

## The Crystal Structure of a New Oxide Chloride of Copper(II) and Selenium(IV): $\text{Cu}_5\text{Se}_2\text{O}_8\text{Cl}_2$

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The oxide chloride  $\text{Cu}_5\text{Se}_2\text{O}_8\text{Cl}_2$  was formed during a chemical transport reaction. The formula was determined by Edax analysis and crystal structure determination. It crystallizes in the monoclinic system, space group  $P2_1/c$ , with the following parameter:  $a=6.039(1)$  Å,  $b=13.765(2)$  Å,  $c=5.572(1)$  Å,  $\beta=95.75(8)^\circ$ . The structure consists in sheets  $(\text{CuO}_2)_n^{2n-}$  parallel to the (010) plane and having a  $b/2$  periodicity; these parallel sheets are connected by a zig-zag string of trigonal bipyramids  $\text{CuO}_3\text{Cl}_2$  sharing edges running along the  $c$ -axis; selenium IV atoms reinforce the network, bridging the strings to the sheets. The three crystallographically independent copper atoms exhibit three different coordination polyhedra; this last problem and the stereochemical activity of the lone pair of selenium (IV) are discussed.

Examination of systems of selenium dioxide and transition metal oxides ( $\text{TiO}_2$ ,  $\text{V}_2\text{O}_5$ ,  $\text{VO}_2$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{NiO}$ ,  $\text{CoO}$ ...) showed the existence of several new compounds.<sup>1</sup> The crystal structures of  $\text{VSe}_2\text{O}_6$ ,  $\text{ZnSe}_2\text{O}_5$  (isostructural with  $\text{NiSe}_2\text{O}_5$  and  $\text{CoSe}_2\text{O}_5$ ) have been reported.<sup>2a,3</sup>

In the  $\text{SeO}_2$ – $\text{CuO}$  system three new compounds have been prepared by solid state reactions and characterized by X-ray single crystal and powder studies:  $\text{CuSe}_2\text{O}_5$ ,  $\text{CuSeO}_3$  and  $\text{Cu}_2\text{SeO}_4$ ; crystals of  $\text{CuSeO}_3$  and  $\text{Cu}_2\text{SeO}_4$  have been obtained by chemical transport, using  $\text{TeCl}_4$  as a vector.<sup>2b</sup> The crystal structure of  $\text{CuSe}_2\text{O}_5$  has been determined.<sup>4</sup>

The chemical transport reactions showed in some cases rather complicated results; in this paper we examine a new compound which appeared in minor amounts as small red-black crystals. The structure and composition of these crystals have been determined by Edax analysis and X-ray single crystal techniques.

### EXPERIMENTAL

An intimate mixture of  $\text{CuSeO}_3$  and  $\text{TeCl}_4$  was prepared in a dry-box and heated in a sealed vycor tube for 24 h. The amount of tellurium tetrachloride was adjusted to follow approximately the rule: 10 mg of  $\text{TeCl}_4$  for a volume of 10  $\text{cm}^3$ .

The tube was introduced in a furnace with the sample in the hotter part (500 °C). Fig. 1 summarizes the final result after analyses by X-ray single crystal and powder techniques.  $\text{CuSeO}_3$  was partially decomposed giving in the different parts of the tube, *i.e.* according to temperature, different phases  $\text{Cu}_2\text{SeO}_4$ ,  $\text{CuSe}_2\text{O}_5$  and  $\text{SeO}_2$ , which have been described elsewhere.<sup>2b,5</sup>

The crystallographic data obtained by Weissenberg technique for the red-black and yellow unknown crystals are summarized in Table I. The crystals were analyzed in an EM300 Philips electron microscope equipped for Edax analysis. After orientation of the crystals in the electron beam by diffraction techniques in order to check the cell parameters of the observed crystals, the qualitative analysis was carried out. The results are given in Table I.

### STRUCTURAL STUDY OF THE RED-BLACK CRYSTALS

The single crystal chosen had a regular shape with small multiple facets. The shape could be approximately assimilated to a sphere of a medium radius 0.06 mm.

