(C$_4$H$_{14}$N$_2$)$_2$[Mo$_8$O$_{26}$]·2H$_2$O: a new molybdate salt

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Crystals of the title compound, 2-(dimethylammonio)-ethanaminium hexacosaoxaoctamolybdate(VI) dihydrate, containing extended chains constructed from centrosymmetric octamolybdate anions, were grown under mild hydrothermal conditions in the presence of N,N-dimethylethylenediamine. An extensive hydrogen-bonding network helps stabilize the crystal structure.

Comment

The chemistry of polyoxomolybdates has been the focus of intense research for many years, owing to their many desirable physical properties. These materials are generally constructed from [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 the presence of several structure types, from the initial report (Lindqvist, 1950) to more recent times (Yan *et al.*, 2003). A series of molecular anions are known which exhibit different forms, the α (Hsieh *et al.*, 1987), β (Harrison *et al.*, 1993), δ (Rarig & Zubieta, 2001) and γ (Niven *et al.*, 1991) forms being the most common. However, octamolybdates are not limited to molecular molybdate anions with associated cations; several compounds that contain extended chains have been reported (Böschen *et al.*, 1974; Chakrabarti & Natarajan, 2002; Xu *et al.*, 2003; Xiao *et al.*, 2005). Our interest in these materials is focused upon molybdate reactions in the presence of both concentrated sulfuric acid and organic amines. A new compound, [C$_4$H$_{14}$N$_2$]$_2$[Mo$_8$O$_{26}$]·2H$_2$O, (I), synthesized in the course of this study, contains infinite [Mo$_8$O$_{26}$]$_n^{2n-}$ chains.

(I)
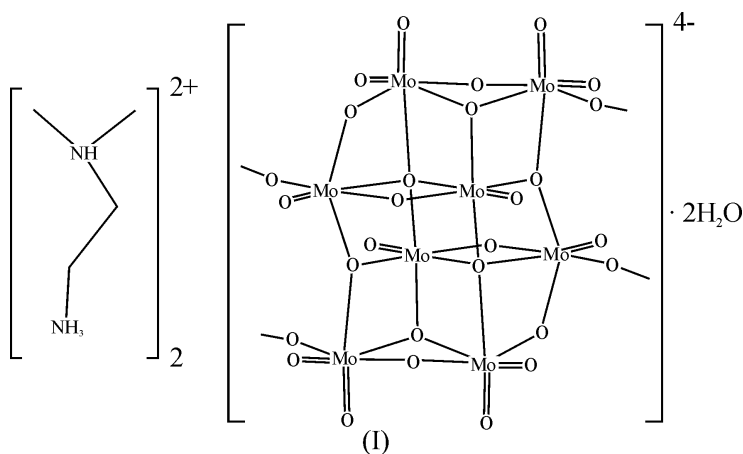
The octamolybdate chains present in (I) (Figs. 1 and 2) are similar to previously reported species (Chakrabarti & Natarajan, 2002; Fang *et al.*, 2004). Four crystallographically distinct
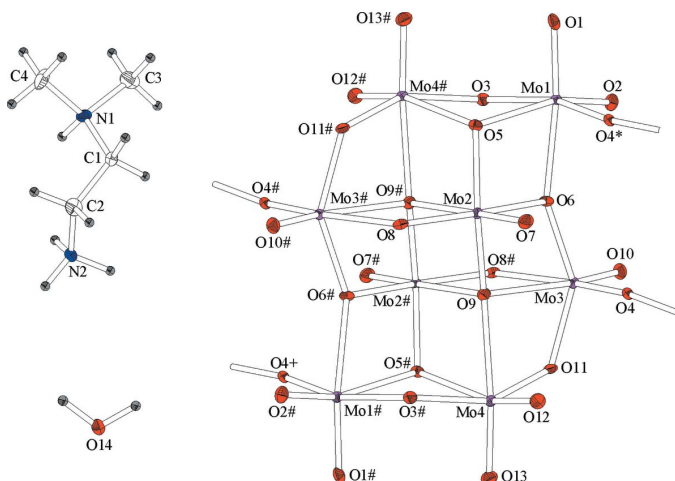
Figure 1
A view of the molecular structure of compound (I), with displacement ellipsoids drawn at the 50% probability level. Atoms labeled with a hash sign (#), plus (+) or asterisk (*) are at the symmetry positions $(2 - x, 1 - y, -z)$, $(1 + x, y, z)$ and $(1 - x, 1 - y, -z)$, respectively.

