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Hemiheptapotassium heminonahydrogen α-hexamolybdoplatinate(IV) 5.5-hydrate

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The title compound, $K_{3.5}[H_{4.5}\alpha\text{-}PtMo_6O_{24}]\cdot5.5H_2O$, containing the hexamolybdoplatinate(IV) polyanion, was isolated at pH 2.85. The complete polyanion has no crystallographic symmetry. The $[H_{4.5}\alpha\text{-}PtMo_6O_{24}]^{3.5-}$ polyanions form an inversion-generated dimer, viz. $[H_9(PtMo_6O_{24})_2]^{7-}$, via seven strong hydrogen bonds, one of which is disordered. One K^+ ion and one water O atom occupy inversion centres.

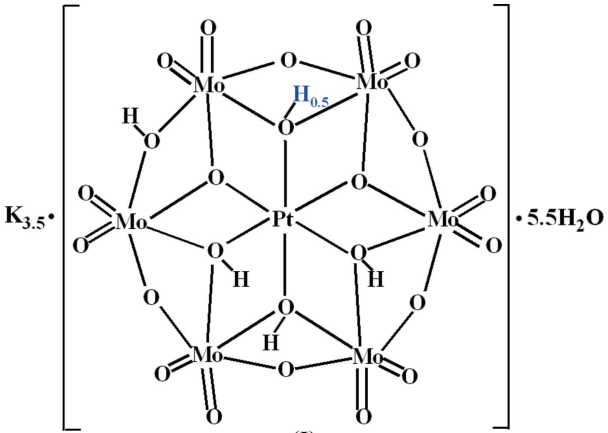
Key indicators

Single-crystal X-ray study
T = 298 K
Mean σ(Mo–O) = 0.007 Å
H-atom completeness 94%
Disorder in solvent or counterion
R factor = 0.043
wR factor = 0.116
Data-to-parameter ratio = 16.2

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

Comment

The α,β-geometric isomerism behaviour of Anderson-type heteropolyoxometallates (Anderson, 1937) has so far been reported only for the hexamolybdoplatinate(IV) system, viz. $[H_{3.5}\alpha\text{-}PtMo_6O_{24}]^{4.5-}$, (II) (Lee & Sasaki, 1994), $[H_4\beta\text{-}PtMo_6O_{24}]^{4-}$, (III) (Lee & Sasaki, 1994; Joo *et al.*, 1994), and $[H_{4.5}\alpha\text{-}PtMo_6O_{24}]^{3.5-}$, (IV) (Lee & Sasaki, 1994). The isolation pHs of these salts were 6.4, 5.4 and 2.5, respectively. The behaviour of this isomerism, with gradual protonation of the polyanion, is a very interesting phenomenon in polyoxometallate chemistry, and this behaviour can be established only by crystal-structure determination.



(I)

The polyanion in the title compound, (I), $[H_{4.5}\alpha\text{-}PtMo_6O_{24}]^{3.5-}$, is isostructural with the same species in (IV). Compound (I) has the same space group, $P\overline{1}$, as compound (IV) and differs only in the incorporation of additional water molecules. The positions of the H atoms in the polyanion were not identified in compound (IV), but all the protonated O atoms in the polyanion of compound (I) were identified in the present study.

Fig. 1 shows the structure of the polyanion of (I). All atoms are located in general positions of the space group, and the symmetry of the polyanion is C_1 (1). The O atoms of the

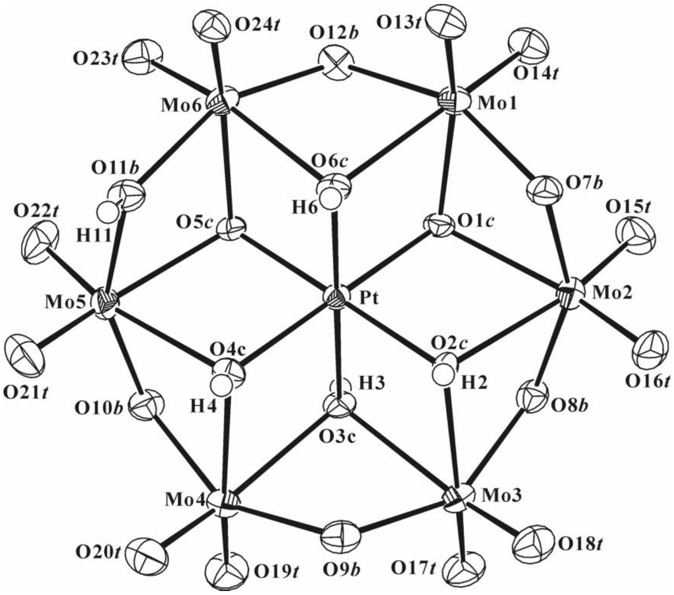


Figure 1
The polyanion structure in (I). Displacement ellipsoids are drawn at the 50% probability level.

cluster were classified in the same way as described previously (Lee & Sasaki, 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 by local structural features, as seen previously (Lee & Joo, 2006*a*,*b*; Table 1). As a result, atoms O2*C*, O3*C*, O4*C*, O6*C* and O11*B* in the polyanion are found to be protonated.

