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Dipotassium Hexahydrogen-α-hexamolybdoplatinate(IV) Pentahydrate, K₂[H₆α-PtMo₆O₂₄].5H₂O

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Abstract

The structure of the fully protonated hexamolybdoplatinate polyanion salt $K_2[H_6\alpha\text{-}PtMo_6O_{24}].5H_2O$ has been determined from X-ray diffraction data. This polyanion has a center of symmetry and protonation of the O atoms is different from that of heteropolyanions having the so-called Anderson structure, $[X^{n+}(OH)_6Mo_6O_{18}]^{(6-n)-}$ (X is a hetero atom), where all the O atoms in the central XO_6 octahedron are protonated. In the present compound, four central (Pt—Oc—Mo2) and two bridging (Mo—Ob—Mo) O atoms are protonated.

Comment

The heteropolymolybdate structure containing platinum(IV) exhibits an $\alpha \rightarrow \beta \rightarrow \alpha$ geometrical isomerism when gradually protonated. The structures of $[H_{3.5}\alpha\text{-}PtMo_6O_{24}]^{4.5-}$ (Lee, 1988), $[H_4\beta\text{-}PtMo_6O_{24}]^{4-}$ and $[H_{4.5}\alpha\text{-}PtMo_6O_{24}]^{3.5-}$ (Lee & Sasaki, 1984) have been determined previously.
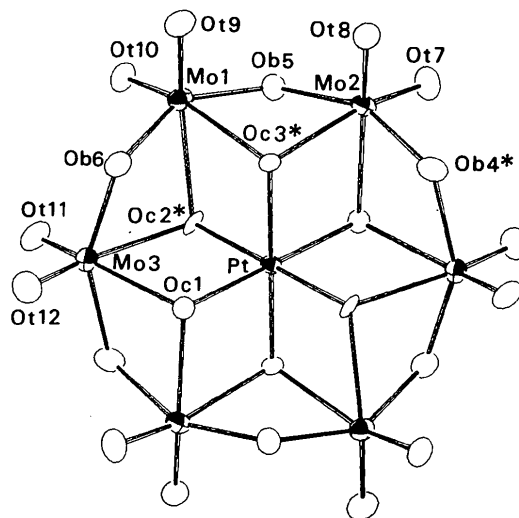

Fig. 1. The structure of the $[H_6\alpha\text{-}PtMo_6O_{24}]^{2-}$ polyanion (H atoms are not shown; starred O atoms are protonated).

The O atoms in the polyanion are classified as either Ot, Ob or Oc atoms, where Ot is a terminal O atom, Ob is bridging between two Mo atoms and Oc is coordinated to one Pt and two Mo atoms (Fig. 1). The ranges of Mo—O distances are Mo—Ot = 1.66–1.75, Mo—Ob = 1.89–2.08 and Mo—Oc = 2.12–2.37 Å.

An important result of this study is the location of the H atoms. Their positions could not be observed in the $\Delta\rho$ maps. Instead, the protonated O atoms were identified from unusually long Mo—O bond distances and short O⋯O contact distances between two polyanions, which suggested hydrogen bonds (Fig. 2). The long Mo1—Oc2, Mo1—Oc3, Mo2—Oc3, Mo2—Ob4, Mo3—Oc2 and Mo3—Ob4 bond distances (Table 2) indicate that the H atoms are bonded to Oc2, Oc3 and Ob4. The average bond-distance elongations of Mo—Oc and Mo—Ob caused by protonation are about 0.19 and 0.16 Å, respectively, suggesting that the Mo—O bond orders are reduced. These values agree well with those of the $[H_{3.5}\alpha\text{-}PtMo_6O_{24}]^{4.5-}$ and $[H_{4.5}\alpha\text{-}PtMo_6O_{24}]^{3.5-}$ polyanions. The H atom of Oc3 does not contribute to the interanion hydrogen bonding.

