

# $[(\text{NH}_4)_2(\text{Mo}_4\text{O}_{13})]_n$ : a novel two-dimensional polyoxomolybdate(VI) framework

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## Key indicators

Single-crystal X-ray study

$T = 293 \text{ K}$

Mean  $\sigma(\text{Mo}-\text{O}) = 0.005 \text{ \AA}$

H-atom completeness 0%

$R$  factor = 0.037

$wR$  factor = 0.104

Data-to-parameter ratio = 11.4

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

The structure of diammonium tetramolybdate,  $[(\text{NH}_4)_2(\text{Mo}_4\text{O}_{13})]_n$ , consists of puckered layers built up from the self-assembly of chains of tetrameric units  $[\text{Mo}_4\text{O}_{13}]^{2-}$  linked through corner-sharing octahedra. The ammonium cations are located between consecutive layers, yielding a three-dimensional array *via* extensive  $\text{N}-\text{H}\cdots\text{O}$  hydrogen bonding, in which terminal oxo groups of the surface network are involved.

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## Comment

A fascinating aspect of the polyoxometalates is their wide structural diversity, which has allowed the possibility of extensive modifications of their physical and chemical properties (Pope & Müller, 1991). As a consequence, these materials have found useful applications in diverse fields (Hill, 1998; Pope & Müller, 1994). Emergent strategies to produce new metal oxide phases with novel compositions and unusual topologies are based on the modification and/or functionalization of the oxidic surface under hydrothermal conditions. Frequently, such strategies are combined with the appropriate selection of charge-compensating agents bearing special structural features (Cheetham *et al.*, 1999; Feng & Xu, 2001; Hagrman *et al.*, 1999; Hagrman *et al.*, 2001; Xu *et al.*, 1996). As part of our attempts to prepare solid materials based on polymolybdates, we have observed a new oxide framework built up from a tetrameric moiety  $[\text{Mo}_4\text{O}_{13}]^{2-}$ , demonstrating the structural versatility of this unit. The hydrothermal synthesis and the X-ray diffraction study of this novel material are reported here.

The structure of the title compound, (I), consists of anionic puckered layers of polyoxomolybdate(VI) parallel to the *ac* plane, with intercalated ammonium cations. The basic building block of the layers is an asymmetric tetranuclear motif  $[\text{Mo}_4\text{O}_{13}]^{2-}$  (Fig. 1), which is built up from the combination of one  $\{\text{MoO}_5\}$  and three  $\{\text{MoO}_6\}$  units. The  $\{\text{MoO}_5\}$  square

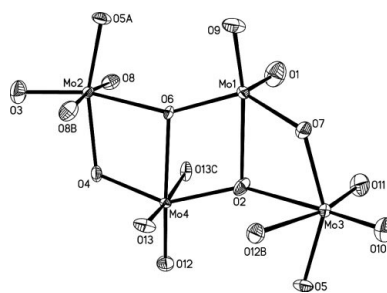
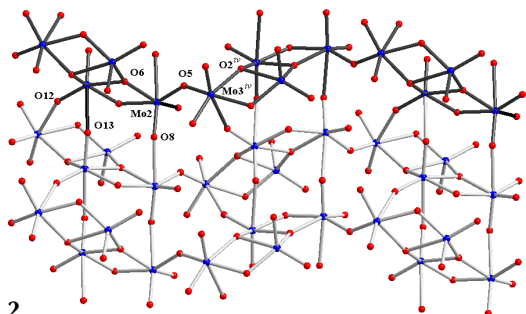


Figure 1

View of the tetranuclear building block  $[\text{Mo}_4\text{O}_{13}]^{2-}$  together with symmetry-generated O atoms to complete the Mo coordination. Symmetry codes: (A)  $x - \frac{1}{2}, y, -\frac{1}{2} - z$ ; (B)  $x, \frac{1}{2} - y, \frac{1}{2} + z$ ; (C)  $x, \frac{1}{2} - y, z - \frac{1}{2}$ , corresponding to (i)–(iii), respectively, in Table 1. Displacement ellipsoids are drawn at the 50% probability level.



