A diprotonated hexatungstoplatinate(IV), Na6[H2PtW6O24]·22H2O

Uk Lee,[a]* Hea-Chung Joo[a] and Ki-Min Park[b]

[a]Department of Chemistry, Pukyong National University, 599-1 Daeyeon-dong Nam-ku, Pusan 608-737, South Korea, and [b]Research Institute of Natural Sciences, Gyeongsang National University, Chinju 660-701, South Korea

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

The novel protonated hexasodium dihydrogen hexatungstoplatinate(IV) doicosahydrate, Na6[H2PtW6O24]·22H2O, was crystallized in the triclinic system in space group $P\bar{1}$. The [H2PtW6O24]$^{6-}$ polyanion has C_i ($\bar{1}$) symmetry. The identification of the protonated O atom in the polyanion is difficult because it does not form interpolyanion hydrogen bonds, and a clear difference was not found in the W—O(H) bond lengths or the W—O(H)—W bond angles to indicate protonation of the O atom.

Comment

The behaviour of gradual protonation in Anderson-structure heteropolyoxometalates (Anderson, 1937; Tsigdinos, 1978) has only been found in hexatungstoplatinate(IV) (Lee *et al.*, 1983; Lee, 2002; Lee & Joo, 2004) and hexamolybdoplatinate(IV) (Lee, 1994; Lee & Sasaki, 1994; Lee & Joo, 2000) systems, where the general formula is [H$_n$PtM_6O24]$^{(8-n)-}$ (M = W or Mo). However, comparing the [H$_n$PtW6O24]$^{(8-n)-}$ polyanion with the [H$_n$PtMo6O24]$^{(8-n)-}$ polyanion, the confirmation of protonated species is not sufficient because only two, *viz.* [H3PtW6O24]$^{5-}$ (Lee *et al.*, 1983; Lee, 2002) and [H2.5PtW6O24]$^{2.5-}$ (Lee & Joo, 2004), have been reported. [H$_n$PtMo6O24]$^{(8-n)-}$ polyanion species are stable in strongly acidic conditions but they are unstable above pH 6. In contrast, [H$_n$PtW6O24]$^{(8-n)-}$ polyanion species are stable at about pH 7, but they cannot be separated under pH 2. Therefore, K6Na2[PtW6O24]·12H2O (Lee *et al.*, 1984) has been prepared at pH 7.0, but the [PtMo6O24]$^{8-}$ salt was not separated at the same pH range. Although the sodium salts of Anderson-structure heteropolyoxometalates containing Pt^{IV} are unstable in air because they include large amounts of water of crystallization, the salts do promote crystallization. We report here the structure of the title compound, (I), which contains the lowest protonated hexatungstoplatinate anion, *viz.* [H2PtW6O24]$^{6-}$.

Fig. 1 shows the [H2PtW6O24]$^{6-}$ polyanion. The polyanion has inversion C_i ($\bar{1}$) symmetry. The O atoms in the anion are classified according to the method reported by Lee *et al.* (1983), *viz.* Oc (O1—O3), Ob (O4—O6), Ot (O7—O12) and OW (O13—O24). The protonated O atoms in the [H2.5W6O24]$^{5.5-}$ polyanion (Lee & Joo, 2004) are definitely indicated by the hydrogen bonding between the polyanions, the elongation of the W—O(H) bond length, and the variations in the W—Oc(H)—W bond angles. The identification of the protonated O atoms in the [H2PtW6O24]$^{6-}$ polyanion was difficult because they do not form interpolyanion hydrogen bonds, and we could not find clear differences in the W—O bond lengths or the W—Oc—W and W—Ob—W bond angles. The W1—O2 [2.257 (6) Å] and W2—O2 [2.244 (6) Å] bond

