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Short Communications

X-Ray Studies on the Mercury(II) Bromates $K_2Hg(BrO_3)_2(NO_3)_2$ and $Hg(BrO_3)_2 \cdot 2H_2O$

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As part of a study of mercury(II) halates, the two compounds $Hg(BrO_3)_2 \cdot 2H_2O$ and $K_2Hg(BrO_3)_2(NO_3)_2$ have been synthesized and structurally investigated. $Hg(BrO_3)_2 \cdot 2H_2O$ crystallizes from a solution obtained by dissolving $NaBrO_3$ in a warm solution of $Hg(NO_3)_2$ in 3 M HNO_3. By exchange of $NaBrO_3$ for $KBrO_3$ the compound $K_2Hg(BrO_3)_2(NO_3)_2$ was prepared. The crystal structures were determined from single crystal X-ray diffraction data collected at room temperature on a CAD-4 four-circle diffractometer. Information on crystal data, the collection and reduction of the intensities and some details of the least-squares refinements are given in Table 1. The fractional coordinates and B_{eq} are given in Table 2. Lists of structure factors and anisotropic temperature coefficients may be obtained from the authors.

Discussion. In mercury(II) compounds two-coordination is prevalent. In the coordination to oxygen, mercury is in most cases linearly or almost linearly bonded at the short distances 2.0–2.2 Å. There are, however, often 3–5 more ligands at 2.4–2.9 Å, implying considerably weaker interactions. Four- and six-coordination for Hg with

Table 1. Crystal data, collection and reduction of intensities and least-squares refinements.

Formula	$K_2Hg(BrO_3)_2(NO_3)_2$	$Hg(BrO_3)_2 \cdot 2H_2O$
F.W.	658.60	492.42
Space group	*Pnnm* (No. 58)	$P2_12_12_1$ (No. 19)
a (Å)	14.170(2)	6.2194(4)
b (Å)	7.254(1)	9.3139(7)
c (Å)	5.656(1)	12.529(1)
V (Å^3)	581.4	727.8
Z	2	4
D_x	3.76	4.49
Crystal size/mm	$0.20 \times 0.09 \times 0.07$	$0.30 \times 0.15 \times 0.12$
Radiation	Mo$K\alpha$	Ag$K\alpha$
θ interval/°	3–32.5	2.5–25
Scan type	$\omega-2\theta$	$\omega-2\theta$
$\Delta\omega$/°	$0.6+0.5\tan\theta$	$0.75+1.0\tan\theta$
Max. scan time/min	4	4.5
μ/cm^{-1}	251	181
Range of trans. factors	0.20–0.27	0.10–0.18
Isotropic extinc. factor	$0.17(2) \times 10^4$	$0.22(4) \times 10^4$
Measured refl.	1651 [a]	2931
Refl. in final refinement	887, $I > 3\sigma(I)$	2083, $I > 3\sigma(I)$
Parameters	54	103
R	0.026	0.055 [b]
R_w	0.034	0.072
S	1.25	1.31

[a] 1228 reflections with $I > 3\sigma(I)$ were averaged to 887 independent ones. [b] Correction for anomalous dispersion made.

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Table 2. Fractional atomic coordinates and B_{eq} (Å^2) with estimated standard deviations in parentheses.

Atom	x	y	z	B_{eq}
$K_2Hg(BrO_3)_2(NO_3)_2$. Hg in position 2(*a*); Br, K, O(3), O(4) and N in 4(*g*); O(1) and O(2) in 8(*h*).				
Hg	0	0	0	1.92(1)
Br	0.38400(5)	0.73193(9)	0	2.00(1)
K	0.2807(1)	0.2438(2)	0	2.60(4)
O(1)	0.1248(3)	0.0882(6)	0.2728(8)	3.21(10)
O(2)	0.4326(4)	0.2049(10)	0.3156(13)	6.97(20)
O(3)	0.2824(4)	0.8385(8)	0	3.11(14)
O(4)	0.1285(7)	0.4812(9)	0	6.51(31)
N	0.0888(5)	0.6265(8)	0	2.80(15)
$Hg(BrO_3)_2 \cdot 2H_2O$. All atoms in position 4(*a*).				
Hg	0.06910(10)	0.07098(6)	0.21727(4)	1.80(1)
Br(1)	0.2126(2)	0.2198(1)	0.6118(1)	1.51(3)
Br(2)	0.3327(2)	0.3408(1)	0.1154(1)	1.62(3)
O(1)	0.3145(22)	0.2425(17)	0.4922(9)	2.82(26)
O(2)	0.1519(21)	0.0460(11)	0.6145(10)	2.49(25)
O(3)	0.4259(21)	0.2190(13)	0.6945(9)	2.63(26)
O(4)	0.2557(22)	0.4932(11)	0.1685(10)	2.55(28)
O(5)	0.4009(24)	0.2316(13)	0.2127(11)	3.31(32)
O(6)	0.1048(18)	0.2659(13)	0.0793(8)	2.45(27)
OW(1)	0.2096(20)	0.5191(13)	0.4022(8)	2.34(25)
OW(2)	0.2288(21)	−0.0190(13)	0.3721(9)	2.54(25)