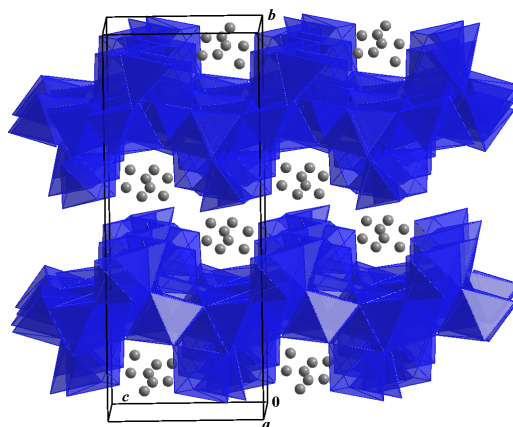
**Figure 2**

Ball-and-stick representation of the layers  $[\text{Mo}_4\text{O}_{13}]_n^{2-}$  observed in the  $bc$ -plane of the crystal structure of (I). [Symmetry code: (iv)  $\frac{1}{2} + x, y, -\frac{1}{2} - z$ .]

pyramid (Mo1) is connected by corner-sharing to one octahedron (Mo2) and by edge-sharing to the two remaining  $\{\text{MoO}_6\}$  octahedra (Mo3 and Mo4). In this configuration, one  $\{\text{MoO}_6\}$  octahedron (Mo4) is linked by edge- and corner-sharing to the other two octahedra (Mo2 and Mo3, respectively). The Mo–O bond distances and angles in (I) lie in the expected ranges (Allen, 2002; Hagrman *et al.*, 1999; Xu *et al.*, 1996)  $[\text{Mo}=\text{O}(\text{t})$ : 1.688 (5)–1.730 (5) Å;  $\text{Mo}-\text{O}(\mu_2)$ : 1.735 (5)–2.398 (5) Å;  $\text{Mo}-\text{O}(\mu_3)$ : 1.865 (5)–2.281 (4) Å; range of bond angles for *cis*-oxo ligands is 71.4 (2)–105.7 (2)°].

The tetranuclear building block forms a kind of extended chain along the  $a$  axis, *via* corner-sharing between two octahedra (Mo2 and Mo3) from different units, in which the bridging atom O5 is involved (dark ball-and-stick in Fig. 2). Two consecutive tetranuclear moieties show a rotation of *ca* 120.9° between them, as estimated from the torsion angle  $\text{O6}-\text{Mo2}-\text{Mo3}^{\text{iv}}-\text{O2}^{\text{iv}}$  [symmetry code: (iv)  $\frac{1}{2} + x, y, -\frac{1}{2} - z$ ], allowing an alternating left–right torsion to the extended chain. Adjacent chains are linked together by corner-sharing through atoms O8, O12 and O13 (see Fig. 2), generating a puckerd two-dimensional network. This puckerd feature appears to be a consequence of the steric requirements of the edge- and corner-sharing modes of the  $\{\text{MoO}_x\}$  polyhedra. The two-dimensional array displays an intricate set of channels along the  $a$  axis, where ammonium cations are located (Fig. 3). The final three-dimensional assembly is achieved by stacking (perpendicular to the  $ac$  plane) of the layers due to extensive hydrogen-bonding  $\text{N}-\text{H}\cdots\text{O}$  interactions (range  $\text{N}\cdots\text{O}$ : 2.80–2.87 Å) between ammonium units and terminal oxo groups of the anion arrays.

The structure of the  $[\text{Mo}_4\text{O}_{13}]_n^{2-}$  tetranuclear unit of (I) is different from those previously reported for the compounds  $[(\text{Hbpa})_2(\text{Mo}_4\text{O}_{13})_n]_n$ , (II) (Hbpa = 4-pyridyl-4'-pyridinium amine) (Zapf *et al.*, 1998),  $[M(\text{tpytrz})_2\text{Mo}_4\text{O}_{13}]_n$ , (III) ( $M = \text{Fe}, \text{Co}, \text{Ni}, \text{Zn}$ ; tpytrz = tripyridyltriazine) (Rarig & Zubieta, 2001), and  $[(\text{Cu}_2(\text{triazolate})_2(\text{H}_2\text{O}))\text{Mo}_4\text{O}_{13}]_n$ , (IV) (Hagrman & Zubieta, 1998). Compounds (II) and (III) display a symmetrical unit built up from two pairs of polyhedra. (II) is defined by edge- and corner-sharing of square-pyramidal  $\{\text{MoO}_5\}$  and octahedral  $\{\text{MoO}_5\text{N}\}$  units generating infinite chains. Compound (III) displays an oxide substructure, described by chains linked *via* corner-sharing of tetrahedral  $\{\text{MoO}_4\}$  and octahedral  $\{\text{MoO}_5\text{N}\}$  moieties. Similar to that



**Figure 3**

Polyhedral representation of the stacking of the two-dimensional networks, showing the intricate set of channels along the  $a$  axis, where the ammonium ions (spheres) are located.

