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Structure of Pentasodium Trihydrogenhexatungstoplatinate(IV) Icosahydrate, $Na_5[H_3PtW_6O_{24}].20H_2O$

By Uk Lee,* Akiko Kobayashi and Yukiyoshi Sasaki

Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Tokyo 113, *Japan*

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Abstract. $M_r = 2160{\cdot}14$, triclinic, $P\bar{1}$, $a = 10{\cdot}576$ (1), $b = 12{\cdot}551$ (1), $c = 10{\cdot}027$ (1) Å, $\alpha = 115{\cdot}06$ (1), $\beta = 99{\cdot}51$ (1), $\gamma = 62{\cdot}32$ (1)°, $U = 1066{\cdot}9$ (1) Å^3, $Z = 1$, $D_m = 3{\cdot}40$, $D_x = 3{\cdot}362$ g cm^{-3}, Mo $K\alpha$, $\mu = 206{\cdot}5$ cm^{-1}, $\lambda = 0{\cdot}71069$ Å, $F(000) = 972$, $T = 293$ K, final $R = 0{\cdot}081$ for 4891 independent reflections. The $[H_3PtW_6O_{24}]^{5-}$ polyanion shows the well known Anderson-type structure and has approximate $\bar{3}m$ symmetry. Mean distances of Pt—W and W—W are 3·28 (2) and 3·28 (4) Å. The W—O bond distances are distributed in three different groups, with mean values of 1·75 (2), 1·94 (2) and 2·21 (3) Å. The PtO_6 octahedron is almost regular and the mean Pt—O bond distance is 2·01 (1) Å. No H atom was identified.

Introduction. A series of heteropolytungstates containing Pt^{IV} were reported by Gibbs (1895), but his studies were rather qualitative and their crystal structures have been entirely unknown. There are some reports on the preparations of Anderson-type heteropolytungstates with the hetero-atoms Te^{6+}, I^{7+}, Mn^{4+} and Ni^{2+}, but a structural study has been made only for $[MnW_6O_{24}]^{8-}$ (Sergienko, Molchanov, Porai-Koshits & Torchenkova, 1979). We report here the synthesis and crystal structure of $Na_5[H_3PtW_6O_{24}].20H_2O$. This heteropolytungstate anion was not contained in Gibb's report. This is the first structural study of a heteropolytungstate containing Pt.

Experimental. Crystals of $Na_5[H_3PtW_6O_{24}].20H_2O$ were obtained by mixing $Na_2Pt(OH)_6$ and Na_2WO_4 solutions in the molar ratio Pt:W = 1:6 and by adjusting the pH to 6·2 with dilute nitric acid. After concentration and cooling, pale-yellow crystals were obtained. Oscillation and Weissenberg photographs indicated triclinic symmetry and the space group $P\bar{1}$ was established in the structure determination. Cell parameters were obtained by least-squares refinement from 25 reflections ($38° < 2\theta < 45°$) at 293 K. The density calculated for $Z = 1$ agrees with that measured by pycnometry. Crystal $0{\cdot}30 \times 0{\cdot}33 \times 0{\cdot}35$ mm (coated with nail enamel), Rigaku automatic four-circle diffractometer, Mo $K\alpha$ radiation monochromatized by a graphite plate, $2\theta \leq 60°$, ω–2θ scan method [scan speed 2° min^{-1} in 2θ, scan range in 2θ $(1{\cdot}3 + 0{\cdot}6 \tan\theta)°$]; three standard reflections monitored every 50 reflections and found to be constant; 6211 measured reflections, intensities corrected for absorption, 4891 independent reflections $[|F_o| > 3\sigma(|F_o|)]$ used for structure determination and refinement. Structure solved by the heavy-atom method and refined by the block-diagonal least-squares method; approximate positions of Pt and W atoms obtained from a three-dimensional Patterson map; anisotropic temperature factors for all atoms; atomic scattering factors from *International Tables for X-ray Crystallography* (1974), including f' and f'' for Pt and W; final $R = 0{\cdot}081$ and $R_w = 0{\cdot}102$, $w^{-1} = \sigma^2(|F_o|) + 0{\cdot}0004|F_o|^2$; computations performed with a local version of *UNICS* (Sakurai, 1967) on a HITAC M-200 H computer at the Computer Centre of the University of Tokyo.

