A novel protonated hexatungstoplatinate(IV), Na$_{5.5}$[H$_{2.5}$PtW$_6$O$_{24}$]·17H$_2$O

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Key indicators

Single-crystal X-ray study
T = 298 K
Mean σ(W–O) = 0.008 Å
H-atom completeness 0%
Disorder in main residue
R factor = 0.039
wR factor = 0.098
Data-to-parameter ratio = 17.6

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

The novel protonated hemiundecasodium hemipentahydrogen hexatungstoplatinate(IV) heptadecahydrate, Na$_{5.5}$[H$_{2.5}$PtW$_6$O$_{24}$]·17H$_2$O, crystallizes in the triclinic system in space group $P\bar{1}$. The protonated O atoms were identified by considering three factors: inter-polyanion hydrogen bonds, elongation of W—O(H) bond distances, and bond angles of W—O(H)—W. The [H$_{2.5}$(PtW$_6$O$_{24}$)]$^{5.5-}$ polyanion has no inversion symmetry, and it forms a dimer, *viz.* [H$_5$(PtW$_6$O$_{24}$)$_2$]$^{11-}$, *via* five strong hydrogen bonds.

Comment

Gradual protonation of the polyanion in Anderson-type heteropolyoxometalates (Anderson, 1937; Tsigdinos, 1978) has been found only in hexamolybdo- (Lee, 1994; Lee & Sasaki, 1994; Lee & Joo, 2000) and hexatungstoplatinate(IV) (Lee *et al.*, 1983; Lee, 2002) systems, when the general formula is [PtM_6O$_{24}$]$^{8-}$ (where M = Mo or W). The preparation of novel protonated hexatungstoplatinates is chemically interesting, and is important for investigating heteropolyoxometalate systems. We had attempted to confirm such protonation in the [PtW$_6$O$_{24}$]$^{8-}$ system. As a result, one type of hexatungstoplatinate(IV), *viz.* [H$_3$PtW$_6$O$_{24}$]$^{5-}$ (Lee *et al.*, 1983; Lee, 2002), was obtained previously. We report here the structure of the title compound, (I), which contains a novel
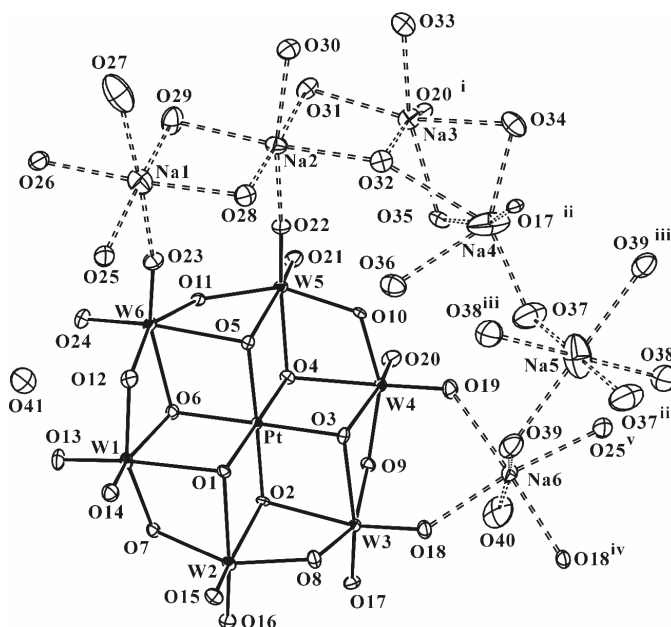
Figure 1
A view of the structure with displacement ellipsoids drawn at the 30% probability level, and showing the full coordination of the cations. H atoms are not shown. [Symmetry codes: (i) 2 − x, 2 − y, 1 − z; (ii) 1 + x, y, z; (iii) 2 − x, 2 − y, −z; (iv) 1 − x, 2 − y, −z; (v) x, 1 + y, z.]
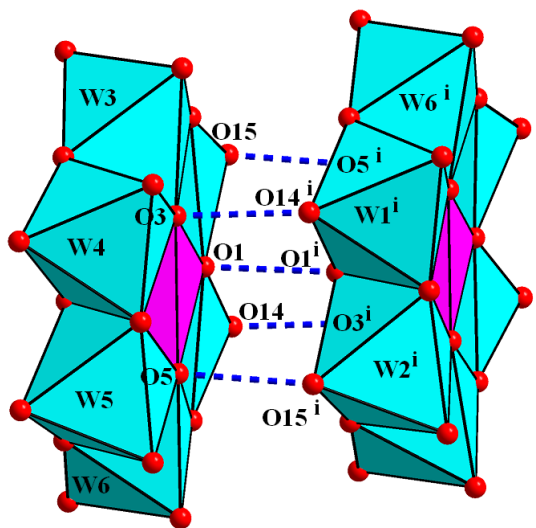
Figure 2
Inter-polyanion hydrogen bonds shown as a polyhedral model. [Symmetry code: (i) $1 - x, 1 - y, -z$.]

