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Tripotassium cis-Dibromo(hydrogenbissulfito)platinate(II) Monohydrate

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Abstract

$K_3[Pt\{(SO_3)_2H\}Br_2].H_2O$ (1), $M_r = 651 \cdot 35$, monoclinic, $P2_1/c$, $a_1 = 8 \cdot 764$ (4), $b_1 = 6 \cdot 934$ (2), $c_1 = 21 \cdot 544$ (9) Å, $\beta_1 = 99 \cdot 32$ (4)°, $Z = 4$, $V = 1292 \cdot 0$ (1·7) Å^3, $D_m = 3 \cdot 47$, $D_c = 3 \cdot 35$ Mg m^{-3}, $F(000) = 1179 \cdot 71$, $\mu(Ag\ K\alpha) = 9 \cdot 87$ mm^{-1}. The structure was solved by Patterson and Fourier methods and refined to $R = 0 \cdot 0248$ and $R_w = 0 \cdot 0288$ (1801 unique reflections). In the distorted square-planar anion, Pt is surrounded by two S and two Br atoms in *cis* positions. Short Pt–S and long Pt–Br bonds (averages 2·244 and 2·488 Å, respectively) suggest a strong *trans* influence of the sulfite ligand. An extremely short asymmetric intramolecular hydrogen bond [O···H···O distance 2·380 (8) Å] links the sulfite ligands to form a six-membered ring. The anions are arranged in layers, held together by three sets of K$^+$ ions to different extents and by hydrogen-bonded H$_2$O molecules. In the anions of (1) and of $K_3[Pt\{(SO_3)_2H\}Cl_2]$ (2) the Pt–S and hydrogen bonds are very similar. The structural arrangements in (1) and (2) show common features, leading to close relations of the cell dimensions of both compounds.

Introduction

As part of our structural studies of sulfito complexes of Pd and Pt, with increasing emphasis on the *trans*

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influence of sulfite in these four-coordinate species (Messer, Breitinger & Haegler, 1979, 1981; Kehr, Breitinger & Bauer, 1980), a series of *cis*-dihalo-(hydrogenbissulfito)platinates(II), $M_3[Pt\{(SO_3)_2H\}X_2]$ ($M = K$, Rb, Cs; $X = Cl$ and Br), was prepared and studied by vibrational spectrometry (Bauer, 1979). The structure of $K_3[Pt\{(SO_3)_2H\}Br_2].H_2O$ (1) and its relations to that of $K_3[Pt\{(SO_3)_2H\}Cl_2]$ (2) (Kehr *et al.*, 1980) will be discussed here.

Experimental

Preparation

Through a suspension of 1·5 g (2·0 mmol) K$_2$PtBr$_6$ and 0·14 g (1·0 mmol) K$_2$CO$_3$ in 10 ml of H$_2$O, SO$_2$ was passed with slight heating (328–333 K). The amounts given in the procedure for (2) (Kehr *et al.*, 1980) should be corrected correspondingly. After dissolution and nearly complete decolorization, the reaction mixture was cooled to room temperature and mixed with 50 ml acetone for precipitation of (1) (analytical data have been deposited). Recrystallization from water yielded single crystals.

Crystal data

Cell parameters were determined by a least-squares refinement of 30 powder reflections, with Pb(NO$_3$)$_2$ as external standard. Systematic absences $h0l$: $l = 2n$, and

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0k0: $k = 2n$ from Weissenberg and precession photographs indicate space group $P2_1/c$.

Data collection

Crystal sphere (0·13 mm diameter); PW 1100 four-circle diffractometer, graphite-monochromated Ag $K\alpha$ radiation, ω scan, scan width (1·0 + 0·2 tan θ)°, scan speed 0·1° s^{-1}, scans repeated up to six times depending on intensity; three standard reflections; 4785 intensities within 3° $\leq \theta \leq$ 18°. $\sigma(F_o)$ was determined after Hornstra & Stubbe (1972). Averaging of equivalent reflections and Lorentz, polarization and absorption corrections for a sphere (Weber, 1969) yielded 1801 unique data [residual index $R_d = 0·0349$, as provided by SHELX 76 (Sheldrick, 1976)].

Structure determination

The structure was solved with the SHELX 76 program by Patterson and Fourier methods and block-diagonal least-squares refinements. Complex scattering factors for K$^+$, Br$^-$ and neutral Pt, S, O and H atoms were taken from International Tables for X-ray Crystallography (1974). The arrangement of Pt and Br atoms was found in a Patterson map. All other non-hydrogen atoms were located in a series of Fourier syntheses. After several steps of anisotropic refinement (with omission of the reflections 302 and 008 on the basis of analyses of variance) the three unlike H atoms could be detected in difference Fourier maps. In a final least-squares refinement including weighting {$w = 0·1460/$ [$\sigma^2(F) + 0·00010F^2$]} and corrections for extinction [$F' = F(1 - 0·001\kappa F^2/\sin \theta)$; $\kappa = 0·0010$] convergence was reached at $R = 0·0248$ and $R_w = 0·0288$. Two maxima of residual electron density (0·72 and 0·57 e Å^{-3}, respectively) 0·79 Å apart from the Pt atoms remained in the final difference Fourier map.

