  type; they are therefore  $TeO_3^{2-}$  analogues of the high-temperature  $K_2SO_4$  structure (O'Keeffe and Hyde, 1985). The alkali cations are in 6–9 coordination.  $Rb_2[TeO_3]$  (**#8**) appears to have a slight monoclinic distortion of the same structure, although the refinement is of poor quality.

$Ca[TeO_3]$  and  $Sr[TeO_3]$  both occur in a large number of polymorphs with large unit cells and low symmetry (**#9–15**). All structures are packings of  $(Ca,Sr)O_{6-8}$  polyhedra containing tunnels, with  $TeO_3$  groups bracing the sides and the tunnels and lone pairs pointing into the central space. The two forms of  $Ba[TeO_3]$  are quite different. One of them (**#16**) has the simple monoclinic structure of  $KClO_3$  (Bats, 1978); the Ba and Te substructure resembles the CrB/TlI type (Helmholtz, 1936), and Ba is in  $7+2$  coordination by oxygen.  $BaTeO_3$  is thus an oxygen-stuffed analogue of TlI, in the same way that baryte,  $BaSO_4$ , is an oxygen-stuffed derivative of the closely related FeB structure (O'Keeffe and



Hyde, 1985). The other dimorph (#17) has an approximately cubic close-packed (*ccp*) array of Ba + Te but a very complex ordering pattern, with Ba in 8–10 coordination.

There are also two synthetic polymorphs with known structures for Pb[TeO<sub>3</sub>]; interestingly, these appear to be distinct from the two mineral species of this composition, triclinic fairbankite (Williams, 1979) and orthorhombic plumbotellurite (Spiridonov and Tananeyva, 1982), both of which remain poorly characterized. The tetragonal form (#18) has a structure very similar to that of scheelite (CaWO<sub>4</sub>) but with ¼ of the oxygens removed in an ordered fashion. The coordination numbers are 6 and 3 for Pb and Te, as opposed to 8 and 4 for Ca and W. The lone pairs of both Pb<sup>2+</sup> and Te<sup>4+</sup> are directed into tunnels running || *z*. The more complex monoclinic structure of #19 has a framework of PbO<sub>4-6</sub> and TeO<sub>3</sub>, again with tunnels (this time || *y*) which act as micelles to contain the lone pairs.

Cd[TeO<sub>3</sub>] (#20) has Te filling interstices in an edge-sharing framework of irregular CdO<sub>6</sub> polyhedra. Sc<sub>2</sub>[TeO<sub>3</sub>]<sub>3</sub> (#21) has edge-sharing layers of ScO<sub>6-7</sub> polyhedra || (020), which are bridged by Te. In Ce<sup>4+</sup>[TeO<sub>3</sub>]<sub>2</sub> (#22), zigzag chains of edge-sharing CeO<sub>8</sub> are linked into a framework by Te. The Th and Pu analogues (#23–24) are isostructural.

#### *Structures with monomeric Te<sup>4+</sup>O<sub>3</sub> and no larger structural unit, but with additional anions or water*

Structures #25–46 are listed in Table 9 (deposited), along with their full references. In Li<sub>3</sub>[TeO<sub>3</sub>](OH) (#25), LiO<sub>3</sub>OH tetrahedra and TeO<sub>3</sub> pyramids form honeycomb-like double layers || (100), which are held together only by long Te··O and lone-pair interactions. Thus, the structure resembles that of the chemically similar but anhydrous phase #1. Na<sub>2</sub>[TeO<sub>3</sub>] · 5H<sub>2</sub>O (#26) has three types of Na. Face-sharing trimers (H<sub>2</sub>O)<sub>2</sub>NaI ≡ (H<sub>2</sub>O)<sub>3</sub> ≡ Na2 ≡ (H<sub>2</sub>O)<sub>3</sub> ≡ NaI(H<sub>2</sub>O)<sub>2</sub> share corners with each other and with square-planar Na3(H<sub>2</sub>O)<sub>2</sub>O<sub>2</sub> to form a very open hydrogen-bonded framework in which TeO<sub>3</sub> is only loosely held. KNa[TeO<sub>3</sub>] · 3H<sub>2</sub>O (#27) has a denser, simpler structure with K(H<sub>2</sub>O)<sub>6</sub>O<sub>3</sub> and Na(H<sub>2</sub>O)<sub>3</sub>O<sub>3</sub> polyhedra sharing faces. The arrangement of K, Na and Te is a threefold ordering of the primitive hexagonal net, so this can be regarded as an O/H<sub>2</sub>O-stuffed derivative of that archetype. The same is also true of K<sub>2</sub>[TeO<sub>3</sub>] · 3H<sub>2</sub>O (#28), although the oxygen positions there are adjusted to give 8–13 coordination. Note that the anhydrous analogue (#6) is

derived by oxygen-stuffing of a different but equally simple hexagonal arrangement of cations.

MgTeO<sub>3</sub> · 6H<sub>2</sub>O ≡ [Mg(H<sub>2</sub>O)<sub>6</sub>][TeO<sub>3</sub>] (#29) has a rhombohedral structure with angle  $\alpha_{rh} = 97.4^\circ$ . It can be regarded as a derivative of the CsCl type, in which Cs<sup>+</sup> and Cl<sup>−</sup> anions are replaced by [Mg(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup> and [TeO<sub>3</sub>]<sup>2−</sup> complexes. As the lone pairs of the Te cations all point in the same direction along *z*, the structure is polar and ferroelectric, with point group *R3*. The structure of Sr[TeO<sub>3</sub>] · H<sub>2</sub>O (#30) is centrosymmetric but strongly anisotropic, with edge-sharing SrO<sub>6</sub>(H<sub>2</sub>O) polyhedra defining layers || (100). The layers are held together via H-bonds and Te lone-pair/secondary bonding interactions. Ba[TeO<sub>3</sub>] · H<sub>2</sub>O (#31) is isostructural, although with *x* and *z* directions exchanged.

The structures of A<sub>3</sub><sup>2+</sup>[TeO<sub>3</sub>]<sub>2</sub>X<sub>2</sub> (*A* = Sr or Ba; *X* = Cl or Br) have a large (*a* ≈ 16 Å) cubic unit cell with the same space group *Fd3m* as diamond (#32–34). Clusters [Sr<sub>6</sub>Te<sub>4</sub>O<sub>12</sub>]<sup>4+</sup> can be distinguished, in which Sr are at the vertices of an octahedron, linked by O along the octahedral edges, and braced by Te above four out of the eight octahedral faces. These clusters are arranged in the same fashion as the C atoms of diamond, and Sr<sub>3</sub> triangles of neighbouring clusters face each other to define a second type of octahedron between them. Halide anions centre both types of octahedron, and also occur in the largest remaining interstices of the structure with six Sr arranged in an almost planar hexagon at 3.6–4.4 Å and six Te above and below the plane at 3.3–3.8 Å. The structure can be regarded as a derivative of the pyrochlore type, with *X* replacing CN8 and CN6 cations of pyrochlore and *A* replacing the framework anions of pyrochlore. Pb<sub>3</sub>[TeO<sub>3</sub>]Cl<sub>4</sub> (#35) is quite different, in that one tellurate oxygen is tetrahedrally coordinated OTePb<sub>3</sub> and the others triangularly coordinated OTePb<sub>2</sub> to make a rod [Pb<sub>3</sub>TeO<sub>4</sub>]<sup>4+</sup> running || *z*. The rod has a rhombic cross-section with the Pb cations (bonded to only 2 or 3 oxygen atoms) on the exterior, and are arranged in a herringbone fashion. They are held together through four crystallographically distinct Cl anions, bonded to 3–5 Pb. Again, the structure is polar due to tilt of all TeO<sub>3</sub> groups in the same sense along the *z* direction.

In Ho[TeO<sub>3</sub>]Cl (#36), Ho<sup>3+</sup> is in pentagonal bipyramidal coordination by five O and two Cl (one apical and one equatorial). The HoO<sub>5</sub>Cl<sub>2</sub> polyhedra form edge-sharing ribbons || *y*, which are again arranged in herringbone fashion but are cross-linked through Te cations. The lone pairs of Te point into well-defined micellar channels that run || *y*, between

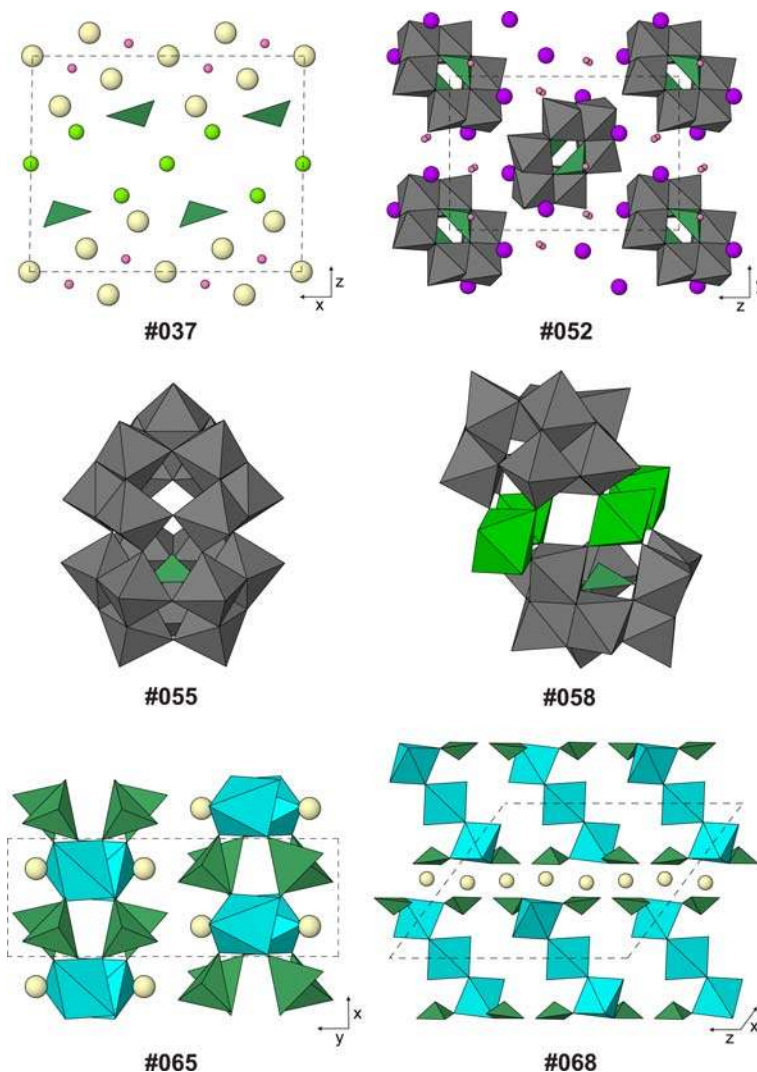


FIG. 17. Examples of structures with monomeric  $\text{TeO}_3$  pyramids that are either weakly bound, or are part of larger structural units that are finite clusters or chains (Tables 9–10, deposited). Small spheres: O (dark pink), when not part of a polyhedron. Medium spheres: Cl (light green). Large spheres: K (purple), rare-earth cations Nd, Dy or Yb (light yellow). Polyhedra: Cu (cyan), Ni (light green), Mo or W (grey) and Te (dark green).

the ribbons.  $\text{Nd}_5[\text{TeO}_3]_2\text{O}_4\text{Cl}_3$  (#37) has three types of  $\text{Nd}^{3+}$  polyhedra:  $\text{NdO}_8$  cubes, irregular  $\text{NdO}_6\text{Cl}$  and  $\text{NdO}_5\text{Cl}_3$  square antiprisms. These form thick layers  $\parallel (001)$ , with  $\text{Cl}^-$  bridging the interlayer regions and Te bracing the outsides of the layers. The  $\text{TeO}_3$  group is canted so that Te makes four long bonds to Cl at 3.19–3.40 Å (Fig. 17).  $\text{Na}_2\text{Lu}_3[\text{TeO}_3]_4\text{I}_3$  (#38) has all the atoms except O in an approximately *ccp* array, with a layer sequence  $(\text{Na}_2\text{Te}_4)$ ,  $\text{Lu}_6$ ,  $(\text{Na}_2\text{Te}_4)$ ,  $\text{I}_6$  alternating

along the *x* direction. Oxygen atoms define nearly-cubic  $\text{LuO}_8$  polyhedra which share edges to form sheets  $\parallel (100)$ . Some oxygen atoms are in tetrahedral coordination ( $\text{OLu}_2\text{NaTe}$ ), while others are displaced away to tetrahedral sites so as to be in nearly plane triangular coordination by  $\text{Lu}_2\text{Te}$ , with a second Te much more distant at 3.15 Å. Thus, the structure can be regarded as a modified superstructure of the fluorite type (the cell parameters correspond to  $2 \times 1 \times 3$  fluorite cubes).

Alternatively, it may be described as a structure in which thick Lu–O sheets are braced by  $\text{Te}^{4+}$ , with  $\text{I}^-$  occupying the interlayer region and  $\text{NaO}_4\text{I}_4$  square antiprisms holding the sheets together.  $\text{Nd}_4\text{Cu}^{1+}[\text{TeO}_3]_5\text{Cl}_3$  (**#39**) has a superficially similar stoichiometry but a quite different structure.  $\text{NdO}_8$ ,  $\text{NdO}_7\text{Cl}$  and  $\text{NdO}_7$  polyhedra share edges to form walls that surround two types of channel running  $\parallel y$ ; large and small channels alternate in a checkerboard fashion. The small channels contain one out of five distinct types of  $\text{TeO}_3$ , which again render the structure polar by all pointing in the same sense along the  $y$  direction. The large channels are lined by the rest of the Te atoms, but still contain enough space to accommodate a zigzag corner-sharing chain  $[\text{Cu}_2\text{Cl}_6]^{4-}$  of  $\text{CuCl}_4$  tetrahedra, held in place by  $\text{Nd3-Cl3}$  links as well as each Cl making two to four long bonds to Te.  $\text{Bi}_2[\text{TeO}_3]_2\text{O}$  (**#40**) has a defect fluorite superstructure (cf. **#38**) with a unit cell corresponding to  $4 \times 1 \times 4$  cubes of fluorite, with  $1/8$  of the anions missing. Overall, Bi + Te form a *ccp* array. They are ordered into columns  $\parallel y$ , with  $1 \times 1$  and rectangular  $2 \times 3$  blocks of Bi separating  $2 \times 1$  and parallelogram-shaped  $2 \times 3$  blocks of Te. If tetrahedral interstices are surrounded by  $\text{Bi}_4$ , then they are occupied by O.  $\text{Bi}_2\text{Te}_2$  tetrahedra have oxygens displaced away from one Te or absent,  $\text{BiTe}_3$  tetrahedra have oxygens linked only to 1 Bi + 1 Te, and  $\text{Te}_4$  tetrahedra are unoccupied. Tellurium lone pairs point along  $\pm y$  for the small Te blocks, but are directed into the interiors of the large blocks, which along with long Bi–O bonds mark the gap between weakly defined thick layers  $\parallel (200)$ . Te2 in this structure is our unique example of ‘2-coordinate’ Te; however, if all Te–O distances out to 3.5 Å are considered, a square-pyramidal coordination polyhedron (Fig. 3e) is defined by oxygens at 1.865, 1.911, 2.519, 2.793 and 3.062 Å. It is possible that the O coordinates are not accurate in this structure, and that the true coordination polyhedron has a narrower spread of bond distances. Smirnite,  $\text{Bi}_2[\text{TeO}_3]_2\text{O}_2$  (**#41**) has yet another defect fluorite superstructure with a unit cell corresponding to  $2 \times 3 \times 1$  fluorite cubes with  $1/6$  of the anions missing, and many of the rest displaced so as to approximate plane triangular coordination by 3Bi or 2Bi + 1Te. The Te atoms are on the outsides of thick layers  $\parallel (100)$ , which are linked only through long  $\text{Bi}\cdots\text{O}$  and  $\text{Te}\cdots\text{O}$  bonds.

In  $\text{Ca}_6[\text{TeO}_3]_5(\text{NO}_3)_2$  (**#42**),  $\text{CaO}_{6-8}$  polyhedra share edges to form undulating layers  $\parallel (100)$  and also bridge these layers into a framework which contains large channels  $\parallel y$ .  $\text{TeO}_3$  pyramids decorate the sides

of these channels, and the channels act as micelles which contain the Te lone pairs and also  $\text{NO}_3^-$  anions. The structure is thus strongly reminiscent of the nitrate-free tellurites **#9–15**.  $\text{Ca}_5[\text{TeO}_3]_4(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  (**#43**) is rather similar, but the Ca layers  $\parallel (200)$  remain completely separate, with no bridges connecting them. Tellurium lone pairs and nitrate groups point into continuous interlayer gaps.

$\text{Sc}_2[\text{TeO}_3](\text{SeO}_3)(\text{SeO}_4)$  (**#44**) has zigzag chains of edge-sharing  $\text{ScO}_7$  polyhedra running  $\parallel x$ .  $\text{TeO}_3$  groups connect the chains into pairs, and the  $\text{SeO}_3$  pyramids connect these further into layers  $\parallel (002)$ , while  $\text{SeO}_4$  tetrahedra share oxygens with four different Sc to link the layers into a rather open framework.

$\text{La}_2[\text{Si}_6\text{O}_{13}][\text{TeO}_3]_2$  (**#45**) contains  $\text{LaO}_9$  and  $\text{TeO}_3$  polyhedra, forming layers  $\parallel (100)$ . These intercalate with a silicate sheet in which *dreier* double chains like those of okenite (Merlino, 1983) link to their neighbours to make a double layer in a disordered fashion, such that  $2/3$  of the Si are  $\text{Q}^4$  and  $1/3$  are  $\text{Q}^3$ , giving an overall composition  $[\text{Si}_6\text{O}_{13}]^{2-}$ . A similar intercalation of La–Te and silicate sheets occurs in the triclinic structure of  $\text{La}_4[\text{Si}_{5.2}\text{Ge}_{2.8}\text{O}_{18}][\text{TeO}_3]_4$  (**#46**) but here, the layers are  $\parallel (010)$ ,  $\text{La}^{3+}$  cations have CN8–10, and the silicate–germanate anion is a loop-branched single sheet which is formed by cross-linking of narsarsukite-like tubes (Peacor and Buerger, 1962) running  $\parallel x$ . Half of the (Si,Ge) are  $\text{Q}^3$  and half are  $\text{Q}^4$ , and Ge > Si in two out of the eight tetrahedral sites.

#### *Structures with monomeric $\text{Te}^{4+}\text{O}_3$ as part of a larger structural unit that is a finite cluster.*

Details for structures **#47–62** are shown in Table 10 (deposited).  $\text{HgTeO}_3 \equiv [\text{Hg}_2(\text{TeO}_3)_2]$  (**#47**) has two types of Hg in quite differently distorted coordination polyhedra. Hg1 has two oxygen nearest neighbours at 2.06–2.12 Å and four more oxygen atoms at 2.54–2.73 Å, while Hg2 has one close oxygen neighbour at 2.14 Å, one at 2.30 Å and three more at 2.40–2.46 Å. Using the parameters of Brese and O’Keeffe (1991), the Hg2 distances correspond to bond valences of 0.57, 0.37 and 0.28–0.24 vu, so a ‘strong bond’ threshold of 0.3 vu would make both Hg atoms 2-coordinate, with O–Hg2–O less symmetrical and less linear than O–Hg1–O. The strong bonds define a structural unit that is a neutral molecule in which Hg1 and Hg2 form a ring with two  $\text{TeO}_3$  groups. These molecules lie in layers  $\parallel (002)$  and are linked through long  $\text{Hg}\cdots\text{O}$  and  $\text{Te}\cdots\text{O}$  bonds. The complex structure of  $\text{Cd}_4\text{V}_2^{5+}\text{Te}_3^{4+}\text{O}_{15} \equiv \text{Cd}_4[\text{VO}_3][(\text{VO}_3)(\text{TeO}_3)](\text{TeO}_3)_2$

(#48) contains several structure-building elements. Pyroxene-like zigzag vanadate chains  $[\text{V}_2\text{O}_6]^{2-}$  run  $\parallel \mathbf{x}$ , although these do not contain Te. The most complex structural unit with Te is a cluster  $[\text{VTeO}_6]^{3-}$  formed by corner-sharing of a  $\text{VO}_4^{3-}$  tetrahedron and a  $\text{TeO}_3^{2-}$  pyramid. The V-bearing structural units act as bridges between layers  $\parallel (020)$  of relatively weakly-bound  $\text{CdO}_{6-8}$  polyhedra. The remaining  $\text{TeO}_3^{2-}$  are attached to the Cd–O layers, and all Te lone pairs point into channels than run  $\parallel \mathbf{x}$ , between the vanadate chains.

In  $\text{Pb}_2[\text{Pd}^{2+}\text{Cl}_2(\text{TeO}_3)_2]$  (#49), two  $\text{TeO}_3$  groups are linked through a  $\text{PdO}_2\text{Cl}_2$  square to make an anionic complex *trans*- $[\text{PdCl}_2(\text{TeO}_3)_2]^{4-}$ . These complexes form layers  $\parallel (002)$  which are linked via irregular  $\text{PbO}_5$  polyhedra, with the long axes of complexes oriented towards  $[120]$  and  $[1\bar{2}0]$  in alternate layers.  $\text{Bi}_2\text{WTe}_2\text{O}_{10} \equiv \text{Bi}_2[\text{WO}_4(\text{TeO}_3)_2]$  (#50) has two  $\text{TeO}_3$  groups linked through a  $\text{WO}_6$  octahedron to make a complex *cis*- $[\text{WO}_4(\text{TeO}_3)_2]^{6-}$ . These V-shaped anions are linked through irregularly coordinated  $\text{Bi}^{3+}$  cations. The six shortest Bi–O bonds out to 2.58 Å define edge-sharing chains of distorted  $\text{BiO}_6$  octahedra  $\parallel \mathbf{y}$ , which with the Te–W anions make layers  $\parallel (200)$ . However, longer Bi–O at 2.83 and 3.27 Å link the Bi chains into continuous sheets  $\parallel (002)$ , alternating with layers of Te–W anions. The cluster anion in  $\text{Nd}_2\text{W}_2\text{Te}_2\text{O}_{13} \equiv \text{Nd}_2[\text{W}_2\text{O}_7(\text{TeO}_3)_2]$  (#51) has two  $\text{TeO}_3$  linked to an edge-sharing pair of octahedra,  $\text{W}_2\text{O}_{10}$ . However, while Te1 is joined to both W atoms to form a 3-ring of cation-centred polyhedra, Te2 is attached only to W1, giving the overall stoichiometry  $[\text{W}_2\text{O}_7(\text{TeO}_3)_2]^{6-}$ . These anions lie in layers  $\parallel (102)$ , and are connected through CN8–9  $\text{Nd}^{3+}$ .

$\text{K}_4[\text{Mo}_6\text{Te}_2\text{O}_{24}] \cdot 6\text{H}_2\text{O}$  (#52) and its isostructural Rb analogue (#53) are our first examples of a large family of salts (mainly telluropoly-molybdates) in which the structural unit is a modified Anderson–Evans anion (Anderson, 1937; Evans, 1948, 1974). Six  $\text{MoO}_6$  octahedra share edges to form a hexagonal ring, but instead of one Te occupying the vacant octahedral site at the ring centre, two pyramidally coordinated Te sit above and below the vacant octahedral position. The hexagonal heteropolyanions lie in layers parallel to  $(10\bar{2})$ , with their planes normal to either  $[11\bar{1}]$  or  $[1\bar{1}1]$  directions. Water molecules and 8–9 coordinated alkali cations lie between them (Fig. 17).

$\text{Cs}_6\text{Na}_2[\text{W}_6\text{Mo}_3\text{S}_4\text{O}_{20}(\text{H}_2\text{O})_3(\text{W}_9\text{TeO}_{33})] \cdot 11.7\text{H}_2\text{O}$  (#54) and the nearly isostructural  $\text{Cs}_{7.15}\text{Na}_{1.85}[\text{W}_6\text{Mo}_3\text{S}_4\text{O}_{20}(\text{H}_2\text{O})_2\text{Cl}(\text{W}_9\text{TeO}_{33})] \cdot$

$11.2\text{H}_2\text{O}$  (#55) have extremely complex heteropolyanions which can be derived from incomplete fragments of the cuboctahedral  $\text{TM}_{12}\text{O}_{40}$  Keggin ion (Keggin, 1934), where  $T$  = a tetrahedral cation and  $M$  = an octahedral cation. The ion is composed of two dissimilar half-cuboctahedral fragments of the Keggin cage. One fragment has composition  $[\text{W}_9\text{O}_{30}(\text{TeO}_3)]$ , and has a  $\text{TeO}_3$  pyramid rather than a  $\text{TO}_4$  tetrahedron bracing a bowl-shaped cluster of  $\text{WO}_6$  octahedra (Fig. 17). The other fragment is  $[\text{W}_6\text{Mo}_3\text{S}_4\text{O}_{26}(\text{H}_2\text{O}, \text{Cl})_3]$ . It has no analogue of the central  $\text{Te}^{4+}$  cation, and has  $\text{Mo}^{6+}$  rather than  $\text{W}^{6+}$  as the cations on one triangular face of the cage. The four anions bonded to two to three Mo and no W are  $\text{S}^{2-}$  rather than  $\text{O}^{2-}$ , and the three anions bonded to one Mo only are  $(\text{H}_2\text{O}, \text{Cl})$ . The two half-cuboctahedra link through six oxygen atoms to form an ellipsoidal cluster that is similar but not identical to the Wells–Dawson cluster (Wells, 1947; Dawson, 1953; Baker and Figgis, 1970). The clusters are held together by additional water molecules and  $\text{Cs}^+$  and  $\text{Na}^+$  cations in a wide range of coordination states.

The heteropolyanion in  $\text{K}_8\text{Na}_2[\text{Pd}_3(\text{W}_9\text{TeO}_{33})_2] \cdot 51\text{H}_2\text{O}$  (#56) consists of two half-Keggin subunits linked into a single, large dumbbell-shaped anion through a set of three square-planar coordinated  $\text{Pd}^{2+}$  cations, to make an expanded version of the cluster in #54–55. These anions are packed around inverse tetrad axes and linked through  $\text{K}(\text{H}_2\text{O})_{7-9}$  and  $\text{Na}(\text{H}_2\text{O})_6$  polyhedra.  $\text{K}_9\text{Na}[\text{Cu}_3(\text{H}_2\text{O})_3(\text{W}_9\text{TeO}_{33})_2] \cdot 16\text{H}_2\text{O}$  (#57) is almost isostructural but has a much lower water content, and each of the bridging  $\text{Cu}^{2+}$  ions also has an  $\text{H}_2\text{O}$  molecule associated, to give it 5-fold rather than 4-fold coordination. Unusually, water molecules are included in the structural unit here and in the clusters below, when they are necessary to fully define the coordination environment of a cluster cation.

$[\text{N}(\text{CH}_3)_4]_2\text{Na}_6[\text{Ni}(\text{H}_2\text{O})_2(\text{Ni}(\text{H}_2\text{O})_3)_2(\text{WO}_2)(\text{W}_9\text{TeO}_{33})_2] \cdot 23\text{H}_2\text{O}$  (#58) and its analogue with  $\text{Zn}^{2+}$  replacing  $\text{Ni}^{2+}$  (#59) have slightly more complex clusters in which the  $\text{W}_9\text{TeO}_{33}$  fragments are not half-cuboctahedra but half-anticuboctahedra, in which two square faces share an edge (Fig. 17). These are linked through two  $M^{2+}\text{O}_3(\text{H}_2\text{O})_3$  octahedra and two octahedra that are 50%  $M^{2+}\text{O}_4(\text{H}_2\text{O})_2$  and 50%  $\text{W}^{6+}\text{O}_6$ . There is also a partially disordered cluster in  $\text{K}_{14}[\text{V}_{12}^{5+}\text{Mo}_{12}^{6+}\text{O}_{69}(\text{TeO}_3)_2] \cdot 27\text{H}_2\text{O}$  (#60), in which two half-Keggin units each have an average composition  $\text{V}_{4.5}\text{Mo}_{4.5}\text{TeO}_{33}$  and are linked through a ring of three  $\text{VO}_4$  tetrahedra alternating with three  $\text{MoO}_6$



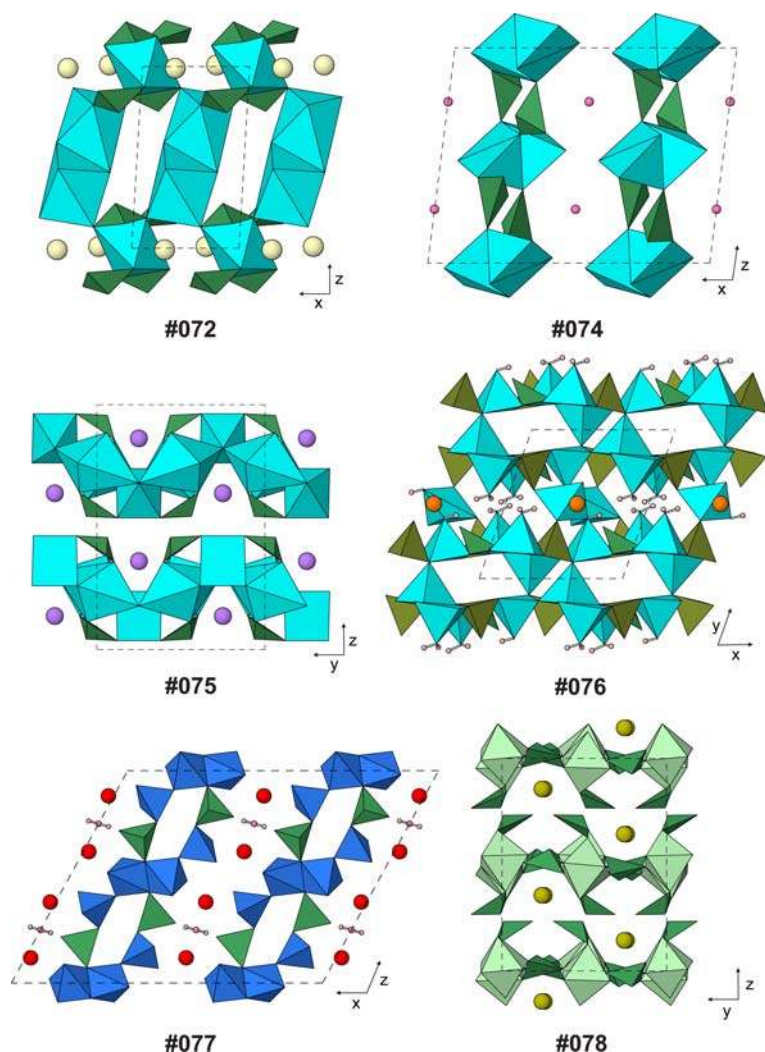


FIG. 18. Examples of structures with monomeric  $\text{TeO}_3$  pyramids as part of larger structural units that are chains or layers (Tables 10–11, deposited). Small spheres: H (pale pink). Medium spheres: O (dark pink), when not part of a polyhedron. Large spheres: Bi (pale violet), Ca (orange), Na (dark yellow), Sr (red) and Yb (light yellow). Polyhedra: As (brown-green), Cu (cyan), Ga (light green), Te (dark green) and V (blue).

octahedra.  $\text{K}_{10}[\text{V}_4(\text{V}_3\text{Mo}_{17}\square)\text{O}_{74}](\text{TeO}_3)] \cdot 15\text{H}_2\text{O}$  (**#61**) has a unique cluster that contains two different kinds of half-Keggin unit. One is  $(\text{V}_3\text{Mo}_5\square)\text{TeO}_{33}$  with partial V–Mo disorder; this has the same topology as the half-Keggin units of **#54–57** and **#60**, with CN3 oxygen atoms centring the three triangular faces around the sides of the ‘bowl’ but not the bottom triangular face. The other half-Keggin unit is  $\text{Mo}_9\text{VO}_{35}$ , of the type found in the Wells–Dawson cluster, in which it is the bottom face that is centred, and with a  $\text{VO}_4$  tetrahedron

instead of a  $\text{TeO}_3$  pyramid. Instead of the two ‘bowls’ facing towards each other, the vanadate bowl is inverted, so that the  $\text{VO}_4$  tetrahedron is pointing away from the centre of the cluster. The two bowls are linked through a ring of alternating V and Mo, as for **#60**. The extraordinarily complex structural unit of  $(\text{NH}_4)[\text{H}(\text{Ru}_4^{4+}\text{O}_6(\text{H}_2\text{O})_9)_2(\text{Fe}^{3+}(\text{H}_2\text{O})_2)_2(\text{W}_9\text{TeO}_{33})_2] \cdot 36\text{H}_2\text{O}$  (**#62**) has two half-anticuboctahedra  $\text{W}_9\text{TeO}_{33}$  similar to those of **#58–59**, linked through a pair of  $\text{FeO}_4(\text{H}_2\text{O})_2$  octahedra and also through three oxygen atoms each of two

tetrahedral clusters or corner-sharing  $\text{RuX}_6$  octahedra,  $\text{Ru}_4\text{O}_9(\text{H}_2\text{O})_9$ .

*Structures with monomeric  $\text{Te}^{4+}\text{O}_3$  as part of a larger structural unit that is a chain*

The next 11 structures (#63–73, Table 10, deposited) have  $\text{TeO}_3$  groups incorporated into infinite heteropolymeric anions. In magnolite,  $[(\text{Hg}_2)(\text{TeO}_3)]$  (#63), each Hg atom is bonded to one other at 2.53 Å to make a  $(\text{Hg}_2)^{2+}$  dimer, and has no other neighbours apart from one close oxygen at 2.06 Å and three more distant at 2.69–3.00 Å. The Hg dimers and  $\text{TeO}_3$  groups form continuous chains  $-\text{O}-\text{Te}-\text{O}-\text{Hg}-\text{Hg}-\text{O}-\text{Te}-\text{O}-$  running  $\parallel y$  and zigzagging in the (001) plane, with Te atoms at the apices of the bends. The chains are held together only by long  $\text{Hg}\cdots\text{O}$  and  $\text{Te}\cdots\text{O}$  bonds.  $\text{BaZn}(\text{TeO}_3)\text{Cl}_2$  (#64), better written for our purposes as  $\text{Ba}_2[\text{Zn}_2\text{Cl}_3(\text{TeO}_3)_2]\text{Cl}$ , has double chains  $\parallel y$  resembling those of the amphibole minerals, in which  $\text{TeO}_3$  pyramids instead of tetrahedra alternate with  $\text{Q}^3 \text{ZnO}_3\text{Cl}$  tetrahedra and  $\text{Q}^2 \text{ZnO}_2\text{Cl}_2$ . The chains lie in double layers  $\parallel (002)$  with additional  $\text{Cl}^-$  and 6–7 coordinate  $\text{Ba}^{2+}$  between them. Dy  $[\text{CuCl}(\text{TeO}_3)_2]$  and its analogues (#65–67) have a loop-branched structural unit, in which  $\text{TeO}_3$  pyramids and  $\text{CuO}_4\text{Cl}$  pyramids make  $\text{CuTeCuTe}$  4-rings, which link into a chain  $\parallel x$  through the Cu atoms (Fig. 17). The chains form layers  $\parallel (002)$ , which are interconnected through zigzag chains of edge-sharing  $\text{DyO}_8$ . The Te lone pairs and Cl are located in channels which run between the Dy chains and the Cu–Te chains. The compound  $\text{Yb}_3[\text{Cu}^{2+}\text{Cl}_2(\text{TeO}_3)_2]_2[\text{Cu}^{1+}\text{Cl}_2]$  (#68) has an open-branched chain  $\parallel y$  in which pyramids  $\text{Cu}^{2+}\text{O}_3\text{Cl}_2$  and  $\text{TeO}_3$  alternate along the chain backbone, while a second type of  $\text{TeO}_3$  acts as a branch sharing an oxygen atom with the Cu. These chains attach on either side of a layer  $\parallel (100)$  of edge-sharing  $\text{YbO}_8$  polyhedra, with isolated, linear  $[\text{Cu}^{1+}\text{Cl}_2]^-$  anions in the interlayer gap (Fig. 17).  $\text{LaNbTeO}_6 \equiv \text{La}[\text{NbO}_3(\text{TeO}_3)]$  (#69) has  $\text{NbO}_6$  octahedra sharing trans corners to make *zweier* chains  $\parallel y$ ; oxygen atoms are shared with Te so as to make two differently oriented  $\text{Nb}_2\text{Te}$  3-rings, which alternate along the chain. Chains are held together via long  $\text{Te}\cdots\text{O}$  bonds and 8-coordinated  $\text{La}^{3+}$ . This compound is isostructural with  $\text{Pb}[\text{MoO}_3(\text{SeO}_3)]$  (Oh *et al.*, 2012).

$\text{Ti}_2[(\text{UO}_2)(\text{TeO}_3)_2] \cdot \beta$  (#70) has  $\text{Te}-\text{U}-\text{Te}-\text{U}$  4-rings which link through  $\text{UO}_6$  octahedra to make loop-branched chains  $\parallel x$ . These pack in a herringbone fashion, and are linked through ribbons of edge-sharing  $\text{TiO}_{5-7}$  polyhedra. The  $\alpha$

polymorph has a layered structure (#221, below).  $\text{Sr}_3(\text{UO}_2)(\text{TeO}_3)_4 \equiv \text{Sr}_3[(\text{UO}_2)(\text{TeO}_3)_2](\text{TeO}_3)_2$  (#71) has similar chains  $\parallel y$ , all sharing a common attitude, and bridging layers  $\parallel (200)$  of  $\text{SrO}_{7-8}$  polyhedra. Additional isolated  $\text{TeO}_3$  brace the Sr layers. The complex chain in  $\text{Yb}_2[\text{Cu}_3\text{Cl}_4(\text{TeO}_3)_4]$  (#72) is again based on linked 4-rings, but the polyhedra are  $\text{CuO}_6$  octahedra at the nodes and  $\text{CuO}_3\text{Cl}_2$  on the loops. One of two types of  $\text{TeO}_3$  acts as an additional bridge between two Cu, making  $\text{Cu}_2\text{Te}$  3-rings, while the other type of  $\text{TeO}_3$  shares an edge with  $\text{CuO}_6$ , so that the bridging oxygens in the Cu chain have CN3. These chains run  $\parallel x$  and are linked through edge-sharing zigzag chains of  $\text{YbO}_8$  to make thick layers  $\parallel (001)$  (Fig. 18). The layers are held together only by long bonds to Te.  $\text{Bi}_2\text{W}_3\text{Te}_2\text{O}_{16} \equiv \text{Bi}_2[\text{W}_3\text{O}_{10}(\text{TeO}_3)_2]$  (#73) again has loop-branched chains of 4-rings, but the polyhedra are all  $\text{WO}_6$ , giving a chain stoichiometry  $\text{W}_3\text{O}_{14}$ .  $\text{TeO}_3$  groups share non-bridging oxygen atoms to make  $\text{W}_2\text{Te}$  3-rings, similar to the  $\text{Cu}_2\text{Te}$  of #72, and giving a final chain composition  $\text{W}_3\text{Te}_2\text{O}_{16}$ . The chains run  $\parallel y$  and lie in layers  $\parallel (002)$ , which cross-link sheets of  $\text{BiO}_8$  polyhedra.

*Structures with monomeric  $\text{Te}^{4+}\text{O}_3$  as part of a larger structural unit that is a layer*

Structures #74–#112 (Table 11, deposited) have infinite two-dimensional structural units.  $[\text{Cu}(\text{NH}_3)(\text{TeO}_3)](\text{H}_2\text{O})$  (#74) has a 3-connected net with 4- and 8-rings, topologically similar to the ‘apophyllite’ layer of mackayite (Fig. 11*i*), but the polyhedra at the nodes are alternately  $\text{TeO}_3$  and square-planar  $\text{CuO}_3(\text{NH}_3)$  (Fig. 18). The polyhedra are tilted so that a very elongated octahedron around Cu is completed by another  $\text{TeO}_3$  oxygen at 2.60 Å and the  $\text{H}_2\text{O}$  molecule at 3.07 Å. The layers are  $\parallel (200)$ , and are connected only through H bonds.  $\text{Bi}[\text{Cu}_3\text{O}_2(\text{TeO}_3)_3]\text{Cl}$  (#75) has a complex layer in which a hexagonal honeycomb array of CN3 oxygen atoms are linked through the two bridging oxygen atoms of  $\text{CuO}_4$  squares. The layer is corrugated because one type of Cu has *trans* bridging oxygen atoms while the other type has *cis*. A Te atom sits above or below each CN3 oxygen, sharing its own oxygens with two *trans* Cu and one *cis* Cu. Elongated octahedra around all Cu are completed by long bonds to Cl. The layers are  $\parallel (002)$  and are connected through  $\text{BiO}_8$  polyhedra and long  $\text{Te}\cdots\text{O}$  bonds (Fig. 18). Juabite,  $\text{Ca}[\text{Cu}_{10}(\text{AsO}_4)_4(\text{TeO}_3)_4(\text{OH})_2] \cdot 4\text{H}_2\text{O}$  (#76) has a structure in which double layers  $\parallel (010)$  are held



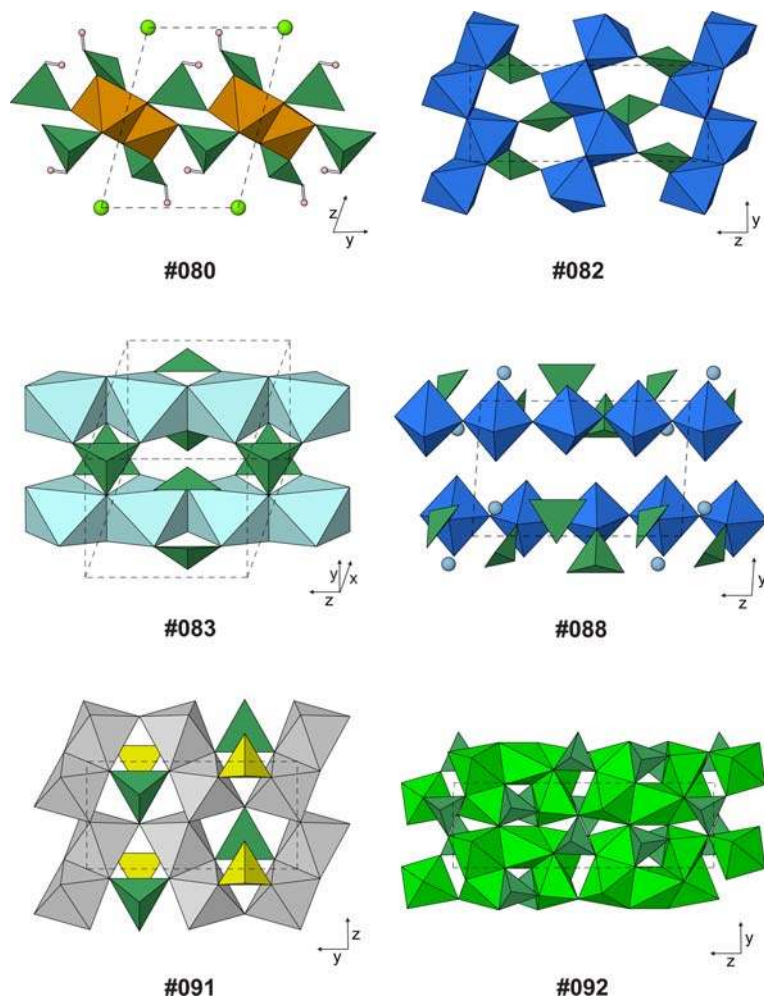


FIG. 19. Examples of structures with monomeric  $\text{TeO}_3$  pyramids as part of larger structural units that are layers (Table 11, deposited). Small spheres: H (pale pink). Large spheres: Cl (yellow-green) and Li (pale blue). Polyhedra: Al (pale grey), Fe (orange-brown), In (pale blue), Ni (bright green), S (yellow), Te (dark green) and V (blue).

together only through long  $\text{Te}\cdots\text{O}$  bonds. The two sublayers contain edge-sharing blocks  $\text{OTe}=\text{Cu}=\text{O}_2=\text{Cu}=\text{O}_2=\text{TeO}$  with long axes  $\parallel [10\bar{1}]$ , which are held together by sharing corners with continuous chains of more  $\text{CuO}_4$  squares and  $\text{AsO}_4$  tetrahedra (Fig. 18). The resulting net is approximately centred-rectangular, and has 8- and 3-rings. Two such sheets are linked by the inward-pointing apical oxygens of  $\text{AsO}_4$  tetrahedra connecting to additional  $\text{Cu}_2\text{O}_4(\text{OH})_2$  dimers. Loosely bound  $\text{H}_2\text{O}$  and  $\text{CN6 Ca}^{2+}$  lie between the two sublayers.

$\text{Sr}_2\text{V}_4^{5+}\text{Te}_2\text{O}_{16} \cdot \text{H}_2\text{O} \equiv \text{Sr}_2[\text{V}_2\text{O}_5(\text{TeO}_3)]_2 \cdot \text{H}_2\text{O}$  (#77) has a structure in which CN5 V1 and CN4 V2

polyhedra share corners with  $\text{TeO}_3$  to make chains  $-\text{V1}-\text{V2}-\text{Te}-\text{V1}-\text{V2}-\text{Te}-$  running  $\parallel z$  and zigzagging in the (100) plane. Such chains at two different heights along  $x$  are linked by edge-sharing of  $\text{VO}_5$  polyhedra to make a layer  $\parallel (200)$  which is strongly corrugated but not topologically a double layer. Thus, the  $\text{TeO}_3$  groups and can be regarded as linking  $[\text{V}_4\text{O}_{14}]$  tetramers (Fig. 18). One oxygen atom of  $\text{TeO}_3$  is directed at the interlayer gap, while the lone pair points into a deep fold in the layer. Water molecules and CN8  $\text{Sr}^{2+}$  are between the layers.

In  $\text{Na}[\text{Ga}(\text{TeO}_3)_2]$  (#78), edge-sharing pairs of  $\text{GaO}_6$  octahedra are linked through corner-sharing

TeO<sub>3</sub> to make layers || (002) consisting exclusively of Ga–Te–Ga–Te 4-rings. A second type of TeO<sub>3</sub> shares the remaining oxygen atoms of the Ga octahedra, forming Ga–Te–Ga 3-ring loops, which occur in pairs to make a Ga<sub>2</sub>Te<sub>2</sub> unit resembling the ‘double triangle’ tetrameric Te unit that occurs in many Te-only polymers (Figs 10f, 10h, 13d, 13i, 15f, 15g and 16c). Layers are linked through CN7 Na<sup>+</sup> ions (Fig. 18). Na[Fe<sup>3+</sup>(TeO<sub>3</sub>)<sub>2</sub>] (#79) is isostructural. Rodalquilarite, Fe<sub>2</sub><sup>3+</sup>Te<sub>4</sub>O<sub>9</sub>(OH)<sub>3</sub>Cl ≡ [Fe<sub>2</sub>(TeO<sub>2</sub>OH)<sub>3</sub>(TeO<sub>3</sub>)]Cl (#80) also has Fe<sub>2</sub>Te<sub>2</sub> ‘double triangles’. These share FeO<sub>6</sub> edges to form zigzag chains || x, which are cross-linked via a second type of TeX<sub>3</sub> into layers || (001). The Cl<sup>−</sup> lie between the layers, and are weakly bonded to Te (Fig. 19). Oxygen atoms that are not bonded to Fe are 100% OH<sup>−</sup> for Te1, 50% O<sup>2−</sup> 50% OH<sup>−</sup> for Te2 (Kampf and Mills, 2011). [(Fe<sup>2+</sup>Fe<sup>3+</sup>)(TeO<sub>3</sub>)<sub>6</sub>]Cl<sub>2</sub> (#81) has three types of Fe polyhedra. (Fe1)O<sub>6</sub> octahedra share two *trans* corners with (Fe3)O<sub>5</sub>. (Fe2)O<sub>6</sub>, share two edges with each other to make zigzag chains || x, and a third edge with Fe3, linking all Fe polyhedra into an undulating layer || (011) with elongated 12-rings. The mean Fe–O distances are very similar for Fe1 and Fe2 (2.03 vs. 2.01 Å), implying that there is little ordering of Fe<sup>2+</sup> and Fe<sup>3+</sup>. Two types of TeO<sub>3</sub> share all oxygen atoms with Fe polyhedra, with lone pairs pointing into the interlayer space. As in rodalquilarite, interlayer Cl<sup>−</sup> are weakly bonded to Te.

The phase α-V<sup>4+</sup>TeO<sub>4</sub> ≡ [VO(TeO<sub>3</sub>)] (#82) is isopuntal with the raspite polymorph of PbWO<sub>4</sub> (Fujita *et al.*, 1977). Edge-sharing, distorted VO<sub>6</sub> octahedra form V<sub>2</sub>O<sub>8</sub> chains || y, analogous to the W<sub>2</sub>O<sub>8</sub> chains of raspite. These are arranged similarly to the corresponding chains in ferberite, FeWO<sub>4</sub> (Ulku, 1967) but with an additional lattice shear so that (1) the anions no longer form a continuous hexagonal close-packed substructure, and (2) the Pb/Te polyhedra are no longer octahedra, but are very irregular (Fig. 19). The structure can be regarded as a distortion of the pucherite type, which is orthorhombic and has an anion array that is still hexagonal close-packed (see discussion of #648–650 below). In raspite, Pb<sup>2+</sup> has seven neighbours at 2.3–2.9 Å and no more within 3.2 Å, while TeVO<sub>4</sub> shows even less regularity: Te<sup>4+</sup> has three strongly bound neighbours at 1.75, 2.00 and 2.25 Å, followed by four more within 3.4 Å, at 2.42, 2.59, 3.04 and 3.17 Å. As is typical for V<sup>4+</sup>, there is one very short bond of 1.73 Å of one of the oxygen atoms that is not linked to Te, although this ligand is also only 2.04 Å from a second V atom. Note that Te<sup>6+</sup> plays the V/W role in

the raspite structure in #650, below. The β polymorph of VTeO<sub>4</sub> has a very different, layered structure (#222, below).

[InCl(TeO<sub>3</sub>)] (#83) and its Br analogue (#84) have edge-sharing chains of InO<sub>4</sub>X<sub>2</sub> octahedra (X = Cl or Br) running || z, sharing oxygen atoms with TeO<sub>3</sub> groups to make In<sub>2</sub>Te 3-rings. The resulting loop-branched chains (similar in topology to the Te chain of Fig. 15c), at two different x heights, are linked through the third oxygen ligand of Te to make a corrugated layer || (100), with layers connected only via long Te...X interactions (Fig. 19). [BiI(TeO<sub>3</sub>)] (#85) has the same space group and similar unit-cell parameters, but is not quite isostructural. The TeO<sub>3</sub> groups are differently oriented, so that they cross-link chains at the same x coordinate, and the structural unit can be described as a double layer rather than a highly corrugated single layer. The Bi coordination polyhedra are BiO<sub>5</sub>I<sub>2</sub> rather than octahedra, and share corners along the chain direction z rather than edges, while making new shared-edge connections between sublayers.

YV<sup>5+</sup>Te<sub>2</sub>O<sub>8</sub> ≡ Y[VO<sub>2</sub>(TeO<sub>3</sub>)](TeO<sub>3</sub>) (#86) has two topological types of TeO<sub>3</sub>. The first type (Te2 and Te3) share corners with VO<sub>6</sub> distorted octahedra to complete V<sub>2</sub>Te 3-rings above and below a corner-sharing VO<sub>4</sub> layer with a square-net topology similar to those of Fig. 11a,f. Layers are || (002), and connect through TeO<sub>3</sub> sharing oxygen atoms with edge-sharing sheets of YO<sub>8</sub> polyhedra. The remaining Te1 and Te4 act as additional braces on the Y layer, and are not part of the larger structural unit.

BaMo<sub>6</sub><sup>6+</sup>TeO<sub>9</sub> ≡ Ba[Mo<sub>2</sub>O<sub>6</sub>(TeO<sub>3</sub>)] (#87) has MoO<sub>6</sub> octahedra sharing corners to form zigzag *zweier* double chains || y, which are cross-linked via TeO<sub>3</sub> into double layers || (002). BaO<sub>10–11</sub> polyhedra lie between the layers. LiV<sub>3</sub><sup>5+</sup>Te<sub>2</sub>O<sub>12</sub> ≡ Li[(V<sup>5+</sup>O<sub>2</sub>)<sub>3</sub>(TeO<sub>3</sub>)<sub>2</sub>] (#88) has strips of distorted VO<sub>6</sub> octahedra sharing edges and CN3 oxygen atoms to form chains || z similar to the Te chain of Fig. 10a. Te1 shares three oxygen atoms with three V of one such chain, making clusters which include a Te<sub>2</sub>V<sub>2</sub> ‘double triangle’ motif, while Te2 shares oxygen ligands with V atoms of two chains, to link them into a double layer || (010). CN6 Li<sup>+</sup> cations sit within corrugations of the layer, and layers are held together through weak Li–O and Te–O bonds (Fig. 19). (NH<sub>4</sub>)V<sup>4+</sup>V<sup>5+</sup>TeO<sub>7</sub> ≡ (NH<sub>4</sub>)[(V<sup>4+</sup>O)V<sup>5+</sup>O<sub>3</sub>(TeO<sub>3</sub>)] (#89) has extremely corrugated layers || (200) in which alternating V<sup>4+</sup>O<sub>6</sub> octahedra and V<sup>5+</sup>O<sub>4</sub> tetrahedra each share three corners to form 6-rings. TeO<sub>3</sub> shares the otherwise non-bridging oxygen ligand of V<sup>5+</sup> and two of V<sup>4+</sup>; the additional

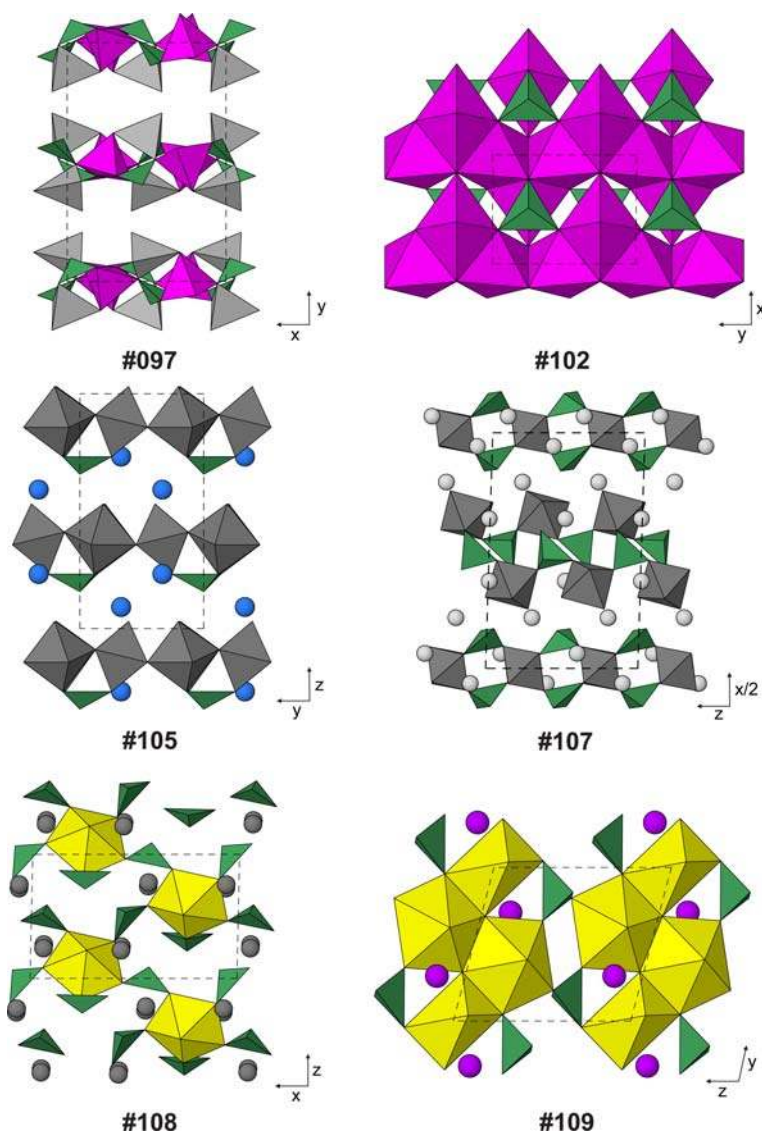


FIG. 20. Examples of structures with monomeric  $\text{TeO}_3$  pyramids that are part of larger structural units that are layers (Table 11, deposited). Large spheres: Ag (pale grey), Cs (blue), K (purple) and Pb (dark grey). Polyhedra: Co (magenta), Mo or W (dark grey), Te (dark green), U (yellow) and Zn (pale grey).

connectivity means that the structural unit can be regarded as a double layer. The remaining ligand of  $\text{V}^{4+}$  is very close (1.61 Å), making a well-defined vanadyl group,  $[\text{V}=\text{O}]^{2+}$ .  $(\text{NH}_4)^+$  ions are in the interlayer gap.  $\text{Cs}_3[(\text{V}^{4+}\text{O})\text{V}^{5+}\text{O}_3(\text{TeO}_3)]_2\text{Cl}$  (#90) has a closely related structure with similar unit-cell dimensions, in which chains  $(\text{V}^{4+}\text{V}^{5+}\text{O}_8) \parallel z$  of alternating  $\text{V}^{4+}\text{O}_6$  and  $\text{V}^{5+}\text{O}_4$  do not form continuous layers, but are linked into a single layer normal

to  $x$  through  $\text{TeO}_3$ . There are four such layers per unit cell, which alternate in their facing direction. The apical oxygen atoms of V polyhedra point towards interlayers that contain  $\text{Cs}^+$  ions only, while Te lone pairs point towards another type of interlayer, which contains both  $\text{Cs}^+$  and  $\text{Cl}^-$ .

