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# Dineodymium dihydrogen $\alpha$-hexamolybdoplatinate(IV) tetradecahydrate, $Nd_2[H_2\alpha\text{-}PtMo_6O_{24}]\cdot 14H_2O$

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The least protonated hexamolybdoplatinate(IV) polyanion, $[H_2\alpha\text{-}PtMo_6O_{24}]^{6-}$, is isolated by using $Nd^{3+}$ as a counter-cation. Two O atoms of the central $PtO_6$ octahedron are protonated. The Mo—Mo distances are 3.244 (2), 3.295 (2) and 3.393 (1) Å, and the Pt—Mo distances are 3.251 (1), 3.332 (2) and 3.338 (1) Å. The anion has the Pt atom on an inversion centre and has close to $\overline{3}m$ symmetry, with Pt—O bond lengths in the range 2.002 (8)–2.015 (8) Å and Mo—O bond lengths in the ranges 1.689 (9)–1.747 (8), 1.890 (8)–2.037 (8) and 2.109 (8)–2.384 (8) Å.

## Comment

Crystallograpic studies of the hexamolybdoplatinate(IV) polyanions $[H_6\alpha\text{-}PtMo_6O_{24}]^{2-}$ (Lee, 1994), $[H_{4.5}\alpha\text{-}PtMo_6O_{24}]^{3.5-}$, $[H_4\beta\text{-}PtMo_6O_{24}]^{4-}$ and $[H_{3.5}\alpha\text{-}PtMo_6O_{24}]^{4.5-}$ (Lee & Sasaki, 1994; Joo *et al.*, 1994) have been reported previously. The behaviour of gradual protonation of the polyanion and geometric isomerism in Anderson-type heteropolyanions was only found in this polyanion system. The $[H_6\alpha\text{-}PtMo_6O_{24}]^{2-}$, $[H_{4.5}\alpha\text{-}PtMo_6O_{24}]^{3.5-}$, $[H_4\beta\text{-}PtMo_6O_{24}]^{4-}$ and $[H_{3.5}\alpha\text{-}PtMo_6O_{24}]^{4.5-}$ polyanion species were isolated at pH 0.7, 2.5, 5.4 and 6.4, respectively. It seems that the $[H_2\alpha\text{-}PtMo_6O_{24}]^{6-}$ species were isolated above pH 8.0, from the process of protonation in this polyanion system. However, it was isolated at pH 3.2 by using $Nd^{3+}$ as the counter-ion.

The present polyanion, $[H_2\alpha\text{-}PtMo_6O_{24}]^{6-}$, has the Pt atom on an inversion centre and has close to $\overline{3}m$ symmetry. The O atoms in the anion can be divided into three groups, O*T*, O*B* and O*C*, where O*T* represents a terminal O atom bound to one Mo atom, O*B* represents a bridging O atom bound to two Mo atoms and O*C* represents a central O atom coordinated to both the Pt and the two Mo atoms. The position of the H atoms, as expected, could not be observed even in the electron-density difference maps. The attached positions of the H atoms were determined from the unusually long Mo—O distances. It was concluded that the H atoms of the polyanion are bound to the O*C*1 atoms from the Mo1—O*C*1 (2.384 Å) and Mo2—O*C*1 (2.345 Å) distances, which are longer than the Mo1—O*C*3 (2.131 Å), Mo2—O*C*2 (2.209 Å), Mo3—O*C*2 (2.109 Å) and Mo3—O*C*3 (2.218 Å) distances. The average bond-distance elongation of Mo—O*C* as a result of protonation is about 0.197 Å. This value agrees well with those of the same family of polyanions. The H atom of O*C*1 does not contribute to the interanion hydrogen bond. The Mo—O*T* bond distances of the O*T* atoms coordinated to $Nd^{3+}$ show elongation.

The $Nd^{3+}$ cation achieves tricapped trigonal prismatic coordination, with O*B*4, O*T*7 and O*T*8 forming one base triangle, O*W*1, O*W*3 and O*T*12 forming the other, and O*W*2, O*W*4 and O*W*5 capping the side faces. The bond distances between Nd and O*W*(1–5) atoms are in the range of 2.451–2.521 Å. The average Nd—O distance is 2.50 Å, which agrees with the typical lanthanide–O bond distance. Of the seven independent water molecules in the crystal structure, five are bonded to the $Nd^{3+}$ ion. The remaining two water molecules in the unit cell only fill the empty space like zeolitic water. The $[H_2\alpha\text{-}PtMo_6O_{24}]^{6-}$ polyanion forms infinite three-dimensional networks with surrounding polyanions *via* six $Nd^{3+}$ ions.