In the B series of polyanions having the so-called Anderson structure, $[H_6X^{3+}Mo_6O_{24}]^{3-}$ [X is Cr^{3+} (Perloff, 1970), Co^{3+} (Nagano, Lee, Ichida & Sasaki, 1990), Rh^{3+} (Ozawa, Hayashi & Isobe, 1991) or Al^{3+} (Lee, Park & Lee, 1991)], each O atom of the central XO_6 octahedron

is protonated. The present polyanion has six protonated O atoms but cannot be classified as belonging to the B series because two of the protons are on Ob instead of Oc atoms.
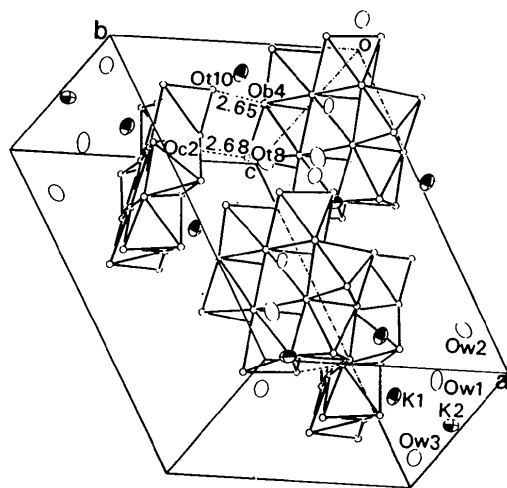

Fig. 2. The crystal packing of $K_2[H_6\alpha\text{-PtMo}_6O_{24}].5H_2O$ in the unit cell shown as polyhedra with interanion hydrogen bonds.

Experimental

The fully protonated title compound was prepared by mixing aqueous solutions of $K_2Pt(OH)_6$ (20 ml) and K_2MoO_4 (20 ml) in the molar ratio 1:6 (4×10^{-4}:2.4×10^{-3} M). The pH was adjusted to 0.7 by adding $1M$ HNO$_3$. The solution was concentrated to about 10 ml by heating on a water bath. Transparent single crystals were isolated at room temperature.

Crystal data

$K_2[H_6\alpha\text{-PtMo}_6O_{24}].5H_2O$
$M_r = 1329.04$
Monoclinic
$C2/c$
$a = 21.100\ (7)$ Å
$b = 12.922\ (3)$ Å
$c = 10.067\ (3)$ Å
$\beta = 105.79\ (3)°$
$V = 2641\ (2)$ Å^3
$Z = 4$
$D_x = 3.343$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 20.0–25.0°$
$\mu = 8.42$ mm^{-1}
$T = 298$ K
Hexagonal prism
$0.25 \times 0.18 \times 0.13$ mm
Lemon yellow

Data collection

Rigaku four-circle diffractometer
ω–2θ scans
Absorption correction:
 by integration from crystal shape
$T_{min} = 0.246$, $T_{max} = 0.621$
4105 measured reflections
3513 independent reflections
2372 observed reflections
 $[F_o > 3.0\sigma(F_o)]$

$R_{int} = 0.0072$
$\theta_{max} = 30.0°$
$h = 0 \rightarrow 29$
$k = 0 \rightarrow 18$
$l = -14 \rightarrow 14$
3 standard reflections
 monitored every 100 reflections
 intensity variation: <1%

Refinement

Refinement on F
$R = 0.055$
$wR = 0.055$
$S = 3.26$
2372 reflections
191 parameters
H atoms not located
$w = 1/[\sigma^2(F_o) + 0.0004F_o^2]$