$[\text{Al}_2(\text{TeO}_3)(\text{SO}_4)(\text{OH})_2]$  (#91) has zigzag edge-sharing ribbons of  $\text{AlX}_6$  octahedra  $\parallel z$ , which in turn share corners with each other to make continuous

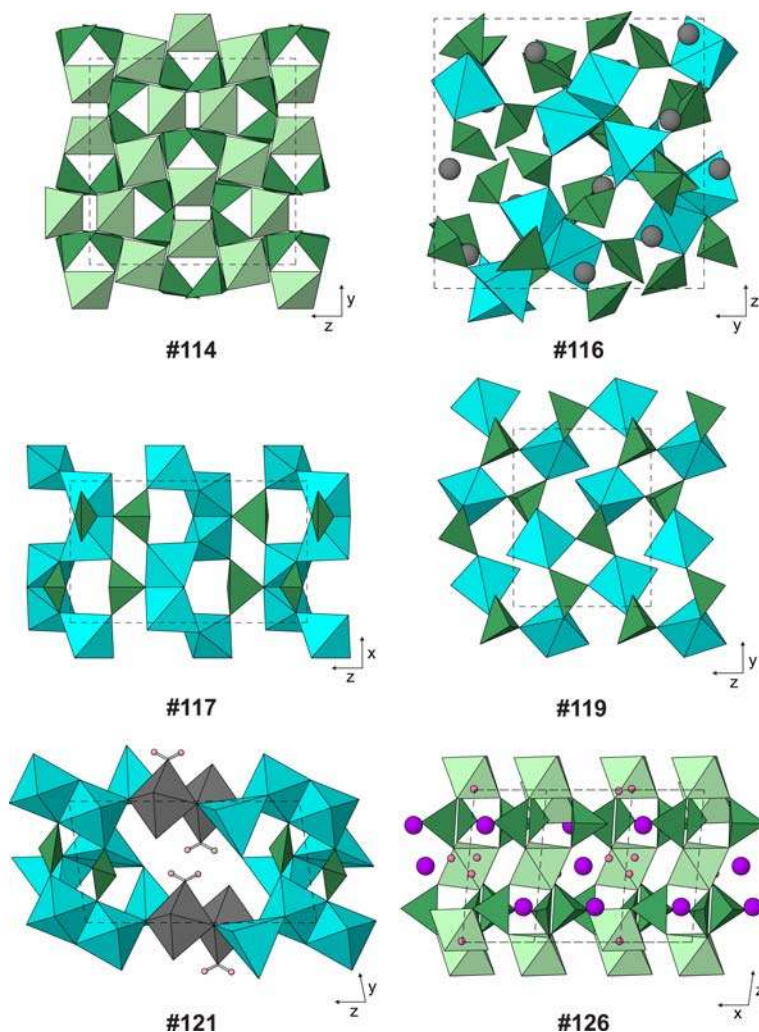


FIG. 21. Examples of structures with monomeric  $\text{TeO}_3$  pyramids that are part of larger structural units that are frameworks (Table 12, deposited). Small spheres: H (pale pink) and O (dark pink), when not part of a polyhedron. Large spheres: K (purple) and Pb (dark grey). Polyhedra: Cu (cyan), Ga (pale green), Mo (dark grey) and Te (dark green).

sheets  $\text{Al}_2\text{O}_5(\text{OH})_2 \parallel (100)$ . The sheets are braced by  $\text{SO}_4$  tetrahedra sharing two oxygen atoms and  $\text{TeO}_3$  pyramids sharing all three, and successive sheets are held together through very long  $\text{Te}\cdots\text{O}$  bonds (Fig. 19). The compounds  $[\text{M}_5\text{X}_2(\text{TeO}_3)_4]$  with  $\text{M}^{2+} = (\text{Ni}, \text{Co} \text{ or } \text{Mg})$ ,  $\text{X}^- = \text{Cl}$  and Br, (**#92–96**) all have a structure with rather dense layers of edge-sharing  $\text{MO}_6$  and  $\text{MO}_5\text{X}$  octahedra  $\parallel (200)$ , braced by  $\text{TeO}_3$  groups. Long  $\text{Te}\cdots\text{X}$  bonds are important in holding the layers together (Fig. 19).

The compounds  $[\text{PTX}_2(\text{TeO}_3)]$  with  $\text{P}^{2+} = (\text{Co}, \text{Cu} \text{ or } \text{Zn})$ ,  $\text{T}^{2+} = \text{Zn}$  and  $\text{X}^- = \text{Cl}$  and also

$[\text{ZnZnBr}_2(\text{TeO}_3)]$  and  $[\text{CoCoBr}_2(\text{TeO}_3)]$  (**#97–101**) have an orthorhombic structure in which  $\text{PO}_5\text{X}$  and  $\text{TO}_2\text{X}_2$  polyhedra share corners to make layers  $\parallel (020)$  (Fig. 20). Although these compounds are not known as minerals, they are isostructural with sphiite,  $[\text{Zn}_2\text{Cl}_2(\text{SeO}_3)]$  (Semenova *et al.*, 1992).  $[\text{Co}_2\text{Cl}_2(\text{TeO}_3)]$  (**#102**), the Cl analogue of **#101**, has a different, monoclinic structure with layers of edge-sharing  $\text{CoO}_4\text{Cl}_2$  and  $\text{CoO}_3\text{Cl}_3$  octahedra  $\parallel (001)$ . In both cases, layers are again braced by  $\text{TeO}_3$  groups and held together through long  $\text{Te}\cdots\text{X}$  bonds (Fig. 20).  $[\text{Cu}_3\text{Br}_2(\text{TeO}_3)_2]$



(#103) has  $\text{CuO}_4$  squares sharing all corners with edge-sharing pairs of  $\text{CuO}_4\text{Br}$  pyramids to make loop-branched chains  $\parallel y$  which feature a Cu analogue of the 'double triangle' motif; these chains are bridged by  $\text{TeO}_3$  groups to make layers  $\parallel (001)$ . Long  $\text{Cu}\cdots\text{Br}$  bonds complete an elongated octahedron of ligands around square-coordinated Cu1, and long  $\text{Te}\cdots\text{Br}$  bonds hold the layers together.

$(\text{NH}_4)_2\text{Mo}_3\text{TeO}_{12} \equiv (\text{NH}_4)_2[\text{Mo}_3\text{O}_9(\text{TeO}_3)]$  and its Cs analogue (#104–105) have a structure in which  $\text{Mo}^{6+}\text{O}_6$  octahedra share four corners to form  $\text{Mo}_3\text{O}_{12}$  layers with the kagome net of 3- and 6-rings. Tellurium atoms share apical oxygen atoms of the Mo octahedra around each 3-ring, to make  $[\text{Mo}_3\text{O}_9(\text{TeO}_3)]^{2-}$  layers  $\parallel (002)$ . Layers are connected through longer  $\text{Te}\cdots\text{O}$  bonds (2.92–2.95 Å) which complete a very distorted octahedron around Te, as well as through interlayer  $\text{NH}_4^+$  or  $\text{Cs}^+$  ions (Fig. 20). The positions of Mo and Te atoms correspond to those of O atoms in the tridymite structure. Alternatively, the  $\text{MoO}_6$  and  $\text{TeO}_{3+3}$  octahedra can be regarded as forming a hexagonal relative of the pyrochlore framework, in which half of the  $\text{Mo}_3$  triangles link to Te above and below the centre of the triangle. The structure is polar (space group  $P6_3$ ) as the  $\text{TeO}_3$  pyramids always point in the same sense along  $z$ .  $\text{Rb}_2[\text{W}_3\text{O}_9(\text{TeO}_3)]$  (#106) is almost isostructural, but with the symmetry reduced to  $P31c$  due to slight collapse of the layers.  $\text{Ag}_6\text{W}_3\text{Te}_4\text{O}_{16} \equiv \text{Ag}_6[\text{W}_2\text{O}_6(\text{TeO}_3)_2][\text{WO}_2(\text{TeO}_3)_2]$  (#107) has two types of infinite, strongly-bound structural unit: a layer  $[\text{W}_2\text{Te}_2\text{O}_{12}]^{4-}$  and a chain  $[\text{WTe}_2\text{O}_8]^{2-}$ ; for classification purposes, the layer takes precedence. The chains are loop-branched, with  $\text{WO}_6$  octahedra sharing four corners with  $\text{TeO}_3$  groups to make  $\text{W}-\text{Te}-\text{W}-\text{Te}$  4-rings. They run  $\parallel z$  and are stacked to make layers  $\parallel (200)$ , which alternate with the continuous  $\text{W}-\text{Te}$  sheets. The latter have  $\text{WO}_6$  and  $\text{TeO}_3$  polyhedra alternating in a 3-connected net of 4- and 8-rings with the 'apophyllite' topology (cf. Fig. 11*i*). Layers are held together through long  $\text{Te}\cdots\text{O}$  links and also three types of interlayer  $\text{Ag}^+$ , in very irregular 5-coordination (Fig. 20).

$\text{Pb}_2[(\text{UO}_2)(\text{TeO}_3)_3]$  (#108) has a structure in which  $\text{UO}_7$  pentagonal dipyramids share four equatorial oxygen atoms and two types of  $\text{TeO}_3$  share two ligands to form layers  $\parallel (020)$  of crumpled 8-rings in which Te and U cations alternate. A third type of  $\text{TeO}_3$  shares the remaining equatorial oxygen ligand of U, and projects into the interlayer gap, where  $\text{Pb}^{2+}$  cations in irregular 7–8 coordination hold the structure together (Fig. 20).

In the compounds  $A_2[(\text{UO}_2)_3\text{O}_2(\text{TeO}_3)_2]$  ( $A = \text{K}$ , Rb and Cs: #109–111), edge-sharing pairs of  $\text{UO}_7$  polyhedra share both CN2 and CN3 oxygen atoms with  $\text{UO}_6$  octahedra to form ribbons  $\parallel y$ , which in turn are bridged by  $\text{TeO}_3$  groups to form layers  $\parallel (101)$ , which are held together by CN7–8 interlayer  $A^+$  cations (Fig. 20).  $\text{K}_4[(\text{UO}_2)_5\text{O}_5(\text{TeO}_3)_2]$  (#112) has a similar structure in which broader edge-sharing ribbons ( $4 \times \text{UO}_7$  and  $1 \times \text{UO}_6$  polyhedra per asymmetric unit) are bridged by  $\text{TeO}_3$  to form layers which are also oriented  $\parallel (101)$ , with 8-coordinated  $\text{K}^+$  in the interlayer.

### *Structures with monomeric $\text{Te}^{4+}\text{O}_3$ as part of a larger structural unit that is a framework*

The  $\text{TeO}_3^{2-}$  pyramid is incorporated into an infinite three-dimensional structural unit in compounds #113–194 (Table 12, deposited). The first two examples are  $\text{Ga}_2(\text{TeO}_3)_3$ - $\alpha$ , which in this context is more appropriately written  $[(\text{Ga}_{2.67}\square_{0.33})(\text{TeO}_3)_4]$ , and  $[(\text{Ga}_2\text{Zn})(\text{TeO}_3)_4]$  (#113–114), which both have the structure of eulytine,  $\text{Bi}_4(\text{SiO}_4)_3 \equiv \text{Si}_3(\text{BiO}_3)_4$  (Menzel, 1931). This framework is made by CN2 oxygen atoms linking one CN4 (Ga, Zn) atom and one CN3 Te atom (Fig. 21). The cation sublattice  $(\text{Ga,Zn})_3\text{Te}_4$  has the same arrangement as the  $\text{Th}_3\text{P}_4$  structure (Meisel, 1939; O'Keeffe and Andersson, 1977; Hyde and Andersson, 1989). The much less dense  $\beta$  polymorph of  $\text{Ga}_2(\text{TeO}_3)_3$  is described below (#136).

The mineral choloalite, ideally  $\text{Pb}_3[(\text{Cu}_{2.67}^{2+}\text{Sb}_{0.33}^{5+})(\text{TeO}_3)_6]\text{Cl}$  is almost isostructural with  $\text{SrCu}(\text{TeO}_3)_2 = \text{Sr}_3[\text{Cu}_3(\text{TeO}_3)_6]\square$  (#115–116). Again, the structure is cubic in symmetry, but rather complex.  $\text{CuO}_4$  squares share all corners with Te, and  $\text{TeO}_3$  groups share two corners with Cu, to form a framework with a large unit cell ( $a \approx 12.5$  Å) and chiral symmetry ( $P4_132$ ). The  $\text{Cl}^-$  anion, if present, is shared by three (Cu,Sb) atoms as a fifth ligand, while (Pb,Sr) is located in large interstices in irregular 9–12 coordination (Sr) or 6–9 (Pb) (Fig. 21). Balyakinite,  $[\text{Cu}(\text{TeO}_3)]$  (#117) has a structure in which edge-sharing pairs  $\text{CuO}_5$  square pyramids link corners to form zigzag chains  $\parallel x$ , which are cross-linked in the  $y$  and  $z$  directions into a rather open framework by  $\text{TeO}_3$  groups (Fig. 21). Structures #142 and #297 are polymorphs. Although the unit-cell parameters and stoichiometry of  $[\text{Zn}(\text{TeO}_3)]$  (#118) are similar to those of balyakinite, the structure is different. It features edge-sharing pairs of  $\text{ZnO}_5$ , but they link with four neighbouring dimers through corners to form continuous corrugated layers  $\parallel (002)$ , with  $\text{TeO}_3$

providing bridges between layers in the *z* direction. Cu(SeO<sub>3</sub>) is not isostructural with balyakinite, but one of its four polymorphs has the structure of Zn(TeO<sub>3</sub>) (Effenberger, 1986; Hawthorne *et al.*, 1986), and another has the perovskite-type structure of high-pressure Cu(TeO<sub>3</sub>) (#142) (Kohn *et al.*, 1976). Teinite, Cu(TeO<sub>3</sub>) · 2H<sub>2</sub>O ≡ [Cu(H<sub>2</sub>O)<sub>2</sub>(TeO<sub>3</sub>)] (#119), the dihydrate of balyakinite, also features square pyramids, although these are CuO<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub>, and do not link to each other. The Cu polyhedra share oxygens with Te so that Cu and Te define an open 3-connected framework in which their locations correspond respectively to Ca and half of the Cl of the CaCl<sub>2</sub> (orthorhombically distorted rutile) structure (van Bever, 1935; Haines *et al.*, 2000). The structure is intrinsically enantiomorphic (space group *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>) and has rather large channels || *y*, which are braced by hydrogen bonds between water molecules and TeO<sub>3</sub> groups, and into which point the lone pairs of Te atoms (Fig. 21). Chalcomenite, Cu(SeO<sub>3</sub>) · 2H<sub>2</sub>O, is isomorphic (Pasero and Perchiazzi, 1989). Less obviously, the structural unit of LiV<sup>5+</sup>TeO<sub>5</sub> ≡ Li[(VO<sub>2</sub>)(TeO<sub>3</sub>)] (#120) is topologically the same as [Cu(H<sub>2</sub>O)<sub>2</sub>(TeO<sub>3</sub>)] of teinite, although change in axial ratios and atomic coordinates close the channels (which would be || *x* if they existed). Additional LiO<sub>5</sub> polyhedra share two oxygen ligands with (Te + V), two with (Li + V) and one with a single V atom only.

[(Cu<sub>6</sub><sup>+</sup>Cl<sub>4</sub>)(Mo<sub>5</sub><sup>+</sup>O<sub>8</sub>)(TeO<sub>3</sub>)<sub>2</sub>] · H<sub>2</sub>O (#121) has a framework made out of two chemically dissimilar components. Square-planar CuX<sub>4</sub>, CuO<sub>4</sub> and Cu<sub>2</sub>O<sub>3</sub>Cl, link corners and some edges to form thick layers || (001), which are braced by TeO<sub>3</sub> groups and additional long Cu...Cl bonds. There are no tetrahedral molybdate complexes: instead, MoO<sub>5</sub> square pyramids share edges to form [Mo<sub>2</sub>O<sub>8</sub>]<sup>4-</sup> dimers in the interlayer region. These share the four non-apical oxygens with Cu of the layers on either side. Half-occupied H<sub>2</sub>O sites complete a very distorted octahedron around Mo: these are at 2.50 Å from the cation, compared to 1.70 Å for the apical oxygen opposite (Fig. 21). [Cu<sub>7</sub>(TeO<sub>3</sub>)<sub>2</sub>(SO<sub>4</sub>)(OH)<sub>6</sub>] (#122) similarly has a framework in which relatively dense layers are connected through sparse bridges. There are five kinds of Cu<sup>2+</sup>, all in square-planar coordination except that Cu5 has a fifth oxygen ligand if the threshold is set at 2.3 Å. Edge-sharing trimers Cu4 = Cu3 = Cu4 and Cu5 = Cu2 = Cu5 link corners to form complex chains || [101], with additional corners shared between Cu4 and bridging Cu1, which further condense the chains into layers || (111). Layers are

linked into a framework through TeO<sub>3</sub> and SO<sub>4</sub> groups, which show some orientational disorder as indicated by splitting of oxygen sites.

[Ge(TeO<sub>3</sub>)<sub>2</sub>] (#123) has a framework in which GeO<sub>6</sub> octahedra and TeO<sub>3</sub> pyramids share corners. Interestingly, the GeTe<sub>2</sub> substructure is a slight monoclinic distortion of the rutile structure, with *x* as the pseudotetrad axis. The Ge–O bonds of argutite (rutile-type GeO<sub>2</sub>; cf. Haines *et al.*, 2000) are replaced by Ge–O–Te links in this compound.

HLi<sub>2</sub>[Ga<sub>3</sub>(TeO<sub>3</sub>)<sub>6</sub>] · 6H<sub>2</sub>O (#124) has Ga–O–Te links between GaO<sub>6</sub> octahedra and TeO<sub>3</sub> pyramids, making a rhombohedral structure with alternating layers of 2 × Ga surrounded by Te in an approximate trigonal prism, and 1 × Ga surrounded octahedrally by Te. LiO<sub>3</sub>(H<sub>2</sub>O)<sub>3</sub> octahedra share faces with the former. There are three of each type of Ga layer per cell. Na<sub>3</sub>[Ga<sub>3</sub>(TeO<sub>3</sub>)<sub>6</sub>] · 7.2H<sub>2</sub>O (#125) has a closely related structure which retains the alternation of sparser and denser Ga layers, but in which Ga is always surrounded by six Te in a trigonal prismatic fashion, and there are only two of each type of Ga layer per unit cell. Na<sub>3</sub>(H<sub>2</sub>O)<sub>5</sub> clusters with each Na bonded to four H<sub>2</sub>O and two tellurite oxygen atoms also lie in the sparse Ga layers, and another water site in the denser layers is 36% occupied. K[Ga(TeO<sub>3</sub>)<sub>2</sub>] · 1.8H<sub>2</sub>O (#126) has Ga of the sparse layers surrounded octahedrally by Te, as for #124. The layers are || (001), but the structure is triclinically distorted. K<sup>+</sup> ions in 7–8 coordination and H<sub>2</sub>O molecules occupy interstices in the sparse Ga layers (Fig. 21). Li<sub>6</sub>[Ga<sub>8.67</sub>(H<sub>2</sub>O)<sub>2</sub>(TeO<sub>3</sub>)<sub>14</sub>] (#127) also has alternating sparse and dense Ga layers, but these are quite different to those of #124–126. The GaO<sub>6</sub> octahedra of the sparse layer have a pseudo-diad axis || *z* rather than a true triad axis, and those of the denser layers occur in edge-sharing dimers Ga<sub>2</sub>O<sub>10</sub>, which link into a honeycomb-like layer through CN3 water molecules. Out of three types of Te, Te2 and Te3 link the two different types of Ga layer, along with CN5 Li<sup>+</sup>, while Te1 sit on triad axes and connect Ga octahedra within the sparse layers.

One dimorph of [Fe<sub>2</sub><sup>3+</sup>(TeO<sub>3</sub>)<sub>3</sub>] (#128) has FeO<sub>6</sub> octahedra in an approximately face-centred orthorhombic array of face-sharing Fe<sub>2</sub>O<sub>9</sub> dimers, all with Fe ≡ Fe vectors || *y*. TeO<sub>3</sub> groups connect an upper oxygen atom of one dimer, lower oxygen atom of a second dimer and middle oxygen atom of a third, to make a continuous framework. The other dimorph (#129) has the same *Pnma* space group but a topologically quite different structure in which FeO<sub>6</sub> octahedra share four corners to form Fe<sub>2</sub>O<sub>8</sub> layers || (020). As the unshared ligands are *cis* to one



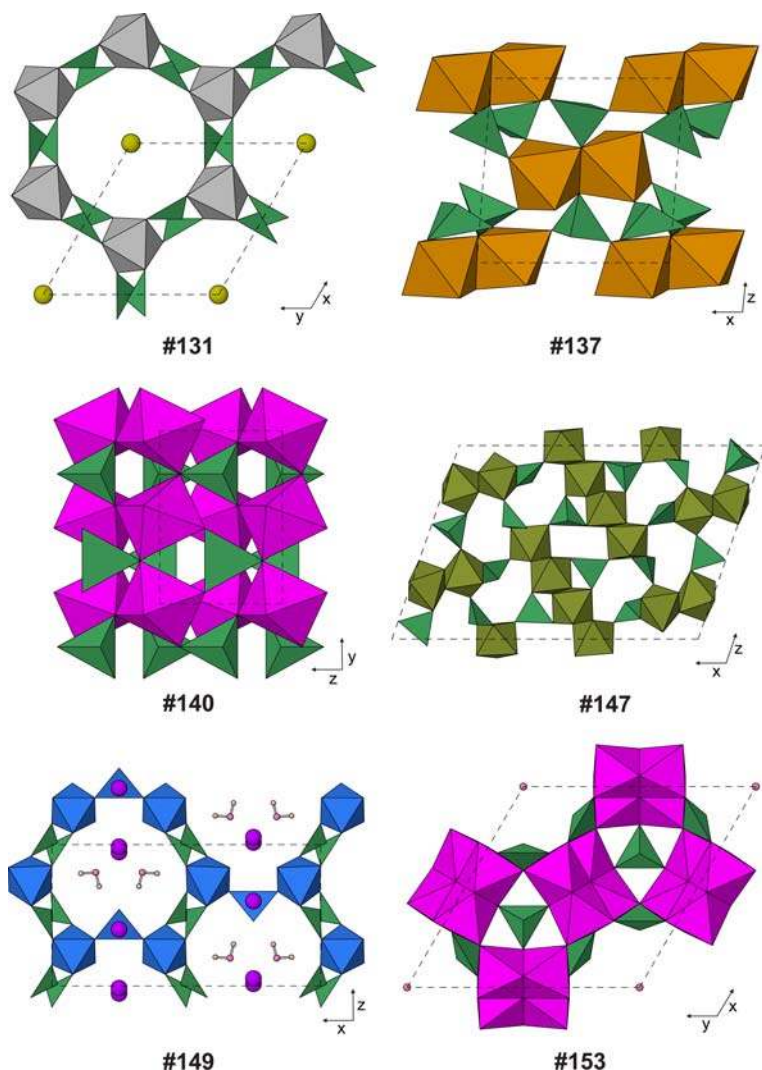


FIG. 22. Examples of structures with monomeric  $\text{TeO}_3$  pyramids that are part of larger structural units that are frameworks (Table 12, deposited). Small spheres: H (pale pink) and O (dark pink), when not part of a polyhedron. Large spheres: K (purple) and Na (dark yellow). Polyhedra: Co (magenta), Fe (orange-brown), Sb (brown-green), Te (dark green), V (blue) and Zn (pale grey).

another, the layers are highly corrugated. One of two types of Te braces the Fe layer, with the lone pair pointing into the interlayer gap, while the other type of Te bridges two Fe layers to make a continuous framework, with its third ligand not bonded to Fe.  $[\text{In}_2(\text{TeO}_3)_3]$  (#130) is isostructural, but was described in a different axial setting.

Structures #131–136 all have the microporous zemannite framework, which has zeolitic ion-exchange properties.  $\text{Na}_2[\text{Zn}_2(\text{TeO}_3)_3]$  (#131) has

face-sharing octahedral dimers  $\text{Zn}_2\text{O}_9$  which are cross-linked through  $\text{TeO}_3$  in a fashion very similar to #128, except that the dimers are arranged in a very open hexagonal honeycomb pattern (Fig. 22). Thus, the resulting framework has hexagonal channels  $\parallel z$  that are very large ( $\sim 10$  Å across). Sodium cations occur in the channels in  $\text{NaH}[\text{Zn}_2(\text{TeO}_3)_3] \cdot 2.67\text{H}_2\text{O}$  (#132) and  $\text{Na}_2[\text{Zn}_2(\text{TeO}_3)_3] \cdot 2.97\text{H}_2\text{O}$  (#133). Cobalt

replaces Zn in **#134**. The negative charge on the framework can be modified by substituting trivalent cations for  $\text{Zn}^{2+}$ , and other channel cations may substitute for  $\text{Na}^+$ . The channel cation is  $\text{Mg}^{2+}$  in the mineral zemannite itself,  $\text{Mg}_{0.45}[(\text{Fe}_{1.12}^{3+}\text{Zn}_{0.80}\text{Mn}_{0.08})(\text{TeO}_3)_3] \cdot 4.08\text{H}_2\text{O}$  (**#135**), which can be idealized as  $\text{Mg}_{0.5}[(\text{Zn}^{2+}\text{Fe}^{3+})(\text{TeO}_3)_3] \cdot 4.5\text{H}_2\text{O}$ , although the data of Miletich (1995a) show that the mean charge on  $M$  can vary over the range 2.33–2.56. The channel contents are arranged as chains  $[\text{Mg}(\text{H}_2\text{O})_6]^{2+} \cdots (\text{H}_2\text{O})_3 \cdots [\text{Mg}(\text{H}_2\text{O})_6]^{2+} \cdots (\text{H}_2\text{O})_3$  that have local trigonal symmetry, but are orientationally and translationally disordered. Kinichilite, ideally  $\text{Mg}_{0.5}[(\text{Mn}^{2+}\text{Fe}^{3+})(\text{TeO}_3)_3] \cdot 4.5\text{H}_2\text{O}$ , and keystoneite,  $\text{Mg}_{0.5}[(\text{Ni}^{2+}\text{Fe}^{3+})(\text{TeO}_3)_3] \cdot 4.5\text{H}_2\text{O}$ , have similar unit-cell parameters to zemannite, but have not had their structures refined (Miletich, 1995a). The new mineral ilirneyite,  $\text{Mg}_{0.5}[(\text{ZnMn}^{3+})(\text{TeO}_3)_3] \cdot 4.5\text{H}_2\text{O}$ , is also isostructural (Pekov *et al.*, 2015). The channels are completely empty and the framework electrostatically neutral in  $[\text{Ga}_2(\text{TeO}_3)_3] \cdot \beta$  (**#136**), much less dense than the  $\alpha$  polymorph with the eulytine structure described above (**#113**). Synthetic selenite analogues of zemannite,  $\text{K}_2\text{M}_2[\text{SeO}_3]_3 \cdot 2\text{H}_2\text{O}$  ( $M = \text{Co}$  or  $\text{Ni}$ ) are also known (Wildner, 1993).

Emmonsite,  $[\text{Fe}_2^+(\text{H}_2\text{O})(\text{TeO}_3)_3]$  (**#137**) is triclinic but has pseudotetragonal symmetry down the  $x$  direction.  $\text{FeX}_6$  octahedra occur in edge-sharing dimers  $\text{Fe}_2\text{O}_8(\text{H}_2\text{O})_2$ , but these stack such that they can be derived from a continuous edge-sharing chain  $\parallel x$  by deletion of every third Fe atom. The Fe dimers of neighbouring chains are connected through  $\text{TeO}_3$  pyramids, which define the walls of nearly-square channels  $\parallel x$ , which accommodate the Te lone pairs (Fig. 22). There is a marked resemblance to the tetragonal structure of minium,  $\text{Pb}^{4+}\text{Pb}_2^{2+}\text{O}_4$  (Gavarri and Weigel, 1975) or schafarikite,  $\text{Fe}^{2+}\text{Sb}_2^{3+}\text{O}_4$  (Fischer and Pertlik, 1975). The atomic arrangement of emmonsite can in fact be regarded as a threefold superstructure of the schafarikite type with ordered vacancies:  $\text{Fe}_2^+\text{Sb}_6^{3+}\text{O}_{12} = (\text{Fe}_2^+\square)(\text{Te}_4^{3+}\square_3)(\text{O}_9(\text{H}_2\text{O})_3)$ .  $\text{Co}_6^+[\text{Te}_6^{6+}\text{O}_6][\text{Te}_4^{4+}\text{O}_3]_2\text{Cl}_2$  (**#678**, below) has a closely related structure.  $[\text{Ga}_2(\text{H}_2\text{O})_3(\text{TeO}_3)_3]$  (**#138**) has the  $\text{Ga}_2\text{Te}_3$  substructure arranged approximately like the atoms of  $\alpha\text{-Ga}_2\text{O}_3$ , which has the corundum structure (Marezio and Remeika, 1967). However, there are  $\text{Te}-\text{O}-\text{Ga}$  links from Te to only three out of the four nearest Ga. There are two types of Ga atom, one bonded to only tellurite oxygen atoms, while the other centres a  $\text{GaO}_3(\text{H}_2\text{O})_3$  octahedron. The structure is polar, as groups  $\text{Ga}1(\text{TeO}_3)_3\text{Ga}2(\text{H}_2\text{O})_3$  all point in the same sense along  $z$ .  $[\text{Nb}_3\text{O}_3(\text{TeO}_3)_4]$

Cl (**#139**) has a quite different type of structure, in which linear chains  $\parallel y$  of corner-sharing  $\text{NbO}_6$  octahedra pack in a trellis-like arrangement, and are cross-linked through  $\text{TeO}_3$ . Lone pairs and  $\text{Cl}^-$  anions are accommodated in large square channels  $\parallel y$ .

The  $[\text{M}(\text{TeO}_3)]$  structures **#140–142** ( $M = \text{Co}$ ,  $\text{Ni}$  or  $\text{Cu}$ ) are all of perovskite type.  $\text{MO}_6$  octahedra share all corners to form a framework, while  $\text{Te}^{4+}$  occupies the cubic cages thus defined. The octahedral tilt system is of  $a^+b^-b^-$  type, as in  $\text{GdFeO}_3$  (Glazer, 1972), producing a unit cell with space group  $Pnma$  and cell parameters  $\sqrt{2} \times 2 \times \sqrt{2}$  of the aristotypical perovskite cube. Bending of  $\text{Fe}-\text{O}-\text{Fe}$  links and displacement of Gd in  $\text{GdFeO}_3$  reduce the Gd coordination from 12 equidistant oxygen atoms to six at 2.26–2.39 Å, two at 2.82 Å and four effectively non-bonded oxygen atoms at  $>3.1$  Å (Coppens and Eibschuetz, 1965). However, the displacement of Te in  $\text{Co}(\text{TeO}_3)$  is much more extreme, giving three O at 1.90–1.92 Å, five at 2.70–2.98 Å and four at  $>3.4$  Å. Thus, Te forms only three strong bonds, and acts as a brace on the  $\text{MO}_3$  framework (Fig. 22). This form of  $\text{Cu}(\text{TeO}_3)$  (**#142**) is a high-pressure polymorph of **#117** and **#297**. Note that  $\text{Te}^{6+}$  in octahedral coordination can act as the smaller ‘B’ cation in the perovskite structure: **#562–584** below, are examples. An unusual example of  $\text{Te}^{4+}$  in the ‘B’ site of a defect perovskite is provided by **#195**, below.

$[\text{Fe}^{3+}\text{F}(\text{TeO}_3)]$  (**#143**) has zigzag *zweier* chains  $\parallel y$  of edge-sharing  $\text{FeO}_4\text{F}_2$  octahedra (the shared edges are alternately  $\text{F}_2$  and  $\text{O}_2$ ).  $\text{TeO}_3$  groups link trios of neighbouring chains to make a framework. In one polymorph of  $\text{V}_2^{3+}\text{Te}_2\text{O}_9 \equiv [\text{V}_2\text{O}_3(\text{TeO}_3)_2]$  (**#144**), alternating  $\text{VO}_5$  and  $\text{VO}_6$  polyhedra ( $\text{V}1$  and  $\text{V}2$  respectively) share corners to make a zigzag *vierer* chain  $\text{V}_2\text{O}_9$ , with  $\text{V}2$  at the angles in the chain. The  $\text{V}1$  polyhedron has a geometry that would be more typical for  $\text{V}^{4+}$  than  $\text{V}^{5+}$ : a square pyramid with four  $\text{V}-\text{O}$  distances 1.78–2.00 Å, and a very short distance of 1.58 Å corresponding to an apical  $\text{V}=\text{O}$  double bond. The  $\text{V}2$  geometry is an extremely distorted octahedron with four distances 1.97–2.30 Å to oxygen atoms that are shared with  $\text{V}1$ , Te or both, and two much shorter *cis* distances 1.60–1.72 Å to unshared oxygen atoms. Thus, the structure appears to contain two types of vanadyl (V) complex,  $[\text{V}=\text{O}]^{3+}$  and  $[\text{O}=\text{V}=\text{O}]^+$ . The V chains lie in layers  $\parallel (100)$ . One of two types of Te shares two oxygen atoms with  $\text{V}1 + 2 \times \text{V}2$  of one chain and the other oxygen atom with  $\text{V}2$  of an adjacent chain. The other type of Te bridges between layers to complete the framework. A second polymorph containing  $\text{Te}_2\text{O}_5$  dimers is described below (**#203**).

Sonoraite,  $\text{Fe}^{3+}(\text{TeO}_3)(\text{OH})\cdot\text{H}_2\text{O} \equiv [\text{Fe}_2^{3+}(\text{OH})_2(\text{H}_2\text{O})(\text{TeO}_3)_2]\cdot\text{H}_2\text{O}$  (**#145**), has edge-sharing octahedral dimers  $\text{Fe}_2\text{O}_8(\text{OH})_2$  and  $\text{Fe}_2\text{O}_4(\text{OH})_5(\text{H}_2\text{O})$  alternating and linked through shared  $\text{OH}^-$  corners to make *vierer* chains  $\parallel [101]$ . The chains are packed in an approximately hexagonal array, and  $\text{TeO}_3$  groups link trios of neighbouring chains into a framework. The non-framework water molecule is loosely held in a structural cage between  $\text{TeO}_3$  groups.  $[\text{Ta}_2\text{O}_3(\text{TeO}_3)_2]$  (**#146**) has a similar stoichiometry for its structural unit, but a quite different structure in which  $\text{TaO}_6$  octahedra share three corners to form a layer  $\parallel (002)$  of 4- and 8-rings. The Te atoms are in the interlayer regions, and half of the  $\text{TeO}_3$  groups share all three ligands while the other half share only two, in order to link the Ta layers into a framework. The structure of stoichiometrically analogous  $[\text{Sb}_2^{5+}\text{O}_3(\text{TeO}_3)_2]$  (**#147**) is again quite different. Half of the  $\text{SbO}_6$  octahedra share four corners and half share two corners to make  $[\text{Sb}_2\text{O}_9]^{8-}$  ribbons of zigzagging 4-rings  $\parallel y$ . These ribbons pack in a herringbone fashion, and are connected into a framework through four crystallographically distinct types of  $\text{TeO}_3$  group (Fig. 22). The wide variety of structures possible for  $M_2\text{Te}_n\text{X}_6$  structural units is demonstrated further by  $\text{Na}_2[\text{W}_2\text{O}_6(\text{TeO}_3)]$  (**#148**), which has a structure in which eight types of  $\text{WO}_6$  octahedron share two to three corners to form corrugated layers  $\parallel (200)$ , which have bands of 4-rings  $\parallel y$  alternating with bands of 8-rings. Two of the four types of Te act as braces on particular W layers, while the other two types link the layers into a framework.  $\text{Na}^+$  cations lie between the layers, in irregular 7–8 coordination.  $\text{K}_3[(\text{V}^{4+}\text{O})_4(\text{V}^{5+}\text{O}_4)(\text{TeO}_3)_4]\cdot 4\text{H}_2\text{O}$  (**#149**) has clusters of five  $\text{VO}_n$  polyhedra: four very distorted octahedra  $\text{V}^{4+}\text{O}_6$  ( $\text{V}-\text{O}$  distances are  $1 \times 1.61$ ,  $4 \times 1.96$ – $2.07$  and  $1 \times 2.26$  Å) and a  $\text{V}^{5+}\text{O}_4$  distorted tetrahedron ( $2 \times 1.63$  and  $2 \times 1.82$  Å). The octahedra form two face-sharing dimers  $\text{V}_2\text{O}_9$ , which each share one of their bridging oxygen atoms with the tetrahedron to make a mixed-valence pentameric anion  $[\text{V}_4^{4+}\text{V}^{5+}\text{O}_{20}]^{19-}$ . All oxygens which are not part of the  $\text{VO}_4$  tetrahedron or the  $[\text{V}=\text{O}]^{2+}$  cation are shared with  $\text{TeO}_3$  groups, which again connect trios of neighbouring vanadate units into an open framework which has large channels (7–8 Å diameter) running  $\parallel y$  and  $z$ . Water molecules and CN 8–10  $\text{K}^+$  ions are in the channels (Fig. 22).

$[\text{Ni}_{11}(\text{TeO}_3)_{10}\text{Cl}_2]$  (**#150**) has five types of  $\text{NiO}_6$  octahedra forming thick layers  $\parallel (001)$ , which are linked into a framework through edge-sharing pairs of  $\text{NiO}_5\text{Cl}$  octahedra. Five types of  $\text{TeO}_3$  brace the

structure, two of which show orientational disorder, evidenced by mutually exclusive split positions for oxygen atoms.  $[\text{Ni}_7(\text{TeO}_3)_6\text{Cl}_2]$  (**#151**) has  $\text{NiO}_5\text{Cl}$  octahedra sharing edges in a very open honeycomb pattern, making very low-density layers  $\parallel (003)$ . The framework is formed by  $\text{TeO}_3$  and additional  $\text{NiO}_6$  between the layers and sharing edges with them.  $\text{Ni}_3(\text{TeO}_3)_2(\text{OH})_2$  (**#152**) is more informatively written  $[\text{Ni}_6(\text{TeO}_3)_4(\text{OH})_3](\text{OH})$ . It, and its Co analogue (**#153**), have an unusual structure in which face-sharing dimers of octahedral  $M_2\text{O}_7(\text{OH})_2$  share additional edges to form zigzag chains  $M_4\text{O}_{10}(\text{OH})_2 \parallel z$ . These chains in turn share corners to act as walls surrounding large channels (9 Å diameter) along the  $6_3$  screw axis of the structure, and small channels along the triad axes (Fig. 22). The overall composition of the resulting nanoporous framework is  $M_{12}\text{O}_{24}(\text{OH})_6$  per unit cell. Two Te occupy the small channels and another six brace the large channels, which contain two more very loosely bound  $\text{OH}^-$  anions to complete the unit-cell content,  $M_{12}(\text{TeO}_3)_8(\text{OH})_8$ .

In  $[\text{Ga}_2\text{Mo}^{6+}\text{O}_4(\text{TeO}_3)_2]$  (**#154**), edge-sharing chains  $\parallel y$  of  $\text{GaO}_6$  octahedra are linked through chains  $[\text{MoO}_4(\text{TeO}_3)]$  of alternating  $\text{TeO}_3$  and distorted  $\text{MoO}_6$  octahedra ( $4 \times 1.71$ – $1.99$  and  $2 \times 2.37$  Å) to form undulating layers  $\parallel (002)$ . A second type of Te connects these layers into a framework.  $\text{K}[\text{Nb}_3\text{O}_6(\text{TeO}_3)_2]$ , its Ta analogue and the corresponding Rb compounds (**#155**–**#158**) have octahedral  $\text{MO}_6$  ( $M = \text{Nb}$  or  $\text{Ta}$ ) sharing four corners to make corrugated layers of 4-rings,  $M_3\text{O}_{12} \parallel (020)$ . Interlayer  $\text{TeO}_3$  shares all three corners to link these layers into a framework. CN12  $\text{K}^+$  ions are also in the interlayer gap.

The structure of  $[\text{Ni}_3(\text{MoO}_4)(\text{TeO}_3)_2]$  (**#159**) bears some resemblance to those of **#152**–**#153**. Four zigzag chains of edge-sharing  $\text{NiO}_6$  and two of corner-sharing  $\text{NiO}_5$ , all chains having the composition  $\text{Ni}_2\text{O}_8$ , share additional corners to form walls around large pseudohexagonal and small pseudotrigonal channels  $\parallel x$ , forming a nanoporous framework  $\text{Ni}_6\text{O}_{18}$ . The small channels are empty, but the large hexagonal channels are braced by four  $\text{TeO}_3$  pyramids and two  $\text{MoO}_4$  tetrahedra. Reduction of some Ni coordination numbers to 5 occurs because of elimination of a bond to an oxygen atom of a neighbouring Ni polyhedron, preventing overbonding of the latter oxygen, which is part of the  $\text{MoO}_4$  group.  $[\text{Co}_7(\text{TeO}_3)_4\text{Br}_6]$  (**#160**) has layers of *cis*- $\text{CoO}_4\text{Br}_2$  octahedra sharing edges to make layers with 7-rings,  $\parallel (200)$ . The layers are linked into a framework via *trans*- $\text{CoO}_2\text{Br}_4$  octahedra, which

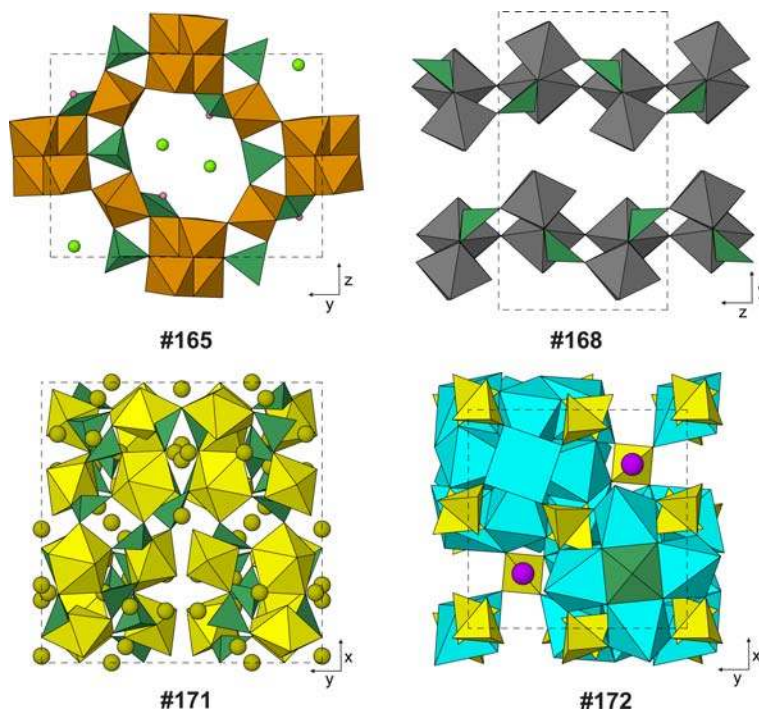


FIG. 23. Examples of structures with monomeric  $\text{TeO}_3$  pyramids that are part of larger structural frameworks (Table 12) and nabokoite, in which a  $\text{TeO}_4$  square pyramid is part of a structural layer (#172, Table 13, deposited). Small spheres: O (dark pink) when not part of a polyhedron. Large spheres: Cl (yellow-green), K (purple) and Na (dark yellow). Polyhedra: Cu (cyan), Fe (orange-brown), Mo (dark grey), S (yellow tetrahedra), Te (dark green) and U (yellow bipyramids).

share faces with octahedra in the layers above and below. Tellurium atoms brace the layers, rather than acting as interlayer bridges.  $[\text{Fe}_2^{3+}(\text{TeO}_3)_2\text{O}_2]$  (#161) has corrugated layers of edge-sharing  $\text{FeO}_6$  octahedra  $\parallel (100)$ , with Te bridging across the interlayers.  $[\text{Co}_2(\text{H}_2\text{O})(\text{SO}_4)(\text{TeO}_3)]$  and its Mn analogue (#162–163) have crankshaft chains  $\parallel z$  of edge-sharing octahedra  $\text{MO}_5(\text{H}_2\text{O})$  ( $M = \text{Co}$  or  $\text{Mn}$ ), which additionally link their  $\text{H}_2\text{O}$  corners to make undulating layers with 6-rings  $\parallel (100)$ . The layers are braced by  $\text{TeO}_3$  but connected into a framework by  $\text{SO}_4$  tetrahedra, which share two oxygen atoms with the layer on one side and one oxygen atom with the layer on the other.  $[\text{Zn}_2(\text{MoO}_4)(\text{TeO}_3)]$  (#164) has alternating  $\text{ZnO}_4$  and  $\text{ZnO}_4$  polyhedra sharing corners to make layers of 6-rings  $\parallel (001)$ .  $\text{TeO}_3$  groups span the 6-rings, acting as braces, while interlayer  $\text{MoO}_4$  tetrahedra share two oxygen atoms with each adjacent Zn layer to make a framework.  $[\text{Fe}_3^{3+}\text{O}(\text{TeO}_3)_3]\text{Cl}$  (#165) has  $\text{FeO}_6$  octahedra sharing edges to make a helical *vierer* chain  $\parallel x$  that is a thin fragment of a

rocksalt-like structure. These chains are linked through two opposite ligands of additional  $\text{FeO}_6$  octahedra to make a very open nanoporous framework with rhombic channels  $\parallel x$  of diameter  $\sim 12 \times 8 \text{ \AA}$  (Fig. 23).  $\text{TeO}_3$  groups reinforce the cross-links, and have their lone pairs pointing into the large channels. While the non-tellurite  $\text{O}^{2-}$  ion is part of the structural unit, in the core of the Fe chain,  $\text{Cl}^-$  is only loosely bound, and sits in the channels.

$\text{K}_2[\text{W}_3\text{O}_9(\text{TeO}_3)]$  (#166) has  $\text{WO}_6$  octahedra sharing four corners to form layers  $\parallel (020)$  with the 3- and 6-rings of the kagome net. Tellurium atoms link these layers into a framework, forming additional 3-rings with two W atoms on one or other side of the interlayer gap. Potassium in the interlayer is 8-coordinated.  $[\text{Ni}_6(\text{Mo}_4\text{O}_{16})(\text{TeO}_3)_2]$  (#167) has rhomb-shaped tetramolybdate anions  $[\text{Mo}_4\text{O}_{16}]^{8-}$  which are held together by two CN3 and four CN2 bridging oxygen atoms. Layers of molybdate anions  $\parallel (200)$  alternate with layers containing zigzag *sechser* chains of edge-sharing  $\text{NiO}_6$  running  $\parallel y$ . The molybdate groups link Ni



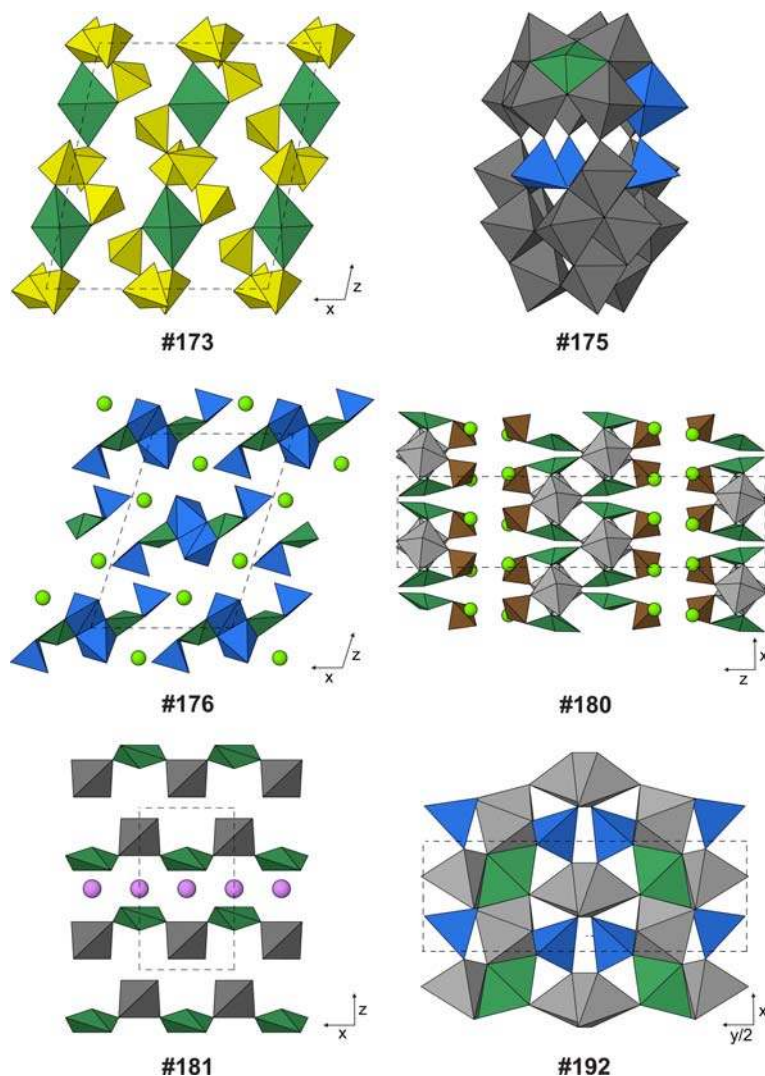


FIG. 24. Examples of structures with monomeric  $\text{TeO}_4$  polyhedra that are part of larger structural units (Table 13, deposited). Large spheres: Ba (yellow-green) and Cd (pink). Polyhedra: Co (magenta), Mo (dark grey), Nb or Zn (pale grey), P (brown), S (yellow), Te (dark green) and V (blue). Only the heteropolyanion cluster is shown for #175.

chains of the same and successive layers to form a framework. Between the molybdate groups, there are channels  $\parallel z$  containing the Te, which also cross-link the Ni layers.  $[(\text{Mo}_2^{5+}\text{Mo}_3^{6+})\text{O}_{13}(\text{TeO}_3)]$  (#168) has five types of Mo in very distorted octahedral coordination. There is a very wide spread of Mo–O distances: all Mo atoms have one very short Mo–O of 1.69–1.71 Å, all except Mo1 have one very long (2.38–2.46 Å), while the rest are 1.78–2.13 Å. The bond-valence parameters of Brese and O’Keeffe (1991) give a correspondingly wide spread of

individual bond valences (0.22–1.78 vu) but a narrow range of bond-valence sums of 5.82–6.12 vu for all Mo, implying that there is no ordering of  $\text{Mo}^{5+}$  and  $\text{Mo}^{6+}$ .  $\text{MoO}_6$  polyhedra share four corners to form layers  $\parallel (002)$ . The layers are of a modified ‘tungsten bronze’ type, in which bands of 4-rings  $\parallel y$  alternate with bands of 3- and 6-rings. Mo2–Mo5, in the 4-rings, share additional corners with octahedral in the layers above and below, connecting the layers into a  $[\text{Mo}_2^{5+}\text{Mo}_3^{6+}\text{O}_{16}]^{4-}$  anionic framework. The charge-balancing  $\text{Te}^{4+}$  ion

sits in the 6-ring of the layer (Fig. 23). The  $\text{TeO}_3$  group shares an edge with the Mo1 octahedron, where 3- and 6-rings meet, and its remaining ligand is one apical oxygen atom of the Mo1 octahedron of the layer either above or below. A high-temperature polymorph is described as #281 below.  $\text{Ba}_2[\text{Nb}_6\text{O}_{15}(\text{TeO}_3)_2]$  and its Ta analogue (#169–170) have octahedral  $\text{MO}_6$  ( $M = \text{Nb}$  or  $\text{Ta}$ ) sharing corners to make a three-cation wide layer that is a slice of  $\text{ReO}_3$ -type structure  $\parallel (221)$  of the cubic  $\text{ReO}_3$  cell. The layers are connected into a framework by sparse shared edges, which separate the interlayer into channels  $\parallel y$  of the resulting monoclinic cell. The channels contain  $\text{CN11 Ba}^{2+}$ , while Te braces the layers but unusually has its lone pair directed in towards the centre of the layer rather than into the interlayer gap.  $\text{Na}_4[(\text{UO}_2)_3(\text{TeO}_3)_5]$  (#171) has a large ( $a \approx 17 \text{ \AA}$ ) unit cell in a low-symmetry cubic space group ( $I2_13$ ).  $\text{UO}_7$  and  $\text{TeO}_3$  polyhedra form a framework in which every equatorial ligand of U links to one of three types of Te. The Te2 and Te3 sites lie on triad axes, and are arranged like  $2 \times 2 \times 2$  unit cubes of the CsCl structure. Three Te1 and three U form a buckled hexagon around each Te2, and the equatorial oxygen atoms of  $\text{UO}_7$  link to the central Te2, the nearest Te3, the two nearest Te1 of the same hexagon and one Te1 of a neighbouring hexagon (Fig. 23). Three types of  $\text{Na}^+$  are weakly held in interstices, in irregular 3–6 coordination.

#### *Structures with neso $\text{Te}^{4+}\text{X}_{4-5}$ as part of the structural unit*

Table 13 (deposited) shows structures #172–194, in which  $\text{TeX}_4$  or  $\text{TeX}_5$  polyhedra do not link to other Te. However, it is interesting to note that unlike  $\text{TeX}_3$ , these polyhedra always link to some other relatively strongly bonded cation, and thus are always part of a larger structural unit. Nabokoite,  $\text{K}[\text{Cu}_7(\text{TeO}_4)(\text{SO}_4)_5]\text{Cl}$  (#172) is the only example of a structure with neso square-pyramidal  $[\text{TeO}_4]^{4-}$  anions (cf. Fig. 4b). Favreauite,  $\text{Pb}[\text{Cu}_6(\text{BiO}_4)(\text{SeO}_3)_4(\text{OH})](\text{H}_2\text{O})$ , is nearly isostructural according to Mills *et al.* (2014b), who noted that the lone-pair cations (Bi, Te) are partially surrounded by corner-sharing  $\text{CuO}_4$  squares to make a thick layer  $\parallel (002)$ , that can be regarded as a slice of the structure of murdochite,  $\text{Cu}_6\text{Pb}^{4+}\text{O}_8$  (Dubler *et al.*, 1983). The resemblance is emphasized if the arrangement is considered of oxygen-centred tetrahedra  $\text{OCu}_3\text{A}$  ( $A = \text{Te}$  and  $\text{Pb}$ ), according to the approach of Krivovichev *et al.* (2013). The layers are braced by  $\text{SO}_4$  tetrahedra, while the interlayers contain  $\text{Cl}^-$ , which is a distant

fifth ligand for one of the  $\text{Cu}^{2+}$  cations, and  $\text{CN8 K}^+$  (Fig. 23). Atlasovite,  $\text{KCu}_6\text{Fe}^{3+}\text{BiO}_4(\text{SO}_4)_5\text{Cl}$ , is closely associated and appears to be isostructural with nabokoite (Popova *et al.*, 1987).

Four-coordinate  $\text{Te}^{4+}$  is rare in the square-pyramidal geometry, but occurs much more often in the ‘trigonal bipyramid – 1’ or ‘folded rhombus/kite’ geometry of Fig. 4c. An example is the pyrosulfate  $[\text{Te}(\text{S}_2\text{O}_7)_2]$  (#173). The  $(\text{S}_2\text{O}_7)^{2-}$  anions are bidentate ligands for the  $\text{Te}^{4+}$  cation, so neutral molecules are formed which consist of butterfly-like pairs of  $\text{Te-S-S}$  3-rings. These are held together through long  $\text{Te}\cdots\text{O}$  bonds (Fig. 24). In  $\text{In}_2[\text{Mo}^{6+}\text{O}_3(\text{TeO}_4)](\text{TeO}_3)$ , (#174),  $\text{InO}_6$  and  $\text{InO}_8$  polyhedra share corners and edges to form a stepped layer  $\parallel (10\bar{1})$ , which is not treated as a structural unit here, given the high coordination number of half of the In cations. The layers are braced by isolated  $(\text{TeO}_3)$  pyramids but also by  $\text{MoO}_4$  tetrahedra and  $\text{TeO}_4$  polyhedra, which share a corner to form the dimeric anion  $[\text{MoO}_3(\text{TeO}_4)]^{3-}$ . Layers are held together by long  $\text{Te}\cdots\text{O}$  bonds. A much more complex finite cluster occurs in  $(\text{NH}_4)_9\text{K}[\text{V}^{4+}\text{V}_8^{5+}\text{Mo}_6^{6+}\text{O}_{65}(\text{TeO}_4)(\text{TeO}_3)_2] \cdot 27\text{H}_2\text{O}$  (#175). The clusters are very similar to the expanded/modified Keggin/Dawson-type anions of #54–62, but are included here because it includes not only two  $\text{TeO}_3$  groups centring its two dissimilar half-cages, but also a  $\text{TeO}_4$  polyhedron as part of one half-cage (Fig. 24). There is considerable (V, Mo) disorder in the half-cuboctahedral cages. One Keggin half-cuboctahedron of composition  $[(\text{V}_{4.25}\text{Mo}_{4.75})\text{O}_{30}(\text{TeO}_3)]$  shares edges and CN3 oxygens with the Mo octahedra of a ring of three  $\text{MoO}_6$  octahedra alternating with three  $\text{V}^{5+}\text{O}_4$  tetrahedra; the Mo and V polyhedra of this ring also share corners with the other half-cuboctahedron  $[(\text{V}_{4.75}\text{Mo}_{4.25})\text{O}_{30}(\text{TeO}_3)]$ , which has the CN4 Te sitting outside one of the square faces, and bonded to the oxygen atoms surrounding that face. The anions pack with their long axes approximately parallel to  $[10\bar{2}]$ , and are held together through weak bonds to  $\text{K}^+$  and  $\text{NH}_4^+$  ions and  $\text{H}_2\text{O}$  molecules.

$\text{BaV}_2^{5+}\text{TeO}_8 \equiv \text{Ba}_2[(\text{VO}_2)_4(\text{TeO}_4)_2]$  (#176) has  $\text{VO}_5$  polyhedra forming edge-sharing dimers  $[\text{V}_2\text{O}_8]^{6-}$  and isolated tetrahedra  $[\text{VO}_4]^{3-}$ .  $\text{TeO}_4$  polyhedra share an edge with  $\text{VO}_5$  and the remaining corners with two  $\text{VO}_4$  groups to form a *zweier* double chain with 8-rings,  $[(\text{VO}_2)_4(\text{TeO}_4)_2]^{4-}$  (Fig. 24). Expressing the V component as vanadyl  $[\text{VO}_2]^+$  complexes is suggested by the bond distances:  $2 \times 1.65$  and  $2 \times 1.78\text{--}1.83 \text{ \AA}$  for  $\text{VO}_4$  and  $2 \times 1.64\text{--}1.65$  and  $3 \times 1.89\text{--}1.99 \text{ \AA}$  for



VO<sub>5</sub>. The chains run  $\parallel y$ , and are flattened  $\parallel (103)$ ; they are linked through CN10 Ba<sup>2+</sup>. The Sr analogue (#177) has a much more complex structure in which eight kinds of VO<sub>n</sub> polyhedron occur as corner-sharing dimers, either O<sub>3</sub>V–O–VO<sub>3</sub> or O<sub>3</sub>V–O–VO<sub>4</sub>, and these are linked through TeO<sub>3</sub> and TeO<sub>4</sub> to make *sechser* double chains with 6- and 10-rings, [V<sub>8</sub>O<sub>18</sub>(TeO<sub>4</sub>)<sub>2</sub>(TeO<sub>3</sub>)<sub>2</sub>]<sup>8-</sup>. The subchains are joined through TeO<sub>4</sub> and VO<sub>5</sub> sharing an edge. Two topologically similar but crystallographically distinct types of such chain run  $\parallel [1\bar{1}0]$ , and are connected through CN8–10 Sr<sup>2+</sup> ions. (NH<sub>4</sub>)<sub>4</sub>[Mo<sub>6</sub>O<sub>16</sub>(TeO<sub>4</sub>)<sub>4</sub>]·2H<sub>2</sub>O and its Rb equivalent (#178–179) have clusters [Mo<sub>6</sub>O<sub>22</sub>]<sup>6-</sup> in which the six Mo atoms are arranged as a pair of tetrahedra sharing an edge; they are held together through two CN4 oxygen atoms at the centres of the tetrahedra and eight CN2 oxygen atoms along edges. These clusters are linked through Te into continuous complex chains  $\parallel z$ , held together through NH<sub>4</sub><sup>+</sup>/Rb<sup>+</sup> and water molecules.

