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Lists of structure factors, anisotropic displacement parameters, angles within the polyanion and probable hydrogen-bond distances have been deposited with the IUCr (Reference: AB1113). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Tetrapotassium Tetrahydrogen- β -hexamolybdoplatinate(IV) Dihydrate, $K_4[H_4\beta\text{-PtMo}_6\text{O}_{24}]\cdot 2H_2O$

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Abstract

The potassium salt containing the $[H_4\beta\text{-PtMo}_6\text{O}_{24}]^{4-}$ 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 $(NH_4)_{4.5}[H_{3.5}\alpha\text{-PtMo}_6\text{O}_{24}]\cdot 3H_2O$ and $(NH_4)_4[H_4\beta\text{-PtMo}_6\text{O}_{24}]\cdot 1.5H_2O$ (Lee & Sasaki, 1984), and $K_{3.5}[H_{4.5}\alpha\text{-PtMo}_6\text{O}_{24}]\cdot 1.5H_2O$

(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 $[H_4\beta\text{-PtMo}_6\text{O}_{24}]^{4-}$ polyanion is therefore very important. Problems encountered in the structure determination of $(NH_4)_4[H_4\beta\text{-PtMo}_6\text{O}_{24}]\cdot 1.5H_2O$ 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.

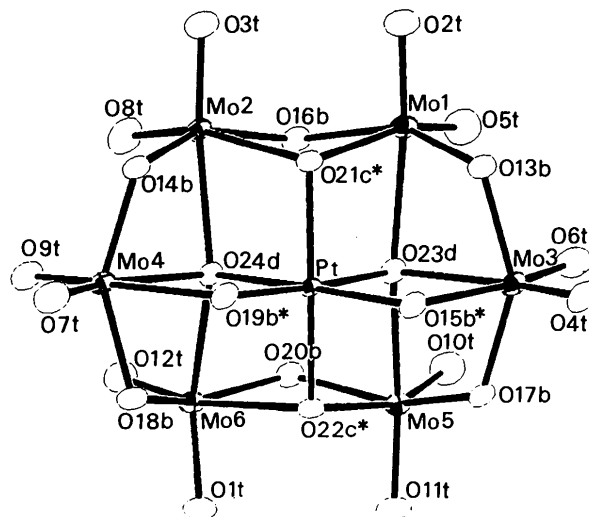


Fig. 1. The structure of the $[H_4\beta\text{-PtMo}_6\text{O}_{24}]^{4-}$ polyanion (H atoms not shown; starred O atoms are protonated).

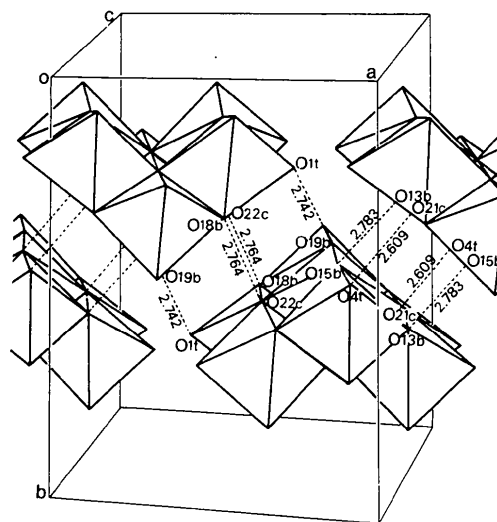


Fig. 2. The crystal packing of the $[H_4\beta\text{-PtMo}_6\text{O}_{24}]^{4-}$ polyanion in the unit cell shown as a polyhedral model with interanion hydrogen bonds.

The structural characteristics of the K₄[H₄β-PtMo₆O₂₄].2H₂O polyanion are the same as those of [H₂SbMo₆O₂₄]⁵⁻ (Ogawa, Yamamoto, Lee, Ichida & Sasaki, 1988). All the atoms of the polyanion are at general positions and the potassium ions and water molecules do not show any disorder. The O atoms in the polyanion are classified as *Ot*, *Ob*, *Oc* and *Od* according to their coordination.

