

Poly[propane-1,3-diammonium [tetra- μ_3 -oxo-hexaoxotrimolybdenum(VI)] dihydrate]

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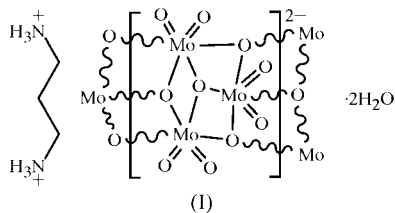
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The crystal structure of the title compound, $\{(C_3H_{12}N_2)[Mo_3O_{10}] \cdot 2H_2O\}_n$, is composed of $[Mo_3O_{10}]^{2-}$ anionic chains, propane-1,3-diammonium cations and solvent water molecules. The $[Mo_3O_{10}]^{2-}$ chain is constructed from edge-sharing MoO_6 octahedra. The protonated propane-1,3-diamine cations and solvent water molecules are located between the chains and are linked to the O atoms of the inorganic chains by hydrogen bonds.

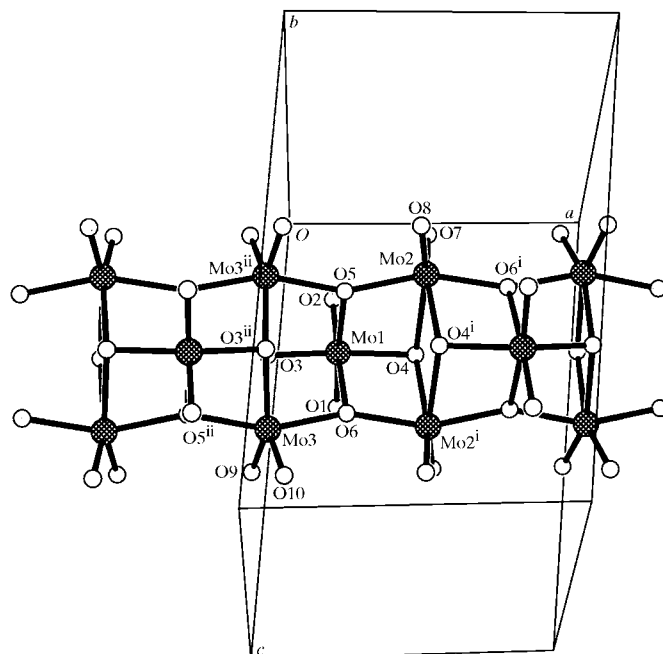
Comment

Hybrid organic–inorganic materials have been attracting extensive interest because of their potential applications in catalysis, electron conductivity, magnetism and photochemistry (Rhule *et al.*, 1998). Exploitation of hydrothermal techniques and the use of organic structure-directing agents proved fruitful in preparing such materials (Hagman *et al.*, 1999; Lin *et al.*, 2003). Influenced by the employed organic components, there exist various inorganic skeletal backbones of metal–oxo polyhedra with different connecting modes through sharing corners, edges and faces. For example, the $[Mo_3O_{10}]^{2-}$ chain in $[Co(bpy)Mo_3O_{10}]$ is made up of MoO_6 octahedra, MoO_5 square pyramids and MoO_4 tetrahedra sharing corners and edges (bpy is 2,2'-bipyridine; Zapf *et al.*, 1997). The $[Mo_3O_{10}]^{2-}$ chain in $(H_2en)[Mo_3O_{10}]$ is made up of

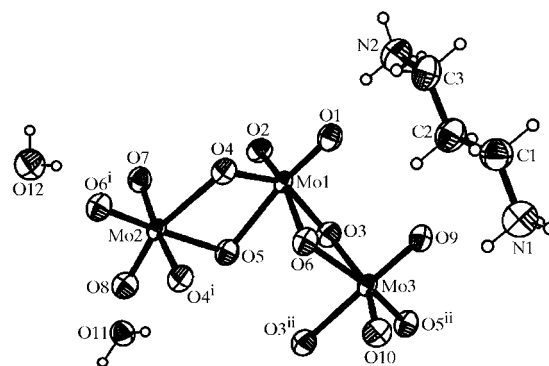


MoO_6 octahedra linked by sharing corners, edges and faces (en is ethylenetriamine; Guillou & Férey, 1997). The present paper reports the synthesis and crystal structure of a new one-dimensional polymeric molybdenum oxide solid, $(H_2pn)[Mo_3O_{10}] \cdot 2H_2O$, (I) (pn is propane-1,3-diamine).