The structural unit of Ba[NbO(PO<sub>3</sub>)(TeO<sub>4</sub>)] (#180) is a highly corrugated layer  $\parallel (002)$ . Corner-sharing NbO<sub>6</sub> octahedra form linear chains  $\parallel y$ . Each pair of adjacent Nb polyhedra then share additional corners with a TeO<sub>4</sub> polyhedron and a PO<sub>4</sub> tetrahedron to form a tetrahedral Nb<sub>2</sub>TeP cluster. The Te atom makes an additional link to Nb in the next chain, thus joining chains into layers. Note that TeO<sub>4</sub> and PO<sub>4</sub> share one oxygen atom: the formula above has been written to emphasize the Te coordination, but the structural unit could equally be written [NbO(PO<sub>4</sub>)(TeO<sub>3</sub>)]<sup>2-</sup>. CN10 Ba<sup>2+</sup> share edges with the phosphate groups, holding the layers together (Fig. 24). CdMo<sup>6+</sup>TeO<sub>6</sub> ≡ [Cd(MoO<sub>2</sub>)(TeO<sub>4</sub>)] (#181) has a layered structure that is a highly modified 1 × 1 × 2 superstructure of the fluorite type with ordered cations and also cation and anion vacancies, (CdMoTe□)(O<sub>6</sub>□<sub>2</sub>) ≡ Ca<sub>4</sub>F<sub>8</sub>. The cations occupy ¾ of the sites in a *ccp* array, with a four-layer sequence along *z* in which layers repeat in the order Cd, (Mo+Te), □, (Mo+Te). Only long Te···O bonds hold the structure together across the layers of vacant cation sites. Cadmium is 8-coordinated by oxygen atoms, but half of the oxygen sites that are not adjacent to Cd are vacant. Displacements of the remaining oxygen atoms reduce the coordination number of Te and Mo from 6 to 4, although the geometries are different: respectively ‘trigonal bipyramid – 1’ and tetrahedral. The TeO<sub>4</sub> and MoO<sub>4</sub> polyhedra share corners to form chains [MoTeO<sub>6</sub>]<sup>2-</sup> that run  $\parallel [110]$  and  $\parallel [1\bar{1}0]$  in alternate layers along *z* (Fig. 24). When smaller divalent cations replace Cd, a small lattice strain reduces the

coordination number from 8 to 6, and the symmetry from tetragonal to orthorhombic, as seen for [M(MoO<sub>2</sub>)(TeO<sub>4</sub>)], (M = Mg, Mn, Co and Zn) (#182–185). Given the close structural relationship and very strong layering, the Cd compound has been grouped with these as having a layer rather than chain structural unit, even though 8-coordination would normally exclude Cd<sup>2+</sup> from the unit as too weakly bonded. In BaMo<sub>2</sub><sup>6+</sup>TeO<sub>9</sub> ≡ Ba[Mo<sub>2</sub>O<sub>5</sub>(TeO<sub>4</sub>)] and its W analogue (#186–187), MO<sub>6</sub> octahedra (M = Mo or W) share three *fac* corners to form undulating layers  $\parallel (001)$  of 6-rings that are in chair configuration. The layers are reinforced by TeO<sub>4</sub> sharing edges with two Mo polyhedra and a corner with a third octahedron, while the layers are held together by CN11 Ba<sup>2+</sup> ions.

The compounds A<sub>2</sub>Mo<sub>2</sub><sup>6+</sup>Te(PO<sub>4</sub>)<sub>2</sub>O<sub>6</sub> ≡ A<sub>2</sub>[Mo<sub>2</sub>P<sub>2</sub>O<sub>10</sub>(TeO<sub>4</sub>)] (A = Rb, Cs and Tl; #188–190) alternating MoO<sub>6</sub> octahedra and PO<sub>4</sub> tetrahedra share corners to form layers [(MoO<sub>3</sub>)<sub>2</sub>(PO<sub>4</sub>)<sub>2</sub>]<sup>6-</sup>  $\parallel (002)$  with a 3-connected net of 4- and 8-rings. Interlayer TeO<sub>4</sub> polyhedra link these layers into a framework, sharing corners to make Te–P–Mo 3-rings. The A<sup>+</sup> cations are in 9-coordination in the interlayer. Note that Tl<sup>+</sup> shows little sign of lone-pair stereoactivity (Tl–O = 2.77–3.17 Å, compared to 2.83–3.17 Å for Rb). Mn<sup>2+</sup>V<sup>4+</sup><sub>2</sub>TeO<sub>7</sub> ≡ [Mn<sup>2+</sup>V<sup>4+</sup><sub>2</sub>O<sub>3</sub>(TeO<sub>4</sub>)] (#191) has double chains  $\parallel [110]$  in which pairs of VO<sub>5</sub> alternate with pairs of VO<sub>6</sub>, sharing edges and CN3 oxygen atoms in a manner similar to the Te chain of Fig. 10a. These chains are linked into double layers  $\parallel (001)$  by markedly asymmetric TeO<sub>3+1</sub> groups (Te–O = 3 × 1.86–1.94 and 1 × 2.34 Å; with no more until 2.87 Å), which share edges with two VO<sub>6</sub> of one chain and a corner with VO<sub>5</sub> of an adjacent chain. The layers are then linked into a framework through MnO<sub>6</sub> octahedra, which also share edges with VO<sub>6</sub> and TeO<sub>4</sub>. For simplicity, the formula above does not indicate that each V atom has one very close (1.64–1.67 Å), approximately double-bonded oxygen ligand, as is typical for V<sup>4+</sup>. The remaining non-tellurite oxygen atom is shared by one VO<sub>6</sub> and two VO<sub>5</sub> polyhedra.

In Zn<sub>3</sub>V<sub>2</sub><sup>5+</sup>TeO<sub>10</sub> ≡ [Zn<sub>3</sub>(VO<sub>3</sub>)<sub>2</sub>(TeO<sub>4</sub>)] (#192), two types of ZnO<sub>5</sub> and one of ZnO<sub>6</sub> polyhedra share edges and corners to make very thick, but looped and low-density layers  $\parallel (020)$ . The higher-valence cations are linked into bow-shaped anions [O<sub>3</sub>V–O–TeO<sub>2</sub>–O–VO<sub>3</sub>]<sup>6-</sup>, which are embedded in the Zn layers, but also cross-link them into a framework through one of the terminal vanadate groups (Fig. 24). Co<sub>6</sub><sup>2+</sup>Te<sub>5</sub>O<sub>16</sub> ≡ [Co<sub>6</sub>(TeO<sub>4</sub>)(TeO<sub>3</sub>)<sub>4</sub>] (#193) has blocks of edge-sharing tetramers of CoO<sub>6</sub> octahedra sharing corners with

edge-sharing dimers of  $\text{CoO}_5$  to make a framework with large channels running  $\parallel y$ . Four types of  $\text{TeO}_n$  groups cross-link across the channels and other interstices between the Co blocks. The only example of  $\text{TeX}_5$  in a framework is  $\text{Co}_3^{2+}\text{Te}_2(\text{PO}_4)_2\text{O}_2(\text{OH})_4 \equiv [\text{Co}_3(\text{PO}_4)_2(\text{TeO}_3(\text{OH})_2)_2]$  (#194), which has *trans* edge-sharing chains of  $\text{CoO}_6$  octahedra running  $\parallel y$ . These are linked into layers  $\parallel (200)$  through corner-sharing chains of alternating  $\text{PO}_4$  tetrahedra and  $\text{TeO}_3(\text{OH})_2$  square pyramids,  $[\text{TePO}_5(\text{OH})_2]^{3-}$ , and then into a framework through interlayer  $\text{CoO}_2(\text{OH})_4$  polyhedra.

#### Dimeric $\text{Te}^{4+}$ oxyanions $[\text{Te}_2\text{X}_n]$ ( $n = 5-9$ )

Compounds with dimeric sorotellurite groups are #195–227, shown in Table 14 (deposited). The simplest example of the  $[\text{Te}_2\text{O}_5]^{2-}$  anion (Fig. 8a) is provided by  $\text{Cs}_2[\text{Te}_2\text{O}_5]$  (#195). Interestingly, the structure can be regarded as a defect perovskite, with  $1/6$  of the anions missing. The orthorhombic unit cell corresponds to a  $2\sqrt{2} \times 2\sqrt{2} \times 2$  supercell of the aristotypical perovskite cube, with  $\text{Cs}^+$  in the large-cation *A* positions and Te in *B* sites. The  $\text{Te}_2\text{O}_5$  dimers are separated from one another by vacancies on the anion sites and asymmetrical  $\text{Te}-\text{O}\cdots\text{Te}$  links, where the short distances are 1.83–1.97 Å and the long ones are 2.68–4.43 Å. The Te–Te vectors of anions point along  $[110]$  or  $[1\bar{1}0]$  in a herringbone pattern (Fig. 25). The  $\text{Cs}^+$  ions are in 9-coordination.  $\text{Ba}_3[\text{Te}_2\text{O}_5](\text{TeO}_3)\text{Br}_2$  (#196) has edge-sharing  $\text{BaO}_8\text{Br}$  and  $\text{BaO}_5\text{Br}_3$  polyhedra forming columns  $\parallel y$ , which share edges sparsely to surround elongated micelles. These channels accommodate the  $\text{Br}^-$  anions and also the lone pairs of the Te dimers and monomers, which brace the micelle walls. In  $\text{Nd}_2[\text{Te}_2\text{O}_5](\text{TeO}_3)(\text{MoO}_4)$  (#197),  $\text{NdO}_8$  polyhedra share edges to form undulating honeycomb layers  $\parallel (200)$ . The layers are braced by molybdate and tellurite groups, and are held together only by long  $\text{Te}\cdots\text{O}$  bonds.

$\text{TiTeO}_3\text{F}_2 \equiv [\text{Ti}_2\text{OF}_4(\text{Te}_2\text{O}_5)]$  (#198) has  $\text{TiO}_2(\text{O}_{0.5}\text{F}_{0.5})_2\text{F}_2$  octahedra sharing corners to make *zweier* double chains of 4-rings,  $[\text{Ti}_4\text{O}_8\text{F}_8]^{8-}$  running  $\parallel x$ .  $\text{Te}_2\text{O}_5$  groups share four oxygen atoms with a square of adjacent Ti atoms in the double chain to make  $\text{Te}_2\text{Ti}_4$  triangular prisms. Long (2.73–2.77 Å)  $\text{Te}\cdots\text{O}$  bonds link the resulting loop-branched double chains into double layers  $\parallel (020)$ , which are then held together through 2.56 Å  $\text{Te}\cdots\text{F}$  bonds (Fig. 25).  $\text{V}_2^{4+}\text{Te}_2\text{O}_7\text{F}_2 \equiv [(\text{VO})_2\text{F}_2(\text{Te}_2\text{O}_5)]$  (#199) has *cis*- $\text{VO}_4\text{F}_2$  octahedra sharing alternately  $\text{O}_2$  and  $\text{F}_2$  edges to make zigzag *zweier* chains  $\parallel x$ .  $\text{Te}_2\text{O}_5$  groups cross-link the V

chains into layers  $\parallel (010)$  in such a way that  $\text{Te} < (\text{V} = \text{V}) > \text{Te}$  ‘double triangle’ clusters are formed. As is typical for  $\text{V}^{4+}$ , the distance to the non-tellurite oxygen ligand is very short (1.595 Å). The layers are held together via long  $\text{Te}\cdots\text{O}$  and  $\text{Te}\cdots\text{F}$  links.  $\text{Fe}_8\text{Cu}_3\text{Te}_{12}\text{O}_{32}\text{Cl}_{10} \equiv [(\text{Fe}^{2+}\text{Fe}^{3+})(\text{Te}_2\text{O}_5)_4(\text{TeO}_3)_4](\text{Cu}_2^{1+}\text{Cl}_6)(\text{Cu}^{1+}\text{Cl}_2)\text{Cl}_2$  (#200) has zigzag chains of edge-sharing  $\text{FeO}_6$  polyhedra  $\parallel z$ , which share corners to make layers  $\parallel (200)$ . These layers are braced by the monomeric and dimeric Te anions. Between the layers lie three types of  $\text{Cl}^-$  anions. One of these makes long bonds to the Te of  $\text{Te}_2\text{O}_5$  in the adjacent layers, while the other  $\text{Cl}^-$  anions form chains of edge-sharing tetrahedra  $\parallel z$ . The tetrahedral interstices are half occupied by  $\text{Cu}^{1+}$ , which also occupies linear twofold coordinated sites in the tetrahedron edges that are  $\parallel y$ . Thus, a chain is formed of alternating  $[\text{Cu}_2\text{Cl}_6]^{4-}$  and  $[\text{CuCl}_2]^-$  anions (Fig. 25).

The elegant framework structure of  $[\text{Cu}_2(\text{Te}_2\text{O}_5)\text{Cl}_2]$  and its Br analogue (#201–202) has square pyramids  $\text{CuO}_4\text{X}$  ( $\text{X} = \text{Cl}$  or  $\text{Br}$ ) that share edges in groups of four to make clusters with a  $\text{Cu}_4\text{O}_4$  cube at the core and have  $\bar{4}$  point symmetry. These clusters sit in columns  $\parallel z$ , and are linked to their neighbours by corner-sharing with  $\text{Te}_2\text{O}_5$  groups, which act as the walls of  $\sim 6$  Å diameter square channels  $\parallel z$ . The channels accommodate the  $\text{X}^-$  anions and Te lone pairs (Fig. 25). Our second polymorph of  $\text{V}_2^{4+}\text{Te}_2\text{O}_9 \equiv [(\text{VO})_2(\text{Te}_2\text{O}_5)]$  (#203) has corner-sharing *zweier* chains of  $\text{VO}_5$  polyhedra that lie in layers  $\parallel (400)$  and run  $\parallel [011]$  or  $[0\bar{1}1]$  in alternate layers.  $\text{Te}_2\text{O}_5$  groups bridge two V chains of one layer and two chains of the next to make a framework. A polymorph with monomeric rather than dimeric  $\text{TeO}_3$  groups was described above (#144).  $\text{Cr}_2^{3+}\text{Te}_4\text{O}_{11} \equiv [\text{Cr}_2(\text{Te}_2\text{O}_5)(\text{TeO}_3)_2]$  (#204) has edge-sharing dimers of  $\text{CrO}_6$  octahedra linked into a framework through Te; only the central oxygen of  $\text{Te}_2\text{O}_5$  does not link to Cr.  $\text{Ni}_{3.4}[\text{Ni}_{30}(\text{Te}_2\text{O}_5)_6(\text{TeO}_3)_{20}]\text{Br}_{14.8}$  (#205) and  $\text{Ni}_{4.5}[\text{Ni}_{30}(\text{Te}_2\text{O}_5)_6(\text{TeO}_3)_{20}]\text{Cl}_{18.45}$  (#206) are isotypical compounds with large cubic unit cells ( $Im\bar{3}$ ,  $a \approx 17.5$  Å). The ordered part of the structure consists of  $\text{NiO}_6$  and  $\text{NiO}_5$  polyhedra which shared edges to form large icosahedral cages, braced by the Te anions,  $[\text{Ni}_{30}^{2+}(\text{Te}_2\text{O}_5)_6(\text{TeO}_3)_{20}]^{8+}$ . The rest of the structure shows substantial disorder. The large cages contain an icosahedral cluster of 12 Ni positions which cannot be  $>50\%$  occupied due to short  $\text{Ni}\cdots\text{Ni}$  distances. Partly occupied halide anion sites are at the core of these clusters, surrounding their exteriors so that the additional  $\text{Ni}^{2+}$  are in approximate 4-coordination by  $(\text{Br}, \text{Cl})^-$ ,

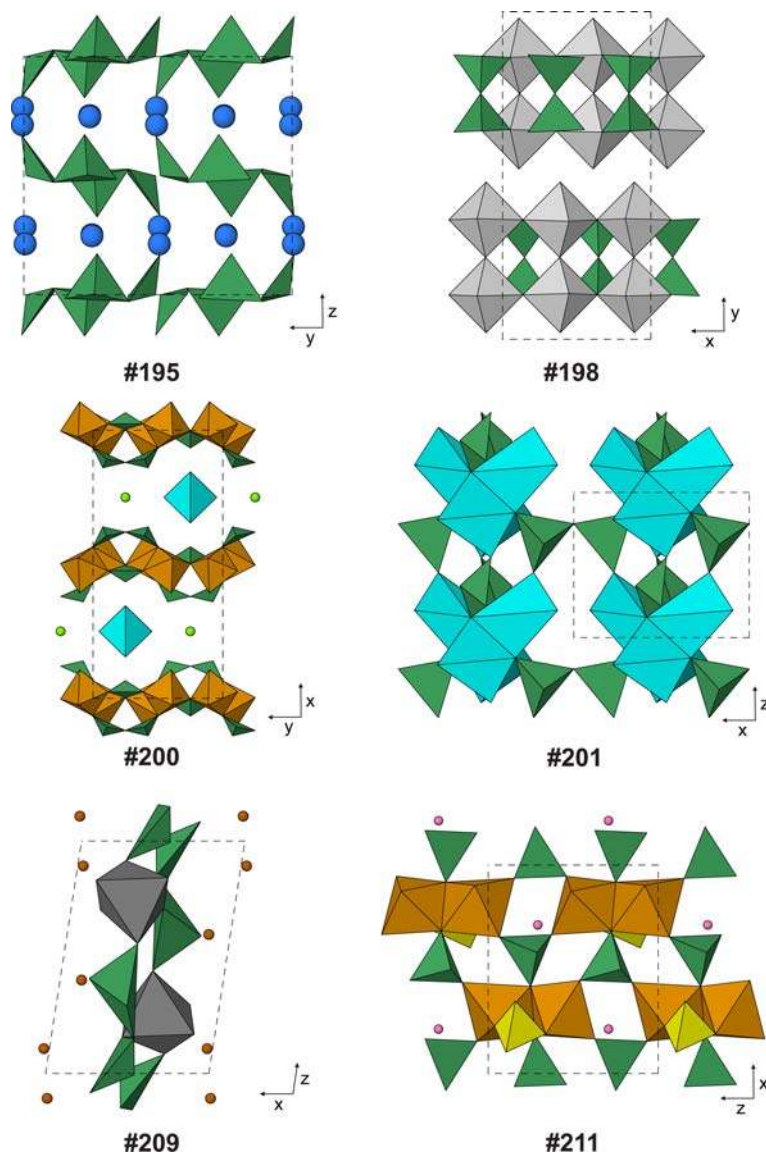


FIG. 25. Examples of structures with  $\text{Te}_2^{4+}\text{O}_{5-6}$  dimers (Table 14, deposited). Small spheres: Cl (yellow-green), N (brown) and O (dark pink) when not part of a polyhedron. Large spheres: Cs (blue). Polyhedra: Cu (cyan), Fe (orange-brown), S (yellow), Te (dark green), Ti (pale grey) and W (dark grey).

and halfway between the Ni clusters in channels  $\parallel <100>$ , making long  $\text{Te}\cdots(\text{Br},\text{Cl})$  bonds.

$\text{Ho}_{11}[\text{Te}_2\text{O}_6]_2(\text{TeO}_3)_{12}\text{Cl}$  (#207) has layers  $\parallel (012)$  of edge-sharing  $\text{HoO}_{6-8}$  polyhedra, sparsely connected into a framework with channels running  $\parallel \mathbf{x}$ . The walls of the channels are braced by six types of monomeric  $(\text{TeO}_3)^{2-}$  and also a dimer in which  $\text{TeO}_3$  shares a corner with  $\text{TeO}_4$  to form the

structural unit,  $[\text{Te}_2\text{O}_6]^{4-}$  (Fig. 8b). The shortest  $\text{Te}-\text{O}$  distance is 2.18 Å; there are no others until 2.47 Å. The  $\text{Cl}^-$  ion is loosely bound in the centre of the channels, into which the Te lone pairs also point. Moctezumite,  $\text{Pb}[(\text{UO}_2)(\text{Te}_2\text{O}_6)]$  (#208) has similar  $\text{Te}_2\text{O}_6$  dimers, fringing zigzag chains of edge-sharing  $\text{UO}_7$  polyhedra to form broad ribbons  $\parallel \mathbf{y}$ . The ribbons lie in layers  $\parallel (10\bar{2})$ , which are held

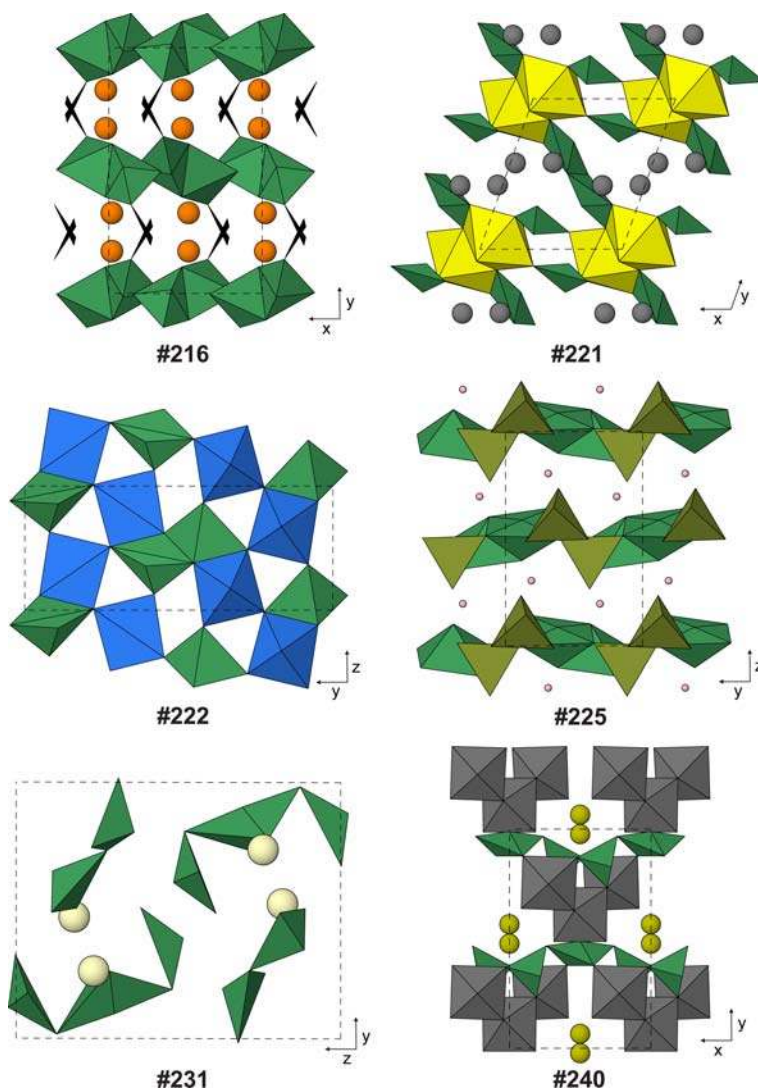


FIG. 26. Examples of structures with soro groups  $\text{Te}_2^{4+}\text{O}_{6-8}$  or  $\text{Te}_3\text{O}_8$  (Tables 14–15, deposited). Large spheres: Ca (orange), Dy (light yellow), Na (dark yellow) and Tl (grey). Black triangles in mroseite, **#216**:  $\text{CO}_3$  groups. Polyhedra: As (brown-green), Mo (grey), Te (dark green), U (yellow) and V (blue).

together by  $\text{PbO}_{3+4}$  polyhedra. A high-pressure (5.09 GPa) structure of  $(\text{NH}_4)_2\text{WTe}_2\text{O}_8 \equiv (\text{NH}_4)_2[\text{WO}_2(\text{Te}_2\text{O}_6)]$  (**#209**) has layers  $\parallel (100)$  in which  $\text{WO}_6$  octahedra share four corners and each Te of  $\text{Te}_2\text{O}_6$  shares two, to form a net of Te–W–Te–Te–W 5-rings which has the topology of the ‘Cairo tiling’ (Hyde and Andersson, 1989), seen in less crumpled form in the tetrahedral sheet of the melilite group of minerals, e.g.  $(\text{Ca},\text{Na})_2[(\text{Al},\text{Si},\text{Mg})_3\text{O}_7]$  (Smith, 1953). Layers are held together by

$\text{NH}_4^+$  ions (Fig. 25).  $\text{InV}^{5+}\text{Te}_2\text{O}_8 \equiv [\text{In}(\text{VO}_2)(\text{Te}_2\text{O}_6)]$  (**#210**) has zigzag corner-sharing chains of  $\text{InO}_6$  octahedra  $\parallel y$ , sharing additional corners with  $\text{VO}_4$  tetrahedra to make In–In–In–V 4-rings.  $\text{Te}_2\text{O}_6$  groups link the resulting ribbons to their neighbours to form thick layers  $\parallel (10\bar{1})$ , held together only through long  $\text{Te}\cdots\text{O}$  bonds. Showing the V as vanadyl is validated by the asymmetry in V–O distances ( $2 \times 1.61\text{--}1.69 \text{ \AA}$  and  $2 \times 1.81\text{--}1.83 \text{ \AA}$ ). Poughite,  $\text{Fe}_2^{3+}\text{Te}_2\text{O}_6(\text{SO}_4) \cdot 3\text{H}_2\text{O} \equiv [\text{Fe}_2(\text{H}_2\text{O})_2$



(SO<sub>4</sub>)(Te<sub>2</sub>O<sub>6</sub>) · H<sub>2</sub>O (**#211**), has an edge-sharing dimer of FeO<sub>5</sub>(H<sub>2</sub>O) octahedra sharing additional corners with an SO<sub>4</sub> tetrahedron to form a finite 3-ring cluster [Fe<sub>2</sub>O<sub>6</sub>(H<sub>2</sub>O)<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub>]<sup>8-</sup>. These are linked together in groups of four through Te<sub>2</sub>O<sub>6</sub> to make layers || (020), with the remaining H<sub>2</sub>O molecule in the interlayer (Fig. 25). Sr[Cu<sub>2</sub>Cl(Te<sub>2</sub>O<sub>6</sub>)]Cl and the isostructural Ba compound (**#212–213**) have Te<sub>2</sub>O<sub>6</sub> sharing all six oxygen atoms with Cu<sub>2</sub>O<sub>6</sub>Cl dimers of CuO<sub>4</sub> and CuO<sub>3</sub>Cl squares, to make a rather open framework, with channels || **x** and **y** which contain the remaining Cl<sup>-</sup> and also (Sr,Ba)<sup>2+</sup> ions, coordinated by 6O + 2Cl.

Pb<sub>3</sub>Te<sub>2</sub>O<sub>6</sub>Cl<sub>2</sub> ≡ Pb<sub>6</sub>[Te<sub>2</sub>O<sub>6</sub>](TeO<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> and its Br analogue (**#214–215**) contain edge-sharing dimers of TeO<sub>4</sub> (Fig. 8c). They have edge-sharing layers || (20 $\bar{1}$ ) of PbO<sub>4</sub>X<sub>4</sub>, PbO<sub>5</sub>X<sub>3</sub> and PbO<sub>8</sub>X polyhedra (X = Cl or Br). The layers are braced by Te<sub>2</sub>O<sub>6</sub> and TeO<sub>3</sub> groups, and loosely held into a framework through Pb–X and Te··X bonds. The Te–O bonds out to 2.05 Å in mroseite (**#216**) define a neutral dimer [Te<sub>2</sub>O<sub>4</sub>]<sup>0</sup>, made from an edge-sharing pair of TeO<sub>3</sub> pyramids, suggesting that the formula be written Ca<sub>2</sub>(Te<sub>2</sub>O<sub>4</sub>)[CO<sub>3</sub>]<sub>2</sub>. However, each Te is only 2.31 Å from a carbonate oxygen atom, so it could also be expressed as Ca[(CO<sub>2</sub>)<sub>2</sub>(Te<sub>2</sub>O<sub>6</sub>)]. The S-shaped [(CO<sub>2</sub>)<sub>2</sub>(Te<sub>2</sub>O<sub>6</sub>)]<sup>4-</sup> heteropolyanions pack in a herringbone pattern to form strongly corrugated layers || (002), which are held together through CN8 Ca<sup>2+</sup> ions (Fig. 26). NaV<sup>5+</sup>TeO<sub>5</sub> ≡ Na<sub>2</sub>[(VO<sub>2</sub>)<sub>2</sub>(Te<sub>2</sub>O<sub>6</sub>)] is atypical with its K<sup>+</sup> and Ag<sup>+</sup> analogues (**#217–219**). In these compounds, edge-sharing Te<sub>2</sub>O<sub>6</sub> dimers share corners with VO<sub>4</sub> tetrahedra to make chains with 4-rings Te–V–Te–V, which extend || [101]. These pack, herringbone fashion, in layers || (020). Large cations between the layers are in 8-fold coordination, but while this is fairly regular for K<sup>+</sup> (K–O = 2.67–2.99 Å), it is less so for the smaller cations (Na–O and Ag–O both = 2.41–2.91 Å). Ba<sub>2</sub>V<sup>5+</sup>Te<sub>2</sub>O<sub>11</sub> ≡ Ba<sub>2</sub>[(VO<sub>2</sub>)(VO<sub>3</sub>)(Te<sub>2</sub>O<sub>6</sub>)] (**#220**) has Te<sub>2</sub>O<sub>6</sub> groups alternating with VO<sub>4</sub> tetrahedra to make a *dreier* chain || **y**, which has a second type of VO<sub>4</sub> as an open branch on one of the central oxygen atoms of each Te<sub>2</sub>O<sub>6</sub>. The chains lie in layers || (200), which have BaO<sub>8–10</sub> polyhedra between them. The α form of Tl<sub>2</sub>(UO<sub>2</sub>)Te<sub>2</sub>O<sub>6</sub> ≡ Tl<sub>4</sub>[(UO<sub>2</sub>)<sub>2</sub>(Te<sub>2</sub>O<sub>6</sub>)(TeO<sub>3</sub>)<sub>2</sub>] (**#221**) has a β dimorph with monomeric TeO<sub>3</sub> in a heteropoly chain structure, **#70** above. The α structure has edge-sharing pairs of UO<sub>7</sub> polyhedra sharing further edges with Te<sub>2</sub>O<sub>6</sub> to make ribbons || [110]. The U polyhedra are bridged by additional TeO<sub>3</sub> to link the ribbons into layers || (1 $\bar{1}$  $\bar{1}$ ) with 12-rings and U–Te–U–Te 4-rings. Between the layers are Tl1 showing

little lone-pair stereoactivity (8 × O at 2.63–3.13 Å) and Tl2 with much less symmetrical coordination (3 × O at 2.49–2.69 Å and four more at 3.27–3.56 Å) (Fig. 26). The β phase of V<sup>4+</sup>TeO<sub>4</sub> ≡ [(VO)<sub>2</sub>(Te<sub>2</sub>O<sub>6</sub>)], stable at high-temperature, has corner-sharing VO<sub>5</sub> making zigzag chains || (**#222**); the V polyhedra share edges with Te<sub>2</sub>O<sub>6</sub> to make layers || (100) (Fig. 26). The vanadyl oxygen atom is at 1.61 Å from V, but also makes three weak bonds to Te of the next layer (2.96–3.25 Å). There is little resemblance to the raspite structure of the α dimorph (**#82**). NiV<sup>5+</sup>Te<sub>2</sub>O<sub>10</sub> ≡ [Ni(VO<sub>2</sub>)<sub>2</sub>(Te<sub>2</sub>O<sub>6</sub>)] (**#223**) has distorted VO<sub>6</sub> octahedra sharing edges to make zigzag chains [V<sub>2</sub>O<sub>8</sub>]<sup>6-</sup> || **x**. Te<sub>2</sub>O<sub>6</sub> groups each bridge four such chains, while NiO<sub>6</sub> octahedra bridge two V chains and two Te<sub>2</sub>O<sub>6</sub> groups, forming a quite dense framework with many Ni–V–V and Ni–V–Te 3-rings.

BaMo<sub>2</sub>Te<sub>2</sub>O<sub>11</sub> · H<sub>2</sub>O ≡ Ba[Mo<sub>2</sub>O<sub>4</sub>(Te<sub>2</sub>O<sub>7</sub>)] · H<sub>2</sub>O (**#224**) has *cis*-corner-sharing MoO<sub>6</sub> octahedra forming helical *vierer* chains || **y**. These are linked into thick layers || (002) via Te dimers which are corner-sharing [Te<sub>2</sub>O<sub>7</sub>]<sup>6-</sup> groups (Fig. 8d), if Te–O distances out to 2.43 Å are included. Water molecules and CN10 Ba<sup>2+</sup> ions are between the layers. Polymorph I of TeO(As<sup>5+</sup>O<sub>3</sub>OH) ≡ [(AsOH)<sub>2</sub>(Te<sub>2</sub>O<sub>8</sub>)] (**#225**), like many compounds of Te with other high bond-valence cations, has Te<sup>4+</sup> in 5-coordination. Here, two TeO<sub>5</sub> pyramids share edges to make a [Te<sub>2</sub>O<sub>8</sub>]<sup>8-</sup> dimer (Fig. 8e). These share corners with [AsO<sub>3</sub>OH]<sup>2-</sup> tetrahedra to make As<(Te=Te)>As clusters which are yet another variant of the common ‘double triangle’ motif (Fig. 26). The remaining unprotonated oxygen atom on As is shared with Te of a neighbouring cluster, linking clusters to form double chains || **y**. Chains are held together through hydrogen bonds and long Te··O bonds. Tellurium polyhedra are condensed further in polymorph II (**#299**, below). The edge-sharing Te<sub>2</sub>O<sub>8</sub> group also features in Ba<sub>2</sub>TeO(PO<sub>4</sub>)<sub>2</sub> ≡ Ba<sub>4</sub>[(PO<sub>2</sub>)<sub>2</sub>(PO<sub>3</sub>)<sub>2</sub>(Te<sub>2</sub>O<sub>8</sub>)] (**#226**), where such groups are bridged by pairs of corner-sharing PO<sub>4</sub> tetrahedra to form *dreier* chains with [–Te = Te–P–] backbones, not unlike the Te–V chains of **#220**. Again, a second type of tetrahedron forms open branches, but this time, the additional PO<sub>4</sub> groups attach to a single Te atom rather than to a bridging oxygen of the chain backbone. The resulting ribbons lie in layers || (10 $\bar{1}$ ), with BaO<sub>9–11</sub> between them. Te<sub>2</sub>O(PO<sub>4</sub>)<sub>2</sub> ≡ [P<sub>2</sub>(Te<sub>2</sub>O<sub>9</sub>)] (**#227**) again has CN5 Te<sup>4+</sup> (cf. **#225**), but this time in corner-sharing dimers [Te<sub>2</sub>O<sub>9</sub>]<sup>10-</sup> (Fig. 8f). The dimers are linked into a framework through



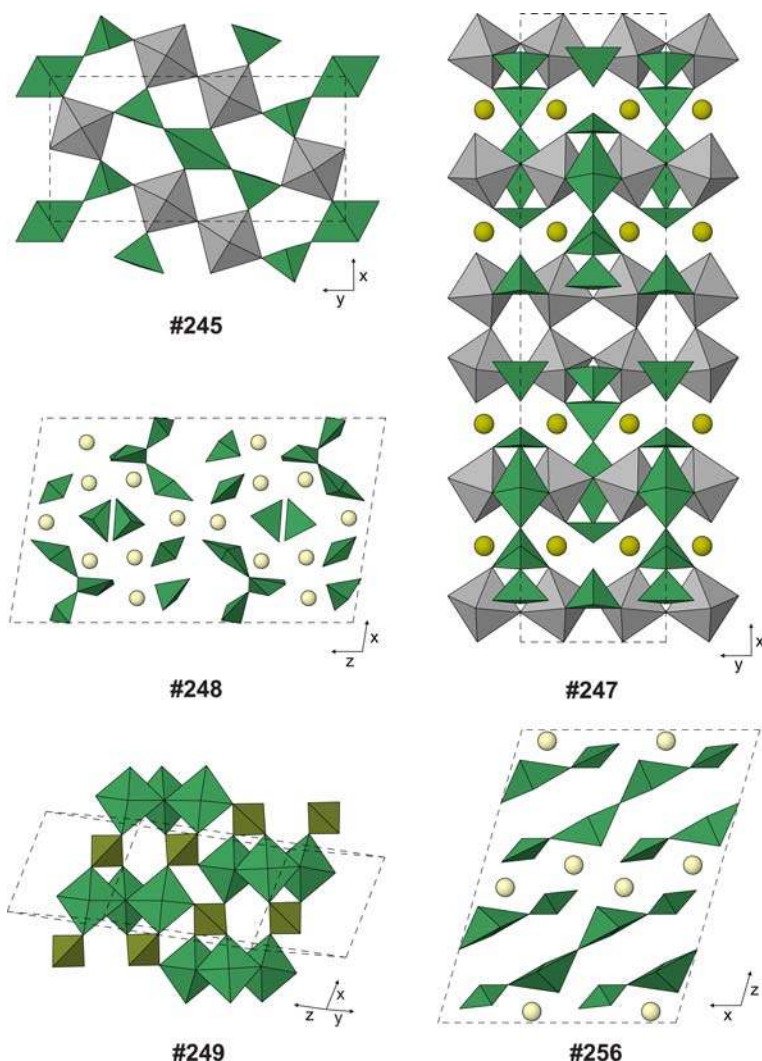


FIG. 27. Examples of structures with soro groups  $\text{Te}_3^{4+}\text{O}_{8-11}$  or  $\text{Te}_4\text{O}_{11}$  (Table 15, deposited). Large spheres: rare-earth elements Dy or La (light yellow) and Na (dark yellow). Polyhedra: As (brown-green), Nb (grey) and Te (dark green).

two types of  $\text{PO}_4$  tetrahedra: one type shares oxygen atoms with Te atoms of four different dimers, whereas the other type links only three dimers, but forms a Te–Te–P 3-ring with both Te atoms of one of them.

#### Trimeric $\text{Te}^{4+}$ oxyanions $[\text{Te}_3\text{X}_n]$ ( $n = 8-11$ )

Trimeric sorotellurite groups occur in structures #228–249 (Table 15, deposited).  $\text{Sr}_3[\text{Te}_3\text{O}_8](\text{TeO}_3)$  (#228) has a triclinic structure in which 2-wide and 4-wide ribbons of edge-sharing  $\text{SrO}_{7-9}$  polyhedra

run  $\parallel x$  and are linked into a framework through a few additional shared edges. Two types of  $[\text{Te}_3\text{O}_8]^{4-}$  (Fig. 8g) and two types of monomeric  $[\text{TeO}_3]^{2-}$  line channels  $\parallel x$  in the Sr–O matrix.  $\text{Ba}_3[\text{Te}_3\text{O}_8](\text{TeO}_3)$  (#229) is nearly isostructural, although with  $x$  and  $z$  axes exchanged, as published. However, it retains a centre of inversion symmetry that is lost in the Sr compound, concomitant with which all  $\text{Te}_3\text{O}_8$  groups are equivalent and  $\text{Ba}^{2+}$  has CN = 8–9. Both structures resemble the unexpectedly complex structures of

the (Ca,Sr)(TeO<sub>3</sub>) phases (#9–15). BaLa<sub>2</sub>[Te<sub>3</sub>O<sub>8</sub>](TeO<sub>3</sub>)<sub>2</sub> (#230) is quite different, in that it has layers || (200) of edge-sharing BaO<sub>12</sub> and LaO<sub>8</sub> polyhedra, which are braced by TeO<sub>3</sub> groups and bridged by Te<sub>3</sub>O<sub>8</sub>. The series A<sub>2</sub>[Te<sub>3</sub>O<sub>8</sub>](Te<sub>2</sub>O<sub>5</sub>) (A = Dy, Ho, Er, Tm, Yb, Lu and Y; #231–237) show even less polymerization of large-cation polyhedra. They have 4-wide ribbons of edge-sharing AO<sub>7–8</sub> polyhedra running || **x**. Interestingly, the Te<sub>3</sub>O<sub>8</sub> groups do not link the ribbons, but only decorate their edges, while Te<sub>2</sub>O<sub>5</sub> groups link the ribbons into thick double layers || (001) (Fig. 26). Long bonds to both types of tellurite anion hold the layers together. Sr<sub>4</sub>[Te<sub>3</sub>O<sub>8</sub>]Cl<sub>4</sub> (#238) has SrO<sub>8</sub>Cl, SrO<sub>4</sub>Cl<sub>5</sub> and SrO<sub>2</sub>Cl<sub>7</sub> polyhedra. These share O<sub>2</sub> edges to form 8-cation-wide ribbons of a fluorite-like structure || **y**, which connect through the longer Sr–Cl bonds into continuous layers || (201), and more sparsely into a three-dimensional framework. The Te<sub>3</sub>O<sub>8</sub> groups brace the Sr–O ribbons. In La<sub>2</sub>[Te<sub>3</sub>O<sub>8</sub>](MoO<sub>4</sub>) (#239), LaO<sub>9</sub> polyhedra share faces, edges and corners to form an open framework La<sub>2</sub>O<sub>11</sub> that has channels || **x** and **y**. Te<sub>3</sub>O<sub>8</sub> groups run down the length of the **y** channels, sharing all oxygen atoms with La, while MoO<sub>4</sub> tetrahedra brace the **x** channels, sharing only three ligands with La.

Na<sub>2</sub>Mo<sub>3</sub>Te<sub>3</sub>O<sub>16</sub> ≡ Na<sub>2</sub>[Mo<sub>3</sub>O<sub>8</sub>(Te<sub>3</sub>O<sub>8</sub>)] and its Ag analogue (#240–241) have MoO<sub>6</sub> octahedra sharing edges to form V-shaped trimers [Mo<sub>2</sub> = Mo1=Mo2], which are linked via Te<sub>3</sub>O<sub>8</sub> groups [Te2–Te1–Te2] to form complex loop-branched *dreier* chains || **x**. The chain has two equivalent backbones –Te1–Te2–Mo2– and –Te1–Mo2–Te2–, which intersect at Te1 and are further braced through Mo1=Mo2 and a CN3 oxygen atom which bonds to Mo1, Mo2 and Te2. Chains are held together via CN6–8 (Na, Ag)<sup>+</sup> (Fig. 26). Ca[Co<sub>2</sub>Cl<sub>2</sub>(Te<sub>3</sub>O<sub>8</sub>)] and its isostructural Sr–Co and Sr–Ni analogues (#242–244) have a structure in which MO<sub>5</sub>Cl octahedra (M = Co or Ni) share edges to form helical *vierer* chains || **y** (cf. #165 and 224). Te<sub>3</sub>O<sub>8</sub> groups bridge these chains to form double layers || (002), the long axes of the Te anions pointing || [110] on one side of the layer and || [110] on the other side. CN8 (Ca,Sr)<sup>2+</sup> ions sit in the cores of the double layers, which are held together through long Te<sup>+</sup>–Cl interactions. Nb<sub>2</sub>Te<sub>3</sub>O<sub>11</sub> ≡ [Nb<sub>2</sub>O<sub>3</sub>(Te<sub>3</sub>O<sub>8</sub>)] (#245) has ladder-like *einer* double chains of 4-rings || **z** of corner-sharing NbO<sub>6</sub> octahedra, arranged in a herringbone pattern. Te<sub>3</sub>O<sub>8</sub> groups share two corners with octahedra in each of the Nb chains in the ±**x** directions and one corner with each of the Nb chains in the ±**y** directions, forming a framework (Fig. 27).

NaNb<sub>3</sub>Te<sub>4</sub>O<sub>16</sub> ≡ Na[Nb<sub>3</sub>O<sub>5</sub>(Te<sub>3</sub>O<sub>8</sub>)(TeO<sub>3</sub>)] (#246) has broader *zweier* triple chains of 4-rings || **y** of NbO<sub>6</sub> octahedra, which are decorated by the TeO<sub>3</sub> monomer, making Nb–Nb–Te 3-rings. The Te<sub>3</sub>O<sub>8</sub> groups link each Nb ribbon to three of its neighbours in a framework. The CN8 Na<sup>+</sup> ion lies between the TeO<sub>3</sub> monomers of neighbouring Nb chains. Na<sub>1.4</sub>Nb<sub>3</sub>Te<sub>4.9</sub>O<sub>18</sub> ≡ Na<sub>1.4</sub>[Nb<sub>3</sub>O<sub>4</sub>(Te<sub>2.9</sub>O<sub>8</sub>)(TeO<sub>3</sub>)<sub>2</sub>] (#247) has a very similar composition and two very similar unit-cell parameters, but the topology is quite different. The NbO<sub>6</sub> octahedra form single and double *zweier* chains || **y**, that alternate in the **x** direction. Te<sub>3</sub>O<sub>8</sub> groups are slightly defective, in that the central Te is only 90% occupied. They link Nb single chains with each other and with neighbouring double chains, forming an open framework with numerous Nb–Nb–Te and Nb–Te–Te 3-rings, while two types of TeO<sub>3</sub> monomer form additional Nb–Nb–Te rings on the double chains. The CN8 Na<sup>+</sup> ions partially occupy sites that lie in channels || **y** (Fig. 27).

Dy<sub>2</sub>(TeO<sub>3</sub>)<sub>3</sub> ≡ Dy<sub>4</sub>[Te<sub>3</sub>O<sub>9</sub>](TeO<sub>3</sub>) (#248) has a surprisingly complex structure with thick, loop-branched layers of edge-sharing DyO<sub>7–8</sub> polyhedra || (100). These are bridged by V-shaped corner-sharing trimers [Te<sub>3</sub>O<sub>9</sub>]<sup>6–</sup>, including Te–O distances out to 2.44 Å (Fig. 8*h*), and three types of independent (TeO<sub>3</sub>)<sup>2–</sup> ion (Fig. 27). The high As<sup>5+</sup>–O bond valence (~1.25 vu) leads to Te adopting 5-coordination in Te<sub>3</sub>O<sub>3</sub>(AsO<sub>4</sub>)<sub>2</sub> ≡ [As<sub>2</sub>(Te<sub>3</sub>O<sub>11</sub>)] (#249). Three TeO<sub>5</sub> pyramids share a common CN3 oxygen atom and two CN2 oxygen atoms to form [Te<sub>3</sub>O<sub>11</sub>]<sup>10–</sup> trimers (Fig. 8*i*). AsO<sub>4</sub> tetrahedra share two corners with one such trimer and one each with two neighbouring trimers to form continuous layers || (010), with Te–Te–As 3-rings, Te–As–Te–As 4-rings and Te–Te–As–Te–Te–As 6-rings. Layers are held together only through long Te···O bonds (Fig. 27).

#### Finite Te<sup>4+</sup> oxyanions [Te<sub>m</sub>X<sub>n</sub>] with m ≥ 4

Na<sub>2</sub>Te<sub>2</sub>O<sub>5</sub> · 2H<sub>2</sub>O ≡ Na<sub>4</sub>[Te<sub>4</sub>O<sub>10</sub>] · 4H<sub>2</sub>O (#250) has linear [Te<sub>4</sub>O<sub>10</sub>]<sup>4–</sup> tetramers with a central shared edge (Fig. 8*j*). These lie in layers || (001) with their long axes all || [110]. Water molecules and CN5–6 Na<sup>+</sup> ions lie between the layers. The analogous NH<sub>4</sub><sup>+</sup> compound (#251) has Te<sub>4</sub>O<sub>10</sub> groups lining up nose-to-tail to form rods || [101], which pack in a hexagonal array, with NH<sub>4</sub><sup>+</sup> ions and H<sub>2</sub>O molecules between them. Sc<sub>2</sub>Te<sub>5</sub>O<sub>13</sub> ≡ Sc<sub>4</sub>[Te<sub>4</sub>O<sub>10</sub>](Te<sub>3</sub>O<sub>8</sub>)<sub>2</sub> (#252) has ScO<sub>6</sub> and ScO<sub>7</sub> polyhedra sharing alternately corners and edges to form zigzag chains || **x**. Linear Te<sub>4</sub>O<sub>11</sub> groups

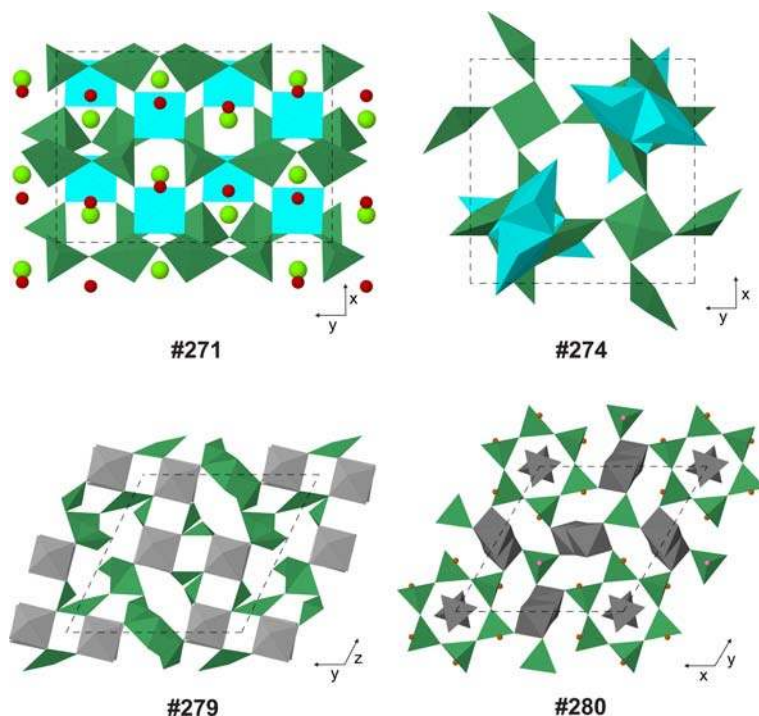


FIG. 28. Examples of structures with soro groups  $\text{Te}_4^+\text{O}_{11}$ ,  $\text{Te}_5\text{O}_{12}$ ,  $\text{Te}_{10}\text{O}_{26}$  or cyclo  $\text{Te}_6\text{O}_{12}$  (Table 15, deposited). Small spheres: N (brown) and O (dark pink) when not part of a polyhedron. Medium spheres: Br (red). Large spheres: Ba (yellow-green). Polyhedra: Cu (cyan), Mo (dark grey), Nb (pale grey) and Te (dark green).

pointing  $\parallel [01\bar{1}]$  connect the Sc chains to make double layers  $\parallel (001)$ , while C-shaped  $\text{Te}_3\text{O}_8$  groups wrap around individual Sc chains. The double layers contain slot-like micelles  $\parallel \mathbf{x}$  which accommodate most of the Te lone pairs; layers are held together through long  $\text{Te}\cdots\text{O}$  bonds.  $\text{Ca}_2[\text{Cu}(\text{Te}_4\text{O}_{10})]\text{Cl}_2$  (#253) has  $\text{Te}_4\text{O}_{10}$  groups pointing  $\parallel [011]$ , sharing corners with  $\text{CuO}_4$  squares to make a continuous layer  $\parallel (011)$ . The  $\text{Ca}^{2+}$  ions form zigzag edge-sharing chains of  $\text{CaO}_7$  polyhedra  $\parallel \mathbf{x}$  between the Cu–Te layers.  $\text{Cl}^-$  ions also lie in the interlayer gap, and complete a very elongated octahedron around  $\text{Cu}^{2+}$  ( $\text{Cu}–\text{Cl} = 2.74 \text{ \AA}$ ).  $\text{Sm}_2\text{Mn}^{2+}\text{Te}_5\text{O}_{13}\text{Cl}_2 \equiv \text{Sm}_4[\text{Mn}_2(\text{Te}_4\text{O}_{10})(\text{Te}_3\text{O}_8)_2]\text{Cl}_4$  and isostructural  $\text{Dy}_4[\text{Cu}_2(\text{Te}_4\text{O}_{10})(\text{Te}_3\text{O}_8)_2]\text{Br}_4$  (#254–255) have Te anions pointing  $\parallel [102]$  and arranged in layers  $\parallel (201)$ ; each layer contains both  $\text{Te}_4\text{O}_{10}$  and  $\text{Te}_3\text{O}_8$  groups. The anions are held together by  $(\text{Mn,Cu})\text{O}_6$  octahedra between the layers, which are considered part of the structural unit, and edge-sharing ribbons of  $(\text{Sm,Dy})\text{O}_8$  polyhedra, which are not. A very open framework results, in which there remain elongated channels  $\parallel \mathbf{y}$  which accommodate  $(\text{Cl,Br})^-$  anions,

which are weakly bonded to Te. Unusually, the  $\text{CuO}_6$  octahedron is not much less regular than  $\text{MnO}_6$  ( $\text{Cu}–\text{O} = 1.99\text{--}2.32 \text{ \AA}$ , vs.  $\text{Mn}–\text{O} = 2.12\text{--}2.28 \text{ \AA}$ ).

The compounds  $A_2[\text{Te}_4\text{O}_{11}]$  ( $A = \text{La–Nd, Sm–Lu}$  and Y; #256–270) show the progressive, monotonic change in parameters and properties with atomic number that is characteristic of the lanthanide elements. In particular, the fourth-shortest  $\text{Te}2\text{–O}$  distance changes so much along the series, from  $2.515 \text{ \AA}$  for the La compound to  $2.354 \text{ \AA}$  for Lu, that the classification of the Te anion(s) changes if the usual ‘strong bond’ threshold of  $2.40\text{--}2.45 \text{ \AA}$  is used. For such a threshold, the compounds of larger  $A$  cations such as La would be regarded as having dimeric  $[\text{Te}_2\text{O}_5] +$  two monomeric  $\text{TeO}_3$  groups. In order to keep this family of isostructural compounds together, a threshold of  $2.53 \text{ \AA}$  is used for all of them, and they all classify as having corner-linked tetramers  $[\text{Te}_4\text{O}_{11}]^{6-}$  (Fig. 8*k*), with the long  $\text{Te}–\text{O}$  bonds linking the terminal Te1 atoms to the core  $\text{Te}2\text{–Te}2$  dimer. The third-shortest  $\text{Te}2\text{–O}$  distance increases slightly from  $1.989$  to  $2.022 \text{ \AA}$  as the  $A$  cation decreases in size from La to Lu. The

structure is relatively simple, with layers  $\parallel$  (002) of edge-sharing  $\text{AO}_8$  polyhedra linked through linear  $\text{Te}_4\text{O}_{11}$  groups that all point  $\parallel$   $[20\bar{1}]$  (Fig. 27).  $\text{Ba}_2[\text{Cu}_2(\text{Te}_4\text{O}_{11})]\text{Br}_2$  (**#271**) has layers in which  $\text{Te}_4\text{O}_{11}$  groups with long axes  $\parallel$   $y$  share corners with  $\text{CuO}_4$  squares to make sheets with Cu–Te–Te 3-rings, Cu–Te–Cu–Te 4-rings and Cu–Te–Te–Cu–Te–Te 6-rings. The sheets are parallel to (001) but have a polarity in the  $z$  direction; a pair of such sheets occurs back-to-back in every  $c$  repeat.  $\text{BaO}_{10}$  polyhedra occur in the interlayer gaps that are faced by Cu, while  $\text{Br}^-$  anions occur in the gap that is lined by Te atoms (Fig. 28). A very similar Cu–Te sheet occurs in  $\text{Ba}_4[\text{Cu}_2^{2+}(\text{Te}_4\text{O}_{11})]_2(\text{Cu}_4^{1+}\text{Cl}_8)$  (**#272**). The sheets again occur in back-to-back pairs, but this time they are parallel to (010), with  $\text{Te}_4\text{O}_{11}$  groups trending  $\parallel$   $[10\bar{1}]$ . Again, the  $\text{Cu}^{2+}$  ions face an interlayer unit of  $\text{BaO}_{10}$  polyhedra. However, the Te side of the sheets faces a wide interlayer space that contains  $[\text{Cu}_4^{1+}\text{Cl}_8]^{4-}$  clusters. These consist of a central pair of edge-sharing  $\text{CuCl}_4$  tetrahedra, linked through corners to two  $\text{CuOCl}_2$  triangles. The long axis of the cluster is  $\parallel$   $[101]$ , approximately perpendicular to that of the  $\text{Te}_4\text{O}_{11}$  groups. The terminal  $\text{Cu}^{1+}$  atoms share the middle oxygen atoms of the Te–O anions, thus providing additional bridges between them, but are not counted as part of the structural unit due to the low valence of Cu.  $[\text{Co}_5^{2+}(\text{Te}_4\text{O}_{11})\text{Cl}_4]$  (**#273**) has thick layers  $\parallel$  (100) of corner- and edge-sharing  $\text{CoO}_4\text{Cl}$  pyramids,  $\text{CoO}_5\text{Cl}$  trigonal prisms and octahedra, and *cis*- $\text{CoO}_4\text{Cl}_2$  octahedra. The layers are braced by  $\text{Te}_4\text{O}_{11}$  groups with their long axes  $\parallel$   $[01\bar{1}]$ , and are held together though long Te...O and Te...Cl bonds.

$[\text{Cu}_4(\text{Te}_5\text{O}_{12})\text{Cl}_4]$  (**#274**) has an elegant tetragonal structure in which the tellurite anion is the pinwheel-like  $\text{Te}_5\text{O}_{12}$  pentamer of Fig. 8*l*.  $\text{CuO}_4\text{Cl}$  square pyramids occur in clusters of four, where the oxygen atoms of the cube-shaped  $\text{Cu}_4\text{O}_4$  cluster core are tetrahedrally coordinated by 3 Cu + 1 Te, thus linking Te and Cu polyhedra into an open framework. The  $\text{Cl}^-$  anions are in channels  $\parallel$   $z$ , and make additional long bonds to Cu and Te (Fig. 28).  $\text{Nd}_5\text{MoTe}_7\text{O}_{23}\text{Cl}_3 \equiv \text{Nd}_5(\text{MoO}_4)[\text{Te}_5\text{O}_{13}](\text{TeO}_3)_2\text{Cl}_3$ , its W analogue and the corresponding Pr analogues (**#275–278**) have edge-sharing columns of (Nd,Pr)  $\text{O}_{7-8}$  polyhedra  $\parallel$   $x$ , which share a few additional edges to make pillared double layers  $\parallel$  (001) with very large channels ( $14 \times 9 \text{ \AA}$ ) running between the sublayers  $\parallel$   $x$ . These are further linked through (Mo,W) $\text{O}_4$  tetrahedra into a very open framework, leaving small interlayer channels containing monomeric  $\text{TeO}_3$  groups, while the large channels are lined by V-shaped  $\text{Te}_5\text{O}_{13}$  pentamers (Fig. 8*m*). The

$\text{Cl}^-$  anions are held loosely, in the centres of large and small channels.  $\text{Nb}_2\text{Te}_4\text{O}_{13} \equiv [\text{Nb}_8\text{O}_8(\text{Te}_{10}\text{O}_{26})(\text{TeO}_3)_6]$  (**#279**) has *zwei* chains of corner-sharing  $\text{NbO}_6$  octahedra  $\parallel$   $x$ . The pseudomonoclinic unit cell contains four distinct such chains, but despite the apparent simplicity of this arrangement, these are connected together through a remarkably complex arrangement of Te atoms. There are eight distinct Te sites. Sites Te2, Te3 and Te5 are in monomeric  $\text{TeO}_3$  groups that share corners with Nb to make 4-cation-wide ribbons  $\parallel$   $x$  with Nb–Nb–Te 3-rings (alternately on each side of the Nb–O backbones, similar to the chain of Fig. 15*c*), Nb–Te–Nb–Te 4-rings and Nb–Nb–Te–Nb–Nb–Nb–Te 7-rings (Fig. 28). The ribbons lie in layers  $\parallel$   $(01\bar{1})$ , which are then bridged by the open-branched decameric anion  $[\text{Te}_{10}\text{O}_{26}]^{12-}$  of Fig. 8*o*, in which a central edge-sharing pair of Te8 are linked through Te6 to Te1, which is then connected to both Te4 and Te7. The long axis of the anion  $\text{Te7}\cdots\text{Te8} = \text{Te8}\cdots\text{Te7}$  is approximately  $\parallel$   $[311]$  in the interlayer gap, while the Te4 branches complete the Nb–Te layers  $\parallel$   $(01\bar{1})$ . Note that this description is valid if the strong bonding threshold for Te is chosen in the range 2.36–2.44 Å; however, two slightly longer Te–O bonds (2.44–2.47 Å) connect the finite decamers into infinite open-branched *achter* chains, in which the additional bridging oxygens are CN3, shared by Te7 of two different decamers and Te2 as a new branch.  $(\text{NH}_4)_6\text{Mo}_8\text{Te}_8\text{O}_{43} \cdot \text{H}_2\text{O} \equiv (\text{NH}_4)_6[(\text{MoO}_3)_6(\text{Te}_6\text{O}_{12})(\text{TeO}_3)_2](\text{Mo}_2\text{O}_7) \cdot \text{H}_2\text{O}$  (**#280**) has the only true cyclo  $\text{Te}^{4+}$  complex of the present study. Hexagonal rings  $[\text{Te}_6\text{O}_{12}]^0$  (Fig. 8*n*) and monomeric  $[\text{TeO}_3]^{2-}$  anions are linked into a layer  $\parallel$  (001) through edge-sharing dimers of  $\text{MoO}_6$  octahedra. Additional corner-sharing dimers of  $\text{MoO}_4$  tetrahedra  $[\text{Mo}_2\text{O}_7]^{2-}$ , with point symmetry  $\bar{3}$ , lie in the centres of the hexagonal rings. The  $\text{NH}_4^+$  cations and water molecules lie in the interlayer gap (Fig. 28).

