

Pentapotassium trihydrogenhexatungstoplatinate(IV) hexahydrate, $K_5[H_3PtW_6O_{24}] \cdot 6H_2O$

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Key indicators

Single-crystal X-ray study

$T = 298\text{ K}$

Mean $\sigma(W-O) = 0.011\text{ \AA}$

R factor = 0.053

wR factor = 0.160

Data-to-parameter ratio = 17.2

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The $[H_3PtW_6O_{24}]^{5-}$ anion has close to $\bar{3}m$ symmetry, with Pt–O bond lengths in the range 1.97 (1)–2.01 (1) Å and W–O bond lengths in the ranges 1.72 (1)–1.78 (1) (O_t), 1.91 (1)–1.96 (1) (O_b) and 2.14 (1)–2.33 (1) Å (O_c), where O_t are terminal atoms, O_b bridge two W atoms, and O_c triply bridge one Pt and two W atoms. The protonated O atoms participate in strong interanion hydrogen bonds.

Comment

While investigating Anderson-type heteropolyoxometallates (Anderson, 1937; Tsigdinos, 1978) containing Pt^{IV}, we found that gradual protonation and α,β -geometric isomerism occur in the hexamolybdoplatinate(IV) anion, $[PtMo_6O_{24}]^{8-}$ (Lee & Sasaki, 1984; Joo *et al.*, 1994; Lee, 1994; Lee & Sasaki, 1994; Lee & Joo, 2000). Only three examples of the corresponding hexatungstoplatinate(IV) anions have been reported: $K_6Na_2[PtW_6O_{24}] \cdot 12H_2O$ (Lee *et al.*, 1984), $Na_5[H_3PtW_6O_{24}] \cdot 20H_2O$ (Lee *et al.*, 1983), and $K_{2.5}[H_{5.5}PtW_6O_{24}] \cdot 2H_2O$ (Lee & Sasaki, 1987). The location of the H atoms in $Na_5[H_3PtW_6O_{24}] \cdot 20H_2O$ could not be determined.

The potassium salt of triprotonated hexatungstoplatinate(IV), $[H_3PtW_6O_{24}]^{5-}$, has now been obtained. The $[H_3PtW_6O_{24}]^{5-}$ anions are packed in a different arrangement compared with the sodium salt. These compounds were prepared under conditions varying over a pH range as wide as 4.5–6.7. Fig. 1 shows the $[H_3PtW_6O_{24}]^{5-}$ anion, with the O atoms classified in the same way as previously (Lee *et al.*, 1984). It forms a dimer, $[H_6(PtW_6O_{24})_2]^{10-}$, by strong hydrogen bonding (Fig. 2). In contrast, hydrogen bonding between adjacent anions does not occur in the sodium salt. Therefore, the potassium salt (4.337 Mg m⁻³) is more densely

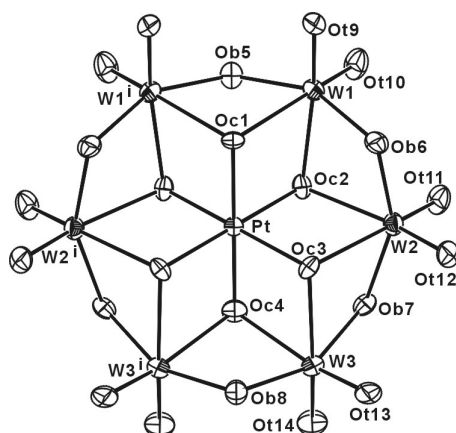


Figure 1

The anion in $K_5[H_3PtW_6O_{24}] \cdot 6H_2O$. Displacement ellipsoids are drawn at the 50% probability level. H atoms are not shown. [Symmetry code: (i) $x, -y, z$.]