protonated hexatungstoplatinate anion, *viz.* $[H_{2.5}PtW_6O_{24}]^{5.5-}$.

Fig. 1 shows the structure of (I) and the atom-labelling scheme of the polyanion. The polyanion consists of six independent $[WO_6]$ and one $[PtO_6]$ octahedra, sharing edges, and the polyanion has C_1 (1) symmetry. The O atoms were classified in the same way as previously (Lee *et al.*, 1984), *viz.* O*c* (O1–O6), O*b* (O7–O12), O*t* (O13–O24), and O*w* (O25–O41). The protonated O atoms, O(H) in the polyanion, were also identified in the same way as reported previously (Lee, 2002).

The protonation of the O*c* atoms causes an increase in the W—O*c*(H) bond lengths, a decrease in the W—O*c*(H)—W bond angles, and an increase in the W—O*b*—W bond angles. The elongation of the W—O*cn*(H) (n = 1, 3 and 5) bond lengths is about 0.16 Å compared with the non-protonated O atoms, as shown in Table 1. Along with the degree of protonation for different $[H_nPtMo_6O_{24}]^{(8-n)-}$ anions, the corresponding Mo—O*c*(H) bonds are elongated, whereas the Pt—O*c*(H) distances do not vary considerably in any protonated hexamolybdo- or hexatungstoplatinate(IV). A distinct bond-length elongation was not found for the W—O*b* bonds. The W···W distance is also affected by the elongation of the W—O*c*(H) bond distance. As a result, the distances W1···W2, W3···W4, and W5···W6, with a mean value of 3.369 Å, are longer than the W1···W6, W2···W3, and W4···W5 distances, with a mean value of 3.237 Å.

The bond angles W—O*cn*—W (n = 1, 3, 5; mean value 93.5°) are smaller than those of the unprotonated W—O*cn*—W groups (n = 2, 4, 6; mean value 97.3°). The W—O*b*—W angles, which are a counterpart of O*c*(H), *i.e.* W—O*bn*—W (n = 7, 9, 11; mean value 121.0°), are larger than the W—O*bn*—W angles (n = 8, 10, 12; mean value 112.3°). For comparison, in the unprotonated $[PtW_6O_{24}]^{8-}$ polyanion (Lee *et al.*, 1984), the bond lengths of W—O*b* and W—O*c* are 1.97 (2) and 2.16 (2) Å, and the bond angles of W—O*b*—W and W—O*c*—W are 110.8 (8) and 97.4 (5)°, respectively.

In the title compound, two $[H_{2.5}PtW_6O_{24}]^{5.5-}$ polyanions form a dimer, $[H_5(PtW_6O_{24})_2]^{11-}$, *via* five strong hydrogen bonds (Fig. 2). The H atom which is involved in the O1···O1($1 - x, 1 - y, -z$) inter-polyanion hydrogen bonding seems to show positional disorder as is the case in the $[H_{3.5}PtMo_6O_{24}]^{4.5-}$ and $[H_{4.5}PtMo_6O_{24}]^{3.5-}$ polyanions (Lee & Sasaki, 1994). The form of dimerization is similar in the $[H_3PtW_6O_{24}]^{5-}$ polyanion (Lee, 2002). These results led us to conclude that atoms O1, O3, and O5 are protonated. Stoichiometry requires, therefore, an average of 2.5 protons for charge compensation.