### Structures with $\text{Te}^{4+}$ complexes that are infinite chains

Structures **#281–334** are inotellurites (Table 16, deposited). The various topological types of chain are summarized in Tables 2 (single chains) and 3 (multiple chains), and depicted in Fig. 9. Our first example is the structure of a high-temperature phase of  $\text{Mo}_5\text{TeO}_{16} \equiv [(\text{Mo}_2^{5+}\text{Mo}_3^{6+})\text{O}_{13}(\text{TeO}_3)]$  (**#281**). As in the polymorph **#168**,  $\text{MoO}_6$  octahedra share four corners to form layers of 3-, 4- and 6-rings  $\parallel$  (010), which then link through the



remaining octahedral vertices to form a framework, and there is no ordering of  $\text{Mo}^{5+}$  and  $\text{Mo}^{6+}$ . As before, Te is in the centre of the hexagonal ring, but this time it is 4-coordinated, and shares oxygen atoms with Te of layers above and below to form a corner-sharing chain  $\parallel y$ . In the long-range average crystal structure the chain is *einer*, but the bridging oxygen is on a twofold split site, which implies that the Te–O–Te configuration is nonlinear and the true local periodicity of a chain is at least *zweier*.  $\text{AgTeO}_2(\text{NO}_3) \equiv \text{Ag}_2[\text{Te}_2\text{O}_4](\text{NO}_3)_2$  (**#282**) has  $\text{TeO}_4$  polyhedra of the type shown in Fig. 4c, sharing edges to make an electrostatically neutral zigzag chain  $[\text{Te}_2\text{O}_4]^{0-} \parallel z$  (Fig. 9a). These lie in layers  $\parallel (020)$ , with interstitial  $\text{NO}_3^-$  and  $\text{CN}_6 \text{Ag}^+$  ions, which themselves form a weakly bonded layer in which  $\text{Ag}^+$  and  $\text{NO}_3^-$  are arranged respectively like the  $\text{Pb}^{2+}$  and  $\text{O}^{2-}$  in the litharge form of  $\text{PbO}$  (Boher *et al.*, 1985). Telluroperite,  $\text{Pb}_3\text{TeO}_4\text{Cl}_2$ , is more precisely written as  $\text{Pb}_2[(\text{Pb}_{0.5}\text{Te}_{0.5})_2\text{O}_4]\text{Cl}_2$  (**#283**). The Te–O complex is a chain topologically similar to Fig. 9a, but with square-pyramidal polyhedra (Fig. 4b) and a net negative charge due to random substitution of 50% of the  $\text{Te}^{4+}$  by  $\text{Pb}^{2+}$ . The (Pb,Te)–O chains and the remaining  $\text{Pb}^{2+}$  cations form litharge-type layers  $\parallel (002)$ , with  $\text{Cl}^-$  anions between the layers (Fig. 29). The resulting structure is isostructural with perite,  $\text{Pb}_2[\text{Bi}_2^{3+}\text{O}_4]\text{Cl}_2$ , and its  $\text{Sb}^{3+}$  analogue nadorite (Kampf *et al.*, 2010f). Rajite,  $[\text{Cu}(\text{Te}_2\text{O}_5)]$ , has the corner-sharing chain of alternating  $\text{CN}_3$  and  $\text{CN}_4 \text{Te}^{4+}$  seen in Fig. 9b (**#284**). The chains run  $\parallel x$ , and are made from finite dimers by the rather long fourth bond to Te2 (2.30 Å). Chains are cross-linked into a framework through  $\text{CuO}_4$  squares, which do not link to each other unless a fifth Cu–O distance (also 2.30 Å) is included, in which case the resulting  $\text{CuO}_5$  pyramids form edge-sharing dimers. Nd  $[\text{Te}_2\text{O}_5]\text{Br}$  (**#285**) has layers  $\parallel (002)$  of edge-sharing  $\text{NdO}_{8-12}$  polyhedra, braced above and below by  $[\text{Te}_2\text{O}_5]^{2-}$  chains  $\parallel y$  which are topologically similar to those of rajite, but have an unusual planar T-shaped geometry for the  $\text{CN}_3$  polyhedron. This may be due to the presence of four interlayer  $\text{Br}^-$  ions at a relatively short distance from the Te cation (3.35–3.47 Å). The structures of the Cl analogue (**#336**) and the Ho analogue of that compound (**#307**) are different (see below).  $\text{Nd}_2[\text{Te}_2\text{O}_5](\text{Te}_2\text{O}_5)(\text{MoO}_4)$  and its Pr analogue (**#286–287**) have edge-sharing zigzag double chains of  $(\text{Nd,Pr})\text{O}_{8-9} \parallel x$ , which are bridged via  $\text{MoO}_4$  tetrahedra to form looped layers  $\parallel (001)$ . Dimeric  $[\text{Te}_2\text{O}_5]^{2-}$  ions (Fig. 8a) brace the layers, while *zweier* chains of the same composition (Fig. 9b) run

$\parallel x$ , and hold the layers together. The chains are the structural unit, for the purposes of this classification. In  $[\text{Ga}_2(\text{Te}_2\text{O}_5)(\text{Te}_2\text{O}_6)]$  (**#288**), the  $\text{Te}_2\text{O}_5$  chains are  $\parallel [1\bar{1}0]$ . These, and dimeric groups  $[\text{Te}_2\text{O}_6]^{4-}$ , which consist of two  $\text{TeO}_3$  units linked by a long (2.35 Å) fourth bond to Te4, cross-link otherwise isolated  $\text{GaO}_5$  and  $\text{GaO}_4$ -polyhedra into a framework.  $[\text{InF}(\text{Te}_2\text{O}_5)]$  (**#289**) has *trans*- $\text{InO}_4\text{F}_2$  octahedra sharing F atoms to form a helical *vierer* chain  $\parallel z$ . These are cross-linked into a framework by  $\text{Te}_2\text{O}_5$  chains, which occur in four layers per unit cell along the  $z$  direction, and run  $\parallel [110]$  and  $\parallel [1\bar{1}0]$  in alternate layers.

$\text{La}_4\text{Ta}_2\text{Te}_6\text{O}_{23} \equiv \text{La}_4[\text{Ta}_2\text{O}_6(\text{Te}_2\text{O}_{5.4})(\text{TeO}_3)_2][\text{Te}_2\text{O}_{5.6}]$  (**#290**) has a somewhat disordered structure with three fundamentally distinct types of Te. One type (Te3) approximates a chain of the *zweier*  $\text{CN}_4$  type  $[\text{Te}_2\text{O}_6]^{4-}$  (Fig. 9c) running  $\parallel z$ . However, the bridging oxygen atoms are only 77–80% occupied. Another type (Te1+Te2) ostensibly forms a similar chain, but the Te atoms are actually on a twofold split site and again the bridging oxygen sites are only partly occupied (71%), implying that the Te atoms are locally in a very strongly asymmetrical 3+1 coordination environment, and that the ‘chain’ is actually a sequence of  $\text{Te}_2\text{O}_5$  dimers (58%) and orientationally disordered  $\text{TeO}_3$  monomers (42%). The Te atoms of the second chain share corners with a parallel *zweier* chain of corner-sharing  $\text{TaO}_6$  octahedra, which are decorated by additional  $\text{TeO}_3$  groups (Te4) to form a second one-dimensional structural unit. All the Te lone pairs point in towards the centres of large rhomb-shaped channels  $\parallel z$  of a trellis-like matrix of edge-sharing  $\text{LaO}_9$  polyhedra (Fig. 29).  $\text{K}[(\text{UO}_2)(\text{Te}_2\text{O}_5(\text{OH}))]$  (**#291**) has chains  $\parallel x$  of Fig. 9c type, which share corners with  $\text{UO}_6$  octahedra to form pleated layers  $\parallel (020)$ . The layers have Te–Te–U 3-rings and Te–Te–U–Te–Te–U 6-rings. The layers are held together by  $\text{CN}_{10} \text{K}^+$  ions, which sit at the centres of the hexagonal rings. There are two types of bridging oxygen atom in the Te chain, with different Te–O distances of 2.07 and 2.28 Å; the latter oxygen atom probably accommodates the  $\text{H}^+$ . Schmitterite,  $\text{UO}_2\text{TeO}_3 \equiv [(\text{UO}_2)_2(\text{Te}_2\text{O}_6)]$  (**#292**), also has its  $\text{TeO}_3$  groups linked into a  $[\text{Te}_2\text{O}_6]^{4-}$  chain ( $\parallel z$ ), and these are linked through U into a pleated sheet  $\parallel (010)$ . However, the  $\text{U}^{6+}$  forms edge-sharing chains of  $\text{UO}_7$  polyhedra, all Te–U links are through  $\text{CN}_3$  oxygen atoms bonding to either  $2\text{Te} + \text{U}$  or to  $\text{Te} + 2\text{U}$ , and layers are held together only through long  $\text{Te}\cdots\text{O}$  bonds (Fig. 29).  $\text{Ti}_3[(\text{UO}_2)_2(\text{Te}_2\text{O}_5(\text{OH}))(\text{Te}_2\text{O}_6)] \cdot 2\text{H}_2\text{O}$  (**#293**) has two symmetrically



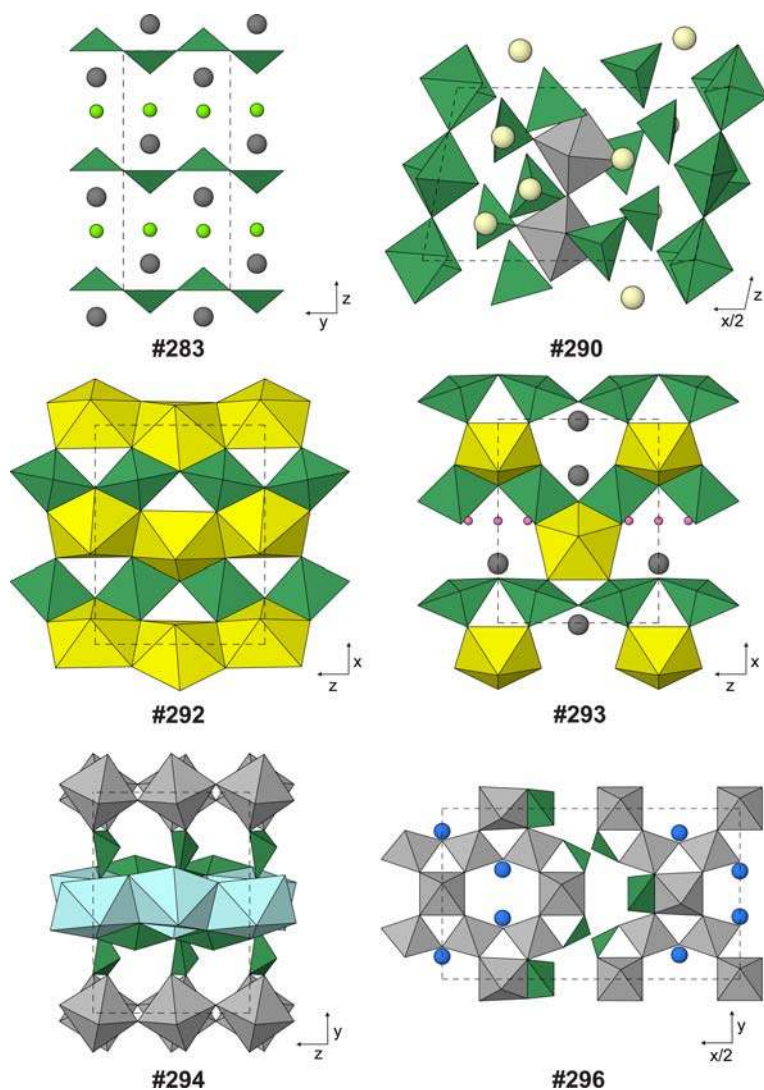


FIG. 29. Examples of structures with *zweier* chains of  $\text{Te}^{4+}$  polyhedra (Table 16, deposited). Small spheres: O (dark pink) when not part of a polyhedron. Medium spheres: Cl (yellow-green). Large spheres: Cs (blue), La (light yellow) and Pb or Tl (grey). Polyhedra: In (pale blue), Nb (grey), Te (dark green) and U (yellow).

distinct  $\text{Te}_2\text{X}_6$  chains running  $\parallel z$ ; as in **#291**, the hydrogen atom can be located by noting the unusually long  $\text{Te2-O7}$  distance: 2.21 Å as opposed to 2.04–2.07 Å for the other bridging oxygen atoms. Isolated  $\text{UO}_7$  polyhedra link the Te chains into corrugated layers  $\parallel (040)$ , held together through three kinds of  $\text{Tl}^+$  ion (CN = 5–9) and water molecules in the interlayers (Fig. 29).

$\text{InNbTe}_2\text{O}_8 \equiv \text{In}_2[\text{NbO}_2(\text{TeO}_3)]_2[\text{Te}_2\text{O}_6]$  (**#294**) has  $\text{NbO}_6$  octahedra sharing four corners to form

a square-net layer  $\parallel (010)$ , resembling the  $(\text{Nb}, \text{Ta})_n\text{O}_{4n}$  layers of **#155–158**. Half of the Te are in monomeric  $\text{TeO}_3$  groups that share additional corners to form Nb–Nb–Te 3-rings that are alternately above and below the Nb layer along the  $x$  direction, while the other half of the Te form *zweier* chains  $\text{Te}_2\text{O}_6 \parallel z$  that do not connect directly to Nb, but brace a layer of edge-sharing  $\text{InO}_7$  polyhedra that holds together the Nb–Te layers. Thus, there are two separate structural units, a

Te chain and a Nb–Te heteropoly layer (Fig. 29). The related compound  $\text{BiNbTe}_2\text{O}_8 \equiv \text{Bi}_2[\text{NbO}_2(\text{TeO}_3)]_2[\text{Te}_2\text{O}_6]$  (**#295**) also has corner-sharing  $\text{Nb}_n\text{O}_{4n}$  sheets, but while the unshared corners are *trans* in **#294** so that the sheets are planar, in the Bi compound the unshared corners are *cis*, and the sheets  $\parallel (002)$  are strongly pleated. Again, half of the  $\text{TeO}_3$  link to the Nb sheets, completing Nb–Nb–Nb–Te 4-rings rather than 3-rings, this time, while the rest of the Te form  $\text{Te}_2\text{O}_6$  chains between the layers, running  $\parallel y$ . The  $\text{BiO}_{4+3}$  polyhedra share edges to form a corrugated layer that is braced by the Te chains and also links to the Te of the Nb–Te units.  $\text{Cs}_3[\text{Nb}_9\text{O}_{20}(\text{Te}_2\text{O}_6)(\text{TeO}_3)_2]$  (**#296**) has very thick layers of  $\text{NbO}_6$  octahedra  $\parallel (200)$  that are slices of a pyrochlore framework. Kagome layers of 3- and 6-rings  $\parallel (011)$  and  $(0\bar{1}1)$  are very prominent in projection down *z*. The pyrochlore framework is displaced by  $\frac{1}{2}c$  on planes  $\parallel (200)$ , which breaks otherwise infinite chains of octahedra running  $\parallel x$  after only four Nb atoms. These chains are terminated by half of the Te rather than Nb, and the offset of the pyrochlore framework allows Te to retain 3-fold rather than 6-fold coordination. Thus, the layers are not condensed any further by strong bonds. The other half of the Te atoms form  $[\text{Te}_2\text{O}_6]$  chains which run  $\parallel z$  in notches in the sides of the thick layers. The  $\text{Cs}^+$  ions are in 6–8 coordination in large interstices within the layers, which are held together only through long-distance  $\text{Te}\cdots\text{O}$  interactions (Fig. 29).  $\text{CuTeO}_3 \equiv [\text{Cu}_2(\text{Te}_2\text{O}_6)]$  (**#297**) is a polymorph of balyakinite (**#117**) and the high-pressure phase **#142**. In this structure,  $\text{CuO}_4$  squares form edge-sharing dimers, condensed into chains  $\parallel x$  through a fifth Cu–O bond at 2.43 Å. The Cu chains lie in layers  $\parallel (020)$ , which are cross-linked into a framework by  $\text{Te}_2\text{O}_6$  chains running  $\parallel [101]$ . Like Cu, Te has a very irregular coordination environment, with three Te–O distances of 1.87–1.92 and the fourth at 2.43 Å; it has no other oxygen atoms within 2.8 Å.  $\text{TlV}^{5+}\text{TeO}_5 \equiv \text{Ti}_2[(\text{VO}_2)_2(\text{Te}_2\text{O}_6)]$  (**#298**) has *trans* corner sharing chains of distorted  $\text{VO}_6$  octahedra in a centred-rectangular array, running  $\parallel x$ . These are cross-linked by  $\text{Te}_2\text{O}_6$  chains running  $\parallel z$  into a framework with large channels  $\parallel x$  and *z*. The resulting three-dimensional net has intersecting layers of kagome topology  $\parallel (011)$  and  $(0\bar{1}1)$ , like the weberite structure (Knop *et al.*, 1982, Fig. 14g, **#672** below). In fact, the framework can be derived from that of weberite by  $\frac{1}{2}a$  displacement of slices  $\parallel (002)$ , thus condensing into chains what would otherwise be isolated Te polyhedra, and adjusting the Te–O–V bonding pattern slightly. In **#298**, oxygen atoms are removed

so that Te has CN = 4 rather than 6, while the environment of V is changed from  $\text{Q}^{0600}$  to  $\text{Q}^{1411}$ , with V making a bond to a CN3 bridging oxygen of the Te chain rather than to the missing anion. The V–O–V bridges are very asymmetrical, one distance being 2.24 Å while the other is 1.66 Å, almost identical to the distance between V and the CN1 ligand. Thus, nonlinear  $[\text{VO}_2]^+$  complexes can be recognized in the structure. The  $\text{Ti}^+$  ions are in very one-sided 7-coordination in the channels.

Polymorph II of  $\text{TeO}(\text{As}^{5+}\text{O}_3\text{OH}) \equiv [(\text{AsOH})_2(\text{Te}_2\text{O}_8)]$  (**#299**), like polymorph I (**#225** above), has Te in 5-fold coordination, but the  $\text{TeO}_5$  polyhedra now form corner-sharing *zweier* chains  $\text{Te}_2\text{O}_8 \parallel y$  (Fig. 9d) rather than edge-sharing dimers.  $[\text{AsO}_3\text{OH}]^{2-}$  tetrahedra share the three unprotonated ligands with the Te chains to form a corrugated layer  $\parallel (002)$  with Te–Te–As 3-rings and Te–Te–As–Te–As 5-rings. Hydrogen bonds brace individual layers, which are held together through long  $\text{Te}\cdots\text{O}$  bonds. The triclinic polymorph of  $\text{TeO}(\text{Se}^{4+}\text{O}_3) \equiv [\text{Se}_2(\text{Te}_2\text{O}_8)]$  (**#300**) has CN5 Te in similar *zweier*  $\text{Te}_2\text{O}_8$  chains  $\parallel x$ . The chain backbones have the asymmetrical crankshaft geometry of the Pb–O chains in massicot (Hill, 1985).  $\text{SeO}_3$  pyramids share all corners with the Te chains to make a framework with hexagonal channels  $\parallel y$ , which accommodate the lone pairs of both Se and Te. The monoclinic (pseudo-orthorhombic) polymorph **#301** is topologically very similar, but slight displacements of atoms mean that the two Te atoms of the chain repeat are now related to each other through a glide plane, rather than being symmetrically independent.

Chekhovichite,  $\text{Bi}_2\text{Te}_4\text{O}_{11} \equiv \text{Bi}_4[\text{Te}_4\text{O}_{10}](\text{TeO}_3)_4$  (**#302**) has the zigzagging *vierer* Te chain of Fig. 9e, with CN3 Te at the sharp bends. The chains trend  $\parallel y$ , and zigzag in layers  $\parallel (002)$ .  $\text{BiO}_{7-8}$  polyhedra share edges to form corrugated sheets with a honeycomb net, between the Te chains, and the monomeric  $\text{TeO}_3$  groups brace the Bi sheets.  $\text{Na}_2\text{MoTe}_4\text{O}_{12} \equiv \text{Na}_2[\text{MoO}_2(\text{Te}_4\text{O}_{10})]$ , its W analogue and the corresponding Ag–Mo compound (**#303–305**) have topologically similar but more contorted *vierer* Te chains, which are cross-linked in pairs through otherwise isolated  $(\text{Mo},\text{W})\text{O}_6$  octahedra to make looped heteropoly chains  $\parallel z$ . These chains lie in layers  $\parallel (200)$ , which are loosely held together through  $\text{CN7}(\text{Na},\text{Ag})^+$  ions. The Te bond threshold for these structures has been set at 2.38 Å. If an additional bond at 2.39–2.48 Å is included, then Te2 atoms of neighbouring chains share edges to join the chain structural units into a continuous layer with 10-rings  $\parallel (200)$ . The

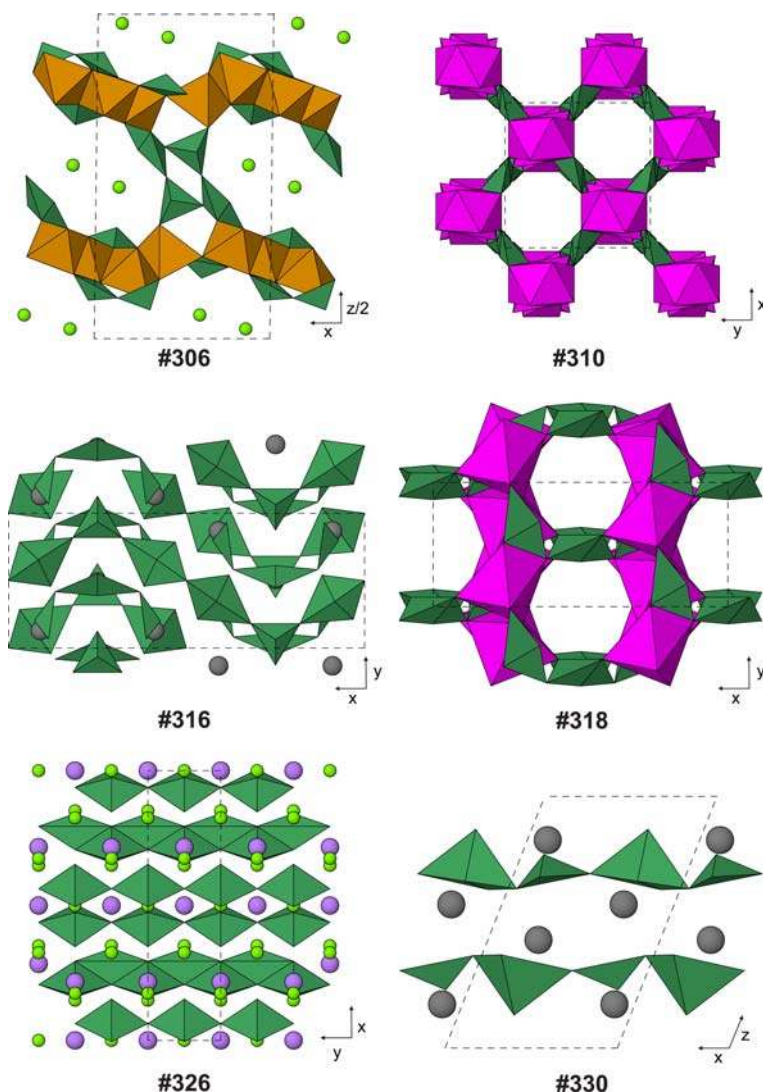


FIG. 30. Examples of structures with *vierer* or *sechser* single chains or with double chains of  $\text{Te}^{4+}$  polyhedra (Table 16, deposited). Medium spheres: Cl (yellow-green). Large spheres: Bi (violet) and Pb or Tl (grey). Polyhedra: Fe (orange-brown), Mn (magenta) and Te (dark green).

compound  $\text{Fe}_8\text{Te}_{12}\text{O}_{32}\text{Cl}_3\text{Br}_3 \equiv [(\text{Fe}_2^{2+}\text{Fe}_6^{3+})(\text{Te}_4\text{O}_{10})(\text{Te}_2\text{O}_5)_2(\text{TeO}_3)_4]\text{Cl}_3\text{Br}_3$  (**#306**) has four types of Fe atom in 5 or 6 coordination, which link in a honeycomb net to form layers  $\parallel (004)$ . The different linkage patterns for Fe1–Fe4 polyhedra are described concisely by Q states as  $Q^{0603}$ ,  $Q^{1502}$ ,  $Q^{1501}$  and  $Q^{2300}$ , respectively. Bond-valence sums indicate that  $\text{Fe}^{2+}$  is ordered at Fe3. Two types of interlayer gap alternate between Fe layers. One gap type contains two-thirds of the loosely bound,

partly-disordered  $(\text{Cl}, \text{Br})^-$  ions, and is lined by  $\text{Te}_2\text{O}_5$  groups which brace the Fe layers. Monomeric  $\text{TeO}_3$  groups decorate the other side of the Fe layers, facing the other type of gap, but on this side, the layers also link to  $\text{Te}_4\text{O}_{10}$  chains running  $\parallel y$ , which join the Fe layers in pairs and thus complete the extremely complex pillared double layer structural unit (Fig. 30). The remaining  $(\text{Cl}, \text{Br})^-$  are in channels  $\parallel y$  between the Te chains. The chains still have alternation of

CN3 and CN4 Te, but are quite different in conformation from those of #302–305: they are helically coiled, with the sharpest bending at the CN4 Te atoms rather than CN3.

In  $\text{HoTe}_2\text{O}_5\text{Cl} \equiv \text{Ho}_2[\text{Te}_4\text{O}_{10}]\text{Cl}_2$  (#307), nearly-cubic  $\text{HoO}_8$  polyhedra share edges to make square-net layers  $\parallel$  (001); half of the Ho atoms have interlayer Cl as a more distant neighbour. The Ho layers are braced by *vierer* Te chains which are a topological isomer of those in #302–306, with a different sequence of CN3 and CN4 Te atoms (Table 2, Fig. 9f). The chains trend  $\parallel$  [1 $\bar{1}$ 0]. Layers are held together only through weak  $\text{Te}\cdots\text{Cl}$  interactions. The compositionally similar Nd compounds #285 and #336 have quite different structures.  $\text{Na}_2\text{Te}_2\text{O}_5 \equiv \text{Na}_4[\text{Te}_4\text{O}_{10}]$  (#308) has yet another isomer of  $\text{Te}_4\text{O}_{10}$  chain, with all Te 4-coordinated, but an alternation of corner- and edge-sharing (Fig. 9g). Chains trend  $\parallel$  [101], and are held together by CN6–7  $\text{Na}^+$  ions. The arrangement of (Na,Te) and O atoms can be described as slightly distorted slabs  $\parallel$  (100) of rocksalt type, alternating with fluorite-like slabs, with there being two of each slab type per unit cell.  $\text{K}_2\text{Te}_2\text{O}_5 \cdot 3\text{H}_2\text{O} \equiv \text{K}_4[\text{Te}_4\text{O}_{10}] \cdot 6\text{H}_2\text{O}$  (#309) has similar *vierer* chains which lie in layers  $\parallel$  (002). The chains run in [110] and [1 $\bar{1}$ 0] directions in alternate layers. Water molecules and CN7–8  $\text{K}^+$  ions lie between the layers. The edge-sharing  $\text{Te}_4\text{O}_{10}$  chains of Fig. 9g are also found in the denningite structure of  $\text{Mn}^{2+}\text{Te}_2\text{O}_5 \equiv \text{Mn}^{2+}[\text{Mn}^{2+}(\text{Te}_4\text{O}_{10})]$  (#310). This nanoporous tetragonal structure has two different types of Mn site, with coordination numbers 8 and 6 respectively, which alternate in edge-sharing chains  $\parallel$  z. The Mn chains are linked to their neighbours by Te chains which also run  $\parallel$  z, so delineate square channels with a minimum diameter of  $\sim 5$  Å (Fig. 30). Note that the CN6 Mn are considered to be part of the overall framework structural unit, while CN8 Mn is not. The CN6  $\text{Mn}^{2+}$  may be substituted by  $\text{Cu}^{2+}$  to produce solid solutions and ultimately the end-member  $\text{Mn}^{2+}[\text{Cu}^{2+}(\text{Te}_4\text{O}_{10})]$  (#311). Although Mn-dominant synthetic compositions have been called ‘denningite’, it seems likely that the mineral denningite itself has Ca replacing Mn in the 8-coordinated cation site. The type material has composition  $(\text{Ca}_{0.60}\text{Mn}_{0.40})[(\text{Mn}_{0.72}\text{Zn}_{0.24}\text{Mg}_{0.04})(\text{Te}_4\text{O}_{10})]$  (Mandarino *et al.*, 1963), and the ideal composition is given as  $\text{CaMn}^{2+}\text{Te}_4^{4+}\text{O}_{10}$  in the IMA list of minerals ([http://ima-cnmnc.nrm.se/IMA\\_Master\\_List\\_2015-05.pdf](http://ima-cnmnc.nrm.se/IMA_Master_List_2015-05.pdf)). Although the refinements of Walitizi (1964, 1965) constrained occupancies to be the same on CN8 and CN6 sites,

Ca would be expected to partition strongly into the larger 8-coordinated site, but the structure needs to be reinvestigated to confirm this. A different polymorph of  $\text{Mn}[\text{Te}_2\text{O}_5]$  is described as #347.

Despite the apparently simple formula,  $\text{K}_2\text{Te}_2\text{O}_5$  (#312) has an open-branched *zweier*  $\text{Te}_4\text{O}_{10}$  chain (Fig. 9h). The chains have a V-shaped cross-section, run  $\parallel$  x and pack in a herringbone fashion. They are cross-linked by undulating layers  $\parallel$  (001) of  $\text{KO}_{7-8}$  polyhedra.  $\text{Ba}_2\text{V}^{5+}\text{Te}_4\text{O}_{12}(\text{OH}) \equiv \text{Ba}_2[\text{VO}_3(\text{Te}_4\text{O}_9(\text{OH}))]$  (#313) contains yet another  $\text{Te}_4\text{X}_{10}$  isomer, the open-branched *dreier* tellurite chain of Fig. 9i. The hydroxide group is located on the CN4 Te atom that does not have the branch (Te4), while a  $\text{VO}_4$  tetrahedron shares an oxygen atom with the branch Te atom (Te1). Chains run  $\parallel$  y and lie in double layers  $\parallel$  (10 $\bar{1}$ ), with the branches directed into the interiors of the double layers.  $\text{BaO}_{8-9}$  polyhedra lie between the double layers.  $(\text{NH}_4)_2\text{WTe}_2\text{O}_8 \equiv (\text{NH}_4)_4[(\text{WO}_2)_2(\text{Te}_4\text{O}_{12})]$  (#314) has *zweier* Te chains with branches attached to CN3 bridging oxygen atoms (Fig. 9j). The chains run  $\parallel$  y, and are cross-linked by individual  $\text{WO}_6$  octahedra, which share four corners to form layers  $\parallel$  (100) with Te–Te–W 3-rings and Te–Te–W–Te–W 5-rings.  $\text{NH}_4^+$  ions are between the layers.  $\text{NiTe}_2\text{O}_5 \equiv [\text{Ni}_4(\text{Te}_6\text{O}_{14})(\text{TeO}_3)_2]$  (#315) has loop-branched *vierer* chains  $\text{Te}_6\text{X}_{14}$ , with CN5 Te at the nodes and CN3 Te in the loops (Fig. 9k). The chains run  $\parallel$  x, and alternate with monomeric  $\text{TeO}_3$  groups in layers  $\parallel$  (002). The tellurite anions are cross-linked into a framework through chains of *trans* edge-sharing  $\text{NiO}_6$  octahedra which run  $\parallel$  y; micelles between these chains accommodate the Te lone pairs.

$\text{Pb}_2\text{Te}_3\text{O}_8 \equiv \text{Pb}_8[\text{Te}_6\text{O}_{16}](\text{Te}_3\text{O}_8)_2$  (#316) has both zigzag *sechser* chains  $\text{Te}_6\text{O}_{16}$  of the type shown in Fig. 9l, and the *soro*  $\text{Te}_3\text{O}_8$  groups of Fig. 8g. Note that the chains contain both CN3 and CN4 Te, with the sharp bends at the CN3 Te atoms. The chains and tritellurite long axes all point  $\parallel$  x. Chains lie in double layers with  $\text{Te}_3\text{O}_8$  groups between the layers, and the resulting thick sheets repeat  $\parallel$  (002). Tellurite anions within the thick sheets are held together by  $\text{Pb}^{2+}$  ions that lie on the outsides of the sheets, and sheets are held together via long  $\text{Pb}\cdots\text{O}$  bonds. Lead is in distorted 7–8 coordination with three short bonds to oxygen atoms (Fig. 30). The compounds  $M_2^+\text{Te}_3\text{O}_8 \equiv [M_4(\text{Te}_6\text{O}_{16})]$  with  $M = \text{Mg}, \text{Mn}, \text{Co}, \text{Ni}, \text{Cu}$  or  $\text{Zn}$  (#317–322) have the spiroffite structure. No structure refinement exists for an Fe compound with this stoichiometry, while those with  $M = \text{Mn}$  and  $\text{Zn}$  are the minerals spiroffite and



zincospiroffite, respectively. The  $MO_6$  octahedra share edges and corners to make honeycomb layers  $\parallel (200)$ , and are linked into a framework by a different  $Te_6X_{16}$  *sechser* chain in which all Te are CN4, but edge-sharing pairs alternate with a polyhedron that shares only corners, at which the chain bends (Fig. 9m). The chains run  $\parallel [10\bar{1}]$  and lie in layers  $\parallel (202)$ . The trellis-like intersection pattern of *M* and Te layers results in 5 Å diameter channels running  $\parallel y$  and  $z$ , which accommodate the Te lone pairs (Fig. 30).

$Fe_3Te_4O_{12} \equiv [Fe_2^{2+}Fe_3^{3+}(Te_6O_{18})(TeO_3)_2]$  (#323) has edge-sharing dimers of  $Fe^{3+}O_6$  octahedra ( $Fe1 = Fe3$ ,  $Fe-O = 1.94-2.15$  Å) and edge-sharing dimers of  $Fe^{2+}O_6$  octahedra ( $Fe2 = Fe2$ ,  $Fe-O = 2.05-2.48$  Å), which share CN3 oxygen atoms to make layers  $\parallel (100)$ . The layers are braced by  $TeO_3$  monomers and linked into a framework through open-branched *vierer* chains  $Te_6O_{18}$  (Fig. 9n). The chains run  $\parallel y$ , but zigzag  $\parallel [101]$ , obliquely to the Fe layers.  $Te_3O_3(PO_4)_2 \equiv [P_4(Te_6O_{22})]$  (#324) also has an open-branched *vierer* chain, but with CN4 and CN5 Te atoms (Fig. 9o). The chains run  $\parallel z$ , with branches extended in the  $y$  direction, and lie in layers  $\parallel (200)$ . Two types of  $PO_4$  tetrahedra share all corners with the Te chains to make a framework which, unusually, has no 3-rings, but does have Te-Te-Te-P and Te-P-Te-P 4-rings and Te-Te-P-Te-P 5-rings.  $Ca_4Te_5O_{14} \equiv Ca_8[Te_8O_{22}](TeO_3)_2$  (#325) has open-branched *sechser* chains (Fig. 9p) running  $\parallel y$  and zigzagging in the  $x$  direction, and lying with  $TeO_3$  monomers in layers  $\parallel (004)$ . The chains wind through a trellis-like framework of  $CaO_7$  polyhedra, which has 7 Å channels  $\parallel z$  accommodating the chain branches.

The next few structures have multiple chains (Table 3). Interestingly, two of them are compounds with  $Fe^{3+}$ , and two are complex compounds with Cd and Cl.  $Bi_3Te_4O_{10}Cl_5 \equiv Bi_3[Te_2O_4](TeO_3)_2Cl_5$  (#326) has the simple *einer*  $[Te_2O_4]^0$  ribbon of Fig. 10a, in which  $Q^{1032}$  Te atoms are linked through CN3 oxygen atoms. These run  $\parallel y$ , and with  $TeO_3$  monomers and  $BiO_4Cl_2$  and  $BiO_4Cl_5$  polyhedra, define layers  $\parallel (201)$ , with the  $Cl^-$  ions in the interlayers. Although the Te double chain is nominally neutral, in reality, Te1 makes weak bonds to  $Cl^-$ , and the non-bridging oxygen is shared with Bi1.  $Cd_7Te_7O_{17}Cl_8 \equiv Cd_7[Te_5O_{12}](Te_2O_5)Cl_8$  (#327) has a commensurately modulated structure in which seven types of Cd polyhedra (variously  $CdO_3Cl_3$ ,  $CdO_4Cl_3$  or  $CdO_3Cl_4$ ) form edge-sharing ribbons, flattened in the  $yz$  plane and running  $\parallel y$ . These ribbons are braced on one side by the rather complex *zweier* double chain  $Te_5O_{12}$  of

Fig. 10b and also by the relatively simple  $Te_2O_5$  single chain of Fig. 9b. The Cd-Te compound layers repeat  $\parallel (200)$ , with  $Cl^-$  ions in the interlayer and long  $Te \cdots Cl$  bonds holding layers together. However, the facing direction of the pair alternates back and forth along the 28 Å  $c$  repeat (Fig. 30).

$Fe^{3+}Te_3O_7Cl \equiv [Fe_2(Te_6O_{14})]Cl_2$  (#328) and the Br analogue (#329) have *dreier* double chains  $Te_6O_{14}$  made out of 5-rings (Fig. 10c), flattened on  $(10\bar{1})$  and running  $\parallel y$ . The chains are linked through edge-sharing dimers of  $FeO_5$  polyhedra to make very thick double layers  $\parallel (100)$ , which contain channels  $\parallel z$ . Halide ions lie in the interlayer spaces, and the layers are held together only through weak  $Te \cdots (Cl, Br)$  and  $Te \cdots O$  interactions. Te2 in this structure has coordination that is strongly 3+1: the third- and fourth-nearest oxygen atoms are at  $\sim 1.95$  and 2.42 Å. If the fourth ligand is not included, the double chain becomes a serpentine *sechser* single chain.  $Tl_2Te_3O_7 \equiv Tl_4[Te_6O_{14}]$  (#330) has a very different  $Te_6O_{14}$  double chain which is only *zweier* but has the subchains linked through edge-sharing Te dimers (Fig. 10d). Thus, the subchains are open-branched but are linked via the branches so that the double chain as a whole is not. The resulting ribbons are flattened on approximately  $(01\bar{1})$  and run  $\parallel x$ . The Te chains interpenetrate with and cross-link layers  $\parallel (010)$  of edge-sharing  $TlO_5$  polyhedra (Fig. 30).  $Fe_2^{3+}Te_4O_{11} \equiv [Fe_4(Te_6O_{16})(Te_2O_6)]$  (#331) has a  $Te_6O_{16}$  chain whose description is again dependent on the Te-O bonding threshold. Here, we include a fourth Te-O link at 2.496 Å, which makes a rather simple *zweier* double chain of 6-rings (Fig. 10e). Without that link to close the rings, the chain is an open-branched *vierer* single chain. The chains are flattened on  $(102)$  and run  $\parallel y$ . The chain is topologically the same as a slice of the aluminosilicate sheet of prehnite,  $Ca_2[Al(AlSi_3O_{10})(OH)_2]$ , which has a similar alternation of  $Q^2$  and  $Q^4$  polyhedra in its 6-rings (Papike and Zoltai, 1967).  $FeO_6$  and  $FeO_5$  polyhedra share a corner to form  $Fe_2O_{10}$  dimers, which cross-link the Te chains, leaving channels  $\parallel y$  which accommodate additional Te in edge-sharing dimers  $Te_2O_6$  (Fig. 8c).  $Na_2Te_4O_9 \equiv Na_4[Te_8O_{18}]$  (#332) has a very complex *zweier* double chain in which the two subchain backbones are linked through the familiar 'double-triangle' tetrameric clusters (Fig. 10f). These chains run  $\parallel y$ , and their parallelogram-shaped cross-section defines the geometry of the unit cell. The chains are held together through layers  $\parallel (100)$  of  $NaO_{5-6}$  polyhedra. The K and  $NH_4$  analogues have a quite different layer structure (#354-355).



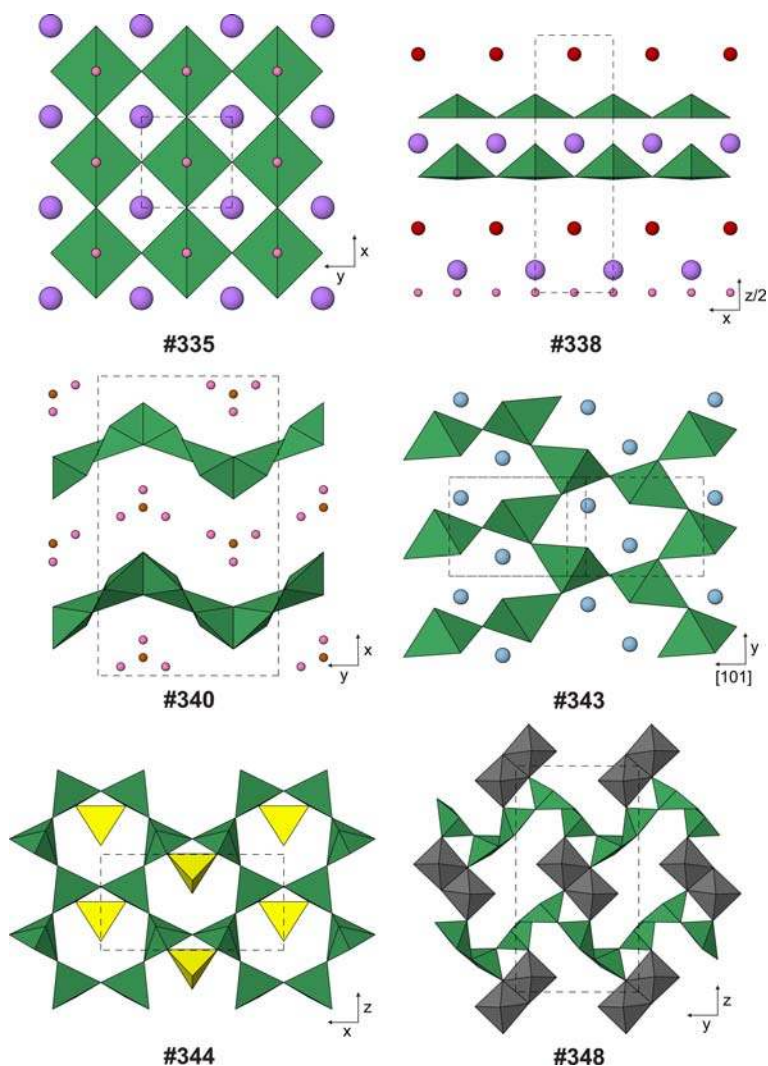


FIG. 31. Examples of structures with layers of  $\text{Te}^{4+}$  polyhedra (Table 17, deposited). Small spheres: N (brown) and O (dark pink) when not part of a polyhedron. N and O constitute interlayer  $\text{NO}_3$  groups in #340. Medium spheres: Br (red). Large spheres: Bi (violet) and Li (pale blue). Polyhedra: Mo (dark grey), S (yellow) and Te (dark green).

We have two instances of chains with multiplicity greater than two.  $\text{Te}_4\text{O}_5(\text{PO}_4)_2 \equiv [\text{P}_2(\text{PO})_2(\text{Te}_8\text{O}_{24})]$  (#333) has the open-branched *zweier* triple chain shown in Fig. 10g. As noted earlier, the central ribbon of 6-rings resembles that of 'biopyr-bole' silicate minerals such as jimthompsonite,  $(\text{Mg},\text{Fe})_5(\text{Si}_6\text{O}_{16})(\text{OH})_2$  (Veblen and Burnham, 1978), except for the increased coordination number of the  $\text{Q}^{2300}$  polyhedra. The Te ribbons are run  $\parallel y$ , and are connected to form strongly pleated layers  $\parallel (201)$  by  $\text{PO}_4$  tetrahedra, half of

which share all four corners and half of which share only three.  $\text{Cd}_4\text{Te}_6\text{O}_{13}\text{Cl}_6 \equiv \text{Cd}_2[\text{Te}_6\text{O}_{13}](\text{Cd}_2\text{Cl}_6)$  (#334) contains the extraordinary quadruple chains of Fig. 10h. The outer two backbones are *zweier*, and contain edge-sharing Te trimers surrounding a  $\text{CN}_3$  oxygen atom, similar to those of Fig. 8i. Conversely, the central backbones are *dreier*, and are linked through shared 'double-triangle' clusters. The resulting ribbons are flattened on  $(012)$  and run  $\parallel x$ . They stack *en échelon*, and are connected into layers  $\parallel (001)$  through edge-sharing ribbons of

$\text{CdO}_7$  and  $\text{CdO}_8$  polyhedra. Between these layers,  $\text{CdCl}_6$  octahedra form edge-sharing ribbons, and the structure is held together by weak  $\text{Te}\cdots\text{Cl}$  bonds.

### Structures with $\text{Te}^{4+}$ complexes that are infinite sheets

Table 17 (deposited) lists phyllotellurites **#335–363**, whose various types of  $\text{Te–O}$  sheet are summarized in Table 4 and shown in Fig. 11 (single layers) or Table 5 and Fig. 12 (double layers).  $\text{Bi}_{10}\text{Te}_2\text{O}_{17}\text{Br}_4 \equiv \text{Bi}_{10}[\text{TeO}_2]_2\text{O}_{13}\text{Br}_4$  (**#335**) has the simple, electrostatically neutral  $\text{TeO}_2$  layer of Fig. 11*a*, with square-pyramidal  $\text{TeO}_4$ . It is a pseudotetragonal with  $a \approx b \approx 4$  Å. The  $\text{Te}$  pyramids share edges with  $\text{BiO}_8$  cubes which have  $\text{BiO}_4$  pyramids on the other side. The composite  $\text{Bi}_2\text{TeO}_4$  layers  $\parallel (001)$  that are thus formed can be regarded as slices of a fluorite-like structure. These layers alternate along  $z$  with topologically similar but  $\text{Te}$ -free  $\text{Bi}_3\text{O}_4$  layers. In both cases, an additional ‘interstitial’ anion site, in an ‘octahedral’ interstice of the cubic close-packed cation slab, is 25% occupied by  $\text{O}^{2-}$  to give a ‘stuffed fluorite slab’ stoichiometry  $(\text{Bi},\text{Te})_3\text{O}_4(\text{O}_{0.25})$ . These interstitial oxygen atoms are weakly bonded to  $\text{Bi}$  and  $\text{Te}$ , but are too far from  $\text{Te}$  (2.51 Å) to be included in the  $\text{Te–O}$  complex of our classification. It should be noted that short  $\text{O}\cdots\text{O}$  distances of 2.38 Å suggest that accommodation of the additional oxygen requires adjustment to other parts of the structure.  $\text{Br}^-$  anions lie between the layers, which are held together through weak  $\text{Bi}\cdots\text{Br}$  and  $\text{Te}\cdots\text{Br}$  interactions (Fig. 31).  $\text{NdTe}_2\text{O}_5\text{Cl} \equiv \text{Nd}[\text{TeO}_2]_2\text{OCl}$  (**#336**) is structurally very similar, although it is truly tetragonal, has all stuffed-fluorite  $\text{NdTe}_2\text{O}_4(\text{O})$  layers equivalent, and thus has a halved  $c$  repeat. The similarity between these compounds is best seen if the formulae are written as  $[(\text{Bi}_2\text{Te})\text{O}_4(\text{O}_{0.25})][\text{Bi}_3\text{O}_4(\text{O}_{0.25})]\text{Br}_2$  and  $[(\text{NdTe}_2)\text{O}_4(\text{O})][(\text{NdTe}_2)\text{O}_4(\text{O})]\text{Cl}_2$ . The fully-occupied interstitial oxygen site has  $8 \times \text{O}$  at 2.58 Å,  $4 \times \text{Nd}$  atoms at 2.86 Å and  $2 \times \text{Te}$  atoms at 2.42 Å. If these oxygen atoms were included as  $\text{Te}$  ligands, then the  $\text{Te}$  coordination would increase from square-pyramidal  $\text{CN}_4$  to  $\text{CN}_5$  (Fig. 4*b,e*), and the  $\text{Te–O}$  complex would be not the single  $[\text{TeO}_2]^0$  layer of Fig. 11*a*, but a double layer  $[\text{Te}_2\text{O}_5]^{2-}$ , in which sublayers of the type shown in Fig. 11*c* are linked by corner-sharing of the additional oxygen atoms. Note the very different chain structures exhibited by the  $\text{Ho}$  analogue (**#307**) and the  $\text{Br}$  analogue (**#285**). Compound

**#337** approximates  $\text{Bi}[\text{Te}_2\text{O}_5]\text{Cl}$ , but is more accurately written  $\text{Bi}_{0.87}[\text{Te}_2\text{O}_{4.9}]\text{Cl}_{0.87}$ . Again, it has a strongly layered structure in which  $\text{Bi}$  atoms are at the core of the layers,  $\text{Te}$  on the outsides, and weak  $\text{Te}\cdots\text{Cl}$  bonds are holding the layers together. However, layers have trigonal rather than (pseudo) tetragonal symmetry, and there is very extensive long-range disorder. Tellurium has one apical ligand  $\text{O1}$  at 2.02 Å, but other oxygen sites at  $3 \times 2.14$  Å ( $\text{O3}$ ),  $3 \times 2.37$  Å ( $\text{O3}$ ) and  $3 \times 2.41$  Å ( $\text{O2}$ ). The  $\text{O2}$  and  $\text{O3}$  sites are only 73% and 24% occupied, respectively, and short  $\text{O}\cdots\text{O}$  distances imply that there must be considerable short-range order. The  $\text{O3}$  sites occur in triangles with  $\text{O3}\cdots\text{O3} = 1.27$  Å, so only one position out of each triplet can be occupied, and each  $\text{O2}$  site has three  $\text{O3}$  at 1.70 Å, so either  $\text{O2}$  or one of those  $\text{O3}$  positions can be occupied. The simplest and most symmetrical occupancy pattern which satisfies these constraints and approximates the refined occupancies of the average structure is shown in Fig. 11*b*. Each  $\text{Te}$  atom has ligands which are  $1 \times \text{O1}$  plus either  $3 \times \text{O2}$  ( $\frac{3}{4}$  of the time) or  $2 \times \text{O2}$  and  $2 \times \text{O3}$  ( $\frac{1}{4}$  of the time). The resulting layer has 3-rings of  $\text{Q}^{1030}$  and  $\text{Q}^{1220}$   $\text{Te}$  polyhedra with the geometry of Fig. 4*d* and a distorted variant of Fig. 4*e* respectively, an ideal stoichiometry  $\text{Te}_2\text{O}_5$ , and a within-layer repeat that is a  $2 \times 2$  superstructure of the crystallographic unit cell. The long-range disorder reflects at least stacking disorder of that ordering pattern, possibly with an admixture of other short-range ordering schemes. Compound **#338** is another  $\text{Bi}$  tellurite halide with an ostensibly simple stoichiometry concealing structural complexity (Fig. 31). It approximates  $\text{BiTeO}_3\text{Br}$ , is more accurately represented by the structural formula  $\text{Bi}_2[\text{TeO}_3][\text{TeO}_2]\text{OBr}_2$ , which if partial occupancies are indicated becomes in turn  $\text{Bi}_{1.93}[\text{TeO}_3][\text{TeO}_2]\text{OBr}_{1.8}$ . Like **#336**, it is a tetragonal structure with  $a \approx 4$  Å. There is a stuffed-fluorite compound layer  $(\text{BiTe}_2)\text{O}_4(\text{O})$  similar to the  $(\text{NdTe}_2)\text{O}_4(\text{O})$  layers of that structure or  $(\text{BiTe}_2)\text{O}_4(\text{O}_{0.25})$  of **#335**. Again, there is a fully-occupied ‘interstitial’ oxygen site, but this is now at 2.87 Å from  $4 \times \text{Bi}$ , 2.59 Å from one  $\text{Te}$  and only 1.88 Å from the other  $\text{Te}$  atom. Thus, individual layers are polar, the  $\text{Te–O}$  complex on one side being the neutral layer  $[\text{TeO}_2]^0$  with  $\text{CN}_4$   $\text{Te}$  (Fig. 11*a*), while that on the other side is anionic  $[\text{TeO}_3]^{2-}$  with  $\text{CN}_5$   $\text{Te}$  (Fig. 11*c*). The full stacking sequence includes two such fluorite-like  $\text{Te1–Bi–Te2}$  slabs of opposing polarity, and also a separate  $\text{Bi}_2\text{O}_2$  layer which is thinner, with a geometry more obviously similar to the litharge form of  $\text{PbO}$

(Boher *et al.*, 1985). Indeed, the overall structure has the same  $P4/nmm$  space group as litharge. Bromium forms double layers between the two fluorite-like slabs and also single layers between fluorite and litharge slabs; the structure is held together through weak  $\text{Te}\cdots\text{Br}$  and  $\text{Bi}\cdots\text{Br}$  bonds.

$(\text{Cu}^{1+}\text{Cl}_2)[\text{Sb}^{3+}\text{TeO}_3]$  (**#339**) has a disordered 50 : 50 mix of  $\text{Sb}^{3+}$  and  $\text{Te}^{4+}$  cations, which are 4-coordinated and form  $(\text{Te},\text{Sb})_2\text{O}_3$  layers of the type seen in Fig. 11*d*, which can be generated by condensing the double chains of Fig. 10*a* through additional corner-sharing. Note that in this compound, the layers are cationic,  $[\text{SbTeO}_3]^+$ . The layers are  $\parallel (201)$ , and between them are intercalated 3-wide ribbons running  $\parallel y$  of  $\text{CuCl}_n$  polyhedra. The outer two Cu positions form well-ordered chains of corner-linked  $\text{CuCl}_4$  tetrahedra, while the central Cu atom is delocalized across triangular 3-fold and linear 2-fold coordinated positions.  $[\text{Te}_2\text{O}_3\text{OH}](\text{NO}_3)$  (**#340**) has corrugated layers  $\parallel (200)$  of the topology shown in Fig. 11*e*, in which  $\text{Q}^{0401}$  polyhedra form a 3-connected net of 6-rings despite having CN4, by virtue of sharing one edge. The Te atoms and O1, which does not participate in the shared edge, form corner-linked chains of massicot-like asymmetrical crankshaft geometry running  $\parallel z$  (cf. Hill, 1985). Te–O distances for O1 (1.89 + 2.05 Å), O2 ( $2 \times 1.93$  Å) and O3 ( $2 \times 2.17$  Å) indicate unambiguously that the H atom is attached to O3. The resulting layers are again cationic,  $[\text{Te}_2\text{O}_3\text{OH}]^+$ , and are held together through their electrostatic attraction to interlayer  $\text{NO}_3^-$  anions (Fig. 31). A layer of the Fig. 11*e* topology also occurs in the mineral tellurite, an orthorhombic polymorph of  $\text{TeO}_2$  (**#341**), where very tightly corrugated layers of this type are  $\parallel (200)$ . These layers are electrostatically neutral, and are held together only by long  $\text{Te}\cdots\text{O}$  bonds. It should be noted that the structure is isopuntal with the brookite polymorph of  $\text{TiO}_2$ , but whereas the Ti atoms of brookite have six oxygen neighbours at 1.863–2.052 Å (Meagher and Lager, 1979), the lone-pair stereoactivity of  $\text{Te}^{4+}$  distorts the coordination octahedron to give only four neighbours in the range 1.88–2.20 Å, an additional neighbour within the layer at 2.64 Å, and a weak Te–O bond across the interlayer gap at 3.07 Å. A variant of the structure with additional anion-anion bonding occurs for the pararammelsbergite form of  $\text{NiAs}_2$  (Fleet, 1972) and intermetallic compounds such as  $\text{AuSn}_2$  (Rodewald *et al.*, 2006). Two other polymorphs of  $\text{TeO}_2$  are discussed as **#364–365** below. At present, there do not appear to be examples of more complex structures that

contain uncharged  $\text{Te}^{4+}\text{--O}$  sheets, although analogues are known for other  $p$ -block elements. The mineral lucabindiite, ideally  $\text{K}[\text{As}_4\text{O}_6]\text{Cl}$  (Garavelli *et al.*, 2013), has planar  $\text{As}_4\text{O}_6$  sheets which direct their lone pairs towards interlayers of  $\text{Cl}^-$ , while the oxygens face interlayers of  $\text{K}^+$ .

$\text{Bi}_4\text{Te}_2\text{O}_9\text{Br}_2 \equiv \text{Bi}_4[\text{Te}_2\text{O}_5]\text{O}_4\text{Br}_2$  (**#342**) is another Bi tellurite containing fluorite-like Bi–Te–O slabs  $\parallel (001)$ , like **#335** and **#338**. In this case,  $a$  and  $b \approx \sqrt{2} \times 4 \text{ Å} \approx 5.6 \text{ Å}$ , as the Te–O component layer contains alternating CN4 and CN5 Te atoms (Fig. 11*f*), and is in effect an ordered intermediate between the layers of Figs 11*a* and 11*c*. It should be noted that the CN4 Te atom is in almost square-planar coordination, which is unusual, and suggests that some atomic coordinates may be incorrect. The  $(\text{Bi}_4\text{Te}_2)\text{O}_8(\text{O})$  stuffed-fluorite slabs are polar, with Te on only one side. Single layers of  $\text{Br}^-$  ions lie between slabs, which are linked through weak  $\text{Te}\cdots\text{Br}$  and  $\text{Bi}\cdots\text{Br}$  bonds.

