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Poly[tris(*p*-xylylenediaminium) [tetradeca-*μ*-oxo-hexadecanonamolybdate(VI)] dihydrate]

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Key indicators

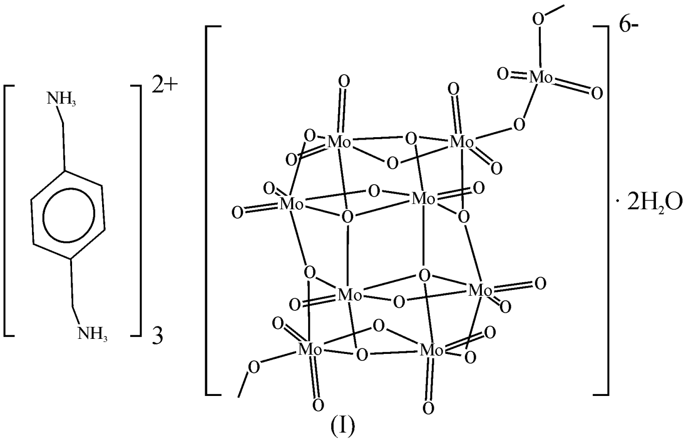
Single-crystal X-ray study
T = 110 K
Mean σ(C–C) = 0.005 Å
R factor = 0.021
wR factor = 0.047
Data-to-parameter ratio = 14.4

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

Crystals of the title compound, $\{[C_8H_{14}N_2]_3[Mo_9O_{30}]\cdot 2H_2O\}_n$, were grown under mild hydrothermal conditions in the presence of *p*-xylylenediamine. $[Mo_9O_{30}]_n^{6n-}$ chains, constructed from $[MoO_6]$ octahedra and $[MoO_4]$ tetrahedra, are separated by protonated *p*-xylylenediaminium cations and occluded water molecules, creating an extensive hydrogen-bonding network. One cation posseses a centre of symmetry; the anion is also centrosymmetric and one Mo atom lies on a crystallographic twofold rotation axis.

Comment

The chemistry of polyoxomolybdates has been the focus of intense research for many years, owing to the host of desirable physical properties that compounds containing such anions can exhibit. The formation of larger polyanions from isolated $[MoO_4]$ tetrahedra is known to occur through many pH-dependent equilibrium steps in which an expansion of the Mo^{VI} coordination number from four to six occurs (Walanda *et al.*, 1999). Anion speciation has also been shown to be highly sensitive to the charge and structure of associated counter-anions in solution, with examples including the selective precipitiation of various polyanions from solutions containing related amines (Himeno, *et al.*, 1997). Our interest in this chemistry is focused upon the role of the cation, specifically protonated organic amines, in the formation of polyoxomolybdates. To this end, a wide range of amines has been used under diverse reaction conditions (Gutnick *et al.*, 2004; Muller, Cannon *et al.*, 2005; Muller, Narducci Sarjeant *et al.*, 2005; Thorn *et al.*, 2005; Nelson *et al.*, 2006*a*,*b*; Veltman *et al.*, 2006).


(I)

The $[Mo_9O_{30}]_n^{6n-}$ chains present in the title compound, (I) (Figs. 1 and 2), exhibit the same connectivity as in previously

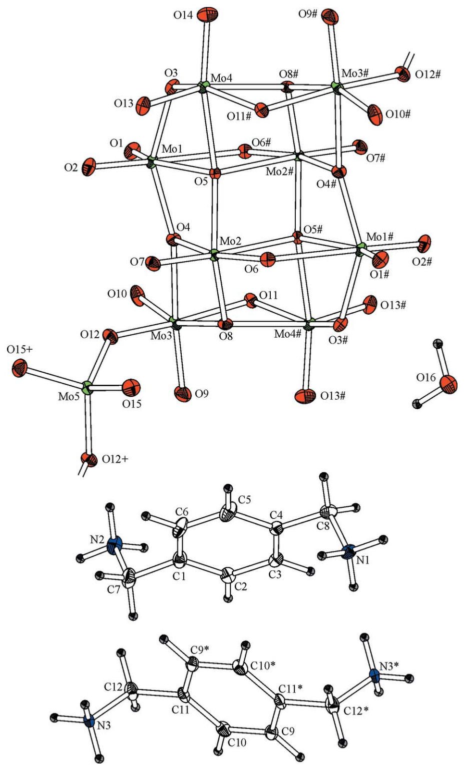


Figure 1
Part of the polymeric structure of (I), with displacement ellipsoids drawn at the 50% probability level (arbitrary spheres for the H atoms). Atoms labeled with a hash (#), plus (+) or asterisk (*) are at the symmetry positions ($\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$), ($1 - x, y, \frac{3}{2} - z$) or ($\frac{1}{2} - x, \frac{1}{2} - y, -z$), respectively.