Table 3. Selected interatomic distances (Å) and angles (°) with estimated standard deviations in parentheses in the structure of $K_2Hg(BrO_3)_2(NO_3)_2$. Notations of the atoms, *cf.* Table 2.

The mercury coordination					
Hg−O(1)	2.433(4)	4X	O(1)−Hg−O(1)	78.7(2)	2X
Hg−O(2)	2.566(7)	4X		101.3(2)	2X
Hg···N	2.988(6)	2X		180	2X
			O(1)−Hg−O(2)	72.0(2)	4X
				78.1(2)	4X
				101.9(2)	4X
				108.0(2)	4X
			O(2)−Hg−O(2)	48.0(3)	2X
				132.0(3)	2X
				180	2X
The bromate group					
Br−O(3)	1.634(6)		O(1)−Br−O(1)	101.5(3)	
Br−O(1)	1.659(4)	2X	O(1)−Br−O(3)	103.3(2)	2X
The nitrate group					
N−O(4)	1.195(10)		O(2)−N−O(2)	116.6(8)	
N−O(2)	1.226(8)	2X	O(2)−N−O(4)	121.7(4)	2X
The potassium coordination					
K−O(4)	2.759(9)		K−O(3)	2.940(6)	
K−O(2)	2.811(6)	2X	K−O(3)	3.044(2)	2X
K−O(1)	2.921(4)	2X	K−O(1)	3.112(4)	2X

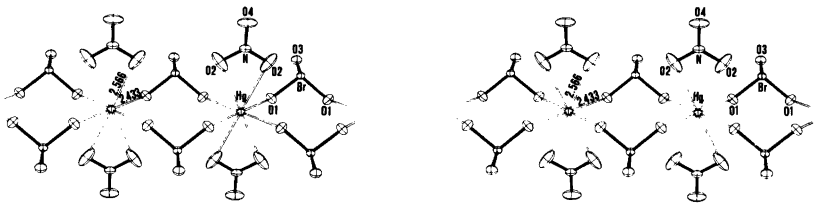

Fig. 1. A stereo view showing the Hg coordination and the linking of Hg by the bromate groups to infinite bands of formula $[Hg(BrO_3)_2(NO_3)_2]_n^{2n-}$ in $K_2Hg(BrO_3)_2(NO_3)_2$.

regard to O are rather unusual and coordination numbers higher than six have so far been reported only for the compound $K_3Hg(NO_2)_4NO_3$,[1,2] containing eight-coordinated Hg in the ions $[Hg(NO_2)_4]^{2-}$. Eight-coordinated Hg has now also been found in the two mercury(II) bromates $K_2Hg(BrO_3)_2(NO_3)_2$ and $Hg(BrO_3)_2 \cdot 2H_2O$.

$K_2Hg(BrO_3)_2(NO_3)_2$. Selected interatomic distances and angles are given in Table 3 and a stereo view showing the coordination of Hg and the linking of Hg by the bromate groups in Fig. 1. A projection of the structure on the *ac* plane is presented in Fig. 2.

Hg is bonded to four oxygens (Hg–O 2.57 Å) from two nitrate ions, which act symmetrically bidentate. The distance Hg···N is 2.99 Å in good agreement with values given for $K_3Hg(NO_2)_4NO_3$.[1] Moreover Hg is coordinated to four oxygens from four bromate groups (Hg–O 2.43 Å) (Fig. 1). The average bond length is 2.50 Å.

In $K_3Hg(NO_2)_4NO_3$ mercury is bonded to eight oxygens from the four bidentate nitrito groups, the coordination polyhedron being a severely distorted square antiprism.[1,2] The Hg–O bonds vary from 2.39 to 2.57 Å; the average value being 2.48 Å. The distances Hg···N are from 2.86 to 2.96 Å. If each NO_2^- group was regarded as forming only one bond to the Hg atom pointing towards the N atom, the four resulting bonds form a slightly deformed tetrahedron.[2]

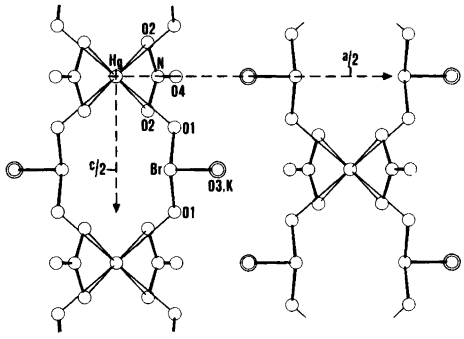

Fig. 2. Projection of the structure on the *ac* plane showing the infinite bands and the K atoms.

