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$[(CH_3)_2NH_2]_4[H_4PMo_{12}O_{40}]Cl_2 \cdot 4H_2O$

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The hydrothermal reaction of an aqueous solution of sodium molybdate, hypophosphorous acid, hydrochloric acid and *N*,*N*-dimethylformamide (DMF) gave rise to tetradimethylammonium tetrahydroxydotriacontaoxo(tetraoxophosphato)-dodecamolybdate dihydrochloride tetrahydrate. The polyanion has a β-Keggin structure, with P—O distances ranging from 1.535 (5) to 1.552 (5) Å and Mo—O distances from 1.664 (4) to 2.509 (4) Å.

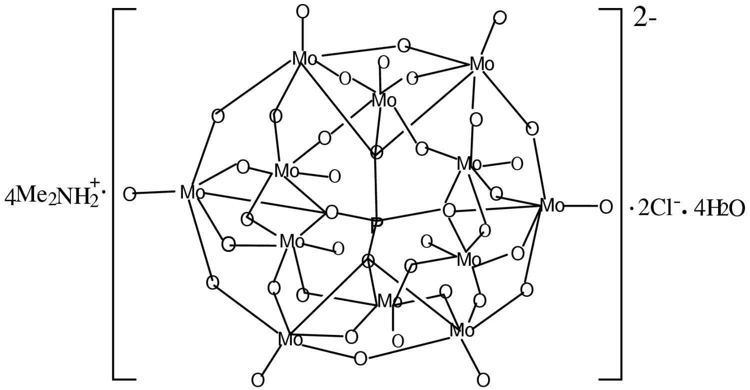
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(N–C) = 0.013 Å
H-atom completeness 55%
R factor = 0.034
wR factor = 0.090
Data-to-parameter ratio = 13.3

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

Comment

The structure of the $[PMo_{12}O_{40}]^{3-}$ heteropolyanion was first reported by Strandberg (1975) and then by D'amour & Allmann (1976). Fruchart and Souchay had shown that reduction of the Keggin-structure anion α-$[PMo_{12}O_{40}]^{3-}$ in aqueous acidic solutions leads to a stable heteropoly blue isomeric β-anion (Fruchart & Souchay, 1968). However, the conclusion had not been structurally proved until 1985 (Barrows *et al.*, 1985). The title compound, (I), is a pseudo-Keggin (Keggin, 1934) heteropoly compound, of which four Mo atoms are reduced (confirmed by cerimetric titration) and four bridging O atoms are protonated. The Mo—O distances range from 2.090 (4) to 2.115 (3) Å (*cf.* 1.92 Å for oxidized structures) and Mo—O—Mo angles from 115.7 (2) to 147.8 (2)° (*cf.* 92° for the oxidized structures) (Barrows *et al.*, 1985).



(I)

As shown in Fig. 1, the $[PMo_{12}O_{40}]^{2-}$ polyanion consists of one {PO_4} tetrahedron and 12 {MoO_6} octahedra. The central almost regular {PO_4} is a tetrahedron with P—O distances ranging from 1.535 (5) to 1.552 (5) Å and O—P—O angles ranging from 109.1 (2) to 110.0 (3)°. The coordination environment for each Mo atom is a distorted octahedron, with Mo—O distances ranging from 1.664 (4) to 2.509 (4) Å and angles involving the neighboring O atoms from 71.2 (1) to

