Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368

Rerefinement of tris(dimethylammonium) dodecamolybdophosphate in the space group $R\bar{3}m$

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Received 26 October 2004
Accepted 1 November 2004
Online 6 November 2004

In the title compound, $(C_2H_8N)_3[Mo_{12}O_{40}P]$, the Keggin ion $[PO_{40}Mo_{12}]^{3-}$ lies on a special position of site symmetry $3m$ and the $[(CH_3)_2NH_2]^+$ cation on a special position of site symmetry m.

Key indicators

Single-crystal X-ray study
T = 295 K
Mean σ(N–C) = 0.009 Å
R factor = 0.027
wR factor = 0.069
Data-to-parameter ratio = 11.2

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

Comment

The Keggin salt, $[(CH_3)_2NH_2]_3^+[PO_{40}Mo_{12}]^{3-}$, which was obtained from the reaction of *N*,*N*-dimethylformamide and $H_3[PO_{40}Mo_{12}]$, has been described in the space group $R\bar{3}$ (Liu *et al.*, 2004). *PLATON* (Spek, 2003) suggests the correct space group to be $R\bar{3}m$. When the structure is rerefined in the higher-symmetry space group, the $[PO_{40}Mo_{12}]^{3-}$ ion lies on a special position of site symmetry $3m$ and the $[(CH_3)_2NH_2]^+$ cation on another special position of site symmetry m.

$$[(CH_3)_2NH_2]_3^+\,[Mo_{12}O_{40}P]^{3-}$$

(I)

The revised structure, (I) (Fig. 1 and Table 1), is isostructural with a molybdophosphate reported as having a carbenium counter-ion, $[(CH_3)_2CH]_3^+\cdot[PO_{40}Mo_{12}]^{3-}$ (Jian *et al.*, 2004), the two structures having essentially identical cell dimensions and atomic coordinates (of non-H atoms). However, as there is no precedent for the existence of a stable carbenium cation in the Cambridge Structural Database (Version 5.25; Allen, 2002), this yellow compound is probably the title ammonium complex; indeed, the structure could be rerefined to a lower R index.

The mixed-metal Keggin compound formulated as $[H_3PO_{40}Mo_6W_6]\cdot3(CH_3)_2O$ was also incorrectly refined in $R\bar{3}$ (Peng *et al.*, 1998); the position of the H atom in the Keggin framework was inferred on the basis of the electroneutrality of the presumed dimethyl ether solvate. The structure features short contacts between the ether O atom and the O atoms of the neutral Keggin molecule. When the space group is revised (Ng & Rae, 1999; Ng & Xie, 2003) to $R\bar{3}$m, the non-H atomic coordinates are again nearly identical to those of the ammonium 12-molybdophosphate. As such, the compound is most likely $[(CH_3)_2NH_2]_3^+[PO_{40}Mo_6W_6]^{3-}$. The metal atoms are statistically disordered.

Experimental

The diffraction data were kindly provided by the senior author of the $R\bar{3}$ structure (Liu *et al.*, 2004).

doi: 10.1107/S1600536804027941

Crystal data

$(C_2H_8N)_3[Mo_{12}O_{40}P]$
$M_r = 1960.53$
Trigonal, $R\bar{3}m$
$a = 16.541$ (2) Å
$c = 25.154$ (7) Å
$V = 5960$ (2) Å^3
$Z = 6$
$D_x = 3.277$ Mg m^{-3}

Mo *Kα* radiation
Cell parameters from 34 reflections
$\theta = 5.0$–$12.9°$
$\mu = 3.81$ mm^{-1}
$T = 295$ (2) K
Block, yellow
0.52 × 0.34 × 0.34 mm

Data collection

Siemens *P*4 four-circle diffractometer
ω scans
Absorption correction: *ψ* scan (North *et al.*, 1968)
$T_{min} = 0.295$, $T_{max} = 0.484$
3044 measured reflections
1304 independent reflections
1150 reflections with $I > 2\sigma(I)$

$R_{int} = 0.037$
$\theta_{max} = 25.0°$
$h = -1 \rightarrow 19$
$k = -19 \rightarrow 1$
$l = -6 \rightarrow 29$
3 standard reflections every 97 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.027$
$wR(F^2) = 0.069$
$S = 1.08$
1304 reflections
116 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.038P)^2 + 0.2473P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.35$ e Å^{-3}
$\Delta\rho_{min} = -0.91$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.00054 (3)

Table 1
Selected geometric parameters (Å, °).