The identities of the O atoms were determined from the strong interanion hydrogen bonds (Fig. 2) and unusually long Mo1—O21*c*, Mo2—O21*c*, Mo5—O22*c*, Mo6—O22*c*, Mo3—O15*b* and Mo4—O19*b* bonds. All protonated O atoms in the polyanion (O21*c*, O22*c*, O15*b* and O19*b*) contribute to the formation of interanion hydrogen bonds (Fig. 2).

Experimental

The title compound was prepared by mixing hot aqueous solutions (total volume 50 ml) of K₂Pt(OH)₆ and K₂MoO₄ in the molar ratio 1:6 (4 × 10⁻⁴:2.4 × 10⁻³ M). The pH was adjusted to ~5.4 by adding dilute HNO₃. The solution was concentrated to about 20 ml by heating on a water bath. Crystals were isolated at room temperature.

Crystal data

K ₄ [H ₄ β-PtMo ₆ O ₂₄].2H ₂ O	Mo Kα radiation
<i>M_r</i> = 1351.47	λ = 0.71069 Å
Triclinic	Cell parameters from 25 reflections
<i>P</i> $\bar{1}$	<i>a</i> = 10.636 (2) Å
<i>b</i> = 12.041 (2) Å	<i>b</i> = 12.041 (2) Å
<i>c</i> = 10.567 (1) Å	<i>c</i> = 10.567 (1) Å
α = 113.68 (1)°	β = 110.54 (1)°
β = 110.54 (1)°	γ = 81.97 (1)°
γ = 81.97 (1)°	<i>V</i> = 1160.6 (3) Å ³
<i>Z</i> = 2	<i>D_x</i> = 3.87 Mg m ⁻³

Data collection

Rigaku AFC-5S diffractometer	<i>R</i> _{int} = 0.0053
ω-2θ scans	θ _{max} = 35°
Absorption correction: by integration from crystal shape	<i>h</i> = 0 → 15
<i>T</i> _{min} = 0.213, <i>T</i> _{max} = 0.647	<i>k</i> = -17 → 17
10231 measured reflections	<i>l</i> = -15 → 15
9170 independent reflections	3 standard reflections monitored every 150 reflections
9126 observed reflections [<i>I</i> > 3.0σ(<i>I</i>)]	intensity variation: <1%

Refinement

Refinement on <i>F</i>	(Δ/σ) _{max} = 0.068
<i>R</i> = 0.044	Δρ _{max} = 3.26 e Å ⁻³
<i>wR</i> = 0.058	Δρ _{min} = -4.15 e Å ⁻³
<i>S</i> = 3.84	Extinction correction: none

9170 reflections
335 parameters
H atoms not located
 $w = 1/[\sigma^2(|F_o|) + |0.02F_o|^2]$

Atomic scattering factors
from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

