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The Crystal Structure of Terlinguaite $Hg_4O_2Cl_2$

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The crystal structure of terlinguaite has been redetermined and refined to a final R-value of 0.089 from three-dimensional X-ray data (CuK) obtained from a native crystal of the mineral. Three mercury atoms in the structure form an equilateral triangle with the triangle edge Hg–Hg = 2.708 ± 0.002 Å. The structure can be described as built up of endless chains of the composition $(Hg_4O_2Cl_2)_n$, fused to a network by contacts Hg–2Cl = 2.84 ± 0.01 Å. Within the chains the interatomic distances are Hg–Cl = 2.60 ± 0.01 Å and Hg–2O = 2.23 ± ± 0.03 Å for mercury atoms belonging to the triangle; for mercury atoms outside the triangle the distances Hg–2O are 2.02 ± 0.03 Å and Hg–Cl ≥ 3.17 Å. In the structure there are mercury atoms of different oxidation numbers. One fourth of them, the atoms outside the triangle are collinearily bonded to two oxygen atoms (2.02 Å) and may be attributed the number 2, while the other ones, forming the triangle, may formally be attributed the number 4/3.

In connection with studies on the crystal chemistry of inorganic mercury(II) compounds,[1] it seemed to be of interest to compare the results obtained with the structural data of some mercury(II) compounds, reported in the literature.[2] The mineral terlinguaite has been the object of an X-ray diffraction study by Ščavničar,[3] based on two-dimensional intensity data. That investigation yielded very interesting results.

In order to get an idea of the accuracy of the structure determination, especially of the positions of the oxygen atoms, the present authors performed a least-squares refinement of the reported structure, based on the intensity material and the parameters given in Ref. 3. The result of these calculations showed, however, considerable changes in the positions of the mercury atoms and indicated that the oxygen atom arrangement did not correspond to the one given earlier.[3] Thus we found it advisable to carry out a renewed investigation of the compound on the basis of a complete three-dimensional intensity material since the two-dimensional data treated earlier had evidently been insufficient.

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PREPARATION, CELL DIMENSIONS AND DENSITY

Native crystals of terlinguaite from Terlingua in Texas were kindly supplied by the Mineralogical Department, the Museum of Natural History, Stockholm. In addition, synthetic single crystals were prepared by hydrothermal heating of yellow HgO(*o-rh*) and Hg_2Cl_2 in the molar ratio 2:1. The moistened sample was sealed in a gold capsule and heated at 300°C and 3000 bars for one week. The synthetic crystals were light yellow. A water analysis was carried out according to Penfield [4] and gave no water content as result. Guinier photographs revealed that the synthetic crystals had the same cell dimensions as the native mineral. The observed density, 9.22 $g \cdot cm^{-3}$, indicated a cell content of four formula units $Hg_4O_2Cl_2$ (calculated density 9.35 $g \cdot cm^{-3}$). The dimensions of the monoclinic unit cell are $a = 19.515 \pm 0.020$ Å, $b = 5.915 \pm 0.001$ Å, $c = 9.478 \pm 0.010$ Å and $\beta = 143.81° \pm 0.04°$. The volume is 646.0 ± 0.6 Å^3. These values of the cell edges and the density are in good agreement with those published earlier.[3] The powder pattern is published elsewhere.[5]

SINGLE CRYSTAL WORK

A single crystal of the mineral of a size about $50 \times 30 \times 15$ μ^3 was investigated by CuK radiation filtered through nickel. Multi-film (3 films) Weissenberg photographs were used to record the reflections of the following layer lines:

Crystal rotated around	Recorded layer lines
[010]	0— 3
[001]	0— 5
[031]	0—11

The Laue symmetry $2/m$ and the characteristic space group $C2/c$ (No. 15 in the International Tables), also given by the previous author,[3] were confirmed. The intensities were estimated visually by comparison with a calibrated scale. The linear absorption coefficient was calculated to be 1871 cm^{-1}.[6] As this value is very large, the corrections for absorption were sometimes considerable. Using a program developed by Werner,[7] the corrections for the absorption in the crystal were calculated as carefully as possible.

As a starting point for the refinement of terlinguaite the crystal structure given in Ref. 3 was used:
Space group: $C2/c$ (No. 15). Coordinates of equivalent positions

$(0,0,0;\frac{1}{2},\frac{1}{2},0) +$
4 Hg_I in 4(c): $\frac{1}{4},\frac{1}{4},0;\frac{3}{4},\frac{1}{4},\frac{1}{2}$;
4 Hg_{II} in 4(e): $\pm(0,y,\frac{1}{4})$, $y = 0.594$;
8 Hg_{III} in 8(f): $\pm(x,y,z)$; $\pm(x,\bar{y},\frac{1}{2}+z)$, $x = 0.047$, $y = 0.197$, $z = 0.200$;
8 Cl in 8(f): $x = 0.188$, $y = 0.282$, $z = 0.230$;
8 O in 8(f): $x = 0.082$, $y = 0.344$, $z = 0.700$.

At first, the intensities of the reflections $h0l$—$h3l$ were treated (408 reflections). Preliminary scale factors were calculated for the structure factors, and a least-squares refinement was performed starting with the parameters given above. The discrepancy factor R decreased to 13 % after 10 cycles of the refinement which, at that point, had produced a considerable displacement, 0.92 Å, of the y parameter of the oxygen atoms, from the value given above. In the last cycle, the shifts in the parameters of the oxygen atoms were

1 % of their deviations, σ ~0.06 Å. The new parameter value was $y_O=0.188\pm0.009$. The other positional parameters changed to a small extent. Thus, the displacements of the atoms were the following: Hg_{II} 0.03 Å; Hg_{III} 0.03 Å; Cl 0.12 Å.