found in (I), compound (IV) also shows an asymmetric tetranuclear unit with one five-coordinated unit and three octahedra. However, the intrinsic polyhedral connection of (IV) allows the formation of the chains with different structural patterns compared with that observed in (I). This analysis reveals the versatility and structural diversity of this tetranuclear building block. As anticipated, other arrays based on tetranuclear  $[\text{Mo}_4\text{O}_{12}]_n^{2-}$  units containing only 12 oxo ligands [see, for example,  $[(\text{ethylenediaminium})(\text{Mo}_4\text{O}_{12})]_n$  (Guillou *et al.*, 1998) and  $[(\text{NMe}_4)_2(\text{Mo}_4\text{O}_{12})]_n$  (Guo *et al.*, 1994)] lead to two-dimensional networks with topologies quite different from that described for (I), whereas the crystal structure of  $(^n\text{Bu}_4\text{N}_2)_2[\text{Mo}_4\text{O}_{12}(\text{picOH})_2]$  (picOH = 3-hydroxypicolinic acid) (Quintal *et al.*, 2001) contains only discrete  $(\text{Mo}_4\text{O}_{12})_n^{2-}$  moieties.

## Experimental

The title compound was obtained by hydrothermal synthesis from the reaction of  $[(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}] \cdot 6\text{H}_2\text{O}$  (STREM Chemical) and 4,4'-bipyridine (bipy) (Merck) in a 1:1 ratio in 9 ml of  $\text{H}_2\text{O}$ . The reaction was carried out at 313 K for 3 d under autogenous pressure. The resulting solid obtained after cooling to room temperature consisted of a mixture of small colourless needle crystals identified as the previously reported  $[(\text{NH}_4)_4(\text{Mo}_8\text{O}_{26})(\text{bipy})_6]$  (Cui *et al.*, 2002), and larger colourless prisms of 1–4 mm corresponding to the characterized product, (I). Attempts to prepare (I) in the absence of bipy were unsuccessful. The IR spectrum was recorded from KBr discs, using a Magna FT-IR 560 Spectrophotometer. IR ( $\text{cm}^{-1}$ ),  $\nu(\text{NH}_4^+)$ : 3200–2800 (*b*), 1685 (*w*), 1399 (*s*);  $\nu(\text{Mo}=\text{O}, \text{Mo}-\text{O}-\text{Mo})$ : 893 (*s*) and 783 (*s*), respectively.

### Crystal data

$(\text{NH}_4)_2[\text{Mo}_4\text{O}_{13}]$   
 $M_r = 627.84$   
 Orthorhombic,  $Pbca$   
 $a = 15.423$  (2) Å  
 $b = 19.0022$  (9) Å  
 $c = 7.6423$  (7) Å  
 $V = 2239.7$  (4) Å<sup>3</sup>  
 $Z = 8$   
 $D_x = 3.724$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation  
 Cell parameters from 25 reflections  
 $\theta = 39.3$ – $39.8^\circ$   
 $\mu = 4.45$  mm<sup>-1</sup>  
 $T = 293$  (2) K  
 Prism, colourless  
 $0.60 \times 0.36 \times 0.20$  mm

## Data collection

Rigaku AFC-7S diffractometer  
 $\omega$ -2 $\theta$  scans  
 Absorption correction: refined from  
 $\Delta F$  (Walker & Stuart, 1983)  
 $T_{\min} = 0.160$ ,  $T_{\max} = 0.411$   
 2166 measured reflections  
 1968 independent reflections  
 1842 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.039$   
 $\theta_{\text{max}} = 25.0^\circ$   
 $h = 0 \rightarrow 18$   
 $k = -2 \rightarrow 22$   
 $l = 0 \rightarrow 9$   
 3 standard reflections  
 every 150 reflections  
 intensity decay: none

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.037$   
 $wR(F^2) = 0.104$   
 $S = 1.24$   
 1968 reflections  
 172 parameters  
 H-atom parameters not located

$w = 1/[\sigma^2(F_o^2) + (0.0611P)^2 + 14.7630P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 1.40 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -2.81 \text{ e } \text{\AA}^{-3}$

