

K₂[O(HgSO₃)₃], a new sulfito-mercurate with an [OHg₃] coreMatthias Weil,^{a*} Stefan Baumann^b and Dietrich K. Breitung^c^aInstitute for Chemical Technologies and Analytics, Division of Structural Chemistry,

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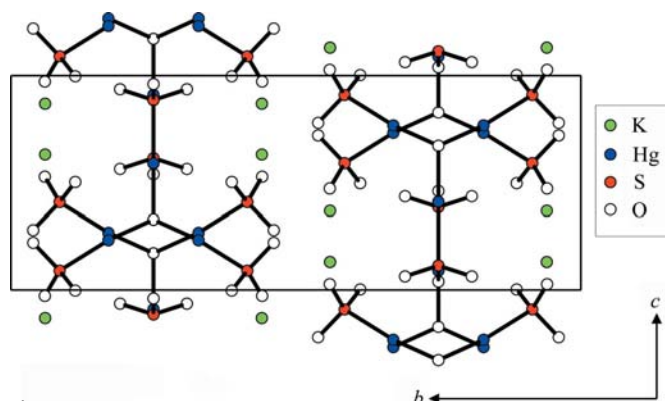
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The structure of dipotassium μ_3 -oxido-tris[sulfitomercurate(II)], K₂[O(HgSO₃)₃], is characterized by segregation of the K⁺ cations and complex [O(HgSO₃)₃]²⁻ anions into layers parallel to (010). The anion has *m* symmetry and is a new example of a μ_3 -oxido-trimercurate complex with a central [OHg₃] core. This unit adopts the shape of a flat, almost trigonal, pyramid (mean O—Hg = 2.072 Å and mean Hg—O—Hg = 110.8°). The two independent Hg—S bonds have nearly the same length (mean Hg—S = 2.335 Å). Due to intermolecular O··Hg donor–acceptor interactions greater than 2.65 Å, the O—Hg—S fragments are slightly bent. The [KO₉] coordination polyhedron of the K⁺ cation approaches a distorted tricapped trigonal prism with a [6+1+2] coordination.

Comment

In a recent project, we have studied the formation conditions and crystal structures of (NH₄)[HgCl(SO₃)] and (NH₄)₂[Hg(SO₃)₂] (Weil *et al.*, 2007). Continuing our work on sulfite complexes of mercury, we have also investigated in some detail the systems K₂SO₃–HgX₂ (*X* = Cl or Br) in aqueous solution and in the solid phases formed therein. Depending on the molar ratios of the components and on the conditions, several phases with the general formula *x*K[XHgSO₃]₃·*y*HgX₂·*z*KX were obtained. A characteristic of all the phases studied structurally so far is the segregation of the K⁺ cations and of the anions and HgX₂ molecules into layers (Weil *et al.*, 2008). On heating solid HgO in an aqueous K₂SO₃ solution, a related phase was obtained, *viz.* a formally basic salt of composition K₂SO₃·2HgSO₃·HgO, or, with respect to the crystal structure determination presented here, K₂[O(HgSO₃)₃].

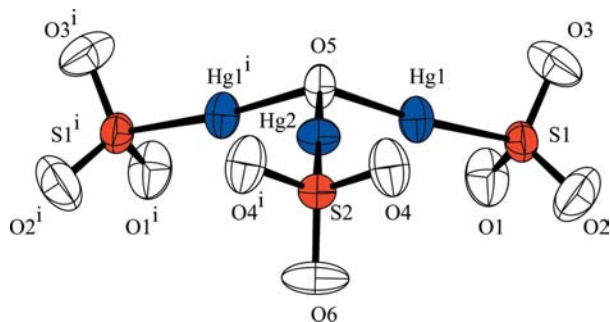
The asymmetric unit of the title compound contains one K, two Hg, two S and six O sites. As in the above-mentioned *x*K[XHgSO₃]₃·*y*HgX₂·*z*KX structures, a segregation of cations

**Figure 1**

The crystal structure of K₂[O(HgSO₃)₃] in projection along [100], showing the layered character of the cations and anions.

(K⁺) and anions [[O(HgSO₃)₃]²⁻] into layers is a characteristic feature of the structure, here with a stacking of the layers parallel to (010) (Fig. 1). The cationic and anionic layers adopt the symmetries (*a:c*).2₁: α -*p*112₁/*a* and (*a:c*).*m*.2₁-*p*2₁/*ma*, respectively (Shubnikov & Koptsik, 1974). The [O(HgSO₃)₃]²⁻ complex anion has site symmetry *m*, with the mirror plane running through atoms O5/Hg2/S2/O6 (Fig. 2). The anion is related to the [O(HgCl)₃]⁺ and [O(HgI)₂(HgOH)]⁺ cationic complexes which are present in the structures of 2HgCl₂·HgO [or, as a more detailed formula, [O(HgCl)₃]Cl] (Aurivillius, 1964) and [O(HgI)₂(HgOH)]ClO₄ (Köhler *et al.*, 1974, 1975). Both the anionic and the two cationic complexes contain flat nearly trigonal–pyramidal [OHg₃] cores, *i.e.* they are all μ_3 -oxido-trimercurate complexes which are representatives of metallo-complexes, and thus they exhibit similar bonding parameters. In the anionic complex, the average O—Hg bond length is 2.07 Å (Table 1), compared with 2.04 and 2.05 Å, respectively, in the cationic complexes. The slight difference may be due to the strong *trans* influence of the sulfite ligands and to the different charges, which is also mirrored in the different average Hg—O—Hg bond angles of 110.8° for the anionic complex and of 118.9 and 119.8° for the cationic complexes.

