

Octasodium hexatungstoptatinate(IV) hexacosahydrate, $\text{Na}_8[\text{PtW}_6\text{O}_{24}] \cdot 26\text{H}_2\text{O}$

Uk Lee* and Hea-Chung Joo

Department of Chemistry, Pukyong National University, 599-1 Daeyeon-3dong Nam-ku, Pusan 608-737, Korea

Correspondence e-mail: uklee@mail.pknu.ac.kr

The symmetry of the hexatungstoptatinate(IV) anion in $\text{Na}_8[\text{PtW}_6\text{O}_{24}] \cdot 26\text{H}_2\text{O}$ is C_i ($\bar{1}$), which is different from the D_{3d} ($\bar{3}m$) and S_6 ($\bar{3}$) symmetry found in $\text{K}_6\text{Na}_2[\text{PtW}_6\text{O}_{24}] \cdot 12\text{H}_2\text{O}$ and $(\text{CH}_6\text{N}_3)_8[\text{PtW}_6\text{O}_{24}]$, respectively. However, this change in symmetry does not significantly affect metal–metal and metal–oxygen distances in the anion.

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Key indicators

Single-crystal X-ray study

$T = 298$ K

Mean $\sigma(\text{W}-\text{O}) = 0.009$ Å

H-atom completeness 0%

R factor = 0.051

wR factor = 0.082

Data-to-parameter ratio = 17.9

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

Comment

Some salts with A-type Anderson–Evans heteropolyoxotungstate structures (Anderson, 1937; Tsigdinos, 1978) have been reported in which the $[\text{X}^{n+}\text{W}_6\text{O}_{24}]^{(12-n)-}$ anion contains heteroatoms in high oxidation states. In $\text{K}_6\text{Na}_2[\text{Mn}^{\text{IV}}\text{W}_6\text{O}_{24}] \cdot 12\text{H}_2\text{O}$ (Sergienko *et al.*, 1979), $\text{K}_6\text{Na}_2[\text{Pt}^{\text{IV}}\text{W}_6\text{O}_{24}] \cdot 12\text{H}_2\text{O}$ (Lee *et al.*, 1984) and $\text{K}_5\text{Na}_2[\text{Sb}^{\text{V}}\text{W}_6\text{O}_{24}] \cdot 12\text{H}_2\text{O}$ (Lee & Sasaki, 1988), the anions have the ideal D_{3d} ($\bar{3}m$) point symmetry. However, the point symmetry of the anion is reduced to C_i ($\bar{1}$) in $\text{Na}_8[\text{MnW}_6\text{O}_{24}] \cdot 18\text{H}_2\text{O}$ (Nolan *et al.*, 2000), S_6 ($\bar{3}$) in $(\text{CH}_6\text{N}_3)_8[\text{PtW}_6\text{O}_{24}]$ (Lee *et al.*, 2003) and C_i ($\bar{1}$) in $\text{Na}_6[\text{TeW}_6\text{O}_{24}] \cdot 22\text{H}_2\text{O}$ (Schmidt *et al.*, 1986). The species having an ideal symmetry is only found in the A-type Anderson–Evans heteropolyoxomolybdate, *viz.* $\text{CoNa}_3[\text{IMo}_6\text{O}_{24}] \cdot 14\text{H}_2\text{O}$ (Rosu & Dickman, 1999). But the point symmetries of $[\text{IMO}_6\text{O}_{24}]^{5-}$ are C_1 ($\bar{1}$) in $\text{K}_5[\text{IMO}_6\text{O}_{24}] \cdot 5\text{H}_2\text{O}$

