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Butane-1,4-diammonium tetrathiomolybdate(VI)

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.004 Å
R factor = 0.026
wR factor = 0.074
Data-to-parameter ratio = 34.0

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

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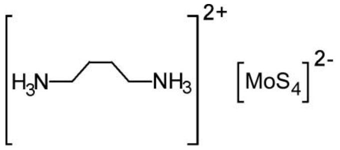
The structure of the title complex, $(C_4N_2H_{14})[MoS_4]$, consists of tetrahedral tetrathiomolybdate dianions connected to butane-1,4-diammonium dications, $(1,4\text{-bnH}_2)^{2+}$, *via* hydrogen bonding. The compound contains two crystallographically independent butane-1,4-diammonium dications in the asymmetric unit, both of which are located around centres of inversion. The anions are located in general positions.

Comment

The chemistry of Mo–S compounds is currently a frontier area of research in view of the emerging importance of MoS_2 in nanomaterials and hydrodesulfurization (HDS) catalysis. The reported use of $(NH_4)_2[MoS_4]$ (Nath *et al.*, 2001) as a precursor for the soft synthesis of MoS_2 nanotubes has generated much interest in the chemistry of tetrathiomolybdates. As part of an overall programme aimed at the synthesis of novel precursors for sulfide materials, we are investigating the synthesis and structural characterization of organic ammonium tetrathiomolybdates. In earlier work, we have demonstrated the structural flexibility of the $[MoS_4]^{2-}$ anion, as it can exist in a variety of structural environments (Ellermeier *et al.*, 1999; Ellermeier & Bensch 2001, 2002; Srinivasan *et al.*, 2004; Srinivasan, Dhuri *et al.*, 2005). The tetrathiomolybdate complexes reported by us exhibit weak hydrogen-bonding interactions between the organic cation and the anion, which affect the Mo—S bond distances. These hydrogen-bonding interactions can be altered by changing the steric bulk and the number of potential hydrogen-bonding donors attached to the N atoms of the organic amines. In the present work, we have employed a long-chain acyclic organic diamine 1,4-butanediamine (1,4-bn) as the source for the organic cation and have structurally characterized the title compound, (I). The acyclic diamine 1,4-bn, also called putrescine (Takusagawa & Koetzle, 1978), plays an important role as a diprotonated cation in biological systems. It interacts with nucleic acids through hydrogen bonds.



(I)

The $(1,4\text{-bnH}_2)^{2+}$ and $[MoS_4]^{2-}$ ions constitute the molecular arrangement of the title complex (Fig. 1), which is isostructural with the corresponding W compound, $(1,4\text{-bnH}_2)[WS_4]$ (Srinivasan, Näther *et al.*, 2005). The lattice

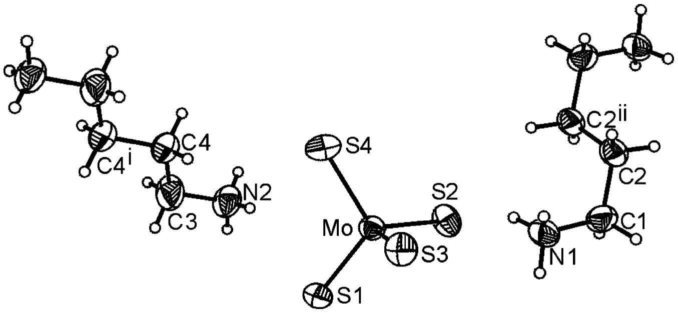


Figure 1
The crystal structure of (I), with the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) $1 - x, 2 - y, 2 - y$; (ii) $1 - x, -y, 1 - z$.]

parameters show a small decrease compared with those of the W compound, with a slightly smaller unit-cell volume [unit-cell volume of the W complex $V = 606.4$ (2) Å^3]. This can be explained by the smaller radius of Mo^{VI}. The related Cr complex, (1,4-bnH$_2$)[CrO$_4$] (Chebbi & Driss 2002), has been reported to crystallize in the space group *Pbca*. Interestingly, in the case of ethylenediamine (en), ethylenediammonium chromate (Srinivasan *et al.*, 2003) is isostructural with the corresponding group VI tetrathiometallates (enH$_2$)[MS$_4$] (*M* is Mo or W; Srinivasan *et al.*, 2001, 2002).

