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$La_2[H_2PtMo_6O_{24}]\cdot16H_2O$

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The title compound, dilanthanum dihydrogen hexamolybdoplatinate(IV) hexadecahydrate, $La_2[H_2PtMo_6O_{24}]\cdot16H_2O$, was obtained by reacting $La(NO_3)_3\cdot6H_2O$ with a sodium salt solution of $[H_nPtMo_6O_{24}]^{(8-n)-}$ at pH 2.0, and it was found to crystallize in the monoclinic system in space group $C2/c$, with the polyanion having the least protonated species and a crystallographical inversion center. Two of the O atoms of the central $[PtO_6]$ octahedron were found to be protonated. The protonated O atoms were identified by elongation of the Mo—O(H) bonds and the values of the Mo—O(H)—Mo bond angles. Inter-polyanion hydrogen bonds are not formed.

Key indicators

Single-crystal X-ray study
T = 298 K
Mean σ(Mo–O) = 0.005 Å
H-atom completeness 0%
Disorder in solvent or counterion
R factor = 0.030
wR factor = 0.074
Data-to-parameter ratio = 16.7

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

Comment

In the B-type Anderson structure heteropolyoxometalate $[H_6XMo_6O_{24}]^{(6-n)-}$(Anderson, 1937; Tsigdinos, 1978), the six H^+ attached to the O atoms of the central $[XO_6]$ octahedron are non-acidic. However, some species of partially protonated Anderson-type polyanions in the $[PtMo_6O_{24}]^{8-}$ system have been reported previously, *viz*. $[H_6PtMo_6O_{24}]^{2-}$ (Lee & Sasaki, 1994), $[H_{4.5}PtMo_6O_{24}]^{3.5-}$, $[H_4PtMo_6O_{24}]^{4-}$, $[H_{3.5}PtMo_6O_{24}]^{4.5-}$ (Lee, 1994; Joo *et al.*, 1994) and $[H_2PtMo_6O_{24}]^{6-}$ (Lee & Joo, 2000). Thus, the confirmation of gradual protonation of the species by crystallographic characterization has become a crystallographically significant challenge in the chemistry of Anderson structure heteropolyoxometalates.

Sometimes the lanthanide cation, having a very large oxide affinity, is useful in isolating polyoxometalates because the lanthanide forms a very stable salt with polyoxometalates. It was anticipated that the $[H_2PtMo_6O_{24}]^{6-}$ species would be isolated above pH 8.0, from the process of protonation in this polyanion system. Although the alkali metal and ammonium salts of the $[H_2PtMo_6O_{24}]^{6-}$ species could not be isolated above pH 8.0 because the $[H_nPtMo_6O_{24}]^{(8-n)-}$ species was unstable above pH 8.0, it has been previously reported that $Nd_2[H_2PtMo_6O_{24}]\cdot14H_2O$ is prepared at pH 3.2 by using Nd^{3+} as the counter-ion and that its crystal structure has been analysed (Lee & Joo, 2000). We report here the structure of the title compound, dilanthanum dihydrogen hexamolybdoplatinate(IV) hexadecahydrate, $La_2[PtMo_6O_{24}]\cdot16H_2O$, (I), a new member in this series.

Fig. 1 shows the structure of (I) and the atom-labeling scheme for the hexamolybdoplatinate anion. The polyanion has inversion C_i ($\bar{1}$) symmetry and a Pt atom at the inversion center. The O atoms in the polyanion are classified in the same way as has been previously reported by Lee & Joo (2000), *viz*. O*c* (O1–O3), O*b* (O4–O6), O*t* (O7–O12), and H_2O (O13–O21). The protonated O atoms, O(H) in the polyanion, were also identified following the same method as that reported by

