

- COPPENS, P., GURU ROW, T. N., LEUNG, P., STEVENS, E. D., BECKER, P. & YANG, Y. W. (1979). *Acta Cryst.* **A35**, 63–72.
- EDWARD, A. R. (1972). *Metall. Trans.* **3**, 1365–1372.
- FRIAUF, J. B. (1927a). *Phys. Rev.* **29**, 35–40.
- FRIAUF, J. B. (1927b). *J. Am. Chem. Soc.* **49**, 3107–3114.
- FUKAMACHI, T. (1971). *Tech. Rep. Inst. Solid State Phys. Tokyo Univ.* B12.
- HAFNER, J. (1979). *Phys. Rev. B*, **19**, 5094–5102.
- HAYDOCK, R. & JOHANNES, R. L. (1975). *J. Phys. F*, **5**, 2055–2067.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.
- KOMURA, Y. (1962). *Acta Cryst.* **15**, 770–778.
- KOMURA, Y. & KITANO, Y. (1977). *Acta Cryst.* **B33**, 2496–2501.
- KOMURA, Y., MITARAI, M., NAKATANI, I., IBA, H. & SHIMIZU, T. (1970). *Acta Cryst.* **B26**, 666–668.
- KOMURA, Y., MITARAI, M., NAKAUE, A. & TSUJIMOTO, S. (1972). *Acta Cryst.* **B28**, 976–978.
- KOMURA, Y., NAKAUE, A. & MITARAI, M. (1972). *Acta Cryst.* **B28**, 727–732.
- KOMURA, Y. & TOKUNAGA, K. (1980). *Acta Cryst.* **B36**, 1548–1554.
- LAVES, F. & WITTE, H. (1935). *Metallwirtsch. Metallwiss. Metalltech.* **14**, 645–649.
- LAVES, F. & WITTE, H. (1936). *Metallwirtsch. Metallwiss. Metalltech.* **15**, 840–842.
- LIESER, K. H. & WITTE, H. (1952). *Z. Metallkd.* **43**, 396–401.
- MERISALO, M. & SOININEN, J. (1979). *Phys. Rev. B*, **19**, 6289–6294.
- OHBA, S., SAITO, Y. & WAKOH, S. (1982). *Acta Cryst.* **A38**, 103–108.
- OHBA, S., SAITO, S. & SAITO, Y. (1981). *Acta Cryst.* **A37**, 697–701.
- RENNERT, P. & RADWAN, A. M. (1977). *Phys. Status Solidi B*, **79**, 167–173.
- SAMSON, S. (1958). *Acta Cryst.* **11**, 851–857.
- STAUDENMANN, J. L. (1977). *Solid State Commun.* **23**, 121–125.
- STAUDENMANN, J. L. (1978). *Solid State Commun.* **26**, 461–468.
- STAUDENMANN, J. L., COPPENS, P. & MULLER, J. (1976). *Solid State Commun.* **19**, 29–33.

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The Structure of Hexapotassium Disodium Hexatungstoplatinate(IV) Dodecahydrate, $K_6Na_2[PtW_6O_{24}]\cdot 12H_2O$

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Abstract. $M_r = 2178.77$, trigonal, $R\bar{3}m$, $a = 9.740$ (1) Å, $\alpha = 84.81$ (1)°, $U = 913.3$ (1) Å³, $Z = 1$, $D_x = 3.961$ g cm⁻³, Mo $K\alpha$ radiation ($\lambda = 0.7107$ Å), $\mu(\text{Mo } K\alpha) = 247.3$ cm⁻¹, $F(000) = 970$, $T = 298$ K. The structure was determined by the heavy-atom method and refined by the block-diagonal least-squares method. The final $R = 0.059$ for 859 independent reflections collected by diffractometry. The heteropolyanion has a structure with point symmetry $D_{3d}(\bar{3}m)$ of the ideal Anderson-type heteropolyanion. The Pt–W and W–W distances are 3.238 (1) Å. Three types of W–O (W–O_a, W–O_b and W–O_c) distances are 1.75 (1), 1.97 (2) and 2.16 (2) Å.

Introduction. Recently we reported the synthesis and crystal structure of $Na_5[H_3PtW_6O_{24}]\cdot 20H_2O$ (Lee, Kobayashi & Sasaki, 1983). Some heteropolytungstates containing platinum have been reported by Gibbs (Pt:W = 1:10, 1:20, 2:30 and 1:30) and Rosenheim (Pt:W = 2:7) (*Gmelin's Handbuch der Anorganischen Chemie*, 1933), but their syntheses could not be

reproduced in our laboratory. We report here the structure of the unprotonated heteropolyanion $[PtW_6O_{24}]^{18-}$ obtained at pH *ca* 7.5.