Fig. 3 shows the three-dimensional network of the structure. Atom Na5 is located on an inversion centre. All Na atoms are six-coordinated by the O atoms of the polyanion and water molecules, and they deviate from the geometry of a regular octahedron. In particular, the $[Na4O_6]$ octahedron is considerably distorted because of an exceptionally long Na4—O32 distance. The dimerized $[H_{2.5}PtW_6O_{24}]^{5.5-}$ polyanion is enclosed by $[NaO_6]$ cluster rings. The octahedra $[Na1O_6]\cdots[Na2O_6]$, $[Na2O_6]\cdots[Na3O_6]$, and $[Na6O_6]\cdots[Na6O_6]$ (symmetry operator for the last Na atom: $1 - x, 2 - y, -z$) are connected by edge-sharing and the octahedra $[Na4O_6]\cdots[Na5O_6]$, $[Na5O_6]\cdots[Na6O_6]$, and $[Na1O_6]\cdots[Na6O_6]$ (symmetry operator for the last Na atom: $x, y - 1, z$) are connected by corner-sharing. The Na3···Na4 distance is shorter than other Na···Na distances because the O atoms O32, O34 and O35 of the corresponding $[Na3O_6]$ and $[Na4O_6]$ octahedra share a common face.

It is worth noting that atom O41 does not show any interaction with the metal atoms, and that it is bonded to other O atoms only by hydrogen bonds. Donor–acceptor distances for possible hydrogen bonding are less than 3.1 Å in (I), as listed in Table 2.

Experimental

Crystals of the title compound were prepared as described in a previous report, by the reaction of $Na_2WO_4\cdot2H_2O$ and $Na_2[Pt(OH)_6]$ at about pH 4.7 (Lee *et al.*, 1983). The crystal used for data collection was coated with epoxy resin.

Crystal data

$Na_{5.5}[H_{2.5}PtW_6O_{24}](H_2O)_{17}]$	$Z = 2$
$M_r = 2117.43$	$D_x = 3.785$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 10.736$ (2) Å	Cell parameters from 30
$b = 12.803$ (3) Å	reflections
$c = 14.877$ (3) Å	$\theta = 9.5–10.5°$
$\alpha = 105.50$ (3)°	$\mu = 22.43$ mm^{-1}
$\beta = 105.13$ (3)°	$T = 298$ (2) K
$\gamma = 97.43$ (3)°	Block, pale yellow
$V = 1858.1$ (9) Å^3	$0.30 \times 0.25 \times 0.24$ mm

Data collection

Stoe Stadi-4 diffractometer	$\theta_{max} = 27.5°$
$\omega/2\theta$ scans	$h = 0 \rightarrow 13$
Absorption correction: numerical	$k = -16 \rightarrow 16$
(*X-SHAPE*; Stoe & Cie, 1996)	$l = -19 \rightarrow 18$
$T_{min} = 0.005$, $T_{max} = 0.010$	3 standard reflections
8526 measured reflections	frequency: 60 min
8526 independent reflections	intensity decay: 3.5%
7210 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.042P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.039$	$+ 22.4365P]$
$wR(F^2) = 0.098$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.13$	$(\Delta/\sigma)_{max} = 0.001$
8526 reflections	$\Delta\rho_{max} = 1.89$ e Å^{-3}
485 parameters	$\Delta\rho_{min} = -2.38$ e Å^{-3}
H atoms not included	Extinction correction: *SHELXL*97
	Extinction coefficient: 0.00196 (5)

Table 1
Selected geometric parameters (Å, °).

