Short Communication

The Crystal Structure of Mercury (I,II) Bromide Oxide, $Hg_8O_4Br_3$*

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Until recently, the mineral terlinguaite, $Hg_4O_2Cl_2$, was the only structurally characterized Hg(I,II) compound.[1,2] Terlinguaite is built up of pleated layers with linearly coordinated Hg(II) atoms and Hg_3 groups forming equilateral triangles with Hg–Hg bonds of 2.708 Å. This distance is much longer than usually found in Hg(I) compounds (2.48–2.54 Å), but considerably shorter than Hg(II)···Hg(II) contacts (> 3.3 Å).

Lately, the structures of two new compounds with the same stoichiometry as terlinguaite, viz. Hg_2OI[3] and $Hg_2O(NO_3)$,[4] have been solved. Both compounds can be described as built up of endless −O−Hg(II)−O− zig-zag chains connected via the O atoms to Hg(I) dimers, thus forming folded layers in which the anions are located in cavities. In an attempt to synthesize Hg_2OBr the compound $Hg_8O_4Br_3$ was obtained, and its crystal structure has now been determined.

Experimental

Single crystals were obtained by hydrothermal synthesis at 460 K from a stoichiometric mixture of yellow HgO and Hg_2Br_2. A dark reddish-brown single crystal of dimensions 0.19 × 0.22 × 0.10 mm was used for the data collection on a Syntex $P2_1$ diffractometer employing monochromated Mo$K\alpha$ radiation. Unit cell dimensions were obtained from 50 θ-values measured at 295 K on the diffractometer; a = 6.8554(9), b = 6.3033(9) and c = 31.093(3) Å, β = 96.09(1)° and V = 1336.0(2) Å^3. The space group is $P2_1/n$ with Z = 4 and D_x = 9.49 g cm^{-3}.

4504 reflections with θ ≤ 30° were measured with ω-scans in one quadrant of reciprocal space. 2412 reflections with $I \geq 3\sigma(I)$ were used in the structure analysis. Three standard reflections were recorded at regular intervals; no systematic variations in their intensities were observed. I and $\sigma(I)$ were corrected for Lp and absorption effects; the transmission factors, evaluated by numerical integration, varied from 0.008 to 0.041 (μ = 1005 cm^{-1}). The heavy atoms, Hg and Br, were found by direct methods,[5] and the oxygen atom positions were localized in Fourier difference maps. The structure was refined by the full-matrix least-squares technique with anisotropic temperature factors for mercury and bromine, and isotropic factors for oxygen. The function minimized was $\Sigma w(|F_o|-|F_c|)^2$ with weights $w^{-1} = (\sigma^2|F_o| + 0.055|F_o|^2 + 1.0)$. The final refinement resulted in R = 0.068, R_w = 0.084 and S = 1.2. A correction for secondary extinction[6] was also included in the refinement and gave g = 0.16(2)·10^4. The computer programs used were those in Ref. 7.

The final positional parameters are given in Table 1, and selected interatomic distances and angles in Table 2. Lists of anisotropic thermal parameters, and observed and calculated structure factors are available from the author on request.

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Table 1. Final positional and isotropic thermal parameters with e.s.d.'s in parentheses.

Atom	*x*	*y*	*z*	U_{iso}/U_{eq}[a]/Å^2
Hg1	0.14270(23)	0.63017(28)	0.00732(5)	0.0254(4)
Hg2	0.44486(23)	0.17071(25)	−0.03868(4)	0.0203(4)
Hg3	0.28525(25)	0.17790(30)	−0.10792(5)	0.0261(5)
Hg4	0.61583(23)	0.62821(25)	0.07005(4)	0.0197(4)
Hg5	0.85163(24)	0.42212(27)	0.12285(4)	0.0225(4)
Hg6	1.20056(23)	0.41288(25)	0.21358(4)	0.0205(4)
Hg7	1.64761(20)	0.63312(25)	0.21946(4)	0.0166(4)
Hg8	0.98918(21)	−0.06945(23)	0.17740(4)	0.0166(4)
Br1	0.88435(66)	−0.00347(75)	0.05623(14)	0.0290(12)
Br2	0.28921(67)	0.68327(73)	0.12923(15)	0.0303(12)
Br3	0.58596(61)	0.14631(72)	0.18884(13)	0.0259(11)
O1	0.4261(36)	0.7748(43)	0.0188(7)	0.015(5)
O2	1.0810(33)	0.2224(39)	0.1587(7)	0.010(4)
O3	1.4009(35)	0.6116(42)	0.2506(7)	0.014(5)
O4	0.9025(38)	−0.3678(45)	0.1929(8)	0.018(5)

[a] $U_{eq} = 1/3\Sigma_i\Sigma_j U_{ij}a^*_i a^*_j \mathbf{a}_i\mathbf{a}_j$.

Table 2. Selected bond distances (Å) and angles (°).