lengths are slightly longer than the other W—Oc bond lengths (mean 2.197 Å). Usually in Anderson-structure hetero-polyoxometalates, atom Oc is protonated in preference to atom Ob. In particular, no difference in length was found between the W—Ob bonds in this polyanion. The W1—O2—W2 and W1—O4—W3 bond angles are 95.1 (2) and 117.1 (3)°, respectively, but the mean W—On—W (n = 1 and 3) and W—Om—W (m = 5 and 6) angles are 96.2 and 114.0°, respectively. From this result, it is postulated that the protons are disordered over all the Oc positions. A polyanion containing the
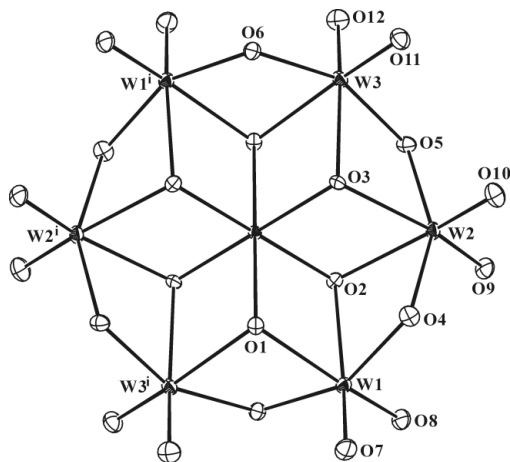
same protonated hexamolybdoplatinate(IV) species was reported in $Nd_2[H_2PtMo_6O_{24}]\cdot14H_2O$ (Lee & Joo, 2000).

Fig. 2 shows the discrete linear cluster of seven $[NaO_6]$ polyhedra in (I). Atom Na4 is located at an inversion center. During the refinement process, reasonable displacement parameters of atom Na2, which is in a general position in space group $P\bar{1}$, were obtained by reducing the occupancy of this atom to 0.5 because of disorder. As a result, the number of Na^+ ions per molecule is six. All Na^+ ions 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 $[Na2O_6]$ octahedron is considerably distorted because of the exceptionally long Na2—O13 and Na2—O19 distances. The Na2···Na3 distance is shorter than other Na···Na distances because atoms O12, O18 and O19 of the corresponding $[Na2O_6]$ and $[Na3O_6]$ octahedra share a common face. All water molecules are coordinated to Na^+ ions.

Fig. 3 shows the unit-cell packing and probable hydrogen-bonding interactions of the O atoms in the polyanion with water molecules of the $[NaO_6]$ clusters. The discrete linear clusters of seven $[NaO_6]$ are connected by the $[H_2PtW_6O_{24}]^{6-}$ polyanion. All O atoms of the polyanion can form hydrogen bonds with the water molecules, as shown in Table 2. Donor–acceptor distances for possible hydrogen bonds less than 3.1 Å in (I) are listed in Table 2.

Figure 1
The anion in $Na_6[H_2PtW_6O_{24}]\cdot22H_2O$. Displacement ellipsoids are drawn at the 30% probability level. H atoms are not shown. [Symmetry code: (i) $1 - x, 1 - y, 1 - z$.]
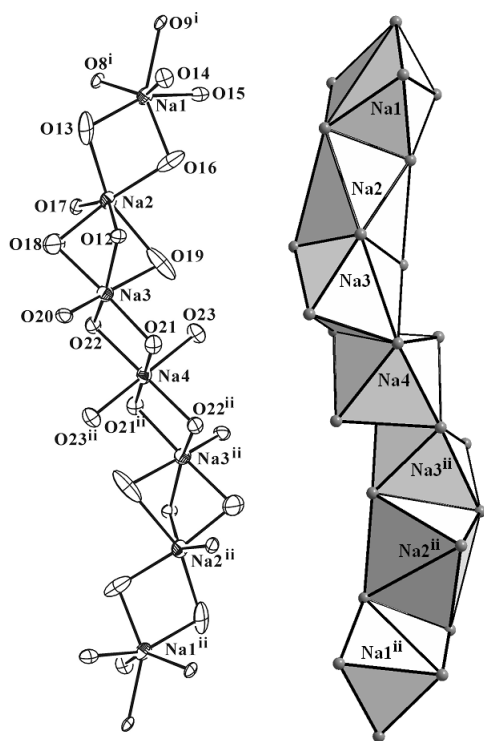

