

retenues aux groupements cationiques par liaisons H uniquement. Jouant un rôle moins important dans l'édification de la structure, elles vont permettre à l'octahydrate de se transformer en hexahydrate à la température relativement basse de 301,5 K. Apparaisent alors forcément dans le sel le moins hydraté deux ponts oxygène intertétraédriques, signalés dans l'article correspondant.

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Hexasodium Tetrasulfitopalladate(II) Dihydrate, $\text{Na}_6[\text{Pd}(\text{SO}_3)_4] \cdot 2\text{H}_2\text{O}$: A Structure with a Pronounced Rod Packing

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Abstract

$\text{Na}_6[\text{Pd}(\text{SO}_3)_4] \cdot 2\text{H}_2\text{O}$ crystallizes in the tetragonal space group $I4_1/a$, with $a = b = 16.488$ (1), $c = 10.663$ (2) Å, $Z = 8$. The final $R = 0.0406$ and $R_w = 0.0338$ for 1969 unique reflections. In the two independent $[\text{Pd}(\text{SO}_3)_4]^{6-}$ complex anions with symmetry $\bar{4}$ all sulfite ligands are coordinated to the Pd atoms through S, yielding non-planar PdS_4 units. Remarkably long Pd–S bonds [2.316 (1) and 2.341 (1) Å] are caused by a strong *trans* influence of the sulfite ligand. The two independent anions are stacked alternately to form rods parallel to *c*. The interconnection of the anionic units within the rods and the coherence of the rods are effected by three independent sets of Na^+ ions. This arrangement of anionic rods produces channels filled with right- and left-handed homodromic helices of water molecules connected by cooperatively strengthened hydrogen bonds [distance O–H...O = 2.684 (10) Å]. Thus, a characteristic feature of the present structure is interpenetrating packings of non-polar (anionic columns) and polar rods (strings of water).

Introduction

Continuing our spectrometric and structural studies of sulfite complexes of platinum-group metals (Messer,

Breitinger & Haegler, 1979; Kehr, Breitinger & Bauer, 1980), we have obtained $\text{Na}_6[\text{Pd}(\text{SO}_3)_4] \cdot 2\text{H}_2\text{O}$ in single-crystal form and performed an X-ray structure analysis.

Experimental

Single crystals of $\text{Na}_6[\text{Pd}(\text{SO}_3)_4] \cdot 2\text{H}_2\text{O}$ have been grown by a gel crystallization method. On a sodium silicate gel, containing 0.33 *M* PdCl_2 , 0.33 *M* acetic acid and free SO_2 , a layer of pure silicate gel was superposed, followed by a third gel layer with 1 *M* NaHSO_3 and 0.5 *M* acetic acid. Analyses for H, Na, Pd and SO_3^{2-} yielded satisfactory results (calculated: H 0.67, Na 22.97, Pd 17.71, SO_3 53.32%; found: H 0.7, Na 23.4, Pd 17.5, SO_3 50.4%).

Crystal data

$\text{Na}_6[\text{Pd}(\text{SO}_3)_4] \cdot 2\text{H}_2\text{O}$, $M_r = 600.6$, tetragonal, $a = b = 16.488$ (1), $c = 10.663$ (2) Å, $V = 2898.8$ (3) Å³, $Z = 8$, $D_m = 2.69$, $D_c = 2.75$ Mg m⁻³, $F(000) = 2272$, $\mu(\text{Mo K}\alpha) = 1.92$ mm⁻¹. Rotation and Weissenberg photographs pointed to systematic absences characteristic for the space group $I4_1/a$, which was later confirmed by the automatic data collection. Cell parameters were refined by least squares from 22

powder reflections with Pb(NO₃)₂ as an external standard.

Data collection

Intensities were collected on a Philips PW 1100 four-circle diffractometer in the ω -scan mode with graphite-monochromatized Mo K α radiation ($\lambda = 0.70926 \text{ \AA}$). The scan range was $(0.80 + 0.20 \tan \theta)^\circ$ with a speed of 0.1° s^{-1} . Each scan was repeated five to 24 times depending on its absolute intensity. The intensities of three standard reflections were checked every two hours. From a needle-shaped crystal (axis parallel to **c**) $0.11 \times 0.11 \times 0.32 \text{ mm}$, 2360 intensities were recorded in one octant of the reflection sphere $\theta \leq 30^\circ$. ψ scans indicated a low absorption coefficient; thus no absorption correction was applied. $\sigma(F_o)$ was determined by the procedure of Hornstra & Stubbe (1972). Equivalent reflections were merged and Lorentz and polarization corrections applied yielding a set of 1969 unique data for further calculations.