Experimental. 0.81 g of $K_2WO_4\cdot 2H_2O$ was dissolved in 40 ml of hot water. To this solution 40 ml of 0.16 g $K_2Pt(OH)_6$ solution (containing a small portion of Na^+ ion) was added dropwise and 3M HNO_3 was used to adjust the pH to *ca* 6.0. After the mixture was heated for half an hour on the water bath and cooled, the pH was adjusted to *ca* 7.5. Small pale-yellow hexagonal crystals were obtained after two days when the solution was concentrated to about 70 ml at room temperature. The crystals are stable in air and a TGA–DSC diagram showed that the water molecules (0.95 w%) were slowly lost from the crystals in the temperature range 356–411 K.

A single crystal of dimensions 0.13 × 0.14 × 0.08 mm, Rigaku automated four-circle diffractometer, graphite monochromator, cell parameters refined by least-squares method on the basis of 25 independent indices ($40 < 2\theta < 45^\circ$), Mo $K\alpha$ radiation ($\lambda = 0.7107$ Å); intensity measurement performed to $2\theta = 60^\circ$ (the $+h$, $+k$, $+l$ set), ω – 2θ scan method, scan

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speed 2° min⁻¹ (θ); three standard reflections monitored every 50 reflections and found to be constant, 992 independent reflections measured, 859 intensities with $F_o > 3\sigma(F_o)$ used for the structure determination; correction for absorption effect; structure solved by Patterson and Fourier methods, refined by block-diagonal least squares on F with anisotropic thermal parameters for all atoms; water molecules located from a difference density map; atomic scattering factors from *International Tables for X-ray Crystallography* (1974), including f' and f'' for Pt and W; $R = 0.059$, $R_w = 0.077$ and $w^{-1} = \sigma^2(F_o) + (0.02F_o)^2$; $(\Delta/\sigma)_{\max} = 0.1$, final $\Delta\rho$ excursions $\leq |4.0| e \text{ \AA}^{-3}$; calculations carried out on a HITAC M-200H computer at the Computer Centre of the University of Tokyo, with a local version of *UNICS* (Sakurai, 1967).

Discussion. Final atomic parameters and equivalent isotropic thermal parameters are in Table 1.*

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38822 (11pp.). 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 isotropic thermal parameters ($\text{\AA}^2 \times 10^2$ for Pt and W; $\times 10$ for Na, K and O) with *e.s.d.*'s in parentheses

$$B_{\text{eq}} = \frac{8}{3} \pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{\text{eq}}(\text{\AA}^2)$
Pt	0	0	0	87 (4)
W	2465 (1)	-2465 (1)	0	90 (2)
Na	2637 (33)	2637 (33)	2637 (33)	28 (5)
K	-3331 (7)	-3331 (7)	1061 (6)	26 (1)
O _b	911 (19)	911 (19)	-3452 (14)	13 (3)
O _c	-1304 (19)	-1304 (19)	1022 (12)	11 (3)
O _t	-1218 (11)	2871 (11)	-3686 (11)	18 (2)
Aq1	1090 (27)	1090 (27)	3702 (19)	29 (5)
Aq2	4207 (29)	4207 (29)	1612 (27)	40 (7)

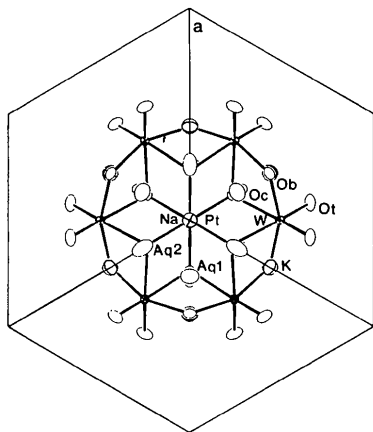


Fig. 1. A view of the crystal structure projected on the (111) plane.