On the basis of Weissenberg photographs, the crystal was found to be monoclinic. Systematic absences observed,  $h0l$   $l=2n+1$  and  $0k0$   $k=2n+1$ , imply the space group  $P2_1/c$ .

The data were collected from the single crystal on a computer-controlled diffractometer Enraf-

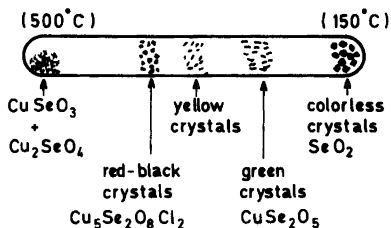


Fig. 1. Scheme of the different crystal deposits in the sealed tube after reaction.

Table 1. Preliminary X-ray and Edax analysis on single crystals.

Crystals	red-black	yellow
System	monoclinic	monoclinic
<i>a</i> (Å)	6.03	11.03
<i>b</i> (Å)	14.05	6.30
<i>c</i> (Å)	5.53	14.80
$\beta$ (°)	96.4	120
Space group	$P2_1/c$	$P2_1/c$
Edax analysis		
Cu	+	+
Se	+	+
Cl	+	+
Te	—	+

Nonius CAD-4 using MoK $\alpha$  radiation ( $\lambda = 0.71069$  Å) and a graphite monochromator. The cell parameters were refined and the intensities recorded at a take-off angle of 5° by  $\omega - 2\theta$  scan techniques (Table 2).

Table 3. Positional and thermal parameters for atoms of Cu<sub>5</sub>Se<sub>2</sub>O<sub>8</sub>Cl<sub>2</sub>.

Atoms	<i>x</i> <sup>a</sup>	<i>y</i>	<i>z</i>	$\beta_{11}$ <sup>b</sup>	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
Cu(1)	.4304(2)	.18958(9)	.5551(2)	96.8(39)	1.3(7)	60.4(41)	5.9(10)	5.0(28)	3.7(11)
Cu(2)	1/2	0	0	60.6(50)	5.2(9)	37.3(55)	3.9(14)	-13.5(39)	6.2(15)
Cu(3)	.2592(2)	-.00361(8)	.4869(2)	46.6(37)	2.9(6)	52.7(43)	-.5(9)	-18.0(28)	-6.8(11)
Se	.0622(2)	.13521(7)	.8996(2)	50.8(30)	1.4(6)	41.7(34)	1.1(8)	-11.6(21)	.3(8)
O(1)	.246(1)	.2220(5)	.815(1)	66(18)	3(3)	60(20)	-4(6)	-8(15)	5(6)
O(2)	.224(1)	.0589(5)	.077(1)	90(19)	5(3)	56(22)	2(6)	12(16)	4(6)
O(3)	.029(1)	.0732(5)	.633(1)	67(18)	4(4)	51(21)	-4(6)	-21(15)	-7(7)
O(4)	.503(1)	.0615(5)	.679(1)	69(18)	1(3)	42(19)	-5(6)	-15(15)	1(6)
Cl	.6709(4)	.1750(2)	.2652(4)	85(7)	6(1)	66(7)	7(2)	5(5)	6(2)

<sup>a</sup> Estimated standard deviations in the least significant figure(s) are given in parentheses in this table.

<sup>b</sup> The form of the anisotropic thermal ellipsoid is:  $\exp -(\beta_{11}h^2 + 2\beta_{23}kl)$ . The quantities given in the table are the thermal coefficients  $\times 10^4$ .

Table 2. Crystal data of the red-black compound, Cu<sub>5</sub>Se<sub>2</sub>O<sub>8</sub>Cl<sub>2</sub>.

System	monoclinic
Space group	$P2_1/c$
Parameters	
<i>a</i> (Å)	6.039(1)
<i>b</i> (Å)	13.765(2)
<i>c</i> (Å)	5.572(1)
$\beta$ (°)	95.75(8)
<i>V</i> (Å <sup>3</sup> )	460.8(3)
$\rho_x$ (g cm <sup>-3</sup> )	4.86
$\mu$ (cm <sup>-1</sup> )	203.1

After collection, reflections with  $I < 3\sigma(I)$  were rejected and the remaining 954 independent reflections were corrected for Lorentz, polarization and absorption effects.