	$B_{eq} = (4/3)\sum_i \beta_j \beta_k a_j a_k$			<i>B</i> _{eq}
	<i>x</i>	<i>y</i>	<i>z</i>	
Pt	0.26247 (3)	0.11887 (2)	0.09688 (3)	0.68 (1)
Mo1	0.50146 (7)	0.30571 (6)	0.16031 (7)	1.09 (2)
Mo2	0.41385 (7)	0.31209 (6)	0.43662 (7)	1.07 (2)
Mo3	0.34378 (7)	0.13561 (6)	-0.17308 (7)	1.05 (2)
Mo4	0.18213 (7)	0.13642 (6)	0.38760 (7)	1.05 (2)
Mo5	0.06664 (6)	0.25817 (6)	-0.11788 (7)	1.00 (2)
Mo6	-0.01211 (6)	0.25707 (6)	0.16591 (7)	1.02 (2)
O1 <i>t</i>	-0.1710 (6)	0.2139 (6)	0.0399 (8)	1.8 (2)
O2 <i>t</i>	0.6653 (7)	0.3025 (7)	0.2649 (8)	2.0 (2)
O3 <i>t</i>	0.5809 (7)	0.3100 (7)	0.5343 (8)	1.9 (2)
O4 <i>t</i>	0.3887 (7)	0.0060 (6)	-0.3000 (7)	1.7 (2)
O5 <i>t</i>	0.4899 (8)	0.4211 (6)	0.1000 (8)	2.0 (2)
O6 <i>t</i>	0.3671 (7)	0.2527 (7)	-0.2144 (8)	2.0 (2)
O7 <i>t</i>	0.1772 (8)	0.0093 (6)	0.4220 (8)	2.0 (2)
O8 <i>t</i>	0.3409 (8)	0.4259 (6)	0.5478 (8)	2.0 (2)
O9 <i>t</i>	0.1303 (7)	0.2525 (7)	0.5162 (7)	2.0 (2)
O10 <i>t</i>	0.1058 (7)	0.3874 (6)	-0.1279 (8)	1.8 (2)
O11 <i>t</i>	-0.0985 (7)	0.2301 (7)	-0.2236 (8)	2.0 (2)
O12 <i>t</i>	-0.0351 (7)	0.3802 (6)	0.3086 (8)	1.8 (2)
O13 <i>b</i>	0.5096 (6)	0.1643 (5)	-0.0080 (6)	1.3 (2)
O14 <i>b</i>	0.3704 (6)	0.1699 (5)	0.4602 (6)	1.3 (2)
O15 <i>b</i>	0.3090 (6)	0.0025 (5)	-0.0784 (6)	1.2 (2)
O16 <i>b</i>	0.4152 (6)	0.3854 (5)	0.3070 (6)	1.3 (2)
O17 <i>b</i>	0.1522 (6)	0.1299 (6)	-0.2441 (6)	1.4 (2)
O18 <i>b</i>	0.0105 (6)	0.1227 (5)	0.2292 (7)	1.3 (2)
O19 <i>b</i>	0.2485 (6)	0.0047 (5)	0.1875 (6)	1.3 (2)
O20 <i>b</i>	0.0479 (6)	0.3373 (5)	0.0731 (6)	1.2 (2)
O21 <i>c</i>	0.4514 (6)	0.1607 (5)	0.2308 (6)	1.0 (1)
O22 <i>c</i>	0.0689 (5)	0.1086 (5)	-0.0273 (6)	1.0 (1)
O23 <i>d</i>	0.2855 (6)	0.2401 (5)	0.0206 (6)	1.0 (1)
O24 <i>d</i>	0.2086 (6)	0.2401 (5)	0.2663 (6)	0.9 (1)
K1	0.2505 (3)	0.4673 (2)	0.7656 (3)	2.20 (6)
K2	0.2215 (3)	0.5335 (2)	0.2047 (3)	2.52 (7)
K3	0.3935 (3)	0.8662 (3)	0.3454 (3)	3.08 (8)
K4	0.1466 (4)	0.8616 (4)	0.5749 (5)	5.1 (2)
O1 <i>w</i>	0.6601 (9)	0.3538 (10)	-0.0954 (12)	3.4 (4)
O2 <i>w</i>	0.8622 (10)	0.3880 (11)	0.5557 (11)	3.7 (4)

Table 2. Selected geometric parameters (Å, °)

