Bis(1,4-Diazoniabicyclo[2.2.2]octane) octamolybdate(VI) tetrahydrate

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The anionic entity in the title octamolybdate, $(C_6H_{14}N_2)_2[Mo_8O_{26}]\cdot4H_2O$, has a chain structure in which the $[Mo_8O_{26}]^{4-}$ units share terminal O atoms. The O atoms in the chain are two-, three- and four-coordinate. The anionic unit occupies a special position of $\bar{1}$ site symmetry and the Mo^{VI} atoms are all octahedrally coordinated.

Comment

Octamolybdates are generally isolated as discrete clusters having MoO_4, MoO_5 and/or MoO_6 polyhedra; occasionally, the anions are linked together in a polymeric structure (Böschen *et al.*, 1974; Gatehouse & Leverett, 1970). To date, some six different octamolybdate cluster types are known and the manner in which the MoO_x polyhedra are linked together is well understood (Hagrman *et al.*, 1999). For their synthesis, the octamolybdates require the use of a structure-directing reagent; with 1,6-hexanediamine as the agent, the resulting octamolybdate, interestingly, has all the Mo atoms in octahedral environments (Xu *et al.*, 1996). The anions are linked into a chain, and it can be viewed either as an oxygen-sharing $[Mo_8O_{28}]^{8-}$ cluster or as a self-aggregation of γ-octamolybdate clusters. The features of the chain are described in detail in that report.

The use of triethylenediamine in place of 1,6-hexanediamine affords the corresponding title octamolybdate, $2C_6H_{14}N_2^{2+}\cdot[Mo_8O_{26}]^{4-}\cdot4H_2O$, (I) (Fig. 1), the anionic unit of which adopts a chain structure (Fig. 2), with the octamolybdate unit on a special position of $\bar{1}$ site symmetry. The structure of (I) is stabilized by extensive hydrogen bonding (Table 2).

(I)
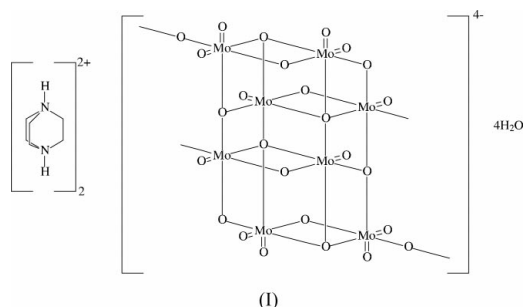
Experimental

Molybdenum trioxide (0.143 g, 1 mmol), triethylenediamine (0.784 g, 0.7 mmol) and water (6 ml) were placed in a 15 ml Teflon-lined stainless-steel bomb, which was then heated at 433 K for 108 h. The bomb was cooled slowly to room temperature and colourless block-like crystals of (I) were isolated in about 45% yield. CHN analysis,
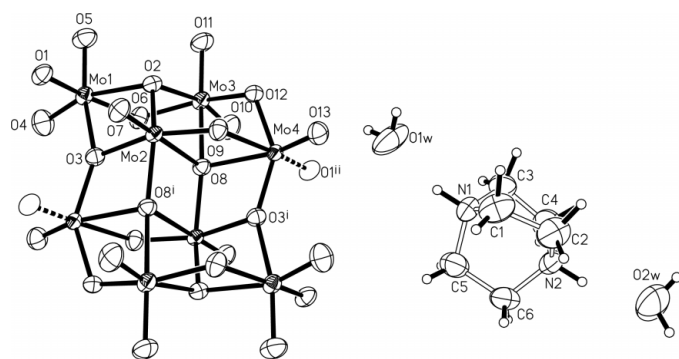
Figure 1
The asymmetric unit of (I), together with the centrosymmetrically-generated other half of the octamolybdate unit, showing the atom-numbering scheme and displacement ellipsoids drawn at the 75% probability level. H atoms are drawn as spheres of arbitrary radii. [Symmetry codes: (i) $-x$, $1 - y$, $1 - z$; (ii) $1 + x$, y, z.]
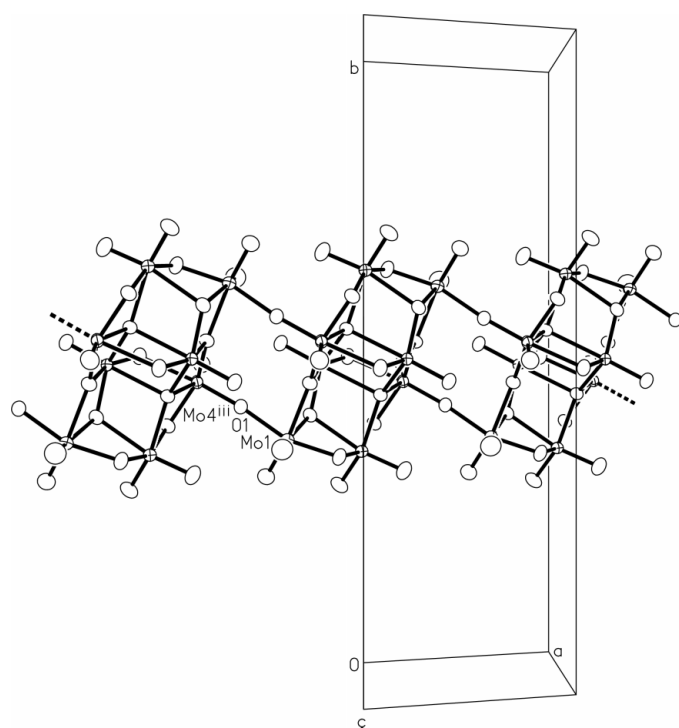

