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Poly[bis(4-aminopyridinium) decaoxotrimolybdate(VI)]

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Key indicators

Single-crystal X-ray study
T = 110 K
Mean σ(C–C) = 0.005 Å
R factor = 0.022
wR factor = 0.046
Data-to-parameter ratio = 14.1

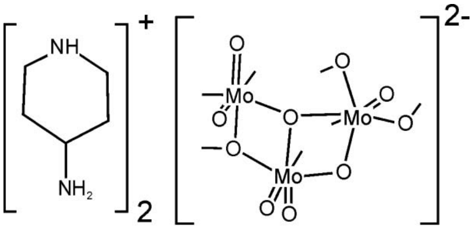
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The hydrothermally synthesized title compound, $\{(C_5H_7N_2)_2[Mo_3O_{10}]\}_n$, contains $[Mo_3O_{10}]_n^{2n-}$ chains, which are generated through inversion symmetry. An extensive N—H···O hydrogen-bonding network is observed between the $C_5H_7N_2^+$ cations and the chains.

Comment

The chemistry of polyoxometalates has been studied extensively owing to a host of desirable physical properties that compounds containing such anions can exhibit. The diverse structural chemistry of polyoxometalates containing molybdenum is well known in the literature, with compounds containing inorganic components whose dimensionalities range between zero and three (Hagrman *et al.*, 1999; Jiang *et al.*, 1999; Cruywagen, 2000) being common.

Compounds containing polyoxomolybdates are often formed under mild hydrothermal conditions (Laudise, 1987) in the presence of organic amines, which can act as charge balancers, structure directors and hydrogen-bond donors (*e.g.* Cruywagen, 2000). Our interest in these materials is focused on 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, Sarjeant *et al.*, 2005; Thorn *et al.*, 2005). This work has been extended through the use of 4-aminopyridine, resulting in the formation of the title compound, $\{(C_5H_7N_2)_2[Mo_3O_{10}]\}_n$, (I).



(I)

The $[Mo_3O_{10}]_n^{2n-}$ chains present in (I) (Figs. 1 and 2) exhibit the same connectivity as in previously reported species (Khan *et al.*, 1993; Guillou & Ferey, 1997). Similar $[WO_3]_n^{2n-}$ chains have also been reported (Yan *et al.*, 2000). Three crystallographically distinct molybdenum centers are present in (I). The complete chains are generated by inversion symmetry. Each Mo^{VI} cation exhibits second-order Jahn–Teller activity (Kunz & Brown, 1995) and resides in a distorted coordination octahedron (Table 1). Both bridging (O_b) and

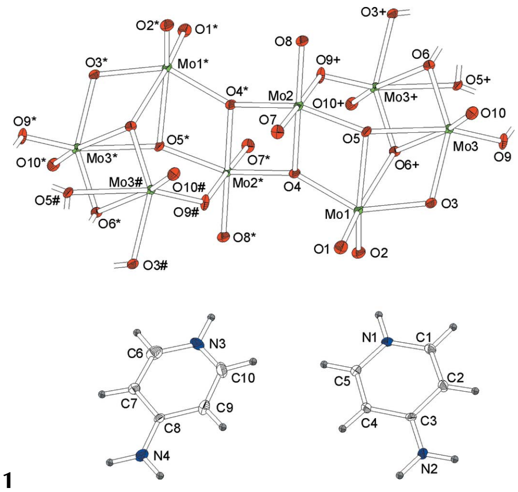


Figure 1
Part of the polymeric structure of (I), with displacement ellipsoids drawn at the 50% probability level. Atoms labeled with a hash (#), plus sign (+) or asterisk (*) are at the symmetry positions (1 + *x*, *y*, *z*), (1 − *x*, −*y*, 2 − *z*) and (2 − *x*, −*y*, 2 − *z*), respectively.

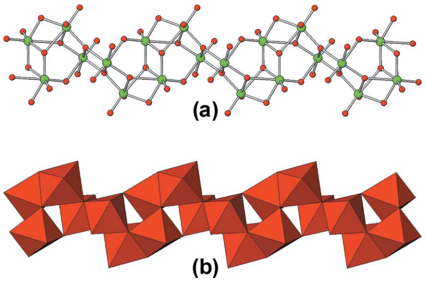


Figure 2
$[Mo_3O_{10}]_n^{2n-}$ chains in (I), shown in both (*a*) ball-and-stick and (*b*) polyhedral representations.

