Ethylenediammonium disulfidodecamolybdate(VI)

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The title compound, $(C_2H_{10}N_2)[MoO_{10}S_2]$, consists of $[MoO_2(SO_4)_2]^{2-}$ chains linked to $[H_3NCH_2CH_2NH_3]^{2+}$ ions, both of which have twofold symmetry. The Mo^{VI} atom is octahedrally surrounded by four sulfate O atoms and two terminal O atoms. The μ_2-O atom connects the MoO_6 octahedra and the SO_4 tetrahedra to form a ring, which extends to form a one-dimensional chain along c.

Comment

Polyoxometalates are of continuing interest in important areas of chemistry, involving diverse compositional range and considerable structural versatility (Pope, 1983; Pope & Müller, 1991, 1994), as well as important magnetic (Clemente-Juan *et al.*, 1999), optical and catalytic properties (Pope, 1983; Pope & Müller, 1991, 1994). Previous studies revealed that sulfate ions react with molybdate to produce many heteropolyanions, such as $[S_2Mo_{18}O_{62}]^{4-}$ and $[S_2Mo_5O_{23}]^{4-}$ (Hori *et al.*, 1989, 1992), α-$[H_3S_2Mo_{18}O_{62}]^{5-}$ (Neier *et al.*, 1995) and $[SMo_{12}O_{40}]^{2-}$ (Hori *et al.*, 1996). However, $[MoO_2(SO_4)_2]^{2-}$ associated with an organic cation is rare.

(I)
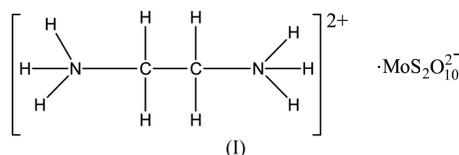
In the title compound, (I), the cation $[MoO_2(SO_4)_2]^{2-}$ is constructed from MoO_6 octahedra and SO_4 tetrahedra, which are joined together *via* shared corners into a one-dimensional chain along c (Fig. 1). The $[H_3N(CH_2)_2NH_3]^{2+}$ cations are located between the chains, on twofold axes (Fig. 2). The Mo atom lies on a twofold axis, and the repeat unit of the chain in (I) is $Mo_{0.5}O(SO_4)$. In the unit of $[MoO_2(SO_4)_2]^{2-}$, the Mo^{VI} atom is in a distorted octahedral coordination, with two short Mo—O5 terminal bonds in a *cis* configuration, two long Mo—O2 bonds *trans* to the short bonds, and two Mo—O1 bonds of intermediate length; all four bridging O atoms belong to different sulfate groups (Fig. 1 and Table 1). In the SO_4^{2-} tetrahedron, the S=O bond lengths of the terminal atoms O3 and O4 are shorter than those of atoms O1 and O2, which are coordinated to the Mo atom. There is extensive hydrogen bonding between the N—H groups of the cations and the O atoms or the S atoms from the inorganic anion chains (Table 2).

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Experimental

Aqueous solutions of $Na_2MoO_4 \cdot 2H_2O$ (0.6 g, 1.24 mol l^{-1}) and $Ti(SO_4)_2$ (0.4 g, 0.83 mol l^{-1}), H_2SO_4 (1.8 ml, 98%), and $H_2N(CH_2)_2NH_2$ (0.3 ml, chemical purity) were mixed together and stirred with a magnetic bar for a few minutes, then sealed in a stainless steel (25 ml) Teflon-lined vessel under autogenous pressure. The reactants were heated at 393 K for 4 d and cooled at a rate of 279 K h^{-1} to room temperature. The resulting product was filtered off, washed with water, and dried in air, and well shaped colourless crystals of (I) were obtained.

Crystal data

$(C_2H_{10}N_2)[MoO_{10}S_2]$
$M_r = 382.18$
Monoclinic, $C2/c$
$a = 9.9305 (7)$ Å
$b = 13.6738 (9)$ Å
$c = 8.7309 (4)$ Å
$\beta = 120.583 (3)°$
$V = 1020.63 (11)$ Å^3
$Z = 4$

$D_x = 2.487$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 12–18°$
$\mu = 1.75$ mm^{-1}
$T = 293 (2)$ K
Block, colourless
$0.25 \times 0.18 \times 0.15$ mm

Data collection

Rigaku Weissenberg IP diffractometer
$\omega–2\theta$ scans
1167 independent reflections
1085 reflections with $I > 2\sigma(I)$