Pt···W1	3.264 (1)	W6—O6	2.174 (7)
Pt···W2	3.2939 (9)	W6—O11	1.942 (7)
Pt···W3	3.305 (1)	W6—O12	1.939 (8)
Pt···W4	3.328 (2)	W6—O23	1.729 (8)
Pt···W5	3.3366 (9)	W6—O24	1.749 (8)
Pt···W6	3.329 (1)	Na1···Na2	3.420 (8)
W1···W2	3.336 (1)	Na1···Na6^i	4.355 (9)
W1···W6	3.239 (2)	Na2···Na3	3.412 (7)
W2···W3	3.234 (1)	Na3···Na4	3.328 (9)
W3···W4	3.384 (2)	Na4···Na5	3.931 (8)
W4···W5	3.239 (1)	Na5···Na6	4.460 (6)
W5···W6	3.387 (2)	Na6···Na6^{ii}	3.50 (1)
Pt—O1	2.026 (7)	Na1—O23	2.30 (1)
Pt—O2	1.987 (7)	Na1—O25	2.33 (1)
Pt—O3	2.025 (7)	Na1—O26	2.39 (1)
Pt—O4	2.009 (6)	Na1—O27	2.46 (2)
Pt—O5	2.010 (7)	Na1—O28	2.48 (1)
Pt—O6	1.988 (7)	Na1—O29	2.38 (1)
W1—O1	2.259 (7)	Na2—O22	2.31 (1)
W1—O6	2.143 (7)	Na2—O28	2.39 (1)
W1—O7	1.943 (7)	Na2—O29	2.48 (1)
W1—O12	1.946 (8)	Na2—O30	2.37 (1)
W1—O13	1.745 (7)	Na2—O31	2.43 (1)
W1—O14	1.755 (7)	Na2—O32	2.47 (1)
W2—O1	2.311 (7)	Na3—O20^{iii}	2.372 (9)
W2—O2	2.154 (7)	Na3—O31	2.47 (1)
W2—O7	1.931 (7)	Na3—O32	2.38 (1)
W2—O8	1.959 (7)	Na3—O33	2.44 (1)
W2—O15	1.763 (7)	Na3—O35	2.47 (1)
W2—O16	1.725 (8)	Na3—O34	2.48 (1)
W3—O2	2.185 (7)	Na4—O17^{iv}	2.32 (1)
W3—O3	2.293 (7)	Na4—O32	2.86 (1)
W3—O8	1.933 (7)	Na4—O34	2.45 (2)
W3—O9	1.952 (7)	Na4—O35	2.33 (1)
W3—O17	1.733 (8)	Na4—O36	2.66 (2)
W3—O18	1.751 (8)	Na4—O37	2.30 (2)
W4—O3	2.325 (7)	Na5—O37^v	2.39 (1)
W4—O4	2.145 (7)	Na5—O37	2.39 (1)
W4—O9	1.921 (7)	Na5—O38	2.45 (2)
W4—O10	1.956 (7)	Na5—O38^v	2.45 (2)
W4—O19	1.769 (8)	Na5—O39^v	2.63 (1)
W4—O20	1.717 (7)	Na5—O39	2.63 (1)
W5—O4	2.140 (7)	Na6—O18	2.348 (9)
W5—O5	2.368 (7)	Na6—O18^{ii}	2.43 (1)
W5—O10	1.965 (7)	Na6—O19	2.41 (1)
W5—O11	1.928 (7)	Na6—O25^{vi}	2.40 (1)
W5—O21	1.726 (8)	Na6—O40	2.44 (2)
W5—O22	1.735 (8)	Na6—O39	2.50 (1)
W6—O5	2.330 (7)		

W1—O1—W2	93.8 (2)	W2—O7—W1	118.9 (3)
W2—O2—W3	96.4 (3)	W3—O8—W2	112.4 (4)
W3—O3—W4	94.3 (3)	W4—O9—W3	121.8 (4)
W5—O4—W4	98.2 (3)	W4—O10—W5	111.4 (3)
W6—O5—W5	92.3 (2)	W5—O11—W6	122.2 (4)
W1—O6—W6	97.2 (3)	W6—O12—W1	113.0 (4)