Preliminary electron density sections $\varrho(x,y,z)$ based on the observed structure factors (*h0l*—*h3l*), were then calculated at different values of y, and also difference syntheses $\varrho''(x,y,z)$, based on structure factors from which the contributions of the mercury and chlorine atoms of the unit cell had been subtracted. (These sections are not given here.) The positional parameters of the mercury and the chlorine atoms were confirmed by inspection of the several sections $\varrho(x,y,z)$, and the new oxygen atom position was supported by, *e.g.*, the appearance of the difference syntheses $\varrho''(x,0.19,z)$. A few other peaks were also found in the difference syntheses, with heights up to 0.7 of an oxygen atom peak in the calculated electron density synthesis. The interatomic distances calculated on the basis of the assumption that these peaks corresponded to different oxygen atom positions, had unacceptable values. The peaks were considered to be caused by termination effects. The preliminary oxygen atom position is thus assumed to be: $x=0.08$, $y=0.19$, $z=0.72$. Scale factors were then calculated and refined for the different layer lines *hk*0—*hk*5 (390 reflections) and for the twelve diagonal layer lines (463 reflections) whereupon averages for all independent structure factors, many of them measured several times in separate layer lines, were computed. A refinement with isotropic temperature factors was then performed using the 646 independent reflections. After ten cycles, the refinement was considered to be complete. The *R*-factor at that point was 0.099 and the shifts in the parameters and their standard deviations were deemed satisfactorily small.

Following the refinement, final electron density difference syntheses $\varrho'(x,y,z)$ and $\varrho'''(x,y,z)$ were calculated where, at first, the contributions of the

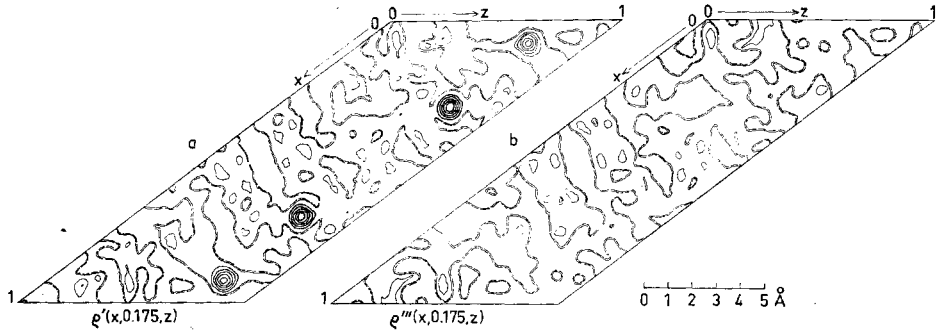

Fig. 1 a. The electron density difference synthesis $\varrho'(x,0.175,z)$, where the contributions of the mercury atoms of the unit cell have been subtracted from the observed structure factors. Two chlorine and two oxygen atoms are seen. Heavy lines are equivalent to two ordinary contour lines.

b. The electron density difference section $\varrho'''(x,0.175,z)$, where the contributions of all atoms in the unit cell are subtracted.

Dashed lines indicate negative values.

Table 1. Final fractional positional parameters and temperature factors and their standard deviations.

Atom	x $\sigma(x)$	y $\sigma(y)$	z $\sigma(z)$	B $\sigma(B)$		
Hg_I	½ —	½ —	0 —	— —		
Hg_{II}	0 —	0.5910 0.0003	½ —	— —		
Hg_{III}	0.0490 0.0001	0.1946 0.0003	0.2016 0.0003	— —		
Cl	0.1946 0.0009	0.295 0.002	0.244 0.002	1.3 0.2		
O	0.079 0.002	0.179 0.004	0.722 0.004	0.57 0.39		
	β_{11} $\sigma(\beta_{11})$	β_{22} $\sigma(\beta_{22})$	β_{33} $\sigma(\beta_{33})$	β_{12} $\sigma(\beta_{12})$	β_{13} $\sigma(\beta_{13})$	β_{23} $\sigma(\beta_{23})$
Hg_I	0.0022 0.0002	0.0067 0.0032	0.0103 0.0006	−0.0002 0.0004	0.0077 0.0006	−0.0007 0.0009
Hg_{II}	0.0029 0.0002	0.0051 0.0032	0.0128 0.0006	0 —	0.0104 0.0006	0 —
Hg_{III}	0.0040 0.0001	0.0061 0.0032	0.0165 0.0006	0.0003 0.0003	0.0142 0.0005	−0.0014 0.0006

Table 2. Analysis of the weighting scheme used in the last cycle of the refinement. The intensity data were made up of 646 independent reflections. $R = 8.9$ %. w is the weighting factor. $\Delta = |F_o| - |F_c|$.

Interval sin θ	Number of independent reflections	$\overline{w\,\Delta^2}$	Interval $\lvert F_o \rvert$	Number of independent reflections	$\overline{w\,\Delta^2}$
0.00—0.46	69	1.58	0— 61	64	0.84
0.46—0.58	71	0.96	61— 89	65	0.87
0.58—0.67	73	1.07	89—116	64	0.79
0.67—0.74	72	0.88	116—141	65	0.99
0.74—0.79	60	0.74	141—170	65	0.84
0.79—0.84	69	0.56	170—197	64	1.00
0.84—0.89	62	0.58	197—243	65	0.77
0.89—0.93	63	0.84	243—293	64	0.92
0.93—0.97	60	0.77	293—377	65	0.81
0.97—1.00	47	1.02	377—844	65	2.14

Table 3. Observed and calculated structure factors *hkl* for $Hg_4O_2Cl_2$. The columns give *h,k,l*, $|F_o|$ and $|F_c|$.