In one form of  $\text{Li}_2[\text{Te}_2\text{O}_5]$  (**#343**; the other polymorph is **#351**),  $\text{Q}^{1300}$  Te polyhedra link to form layers of 6-rings, topologically equivalent to the silicate sheets of the ‘micas’ (Fig. 11*g*). Resemblance to micas is further enhanced by the fact that such sheets occur in pairs, and their apical oxygen atoms are directed inwards, towards a ‘sandwich filling’ layer of electropositive cations. In this compound, however, the core of the layer is composed of tetrahedrally coordinated  $\text{Li}^+$  cations, rather than higher-valence species in octahedral coordination. The compound mica-like layers are  $\parallel (10\bar{1})$ , with Te lone pairs directed into the interlayer gap and only weak  $\text{Te}\cdots\text{O}$  bonds connecting layers (Fig. 31).  $(\text{Te}_2\text{O}_3)(\text{SO}_4) \equiv [(\text{SO}_2)(\text{Te}_2\text{O}_5)]$  (**#344**) also has phyllostellurite sheets  $\parallel (010)$  with the topology of Fig. 11*g*, but the non-bridging oxygen atoms are not all on one side of the sheet. Hexagonal rings are bent in a boat configuration, and pairs of apical oxygen atoms point alternately up and down along  $y$ . All ‘up’ or ‘down’ pairs have  $\text{Te}\text{--Te} \parallel x$ , and individual 6-rings have either four ‘up’ polyhedra and two ‘down’ or *vice versa* (Fig. 31). This is an analogue of the silicate sheet found in sanbornite,  $\text{Ba}[\text{Si}_2\text{O}_5]$  (Hesse and Liebau, 1980), rather than the mica structure type. Each pair of apical oxygen atoms is shared with a  $\text{SO}_4$  tetrahedron, thus completing the heteropoly layer structural unit. Layers are held together through long bonds between the Te of one layer and the non-bridging sulfate oxygen atoms of the next. Tilt of the  $\text{SO}_4$  groups and asymmetry of the Te–O–Te angles make the structure polar  $\parallel z$ . The layer  $\parallel (010)$  of  $(\text{Te}_2\text{O}_3)(\text{PO}_3\text{OH}) \equiv (\text{POOH})[\text{Te}_2\text{O}_5]$

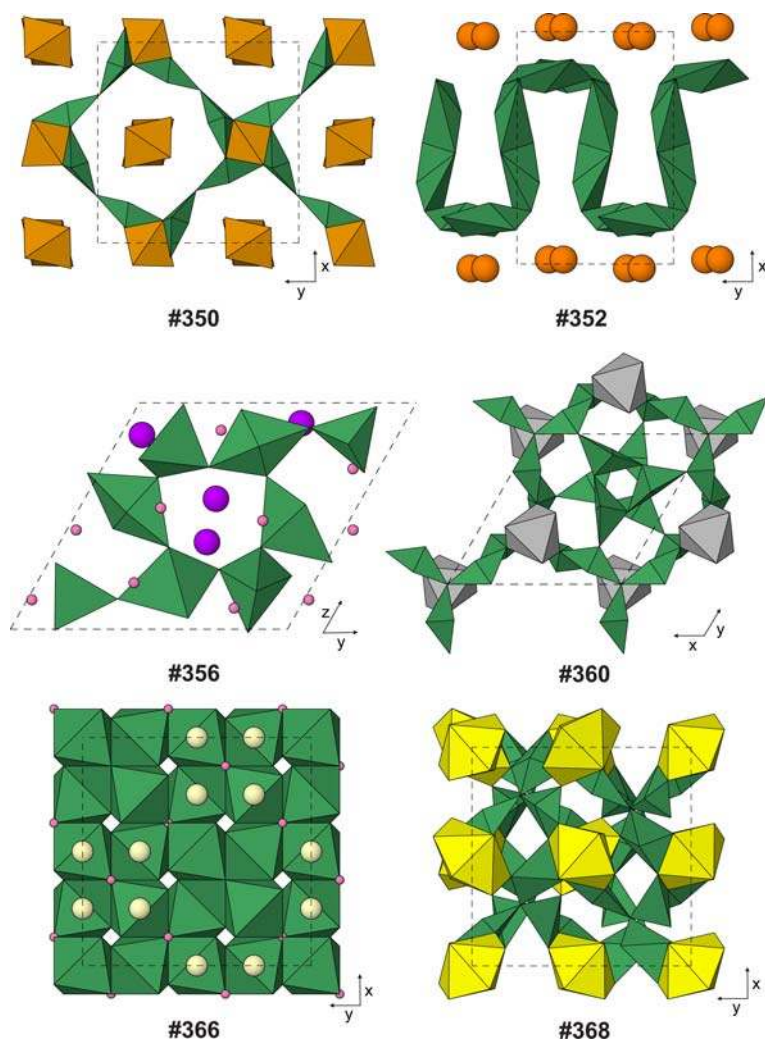


FIG. 32. Examples of structures with layers or frameworks of  $\text{Te}^{4+}$  polyhedra (Tables 17–18, deposited). Small spheres: O (dark pink) when not part of a polyhedron. Large spheres: Ca (orange), K (purple) and Pr (pale yellow). Polyhedra: Fe (orange-brown), Te (dark green), U (yellow) and Zn (pale grey).

(#345) also has pairs of ‘up’ or ‘down’ Te polyhedra, but each 6-ring has three of each, and the ‘up’ (or ‘down’) pairs are arranged in a herringbone pattern. The  $\text{PO}_3\text{OH}$  tetrahedra again share two corners with adjacent Te polyhedra of a layer. Interatomic distances indicate that the H atom is attached to the non-bridging phosphate oxygen atom O7, and forms hydrogen bonds that brace the layer, rather than connecting between layers. Layers are connected by weak bonds between Te and the other non-bridging phosphate ligand O5, and the overall structure is polar  $\parallel z$  for the same reasons as #344. The *b*

parameters of these two structures are very similar, reflecting the similarity of layers and their stacking.

$[\text{Mg}(\text{Te}_2\text{O}_5)]$  and the  $\beta$  polymorph of  $[\text{Mn}(\text{Te}_2\text{O}_5)]$  (#346–347) have layers  $\parallel (020)$  with 6-rings of the ‘four up/two down’ type, like #344, but the 6-rings are distorted so that ‘up’ Te–Te pairs point along  $[102]$  while ‘down’ pairs point  $\parallel [10\bar{2}]$ . Layers are cross-linked into a framework through zigzag edge-sharing chains of  $\text{MO}_6$  octahedra ( $\text{M} = \text{Mg}$  or  $\text{Mn}$ ). The octahedral chains run  $\parallel z$ , with small channels between them that can accommodate the Te lone pairs. The ‘denningite’ polymorph



of the Mn compound was discussed above (#310).  $\text{MoTe}_2\text{O}_7 \equiv [(\text{MoO}_2)(\text{Te}_2\text{O}_5)]$  (#348) also has ‘four up/two down’ layers, this time  $\parallel (002)$ , but the layers are strongly pleated so that the Te–Te pairs point obliquely to the overall trend of the layer,  $\parallel [232]$  (‘down’ pairs relative to  $+z$ ) or  $[23\bar{2}]$  (‘up’). Layers contain very obvious massicot-like Te–O–Te–O chains  $\parallel x$ . Tellurium layers are linked into a framework through  $\text{MoO}_6$  octahedra chains, which occur as edge-sharing  $\text{Mo}_2\text{O}_{10}$  dimers which then share four additional corners to make ladder-like double chains  $\parallel x$  (Fig. 31).

$\text{La}_2[\text{Te}_3\text{O}_7]_2(\text{WO}_4)$  (#349) has the unique layers of 3- and 6-rings shown in Fig. 11*h*; note that the node where three 6-rings join is a CN3 oxygen atom. These layers are  $\parallel (002)$ , and the non-bridging oxygen atoms of the  $\text{Q}^{1210}$  Te polyhedra all point inwards from two such layers towards a central sheet of  $\text{LaO}_{10}$  polyhedra. Between the 6-rings of the two Te sheets are large interstices which contain  $\text{WO}_4$  tetrahedra, disordered between ‘up’ and ‘down’ orientations. Mackayite,  $\text{Fe}^{3+}(\text{Te}_2\text{O}_5)(\text{OH})$  (#350) has layers that should be written  $\text{Te}_4\text{O}_{10}$  to reflect the translational periodicity. These have 4- and 8-rings similar to the ‘apophyllite’ type, as seen in Fig. 11*i*. In the mackayite layer, individual ‘upward’ and ‘downward’ pointing polyhedra alternate, unlike apophyllite, where whole 4-rings of ‘up’ and ‘down’ tetrahedra alternate (Colville *et al.*, 1971). The layers lie  $\parallel (004)$ , repeated by a screw tetrad axis. The layers are held together by edge-sharing dimers of Fe octahedra,  $\text{Fe}_2\text{O}_8(\text{OH})_2$  (Fig. 32). Our second polymorph of  $\text{Li}_2\text{Te}_2\text{O}_5 \equiv \text{Li}_4[\text{Te}_4\text{O}_{10}]$  (#351) like its dimorph #343 has Te layers  $\parallel (020)$  in which all Te are CN4; however, the polyhedra form 10-rings, and some of them are only 2-connected, occurring as edge-sharing  $\text{Q}^{1301}$  pairs rather than the  $\text{Q}^{1300}$  polyhedra typical of silicate-like sheets (Fig. 11*j*). The edge-sharing dimers act as bridges between bands where the other Te tetrahedra point downwards and bands where they point upwards. The pointing direction reverses every  $\frac{1}{2}c$ . Tellurium sheets are held together through the non-bridging oxygen atoms, which link to  $\text{LiO}_4$  tetrahedra, which occur as pairs of *vierer* corner-sharing helices (cf.  $\text{Li}_2[\text{TeO}_3]$ , #1) running  $\parallel x$  between Te layers. The regular inversion of pointing direction in the Te layers, and breakup of the Li component into discrete ribbons, gives this structure a resemblance to commensurately modulated phyllosilicates such as sepiolite,  $\text{Mg}_4[\text{Si}_6\text{O}_{15}](\text{OH})_2 \cdot 6\text{H}_2\text{O}$  (Post *et al.*, 2007). The  $\text{Te}_4\text{O}_{10}$  layer of  $\text{Ca}[\text{Te}_2\text{O}_5]$  (#352) also has 10-rings and edge-sharing dimers

of Te polyhedra; however, the latter are now 3-connected  $\text{Q}^{0401}$  type, as seen in Fig. 11*k*. The layers are crumpled and rather thick, with the edge-sharing Te=Te vectors almost normal to the overall layer plane (100). Layers are linked through sheets of  $\text{CaO}_7$  polyhedra (Fig. 32). Note that this description requires a slightly longer than usual strong-bonding distance threshold; if a Te–O distance of 2.450 Å is not included, the layer breaks up into finite  $\text{Te}_4\text{O}_{10}$  tetramers of the type seen in Fig. 8*j*, #250–255. A similar topology of layer, less tightly corrugated, occurs  $\parallel (10\bar{1})$  in  $\text{Ti}_2[\text{Te}_2\text{O}_5]$  (#353). Layers are linked through very irregular  $\text{TiO}_{5-7}$  polyhedra.  $\text{K}_2[\text{Te}_4\text{O}_9]$  (#354) and its  $\text{NH}_4^+$  analogue #355 are isopuntal, but giving them a common description again requires a careful choice of Te–O bonding threshold, which is 2.43 Å here. This excludes additional neighbours at 2.433 and 2.489 Å to respectively Te1 and Te2 of the K compound, which are at 2.713 and 2.615 Å and hence clearly not strongly bonded in #355. The convoluted  $\text{Te}_8\text{O}_{18}$  layers  $\parallel (100)$  in these structures have the topology of Fig. 11*l*, with 6- and very elongated 14-rings containing both CN3 and CN4 Te polyhedra. The layers are held together by large cations, 7–8 coordinated by oxygen in the case of  $\text{K}^+$ . This structure is very different from the double-chain type of the Na analogue (#332, Fig. 10*f*). Although  $\text{K}_2[\text{Te}_4\text{O}_9] \cdot 3.2\text{H}_2\text{O}$  (#356) is triclinic, it is strongly pseudohexagonal ( $b \approx c$ ,  $\alpha \approx 60^\circ$ ) and has rather symmetrical  $\text{Te}_8\text{O}_{18}$  layers  $\parallel (100)$  containing two types of 6-ring (Fig. 11*m*). One quarter of the rings are regular hexagons containing only CN4 Te, with non-bridging ligands pointing alternately ‘up’ and ‘down’. The rest of the rings are elliptical, and three of these meet at a CN3 Te atom. Between the Te layers are a central plane of water molecules and  $\text{K}^+$  ions in 7–8 coordination (Fig. 32).  $(\text{NH}_4)\text{Rb}[\text{Te}_4\text{O}_9] \cdot 2\text{H}_2\text{O}$  and the corresponding compound with Cs replacing Rb (#357–358) have a rather complex  $\text{Te}_{16}\text{O}_{36}$  layer (Fig. 11*n*). The layers are  $\parallel (002)$ , and can be regarded as formed by condensation of  $\text{Te}_8\text{O}_{20}$  clusters. The clusters, in turn, consist of a central edge-sharing pair of  $\text{Q}^{0501}$  Te atoms, common to two 4-rings which are each completed by a pair of  $\text{Q}^{1300}$  Te atoms, each 4-ring in turn sharing one side with a 3-ring formed by links to a  $\text{Q}^{0300}$  Te atom. The remaining corners of the 4-rings and the CN3 Te atom of the 3-rings then link to other clusters to make a continuous layer, which has very elongate 12-rings. Large cations and water molecules are between the layers.

Our final single-layer structure,  $\text{Ba}_6[\text{Te}_{10}\text{O}_{25}]\text{Br}_2$  (#359), also has an extraordinarily complex layer



with a translational repeat  $\text{Te}_{40}\text{O}_{100}$  and ten symmetrically distinct types of Te (Fig. 11*o*). The layers are  $\parallel$  (002) and are rather thick but looped rather than double, with tubular cavities running  $\parallel$   $x$  which contain the  $\text{Br}^-$  ions.  $\text{Ba}^{2+}$  cations between the layers link to 8–9 O atoms of the tellurite layer and 0–1 Br. Again, the layer is most simply described if an unusually long bonding threshold of 2.52 Å is used. This includes all the moderately strong Te–O bonds: seven out of the ten Te sites have oxygen neighbours in the 2.41–2.52 Å range, while none have any other neighbours within 2.98 Å. With the Te–O bond network thus defined, Te are CN4 (Te1–Te2, Te4 =  $\text{Q}^{0400}$ , Te9 =  $\text{Q}^{1300}$  and Te5–Te8 =  $\text{Q}^{2200}$ ) except Te3 ( $\text{Q}^{0300}$ ). Two types of tube alternate, both with flattened elliptical cross-sections. The denser type contains a ribbon of 4-rings (Te2–Te9–Te2–Te9) and 8-rings (Te2–Te3–Te1–Te9–Te2–Te3–Te1–Te9), with arches of three additional Te atoms completing 7-rings (Te4–Te8–Te7–Te3–Te2–Te9–Te1). These tubes are linked into a layer through Te10 and bridges –Te5–Te6– but the second type of tube defined by those is much more sparsely connected, its smallest rings having 9 and 10 members.

The compounds  $[\text{M}^{2+}(\text{Te}_6\text{O}_{13})]$  ( $\text{M} = \text{Zn}, \text{Fe}$  and  $\text{Mg}$ ; #360–362) have  $\text{Te}_6\text{O}_{13}$  double layers (Fig. 12*a*). These stack  $\parallel$  (003) and are linked through corner-sharing with  $\text{MO}_6$  octahedra. The individual sublayers contain triplets of  $\text{Q}^{0311}$  Te1 sharing a common CN3 oxygen atom, connecting to 3-rings of  $\text{Q}^{1300}$  Te2 so as to form crumpled 12-rings of Te1 and Te2, which surround the M cations. Two such sublayers are linked by their Te1 atoms sharing an edge (Fig. 32).  $(\text{Te}_3\text{O}_5)(\text{Se}^{4+}\text{O}_3) \equiv [(\text{SeO})_2(\text{Te}_6\text{O}_{14})]$  (#363) has a double layer  $\parallel$  (001) with three types of Te polyhedron:  $\text{Q}^{0300}$ ,  $\text{Q}^{1300}$  and  $\text{Q}^{1400}$  (Fig. 12*b*). Each sublayer has a net of 3-connected 8-rings, with CN4 and CN5 Te atoms at the nodes and CN3 Te making two links within the sublayer. These links result in smaller 4- and 6-rings that are shared by the sublayers. Two such sublayers are held together by links between CN3 Te of one and CN5 Te of the other. The  $\text{SeO}_3$  pyramids are on the outside of the double layer, sharing one oxygen atom with CN5 Te and one with CN4 Te. Layers are held together by weak  $\text{Te}\cdots\text{O}$  and  $\text{Se}\cdots\text{O}$  bonds.

### Structures with $\text{Te}^{4+}$ complexes that are infinite frameworks

Tectotellurite structures #364–375 are listed in Table 18 (deposited), summarized in Table 5 and have their Te–O frameworks depicted in Fig. 12.

The structure of the paratellurite polymorph of  $\text{TeO}_2$  (#364, Fig. 12*c*) is derived from that of the rutile form of  $\text{TiO}_2$  (cf. Meagher and Lager, 1979) in a way analogous to the derivation of the tellurite structure from brookite (#341 above). The lone-pair stereoactivity of the  $\text{Te}^{4+}$  changes the coordination environment from the relatively regular octahedron of rutile to a strongly distorted 4 + 2 pattern with  $2 \times \text{O}$  at 1.88 Å,  $2 \times \text{O}$  at 2.12 Å and  $2 \times \text{O}$  at 2.87 Å. However, unlike tellurite, the lengthening and weakening of two bonds per Te atom does not disrupt the framework of the  $\text{TiO}_2$  aristotype. However, the tetragonal  $c$  repeat is doubled, and the  $4_2$  screw axis of rutile becomes a  $4_3$  (or  $4_1$ ) axis in paratellurite. Paratellurite is  $\sim 4.5\%$  denser than tellurite. Interestingly, not only is the structure a distortion of the rutile structure, but it is isopuntal and topologically equivalent to the metastable low-temperature  $\alpha$ -cristobalite form of  $\text{SiO}_2$  (cf. Downs and Palmer, 1994). This suggests that the paratellurite geometry provides a pathway for diffusionless structural transformation of the type discussed by Christy (1993), between the relatively low-density cristobalite structure type (stable at relatively high temperature and low pressure in the  $\text{SiO}_2$  system, for instance) and the high-density rutile type (stable at very high pressure for  $\text{SiO}_2$ , as stishovite). At high pressure ( $\sim 0.95$  GPa), paratellurite undergoes a continuous, displacive phase transition to a topologically similar but orthorhombic variant  $\text{TeO}_2\text{-}\gamma$ , whose structure has been refined at 1.98 GPa (#365). Paratellurite and the high-pressure phase are isostructural with, respectively, the  $\beta$  and  $\gamma$  phases of  $\text{SnF}_2$ , as noted by Denes *et al.* (1980), who also discuss transformations involving the cristobalite and rutile structures.

$\text{Pr}_2[\text{Te}_2\text{O}_6]\text{O}$  (#366) has a structure of the well-known pyrochlore type, which can be derived from a  $2 \times 2 \times 2$  block of face-centred cubes of the fluorite structure by slight displacement of  $\frac{1}{4}$  of the anions so that half of the cations are in octahedral coordination by them, forming a continuous framework (Fig. 12*d*) and omission of half of the remaining anions. The overall stoichiometry is  $A_2[B_2X_6]Y$ , where the larger cation type  $A$  is coordinated by  $6X + 2Y$  while  $B$  bonds to  $6X$  only. In this case,  $B$  is  $\text{Te}^{4+}$ , which usually is in rather regular octahedral coordination by oxygen, with no lone-pair stereoactivity (Fig. 32). The next few structures are also fluorite derivatives.  $\text{K}[\text{Ga}(\text{Te}_6\text{O}_{14})]$  (#367) has a similar-sized  $a \approx 11$  Å cubic unit cell to #366, but  $\frac{1}{8}$  of the cations are 8-coordinated  $\text{K}^+$ ,  $\frac{1}{8}$  are 6-coordinated  $\text{Ga}^{3+}$ , and the rest are 4-coordinated  $\text{Te}^{4+}$ . The K, six Te and Ga are arranged in the  $\text{LiCa}_6\text{Ge}$

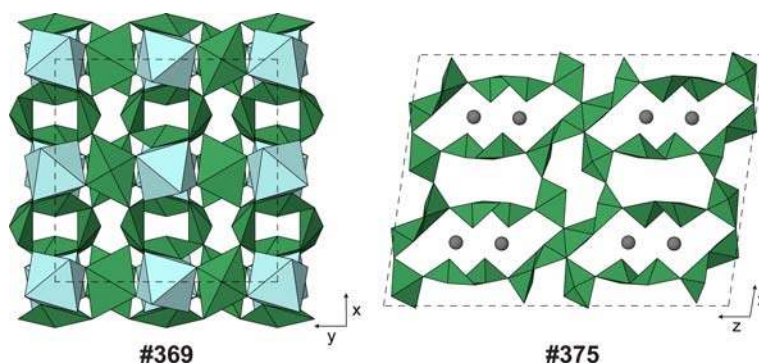


FIG. 33. Examples of structures with frameworks of  $\text{Te}^{4+}$  polyhedra (Table 18, deposited). Large spheres: Pb (dark grey). Polyhedra: Sn (pale blue) and Te (dark green).

pattern (Pavlyuk *et al.*, 1993), a superstructure of the common  $\text{Cu}_3\text{Au}$  type (Kear and Wilsdorf, 1962). Relative to fluorite,  $1/8$  of the anions are missing, as for pyrochlore. The remaining anions are of three types, bonded respectively to  $2\text{Te} + \text{K}$ ,  $\text{Te} + \text{Ga}$  and  $3\text{Te} + \text{K}$ . If we consider only the Te–O substructure, it has  $\text{Te}_6\text{O}_{14}$  stoichiometry and  $\text{Q}^{1210}$  Te polyhedra forming the complex network shown in Fig. 12e. The Ga octahedra reinforce this framework. Cliffordite,  $[(\text{UO}_2)(\text{Te}_3\text{O}_7)]$  (#368), has  $\text{Te}^{4+}$  and  $\text{U}^{6+}$  in a 3:1 ratio, ordered in the  $\text{Cu}_3\text{Au}$  arrangement like Te and (K+Ga) of #367 (Fig. 32). As for that structure, the Te–O framework has  $\text{Q}^{1210}$  Te polyhedra and  $\text{Te}_6\text{O}_{14}$  stoichiometry, but the topology is different (Fig. 12f), and whereas  $\text{TeO}_4$  polyhedra share corners with  $\text{GaO}_6$  octahedra in #367, they share edges with  $\text{UO}_8$  bipyramids in cliffordite. Note that the total anion content is higher than that of fluorite: while the uranyl oxygen positions and those of the oxygen atoms that link U to Te can all be derived by small displacements from their counterparts in the fluorite aristotype, this is not true for O5 of cliffordite, which joins 3 Te. Very closely related is the winstanleyite structure type of compounds  $[\text{A}^{4+}(\text{Te}_3\text{O}_8)]$  (#369–373), where  $\text{A} = \text{Ti}$  in the mineral winstanleyite (#372),  $(\text{Fe}_{0.67}^{3+}\text{Te}_{0.33})$  in walfordite (#373), and Sn, Zr or Hf in synthetic analogues (Fig. 33). Again, Te and A atoms are in the  $\text{Cu}_3\text{Au}$  pattern. The oxygen atoms of the fluorite aristotype are all present, but are displaced so as to form quite regular octahedra around the A cations and the common ‘folded rhombus’ arrangement of Fig. 4c around Te. The Te polyhedra are  $\text{Q}^{2020}$ , and form a framework (Fig. 12g) where the non-bridging ligands share corners with A octahedra. Note that for taxonomic purposes, the minority  $\text{Te}^{6+}$  content of the A sites of walfordite is ignored.  $\text{Cs}_2[\text{Te}_4\text{O}_9]$

(#374) has a tetragonal unit cell with the  $a$  parameter similar to that of #366–373 but  $c$  about twice as large. The Cs and Te atoms form two cubes of the  $\text{MgCu}_2$  Friauf-Laves structure arrangement (Friauf, 1927; Hyde and Andersson, 1989). That is, they are geometrically equivalent to, respectively, the  $D$  and  $T$  cubic lattice complexes of Fischer and Koch (2006). This is also the pattern of Mg and Al atoms in normal spinel,  $\text{MgAl}_2\text{O}_4$ , and of  $\text{YB}_2$  atoms in the  $\text{A}_2\text{B}_2\text{X}_6\text{Y}$  pyrochlore structure. However, whereas the B cations of the pyrochlore framework are linked through X to six B neighbours (cf. #366 above), the Te atoms of #374 are bonded to only a subset of these: half of them are CN4 ( $\text{Q}^{0400}$ ) and the other half are CN3 ( $\text{Q}^{1300}$ ). There are no 3- or 6-rings, as in the pyrochlore framework: every CN3 Te atom is a member of one 4-ring, while the CN4 atoms join two such rings, and the next-smallest rings have 8 members (Fig. 12h). Vacant sites which would be occupied by oxygen atoms in a pyrochlore allow a more open framework, with rather large interstices to accommodate  $\text{Cs}^+$  ions in 9–10 coordination.  $\text{Pb}[\text{Te}_5\text{O}_{11}]$  has a very complex, open framework with five symmetrically different types of Te atom (#375). If Te–O distances out to 2.45 Å are included as bonds, then the topology is as seen in Fig. 12i. Te1, Te2 and Te3 (respectively  $\text{Q}^{0312}$ ,  $\text{Q}^{1210}$  and  $\text{Q}^{0401}$ ) form complex double chains that run  $\parallel [1\bar{1}0]$  at  $z = 0$  and  $\parallel [110]$  at  $z = 1/2$ . These are in turn made from  $\text{Te3}=\text{Te1}=\text{Te3}$  tetramers which are joined by Te2, which shares a CN3 oxygen with 2Te1 and a CN2 oxygen with Te3 (Fig. 33). Between these double chains, Te4 and Te5 (both  $\text{Q}^{1300}$ ) form massicot-like single chains (cf. Hill, 1985) which run  $\parallel y$  at  $z = 1/4$  and  $3/4$ . The component chains are joined in three dimensions by Te4 linking to Te3 on one side of these chains, while Te5 links to Te2 on

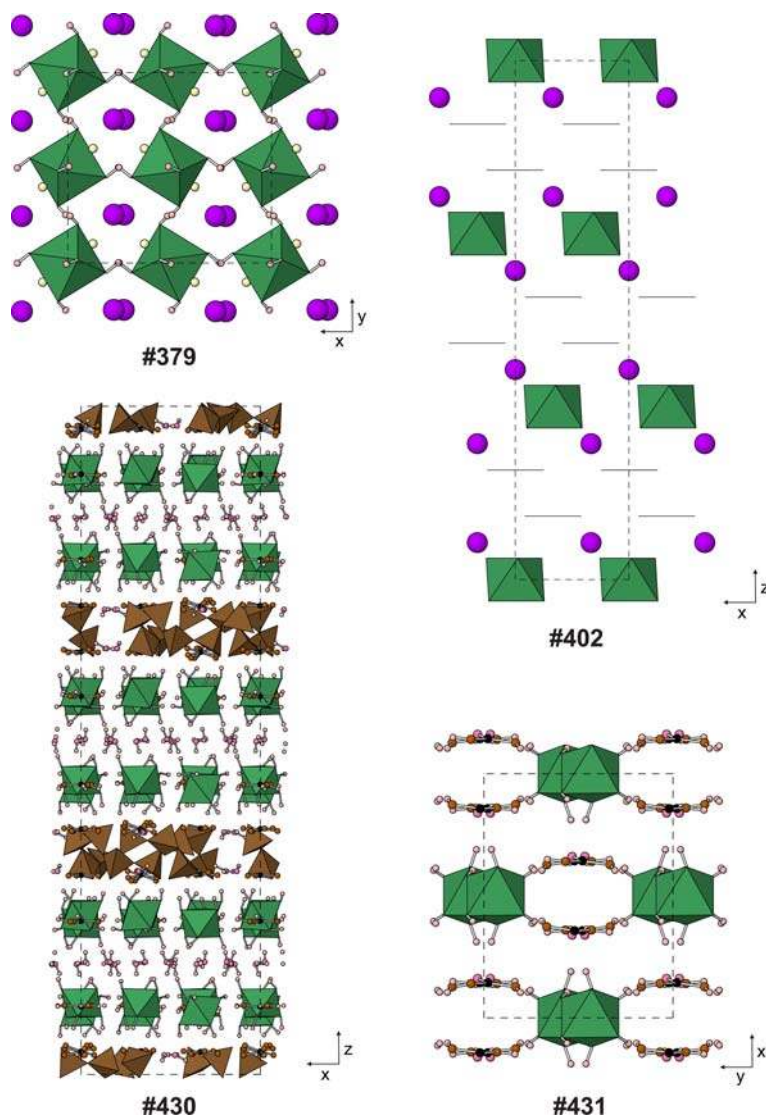


FIG. 34. Examples of structures of  $\text{Te}^{6+}(\text{OH})_6$  adducts (Table 19, deposited). Small spheres: C (black), H (pale pink), N (brown) and O (dark pink) when not part of a polyhedron. Large spheres: K (purple). Horizontal lines in **#402** indicate planes of oxygen triangles of pyramidal  $\text{I}^{5+}\text{O}_5$  anions; I atoms are not shown. Polyhedra: P (brown) and Te (dark green).

the other. Lead atoms are in 8-coordination between the massicot-like chains.

#### $\text{Te}^{6+}(\text{OH})_6$ and its adducts

Our first examples of  $\text{Te}^{6+}$  compounds are polymorphs and derivatives of orthotelluric acid,  $\text{Te}^{6+}(\text{OH})_6$ . The large valence ( $\sim 1$  vu) of bonds to O from both Te and H means that any additional

bonding must be weak, so the compound  $\text{Te}(\text{OH})_6$  has discrete octahedral molecules which are held together only through hydrogen bonds. Unsurprisingly, it is hygroscopic, extremely water-soluble, and unknown in minerals. As the molecule has six oxygen atoms, each of which carries one donor H atom and is able to accept low-valence bonds from other electron donors outside the molecule,  $\text{Te}(\text{OH})_6$  is able to co-crystallize with

a wide range of other compounds to form adducts. The other components may be polar organic molecules, simple salts of large cations such as alkali halides, or salts with larger and more complex anions such as polyphosphate species. These adducts are physically and crystal-chemically distinctive enough that they are considered separately from other  $\text{Te}^{6+}$  compounds. In many cases, small tilts of Te octahedra or changes to the H-bonding pattern may result in very similar molecular arrangements occurring in a range of different space groups and unit-cell shapes. The  $\text{TeO}_6$  octahedron (Fig. 4*h*) is always rather regular, with  $\text{Te}-\text{O} = 1.90\text{--}2.07$  Å, corresponding to bond valences of 1.04–0.77 vu using the parameters of Mills and Christy (2013). The individual structures #376–431 are listed in Table 19 (deposited).

The cubic polymorph of  $[\text{Te}(\text{OH})_6]$  itself has the molecules packed in a *fcc* array, but with the octahedra tilted and hydrogen bonded so that the cell repeat is doubled to 15.71 Å, and the space group is *Fd3c* (#376). There is also a monoclinic polymorph (#377), where  $\text{Te}\cdots\text{Te}$  distances shorter than 6.3 Å define 12 nearest neighbours in a monoclinically sheared face-centred cube, with pseudocube edges  $\parallel [100]$ ,  $[101]$  and  $[010]$  of the  $P2_1/n$  cell.  $(\text{NaF}) \cdot [\text{Te}(\text{OH})_6]$  (#378) retains a *fcc* arrangement of  $\text{Te}(\text{OH})_6$  molecules, albeit with rhombohedral distortion.  $\text{Na}^+ \text{--} \text{F}^-$  ion pairs occur in the octahedral interstices between them, so that  $(\text{NaF})$  units and  $\text{Te}(\text{OH})_6$  molecules form a rocksalt arrangement. Similarly,  $(\text{KF})_2 \cdot [\text{Te}(\text{OH})_6]$  (#379) has  $\text{K}^+ \text{--} \text{F}^-$  ion pairs in the tetrahedral interstices of an orthorhombically distorted *fcc* array of  $\text{Te}(\text{OH})_6$  molecules, so that  $(\text{KF})$  and  $\text{Te}(\text{OH})_6$  are arranged like F and Ca of the fluorite structure (Fig. 34). Such ion pairs are almost unknown in mineral structures, although the  $\text{Ca}^{2+} \text{--} \text{CO}_3^{2-}$  pair occurs in a matrix of H-bonded water molecules in ikaite,  $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$  (Swainson and Hammond, 2003) and hsianghualite,  $(\text{LiF})_2\text{Ca}_3[\text{Be}_3\text{Si}_3\text{O}_{12}]$ , can be regarded geometrically as having ion pairs  $\text{Li}^+ \text{--} \text{F}^-$  replacing the  $\text{Cs}^+$  of pollucite,  $\text{Cs}_2\Box_3[\text{Al}_2\text{Si}_4\text{O}_{12}]$ , or water of analcime,  $(\text{H}_2\text{O})_2(\text{Na}_2\Box)[\text{Al}_2\text{Si}_4\text{O}_{12}]$  (Rastsvetaeva *et al.*, 1991). However, the bond distances and the parameters of Brese and O’Keeffe (1991) indicate that the Li–F bond is not unusually strong, bond valences being  $\sim 0.25$  vu for all bonds from Li to F + 3 O and to F from Li + 3 Ca.

Alkali halide adducts with larger ions do not have ion pairs intercalated into a matrix of *fcc*  $\text{Te}(\text{OH})_6$ .  $(\text{CsCl})_2 \cdot [\text{Te}(\text{OH})_6]$  (#380) has Te and Cl forming an array of monoclinically distorted  $\text{CaCl}_2$  (or collapsed rutile) type, with Cs located in

tetrahedra of four Cl.  $(\text{RbCl})_3 \cdot [\text{Te}(\text{OH})_6]$  (#381) has a quite different rhombohedral structure in which  $\text{Te}(\text{OH})_6$  octahedra alternate with  $\text{Cl}_3$  triangles to form rods  $\parallel z$  which are linked through Rb, with each Rb having five Cl neighbours and *vice versa*.

$\text{Na}_2(\text{SO}_4) \cdot [\text{Te}(\text{OH})_6]$  (#382) has a unique structure in which  $\text{Te}(\text{OH})_6$  octahedra form a primitive hexagonal array, and alternate trigonal prisms of such molecules contain either two Na or  $\text{SO}_4$  tetrahedra. The pseudohexagonal layers of Te are  $\parallel (002)$ , with layers of Na and  $\text{SO}_4$  groups between them. One type of Na bonds to only two  $\text{SO}_4$  while the other type bonds to three  $\text{SO}_4$ , and their arrangement makes the structure polar in the (010) plane. There are a very large number of adducts of the type  $A_2(\text{TO}_4) \cdot [\text{Te}(\text{OH})_6]$ , with larger cations  $A = (\text{K}, \text{Rb}, \text{Cs}, \text{Tl} \text{ and } \text{NH}_4)$  and  $T = (\text{S} \text{ or } \text{Se})$  (#383–398). Despite the apparent diversity of symmetries and cell parameters, all of these are again based on a *fcc* array of  $\text{Te}(\text{OH})_6$  molecules, with the tetrahedral anion occupying octahedral interstices and the *A* cations occupying tetrahedral interstices. The edges of the pseudocubic cell have different indices depending on the axial setting chosen by authors, as follows.  $\text{K}_2(\text{SO}_4) \cdot [\text{Te}(\text{OH})_6]$  (#383) has space group  $P\bar{1}$ , with pseudocube edge vectors are  $\frac{1}{2}[1\bar{1}\bar{1}]$ ,  $\frac{1}{2}[311]$  and  $\frac{1}{2}[13\bar{1}]$ . The monoclinic structures with space group  $C2/c$ ,  $Cc$ ,  $P2_1/a$ ,  $P2_1/c$ ,  $P2_1/n$  or  $Pn$  all have pseudocube edges  $\frac{1}{2}[10\bar{1}]$ ,  $\frac{1}{2}[121]$  and  $\frac{1}{2}[1\bar{2}1]$  (#384–390 and 392–397) except for  $(\text{NH}_4)_{1.16}\text{K}_{0.84}(\text{SO}_4) \cdot [\text{Te}(\text{OH})_6]$  (#391), which was published in a different axial setting where the pseudocube edges are  $\frac{1}{2}[102]$ ,  $\frac{1}{2}[120]$  and  $\frac{1}{2}[\bar{1}20]$ . Note that these structures include centrosymmetric and acentric polymorphs of  $\text{K}_2(\text{SeO}_4) \cdot [\text{Te}(\text{OH})_6]$  (#384 and 385), structures in which two *A* species occur in solid solution and others in which they are ordered, such as  $\text{CsK}(\text{SO}_4) \cdot [\text{Te}(\text{OH})_6]$  (#397), and that there may be one or two symmetrically distinct types of  $\text{Te}(\text{OH})_6$  octahedron per unit cell.  $\text{Cs}_2(\text{SO}_4) \cdot [\text{Te}(\text{OH})_6]$  (#398) has a rhombohedrally distorted structure, in which the pseudocube edges are  $\frac{1}{3}[2\bar{2}1]$ ,  $\frac{1}{3}[42\bar{1}]$  and  $\frac{1}{3}[241]$ . Hydrogen ions may be quite mobile in these compounds; Dammak *et al.* (2005) investigated the protonic conductivity behaviour of  $\text{Cs}_{0.86}(\text{NH}_4)_{1.14}(\text{SO}_4) \cdot [\text{Te}(\text{OH})_6]$ , which has the  $P2_1/c$  variant of the structure but has been excluded from this study because of some unrealistically short Te–O distances in the refinement.

$\text{K}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2 \cdot [\text{Te}(\text{OH})_6]$  (#399) has a layered structure  $\parallel (001)$  not unlike that of #382, in which Te octahedra form a monoclinically



sheared primitive-hexagonal array with trigonal prisms containing the other components. Conversely,  $(\text{Cs}_{3.5}\text{Rb}_{0.5})(\text{SeO}_3)_{1.7}(\text{SO}_3)_{0.3} \cdot [\text{Te}(\text{OH})_6]_3$  (**#400**) has the familiar *fcc* array of Te, although this time, large cations occupy only  $\frac{2}{3}$  of the tetrahedral interstices, pyramidal anions are in the other  $\frac{1}{3}$  of the tetrahedral voids, and the octahedral positions are empty. The pseudocubic edge vectors are  $[010]$ ,  $\frac{1}{2}[203]$  and  $\frac{1}{6}[20\bar{3}]$  of the orthorhombic cell. The iodate adducts all have layered structures.  $\text{K}(\text{IO}_3) \cdot [\text{Te}(\text{OH})_6]$  (**#401**) has K+Te and I layers alternating  $\parallel (001)$ , while  $\text{K}_2(\text{IO}_3)_2 \cdot [\text{Te}(\text{OH})_6]$  (**#402**) has thicker layers  $\text{I}-\text{K}-\text{Te}-\text{K}-\text{I} \parallel (003)$ , with the lone pairs of  $\text{I}^{5+}$  cations directed into the interlayer gap (Fig. 34).  $(\text{NH}_4)(\text{IO}_3)(\text{H}_2\text{O}) \cdot [\text{Te}(\text{OH})_6]$  (**#403**) has layers of Te + I alternating with  $\text{NH}_4 + \text{H}_2\text{O} \parallel (200)$ .

A very large number of adducts have been made that contain phosphate anions, along with large cations Na, K, Rb, Ag, Tl or  $\text{NH}_4$ . The phosphate groups range from tetrahedral monomers  $[\text{PO}_3\text{OH}]^{2-}$  or  $[\text{PO}_2(\text{OH})_2]^-$  (**#404–412**) through diphosphates  $[\text{P}_2\text{O}_6\text{OH}]^{3-}$  or  $[\text{P}_2\text{O}_5(\text{OH})_2]^{2-}$  (**#413–415**), cyclo triphosphates  $[\text{P}_3\text{O}_9]^{3-}$  (**#416–422**),  $[\text{P}_4\text{O}_{12}]^{4-}$  (**#423–424**),  $[\text{P}_6\text{O}_{18}]^{6-}$  (**#425–427**),  $[\text{P}_8\text{O}_{24}]^{8-}$  (**#428–429**) and even  $[\text{P}_{12}\text{O}_{36}]^{12-}$  (**#430**). Most of these compounds have layered structures with large unit cells, mainly of low symmetry, and will not be discussed in detail here. However, we note that  $\text{K}_3\text{Na}_3(\text{P}_3\text{O}_9)_2 \cdot [\text{Te}(\text{OH})_6]$  has monoclinic and rhombohedral dimorphs (**#420–421**), with alternation of (pseudo)hexagonal layers of Te + P and Na + K  $\parallel (200)$  and  $(003)$ , respectively. Most of the phosphate adducts are crystal-chemically unique: there are few examples of more than one compound sharing the same stoichiometry, and even when they do, the structures are different. Thus, despite the apparent chemical similarity,  $(\text{NH}_4)_4(\text{P}_4\text{O}_{12})(\text{H}_2\text{O})_2 \cdot [\text{Te}(\text{OH})_6]$  and its K analogue (**#423–424**) are not isostructural, and the same is true for  $(\text{NH}_4)_8(\text{P}_8\text{O}_{24})(\text{H}_2\text{O})_2 \cdot [\text{Te}(\text{OH})_6]$  and the corresponding K compound (**#428–429**). The most complex phosphate adduct,  $(\text{C}(\text{NH}_2)_3)_{12}(\text{P}_{12}\text{O}_{36})(\text{H}_2\text{O})_{24} \cdot [\text{Te}(\text{OH})_6]_{12}$  (**#430**), has as a counterion not an alkali metal cation but guanidinium,  $[\text{C}(\text{NH}_2)_3]^+$ . This compound has six Te layers and three polyphosphate layers in its rhombohedral cell with  $c \approx 51 \text{ \AA}$ . The threefold rotational symmetry is inherited from the Te octahedra, triangular planar guanidinium complexes and cyclophosphate rings (Fig. 34). The final adduct described here also has a small organic molecular component, the neutral urea molecule in  $(\text{CO}(\text{NH}_2)_2)_2 \cdot [\text{Te}(\text{OH})_6]$  (**#431**).

This compound has a rather simple structure in which each Te octahedron has four neighbours at 5.1–6.6 Å, in a monoclinically distorted version of the diamond arrangement. Each Te octahedron also has four nearby urea molecules ( $\text{Te} \cdots \text{C} = 4.2\text{--}4.5 \text{ \AA}$ ), and with them defines dense layers in the structure  $\parallel (20\bar{2})$ . Hydrogen bonds link molecules both within and between these layers (Fig. 34).

A few additional compounds containing Te  $(\text{OH})_6$  molecules as hydrogen-bonded adducts along with other Te in other environments are included below at **#498–502**, **504** and **631**.

### Monomeric $\text{Te}^{6+}\text{X}_n$ anions ( $n = 4\text{--}6$ )

#### $\text{Te}^{6+}\text{X}_4$ and $\text{Te}^{6+}\text{X}_5$

$\text{Te}^{6+}$  almost always occurs in octahedral coordination with oxygen, as noted above and by Mills and Christy (2013). However, we have a very small group of compounds in which the coordination number is 4 or 5. Ligands distribute themselves symmetrically around the closed-shell  $\text{Te}^{6+}$  cation, unlike the situation with  $\text{Te}^{4+}$ , which usually has a strongly stereoactive lone pair of electrons. The coordination polyhedron for CN4  $\text{Te}^{6+}$  is a tetrahedron (Fig. 4f), while that for CN5  $\text{Te}^{6+}$  is a trigonal bipyramid (Fig. 4g).  $\text{Cs}_2[\text{TeO}_4]$  (**#432**) has the  $\text{K}_2\text{SO}_4$ - $\beta$  structure, in which Te and Cs form the same arrangement as Pb and Cl in cotunnite,  $\text{PbCl}_2$  (O’Keeffe and Hyde, 1985) (Fig. 35).  $\text{Cs}_2\text{K}_2[\text{TeO}_5]$  (**#433**) has a tetragonal structure in which  $\text{TeO}_5$  polyhedra are linked through CN6  $\text{K}^+$  and CN6–8  $\text{Cs}^+$ .  $\text{Rb}_6[\text{TeO}_5][\text{TeO}_4]$  (**#434**) contains both types of Te polyhedron. In this compound, Rb and Te together form an approximately cubic close-packed array with pseudocube edge vectors  $[\frac{1}{2}00]$ ,  $[0\frac{1}{2}0]$  and  $[\frac{1}{4}0\frac{1}{2}]$  of the monoclinic cell. Rubidium atoms are in 6–8 coordination by oxygen (Fig. 35). Note that in all these structures, the counterions are large, weakly-bonding alkali metal species. Details for these structures are summarized in Table 20 (deposited).

#### Monomeric $\text{Te}^{6+}\text{X}_6$ that are not part of a larger structural unit.

Although  $\text{Te}^{6+}$  occurs almost exclusively in one type of coordination polyhedron, and the range of Te–O polymers that it forms is very restricted compared with  $\text{Te}^{4+}$ , the monomeric tellurate octahedron  $\text{TeX}_6$  is the single most prolific structure-forming Te–O complex in the present study: there are 172 compounds with such octahedral anions (**#435–616** below), in addition



to the 56 adducts of neutral molecular  $\text{Te}(\text{OH})_6$  that were briefly described above. Nesotellurates up to #456, with no larger structural unit including strongly-bonding non-Te cations, are listed in Table 20 and described here.

$(\text{NH}_4)_2[\text{TeO}_2(\text{OH})_4]$  (#435) has a simple structure in which Te octahedra form a centred regular net in layers  $\parallel (001)$ , with layers of  $\text{NH}_4$  cations between them. The Te–O distances show that the unprotonated oxygens (O1) are ordered in *trans* positions in the octahedron, with O–Te–O vectors  $\parallel [201]$ .  $\text{K}_3\text{Na}_2\text{Li}[\text{TeO}_6]$  (#436) has layers of K alternating with layers of Na+Li+Te  $\parallel (020)$ . Within the latter layers,  $\text{TeO}_6$  octahedra and  $\text{LiO}_4$  tetrahedra form edge-sharing chains  $\parallel [101]$ , alternating with chains of  $\text{NaO}_{5-6}$  polyhedra. The three types of K atom are in 6–8 coordination.  $\text{K}_3\text{Li}_3[\text{TeO}_6]$  (#437), somewhat similarly, has alternation of K and Te+Li layers  $\parallel (200)$ . Within the Te+Li layers, chains  $\parallel y$  of corner-linked  $\text{LiO}_4$  tetrahedra alternate with chains of edge-sharing  $\text{TeO}_6$  octahedra and unusual square-planar  $\text{LiO}_4$  groups. The Li–O distances in the distorted tetrahedra are 1.94–2.05 Å; those in the squares are similar, at 2.01–2.11 Å, with no additional O neighbours until two at 3.27–3.29 Å, which complete a very elongated octahedron around Li. Potassium is 8–9 coordinated.  $\text{K}_4\text{Na}_2[\text{TeO}_6]$  (#438) has K layers alternating with Te+Na  $\parallel (001)$ . The Te form a face-centred rectangular net, and  $\text{NaO}_6$  octahedra share two opposite faces with neighbouring  $\text{TeO}_6$  octahedra to complete the layer. Potassium coordination is 6–8.

The structure of  $\text{KNa}_5[\text{TeO}_6]$  (#439) is best described as having cations in a *hcp* array, with layers of composition  $\text{KNa}_3$  and  $\text{Te}(\text{Na}_{0.67}\square_{0.33})_3$  alternating along *z*, and two of each layer type per cell. Oxygen atoms are all equivalent and in octahedral interstices in the cation array, coordinated by  $\text{Te} + \text{K} + 2\text{Na} + 2(\text{Na}_{0.67})$ . The coordination environments for all alkali cations are slightly unusual: trigonal prismatic for K (K–O = 2.79 Å), square planar for partially occupied Na1 and square pyramidal for fully occupied Na2 (Na–O = 2.35 Å in both cases), while Te is in very regular octahedral coordination with Te–O = 1.94 Å (Fig. 35).  $\text{K}[\text{TeO}(\text{OH})_5] \cdot \text{H}_2\text{O}$  (#440) has  $\text{KO}_9$  polyhedra sharing edges and faces to make a sheet with a honeycomb net  $\parallel (100)$ . The  $\text{TeX}_6$  octahedra are bound to this sheet to make a compound layer, with  $\text{H}_2\text{O}$  molecules in the interlayer gaps. The layers are held together only by hydrogen bonds.

$\text{Na}[\text{TeO}(\text{OH})_5]$  (#441) is very different from the above structures. It has a  $2 \times 2 \times 2$  cubic superstructure of the  $\text{ReO}_3$  type with alternation of  $\text{Na}^+$  and  $\text{Te}^{6+}$  in octahedral coordination and no

long-range order of  $\text{O}^{2-}$  and  $\text{OH}^-$ , and is thus isotypical with wickmanite,  $\text{Mn}^{2+}[\text{Sn}^{4+}(\text{OH})_6]$  and a family of related hydroxostannates, germanates and antimonates, including several mineral species (Basciano *et al.*, 1998). Because of nonlinear *M*–*O*–*M'* links and orientational order of O–H groups, these compounds do not have  $Fm\bar{3}m$  symmetry but either  $Pn\bar{3}m$  (Strunz and Contag, 1960),  $Pn\bar{3}$  (Morgenstern Badarau and Michel, 1976; Cohen-Addad, 1977; Basciano *et al.*, 1998) or  $P4_2/n$  (Mikhaylov *et al.*, 2011; Kleppe *et al.*, 2012; Lafuente *et al.*, 2015).  $\text{Na}[\text{TeO}(\text{OH})_5]$  may either be orientationally disordered, or may actually crystallize in one of these lower symmetry space groups. The  $\text{ReO}_3$  and wickmanite structure types are derivatives of the  $ABX_3$  perovskite type in which large cations *A* are absent, leaving only octahedrally coordinated species *B*. Many other perovskite-related tellurates are described below (#562–584), while here, we include two unusual examples which have large cations in both *A* and *B* positions. These are  $\text{Sr}_3[\text{TeO}_6]$  and  $\text{Ba}_3[\text{TeO}_6]$  (#442–443) whose unit cells are very large superstructures of the basic perovskite cube (the cells reported are respectively  $4 \times 4 \times 4$  and  $\sqrt{20} \times \sqrt{20} \times 8$  of the  $\sim 4$  Å cube), with rather low symmetry: the triclinic structure of #442 has eight distinct Te sites, four ‘*B*-type’ Sr sites and eight ‘*A*-type’ Sr, while for #443, which is tetragonal, the corresponding numbers of distinct sites are five, five and 13. Substantial rotations of  $\text{TeO}_6$  octahedra allow some ‘*B*-type’ (Sr,Ba) to increase their coordination number from 6 to 7 (Sr) or even 8 (Ba).

Rhombohedral  $\text{Li}_6[\text{TeO}_6]$  and  $\text{Tl}_6[\text{TeO}_6]$  (#444–445) are isopuntal, even though the great difference in size and stereochemistry between  $\text{Li}^+$  and  $\text{Tl}^+$  means that their coordination environments are rather different. These compounds have defect superstructures of rocksalt, in which (Li,Tl) and Te are ordered on a *ccp* array. In #444, oxygen atoms occupy  $7/8$  of the octahedral interstices. Tellurium has six oxygen neighbours at 1.93 Å, Li has four at 1.94–2.08 Å and one at 2.37 Å, and oxygen is surrounded by  $\text{Te} + 5\text{Li}$ . In the Tl compound, the inter-cation distances and cell parameters are much larger, and the oxygen atoms are in one of the triangular faces shared by an octahedral and a tetrahedral interstice of the *ccp* array. While the  $\text{TeO}_6$  octahedron itself is little changed (Te–O = 1.95 Å), Tl is very irregularly coordinated by six oxygen neighbours at 2.11, 2.46, 2.86, 3.60, 3.88 and 3.90 Å. There is a remarkable relationship between the structure of  $\text{Tl}_6^{1+}[\text{TeO}_6]$  and that of  $[\text{Tl}_6^{3+}(\text{TeO}_6)\text{O}_6]$  (#616, below), which can be

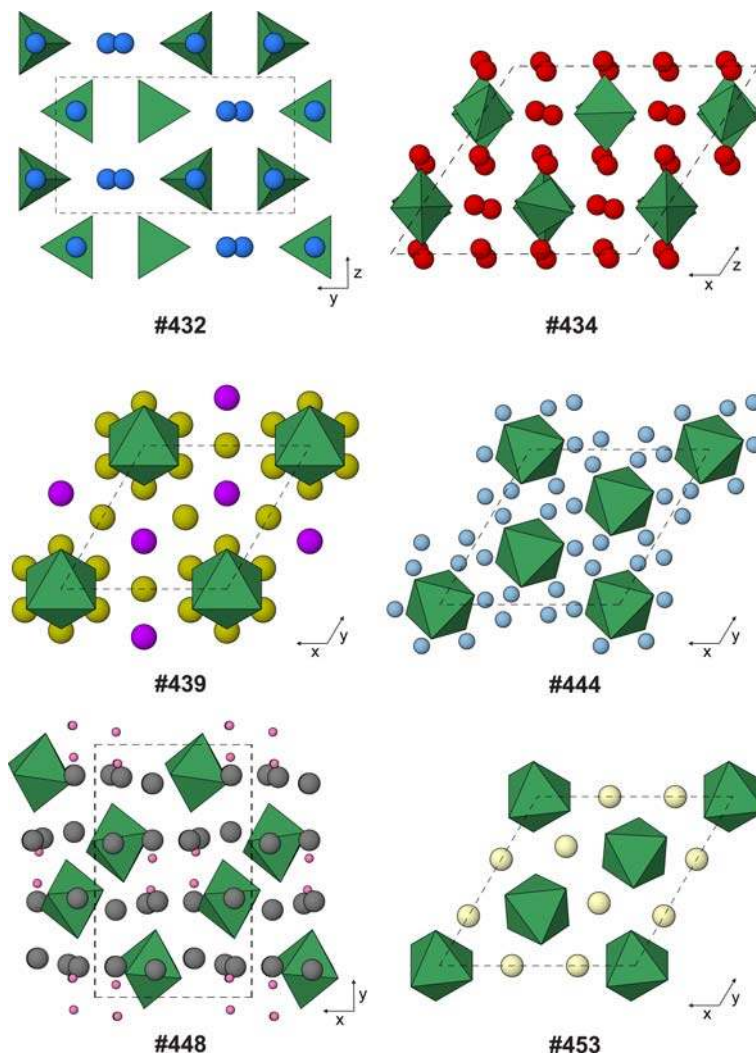


FIG. 35. Examples of structures with monomeric  $\text{Te}^{6+}\text{O}_{4-6}$  anions that are not part of a larger structural unit (Table 20, deposited). Small spheres: O (dark pink) when not part of a polyhedron. Large spheres: Cs (deep blue), K (purple), Li (pale blue), Na (dark yellow), Pb (grey), Rb (red) and Sc (pale yellow). Polyhedra: Te (dark green).

derived from it by stuffing with additional oxygen atoms (Fig. 35).  $\text{Li}_4\text{Zn}[\text{TeO}_6]$  (#446) also has a defect rocksalt superstructure, but this time, there are no vacancies. Edge vectors of a face-centred pseudocube are  $[\frac{1}{2}0\frac{1}{2}]$ ,  $[\frac{1}{2}\frac{1}{2}\frac{1}{2}]$  and  $[\frac{1}{2}\frac{1}{2}\frac{1}{2}]$  of the true monoclinic cell. Lithium and Zn are partially ordered on three types of octahedral site, although Li is dominant in all cases.

$\text{Ag}_2[\text{TeO}_2(\text{OH})_4]$  (#447) has  $\text{TeX}_6$  octahedra arranged on the  $D$  lattice complex (Fischer and Koch, 2006) of its  $Fdd2$  space group. The

unprotonated oxygen atoms (O1) are ordered in a *cis* fashion, and their orientation defines the polarity of the structure along the  $z$  direction. The Te octahedra are linked by  $\text{Ag}^+$  ions in irregular tetrahedral coordination ( $\text{Ag}-\text{O}=2.23\text{--}2.58\text{ \AA}$ ). Silver and the hydroxide oxygen O2 form massicot-like chains (cf. Hill, 1985) which lie in layers  $\parallel (400)$  between the Te octahedra, and run  $\parallel [011]$  or  $[0\bar{1}1]$  in alternate layers.  $\text{Pb}_5[\text{TeO}_6]\text{O}_2$  (#448) has an unusual, very dense arrangement of Pb and Te atoms. Cations lie in rods  $\parallel x$  that are in a

pseudohexagonal array ( $\sqrt{\frac{3b}{c}} = 1.95 \approx 2$ ), but the  $x$  coordinates are such that the cation substructure is not conventionally close-packed. Layers of cations  $\parallel$  (040) form nets in which cations form squares and triangles, such that the connectivity is  $3^6, 3^3 4^2, 3^3 4^2$  and then repeats along the  $z$  direction (Fig. 35). The arrangement can be generated from thinned and faulted  $2 \times 3$  blocks of hexagonal close-packing. Each cation has from 11 to 13 cation next-nearest neighbours at 3.6–4.6 Å, while the oxygen coordination number of  $\text{Pb}^{2+}$  is 5–8. Oxygen atoms are in interstices such that layers  $\parallel$  (040) of tetrahedrally coordinated oxygen alternate with layers where CN = 5–6.  $\text{Pb}_6\text{Cd}[\text{TeO}_6]\text{O}_4$  (#449) has an approximately *ccp* array of Pb, Cd and Te atoms, the unit cell containing a  $2 \times 2 \times 2$  array of distorted face-centred cubes, with irregular  $\text{PbO}_{4-6}$  polyhedra,  $\text{CdO}_6$  trigonal prisms and  $\text{TeO}_6$  octahedra.

The compounds  $A_2^{3+}[\text{TeO}_6]$  ( $A = \text{Y, La and Gd}$ ; #450–452) have the enantiomorphic ( $P2_12_12_1$ ) structure of the orthorhombic form of  $\text{Nd}_2\text{WO}_6$  (Efremov *et al.*, 1984). The  $\text{TeA}_2$  substructure is in the cotunnite ( $\text{PbCl}_2$ ) arrangement (Léger *et al.*, 1996, and cf. #432 above), with oxygen atoms coordinated by  $\text{Te} + 2A$  or  $\text{Te} + 3A$  so as to form two different types of  $\text{AO}_7$  polyhedron. Conversely,  $A_2^{3+}[\text{TeO}_6]$  with  $A = \text{Sc, Yb, In or Tl}^{3+}$  adopt a different, trigonal structure (#453–456). These compounds have either smaller  $A$ –O bonded distances than those above or  $A$  cations with relatively large non-bonded radii in the sense of O’Keeffe and Hyde (1981), so all oxygen atoms are 3-coordinate. The structure adopted is shared with malladrite,  $\text{Na}_2[\text{SiF}_6]$  (Babel, 1967). The oxygen atoms are approximately *hcp*, with ( $A$ , Te) cations filling variously  $\frac{4}{9}$  or  $\frac{5}{9}$  of the octahedral interstices between alternate oxygen layers, and the smaller minority cation ( $\text{Te} \equiv \text{Si}$ ) forming a substructure with the  $\text{AlB}_2$  arrangement (Hofmann and Jäniche, 1935). Every occupied cation site alternates with vacancies along  $z$ , so as to avoid face-sharing of octahedra (Fig. 35). Note that #453–456 could be considered as examples of  $[A_2^{3+}(\text{TeO}_6)]$  frameworks, given the relatively low CN and high bond valence for the  $A$  cations, but they are included here because of the chemical similarity to #450–452 and the isostructurality with malladrite, in which the  $A$  cation  $\text{Na}^+$  is much more weakly bound.

#### Monomeric $\text{Te}^{6+}\text{X}_6$ as part of a larger structural unit that is a finite cluster

Table 21 (deposited) lists compounds #457–502, in which monomeric  $\text{TeX}_6$  anions are strongly bound to

non-Te cations as part of a larger structural unit. The first of these compounds is unusual, in that the structural unit is in part organic: it is *tris*(tetramethyldisilyl) tellurate,  $[(\text{CH}_3)_2\text{Si}-\text{Si}(\text{CH}_3)_2]_3(\text{TeO}_6)$  (#457). The three tetramethyldisilyl groups each bond to two oxygens of the tellurate octahedron, to form a propellor-shaped neutral molecule. The monoclinic cell contains four such molecules, two of opposite rotational senses with their local pseudotriad axes pointing  $\parallel \pm[011]$ , and two with their pseudotriad axes  $\parallel \pm[0\bar{1}1]$  (Fig. 36).