In $K_2Hg(BrO_3)_2(NO_3)_2$ mercury is, as stated above, bonded to eight oxygens. The coordination polyhedron is a highly distorted cube. If the same reasoning is applied as for $K_3Hg(NO_2)_4NO_3$, *viz.* that each NO_3^- ion in $K_2Hg(BrO_3)_2(NO_3)_2$ only forms one bond to Hg, pointing towards the N atom, the then occurring six bonds form a rather regular octahedron, the four bromate oxygens forming the central square and the assumed bonds the apices. The polyhedra are linked by O(1)–Br–O(1) bonds (Br–O 1.66 Å) to infinite bands of formula $[Hg(BrO_3)_2(NO_3)_2]_n^{2n-}$ running parallel to the *bc* plane (Fig. 2). Another description of the bands is that they are formed from four-membered chelate rings $[HgO_2N]$ and eight-membered rings $[Hg_2O_4Br_2]$ sharing the Hg atoms (Fig. 1).

The potassium ions are located in cavities in the structure (Fig. 2). They are irregularly surrounded by ten oxygens at distances varying from 2.76 to 3.11 Å in accordance with data on the coordination K–O (coord. number 10) reported in the literature (2.71–3.03 Å).[3] The infinite bands are connected to a three-dimensional network by the K–O contacts.

The mean values of the Br–O distances and O–Br–O angles (Table 3) are 1.653(3) Å and 102.9(1)° in good agreement with data reported for $NaBrO_3$.[4] The pyramidal BrO_3^- ion is somewhat distorted due to an elongation of the bridging Br–O(1) distances. Similar elongations are also found for the bridging Cr–O and S–O distances in *e.g.* $HgCrO_4 \cdot \frac{1}{2}H_2O$[5] and $Hg_3(OH)_2(SO_4)_2 \cdot H_2O$.[6]

The mean values of the N–O distances and O–N–O angles (Table 3) are 1.217(5) Å and 120.7(3)° also in accordance with values given in literature (1.22–1.27 Å).[3] A small elongation of the N–O(2) distance was found, O(2) bonded to Hg.

Work is in progress on the compound $K_2Cd(BrO_3)_2(NO_3)_2$. It has most probably a structure very close to that of the Hg-compound.

$Hg(BrO_3)_2 \cdot 2H_2O$. Mercury is eight-coordinated, bonded to two water oxygens (Hg–OW(1,2) 2.33, 2.34 Å) and to six oxygens, the atoms O(2)–O(6) (Table 2), from two crystallographically independent

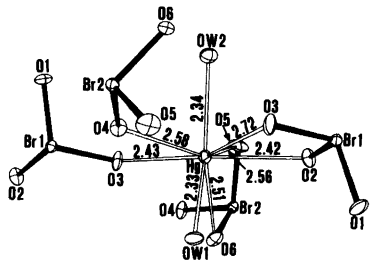

Fig. 3. The mercury coordination in $Hg(BrO_3)_2 \cdot 2H_2O$.

bromate groups (Hg – O 2.42 – 2.58, 2.72 Å) (Fig. 3). The irregular polyhedra around Hg are linked to a three-dimensional network. The Br – O bonds vary from 1.64 to 1.68 Å with a mean value of 1.65 Å.

The average value of the O – Br – O angles is 103.1°. A neutron diffraction work is now in progress to refine the structure and to locate the hydrogen bonds. A full report of the structure will be given elsewhere.

There also exists an analogous Cd compound with the formula $Cd(BrO_3)_2 \cdot 2H_2O$,[7] isomorphous with $Hg(BrO_3)_2 \cdot 2H_2O$. Cd is described as seven-coordinated, bonded to two water oxygen and five bromate oxygen atoms (Cd – OW 2.30, 2.32 Å; Cd – O 2.33 – 2.53 Å). As in the case of $Hg(BrO_3)_2 \cdot 2H_2O$ there is an oxygen atom at a longer distance (Cd – O 2.73 Å) making up an eight-coordination. The hydrogen atom positions were not determined for $Cd(BrO_3)_2 \cdot 2H_2O$.

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