0	0	2	557.6	564.9	15	1	-6	67.7	54.2	20	2	-5	111.1	108.9	2	2	0	114.3	98.0
0	0	4	526.3	502.4	15	1	-7	107.9	77.9	20	2	-6	177.3	171.0	2	2	-1	479.4	485.1
0	0	6	20.1	16.0	15	1	-8	81.4	77.5	20	2	-7	37.4	37.8	2	2	-2	229.6	223.0
0	0	8	20.1	16.0	15	1	-9	270.8	242.9	20	2	-10	288.3	303.9	2	2	-3	261.6	255.2
2	0	0	453.4	426.7	15	1	-10	121.6	102.1	20	2	-11	76.9	56.7	2	2	-4	363.1	401.4
2	0	2	644.2	809.5	15	1	-11	143.9	139.2	18	2	-3	181.5	225.1	2	2	-5	67.6	73.3
2	0	4	195.9	203.2	13	1	0	115.3	114.4	18	2	-4	84.4	75.1	2	2	-6	108.9	93.7
2	0	6	214.9	244.3	13	1	-1	334.3	347.7	18	2	-5	270.2	261.2	0	2	6	166.6	167.7
2	0	-2	712.9	692.6	13	1	-2	130.1	119.6	18	2	-6	152.7	130.2	0	2	5	127.1	104.6
2	0	-4	195.9	172.3	13	1	-3	110.0	83.1	18	2	-7	215.7	202.3	0	2	4	248.8	241.7
2	0	-6	41.7	43.4	13	1	-4	103.7	80.1	18	2	-8	246.7	273.8	0	2	3	293.6	285.3
4	0	0	648.2	709.3	13	1	-5	122.7	108.4	18	2	-9	97.2	86.4	0	2	2	71.5	44.5
4	0	2	317.9	265.7	13	1	-6	34.9	31.0	18	2	-10	106.8	86.3	0	2	1	466.6	475.3
4	0	4	437.7	477.6	13	1	-7	297.2	358.3	16	2	-2	53.4	42.9	0	2	0	627.9	694.4
4	0	-2	169.9	169.3	13	1	-9	39.1	23.8	16	2	-3	250.9	232.8	21	3	-6	84.5	88.4
4	0	-4	110.5	107.9	13	1	-10	36.0	36.3	16	2	-4	318.2	299.8	21	3	-7	149.5	163.8
4	0	-6	300.2	308.2	13	1	-11	96.3	104.0	16	2	-5	332.1	319.9	21	3	-8	176.6	178.4
4	0	-8	75.0	61.6	11	1	2	111.1	120.9	16	2	-7	256.3	241.2	21	3	-9	92.1	93.4
6	0	0	158.4	121.6	11	1	1	307.8	337.0	16	2	-8	192.2	196.2	21	3	-10	214.6	198.4
6	0	2	406.5	425.0	11	1	0	194.6	193.7	16	2	-9	194.3	188.4	19	3	-4	82.4	85.6
6	0	4	130.3	130.4	11	1	-1	150.2	136.8	16	2	-10	183.7	191.3	19	3	-5	246.2	268.5
6	0	-2	160.5	134.0	11	1	-2	279.2	285.0	16	2	-11	47.0	50.2	19	3	-6	94.3	102.9
6	0	-4	400.2	447.3	11	1	-3	465.4	458.6	14	2	0	168.7	193.8	19	3	-9	159.3	158.3
6	0	-6	82.3	95.6	11	1	-4	220.0	196.9	14	2	-1	86.5	84.3	19	3	-10	186.4	173.7
6	0	-8	96.9	93.8	11	1	-5	160.8	177.8	14	2	-2	157.0	127.5	19	3	-11	85.6	93.0
8	0	0	44.6	37.0	11	1	-6	99.4	104.1	14	2	-3	258.4	218.7	17	3	-3	264.4	303.1
8	0	2	140.7	128.6	11	1	-7	83.6	36.2	14	2	-4	82.2	60.0	17	3	-4	171.2	186.5
8	0	-2	565.9	564.2	11	1	-8	59.2	40.1	14	2	-5	344.9	352.1	17	3	-5	101.9	92.1
8	0	-6	216.8	202.7	11	1	-9	317.3	289.8	14	2	-6	320.3	304.2	17	3	-6	176.6	146.9
8	0	-8	297.0	301.7	9	1	3	173.5	180.4	14	2	-7	292.6	308.3	17	3	-7	279.6	326.1
10	0	0	255.3	232.3	9	1	2	133.3	130.8	14	2	-8	47.0	13.5	17	3	-9	56.4	35.8
10	0	2	115.7	114.9	9	1	1	116.4	97.9	14	2	-9	257.3	253.6	17	3	-10	97.5	82.3
10	0	-2	200.1	182.3	9	1	0	257.0	238.8	14	2	-10	157.6	144.3	17	3	-11	96.4	116.4
10	0	-4	99.0	79.5	9	1	-1	643.1	646.3	14	2	-11	108.9	119.7	15	3	-1	185.3	233.3
10	0	-6	507.5	579.3	9	1	-2	359.6	325.4	12	2	0	61.9	36.8	15	3	-2	50.9	40.8
10	0	-8	274.5	273.3	9	1	-3	254.9	241.3	12	2	-2	348.1	334.3	15	3	-3	123.5	106.0
10	0	-10	457.5	426.0	9	1	-4	248.8	322.6	12	2	-3	159.1	137.8	15	3	-4	151.7	149.4
12	0	0	80.2	73.3	9	1	-5	415.7	513.2	12	2	-4	181.5	157.3	15	3	-5	432.4	483.6
12	0	-2	168.8	141.5	9	1	-6	181.9	183.2	12	2	-5	290.9	295.4	15	3	-6	218.9	192.2
12	0	-4	499.2	491.7	9	1	-7	137.5	136.2	12	2	-6	84.4	78.0	15	3	-7	162.6	162.9
12	0	-6	206.8	205.8	9	1	-8	95.2	76.3	12	2	-7	340.6	357.8	15	3	-8	127.9	110.7
12	0	-8	549.2	604.3	9	1	-10	29.6	27.9	12	2	-8	286.2	287.7	15	3	-9	325.1	335.3
12	0	-10	176.1	127.8	7	1	4	39.1	44.7	12	2	-9	293.6	289.5	13	3	0	70.4	71.0
14	0	0	73.0	69.8	7	1	3	112.1	113.3	12	2	-10	36.3	40.9	13	3	-1	86.7	74.5
14	0	-2	345.0	346.4	7	1	2	137.5	115.2	10	2	0	366.3	370.3	13	3	-3	324.0	313.1
14	0	-4	286.8	244.7	7	1	1	396.7	362.0	10	2	-1	100.4	74.5	13	3	-4	164.7	152.8
14	0	-6	634.7	742.4	7	1	0	277.1	243.6	10	2	-2	83.3	84.5	13	3	-5	113.8	94.4
14	0	-8	330.6	286.2	7	1	-1	298.3	238.3	10	2	-3	59.8	33.3	13	3	-6	263.3	268.9
14	0	-10	368.9	353.8	7	1	-2	355.4	365.9	10	2	-4	347.0	356.2	13	3	-7	394.5	443.3