$\theta_{max} = 27.5°$
$h = 0 \to 12$
$k = 0 \to 17$
$l = -11 \to 9$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.020$
$wR(F^2) = 0.057$
$S = 1.00$
1167 reflections
79 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.033P)^2 + 1.486P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.46$ e Å^{-3}
$\Delta\rho_{min} = -0.66$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Mo—O5	1.6959 (16)	S—O4	1.4562 (16)
Mo—O1^i	2.0208 (15)	S—O2	1.4911 (16)
Mo—O2	2.1938 (15)	S—O1	1.5223 (16)
S—O3	1.4376 (15)		
O5—Mo—O5^{ii}	103.34 (12)	O5—Mo—O2	164.17 (7)
O5—Mo—O1^i	97.32 (8)	O1^i—Mo—O2	85.98 (7)
O5—Mo—O1^{iii}	94.90 (7)	O1^{iii}—Mo—O2	78.21 (6)
O1^i—Mo—O1^{iii}	160.24 (10)	O2^{ii}—Mo—O2	73.72 (8)
O5—Mo—O2^{ii}	91.74 (7)		

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

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N—H3$\cdots$O4^{iv}	0.77	2.09	2.865 (3)	174
N—H4$\cdots$O3^v	0.85	2.03	2.815 (3)	153
N—H5$\cdots$O4^{vi}	0.81	2.28	3.039 (3)	157
N—H5$\cdots$O5^{vii}	0.81	2.64	3.140 (3)	122
N—H5$\cdots$S^{vi}	0.81	2.95	3.537 (3)	131

Symmetry codes: (iv) $1+x, y, z$; (v) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; (vi) $\frac{3}{2}+x, \frac{3}{2}-y, \frac{1}{2}+z$; (vii) $1+x, 1-y, \frac{1}{2}+z$.

All H atoms were positioned geometrically and fixed. Information of the range of hkl for the original data set are missing, because the
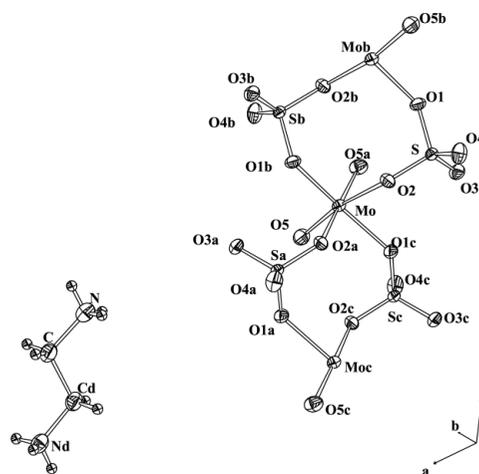

Figure 1
A view of the structure of (I), showing 50% displacement ellipsoids for non-H atoms. A part of the $[MoO_2(SO_4)_2]^{2-}$ chain is shown together with a cation. Letters a–d denote symmetry-generated atoms.
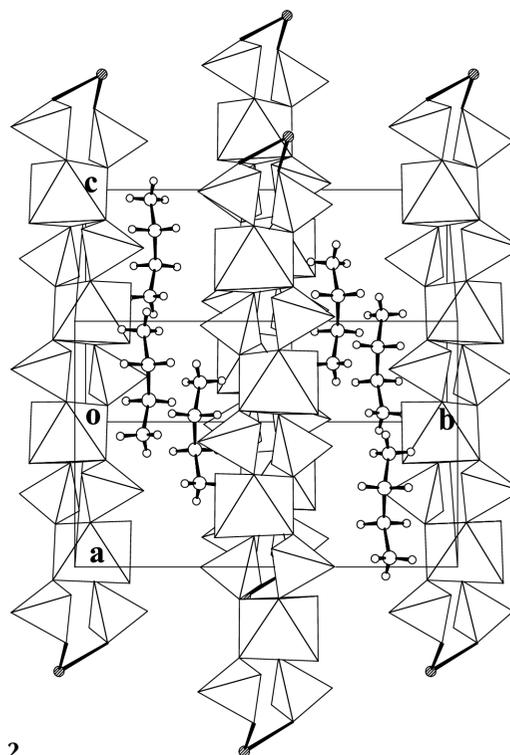

Figure 2
Crystal structure of (I), in which MoO$_6$ and SO$_4$ are connected by sharing corners.

authors received only the averaged data and the original data in the machine have been deleted ($R_{int} = 0.034$).

Data collection: *TEXRAY* (Molecular Structure Corporation, 1999); cell refinement: *TEXRAY*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1999); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEX* (McArdle, 1995); software used to prepare material for publication: *SHELXL*97.

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