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Key indicators

Single-crystal X-ray study
 T = 150 K
 Mean $\sigma(\text{C}-\text{C}) = 0.006 \text{ \AA}$
 R factor = 0.033
 wR factor = 0.071
 Data-to-parameter ratio = 19.2

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

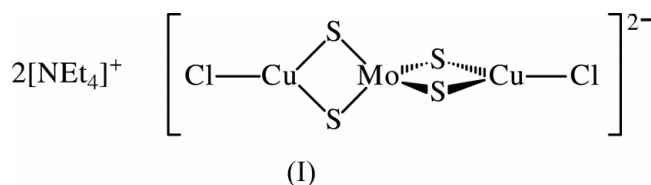
Bis(tetraethylammonium) μ -tetrathio-molybdate(VI)-bis[chlorocopper(I)]

The title compound, $(\text{Et}_4\text{N})_2[\text{MoS}_4(\text{CuCl})_2]$, consists of tetraethylammonium cations of expected geometry, and trinuclear anions in which two opposite edges of an MoS_4^{2-} tetrahedron are bridged by CuCl units. The bridging of Mo and Cu centres by all four S atoms hardly affects the tetrahedral coordination of Mo and leads to a distorted trigonal planar coordination geometry for Cu, with both chloro ligands terminal.

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Comment

The title compound, (I), was obtained as an unexpected side product in the synthesis and study of a range of complexes in which tetrathiomolybdate or tetrathiotungstate anions $[\text{MS}_4]^{2-}$ are bridged by Cu^{I} atoms carrying pyrazolylborate ligands (Beheshti *et al.*, 2001; Beheshti, Clegg & Hosaini Sadr, 2002; Beheshti, Clegg, Hyvadi & Fereshteh Hekmat, 2002; Hosaini Sadr *et al.*, 2003). The asymmetric unit contains two tetraethylammonium cations and a trinuclear $[\text{MoS}_4(\text{CuCl})_2]^{2-}$ anion (Fig. 1) in which two opposite edges of an $[\text{MoS}_4]^{2-}$ tetrahedron are each bridged by a chlorocopper(I) unit. Bond lengths and angles of the anion are given in Table 1.



Salts of anions $[\text{MoS}_4(\text{CuX})_n]^{2-}$, in which three or four edges of the MoS_4 tetrahedron are bridged by neutral halo-

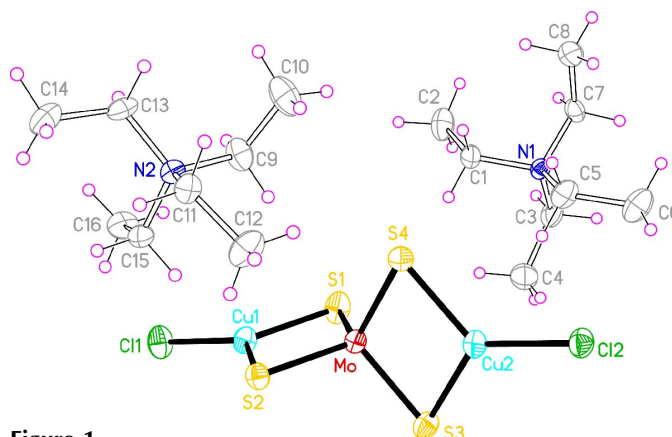


Figure 1
 The molecular structure of (I), with atom labels and 50% probability ellipsoids for non-H atoms.

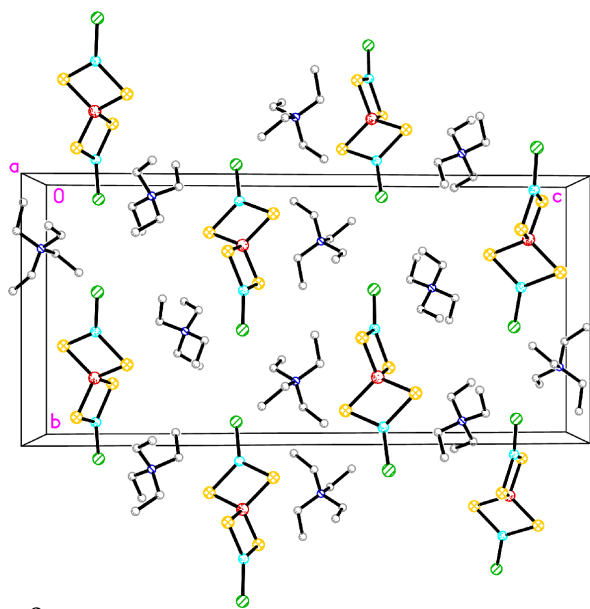


Figure 2

The packing of cations and anions, viewed down the *a* axis. H atoms have been omitted.

genocopper(I) units have been crystallographically characterized (Bernès *et al.*, 1992; Clegg *et al.*, 1983; Nicholson *et al.*, 1983; Potvin *et al.*, 1984; Sécheresse *et al.*, 1991; Müller *et al.*, 1989). Some of these are discrete mononuclear anions, while others form oligomers or polymers as a result of bridging of copper(I) centres by halide ligands. The anion with two CuX units per Mo atom has not previously been reported, although the analogous tungsten complex is known, as its tetraphenylphosphonium salt (Sécheresse *et al.*, 1986). A few other complexes have been reported, in which the halide is replaced by a different monoanionic ligand (cyanide, thiocyanate, thiolate or dithiocarboxylate) (Müller *et al.*, 1981; Acott *et al.*, 1983; Gheller *et al.*, 1984; Jin *et al.*, 1992; Clegg *et al.*, 2002). In each of these cases, as in the title compound, the two CuX units bridge opposite edges of the central tetrahedron.