16	0	-2	154.2	146.4	7	1	-3	874.9	912.9	10	2	-5	95.0	99.3	13	3	-8	261.2	247.7
16	0	-4	589.9	542.7	7	1	-4	306.8	358.9	10	2	-6	224.2	233.4	13	3	-9	103.0	83.5
16	0	-6	336.0	299.4	7	1	-5	288.8	290.2	10	2	-7	206.1	205.7	13	3	-10	130.0	126.2
16	0	-8	451.3	473.9	7	1	-6	214.7	232.2	10	2	-9	202.9	200.1	11	3	1	92.1	62.2
16	0	-10	38.0	22.8	7	1	-7	388.2	398.3	10	2	-10	211.4	222.6	11	3	0	209.2	202.8
18	0	-4	120.1	128.7	7	1	-8	118.5	109.2	8	2	3	112.1	113.1	11	3	-1	208.1	196.6
18	0	-6	382.5	370.0	7	1	-9	70.9	51.3	8	2	2	287.2	264.8	11	3	-2	214.6	202.5
18	0	-8	67.5	36.7	5	1	5	163.0	206.3	8	2	1	96.1	75.6	11	3	-3	65.0	51.1
18	0	-10	40.6	32.4	5	1	4	48.7	43.3	8	2	0	173.0	138.1	11	3	-4	84.5	64.1
20	1	-4	267.8	305.7	5	1	2	111.1	98.8	8	2	-2	619.3	704.9	11	3	-5	368.5	423.4
20	0	-8	162.0	146.2	5	1	1	367.0	381.2	8	2	-3	38.4	33.1	11	3	-6	108.4	110.5
20	0	-10	210.5	153.9	5	1	0	240.3	231.4	8	2	-4	207.2	215.4	11	3	-7	144.1	129.0
22	0	-6	41.3	32.3	5	1	-1	391.4	417.8	8	2	-5	39.8	38.0	11	3	-8	184.2	183.2
22	0	-8	204.9	215.4	5	1	-2	340.6	365.0	8	2	-6	374.6	405.1	11	3	-9	339.2	349.9
22	0	-10	51.1	26.3	5	1	-3	114.2	129.1	8	2	-7	144.2	127.9	11	3	-10	133.3	137.5
23	1	-7	284.5	305.0	5	1	-4	378.7	386.2	8	2	-8	110.0	96.1	9	3	2	108.4	100.1
23	1	-9	153.4	144.9	5	1	-5	552.2	599.2	8	2	-9	151.6	136.0	9	3	1	172.3	170.6
23	1	-9	153.0	167.3	5	1	-6	272.9	275.1	6	2	4	36.3	36.7	9	3	0	264.4	242.6
23	1	-10	141.7	136.9	5	1	-7	94.1	61.3	6	2	3	169.5	163.2	9	3	-1	153.1	163.4
23	1	-11	289.8	296.7	5	1	-8	155.5	152.0	6	2	2	195.4	174.2	9	3	-2	328.4	333.5
21	1	-5	142.8	108.0	3	1	5	94.1	78.4	6	2	1	205.0	168.3	9	3	-3	243.8	236.0
21	1	-6	129.0	126.1	3	1	3	313.1	318.1	6	2	0	376.9	371.8	9	3	-4	225.4	253.6
21	1	-7	67.7	64.5	3	1	2	29.6	23.8	6	2	-1	64.1	62.7	9	3	-5	68.3	62.8
21	1	-8	186.2	176.4	3	1	1	155.5	95.2	6	2	-2	149.5	141.9	9	3	-6	78.0	60.0
21	1	-9	368.6	349.0	3	1	0	119.5	92.0	6	2	-3	60.9	32.5	9	3	-7	329.4	344.0
21	1	-10	194.6	191.0	3	1	-1	230.5	228.7	6	2	-4	565.9	659.3	9	3	-8	93.2	61.8
21	1	-11	155.5	126.8	3	1	-2	149.3	210.3	6	2	-5	74.7	58.6	9	3	-9	87.8	75.9
21	1	-12	112.1	111.0	3	1	-3	543.7	572.2	6	2	-6	120.7	139.5	7	3	3	540.8	229.6
19	1	-4	50.8	48.0	3	1	-4	240.1	253.4	6	2	-8	205.0	226.0	7	3	1	66.1	60.9
19	1	-5	185.1	180.7	3	1	-5	196.7	167.2	4	2	5	175.1	173.6	7	3	0	207.0	176.2
19	1	-6	183.7	98.4	3	1	-6	213.7	205.7	4	2	4	243.5	238.4	7	3	-1	235.2	222.3
19	1	-7	251.7	250.2	3	1	-7	389.3	397.7	4	2	3	301.1	289.0	7	3	-2	318.6	349.6
19	1	-8	205.2	196.2	3	1	-8	118.5	128.2	4	2	2	64.1	46.5	7	3	-3	242.7	238.1
19	1	-9	122.7	104.4	1	1	6	88.9	81.1	4	2	1	411.1	346.6	7	3	-4	300.2	352.9
19	1	-10	192.5	174.9	1	1	5	159.7	163.2	4	2	0	281.9	261.3	7	3	-5	195.1	191.4
19	1	-11	363.9	308.4	1	1	4	82.5	70.8	4	2	-1	254.1	255.9	7	3	-6	188.6	183.7
19	1	-12	110.0	142.7	1	1	2	50.8	40.8	4	2	-2	404.7	471.9	7	3	-7	83.4	73.6
17	1	-2	37.0	33.9	1	1	1	643.1	636.7	4	2	-3	75.8	88.0	7	3	-9	170.1	190.3
17	1	-3	236.9	245.0	1	1	0	46.5	47.5	4	2	-4	130.3	124.1	5	3	4	100.8	95.6
17	1	-5	122.7	99.5	1	1	-2	130.1	108.8	4	2	-5	35.2	32.4	5	3	3	110.5	106.4
17	1	-7	224.2	195.1	1	1	-3	260.2	252.9	4	2	-6	383.3	433.1	5	3	2	91.0	77.8
17	1	-8	117.4	106.5	1	1	-4	152.3	152.0	4	2	-7	31.0	26.8	5	3	1	454.1	491.2
17	1	-9	279.2	265.8	1	1	-5	312.0	314.1	4	2	-8	45.9	40.8	5	3	0	97.5	65.0
17	1	-10	160.8	156.2	1	1	-6	157.6	144.9	2	2	6	85.4	93.4	5	3	-2	311.0	324.8
17	1	-11	121.6	97.6	1	1	-7	64.5	59.6	2	2	5	179.4	183.6	5	3	-3	282.8	313.8
15	1	-1	131.2	120.2	22	2	-8	279.8	324.2	2	2	4	78.0	61.8	5	3	-4	376.0	416.0
15	1	-2	86.7	79.4	22	2	-9	39.5	31.5	2	2	3	375.9	364.9	5	3	-5	133.3	133.2
15	1	-4	85.7	60.9	22	2	-10	118.5	90.6	2	2	2	434.6	408.3	5	3	-6	322.9	315.2
15	1	-5	416.8	443.6	20	2	-4	116.4	136.3	2	2	1	552.1	510.5	5	3	-7	194.0	183.8
															5	3	-8	149.5	150.5