There are two crystallographically independent (1,4-bnH$_2$)$^{2+}$ cations in the asymmetric unit of (I) and both are located around centres of inversion. The bond lengths and angles of the (1,4-bnH$_2$)$^{2+}$ cation (Table 1) are in good agreement with those reported for other compounds containing this cation (Chebbi & Driss 2002; Srinivasan, Näther *et al.*, 2005). The MoS$_4$ tetrahedron is slightly distorted, with S—Mo—S angles between 108.56 (3) and 110.28 (3)° (Table 1). The Mo—S bond lengths range from 2.1749 (8) to 2.1992 (7) Å with a mean Mo—S distance of 2.1814 Å. All structural parameters of (I) are comparable with those reported for other compounds containing the [MoS$_4$]$^{2-}$ anions, such as (enH$_2$)[MoS$_4$] (Srinivasan *et al.*, 2001), and (1,3-pnH$_2$)[MoS$_4$] (1,3-pn is 1,3-propanediamine) and (tmenH$_2$)[MoS$_4$] (tmen is *N*,*N*,*N*′,*N*′-tetramethylethylenediamine) (Srinivasan, Dhuri *et al.*, 2005).

The cations and anions are further connected *via* hydrogen bonding and the resulting three-dimensional hydrogen-bonded network is depicted in Fig. 2. Three of the Mo—S bonds in (I) are shorter than the mean Mo—S bond distance, while the longest Mo—S bond is observed at a distance of 2.1992 (7) Å. In all, seven short hydrogen-bonding contacts ranging from 2.35 to 2.72 Å (Table 2) are observed in the title complex, and all these interactions are shorter than the sum of the van der Waals radii of S and H (Bondi, 1964). These values are comparable with the S···H distances of 2.494–2.827 Å observed for (1,3-pnH$_2$)[MoS$_4$] (Srinivasan, Dhuri *et al.*, 2005). The N···S distances for one of the cations fall in the range 3.263 (3)–3.410 (2) Å, while the N···S distances for the second cation are shorter, at 3.238 (3)–3.324 (3) Å. The difference between the longest and shortest Mo—S bond Δ is 0.0143 Å, and this is in the range of Δ values of 0.0111 and 0.0183 Å observed for (enH$_2$)[MoS$_4$] and (1,3-pnH$_2$)[MoS$_4$], respectively. This indicates that the use of a long-chain spacer between the amino N atoms in acyclic diamines does not affect the Mo—S bond lengths significantly.

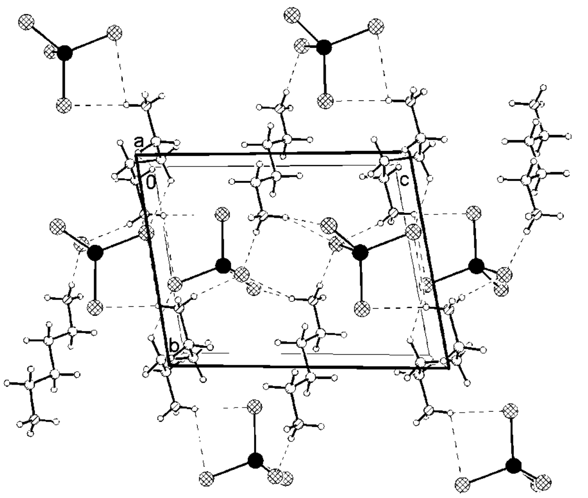


Figure 2
The crystal structure of (I), viewed along the *a* axis. Intermolecular hydrogen bonding is shown as dashed lines.

Experimental

Molybdic acid (1 g) was dissolved in 1,4-bn (2 ml) and distilled water (10 ml). Into this clear solution, a rapid stream of H$_2$S gas was passed while maintaining the temperature of the reaction mixture at 333 K. After about 30 min, when crystals started to appear, the gas flow was stopped and the reaction mixture was cooled to room temperature and then kept in a refrigerator. This resulted in the formation of red crystals of the title complex, which were isolated by filtration, washed with ice-cold water (5 ml), propan-2-ol (20 ml) and diethyl ether (20 ml), and dried in a vacuum (yield 1.4 g; 64% based on Mo). The crystals are quite stable in air, slightly soluble in water and quite soluble in aqueous ammonia. Analysis, calculated for C$_4$H$_{14}$N$_2$MoS$_4$: C 15.28, H 4.50, N 8.91, S 40.80%; found: C 15.32, H 4.55, N 8.86 S 41.63%.