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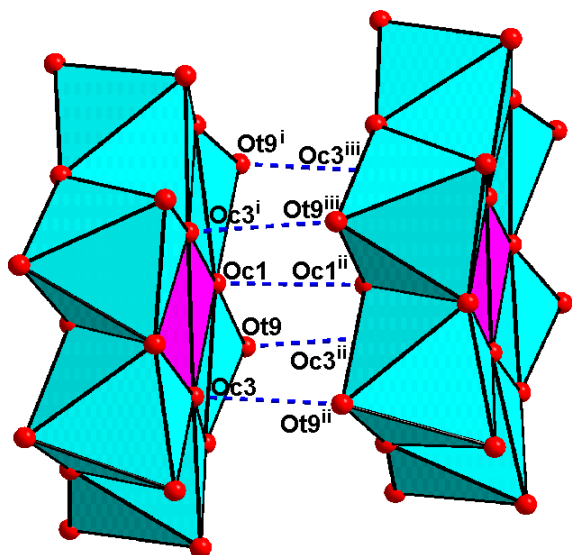


Figure 2
Interanion hydrogen bonds shown in a polyhedral model. [Symmetry codes: (i) $x, -y, z$; (ii) $-x, y, -z$; (iii) $-x, -y, -z$.]

packed than the sodium salt (3.362 Mg m^{-3}). The protonated O atoms in the anion can be identified by examining the W—O distances and the W—Ob—W angles. Protonation increases the W—O distances and decreases the W—Ob—W angles by about 10° . The elongation of the W—Oc bond distance is especially notable. From this result, it can be concluded that the Oc3 and Oc1 atoms are protonated, giving three protons as required by the stoichiometry.

The K^+ ions are coordinated at distances of 2.7 to 3.4 Å by six or eight O atoms from anions or water molecules. All water molecules are coordinated to K^+ ions and form hydrogen bonds with neighbouring water molecules or with the O atoms of anions. Fig. 3 shows the unit-cell packing.

Experimental

Crystals of the title compound were isolated as described previously, by reaction of K_2WO_4 and $\text{K}_2[\text{Pt}(\text{OH})_6]$ at pH 4.5 (Lee *et al.*, 1983).

Crystal data

$\text{K}_5[\text{H}_3\text{PtW}_6\text{O}_{24}] \cdot 6\text{H}_2\text{O}$	$D_x = 4.337 \text{ Mg m}^{-3}$
$M_r = 1988.81$	Mo $K\alpha$ radiation
Monoclinic, $C2/m$	Cell parameters from 30 reflections
$a = 11.449 (7) \text{ \AA}$	$\theta = 13.5\text{--}16.3^\circ$
$b = 19.829 (10) \text{ \AA}$	$\mu = 27.92 \text{ mm}^{-1}$
$c = 13.688 (14) \text{ \AA}$	$T = 298 (2) \text{ K}$
$\beta = 101.43 (7)^\circ$	Truncated octahedron, yellow
$V = 3046 (4) \text{ \AA}^3$	$0.28 \times 0.16 \times 0.16 \text{ mm}$
$Z = 4$	

Data collection

Stoe Stadi-4 diffractometer	$\theta_{\text{max}} = 27.5^\circ$
$\omega/2\theta$ scans	$h = -14 \rightarrow 14$
Absorption correction: numerical (<i>X-SHAPE</i> ; Stoe & Cie, 1996)	$k = 0 \rightarrow 25$
$T_{\text{min}} = 0.013, T_{\text{max}} = 0.128$	$l = 0 \rightarrow 17$
3601 measured reflections	3 standard reflections
3601 independent reflections	frequency: 60 min
3084 reflections with $I > 2\sigma(I)$	intensity decay: 3.8%