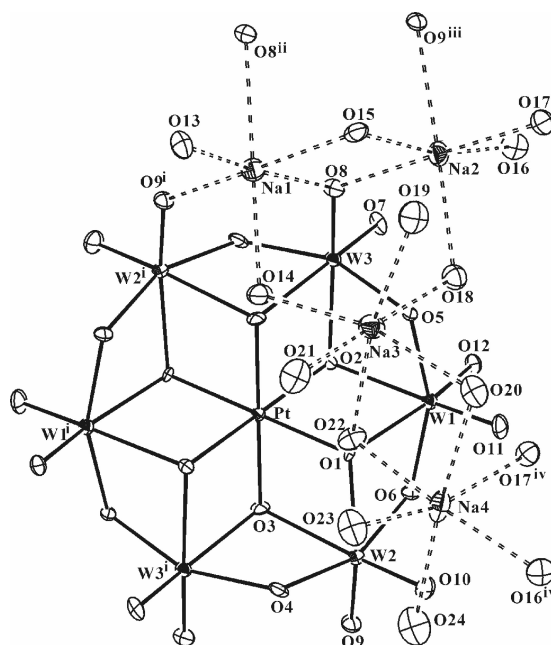


Figure 1

The $[\text{PtW}_6\text{O}_{24}]^{8-}$ anion and surrounding Na^+ cations in $\text{Na}_8[\text{PtW}_6\text{O}_{24}] \cdot 26\text{H}_2\text{O}$, with displacement ellipsoids drawn at the 30% probability level. H atoms and atom O25 are not shown. [Symmetry codes: (i) $1 - x, 1 - y, 1 - z$; (ii) $1 - x, 2 - y, 1 - z$; (iii) $x, 1 + y, z$; (iv) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{3}{2} - z$.]

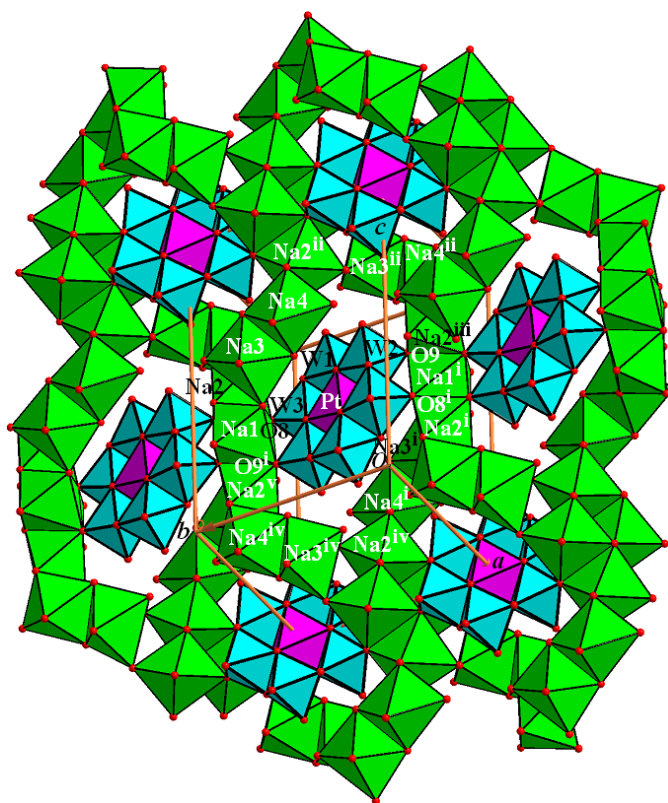


Figure 2
Two-dimensional network of $[\text{PtW}_6\text{O}_{24}]^{8-}$ anions with $[\text{NaO}_6]$ clusters. [Symmetry codes: (i) $1-x, 1-y, 1-z$; (ii) $\frac{1}{2}-x, y-\frac{1}{2}, \frac{3}{2}-z$; (iii) $x, y-1, z$; (iv) $\frac{1}{2}+x, \frac{3}{2}-y, z-\frac{1}{2}$; (v) $1-x, 2-y, 1-z$.]

(Kondo *et al.*, 1980) and C_i ($\bar{1}$) in $\text{Na}_2\text{Cr}[\text{IMo}_6\text{O}_{24}]\cdot 24\text{H}_2\text{O}$ (Rosu & Weakley, 2000). The point symmetry of $[\text{TeMo}_6\text{O}_{24}]^{6-}$ is C_i ($\bar{1}$) in $(\text{NH}_4)_6[\text{TeMo}_6\text{O}_{24}]\cdot \text{Te}(\text{OH})_6\cdot 7\text{H}_2\text{O}$ (Evans, 1974).