#### STRUCTURE DETERMINATION AND REFINEMENT

The structure was solved by the heavy atom method and refined by least-squares techniques. The scattering factors were those of Cromer and Waber<sup>6</sup> for neutral copper, selenium and oxygen, the anomalous dispersion correction being also included except for oxygen atoms.

The calculations were performed on a CII Iris 80 computer. In addition to local programs, local modifications of the following programs were employed: Zalkin's FORDAP Fourier program, Johnson's ORTEP II thermal plotting program,

Busing and Levy's ORFFE program and the Doedens and Ibers' NUCLS least-squares program.

From a vector map, the positions of heavy atoms were found and the lighter atoms revealed by difference syntheses.

The final positional and thermal parameters of the atoms are given in Table 3 and selected interatomic distances and angles are summarized in Table 4. These data correspond to the minimum value of  $R = \sum |KF_o - |F_c|| / \sum KF_o = 0.055$ .

Table 4. Interatomic distances (Å) and angles (°) in  $\text{Cu}_5\text{Se}_2\text{O}_8\text{Cl}_2$ .

Cu(1)	Cu(2)		
Cu(1)–Cu(1i)	Cu(2)–Cu(3)		
Cu(1)–O(4)	Cu(2)–O(2)	1.940	
Cu(1)–O(11)	Cu(2)–O(2ii)	1.940	
Cu(1)–Cl(1)	Cu(2)–O(4)	1.982	
Cu(1)–O(1)	Cu(2)–O(4ii)	1.982	
Cu(1)–Cl	Cu(2)–Cl	2.957	
	Cu(2)–Cl(ii)	2.957	
Cu(3)–Cu(3ii)	Se–O(1)	1.709	
Cu(3)–Cu(3ii)	Se–O(2)	1.682	
Cu(3)–O(2)	Se–O(3)	1.728	
Cu(3)–O(3)	O(1)–O(3)	2.587	
Cu(3)–O(4)	O(3)–O(2)	2.642	
Cu(3)–O(4ii)	O(1)–O(2)	2.679	
Cu(3)–O(3ii)	O(3)–Se–O(2)	102.3	
Cu(3)–Cl(ii)	O(2)–Se–O(1)	103.5	
	O(3)–Se–O(1)	97.7	
Cu(1)	Cu(1)		
O(4)–O(1)	O(4)–Cu(1)–O(1i)	150.1	
O(1i)–Cl(1)	O(1i)–Cu(1)–Cl(1)	96.2	
Cl(1)–O(4)	Cl(1)–Cu(1)–O(4)	113.7	
O(1)–O(4)	O(1)–Cu(1)–Cl	171.0	
O(1)–O(1i)	O(1)–Cu(1)–O(4)	93.9	
O(1)–Cu(i)	O(1)–Cu(1)–O(1i)	92.2	
Cl–O(4)	O(1)–Cu(1)–Cl(1)	80.5	
Cl–O(4)	Cl–Cu(1)–O(4)	91.9	
Cl–O(1i)	Cl–Cu(1)–O(1i)	86.2	
Cl–Cl(i)	Cl–Cu(1)–Cl(i)	90.9	
Cu(2)	Cu(2)		
O(2)–O(4)	O(2)–Cu(2)–O(4)	96.1	
O(2ii)–O(4ii)	O(2ii)–Cu(2)–O(4)	83.9	
O(2)–O(4ii)	O(2)–Cu(2)–O(4ii)	83.9	
O(4)–O(2ii)	O(4)–Cu(2)–O(2ii)	180.	
Cl–O(2)	Cl–Cu(2)–Cl(ii)	79.1	
Cl–O(4ii)	Cl–Cu(2)–O(2)	93.9	
Cl–O(2ii)	Cl–Cu(2)–O(4)	86.1	
Cl–O(4)	Cl–Cu(2)–O(2ii)	100.9	