Atomic parameters and U_{eq} values are given in Table 1.*

Discussion

The structure consists of cis-|Pt{(SO$_3$)$_2$H}Br$_2$|$^{3-}$ anions arranged to form layers containing the (102) planes,

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* Lists of structure factors and anisotropic thermal parameters, and analytical data and the equation for the best plane of the anion have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38008 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional coordinates* ($\times 10^4$) *and equivalent values* [U_{eq} (Å$^2 \times 10^4$)] *of the anisotropic temperature factors* U_{ij}, *with e.s.d.'s in parentheses*

$$U_{eq} = \tfrac{1}{3}(U_{11} + U_{22} + U_{33} + 2U_{13} \cos \beta).$$

	x	y	z	U_{eq}
Pt	2204·1 (3)	2716·4 (4)	8723·8 (1)	163 (2)
Br(1)	4829·6 (8)	1228·0 (11)	8810·8 (4)	312 (4)
Br(2)	1789·3 (9)	840·3 (11)	9660·0 (4)	347 (4)
S(1)	2797 (2)	4307 (2)	7892 (1)	215 (8)
S(2)	−95 (2)	4142 (2)	8744 (1)	206 (8)
O(1)	−1345 (6)	2773 (7)	8787 (3)	355 (17)
O(2)	1405 (6)	5381 (8)	7527 (3)	451 (17)
O(3)	3316 (6)	3046 (7)	7425 (3)	295 (16)
O(4)	4006 (6)	5748 (7)	8108 (3)	339 (16)
O(5)	−618 (5)	5345 (7)	8142 (2)	291 (16)
O(6)	46 (6)	5500 (7)	9267 (3)	342 (16)
H(3)	214 (18)	4934 (18)	7758 (17)	499 (19)*
K(1)	3517 (2)	5961 (2)	2386 (1)	294 (8)
K(2)	2600 (2)	6018 (3)	136 (1)	365 (9)
K(3)	1408 (2)	1086 (2)	1260 (1)	386 (9)
O(7)	4905 (8)	3416 (9)	622 (3)	678 (17)
H(1)	3965 (18)	3394 (18)	807 (17)	461 (18)*
H(2)	5658 (18)	3452 (18)	945 (16)	462 (18)*

* Isotropic.

three independent sets of K$^+$ ions with different connection functions within and between the layers. and water molecules as constituents of the layers. A projection of the structure along b$_1$ is shown in Fig. 1.
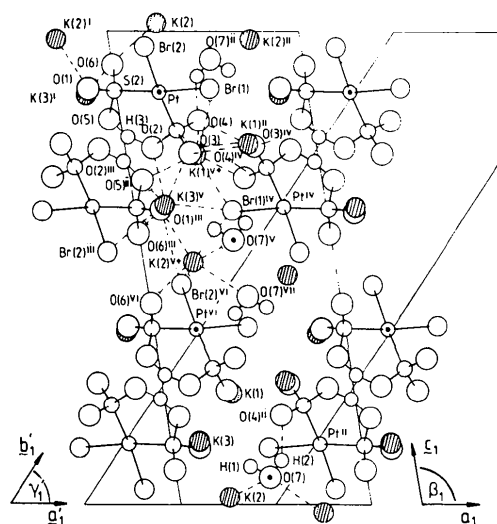

Fig. 1. Projection of the structure of K$_3$|Pt{(SO$_3$)$_2$H}Br$_2$|.H$_2$O along b$_1$. Potassium ions are hatched. and platinum atoms and water molecules around the $y = \frac{1}{4}$ level are marked with a dot. The transformed unit cell with two of the transformed basis vectors (see Table 3) is outlined.