Compounds #458–461 have stoichiometry of the form  $\text{Na}_3[M^{3+}(\text{TeO}_4(\text{OH})_2)_2] \cdot 16\text{H}_2\text{O}$ , where  $M = \text{Cu, Ag and Au}$ , except that #459 is a variant of #458 with 13% of the  $\text{Na}^+$  replaced by  $\text{H}^+$ . All are isostructural. Two  $\text{TeX}_6$  octahedra share *trans* edges of a  $\text{MO}_4$  square in these compounds, the square-planar coordination being typical for  $M^{3+}$  in a low-spin  $d^8$  electronic configuration. The hydrogen atoms were located in the refinement of #461, where they are located on the Te ligands that lie out of the principal plane of the cluster. The corresponding Te–O distances are long, 1.98–1.99 Å, compared to 1.97 Å for the  $\text{Au}=\text{Te}$  bridging oxygens and 1.85–1.86 Å for the unprotonated non-bridging Te ligands opposite the  $\text{Te}=M$  shared edge. The lath-shaped  $[\text{Te}=M=\text{Te}]$  clusters all have their long axes  $\parallel [111]$  of the triclinic cell, and their principal plane approximately  $\parallel (2\bar{1}\bar{1})$ . These structural units cross-link layers  $\parallel (10\bar{1})$  of  $\text{NaX}_6$  polyhedra, which contain the additional  $\text{H}_2\text{O}$  molecules (Fig. 36).

The next three compounds #462–464 feature similar trimeric  $[\text{Te}=M=\text{Te}]$  heteropoly clusters containing a high-valence noble metal cation, but the central polyhedron is an  $\text{MX}_6$  octahedron rather than an  $\text{MX}_4$  square. The three structures are all different.  $\text{K}_6\text{Na}_2[\text{Pt}^{4+}(\text{OH})_2(\text{TeO}_5\text{OH})_2] \cdot 12\text{H}_2\text{O}$  (#462) has all  $[\text{Te}=\text{Pt}=\text{Te}]$  clusters parallel, with long axes  $\parallel [10\bar{1}]$  and equatorial planes of octahedra  $\parallel (101)$ . The clusters are held together through separate  $\text{Na}(\text{H}_2\text{O})_6$  octahedra and  $\text{K}^+$  ions in 6–8 coordination. In  $\text{Rb}_2\text{Na}_4[\text{Os}^{6+}\text{O}_2(\text{TeO}_4(\text{OH})_2)_2] \cdot 16\text{H}_2\text{O}$  (#463), the  $[\text{Te}=\text{Os}=\text{Te}]$  complexes have their long axes  $\parallel [010]$  and equatorial planes  $\parallel (102)$ . They share the two  $\text{O}^{2-}$  ligands of one Te ( $\text{Te}_2$ ) with similarly oriented edge-sharing tetramers of  $\text{NaX}_6$  octahedra,  $\text{Na}_4\text{O}_2(\text{H}_2\text{O})_{16}$ , to form long structural rods  $\parallel y$ , which are held together by 8-coordinated  $\text{Rb}^+$ . Despite the similar stoichiometry,  $\text{Na}_6[\text{Ru}^{6+}\text{O}_2(\text{TeO}_4(\text{OH})_2)_2] \cdot 16\text{H}_2\text{O}$  (#464) has a very different triclinic structure with trimer long axes  $\parallel [2\bar{2}\bar{3}]$  and equatorial planes  $\parallel (302)$ . These structural units act as bridges between

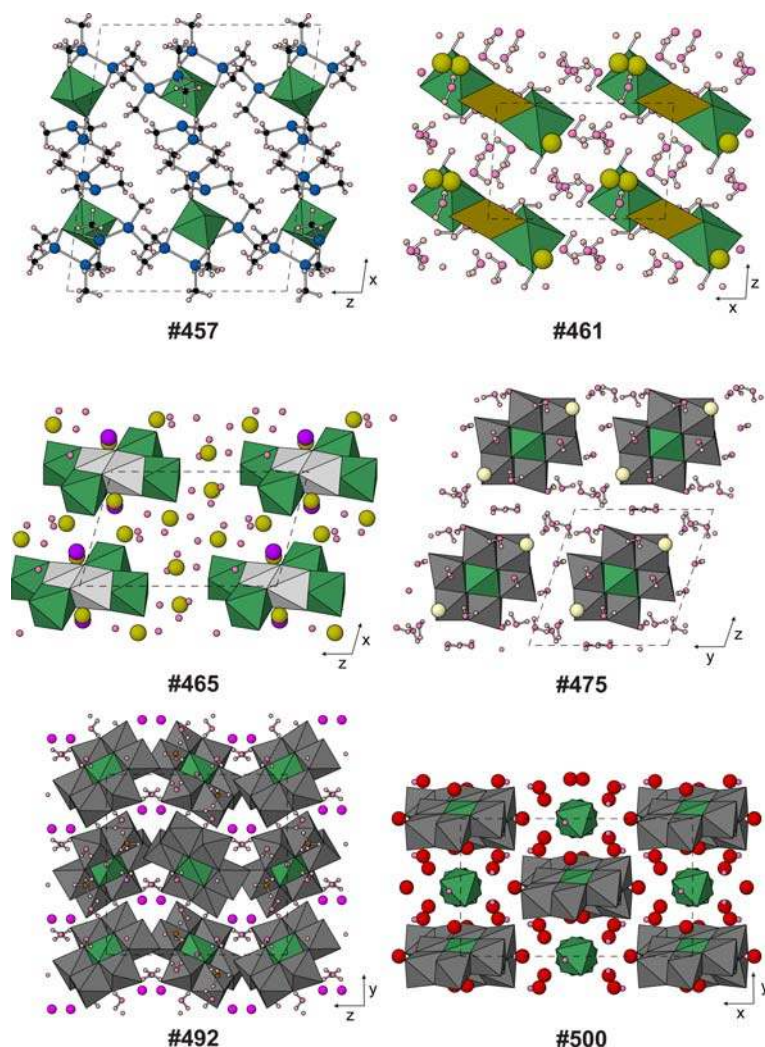


FIG. 36. Examples of structures with monomeric  $\text{Te}^{6+}\text{O}_{4-6}$  anions that are part of a larger structural cluster (Table 21, deposited). Small spheres: C (black), H (pale pink) and O (dark pink) when not part of a polyhedron. Medium spheres: Mn (magenta) and Si (blue). Large spheres: Ce (pale yellow), K (purple), Na (dark yellow) and Rb (red). Polyhedra: Au (yellow-brown), Mo (dark grey), Pd (pale grey) and Te (dark green).

layers  $\parallel (100)$  in which  $\text{NaX}_6$  octahedra share corners, edges and faces with each other. The H atoms were located in this refinement, and are again confirmed to be located on the oxygen atoms away from the principal plane of the cluster ( $\text{Te}-\text{O} = 1.98\text{--}2.01 \text{ \AA}$ ), rather than the terminal oxygen ligands in that plane ( $\text{Te}-\text{O} = 1.85\text{--}1.86 \text{ \AA}$ ).  $\text{K}_2\text{Na}_8[\text{Pd}_2^+\text{Te}_4\text{O}_{18}(\text{OH})_6] \cdot 20\text{H}_2\text{O}$  (#465) has a heteropoly hexameric cluster with a central core of two edge-sharing  $\text{PdX}_6$  octahedra. Each shares its *trans* edge with a Te1 cation, while the two Te2

octahedra share the remaining Pd ligands to form 3-rings with both Pd atoms, and in addition make a third bond to the oxygen atoms of the  $\text{Pd}=\text{Pd}$  edge. The hydroxide H atoms are not located in the structure. They are most probably located on the non-bridging oxygen atoms of  $\text{TeX}_6$  (of which there are 14 per cluster), but only two of these have long  $\text{Te}-\text{O}$  distances ( $\text{Te1}-\text{O4} = 1.99 \text{ \AA}$ ) as opposed to the typical  $1.80\text{--}1.83 \text{ \AA}$ . The rhombus-shaped clusters have long axes  $\parallel [011]$  and are flattened  $\parallel (1\bar{1}1)$ . They lie in layers parallel to that plane with



$\text{NaX}_6$  octahedra, while additional  $\text{NaX}_6$  and  $\text{KX}_7$  lie between the layers (Fig. 36).

A large group of structures feature the  $[\text{M}_6^{6+}\text{Te}_6^{6+}\text{O}_{24}]^{6-}$  Anderson–Evans heteropolyanion, where  $M$  = (Mo or W), and six  $\text{MO}_6$  octahedra form a hexagonal ring around a central  $\text{TeO}_6$  octahedron (Anderson, 1937; Evans, 1948, 1974). The shape and size of the unit cell is controlled largely by the stacking of these large, tabular structural units, which are held together principally by hydrogen bonds to hydrated alkali cations or  $\text{NH}_4^+$  (#466–470), hydrated lanthanide cations (#471–487) or both (#488–490), hydrated transition elements (#491–497) or alkalis plus additional molecular  $\text{Te}(\text{OH})_6$  (#498–502).

Although the alkali tellurohexamolybdates and tungstates are all triclinic with very similar cell dimensions, they differ in detail.  $\text{Li}_6[\text{Mo}_6\text{TeO}_{24}] \cdot 18\text{H}_2\text{O}$  (#466) has the planes of the Mo–Te hexagons  $\parallel (2\bar{3}3)$ , with  $\text{LiX}_6$  octahedra between them, sharing edges to form rods of rocksalt-like structure  $\parallel [01\bar{1}]$ .  $\text{Na}_6[\text{Mo}_6\text{TeO}_{24}] \cdot 22\text{H}_2\text{O}$  and its W analogue (#467–468) have layers of  $\text{NaX}_6$  polyhedra  $\parallel (1\bar{1}0)$ , between M–Te hexagons that lie parallel to approximately  $(6\bar{4}3)$ .  $\text{Rb}_6[\text{Mo}_6\text{TeO}_{24}] \cdot 10\text{H}_2\text{O}$  (#469) has hexagons  $\parallel (1\bar{1}1)$ , sitting in voids in a three-dimensional framework of  $\text{RbX}_{7-9}$  polyhedra.  $(\text{NH}_4)_2\text{Na}_4[\text{Mo}_6\text{TeO}_{24}] \cdot 16\text{H}_2\text{O}$  (#470) has layers  $\parallel (001)$  of  $\text{NH}_4^+$  and Mo–Te ions, alternating with layers of monomeric  $\text{NaX}_6$  octahedra and  $\text{Na}_2\text{X}_{10}$  dimers.

$(\text{Ce}(\text{H}_2\text{O})_4)_2[\text{Mo}_6\text{TeO}_{24}] \cdot 3\text{H}_2\text{O}$  and the Nd analogue (#471–472) have Mo–Te hexagons that lie in layers  $\parallel (020)$ , and are canted slightly relative to that plane in opposite senses in alternate layers. Layers are cross-linked by  $\text{AX}_9$  polyhedra ( $A$  = Ce or Nd), while additional  $\text{H}_2\text{O}$  molecules lie in the Mo–Te layers. The next several compounds are all triclinic with similar unit-cell dimensions, with only a single orientation of Mo–Te hexagon. Again, these lie in layers with some of the water molecules, while  $\text{AX}_n$  polyhedra lie between the layers and bridge them. The coordination number,  $n$ , is usually 9, although it is reduced to 8 for the smaller  $\text{Eu}^{3+}$ ,  $\text{Ho}^{3+}$  and  $\text{Yb}^{3+}$  cations in #485–487. The layers are usually  $\parallel (100)$ , although they are  $\parallel (110)$  for  $(\text{Sm}(\text{H}_2\text{O})_5)_2[\text{Mo}_6\text{TeO}_{24}] \cdot 6\text{H}_2\text{O}$  (#482), which has a different axial setting. The orientation of the Mo–Te hexagons varies depending on the hydration state and cation size. For  $(\text{La}(\text{H}_2\text{O})_7)_2[\text{Mo}_6\text{TeO}_{24}] \cdot 6\text{H}_2\text{O}$  (#473), the hexagons are  $\parallel (10\bar{1})$ , while for the less hydrated  $(\text{La}(\text{H}_2\text{O})_6)_2[\text{Mo}_6\text{TeO}_{24}] \cdot 6\text{H}_2\text{O}$  (#474) and its Ce analogue (#475), they lie flatter, approximately  $\parallel (411)$  (Fig. 36). The hexagons also lie flatter for the Nd compounds:  $\parallel (411)$  in (Nd

$(\text{H}_2\text{O})_6)_2[\text{Mo}_6\text{TeO}_{24}] \cdot 6\text{H}_2\text{O}$  (#479),  $\parallel (611)$  in (Nd  $(\text{H}_2\text{O})_7)_2[\text{Mo}_6\text{TeO}_{24}] \cdot 5\text{H}_2\text{O}$  (#480) and  $\parallel (41\bar{1})$  in  $(\text{Nd}(\text{H}_2\text{O})_7)_2[\text{Mo}_6\text{TeO}_{24}] \cdot 5\text{H}_2\text{O}$  (#481), although they are strongly canted  $\parallel (20\bar{1})$  in the Pr analogue of the latter compound (#478). In  $\text{K}_6(\text{Eu}(\text{H}_2\text{O})_7)_2[\text{Mo}_6\text{TeO}_{24}]_2 \cdot 16\text{H}_2\text{O}$  (#488), layers of two differently oriented and symmetrically independent Mo–Te hexagons alternate along the  $z$  axis; one type has  $\text{EuO}_2(\text{H}_2\text{O})_7$  polyhedra connecting them into columns  $\parallel y$ , while the other type does not. A matrix of CN9–10 hydrated  $\text{K}^+$  ions holds the layers together. The Gd analogue (#489) is nearly isostructural, but is in a different axial setting, with the layers of hexagons  $\parallel (010)$  not  $(001)$ , and the Gd–Mo–Te columns  $\parallel x$ , not  $y$ . Also, slight atomic rearrangements lead to doubling of the  $c$  parameter relative to the corresponding  $a$  parameter of #488.

$(\text{Co}(\text{H}_2\text{O})_6)_3[\text{Mo}_6\text{TeO}_{24}]$  and its Ni analogue (#490–491) have a simple, highly symmetrical rhombohedral structure in which  $[\text{Mo}_6\text{TeO}_{24}]^{6-}$  hexagons alternate with triangles of  $[\text{M}(\text{H}_2\text{O})_6]^{2+}$  octahedra ( $M$  = Co or Ni) to make columns running along the threefold rotation axes.  $(\text{NH}_4)_2(\text{M}^{2+}(\text{H}_2\text{O})_3)_2[\text{Mo}_6\text{TeO}_{24}] \cdot \text{H}_2\text{O}$  ( $M$  = Mn, Co, Ni, Cu and Zn; #492–496) (Fig. 36) and the Ni–W analogue (#497) are also highly symmetrical (cubic, space group  $Pa\bar{3}$ ,  $a \approx 14$  Å). The  $\text{TeM}_2$  part of the structure forms a distorted fluorite array of the type found as predicted for  $\text{SiO}_2$  at very high pressure by Park *et al.* (1988) and found experimentally for  $\text{SnO}_2$  above 21 GPa by Haines and Léger (1997). Because of the distortion,  $\text{M}^{2+}$  bonds to only three of its four nearest Mo–Te hexagons, as well as to three water molecules. The other components in the structure,  $\text{NH}_4^+$  ions and the remaining  $\text{H}_2\text{O}$  molecule (O6) form hydrogen-bonded dumbbells ( $\text{N} \cdots \text{O} = 2.84$  Å) which, together with the Te atoms, are arranged similarly to the covalent  $[\text{S}_2]^{2-}$  dumbbells and Fe in pyrite,  $\text{FeS}_2$ .

The remaining compounds of this section are alkali tellurohexamolybdates which also contain  $\text{Te}(\text{OH})_6$  molecules as adducts.  $\text{Li}_6[\text{Mo}_6\text{TeO}_{24}] (\text{H}_2\text{O})_{18} \cdot [\text{Te}(\text{OH})_6]$  (#498) has sinuous chains of  $\text{LiX}_{4-6}$  polyhedra and  $\text{Te}(\text{OH})_6 \parallel y$ , which cross-link Mo–Te hexagons that are oriented  $\parallel (103)$ .  $\text{Cs}_6[\text{Mo}_6\text{TeO}_{24}](\text{H}_2\text{O})_2 \cdot [\text{Te}(\text{OH})_6]_2$  (#499) has one Mo–Te anion per unit cell oriented  $\parallel (112)$ , embedded in a trellis-like open framework of  $\text{CsX}_{7-10}$  and  $\text{Te}(\text{OH})_6$  polyhedra.  $\text{Rb}_6[\text{Mo}_6\text{TeO}_{24}](\text{H}_2\text{O})_6 \cdot [\text{Te}(\text{OH})_6]_2$  (#500) has a  $C$ -centred monoclinic cell with strong  $\frac{1}{2}c$  pseudosymmetry, and thus four Mo–Te hexagons per cell. These are all oriented  $\parallel (010)$  and alternate with  $\text{Te}(\text{OH})_6$  molecules along the  $y$



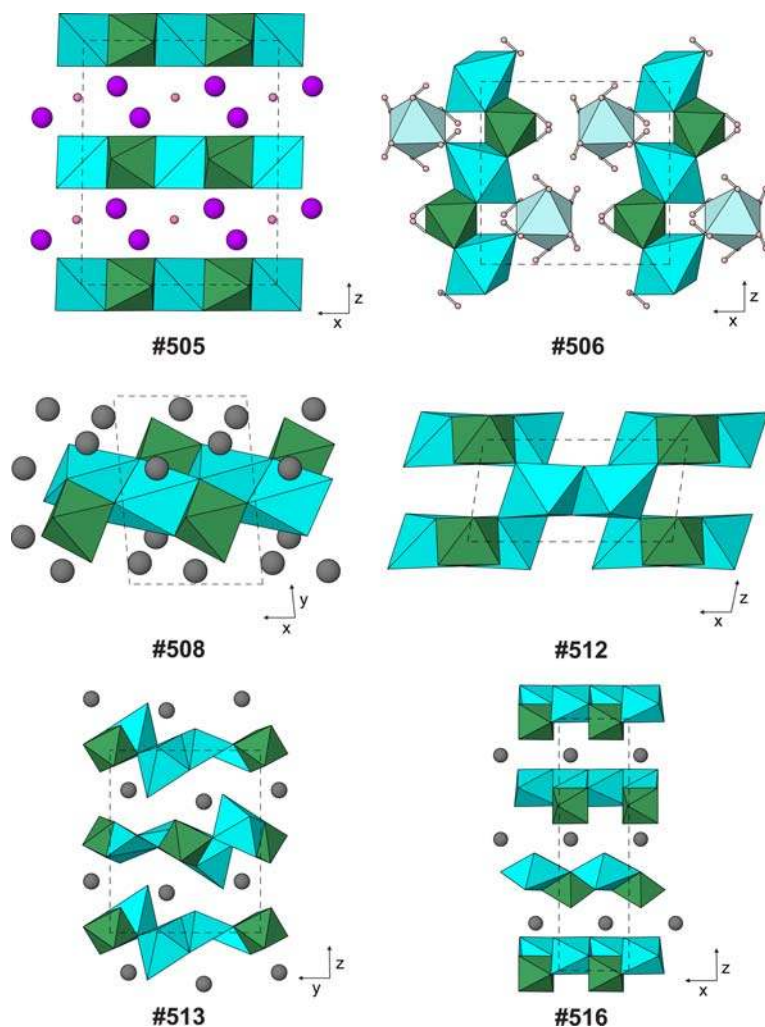


FIG. 37. Examples of structures with monomeric  $\text{Te}^{6+}\text{O}_6$  anions that are part of a larger structural chain or layer (Table 22, deposited). Small spheres: H (pale pink) and O (dark pink), when not part of a polyhedron. Large spheres: K (purple) and Pb or Tl (grey). Polyhedra: Cu (cyan), Mg (pale blue) and Te (dark green). Additional long Cu–O bonds complete octahedra in frankhawthorneite (#512) and link layers into a framework.

direction, forming Te-rich rods in a matrix of  $\text{RbX}_{7-9}$  polyhedra (Fig. 36). The ordered K– $\text{NH}_4$  compound #501 is nearly isostructural, as is the more highly hydrated  $\text{NH}_4$  compound #502 (although this is in an *A*-centred axial setting).

*Monomeric  $\text{Te}^{6+}\text{X}_6$  as part of a larger structural unit that is an infinite chain*

The next few structures have  $\text{TeX}_6$  anions that are strongly bound with other cations into one-dimensional structural units. They are listed in

Table 22 (deposited).  $[\text{Hg}^{2+}(\text{TeO}_2(\text{OH})_4)]$  (#503) has  $\text{TeX}_6$  octahedra linked via their *cis* unprotonated ligands through linear 2-coordinated  $\text{Hg}^{2+}$  into chains  $\parallel y$ , which pack in a hexagonal array. Chains are connected only through hydrogen bonds and long, weak  $\text{Hg}\cdots\text{O}$  bonds (within-chain Hg–O distances are 2.02–2.05 Å, while the two next nearest oxygen atoms to Hg are at 2.67 and 2.75 Å). In  $[(\text{Hg}_2^{2+})(\text{TeO}_2(\text{OH})_4)] \cdot [\text{Te}(\text{OH})_6] \cdot 2\text{H}_2\text{O}$  (#504),  $\text{TeX}_6$  octahedra linked through *trans* unprotonated ligands to linear  $[\text{Hg}–\text{Hg}]^{2+}$  dimers,

forming infinite chains  $\parallel [101]$ . These lie in layers  $\parallel (010)$ , which alternate with layers containing Te  $(\text{OH})_6$  and  $\text{H}_2\text{O}$  molecules. Mercury is even more strongly 2-coordinate than in the previous compound, with one O neighbour at 2.11 Å, one Hg at 2.50 Å, and the next O neighbours not until 2.91 and 2.93 Å.  $\text{K}_2[\text{Cu}(\text{TeO}_4(\text{OH})_2)] \cdot \text{H}_2\text{O}$  (#505) has  $\text{TeX}_6$  octahedra sharing opposite edges with  $\text{CuO}_4$  squares to form straight chains, which lie in layers  $\parallel (002)$ . Chains of alternate layers run  $\parallel$  to  $[110]$  or to  $[1\bar{1}0]$ . Water molecules and CN8–9  $\text{K}^+$  ions lie between the layers (Fig. 37). Copper has no additional ligands within 3 Å. Very slight tilts and displacements reduce the symmetry from orthorhombic and centrosymmetric (space group *Cccm*) to monoclinic and acentric (*Cc*). The mineral raisaite,  $(\text{Mg}(\text{H}_2\text{O})_6)[\text{Cu}(\text{TeO}_4(\text{OH})_2)]$  (#506) has  $\text{TeX}_6$  octahedra sharing edges which are not opposite with  $\text{CuO}_4$  squares ( $\text{Cu}-\text{O} = 1.94\text{--}1.98$  Å), to form zigzag chains  $\parallel \mathbf{z}$ . These form a centred-rectangular array, which have  $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$  octahedra lying between them. The structure is held together through hydrogen bonds, and also weak  $\text{Cu}\cdots\text{O}$  bonds: Cu has two O atoms of water molecules at 2.78 Å, completing an elongated octahedron of ligands (Fig. 37).  $\text{Ag}_4[\text{Cu}(\text{TeO}_6)]$  (#507) has  $\text{TeO}_6$  octahedra sharing an edge with one  $\text{CuO}_4$  square and corners with two others to make a double chain running  $\parallel \mathbf{z}$  that zigzags in the (100) plane. The double chain consists of  $\text{Cu}=\text{Te}-\text{Cu}=\text{Te}$  4-rings, united by the shared edges. Two additional O ligands are much closer to Cu than in #506 above ( $\text{Cu}-\text{O} = 2 \times 1.98, 2 \times 2.00$  and  $2 \times 2.49$  Å). If these are included to complete a  $\text{CuO}_{4+2}$  octahedron, the chains become ribbons of edge-sharing Cu and Te octahedra in which Cu atoms form a central zigzag backbone while Te sit on the outside of the ribbon. The chains form a centred-rectangular array, and are held together by three types of  $\text{Ag}^+$  ions in distorted octahedral coordination ( $\text{Ag}-\text{O} = 2.27\text{--}2.83$  Å). The oxygen atoms approximate *ccp*, with pseudo-cube edge vectors  $\parallel [\frac{1}{4}0\frac{1}{4}]$ ,  $[\frac{1}{4}\frac{1}{2}\frac{1}{4}]$  and  $[\frac{1}{4}\frac{1}{2}\frac{3}{4}]$ . If the structure is considered as a packing of (Ag, Cu, Te) octahedra, then it is a superstructure of the rocksalt type.  $\text{Ti}_4[\text{Cu}(\text{TeO}_6)]$  (#508) has Cu–Te chains with the same topology as those of #507 and also forming an approximately centred-rectangular array, but this time running  $\parallel \mathbf{x}$  and zigzagging in the (011) plane of the triclinic cell. The oxygens do not form a continuous close-packed array as in #507, but discrete close-packed ribbons which surround large channels  $\parallel \mathbf{x}$ . Four types of  $\text{Ti}^{4+}$  ions in irregular 5–7 coordination hold the chains together, with their lone pairs pointing into the channels (Fig. 37).

$(\text{NH}_4)_2\text{V}_2^{5+}\text{TeO}_8(\text{OH})_2 \equiv (\text{NH}_4)_2[(\text{VO}_2)_2(\text{TeO}_4(\text{OH})_2)]$  (#509) has  $\text{TeX}_6$  octahedra sharing non-opposed edges with edge-sharing dimers  $\text{V}_2\text{O}_8$  of  $\text{VO}_5$  square pyramids. One of the bridging oxygens links to 1 Te + 1 V, while the other connects to 1 Te + 2 V atoms. Small atomic displacements break the potential  $2/a$  symmetry of the chain, so that there are two distinct Te atoms and four distinct V atoms per repeat unit. These chains run  $\parallel \mathbf{x}$  and lie in layers  $\parallel (002)$ , with  $\text{NH}_4^+$  ions between the layers.

### Monomeric $\text{Te}^{6+}\text{X}_6$ as part of a larger structural unit that is an infinite layer

Table 22 also includes structures #510–547, where monomeric  $\text{TeX}_6$  octahedra are linked with non-Te cations to form two-dimensional structural units.  $\text{Na}_2[\text{Cu}_2(\text{TeO}_6)]$  (#510) has a Cu–Te layer  $\parallel (001)$  that can be regarded as an ordered version of a brucite-like trioctahedral sheet, but with strong Jahn–Teller distortion of the  $\text{CuO}_6$  octahedra, giving Cu a square of four O neighbours at 1.98–2.00 Å and two more distant ligands at 2.53 Å. If all six neighbours are considered, then the structural unit has the same bond topology as those of #538–541 below. However, unlike those structures, the oxygen atoms of #510 are approximately *ccp* in three dimensions, and Na atoms are ordered in  $\frac{2}{3}$  of the octahedral sites between  $[\text{Cu}_2(\text{TeO}_6)]^{2-}$  layers. The structure can be regarded as an ordered defect derivative of the rocksalt type.  $\text{NaTi}_3^+[\text{Cu}_4^+(\text{TeO}_6)_2]$  (#511) has similarly distorted Cu–Te layers  $\parallel (200)$ , alternating with layers that contain an ordered array of  $\text{Na}^+$  in octahedral coordination and  $\text{Ti}^{4+}$  in very irregular 6-fold coordination. The three-dimensional arrangement of oxygen atoms can again be considered a derivative of cubic close-packing, except that the coordination requirements of Ti cause the Cu–Te–O layers to undulate, and lead to the Ti atoms being far from the centres of octahedral interstices.

Frankhawthorneite,  $[\text{Cu}_2(\text{TeO}_4(\text{OH})_2)]$ , (#512), has oxygen atoms forming a slightly distorted *hcp* array, with close-packed layers  $\parallel (002)$ . Copper and Te atoms occupy octahedral interstices to form ribbons in which one Te atom alternates with two Cu along the  $\mathbf{y}$  direction. Ribbons form a centred rectangular array, and share corners with their neighbours. However, Jahn–Teller distortion of the Cu coordination polyhedron is of a similar degree to that in #507–508 above ( $\text{Cu}-\text{O} = 4 \times 1.98\text{--}2.06$  Å and  $2 \times 2.46\text{--}2.52$  Å), so only the four shortest bonds are counted when defining the structural unit, which is hence not a framework but a layer  $\parallel (10\bar{1})$ . In frankhawthorneite, the component

ribbons of the layer have each Te octahedron sharing two opposite edges with  $\text{CuO}_4$  squares, and ribbons are linked through CN3 oxygen atoms in a stepped pattern. The Jahn-Teller distortion also reduces the symmetry to monoclinic  $P2_1/n$  from orthorhombic  $Pmnn$ , and allows ordering of the H atom on O2, as shown by long Te–O bonds (1.99 rather than 1.91–1.92 Å). Layers are held together by long  $\text{Cu}\cdots\text{O}$  bonds and hydrogen bonds (Fig. 37). A similar arrangement of more regular octahedra is found in kotoite,  $\text{Mg}_3(\text{BO}_3)_2$ , which has similar unit-cell dimensions but the orthorhombic space group, and has additional B atoms in triangular coordination, providing strong links between ribbons (Berger, 1988). The octahedral arrangement in the average structure of one form of  $(\text{H,Li})_2[\text{Ti}(\text{TeO}_6)]$  is also very similar (#585, below). Paratimroseite,  $\text{Pb}[\text{Cu}_2(\text{TeO}_6)] \cdot \text{H}_2\text{O}$  (#513) has stepped layers  $\parallel (002)$  composed by condensation of ribbons  $\parallel x$ , in exactly the same topology as frankhawthorneite (#512), but the layers are separated widely and also alternate between two orientations related by a screw diad axis, so their anions form disconnected oblique slices of *hcp* structure rather than constituting a three-dimensionally continuous close-packed substructure. Water molecules and  $\text{Pb}^{2+}$  cations in irregular 9-coordination lie between the layers, and the Pb coordination geometry causes shift of the layers in the  $x$  direction such that any reflection symmetries are eliminated, and the space group is  $P2_12_12_1$  rather than the  $Pbca$  or  $Pbcm$  of hypothetical aristotypes. An elongated coordination octahedron around Cu is completed by an interlayer water molecule at 2.42 Å and an additional tellurate oxygen atom at 2.54 Å (Fig. 37). The structure of timroseite is closely related (#555, below).  $\text{Sr}_2[\text{Cu}_2(\text{TeO}_6)]\text{Br}_2$  (#514) has edge-sharing ribbons of  $\text{CuO}_{4+1}$  square pyramids ( $\text{Cu}-\text{O} = 4 \times 1.93\text{--}2.02$  Å and  $1 \times 2.36$  Å) and  $\text{TeO}_6$  octahedra running  $\parallel y$ , which share corners with each other so as to form a continuous layer  $\parallel (100)$  in which the oxygen atoms again form the stepped, *hcp* slice of #512–513. Interlayer  $\text{SrO}_4\text{Br}_3$  polyhedra hold the structure together. The  $\text{Br}^-$  anion is also a very distant sixth ligand for  $\text{Cu}^{2+}$  (2.97 Å). In bairdite,  $\text{Pb}_2[\text{Cu}_4(\text{TeO}_5\text{OH})_2(\text{SO}_4) \cdot \text{H}_2\text{O}$  (#515), two stepped Cu–Te layers  $\parallel (100)$  stack adjacent to each other, related by a screw diad axis, and are linked through long  $\text{Cu}\cdots\text{O}$  bonds so as to form a double layer ( $\text{Cu}_2\text{--O}_4 = 2.36$  Å, as opposed to 1.94–2.04 Å for the four shortest Cu–O bonds, and 2.57 Å for an additional within-layer distance that completes the octahedron). O4 also has another

$\text{Cu}_2$  at 2.00 Å and an unusually long distance of 2.03 Å to Te, and is where the H is located. Between Cu–Te double layers are Pb atoms which show some positional disorder, and  $\text{SO}_4$  tetrahedra. Cu1 has a square of O atoms at 1.91–2.00 Å and one at 2.41 Å within the Cu–Te layer, and a sulfate oxygen atom at 2.46 Å. A differently oriented oblique slice through an *hcp* anion array is an element of the ‘tri-harmunite’ structure of #598, below.

The polytypes of khinite ( $-3T$  and  $-4O$ ),  $\text{Pb}[\text{Cu}_3(\text{OH})_2(\text{TeO}_6)]$  (#516–517) share a more complex layer type, in which rows of edge-sharing  $\text{CuO}_4$  squares  $=\text{Cu}_1=\text{Cu}_2=$  alternate with rows of  $\text{CuO}_4$  squares and  $\text{TeO}_6$  octahedra,  $=\text{Cu}_3=\text{Te}=$ . The coordination octahedron of the Te is completed by sharing bridging oxygen atoms of the all-Cu chain, thus making a layer containing 5-rings  $[-\text{Te}=\text{Cu}_3=\text{Te}-\text{Cu}_1=\text{Cu}_2-]$ . In projection normal to the layer, the cations form a hexagonal net, but the all-Cu chain is at a different height from the Cu–Te chain, so the layer has an overall polarity (Fig. 37). In the  $3T$  polytype (originally known as ‘parakhinite’), the subchains of layers point along  $x$ ,  $y$  or  $-[110]$ , successive layers rotating by  $120^\circ$ , consistent with a screw triad axis. There are three layers  $\parallel (003)$  per  $P3_2/P3_1$  unit cell. In the  $4O$  polytype, layers are  $\parallel (004)$ , alternate layers have subchains  $\parallel [110]$  or  $[1\bar{1}0]$ , and the layers are related by the  $d$  glides of the space group  $Fdd2$ . Note that  $a_{4O} \approx a_{3T}$ , and that a pseudo-hexagonal metric is retained, as  $b_{4O} \approx \sqrt{3}a_{4O}$ . In both cases,  $\text{Pb}^{2+}$  lies between the layers, in 8-fold coordination. Agaite,  $\text{Pb}_3[\text{Cu}(\text{TeO}_5\text{OH})(\text{CO}_3)(\text{OH})]$  (#518) has layers  $\parallel (020)$  in which alternating  $\text{TeX}_6$  and  $\text{CuX}_5$  polyhedra form a  $6^3$  honeycomb net. These polyhedra share non-opposing edges to form zigzag chains trending  $\parallel x$ , which are joined in the  $z$  direction by sharing of a fifth corner. Between the Cu–Te layers lie triple layers of CN8  $\text{Pb}^{2+}$  ions, additional  $\text{OH}^-$  ions (bound to 3 Pb) and a central plane of  $\text{CO}_3^{2-}$  ions (each oxygen atom bound to 3 Pb as well as to C). The orientation of Cu=Te zigzags in the structural unit and the pointing direction of  $\text{CO}_3$  triangles both define a polarity in the  $z$  direction (Fig. 38).

$\text{Na}_{1.8}[(\text{Sn}_{0.9}\text{Te}_{0.1})_2(\text{TeO}_6)]$  and  $\text{Na}_2[\text{Ge}(\text{TeO}_6)]$  (#519–520) both have a trigonal structure in which oxygen atoms approximate *hcp* (cf. #512). It is a superstructure of one of the  $\text{TiSbO}_3$  polytypes (Bouchama and Tournoux, 1975). The other such polytype has the structure of ilmenite ( $\text{Fe}^{2+}\text{Ti}^{4+}\text{O}_3$ ) in that  $\frac{2}{3}$  of the octahedral interstices between each pair of oxygen layers are occupied by cations, and

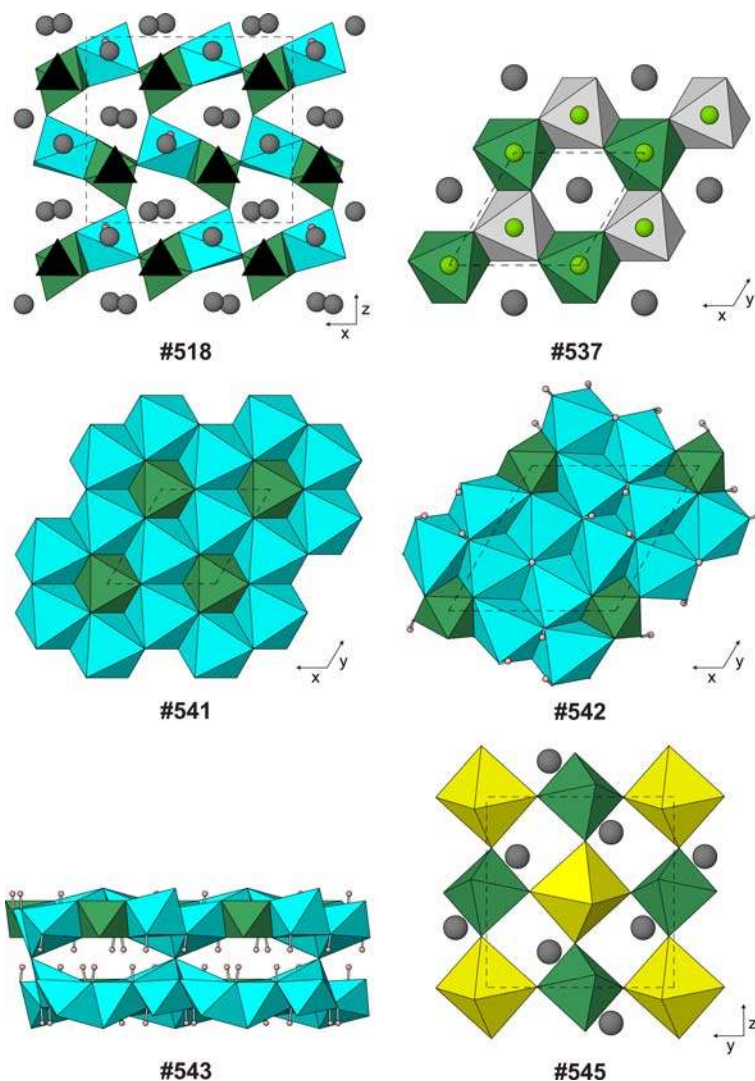


FIG. 38. Examples of structures with monomeric  $\text{Te}^{6+}\text{O}_6$  anions that are part of a larger structural layer (Table 20, deposited). Small spheres: H (pale pink) and O (dark pink) when not part of a polyhedron. Large spheres: Cl (green-yellow) and Pb (grey). Black triangles in **#518**:  $\text{CO}_3$  groups. Polyhedra: Al (pale grey), Cu (cyan), Te (dark green) and U (yellow).

that two types of cation occupy alternate cation layers. However, whereas the vacant octahedral sites in the ilmenite polytype are offset in a sequence *ABCABC* so as to produce a 6-layer rhombohedral cell (space group  $R\bar{3}$ ), the vacant sites in the current structures are arranged in a pattern *ABAC*, giving a 4-layer trigonal cell with space group  $P\bar{3}1c$ . In these tellurate compounds, layers of Na cations alternate with layers of ( $M^{4+} +$

$\text{Te}^{6+}$ ), where  $M = (\text{Sn or Ge})$ .  $\text{NaO}_6$  octahedra share faces with  $\text{TeO}_6$  octahedra above and below along the *z* direction, while  $M^{4+}\text{O}_6$  octahedra have vacant sites above and below. Note that such face-sharing relationships would not be achievable in an ilmenite-like polytype, where every occupied octahedron shares one face with another that is occupied.  $\text{Sr}[\text{Ge}(\text{TeO}_6)]$  (**#521**) also has *hcp* oxygen atoms, and a primitive trigonal cell that



has the same  $\sim 5 \text{ \AA}$   $a$  parameter but half the  $c$  parameter of **#519–520**. (Ge+Te) atoms occupy  $\frac{2}{3}$  of the octahedral sites every other octahedral cation layer, forming a honeycomb pattern with Ge and Te alternating, while Sr atoms are in the intervening layers, above and below the vacant sites in the (Ge+Te layer). This is the  $P312$  structure of  $\text{NaNi}^{4+}\text{I}^{7+}\text{O}_6$  (Brown, 1969), which is a cation-ordered superstructure of the  $P\bar{3}1m$  type of  $\text{Li}_2\text{ZrF}_6$  (Brunton, 1973) or rosiite,  $\text{Pb}^{2+}\text{Sb}^{5+}\text{O}_6$  (Basso *et al.*, 1996). The compounds  $A^3+[\text{Cr}^{3+}(\text{Te}^{6+}\text{O}_6)]$  ( $A = \text{La, Pr, Nd, Sm–Yb}$  and  $\text{Y}$ ; **#522–534**) and  $\text{La}[\text{Fe}(\text{TeO}_6)]$  (**#535**) have a polytypical relative of the  $\text{Sr}[\text{Ge}(\text{TeO}_6)]$  structure in which the  $c$  repeat is doubled from  $5.4 \text{ \AA}$  to  $\sim 10 \text{ \AA}$  and the space group changes to  $P\bar{3}$ , because the relative positions of (Cr, Fe) and Te are reversed in alternate Cr–Fe–Te layers. This structure is also that of colquiriite,  $\text{CaLi}[\text{AlF}_6]$  (Yin and Keszler, 1992). Compound **#535** shows some Fe–Te disorder which may imply short-range mixing of the two cations, but given the large difference in charge, more probably implies displacement of layers by stacking faults, while retaining two-dimensional order within layers. Thus, it may have a nanoscale intergrowth of rosiite and colquiriite structure types.

$\text{Ba}[\text{Ge}(\text{TeO}_6)]$  (**#536**), despite the chemical similarity to its Sr analogue **#521**, has a different structure with the same  $P312$  space group. Oxygen atoms are double-hexagonal close-packed ( $AABB$  stacking), and layers of (Ge+Te) in octahedral coordination alternate with layers of  $\text{BaO}_6$  trigonal prisms. Backite,  $\text{Pb}_2[\text{Al}(\text{TeO}_6)]\text{Cl}$  (**#537**) has dioctahedral  $\text{AlTeO}_6$  layers resembling the  $M\text{TeO}_6$  unit in structures **#519–536** (Fig. 38). However, these layers are now widely spaced, and the oxygen atoms are not three-dimensionally close-packed. Instead, the unit cell contains one such layer, separated from the next by layers of Pb, Cl and Pb such that each Pb atom lies above a vacant octahedral site of the Al–Te layer and is coordinated by  $3\text{O} + 6\text{Cl}$ . The compounds  $\text{Na}_{2-x}[\text{M}_2(\text{TeO}_6)]$  ( $M = \text{Ni, Zn}$  and  $\text{Co}$ ,  $x = 0–0.05$ ; **#538–540**) are based upon a  $AABB$  stacking of oxygen atoms, like **#536**.  $M$  and Te cations are in octahedral coordination, and form a structural unit that is an ordered brucite-like trioctahedral layer, with Na cations partially occupying the trigonal prismatic sites between the  $M$ –Te layers. The  $\text{Na}^+$  ions are highly mobile, leading to fast-ion conduction in these compounds (Evstigneeva *et al.*, 2011). Small atomic displacements result in the Zn and Co compounds being acentric ( $P6_322$ ), while the Ni compound has space group  $P6_3/mcm$ . The Cu

analogue of these compounds was discussed above (**#510**).

Leisingite,  $(\text{Mg}(\text{H}_2\text{O})_6)[\text{Cu}_2(\text{TeO}_6)]$  (**#541**) has a layered  $[\text{Cu}_2(\text{TeO}_6)]^{2-}$  structural unit  $\parallel (001)$  which resembles the trioctahedral layers of **#538–540**, with no evident Jahn–Teller distortion of  $\text{CuO}_6$  octahedra ( $\text{Cu–O} = 6 \times 2.11 \text{ \AA}$ ), unlike the layers of **#510–511**. Isolated  $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$  octahedra lie between these layers, and connect them through hydrogen bonding. Apart from a  $30^\circ$  rotation of the Mg octahedron and the locations of H atoms, this mineral is isotypical with zincalstibite (Bonaccorsi *et al.*, 2007), a member of the cualstibite group of the hydrotalcite supergroup of Mills *et al.* (2012). The correspondence can be shown as  $[\text{Cu}_2(\text{TeO}_6)][\text{Mg}(\text{H}_2\text{O})_6]$  (leisingite)  $\equiv [\text{Zn}_2\text{Al}(\text{OH})_6][\text{Sb}(\text{OH})_6]$  (zincalstibite). Zincalstibite has a lower-symmetry space group ( $P\bar{3}$  as opposed to  $P\bar{3}1m$ ), but very similar unit-cell parameters  $a = 5.321(1) \text{ \AA}$  and  $c = 9.786(2) \text{ \AA}$  (Fig. 38).

Mojaveite,  $[\text{Cu}_6(\text{TeO}_4(\text{OH})_2)(\text{OH})_7]\text{Cl}$  (**#542**), has brucite-like octahedral sheets in which  $\frac{1}{7}$  of the cations are Te and  $\frac{6}{7}$  are Cu, while  $\frac{1}{14}$  of the anions are Cl, and thus are not counted as part of the structural unit. The degree of Jahn–Teller distortion is relatively small, half the Cu are regarded as coordinated by five (O,OH) ligands (+1 Cl) while the other half have six O neighbours. The ordering pattern of cations and anions forces the structure to adopt the relative low-symmetry polar space group  $R3$ . The layers are held together by hydrogen bonds (Fig. 38). The mineral is isostructural with bluebellite,  $\text{Cu}_6[\text{I}^{5+}\text{O}_3(\text{OH})_3](\text{OH})_7\text{Cl}$ , which is unusual in that  $\text{Te}^{6+}$  does not have a lone pair of electrons while  $\text{I}^{5+}$  does so (Mills *et al.*, 2014a). The substitution is presumably facilitated by the polar symmetry of the Te/I site, which frees the coordination environment to distort. Fuettererite,  $\text{Pb}_3\text{Cu}_6(\text{TeO}_6)(\text{OH})_7\text{Cl}_5 \equiv (\text{Pb}_3(\text{OH})\text{Cl}_3)_2[\text{Cu}_6(\text{TeO}_6)(\text{OH})_6]_2\text{Cl}_4$  (**#543**), has Cu–Te layers very similar to those of mojaveite, although all Cu atoms now have one Cl as a sixth ligand, rather than just half of them. There are Cl atoms on both sides of the layer, and the structure retains a centre of inversion symmetry. Pairs of Cu–Te–O layers are linked through a shared Cl atom, and these layers are stacked with the other components between them in the sequence  $[\text{Cu}_6(\text{TeO}_6)(\text{OH})_6] \cdots \text{Cl} \cdots [\text{Cu}_6(\text{TeO}_6)(\text{OH})_6] \cdots \text{Cl} \cdots (\text{Pb}_3(\text{OH})\text{Cl}_3) \cdots \text{Cl} \cdots (\text{Pb}_3(\text{OH})\text{Cl}_3) \cdots \text{Cl}$  (Fig. 38).

Markcooperite and its synthetic analogue, ideally  $\text{Pb}_2^{2+}[(\text{U}^{6+}\text{O}_2)(\text{TeO}_6)]$ , have a quite different type of layer (**#544–545**).  $\text{TeO}_6$  and  $\text{UO}_6$  octahedra



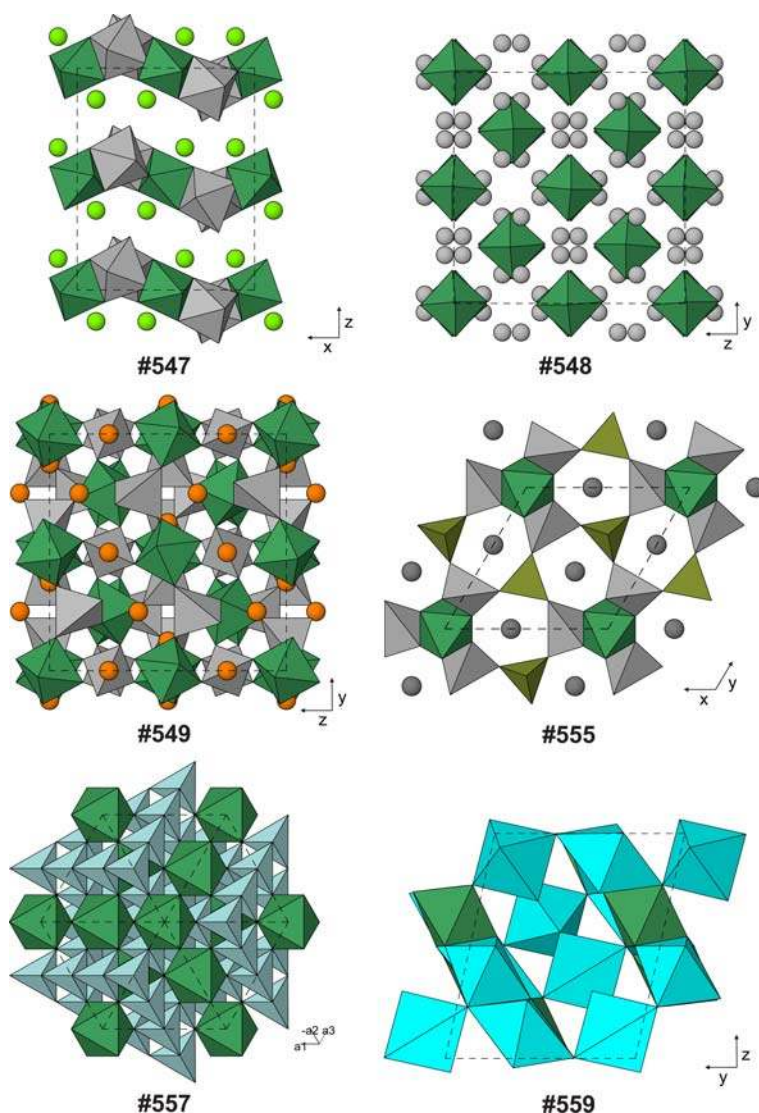


FIG. 39. Examples of structures with monomeric  $\text{Te}^{6+}\text{O}_6$  anions that are part of a larger structural layer or framework (Tables 22–23, deposited). Large spheres: Ba (yellow-green), Ca (orange), Hg (pale grey) and Pb (dark grey). Polyhedra: As (brown-green), Be (pale blue), Cu (cyan), Nb (grey octahedra), Te (dark green) and Zn (grey tetrahedra).

In #548, the two Hg–O bonds per Hg atoms are omitted for clarity.

both share four corners to form a layer with 4-rings, similar to that of Fig. 14c but with alternation of Te and U atoms. These layers lie  $\parallel (100)$  and have CN7  $\text{Pb}^{2+}$  ions between them. In the end-member synthetic compound (#545), the Te octahedron is relatively regular ( $\text{Te–O} = 2 \times 1.91, 2 \times 1.94$  and  $2 \times 1.95$  Å) while the U octahedron is strongly compressed ( $\text{U–O} = 2 \times 1.84, 2 \times 2.24$  and  $2 \times 2.29$  Å), consistent

with the presence of linear  $[\text{O}=\text{U}=\text{O}]^{2+}$  groups (Fig. 38). The natural mineral shows 25% substitution of Te on the U site, but the pattern of bond-length variation remains similar. The substitution makes the structure transitional towards those with continuous layers of corner-sharing  $\text{TeO}_6$  octahedra (Fig. 14c), such as #688–670 below.

$\text{ThV}_2^{5+}\text{TeO}_{10} \cdot 2\text{H}_2\text{O} \equiv \text{Th}[(\text{VO}_2)_2(\text{TeO}_6)] \cdot 2\text{H}_2\text{O}$  (#546) has layers  $\parallel (200)$  consisting of  $\text{TeO}_6$  octahedra,  $\text{VO}_5$  (V1) trigonal bipyramids and  $\text{VO}_4$  tetrahedra (V2). V1 polyhedra share an edge with Te on one side and a corner with Te on the other side in the  $z$  direction, while V2 tetrahedra share a corner with Te on each side in the  $y$  direction, so the layer has square-shaped 8-rings of alternating Te and V in which Te is 4-connected while V is always only 2-connected. Each V atom has two non-bridging ligands with short V–O distances (1.63–1.67 Å as opposed to 1.77–2.04 Å), validating their description as vanadyl groups  $[\text{VO}_2]^+$ .  $\text{Th}^{4+}$  ions are in 9-coordination between the layers.  $\text{Ba}_2\text{Nb}_2\text{TeO}_{10} \equiv \text{Ba}_2[\text{Nb}_2\text{O}_4(\text{TeO}_6)]$  (#547) has corrugated layers  $\parallel (020)$  containing *zweier* chains of corner-sharing  $\text{NbO}_6$  octahedra which run  $\parallel x$ . The  $\text{TeO}_6$  octahedron shares one edge and one corner with a pair of Nb octahedra in the chain on one side, making an  $[-\text{Nb}=\text{Te}=\text{Nb}-]$  3-ring, and the same with the next chain on the other side, so that the layer has 3- and 6-rings with the topology of the kagome net.  $\text{Ba}^{2+}$  ions between the layers are 9-coordinated. Although the layer contains four non-tellurate oxygen atoms per formula unit, only two of these are non-bridging oxygen atoms with short Nb–O distances (1.78 Å; compare 1.90–2.26 Å for all other Nb–O) (Fig. 39).

#### Monomeric $\text{Te}^{6+}\text{X}_6$ as part of a larger structural unit that is a framework

A large group of compounds have  $\text{TeX}_6$  octahedra strongly bound to non-Te cations to form a three-dimensional framework. These are listed as #548–618 in Table 23 (deposited).  $[\text{Hg}_3^{2+}(\text{TeO}_6)]$  (#548) has a highly symmetrical structure with a large cubic unit cell ( $Ia\bar{3}$ ,  $a \approx 13$  Å). Two types of Te atom are arranged as a  $2 \times 2 \times 2$  block of CsCl unit cubes, while the Hg atoms are positioned so as to form, in combination with Te, a slightly perturbed  $2 \times 2 \times 2$  array of cubes with the  $\text{Cr}_3\text{Si}$  arrangement (Boren, 1933; Andersson, 1978), analogous to the cations of the garnet structure (O’Keeffe and Andersson, 1977; Grew *et al.*, 2013; #549–553 below), which has the same space group and similar unit-cell parameter. However,  $\text{Hg}^{2+}$  has linear two-fold coordination, unlike the CN4/CN8 cations of garnet: two Hg–O distances are 2.06 Å, while the next neighbours are not until 2.57, 2.59, 2.76 and 2.83 Å. Links  $\text{Te}-\text{O}-\text{Hg}-\text{O}-\text{Te}$  connect each Te atom to six out of the eight neighbouring Te of the other type (Fig. 39).

The important garnet structure is an ordered and anion-stuffed superstructure of the  $\text{Cr}_3\text{Si}$  type

(Geller, 1967; O’Keeffe and Hyde, 1985). The  $Ia\bar{3}d$  cubic cell of typical garnets  $A_3B_2C_3X_{12}$  has a  $2 \times 2 \times 2$  array of body-centred cubes of  $B$  atoms corresponding to Si of  $\text{Cr}_3\text{Si}$ , and non-intersecting rods  $\parallel \langle 100 \rangle$  directions of alternating  $A$  and  $C$  atoms corresponding to Cr. Anions  $X$  occupy distorted tetrahedral interstices, so that each anion is bonded to  $2A + B + C$ , while coordination numbers of  $A$ ,  $B$  and  $C$  are, respectively, 8, 6 and 4. The numerous mineralogical examples of garnets were reviewed by Grew *et al.* (2013). The  $B_2C_3X_{12}$  substructure forms a framework in which each  $X$  links to one cation of each type. Depending on the relative bond valences, it may be reasonable to identify within this framework either  $BX_6$  or  $CX_4$  as a principal anionic complex. An example of the former would be cryolithionite,  $\text{Na}_3\text{Al}_2\text{Li}_3\text{F}_{12} \equiv \text{Na}_3\text{Al}_2[\text{LiF}_4]_3$  more appropriately than  $\text{Na}_3\text{Li}_3[\text{AlF}_6]_2$ , while silicate garnets are examples where the strongest-bound cation is in the tetrahedron: grossular,  $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12} = \text{Ca}_3\text{Al}_2[\text{SiO}_4]_3$ . Several tellurate garnets are known, in which the  $B$  cation is  $\text{Te}^{6+}$ ; these compounds are of the first type, because of the high Te–O bond valence. These include the mineral yafsoanite (Fig. 39),  $\text{Ca}_3[\text{Zn}_3(\text{TeO}_6)_2]$  (#549) and also synthetic  $\text{Na}_3[M_3^{3+}(\text{TeO}_6)_2]$  ( $M = \text{Fe}_{0.5}\text{Al}_{0.5}$  or Ga, #550–551).  $\text{Nd}_3\text{Li}_{3.05}[(\text{Te}_{0.975}\text{Sb}_{0.025})\text{O}_6]_2$  (#552) and  $\text{Nd}_3\text{Li}_4[(\text{Te}_{0.5}\text{Sb}_{0.5})\text{O}_6]_2$  (#553) are included here because they still have the garnet structure, albeit slightly modified. However, the  $C$  cation Li is now so low in charge that it no longer forms a structural unit with the octahedral cations: the Nd–O bond valence (0.375) is larger than that of Li–O (0.25). Furthermore, both these compounds have considerably higher Li contents than the 2 atoms per formula unit expected for a normal garnet, due to stuffing of additional Li into normally vacant interstices, and the Li are very mobile in the structure, making the compounds fast-ion conductors (O’Callaghan *et al.*, 2008).

$\text{LaV}_3^{5+}\text{TeO}_{12} \cdot 3\text{H}_2\text{O} \equiv \text{La}[(\text{VO}_2)_3(\text{TeO}_6)] \cdot 3\text{H}_2\text{O}$  (#554) has a framework in which an approximately primitive cubic array of  $\text{TeO}_6$  octahedra are linked to all six of their neighbours through 2-connected  $\text{VO}_4$  tetrahedra.  $\text{La}^{3+}$  ions are near the centre of each cube. Thus, the  $\text{LaTeV}_3$  substructure corresponds to the atomic arrangement of an  $ABX_3$  perovskite. The La atom is coordinated by six oxygen atoms of the framework but also by three water molecules which all lie on one side of La, reducing the symmetry to polar rhombohedral  $R3c$ . Relative to a cubic metric, the structure is slightly stretched along the rhombohedral triad axis

( $c/a = 2.48 = \sqrt{6.15}$ , rather than  $\sqrt{6}$ ). As is typical for vanadyl tellurates, V–O distances are much shorter (1.63–1.64 Å) for the V–O–La oxygens than for the V–O–Te oxygens (1.80–1.84 Å).

The minerals of the dugganite group include dugganite itself,  $\text{Pb}_3[\text{Zn}_3(\text{TeO}_6)(\text{AsO}_4)_2]$  (#555), its phosphate analogue kuskite (#556) and also cheremnykhite (the vanadate analogue),  $\text{Pb}_3[\text{Zn}_3(\text{TeO}_6)(\text{VO}_4)_2]$  (Kim *et al.*, 1990), whose structure has not been refined, and joëlbругgerite, ideally  $\text{Pb}_3[\text{Zn}_3(\text{Sb}^{5+}\text{O}_6)(\text{AsO}_{3.5}(\text{OH})_{0.5})_2]$  (Mills *et al.*, 2009c), which has only minor Te substituting for Sb. The dugganite structure has layers  $\parallel (001)$  in which 3-connected  $\text{AsO}_4$  on triad axes and 2-connected  $\text{ZnO}_4$  tetrahedra share corners to form a net of trefoil-shaped 12-rings in which Zn and As alternate. One third of the triad axes does not have an As tetrahedron, but instead have Te octahedra between two Zn–As layers and linking the layers. Each  $\text{TeO}_6$  octahedron links to three Zn tetrahedra below and to three more above. Thus, the three-dimensional framework that results contains  $[\text{Zn–Te–Zn–Te}]$  4-rings and  $[\text{Zn–As–Zn–Te–Zn–As}]$  6-rings (Fig. 39).