Hg1−Hg1^{i}	2.557(3)	Hg2−O1	2.10(2)	Hg5−O2	2.22(2)
Hg2−Hg3	2.517(2)	Hg−O1^{ii}	2.57(3)	Hg5−O4^{iv}	2.54(2)
Hg4−Hg5	2.536(2)	Hg3−O2^{iii}	2.24(2)		
Hg1−O1	2.14(2)	Hg4−O1	2.16(2)		
Hg1^{i}−Hg1−O1	165.1(7)			Hg5−Hg4−O1	172.4(7)
Hg3−Hg2−O1	169.6(7)			Hg4−Hg5−O2	169.8(5)
Hg3−Hg2−O1^{ii}	102.0(5)			Hg4−Hg5−O4^{iv}	107.9(6)
O1−Hg2−O1^{ii}	88.2(9)			O2−Hg5−O4^{iv}	80.8(8)
Hg2−Hg3−O2^{iii}	165.4(6)				
Hg6−O3	2.11(2)	Hg6−O4^{iv}	2.50(3)	Hg8−O4	2.04(3)
Hg6−O2	2.18(2)	Hg7−O4^{vi}	2.01(2)	Hg8−O2	2.05(2)
Hg6−O3^{v}	2.34(2)	Hg7−O3	2.04(2)	Hg8−O3^{v}	2.55(2)
O2−Hg6−O3	157.9(8)			O3−Hg7−O4^{vi}	174.3(10)
O2−Hg6−O3^{v}	79.6(8)			O2−Hg8−O4	176.7(9)
O3−Hg6−O3^{v}	115.5(4)				

Symmetry code: *i*: −*x*, 1−*y*, −*z*; *ii*: 1−*x*, 1/2+*y*, −*z*; *iii*: 2−*x*, 1−*y*, −*z*; *iv*: *x*, 1+*y*, *z*; *v*: 1/2−*x*, −1/2+*y*, 1/2−*z*; *vi*: 1+*x*, 1+*y*, *z*.

Results and discussion

The structure is quite different from those of the earlier investigated mercury(I,II) compounds $Hg_4O_2Cl_2$,[1,2] Hg_2OI[3] and $Hg_2O(NO_3)$.[4] There are five Hg(I) atoms (Hg1−Hg5) and three Hg(II) atoms (Hg6−Hg8) in the asymmetric unit. The Hg(I) atoms form three Hg(I) pairs with Hg−Hg distances of 2.517(2)–2.557(3) Å, the latter distance being somewhat longer than normally found in Hg(I) compounds.[8] The Hg(I) atoms are further bonded to the oxygen atoms O1 and O2, which with Hg2−Hg5 form 12-membered −O−Hg−Hg−O− rings having Hg−O bond

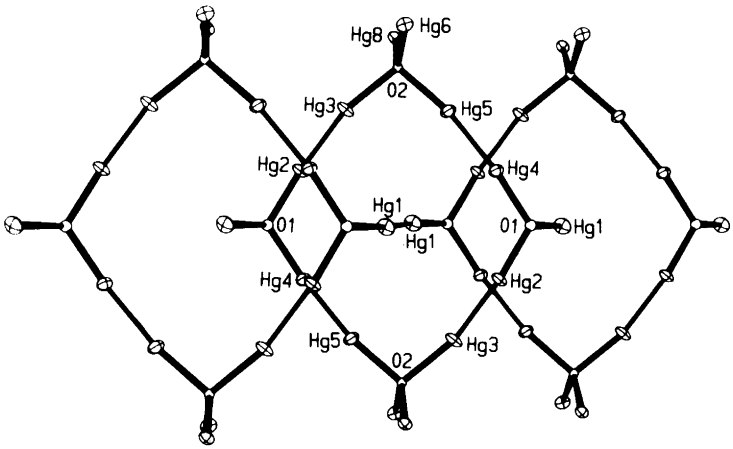

Fig. 1. Interlocking −O−Hg(I)−Hg(I)−O− chains.

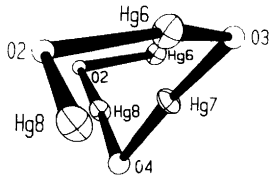

Fig. 2. The spiral −O−Hg(II)−O− chain.

lengths in the range 2.10–2.14 Å (Table 2). Hg1−Hg1 dimers connect the rings to form endless interlocking chains (Fig. 1). The Hg(II) atoms, Hg6−Hg8, are diagonally coordinated by the oxygen atoms O2−O4 in spiral chains (Fig. 2). Hg7 and Hg8 are almost linearly coordinated at short Hg−O distances (2.01–2.05 Å), as found, e.g., for the two modifications of HgO.[9-11] The two Hg6−O bonds within a spiral chain are elongated (2.11, 2.18 Å) with an O−Hg6−O angle of only 157.9°. This is caused by the binding of a third oxygen atom to Hg6 from a neighbouring spiral chain at 2.34 Å. The atom O2 links the Hg(I) and Hg(II) parts to form a three-dimensional network with the bromine atoms located in cavities; the shortest Hg−Br distance (Hg4−Br1) is 3.02 Å.

All oxygen atoms have four Hg neighbours (O−Hg < 2.90 Å, Table 2) and the Hg−O network in the structure may also be described on the basis of connecting OHg_4 groups. Atom O1 coordinates only to Hg(I)-dimers, O2 and O4 to both Hg(I) and Hg(II), and O3 only to Hg(II) atoms. The Hg atoms around O2 form a fairly regular tetrahedron (O−Hg 2.05–2.24 Å, O−Hg−O 100.4–115.4°), while the other OHg_4 groups deviate considerably from tetrahedral geometry.

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