The anions in $K_3[Pt\{(SO_3)_2H\}Br_2].H_2O$ (1) (Fig. 2) adopt a structure with *cis* coordination of two Br and two S atoms about the Pt atom, analogous to the findings for $K_3[Pt\{(SO_3)_2H\}Cl_2]$ (2), with the anions in (1) clearly deviating from the mirror symmetry found in (2). There are deviations of Pt and the atoms bound to it from their best plane of up to 0·52 Å (the equation for the plane has been deposited). The Pt–S bond lengths do not differ significantly from those in (2) [2·247 (2) Å] (Kehr *et al.*, 1980). In the recently reported *trans*-bis(methylsulfito)platinum(II) complex [Pt(SO₃Me)₂(PPh₃)₂] the Pt–S bonds are much longer [2·308 (1) Å] (Hughes, Minshall & Mingos, 1979), caused by the mutual *trans* influence of the methyl-sulfito ligands. In contrast to the short Pt–S bonds the Pt–Br bonds are unusually long, once more indicating a strong *trans* influence of the sulfito ligand (*cf.* Messer *et al.*, 1981, and references therein). Up to now comparable Pt–Br bonds range between 2·408 (9) Å for a bromo(diethylenetriamine)platinum(II) complex (Melanson, Rochon & Hubert, 1979) and 2·445 (2) Å for K_2PtBr_4 (Kroening, Rush, Martin & Clardy, 1974); only a few additional, similar Pt–Br bond lengths were given in the literature (Melanson, Hubert & Rochon, 1975; Lock & Pilon, 1981; Keller, Keppler, Ledezma-Sanchez & Steiger, 1981). For $K[Pt(C_2H_4)Br_3].H_2O$ an unusually long Pt–Br bond (2·52 Å, *trans* to ethylene) was reported (Bokii & Kukina, 1965).

The geometries of the S-coordinated sulfito ligands are comparable to those in (2). Thus, the averages of the terminal S–O bond lengths are almost exactly the same [1·464 in (1) and 1·465 Å in (2)]. The long S(1)–O(2) and S(2)–O(5) bonds, approaching S–O single bonds, are caused by the involvement of both O atoms in the strong hydrogen bond (see below). On the whole, the S–O bond lengths in both (1) and (2) show

similar gradation as in the mentioned bis(methyl-sulfito)platinum(II) complex (Hughes *et al.*, 1979) or in $K_2[Pd(SO_3)_2].H_2O$ (Messer *et al.*, 1979).

The very short hydrogen bond O(2)···H(3)···O(5) of 2·380 (8) Å in (1) has almost exactly the same length as in (2) [2·382 (6) Å]; they are among the shortest known (*cf.* the compilation by Kehr *et al.*, 1980). As a further recent example, the linear and symmetric hydrogen bond between coordinated acetate ligands with O···H···O 2·370 (10) Å (Rozière & Belin, 1979) should be mentioned. In the present case, the hydrogen bond is clearly asymmetric and bent, in consequence of its sensitivity to the asymmetry of the environment.

The potassium ions in three independent sets show quite different coordination (Fig. 1 and Table 2). Thus, $K(1^{v+})$ is surrounded by five oxygens from four different anions in a rather narrow range of distances, and two bromines form two anions out of the four; a sulfur atom S(1) also approaches $K(1^{v+})$ [*cf.* a similar finding for (2)]. In its coordination sphere $K(2^{v+})$ has only two oxygens from two anions, but also two water molecules, which in turn are linked to anions by hydrogen bonds; the coordination is completed by one bromine from each of three anions. Finally, in the surroundings of $K(3^v)$ there are five O atoms from three anions with the shortest and longest K···O contacts in the present structure. One of the three K(3)···Br contacts is also the shortest and comparable to the K···Br distance [3·385 (1) Å] in K_2PtBr_4 (Kroening *et al.*, 1974).

The water molecule [bond lengths O(7)–H(1) 0·97 (3) and O(7)–H(2) 0·88 (3) Å, angle H(1)–O(7)–H(2) 104·6 (2·3)°] is involved in a moderately
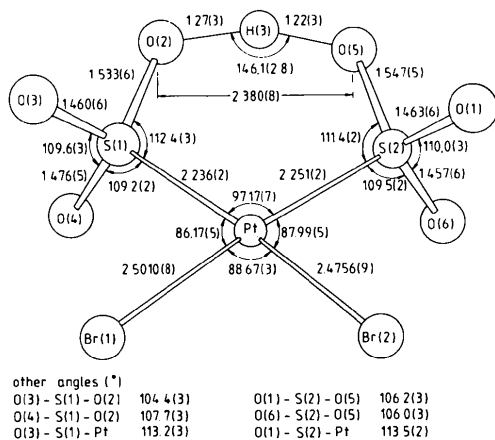

Fig. 2. The $[Pt\{(SO_3)_2H\}Br_2]^{3-}$ anion.

other angles (°)
O(3)–S(1)–O(2)	104.4(3)	O(1)–S(2)–O(5)	106.2(3)
O(4)–S(1)–O(2)	107.7(3)	O(6)–S(2)–O(5)	106.0(3)
O(3)–S(1)–Pt	113.2(3)	O(1)–S(2)–Pt	113.5(2)

Table 2. *Interatomic distances* (Å) *in the environments of the potassium ions* K(1), K(2) *and* K(3)

Atoms with superscripts are related to those in Table 1 by (i) $-x$, $1 - y$, $1 - z$; (ii) $1 - x$, $1 - y$, $1 - z$; (iii) $-x$, $\frac{1}{2} + y$, $\frac{3}{2} - z$; (iv) $1 - x$, $\frac{1}{2} + y$, $\frac{3}{2} - z$; (v) x, $\frac{1}{2} - y$, $\frac{1}{2} + z$; (vi) x, $\frac{1}{2} - y$, $-\frac{1}{2} + z$; (vii) $1 - x$, $\frac{1}{2} + y$, $\frac{1}{2} - z$. Additional $+$ or $-$ sign indicates positive or negative translation by one unit of b_1.