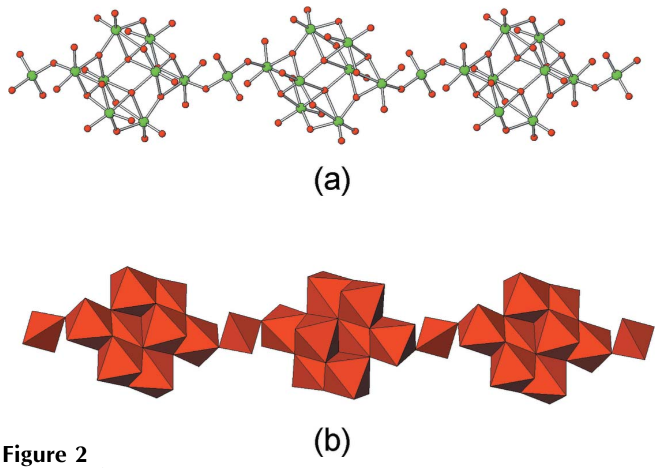


Figure 2
$[\mathrm{Mo_9O_{30}}]_n^{6n-}$ chains in (I), shown in both (*a*) ball- and-stick and (*b*) polyhedral representations.

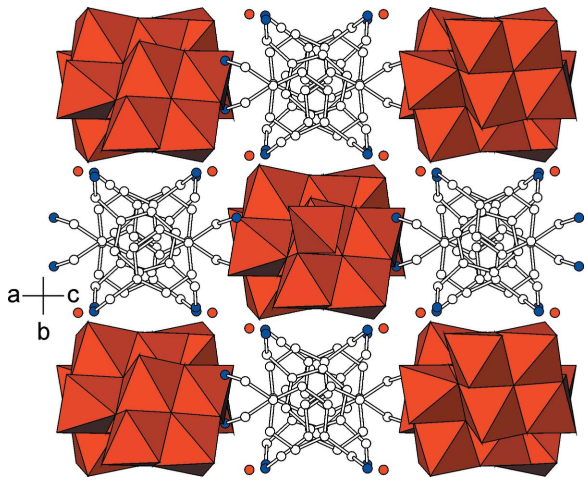


Figure 3
Three-dimensional packing of (I). Red octahedra and tetrahedra represent $[\mathrm{MoO_6}]$ and $[\mathrm{MoO_4}]$ groups, respectively. H atoms have been omitted for clarity.

reported species (Yamase *et al.*, 1996). Five crystallographically distinct Mo centers are present. The $[\mathrm{Mo_9O_{30}}]_n^{6n-}$ chains are constructed from $[\mathrm{Mo_8O_{26}}]$ clusters that are linked to one another through $[\mathrm{MoO_4}]$ bridging tetrahedra. Inversion symmetry within the $[\mathrm{Mo_8O_{26}}]$ clusters generates the complete chains. Four of the five unique Mo sites are part of $[\mathrm{MoO_6}]$ octahedra, in which the $\mathrm{Mo^{VI}}$ cations are second-order Jahn–Teller active and distorted from the centers of their respective coordination polyhedra (Kunz & Brown, 1995). Mo5 lies on a crystallographic twofold rotation axis. Both bridging ($\mathrm{O_b}$) and terminal ($\mathrm{O_t}$) oxo ligands are observed. $\mathrm{Mo{-}O_t}$ bonds [1.705 (2)–1.754 (2) Å] are generally shorter than $\mathrm{Mo{-}O_b}$ bonds [1.815 (2)–2.386 (2) Å]. Greater variablity in the $\mathrm{Mo{-}O_b}$ bond lengths is observed because bridging oxo ligands can be bound to two, three or four adjacent Mo centers.

Two unique $[\mathrm{C_8H_{14}N_2}]^{6+}$ cations are present in the title compound; one of these possesses a centre of symmetry. These cations reside between chains and stack along the [101] direction. Aromatic π–π stacking between neighboring cations is observed at distances of 3.938 (2) and 4.407 (2) Å. Columns of cations, which stack along the [101] direction, are formed by a twofold axis of rotation at ($\frac{1}{2}, y, \frac{1}{4}$).