Figure 2
The discrete linear cluster of seven $[NaO_6]$ polyhedra in (I), with displacement ellipsoids drawn at the 30% probability level. H atoms are not shown. [Symmetry codes: (i) $-x, 1 - y, 1 - z$; (ii) $1 - x, 2 - y, -z$.]
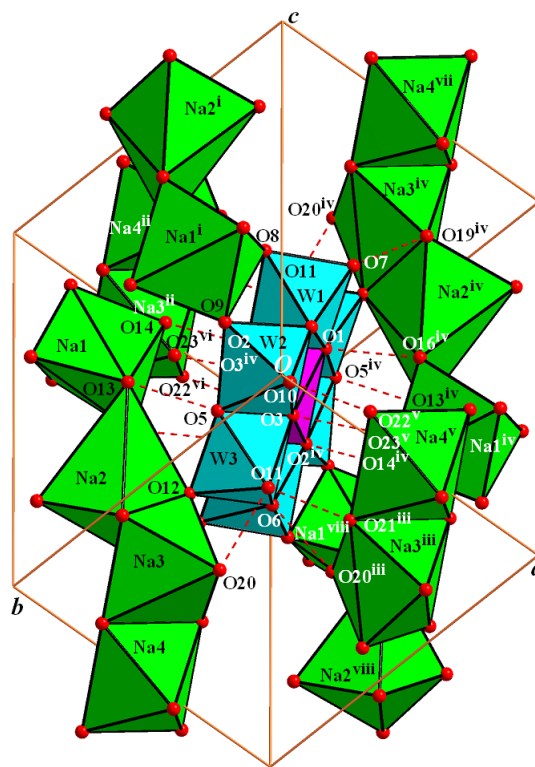

Figure 3
The unit-cell packing represented by a polyhedral model and probable hydrogen-bonding interactions in the polyanion with water molecules of $[NaO_6]$ clusters. [Symmetry codes: (i) $-x, 1 - y, 1 - z$; (ii) $x, y, 1 + z$; (iii) $1 - x, 1 - y, -z$; (iv) $1 - x, 1 - y, 1 - z$; (v) $x, y - 1, z$; (vi) $1 - x, 2 - y, 1 - z$; (vii) $x, y - 1, 1 + z$; (viii) $1 + x, y, z$.]

Experimental

Crystals of the title compound were prepared as described previously, by the reaction of $Na_2WO_4 \cdot 2H_2O$ and $Na_2[Pt(OH)_6]$ at about pH 5.5 (Lee *et al.*, 1983). The crystal used for data collection was coated with epoxy resin.

Crystal data

$Na_6[H_2PtW_6O_{24}] \cdot 22H_2O$	$Z = 1$
$M_r = 2218.50$	$D_x = 3.440$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 10.028\ (1)$ Å	Cell parameters from 27
$b = 10.591\ (1)$ Å	reflections
$c = 12.109\ (3)$ Å	$\theta = 9.6$–$10.5°$
$\alpha = 113.13\ (1)°$	$\mu = 19.48$ mm^{-1}
$\beta = 107.17\ (1)°$	$T = 298\ (2)$ K
$\gamma = 99.48\ (1)°$	Hexagonal prism, pale yellow
$V = 1070.8\ (3)$ Å^3	$0.26 \times 0.13 \times 0.10$ mm

Data collection

Stoe Stadi-4 diffractometer	$\theta_{max} = 27.5°$
ω–2θ scans	$h = 0 \rightarrow 13$
Absorption correction: numerical	$k = -13 \rightarrow 13$
(X-$SHAPE$; Stoe & Cie, 1996)	$l = -15 \rightarrow 14$
$T_{min} = 0.051$, $T_{max} = 0.156$	3 standard reflections
4896 measured reflections	frequency: 60 min
4896 independent reflections	intensity decay: 3.7%
4223 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0492P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.035$	$+ 10.2521P]$
$wR(F^2) = 0.096$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.11$	$(\Delta/\sigma)_{max} < 0.001$
4896 reflections	$\Delta\rho_{max} = 2.62$ e Å^{-3}
275 parameters	$\Delta\rho_{min} = -2.18$ e Å^{-3}
H-atom parameters not refined	Extinction correction: $SHELXL$97
	Extinction coefficient: 0.0073 (2)

Table 1
Selected geometric parameters (Å, °).