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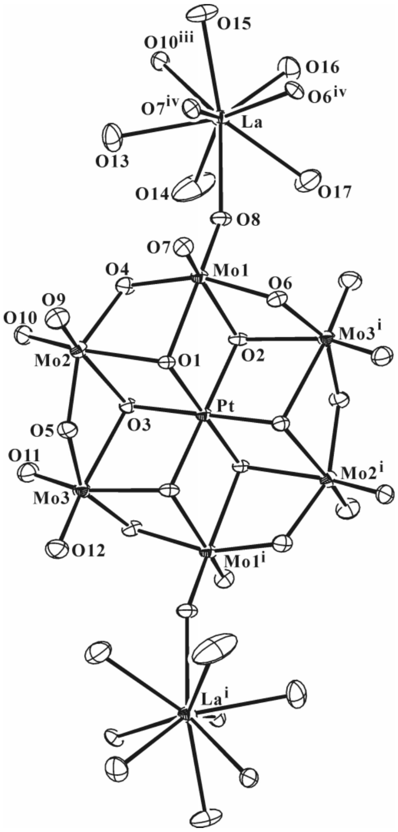

Figure 1
A view of (I) (30% probability displacement ellipsoids), showing the coordination of the cation and the structure of the anion. Uncoordinated water molecules (O18–O21) are not shown. [Symmetry codes: (i) $\frac{1}{2} - x$, $\frac{1}{2} - y$, $1 - z$; (ii) $1 - x$, y, $\frac{1}{2} - z$; (iii) $1 - x$, $1 - y$, $1 - z$; (iv) $1 - x$, y, $\frac{3}{2} - z$.]

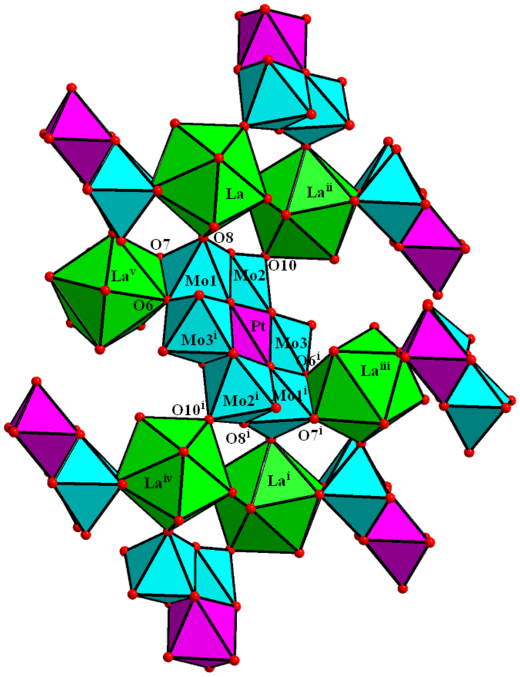

Figure 2
The [LaO$_9$] cluster–polyanion represented by a polyhedral model. Uncoordinated water molecules (O18–O21) are not shown. [Symmetry codes: (i) $\frac{1}{2} - x$, $\frac{1}{2} - y$, $1 - z$; (ii) $1 - x$, $1 - y$, $1 - z$; (iii) $x - \frac{1}{2}$, $\frac{1}{2} - y$, $z - \frac{1}{2}$; (iv) $x - \frac{1}{2}$, $y - \frac{1}{2}$, z; (v) $1 - x$, y, $\frac{3}{2} - z$.]

Lee (2002). The Mo—O*c*(H) bond lengths are increased, the Mo—O*c*(H)—Mo bond angles are decreased, and the Mo—O*b*—Mo bond angles are increased by protonation of the O*c* atom. Table 1 shows that among the Mo—O*c* bonds, the Mo—O3 bond is 0.194 Å longer than the Mo—O1 and Mo—O2 bonds. Similarly, among the Mo—O*b* bonds, the Mo1—O6 and Mo2—O4 bonds are elongated but the Mo1—O4 and Mo3—O6 bonds are normal. However, as is common in the Anderson structure heteropolyoxometalates, the O*c* atom is protonated in preference to the O*b* atom. The possibility of protonation of O*b* atoms is low from a stoichiometric point of view. The Mo···Mo distance is affected by the elongation of the Mo—O*c*(H) bond. As a result, the Mo2···Mo3 distances are greater than Mo1···Mo2 and Mo1···Mo3. The Mo2—O3—Mo3 bond angles are smaller than those of the unprotonated Mo—O*n*—Mo (n = 1, 2). The Mo—O*b*—Mo angle, which is a counterpart of O*c*(H), *i.e.* Mo—O5 —Mo, is larger than Mo—O*n*—Mo (n = 4,6).