The crystal structure of (I) is composed of $[Mo_3O_{10}]^{2-}$ anionic chains, $(H_2pn)^{2+}$ cations and solvent water molecules. The $[Mo_3O_{10}]^{2-}$ chain is built up of MoO_6 octahedra by sharing edges and expansion along the *a* axis (Fig. 1). The coordination environments around the Mo sites are shown in Fig. 2. The octahedral geometry of each Mo atom is defined by two terminal and four triply bridging O atoms, where the two terminal O atoms are in a *cis* arrangement. As listed in Table 1, each octahedron exhibits two short, two medium and two long Mo–O bonds with lengths of 1.690 (2)–1.7032 (17), 1.884 (2)–1.976 (2) and 2.215 (2)–2.342 (2) Å, respectively. These values are in accordance with those observed in reported molyb-


Figure 1

The infinite one-dimensional edge-sharing MoO_6 chains extending along the *a* axis in (I). The large cross-hatched and open circles denote Mo and O atoms, respectively. [Symmetry codes: (i) $-x + 1, -y + 1, -z + 1$; (ii) $-x, -y + 1, -z + 1$.]


Figure 2

The asymmetric unit in (I), showing the metal-atom coordination environments with 50% probability displacement ellipsoids. [Symmetry codes: (i) $-x + 1, -y + 1, -z + 1$; (ii) $-x, -y + 1, -z + 1$.]

denum oxides, such as $(\text{H}_2\text{en})[\text{Mo}_3\text{O}_{10}]$ (Guillou & Férey, 1997), $\text{Na}(\text{NH}_4)[\text{Mo}_3\text{O}_{10}]$ (Xu *et al.*, 1996) and $(\text{C}_6\text{H}_5\text{NH}_3)_2[\text{Mo}_3\text{O}_{10}]\cdot 4\text{H}_2\text{O}$ (Lasocha *et al.*, 1995). As displayed in Fig. 1, two MoO_6 octahedra surrounding Mo2 and one of its symmetry-related sites, or Mo3 and one of its symmetry-related sites, share one edge to form a dimer. This dimer is then linked by one MoO_6 octahedron around Mo1 to an Mo_3O_{10} unit by sharing two edges. Such units are further interlinked through sharing two other edges of the middle octahedron around Mo1 to form an infinite one-dimensional molybdenum–oxo chain. The one-dimensional molybdenum–oxo chain in (I) is similar to those found in $\text{Na}(\text{NH}_4)[\text{Mo}_3\text{O}_{10}]$ (Xu *et al.*, 1996) and $(\text{C}_6\text{H}_5\text{NH}_3)_2[\text{Mo}_3\text{O}_{10}]\cdot 4\text{H}_2\text{O}$ (Lasocha *et al.*, 1995). However, this one-dimensional chain is distinctly different from those with similar composition $[\text{Mo}_3\text{O}_{10}]$ or $[\text{Mo}_9\text{O}_{30}]$. As mentioned above, the $[\text{Mo}_3\text{O}_{10}]^{2-}$ chain in $[\text{Co}(\text{bpy})\text{Mo}_3\text{O}_{10}]$ is built up of three types of MoO_n polyhedra (Zapf *et al.*, 1997). The chain in $\text{K}_2[\text{Mo}_3\text{O}_{10}]$ is composed of edge-sharing MoO_6 octahedra and MoO_5 square pyramids (Gatehouse & Leverett, 1968). The $[\text{Mo}_9\text{O}_{30}]^{6-}$ chain in $(\text{H}_3\text{dien})_2[\text{Mo}_9\text{O}_{30}]$ is constructed from $[\text{Mo}_8\text{O}_{26}]^{4-}$ clusters and MoO_6 octahedra through sharing vertices (dien is diethylenetriamine; Xu *et al.*, 2003). In contrast, the $[\text{Mo}_3\text{O}_{10}]^{2-}$ chain in (I) is built up of edge-sharing MoO_6 octahedra.