Table 3. Continued.

3	3	3	393.4	408.9	-2	4	4	299.2	303.6	-11	5	1	123.5	126.4	6	5	3	46.9	39.8
3	3	2	320.6	294.5	-6	4	4	377.5	350.7	1	5	2	391.7	452.2	6	5	0	306.4	314.7
3	3	1	144.1	141.1	-10	4	4	271.4	282.4	3	5	2	483.5	423.7	6	5	1	152.5	152.2
3	3	0	237.3	246.6	-12	4	4	59.2	57.3	5	5	2	193.5	209.6	6	5	1	192.4	209.8
3	3	-1	507.2	449.0	-14	4	4	199.9	195.9	7	5	2	106.1	110.7	4	6	1	91.3	98.4
3	3	-2	41.2	41.0	-16	4	4	106.1	95.3	-1	5	2	345.7	396.4	6	6	1	43.2	41.1
3	3	-3	112.7	91.6	-18	4	4	136.7	134.9	-3	5	2	223.8	218.4	-2	6	1	167.8	140.6
3	3	-4	176.8	176.3	2	4	5	46.0	33.8	-5	5	2	90.9	77.8	-4	6	1	54.3	40.8
3	3	-5	186.4	174.5	0	4	5	126.2	117.1	-7	5	2	116.6	111.4	-6	6	1	227.0	190.5
3	3	-6	209.2	200.8	-2	4	5	195.5	200.4	-9	5	2	134.1	128.6	-8	6	1	227.0	194.9
3	3	-7	129.0	114.9	-4	4	5	372.0	377.3	-11	5	2	51.3	40.5	-10	6	1	192.4	232.9
1	3	5	306.7	284.7	-6	4	5	407.7	433.9	-13	5	2	127.1	130.7	8	6	2	118.4	129.1
1	3	4	130.0	121.8	-8	4	5	320.6	313.9	1	5	3	204.0	204.3	2	6	2	119.7	124.8
1	3	3	162.6	140.0	-10	4	5	220.8	230.1	3	5	3	54.6	51.6	4	6	2	80.2	86.5
1	3	2	347.9	383.1	-12	4	5	42.4	37.2	-1	5	3	67.4	91.1	-2	6	2	207.2	233.4
1	3	1	626.4	678.6	-14	4	5	146.3	133.6	-3	5	3	200.5	209.3	-4	6	2	48.1	43.8
1	3	0	295.8	305.9	-16	4	5	128.5	127.0	-5	5	3	136.4	146.5	-6	6	2	446.6	395.1
1	3	-1	212.4	200.9	-18	4	5	97.2	96.6	-7	5	3	179.5	165.2	-8	6	2	159.1	137.9
1	3	-2	213.5	204.7	0	4	6	135.2	134.7	-9	5	3	181.9	190.5	-10	6	2	310.9	329.5
1	3	-3	434.6	458.7	-2	4	6	243.5	249.4	-11	5	3	124.7	141.3	0	6	3	58.0	47.3
1	3	-5	36.8	40.2	-4	4	6	288.2	280.6	-13	5	3	94.4	91.6	2	6	3	140.8	139.0
1	3	-6	136.5	110.2	-10	4	6	132.9	98.9	-15	5	3	181.9	154.8	-4	6	3	185.0	193.8
0	4	0	148.6	159.3	-12	4	6	234.6	224.0	1	5	4	229.7	235.6	-6	6	3	286.2	278.2
2	4	0	283.7	297.7	-14	4	6	141.9	100.8	-1	5	4	144.6	159.1	-8	6	3	271.4	243.3
4	4	0	86.0	88.7	-16	4	6	218.9	177.6	-5	5	4	191.2	183.8	-10	6	3	203.5	214.2
6	4	0	271.4	283.6	-20	4	6	169.8	177.3	-7	5	4	113.1	119.6	-12	6	3	49.3	35.3
10	4	0	217.8	234.0	-4	4	7	223.4	206.4	-9	5	4	59.5	45.8	0	6	4	145.6	165.2
0	4	1	151.9	143.3	-6	4	7	232.3	241.2	-11	5	4	137.6	106.4	-2	6	4	37.0	27.8
2	4	1	223.4	229.5	-8	4	7	129.6	113.3	-13	5	4	286.8	296.0	-4	6	4	345.4	359.2
4	4	1	85.9	82.1	-10	4	7	43.5	33.2	-15	5	4	255.3	272.8	-6	6	4	190.0	143.9
6	4	1	119.5	111.1	-12	4	7	156.4	153.1	-1	5	5	143.4	143.6	-8	6	4	417.0	340.3
8	4	1	155.3	170.9	-14	4	7	134.2	132.0	-3	5	5	134.4	149.9	-10	6	4	215.4	214.8
10	4	1	236.3	267.0	-16	4	7	101.6	74.4	-5	5	5	137.6	136.1	-12	6	4	58.0	64.4
12	4	1	131.8	119.6	-20	4	7	188.8	143.6	-7	5	5	141.1	142.2	-2	6	5	85.1	108.4
-4	4	1	143.0	134.6	-6	4	8	151.9	169.0	-9	5	5	167.9	148.6	-4	6	5	180.1	220.7
-6	4	1	341.8	333.6	-8	4	8	52.5	43.2	-11	5	5	145.7	117.0	-6	6	5	212.2	249.7
-8	4	1	356.3	361.1	-10	4	8	160.8	152.1	-13	5	5	220.3	197.9	-8	6	5	146.8	148.6
-10	4	1	413.3	400.0	-12	4	8	78.2	73.2	-15	5	5	74.6	51.7	-10	6	5	177.6	98.5
-12	4	1	221.2	222.6	-14	4	8	188.8	176.7	-17	5	5	141.2	136.3	-12	6	5	98.7	88.9
-14	4	1	85.9	93.0	-18	4	8	255.8	253.0	-3	5	6	73.4	58.8	-14	6	5	119.7	138.2
0	4	2	230.1	239.4	-10	4	9	62.6	45.9	-5	5	6	176.8	148.7	-10	6	7	30.8	29.1
2	4	2	83.6	97.0	-12	4	9	154.1	141.8	-9	5	6	121.2	104.6	-12	6	7	151.7	158.1
4	4	2	221.2	206.1	-14	4	9	100.5	71.7	-11	5	6	269.3	263.6	-14	6	7	136.9	121.0
6	4	2	80.1	74.5	-16	4	9	57.0	47.0	-13	5	6	426.7	403.9	1	7	0	63.1	58.6
8	4	2	186.5	148.9	-18	4	9	173.1	144.4	-15	5	6	356.7	321.0	3	7	0	48.7	38.2
-2	4	2	73.7	81.4	-20	4	9	259.1	240.3	-17	5	6	272.8	269.4	5	7	0	105.1	103.3
-4	4	2	338.4	343.2	-14	4	10	33.5	41.8	-5	5	7	101.4	105.6	1	7	1	182.6	155.4
-6	4	2	43.6	21.1	-16	4	10	163.1	163.0	-7	5	7	142.2	123.9	3	7	1	321.8	326.4
-8	4	2	382.0	374.1	3	5	4	256.5	299.5	-9	5	7	109.6	100.2	-1	7	1	425.6	373.6
-12	4	2	252.4	255.2	1	5	0	431.3	478.9	-11	5	7	207.5	170.8	-5	7	1	212.8	190.4
-14	4	2	58.1	94.0	3	5	0	384.7	405.4	-15	5	7	222.7	200.6	-7	7	1	128.7	145.1
2	4	3	160.8	159.0	5	5	0	124.7	106.1	-17	5	7	47.8	38.9	-1	7	2	48.6	49.2
4	4	3	110.6	109.2	9	5	0	106.1	86.6	-9	5	8	143.5	143.5	-3	7	2	64.4	57.7
-2	4	3	107.2	81.9	11	5	0	64.1	79.6	-11	5	8	277.5	297.4	-5	7	2	233.6	205.4
-4	4	3	338.6	342.3	1	5	1	65.4	75.6	-13	5	8	333.4	366.1	-7	7	2	194.4	201.5
-6	4	3	450.1	466.9	3	5	1	249.5	245.0	-15	5	8	267.0	231.6	-1	7	3	32.8	36.6
-8	4	3	417.8	439.5	5	5	1	87.4	88.5	-17	5	8	190.0	180.1	-3	7	3	176.0	161.5
-10	4	3	430.0	399.1	7	5	1	143.4	160.7	-13	5	9	141.1	172.3	-5	7	3	134.0	132.8
-12	4	3	137.4	137.5	-1	5	1	262.3	259.9	-15	5	9	53.6	49.6	-7	7	3	46.0	49.3
-16	4	3	77.1	72.0	-3	5	1	83.9	90.3	-17	5	9	142.2	154.2	-9	7	3	136.9	170.2
0	4	4	83.8	77.1	-5	5	1	216.8	203.3	0	6	0	141.9	127.4	-5	7	4	211.5	242.3
2	4	4	199.9	190.9	-7	5	1	132.9	130.6	2	6	0	133.2	120.6	-7	7	4	190.5	202.0
4	4	4	81.5	72.7	-9	5	1	124.7	132.9	4	6	0	249.2	233.3	-9	7	4	155.0	170.7
															3	3	5	42.3	33.3
															3	3	4	210.2	199.8