Structure determination and refinement

The structure was solved with *SHELX 76* (Sheldrick, 1976) by Patterson and Fourier methods and full-matrix least-squares refinement. Complex scattering factors for Na⁺, Pd²⁺ and neutral S, O and H atoms were taken from *International Tables for X-ray Crystallography* (1974). The arrangement for Pd and S was found in a Patterson synthesis. A series of step-by-step difference syntheses allowed the location of the remaining Na and sulfito O atoms. Least-squares refinement converged only when all these atoms were included because of strong coupling of parameters. The

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

Site	x	y	z	U_{eq}^\dagger
Na(1)	16(f) 3119 (1)	2303 (1)	1251 (2)	234 (8)
Na(2)	16(f) 4292 (1)	498 (1)	908 (2)	308 (9)
Na(3)	16(f) 3741 (1)	4482 (1)	1826 (2)	324 (10)
Pd(1)	4(a) 0	2500	1250	132 (3)
Pd(2)	4(b) 0	2500	6250	133 (3)
S(1)	16(f) 567 (1)	3772 (1)	1536 (1)	149 (4)
S(2)	16(f) 1081 (1)	3401 (1)	6549 (1)	151 (4)
O(11)	16(f) 790 (2)	4196 (2)	347 (3)	225 (13)
O(12)	16(f) -15 (2)	4306 (2)	2215 (3)	216 (13)
O(13)	16(f) 1295 (2)	3692 (2)	2352 (3)	227 (13)
O(21)	16(f) 1493 (2)	3628 (2)	5354 (3)	234 (13)
O(22)	16(f) 792 (2)	4148 (2)	7172 (3)	269 (15)
O(23)	16(f) 1697 (2)	3024 (2)	7391 (3)	253 (14)
O(W)	16(f) 2619 (4)	4934 (4)	3740 (7)	1282 (27)
H(1)	16(f) 2438 (21)	4904 (22)	2831 (14)	524 (28)

$$\dagger U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^*$$

O atom of the water molecule could be fixed with abnormal thermal parameters and only one of the two water H atoms was detected in a difference map (for explanation see below). In a final refinement with anisotropic thermal parameters convergence was reached at $R = 0.0406$ and $R_w = \sum w^{1/2} \Delta / \sum w^{1/2} |F_o| = 0.0338$, with the weighting scheme $w = 0.1327/\sigma^2(F) + 0.000030F^2$ (based on analyses of variance as provided by *SHELX 76*).

Table 1 gives the resulting atomic parameters and the equivalent values U_{eq} of the anisotropic thermal parameters U_{ij} .*

Results and discussion

A projection of the crystal structure down **c** is shown in Fig. 1. The structure is made up of isolated [Pd(SO₃)₄]⁶⁻ disk units, stacked into columns along **c**.

The interconnections of both complex units and columns in the lattice are effected by the Na⁺ ions *via* purely electrostatic forces. In this framework of parallel

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35651 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

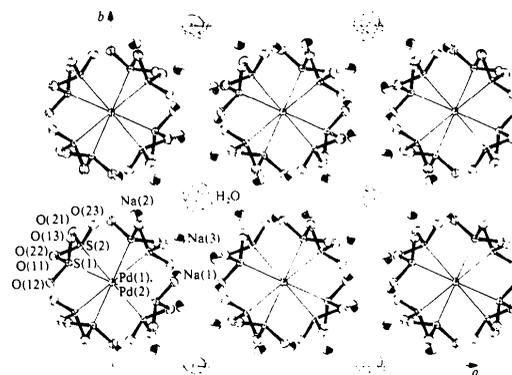


Fig. 1. Projection of the structure onto the (001) plane.