Table 1

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

Mo1—O9	1.706 (5)	Mo3—O11	1.723 (5)
Mo1—O1	1.730 (5)	Mo3—O5	1.877 (5)
Mo1—O7	1.877 (5)	Mo3—O7	1.982 (5)
Mo1—O6	1.893 (5)	Mo3—O2	2.173 (5)
Mo1—O2	2.281 (5)	Mo3—O12 <sup>ii</sup>	2.330 (5)
Mo2—O3	1.688 (5)	Mo4—O12	1.735 (5)
Mo2—O8	1.734 (5)	Mo4—O13	1.736 (5)
Mo2—O5 <sup>i</sup>	1.902 (5)	Mo4—O2	1.865 (5)
Mo2—O4	1.999 (5)	Mo4—O4	1.923 (4)
Mo2—O6	2.149 (5)	Mo4—O6	2.158 (5)
Mo2—O8 <sup>ii</sup>	2.288 (5)	Mo4—O13 <sup>iii</sup>	2.398 (5)
Mo3—O10	1.719 (5)		
O9—Mo1—O1	104.3 (2)	O5—Mo3—O7	150.4 (2)
O9—Mo1—O7	101.3 (2)	O10—Mo3—O2	162.2 (2)
O1—Mo1—O7	105.7 (2)	O11—Mo3—O2	92.7 (2)
O9—Mo1—O6	103.7 (2)	O5—Mo3—O2	83.93 (19)
O1—Mo1—O6	104.3 (2)	O7—Mo3—O2	73.73 (18)
O7—Mo1—O6	134.3 (2)	O10—Mo3—O12 <sup>ii</sup>	85.6 (2)
O9—Mo1—O2	162.1 (2)	O11—Mo3—O12 <sup>ii</sup>	168.5 (2)
O1—Mo1—O2	93.6 (2)	O5—Mo3—O12 <sup>ii</sup>	81.81 (19)
O7—Mo1—O2	73.09 (18)	O7—Mo3—O12 <sup>ii</sup>	74.64 (18)
O6—Mo1—O2	71.39 (18)	O2—Mo3—O12 <sup>ii</sup>	77.41 (17)
O3—Mo2—O8	104.0 (2)	O12—Mo4—O13	102.6 (2)
O3—Mo2—O5 <sup>i</sup>	102.2 (2)	O12—Mo4—O2	105.1 (2)
O8—Mo2—O5 <sup>i</sup>	98.4 (2)	O13—Mo4—O2	99.9 (2)
O3—Mo2—O4	95.8 (2)	O12—Mo4—O4	99.3 (2)
O8—Mo2—O4	96.1 (2)	O13—Mo4—O4	98.6 (2)
O5 <sup>i</sup> —Mo2—O4	153.45 (19)	O2—Mo4—O4	145.1 (2)
O3—Mo2—O6	157.3 (2)	O12—Mo4—O6	158.8 (2)
O8—Mo2—O6	96.6 (2)	O13—Mo4—O6	98.2 (2)
O5 <sup>i</sup> —Mo2—O6	84.10 (18)	O2—Mo4—O6	74.86 (18)
O4—Mo2—O6	72.18 (18)	O4—Mo4—O6	73.42 (18)
O3—Mo2—O8 <sup>ii</sup>	85.2 (2)	O12—Mo4—O13 <sup>iii</sup>	80.2 (2)
O8—Mo2—O8 <sup>ii</sup>	170.8 (2)	O13—Mo4—O13 <sup>iii</sup>	176.0 (3)
O5 <sup>i</sup> —Mo2—O8 <sup>ii</sup>	80.63 (19)	O2—Mo4—O13 <sup>iii</sup>	81.93 (18)
O4—Mo2—O8 <sup>ii</sup>	81.55 (18)	O4—Mo4—O13 <sup>iii</sup>	77.99 (18)
O6—Mo2—O8 <sup>ii</sup>	74.22 (17)	O6—Mo4—O13 <sup>iii</sup>	78.74 (17)
O10—Mo3—O11	103.7 (2)	Mo3—O5—Mo2 <sup>iv</sup>	144.1 (3)
O10—Mo3—O5	98.9 (2)	Mo2—O8—Mo2 <sup>iii</sup>	143.3 (3)
O11—Mo3—O5	103.2 (2)	Mo4—O12—Mo3 <sup>iii</sup>	152.7 (3)
O10—Mo3—O7	97.0 (2)	Mo4—O13—Mo4 <sup>ii</sup>	135.0 (3)
O11—Mo3—O7	97.1 (2)		

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

During the least-squares refinement of the crystal structure of (I), the H atoms could not be located in acceptable positions, and so they were not included. After refinement, the highest peak and the deepest hole were located 1.40 and 0.06  $\text{\AA}$  from atoms O8 and Mo4, respectively.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1999); program(s) used to solve structure: *SHELXLTL-NT* (Bruker, 1998); program(s) used to refine structure: *SHELXLTL-NT*; molecular graphics: *SHELXLTL-NT*; software used to prepare material for publication: *SHELXLTL-NT*.

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