molybdenum centers are observed and the complete anion is generated by inversion symmetry. Each Mo^{6+} cation resides near to the center of a coordination octahedron. Distinct distortions from the centers of these octahedra are observed, a result of the second-order Jahn–Teller activity of Mo^{6+} (Pearson, 1969; Wheeler *et al.*, 1986; Kunz & Brown, 1995; Halasyamani, 2004). Both bridging (O_b) and terminal (O_t) oxo ligands are observed.

The $Mo-O_t$ bonds [1.692 (4)–1.720 (4) Å] are shorter than the $Mo-O_b$ bonds [1.792 (4)–2.365 (4) Å; Table 1]. Eight $[MoO_6]$ octahedra share both edges and vertices, forming the $[Mo_8O_{26}]_n^{2n-}$ chains.

The extended chains in (I) are located at $(x, 0, \frac{1}{2})$ and run along the a axis (Figs. 2 and 3). $[C_4H_{14}N_2]^{2+}$ cations and occluded water molecules reside between chains (Fig. 2), and participate in an extensive hydrogen-bonding network (Table 2). Each $[C_4H_{14}N_2]^{2+}$ cation donates four hydrogen bonds. The H atom bound to N1 donates a hydrogen bond to molybdate atom O8, while the H atoms bound to N2 donate bonds to O atoms of adjacent chains (O1 and O2) and the occluded water molecule containing O14. This water molecule in turn donates two hydrogen bonds to O atoms of two neighboring chains (both O3). This extensive network helps stabilize the structure.

Experimental

The title compound was synthesized by the addition of MoO_3 (0.5051 g, 3.509×10^{-3} mol), H_2SO_4 (0.0937 g, 9.56×10^{-3} mol), *N,N*-dimethylethylenediamine (0.1390 g, 1.58×10^{-3} mol) and deionized water (1.0323 g, 5.735×10^{-2} mol) to a 23 ml Teflon-lined pressure vessel. The reaction gel was heated at 453 K for 24 h, and then cooled slowly to room temperature over an additional 24 h. The vessel was opened in air and the reaction products were recovered by filtration.
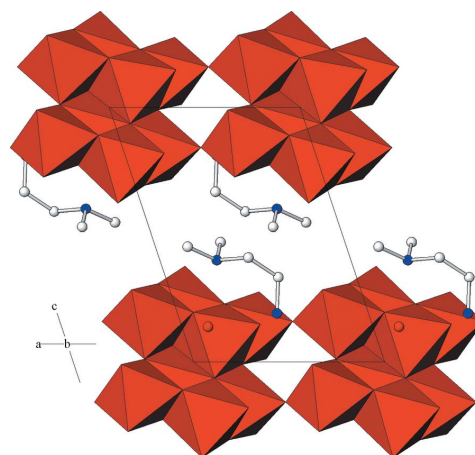
Figure 2
Three-dimensional packing of compound (I). Red octahedra represent $[MoO_6]$. H atoms have been omitted for clarity.
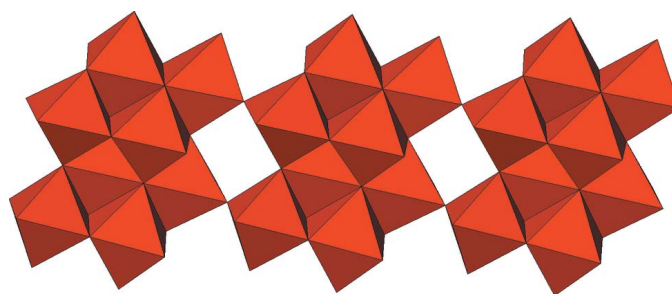
Figure 3
$[Mo_8O_{26}]_n^{2n-}$ chains in compound (I). Red octahedra represent $[MoO_6]$.