In $\text{Na}_8[\text{PtW}_6\text{O}_{24}]\cdot 26\text{H}_2\text{O}$, the $[\text{PtW}_6\text{O}_{24}]^{8-}$ anion has inversion symmetry, as shown in Fig. 1. The O atoms are classified into O_c (O1–O3), O_b (O4–O6), O_t (O7–O12) and O_w (O13–O25), as described previously (Lee *et al.*, 1984). The average bond distances and angles in the $[\text{PtW}_6\text{O}_{24}]^{8-}$ anion are very similar to those in $\text{K}_6\text{Na}_2[\text{PtW}_6\text{O}_{24}]\cdot 12\text{H}_2\text{O}$ (Lee *et al.*, 1984) and $(\text{CH}_6\text{N}_3)_8[\text{PtW}_6\text{O}_{24}]$ (Lee *et al.*, 2003).

All Na^+ cations are coordinated by the O atoms of the $[\text{PtW}_6\text{O}_{24}]^{8-}$ anion and water molecules in a distorted octahedral geometry. Fig. 2 shows the two-dimensional network of $[\text{PtW}_6\text{O}_{24}]^{8-}$ anions with $[\text{NaO}_6]$ clusters. The polyanion is enclosed by the cluster ring of 16 $[\text{NaO}_6]$. The polyanion is connected to the ring of $[\text{NaO}_6]$ cluster by two O8 and two O9 atoms. The octahedra $[\text{Na}_1\text{O}_6]\cdots[\text{Na}_2\text{O}_6]$, $[\text{Na}_3\text{O}_6]\cdots[\text{Na}_4\text{O}_6]$ and $[\text{Na}_4\text{O}_6]\cdots[\text{Na}_2\text{O}_6]$ (symmetry code for the last Na2 atom: $\frac{1}{2}-x, y-\frac{1}{2}, \frac{3}{2}-z$) are connected by edge-sharing, and the octahedra $[\text{Na}_1\text{O}_6]\cdots[\text{Na}_3\text{O}_6]$ and $[\text{Na}_2\text{O}_6]\cdots[\text{Na}_3\text{O}_6]$ are connected by corner-sharing. The two-dimensional planes are connected to each other by hydrogen bonds.

It is worth noting that atom O25, belonging to a water molecule, does not show any interaction with the metal ions

and only forms hydrogen bonds to other O atoms. All the O atoms of the anion form hydrogen bonds with water molecules, except for atoms O8 and O9, which are coordinated to two Na^+ ions. Donor–acceptor distances less than 3.1 Å for possible hydrogen bonding are listed in Table 2.

Experimental

Crystals of the title compound were prepared by the reaction of $\text{Na}_2\text{WO}_4\cdot 2\text{H}_2\text{O}$ and $\text{Na}_2[\text{Pt}(\text{OH})_6]$ at about pH 7.2, as described in a previous report (Lee *et al.*, 1983).

Crystal data

$\text{Na}_8[\text{PtW}_6\text{O}_{24}]\cdot 26\text{H}_2\text{O}$
 $M_r = 2334.53$
 Monoclinic, $P2_1/n$
 $a = 10.873$ (1) Å
 $b = 11.785$ (1) Å
 $c = 18.116$ (1) Å
 $\beta = 93.56$ (1)°
 $V = 2316.9$ (3) Å³
 $Z = 2$

$D_x = 3.346$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 39 reflections
 $\theta = 9.6$ – 16.2°
 $\mu = 18.04$ mm⁻¹
 $T = 298$ (2) K
 Block, pale yellow
 $0.25 \times 0.19 \times 0.13$ mm

Data collection

Stoe Stadi-4 diffractometer
 $\omega/2\theta$ scans
 Absorption correction: numerical
 (*X-SHAPE*; Stoe & Cie, 1996)
 $T_{\min} = 0.034$, $T_{\max} = 0.114$
 5299 measured reflections
 5299 independent reflections
 4017 reflections with $I > 2\sigma(I)$

$\theta_{\max} = 27.5^\circ$
 $h = -14 \rightarrow 14$
 $k = 0 \rightarrow 15$
 $l = 0 \rightarrow 23$
 3 standard reflections
 frequency: 60 min
 intensity decay: 4.3%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.051$
 $wR(F^2) = 0.082$
 $S = 1.67$
 5299 reflections
 296 parameters
 H atoms not located

$w = 1/[\sigma^2(F_o^2)]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 2.79$ e Å⁻³
 $\Delta\rho_{\min} = -2.25$ e Å⁻³
 Extinction correction: *SHELXL97*
 Extinction coefficient: 0.00172 (3)

Table 1

Selected bond distances (Å).