$[\text{Be}_4\text{O}(\text{TeO}_6)]$  (#557) has a simple face-centred cubic structure in which  $\text{Be}_4\text{O}_6$  tetrahedra, with Be atoms at the corners and O1 oxygen atoms along the edges, and additional oxygen atoms (O2) are arranged in the ‘zincblende’ arrangement. Thus, there is a rather open  $[\text{Be}_4\text{O}_7]^{6-}$  framework in which O2 is at the centre of an anion-centred tetrahedron, where four  $\text{BeO}_4$  tetrahedra meet. Oxygen atoms occupy  $7/8$  of the positions of *ccp*, with the eighth position vacant, and the sixth O1 oxygen atom defines an octahedral interstice that contains Te (Fig. 39). The structure may be compared with that of swedenborgite,  $\text{Na}[\text{Be}_4\text{O}(\text{Sb}^{5+}\text{O}_6)]$ , which has a similar stoichiometry. In swedenborgite (Huminicki and Hawthorne, 2001), the oxygen atoms again occupy  $7/8$  of the positions of *ccp*, but the stacking of close-packed layers is now *ABAC* rather than *ABC*, and the eighth position contains CN12  $\text{Na}^+$  ions. There is also a unique octahedral interstice, which contains Sb, and a  $\text{Be}_4\text{O}_7$  framework in which  $\text{Be}_4\text{O}_6$  tetrahedra can be identified. However, the additional oxygen atom that connects the tetrahedra is no longer bonded to four Be, but instead to two Be + Sb, while the oxygen that centres an  $\text{OBe}_4$  tetrahedron is now part of the  $\text{Be}_4\text{O}_6$  tetrahedron. Apart from #557 and swedenborgite, isolated  $\text{OBe}_4$  tetrahedra have also been reported from two polymorphs of  $(\text{Be}_4\text{O})(\text{NO}_3)_6$  (Haley *et al.*, 1997; Troyanov *et al.*, 2000; Krivovichev *et al.*, 2013).

$\text{Pb}[\text{Cu}_3\text{O}(\text{TeO}_6)]$  (#558) has Cu–Te–O rods running  $\parallel y$  in which the oxygen atoms approximate small blocks of cubic close-packed structure. Relatively regular  $\text{TeO}_6$  octahedra alternate with pairs of Cu1 atoms in elongated  $\text{CuO}_{4+2}$  polyhedra, while  $\text{Cu}_2\text{O}_4$  squares brace the sides of the rods, as well as sharing corners with Te and Cu1 atoms of neighbouring rods to form a framework with large channels  $\parallel y$ , which contain CN7  $\text{Pb}^{2+}$  ions. Jensenite,  $\text{Cu}_3\text{TeO}_6 \cdot 2\text{H}_2\text{O} \equiv [\text{Cu}_3(\text{H}_2\text{O})_2(\text{TeO}_6)]$  (#559), has brucite-like  $\text{Cu}_2\text{TeO}_6$  layers  $\parallel (10\bar{1})$  in which Cu and Te are ordered in a honeycomb pattern. While the Te octahedra are quite regular (Te–O = 1.89–1.98 Å), the Cu polyhedra show the usual Jahn–Teller distortion, with Cu–O =  $4 \times 1.94$ – $2.06$  Å and  $2 \times 2.32$ – $2.45$  Å. The layers are bridged into a framework by an additional Cu cation in the interlayer gap that is in strict square-planar coordination. This Cu atom (Cu1) has as ligands two interlayer water molecules, plus a tellurate oxygen atom in each layer (Fig. 39).

Timroseite,  $\text{Pb}_2[\text{Cu}_5(\text{TeO}_6)_2](\text{OH})_2$  (#560) has stepped *hcp* layers  $\parallel (002)$  of the type previously seen in frankhawthorneite, paratimroseite,  $\text{Sr}_2[\text{Cu}_2(\text{TeO}_6)]\text{Br}_2$  and bairdite (#512–515, above). As in paratimroseite, the layers are in two different orientations which alternate, but in timroseite, they are connected into a three-dimensional framework through additional  $\text{CuO}_4$  squares (Fig. 40). Large channels remain  $\parallel x$ , which contain  $\text{OH}^-$  anions and  $\text{Pb}^{2+}$  in 8–10 coordination. All Cu are in square-planar coordination if a bonding cutoff of  $<2.27$  Å is used, but all Cu atoms also have one channel  $\text{OH}^-$  anion at 2.27–2.64 Å, and Cu1 and Cu2 within the *hcp* layers, also have an additional tellurate oxygen at 2.47–2.71 Å. Quetzalcoatite,  $[\text{Zn}_6\text{Cu}_3(\text{TeO}_6)_2(\text{OH})_6] \cdot (\text{Ag}_x\text{Pb}_y\text{Cl}_{x+2y})$  (#561), has a more explicitly nanoporous structure in which hexagonal rings of six corner-sharing  $\text{ZnO}_2(\text{OH})_2$  tetrahedra alternate along *z* with layers  $\parallel (001)$  in which  $\text{TeO}_6$  octahedra share edges with  $\text{CuO}_4$  squares to form a honeycomb net with walls  $\text{Te}=\text{Cu}=\text{Te}$  surrounding large hexagonal voids. The hexagonal channels contain rods of alternating, partially occupied ( $\text{Ag}^+$ ,  $\text{Pb}^{2+}$ ) and  $\text{Cl}^-$  sites (Fig. 40).

A large group of tellurate compounds have a superstructure of the perovskite type (#562–584). An aristotypical  $\text{ABO}_3$  perovskite has a unit cube with  $Z = 1$ ,  $a \approx 4$  Å and space group  $\text{Pm}\bar{3}m$ . The compounds described here all have two types of octahedrally coordinated *B* atom, one of which is  $\text{Te}^{6+}$ . Other perovskite variants have been described earlier, including  $\text{M}^{2+}\text{Te}^{4+}\text{O}_3$  ( $\text{M} = \text{Co}$ ,  $\text{Ni}$  and  $\text{Cu}$ )

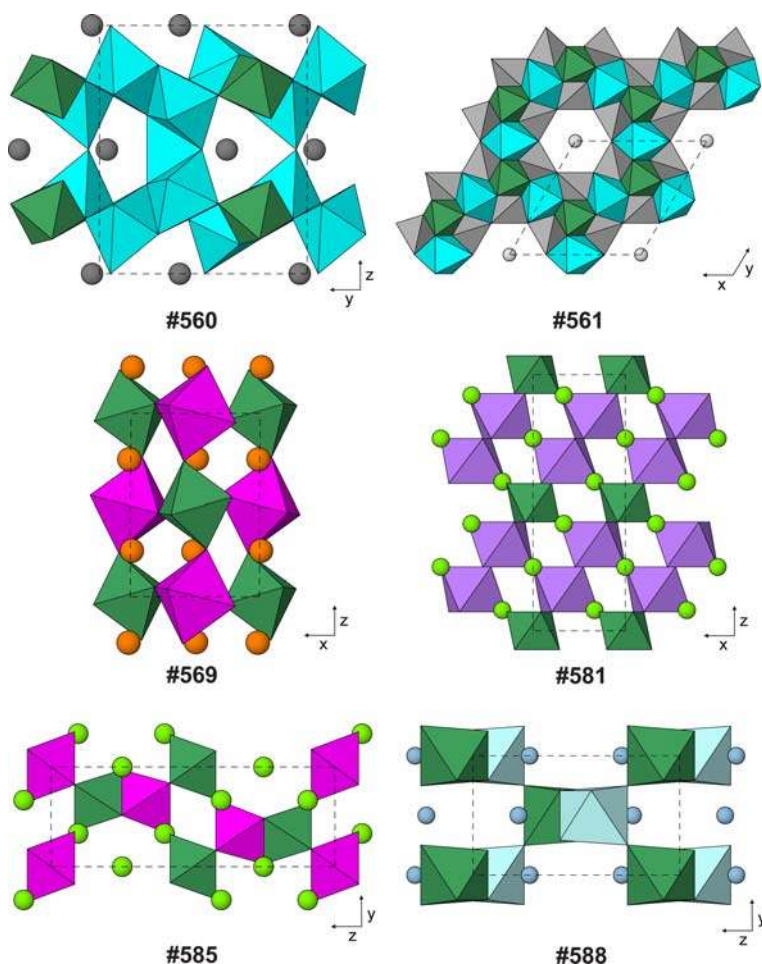


FIG. 40. Examples of structures with monomeric  $\text{Te}^{6+}\text{O}_6$  anions that are part of a larger structural framework (Table 23, deposited). Large spheres: Ag (pale grey), Ba (yellow-green), Ca (orange), Li (pale blue) and Pb (dark grey). Polyhedra: Bi (violet), Co (magenta), Cu (cyan), Sn (pale blue), Te (dark green) and Zn (pale grey).

with  $\text{Te}^{4+}$  as the *A* cation (**#140–142**),  $\text{Cs}_2[\text{Te}_2^{4+}\text{O}_5]$  with  $\text{Te}^{4+}$  as the *B* cation and some ordered oxygen vacancies (**#195**), the wickmanite-like  $\text{Na}[\text{Te}^{6+}\text{O}(\text{OH})_5]$ , with a vacant *A* site (**#441**), and the complex superstructures of  $M_3[\text{Te}^{6+}\text{O}_6]$  (*M* = Sr and Ba; **#442–443**). One form of  $\text{Pb}_2[\text{Co}^{2+}(\text{TeO}_6)]$  (**#562**) has Te alternating with Co in the *B* sites, a  $\sqrt{2} \times \sqrt{2} \times 2$  superstructure of the basic perovskite type, and tetragonal space group *I4/mmm*, consistent with slight tetragonal distortion but no octahedral tilt. Howard *et al.* (2003), in their analysis of possible octahedral tilt systems (Glazer, 1972) and symmetries of ordered perovskites, expressed scepticism about the existence of such structures

in the absence of strong Jahn-Teller or other distortion (as occurs in ‘ $\text{CsAuCl}_3$ ’ =  $\text{Cs}_2[\text{Au}^{1+}\text{Cl}_2][\text{Au}^{3+}\text{Cl}_4]$ ; Tindemans-van Eijndhoven and Verschoor, 1974). It is possible that the oxygen positions in this structure need reinvestigation. A rhombohedral polymorph occurs at high and at low temperature (**#582**, below).  $A_2[\text{Cu}^{2+}(\text{TeO}_6)]$  (*A* = Sr and Ba; **#563–564**) have similar cell dimensions to **#562** but the tetragonal space group *I4/m* is obtained by octahedra tilt according to the  $a^0a^0c^-$  pattern in these compounds, independent of the Jahn-Teller distortion of the  $\text{CuO}_{4+2}$  octahedra (Howard *et al.*, 2003; Howard and Carpenter, 2010). The ICSD gives as the archetype of this



perovskite structure  $\text{Sr}_2\text{NiWO}_6$  (Köhl, 1973).  $\text{Ba}_2[\text{Cu}(\text{TeO}_6)]$  (#564) has another polymorph whose structural topology is polytypically related to that of normal perovskites (#587, below).

$\text{NaLa}[\text{Mg}(\text{TeO}_6)]$  (#565) has similar cell dimensions again but in addition to two types of  $B$  cation ordered in a ‘rocksalt’ fashion, there are two types of  $A$  cation ordered layerwise along the  $z$  direction, and the symmetry is monoclinic,  $P2_1/m$ . However, most of the perovskites with  $\sqrt{2} \times \sqrt{2} \times 2$  superstructure have the  $P2_1/n$  space group exhibited by cryolite,  $\text{Na}_3\text{AlF}_6 = \text{Na}_2[\text{Na}(\text{AlF}_6)]$  (Hawthorne and Ferguson, 1975). These include compounds  $A_2[B(\text{TeO}_6)]$  with  $A = \text{Ca}$  or  $\text{Sr}$  and  $B = \text{Ca}$  or  $\text{Co}$  (#566, 569–571) (Fig. 40),  $\text{Cd}_2[\text{Cd}(\text{TeO}_6)]$  (#567),  $\text{Na}_2[\text{Sn}^{4+}(\text{TeO}_6)]$  (#568) and  $A =$  disordered  $(\text{Ca}_{0.5}\text{Pr}_{0.5}^{3+})$ ,  $(\text{Sr}_{0.5}\text{Pr}_{0.5}^{3+})$  or  $(\text{Sr}_{0.5}\text{Eu}_{0.5}^{3+})$ ,  $B = \text{Li}$  (#572–574).

$\text{Sr}_2[\text{Ni}(\text{TeO}_6)]$  has a larger  $2 \times 2 \times 2$  superstructure than the perovskites above, and  $C2/m$  symmetry (#575), although it is nearly cubic, with all three cell parameters within 0.3% of their mean value, and  $\beta \approx 90.4^\circ$ . The next five compounds have the truly cubic ‘double perovskite’ structure of elpasolite ( $\text{K}_2\text{Na}[\text{AlF}_6]$ ; Sabelli, 1987), with a  $2 \times 2 \times 2$  supercell but  $Fm\bar{3}m$  symmetry. In all these compounds,  $\text{Te}$  alternates in the  $B$  sites in a ‘rocksalt’ fashion with  $\text{Ni}$  (#575),  $\text{Ca}$  (#576),  $\text{Li}$  (#577–578),  $\text{Mg}$  (#579) or partially occupied  $\text{Bi}$  (#580), while in #577 and 578, the alkaline earth cation  $\text{Ba}^{2+}$  and lanthanides  $(\text{La}, \text{Pr})^{3+}$  are disordered in the  $A$  site, analogous to the situation in #572–574 above.

Our final group of perovskites have trigonal cells with  $a \approx \sqrt{2}$  and  $c \approx 2\sqrt{3}$  times the edge of the fundamental perovskite cube. This is an alternative axial setting for a structure produced by compression or extension of a  $2 \times 2 \times 2$  cube along one  $[111]$  direction. The lattice type for such a perovskite is  $R$  in most cases, but in  $\text{Ba}_3[\text{Bi}_2\text{O}_3(\text{TeO}_6)]$  (#581), the unusual ordering pattern, with  $\text{Te}$  in only  $1/3$  of the  $B$  sites, reduces the symmetry to  $P\bar{3}c1$  (Fig. 40). The space group is  $R\bar{3}$  or  $R\bar{3}m$  for the other structures #582–584, which have the standard ‘double perovskite’ cation arrangement, and include the rhombohedral polymorph of  $\text{Pb}_2[\text{Co}(\text{TeO}_6)]$  (cf. #562 above). Three additional compounds in the present study could be regarded as aberrant examples of rhombohedral double perovskites, but are more usefully considered as superstructures of the corundum type. These are  $[\text{Ni}_3(\text{TeO}_6)]$  and its relatives, #599–601 below.

In the  $ABX_3$  cubic perovskite structure, the large cations  $A$  and anions  $X$  together form a cubic

close-packed array, with  $X_3A$  ordered in the  $\text{Cu}_3\text{Au}$  pattern. The structure can thus be described as an  $ABC$  stacking of  $AX_3$  layers, with  $B$  cations filling the  $X_6$  octahedral interstices. Other ‘perovskite polytypes’ can be produced by stacking  $AX_3$  differently (Mitchell, 2002). These structures require some  $BX_6$  octahedra to share faces, implying short  $B \cdots B$  distances and the possibility that they may require some  $B \cdots B$  bonding interaction to be stable. Most mineralogical perovskites are derived from only the  $3C$  polytype, although some examples with face-sharing octahedra are known for antiperovskite polytypes, with anions  $\text{O}^{2-}$ ,  $\text{F}^-$  or  $\text{Cl}^-$  in the  $B$  sites (Krivovichev, 2008). The synthetic compound  $\text{Ba}_2[\text{Co}(\text{TeO}_6)]$  (#585) has very similar unit-cell parameters to #584 but a different space group and structural topology. Unlike its analogues with  $\text{Ca}$ ,  $\text{Sr}$  and  $\text{Mn}$  in  $B$  sites (#576, 583 and 584 above), it is based on a  $6H$   $ABACBC$  stacking of  $\text{BaO}_3$  layers: the  $hkk$  sequence, where ‘ $h$ ’ = ‘hcp-like (layers above and below superimposed)’ and ‘ $k$ ’ = ‘ccp-like (layers above and below not superimposed)’. A very different  $6H$  perovskite is described as #620, below. Because layers of  $\text{Co}^{2+}$  and  $\text{Te}^{6+}$  cations alternate along  $z$  in #585, there are 12 oxygen layers altogether in the unit cell, which has space group  $P\bar{3}m1$ , and two crystallographic types each of  $\text{Co}$  and  $\text{Te}$ .  $\text{Co}2$  and  $\text{Te}2$  octahedra each share one face with each other, while  $\text{Co}1$  and  $\text{Te}1$  share only corners (Fig. 40). In contrast,  $\text{Ba}_2[\text{Ni}(\text{TeO}_6)]$  (#586) has a  $12R$  ( $hhkk$ ) layer sequence (space group  $R\bar{3}m$ ), in which corner-sharing octahedra  $(\text{Te}1)\text{O}_6$  alternate along  $z$  with columns of three face-sharing octahedra,  $\text{Ni} \equiv (\text{Te}2) \equiv \text{Ni}$ .  $\text{Ba}_2[\text{Cu}(\text{TeO}_6)]$  (#587) has the same topology, but distortion of the  $\text{CuO}_6$  octahedra reduces the symmetry to triclinic  $P\bar{1}$ . The distortion is not the usual symmetrical elongation, but gives  $\text{Cu}^{2+}$  five oxygen neighbours at 1.98–2.11 Å and the sixth at 2.26 Å. The triclinic (001) plane corresponds to (003) of the pseudorhombohedral cell, while the pseudotriad axis is  $[113]$  in the triclinic axial setting. A tetragonally distorted  $3C$  perovskite polymorph of this compound was discussed at #564, above.

The next four closely-related compounds have structures derived from the  $\text{LiSbO}_3$  type (Genkina, 1992). This structure has a  $hcp$  oxygen substructure, as for the corundum superstructures of  $\text{LiNbO}_3$  and  $\text{NaSbO}_3$ , but a quite different arrangement of cations.  $\text{LiSbO}_3$  has an orthorhombic structure with space group  $Pncn$ , which is permuted into the  $Pnma$  axial setting here. Then,

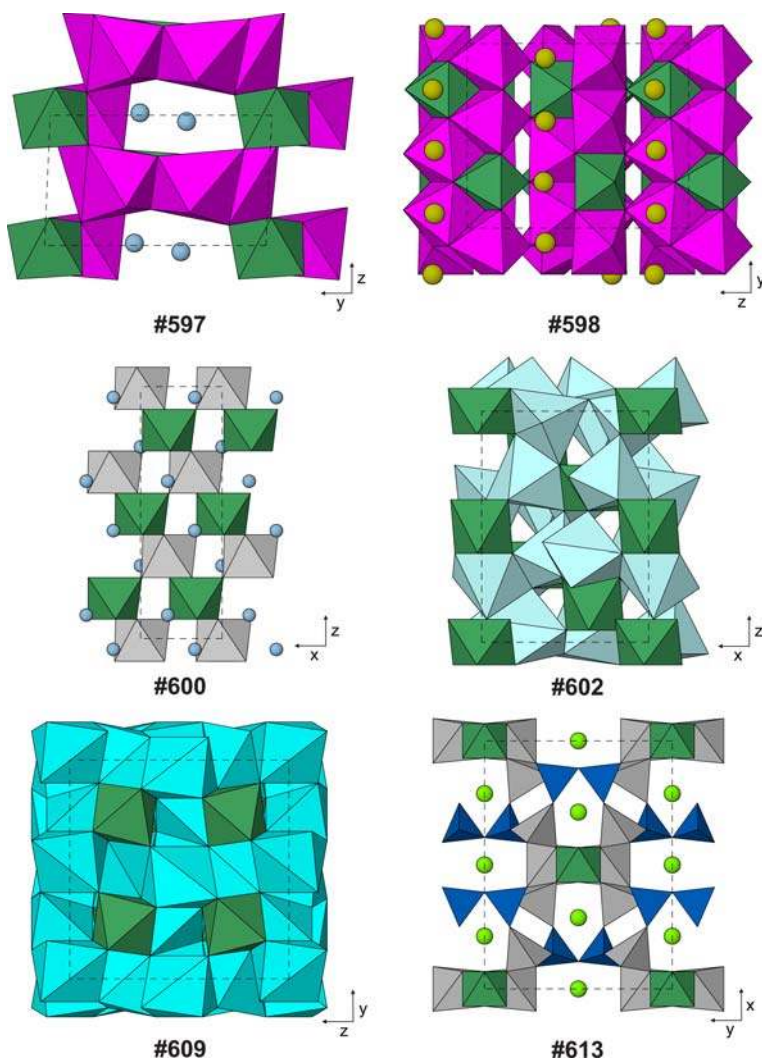


FIG. 41. Examples of structures with monomeric  $\text{Te}^{6+}\text{O}_6$  anions as part of a larger structural framework (Table 23, deposited). Large spheres: Ba (yellow-green), Li (pale blue) and Na (dark yellow). Polyhedra: Cu (cyan), Mg (pale blue), Mn (magenta), Si (dark blue), Te (dark green), Zn (grey tetrahedra) and Zr (pale grey octahedra).

cell parameters  $a$ ,  $b$ ,  $c \approx \sqrt{3}$ ,  $\sqrt[8]{3}$  and 3, measured in units of the mean 'close-packed'  $\text{O}\cdots\text{O}$  distance. There are two close-packed anion layers per cell (as opposed to six for corundum/ilmenite)  $\parallel (020)$ , and between each layer pair, Li and Sb each occupy  $\frac{1}{3}$  of the octahedral interstices.  $\text{SbO}_6$  octahedra form edge-sharing chains  $\parallel x$ , and these share corners with the chains above and below to form a framework. The vacant octahedral sites of each cation layer lie above and below Sb, so that  $\text{SbO}_6$  octahedra do not share faces.  $\text{LiO}_6$

octahedra do not form edge-sharing chains, but do form face-sharing columns  $\parallel y$ . Even in the idealized structure,  $a$  and  $b$  are only  $\sim 6\%$  different, so the structure is metrically pseudotetragonal with pseudotetrad axis  $\parallel z$ , and the two types of cation are arranged similarly to Ca and W of the scheelite structure (Hazen *et al.*, 1985), although the disposition of oxygen atoms is quite different. The compounds  $\text{Li}_2[\text{M}^{4+}(\text{TeO}_6)]$  ( $M = \text{Sn}$  or  $\text{Ti}$ ; #588–589) have this structure, but with  $M$  and Te alternating in the zigzag chains, which reduces the

symmetry to  $Pnn2$  (Fig. 40). Partial leaching of  $\text{Li}^+$  from the Ti compound and replacement with  $\text{H}^+$  indicated no structural change for small degrees of leaching (Crosnier *et al.*, 1992), but  $(\text{H}_{1.68}\text{Li}_{0.32})[\text{Ti}(\text{TeO}_6)]$  showed considerable redistribution of non-Te cations, while preserving the (Te + O) substructure. A significant proportion of Ti occupied former Li or vacant sites (#590), giving an arrangement with the space group  $Pnnm$ , which is in effect a tri- $\text{CaCl}_2$  (orthorhombically collapsed trirutile) structure. The structure of frankhawthorneite,  $[\text{Cu}_2(\text{TeO}_4(\text{OH})_2)]$ , is closely related (#512 above). Annealing of this compound re-ordered the octahedral site occupancies to give a tetragonal but acentric trirutile structure with space group  $P4_2nm$  (#591). More conventional  $P4_2/mnm$  trirutile structures are covered below (#594–596).

$\text{Pb}_6[\text{Co}_9(\text{TeO}_6)_5]$  and its Ni analogue (#592–593) have an unusual structure containing defect brucite-like layers with  $1/6$  of the cations missing,  $(M_7^{2+}\text{Te}_3\Box_2)\text{O}_{24}$  ( $M = \text{Co}$  or  $\text{Ni}$ ). These are connected into a framework through additional  $M \equiv \text{Te}$  face-sharing dimers, which share corners with the layers above and below to form a pillared-layer structure with very large interlayer channels, which contain the Pb atoms (Fig. 41).  $[M_2^{2+}(\text{TeO}_6)]$  with  $M = \text{Cr}$ ,  $\text{Fe}$  or  $\text{Ga}$  (#594–596) have the well-known trirutile structure also known for minerals such as the byströmite and tapiolite groups,  $M^{2+}\text{Sb}_2^{5+}\text{O}_6$  ( $M = \text{Mg}$  or  $\text{Zn}$ ) and  $M^{2+}\text{Ta}_2^{5+}\text{O}_6$  ( $M = \text{Fe}$  or  $\text{Mn}$ ) (Byström *et al.*, 1942). The space group is the same as rutile,  $P4_2/mnm$ , while the  $c$  repeat is tripled due to cation ordering. An unusual acentric trirutile phase with  $M1-M2-\Box$  ordering along its pseudotetrad direction was discussed above (#586).  $\text{Li}[\text{Mn}^{2+}\text{Mn}^{3+}(\text{TeO}_6)]$  (#597) again has slightly distorted *hcp* of oxygen atoms, a pseudotetragonal unit-cell metric, and cell dimensions very similar to #583–586 and #594–596 above. However, a greater proportion of the octahedral sites are occupied, although it should be noted that irregularity of the octahedra and off-centring of cations mean that the coordination number is unambiguously 6 only for Te1, Te2 and Mn1–3, while Mn4 and Li2 are CN7 and Li3 is CN8, if all cation–oxygen distances within 3 Å are included. Bond-valence sums using the parameters of Brese and O’Keeffe (1991) indicate that Mn1 and Mn3 are  $\text{Mn}^{2+}$ , while Mn2 and Mn4 are  $\text{Mn}^{3+}$ . The approximate close-packed oxygen layers are  $\parallel (002)$ , with the pseudotetrad direction  $\parallel y$ . Cations are arranged such that two out of every three sites are occupied along the  $y$  direction. Two types of cation layer alternate. In one of these, Te1 and Mn2 share edges to form a zigzag

chain  $\parallel x$ , with an adjacent zigzag of Li2 and Li3 on one side. In the other layer, zigzag chains  $\parallel x$  are formed by Te2 and Mn4 and by Mn1 and Mn3. The vacancies of the second layer share faces with Te1 and Mn2, while the vacancies of the first layer share faces with Mn1 and Mn3. The refinement indicates some mixing (17%) of Li on Mn4 and of Mn on Li3, but if this is ignored, all ‘Li’ sites excluded from the structural unit and all ‘Mn’ sites included, then we define a framework in which layers of 2-wide and 4-wide octahedral ribbons share edges, with channels between them  $\parallel x$  which accommodate  $\text{Li}^+$  ions.  $\text{Na}_3[(\text{Mn}_3^{2+}\text{Mn}^{3+})(\text{TeO}_6)_2]$  (#598) has a ‘tri-harmunite’ structure which can be derived from the  $Pnma$  structure of harmunite,  $\text{CaFe}_2^{3+}\text{O}_4$  (Gaulskina *et al.*, 2014), one of three closely related structures known to high-pressure researchers as ‘post-spinel’ phases, as they have the same cation: oxygen ratio as spinel but larger coordination numbers, making them potential high-pressure polymorphs (cf. Yamanaka *et al.*, 2013). These structures all have frameworks made by corner sharing between 2-wide edge-sharing ribbons of octahedra, with channels which contain CN8 cations (Fig. 41). In #598, the octahedral ribbons run  $\parallel y$ , but ordering of Te and mixed-valence Mn triples the unit cell repeat in this direction. Na occupies the CN8 site. Note that the octahedral ribbons define oblique, stepped slices of cations in an *hcp* anion array, repeated by twinning on (020), as noted by Hyde and Andersson (1989). The hexagonal close-packed planes are  $\parallel (210)$  or  $(2\bar{1}0)$  in alternate twin lamellae. The oblique *hcp* slices differ from those of frankhawthorneite etc (#512–515) in that the ribbon direction is parallel to an octahedral edge, rather than perpendicular.

$[\text{Ni}_3(\text{TeO}_6)]$  (#599) has a *hcp* array of oxygen atoms in which  $2/3$  of the octahedral interstices are filled in the same pattern as corundum,  $\text{Al}_2\text{O}_3$ . However, alternate cation layers along the  $z$  direction are either all Ni or are Ni+Te, ordered so as to reduce the symmetry to the polar space group  $R3$ . The resulting structure is a superstructure not just of the corundum type ( $R3c$ ), but also of its two *zellengleich* 1 : 1 superstructures: ilmenite ( $\text{FeTiO}_3$ ;  $R\bar{3}$ ) and  $\text{LiNbO}_3$  ( $R3c$ ). Ilmenite-structure compounds in which there is alternation of cation layers with Na and with disordered ( $M^{4+} + \text{Te}^{6+}$ ) are discussed below at #664–665. The compounds  $\text{Li}_2[M^{4+}(\text{TeO}_6)]$  ( $M = \text{Zr}$  or  $\text{Ge}$ ; #600–601) are placed here because they are isopuntal, although cation layers of (Li1 +  $M$ ) and (Li2 + Te) now alternate along  $z$ . Lithium octahedra share faces with  $M$  or Te octahedra, and the Li cations are

displaced strongly away from these neighbours along *z*, in accord with the polar symmetry of the structure (Fig. 41). If the low-valence Li atoms are excluded from the structural unit, the remaining  $M\text{TeO}_6$  framework has a rhombohedrally stretched version of the ‘double perovskite’ type. The *c/a* ratio is 17% larger in **#601** than the value of  $\sqrt{12}$  which would correspond to a primitive cubic arrangement of cations. As Li can be regarded as an off-centre ‘*A*’ cation in the  $A_2BB'X_6$  double perovskite topology, these compounds could in fact be classified with the rhombohedral double perovskites **#582–584** above, which have similar cell dimensions. Thus, the range of cation valences in these compounds, and the resulting choice of whether or not to include cations in the structural unit, highlight a relationship between perovskite and corundum structure families which is not otherwise obvious.

$[\text{Mg}_3(\text{TeO}_6)]$  (**#602**) is an archetype for several isostructural tellurates of Mn, Mn+Cu or Cd+Mn (**#603–605**). The rather dense structure is not conventionally close-packed, but the key to comprehending it is to note that the rhombohedral cell parameters for Mg are  $a_{rh} = 6.047 \text{ \AA}$  and  $\alpha_{rh} = 90.86^\circ$ , with Te atoms forming an almost perfect body-centred cubic array (more precisely a CsCl-type array, as there are two nonequivalent Te atoms per cell) (Fig. 41). Like  $[\text{Hg}_3(\text{TeO}_6)]$  (**#548**) and the tellurate garnets (**#549–553**) above, these compounds have an oxygen-stuffed  $\text{Cr}_3\text{Si}$  structure, with oxygen atoms occupying a different set of tetrahedral interstices than those that they do in garnets, such that each oxygen bonds to 3 Mg ( $\equiv \text{Cr}$ ) and 1 Te ( $\equiv \text{Si}$ ), while Mg and Te are all in octahedral coordination. There is no long-range order of Cd and Mn in  $[(\text{Cd}_2\text{Mn})(\text{TeO}_6)]$  (**#605**). The Co and Zn analogues have monoclinically distorted superstructures (**#606–607**). The Co and Zn compounds have space group  $C2/c$ , with  $a_{mon} \sim \sqrt{3}a_{trig}$ ,  $b_{mon} \approx b_{trig}$ ,  $c_{mon} \approx c_{trig}$ ,  $\beta = 92\text{--}95^\circ$ . There are still two distinct Te sites per cell, but the single octahedrally-coordinated  $M^{2+}$  site of the rhombohedral phases splits into five distinct sites with a wider range of coordination numbers: CN = 6, 6, 5, 6 and 4 for  $[\text{Co}_3(\text{TeO}_6)]$  (**#606**) and CN = 4, 4, 5, 5 and 6 for  $[\text{Zn}_3(\text{TeO}_6)]$  (**#607**). The ordered Cu–Zn compound  $[\text{Cu}_5\text{Zn}_4(\text{TeO}_6)_3]$  (**#608**) has similar cell parameters, but additional displacements of atoms which reduce the symmetry further to  $C2$ . There are three Te sites, six Cu sites and four Zn sites. While Te is in fairly regular octahedral coordination, the Cu atoms are in Jahn–Teller distorted 4+2 coordination if the threshold between

strong and weak bonding is set at  $\text{Cu–O} = 2.2 \text{ \AA}$ , except for Cu2, which is 4+3 coordinated, with three oxygen ligands in the range 2.5–2.8  $\text{\AA}$ . Two Zn atoms are 4-coordinated and two are 5-coordinated.

The mineral mcalpineite has been recently redefined as anhydrous  $[\text{Cu}_3(\text{TeO}_6)]$  (Carbone *et al.*, 2013). It is interesting to note that its structure (**#609**) is the explicitly ternary variant of the ‘*C*-sesquioxide’ structure of heavy rare-earth oxides and the bixbyite group of minerals  $M_2^{3+}\text{O}_3$ , where  $M = \text{Mn, Tl, Y and Sc}$ , in respectively, bixbyite (Zachariasen, 1928), avicennite (Radtke *et al.*, 1978), yttriaite-(Y) (Mills *et al.*, 2011) and kangite (Ma *et al.*, 2013) (Fig. 41). This is another structure like the pyrochlore type (cf. **#366, 700**) which can be regarded as a defect fluorite. Again, the overall cation array is cubic close-packed and there is a cubic unit cell with  $a \approx 10 \text{ \AA}$ , corresponding to  $2 \times 2 \times 2$  fluorite unit cubes, but this time,  $\frac{1}{4}$  of the anions are missing, which correspond to O2 in the winstanleyite structure (**#369–373**), which has similar cell dimensions and the same  $Ia\bar{3}$  space group. As in winstanleyite, the cations are split into two distinct types in a 3:1 ratio. All cations are 6-coordinate in mcalpineite, but one type ( $\text{Te}^{6+}$ , here) has a coordination polyhedron that is close to regular octahedral geometry, while the other ( $\text{Cu}^{2+}$ ) has a less regular geometry that is best described as twisted trigonal prismatic. Up to half the Cu may be substituted by Co or Zn, with no further ordering (**#610–612**). Some Te-free synthetic isotypes are also rich in Cu, such as the phases  $\text{Cu}_{2-x}^2+\text{Fe}_{2x}^{3+}\text{Ti}_{2-x}^4\text{O}_6$  (Mouron *et al.*, 1985) and  $\text{Cu}_2^2+M^{3+}\text{Sb}^{5+}\text{O}_6$  ( $M = \text{Mn, Fe and Ga}$ ; Bazuev *et al.*, 1994).

$\text{Ba}_3[\text{Zn}_6(\text{Si}_2\text{O}_7)_2(\text{TeO}_6)]$  (**#613**) has a unique zincotellurosilicate framework, with 9- and 12-coordinate  $\text{Ba}^{2+}$  ions in large cages. Paired  $\text{ZnO}_6$  and single  $\text{TeO}_6$  octahedra share edges to form ribbons running  $\parallel z$  that resemble the  $\text{Cu}_2\text{Te}$  octahedral ribbons of frankhawthorneite and related compounds (**#512–515**). These ribbons are linked into a framework by sharing corners with corrugated layers  $\parallel (200)$  of  $\text{ZnO}_4$  tetrahedra and  $\text{Si}_2\text{O}_7$  tetrahedral dimers. The tetrahedral layers contain  $[\text{Zn–Si–Zn–Si}]$  4-rings and  $[\text{Zn–Si–Si–Zn–Si–Si}]$  6-rings (Fig. 41).

$[\text{M}_6^{3+}(\text{TeO}_6)\text{O}_6]$  ( $M = \text{Y, In and Tl}$ ; **#614–616**) again have a defect fluorite structure like the bixbyite isotypes **#609–612** above, but the rhombohedral structure is more complex, with approximately cubic close-packed cations ordered into two types in a 6:1 ratio,  $\frac{1}{6}$  of the anions missing, and the rest split into two types, coordinated either by  $2M + 1 \text{ Te}$  or by  $4M$ . All cations are 6-coordinate.



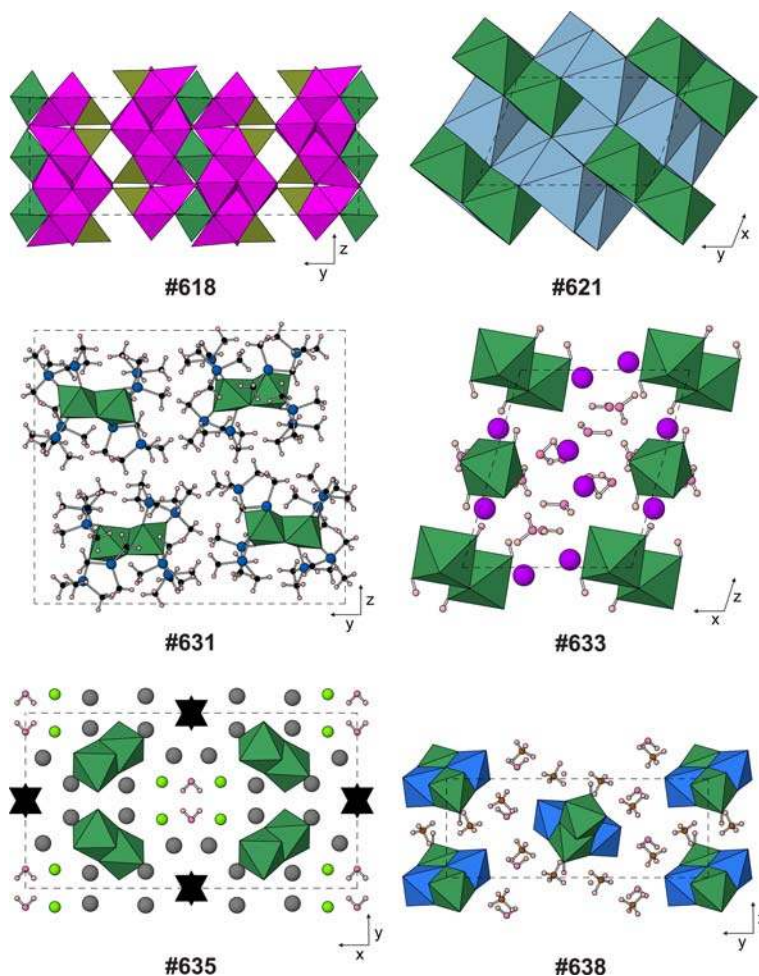


FIG. 42. Examples of structures with monomeric  $\text{Te}^{6+}\text{O}_6$  as part of a larger structural framework (**#618**, Table 23, deposited) and with soro dimers of  $\text{TeO}_6$  octahedra (Table 24). Small spheres: C (black), H (pale pink), N (brown) and O (dark pink) when not part of a polyhedron. Medium spheres: Si (blue) and Cl (yellow-green). Large spheres: K (purple) and Pb (grey). Black triangles in **#635**:  $\text{CO}_3$  groups. Polyhedra: As (brown-green), Co (magenta), Li (grey-blue) and V (bright blue).

This structure is also known for compounds such as  $\text{Y}_6(\text{U}^{6+}\text{O}_6)\text{O}_6$  (Bartram, 1966), the meteoritic mineral allendeite,  $\text{Sc}_4\text{Zr}_3\text{O}_{12} \equiv [(\text{Sc}_4\text{Zr}_2)(\text{ZrO}_6)\text{O}_6]$  (Thornber *et al.*, 1968; Ma *et al.*, 2014) and  $\text{Pr}_7\text{O}_{12} \equiv [(\text{Pr}_4^{3+}\text{Pr}_2^{4+})(\text{Pr}^{4+}\text{O}_6)\text{O}_6]$  (von Dreele *et al.*, 1975). Remarkably,  $\text{Ti}_6^{1+}[\text{TeO}_6]$  (**#445**, above) has the same space group and cation substructure, and very nearly the same cell parameters as  $\text{Ti}_6^{3+}(\text{TeO}_6)$  (**#616**). However, all the non-tellurate oxygen atoms are missing in **#445**, and the Ti–O bonds to the remaining oxygen atoms are longer and less regular.

This section concludes with two Co-rich frameworks.  $\text{Na}_5\text{Co}_{15.5}^{2+}(\text{TeO}_6)_6 \equiv \text{Na}_{2.5}(\text{Na}_{2.5}\text{Co}_{1.5})[\text{Co}_{14}(\text{TeO}_6)_6]$  (**#617**) has a nanoporous hexagonal structure in which Co1 and Te octahedra share edges to form 2-wide ribbons running  $\parallel z$ . These ribbons link at corners to delineate relatively large hexagonal tunnels (diameter  $\approx 6.5$  Å) and smaller ditrigonal tunnels, which are internally braced by Co2 atoms in trigonal prismatic coordination, to complete a framework  $[(\text{Co1})_{12}(\text{Co2})_2(\text{TeO}_6)_6]^{8-}$ . An additional site in the small channels is occupied by mixed Na + Co, while the remaining  $\text{Na}^+$  ions

are in the large channels.  $[\text{Co}_8^{2+}(\text{TeO}_6)(\text{AsO}_4)_2\text{O}_2]$  (**#618**) has four types of  $\text{Co}^{2+}$  ion (CN = 4, 6, 6 and 6) sharing edges and corners to make thick double layers  $\parallel (020)$ .  $\text{TeO}_6$  octahedra act as internal braces in the middle of the double layers, while  $\text{AsO}_4$  tetrahedra cross-link the layers into a three-dimensional framework (Fig. 42).

### Soro or cyclo finite polymers $\text{Te}_m^{6+}\text{X}_n$

Structures **#619–645** contain  $\text{Te}^{6+}\text{O}_6$  octahedra that are linked into finite polymers  $\text{Te}_m\text{X}_n$  ( $m = 2\text{--}6$ ); these are listed in Table 24 (deposited). Our first two examples are closely related to each other.  $\text{Ba}_3[\text{Te}_2\text{O}_9]$  (**#619**) has a simple hexagonal structure containing the face-sharing dimer of Fig. 13*a*. These groups lie with  $\frac{1}{3}$  of the  $\text{Ba}^{2+}$  ions in layers  $\parallel (002)$ , which alternate with layers containing the other  $\frac{2}{3}$  of the  $\text{Ba}^{2+}$  ions.  $\text{Ba}_3[\text{Fe}^{3+}(\text{Fe}^{3+}\text{Te}^{6+})\text{O}_9]$  (**#620**) has the same  $P6_3/mmc$  space group and nearly identical unit-cell parameters. It contains the same dimeric anion, except that 50% of the  $\text{Te}^{6+}$  is now randomly substituted by  $\text{Fe}^{3+}$ , and charge balance is maintained by insertion of additional  $\text{Fe}^{3+}$  ions into octahedral interstices which were vacant in **#619**. The additional Fe octahedra in **#620** join corners with the face-sharing dimers to form a three-dimensional framework which is a  $6H$  perovskite polytype, with  $hkk$  stacking of  $(\text{BaO}_3)$  close-packed layers. It is thus very closely related to  $\text{Ba}_2[\text{Co}(\text{TeO}_6)]$  (**#585**), where the different cation-ordering pattern results in lower symmetry. The relationship to these phases shows that **#619** can be considered a defect  $6H$  perovskite with ordered  $B$ -site vacancies.

$\text{Li}_4\text{TeO}_5 \equiv \text{Li}_8[\text{Te}_2\text{O}_{10}]$  and its Na analogue (**#621–622**) has the edge-sharing dimeric anion of Fig. 13*b*. All atoms are 6-coordinated, with each oxygen atom linked to 5 Na + 1 Te or to 4 Na + 2 Te. The cation array is  $ccp$  and the structure is actually a superstructure of the rocksalt type, with the pseudocube edge vectors parallel to  $[0\frac{1}{2}\frac{1}{2}]$  and approximately  $[\frac{5}{12}\frac{1}{12}\frac{3}{4}]$  and  $[\frac{5}{6}\frac{1}{3}\frac{1}{12}]$  of the triclinic cell in **#622**. The Te = Te dimer axes are oriented  $\parallel [331]$  (Fig. 42). The Ag analogue (**#623**) has a monoclinic structure in which layers of close-packed cations stack  $\parallel (004)$  in an  $ABAC$  sequence (alternating  $h$  and  $k$  layers). All cations and anions again occupy 6-coordinated interstices of the opposite substructure, so while  $\text{Ag}^+$  and  $\text{Te}^{6+}$  of the  $k$  cation layers are in octahedral coordination, the  $\text{Ag}^+$  ions of  $h$  layers are in trigonal prisms. Within the  $k$  layers, edge-sharing Te=Te dimers alternate with  $\text{Ag}=\text{Ag}=\text{Ag}$  triplets along rows  $\parallel x$ .

$\text{K}_4[\text{Te}_2\text{O}_6(\text{OH})_4] \cdot 5\text{H}_2\text{O}$  (**#624**) has a simple but incompletely determined structure in which dimers with Te=Te axes  $\parallel x$  are linked into layers  $\parallel (020)$  through  $\text{K}^+$  ions. Water molecules were not located, but are presumably in the interlayer gap and complete the coordination polyhedra of the  $\text{K}^+$  ions. The structure of  $\text{K}_4[\text{Te}_2\text{O}_6(\text{OH})_4] \cdot 8\text{H}_2\text{O}$  (**#625**) is more completely determined, with all O and H atoms located, and bears little resemblance to that of its lower hydrate. Again, all Te=Te dimers are parallel ( $\parallel [011]$ ), and lie in layers  $\parallel (200)$ , which alternate with layers of  $\text{KO}_{8-9}$  polyhedra.  $\text{Rb}_4[\text{Te}_2\text{O}_6(\text{OH})_4] \cdot 10\text{H}_2\text{O}$  (**#626**) is somewhat similar, but in this triclinic cell, the layering is  $\parallel (110)$ , Te=Te axes are  $\parallel [2\bar{1}4]$ , and the Rb atoms are 8–10 coordinated and lie in less convoluted layers.  $\text{Cs}_3[\text{Te}_2\text{O}_5(\text{OH})_5] \cdot 4\text{H}_2\text{O}$  (**#627**) has one Te=Te group per triclinic cell, aligned  $\parallel [322]$ , in a matrix of water molecules and CN10  $\text{Cs}^+$  ions, while  $\text{Cs}_4[\text{Te}_2\text{O}_4(\text{OH})_4] \cdot 8\text{H}_2\text{O}$  (**#628**) has a more obviously layered structure in which Te=Te groups pointing  $\parallel [2\bar{1}2]$  and  $\text{CsX}_{9-10}$  polyhedra form sheets  $\parallel (10\bar{1})$ , which are linked only through hydrogen bonds.  $\text{K}_4\text{Na}_2[\text{Te}_2\text{O}_8(\text{OH})_2] \cdot 14\text{H}_2\text{O}$  (**#629**) has a body-centred array of Te=Te dimers pointing  $\parallel z$ , which bridge layers  $\parallel (10\bar{1})$  of water molecules, CN8  $\text{K}^+$  and CN6  $\text{Na}^+$  ions.  $\text{K}_7\text{Na}[\text{Te}_2\text{O}_6(\text{OH})_4]_2 \cdot 12\text{H}_2\text{O}$  (**#630**) has Te=Te dimers  $\parallel x$ , lying in undulating layers  $\parallel (020)$  that are connected weakly through CN6–10  $\text{K}^+$  and CN6  $\text{Na}^+$  ions.

The next two compounds are ditellurates of organic complexes.  $(\text{C}(\text{CH}_3)_3\text{Si})_8[\text{Te}_2\text{O}_{10}]$  (**#631**) has a trimethylsilyl group strongly bonded (1 vu) to each of the eight non-bridging oxygen atoms of the Te=Te anion, to form a large neutral molecule that has only point symmetry 1, with two distinct Te and eight distinct Si atoms. Four such molecules in slightly different orientations pack together per unit cell (Fig. 42).  $(\text{C}(\text{NH}_2)_3)_4[\text{Te}_2\text{O}_6(\text{OH})_4]$  (**#632**) is not molecular, having well-defined guanidinium cations  $[\text{C}(\text{NH}_2)_3]^+$  and tellurate anions  $[\text{Te}_2\text{O}_6(\text{OH})_4]^{4-}$ . However, the structure is surprisingly complex, with four distinct C atoms and two types of Te=Te anion per unit cell. Te1 dimers pointing  $\parallel [221]$  form layers  $\parallel (100)$ , which alternate with layers that contain both Te2 dimers pointing  $\parallel [2\bar{1}1]$  and one type of guanidinium group. The other three types of guanidinium lie between the Te layers.

Two structures have edge-sharing  $\text{Te}_2\text{X}_{10}$  (Fig. 13*b*) in combination with monomeric  $\text{TeX}_6$  octahedra.  $\text{K}_6[\text{Te}_2\text{O}_6(\text{OH})_4](\text{TeO}_2(\text{OH})_4) \cdot 12\text{H}_2\text{O}$  (**#633**) has Te=Te dimers (Te2) aligned  $\parallel [110]$ , alternating along  $z$  with monomeric octahedra

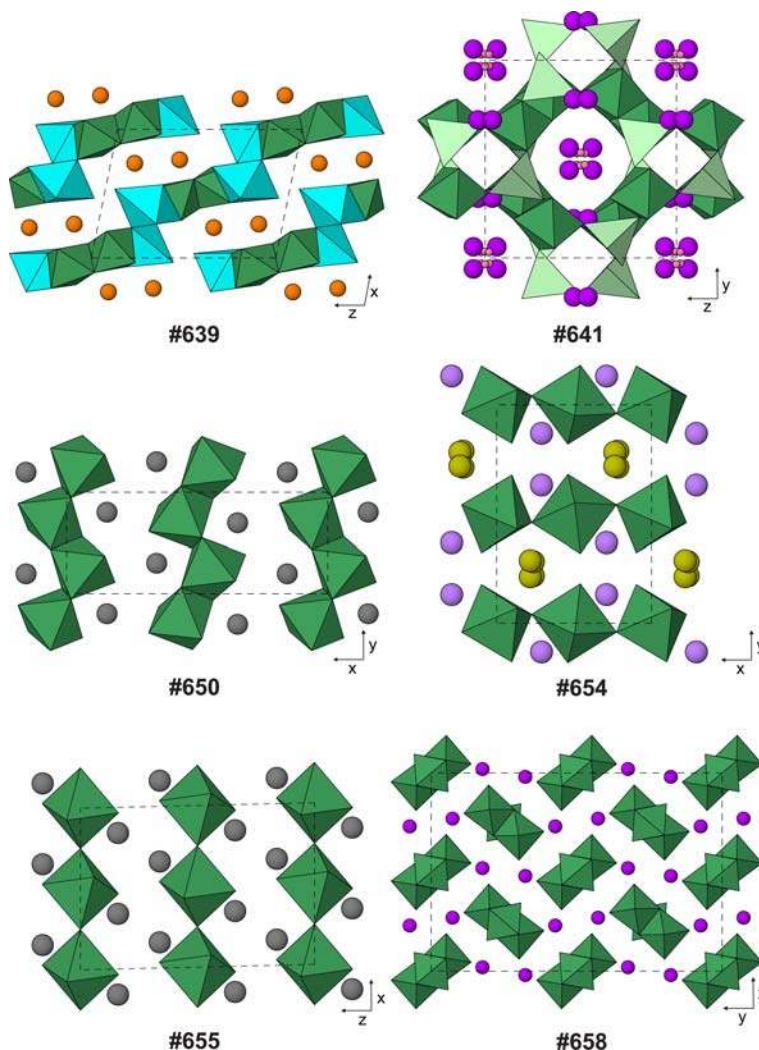


FIG. 43. Examples of structures with  $\text{Te}_2\text{O}_{10}$  octahedral dimers as part of a larger structural layer or framework (Table 24, deposited) and of infinite chains of  $\text{TeO}_6$  octahedra (Table 25). Small spheres: O (dark pink) when not part of a polyhedron. Large spheres: Bi (violet), Ca (orange), K (purple), Na (dark yellow) and Pb (grey). Polyhedra: Cu (cyan), Ga (pale green) and Te (dark green).

(Te1). The rows of Te anions lie between layers  $\parallel (1\bar{1}0)$  of CN8–10  $\text{K}^+$  ions (Fig. 42).  $\text{Cs}_2[\text{Te}_2\text{O}_4(\text{OH})_6] \cdot (\text{Te}(\text{OH})_6)$  (#634) has  $\text{Te}=\text{Te}$  pointing  $\parallel [2\bar{1}1]$  and lying in layers  $\parallel (001)$ , which alternate with layers of CN9  $\text{Cs}^+$  ions and neutral  $\text{Te}(\text{OH})_6$  molecules. Note that this is a special case of an orthotelluric acid adduct, more conventional examples of which are described as #376–431 above.

Thorneite,  $\text{Pb}_6[\text{Te}_2\text{O}_{10}](\text{CO}_3)\text{Cl}_2 \cdot \text{H}_2\text{O}$  (#635, see front cover image), has  $\text{Te}=\text{Te}$  dimers pointing

$\parallel [12\bar{4}]$  or  $\parallel [1\bar{2}4]$ , lying in sheets  $\parallel (200)$ . The Te sheets have on each side of them  $\text{PbO}_7\text{Cl}$ ,  $\text{PbO}_6\text{Cl}_2$  and  $\text{PbO}_5\text{Cl}_2$  polyhedra which complete thick layers, and carbonate groups and water molecules lie between the layers (Fig. 42).  $\text{K}_3[\text{Ga}(\text{Te}_2\text{O}_8(\text{OH})_2)] \cdot \text{H}_2\text{O}$  (#636) has  $\text{Te}=\text{Te}$  dimers alternating with  $\text{GaO}_4$  tetrahedra to form loop-branched *vierer* chains  $\parallel z$ . The Te and Ga polyhedra between them form ‘double-triangle’ clusters; for a topologically similar chain made only of Te octahedra, see  $\text{K}_2[\text{Te}_3\text{O}_8(\text{OH})_4]$  below (#658;

Fig. 13*i*). The chains form an approximately hexagonal rod packing, and are held together through CN7–8  $K^+$  ions and water molecules.  $Tl_6^{1+}[Cu^{2+}(Te_2O_{10})]$  (#637) has chains that are very similar in topology, but the non-Te component is a  $CuO_4$  square rather than  $GaO_4$  tetrahedron. The four shortest Cu–O distances are 1.96–1.98 Å, but a fifth neighbour to Cu at 2.52 Å provides an additional brace along the chain. The chains run  $\parallel x$  and are arranged in a checkerboard fashion, leaving large square channels.  $Tl^+$  ions line the sides of these channels, and are in one-sided 5–8 coordination.  $(NH_4)_2V^{5+}TeO_6(OH) \cdot H_2O \equiv (NH_4)_4[(V^{5+}O_2)_2(Te_2O_8(OH)_2)] \cdot 2H_2O$  (#638) has a loop-branched *dreier* chain made from regular Te octahedra and very distorted  $VO_6$  octahedra. Edge-sharing Te=Te and V=V pairs alternate along the chain  $\parallel z$ . Every Te atom shares an oxygen ligand with each V of its adjacent dimer, and also a CN3 oxygen atom with both of them. V–O distances are 1.65–1.66 Å (non-bridging oxygen), 1.95–1.96 Å (CN2 bridging oxygen) and 2.16 and 2.47 Å (CN3 bridging oxygen), consistent with its description as the core of a  $[VO_2]^+$  cation. The chains pack in a centred-rectangular array, with  $NH_4^+$  ions and  $H_2O$  molecules between them (Fig. 42).

Eckhardite,  $Ca_2[Cu_2(Te_2O_{10})] \cdot 2H_2O$  (#639) has  $TeO_6$  and  $CuO_{4+2}$  polyhedra sharing edges to form layers  $\parallel (101)$ . The Cu ligands form a slightly twisted square at 1.96–2.02 Å, plus two more completing an elongated octahedron at 2.51 and 2.67 Å (Fig. 43). The oxygen atoms associated with all these polyhedra form a stepped, oblique slice through a *hcp* array, somewhat similar to the layer seen in the frankhawthorneite-related structures #512–515 above. However, while the frankhawthorneite layer ‘steps’ are edge-sharing ribbons which alternate between two octahedra in width (Cu=Cu) and one (Te), the eckhardite ribbons alternate between three octahedra (Cu= $\square$ =Cu) and two (Te=Te) in width. These run  $\parallel y$ . Between the layers lie CN7  $Ca^{2+}$  ions.  $Ag[(UO_2)(Te_2O_8(OH)_2)]$  (#640) has edge-sharing ribbons of  $UO_7$  pentagonal bipyramids running  $\parallel x$ , which share CN3 oxygen atoms with  $Te_2O_{10}$  dimers to form layers  $\parallel (020)$ . The layer topology contains ‘double-triangle’ clusters  $U < (Te=Te) > U$ . The  $Ag^+$  ions are in irregular 5-fold coordination between the layers. In  $K_2[Ga_2(Te_2O_{10})] \cdot 2H_2O$  (#641),  $GaO_4$  tetrahedra and  $Te_2O_{10}$  octahedral pairs share corners to form a three-dimensional framework. Two ligands of each Ga connect it to a neighbouring Te = Te dimer as part of a ‘double triangle’  $Ga < (Te = Te) > Ga$ , while the other two ligands link Ga

to two other dimers, as part of a  $[Ga-Te-Ga-Te]$  4-ring. The double triangles and 4-rings alternate, forming crankshaft ribbons  $\parallel z$ , which are arranged in a centred-rectangular array and are connected into a framework via the remaining Ga–O–Te links. The framework is very open, with 6–8 Å diameter channels  $\parallel x$  and  $z$ , which contain water molecules and CN9–11  $K^+$  ions, and has very strong pseudotetragonal symmetry in projection down  $x$  (Fig. 43).

Schieffelinite,  $Pb_{10}[Te_2O_8(OH)_3]_2(TeO_2(OH)_4)_2(SO_4) \cdot 5H_2O$ , and its chromate analogue chromschiefelinite (#642–643), have as their structural unit the corner-sharing  $Te_2X_{11}$  dimer of Fig. 13*c*. The Te–Te dimers lie in undulating layers  $\parallel (020)$ , with CN8–10  $Pb^{2+}$  ions on either side. Water molecules, additional  $TeX_6$  monomers and orientationally disordered  $SO_4^{2-}$  or  $CrO_4^{2-}$  tetrahedra lie between the layers.

We have two examples of cyclo anions made from  $Te^{6+}$  octahedra.  $K_2[Te_4O_8(OH)_{10}]$  (#644) has an edge-sharing pair of octahedra joining the two halves of a  $Te_4X_{18}$  ‘double triangle’ tetramer (Fig. 13*d*). These isolated clusters are arranged in a herringbone pattern in layers  $\parallel (100)$ , with CN10  $K^+$  ions between the layers.  $K_{8.5}(H_3O)_{0.5}[Te_6O_{18}(OH)_9] \cdot 17H_2O$  (#645) has ditrigonal rings  $Te_6X_{27}$  in which Te octahedra alternately share corners and edges with their neighbours (Fig. 13*e*). Rings are in two different orientations with the ring plane always normal to  $z$ , and form pseudo-hexagonal columns running  $\parallel z$ , which are arranged in a hexagonal rod packing, with hydronium and CN6–11  $K^+$  ions between them. Successive layers of the rods  $\parallel (200)$  are shifted by  $\frac{1}{4}c$ , which reduces the symmetry to monoclinic.