In the title compound, the average Hg—S bond length is 2.335 Å (Table 1), and the O—Hg—S structural fragments are slightly bent with only a minor deviation from linearity (mean O—Hg—S angle = 174.7°), due to the intermolecular donor–acceptor interactions with S—O··Hg > 2.65 Å. These interactions cause linking of the anions to the above-mentioned layers and the remote O atoms expand the coordination spheres of the Hg²⁺ cations to five- and six-coordination if Hg—O distances > 3.0 Å are neglected. The average Hg—S bond length is similar to the average Hg—Cl distance of 2.31 Å in [O(HgCl)₃]Cl and in good agreement with the Hg—S bond lengths in the sulfitomercurates (NH₄)[HgCl(SO₃)] and (NH₄)₂[Hg(SO₃)₂] (Weil *et al.*, 2007), and Na₂[Hg(SO₃)₂]·H₂O (Nyberg & Cynkier, 1972), with average values of 2.394, 2.364 and 2.406 Å, respectively. In contrast with K₂[O(HgSO₃)₃], in the latter structures, Cl—Hg—SO₃ and O₃S—Hg—SO₃ moieties are present. Nevertheless, in agreement with the preference of mercury for linear coordi-


Figure 2

The $[\text{O}(\text{HgSO}_3)_3]^{2-}$ anion with the atom-labelling scheme. Displacement ellipsoids are drawn at the 90% probability level. [Symmetry code: (i) $x, -y + \frac{1}{2}, z$.]

nation, the Cl–Hg–S and S–Hg–S angles are close to 180° , *viz.* 165.5, 174.4 and 172.8° , respectively.

The S–O bond lengths of the two independent SO_3 groups in $\text{K}_2[\text{O}(\text{HgSO}_3)_3]$ differ slightly (mean S–O = 1.460 and 1.473 Å) because of their different roles in the linking within and between the cationic and anionic layers. Not all of the O atoms of the sulfite groups are involved in donor–acceptor interactions within the anionic layers, and only some of the O atoms are coordinated to the K^+ cation, and thus contribute to the linking of the cationic and anionic layers. The K^+ cation has nine O-atom neighbours with a [6+1+2] coordination and with K–O distances ranging from 2.801 (4) to 3.276 (5) Å (Table 1). The resulting coordination polyhedron may be described as a distorted tricapped trigonal prism.

Results from bond-valence-sum calculations (Brown, 2002), using the parameters of Brese & O’Keeffe (1991), are in good agreement with the expected values for K, Hg and O (1, 2 and 2, respectively): Hg1/Hg2 (including all distances < 3.0 Å) 1.99 and 2.10; K 1.07; O1 [coordination number (CN) = 5; 1 S, 2 Hg, 2 K] 1.94, O2 (CN = 4; 1 S, 3 K) 1.97, O3 (CN = 4; 1 S, 3 K) 2.11, O4 (CN = 4; 1 S, 1 Hg, 2 K) 1.90, O5 (CN = 3; 3 Hg) 2.29, and O6 (CN = 4; 1 S, 3 Hg) 2.04. Following this concept, the S atoms are considerably ‘overbonded’, with valence units of 5.87 for S1 and 5.75 for S2. This behaviour is attributed to the additional metal–sulfur coordination *via* the lone-pair electrons of the S atoms, which leads to enhanced S–O π -bonding as a consequence (Cruickshank, 1961), and thus to shorter S–O bond lengths. So, in comparison with other sulfates(IV) of the formula type $\text{MS}^{\text{IV}}\text{O}_3$ (*M* is a divalent metal) where the S atom is not coordinated to the metal centres, the overall S–O distance is significantly shorter here (1.47 *versus* 1.54 Å). Nevertheless, the bonding situation in the title compound is in agreement with the HSAB (hard and soft acids and bases) concept (Pearson, 1997), where the soft acid Hg^{2+} prefers bonding to the soft base S^{IV} with its lone-pair electrons.

Experimental

All chemicals used were of analytical grade (Merck) and employed without further purification. The title compound was obtained on dissolution of freshly precipitated HgO (25 mg, 0.115 mmol) in a boiling aqueous solution of K_2SO_3 (50 ml, 180 mg, 1.1 mmol). After

Table 1

Selected geometric parameters (Å, °).

