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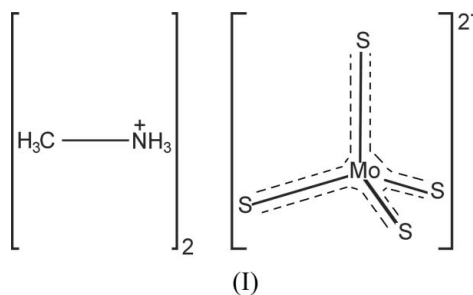
Key indicators

Single-crystal X-ray study
T = 170 K
Mean $\sigma(o-S)$ = 0.001 Å
R factor = 0.028
wR factor = 0.074
Data-to-parameter ratio = 26.0For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

Bis(methylammonium) tetrathiomolybdate(VI)

The structure of the title complex, $(\text{CNH}_6)_2[\text{MoS}_4]$, consists of tetrahedral tetrathiomolybdate dianions, $[\text{MoS}_4]^{2-}$, and two crystallographically independent methylammonium cations, MeNH_3^+ , all of which are located on mirror planes. The tetrathiomolybdate anions are linked to the organic cations *via* hydrogen bonding.Received 9 June 2006
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Comment

As part of an ongoing research programme, we are investigating the synthesis and structural characterization of organic ammonium tetrathiomolybdates (Srinivasan *et al.*, 2005, 2006). In the present work, we report the structure of bis(methylammonium) tetrathiomolybdate, (I), which is isotypic with $\text{Rb}_2[\text{MoS}_4]$ (Ellermeier *et al.*, 1999).

The formula unit of (I) consists of a tetrahedral $[\text{MoS}_4]^{2-}$ ion and two crystallographically independent methylammonium cations, MeNH_3^+ , all of which are located on crystallographic mirror planes (Fig. 1), so that half of each of these ions make up the asymmetric unit. The MoS_4 tetrahedron is slightly distorted, with $\text{Mo}-\text{S}$ bond lengths ranging from 2.1762 (5) to 2.1961 (7) Å (Table 1). All structural parameters of (I) are in good agreement with those reported for other compounds containing the $[\text{MoS}_4]^{2-}$ anion (Srinivasan *et al.*, 2006). The observed $\text{Mo}-\text{S}$ bond distances can be rationalized on the basis of the number and strength of hydrogen-bonding interactions. In general, unshared hydrogen bonds have a considerably stronger effect than bifurcated ones, while the effect of trifurcated hydrogen bonds is quite weak (Jeffrey, 1997). Atoms H1N1 and H2N1 are involved in bifurcated hydrogen bonding, while H2N2 makes a trifurcated hydrogen bond and H1N2 forms an unshared hydrogen bond. The weakness of the trifurcated hydrogen bond is also evident from the observed longer $\text{S}\cdots\text{H}$ distances accompanied by smaller $\text{N}-\text{H}\cdots\text{S}$ angles. Atom S1 is involved in an unshared hydrogen bond with a $\text{H}\cdots\text{S}$ distance of 2.66 Å. The effect of this contact is stronger than the rest of the contacts and can explain the elongation of the $\text{Mo}-\text{S1}$

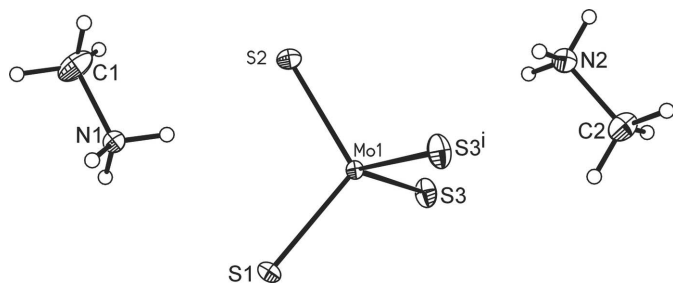


Figure 1
Perspective view of (I), with labelling and displacement ellipsoids drawn at the 50% probability level. [Symmetry code: (i) $x, -y + \frac{1}{2}, z$.]

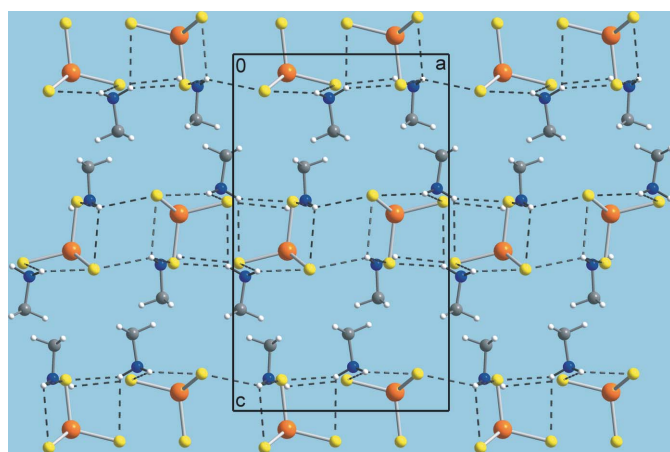


Figure 2
Crystal structure of (I), with a view along the *b* axis (intermolecular N—H...S hydrogen bonding is shown as dashed lines).

