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Dipotassium Disulfitopalladate(II) Monohydrate, $K_2[Pd(SO_3)_2] \cdot H_2O$: Structure and Connexion Modes

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Abstract

$K_2[Pd(SO_3)_2] \cdot H_2O$ crystallizes in the orthorhombic space group *Pnma*, with $a = 7.037$ (3), $b = 14.749$ (6), $c = 7.441$ (3) Å, $Z = 4$. The structure has been determined from diffractometer data by Patterson and Fourier methods and refined by a full-matrix least-squares procedure to $R = 0.034$ for 1268 observed reflections. The nearly planar distorted-square environment of Pd is formed by two *cis*-coordinated S and two O atoms [Pd–S and Pd–O distances of 2.241 (1) and 2.121 (3) Å, respectively], belonging to four different sulfite groups. Two adjacent Pd atoms are linked by two bidentate sulfite ligands to form infinite undulating chains of six-membered rings running along the a axis. These chains are held together by coordination of the K ions to the O atoms of three different chains. The 6 + 2 coordination (extended octahedron) of two K ions is completed by a water molecule common to both.

Introduction

During our spectrometric studies of sulfite complexes of heavy metals we have turned our attention to such pure and mixed complexes of the platinum metals. For $K_2[Pd(SO_3)_2] \cdot H_2O$, vibrational spectra have suggested one of four possible chain structures (Haegler, 1976). An X-ray structure analysis has been performed in order to check the spectroscopic suggestions.

Experimental

Single crystals of $K_2[Pd(SO_3)_2] \cdot H_2O$ were prepared by a diffusion method using solutions of K_2SO_3 and $K_2S_2O_5$ (both 0.25 *M*) and a 0.20 *M* $PdCl_2$ solution in 0.01 *M* HCl both separated by a layer of water. Satisfactory analytical data have been obtained.

Crystal data

$K_2[Pd(SO_3)_2] \cdot H_2O$, $M_r = 362.7$, orthorhombic, $a = 7.037$ (3), $b = 14.749$ (6), $c = 7.441$ (3) Å, $V = 772.3$ (4) Å³, $Z = 4$; $D_m = 3.05$, $D_c = 3.12$ Mg m⁻³; $F(000) = 680$, $\mu(Mo K\alpha) = 3.74$ mm⁻¹. The systematic absences $0kl$: $k + l = 2n + 1$, and $hk0$: $h = 2n + 1$, obtained from Weissenberg and precession photographs, indicated the space group to be *Pnma* or *Pn2₁a*, the centrosymmetric group being proposed by intensity statistics and later confirmed by the structure determination. Unit-cell parameters were refined by a least-squares method from 25 powder reflexions with $Pb(NO_3)_2$ as an external standard.

Data collection

Three-dimensional intensity data were collected with a scintillation counter on a PW 1100 four-circle diffractometer in the ω -scan mode, using graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 0.70926$ Å). The scan range was $(0.80 + 0.20 \tan \theta)^\circ$ with a speed

of $0.08^\circ \text{ s}^{-1}$. The intensities of three standard reflexions were checked every 180 min. From a crystal of approximate dimensions $0.18 \times 0.05 \times 0.12 \text{ mm}$, shaped as a truncated bipyramid along the b axis, a total of 5226 intensities were recorded within four octants of the reflexion sphere $1 \leq \theta \leq 35^\circ$. Lorentz and polarization corrections were applied, but no absorption correction was made because of the low μr value ($\mu r < 0.35$) and as ψ scans on various reflexions did not indicate any significant absorption effects. Equivalent reflexions were merged to yield 1598 unique data, of which 1269 had intensities $I > 3\sigma(I)$, $\sigma(I)$ being the standard deviation calculated from the total count and the background values. The structure amplitudes with $I < 3\sigma(I)$ were regarded as unobserved and not included in the refinements.

Structure determination and refinement

The structure was solved by Patterson and Fourier methods and refined by a full-matrix least-squares procedure, using the *SHELX 76* program package (Sheldrick, 1976). Complex atomic scattering factors for K^+ , Pd^{2+} and neutral S and O atoms were taken from *International Tables for X-ray Crystallography* (1974). The position of Pd was found in a Patterson synthesis; a difference Fourier map revealed the remaining K, S and O atoms. Pd was refined with anisotropic thermal parameters, K and S with isotropic ones, while the O atoms had to be kept fixed at their values obtained from the difference Fourier synthesis. After a step-by-step refinement with anisotropic parameters for all non-hydrogen atoms, convergence was reached at $R = 0.034$ [$R = \sum (|F_o| - |F_c|) / \sum |F_o|$], using unit weights during all stages of the calculations. In the final cycle the parameter shifts were a maximum of 0.14 (typically 0.02) times the corresponding standard deviations. An attempt to locate the H atoms of the water molecule by a difference Fourier synthesis using these data was unsuccessful. The final atomic parameters are given in Table 1.*

Results and discussion

The crystal structure is shown in Fig. 1. The structure may be described in terms of $[\text{Pd}(\text{SO}_3)_{4/2}]^{2-}$ chains, connected by K^+ cations and water molecules.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34065 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The coordination of palladium

Pd is surrounded by two S and two O atoms in a *cis* configuration yielding a distorted square. Bond distances and angles are given in Table 2.

