

**K<sub>2</sub>[Hg(SO<sub>3</sub>)<sub>2</sub>]·2.25H<sub>2</sub>O**Matthias Weil,<sup>a\*</sup> Stefan O. Baumann<sup>a‡</sup> and Dietrich K. Breiting<sup>b</sup><sup>a</sup>Institute for Chemical Technologies and Analytics, Division of Structural Chemistry, Vienna University of Technology, Getreidemarkt 9/164-SC, A-1060 Vienna, Austria, and <sup>b</sup>University of Erlangen–Nürnberg, Egerlandstrasse 1, D-91058 Erlangen, Germany

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The characteristic feature of the structure of the title compound, dipotassium bis(sulfite- $\kappa$ S)mercurate(II) 2.25-hydrate, is a layered arrangement parallel to (001) where each of the two independent [Hg(SO<sub>3</sub>)<sub>2</sub>]<sup>2-</sup> anions are grouped into centrosymmetric pairs and are surrounded by two K<sup>+</sup> cations to give the overall layer composition {K<sub>2</sub>[Hg(SO<sub>3</sub>)<sub>2</sub>]<sub>2</sub>}<sup>2-</sup>. The remaining cations and the uncoordinated water molecules are situated between these layers. Within the [Hg(SO<sub>3</sub>)<sub>2</sub>]<sup>2-</sup> anions, the central Hg atoms are twofold coordinated by S atoms, with a mean Hg–S bond length of 2.384 (2) Å. The anions are slightly bent [174.26 (3) and 176.99 (3)°] due to intermolecular O···Hg interactions greater than 2.8 Å. All coordination polyhedra around the K<sup>+</sup> cations are considerably distorted, with coordination numbers ranging from six to nine. Although the H atoms of the five water molecules (one with symmetry 2) could not be located, O···O separations between 2.80 and 2.95 Å suggest a system of medium to weak O–H···O hydrogen bonds which help to consolidate the structural set-up. Differences and similarities between the bis(sulfite- $\kappa$ S)mercurate(II) anions in the title compound and those in the related salts (NH<sub>4</sub>)<sub>2</sub>[Hg(SO<sub>3</sub>)<sub>2</sub>] and Na<sub>2</sub>[Hg(SO<sub>3</sub>)<sub>2</sub>]·H<sub>2</sub>O are discussed.

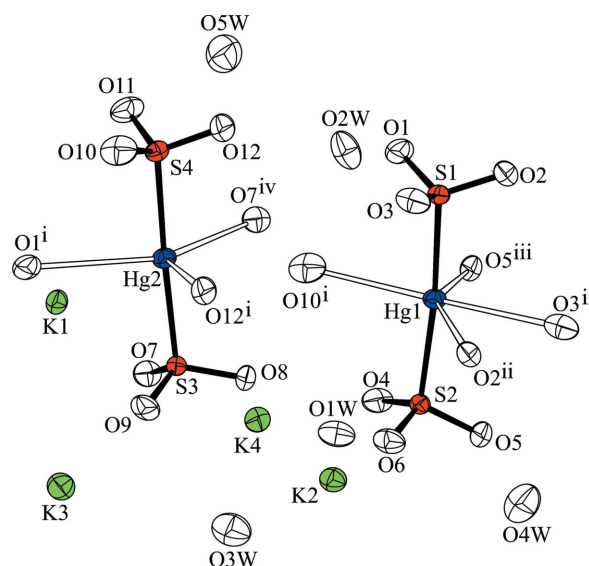
**Comment**

From a structural point of view, sulfite complexes of mercury(II) are interesting because the primary coordination of the metal is not accomplished through the O atoms of the SO<sub>3</sub><sup>2-</sup> anion, but through the lone-pair of electrons of the S<sup>IV</sup> atom. The  $\kappa$ S-coordination mode to the metal leads to an enhanced S–O  $\pi$ -bonding (Cruickshank, 1961) and consequently to considerably shorter S–O bond lengths ( $\approx$  1.47 Å) compared with a  $\kappa$ O-coordination mode [ $d$ (S–O)  $\approx$  1.54 Å]. Structurally well characterized examples of such S-bonded mercury(II) complexes include Na<sub>2</sub>[Hg(SO<sub>3</sub>)<sub>2</sub>]·H<sub>2</sub>O (Nyberg

& Cynkier, 1972), (NH<sub>4</sub>)[HgCl(SO<sub>3</sub>)], (NH<sub>4</sub>)<sub>2</sub>[Hg(SO<sub>3</sub>)<sub>2</sub>] (Weil *et al.*, 2007), K<sub>2</sub>[O(HgSO<sub>3</sub>)<sub>3</sub>] (Weil *et al.*, 2008a) and several compounds of general composition  $xM$ [HgX(SO<sub>3</sub>)<sub>2</sub>] $\cdot$  $y$ HgX<sub>2</sub> $\cdot$  $zMX$  $\cdot$  $n$ H<sub>2</sub>O ( $M$  = NH<sub>4</sub>, K;  $X$  = Cl, Br;  $x$ ,  $y$ ,  $z$ ,  $n$  = 0–2; Weil *et al.*, 2008b). Continuing our studies of sulfite complexes of mercury, we have obtained single crystals of the title compound, K<sub>2</sub>[Hg(SO<sub>3</sub>)<sub>2</sub>]·2.25H<sub>2</sub>O, (I), and report its crystal structure here.