$(\Delta/\sigma)_{max} = 0.42$
$\Delta\rho_{max} = 4.0$ e Å^{-3}
$\Delta\rho_{min} = -3.0$ e Å^{-3}
Atomic scattering factors from International Tables for X-ray Crystallography (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Pt	1/4	1/4	0	0.97 (1)
Mo1	0.3481 (1)	0.2371 (1)	0.3277 (1)	1.49 (3)
Mo2	0.1962 (1)	0.3300 (1)	0.2627 (1)	1.49 (3)
Mo3	0.4035 (1)	0.1572 (1)	0.0647 (2)	1.68 (3)
Oc1	0.3288 (5)	0.2522 (8)	-0.0731 (10)	1.1 (2)
Oc2	0.3030 (5)	0.1429 (8)	0.1249 (10)	1.2 (2)
Oc3	0.2826 (5)	0.3437 (8)	0.1617 (11)	1.3 (2)
Ob4	0.1477 (7)	0.4270 (10)	0.1020 (13)	2.4 (3)
Ob5	0.2590 (6)	0.2263 (9)	0.3426 (12)	1.8 (3)
Ob6	0.4049 (5)	0.2526 (11)	0.2082 (11)	1.9 (3)
O7	0.1288 (6)	0.2906 (11)	0.3100 (14)	2.6 (4)
O8	0.2261 (7)	0.4424 (10)	0.3555 (13)	2.4 (3)
O9	0.3790 (7)	0.3375 (9)	0.4375 (13)	2.3 (3)
O10	0.3796 (6)	0.1275 (9)	0.4134 (13)	2.2 (3)
O11	0.4280 (7)	0.0455 (11)	0.1530 (14)	2.7 (4)
O12	0.4658 (7)	0.1964 (12)	0.0060 (15)	3.0 (4)
K1	0	0.3711 (6)	1/4	4.0 (2)
K2†	-0.0091 (6)	0.0638 (9)	0.0588 (12)	4.3 (3)
Ow1	0.1158 (11)	0.0604 (13)	0.0981 (21)	5.2 (6)
Ow2	0.1757 (9)	0.0259 (12)	0.3770 (17)	3.9 (5)
Ow3	0	0.0859 (17)	-1/4	4.3 (8)

† Occupancy factor of 0.5.

Table 2. *Selected geometric parameters* (Å, °)

Pt—Mo1	3.388 (1)	Mo1—Mo3	3.336 (3)
Pt—Mo2	3.314 (2)	Mo2—Mo3^i	3.397 (2)
Pt—Mo3	3.347 (2)	Pt—Oc2	2.00 (1)
Pt—Oc1	1.99 (1)	Mo1—Oc2†	2.35 (1)
Pt—Oc3	2.00 (1)	Mo2—Oc1^i	2.12 (1)
Mo1—Oc3†	2.31 (1)	Mo3—Oc1	2.17 (1)
Mo2—Oc3†	2.32 (1)	Mo1—Ob5	1.93 (1)
Mo3—Oc2†	2.37 (1)	Mo2—Ob5	1.90 (1)
Mo1—Ob6	1.93 (1)	Mo2—Ob4†	2.08 (1)
Mo3—Ob6	1.89 (1)	Mo1—O9	1.71 (1)
Mo3—Ob4^i†	2.05 (1)	Mo2—O7	1.70 (1)
Mo1—O10	1.70 (1)	Mo3—O11	1.70 (1)
Mo2—O8	1.75 (1)	Ob4$\cdots$O10^{ii}‡	2.65 (2)
Mo3—O12	1.66 (2)	Oc2$\cdots$O8^{iii}‡	2.68 (2)
Mo1—Mo2	3.317 (3)		
Mo1—Pt—Mo2	59.31 (3)	Mo1—Pt—Mo3	59.39 (4)
Mo2—Pt—Mo3	118.67 (4)	Oc1—Pt—Oc2	82.1 (4)
Oc1—Pt—Oc3	98.9 (4)	Oc2—Pt—Oc3	84.1 (4)

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

† Indicates protonated O atom.
‡ Interpolyanion hydrogen-bond distance.

The position of the Pt atom was obtained from the Harker line and plane (Buerger, 1959) of the $C2/c$ space group. Refinement was by block-diagonal least-squares methods. The programs used were *UNICS*III (Sakurai & Kobayashi, 1979) and *ORTEP* (Johnson, 1965). All calculations were carried out on a HITAC M280-H computer at the Computer Centre of the University of Tokyo.