Table 2. Interatomic distances (\AA) and bond angles ($^\circ$) in the two independent [Pd(SO₃)₄]⁶⁻ units

Pd(1) S(1)	2.316 (1)	Pd(2)-S(2)	2.341 (1)
<i>cis</i> -		<i>cis</i> -	
[S(1)-Pd(1)-S(1)]	91.00 (3)	[S(2)-Pd(2)-S(2)]	91.06 (3)
<i>trans</i>		<i>trans</i> -	
[S(1)-Pd(1)-S(1)]	164.86 (15)	[S(2)-Pd(2)-S(2)]	164.34 (15)
S(1)-O(11)	1.494 (3)	S(2)-O(21)	1.492 (3)
S(1)-O(12)	1.490 (3)	S(2)-O(22)	1.479 (3)
S(1)-O(13)	1.489 (3)	S(2)-O(23)	1.492 (3)
O(11)-S(1)-O(12)	107.10 (16)	O(21)-S(2)-O(22)	108.75 (18)
O(11)-S(1)-O(13)	109.79 (17)	O(21)-S(2)-O(23)	107.94 (17)
O(12)-S(1)-O(13)	106.73 (16)	O(22)-S(2)-O(23)	107.25 (17)
Pd(1)-S(1)-O(11)	114.29 (12)	Pd(2) S(2)-O(21)	112.92 (12)
Pd(1) S(1)-O(12)	109.82 (12)	Pd(2)-S(2)-O(22)	110.17 (12)
Pd(1)-S(1)-O(13)	108.85 (11)	Pd(2)-S(2)-O(23)	109.64 (12)

rods, channels are produced, which are filled with strings of hydrogen-bonded water molecules.

The $[\text{Pd}(\text{SO}_3)_4]^{6-}$ disk units

There are two crystallographically independent $[\text{Pd}(\text{SO}_3)_4]^{6-}$ anions, both with symmetry $\bar{4}$. Distances and angles are given in Table 2. In contrast to $\text{K}_2[\text{Pd}(\text{SO}_3)_2] \cdot \text{H}_2\text{O}$ (Messer *et al.*, 1979), the sulfite ligands are exclusively S-coordinated to Pd. The two different PdS_4 skeletons deviate from planarity, with S(1) and S(2) shifted from planes through the Pd atoms and parallel to (001) by 0.305 and 0.319 Å respectively. The deviations of the entire $[\text{Pd}(\text{SO}_3)_4]^{6-}$ units from idealized $42m$ symmetry are caused by a slight twist of the sulfite groups around the Pd–S bonds by 2.1 and 6.2°. Compared with other sulfite Pd complexes (Messer *et al.*, 1979, and references cited therein) the Pd–S bonds are drastically lengthened. As the dominating reason for this lengthening we suggest the strong *trans* influence of the sulfite ligand (Kehr, Breitinger & Bauer, 1980, and reference cited therein; Elder, Heeg, Payne, Trkula & Deutsch, 1978; Raston, White & Yandell, 1979, and references cited therein); however, the cooperative repulsion of the highly charged sulfite ligands and their coordination by Na^+ ions may act in the same direction.

As to the internal geometry of the sulfite ligands, all the S–O lengths are the same throughout and in the usual range for S-coordinated sulfite complexes. The deviations of the O–S–O angles from tetrahedral values are insignificant. However, for both independent complex units the angles Pd–S–O (the planes of which are approximately perpendicular to the

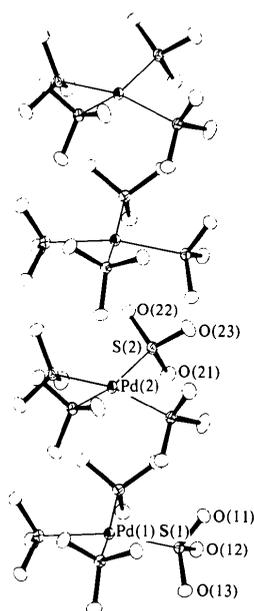


Fig. 2. Stacking of the anions into columns.

idealized PdS_4 planes) are enhanced (114.3 and 112.9° respectively); this means that the sulfite groups as a whole have been tilted (away from the idealized PdS_4 planes) in the same sense as the S atoms have been shifted.