Crystal data

$(C_4H_{14}N_2)_2[Mo_8O_{26}]\cdot2H_2O$	$Z = 1$
$M_r = 1399.88$	$D_x = 2.928$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 7.7451$ (9) Å	Cell parameters from 3137
$b = 10.3145$ (10) Å	reflections
$c = 10.8614$ (11) Å	$\theta = 0.6$–9.8°
$\alpha = 79.304$ (8)°	$\mu = 3.16$ mm^{-1}
$\beta = 70.145$ (10)°	$T = 110$ K
$\gamma = 78.793$ (9)°	Rod, colorless
$V = 793.79$ (15) Å^3	$0.18 \times 0.05 \times 0.03$ mm

Data collection

Oxford Diffraction CrysAlis CCD diffractometer	3918 independent reflections
ω scans	2754 reflections with $I > 3\sigma(I)$
Absorption correction: analytical (multifaceted crystal model; Clark & Reid, 1995)	$R_{int} = 0.02$
	$\theta_{max} = 28.3°$
	$h = -10 \rightarrow 9$
$T_{min} = 0.584$, $T_{max} = 0.908$	$k = -13 \rightarrow 13$
7063 measured reflections	$l = -14 \rightarrow 8$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.027$	Weighting scheme: see below
$wR(F^2) = 0.055$	$(\Delta/\sigma)_{max} = 0.001$
$S = 0.90$	$\Delta\rho_{max} = 1.33$ e Å^{-3}
2754 reflections	$\Delta\rho_{min} = -0.91$ e Å^{-3}
217 parameters	

Table 1
Selected geometric parameters (Å, °).

Mo1—O1	1.720 (4)	Mo3—O9	2.275 (4)
Mo1—O2	1.708 (4)	Mo3—O10	1.693 (4)
Mo1—O3	1.939 (4)	Mo3—O11	1.888 (4)
Mo1—O4^i	2.022 (4)	Mo4—O3^{ii}	1.964 (4)
Mo1—O5	2.222 (4)	Mo4—O5^{ii}	2.259 (4)
Mo1—O6	2.154 (3)	Mo4—O9	2.265 (4)
Mo2—O5	1.885 (4)	Mo4—O11	1.965 (4)
Mo2—O6	2.130 (4)	Mo4—O12	1.709 (4)
Mo2—O7	1.692 (4)	Mo4—O13	1.711 (4)
Mo2—O8	1.795 (4)	N1—C1	1.518 (7)
Mo2—O9	1.924 (4)	N1—C3	1.497 (8)
Mo2—O9^{ii}	2.365 (4)	N1—C4	1.482 (7)
Mo3—O4	1.792 (4)	N2—C2	1.504 (7)
Mo3—O6	1.911 (3)	C1—C2	1.501 (8)
Mo3—O8^{ii}	2.190 (3)		

