

Poly[tetrakis(4-aminopyridinium) [hexadeca- $\mu$ -oxo-decaoxooctamolybdate(VI)]]James R. Nelson,<sup>a</sup> Amy Narducci Sarjeant<sup>b</sup> and Alexander J. Norquist<sup>a\*</sup><sup>a</sup>Department of Chemistry, Haverford College, 370 Lancaster Avenue, Haverford, PA 19041, USA, and <sup>b</sup>Department of Chemistry, Johns Hopkins University, Baltimore, MD 21218, USA

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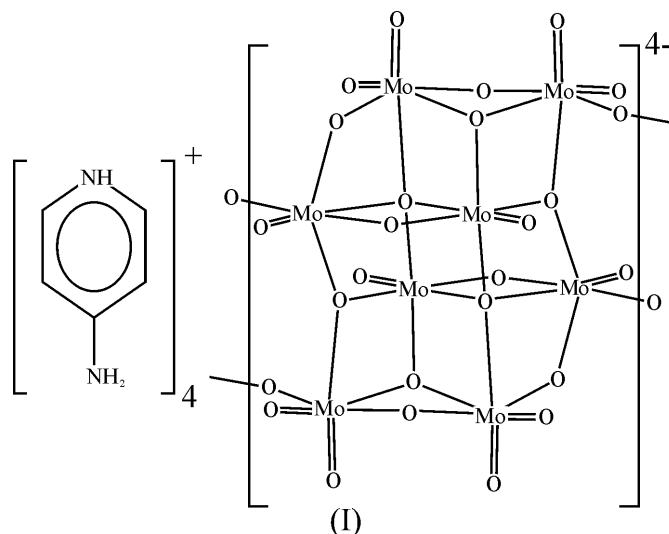
## Key indicators

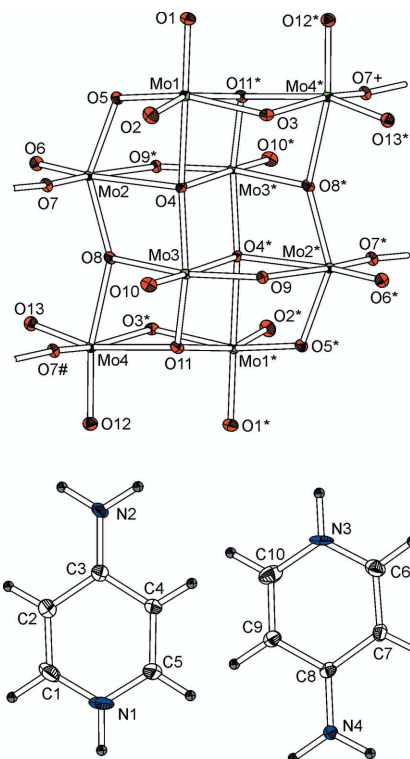
Single-crystal X-ray study  
 $T = 110$  K  
Mean  $\sigma(\text{C}-\text{C}) = 0.007$  Å  
 $R$  factor = 0.022  
 $wR$  factor = 0.047  
Data-to-parameter ratio = 11.4For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.The title compound,  $\{(\text{C}_5\text{H}_7\text{N}_2)_4[\text{Mo}_8\text{O}_{26}]\}_n$ , contains extended  $[\text{Mo}_8\text{O}_{26}]_n^{4n-}$  chains, built up from distorted  $\text{MoO}_6$  octahedra sharing vertices and edges. A network of  $\text{N}-\text{H} \cdots \text{O}$  hydrogen bonds helps to stabilize the crystal packing.

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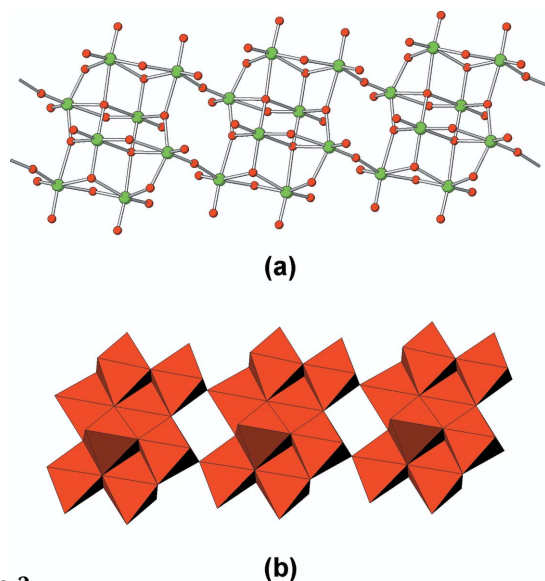
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## Comment