Discussion. Atomic fractional coordinates and equivalent isotropic thermal parameters are given in Table 1.† The $[H_3PtW_6O_{24}]^{5-}$ polyanion has approximate D_{3d} ($\bar{3}m$) symmetry, which is analogous to the Anderson-type heteropolytungstate anion found in $[MnW_6O_{24}]^{8-}$. The polyanion structure is illustrated in Fig. 1 and a view of the crystal structure projected along the z axis is shown in Fig. 2. Average interatomic distances and angles in the $[H_3PtW_6O_{24}]^{5-}$ polyanion are listed in Table 2. The Pt atom and the six W atoms are coplanar and these W atoms form a nearly regular hexagon around the Pt atom. All the Pt and W atoms are octahedrally surrounded by the O atoms. This heteropolyanion has three types of O atoms, denoted O_t, O_b and O_c, where O_t is the terminal O atom bonded to a W atom, O_b is the bridging atom between two W atoms and O_c is the central atom coordinated to the Pt and two W atoms. Six O_c atoms make up the central PtO_6 octahedron. From the result of the structural determination of $[H_6CrMo_6O_{24}]^{3-}$ (Perloff, 1970), six H

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* Permanent address: Department of Chemistry, College of Natural Science, Busan National University, Busan 607, Korea.

† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38443 (35 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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atoms are bonded to the O_c atoms. We could not find the positions of the H atoms but we presume that three H atoms are bonded to the six O_c atoms with positional disorder in this hexatungstoplatinate polyanion.

The coordination forms of three Na^+ ions are: $Na(1)(H_2O)_4(O_t)_2$, $Na(2)(H_2O)_5(O_t)$ and $Na(3)(H_2O)_6$. Na(3) is on the special position $(0,\frac{1}{2},0)$. The O atoms which are coordinated to Na^+ ions are shown partially in Fig. 2 and $Na^+—O$ distances are given in Table 3. The heteropolyanions are joined to each other by means of hydrogen bonds and coordination to the Na^+ ions. A list of all probable hydrogen-bond distances within 3·1 Å is given in Table 4. All O_c atoms are bonded to the water (Aq) molecules. In particular two $Aq—O_c$ [$Aq(8)—O_c(12)$ and $Aq(7)—O_c(11)$] distances are short.

In comparison with the distances $M—W$ and $M—O_c$ (M: Pt or Mn) in $[H_3PtW_6O_{24}]^{5-}$ and $[MnW_6O_{24}]^{8-}$ (see Table 2), Pt—W and $Pt—O_c$ are longer than Mn—W and $Mn—O_c$. This is explained by the different ionic radii of the hetero-atoms (Pt^{4+}: 0·70 Å and Mn^{4+}: 0·54 Å). However, $W—O_b$ and $W—O_t$ bond distances are almost independent of the ionic radii of the hetero-atoms. This tendency is similar to that found for hexamolybdo heteropolyanions (Kondo, Kobayashi & Sasaki, 1980).

Table 1. *Fractional coordinates* (×10⁴) *and equivalent isotropic thermal parameters* (Å² × 10) *with e.s.d.'s in parentheses*

$$B_{eq} = \tfrac{4}{3}(B_{11}a^2 + B_{22}b^2 + B_{33}c^2 + 2B_{12}ab\cos\gamma + 2B_{23}bc\cos\alpha + 2B_{13}ca\cos\beta).$$