Experimental

A mixture of $\mathrm{MoO_3}$ (0.0852 g, 0.592 mmol), *p*-xylylenediamine (0.4632 g, 0.145 mmol), $\mathrm{H_2SO_4}$ (0.1969 g, 2.009 mmol) and deionized water (1.9937 g, 0.111 mol) was added to a 23 ml Teflon-lined pressure vessel. The reaction gel was heated to 453 K for 24 h, and then cooled slowly to room temperature at a rate of 6 K $\mathrm{h^{-1}}$. The vessel was opened in air and the reaction products were recovered by filtration.

Crystal data

$(\mathrm{C_8H_{14}N_2})_3[\mathrm{Mo_9O_{30}}]\cdot 2\mathrm{H_2O}$
$M_r = 1794.13$
Monoclinic, $C2/c$
$a = 16.850$ (3) Å
$b = 13.656$ (3) Å
$c = 21.441$ (4) Å
$\beta = 105.908$ (15)°
$V = 4744.7$ (16) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 2.40\ \mathrm{mm^{-1}}$
$T = 110$ (2) K
0.25 × 0.14 × 0.03 mm

Data collection

Oxford Diffraction CrysAlis CCD area-detector diffractometer
Absorption correction: analytical (multifaceted crystal model; Clark & Reid, 1995)
$T_{\min} = 0.540$, $T_{\max} = 0.930$
49286 measured reflections
7576 independent reflections
4638 reflections with $I > 3\sigma(I)$
$R_{\mathrm{int}} = 0.02$

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Refinement

$R[F^2 > 2\sigma(F^2)] = 0.021$
$wR(F^2) = 0.047$
$S = 0.86$
4638 reflections
321 parameters
H-atom parameters constrained
$\Delta\rho_{\max} = 0.58$ e Å^{-3}
$\Delta\rho_{\min} = -0.56$ e Å^{-3}

Table 1
Selected bond lengths (Å).

Mo1—O1	1.733 (2)	Mo3—O11	1.939 (2)
Mo1—O2	1.718 (2)	Mo3—O12	2.007 (2)
Mo1—O3	1.929 (2)	Mo4—O3	1.962 (2)
Mo1—O4	1.904 (2)	Mo4—O5	2.209 (2)
Mo1—O5	2.228 (2)	Mo4—O8^{i}	2.303 (2)
Mo1—O6^{i}	2.369 (2)	Mo4—O11^{i}	1.942 (2)
Mo2—O4	2.145 (2)	Mo4—O13	1.723 (2)
Mo2—O5	1.942 (2)	Mo4—O14	1.708 (2)
Mo2—O5^{i}	2.386 (2)	Mo5—O12	1.815 (2)
Mo2—O6	1.754 (2)	Mo5—O12^{ii}	1.815 (2)
Mo2—O7	1.705 (2)	Mo5—O15	1.726 (2)
Mo2—O8	1.886 (2)	Mo5—O15^{ii}	1.726 (2)
Mo3—O4	2.177 (2)	N1—C8	1.506 (4)
Mo3—O8	2.223 (2)	N2—C7	1.506 (5)
Mo3—O9	1.708 (2)	N3—C12	1.499 (4)
Mo3—O10	1.718 (2)		

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

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O16—H1···O10^{ii}	1.00	2.16	2.825 (4)	122
O16—H2···O9	1.00	1.82	2.792 (4)	164
N1—H9···O7^{iii}	1.00	1.89	2.792 (4)	149
N1—H10···O13^{iv}	1.00	2.03	2.862 (4)	139
N1—H11···O2^{iv}	1.00	1.98	2.883 (4)	149
N2—H15···O16	1.00	1.79	2.716 (4)	153
N2—H16···O15^{v}	1.00	2.03	2.860 (4)	139
N3—H21···O1^{vi}	1.00	1.96	2.876 (4)	150
N3—H22···O11^{vii}	1.00	1.94	2.891 (4)	158

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

H atoms were positioned geometrically after each cycle in idealized locations, with C—H = 1.00–1.01 Å and N—H = 1.00 Å, and refined as riding on their parent atoms, with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(parent) in all cases.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2004); cell refinement: *CrysAlis RED*; data reduction: *CrysAlis RED* (Oxford Diffraction, 2004); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *CRYSTALS* (Betteridge *et al.*, 2003); molecular graphics: *ATOMS* (Dowty, 2002); software used to prepare material for publication: *CRYSTALS*.

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