Hg1–O5	2.084 (3)	K–O2 ^{vii}	2.824 (4)
Hg1–S1	2.3395 (15)	K–O3 ^{viii}	2.845 (4)
Hg1–O6 ⁱ	2.688 (4)	K–O3 ^{ix}	2.852 (5)
Hg1–O1 ⁱⁱ	2.837 (5)	K–O1 ^x	2.895 (4)
Hg1–O4 ⁱⁱⁱ	2.941 (4)	K–O2 ^{ix}	3.021 (5)
Hg1–O3	3.074 (4)	K–O2 ^{iv}	3.253 (5)
Hg2–O5	2.049 (5)	K–O1 ⁱⁱ	3.276 (5)
Hg2–S2	2.325 (2)	S1–O2	1.453 (4)
Hg2–O6 ^{iv}	2.654 (5)	S1–O3	1.455 (4)
Hg2–O4 ^v	2.913 (4)	S1–O1	1.472 (4)
Hg2–O4 ⁱⁱⁱ	2.913 (4)	S2–O6	1.472 (5)
Hg2–O1 ^{vi}	2.932 (5)	S2–O4	1.473 (4)
K–O4	2.801 (4)	S2–O4 ^{xi}	1.473 (4)
K–O3 ⁱⁱ	2.821 (5)		
O5–Hg1–S1	172.45 (14)	O6–S2–O4 ^{xi}	110.7 (2)
O5–Hg2–S2	179.14 (14)	O4–S2–O4 ^{xi}	111.0 (3)
O2–S1–O3	112.5 (3)	O6–S2–Hg2	105.9 (2)
O2–S1–O1	112.5 (3)	O4–S2–Hg2	109.22 (18)
O3–S1–O1	111.2 (3)	O4 ^{xi} –S2–Hg2	109.22 (18)
O2–S1–Hg1	107.4 (2)	Hg2–O5–Hg1 ^{xi}	114.25 (16)
O3–S1–Hg1	105.82 (17)	Hg2–O5–Hg1	114.25 (16)
O1–S1–Hg1	106.98 (18)	Hg1 ^{xi} –O5–Hg1	103.9 (2)
O6–S2–O4	110.7 (2)		

Symmetry codes: (i) $x, y, z + 1$; (ii) $x - \frac{1}{2}, y, -z + \frac{3}{2}$; (iii) $x + \frac{1}{2}, y, -z + \frac{1}{2}$; (iv) $x - \frac{1}{2}, y, -z + \frac{1}{2}$; (v) $x + \frac{1}{2}, -y + \frac{1}{2}, -z + \frac{1}{2}$; (vi) $x - \frac{1}{2}, -y + \frac{1}{2}, -z + \frac{3}{2}$; (vii) $-x + \frac{1}{2}, -y, z - \frac{1}{2}$; (viii) $x, y, z - 1$; (ix) $-x, -y, -z + 1$; (x) $x - 1, y, z - 1$; (xi) $x, -y + \frac{1}{2}, z$.

cooling to ambient temperature, aggregated yellow crystals up to 2 mm in length with a lancet-like habit were formed within 2 d. The crystals were not stable over a long period and decomposed within a few days under formation of elemental mercury and SO_2 . However, when the crystals were embedded in perfluorinated ether, collection of a complete data set with high redundancy was possible without difficulty.

Crystal data

$\text{K}_2[\text{Hg}_3\text{O}(\text{SO}_3)_3]$	$V = 1185.9 (11) \text{ \AA}^3$
$M_r = 936.15$	$Z = 4$
Orthorhombic, $Pnma$	Mo $K\alpha$ radiation
$a = 7.352 (4) \text{ \AA}$	$\mu = 40.01 \text{ mm}^{-1}$
$b = 20.734 (11) \text{ \AA}$	$T = 298 (2) \text{ K}$
$c = 7.780 (4) \text{ \AA}$	$0.12 \times 0.11 \times 0.04 \text{ mm}$

Data collection

Bruker SMART APEX CCD area-detector diffractometer	12066 measured reflections
Absorption correction: numerical (<i>HABITUS</i> ; Herrendorf, 1997)	1763 independent reflections
$T_{\min} = 0.086, T_{\max} = 0.327$	1612 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.046$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.023$	89 parameters
$wR(F^2) = 0.055$	$\Delta\rho_{\max} = 1.56 \text{ e \AA}^{-3}$
$S = 1.06$	$\Delta\rho_{\min} = -1.27 \text{ e \AA}^{-3}$
1763 reflections	

The highest remaining peak in the final difference Fourier map was 0.76 Å from atom Hg2 and the deepest hole 0.90 Å from Hg1.

Data collection: *SMART* (Bruker, 2003); cell refinement: *SAINTE* (Bruker, 2003); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ATOMS* (Dowty, 2006); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: IZ3045). Services for accessing these data are described at the back of the journal.

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