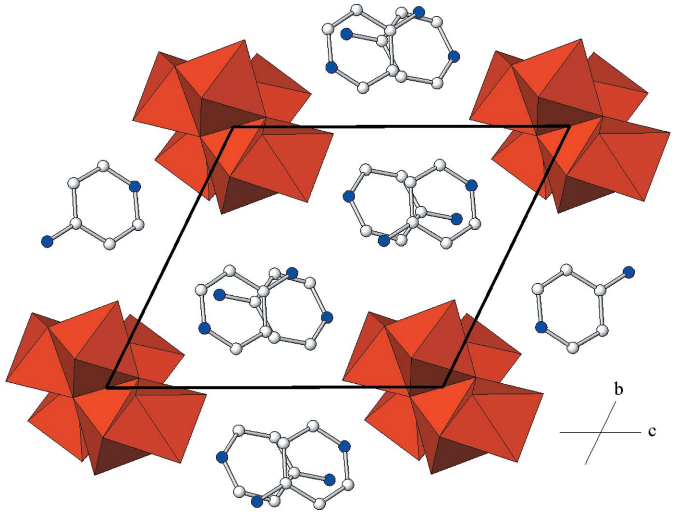


Figure 3
Three-dimensional packing of (I). Red octahedra represent $[MoO_6]$ groups. H atoms have been omitted for clarity.

terminal (O_t) oxo ligands are observed. The Mo—O_t bonds [1.700 (2) − 1.720 (2) Å] are shorter than the Mo—O_b bonds [1.852 (2) − 2.424 (2) Å]. The chains propagate along [100] (Fig. 3).

Two unique organic cations are present in (I); only the pyridine N atom in each 4-aminopyridine molecule is protonated, resulting in the formation of $C_5H_7N_2^+$ ions. These cations reside between the molybdate chains and interact with them by way of N—H⋯O hydrogen bonds (Table 2). Each cation donates three hydrogen bonds to neighboring oxo ligands on the $[Mo_3O_{10}]_n^{2n-}$ chains, forming an extensive hydrogen-bonding network. Aromatic π–π stacking interactions between the cations are observed along the *a* axis.

Experimental

MoO_3 (0.0843 g, 0.583 mmol), 4-aminopyridine (0.3236 g, 3.443 mmol), H_2SO_4 (0.2129 g, 2.127 mmol) and deionized water (0.5191 g, 0.028 mol) were 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 h^{-1}. The vessel was opened in air and the reaction products were recovered by filtration.

Crystal data

$(C_5H_7N_2)_2[Mo_3O_{10}]$
$M_r = 638.06$
Triclinic, $P\overline{1}$
$a = 8.045$ (3) Å
$b = 10.376$ (5) Å
$c = 11.538$ (4) Å
$\alpha = 65.05$ (4)°
$\beta = 89.94$ (3)°
$\gamma = 72.91$ (3)°
$V = 826.3$ (7) Å^3
$Z = 2$
$D_x = 2.565$ Mg m^{-3}
Mo *Kα* radiation
$\mu = 2.31$ mm^{-1}
$T = 110$ (2) K
Needle, colorless
0.22 × 0.10 × 0.07 mm

Data collection

Oxford Diffraction CrysAlis CCD diffractometer
ω scans
Absorption correction: analytical multifaceted crystal model (Clark & Reid, 1995)
$T_{min} = 0.76$, $T_{max} = 0.85$
11942 measured reflections
5309 independent reflections
3432 reflections with $I > 3\sigma(I)$
$R_{int} = 0.02$
$\theta_{max} = 32.2$°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.022$
$wR(F^2) = 0.046$
$S = 0.86$
3432 reflections
244 parameters
H-atom parameters constrained
$w = [1 - (F_o - F_c)^2/36\sigma^2(F)]^2/[(1.76 \times 10^4)T_o(x) - (2.27 \times 10^4)T_1(x) + (2.15 \times 10^4)T_2(x) - (7.68 \times 10^3)T_3(x) + (4.06 \times 10^3)T_4(x)]$, where T_i are the Chebychev polynomials and $x = F_c/F_{max}$ (Prince, 1982; Watkin, 1994)
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.56$ e Å^{-3}
$\Delta\rho_{min} = -0.55$ e Å^{-3}

Table 1
Selected bond lengths (Å).

Mo1—O1	1.709 (2)	Mo2—O7	1.700 (2)
Mo1—O2	1.713 (2)	Mo2—O8	1.720 (2)
Mo1—O3	1.931 (2)	Mo2—O9^{i}	2.424 (2)
Mo1—O4	1.938 (2)	Mo3—O3	1.990 (2)
Mo1—O5	2.247 (2)	Mo3—O5	2.280 (2)
Mo1—O6^{i}	2.358 (2)	Mo3—O6	1.852 (2)
Mo2—O4	2.188 (2)	Mo3—O6^{i}	2.258 (2)
Mo2—O4^{ii}	2.002 (2)	Mo3—O9	1.735 (2)
Mo2—O5	1.877 (2)	Mo3—O10	1.708 (2)

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

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N1—H1⋯O6^{i}	1.00	1.96	2.877 (3)	151
N2—H6⋯O3^{iii}	1.00	1.97	2.967 (4)	173
N2—H7⋯O1^{iv}	1.00	2.05	3.043 (4)	172
N3—H8⋯O3^{iv}	1.00	1.99	2.883 (4)	148
N4—H13⋯O8^{ii}	1.00	2.00	2.997 (4)	173
N4—H14⋯O10^{v}	1.00	2.19	2.864 (4)	124

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

H atoms were positioned geometrically after each cycle in idealized locations and refined as riding on their carrier atoms [C—H = 1.00 Å and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(carrier atom)]. The highest residual electron density peak is 0.95 Å from N2.

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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