Crystal structure of bis(tetramethylammonium) trismolybdenumtrideca-sulfide, $[N(CH_3)_4]_2Mo_3S_{13}$

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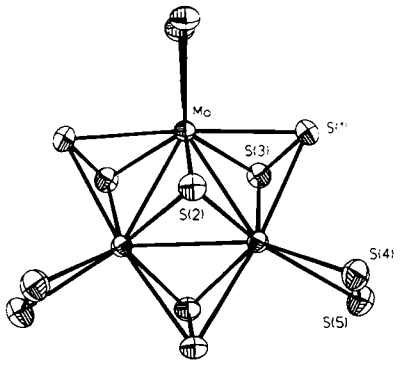

Fig. 1. Mo_3S_{13} cluster.

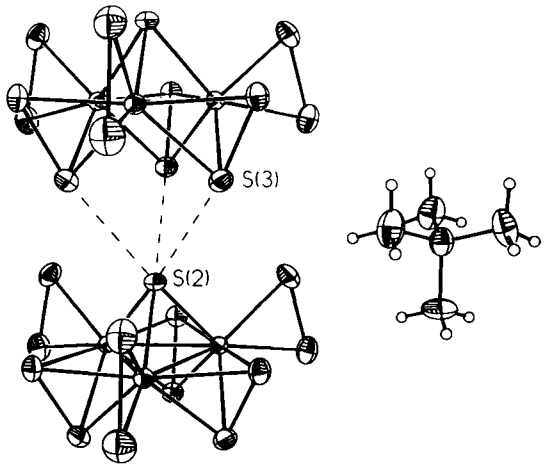

Fig. 2. Arrangement of the Mo_3S_{13} clusters along the *c* axis. The broken lines indicate the weak S–S interaction (3.130 Å).

Source of material: Single crystals of $[N(CH_3)_4]_2Mo_3S_{13}$ were obtained in a hydrothermal reaction of MoO_3 with elemental sulfur, $Na_3SbS_4 \cdot 9H_2O$ and tetramethylammoniumchloride (molar ratio = 1:5:2:1) in a 0.2 mol aqueous ammonia solution within 6 days. The reaction product consists of dark red hexagonal prisms up to 5 mm long.

The cluster Mo_3X_{13} (X=S, Se) is found in different compounds as isolated (see refs. 1, 2, 3) or interlinked species (see refs. 4, 5). It is build up from a molybdenum triangle held together by an apical chalcogen atom and six dichalcogen ligands. Three of them are bridging and three are terminal ligands (see Fig. 1, Mo–Mo 2.733(2) Å, Mo–S(1) 2.497(2) Å, Mo–S(2) 2.368(3) Å, Mo–S(3) 2.426(2) Å, Mo–S(4) 2.417(3) Å, Mo–S(5) 2.474(3) Å, S(1)–S(3) 2.022(4) Å, S(4)–S(5) 2.082(4) Å). In the title compound as well as in the isotypic selenide $[N(CH_3)_4]_2Mo_3Se_{13}$ (see ref. 6), the apical chalcogen atom shows weak interaction to three of the chalcogen atoms from the bridging X_2 (X=S, Se) ligands of the neighboured cluster, forming columnar stacks along the *c*-axis (see Fig. 2). The interaction seems to be less pronounced than in the selen compound as indicated by the nearest intercluster S–S distances of 3.130 Å compared to 3.174 Å for the Se–Se distance. We note that a shorter intercluster S–S distance type of 3.026 Å was reported for $(NH_4)_2Mo_3S_{13} \cdot H_2O$ (see ref. 1). In addition the shortest intracluster S–S distances from the apical sulfur atom to the bridging S_2 groups increases slightly from 3.281 Å (mean value) in the ammonium compound to 3.307 Å in the title compound whereas the distance to the terminal S_2 groups decreases from 3.504 Å to 3.467 Å.

$C_8H_{24}Mo_3N_2S_{13}$, trigonal, *P*31*m* (No. 157), a =11.223(5) Å, c =5.887(3) Å, V =642.2 Å^3, Z =1, $R(F)$ =0.036, $R_w(F^2)$ =0.109.

Table 1. Parameters used for the X-ray data collection

Crystal:	dark red, hexagonal needle, size 0.16 x 0.16 x 0.8 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	25.01 cm^{-1}
Diffractometer:	STOE AED II
Scan mode:	ω/θ
$T_{measurement}$:	293 K
$2\theta_{max}$:	65°
$N(hkl)_{unique}$:	1268
Criterion for I_o:	$I_o > 2\,\sigma(I_o)$
$N(param)_{refined}$:	49
Programs:	SHELXS-86, SHELXL-93

Table 2. Final atomic coordinates and displacement parameters (in Å^2)

Atom	Site	Occ.	*x*	*y*	*z*	U_{iso}
H(1A)	6*d*	0.33	0.6707	0.4159	0.1567	0.081
H(1B)	6*d*	0.33	0.5841	0.2548	0.1567	0.081
H(1C)	6*d*	0.33	0.7452	0.3293	0.1567	0.081
H(2A)	6*d*		0.7961	0.5377	0.4993	0.073
H(2B)	6*d*		0.8729	0.4535	0.4852	0.073
H(2C)	6*d*		0.8020	0.4571	0.7125	0.073

Table 3. Final atomic coordinates and displacement parameters (in $Å^2$)

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mo(1)	3*c*	0.14059(5)	0	0.0126(1)	0.0189(2)	0.0194(3)	0.0187(3)	$U_{11}/2$	–0.0011(2)	0
S(1)	3*c*	–0.2562(2)	0	0.0351(5)	0.0226(6)	0.031(1)	0.035(1)	$U_{11}/2$	0.0015(8)	0
S(2)	1*a*	0	0	0.3126(7)	0.028(1)	U_{11}	0.016(2)	$U_{11}/2$	0	0
S(3)	3*c*	–0.1714(2)	0	–0.2680(4)	0.0281(6)	0.0315(9)	0.025(1)	$U_{11}/2$	–0.0037(7)	0
S(4)	3*c*	0.3081(2)	0	0.2706(5)	0.0327(7)	0.036(1)	0.040(1)	$U_{11}/2$	–0.0122(9)	0
S(5)	3*c*	0.3567(2)	0	–0.0706(6)	0.0306(7)	0.043(1)	0.052(2)	$U_{11}/2$	0.0066(9)	0
N(1)	2*b*	2/3	1/3	0.477(2)	0.030(3)	U_{11}	0.043(8)	$U_{11}/2$	0	0
C(1)	2*b*	2/3	1/3	0.211(3)	0.071(7)	U_{11}	0.020(6)	$U_{11}/2$	0	0
C(2)	6*d*	0.7957(8)	0.4562(8)	0.550(2)	0.034(3)	0.035(3)	0.070(8)	0.013(3)	–0.015(4)	–0.008(4)

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