In the crystal structure of (I), the protonated propane-1,3-diamine cations and solvent water molecules are located between these edge-sharing MoO_6 octahedral chains and are linked to the O atoms of the molybdenum units by hydrogen bonds, with $\text{O}\cdots\text{O}$ distances of 2.812 (3)–3.142 (3) Å and $\text{N}\cdots\text{O}$ distances 2.657 (4)–2.866 (4) Å (Table 2). These hydrogen-bonding interactions make the crystal structure of (I) more stable, and hold the components together in a three-dimensional supramolecular network (Fig. 3).

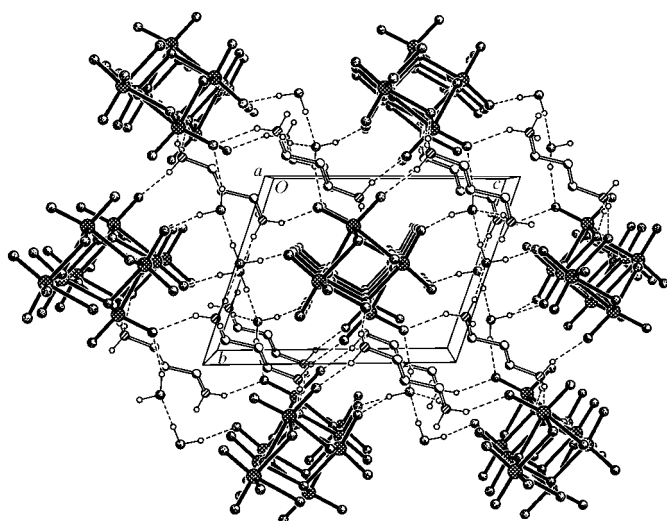


Figure 3

A projection of the crystal structure of (I) along the *a* axis. The large cross-hatched, large open, striped, shaded and small open circles denote Mo, O, N, C and H atoms, respectively, while the H atoms attached to C atoms have been omitted for clarity.

Experimental

Compound (I) was synthesized hydrothermally under autogenous pressure. A mixture of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$, propane-1,3-diamine and water in the molar ratio 1:3.6:833.3 was sealed in a 17 ml Teflon-lined autoclave and heated at 433 K for 60 h. The reaction mixture was cooled slowly to room temperature at a rate of 10 K h^{-1} and colorless needle-shaped crystals of (I) were obtained. The pH of the reaction system was adjusted using 5 mol dm^{-3} HCl solution to 5.04 before the reaction, and it reached 4.98 after the reaction. The resulting crystals were filtered off, washed with distilled water and dried in air (65% yield based on Mo). The strong features at 928 and 915 cm^{-1} in the IR spectrum of (I) are associated with Mo–O stretching vibrations, and the bands at 1491, 1314, 1225, 1114 and 1052 cm^{-1} are related to C–C and C–N stretchings. The weight loss of 6.36% between 389 and 433 K corresponds to the removal of the solvent water molecules, and the weight loss in the temperature range 443–663 K is attributed to the release of the organic amines. The total observed loss of 20.12% is consistent with the calculated value of 20.03%. Analysis calculated for $\text{C}_3\text{H}_{16}\text{Mo}_3\text{N}_2\text{O}_{12}$: C 6.43, H 2.88, N 5.00%; found: C 6.64, H 3.12, N 4.92%.