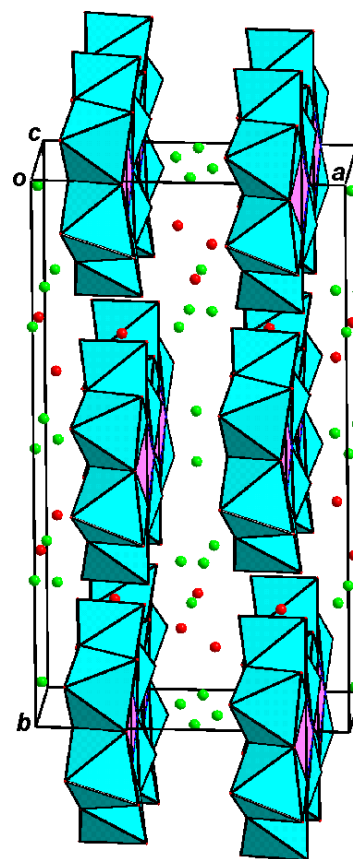


Figure 3
Crystal packing of $\text{K}_5[\text{H}_3\text{PtW}_6\text{O}_{24}] \cdot 6\text{H}_2\text{O}$. Red circles are K^+ and green circles are H_2O .

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0929P)^2 + 140.7849P]$
$R[F^2 > 2\sigma(F^2)] = 0.053$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.160$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.11$	$\Delta\rho_{\text{max}} = 2.84 \text{ e \AA}^{-3}$
3601 reflections	$\Delta\rho_{\text{min}} = -2.77 \text{ e \AA}^{-3}$
209 parameters	Extinction correction: <i>SHELXL97</i>
H-atom parameters not located	Extinction coefficient: 0.00046 (4)

Table 1

Selected geometric parameters ($\text{\AA}, ^\circ$).

W1—W1 ⁱ	3.397 (2)	W2—Or11	1.721 (11)
W1—W2	3.240 (3)	W2—Or12	1.740 (10)
W2—W3	3.381 (3)	W2—Ob6	1.934 (11)
W3—W3 ⁱ	3.205 (2)	W2—Ob7	1.956 (10)
Pt—Oc2	1.973 (10)	W2—Oc2	2.203 (10)
Pt—Oc1	1.990 (14)	W2—Oc3	2.333 (10)
Pt—Oc4	2.007 (16)	W3—Or14	1.727 (12)
Pt—Oc3	2.014 (10)	W3—Or13	1.758 (11)
W1—Or10	1.720 (11)	W3—Ob7	1.913 (11)
W1—Or9	1.775 (12)	W3—Ob8	1.940 (8)
W1—Ob6	1.927 (11)	W3—Oc4	2.135 (10)
W1—Ob5	1.949 (8)	W3—Oc3	2.334 (11)
W1—Oc2	2.174 (11)	Ob6—Ob6 ⁱⁱ	3.16 (2)
W1—Oc1	2.315 (11)		
W1—W2—W3	119.54 (6)	W1—Ob6—W2	114.1 (5)
W3 ⁱ —W3—W2	120.47 (3)	W3—Ob7—W2	121.8 (5)
W2—W1—W1 ⁱ	119.97 (3)	W3—Ob8—W3 ⁱ	111.4 (7)
W1 ⁱ —Ob5—W1	121.3 (8)		

Symmetry codes: (i) $x, -y, z$; (ii) $-x, y, -z$.

Table 2

 Hydrogen-bonding $D \cdots A$ distances (Å).

Oc1...Oc1 ⁱⁱ	2.64 (3)	Ow1...Or10 ^v	3.08 (4)
Oc3...Or9 ⁱⁱ	2.582 (16)	Ow2...Or14 ^{iv}	3.04 (3)
Ow1...Ob7 ⁱⁱⁱ	2.83 (3)	Ow3...Or9 ^v	3.18 (3)
Ow1...Ow4 ^{iv}	2.93 (6)	Ow4...Or13 ^{iv}	2.92 (4)

 Symmetry codes: (ii) $-x, y, -z$; (iii) $1-x, y, 1-z$; (iv) $\frac{1}{2}-x, \frac{1}{2}-y, 1-z$; (v) $x, y, 1+z$.

H atoms were not located. The maximum and minimum electron-density peaks are 0.83 Å from W1 and 1.12 Å from OC4, respectively.

Data collection: *STADI-4* (Stoe & Cie, 1996); cell refinement: *STADI-4*; data reduction: *X-RED* (Stoe & Cie, 1996); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Version 1.07; Farrugia, 1997) and *DIAMOND* (Brandenburg, 1998); software used to prepare material for publication: *SHELXS97*.

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