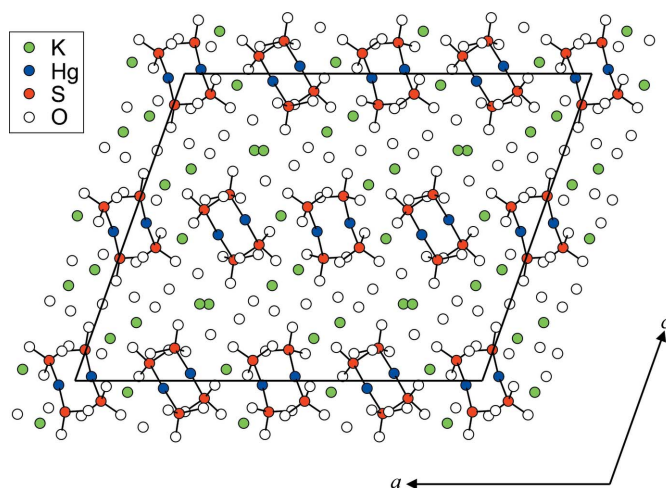
The asymmetric unit of (I) (Fig. 1) contains four K, two Hg, four S and 17 O atoms, five of which are associated with water molecules. Except for one H<sub>2</sub>O molecule (OW1) on a special position (4e, symmetry 2), all other atoms occupy general sites (8f). The two independent but very similar [Hg(SO<sub>3</sub>)<sub>2</sub>]<sup>2-</sup> sulfite-mercurate anions are arranged in two centrosymmetric pairs {[Hg(SO<sub>3</sub>)<sub>2</sub>]<sub>2</sub>}<sup>4-</sup>, which, in turn, are linked into layers parallel to (001) through weak S–O···Hg interactions. In addition, two of the four independent K<sup>+</sup> cations (K1 and K2) are embedded within these layers, leading to an overall layer composition of {K<sub>2</sub>[Hg(SO<sub>3</sub>)<sub>2</sub>]<sub>2</sub>}<sup>2-</sup> (Fig. 2). The layers are stacked along [001], with an interlayer distance  $\sin\beta\cdot c/2$  of 9.0719 Å. This distance corresponds to the most intense reflection (002) in the X-ray powder pattern. These mixed anionic sheets adopt layer symmetry (a/b)· $\bar{1}$ · $p\bar{1}$  (Shubnikov & Koptsik, 1974). The remaining K<sup>+</sup> ions (K3, K4) are spread between the anionic layers; their layer symmetry is (a/b)·2· $p121$ .

In the two slightly bent [Hg(SO<sub>3</sub>)<sub>2</sub>]<sup>2-</sup> anions, which both approach an eclipsed conformation, the four Hg–S bonds have virtually the same lengths, with an average of 2.384 (2) Å (Table 1). The coordination spheres of the two Hg<sup>II</sup> atoms are augmented by remote O atoms at distances greater than 2.8 Å. When a bonding interaction between mercury and oxygen is considered to be relevant for Hg–O distances less than 3.1 Å,

**Figure 1**

The asymmetric unit of K<sub>2</sub>[Hg(SO<sub>3</sub>)<sub>2</sub>]·2.25H<sub>2</sub>O, showing the atom labelling and with displacement ellipsoids drawn at the 74% probability level. The additional O atoms augmenting the coordination sphere of the Hg<sup>II</sup> atoms are also shown. K–O bonds and O···O interactions have been omitted for clarity. [Symmetry codes: (i)  $-x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1$ ; (ii)  $-x, -y + 1, -z + 1$ ; (iii)  $-x, -y, -z + 1$ ; (iv)  $-x + \frac{1}{2}, -y - \frac{1}{2}, -z + 1$ .]