The Pd atom is shifted by 0.024 Å from the plane spanned by the coordinated S and O atoms towards the O(2) atoms of the S-bonded sulfite groups.

The Pd–S distances are very similar to those in sulfotriamminepalladium(II) [2.245 (6) Å; Spinnler & Becka, 1967], but significantly shorter than in disodium *trans*-disulfotodiamminepalladate(II) hexahydrate [2.294 (6) Å; Capparelli & Becka, 1969]. To our knowledge no further comparable data for sulfite palladium complexes are available in the literature. The Pd–O bond lengths observed in this compound are near to the upper limit of the range for Pd–O bonds (1.97–2.16 Å; Brown, Brown & Hawthorne, 1975). Possible reasons for the long Pd–O distances are discussed in the following section dealing with the internal structure of the sulfite group.

Table 1. Atomic parameters

The estimated standard deviations are given in parentheses and refer to the last figures of respective values.

	Site	x	y'	z
K	8(<i>d</i>)	0.1424 (1)	0.0725 (1)	0.8704 (1)
Pd	4(<i>c</i>)	0.2684 (1)	0.25	0.2196 (1)
S	8(<i>d</i>)	0.1265 (1)	0.1361 (1)	0.3671 (1)
O(1)	8(<i>d</i>)	−0.0694 (4)	0.1590 (2)	0.4389 (5)
O(2)	8(<i>d</i>)	0.1086 (4)	0.0599 (2)	0.2402 (5)
O(3)	8(<i>d</i>)	0.2451 (4)	0.1115 (2)	0.5226 (4)
O(4)	4(<i>c</i>)	0.0151 (7)	0.25	0.8051 (8)

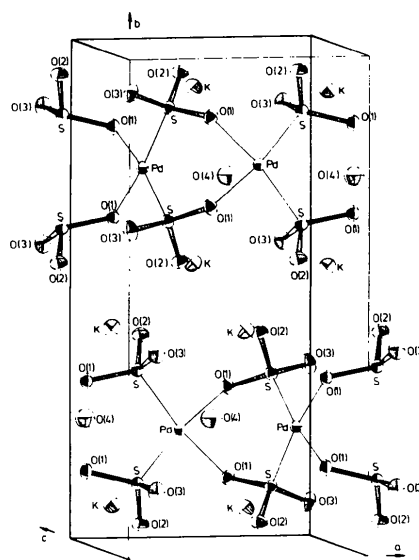


Fig. 1. The arrangement of atoms in the unit cell.

The sulfite group

The sulfite group acts as a bidentate ligand bridging two Pd atoms by coordination through S and one O atom [O(1)]. Distances and angles within the sulfite group are given in Table 3. All the angles around the S atom are nearly tetrahedral, including those between the Pd, S and O atoms.

As has been pointed out by Cruickshank (1961), S coordination of the sulfite group strengthens all S—O bonds by enhancement of π bonding. In accordance with this theory the terminal S—O bonds in the present structure are rather short (1.47 Å) and near the lower limit of the range of S—O bond lengths in sulfite compounds (*cf. e.g.* Maslen, Raston, White & Yandell, 1975). Due to coordination of O(1) to Pd, the S—O(1) bond is weaker and longer (1.52 Å) than the terminal bonds by about 3%. As a consequence of the different S—O bond lengths, the S—O valence vibrations are shifted to higher [terminal S—O(2) and S—O(3) bonds] and lower [bridging S—O(1) bond] frequencies, respectively, than in a free sulfite ion. The complete vibrational spectra will be discussed in full in a forthcoming paper.

Table 2. *Interatomic distances (Å) and bond angles (°) for atoms surrounding Pd*

Greek letters α and β refer to atoms at (x, y, z) and $(x, \frac{1}{2} - y, z)$, respectively.

Pd—O(1)	2.121 (3)	O(1 α)—Pd—O(1 β)	78.54 (12)
Pd—S	2.241 (1)	S(α)—Pd—O(1 α)	92.17 (9)
		S(α)—Pd—S(β)	97.09 (4)
S(α)—S(β)	3.360 (2)		
O(1 α)—O(1 β)	2.685 (4)	S(α)—Pd—O(1 β)	170.6 (8)
S(α)—O(1 α)	3.143 (3)		

Table 3. *Interatomic distances (Å) and angles (°) in the sulfite group*

S—O(1)	1.516 (3)	Pd—S—O(1)	114.3 (1)
S—O(2)	1.474 (3)	Pd—S—O(2)	107.2 (1)
S—O(3)	1.472 (3)	Pd—S—O(3)	108.5 (1)
O(1)—S—O(2)	108.6 (2)	Pd—O(1)—S	115.7 (1)
O(1)—S—O(3)	107.0 (2)		
O(2)—S—O(3)	111.4 (2)		

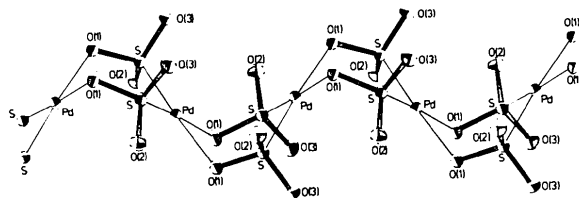


Fig. 2. The $\frac{1}{\infty}[\text{Pd}(\text{SO}_3)_{4/2}]^{2-}$ chain.