Crystal data

(C$_4$H$_{14}$N$_2$)[MoS$_4$]
$M_r = 314.35$
Triclinic, $P\overline{1}$
$a = 7.1447$ (11) Å
$b = 8.2159$ (12) Å
$c = 10.5031$ (19) Å
$\alpha = 79.558$ (10)°
$\beta = 81.561$ (13)°
$\gamma = 83.701$ (12)°
$V = 597.57$ (17) Å^3

$Z = 2$
$D_x = 1.747$ Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 104 reflections
$\theta = 15$–18.5°
$\mu = 1.75$ mm^{-1}
$T = 293$ (2) K
Block, red
0.12 × 0.09 × 0.07 mm

Data collection

Stoe AED-II four-circle diffractometer
$\omega/2\theta$ scans
Absorption correction: numerical (*X-SHAPE*; Stoe & Cie, 1998)
$T_{\min} = 0.824$, $T_{\max} = 0.887$
3726 measured reflections
3467 independent reflections
2852 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.027$
$\theta_{\max} = 30.0$°
$h = 0 \rightarrow 10$
$k = -11 \rightarrow 11$
$l = -14 \rightarrow 14$
4 standard reflections frequency: 120 min intensity decay: none

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Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.027$
$wR(F^2) = 0.074$
$S = 1.04$
3467 reflections
102 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0377P)^2 + 0.2604P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.71$ e Å^{-3}
$\Delta\rho_{min} = -0.65$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Mo—S1	2.1749 (8)	C1—C2	1.518 (3)
Mo—S4	2.1750 (8)	C2—C2^{i}	1.503 (5)
Mo—S3	2.1765 (8)	N2—C3	1.472 (4)
Mo—S2	2.1992 (7)	C3—C4	1.486 (4)
N1—C1	1.485 (3)	C4—C4^{ii}	1.504 (5)
S1—Mo—S4	108.56 (3)	S3—Mo—S2	109.14 (3)
S1—Mo—S3	109.58 (3)	N1—C1—C2	111.8 (2)
S4—Mo—S3	110.28 (3)	C2^{i}—C2—C1	113.0 (3)
S1—Mo—S2	109.41 (3)	N2—C3—C4	113.0 (3)
S4—Mo—S2	109.87 (3)	C3—C4—C4^{ii}	112.5 (3)

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

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···S4^{iii}	0.89	2.39	3.263 (3)	168
N1—H1B···S3^{iv}	0.89	2.55	3.410 (2)	163
N1—H1C···S2	0.89	2.48	3.297 (3)	153
N2—H2C···S4^{v}	0.89	2.35	3.238 (3)	178
N2—H2D···S2^{vi}	0.89	2.37	3.240 (3)	165
N2—H2E···S4	0.89	2.63	3.324 (3)	136
N2—H2E···S1	0.89	2.72	3.417 (3)	136

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

N-bound H atoms were positioned with idealized geometry, with N—H = 0.89 Å, allowed to rotate but not tip and refined with fixed isotropic displacement parameters using a riding model, with U_{iso}(H) = 1.2U_{eq}(N). C-bound H atoms were positioned with idealized geometry, with C—H = 0.97 Å, and refined with fixed isotropic displacement parameters using a riding model, with U_{iso}(H) = 1.2U_{eq}(C).

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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References

Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.
Bruker (1998). *SHELXTL*. Version 5.10 Bruker AXs Inc., Madison, Wisconsin, USA.
Chebbi, H. & Driss A. (2002). *Acta Cryst.* E**58**, m147–m149.
Ellermeier, J. & Bensch, W. (2001). *Z. Naturforsch. Teil B*, **56**, 611–619.
Ellermeier, J. & Bensch, W. (2002). *Monatsh. Chem.* **133**, 945–957.
Ellermeier, J., Näther, C.& Bensch, W. (1999). *Acta Cryst.* C**55**, 501–503.
Nath, M., Govindaraj, A. & Rao, C. N. R. (2001). *Adv. Mater.* **13**, 283–285.
Sheldrick, G. M. (1997) *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Srinivasan, B. R., Dhuri, S. N., Näther, C. & Bensch, W. (2002). *Acta Cryst.* E**58**, m622–m624.
Srinivasan, B. R., Dhuri, S. N., Näther, C. & Bensch, W. (2003). *Indian J. Chem. Sect A*, **42**, 2735–2741.
Srinivasan, B. R., Dhuri, S. N., Näther, C. & Bensch, W. (2005). *Inorg. Chim. Acta*, **358**, 279–287.
Srinivasan, B. R., Dhuri, S. N., Poisot, M., Näther, C. & Bensch, W. (2004). *Z. Naturforsch. Teil B*, **59**, 1083–1092.
Srinivasan, B. R., Näther, C., Dhuri, S. N. & Bensch, W. (2005). *Monatsh. Chem.* In the press.
Srinivasan, B. R., Vernekar, B. K. & Nagarajan, K. (2001). *Indian J. Chem. Sect A*, **40**, 563–567.
Stoe & Cie (1998). *DIF4*, *REDU4* and *X-SHAPE* (Version 1.03). Stoe & Cie, Darmstadt, Germany.
Takusagawa, F. & Koetzle, T. F. (1978). *Acta Cryst.* B**34**, 1910–1915.

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