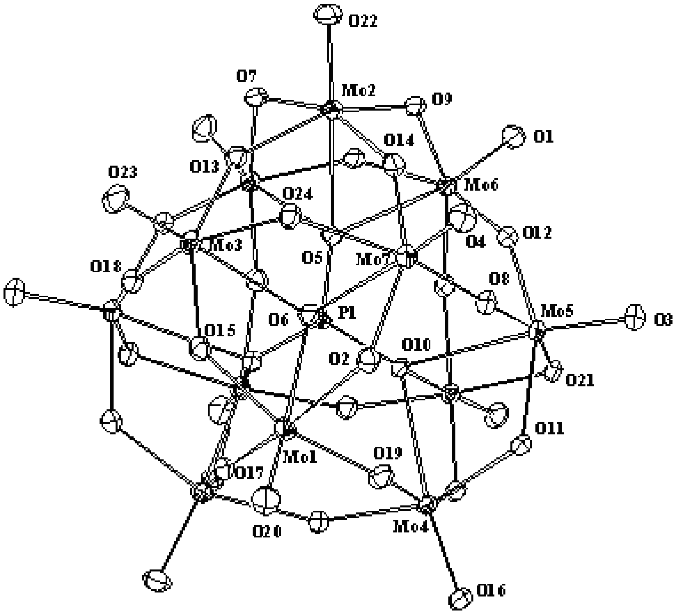


Figure 1
The structure of the $[(H_4PMo_{12}O_{40})]^{2-}$ anion.

105.6 (2)°. The $\{PO_4\}$ tetrahedron and 12 $\{MoO_6\}$ octahedra are linked together through μ_4-O atoms. All O atoms of the anion can be divided into three groups: terminal O atoms, μ_2-O atoms and μ_4-O atoms. The distances between terminal O atoms and Mo atoms range from 1.664 (4) to 1.678 (4) Å, while that of μ_2-O atoms and μ_4-O atoms range from 1.865 (4) to 2.115 (3) Å and from 2.406 (3) to 2.509 (4) Å, respectively.

The title compound contains two chlorine anions in its crystal structure. The $(CH_3)_2NH_2^+$ and Cl^- ions and water molecules in the unit cell are shown in Fig. 2. Finally, it should also be pointed out, as no $(CH_3)_2NH_2^+$ ion was added to the reaction, the cation might derive from DMF; however, the mechanism is still to be further studied.

Experimental

The title compound was prepared by hydrothermal synthesis from a mixture of $Na_2MoO_4{\cdot}2H_2O$ (1.21 g, 5 mmol), DMF (0.5 ml), 35% HCl (2.5 ml), 35% H_3PO_2 (0.2 ml) in H_2O (8 ml), heated at 433 K for one day and cooled. After filtration, the filtrate was allowed to stand in air for about one week, whereupon blue crystals suitable for X-ray diffraction study were obtained. Elemental analysis, calculated: Mo 53.46, P 1.44, Cl 3.29, C 4.46, N 2.60, H 2.06%; found: Mo 53.39, P 1.39, Cl 3.30, C 4.41, N 2.54, H 2.02%.

Crystal data

$(C_2H_6NH_2)_4[H_4PMo_{12}O_{40}]Cl_2{\cdot}4H_2O$
$M_r = 2153.62$
Orthorhombic, *Pnma*
$a = 14.9803\ (7)$ Å
$b = 15.0682\ (8)$ Å
$c = 22.6217\ (12)$ Å
$V = 5106.3\ (5)$ Å^3
$Z = 4$
$D_x = 2.801$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5625 reflections
$\theta = 1.6$–$25.0°$
$\mu = 3.09$ mm^{-1}
$T = 293\ (2)$ K
Prism, blue
$0.45 \times 0.25 \times 0.20$ mm