Crystal data

$(\text{C}_3\text{H}_{12}\text{N}_2)[\text{Mo}_3\text{O}_{10}]\cdot 2\text{H}_2\text{O}$	$\gamma = 94.816 (6)^\circ$
$M_r = 560.00$	$V = 696.1 (2) \text{ \AA}^3$
Triclinic, $P\bar{1}$	$Z = 2$
$a = 7.6330 (15) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 8.7000 (17) \text{ \AA}$	$\mu = 2.72 \text{ mm}^{-1}$
$c = 11.174 (2) \text{ \AA}$	$T = 291 (2) \text{ K}$
$\alpha = 107.86 (2)^\circ$	$0.18 \times 0.08 \times 0.05 \text{ mm}$
$\beta = 96.556 (7)^\circ$	

Data collection

Bruker SMART APEXII CCD area-detector diffractometer	5476 measured reflections
Absorption correction: multi-scan (SADABS; Bruker, 2002)	2738 independent reflections
$T_{\min} = 0.640$, $T_{\max} = 0.876$	2699 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.003$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.046$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.136$	
$S = 1.04$	$\Delta\rho_{\text{max}} = 0.96 \text{ e \AA}^{-3}$
2738 reflections	$\Delta\rho_{\text{min}} = -0.95 \text{ e \AA}^{-3}$
195 parameters	
6 restraints	

Table 1

Selected bond lengths (Å).

Mo1–O1	1.690 (2)	Mo2–O5	1.976 (2)
Mo1–O2	1.7032 (17)	Mo2–O4 ⁱ	2.215 (2)
Mo1–O3	1.884 (2)	Mo2–O4	2.342 (2)
Mo1–O4	1.932 (2)	Mo3–O9	1.6923 (19)
Mo1–O6	2.245 (2)	Mo3–O10	1.6989 (18)
Mo1–O5	2.278 (2)	Mo3–O5 ⁱⁱ	1.942 (2)
Mo2–O7	1.6980 (17)	Mo3–O6	1.962 (2)
Mo2–O8	1.699 (2)	Mo3–O3	2.246 (2)
Mo2–O6 ⁱ	1.957 (2)	Mo3–O3 ⁱⁱ	2.312 (3)

Symmetry codes: (i) $-x + 1, -y + 1, -z + 1$; (ii) $-x, -y + 1, -z + 1$.

While the H atoms attached to C and N atoms were placed in calculated positions, those on water molecules were located in a difference Fourier map and then refined with O–H distances restrained to 0.96 (4) Å and H–O–H angles restrained to 104.4 (4)°.

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

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O11—H11A...O8	0.939 (19)	2.52 (3)	3.142 (3)	124 (3)
O11—H11A...O9 ⁱⁱ	0.939 (19)	2.00 (3)	2.812 (3)	143 (3)
O11—H11B...O2 ⁱⁱⁱ	0.927 (17)	2.03 (2)	2.861 (3)	148 (3)
O12—H12A...O7	0.94 (2)	2.18 (3)	3.044 (4)	152 (3)
O12—H12B...O11 ^{iv}	0.92 (2)	2.03 (3)	2.911 (4)	161 (3)
N1—H1C...O2 ^v	0.89	2.04	2.851 (4)	151
N1—H1D...O11 ⁱⁱ	0.89	1.97	2.807 (4)	156
N1—H1E...O12 ⁱ	0.89	1.95	2.815 (5)	164
N2—H2C...O4 ^{vi}	0.89	1.79	2.657 (4)	165
N2—H2D...O1	0.89	2.07	2.866 (4)	149
N2—H2E...O3 ^{vii}	0.89	1.92	2.747 (4)	154

Symmetry codes: (i) $-x + 1, -y + 1, -z + 1$; (ii) $-x, -y + 1, -z + 1$; (iii) $x, y + 1, z$; (iv) $-x + 1, -y + 1, -z$; (v) $x, y, z + 1$; (vi) $-x + 1, -y, -z + 1$; (vii) $-x, -y, -z + 1$.

All H atoms were included in the refinement, with $U_{\text{iso}}(\text{H})$ values of $1.2U_{\text{eq}}(\text{parent atom})$.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SAINTE* (Bruker, 2001); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2000); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GZ3086). Services for accessing these data are described at the back of the journal.

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