O1—Mo1—O2	104.21 (18)	O8^{ii}—Mo3—O11	81.19 (14)
O1—Mo1—O3	98.01 (16)	O9—Mo3—O10	159.19 (15)
O2—Mo1—O3	96.25 (16)	O9—Mo3—O11	74.12 (15)
O1—Mo1—O4^i	89.90 (16)	O10—Mo3—O11	103.01 (17)
O2—Mo1—O4^i	101.22 (16)	O3^{ii}—Mo4—O5^{ii}	74.17 (14)
O3—Mo1—O4^i	158.45 (16)	O3^{ii}—Mo4—O9	84.15 (14)
O1—Mo1—O5	92.88 (15)	O5^{ii}—Mo4—O9	72.17 (12)
O2—Mo1—O5	162.00 (16)	O3^{ii}—Mo4—O11	152.05 (15)
O3—Mo1—O5	75.48 (14)	O5^{ii}—Mo4—O11	83.48 (13)
O4^i—Mo1—O5	84.16 (14)	O9—Mo4—O11	73.01 (14)
O1—Mo1—O6	160.38 (16)	O3^{ii}—Mo4—O12	95.77 (16)
O2—Mo1—O6	93.86 (16)	O5^{ii}—Mo4—O12	161.23 (16)
O3—Mo1—O6	87.38 (14)	O9—Mo4—O12	91.34 (16)
O4^i—Mo1—O6	78.99 (13)	O3^{ii}—Mo4—O13	99.85 (17)
O5—Mo1—O6	70.12 (13)	O5^{ii}—Mo4—O13	92.35 (15)
O5—Mo2—O6	77.29 (14)	O9—Mo4—O13	162.45 (15)
O5—Mo2—O7	103.89 (17)	O11—Mo4—O12	100.56 (16)
O6—Mo2—O7	99.51 (16)	O11—Mo4—O13	97.59 (16)
O5—Mo2—O8	100.07 (15)	O12—Mo4—O13	105.14 (18)
O6—Mo2—O8	157.90 (14)	Mo1—O3—Mo4^{ii}	113.22 (17)
O7—Mo2—O8	102.40 (17)	Mo1^i—O4—Mo3	172.7 (2)
O5—Mo2—O9	144.12 (15)	Mo1—O5—Mo2	108.59 (16)
O6—Mo2—O9	74.72 (14)	Mo1—O5—Mo4^{ii}	93.33 (13)
O7—Mo2—O9	102.49 (17)	Mo2—O5—Mo4^{ii}	113.08 (16)
O8—Mo2—O9	97.54 (16)	Mo1—O6—Mo2	102.52 (14)
O5—Mo2—O9^{ii}	76.71 (14)	Mo1—O6—Mo3	149.2 (2)
O6—Mo2—O9^{ii}	80.80 (13)	Mo2—O6—Mo3	108.09 (16)
O7—Mo2—O9^{ii}	179.37 (16)	Mo2—O8—Mo3^{ii}	116.38 (17)
O8—Mo2—O9^{ii}	77.27 (14)	Mo2—O9—Mo2^{ii}	102.95 (15)
O9—Mo2—O9^{ii}	77.05 (15)	Mo2—O9—Mo3	102.08 (16)
O4—Mo3—O6	94.84 (15)	Mo2^{ii}—O9—Mo3	93.93 (13)
O4—Mo3—O8^{ii}	168.54 (15)	Mo2—O9—Mo4	154.47 (19)
O6—Mo3—O8^{ii}	81.95 (14)	Mo2^{ii}—O9—Mo4	96.80 (13)
O4—Mo3—O9	96.23 (15)	Mo3—O9—Mo4	92.43 (13)
O6—Mo3—O9	71.56 (14)	Mo3—O11—Mo4	116.54 (18)
O8^{ii}—Mo3—O9	72.30 (13)	C1—N1—C3	109.1 (4)
O4—Mo3—O10	104.57 (18)	C1—N1—C4	111.7 (4)
O6—Mo3—O10	106.49 (17)	C3—N1—C4	111.0 (5)
O8^{ii}—Mo3—O10	86.89 (15)	N1—C1—C2	116.0 (4)
O4—Mo3—O11	95.65 (16)	N2—C2—C1	112.1 (4)
O6—Mo3—O11	144.96 (16)		

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

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O14—H1$\cdots$O3^{ii}	1.00	1.91	2.825 (5)	151
O14—H2$\cdots$O3^{iii}	1.00	1.91	2.835 (5)	153
N1—H3$\cdots$O8	1.00	2.00	2.838 (6)	139
N2—H4$\cdots$O14	1.00	2.05	2.815 (6)	132
N2—H5$\cdots$O2^i	1.00	1.94	2.809 (6)	144
N2—H6$\cdots$O1^{iii}	1.00	2.15	3.036 (6)	147