mercury atoms and then of all atoms in the unit cell have been subtracted from the observed structure factors. The sections were calculated at intervals of $\Delta y=0.025$ ($\Delta y=0.15$ Å) from $y=0.000$ to $y=0.250$. The whole unit cell in the x and z directions was studied. The section $\varrho'(x,0.175,z)$, showing two chlorine and two oxygen atoms, intersected respectively 0.18 Å and 0.015 Å from their midpoints, is given in Fig. 1 a. The appearance, the heights and the positions of the peaks in this section and in all the other calculated ones are in a very good agreement with the now deduced parameter values. In the sections $\varrho'''(x,y,z)$ (*e.g.* $\varrho'''(x,0.175,z)$ in Fig. 1 b), the highest peaks and the deepest pits are smaller than 0.25 of the height of an oxygen atom peak in the calculated electron density synthesis.

A final least-squares refinement of the 646 independent reflections was then made using the program LALS,[8] the isotropic temperature factors for the mercury atoms converted into anisotropic ones. Altogether 36 parameters were refined: 10 positional parameters, 16 anisotropic and 2 isotropic tempera-

Table 4. Interatomic distances (Å units) and bond angles in the structure of $Hg_4O_2Cl_2$ (*cf.* Figs. 3 b and 4). The values are corrected for thermal motion.

Bond	Distance	e.s.d.
$Hg_{II}-2Hg_{III}$	2.708	0.002
$Hg_{III}-Hg_{III}$	2.708	0.002
Hg_I-2Hg_{II}	3.412	0.004
Hg_I-2Hg_{III}	3.520	0.003
$Hg_{III}-Hg_{III}$	3.429	0.004
Hg_I-2O	2.02	0.03
$Hg_{II}-2O$	2.23	0.03
$Hg_{II}-2Cl$	2.84	0.01
$Hg_{III}-Cl$	2.60	0.01
$Hg_{III}-O$	2.26	0.03
$Hg_{III}-O$	2.49	0.03
Cl—Cl	≷ 3.41	0.02
Cl—O	≷ 3.23	0.03
O—O	≷ 3.28	0.05
$\angle Hg_{III}-Hg_{II}-Hg_{III}$	60.0° ± 0.1°	
$\angle Hg_{II}-Hg_{III}-Hg_{III}$	60.0° ± 0.1°	
$\angle Hg_{III}-Hg_{III}-Cl$	158.7° ± 0.2°	
$\angle O-Hg_I-O$	180.0° ± 0.0°	

ture factors and 8 interlayer scale factors. The weighting factor scheme recommended by Cruickshank,[9] was used. The refinement was considered to be complete after 5 cycles when the shifts in the coordinates of the oxygen atoms were well below 0.1 % of their standard deviations and when there were no shifts in the coordinates of the mercury and the chlorine atoms. The *R*-value was then 0.089. In Table 1 are given the final fractional parameters and their corresponding standard deviations and also the temperature factors and their standard deviations. Isotropic thermal parameters *B* are given in Å^2 and the anisotropic parameters β are dimensionless. The weight analysis after the last cycle of the refinements is given in Table 2. It presents an overall view of the