Data collection

SMART CCD diffractometer
φ and ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.308$, $T_{max} = 0.638$
16 093 measured reflections
4616 independent reflections
3868 reflections with $I > 2\sigma(I)$
$R_{int} = 0.045$
$\theta_{max} = 25.0°$
$h = -16 \rightarrow 17$
$k = -17 \rightarrow 17$
$l = -16 \rightarrow 26$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.090$
$S = 1.10$
4616 reflections
346 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0451P)^2 + 4.5711P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.77$ e Å^{-3}
$\Delta\rho_{min} = -1.45$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Mo1—O20	1.668 (4)	Mo4—O10	2.415 (5)
Mo1—O17	1.893 (1)	Mo5—O3	1.669 (4)
Mo1—O15	1.930 (4)	Mo5—O8	1.865 (4)
Mo1—O2	1.941 (4)	Mo5—O12	1.866 (3)
Mo1—O19	2.026 (4)	Mo5—O11	1.933 (3)
Mo1—O6	2.406 (3)	Mo5—O21	2.115 (3)
Mo2—O22	1.672 (4)	Mo5—O10	2.497 (3)
Mo2—O9	1.866 (4)	Mo6—O1	1.672 (5)
Mo2—O14	1.881 (4)	Mo6—O12	1.933 (4)
Mo2—O13	1.949 (4)	Mo6—O9	1.943 (4)
Mo2—O7	2.096 (2)	Mo6—O5	2.442 (5)
Mo2—O5	2.486 (3)	Mo7—O4	1.663 (4)
Mo3—O23	1.678 (4)	Mo7—O8	1.879 (4)
Mo3—O18	1.869 (1)	Mo7—O2	1.892 (4)
Mo3—O13	1.873 (4)	Mo7—O14	1.899 (4)
Mo3—O15	1.896 (4)	Mo7—O24	2.090 (3)
Mo3—O24	2.104 (4)	Mo7—O6	2.508 (4)
Mo3—O6	2.505 (3)	P1—O5	1.535 (5)
Mo4—O16	1.676 (5)	P1—O6	1.545 (4)
Mo4—O11	1.921 (4)	P1—O10	1.552 (5)
Mo4—O19	1.958 (4)		
O5—P1—O6	109.1 (2)	Mo4—O10—Mo5	88.8 (1)
O5—P1—O10	109.2 (3)	Mo5^{i}—O10—Mo5	91.6 (2)
O6—P1—O10	109.7 (2)	Mo4—O11—Mo5	126.3 (2)
Mo7—O2—Mo1	126.8 (2)	Mo5—O12—Mo6	149.0 (2)
Mo6—O5—Mo2	88.3 (1)	Mo3—O13—Mo2	148.2 (2)
Mo2^{i}—O5—Mo2	95.0 (2)	Mo2—O14—Mo7	149.4 (2)
Mo1—O6—Mo3	88.3 (1)	Mo3—O15—Mo1	126.9 (2)
Mo1—O6—Mo7	88.4 (1)	Mo1—O17—Mo1^{i}	156.7 (3)
Mo3—O6—Mo7	90.8 (1)	Mo3—O18—Mo3^{i}	158.5 (3)
Mo2^{i}—O7—Mo2	122.0 (2)	Mo4—O19—Mo1	147.8 (2)
Mo5—O8—Mo7	158.2 (2)	Mo5^{i}—O21—Mo5	115.7 (2)
Mo2—O9—Mo6	128.5 (2)	Mo7—O24—Mo3	116.6 (2)
Mo4—O10—Mo5^{i}	88.8 (1)		

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

Only the H atoms based on C and N atoms were generated geometrically; other H atoms were not located. The highest residual peak is located at (0.1216, 0.2500, 0.3588), 1.10 Å from O1; the deepest hole is located at (0.5480, 0.2500, 0.4682), 0.91 Å from Mo4.

Data collection: *SMART* (Siemens, 1994); cell refinement: *SMART* and *SAINT* (Siemens, 1996); data reduction: *XPREP* in *SHELXTL* (Siemens, 1994); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXS*97 (Sheldrick, 1997).

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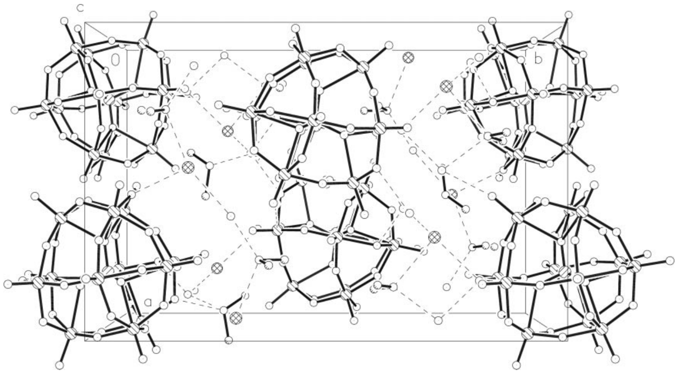

Figure 2
Packing diagram viewed down the *a* axis.

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