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

A Chebychev polynomial (Watkin, 1994, Prince, 1982) was used in the weighting scheme, [weight] = $1.0/[A_0T_0(x) + A_1T_1(x) + \cdots + A_{n-1}T_{n-1}(x)]$, where A_i are the Chebychev coefficients 21.5, 18.7, 19.2, 3.32 and 3.23, and $x = F/F_{max}$; robust weighting (Prince, 1982) $W = [weight][1 - (\delta F/6\sigma F)^2]^2$. H atoms were positioned geometrically after each cycle in idealized locations and refined as riding on their carrier atoms, with C—H = 1.0 Å and $U_{iso}(H) = 1.2U_{eq}$(carrier atom). The highest electron-density peak is located 0.7166 (7) Å from atom N2 and the deepest electron-density hole is located 0.7254 (7) Å from Mo4.

Data collection: *CrysAlisCCD* (Oxford Diffraction, 2004); cell refinement: *CrysAlisRED* (Oxford Diffraction, 2004); data reduction: *CrysAlisRED*; 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*.

References

Altomare, A., Cascarano, G., Giacovazzo, G., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.
Betteridge, P. W., Carruthers, J. R., Cooper, R. I., Prout, K. & Watkin, D. J. (2003). *J. Appl. Cryst.* **36**, 1487.
Böschen, V. I., Buss, B. & Krebs, B. (1974). *Acta Cryst.* B**30**, 48–56.
Chakrabarti, S. & Natarajan, S. (2002). *Cryst. Growth Des.* **2**, 333–335.
Clark, R. C. & Reid, J. S. (1995). *Acta Cryst.* A**51**, 887–897.
Dowty, E. (2002). *ATOMS*. Version 6.0. Shape Software, Kingsport, TN, USA.
Fang, R.-Q., Zhang, X.-M., Wu, H.-S. & Ng, S. W. (2004). *Acta Cryst.* E**60**, m359–m361.
Halasyamani, P. S. (2004). *Chem. Mater.* **16**, 3586–3592.
Harrison, W. T. A., Stucky, G. D. & Gier, T. E. (1993). *Acta Cryst.* C**49**, 1900–1902.
Hsieh, T.-C., Shaikh, S. N. & Zubieta, J. (1987). *Inorg. Chem.* **26**, 4079–4089.
Kunz, M. & Brown, I. D. (1995). *J. Solid State Chem.* **115**, 395–406.
Lindqvist, I. (1950). *Ark. Kemi.* **3**, 349–355.
Niven, M. L., Cruywagen, J. J. & Heyns, J. B. B. (1991). *J. Chem. Soc. Dalton Trans.* pp. 2007–2010.
Oxford Diffraction (2004). *CrysAlisCCD* and *CrysAlisRED*. Oxford Diffraction Ltd., Abingdon. England.
Pearson, R. G. (1969). *J. Am. Chem. Soc.* **91**, 4947–4955.
Prince, E. (1982). *Mathematical Techniques in Crystallography and Materials Science.* New York: Springer-Verlag.
Rarig, R. S. & Zubieta, J. (2001). *Inorg. Chim. Acta*, **312**, 188–196.
Watkin, D. J. (1994). *Acta Cryst.* A**50**, 411–437.
Wheeler, R. A., Whangbo, M. H., Hughbanks, T., Hoffmann, R., Burdett, J. K. & Albright, T. A. (1986). *J. Am. Chem. Soc.* **108**, 2222–2236.
Xiao, D., An, H., Wang, E. & Xu, L. (2005). *J. Mol. Struct.* **738**, 217–225.
Xu, L., Qin, C., Wang, X., Wei, Y. & Wang, E. (2003). *Inorg. Chem.* **42**, 7342–7344.
Yan, Y., Wu, C.-D., Liu, J.-H., Zhang, Q.-Z. & Lu, C.-Z. (2003). *Acta Cryst.* E**59**, m102–m104.