

## Dipotassium hexahydrogen hexamolybdoplatinate(IV) hexahydrate

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## Key indicators

Single-crystal X-ray study  
 $T = 298\text{ K}$   
 Mean  $\sigma(\text{Mo}-\text{O}) = 0.005\text{ \AA}$   
 H-atom completeness 78%  
 Disorder in solvent or counterion  
 $R$  factor = 0.033  
 $wR$  factor = 0.081  
 Data-to-parameter ratio = 14.6

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

The title compound,  $\text{K}_2[\text{H}_6\text{PtMo}_6\text{O}_{24}]\cdot 6\text{H}_2\text{O}$ , containing the hexamolybdoplatinate(IV) polyanion with the highest level of protonation, was isolated at pH 1.60. The anion has the Pt atom at an inversion center and exhibits a local symmetry close to  $\bar{3}m$ . Four O atoms of the central  $\text{PtO}_6$  octahedron and two O atoms of the edge-shared  $\text{MoO}_6$  octahedron are protonated. One  $\text{K}^+$  ion and one O atom of a water molecule are located on twofold axes; the positions of a second  $\text{K}^+$  ion and one water molecule, both on general sites, are half-occupied.

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## Comment

The gradual protonation behavior of Anderson-type heteropolyoxometalates (Anderson, 1937) has been characterized by crystal structure analysis in the hexamolybdoplatinate system, *viz.*  $[\text{H}_2\text{PtMo}_6\text{O}_{24}]^{6-}$  (Lee & Joo, 2000, 2004),  $[\text{H}_{3.5}\text{PtMo}_6\text{O}_{24}]^{4.5-}$  (Lee & Sasaki, 1994),  $[\text{H}_4\text{PtMo}_6\text{O}_{24}]^{4-}$  (Lee & Sasaki, 1994; Joo *et al.*, 1994),  $[\text{H}_{4.5}\text{PtMo}_6\text{O}_{24}]^{3.5-}$  (Lee & Sasaki, 1994) and  $[\text{H}_6\text{PtMo}_6\text{O}_{24}]^{2-}$  (Lee, 1994). The behavior of these protonated polyanions is a very interesting phenomenon in polyoxometalate chemistry, and the pH range of the polyanions existing in aqueous solution can be established only by crystal structure determination.

This study was carried out to confirm the presence of the most highly protonated species that exists at very low pH. The same polyanion,  $[\text{H}_6\text{PtMo}_6\text{O}_{24}]^{2-}$ , as in the title compound, (I), has been isolated at pH 0.70 and 0.48, respectively, yielding the two compounds  $\text{K}_2[\text{H}_6\text{PtMo}_6\text{O}_{24}]\cdot 5\text{H}_2\text{O}$ , (II) (Lee, 1994), and  $\text{KNa}[\text{H}_6\text{PtMo}_6\text{O}_{24}]\cdot 6\text{H}_2\text{O}$ , (III) (Lee & Joo, 2006). Compound (I) has the same space group,  $C2/c$ , as compound

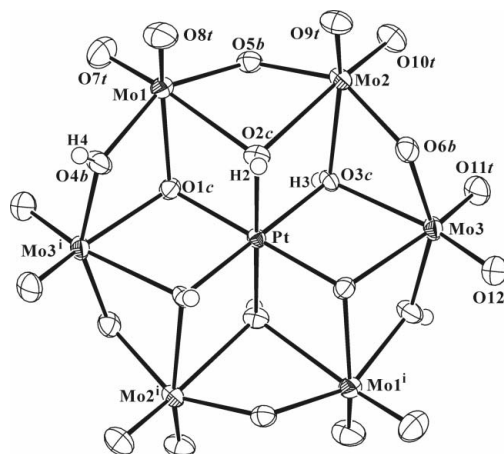
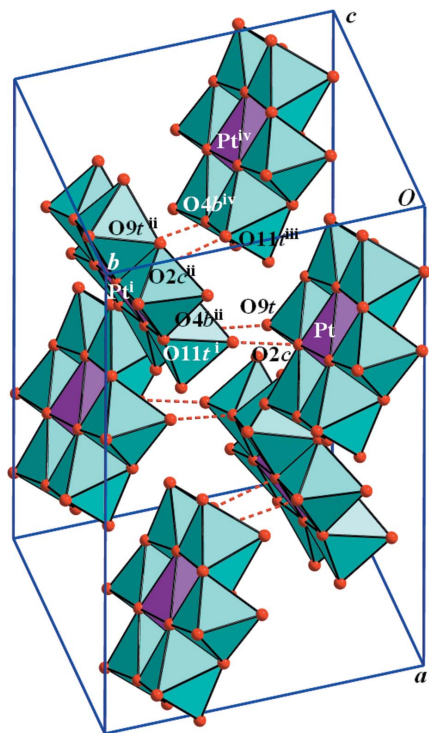


Figure 1

The structure of the polyanion in (I). Displacement ellipsoids are drawn at the 50% probability level for all non-H atoms. [Symmetry code:  $(i) \frac{1}{2} - x, \frac{1}{2} - y, -z$ .]