The anionic chains

In a discussion of the bonding capabilities of sulfite groups Newman & Powell (1963) suggested a bridged structural unit with S- and O-bonded bidentate sulfite from which several possible chain structures for anions $[\text{M}(\text{SO}_3)_2]^{2-}$ may be derived.

A first example of a simple chain $\frac{1}{\infty}[\text{M}^1(\text{SO}_3)_{2/2}]^-$ built up by only one bridging sulfite group between two metal atoms has been found in $\text{NaAgSO}_3 \cdot 2\text{H}_2\text{O}$ (Niinistö & Larsson, 1973). The quite different (until now unique) case of a twin-chain $\frac{1}{\infty}[\text{M}^{II}(\text{SO}_3)_{4/2}]^{2-}$ in $\text{K}_2\text{Pd}(\text{SO}_3)_2 \cdot \text{H}_2\text{O}$ is shown in Fig. 2. The connexion principle in this undulating ribbon may be described in terms of tilted squares double-linked by trigonal pyramids. Subsequent squares around the Pd atoms within the chain are approximately perpendicular to each other (tilt angle 86°). This type of connexion produces six-membered rings in the boat configuration linked bow to stern, the bottom of the boat facing alternately up and down. The symmetry operations of such an isolated chain constitute a rod group $(a)2_m$, corresponding to $p2_1ma$ in international notation (*cf.* Shubnikov & Koptsik, 1974) with one-dimensional translations parallel to the a axis.

Packing considerations

The arrangement of the chains is depicted in Fig. 3. It may be derived from a two-dimensional pseudo-hexagonal array of polar rods, such that the given unit cell contains two antiparallel chains (indicated by plus and minus signs) as is required by space-group symmetry. In the array as a whole each of the chains is surrounded by two parallel and four antiparallel ones.

The water molecules are located on the mirror planes between parallel chains above the trough formed by the above-mentioned six-membered rings. On the other hand the H_2O molecules are common to pairs of K ions (correlated by the mirror operation) each in turn connecting three chains.

The coordination on potassium

The environment of K is shown in Fig. 4; atoms with superscripts (i) and (iii) belong to parallel chains, those

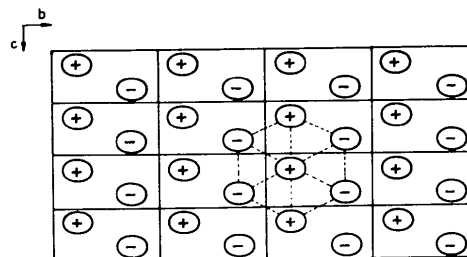


Fig. 3. The pseudo-hexagonal packing of chains.

with (ii) to the antiparallel chain. K is surrounded by one water molecule and six sulfite groups. Six K—O distances are found in the narrow range from 2.748 to 2.810 Å [the latter value being the K—O(water) distance], and two longer ones at 2.964 and 3.045 Å. The complicated coordination polyhedron may best be discussed on the basis of an octahedron, with a twofold coordinated sulfite group opposite the water molecule, and an additional sulfite O atom above an octahedral face adjacent to H₂O.

The possible orientation of the water molecules

The positions of the H atoms in the H₂O molecules have not been found. The high frequencies of the sharp O—H valence vibration bands in the IR spectrum preclude hydrogen bonding, which is furthermore excluded by the absence of potential acceptor atoms at a reasonable distance from the water molecules. If it is

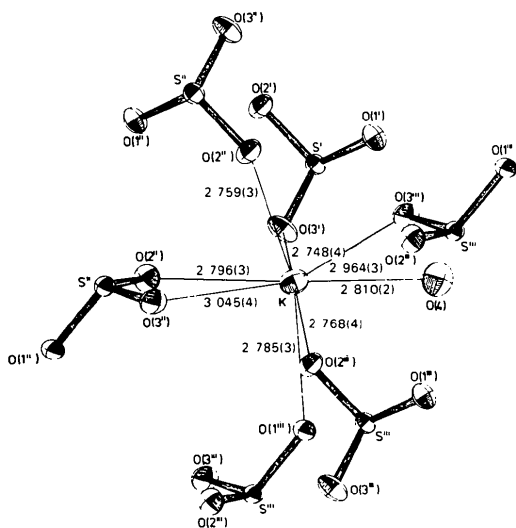


Fig. 4. The environment of the potassium, showing K—O interatomic distances (Å).

assumed that the inert pairs of H₂O are directed towards the two K⁺ ions (correlated by the mirror operation, see above) the two H atoms are pushed into the mirror plane for electrostatic and symmetry reasons. The most probable orientation in the mirror plane is such that one of the two H—O vectors is pointing to the center of the region between the two O(1) atoms.

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