### Infinite polymers $Te_m^{6+}X_n$

#### Inotellurates

In structures #646–677  $Te^{6+}$  octahedra are linked to form infinite polymers (Table 25, deposited). Our first examples of ino tellurates have edge-sharing *zweier* chains  $Te_2X_8$ . In all cases, the shared edges of an octahedra are not *cis* to one another, so the chain zigzags (Fig. 13*f*). The database includes two polymorphs of  $Na_2TeO_4 \equiv Na_4[Te_2O_8]$ . The *Pbcn* polymorph (#646) has Te chains  $\parallel z$ , arranged in a centred-rectangular array. The chains are flanked by edge-sharing ribbons of  $NaO_6$  polyhedra which hold the structure together. Overall, the oxygen arrangement approximates *hcp*, with close-packed planes  $\parallel (200)$  and (Na+Te) occupying  $\frac{3}{4}$  of the octahedral interstices between each pair of



layers. The  $P2_1/c$  polymorph (#647) has a slightly sheared version of the same structure, with  $\mathbf{x}_{\text{mon}} = \left[\frac{3}{2}, \frac{1}{2}, 0\right]_{\text{orth}}$  and  $\mathbf{z}_{\text{mon}} = [1\bar{1}0]_{\text{orth}}$ . The isostructural pair of compounds  $\text{CaTeO}_4$  and  $\text{SrTeO}_4$  (#648–649) have the same space group as #646 ( $Pbcn$ , although strongly pseudo- $Cmnm$ ), very similar cell parameters, and the same type of Te chain. However, only half of the Na sites of #646 are occupied by alkaline earth cations.  $(\text{Ca}, \text{Sr})\text{O}_6$  and  $\text{TeO}_6$  octahedra together form open-branched *zweier* chains of edge-sharing octahedra running  $\parallel \mathbf{z}$  between each pair of close-packed anion layers, thus avoiding shared faces between  $(\text{Ca}, \text{Sr})$  octahedra. This structure is shared with the pucherite polymorph of  $\text{BiVO}_4$  (Qurashi and Barnes, 1953) and aluminotantite,  $\text{AlTaO}_4$  (Ercit *et al.*, 1992) as well as synthetic  $\text{MUO}_4$  ( $\text{M} = \text{Cr}, \text{Fe}$  and  $\text{Ni}$ ; Hoekstra and Marshall, 1967). A Te-rich variety of raspite,  $\text{Pb}[(\text{W}_{0.56}\text{Te}_{0.44})\text{O}_4]$  (#650) is included in this review, as the W:Te ratio is close to 1:1. Raspite is ideally  $\text{PbWO}_4$  (Fujita *et al.*, 1977), and was discussed earlier, as one of the forms of  $\text{Te}^{4+}\text{V}^{4+}\text{O}_4$  is isostructural (#82, above). While  $\text{Te}^{4+}$  may occupy large, irregularly-coordinated sites like  $\text{Pb}^{2+}$ , also a cation with a stereoactive lone pair,  $\text{Te}^{6+}$  readily enters octahedral sites, and so behaves analogously to W in raspite or V in  $\text{TeVO}_4$ . The raspite structure is a monoclinically sheared derivative of the pucherite type, in which the anion arrangement is strongly perturbed away from hexagonal close-packing and the larger cation is irregularly 7-coordinated. The  $P2_1/a$  axial setting can be related back to the  $Pbcn$  setting of pucherite through the relations  $\mathbf{x}_{\text{puch}} = \mathbf{z}_{\text{rasp}}$ ,  $\mathbf{y}_{\text{puch}} = [101]_{\text{rasp}}$  and  $\mathbf{z}_{\text{puch}} = \mathbf{y}_{\text{rasp}}$ ; a pucherite-like cell for raspite would have space group  $P112_1/n$ ,  $a = 5.59 \text{ \AA}$ ,  $b = 13.03 \text{ \AA}$ ,  $c = 5.02 \text{ \AA}$  and  $\beta = 96.1^\circ$  (Fig. 43).  $\text{KTeO}_3(\text{OH}) \equiv \text{K}_2[\text{Te}_2\text{O}_6(\text{OH})_2]$  (#651) has similar cell parameters to #646–649 and a very similar arrangement of Te chains, although chains in successive layers  $\parallel (020)$  are translated by  $\frac{1}{2}a$  relative to their positions in the pucherite structure, the K atoms are near positions that are vacant octahedra of  $(\text{Ca}, \text{Sr})\text{TeO}_4$  and are in 7- rather than 6-coordination, and the symmetry is monoclinic  $P2_1/a$ , but this time not as a subgroup of pucherite symmetry.  $(\text{NH}_4)\text{TeO}_3(\text{OH})$  (#652) has a triclinic distortion of this structure with  $\mathbf{x}_{\text{orth}} = [011]_{\text{icl}}$  and  $\mathbf{y}_{\text{orth}} = [01\bar{1}]_{\text{icl}}$ .

The corner sharing *zweier* chains  $\text{Te}_2\text{X}_{10}$  of the present study all have their bridging oxygen atoms *trans* to each other across a Te octahedron, but zigzag nevertheless due to having non-linear Te–O–Te links (Fig. 13g).  $\text{KTeO}_2(\text{OH})_3 \equiv \text{K}_2[\text{Te}_2$

$\text{O}_4(\text{OH})_6]$  (#653) has such chains running  $\parallel \mathbf{z}$  of the tetragonal structure, with bridging oxygen atoms disordered on a quadruply split site. Large square channels between the chains accommodate  $\text{K}^+$  ions in 8-fold coordination.  $\text{NaBiTeO}_5 \equiv \text{Na}_2\text{Bi}_2[\text{Te}_2\text{O}_{10}]$  (#654) has *zweier*  $\text{Te}_2\text{O}_{10}$  chains running  $\parallel \mathbf{x}$ , which form a pseudohexagonal array. Sodium and Bi atoms occupy trigonal prismatic interstices between Te atoms; both form zigzag chains  $\parallel \mathbf{z}$ , and are ordered in a checkerboard fashion. The  $\text{Te}(\text{NaBi})$  cation array is similar but not identical to the ordered form of the  $\text{CeCu}_2$  type (Larson and Cromer, 1961), apart from the strong monoclinic shear ( $\beta = 106.8^\circ$ ) of the structure in #654. The oxygen coordination number of both Na and Bi is 7 (Fig. 43). The mineral ottoite,  $\text{Pb}_2\text{TeO}_5 \equiv \text{Pb}_4[\text{Te}_2\text{O}_{10}]$  (#655) has a very similar structure but with monoclinic shear much smaller ( $\beta = 91.3^\circ$ ) and in a different direction ( $\mathbf{y}$  and  $\mathbf{z}$  are reversed relative to #654) and Na and Bi positions merged into a single Pb site (Fig. 43). The Pb is in irregular 7-coordination ( $\text{Pb–O} = 2.37, 2.37, 2.53, 2.59, 2.71, 2.88$  and  $3.04 \text{ \AA}$ ; no others at  $<3.4 \text{ \AA}$ ).  $\text{Hg}_2\text{TeO}_5$  (#656) has cell parameters quite close to those of ottoite, and the structure looks very similar in projection down  $\mathbf{x}$ . However, the symmetry is now orthorhombic ( $Pna2_1$ ). The Te chains are displaced along  $\mathbf{x}$  so that the Te substructure has elongate octahedral and tetrahedral interstices rather than trigonal prismatic ones, and Hg atoms are split into two distinct types, both of which lie at the centres of Te triangles. Both Hg atoms have 7 oxygen neighbours within  $3.1 \text{ \AA}$ , but the bond-length variation is such that Hg1 coordination is best regarded as plane-triangular ( $\text{Hg–O}$  at  $2.13, 2.21$  and  $2.31 \text{ \AA}$ ; no more until  $2.49 \text{ \AA}$ ) and Hg2 as linear 2-coordinate ( $\text{Hg–O}$  at  $2.07$  and  $2.08 \text{ \AA}$ , with no more until  $2.53 \text{ \AA}$ ). Because of the large bond valence of the short Hg–O bonds, this structure is regarded as having a Hg–Te heteropolyhedral framework.

$\text{Ag}_3\text{TeO}_4\text{I} \equiv \text{Ag}_9[\text{Te}_3\text{O}_{12}]\text{I}_3$  (#657) has an edge-sharing *dreier* chain  $\text{Te}_3\text{X}_{12}$  in which again the shared edges are not *trans* (Fig. 13h). The chains spiral helically  $\parallel \mathbf{y}$ , and are surrounded by nine types of  $\text{Ag}^+$  ion so as to form thick layers  $\parallel (200)$ , with  $\Gamma^-$  anions in the interlayer gaps. Ag atoms are irregularly coordinated by  $3 \text{ O} + \text{I}, 2 \text{ O} + 2 \text{ I}, \text{O} + 3 \text{ I}$  or  $2 \text{ O} + \text{I}$ .  $\text{K}_2[\text{Te}_3\text{O}_8(\text{OH})_4]$  and its  $\text{NH}_4$  analogue (#658–659) have a quite different  $\text{Te}_3\text{X}_{12}$  chain, with a  $\text{Q}^{2400}$  octahedron alternating with a pair of  $\text{Q}^{2401}$  octahedra to make a loop-branched *zweier* type as seen in Fig. 13i. This chain represents a condensation of the ‘double triangle’ cluster that is

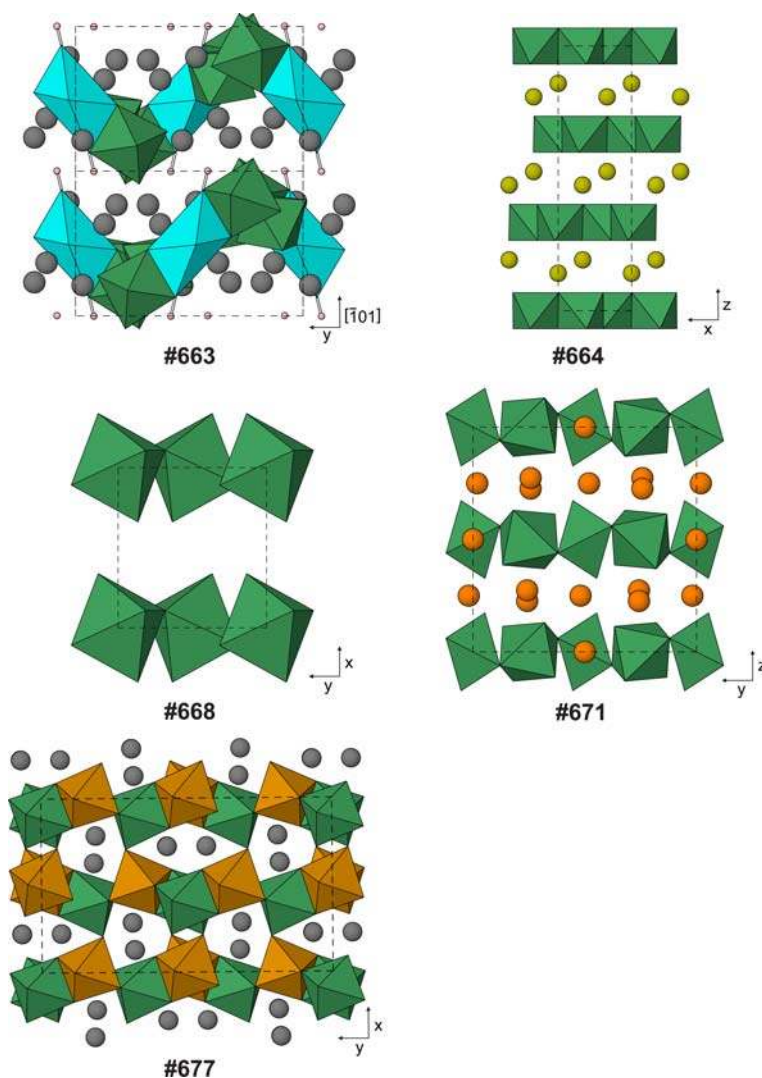


FIG. 44. Examples of structures with  $\text{TeO}_6$  linked to form infinite layers or frameworks (Table 25, deposited). Small spheres: H (pale pink). Large spheres: Ca (orange), Li (pale blue), Na (dark yellow) and Pb (grey). Polyhedra: Cu (cyan), Fe (orange-brown) and Te (dark green). There is substantial Fe–Te disorder in **#677**.

seen in isolation in  $\text{K}_2[\text{Te}_4\text{O}_8(\text{OH})_{10}]$  (**#644**, Fig. 13*d*). Eight such chains per unit cell run  $\parallel z$  and pack in a herringbone arrangement, held together by large cations in 8-coordination (Fig. 43). Similar chains of double triangles occur in  $\text{Ag}_2\text{TeO}_4 \equiv \text{Ag}_6[\text{Te}_3\text{O}_{12}]$  (**#660**) and  $\text{Ag}_2[\text{Hg}_2(\text{Te}_3\text{O}_{12})]$  (**#661**). In the first of these compounds, the pseudotetragonal cell has chains that lie in layers  $\parallel (002)$ , and chains run  $\parallel [110]$  or  $[\bar{1}\bar{1}0]$  in alternate layers. Silver atoms lie between the layers in 2–4 coordination. In **#661**, the Te

chains all are  $\parallel x$ , and linear 2-coordinated  $\text{Hg}^{2+}$  link the chains to form layers  $\parallel (002)$ . Ag atoms lie between the layers in irregular 6-coordination.

$\text{Li}_2\text{TeO}_4 \equiv \text{Li}_8[\text{Te}_4\text{O}_{12}]$  (**#662**) has a chain that is the *vierer* analogue of the *dreier* chain in **#657**. This time, the nonlinear  $\text{Te}=\text{Te}=\text{Te}$  links result in a helical chain with periodicity four (Fig. 13*j*), which spirals around a screw tetrad axis in the structure, winding through a matrix of  $\text{LiO}_4$  tetrahedra. Our final inotellurate is the mineral housleyite,  $\text{Pb}_6[\text{Cu}(\text{Te}_4\text{O}_{18}(\text{OH})_2)]$  (**#663**), in which the *vierer* chain is

entirely corner-sharing, but differs from the *zweier* chain of *ottoite* (#655) in that there is alternation of Te octahedra with *trans* bridging oxygen atoms and octahedra with *cis* bridging oxygen atoms (Fig. 13*k*). Tellurium chains run  $\parallel$  [101], and are linked through  $\text{CuO}_{4+2}$  polyhedra to form corrugated layers  $\parallel$  (10 $\bar{1}$ ). Copper shares corners with two adjacent Te octahedra in the chains on each side, to make a pair of [Cu–Te–Te] 3-rings (Fig. 44). The four shortest Cu–O distances are 1.96–1.97 Å; two more neighbours at 2.65 Å complete an elongated octahedron, and further brace the structural layer. Pb atoms in irregular 7–8 coordination decorate the outsides of the layers and link them. Fortuitously, the structure has a pseudotetragonal aspect in projection down *x*, with the Te atoms appearing to form an apophyllite-like net of 4- and 8-rings, but the component Te chains are linked only through Cu atoms, so this pattern has little structural significance.

### Phyllotellurates

The simplest layer tellurates have an edge-sharing dioctahedral sheet  $\text{MX}_3$  of the topology seen in gibbsite and other polymorphs of  $\text{Al}(\text{OH})_3$  (Fig. 14*a*). Note that a  $\text{Te}^{6+}\text{O}_3$  sheet would be electrostatically neutral and that a protonated sheet would be charged positively. In all the cases described here, some of the *M* cations are a different element of lower valence than Te, thus achieving a negative charge on the sheet. What is unusual is that even though the two elements are present in a 50:50 ratio in all cases, there is no evidence for long-range three-dimensional order of the cations. It is quite feasible that two-dimensional order occurs within the layers, but the *M* cations are treated as disordered here in the absence of experimental evidence to the contrary. The isostructural pair  $\text{Na}_2[(\text{GeTe})\text{O}_6]$  (#664) and  $\text{Na}_2[(\text{TiTe})\text{O}_6]$  (#665) have the ilmenite ( $\text{FeTiO}_3$ ) structure, which is in turn a superstructure of the corundum type. Oxygen atoms are *hcp*, and between each pair of layers,  $\frac{2}{3}$  of the octahedral interstices are occupied either by Na or by disordered ( $\text{M}^{4+} + \text{Te}^{6+}$ ). Discrete layers  $\parallel$  (003) can be identified as structural units because of the weakly bonded Na layers that lie between them (Fig. 44). Brizziite,  $\text{NaSb}^{5+}\text{O}_3$ , is compositionally close and shares the same structure (Olmi and Sabelli, 1994). A superstructure of the ilmenite type, in which additional cation ordering results in isolated  $\text{TeO}_6$  octahedra, occurs for  $\text{Ni}_3(\text{TeO}_6)$  and its relatives, discussed as #599–601 above.

Burckhardtite,  $\text{Pb}_2[(\text{Fe}^{3+}\text{Te}^{6+})\text{O}_6][\text{AlSi}_3\text{O}_8]$  (#666) has  $[(\text{Fe}^{3+}\text{Te}^{6+})\text{O}_6]^{3-}$  layers of the same type, alternating with aluminosilicate double layers  $[\text{AlSi}_3\text{O}_8]^-$  of the topology seen in minerals such as cymrite,  $\text{Ba}[\text{Al}_2\text{Si}_2\text{O}_8] \cdot \text{H}_2\text{O}$  (Drits *et al.*, 1975).

$\text{Sr}[(\text{Mn}^{4+}\text{Te}^{6+})\text{O}_6]$  (#667) has a hexagonal cell with a parameter similar to those of #664–666, and a *c* parameter suggesting that it might be isotypical with *rosiaite*-type compounds such as  $\text{Sr}[\text{Ge}(\text{TeO}_6)]$  (#521 above), in which layers of Sr octahedra alternate with layers of ( $\text{M}^{4+} + \text{Te}$ ). However, the structural refinement reveals that Mn and Te are disordered in trigonal prisms (Fig. 14*b*) rather than in octahedra, which is reflected in the different space group,  $P\bar{6}2m$  as opposed to  $P\bar{3}1m$  for disordered *rosiaite* (e.g.  $\text{Pb}[\text{Sb}_2\text{O}_6]$ ) or  $P312$  for ordered *rosiaite* (#521).

$[\text{TeO}_2(\text{OH})_2]$  (#668) has  $\text{TeX}_6$  octahedra sharing four corners with neighbours to form a slightly crumpled square net (Fig. 14*c*). The layers are  $\parallel$  (100), and are held together only by hydrogen bonds (Fig. 44).  $(\text{Bi}_2\text{O}_2)[\text{TeO}_4]$  (#669) has topologically similar but geometrically more regular square layers  $\parallel$  (020), which intercalate with cationic sheets  $[\text{Bi}_2\text{O}_2]^{2+}$  which have the litharge structure (Boher *et al.*, 1985). The two types of unit are held together by long  $\text{Bi}\cdots\text{O}$  bonds.  $[\text{Cu}(\text{TeO}_4)]$  (#670) also has square  $[\text{TeO}_4]^{2-}$  layers  $\parallel$  (020), but corner-sharing chains of  $\text{CuO}_4$  squares run  $\parallel$  [101] that share edges with  $\text{TeO}_6$  octahedra above or below to link the whole structure into a strongly-bonded framework. The four shortest Cu–O are in the range 1.90–2.12 Å, but the Jahn–Teller elongation of the  $\text{CuO}_{4+2}$  octahedron is unusually small, as the next neighbours are at only 2.22–2.26 Å. Alternation of  $\text{Te}^{6+}$  with  $\text{U}^{6+}$  in a square-net layer such as those of #668–670 produces the heteropoly structural layer of markcooperite (#544–545 above).

$\text{Ca}_5[\text{Te}_3\text{O}_{14}]$  (#671) has more complex corner-sharing layers of the type shown in Fig. 14*d*, with  $\text{Q}^{2400}$  and  $\text{Q}^{4200}$  octahedra. It is isotypical with chiolite,  $\text{Na}_5[\text{Al}_3\text{F}_{14}]$  (Jacoboni *et al.*, 1981), although with a slight orthorhombic distortion (chiolite is tetragonal,  $P4/mnc$ ). This compound thus represents another valence-doubled structural analogy between tellurates and hexafluoroaluminates, along with examples such as the perovskite-superstructure phases  $\text{Ca}_3\text{TeO}_6$  (#561) and cryolite,  $\text{Na}_3\text{AlF}_6$  (Hawthorne and Ferguson, 1975),  $\text{Ba}_2\text{CaAlF}_6$  (#571) and elpasolite,  $\text{K}_2\text{NaAlF}_6$  (Sabelli, 1987), and the gamet-structure minerals yafsoanite,  $\text{Ca}_3\text{Zn}_2(\text{TeO}_6)_2$  (#587) and cryolithionite,  $\text{Na}_3\text{Li}_2(\text{AlF}_6)_2$  (Geller, 1971). In #671, tellurate

layers are  $\parallel$  (002), with CN7–8  $\text{Ca}^{2+}$  ions lying between them (Fig. 44). Other fluoride-tellurate analogies were noted in the discussion of Fig. 14f–g, above.

### Tectotellurates

$[(\text{Co}^{2+}\text{Te}^{6+})\text{O}_4]$  and its Ni analogue (#672–673) have long-range disorder of the divalent cation and Te in octahedral sites, similar to the situation in the phyllostellurates #664–667 above. However, in these compounds, the octahedra share two *trans* edges and all corners to form a framework with the same topology as the rutile form of  $\text{TiO}_2$ , but a strong monoclinic distortion (Fig. 14e). Thus, they are isostructural with tugarinovite,  $\text{Mo}^{4+}\text{O}_2$  (Brandt and Skapski, 1967). The pseudotetrad direction is  $\mathbf{x}$ , while vectors [010] and  $[\frac{1}{2}01]$  correspond to the  $\mathbf{x}$  and  $\mathbf{y}$  lattice vectors of the tetragonal rutile cell.  $[\text{TeO}_3]$  (#674) has the rhombohedral  $\text{FeF}_3$  type of structure (Hepworth *et al.*, 1957) in which an octahedron shares each corner with a different neighbour (Fig. 14f). Topologically, the structure is the same as that of the cubic defect perovskite  $\text{ReO}_3$ , but the Te–O–Te angles are reduced from  $180^\circ$  so as to collapse the structure and achieve approximate hexagonal packing of oxygen atoms. These and other related structures are discussed by Hyde and Andersson (1989), and an analogous relationship between stuffed variants of these structures, namely the ilmenite/corundum structure and  $ABX_3$  perovskite, was discussed in connection with  $\text{Ni}_3\text{TeO}_6$  and its isotypes, #599–601 above.  $\text{Na}_2[\text{Te}_2\text{O}_7]$  and its Ag analogue (#675–676) have the same framework as weberite,  $\text{Na}_2(\text{MgAlF}_7)$  (Knop *et al.*, 1982), depicted in Fig. 14g. The extra-framework cations are in similar environments, Na having eight oxygen neighbours at 2.26–2.79 Å while Ag–O distances are in the range 2.39–2.81 Å.  $\text{Pb}_3[\text{Fe}_2^{3+}\text{Te}_2\text{O}_{12}]$  (#677) has partial ordering of Fe and Te on four distinct octahedral sites. Te1 and Te2 are  $(\text{Te}_{0.75}\text{Fe}_{0.25})$ , while ‘Te3’ and ‘Te4’ are actually  $(\text{Fe}_{0.75}\text{Te}_{0.25})$ . Tellurium- and Fe-rich octahedra are related via a pseudo-*a*-glide reflection  $\parallel$  (002). Here, all are considered as of equal status in the structural unit. Te-dominant and Fe-dominant octahedra alternate in the unique framework of Fig. 14h, which is strongly layered  $\parallel$  (200). Within a layer, zigzag *zweier* chains of Te2 and Te4 alternate, both running  $\parallel$   $\mathbf{z}$ . The Te1 atoms share corners to make 3-ring loops on the Te4 chains, while Te3 do the same for the Te2 chains. The Te1 of one chain and Te3 of an adjacent chain then share edges, so as to make 8-rings and complete the layer, and the

layers are bridged further to link them in three dimensions through additional Te1–Te3 and Te2–Te4 links, which create 4- and 6-rings. The Pb atoms in 7–8 lie between the dense layers coordination (Fig. 44).

### Mixed-valence $\text{Te}^{4+}$ and $\text{Te}^{6+}$

Table 26 (deposited) lists structures #678–703, which feature Te in both +4 and +6 valence states. The first of these compounds,  $[\text{Co}_6^{2+}(\text{Te}^{6+}\text{O}_6)(\text{Te}^{4+}\text{O}_3)_2\text{Cl}_2]$  (#678) is a somewhat trivial example in that it contains isolated  $[\text{Te}^{6+}\text{O}_6]^{6-}$  octahedra and  $[\text{Te}^{4+}\text{O}_3]^{2-}$  trigonal pyramids. However, the structure is related closely to the interesting schafarzikite–apuanite–versiliaite polysomatic series of minerals. Schafarzikite,  $\text{Fe}^{2+}\text{Sb}_2^{3+}\text{O}_4$ , is isostructural with minium,  $\text{Pb}^{4+}\text{Pb}_2^{3+}\text{O}_4$  (Fischer and Pertlik, 1975; Gavarri and Weigel, 1975) and has rutile-like edge-sharing chains of octahedra containing  $\text{Fe}^{2+}$  running  $\parallel$   $\mathbf{z}$ , connected through chains of corner-sharing lone-pair cations,  $[\text{Sb}_2\text{O}_4]^{2-}$ . The overall structure has the same tetragonal space group  $P4_2/mbc$  as #678,  $a = 8.59$  Å and  $c = 5.91$  Å. A series of additional phases is produced if some pairs of  $\text{Sb}^{3+}$  ions and their lone pairs ( $\text{Sb}^{3+} \cdot \cdot \text{Sb}^{3+}$ ) are replaced by  $(\text{Fe}^{3+} \cdot \cdot \text{S} \cdot \cdot \text{Fe}^{3+})$  bridges, with oxidation of some octahedral  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  in order to maintain electroneutrality (Mellini and Merlino, 1981). Chemically, the maximally substituted end-member, with all Fe oxidized, would be  $(\text{Fe}_2^{3+})(\text{Sb}_2\text{Fe}_2^{3+})\text{O}_8(\square\text{S})$ . Versiliaite, with a  $c$  parameter doubled relative to schafarzikite and with orthorhombic symmetry, represents 50% substitution,  $(\text{Fe}_2^{3+}\text{Fe}_2^{3+})(\text{Sb}_6\text{Fe}_2^{3+})\text{O}_{16}(\square_3\text{S})$ , while apuanite, with a tripled  $c$  parameter and  $P4_2/mbc$  symmetry, has the 67% substituted composition,  $(\text{Fe}^{2+}\text{Fe}_2^{3+})(\text{Sb}_4\text{Fe}_2^{3+})\text{O}_{12}(\square_2\text{S})$ . Compound #678 has very similar cell parameters to apuanite (for which  $a = 8.37$  and  $c = 17.97$  Å) and is nearly isotypical with it, as evident if its formula is written  $(\text{Te}^{6+}\text{Co}_2^{2+})(\text{Co}_4^{2+}\text{Te}_2^{4+})\text{O}_{12}(\text{Cl}_2\square)$ . It thus represents an intermediate member of a series between two hypothetical end-members, with the interesting complication that it is not possible to write a formula that both makes crystal-chemical sense and is electrostatically neutral. The extreme compositions that correspond to those of the schafarzikite family are  $[\text{Te}^{6+}\text{Co}_2^{2+}\text{O}_4\text{Cl}]^{1+}$  and  $[\text{Co}_2^{2+}(\text{Co}_2^{2+}\text{Te}_2^{4+})\text{O}_{12}(\text{Cl}\square)]^{1-}$ . The ordering of Co and Te is consistent with these, such that octahedral  $\text{Co}^{2+}$  is closely associated with pyramidal  $\text{Te}^{4+}$ , while octahedral  $\text{Te}^{6+}$  is close to tetrahedral  $\text{Co}^{2+}$ . The



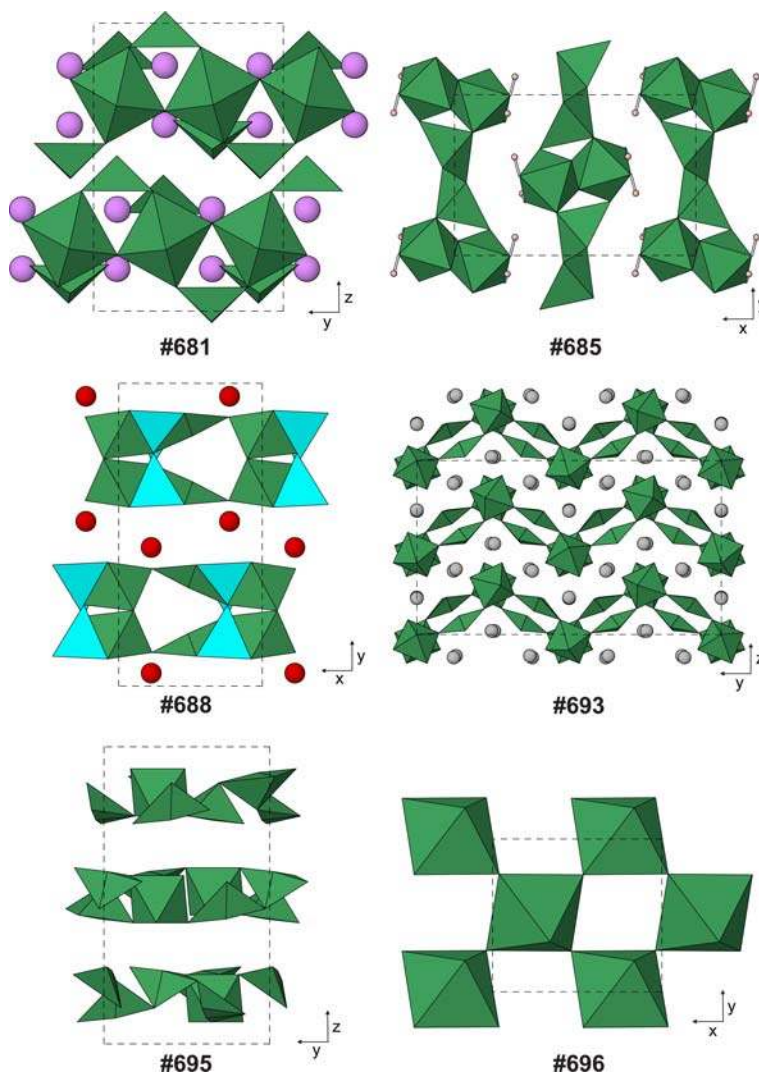


FIG. 45. Examples of structures containing both  $\text{Te}^{4+}$  and  $\text{Te}^{6+}$  (Table 26, deposited). Small spheres: H (pale pink). Large spheres: Cd (purple-pink), Hg (pale grey) and Sr (red). Polyhedra: Cu (cyan) and Te (dark green). The Te layers of **#693** are further linked into a framework through linear O–Hg–O links, which are not shown for clarity. The  $\text{Te}^{6+}$  cations are in nearly regular octahedra; the  $\text{Te}^{4+}$  cations are not.

structure of emmonsite,  $[\text{Fe}_2^{3+}(\text{H}_2\text{O})(\text{Te}^{4+}\text{O}_3)_3]$  (**#137**, above) is closely related.

It is noteworthy that there are no structures in which  $\text{Te}^{4+}$  and  $\text{Te}^{6+}$  polyhedra are linked together into a finite Te–O complex. The simplest Te–O polymers that contain both valence states are infinite chains. In  $\text{Bi}[(\text{Bi}^{3+}\text{Te}^{4+})\text{Te}^{6+}\text{O}_8]$ , **#679**, half of the Bi atoms occupy 8-coordinated sites (Bi1), while the other half (Bi2) randomly share a split site with Te2. The Bi atoms are displaced by

$\sim 0.38 \text{ \AA}$  from the Te position, so as to acquire an additional oxygen neighbour. The lone-pair cations and  $\text{Te}^{6+}$  link to form as a structural unit the loop-branched *zweier* chain of Fig. 15a. Note that this is a mixed-valence version of the chain that occurs in  $\text{K}_2[\text{Te}_3^{6+}\text{O}_8(\text{OH})_4]$  (**#658**, Fig. 13i), and that both are built from the very frequently occurring ‘double-triangle’ clusters. In **#679**, chains lie in layers  $\parallel (002)$ , and chains of alternate layers run either  $\parallel [110]$  or  $\parallel [\bar{1}\bar{1}0]$ . The Bi1 cations lie

between the chains and link them. Interestingly, Bi1 and octahedral Te1 also lie in layers, this time  $\parallel$  (200), and form a square net in which  $\text{TeO}_6$  octahedra share two *trans* edges with Bi atoms, and the remaining corners with another two Bi atoms. Layers of (Bi2, Te2) alternate with those of (Bi1 + Te1). The structure can be regarded as an extreme derivative of the fluorite type, given the 1:2 cation:oxygen ratio, and the fact that cations lie in an approximate *ccp* array with pseudocube edge vectors  $[00\frac{1}{2}]$ ,  $[010]$  and  $[\frac{1}{4}0\frac{1}{2}]$  of the monoclinic cell, with lengths respectively 5.14, 5.56 and 5.82 Å.

$\text{Cd}_2\text{Te}^{4+}\text{Te}^{6+}\text{O}_7 \equiv \text{Cd}_4[\text{Te}^{4+}\text{Te}_2^{6+}\text{O}_{11}](\text{Te}^{4+}\text{O}_3)$  (#680) has two types of  $\text{Te}^{4+}$  (Te1 and Te3) and of  $\text{Te}^{6+}$  (Te2 and Te4). The  $\text{Te}^{6+}$  octahedra form the backbones of *zweier* chains  $\parallel \mathbf{x}$ , with Te3 attached to them to form 3-ring loops (Fig. 15b). The independent Te1 atom forms pyramidal  $[\text{TeO}_3]^{2-}$  anions that lie between the loops. Te–O anions are embedded in a matrix of edge-sharing  $\text{CdO}_{6-8}$  polyhedra.  $\text{Cd}_2\text{Te}_2^{4+}\text{Te}^{6+}\text{O}_9 \equiv \text{Cd}_4[\text{Te}_2^{4+}\text{Te}_2^{6+}\text{O}_{12}](\text{Te}^{4+}\text{O}_3)_2$  (#681) is rather similar, although the *zweier* tellurate chain is  $\parallel \mathbf{y}$ , has twice as many 3-ring loops (Fig. 15c) and twice as many associated but separate tellurite pyramids. The chains lie *en échelon* in well-defined layers  $\parallel$  (100), which alternate with layers of edge-sharing  $\text{CdO}_7$  polyhedra (Fig. 45). The tendency of  $\text{Cd}^{2+}$  ions to form rather complex structures was noted previously (#327 and 334, above).

$(\text{NH}_4)[\text{Te}^{4+}\text{Te}^{6+}\text{O}_5(\text{OH})]$  (#682) has infinite Te–O layers  $\parallel$  (002) in which  $\text{Te}^{6+}\text{O}_6$  octahedra share corners to form *zweier* chains  $\parallel \mathbf{x}$ , and CN5  $\text{Te}^{4+}$  share corners with two octahedra from each of a pair of chains to form a net with 3- and 4-rings (Fig. 15d). Thus, the layer contains looped chain elements similar to the anions of #680–681.  $\text{Te}^{6+}$  octahedra are  $Q^{0600}$ , while  $\text{Te}^{4+}$  polyhedra are  $Q^{1400}$  in connection pattern.  $\text{NH}_4^+$  cations lie between the layers. The  $\text{OH}^-$  group was not located, but is presumably the unique non-bridging anion attached to  $\text{Te}^{4+}$ .  $\text{Ba}[\text{Te}^{4+}\text{Te}^{6+}\text{O}_6]$  (#683) has a topologically identical Te–O layer  $\parallel$  (020), with  $\text{Te}^{6+}$  chains running  $\parallel \mathbf{z}$ . The  $\text{Ba}^{2+}$  ions between the layers are in 10-coordination. The third structure with this layer topology is polymorph II of  $\text{Ag}_2[\text{Te}^{4+}\text{Te}^{6+}\text{O}_6]$  (#684). In this monoclinic structure, the Te–O layers are  $\parallel$  (001) with  $\text{Te}^{6+}$  chains  $\parallel \mathbf{y}$ , and layers are connected through sheets of  $\text{Ag}^+$  ions in irregular 6-fold coordination. Two other polymorphs are described below (#686–687).  $[\text{Te}^{4+}\text{Te}^{6+}\text{O}_4(\text{OH})_2]$  (#685) has layers  $\parallel$  (200) which again contain *zweier* chains of  $\text{Te}^{6+}$  octahedra (Te1),  $\parallel \mathbf{z}$  this time,

and have  $\text{Te}^{4+}$  (Te2) polyhedra making 3-rings with adjacent pairs of octahedra. However, the layer is completed by  $\text{Te}^{4+}$  polyhedra linking to each other, to form (Te1–Te2–Te2–Te2–Te1) 5-rings (Fig. 15e) (Fig. 45). The polymerization state of Te1 is  $Q^{2400}$  while that of Te2 is  $Q^{0400}$ ; the hydrogen atoms are located on the non-bridging ligands of Te1, with layers held together via both hydrogen bonds and long  $\text{Te}2\cdots\text{O}$  interactions. The polarity of the structure along  $\mathbf{z}$  is due to the orientation of both O–H groups and  $\text{Te}^{4+}$  lone pairs. Polymorphs I and III of  $\text{Ag}_2[\text{Te}^{4+}\text{Te}^{6+}\text{O}_6]$  (#686–687) have layer topologies that are quite distinct from each other and from that of polymorph II (#684). In polymorph I, layers are  $\parallel$  (10 $\bar{1}$ ) and contain ‘double-triangle’ clusters of  $Q^{1501}$   $\text{Te}^{6+}$  and  $Q^{1300}$   $\text{Te}^{4+}$ , which link to form a net which has 8-rings as well as 3-rings (Fig. 15f). Note that the positions of  $\text{Te}^{4+}$  and  $\text{Te}^{6+}$  in the double triangle are reversed relative to their locations in the chain of  $\text{Bi}[(\text{Bi}^{3+}\text{Te}^{4+})\text{Te}^{6+}\text{O}_8]$  (#679, Fig. 15a). Sheets of edge- and face-sharing  $\text{AgO}_{6-7}$  polyhedra lie between the Te–O layers. The Te–O layer of polymorph III is very similar, but is oriented  $\parallel$  (100) in its structure, and an additional short  $\text{Te}^{4+}$ –O distance of 2.41 Å renders all oxygen ligands as ‘bridging’ and breaks the 8-rings into pairs of 4-rings (Fig. 15g). The  $\text{Ag}^+$  ions between the layers are in irregular 5–6 coordination.

There are a number of polytypical compounds with the formula  $A^2+[M^{2+}(\text{Te}^{4+}\text{Te}^{6+}\text{O}_7)]$ , where  $A = \text{Sr}$ ,  $\text{Pb}$  or  $\text{Ba}$  and  $M = \text{Cu}$  (#688–690),  $\text{Mg}$  (#691) or  $\text{Zn}$  (#692). All structures have similar-sized unit cells. The symmetries are primitive but centrosymmetric *Pbcm* for one polytype (#688–689) or centred but without inversion symmetry for the other (#688–689); the *Ama2* space group used for the latter subgroup has  $\mathbf{x}$  and  $\mathbf{z}$  directions reversed relative to the *P* subgroup, and would be written *C2cm* in the same axial setting. In #688,  $Q^{2400}$   $\text{Te}^{6+}$  octahedra (Te1) share *cis* corners to form zigzag *zweier* chains  $\parallel \mathbf{z}$ . Each octahedron also shares another pair of *trans* corners with  $Q^{2200}$   $\text{Te}^{4+}$  (Te2) to make zigzag chains  $\parallel \mathbf{x}$ , thus forming strongly corrugated layers  $\parallel$  (020) with four 6-rings meeting at each  $\text{Te}^{6+}$  cation (Fig. 15h). The *M* cations, Cu in this case, are in square-pyramidal 5-fold coordination above or below the Te sheet, and share corners with three Te1 atoms of one chain and two adjacent Te2 atoms, producing a structural unit that is a rather dense double layer (Fig. 45). The positioning of the Cu atoms is the main topological factor that gives the layer a polarity along the  $\mathbf{x}$  direction. The  $\text{Sr}^{2+}$  ions lie between the layers in 10-coordination. In this

polytype, layers stack along *y* so that Te1 chains of successive layers superpose, but the polarity along *x* reverses from layer to layer. In the *C2cm* polytype, there is a displacement of  $\frac{1}{2}a$  between adjacent layers, but the polarity is the same for all of them. The  $\beta$  and  $\alpha$  polymorphs of  $[\text{Hg}_2^{2+}(\text{Te}^{4+}\text{Te}^{6+}\text{O}_7)]$  (**#693–694**) also have Te–O layers with the topology of Fig. 15*h*. The layer in the  $\beta$  phase is corrugated very similarly to that of **#688–692**, while that of the  $\alpha$  phase is much flatter, as the  $\text{Te}^{6+}$  octahedra are connected through *trans* corners. The  $\beta$  phase (**#693**) has layers  $\parallel (002)$ , with chains of  $\text{Te}^{6+}$  running  $\parallel x$ . There are five types of Hg atoms between the layers, linking them into a framework. All Hg atoms have two close oxygen neighbours at 2.03–2.31 Å. However, while there is a distinct gap in distances before next-nearest neighbours for Hg1, Hg2 and Hg4, this is not true for Hg3 or Hg5, which have six neighbours in the ranges 2.24–2.38 and 2.30–2.36 Å, respectively (Fig. 45). This wide range of stereochemistries for Hg in the same compound is not unusual. Mercury and Te atoms form approximately close-packed layers  $\parallel (080)$ , which form two repeats of the four-layer *ABCB* sequence along *y*. Within each layer, Te and Hg alternate in the *z* direction, while  $\text{Te}^{4+}$  and  $\text{Te}^{6+}$  alternate along *y* in the corrugated Te layers. In the  $\alpha$  phase (**#694**), layers are  $\parallel (20\bar{2})$  with  $\text{Te}^{6+}$  chains  $\parallel y$ . Mercury atoms between the layers are of four different types, each with two close oxygen neighbours at 2.05–2.28 Å and no more until 2.40–2.73 Å. Mercury and Te atoms lie on a *ccp* array, ordered layer-wise in a CuAu-type fashion. Cubic pseudocell edge vectors are  $[\frac{1}{4}\frac{1}{2}\frac{1}{4}]$  and  $[\frac{1}{4}\frac{1}{2}\frac{1}{4}]$  (5.20 Å long) and  $[\frac{1}{4}0\frac{1}{4}]$  (5.43 Å), with layers of Hg and Te alternating  $\parallel (20\bar{2})$  and  $\text{Te}^{4+}$  and  $\text{Te}^{6+}$  alternating along  $[101]$  within the Te layers.

$[\text{Te}_3^{4+}\text{Te}^{6+}\text{O}_9]$  (**#695**) has a rhombohedral structure with layers  $\parallel (003)$  of the form shown in Fig. 15*i*. Rings of six  $\text{Q}^{0400}$   $\text{Te}^{4+}$  polyhedra surround  $\frac{1}{3}$  of the triad axes, which are linked through  $\text{Q}^{0600}$   $\text{Te}^{6+}$  octahedra which are located on the remaining triads. The resulting net has 3-, 4- and 6-rings, such that the ring pattern around  $\text{Te}^{4+}$  is 6.3.4.3, while that around  $\text{Te}^{6+}$  is 3.4.3.4.3.4. Layers are held together only through long  $\text{Te}^{4+}\cdots\text{O}$  bonds (Fig. 45).

$[\text{Te}^{4+}\text{Te}^{6+}\text{O}_5]$  (**#696**), like **#695**, has CN4  $\text{Te}^{4+}$  and CN6  $\text{Te}^{6+}$  sharing all vertices of their coordination polyhedra, but for this compound, the resulting structure is a three-dimensional framework (Fig. 16*a*). The  $\text{Te}^{6+}$  octahedra (Te1) share four vertices with other  $\text{Te}^{6+}$  cations to form sheets of 4-rings  $\parallel (001)$ , as found in **#668–670**.

Half of the Te–O–Te links in these sheets are decorated by  $\text{Te}^{4+}$  (Te2) so as to form (Te1–Te1–Te2) 3-rings, which define loop-branched *zweier* chains (cf. **#681**) running  $\parallel y$ . The Te2 cations associated with adjacent Te1 sheets then share remaining ligands with each other to link the sheets together; thus, the Te2 polyhedra in isolation form corner-sharing chains with a massicot-like geometry (Hill, 1985) (Fig. 45).

Carlfriesite,  $\text{Ca}[\text{Te}_2^{4+}\text{Te}^{6+}\text{O}_8]$  (**#697**) has a nanoporous framework that contains loop-branched *vierer* chains of 4-rings, with  $\text{Q}^{2400}$   $\text{Te}^{6+}$  at the nodes linked through  $\text{Te}^{4+}$  on the loops, that run  $\parallel z$  and are flattened  $\parallel (010)$ . A centred-rectangular array of such chains is linked by  $\text{Te}^{4+}$  of neighbouring chains sharing edges to form a framework with  $\sim 6$  Å wide channels  $\parallel z$ , which contain CN8  $\text{Ca}^{2+}$  ions (Fig. 16*b*) (Fig. 46). The Sr analogue,  $\text{Sr}[\text{Te}_2^{4+}\text{Te}^{6+}\text{O}_8]$  (**#698**) has a quite different tetragonal structure which contains chains of ‘double-triangle’ clusters similar to those in **#679** above (Fig. 15*a*). These chains run  $\parallel z$  and share corners to produce a framework with narrow ( $\sim 4$  Å) channels, which contain CN8  $\text{Sr}^{2+}$  ions (Fig. 16*c*).

The remaining structures all feature Te polyhedra that share corners to form the hexagonal tungsten bronze or kagome net of hexagons and triangles, and all have at least one  $\sim 7.3$  Å unit-cell parameter which corresponds to the repeat unit of that net.  $\text{Ag}_2[\text{Te}_2^{4+}\text{Te}^{6+}\text{O}_{11}]$  (**#699**) has a strongly pseudohexagonal but intrinsically triclinic structure. Te1 and Te2 (CN6  $\text{Te}^{6+}$ ) and Te3 (CN5  $\text{Te}^{4+}$ ) form two layers of kagome type  $\parallel (001)$ , which share corners but are offset relative to each other. These double layers are then linked into a framework via edge-sharing  $\text{Te4} = \text{Te4}$  dimers of CN5  $\text{Te}^{4+}$ , which form additional 3-rings with Te1 and Te3 above and below (Fig. 16*d*). The  $\text{Ag}^+$  ions, in irregular 6–8 coordination, lie in the hexagonal rings of the kagome layers, and between rows of Te4 atoms (Fig. 46).  $\text{Cs}_2[\text{Te}^{4+}\text{Te}_3^{6+}\text{O}_{12}]$  (**#700**) has a rhombohedrally distorted pyrochlore framework (Fig. 16*e*). Both valence states of Te are in nearly regular octahedral coordination, which is extremely unusual for  $\text{Te}^{4+}$ , although it is also found in the pyrochlore  $\text{Pr}_2[\text{Te}_2^{4+}\text{O}_6]\text{O}$  (**#366** above). Note that the lone pair of electrons is not stereochemically active in these compounds. When it occurs, stereoactivity usually causes strong distortion of the  $\text{Te}^{4+}\text{O}_6$  polyhedra (cf. Christy and Mills, 2013). Ordering of  $\text{Te}^{4+}$  and  $\text{Te}^{6+}$  in the octahedral sites is the cause of the symmetry reduction from cubic. As is typical for ‘inverse pyrochlores’, the very large

TABLE 27. Unit-cell data and references for additional minerals, where no structure refinement is available.

Compound (Mineral name)	SG	<i>a</i> /Å	<i>b</i> /Å	<i>c</i> /Å	$\alpha, \beta, \gamma/^\circ$	Reference
Mg <sub>0.5</sub> [(Mn <sup>2+</sup> Fe <sup>3+</sup> )(Te <sup>4+</sup> O <sub>3</sub> ) <sub>3</sub> ] · 4.5H <sub>2</sub> O (Kinichilite)	<i>P</i> <sub>6<sub>3</sub>/m</sub>	9.451(7)	9.451(7)	7.687(9)	90, 90, 120	Miletich (1995 <i>a</i> )
Mg <sub>0.5</sub> [(Ni <sup>2+</sup> Fe <sup>3+</sup> )(Te <sup>4+</sup> O <sub>3</sub> ) <sub>3</sub> ] · 4.5H <sub>2</sub> O (Keystoneite)	<i>P</i> <sub>6<sub>3</sub>/m or <i>P</i><sub>6<sub>3</sub></sub></sub>	9.344(2)	9.344(2)	7.607(3)	90, 90, 120	Miletich (1995 <i>a</i> )
Mg <sub>0.5</sub> [(Zn <sup>2+</sup> Mn <sup>3+</sup> )(Te <sup>4+</sup> O <sub>3</sub> ) <sub>3</sub> ] · 4.5H <sub>2</sub> O (Ilimevite)	<i>P</i> <sub>6<sub>3</sub>/m</sub>	9.40(2)	9.40(2)	7.657(17)	90, 90, 120	Pekov <i>et al.</i> (2015)
Cu(Te <sup>4+</sup> O <sub>3</sub> ) · 2H <sub>2</sub> O (Millsite)	<i>P</i> <sub>2<sub>1</sub>/c</sub>	7.4049(2)	7.7873(2)	8.5217(2)	90, 110.203(3), 90	Rumsey <i>et al.</i> (2016)
[Fe <sub>2</sub> <sup>3+</sup> (H <sub>2</sub> O) <sub>3</sub> (Te <sup>4+</sup> O <sub>3</sub> ) <sub>3</sub> ] · 3H <sub>2</sub> O (Telluromandarinite)	<i>P</i> <sub>2<sub>1</sub>/c</sub>	16.9356(5)	7.8955(3)	10.1678(3)	90, 98.006(1), 90	Back <i>et al.</i> (2011)
(K <sub>1.5</sub> □ <sub>0.5</sub> )(Te <sub>1.25</sub> W <sub>0.25</sub> □ <sub>0.5</sub> )W <sub>5</sub> <sup>6+</sup> O <sub>19</sub> ] (Tewite)	<i>P</i> <i>ban</i>	7.2585(4)	25.8099(15)	3.8177(2)	90, 90, 90	Li <i>et al.</i> (2014)
PbMn <sup>4+</sup> (Te <sup>6+</sup> O <sub>6</sub> ) (Kuranakhite)	orth. <i>C</i> ?	5.11(1)	8.91(1)	5.32(1)	90, 90, 90	Yablokova <i>et al.</i> (1975)
Ca <sub>2</sub> Mn <sub>2</sub> <sup>4+</sup> (Te <sup>6+</sup> O <sub>6</sub> ) <sub>2</sub> · H <sub>2</sub> O (Xocolatlite)	<i>P</i> <sub>2<sub>1</sub>/m</sub> , <i>P</i> <sub>2</sub> , or <i>P</i> <i>m</i>	10.757(3)	4.928(3)	8.492(2)	90, 102.39(3), 90	Grundler <i>et al.</i> (2008)
Pb <sub>3</sub> [Zn <sub>3</sub> (TeO <sub>6</sub> )(VO <sub>4</sub> ) <sub>2</sub> ] (Cheremnykhite)	orth. <i>C</i> ?	8.58(3)	14.86(5)	5.18(3)	90, 90, 90	Kim <i>et al.</i> (1990)
Pb <sub>2</sub> [Cu <sub>2</sub> (Te <sub>2</sub> <sup>6+</sup> O <sub>10</sub> ) · 2H <sub>2</sub> O] (Andychristite)	<i>P</i> $\bar{1}$	5.322(3)	7.098(4)	7.511(4)	83.486(7), 76.279(5), 70.742(5)	Kampf <i>et al.</i> (2016)



$\text{Cs}^+$  cation occupies the  $Y$  site of the  $A_2B_2X_2Y$  pyrochlore pattern, while the CN8  $A$  sites are vacant. The K analogue of #700,  $\text{K}_2[\text{Te}^{4+}\text{Te}_3^{6+}\text{O}_{12}]$  (#701) has a variant of the same structure that is monoclinically sheared. The monoclinic cell axes correspond to the hexagonal axes of #700 as follows:  $\mathbf{a}_{\text{mon}} = [1\bar{1}0]_{\text{hex}}$ ,  $\mathbf{b}_{\text{mon}} = \mathbf{b}_{\text{hex}}$ ,  $\mathbf{c}_{\text{mon}} = [\frac{1}{3}\sqrt{3}z]_{\text{hex}}$ . The distortion reduces the coordination number of  $\text{Te}^{4+}$  from 6 to 5 (Fig. 16f), which allows the lone pair to become stereoactive, and the coordination number of  $\text{K}^+$  decreases from 12 to 10. The compound  $(\text{Na}_{1.6}\text{Ag}_{0.4})[\text{Te}_2^{4+}\text{Te}_3^{6+}\text{O}_{14}]$  (#702) has kagome layers of  $\text{Te}^{6+}$  octahedra  $\parallel (100)$ , which are linked through corner-sharing dimers of CN4  $\text{Te}^{4+}$  polyhedra (Fig. 16g) in a manner reminiscent of the linkage via edge-sharing CN5 dimers in #699 above. Again, the  $\text{Te}^{4+}$  dimers form 3-rings with pairs of  $\text{Te}^{6+}$  octahedra in the kagome layers above and below, and weakly bound 8-coordinated cations (Na,Ag) lie in the hexagonal holes of the kagome net and between the  $\text{Te}^{4+}$  dimers. The ordered distribution of the interlayer (Na,Ag) and an associated undulation of the kagome layers results in the very long ( $\sim 25$  Å)  $b$  repeat (Fig. 46).  $\text{Rb}_4[\text{Te}_3^{4+}\text{Te}_5^{6+}\text{O}_{23}]$  (#703) has a defect pyrochlore superstructure. Intact kagome layers of mixed  $\text{Te}^{4+}$  and  $\text{Te}^{6+}$  polyhedra occur  $\parallel (220)$  and  $(2\bar{2}0)$  of the orthorhombic cell. However, there are also modified kagome layers  $\parallel (201)$  and  $(20\bar{1})$ , with some oxygen atoms missing so as to allow reduction of the  $\text{Te}^{4+}$  coordination number from 6 to 5, and to provide space for accommodation of the stereoactive lone pairs (Fig. 16h). CN8–10  $\text{Rb}^+$  ions occupy the large interstices in the framework.

### Additional tellurium oxyminerals

In the section above on zemannite and related compounds (#131–136), we mentioned the minerals kinichilite, keystoneite and ilirneyite as isostructural with zemannite itself, although their crystal structures have not been published. For completeness, the available data on these species are included in Table 27, along with several other minerals for which refinements are not yet available, but for which some structural details can be deduced. Such species could not be included in the classification above, as quantitative bond-distance data are not available.

Millsite,  $\text{Cu}(\text{Te}^{4+}\text{O}_3) \cdot 2\text{H}_2\text{O}$  (Rumsey *et al.*, 2016), is a new dimorph of teineite (#119) with a unique structure in which  $\text{TeO}_3^{2-}$  pyramids cross-link  $\text{Cu}_2\text{O}_2(\text{H}_2\text{O})_4$  dimers to form a two-dimensional layer. Telluromandarinite

$\text{Fe}_2^{3+}(\text{Te}^{4+}\text{O}_3)_3 \cdot 6\text{H}_2\text{O}$  (Back *et al.*, 2011), is the Te analogue of the selenite mineral mandarinite, and has similar symmetry and unit-cell dimensions. If the two minerals are isostructural, then two symmetrically distinct  $[\text{TeO}_3]^{2-}$  pyramids share corners with  $\text{FeX}_6$  octahedra to form layers  $\parallel (100)$  with 8-rings of alternating Fe and Te, which are bridged by a third type of  $\text{TeO}_3$  group to form a very open  $[\text{M}_2\text{Y}_3(\text{TeX}_3)_3]$  framework with additional water molecules in large cavities (cf. Hawthorne, 1984). Such a structure would follow  $\text{Sb}_2^{5+}\text{O}_3(\text{TeO}_3)_2$  (#147) in our tables. The full description has not yet been published for the mineral tewite,  $(\text{K}_{1.5}\square_{0.5})[(\text{Te}_{1.25}^{4+}\text{W}_{0.25}^{6+}\square_{0.5})\text{W}_5^{6+}\text{O}_{19}]$ , but the W-rich composition suggests that it is a tungsten bronze-like phase containing layers of corner-sharing  $\text{WO}_6$  octahedra, with layers oriented normal to the very short (3.8 Å)  $c$  repeat, along which W–O–W links connect them into a framework. There may be some modification of the kagome net due to replacement of some W by  $\text{Te}^{4+}$  with stereoactive lone-pair electrons, as in structures #699–703 above. Note in particular that  $a \approx 7.3$  Å and  $b \approx 25.8$  Å are very similar to  $a \approx 7.3$  Å and  $b \approx 24.7$  Å for  $(\text{Na}_{1.6}\text{Ag}_{0.4})[\text{Te}_2^{4+}\text{Te}_3^{6+}\text{O}_{14}]$  (#702). However, tewite contains only  $\text{Te}^{4+}$ . It cannot be placed more precisely in our classification without knowledge of the coordination environment of the Te atoms.

Kuranakhite,  $\text{PbMn}^{4+}(\text{Te}^{6+}\text{O}_6)$ , is a long-known mineral (Yablokova *et al.*, 1975) whose structure has never been fully determined. However, its unit cell parameters suggest that it is structurally related to the  $\text{Li}_2[\text{M}^{4+}(\text{TeO}_6)]$  phases #583–585, based upon a *hcp* array of oxygen atoms, but with one  $\text{Pb}^{2+}$  replacing two  $\text{Li}^+$  ions. Grundler *et al.* (2008) suggested that the hydrated Ca analogue xocolatlite was structurally related to kuranakhite, which seems feasible. Cheremnykhite,  $\text{Pb}_3[\text{Zn}_3(\text{TeO}_6)(\text{VO}_4)_2]$ , was noted earlier as probably isotypical with dugganite and kuksite (#550–551), on the basis of its stoichiometry and unit-cell dimensions. However, although it has a strongly pseudo-hexagonal unit-cell metric with  $b = \sqrt{3}a$ , note that its symmetry is reported as orthorhombic,  $Cmmm$ ,  $Cmm2$ ,  $Cm2m$  or  $C222$ . None of these can be correct if the symmetry is a subgroup of the  $P321$  space group exhibited by #550–551. Such a relationship would imply that cheremnykhite is actually monoclinic  $C211$ , with  $\alpha \approx 90^\circ$ . Andychristyite,  $\text{Pb}_2[\text{Cu}_2(\text{Te}_2^{6+}\text{O}_{10})] \cdot 2\text{H}_2\text{O}$  (Kampf *et al.*, 2016), is a new mineral that is chemically the Pb analogue of eckhardite (#639). However, although the structures of the two minerals are related, they are not the same. Both contain

edge-sharing  $[\text{Te}_2\text{O}_{10}]^{8-}$  dimers, and both have structure units based upon stepped oblique slices through a *hcp* anion array (cf. #512–515), but the component ribbons of the slices and disposition of the Te=Te dimers are different.

There remain several Te minerals for which structures have never been determined, and even the true valence state of Te remains unknown. This is the case even for apparently simple species such as cesbronite,  $\text{Cu}_5(\text{Te}^{4+}\text{O}_3)_2(\text{OH})_6 \cdot 2\text{H}_2\text{O}$  (Williams, 1974) and xocometatlite,  $\text{Cu}_3\text{Te}^{6+}\text{O}_4(\text{OH})_4$  (Williams, 1975). As these minerals become better characterized and additional natural and synthetic Te oxycompounds are discovered, the diversity of known structures is likely to increase. However, the dataset and classification of the present study are sufficiently large to provide a robust framework into which new structural architectures can be fitted.

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