**Figure 2**

Polyhedral view of the packing of the heteropolyanion in (I), with O...O contacts of the inter-anion hydrogen bonds shown as dashed lines. [Symmetry codes: (i)  $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$ ; (ii)  $x, 1 - y, \frac{1}{2} + z$ ; (iii)  $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$ ; (iv)  $x, y, 1 + z$ ]

(II) and differs only in the incorporation of an additional water molecule. The unit cell of (III) contains two discrete, centrosymmetric  $[\text{H}_6\text{PtMo}_6\text{O}_{24}]^{2-}$  polyanions. As a result, we may conclude that the  $[\text{H}_6\text{PtMo}_6\text{O}_{24}]^{2-}$  polyanion exists in a wide pH range of about 0.48–1.60.

Fig. 1 shows the structure of the  $[\text{H}_6\text{PtMo}_6\text{O}_{24}]^{2-}$  polyanion. The Pt atom lies on an inversion center, and the overall symmetry of the anion is close to  $D_{3h}(\bar{3}m)$ . The O atoms of the cluster were classified in the same way as previously (Lee, 1994). The protonated O atoms in the polyanion were identified by the location in difference maps of the H atoms bound to O atoms and of local structural features, *viz.* bond lengths, angles and Mo...Mo distances. The protonation of the Ob and Oc atoms causes an increase in the Mo–Ob and Mo–Oc bond lengths and Mo...Mo distances, as well as a decrease in the Mo–Ob(H)–Mo and Mo–Oc(H)–Mo bond angles. These tendencies have also been found in (II) and (III). The structure of (I) confirms the protonation of atoms O2c, O3c and O4b. The mean elongations of the Mo–Onc ( $n = 2$  and 3) and Mo–O4b bond lengths, compared with those of the non-protonated Oc and Ob atoms, are about 0.190 (5) and 0.136 (5) Å, respectively, as shown in Table 1. In the crystal structure of (I), the  $[\text{H}_6\text{PtMo}_6\text{O}_{24}]^{2-}$  polyanions link together *via* medium interanion O–H...O hydrogen bonds (Fig. 2 and Table 2); however, O3c(H) does not contribute to these bonds.

Reasonable displacement parameters of K2 and O15w were obtained by reducing its site occupancy to 0.5. The K<sup>+</sup> ions are variously coordinated by O atoms as  $[\text{K1}(\text{Ot})_6(\text{Ow})]^+$  and

$[\text{K2}(\text{Ot})_2(\text{Ow})_5]^+$ , respectively, where Ot is a terminal cluster O atom and Ow is an O atom of a water molecule. The bond-valence sums (BVS; Brown & Altermatt, 1985; Brese & O'Keeffe, 1991) of the K ions are 1.025 valence units (v.u.) for K1 and 1.144 v.u. for K2, in good accord with charge-balancing requirements. The O16w water molecule does not coordinate to any cation and is solely bonded to other water molecules *via* hydrogen bonding, with four donor–acceptor distances in the range 2.789 (11) Å (O14w;  $x, -y, z - \frac{1}{2}$ ) to 3.076 (11) Å (O14w;  $1 - x, y, \frac{1}{2} - z$ ).

## Experimental

Crystals of compound (I) were prepared by the reaction of  $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$  and  $\text{K}_2\text{Pt}(\text{OH})_6$  at pH 1.60 as described in a previous report (Lee, 1994).

### Crystal data

$\text{K}_2[\text{H}_6\text{PtMo}_6\text{O}_{24}] \cdot 6\text{H}_2\text{O}$   
 $M_r = 1347.07$   
 Monoclinic,  $C2/c$   
 $a = 21.178$  (3) Å  
 $b = 12.940$  (2) Å  
 $c = 10.110$  (2) Å  
 $\beta = 105.77$  (1)°  
 $V = 2666.3$  (8) Å<sup>3</sup>

$Z = 4$   
 $D_x = 3.356$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 $\mu = 8.38$  mm<sup>-1</sup>  
 $T = 298$  (2) K  
 Hexagonal block, pale yellow  
 0.42 × 0.36 × 0.12 mm