Pt–O1	2.012 (9)	Na1–O9 ⁱ	2.35 (1)
Pt–O2	2.009 (9)	Na1–O13	2.38 (1)
Pt–O3	2.004 (9)	Na1–O14	2.41 (2)
W1–O1	2.138 (9)	Na1–O15	2.35 (1)
W1–O2	2.152 (9)	Na2–O8	2.42 (1)
W1–O5	1.962 (9)	Na2–O9 ⁱⁱⁱ	2.50 (1)
W1–O6	1.946 (9)	Na2–O15	2.42 (1)
W1–O11	1.75 (1)	Na2–O16	2.36 (1)
W1–O12	1.765 (9)	Na2–O17	2.36 (1)
W2–O1	2.139 (9)	Na2–O18	2.45 (1)
W2–O3	2.177 (9)	Na3–O14	2.41 (1)
W2–O4	1.938 (9)	Na3–O18	2.44 (1)
W2–O6	1.97 (1)	Na3–O19	2.47 (2)
W2–O9	1.771 (9)	Na3–O20	2.52 (1)
W2–O10	1.78 (1)	Na3–O21	2.41 (1)
W3–O2	2.155 (9)	Na3–O22	2.41 (1)
W3–O3 ⁱ	2.151 (9)	Na4–O16 ^{iv}	2.36 (1)
W3–O4 ⁱ	1.96 (1)	Na4–O17 ^{iv}	2.40 (1)
W3–O5	1.96 (1)	Na4–O20	2.55 (2)
W3–O7	1.767 (9)	Na4–O22	2.33 (1)
W3–O8	1.76 (1)	Na4–O23	2.37 (1)
Na1–O8	2.51 (1)	Na4–O24	2.51 (2)
Na1–O8 ⁱⁱ	2.57 (1)		

Symmetry codes: (i) $1-x, 1-y, 1-z$; (ii) $1-x, 2-y, 1-z$; (iii) $x, 1+y, z$; (iv) $\frac{1}{2}-x, y-\frac{1}{2}, \frac{3}{2}-z$.

Table 2
Hydrogen-bonding $D \cdots A$ distances (Å).

O13...O7 ⁱⁱ	2.72 (2)	O19...O11 ^{viii}	2.82 (2)
O13...O19 ^v	2.75 (2)	O20...O7 ^{ix}	2.82 (1)
O13...O12 ^{vi}	2.84 (2)	O21...O4 ^x	2.87 (2)
O14...O3 ⁱ	2.76 (2)	O21...O23	2.93 (2)
O14...O25 ^{vi}	2.99 (2)	O21...O24 ^x	2.76 (2)
O15...O19	2.72 (2)	O22...O1	2.80 (2)
O15...O4 ⁱⁱⁱ	2.83 (1)	O22...O23 ^x	2.82 (2)
O16...O25	2.82 (2)	O23...O2 ^{ix}	2.74 (2)
O16...O12 ^{vii}	2.90 (2)	O24...O10	2.83 (2)
O17...O11 ^{viii}	2.73 (2)	O24...O25 ^{iv}	3.09 (2)
O17...O10 ⁱⁱⁱ	2.85 (2)	O25...O6 ^{vii}	2.77 (2)
O18...O5	2.75 (2)	O25...O12	2.79 (2)
O18...O10 ^{viii}	3.04 (2)		

Symmetry codes: (i) $1-x, 1-y, 1-z$; (ii) $1-x, 2-y, 1-z$; (iii) $x, 1+y, z$; (iv) $\frac{1}{2}-x, y-\frac{1}{2}, \frac{3}{2}-z$; (v) $-x, 2-y, 1-z$; (vi) $x-\frac{1}{2}, \frac{3}{2}-y, z-\frac{1}{2}$; (vii) $\frac{3}{2}-x, \frac{1}{2}+y, \frac{3}{2}-z$; (viii) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{3}{2}-z$; (ix) $x-1, y, z$; (x) $-x, 1-y, 1-z$.

The highest peak in the difference map is 0.84 Å from Pt and the deepest hole is 1.46 Å from O4.

Data collection: *Stadi4* (Stoe, 1996); cell refinement: *Stadi4*; data reduction: *X-RED32* (Stoe, 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: *SHELXL97*.

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