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**Figure 2**  
The crystal structure of  $K_2[Hg(SO_3)_2] \cdot 2.25H_2O$  in a projection along  $[010]$  showing the alternating anionic and cationic layers in the  $ab$  plane.

the resulting coordination polyhedra are a distorted  $HgS_2O_4$  octahedron for Hg1 and a distorted  $HgS_2O_3$  trigonal bipyramid for Hg2, each with the S atoms in the respective axial positions. The four S atoms adopt a tetrahedral  $SHgO_3$  coordination with a slight angular distortion in which the O—S—O angles [mean  $110.4(6)^\circ$ ] are somewhat greater than the O—S—Hg angles [mean  $108.5(18)^\circ$ ]. The 12 S—O bond lengths scatter marginally [ $\bar{d}(S—O) = 1.472(6) \text{ \AA}$ ], as the individual O atoms are involved to a different extent in the effective coordination spheres of Hg, in the coordination to the  $K^+$  cations, and as acceptors in hydrogen bonds from the  $H_2O$  molecules.

The four independent  $K^+$  ions show different coordination behaviour. K1 is a component of the mixed anionic layer and is coordinated by six O atoms of the sulfite ligands at short distances [ $2.662(3)$ – $2.788(3) \text{ \AA}$ ] in the form of a distorted octahedron. K2 is already situated at the outer margin of the anionic layer and thus also bonds to three interlayer water molecules. This leads to an increase of the coordination number to eight with K—O distances ranging from  $2.708(3)$  to  $3.080(4) \text{ \AA}$ . K3 and K4 are part of the cationic layer and are coordinated both to sulfite O atoms and to water molecules. Their coordination numbers are eight and nine, with K—O distances ranging from  $2.666(3)$  to  $3.097(3) \text{ \AA}$ . The resulting coordination spheres are considerably distorted and difficult to derive from simple polyhedra.

Although the H atoms of the water molecules could not be located, the O···O separations (Table 2) between the water molecules and between water molecules and neighbouring O atoms of the sulfite groups are indicative of typical donor–acceptor distances for medium-to-weak O—H···O hydrogen bonds which leads to an additional stabilization of the structure.

In relation to the two other  $[Hg(SO_3)_2]^{2-}$  anions structurally characterized so far, the atomic distances and angles for the two anions in (I) are very similar (Table 1). The Hg—S bond lengths are slightly shorter than in  $(NH_4)_2[Hg(SO_3)_2]$ , (II), and  $Na_2[Hg(SO_3)_2] \cdot H_2O$ , (III), due to differences in the

effective coordination of  $Hg^{II}$  in the three structures. However, compared with the average Hg—S distance of  $2.371(19) \text{ \AA}$  in structures comprising the (halidosulfito- $\kappa S$ )-mercurate anion  $[HgX(SO_3)]^-$  ( $X = Br, Cl$ ; Weil *et al.*, 2007, 2008b), an increase of the Hg—S bond length is observed which we ascribe to the mutual *trans* influence of the two sulfite ligands in the  $[Hg(SO_3)_2]^{2-}$  anion. As for Hg1 in (I), the coordination polyhedra of the  $Hg^{II}$  atoms in (II) and (III) show a distinct  $[2 + 4]$  coordination, however, with differences with respect to the Hg—O bond lengths [ $2.733(3)$ – $2.844(3) \text{ \AA}$  for (II) and  $2.80(2)$ – $3.070(19) \text{ \AA}$  for (III)]. In all three structures, similar angular distortions are found for the tetrahedrally coordinated S atom, whereas in (II) and (III) the mean S—O bond lengths of the sulfite moiety differ slightly from that of (I), with a value of  $1.481(8) \text{ \AA}$  for (II) and  $1.467(16) \text{ \AA}$  for (III). The  $[Hg(SO_3)_2]^{2-}$  anions in all three structures are nearly linear and approach an eclipsed conformation. Comparison of the four bis(sulfito- $\kappa S$ )mercurate(II) anions reveals a rather rigid structure for this unit with only slight deviations that mainly originate from the outer coordination spheres of the  $Hg^{II}$  atoms involving remote O atoms, from the role of the sulfite O atoms as acceptors in hydrogen bonding, and from bonding of the individual  $SO_3$  units to the different counter-cations ( $K^+$ ,  $NH_4^+$  and  $Na^+$ ) *via* ionic or hydrogen-bonding interactions. The number of lattice water molecules and their bonding to the respective cations and further involvement in hydrogen bonding also contribute to these differences. Whereas in (I) 2.25 water molecules per anion are present, (II) contains no additional water molecules and (III) contains one water molecule per anion. The different numbers of lattice water molecules also influence the packing of the three structures. In contrast to the layered arrangement in (I) which contains a comparatively high number of water molecules, (III) includes less water and is characterized by a rod-like arrangement of the bis(sulfito- $\kappa S$ )mercurate(II) anions, which are separated by the  $Na^+$  cations and water molecules. Finally, (II), containing no water molecules, is made up of a three-dimensional anionic framework where the  $NH_4^+$  cations are situated in the voids.