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Tetrapotassium Tetrahydrogen-β-hexamolybdoplatinate(IV) Dihydrate, $K_4[H_4\beta\text{-PtMo}_6O_{24}].2H_2O$

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Abstract

The potassium salt containing the $[H_4\beta\text{-PtMo}_6O_{24}]^{4-}$ polyanion, which has approximate $2mm$ symmetry (bent structure), has been isolated and its structure determined by single-crystal X-ray diffraction. This polyanion is an isomeric form of the $\bar{3}m$ (flat-structure) species.

Comment

The hexamolybdoheteropolyanion (the so-called Anderson-structure heteropolyanion) has possible flat and bent isomeric forms. This isomerism was investigated initially by the structure determinations of $(NH_4)_{4.5}[H_{3.5}\alpha\text{-PtMo}_6O_{24}].3H_2O$ and $(NH_4)_4[H_4\beta\text{-PtMo}_6O_{24}].1.5H_2O$ (Lee & Sasaki, 1984), and $K_{3.5}[H_{4.5}\alpha\text{-PtMo}_6O_{24}].1.5H_2O$

(Lee, 1988; Lee & Sasaki, 1994). Surprisingly, the isomerism occurs because of a change of only 0.5 in the number of non-acidic H atoms attached to the polyanion. It seems that the gradual protonation of the polyanion plays an important role in the isomerism; the characterization of the $[H_4\beta\text{-PtMo}_6O_{24}]^{4-}$ polyanion is therefore very important. Problems encountered in the structure determination of $(NH_4)_4[H_4\beta\text{-PtMo}_6O_{24}].1.5H_2O$ made detailed discussion difficult. These included disordered NH_4^+ ions and water molecules, distinction between the $N(NH_4^+)$ and $O(H_2O)$ atoms, and determining which O atoms in the polyanion were protonated. These problems are solved by the structure determination of the title compound.
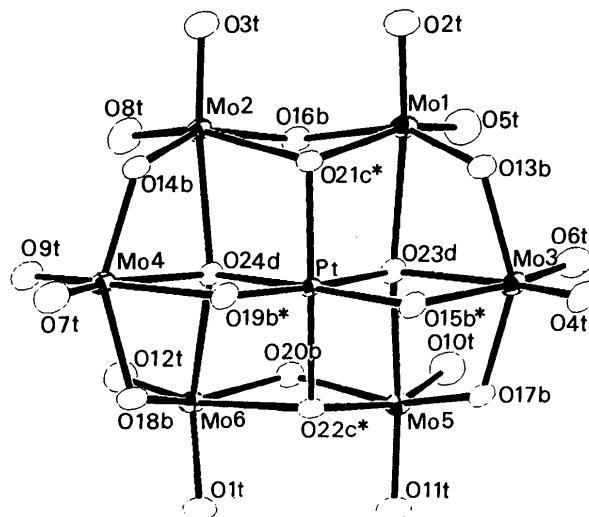

Fig. 1. The structure of the $[H_4\beta\text{-PtMo}_6O_{24}]^{4-}$ polyanion (H atoms not shown; starred O atoms are protonated).
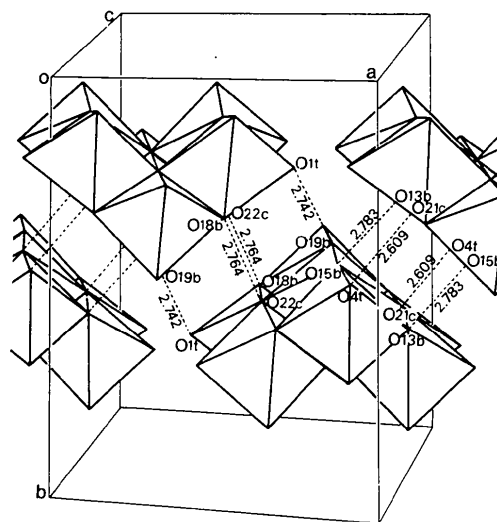

Fig. 2. The crystal packing of the $[H_4\beta\text{-PtMo}_6O_{24}]^{4-}$ polyanion in the unit cell shown as a polyhedral model with interanion hydrogen bonds.