$K(1^{v+})$–O(4)	2·756 (5)	$K(1^{v+})$–Br(1⁺)	3·450 (2)
O(5ⁱⁱⁱ)	2·763 (5)	Br(1ⁱᵛ)	3·709 (2)
O(3⁺)	2·786 (5)		
O(3ⁱᵛ)	2·824 (5)	$K(1^{v+})$–S(1)	3·384 (3)
O(4ⁱᵛ)	2·828 (6)		
$K(2^{v+})$–O(6ᵛⁱ⁺)	2·700 (5)	$K(2^{v+})$–Br(1ⁱᵛ)	3·495 (2)
O(1ⁱⁱⁱ)	2·850 (7)	Br(2ᵛⁱ)	3·536 (2)
$K(2^{v+})$–O(7ᵛ⁺)	2·784 (7)	Br(2ᵛⁱ⁺)	3·770 (2)
O(7ᵛⁱⁱ)	2·958 (8)		
$K(3^v)$–O(1ⁱⁱⁱ)	2·678 (5)	$K(3^v)$–Br(2ⁱⁱⁱ)	3·430 (2)
O(6ⁱⁱⁱ⁻)	2·837 (5)	Br(2ᵛⁱ)	3·520 (2)
O(3)	2·846 (5)	Br(1ⁱᵛ)	3·692 (2)
O(2)	2·912 (6)		
O(5ⁱⁱⁱ⁻)	2·924 (5)		

Table 3. *Transformed cell parameters of* $K_3[Pt\{(SO_3)_2H\}Br_2].H_2O$ (1) *and of* $K_3[Pt\{(SO_3)_2H\}Cl_2]$ (2) *in comparison*

Transformations and transformed cell parameters

	Compound (1)			Compound (2)	
a_1'	a_1	a_1' 8·764 (4) Å	$a_2' - (a_2 - b_2)/2$	a_2'	9·207 (2) Å
b_1'	$2a_1 + c_1$	b_1' 25·477 (13)	$b_2' - b_2$	b_2'	10·490 (3)
c_1'	b_1	c_1' 6·934 (2)	$c_2' - c_2$	c_2'	7·054 (1)
		γ_1' 56·56 (6)°		γ_2'	55·27 (2)°

Layer distances

$a_1' \sin \gamma_1'$ 7·313 (6) Å $a_2/2 - a_2' \sin \gamma_2'$ 7·567 (2) Å

strong hydrogen bond to $O(4^{ii})$ |distances $O(7)\cdots$ $O(4^{ii})$ 2·809 (8) and $H(2)\cdots O(4^{ii})$ 2·09 (3) Å, angle $O(7)-H(2)\cdots O(4^{ii})$ 138·6 (2·3)°| (Fig. 1, lower part). $H(1)$ has no potential acceptor for a hydrogen bond at a reasonable distance. However, $K(2)$ and $K(3)$ are close enough $|H(1)\cdots K(2)$ 2·50 (2) and $H(1)\cdots K(3)$ 3·04 (2) Å| to influence the orientation of the water molecule by repulsion of $H(1)$. The type of coordination to two $K(2)$ ions (Table 2) and the surroundings of this H_2O molecule do not match any class of the classification of Ferraris & Franchini-Angela (1972).

For a brief comparison of the structures of (1) and (2) both cells are transformed, *viz* (1) by 1,0,0; 2,0,1; 0,−1,0 (setting $P2_1/b$, new cell indicated in Fig. 1) and (2) ($Cmc2_1$) (Kehr *et al.*, 1980) into a primitive monoclinic cell by $\frac{1}{2},-\frac{1}{2},0; 0,-1,0; 0,0,-1$ (Table 3). In both (1) and (2) the anions are arranged in similar ways to form layers with almost the same basis vectors c_1' and c_2'. Orthogonal to the c' vectors, but within the layers, the translational unit b_1' is more than twice b_2', due to the additional inversion center and the insertion of H_2O molecules in (1). Again, the a' parameters and the correlated layer distances are quite similar in both cases. However, the repeat units along the stacking directions comprise four layers in (1) (stacking sequence *ABCD...*), but only two layers in (2) (*AB...*). A detailed discussion of the structural relationship and its group-theoretical background will be given elsewhere.

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