Mo1—O1	1.680 (4)	Mo2—O6	1.687 (3)
Mo1—O2	1.910 (1)	Mo2—O7	1.926 (3)
Mo1—O3	1.922 (3)	Mo2—O10	2.450 (3)
Mo1—O10	2.423 (4)	Mo3—O7	1.913 (3)
Mo2—O3	1.907 (3)	Mo3—O8	1.927 (2)
Mo2—O4	1.909 (1)	Mo3—O9	1.676 (4)
Mo2—O5	1.922 (2)	Mo3—O11	2.443 (4)
O1—Mo1—O2	101.8 (2)	O4—Mo2—O10	83.4 (1)
O1—Mo1—O3	102.0 (1)	O5—Mo2—O6	101.0 (2)
O1—Mo1—O10	173.4 (2)	O5—Mo2—O7	87.7 (2)
O2—Mo1—O2^{i}	85.1 (2)	O5—Mo2—O10	72.1 (1)
O2—Mo1—O3	156.2 (2)	O6—Mo2—O7	102.3 (1)
O2—Mo1—O3^{ii}	89.0 (2)	O6—Mo2—O10	171.0 (1)
O2—Mo1—O10	83.0 (1)	O7—Mo2—O10	83.4 (1)
O3—Mo1—O3^{ii}	87.2 (2)	O7—Mo3—O7^{iii}	86.3 (2)
O3—Mo1—O10	73.3 (1)	O7—Mo3—O8	156.7 (1)
O3—Mo2—O4	89.9 (2)	O7—Mo3—O8^{iv}	88.3 (2)
O3—Mo2—O5	87.4 (2)	O7—Mo3—O9	102.6 (1)
O3—Mo2—O6	101.5 (1)	O7—Mo3—O11	84.0 (1)
O3—Mo2—O7	156.2 (1)	O8—Mo3—O8^{iv}	87.8 (2)
O3—Mo2—O10	72.9 (1)	O8—Mo3—O9	100.7 (2)
O4—Mo2—O5	155.1 (2)	O8—Mo3—O11	72.9 (1)
O4—Mo2—O6	103.8 (2)	O9—Mo3—O11	170.9 (2)
O4—Mo2—O7	85.0 (2)		

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

The H atoms were placed at calculated positions [N—H = 0.90 Å, C—H = 0.97 Å and $U_{iso}(H) = 1.5U_{eq}(N,C)$] and were included in the refinement in the riding-model approximation. The final difference Fourier map had a large residual electron-density peak located 3.5 Å from the nearest atom (H1*b*). However, the electron density could not be refined as a water O atom.

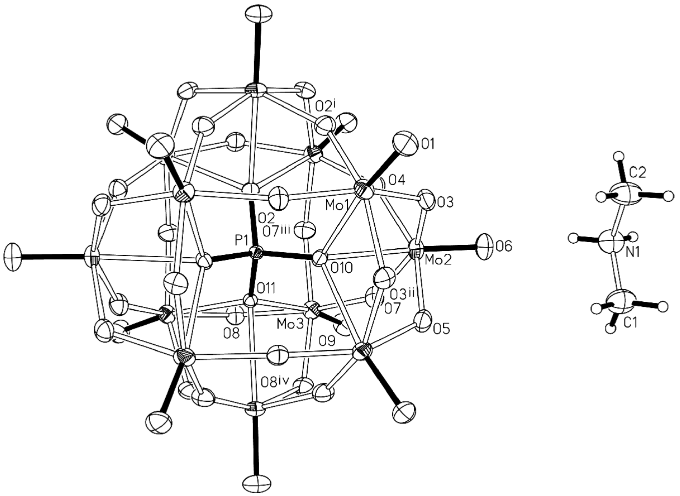

Figure 1
*ORTEP*II (Johnson, 1976) plot of (I); displacement ellipsoids are drawn at the 50% probability level. Symmetry labels refer to the codes in Table 1.

Data collection: *XSCANS* (Bruker, 1994); cell refinement: *LEAST SQUARES* in *XSCANS* (Bruker, 1994); data reduction: *REDUCE* in *XSCANS* (Bruker, 1994); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*97.

The author thanks Professor Shu-Xia Liu of Northeast Normal University for the four-circle diffraction data, Professor Jian-Jian Fang of the Qingdao University of Science and Technology for the area-detector diffraction data, and the University of Malaya for supporting this study.

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