Fig. 1 shows the crystal structure projected on (111). This heteropolyanion has the ideal Anderson-type structure with point symmetry D_{3d} . The W atoms are located at the corners of the regular hexagon, the Pt atom is located at its centre. There are three types of O atoms denoted as O_p, O_b and O_c. The W(O_b)₂(O_c)₂(O_t)₂ octahedra are joined to the central Pt(O_c)₆ octahedron by edge sharing. Interatomic distances and angles of the polyanion are listed in Table 2. Although the W—O_c bond distances of [H₃PtW₆O₂₄]⁵⁻ (Lee, Kobayashi & Sasaki, 1983) are longer than those of [PtW₆O₂₄]⁸⁻, the Pt—O_c bond distances are almost the same. The Pt—O bond distance of the [Pt(OH)₆]²⁻ anion is 2.05 Å (Trömel & Lupprich, 1975). Consequently, the average Pt—W and W—W distances in the former structure are longer than those of the latter. This difference can be explained by assuming that the O_c atoms in this anion are not protonated. Compared with the [MnW₆O₂₄]⁸⁻ anion (Sergienko, Molchanov, Porai-Koshits & Torchenkova, 1979), the WO₆ octahedra are found to be affected by the ionic radius of each central heteroatom. As a result, the angles O_c—W—O_c, W—O_b—W in this polyanion are greater than those of [MnW₆O₂₄]⁸⁻.

Fig. 2 shows the possible hydrogen bonds and the coordination features of Na⁺ and K⁺ ions in the polyanions. The Na⁺ ion is coordinated by six water molecules as [Na(Aq1)₃(Aq2)₃]⁺ and K⁺ ion as [K(Aq1)₂(Aq2)(O_c)(O_t)₄]⁺. The [K₃Na(Aq)₆]⁴⁺ fragment with 3*m* symmetry is placed in all the cavities among the polyanions. The Na⁺—O and K⁺—O distances less than 3.1 Å are given in Table 3. The Aq1—O_b distances are 2.75 (2) and 2.92 (3) Å and Aq2—O_t is 2.84 (3) Å. The [PtW₆O₂₄]⁸⁻ polyanions form a three-dimensional network by the hydrogen bonds and coordination to K⁺ ions.

Table 2. Interatomic distances (Å) and angles (°) in the [PtW₆O₂₄]⁸⁻ anion

(a) Distances. The prime (') refers to the atoms on the opposite side of the W₆ plane.

Pt—W	3.238 (1)	Pt—O _c	2.01 (2)
W—W	3.238 (1)	W—O _c	2.16 (2)
W—O _b	1.97 (2)	W—O _t	1.75 (1)
O _c —O _c	3.06 (3)	O _c —O _c '	2.62 (4)
O _c —O _b	2.87 (2)	O _c —O _b '	2.50 (2)
O _c —O _t	2.81 (2)	O _b —O _t	2.70 (2)
O _b —O _t '	2.86 (2)	O _t —O _t	2.77 (2)

(b) Angles. *anti* indicates that the two O atoms are on opposite sides of the W₆ plane, *syn* indicates that they are on the same side.

W—Pt—W	60.0	W—Pt—W	120.0
W—O _c —W	97.4 (5)	W—O _c —Pt	101.9 (8)
W—O _b —W	110.8 (8)		
O _c —Pt—O _c (<i>syn</i>)	98.8 (7)	O _c —Pt—O _c (<i>anti</i>)	81.2 (7)
O _c —W—O _c (<i>anti</i>)	74.9 (6)	O _c —W—O _b (<i>syn</i>)	88.1 (7)
O _c —W—O _b (<i>anti</i>)	74.5 (7)	O _c —W—O _t (<i>syn</i>)	91.2 (6)
O _c —W—O _t (<i>anti</i>)	161.4 (6)	O _b —W—O _t (<i>syn</i>)	93.0 (6)
O _b —W—O _t (<i>anti</i>)	100.4 (6)	O _b —W—O _b (<i>anti</i>)	158.2 (7)
O _t —W—O _t (<i>anti</i>)	104.7 (5)		

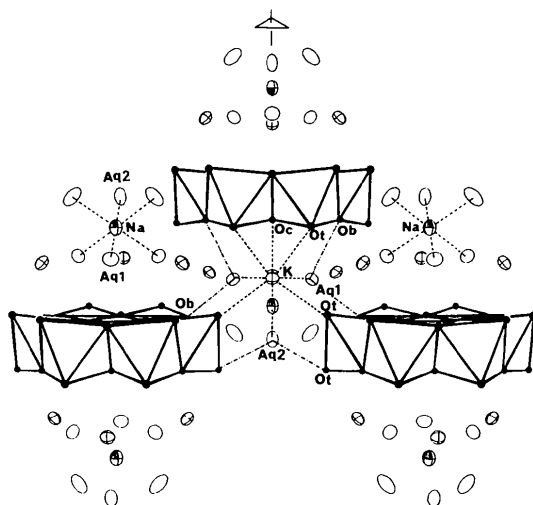


Fig. 2. Some possible hydrogen bonds and the coordination feature of the cations.