In the anion of the title compound, the distortion of the tetrahedral coordination of Mo is small, and both Cu^I centres have essentially planar coordination, as expected (sum of angles 359.9°). The main distortion from ideal trigonal planar geometry is the reduction of the S—Cu—S angle from 120° as a consequence of the double sulfide bridges, which have geometry typical of such complexes. The acute angle of these bridges (Table 1) results in short Mo...Cu distances of 2.6178 (6) and 2.5969 (6) Å, which are not generally regarded as direct metal–metal bonds.

The cations have unremarkable geometry, and there are no unusual intermolecular interactions (Fig. 2).

Experimental

Deep violet crystals of the title compound were obtained as a bunch of needles on the walls of a flask containing an acetone solution of (NEt₄)₂[MoS₄(CuBp)₂] (Bp = bispyrazolylborate) contaminated with diethyl ether. They were formed probably as a result of partial decomposition of this compound, which has been characterized by

spectroscopy and elemental analysis. The IR spectrum of the title compound contains a strong band at 466 cm⁻¹ for Mo—S stretching. Uv–Vis maxima (ϵ in parentheses; spectrum measured for DMF solution) are at 266.7 (1.040), 321.3 (1.194) and 503.6 (0.413) nm. These observations indicate four equivalent Mo—S bonds in the MoS₄ core and are in agreement with data reported previously for similar complexes with *D*_{2d} symmetry (Manoli *et al.*, 1988).

Crystal data

(C₈H₂₀N)₂[CuMoCl₂S₄]
M_r = 682.66
 Monoclinic, *P*2₁/*n*
a = 7.5052 (5) Å
b = 13.2537 (9) Å
c = 27.9439 (18) Å
 β = 93.175 (1)°
V = 2775.4 (3) Å³
Z = 4

D_x = 1.634 Mg m⁻³
 Mo *K* α radiation
 Cell parameters from 1000 reflections
 θ = 2.5–25.0°
 μ = 2.46 mm⁻¹
T = 150 (2) K
 Block, deep violet
 0.18 × 0.12 × 0.10 mm

Data collection

Bruker SMART 1K CCD diffractometer

Thin-slice ω scans

Absorption correction: multi-scan (SADABS; Sheldrick, 2002)

*T*_{min} = 0.698, *T*_{max} = 0.782

15663 measured reflections

4845 independent reflections
 3525 reflections with *I* > 2 σ (*I*)
*R*_{int} = 0.048
 θ _{max} = 25.0°
h = -8 → 8
k = -15 → 15
l = -33 → 30

Refinement

Refinement on *F*²

R[*F*² > 2 σ (*F*²)] = 0.033

wR(*F*²) = 0.071

S = 1.04

4845 reflections

252 parameters

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0256P)^2 + 0.3229P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.43 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.47 \text{ e } \text{Å}^{-3}$

Table 1

Selected geometric parameters (Å, °).

Mo—S1	2.2102 (11)	Cu1—S2	2.2235 (11)
Mo—S2	2.2174 (10)	Cu1—Cl1	2.1656 (11)
Mo—S3	2.2162 (11)	Cu2—S3	2.2163 (11)
Mo—S4	2.2156 (10)	Cu2—S4	2.2169 (11)
Cu1—S1	2.2165 (12)	Cu2—Cl2	2.1584 (10)
S1—Mo—S2	107.84 (4)	S2—Cu1—Cl1	126.61 (4)
S1—Mo—S3	109.57 (4)	S3—Cu2—S4	108.23 (4)
S1—Mo—S4	110.04 (5)	S3—Cu2—Cl2	126.51 (4)
S2—Mo—S3	109.71 (4)	S4—Cu2—Cl2	125.21 (4)
S2—Mo—S4	111.38 (4)	Mo—S1—Cu1	72.51 (4)
S3—Mo—S4	108.28 (4)	Mo—S2—Cu1	72.24 (3)
S1—Cu1—S2	107.41 (4)	Mo—S3—Cu2	71.73 (3)
S1—Cu1—Cl1	125.94 (5)	Mo—S4—Cu2	71.73 (3)

H atoms were positioned geometrically and refined with a riding model (including free rotation about C—C bonds), and with *U*_{iso} values constrained to be 1.2 (1.5 for methyl groups) times *U*_{eq}(C).

Data collection: SMART (Bruker, 2001); cell refinement: SAINT (Bruker, 2001); data reduction: SAINT; program(s) used to solve structure: SHELXTL (Sheldrick, 2001); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL and local programs.

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