Cu(3)	Cu(3)		
O(2)–O(3)	O(3)–Cu(3)–O(4)	93.1	
O(2)–O(4)	O(4)–Cu(3)–O(4ii)	84.1	
O(2)–O(4ii)	O(4ii)–Cu(3)–O(3ii)	107.2	
O(2)–O(4ii)	O(3ii)–Cu(3)–O(3)	77.0	
O(3)–O(4)	O(2)–Cu(3)–O(3)	101.3	
O(4)–O(4ii)	O(2)–Cu(3)–O(4)	109.9	
O(4ii)–O(3ii)	O(2)–Cu(3)–O(4ii)	72.5	
O(3ii)–O(3)	O(2)–Cu(3)–O(3ii)	82.5	
O(2ii)–Cl(ii)	O(2)–Cu(3)–O(2ii)	143.4	
O(4ii)–Cl(ii)	O(2)–Cu(3)–Cl(ii)	140.6	
O(4)–Cl(ii)	O(2i)–Cu(3)–Cl(ii)	75.9	
O(3ii)–Cl(ii)			
O(3)–Cl(ii)			

The resulting composition of the red-dark crystal is  $\text{Cu}_5\text{Se}_2\text{O}_8\text{Cl}_2$ . Such a formula is in full agreement with the oxidation states (II) and (IV) of copper and selenium atoms.

#### DESCRIPTION OF THE STRUCTURE

A ball-and-spoke drawing of the structure, projected on to (001), is given in Fig. 2.

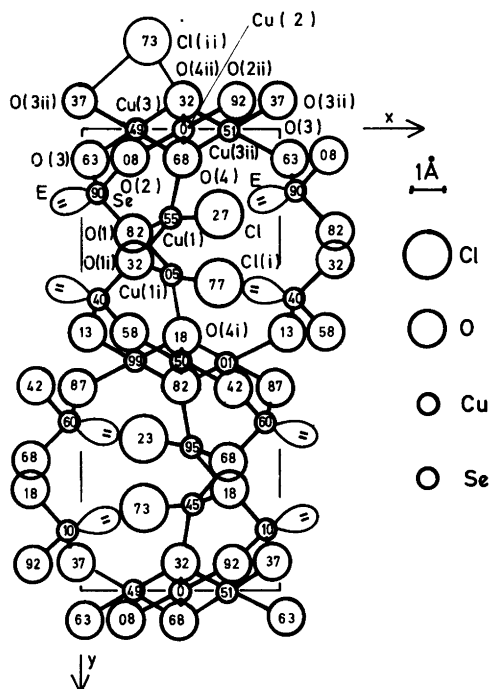


Fig. 2. Ball-and-spoke projection drawing of the crystal structure of  $\text{Cu}_5\text{Se}_2\text{O}_8\text{Cl}_2$  on the (001) plane.

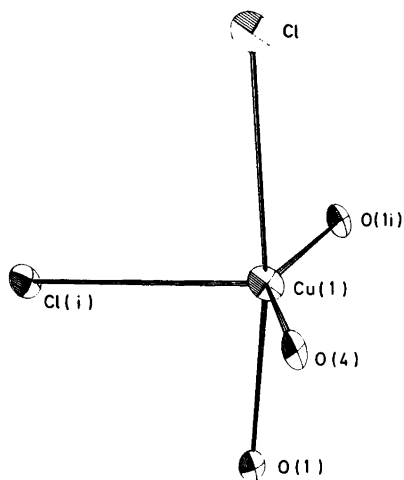


Fig. 3. Fivefold coordination of Cu(1) in form of a trigonal bipyramid:  $\text{Cu}(1)\text{O}_3\text{Cl}_2$ .