The stacking of the disks to form columns

As shown in Fig. 2, the two independent disk units *A* and *B* are stacked into columns parallel to *c* in the sequence *ABAB*..., with *B* rotated relative to *A* through an angle of 26.1° (pseudostaggered arrangement), thus minimizing the intermolecular repulsion. Metal–metal interactions can be excluded, because of the large Pd...Pd distance of 5.33 Å. The connection within a column is caused by the peripheral coordination of Na^+ ions to O atoms of different disks.

The coordination about sodium

The cell contains three crystallographically independent Na^+ ions, each connecting three disks from two different columns.

Both $\text{Na}^+(1)$ and $\text{Na}^+(2)$ show sixfold coordination (Figs. 3 and 4), derived from tetragonal pyramids, the apices of which are occupied by bidentate sulfite ligands. Differences arise in so far as $\text{Na}^+(1)$ is surrounded by five sulfites from three anions (see above), whereas $\text{Na}^+(2)$ coordinates to four sulfites (two being bidentate).

The highly distorted octahedral environment of $\text{Na}^+(3)$ is built up by the O atoms of four sulfite groups and two water molecules *W*, the latter with rather different distances (Fig. 5).

The Na...O distances may be divided into two groups, viz 2.31 to 2.44 Å (I) and 2.48 to 2.90 Å (II). With bidentate sulfites one Na...O distance belongs to group (I), the other to group (II) in all cases.

Packing of the columns

The stacking of the disks, as discussed above, yields columns with internal symmetry $(c)\bar{4}$, corresponding

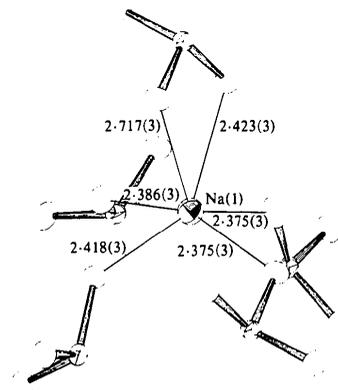


Fig. 3. The environment of $\text{Na}(1)$.

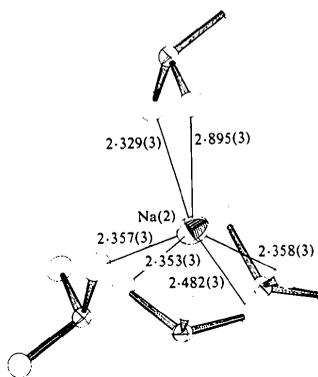


Fig. 4. The environment of Na(2).

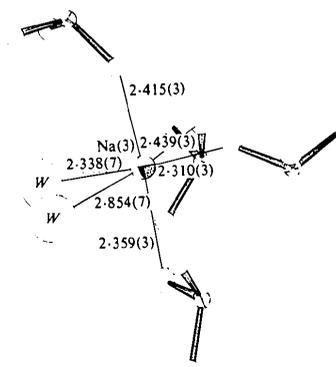


Fig. 5. The environment of Na(3).

to $p\bar{4}$ in international notation (Shubnikov & Koptsik, 1974). A closer consideration reveals that there are, in fact, two crystallographically independent, coaxial columns with symmetry $(c)\cdot\bar{4} - p\bar{4}$ each. The arrangement of these columns is depicted in Fig. 6. The details of these arrays may be discussed in two alternative ways:

(i) The two combined independent sets of disks *A* and *B* (white and hatched in Fig. 6) are arranged in a way related to the cubic face-centered array [multi-stage group-super-group relation of the respective space groups $I4_1/a$ and $Fm\bar{3}m$ (Neubüser & Wondratschek, 1970)].

(ii) A primitive tetragonal rod packing (O'Keeffe & Andersson, 1977) is transformed into the present *I*-centered structure by the doubling of *a* and the introduction of right- and left-handed 4_1 axes along $[\frac{1}{4}\frac{1}{4}z]$ and $[\frac{1}{4}\frac{3}{4}z]$ in the enlarged cell.

The resulting arrangement of columns contains channels with symmetry $(c)\cdot 4_1 - p4_1$ (Shubnikov & Koptsik, 1974), filled with strings of water molecules (see below). An essential feature of this structure is a combination of non-polar and polar rods, with appropriate symmetry correlations.