Figure 2
A view of the polyanionic $[Mo_8O_{26}]^{4-}$ chain. [Symmetry code: (iii) $x - 1$, y, z.]

found: C 9.63, H 2.49, N 3.72%; calculated for $C_{12}H_{36}N_4O_{30}Mo_8$: C 9.59, H 2.53, N 3.68%.

Crystal data

$(C_6H_{14}N_2)_2[Mo_8O_{26}]\cdot4H_2O$
$M_r = 1483.97$
Monoclinic, $P2_1/n$
$a = 7.8880\ (3)$ Å
$b = 22.9733\ (9)$ Å
$c = 10.3234\ (4)$ Å
$\beta = 111.704\ (1)°$
$V = 1738.1\ (1)$ Å^3
$Z = 2$

$D_x = 2.835$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 8568 reflections
$\theta = 2.3$–27.0°
$\mu = 2.90$ mm^{-1}
$T = 298\ (2)$ K
Block, colourless
$0.42 \times 0.33 \times 0.15$ mm

Data collection

Bruker APEX CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)
$T_{min} = 0.437$, $T_{max} = 0.670$
8501 measured reflections

2925 independent reflections
2885 reflections with $I > 2\sigma(I)$
$R_{int} = 0.017$
$\theta_{max} = 25.0°$
$h = -9 \rightarrow 8$
$k = -27 \rightarrow 27$
$l = -10 \rightarrow 12$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.021$
$wR(F^2) = 0.054$
$S = 1.06$
2925 reflections
244 parameters
H-atom parameters constrained