### Data collection

Stoe Stadi-4 diffractometer  
 $\omega/2\theta$  scans  
 Absorption correction: numerical  
 (*X-SHAPE*; Stoe & Cie, 1996)  
 $T_{\text{min}} = 0.229$ ,  $T_{\text{max}} = 0.376$   
 3078 measured reflections  
 3056 independent reflections

2608 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.010$   
 $\theta_{\text{max}} = 27.5^\circ$   
 3 standard reflections  
 frequency: 60 min  
 intensity decay: 3.2%

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.033$   
 $wR(F^2) = 0.081$   
 $S = 1.16$   
 3056 reflections  
 210 parameters  
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0368P)^2 + 9.1413P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 0.97$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -1.27$  e Å<sup>-3</sup>

**Table 1**

Selected geometric parameters (Å, °).

|                           |             |                          |           |
|---------------------------|-------------|--------------------------|-----------|
| Pt–O1c                    | 2.010 (4)   | Mo2–O5b                  | 1.934 (5) |
| Pt–O2c                    | 2.003 (4)   | Mo2–O6b                  | 1.953 (5) |
| Pt–O3c                    | 1.995 (4)   | Mo2–O9t                  | 1.702 (5) |
| Mo1–O1c                   | 2.169 (4)   | Mo2–O10t                 | 1.695 (5) |
| Mo1–O2c                   | 2.391 (5)   | Mo3–O1c <sup>i</sup>     | 2.137 (4) |
| Mo1–O4b                   | 2.044 (5)   | Mo3–O3c                  | 2.335 (5) |
| Mo1–O5b                   | 1.909 (5)   | Mo3–O4b <sup>i</sup>     | 2.073 (5) |
| Mo1–O7t                   | 1.696 (6)   | Mo3–O6b                  | 1.895 (5) |
| Mo1–O8t                   | 1.706 (5)   | Mo3–O11t                 | 1.724 (5) |
| Mo2–O2c                   | 2.336 (5)   | Mo3–O12t                 | 1.688 (5) |
| Mo2–O3c                   | 2.308 (4)   |                          |           |
| Mo3 <sup>i</sup> –O1c–Mo1 | 104.58 (18) | Mo1–O4b–Mo3 <sup>i</sup> | 111.7 (2) |
| Mo2–O2c–Mo1               | 90.27 (16)  | Mo1–O5b–Mo2              | 121.3 (2) |
| Mo2–O3c–Mo3               | 91.55 (15)  | Mo3–O6b–Mo2              | 119.7 (2) |

Symmetry code: (i)  $-x + \frac{1}{2}, -y + \frac{1}{2}, -z$ .

**Table 2**  
Hydrogen-bond geometry (Å, °).

| $D-H\cdots A$              | $D-H$    | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|----------------------------|----------|-------------|-------------|---------------|
| $O2c-H2\cdots O11r^{ii}$   | 0.86 (7) | 1.89 (7)    | 2.720 (6)   | 160 (8)       |
| $O4b-H4\cdots O9r^{iii}$   | 0.81 (8) | 1.86 (9)    | 2.659 (7)   | 174 (14)      |
| $O13w-H13\cdots O5b$       | 0.75 (7) | 2.21 (8)    | 2.850 (9)   | 144 (11)      |
| $O14w-H14A\cdots O1c^{iv}$ | 0.96 (8) | 1.79 (9)    | 2.707 (8)   | 159 (12)      |
| $O15w-H15B\cdots O12r^{v}$ | 0.97     | 2.20        | 3.041 (15)  | 144           |
| $O15w-H15B\cdots O10t$     | 0.97     | 2.46        | 2.988 (14)  | 114           |
| $O15w-H15A\cdots O7r^{v}$  | 0.97     | 2.20        | 3.056 (16)  | 147           |

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

The  $Oc$ - and  $Ob$ -bound H atoms in the polyanion, as well as  $O13w$ - and  $O14w$ -bound H atoms, were found in a difference Fourier map and were refined with a distance restraint of  $O-H = 0.85$  (2) Å. The  $U_{iso}(H)$  parameters were freely refined. H atoms of the  $O15w$  water molecule were placed in calculated positions with a distance constraint of  $O-H = 0.85$  Å. They were included in the refinement in the riding-model approximation, with  $U_{iso}(H) = 1.5U_{eq}(O)$ . The H atoms of  $O16w$  could not be positioned geometrically because they are not coordinated to any cations, and could not be reasonably located in an electron density map. The highest peak in the difference map is 1.00 Å from Pt and the largest hole is 0.87 Å from Pt.

Data collection: *STADIA* (Stoe & Cie, 1996); cell refinement: *STADIA*; data reduction: *X-RED* (Stoe & Cie, 1996); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *DIAMOND* (Brandenburg, 1998); software used to prepare material for publication: *SHELXL97*.

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