In the unit cell, there are three crystallographically different copper atoms. Cu(1) has a fivefold coordination; three oxygen and two chlorine atoms are at the corners of a distorted trigonal bipyramid ( $\text{Cl}-\text{O}(1)\text{O}(4)\text{Cl}(i)\text{O}(1)$ ); O(1), O(4), Cl(i) forming the equatorial base (Fig. 3). Cu(2), at a center of symmetry, has a 4+2 coordination type (Fig. 4); O(2)O(4)O(2ii) and O(4ii) form a planar square

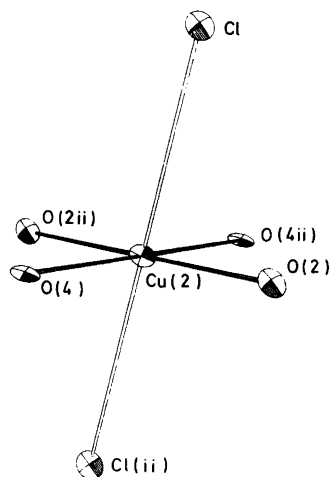


Fig. 4. (4+2) Coordination of Cu(2); square plane of oxygen atoms + two apical chlorine atoms making a distorted octahedron  $\text{Cu}(2)\text{O}_4\text{Cl}_2$ .

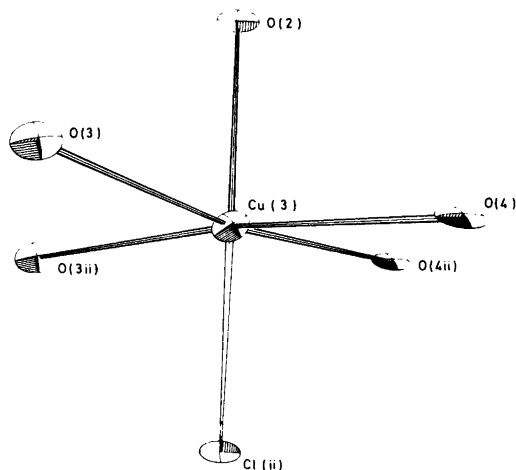


Fig. 5. (4+2) Coordination of Cu(3) with one oxygen atom and one chlorine atom at the apices of a distorted octahedron.

around Cu(2) and two chlorines, Cl and Cl(ii) complete a distorted octahedron  $\text{Cl}-\text{O}(2)\text{O}(4)-\text{O}(2ii)\text{O}(4ii)-\text{Cl}(ii)$ . We find around Cu(3) a distorted square of oxygens O(3)O(4)O(4ii)O(3ii) and two extra atoms O(2) and Cl(ii) complete again a coordination of the 4+2 type of a very distorted octahedron (Fig. 5). The selenium atom has a threefold coordination, Se O(1)O(2)O(3), of a trigonal pyramid type (Fig. 6).

The squares  $\text{Cu}(3)\text{O}_4$  share two opposite edges [ $\text{O}(3)-\text{O}(3ii)$  and  $\text{O}(4)-\text{O}(4ii)$ ] giving rise to an infinite ribbon parallel to the  $a$ -axis. These ribbons are held together by corners shared with  $\text{Cu}(2)\text{O}_4$  squares. Such sheets are parallel to (010) with the  $b/2$  periodicity and the composition  $[\text{CuO}_2]_n^{2n-}$  (Fig. 7).

The trigonal bipyramids  $\text{Cu}(1)\text{O}_3\text{Cl}_2$  are linked together by edge sharing [equatorial  $\text{O}(1i)-\text{Cl}$  and axial  $\text{O}(1)\text{Cl}(i)$  edges] and form infinite strings parallel to the  $c$ -axis. These strings, with the former composition  $[\text{CuO}_2\text{Cl}]_n^{3n-}$ , are bridging the  $[\text{CuO}_2]_n^{2n-}$  by corner sharing with the  $\text{SeO}_3$  pyramids. The  $\text{SeO}_3$  pyramids also share corners with the  $\text{CuO}_4$  squares.

The resulting crystal structure of  $\text{Cu}_3\text{Se}_2\text{O}_8\text{Cl}_2$  is a three-dimensional network. A tunnel parallel to the  $c$ -axis appears bordered by chlorine, selenium and the O(1) oxygen atoms. This tunnel is filled by the lone pairs E of the selenium (IV).