Symmetry codes: (i) $x, y - 1, z$; (ii) $1 - x, 2 - y, -z$; (iii) $2 - x, 2 - y, 1 - z$; (iv) $1 + x, y, z$; (v) $2 - x, 2 - y, -z$; (vi) $x, 1 + y, z$.
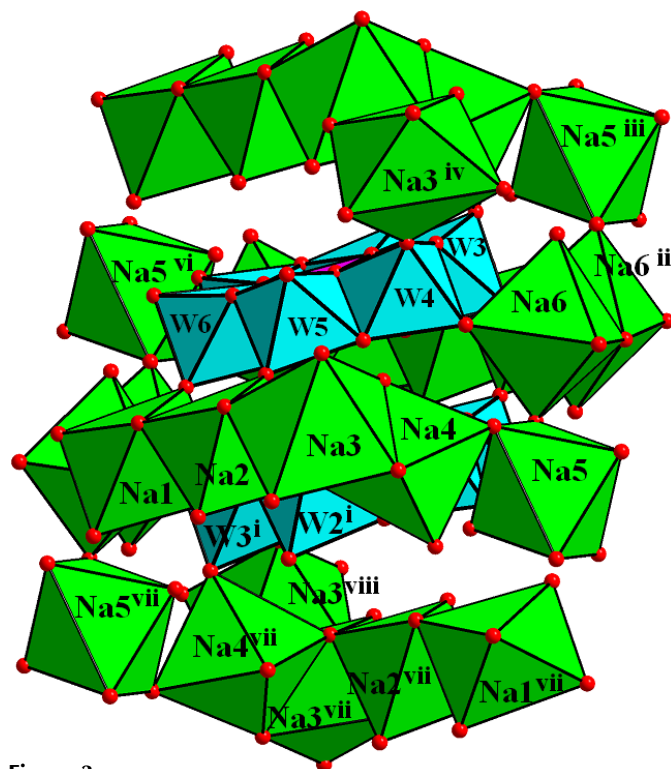

Figure 3
The three-dimensional network of (I) represented as a polyhedral model. The unit cell is outlined. [Symmetry codes: (i) $1 - x, 2 - y, -z$; (ii) $x - 1, y, z$; (iii) $x - 1, y - 1, z$; (iv) $x - 1, y - 1, z$; (v) $x, y - 1, z$; (vi) $2 - x, 1 - y, -z$; (vii) $2 - x, 2 - y, -z$; (viii) $1 - x, 1 - y, -z$.]

Table 2
Hydrogen-bonding geometry (Å).

O1···O1^i	2.60 (1)	O30···O41^{iv}	2.83 (1)
O3···O14^i	2.56 (1)	O31···O24^{iii}	2.90 (1)
O5···O15^i	2.60 (1)	O31···O33	3.08 (1)
O25···O8^i	2.82 (1)	O32···O2^{iv}	2.80 (1)
O25···O23	3.04 (2)	O32···O36	2.81 (2)
O25···O38^{ii}	2.90 (2)	O33···O4^{iv}	2.82 (1)
O26···O19^{ii}	2.90 (1)	O33···O34^v	2.80 (2)
O26···O21^{iii}	2.84 (1)	O34···O9^{iv}	2.82 (1)
O26···O27	3.05 (2)	O34···O35	3.03 (1)
O26···O31^{iii}	2.80 (1)	O35···O10	2.81 (1)
O27···O13^{iv}	2.68 (2)	O35···O20^{vi}	3.06 (1)
O27···O37^{ii}	2.80 (2)	O35···O21^{vi}	2.91 (1)
O27···O41^{iv}	2.76 (2)	O36···O10	2.83 (1)
O28···O7^{iv}	2.83 (1)	O36···O15^i	3.01 (1)
O28···O15^i	2.96 (1)	O36···O16^{iv}	2.98 (1)
O29···O11^{iii}	3.04 (1)	O37···O19	3.06 (2)
O29···O29^{iii}	2.95 (2)	O38···O16^{vii}	3.07 (2)
O30···O6^{iv}	2.73 (1)	O38···O17^{vii}	3.00 (2)
O30···O31	3.05 (1)	O39···O14^i	3.03 (1)
O30···O33	2.93 (1)	O40···O12^{viii}	2.98 (2)

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

H atoms were not located. The highest peak in the difference map is 0.76 Å from W6 and the deepest hole is 0.90 Å from Pt.

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