During the refinement process, reasonable displacement parameters of O21 and O22, which are in general positions in the space group $P\overline{1}$, were obtained by reducing the occupancy of these atoms to 0.5 because of disorder. The coordination environment of the La^{3+} ion in the title compound is similar to that of Nd^{3+} in Nd$_2$[H$_2$PtMo$_6$O$_{24}$]·14H$_2$O. Of the nine independent water molecules (atoms O13–O21) in the crystal structure, five are bonded to the La^{3+} ion. Only the remaining four water molecules (atoms O18–O21) in the unit cell fill the empty space like zeolitic water. The [H$_2$PtMo$_6$O$_{24}$]$^{6-}$ polyanion forms infinite three-dimensional networks with the surrounding polyanions through six [LaO*b*(O*t*)$_3$(H$_2$O)$_5$)] clusters (see Fig. 2). Interconnection of [LaO*b*(O*t*)$_3$(H$_2$O)$_5$)] clusters does not occur. All O atoms of the polyanion can hydrogen bond 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.

Experimental

The sodium salt of hexamolybdoplatinate was prepared as described previously, by the reaction of Na$_2$MoO$_4$·2H$_2$O (0.6 m*M*/20 ml) and Na$_2$[Pt(OH)$_6$] (0.1 m*M*/20 ml) at about pH 4.0 (Lee & Sasaki, 1994). The title compound was prepared by mixing a hot aqueous solution of sodium hexamolybdoplatinate (0.1 m*M*/40 ml) and La(NO$_3$)$_3$·6H$_2$O (0.2 m*M*/20 ml). The pH was adjusted to 2.0 by adding 3.0 *M* HNO$_3$. After 3 d, crystals of the title compound were obtained at room temperature.

Crystal data

La$_2$[H$_2$PtMo$_6$O$_{24}$]·16H$_2$O
M_r = 1722.82
Monoclinic, $C2/c$
a = 21.147 (2) Å
b = 10.664 (1) Å
c = 15.949 (2) Å
β = 109.62 (1)°
V = 3387.9 (7) Å^3
Z = 4

D_x = 3.378 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 9.5–10.4°
μ = 8.85 mm^{-1}
T = 298 (2) K
Block, colorless
0.20 × 0.13 × 0.13 mm

Data collection

Stoe Stadi-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: numerical (*X-SHAPE*; Stoe & Cie, 1996)
$T_{\min} = 0.251$, $T_{\max} = 0.357$
3893 measured reflections
3893 independent reflections
3493 reflections with $I > 2\sigma(I)$

$\theta_{\max} = 27.5°$
$h = -27 \rightarrow 25$
$k = 0 \rightarrow 13$
$l = 0 \rightarrow 20$
3 standard reflections
frequency: 60 min
intensity decay: 3.7%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.030$
$wR(F^2) = 0.074$
$S = 1.11$
3893 reflections
233 parameters
H atoms not located

$w = 1/[\sigma^2(F_o^2) + (0.0295P)^2 + 55.4435P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 1.33$ e Å^{-3}
$\Delta\rho_{\min} = -0.82$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.000281 (19)

Table 1
Selected geometric parameters (Å, °).