## Experimental

The title compound was prepared by mixing a hot aqueous solution of $[H_2\alpha\text{-}PtMo_6O_{24}]^{8-}$ (0.5 m*M*, 20 ml) and $Nd(NO_3)_3\cdot 6H_2O$ (0.1 m*M*, 20 ml). The pH was adjusted to 3.2 by adding 3.0 *M* $HNO_3$. The solution was concentrated to about 20 ml by heating in a water bath. After a day, monoclinic grey crystals were obtained at room temperature.

### *Crystal data*

$Nd_2[H_2PtMo_6O_{24}]\cdot 14H_2O$
$M_r = 1697.45$
Monoclinic, $C2/c$
$a = 21.079$ (2) Å
$b = 10.324$ (4) Å
$c = 15.8637$ (18) Å
$\beta = 109.780$ (9)°
$V = 3248.5$ (13) Å$^3$
$Z = 4$

$D_x = 3.471$ Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 28 reflections
$\theta = 10.0$–11.4°
$\mu = 9.784$ mm$^{-1}$
$T = 298$ (2) K
Monoclinic, grey
0.12 × 0.08 × 0.06 mm

### *Data collection*

Stoe Stadi-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: numerical (Stoe & Cie, 1996)
$T_{min} = 0.185$, $T_{max} = 0.340$
3719 measured reflections
3719 independent reflections
2851 reflections with $I > 2\sigma(I)$

$\theta_{max} = 27.45°$
$h = -27 \rightarrow 25$
$k = 0 \rightarrow 13$
$l = 0 \rightarrow 20$
3 standard reflections
frequency: 60 min
intensity decay: 5.0%

### *Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.050$
$wR(F^2) = 0.120$
$S = 1.132$
3719 reflections
214 parameters
H-atom parameters not refined

$w = 1/[\sigma^2(F_o^2) + (0.0476P)^2 + 51.4635P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 2.68$ e Å$^{-3}$
$\Delta\rho_{min} = -2.09$ e Å$^{-3}$

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| Pt—O*C*3 | 2.002 (8) | Mo1—O*B*6 | 2.014 (9) |
| Pt—O*C*1 | 2.006 (8) | Mo1—O*C*3 | 2.131 (8) |
| Pt—O*C*2 | 2.015 (8) | Mo1—O*C*1$^{\rm iii}$ | 2.384 (8) |
| Pt—Mo3 | 3.2511 (11) | Mo1—Mo3 | 3.2437 (16) |
| Pt—Mo1 | 3.3318 (15) | Mo1—Mo2$^{\rm iii}$ | 3.3927 (14) |
| Pt—Mo2 | 3.3379 (12) | Mo2—O*T*9 | 1.703 (9) |
| Nd—O*B*4$^{\rm i}$ | 2.451 (8) | Mo2—O*T*10 | 1.715 (9) |
| Nd—O*W*4 | 2.470 (10) | Mo2—O*B*4 | 1.947 (8) |
| Nd—O*W*2 | 2.478 (10) | Mo2—O*B*5 | 1.975 (9) |
| Nd—O*T*7 | 2.494 (9) | Mo2—O*C*2 | 2.209 (8) |
| Nd—O*W*1 | 2.501 (10) | Mo2—O*C*1 | 2.345 (9) |
| Nd—O*W*5 | 2.518 (10) | Mo2—Mo3 | 3.2945 (18) |
| Nd—O*W*3 | 2.521 (9) | Mo3—O*T*7 | 1.723 (9) |
| Nd—O*T*12$^{\rm ii}$ | 2.530 (9) | Mo3—O*T*8 | 1.736 (9) |
| Nd—O*T*8$^{\rm i}$ | 2.567 (9) | Mo3—O*B*6 | 1.890 (8) |
| Nd—Mo3$^{\rm i}$ | 3.5521 (12) | Mo3—O*B*4 | 2.037 (8) |
| Mo1—O*T*11 | 1.689 (9) | Mo3—O*C*2 | 2.109 (8) |
| Mo1—O*T*12 | 1.747 (8) | Mo3—O*C*3 | 2.218 (9) |
| Mo1—O*B*5$^{\rm iii}$ | 1.904 (9) | | |
| O*C*3—Pt—O*C*1 | 97.5 (3) | Mo3—Pt—Mo2 | 59.98 (3) |
| O*C*3—Pt—O*C*2 | 81.1 (3) | Mo1—Pt—Mo2 | 118.85 (3) |
| O*C*1—Pt—O*C*2 | 83.6 (3) | Mo1—Pt—Mo2$^{\rm iii}$ | 61.15 (3) |
| Mo3—Pt—Mo1 | 59.03 (3) | | |

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

The largest difference peak lies 2.93 Å from the nearest atom (O*W*5) and 4.66 Å from the Nd atom. It may represent an additional partially occupied disordered water molecule site.

Data collection: *STADI*4 (Stoe & Cie, 1996); cell refinement: *STADI*4; data reduction: *X-RED* (Stoe & Cie, 1996); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); software used to prepare material for publication: *SHELXL*97.

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