Pt—O1	2.008 (6)	Na3···Na4	3.498 (4)
Pt—O2	2.008 (6)	Na1—O8^{ii}	2.372 (8)
Pt—O3	2.013 (6)	Na1—O9^{ii}	2.544 (8)
W1—O1	2.166 (6)	Na1—O13	2.47 (1)
W1—O2	2.257 (6)	Na1—O14	2.420 (9)
W1—O4	1.949 (6)	Na1—O15	2.45 (1)
W1—O6^i	1.940 (6)	Na1—O16	2.406 (9)
W1—O7	1.737 (7)	Na2—O12	2.388 (11)
W1—O8	1.745 (6)	Na2—O13	2.85 (2)
W2—O2	2.244 (6)	Na2—O16	2.62 (2)
W2—O3	2.227 (6)	Na2—O17	2.49 (2)
W2—O4	1.945 (6)	Na2—O18	2.35 (2)
W2—O5	1.955 (6)	Na2—O19	2.83 (2)
W2—O9	1.740 (6)	Na3—O12	2.424 (8)
W2—O10	1.739 (6)	Na3—O18	2.44 (1)
W3—O1^i	2.170 (6)	Na3—O19	2.40 (1)
W3—O3	2.224 (6)	Na3—O20	2.399 (9)
W3—O5	1.958 (6)	Na3—O21	2.423 (9)
W3—O6	1.948 (6)	Na3—O22	2.435 (9)
W3—O11	1.757 (6)	Na4—O21	2.439 (8)
W3—O12	1.718 (7)	Na4—O22	2.465 (7)
Na1···Na2	3.76 (1)	Na4—O23	2.418 (8)
Na2···Na3	3.19 (1)		
W1—O1—W3^i	96.3 (2)	W2—O4—W1	117.1 (3)
W2—O2—W1	95.1 (2)	W2—O5—W3	115.6 (3)
W3—O3—W2	96.1 (2)	W1^i—O6—W3	112.3 (3)

Symmetry codes: (i) $1-x, 1-y, 1-z$; (ii) $-x, 1-y, 1-z$.

Table 2
Hydrogen-bond distances (Å).

O13···O5	2.81 (1)	O18···O5^{iii}	2.89 (1)
O13···O14^{ii}	2.99 (2)	O18···O12	2.88 (1)
O13···O20^{iii}	2.79 (1)	O18···O18^{iii}	2.79 (3)
O14···O2	2.671 (9)	O19···O4^v	2.67 (1)
O14···O9^{ii}	3.07 (1)	O19···O7^i	2.80 (1)
O14···O23^{iv}	2.73 (1)	O19···O12	3.02 (1)
O15···O8^v	2.97 (1)	O19···O23	3.01 (2)
O15···O17^{vi}	2.79 (2)	O20···O6^{vii}	2.755 (9)
O15···O21^{iv}	2.95 (1)	O20···O11	2.94 (1)
O16···O1^i	2.84 (1)	O20···O13^{iii}	2.79 (1)
O16···O7^v	2.82 (1)	O21···O11^{vii}	2.80 (1)
O17···O10^v	3.10 (2)	O21···O15^{iv}	2.95 (1)
O17···O11^{iii}	2.95 (2)	O22···O9^{iii}	2.92 (1)
O17···O15^{vi}	2.79 (2)	O22···O10^v	2.85 (1)
O17···O18	2.81 (2)	O23···O3^v	2.661 (9)

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

H atoms were not located. The highest peak in the difference map is 1.31 Å from atom Na2, and the deepest hole is 0.81 Å from atom Pt.

Data collection: *STADI*4 (Stoe & Cie, 1996); cell refinement: *STADI*4 (Stoe & Cie, 1996); data reduction: *X-RED* (Stoe & Cie, 1996); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97-2 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997) and *DIAMOND* (Brandenburg, 1998); software used to prepare material for publication: *SHELXL*97-2 (Sheldrick, 1997).

References

Anderson, J. S. (1937). *Nature* (*London*), **150**, 850.
Brandenburg, K. (1998). *DIAMOND*. Version 2.1. Crystal Impact GbR, Bonn, Germany.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Lee, U. (1994). *Acta Cryst.* C**50**, 1657–1659.
Lee, U. (2002). *Acta Cryst.* E**58**, i130–i132.
Lee, U., Ichida, H., Kobayashi, A. & Sasaki, Y. (1984). *Acta Cryst.* C**40**, 5–7.
Lee, U. & Joo, H. C. (2000). *Acta Cryst.* C**56**, e311–e312.
Lee, U. & Joo, H. C. (2004). *Acta Cryst.* E**60**, i33–i36.
Lee, U., Kobayashi, A. & Sasaki, Y. (1983). *Acta Cryst.* C**39**, 817–819.
Lee, U. & Sasaki, Y. (1994). *Bull. Korean Chem. Soc.* **15**, 37–45.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1997). *SHELXL*97-2. University of Göttingen, Germany.
Stoe & Cie (1996). *STADI*4, *X-RED* and *X-SHAPE*. Stoe & Cie Gmbh, Hilpertstraße 10, D-64295 Darmstadt, Germany.
Tsigdinos, G. A. (1978). *Top. Curr. Chem.* **76**, 36–40.