## Experimental

All chemicals employed were of 'p.A.' quality and were purchased from Merck. Freshly prepared HgO, obtained by precipitation of a saturated aqueous  $HgCl_2$  solution with KOH, was dissolved in a concentrated  $K_2SO_3$  solution ( $HgO:K_2SO_3$  molar ratio = 1:3). After removal of unreacted HgO by filtration, the colourless solution was left to stand in a refrigerator (280 K) for several days. Colourless crystals with a typical sword-like habit and maximum edge lengths of about 0.6 mm were obtained.

### Crystal data

$K_2[Hg(SO_3)_2] \cdot 2.25H_2O$	$V = 3728.4(5) \text{ \AA}^3$
$M_r = 479.45$	$Z = 16$
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
$a = 24.0774(19) \text{ \AA}$	$\mu = 17.87 \text{ mm}^{-1}$
$b = 8.5348(7) \text{ \AA}$	$T = 100 \text{ K}$
$c = 19.2633(15) \text{ \AA}$	$0.30 \times 0.12 \times 0.02 \text{ mm}$
$\beta = 109.634(1)^\circ$	

## Data collection

Bruker SMART CCD diffractometer	21048 measured reflections
Absorption correction: multi-scan (SADABS; Bruker, 2006)	5912 independent reflections
$T_{\min} = 0.075$ , $T_{\max} = 0.674$	5360 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.039$

## Refinement

$R[F^2 > 2\sigma(F^2)] = 0.023$	240 parameters
$wR(F^2) = 0.058$	H-atom parameters not refined
$S = 1.02$	$\Delta\rho_{\text{max}} = 1.67 \text{ e } \text{\AA}^{-3}$
5912 reflections	$\Delta\rho_{\text{min}} = -0.98 \text{ e } \text{\AA}^{-3}$

Table 1

Comparative geometric parameters ( $\text{\AA}$ ,  $^\circ$ ) for structures containing the  $[\text{Hg}(\text{SO}_3)_2]^{2-}$  anion.

Structure	Hg—S	S—O	S—Hg—S
(I)†	Hg1—S2 2.3831 (8)	S1—O1 1.469 (3)	S2—Hg1—S1 174.26 (3)
	Hg1—S1 2.3876 (9)	S1—O2 1.471 (3)	S3—Hg2—S4 176.99 (3)
	Hg2—S3 2.3826 (8)	S1—O3 1.472 (3)	
	Hg2—S3 2.3829 (9)	S2—O4 1.462 (3)	
		S2—O5 1.474 (3)	
		S2—O6 1.480 (3)	
		S3—O7 1.470 (3)	
		S3—O8 1.470 (3)	
		S3—O9 1.471 (3)	
		S4—O10 1.461 (3)	
		S4—O11 1.479 (3)	
		S4—O12 1.481 (3)	
	(II)‡	Hg—S1 2.3935 (7)	S1—O6 1.470 (3)
Hg—S2 2.3935 (8)		S1—O5 1.480 (3)	
		S1—O2 1.491 (3)	
		S2—O3 1.475 (3)	
		S2—O4 1.483 (3)	
		S2—O1 1.487 (3)	
		S1—O5 1.466 (20)	S1—Hg—S2 172.8 (2)
(III)§	Hg—S1 2.402 (6)	S1—O1 1.480 (21)	
	Hg—S2 2.411 (6)	S1—O2 1.486 (20)	
		S2—O4 1.441 (22)	
		S2—O6 1.458 (22)	
		S2—O3 1.469 (22)	

† This work. ‡  $(\text{NH}_4)_2[\text{Hg}(\text{SO}_3)_2]$  (Weil *et al.*, 2007). §  $\text{Na}_2[\text{Hg}(\text{SO}_3)_2] \cdot \text{H}_2\text{O}$  (Nyberg & Cynkier, 1972).

Table 2

Selected interatomic distances ( $\text{\AA}$ ) in (I).

O1...O2W	2.845 (4)	O11...O5W	2.857 (5)
O2...O5W <sup>i</sup>	2.889 (5)	O12...O2W	2.790 (4)
O5...O4W	2.901 (5)	O3W...O5W <sup>ii</sup>	2.945 (5)
O6...O1W	2.863 (4)	O4W...O5W <sup>iii</sup>	2.849 (5)

Symmetry codes: (i)  $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$ ; (ii)  $-x + \frac{1}{2}, -y - \frac{1}{2}, -z + 1$ ; (iii)  $x - \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$ .

The H atoms of water molecules O1W–O5W were not discernible from difference Fourier maps and hence were not included in the final refinement. The highest peak in the final Fourier map is 0.65  $\text{\AA}$  from Hg2 and the deepest hole is 1.35  $\text{\AA}$  from the same atom.

Data collection: *SMART* (Bruker, 2006); cell refinement: *SAINTE* (Bruker, 2006); 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: SQ3257). Services for accessing these data are described at the back of the journal.

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