$w=1/[\sigma^2(F_o^2) + (0.0248P)^2 + 5.4418P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.13$ e Å^{-3}
$\Delta\rho_{min} = -0.64$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Mo1—O1	2.051 (2)	Mo2—O3	2.153 (3)
Mo1—O2	2.319 (2)	Mo3—O6	1.921 (3)
Mo1—O3	2.153 (2)	Mo3—O8	2.228 (2)
Mo1—O4	1.692 (3)	Mo3—O10	1.710 (3)
Mo1—O5	1.707 (3)	Mo3—O11	1.719 (3)
Mo1—O6	1.928 (2)	Mo3—O12	1.985 (3)
Mo2—O2	1.867 (2)	Mo4—O1^{ii}	1.782 (2)
Mo2—O7	1.692 (3)	Mo4—O3^{i}	1.896 (2)
Mo2—O8	2.433 (2)	Mo4—O8	2.228 (3)
Mo2—O8^{i}	1.964 (2)	Mo4—O9	2.226 (2)
Mo2—O9	1.774 (3)	Mo4—O12	1.896 (2)
Mo3—O2	2.279 (2)	Mo4—O13	1.699 (3)
O1—Mo1—O2	85.1 (1)	O6—Mo3—O12	153.1 (1)
O1—Mo1—O3	77.8 (1)	O8—Mo3—O10	92.0 (1)
O1—Mo1—O4	101.2 (1)	O8—Mo3—O11	160.3 (1)
O1—Mo1—O5	90.1 (1)	O8—Mo3—O12	72.5 (1)
O1—Mo1—O6	157.3 (1)	O10—Mo3—O11	104.3 (1)
O2—Mo1—O3	68.5 (1)	O10—Mo3—O12	100.6 (1)
O2—Mo1—O4	160.8 (1)	O11—Mo3—O12	93.3 (1)
O2—Mo1—O5	92.9 (1)	O1^{ii}—Mo4—O3^{i}	97.2 (1)
O2—Mo1—O6	73.4 (1)	O1^{ii}—Mo4—O8	98.8 (1)
O3—Mo1—O4	94.9 (1)	O1^{ii}—Mo4—O9	171.1 (1)
O3—Mo1—O5	158.3 (1)	O1^{ii}—Mo4—O12	95.6 (1)
O3—Mo1—O6	87.5 (1)	O1^{ii}—Mo4—O13	104.2 (1)
O4—Mo1—O5	105.1 (1)	O3^{i}—Mo4—O8	72.8 (1)
O4—Mo1—O6	97.1 (1)	O3^{i}—Mo4—O9	82.2 (1)
O5—Mo1—O6	98.1 (1)	O3^{i}—Mo4—O12	146.0 (1)
O2—Mo2—O3	77.3 (1)	O3^{i}—Mo4—O13	105.2 (1)
O2—Mo2—O7	104.2 (1)	O8—Mo4—O9	72.5 (1)
O2—Mo2—O8	77.1 (1)	O8—Mo4—O12	74.1 (1)
O2—Mo2—O8^{i}	143.0 (1)	O8—Mo4—O13	156.9 (1)
O2—Mo2—O9	101.2 (1)	O9—Mo4—O12	80.4 (1)
O3—Mo2—O7	100.4 (1)	O9—Mo4—O13	84.4 (1)
O3—Mo2—O8	80.7 (1)	O12—Mo4—O13	101.9 (1)
O3—Mo2—O8^{i}	73.3 (1)	Mo1—O1—Mo4^{iii}	172.7 (2)
O3—Mo2—O9	156.1 (1)	Mo1—O2—Mo2	108.4 (1)
O7—Mo2—O8	178.4 (1)	Mo1—O2—Mo3	91.6 (1)
O7—Mo2—O8^{i}	102.7 (1)	Mo2—O2—Mo3	112.4 (1)
O7—Mo2—O9	103.1 (1)	Mo1—O3—Mo2	104.5 (1)
O8—Mo2—O8^{i}	76.5 (1)	Mo1—O3—Mo4^{i}	147.7 (1)
O8—Mo2—O9	75.7 (1)	Mo2—O3—Mo4^{i}	107.7 (1)
O8^{i}—Mo2—O9	96.8 (1)	Mo1—O6—Mo3	117.8 (1)
O2—Mo3—O6	74.5 (1)	Mo2—O8—Mo4	94.4 (1)
O2—Mo3—O8	74.1 (1)	Mo2—O8—Mo2^{i}	103.5 (1)
O2—Mo3—O10	163.9 (1)	Mo2—O8—Mo4	95.5 (1)
O2—Mo3—O11	91.0 (1)	Mo2^{i}—O8—Mo3	153.3 (1)
O2—Mo3—O12	83.2 (1)	Mo2^{i}—O8—Mo4	102.4 (1)
O6—Mo3—O8	87.0 (1)	Mo2—O9—Mo4	117.2 (1)
O6—Mo3—O10	97.2 (1)	Mo3—O8—Mo4	94.5 (1)
O6—Mo3—O11	101.7 (1)	Mo3—O12—Mo4	115.0 (1)

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

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1W—H1W1···O13	0.85	2.01	2.819 (4)	161
O1W—H1W2···O12^i	0.86	2.13	2.946 (4)	159
O2W—H2W1···O10^{ii}	0.86	1.96	2.788 (4)	161
O2W—H2W2···O11^{iii}	0.88	2.03	2.908 (5)	175
N1—H1···O1W	0.91	1.75	2.636 (5)	163
N2—H2···O2W	0.91	1.81	2.682 (5)	161

Symmetry codes: (i) $-x, 1-y, -z$; (ii) $\frac{3}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; (iii) $1-x, 1-y, -z$.

The H atoms of the cation were placed at calculated positions [C—H = 0.97 Å and $U_{iso}(H) = 1.2U_{eq}(C)$] in the riding-nstrmodel approximation. The water H atoms could not be located; they were found using the *HYDROGEN* option (Nardelli, 1999) in the *WinGX* package (Farrugia, 1999) but were not refined. For these four H atoms, $U_{iso}(H)$ was set to $1.2U_{eq}(O)$. In the final difference Fourier map, the largest peak was about 1 Å from the O2W atom.

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*97.

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