	x	y	z	B_{eq}
Pt(1)	0	0	0	6 (<1)
W(1)	3065 (1)	−604 (1)	1612 (1)	9 (<1)
W(2)	−2789 (1)	2818 (1)	1434 (1)	9 (<1)
W(3)	254 (1)	2248 (1)	3163 (1)	9 (<1)
$O_t(1)$	3406 (15)	−680 (13)	3332 (12)	16 (4)
$O_t(2)$	4649 (14)	−878 (14)	932 (15)	18 (5)
$O_t(3)$	−2976 (17)	4391 (14)	1752 (16)	21 (5)
$O_t(4)$	−4389 (14)	3121 (13)	2064 (15)	15 (4)
$O_t(5)$	122 (17)	3776 (14)	3505 (16)	23 (6)
$O_t(6)$	627 (14)	2062 (13)	4847 (12)	14 (4)
$O_b(7)$	−3104 (14)	2349 (12)	−660 (13)	12 (4)
$O_b(8)$	2103 (14)	1285 (13)	2217 (16)	15 (4)
$O_b(9)$	−1740 (13)	2621 (13)	3186 (14)	12 (4)
$O_c(10)$	−2072 (12)	713 (11)	505 (13)	9 (4)
$O_c(11)$	−461 (13)	1915 (11)	864 (13)	9 (4)
$O_c(12)$	739 (12)	130 (11)	2027 (13)	8 (4)
Na(1)	2326 (10)	282 (9)	−4304 (9)	22 (3)
Na(2)	3100 (10)	4527 (9)	1993 (10)	25 (3)
Na(3)	0	5000	0	26 (5)
Aq(1)	2491 (32)	−1913 (21)	4811 (20)	55 (12)
Aq(2)	3703 (30)	4995 (25)	4611 (25)	61 (10)
Aq(3)	3910 (18)	−3930 (16)	2167 (19)	24 (6)
Aq(4)	3470 (26)	−303 (25)	−2272 (24)	46 (12)
Aq(5)	3109 (27)	2455 (21)	1199 (34)	65 (11)
Aq(6)	−581 (18)	4562 (16)	−2598 (18)	25 (6)
Aq(7)	504 (21)	2762 (18)	−577 (20)	30 (7)
Aq(8)	43 (19)	1076 (17)	−3156 (20)	28 (7)
Aq(9)	3412 (17)	1843 (17)	−3300 (21)	29 (6)
Aq(10)	2512 (18)	4195 (17)	−525 (17)	23 (6)

Table 2. *Average bond distances* (Å) *and bond angles* (°) *in* $[H_3PtW_6O_{24}]^{5-}$ *and* $[MnW_6O_{24}]^{8-}$ (*Sergienko et al.*, 1979)

Estimated standard deviations are given in parentheses; X indicates Pt^{4+} or Mn^{4+}.

(*a*) Bond distances (a prime refers to atoms on the opposite side of the W_6 plane)

	$[H_3PtW_6O_{24}]^{5-}$		$[MnW_6O_{24}]^{8-}$
	Average distance	Range	Distance
$X—W$	3·28 (2)	3·268–3·307	3·183 (1)
W—W	3·28 (4)	3·226–3·316	3·183 (10)
$X—O_c$	2·01 (1)	2·005–2·020	1·943 (7)
$W—O_c$	2·21 (3)	2·170–2·235	2·155 (16)
$W—O_b$	1·94 (2)	1·905–1·967	1·967 (17)
$W—O_t$	1·75 (2)	1·720–1·779	1·750 (11)
$O_c—O_c$	3·02 (2)	3·018–3·032	2·919 (5)
$O_c—O_c'$	2·66 (2)	2·652–2·660	2·566 (11)
$O_c—O_b$	2·84 (5)	2·742–2·885	2·825 (7)
$O_c—O_b'$	2·47 (4)	2·416–2·510	2·534 (12)
$O_c—O_t$	2·84 (3)	2·815–2·900	2·835 (13)
$O_b—O_t$	2·72 (3)	2·687–2·770	2·691 (11)
$O_b—O_t'$	2·85 (3)	2·811–2·895	2·873 (12)
$O_t—O_t$	2·79 (3)	2·768–2·806	2·798 (11)