The chemistry of polyoxomolybdate anions has been the focus of intense research for many years owing to a presence of a host of desirable physical properties associated with compounds containing such groupings. These materials are generally constructed from  $[\text{MoO}_x]$  polyhedra that share common edges and vertices with one another, forming large anionic architectures. Special attention has been focused upon octamolybdates owing to their great structural diversity. Compounds containing both a range of molecular (Lindqvist, 1950) and extended (Böschchen *et al.*, 1974) octamolybdate anions are well known. These compounds often include organic amines, which can act as charge-balancers, structure directors and hydrogen-bond donors (Cruywagen, 2000).Our interest in polyoxomolybdates is focused upon the relationship between the structure of the organic amine and the resulting solid. In order to elucidate the factors governing this relationship, a wide range of organic amines has been used under diverse reaction conditions (Gutnick *et al.*, 2004; Muller, Cannon *et al.*, 2005; Muller, Narducci Sarjeant & Norquist, 2005; Thorn *et al.*, 2005; Nelson *et al.*, 2006; Veltman *et al.*, 2006). As a continuation of these studies, the title compound, (I), was synthesized under mild hydrothermal conditions; it contains extended  $[\text{Mo}_8\text{O}_{26}]_n^{4n-}$  chains.

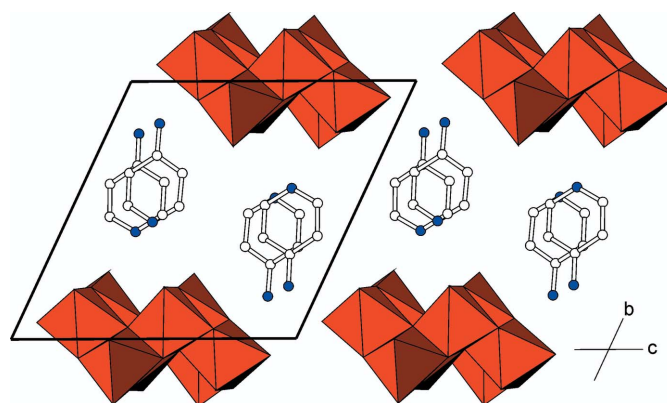

**Figure 1**

The asymmetric unit of (I), together with additional atoms to complete the octamolybdate unit and its connections with other units, with displacement ellipsoids drawn at the 50% probability level (spheres of arbitrary radius for the H atoms). Atoms labeled with a hash (#), plus (+) or asterisk (\*) are at the symmetry positions  $(-x, -y, 1-z)$ ,  $(1+x, y, z)$  or  $(1-x, -y, 1-z)$ , respectively.


**Figure 2**

The  $[\text{Mo}_8\text{O}_{26}]_n^{4-}$  chains in (I), shown in both (a) ball-and-stick and (b) polyhedral representations.

Four crystallographically distinct molybdenum centers are observed in (I). The  $\text{Mo}^{\text{VI}}\text{O}_6$  octahedra are typically distorted as a result of the second-order Jahn–Teller activity of  $\text{Mo}^{\text{VI}}$  (Kunz & Brown, 1995). Both bridging ( $\text{O}_b$ ) and terminal ( $\text{O}_t$ ) oxo ligands are observed. The  $\text{Mo}-\text{O}_t$  bonds [1.693 (3)–


**Figure 3**

The packing of (I). Red octahedra represent  $[\text{MoO}_6]$  groups. H atoms have been omitted for clarity.

1.712 (3) Å] are shorter than the  $\text{Mo}-\text{O}_b$  bonds [1.777 (3)–2.373 (3) Å] (Fig. 1).

The infinite  $[\text{Mo}_8\text{O}_{26}]_n^{4n-}$  chains are generated through inversion symmetry. This chain connectivity has been observed previously (Chakrabarti & Natarajan, 2002; Fang *et al.*, 2004; Thorn *et al.*, 2005) (Fig. 2). The chains propagate along [100] (Fig. 3).

Two unique  $[\text{C}_5\text{H}_7\text{N}_2]^+$  cations are present in (I); only the pyridine N atom in each 4-aminopyridine molecule is protonated. These cations reside between the  $[\text{Mo}_8\text{O}_{26}]_n^{4n-}$  chains, and act as both charge-balancers and  $\text{N}-\text{H}\cdots\text{O}$  hydrogen-bond donors (Table 2). Aromatic  $\pi-\pi$  stacking interactions between the cations are observed along [100] at a distance of 3.662 (3) Å.

## Experimental

A mixture of  $\text{MoO}_3$  (0.4637 g, 3.221 mmol), 4-aminopyridine (0.0712 g, 0.757 mmol),  $\text{H}_2\text{SO}_4$  (0.1968 g, 2.008 mmol) and deionized water (6.2327 g, 0.346 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  $\text{h}^{-1}$ . The vessel was opened in air and the reaction products were recovered by filtration.