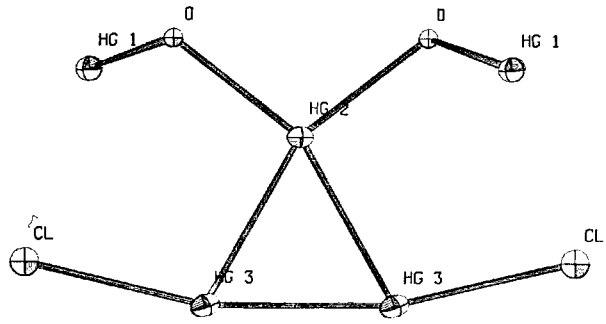

Fig. 2. Part of a $(Hg_4O_2Cl_2)_n$-chain, showing the anisotropic character of the thermal vibrations of the mercury atoms.

Table 5. Root-mean-square components R_i (Å) of thermal vibration along principal axes of the ellipsoids of vibration.

Atom	R_1 $\sigma(R_1)$	R_2 $\sigma(R_2)$	R_3 $\sigma(R_3)$
Hg_I	0.096 0.022	0.117 0.011	0.129 0.008
Hg_{II}	0.080 0.027	0.118 0.024	0.142 0.006
Hg_{III}	0.086 0.023	0.131 0.018	0.165 0.005

deviations $|F_o|-|F_c|$ in the calculations. The observed and calculated structure factors are given in Table 3 and the interatomic distances and angles of interest in Table 4. The anisotropic character of the thermal vibrations of the mercury atoms is shown in Fig. 2 and in Table 5.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

From a two-dimensional X-ray intensity material, Ščavničar [3] found that the structure of terlinguaite was built up of two separate elements, *viz.* endless zig-zag —O—Hg—O— chains, and molecules Hg_2Cl_2, forming a layer structure. A mercury-oxygen distance of 2.40 Å, which is too long to represent a chemical bond, was the shortest one found between atoms belonging to different structure elements (Fig. 3 a). Consequently, the formula of the mineral was written $2HgO{\cdot}Hg_2Cl_2$. Three mercury atoms with Hg—Hg distances of 2.70, 2.70, and 2.66 Å formed a triangle. One of these atoms was described to belong to the HgO-chain and the two others to form the Hg_2Cl_2-molecule. Thus, one of

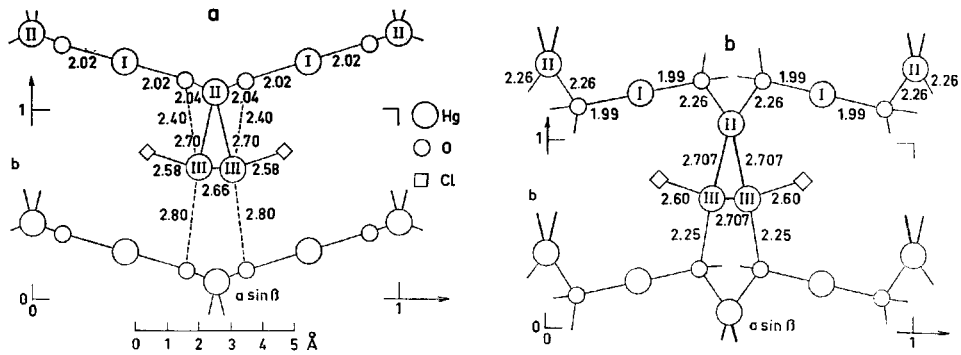

Fig. 3. Projection of the structure of terlinguaite along [001];
a) the coordinates of the atoms according to the previous author.[3]
b) the coordinates of the atoms according to the present authors. The distances are not corrected for thermal motion.

them was considered to be divalent and the other two monovalent. A similar description is given in a short communication by Baird and Harris.[10]

From three-dimensional intensity data (CuK), the present authors have found oxygen atom positions quite different from those given in Ref. 3 and also some changes in the parameters of the chlorine and the mercury atoms. The result has revealed that the structure is more complicated than described above. Thus, it is no longer possible to discern separate HgO-chains or Hg_2Cl_2-molecules. In spite of that, when describing the structure it is convenient to start from the same building elements as given by Ščavničar, *viz.* the Hg_2Cl_2-molecule and the HgO-chain.

On account of a strong interaction between the mercury atoms of the imaginary endless HgO-chain and those of the mercury doublet of the imagined calomel molecule, there is formed a "mercury triangle" which is equilateral within the limits of error ($\sigma = \pm 0.002$ Å) (Fig. 3 b). The distances between these atoms, denoted Hg_{II} and Hg_{III} (Table 4) are short, being 2.708 Å. Equilateral "mercury triangles", with normal Hg—Hg distances (*cf.* the structure of HgO(*o-rh*)[11]) are found in Hg_3OCl_4[12] and in $Hg_3S_2Cl_2$,[13] the distances Hg—Hg being 3.532 Å and 3.543 Å, respectively, with standard deviations of 0.003 Å. On the other hand the reported Hg—Hg distance in Hg_2Cl_2[14] is 2.53 Å. Thus, the three mercury atoms Hg_{II} and Hg_{III} may be bonded mutually to each other. Further, as seen from the interatomic distances, there seems to be no reason to assign different oxidation numbers to them. In the structure all other mercury-mercury distances are much longer, ≥ 3.41 Å.