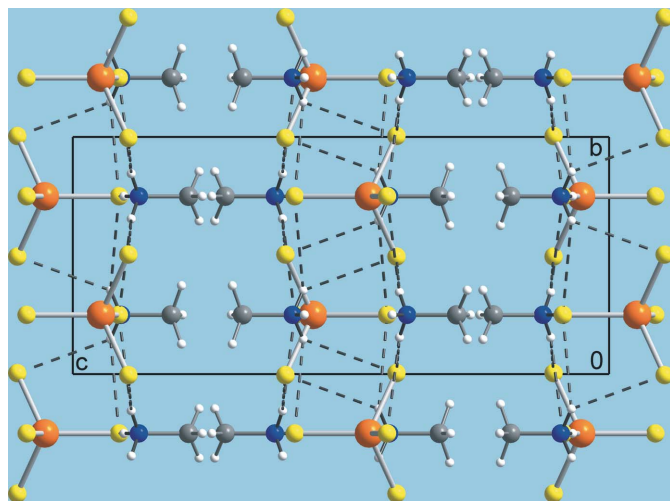


Figure 3
Crystal structure of (I), with a view along the *a* axis (intermolecular N—H...S hydrogen bonding is shown as dashed lines).

bond, the longest observed Mo—S distance for (I). These results are in agreement with similar observations for piperidinium thiotungstates (Siemeling *et al.*, 2006). All eight short S...H contacts (ranging from 2.40 to 2.95 Å) are shorter than the sum of their van der Waals radii (Bondi, 1964). As a result

of hydrogen-bonding interactions, the organic cations are organized such that the ammonium groups always point towards the S atoms of tetrathiomolybdate *viz.* MoS₄·H₃NMe·MeNH₃·MoS₄· and so on (Fig. 2).

Experimental

Molybdic acid (3 g) was dissolved in a mixture of 40% MeNH₂ (10 ml) and distilled water (5 ml). A rapid stream of H₂S gas was bubbled into this for 30 min, resulting in the formation of a red solid. The reaction mixture was cooled to room temperature and the red solid filtered off. The filtrate was left aside at room temperature for 2 d, resulting in the formation of crystalline blocks of the title compound used for the structure determination. The crystals were isolated by filtration, washed with isopropyl alcohol (20 ml) and diethyl ether (20 ml), and dried under vacuum. The product was satisfactorily analysed.

Crystal data

(CH ₆ N) ₂ [MoS ₄]	Z = 4
<i>M_r</i> = 288.32	<i>D_x</i> = 1.845 Mg m ⁻³
Orthorhombic, <i>Pnma</i>	Mo <i>K</i> α radiation
<i>a</i> = 9.5190 (7) Å	<i>μ</i> = 2.00 mm ⁻¹
<i>b</i> = 6.9424 (4) Å	<i>T</i> = 170 (2) K
<i>c</i> = 15.7041 (11) Å	Block, red
<i>V</i> = 1037.80 (12) Å ³	0.12 × 0.12 × 0.08 mm

Data collection

Stoe IPDS-1 diffractometer	6261 measured reflections
<i>φ</i> scans	1354 independent reflections
Absorption correction: numerical (<i>X-SHAPE</i> ; Stoe & Cie, 1998)	1166 reflections with <i>I</i> > 2σ(<i>I</i>)
<i>T</i> _{min} = 0.779, <i>T</i> _{max} = 0.949	<i>R</i> _{int} = 0.028
	<i>θ</i> _{max} = 28.0°

Refinement

Refinement on <i>F</i> ²	H-atom parameters constrained
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.028	<i>w</i> = 1/[σ ² (<i>F</i> _o ²) + (0.0531 <i>P</i>) ²]
<i>wR</i> (<i>F</i> ²) = 0.074	where <i>P</i> = (<i>F</i> _o ² + 2 <i>F</i> _c ²)/3
<i>S</i> = 1.09	(Δ/σ) _{max} = 0.001
1354 reflections	Δρ _{max} = 0.48 e Å ⁻³
52 parameters	Δρ _{min} = -1.03 e Å ⁻³

Table 1

Selected geometric parameters (Å, °).

Mo1—S3	2.1762 (5)	Mo1—S1	2.1961 (7)
Mo1—S2	2.1881 (8)		
S3 ⁱ —Mo1—S3	108.35 (3)	S3—Mo1—S1	110.51 (2)
S3—Mo1—S2	108.530 (19)	S2—Mo1—S1	110.34 (3)

Symmetry code: (i) $x, -y + \frac{1}{2}, z$.

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H1N1...S2	0.88	2.40	3.219 (3)	155
N1—H1N1...S1	0.88	2.86	3.380 (2)	119
N1—H2N1...S3 ⁱⁱ	0.88	2.58	3.326 (2)	144
N1—H2N1...S1 ⁱⁱⁱ	0.88	2.88	3.5316 (5)	132
N2—H1N2...S1 ^{iv}	0.88	2.66	3.451 (3)	150
N2—H2N2...S3	0.88	2.77	3.445 (3)	135
N2—H2N2...S2 ^v	0.88	2.94	3.5172 (5)	125
N2—H2N2...S3 ^v	0.88	2.95	3.489 (2)	121

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

H atoms were located in a difference map, but their bond lengths were set to ideal values and they were refined using a riding model, with C–H = 0.98 Å and N–H = 0.88 Å. The $U_{\text{iso}}(\text{H})$ values were set to $1.5U_{\text{eq}}(\text{C,N})$. The deepest hole in the electron-density map is located 0.79 Å from atom Mo1.

Data collection: *DIF4* (Stoe & Cie, 1998); cell refinement: *DIF4*; data reduction: *REDU4* (Stoe & Cie, 1998); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *CIFTAB* in *SHELXTL*.

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