A first inspection of the present structure suggests relations to the $K_2[PtCl_4]$ type ($P4/mmm$) with primitive tetragonal rod packings of both cations and anions. Formally, there is a group-subgroup relation between the space groups $P4/mmm$ and $I4_1/a$ (Neubüser & Wondratschek, 1969/1977). However, a more detailed consideration reveals that the structure under discussion cannot be derived from that of $K_2[PtCl_4]$ by mere descent in symmetry.

The strings of water molecules

The O atoms of the water molecules form two sets of right- and left-handed nearly linear helical strings, running in the above-mentioned channels. The $O(W)\cdots O(W)$ distances of 2.684 (10) Å are slightly shorter than those in the different forms of ice (Wells, 1975), and therefore hydrogen bonds have to be assumed. A difference synthesis enabled us to locate one of the H atoms involved in an asymmetric bent hydrogen bond between two O atoms [O—H and H \cdots O distances of 1.016 (19) and 1.696 (17) Å respectively; angle O—H \cdots O 163°]. Further difference syntheses revealed a second electron density maximum diagonal to the short O—H bond at a distance of 0.67 Å from the O atom. This maximum may be understood as the center of the basis of a cone, formed by the statistically oriented second O—H bond of each water molecule.

On the whole, infinite homodromic chains (nomenclature after Saenger, 1979*a*) of water molecules with both donor and acceptor properties result [similar to type *I*A hydroxyls in carbohydrates (Jeffrey & Takagi, 1978)]. These water molecules are connected by hydrogen bonds strengthened by a cooperative effect predicted by quantum-mechanical calculations (Del Bene, 1971; Del Bene & Pople, 1970, 1973; Saenger, 1979*b*). Similar situations are found in some carbohydrate structures (Jeffrey & Takagi, 1978; Saenger, 1979*a*; Saenger & Lindner, 1980).

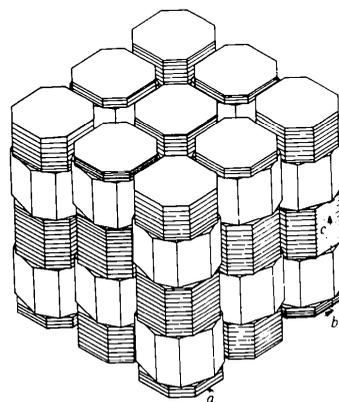


Fig. 6. The arrangement of the anionic columns.

In addition to the engagement in the hydrogen-bond system each water molecule is coordinated to two $\text{Na}^+(3)$ ions with different distances $\text{O}(W)\cdots\text{Na}(3)$ of 2.338 (7) and 2.854 (7) Å respectively (Fig. 5) and angle $\text{Na}(3)\cdots\text{O}(W)\cdots\text{Na}(3) = 104.46(8)^\circ$; hence it may be assigned to class 2A in the classification given by Ferraris & Franchini-Angela (1972).

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The Structure of 1,5-Dichlorocyclotetra(azathiene)

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Abstract

The structure of monoclinic $\text{S}_4\text{N}_4\text{Cl}_2$ [space group $P2_1/c$, $a = 9.077(4)$, $b = 6.580(2)$, $c = 13.311(6)$ Å, $\beta = 108.46(4)^\circ$, $U = 754.1$ Å³, $Z = 4$, $M_r = 255.19$, $D_m = 2.25$, $D_x = 2.25$ Mg m⁻³] was refined to $R = 0.094$ for 1235 densitometer intensities. The structure consists of $\text{S}_4\text{N}_4\text{Cl}_2$ molecules with covalent S–Cl bonds. The average bond lengths are S–N 1.59 and S–Cl 2.18 Å; the angles are S–N–S 119, N–S–N 109 and N–S–Cl 104°.

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Introduction

According to Meuwesen (1931) the chlorination of S_4N_4 yields 1,3,5-trichlorocyclotri(azathiene), $\text{S}_3\text{N}_3\text{Cl}_3$. However, the kinetics of the reaction in CS_2 (Nelson & Heal, 1970) suggests that the process proceeds *via* some intermediate, which decomposes to $\text{S}_3\text{N}_3\text{Cl}_3$ and SNCl . Its composition has been proposed, by analogy with $\text{S}_4\text{N}_4\text{F}_4$ and from the stoichiometry of the chlorination, as $\text{S}_4\text{N}_4\text{Cl}_4$. Zbořilová & Gebauer (1979a,b) have isolated the intermediate and identified

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