### Crystal data

$4\text{C}_5\text{H}_7\text{N}_2^+ \cdot \text{Mo}_8\text{O}_{26}^{4-}$   
 $M_r = 1564.00$   
 Triclinic,  $P\bar{1}$   
 $a = 7.7680$  (18) Å  
 $b = 11.923$  (2) Å  
 $c = 12.208$  (4) Å  
 $\alpha = 63.03$  (2)°  
 $\beta = 74.37$  (2)°  
 $\gamma = 79.220$  (17)°

$V = 967.7$  (5) Å<sup>3</sup>  
 $Z = 1$   
 $D_x = 2.684$  Mg  $\text{m}^{-3}$   
 Mo  $K\alpha$  radiation  
 $\mu = 2.61$  mm<sup>-1</sup>  
 $T = 110$  K  
 Block, colorless  
 $0.07 \times 0.04 \times 0.02$  mm

### Data collection

Oxford Diffraction Xcalibur3 diffractometer  
 $\omega$  scans  
 Absorption correction: multi-scan (DENZO/SCALEPACK; Otwinowski & Minor, 1997)  
 $T_{\text{min}} = 0.88$ ,  $T_{\text{max}} = 0.95$

10827 measured reflections  
 5089 independent reflections  
 3196 reflections with  $I > 3\sigma(I)$   
 $R_{\text{int}} = 0.0209$   
 $\theta_{\text{max}} = 29.1^\circ$

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.022$   
 $wR(F^2) = 0.047$   
 $S = 0.88$   
 3196 reflections  
 281 parameters  
 H-atom parameters constrained  
 $w = [1 - (F_o - F_c)^2/36\sigma^2(F)]^2 /$   
 $[5110T_o(x) - 6330T_1(x) +$   
 $5870T_2(x) - 2030T_3(x) +$   
 $891T_4(x)]$

where  $T_i$  are the Chebyshev  
 polynomials and  $x = F_c/F_{max}$   
 (Prince, 1982; Watkin, 1994)  
 $(\Delta/\sigma)_{max} < 0.001$   
 $\Delta\rho_{max} = 0.78 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{min} = -0.71 \text{ e } \text{Å}^{-3}$   
 Extinction correction: Larson  
 (1970)  
 Extinction coefficient: 3.2 (7)

Table 1

Selected bond lengths (Å).

Mo1—O1	1.712 (3)	Mo3—O4	1.943 (3)
Mo1—O2	1.693 (3)	Mo3—O4 <sup>i</sup>	2.373 (3)
Mo1—O3	1.936 (3)	Mo3—O8	2.147 (3)
Mo1—O4	2.204 (3)	Mo3—O9	1.777 (3)
Mo1—O5	1.994 (3)	Mo3—O10	1.696 (3)
Mo1—O11 <sup>i</sup>	2.314 (3)	Mo3—O11	1.875 (3)
Mo2—O4	2.261 (3)	Mo4—O3 <sup>i</sup>	1.918 (3)
Mo2—O5	1.886 (3)	Mo4—O7 <sup>ii</sup>	2.029 (3)
Mo2—O6	1.701 (3)	Mo4—O8	2.187 (3)
Mo2—O7	1.785 (3)	Mo4—O11	2.260 (3)
Mo2—O8	1.899 (3)	Mo4—O12	1.709 (3)
Mo2—O9 <sup>i</sup>	2.228 (3)	Mo4—O13	1.702 (3)

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

Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1 <sup>i</sup> ···O10	1.00	2.04	2.859 (5)	138
N1—H1 <sup>i</sup> ···O13 <sup>ii</sup>	1.00	2.15	2.854 (5)	126
N2—H6 <sup>i</sup> ···O1 <sup>iii</sup>	1.00	1.88	2.861 (5)	165
N2—H7 <sup>i</sup> ···O11 <sup>iv</sup>	1.00	1.95	2.932 (5)	166
N3—H8 <sup>i</sup> ···O3 <sup>v</sup>	1.00	2.25	2.934 (5)	125
N3—H8 <sup>i</sup> ···O9 <sup>v</sup>	1.00	2.26	2.955 (5)	125
N4—H13 <sup>i</sup> ···O12 <sup>vi</sup>	1.00	2.05	3.004 (5)	158
N4—H14 <sup>i</sup> ···O5 <sup>i</sup>	1.00	1.87	2.867 (5)	174

Symmetry codes: (i)  $-x + 1, -y, -z + 1$ ; (ii)  $-x, -y, -z + 1$ ; (iii)  $-x + 1, -y + 1, -z$ ; (iv)  $-x, -y + 1, -z + 1$ ; (v)  $-x + 1, -y + 1, -z + 1$ ; (vi)  $-x, -y, -z + 2$ .

H atoms were positioned geometrically after each cycle in idealized locations ( $C-H = 1.00-1.01 \text{ Å}$  and  $N-H = 1.00 \text{ Å}$ ) and refined as riding on their carrier atoms, with  $U_{iso}(H) = 1.2U_{eq}(\text{carrier atom})$ .

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2004); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2004); data reduction: *CrysAlis RED*; 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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