(*b*) Bond angles (*anti* indicates that the two O atoms are on the opposite sides of the WO_6 plane, *syn* indicates that they are on the same side)

	$[H_3PtW_6O_{24}]^{5-}$		$[MnW_6O_{24}]^{8-}$
	Average angle	Range	Angle
$O_c—X—O_c$ (*syn*)	97·4 (5)	97·3–97·5	97·4 (3)
$O_c—X—O_c$ (*anti*)	82·6 (5)	82·5–82·7	82·6 (3)
$O_c—W—O_c$ (*anti*)	73·7 (5)	73·2–74·0	73·4 (3)
$O_c—W—O_b$ (*syn*)	86·6 (8)	85·1–87·1	86·9 (9)
$O_c—W—O_b$ (*anti*)	72·2 (18)	70·4–75·0	76·1 (3)
$O_c—W—O_t$ (*syn*)	90·4 (13)	88·9–92·3	92·1 (4)
$O_c—W—O_t$ (*anti*)	161·4 (7)	161·1–161·9	161·6 (4)
$O_b—W—O_b$ (*anti*)	153·2 (20)	151·3–156·0	158·9 (4)
$O_b—W—O_t$ (*syn*)	95·2 (15)	93·1–97·4	92·3 (4)
$O_b—W—O_t$ (*anti*)	100·9 (13)	99·0–102·5	100·7 (4)
$O_t—W—O_t$ (*anti*)	106·1 (11)	104·6–107·0	104·2 (4)

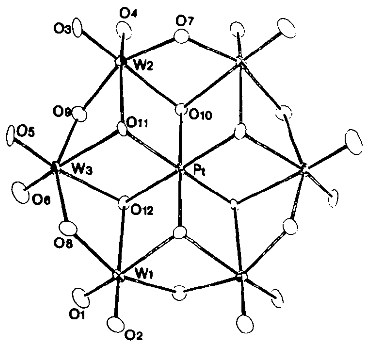

Fig. 1. View of the $[H_3PtW_6O_{24}]^{5-}$ polyanion (except for H atoms). The thermal ellipsoids are drawn at the 50% probability level.

Table 3. Na—O *distances* (Å) *within* 3·0 Å

Na(1)—Aq(1^{i})	2·44 (3)	Na(2)—Aq(2)	2·48 (3)
Aq(4)	2·41 (3)	Aq(3^{iii})	2·39 (3)
Aq(8)	2·42 (3)	Aq(5)	2·37 (3)
Aq(9)	2·49 (3)	Aq(6^{iv})	2·43 (2)
O_t(1^{i})	2·36 (2)	Aq(10)	2·40 (2)
O_t(6^{i})	2·51 (2)	O_t(4^{ii})	2·42 (2)
Na(3)—Aq(6)	2·46 (2)		
Aq(6^{iv})	2·46 (2)		
Aq(7)	2·42 (2)		
Aq(7^{iv})	2·42 (2)		
Aq(10)	2·42 (2)		
Aq(10^{iv})	2·42 (2)		

Superscripts refer to the following symmetry operations: (i)*x*, *y*, *z*−1; (ii)1 + *x*, *y*, *z*; (iii)*x*, 1 + *y*, *z*; (iv)−*x*, 1−*y*, −*z*.

Table 4. *Probable hydrogen-bond distances* (<3·1 Å)