In the crystal structure of (I), two $[H_{4.5}\alpha\text{-}PtMo_6O_{24}]^{3.5-}$ polyanions form an $[H_9(\alpha\text{-}PtMo_6O_{24})_2]^{7-}$ dimer, via seven strong hydrogen bonds (Fig. 2, Table 1). The H atom involved in the O6*C*···O6*C*^{i} [symmetry code: (i) $1 - x, -y, 1 - z$] inter-polyanion hydrogen bond seems to show positional disorder, as is the case in the polyanions of (II) and $[H_{2.5}\alpha\text{-}PtW_6O_{24}]^{5.5-}$ (Lee & Joo, 2004). This is consistent with the overall stoichiometry, which requires 4.5 H atoms per cluster for charge compensation. The H atom on O3*C* does not contribute to the formation of inter-polyanion hydrogen bonds because it is located on the opposite side of the cluster (Fig. 2).

The K2 ion and O30*W* water molecule are located on inversion centres. The K^+ ions are variously coordinated by O atoms as $[K1(OB)(OT)_2(OW)_4]^+$, $[K2(OB)_2(OT)_6]^+$, $[K3(OB)(OT)_5(OW)_2]^+$ and $[K4(OT)_5(OW)_2]^+$, where O*T* is a terminal cluster O atom, O*B* is an edge-shared cluster O atom and O*W* is an O atom of a water molecule. The O30*W* water molecule does not coordinate to any cation and does not form hydrogen bonds with any other O atoms.

Experimental

Crystals of (I) were prepared by the reaction of $K_2MoO_4\cdot2H_2O$ and $K_2Pt(OH)_6$ at pH 2.85, as described in a previous report (Lee & Sasaki, 1994).

Crystal data

$K_{3.5}[H_{4.5}PtMo_6O_{24}]\cdot5.5H_2O$
$M_r = 1395.20$
Triclinic, $P\overline{1}$
$a = 10.104$ (2) Å
$b = 12.214$ (2) Å
$c = 12.419$ (2) Å
$\alpha = 68.72$ (1)°
$\beta = 69.33$ (2)°
$\gamma = 83.634$ (8)°
$V = 1335.9$ (5) Å^3
$Z = 2$
$D_x = 3.468$ Mg m^{-3}
Mo *K*α radiation
$\mu = 8.60$ mm^{-1}
$T = 298$ (2) K
Block, pale yellow
0.25 × 0.13 × 0.13 mm

Data collection

Stoe STADI4 diffractometer
$\omega/2\theta$ scans
Absorption correction: numerical (*X-SHAPE*; Stoe & Cie, 1996)
$T_{min} = 0.282$, $T_{max} = 0.404$
6100 measured reflections
6100 independent reflections
5081 reflections with $I > 2\sigma(I)$
$\theta_{max} = 27.5°$
3 standard reflections
frequency: 60 min
intensity decay: 3.2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.116$
$S = 1.11$
6100 reflections
376 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0558P)^2 + 7.7029P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 1.61$ e Å^{-3}
$\Delta\rho_{min} = -2.47$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Pt—O1*C*	1.969 (6)	Mo3—O9*B*	1.931 (7)
Pt—O5*C*	1.992 (6)	Mo3—O17*T*	1.700 (6)
Pt—O6*C*	1.990 (5)	Mo3—O18*T*	1.722 (7)
Pt—O2*C*	2.011 (6)	Mo4—O3*C*	2.283 (6)
Pt—O3*C*	2.039 (5)	Mo4—O4*C*	2.335 (6)
Pt—O4*C*	2.019 (6)	Mo4—O9*B*	1.940 (7)
Mo1—O1*C*	2.118 (6)	Mo4—O10*B*	1.944 (6)
Mo1—O6*C*	2.316 (6)	Mo4—O19*T*	1.706 (6)
Mo1—O7*B*	1.977 (6)	Mo4—O20*T*	1.696 (7)
Mo1—O12*B*	1.977 (6)	Mo5—O4*C*	2.291 (6)
Mo1—O13*T*	1.753 (6)	Mo5—O5*C*	2.164 (6)
Mo1—O14*T*	1.713 (7)	Mo5—O10*B*	1.907 (6)
Mo2—O1*C*	2.212 (6)	Mo5—O11*B*	2.071 (6)
Mo2—O2*C*	2.300 (6)	Mo5—O21*T*	1.716 (7)
Mo2—O7*B*	1.991 (6)	Mo5—O22*T*	1.705 (7)
Mo2—O8*B*	1.934 (6)	Mo6—O5*C*	2.095 (5)
Mo2—O15*T*	1.703 (7)	Mo6—O6*C*	2.285 (6)
Mo2—O16*T*	1.728 (7)	Mo6—O11*B*	2.100 (7)
Mo3—O2*C*	2.327 (5)	Mo6—O12*B*	1.868 (6)
Mo3—O3*C*	2.288 (6)	Mo6—O23*T*	1.704 (6)
Mo3—O8*B*	1.945 (6)	Mo6—O24*T*	1.760 (6)
Mo1—O1*C*—Mo2	96.5 (2)	Mo1—O7*B*—Mo2	109.0 (3)
Mo2—O2*C*—Mo3	92.7 (2)	Mo2—O8*B*—Mo3	119.4 (3)
Mo4—O3*C*—Mo3	94.3 (2)	Mo3—O9*B*—Mo4	119.9 (3)
Mo5—O4*C*—Mo4	92.3 (2)	Mo5—O10*B*—Mo4	120.0 (3)
Mo6—O5*C*—Mo5	104.3 (2)	Mo5—O11*B*—Mo6	107.4 (3)
Mo6—O6*C*—Mo1	91.0 (2)	Mo6—O12*B*—Mo1	117.2 (3)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2*C*—H2···O24*T*$^{\rm i}$	0.97 (6)	1.62 (7)	2.574 (8)	168 (8)
O4*C*—H4···O13*T*$^{\rm i}$	0.95 (7)	1.61 (7)	2.556 (8)	175 (9)
O6*C*—H6···O6*C*$^{\rm i}$	0.98	1.61	2.573 (12)	168
O11*B*—H11···O7*B*$^{\rm i}$	0.95 (8)	1.91 (8)	2.820 (9)	161 (10)
O25*W*—H25*A*···O13*T*$^{\rm ii}$	0.97	2.26	3.100 (12)	144
O26*W*—H26*A*···O7*B*$^{\rm iii}$	0.96	2.41	2.972 (13)	117
O26*W*—H26*B*···O21*T*$^{\rm iv}$	0.96	2.41	3.081 (15)	126
O27*W*—H27*A*···O1*C*$^{\rm v}$	0.97	2.06	2.812 (11)	133
O27*W*—H27*B*···O29*W*$^{\rm v}$	0.97	2.50	2.958 (15)	109
O27*W*—H27*B*···O5*C*	0.97	2.20	2.980 (10)	136
O28*W*—H28*A*···O15*T*$^{\rm v}$	0.97	1.94	2.892 (11)	166
O28*W*—H28*B*···O18*T*$^{\rm iii}$	0.97	2.14	3.028 (11)	151
O29*W*—H29*B*···O3*C*$^{\rm v}$	0.96	1.93	2.586 (9)	123
O29*W*—H29*A*···O12*B*	0.96	2.10	3.014 (9)	158