Mo1—Mo2	3.2475 (8)	Mo1—O4	1.893 (5)
Mo1—Mo3^{i}	3.2814 (8)	Mo1—O6	2.037 (4)
Mo2—Mo3	3.3897 (8)	Mo1—O7	1.737 (4)
Pt—O1	2.004 (4)	Mo1—O8	1.729 (4)
Pt—O2	2.011 (4)	Mo2—O1	2.129 (4)
Pt—O3	2.006 (4)	Mo2—O3	2.387 (4)
La—O6^{ii}	2.479 (4)	Mo2—O4	2.012 (5)
La—O7^{ii}	2.614 (4)	Mo2—O5	1.899 (4)
La—O8	2.561 (4)	Mo2—O9	1.701 (5)
La—O10^{iii}	2.590 (4)	Mo2—O10	1.736 (4)
La—O13	2.556 (6)	Mo3—O2^{i}	2.186 (4)
La—O14	2.557 (7)	Mo3—O3	2.331 (4)
La—O15	2.535 (5)	Mo3—O5	1.973 (5)
La—O16	2.550 (5)	Mo3—O6^{i}	1.952 (5)
La—O17	2.549 (5)	Mo3—O11	1.716 (5)
Mo1—O1	2.216 (4)	Mo3—O12	1.716 (5)
Mo1—O2	2.128 (4)		
Mo2—O1—Mo1	96.7 (2)	Mo1—O4—Mo2	112.5 (2)
Mo1—O2—Mo3^{i}	99.1 (2)	Mo2—O5—Mo3	122.1 (2)
Mo3—O3—Mo2	91.8 (2)	Mo3^{i}—O6—Mo1	110.7 (2)

Symmetry codes: (i) $\frac{1}{2}-x, \frac{1}{2}-y, 1-z$; (ii) $1-x, y, \frac{3}{2}-z$; (iii) $1-x, 1-y, 1-z$.

Table 2
Hydrogen-bonding geometry (Å).

O13···O4^{i}	2.703 (7)	O16···O5^{iii}	2.785 (7)
O13···O7^{ii}	2.920 (7)	O16···O17	2.849 (7)
O13···O10^{i}	2.923 (7)	O17···O8	2.721 (7)
O13···O21^{i}	2.75 (2)	O17···O12^{iv}	2.805 (7)
O14···O17	2.98 (1)	O17···O19^{v}	2.673 (9)
O14···O19^{i}	2.99 (1)	O18···O3	2.732 (7)
O14···O20^{iii}	2.72 (2)	O18···O9^{vi}	2.964 (7)
O14···O21	2.54 (2)	O18···O19^{i}	2.809 (9)
O15···O6^{ii}	2.967 (7)	O19···O2^{i}	2.685 (7)
O15···O7^{ii}	2.911 (7)	O20···O9^{vii}	2.72 (2)
O15···O1^{ii}	2.647 (6)	O20···O12	2.65 (2)
O15···O10^{i}	2.770 (7)	O20···O14^{viii}	2.72 (2)
O15···O11^{i}	2.811 (7)	O20···O21^{ix}	2.64 (2)

Symmetry codes: (i) $1-x, 1-y, 1-z$; (ii) $1-x, y, \frac{3}{2}-z$; (iii) $\frac{1}{2}+x, y-\frac{1}{2}, z$; (iv) $\frac{1}{2}-x, \frac{1}{2}-y, 1-z$; (v) $x, y-1, z$; (vi) $x, 1-y, z-\frac{1}{2}$; (vii) $\frac{1}{2}-x, \frac{3}{2}-y, 1-z$; (viii) $x-\frac{1}{2}, \frac{1}{2}+y, z$; (ix) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$.

H atoms were not located. The highest peak in the difference map is 0.84 Å from O19 and the deepest hole is 1.17 Å from O5.

Data collection: *Stadi*4 (Stoe & Cie, 1996); cell refinement: *Stadi*4; data reduction: *X-RED*32 (Stoe & Cie, 1996); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Version 1.07; Farrugia, 1997) and *DIAMOND* (Brandenburg, 1998); software used to prepare material for publication: *SHELXL*97.

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