Aq(1)—O_t(1)	3·06 (4)	Aq(5)—O_b(8)	2·72 (4)
Aq(3)	2·79 (3)	Aq(7)	2·98 (3)
O_b(9^{ii})	2·86 (4)	O_t(2^{vi})	2·80 (3)
Aq(8^{i})	2·90 (3)	O_t(4^{iv})	3·02 (4)
Aq(2)—O_t(4^{iv})	2·89 (3)	Aq(6)—O_t(6^{vii})	2·93 (2)
Aq(2^{iii})	2·73 (7)	O_t(5^{viii})	2·85 (3)
O_b(9^{v})	2·88 (2)		
		Aq(7)—O_c(11)	2·66 (3)
Aq(3)—O_b(7^{i})	2·74 (3)	Aq(8)	2·70 (3)
Aq(4)—O_c(10^{i})	2·82 (4)	Aq(8)—O_c(12^{i})	2·68 (3)
O_t(2^{vi})	2·85 (4)	O_t(6^{vii})	3·02 (2)
		Aq(9)—Aq(10)	2·94 (2)
		O_t(1^{vi})	2·98 (2)
		Aq(10)—O_t(3^{viii})	2·79 (3)

Superscripts refer to the following symmetry operations: (i)*x*, *y*, −*z*; (ii)−*x*, −*y*, 1−*z*; (iii)1−*x*, 1−*y*, 1−*z*; (iv)1 + *x*, *y*, *z*; (v)−*x*, 1−*y*, 1−*z*; (vi)1−*x*, −*y*, −*z*; (vii)*x*, *y*, −1 + *z*; (viii)−*x*, 1−*y*, −*z*.

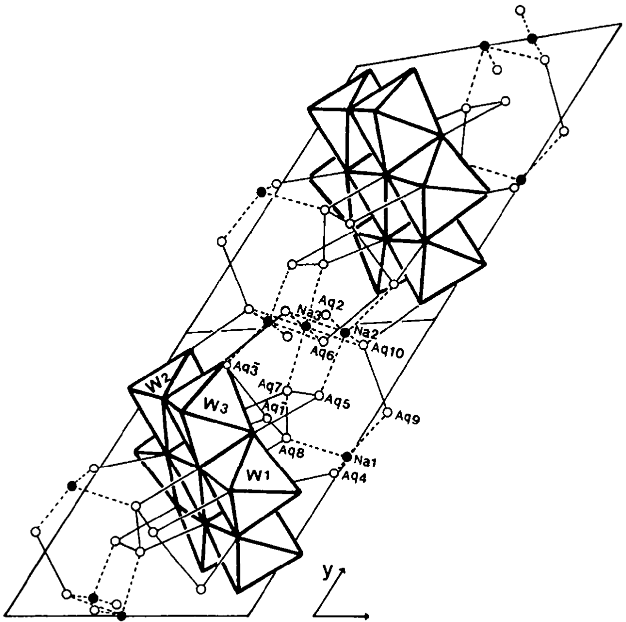

Fig. 2. Projection of the structure on the *xy* plane.

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Pentapotassium Disulfite Tris(hydrogensulfite), $K_5(HSO_3)_3(S_2O_5)$

By Astrid Magnusson, Lars-Gunnar Johansson and Oliver Lindqvist

Department of Inorganic Chemistry, Chalmers University of Technology and the University of Göteborg, S-412 96 Göteborg, Sweden

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Abstract. $M_r = 582·82$, monoclinic, $C2/m$, $a = 20·3475$ (11), $b = 5·9114$ (6), $c = 14·7733$ (9) Å, $\beta = 104·380$ (5)°, $V = 1721·3$ (2) Å^3, $Z = 4$, $D_x = 2·249$ (1) Mg m^{-3}, Mo $K\alpha$, $\lambda = 0·7107$ Å, $\mu = 1·90$ mm^{-1}, $T = 298$ K, $F(000) = 1160$; $R = 0·039$ was obtained for 1751 observed reflections. The disulfite ion has m (C_s) symmetry and consists of a thionite and a thionate group linked by an S—S bond of 2·226 (2) Å. The S—O distances are 1·489 (3) Å in the thionite group and 1·462 (4)—1·463 (3) Å in the thionate group. There are three crystallographically different HSO_3^- ions in the cell, with average S—O distances of 1·419 (3), 1·451 (2), and 1·445 (2) Å, respectively. The H atom is bonded to the S atom in all three HSO_3^- ions, with H—S distances of 1·31 (6), 1·16 (7), and 1·16 (5) Å, respectively.

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