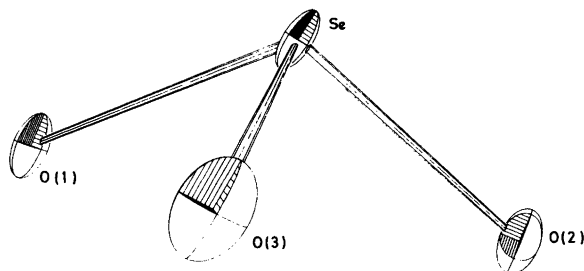


Fig. 6. Threefold coordination of the selenium atom.

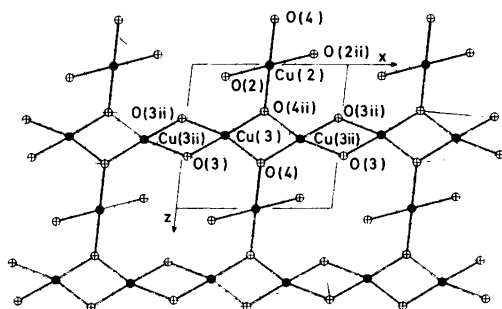


Fig. 7. The sheets  $(\text{CuO}_2)_{2n}^{2-}$  formed by the ribbons of  $\text{CuO}_4$  squares sharing edges bridged by independent  $\text{CuO}_4$  squares. The sheets are parallel to the (010) plane.

## DISCUSSION

The distorted trigonal bipyramid  $\text{Cu}(1)\text{O}_3\text{Cl}_2$  is one of the unusual features in this rather complex structure *versus* the small size of the cell. The distortion  $\Delta$  has been appreciated using the Muetterties and Guggenberger<sup>7</sup> description by comparison of the observed dihedral angles ( $\delta$ ) formed by the normal to adjacent polytopal faces with the ones of the ideal trigonal bipyramid ( $\Delta=1$ ) (Table 5); the value of  $\Delta$ , around 32%, indicates that the  $\text{Cu}(1)\text{O}_3\text{Cl}_2$  polyhedron is close to TBP. The Cu–O and Cu–Cl distances may be compared with those found in the structure of CuO (determined: Ref. 8; refined: Ref. 9) and  $\text{CuCl}_2$  studied by Wells<sup>10</sup> (Table 6), one of these Cu(1)–Cl(1)=2.57 Å being

Table 5. Distortions  $\Delta$  of the  $\text{Cu}(1)\text{O}_3\text{Cl}_2$  polyhedron.  $\Delta$  is calculated using the following formula:  
 $\Delta = |\delta a_1 + \delta a_3 + \delta a_4 + \delta a_6 - 406|/164.7 + |\delta e_1 + \delta e_2 - 106.2|/203.4 + |203 - \delta a_2 - \delta a_5|/232.2 + |53.1 - \delta e_3|/477.9$ .

Dihedral angle	Polyhedron		
	Ideal trigonal bipyramid (TBP) (°)	$\text{Cu}(1)\text{O}_3\text{Cl}_2$ (°)	Ideal tetragonal pyramid (TP) (°)
$\delta a_1$	101.5	106.5 O(1i)–O(4)–Cl–Cl(i)]	119.8
$\delta a_3$	101.5	113.6 [Cl(i)–O(1i)–Cl–O(4)]	119.8
$\delta a_4$	101.5	97.4 [Cl(1)–O(1)–O(4)–O(1i)]	119.8
$\delta a_6$	101.5	107.0 [Cl(1)–O(1)–O(1i)–O(4)]	119.8
$\delta e_1$	53.1	66.8 [Cl–O(4)–Cl(1)–O(1)]	75.7
$\delta e_2$	53.1	58.2 [Cl–O(1i)–Cl(1)–O(1)]	75.7
$\delta a_2$	101.5	92.7 [O(4)–Cl–Cl(i)–O(1i)]	75.7
$\delta a_5$	101.5	93.5 [O(4)–O(1)–Cl(i)–O(1i)]	75.7
$\delta e_3$	53.1	34.6 [Cl–O(4)–O(1i)–O(1)]	0
$\Delta$	0	0.32	1

Table 6. Environments of Cu(II) atoms in some crystal structures.