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Uranyl Hydroxide Sulphamate Trihydrate,* $\text{UO}_2(\text{OH})(\text{NH}_2\text{SO}_3)\cdot 3\text{H}_2\text{O}\dagger$

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Abstract. $M_r = 437.16$, monoclinic, $P2_1/c$, $a = 6.1249(7)$, $b = 17.3612(17)$, $c = 9.0544(7)$ Å, $\beta = 117.195(7)^\circ$, $V = 856.37(14)$ Å³, $Z = 4$, $D_x = 3.390(1)$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu(\text{Mo } K\alpha) = 181.8$ cm⁻¹, $F(000) = 784$, $T = 294$ K, $R = 0.029$ for 1957 observed unique reflections [$I \geq 3\sigma(I)$]. The seven-coordinated uranium lies at the centre of a distorted pentagonal bipyramid. Two bridging hydroxide groups connect the two polyhedra into a dimer. The remaining three equatorial O atoms in the bipyramid are from two water molecules and from one sulphamate group. The dimers are connected to each other by a complex hydrogen-bonding network.

Introduction. Whereas the structural features of uranyl sulphates have been widely investigated (Serezhkin, 1982) there are rather few studies on the related uranyl sulphamates (Capestan, 1960; Sampath &

Table 3. $\text{Na}^+ - \text{O}$ and $\text{K}^+ - \text{O}$ distances (Å) less than 3.1 Å

Na–Aq1	2.34 (4)	K–O _c	2.91 (2)
Aq1 ^{i,ii}	2.34 (4)	O _{i,ii}	2.81 (1)
Aq2	2.36 (4)	O _{i^{vi,vii}}	2.89 (1)
Aq2 ^{i,ii}	2.36 (4)	Aq1 ^{iii,v}	2.91 (3)
		Aq2 ^{iv}	3.03 (3)

Symmetry code: (i) x, z, y ; (ii) z, x, y ; (iii) $-z, -y, -x$; (iv) $-x, -y, -z$; (v) $-x, -z, -y$; (vi) $-y, -1-z, -x$; (vii) $-1-z, -y, -x$.

References

- Gmelin's *Handbuch der Anorganischen Chemie* (1933). Vol. 54, pp. 396–397. Berlin: Verlag Chemie.
- International Tables for X-ray Crystallography* (1974). Vol. IV, pp. 71–98. Birmingham: Kynoch Press.
- LEE, U., KOBAYASHI, A. & SASAKI, Y. (1983). *Acta Cryst.* **C39**, 817–819.
- SAKURAI, A. (1967). *The Universal Crystallographic Computation Program System*, Crystallographic Society of Japan.
- SERGIENKO, V. S., MOLCHANOV, V. N., PORAI-KOSHITS, M. A. & TORCHENKOVA, E. A. (1979). *Koord. Khim.* **5**, 936–942.
- TRÖMEL, M. & LUPPRICH, L. (1975). *Z. Anorg. Allg. Chem.* **414**, 160–168.

Aravamudan, 1971). All in all, it seems that the structural information on sulphamates is rather sparse (Benson & Spillane, 1980) with complete crystal structures known only for KNH_2SO_3 (Brown & Cox, 1940; Cox, Sabine, Padmanabhan, Ban, Chung & Surjadi, 1967) and for $\text{NH}_4\text{NH}_2\text{SO}_3$ (Wadhawan & Padmanabhan, 1972; Cain & Kanda, 1972). In this work the crystal structure of uranyl hydroxide sulphamate is reported.

Experimental. Title compound prepared as outlined by Capestan (1960) by mixing 1.0 g of uranium trioxide and 0.5 g of sulphamic acid in 10 cm³ of hot water. Solution filtered and concentrated at 353 K. Upon cooling to room temperature well formed yellow prismatic crystals appeared. Contrary to the neutral uranyl sulphamate obtained by Capestan (1960) the product turned out to be uranyl hydroxide sulphamate.

Details of data collection are shown in Table 1. Empirical absorption correction made from ψ -scan data after which the net intensities were corrected for Lorentz and polarization effects. Structure solved by

* Di- μ -hydroxo-bis(diaquadioxo(sulphamato)uranium(VI)) dihydrate.

† Uranyl(VI) Compounds. IV. For part III, see Toivonen & Niinistö (1983).