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

The H atoms bonded to atoms O2*C*, O4*C* and O11*B* in the polyanion were located in a difference Fourier map and refined with a distance restraint of O—H = 0.85 (1) Å. Their displacement parameters were freely refined. The H atoms of the O3*C* and O6*C* cluster atoms and all O*W* water molecules were placed in calculated positions with a distance restraint of O—H = 0.85 (1) Å, except the O30*W* water molecule. They were included in the refinement in the riding-model approximation, with $U_{\rm iso}({\rm H}) = 1.5U_{\rm eq}({\rm O})$. The occupancy of the H atom on atom O6*C* was fixed at 0.5 because of disorder. The H atoms of O30*W* could not be positioned geometrically or be reasonably located in an electron-density map. The highest peak in the difference map is 0.95 Å from K1, and the deepest hole is 0.74 Å from Pt.

Data collection: *STADI4* (Stoe & Cie, 1996); cell refinement: *STADI4*; data reduction: *X-RED* (Stoe & Cie, 1996); program(s) used to solve structure: *SHELXS97-2* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97-2* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *DIAMOND* (Brandenburg, 1998); software used to prepare material for publication: *SHELXL97-2*.

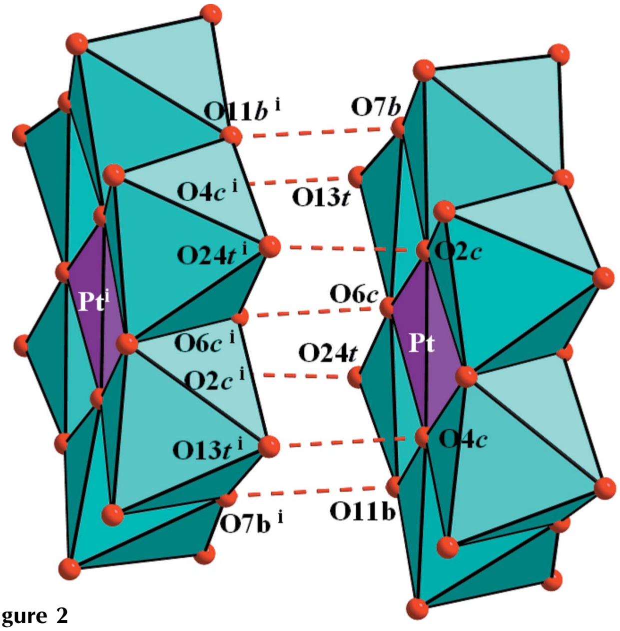


Figure 2
A polyhedral view of a pair of heteropolyanions in (I), with the O···O contacts of the inter-anion hydrogen bonds shown as dashed lines. [Symmetry code: (i) $1-x, -y, 1-z$].

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