Compound	Distances (Å)		
CuO	2 O	1.961	
	2 O	1.951	(square)
	2 O	2.784	(apical)
CuCl <sub>2</sub>	4 Cl	2.30	(square)
	2 Cl	2.95	(apical)
Cu <sub>2</sub> Cl(OH) <sub>3</sub> Atacamite	Cu(1)		
	2 O	2.04	
	2 O	2.00	(square)
	2 Cl	2.76	(apical)
	Cu(2)		
	2 O	1.94	
	2 O	2.07	(square)
	O	2.36	
	Cl	2.75	(apical)

intermediate between the shortest (2.30 Å) and the longest (2.95 Å) Cu–Cl distances.

Looking at the arrangement of the six nearest atoms of copper Cu(2) it is seen that the four oxygens and the two chlorines are at distances very similar to the ones found by Wells<sup>10</sup> in the crystal structure of atacamite Cu<sub>2</sub>Cl(OH)<sub>3</sub> for the copper in crystallographic site Cu(I) (Table 6). The elongation along the Cl–Cl axis is generally explained as a consequence of the Jahn-Teller effect; it may be noticed that the elongation, as it has been pointed out by Åsbrink and Norrby<sup>9</sup> for CuO, does not take place purely along the fourfold axis of the octahedron but is tilted 11° from that direction (17° in CuO).

The last copper Cu(3) coordination polyhedron can be compared (Tables 4 and 6), with the Cu(II) polyhedron found in atacamite.

It is interesting to note that the ribbons [CuO<sub>2</sub>]<sub>n</sub> found in Cu<sub>5</sub>Se<sub>2</sub>O<sub>8</sub>Cl<sub>2</sub> are also present in CuO and that they are almost identical, distortions included. Using this particular description based on ribbons, CuO can be described as an interpenetrating network of such units.

Finally, selenium (IV), with its stereochemically active lone pair E at the apex of the tetrahedron formed with the three-bonded oxygen atoms, is not connected *via* oxygen to other SeO<sub>3</sub>E groups as in many other structures (SeO<sub>2</sub> chains in the dioxide SeO<sub>2</sub>,<sup>5</sup> Se<sub>2</sub>O<sub>5</sub><sup>2-</sup> groups in VSe<sub>2</sub>O<sub>6</sub>, for example, Ref. 2a). The role of the lone pair E in the structures

Table 7. Oxygen positions.

	Calc.			Obs.		
	x	y	z	x	y	z
O <sub>1</sub>	.25	.25	.83	.25	.22	.82
O <sub>2</sub>	.25	.06	.17	.22	.06	.08
O <sub>3</sub>	0	.06	.67	.03	.07	.63
O <sub>4</sub>	.50	.06	.67	.50	.06	.68

has been discussed in detail in earlier papers.<sup>11,12</sup>

Such a role of selenium(IV) in the linkage of a network has also been found in Se<sub>2</sub>TiO<sub>5</sub> where isolated TiO<sub>6</sub> octahedra are held together by selenium atoms.<sup>13</sup>

The oxygen packing of this structure is interesting to analyse. The [CuO<sub>2</sub>]<sub>n</sub> layers can be described as partly cubic closepacking of oxygens, built up of halfcube-octahedra. The polyhedron has a hexagonal face which is shared with a corresponding face of a Frank-Kasper polyhedron, a so-called 15-hedron. This is surrounded by three hexagon faces, and eight tetrahedra. Of the three hexagons, one is shared with the cube-octahedron, and the other two with identical 15-hedra. This is a simple arrangement of polyhedra that describes all the oxygen positions fairly accurately. The unit cell can be calculated to  $a = 6.10$  Å,  $b = 14.57$  Å and  $c = 5.28$  Å, and the calculated oxygen positions are given in Table 7.

One chlorine ion and one lone pair of Se are situated in each 15-hedron. Using the models proposed by Galy, Meunier, Andersson and Åström<sup>12</sup> the E–Cl distance becomes ~2.10 Å. This is unusually short and it is natural to assume some kind of interaction. Each chlorine is bonded to two Cu<sup>2+</sup> which are both on the same side of the chlorine ion, giving it an asymmetrical charge distribution. We believe similar lone pair-large anion attractions could explain many structures, and we intend to explore this phenomenon further.

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