Pt—Mo1	3.341 (1)	Mo1—Mo2	3.333 (1)
Pt—Mo2	3.343 (1)	Mo1—Mo3	3.231 (1)
Pt—Mo3	3.342 (1)	Mo2—Mo4	3.240 (1)
Pt—Mo4	3.389 (1)	Mo3—Mo5	3.241 (1)
Pt—Mo5	3.327 (1)	Mo4—Mo6	3.220 (1)
Pt—Mo6	3.316 (1)	Mo5—Mo6	3.390 (1)
Pt—O15 <i>b</i> †	2.001 (6)	Mo1—O23 <i>d</i>	2.296 (5)
Pt—O19 <i>b</i> †	2.010 (8)	Mo2—O24 <i>d</i>	2.297 (5)
Pt—O21 <i>c</i> †	2.003 (5)	Mo3—O23 <i>d</i>	2.182 (6)
Pt—O22 <i>c</i> †	2.006 (5)	Mo4—O24 <i>d</i>	2.218 (7)
Pt—O23 <i>d</i>	2.006 (7)	Mo5—O23 <i>d</i>	2.309 (5)
Pt—O24 <i>d</i>	2.013 (6)	Mo6—O24 <i>d</i>	2.230 (5)
Mo1—O21 <i>c</i> †	2.339 (8)	Mo2—O21 <i>c</i> †	2.332 (6)
Mo5—O22 <i>c</i> †	2.350 (7)	Mo6—O22 <i>c</i> †	2.445 (6)
Mo1—O13 <i>b</i>	1.924 (5)	Mo1—O2 <i>t</i>	1.710 (7)
Mo1—O16 <i>b</i>	1.929 (7)	Mo1—O5 <i>t</i>	1.721 (9)
Mo2—O14 <i>b</i>	1.963 (8)	Mo2—O3 <i>t</i>	1.716 (7)
Mo2—O16 <i>b</i>	1.909 (8)	Mo2—O8 <i>t</i>	1.706 (8)
Mo3—O13 <i>b</i>	1.950 (5)	Mo3—O4 <i>t</i>	1.738 (6)
Mo3—O15 <i>b</i> †	2.328 (8)	Mo3—O6 <i>t</i>	1.71 (1)
Mo3—O17 <i>b</i>	1.910 (6)	Mo4—O7 <i>t</i>	1.721 (9)
Mo4—O14 <i>b</i>	1.913 (6)	Mo4—O9 <i>t</i>	1.700 (7)
Mo4—O18 <i>b</i>	1.969 (6)	Mo5—O10 <i>t</i>	1.717 (9)
Mo4—O19 <i>b</i> †	2.351 (6)	Mo5—O11 <i>t</i>	1.713 (6)
Mo5—O17 <i>b</i>	1.949 (6)	Mo6—O1 <i>t</i>	1.735 (6)

Mo5—O20b	1.925 (7)	Mo6—O12f	1.701 (6)
Mo6—O18b	1.942 (8)	Mo6—O20b	1.917 (8)
O22c...O18b [†] ‡	2.764 (7)	O21c...O4f [†] ‡	2.609 (9)
O15b...O13b [†] ‡	2.783 (9)	O19b...O1f [†] ‡	2.742 (8)
Mo1—Pt—Mo2	59.82 (2)	Mo1—Pt—Mo4	117.36 (2)
Mo1—Pt—Mo5	84.78 (2)	Mo2—Pt—Mo6	82.75 (2)
Mo3—Pt—Mo4	173.55 (2)	Mo5—Pt—Mo6	61.38 (2)
Mo2—Mo1—Mo5	89.06 (2)	Mo1—Mo2—Mo6	91.67 (2)
Mo1—Mo5—Mo6	89.31 (2)	Mo2—Mo6—Mo5	89.92 (2)
O15b—Pt—O23d	82.1 (3)	O15b—Pt—O24d	177.0 (2)
O21c—Pt—O22c	170.0 (2)	O19b—Pt—O23d	175.9 (2)
O23d—Pt—O24d	95.9 (3)	O19b—Pt—O24d	81.7 (3)
O23d—Mo3—O15b	71.3 (2)	O24d—Mo4—O19b	70.3 (2)

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

† Indicates protonated O atom.

‡ Interpolyanion hydrogen-bond distance.

The structure was solved by the heavy-atom method with UNICSIII (Sakurai & Kobayashi, 1979) and refined by block-diagonal least-squares methods. Figures were produced using ORTEP (Johnson, 1965). All computations were performed on a HITAC M-680H computer at the Computer Centre of the University of Tokyo.

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Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: DU1074). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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