In the linear molecule of Hg_2Cl_2, the distances Hg—Hg and Hg—Cl are reported to be 2.53 Å and 2.52 Å, respectively.[14] The corresponding group in the present structure is distorted, giving longer interatomic distances. Thus, the distance Hg—Hg, identical to the triangle edge, is 2.708 ± 0.002 Å and Hg—Cl is 2.60 ± 0.01 Å. The angle Cl—Hg—Hg is $158.7° \pm 0.2°$ (Table 4). In the endless, planar zig-zag chain of HgO(*o-rh*) the distances Hg—O are 2.07 Å and 2.04 Å ($\sigma = \pm 0.03$ Å) and the angles O—Hg—O $180° \pm 1°$ and Hg—O—Hg $107° \pm 2°$.[11] A large and important deformation of this structure element has occurred in the present structure, causing the distances Hg_I—O to be 2.02 Å and Hg_{II}—O 2.23 Å ($\sigma = \pm 0.03$ Å) and the angles O—Hg_I—O $180° \pm 0°$ and O—Hg_{II}—O $105° \pm 1°$. The angles Hg_I—O—Hg_{II} are $107° \pm 1°$ (Fig. 3 b, Table 4).

Furthermore, the distances from the mercury atoms (Hg_{III}) of the deformed "Hg_2Cl_2-molecule" to the oxygen atoms of the "HgO-chain" are rather short, being 2.26 ± 0.03 Å, the same distance as found for tetrahedral bonding Hg—O in $Hg(OHg)_4Br_2$.[15] Thus, there seem to be but formal and didactic reasons for describing the structure of terlinguaite as being built up of separate Hg_2Cl_2-molecules and HgO-chains, even severely distorted ones.

The structure is thus more correctly described as built up of endless, slightly puckered chains of the composition $(Hg_4O_2Cl_2)_n$ (Fig. 4), joined by mercury-to-chlorine contacts into a three-dimensional network. The contact distances are those between mercury and chlorine atoms of different chains Hg_{II}—2Cl = 2.84 Å (Table 4), somewhat shorter than between a mercury atom within the ion $OHg_3Cl_3^+$ and chloride ion (2.99 Å) in the structure of Hg_3OCl_4.[12]

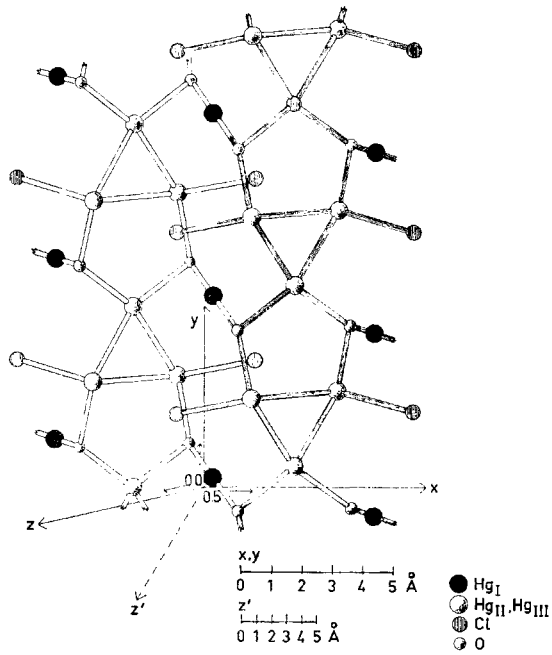

Fig. 4. Perspective view of the structure of terlinguaite, showing one chain $(Hg_4O_2Cl_2)_n$. *x,y,z* correspond to the crystallographic axes. *z'* denotes a line perpendicular to the crystallographic *xy* plane. The part of the chain where the bonding distances are shaded lies near the plane $z=0.75$. The other part lies near $z=0.25$. Filled circles show the mercury atoms Hg_I and empty small ones the oxygen atoms. These atoms form the short mercury-oxygen bonds of 2.02 Å.

Two such chains $(Hg_4O_2Cl_2)_n$ are running parallel to the *y*-axis through the unit cell. They are crystallographically equivalent. *Geometrically*, the chain can be described as built up of two parts of the composition $(Hg_3O_2Cl_2)_n$, connected by divalent mercury atoms, the atoms Hg_I (Fig. 4), with short mercury-oxygen distances of 2.02 Å. The $O-Hg_I-O$ bonding is linear. One part of the chain is lying near the plane $z=0.25$ and the other near $z=-0.25$. The maximum distance of an atom of a part of the chain to the respective plane is ± 0.45 Å.

The coordination conditions of the various atoms of the structure may be summarized as follows:

Two of the mercury atoms of the "mercury triangle" (the atoms denoted Hg_{III}) are each further surrounded by one chlorine atom (2.60 Å) and one oxygen atom (2.26 Å). An atom Hg_{III}, of point symmetry 1 and its four nearest neighbours, *viz.* two mercury atoms, one chlorine and one oxygen atom form a very flat square pyramid with the central atom Hg_{III} at its vertex (Fig. 4).

The third mercury atom Hg_{II} (point symmetry *2*) of the triangle is surrounded by two oxygen atoms (2.23 Å), two chlorine atoms (2.84 Å) and the two mercury atoms Hg_{III} (2.71 Å), the six atoms forming a deformed octahedron.

The atoms Hg_I which are situated at a centre of symmetry are surrounded by six atoms, *viz.* two oxygen atoms (2.02 Å) and four chlorine atoms (3.17 Å). The resulting polyhedron is a deformed octahedron.

The oxygen atoms in acentric positions are each surrounded by four mercury atoms in the shape of a deformed tetrahedron. The same polyhedron is formed by four mercury atoms around all chlorine atoms, also in acentric positions.

In the structure of terlinguaite there are mercury atoms of different oxidation numbers. Šćavničar stated that half of them were monovalent and half divalent. The present authors prefer to write the formula of the mineral in its original form $Hg_4O_2Cl_2$ or possibly $Hg(Hg_3O_2Cl_2)$ instead of $2HgO{\cdot}Hg_2Cl_2$. To one quarter of the mercury atoms, the atoms Hg_I, collinearily bonded to two oxygen atoms, the oxidation number 2 may be attributed while the others, *viz.* Hg_{II} and Hg_{III}, may formally be considered to have the oxidation number 4/3.

More information concerning the valency stages of the mercury atoms in terlinguaite, is expected to issue from spectroscopic studies now in progress. It is hoped that these studies will give more exact indications concerning the correct oxidation numbers of Hg_{II} and Hg_{III}.

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