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A second tetragonal polymorph of bis(tetra-*n*-butylammonium) tetrakis[chloro(μ_3-sulfido)-copper(I)]molybdate(VI)

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The title compound, bis(tetra-*n*-butylammonium) tetrachlorotetra-μ_3-sulfidotetracopper(I)molybdenum(VI), $(C_{16}H_{36}N)_2[MoS_4(CuCl)_4]$, has been obtained in a second polymorphic form. The anion, in which four of the six S···S edges of the central MoS_4 tetrahedron are bridged by CuCl neutral molecular units to give a planar pentanuclear $MoCu_4$ framework, is disordered on a crystallographic fourfold rotation axis, requiring equal occupancy of two sets of four positions for the S atoms. There is additional disorder as a result of 8.2 (2)% substitution of Cl by Br, arising from tetra-*n*-butylammonium bromide used in the synthesis. Copper has distorted trigonal planar coordination, involving two μ_3-S atoms and a terminal halogen atom. The two independent cations lie on positions of symmetry $\bar{4}$.

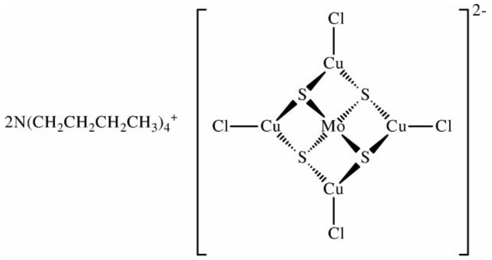
Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.003 Å
Disorder in main residue
R factor = 0.024
wR factor = 0.058
Data-to-parameter ratio = 23.5

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

Comment

The title compound, (I), was prepared as a precursor for the synthesis of complexes with the MoS_4Cu_4 core and a range of terminal ligands. It was found to crystallize with slightly different tetragonal unit-cell parameters from those reported previously (Sécheresse *et al.*, 1991); the previous structure was in the non-centrosymmetric space group $I\bar{4}$ [reported as $I\bar{4}/m$ in the original publication, but corrected to $I\bar{4}$ in entry SORLAM of the Cambridge Structural Database (CSD, Version 5.25, November 2003; Allen, 2002); one of the two cations is missing from the list of coordinates in the publication and in the CSD, as confirmed by the identification of major voids in the structure by *PLATON* (Spek, 2003)], but the new polymorph has the centrosymmetric space group $P4/n$ with pseudo-body-centring (see *Experimental*). In both cases, Z = 2.



(I)

The tetrahedral MoS_4^{2-} anion (and its tungsten analogue) can form heterometallic complexes with up to six Cu^I atoms, which bridge the S···S edges of the tetrahedron. Many of these complexes are formed from Cu^I halides, though other anionic and neutral ligands have also been used. When five or six Cu^I atoms are attached to the central tetrahedron, the

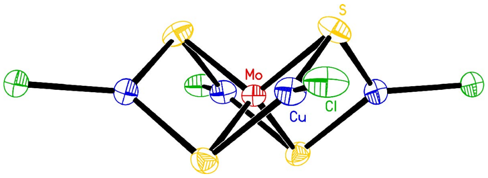


Figure 1
The structure of the anion, with atom labels for the asymmetric unit and 50% probability ellipsoids. Only one component of the disorder is shown for the S atoms, and the minor substitution component of Br for Cl is not included.

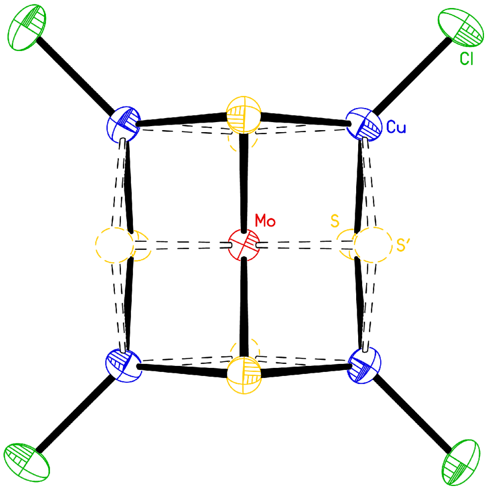


Figure 2
The anion with both disorder components, viewed along the crystallographic fourfold rotation axis. The second disorder component is shown with dashed ellipsoids and bonds; four of the Mo—S bonds are obscured by the four that are visible.

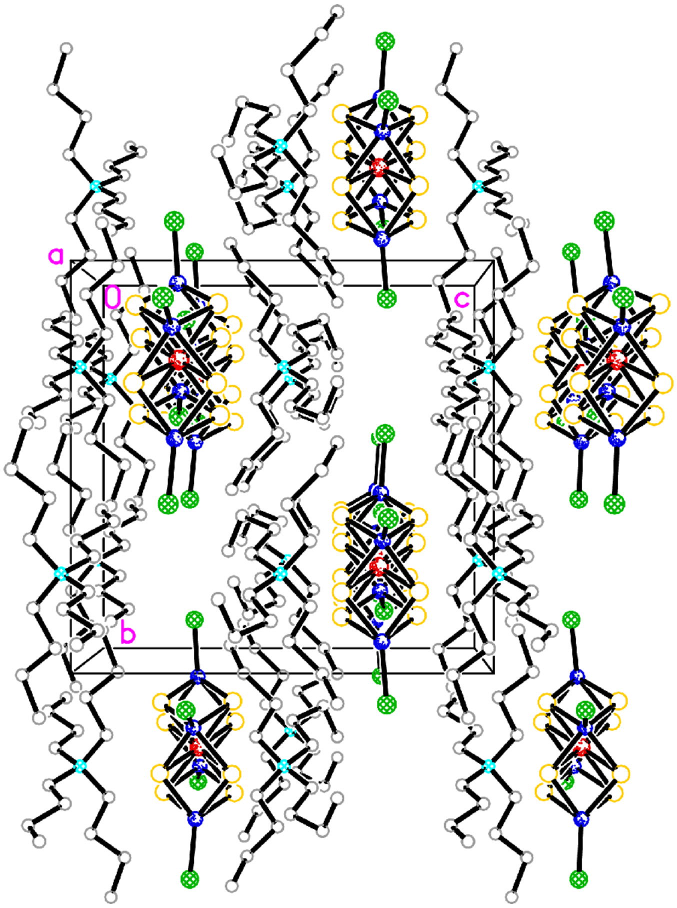


Figure 3
The packing, viewed along the *a* axis. H atoms have been omitted, but all disordered atoms are shown.

resulting structures involve both terminal and bridging ligands on Cu. With 2–4 Cu^I atoms, simpler structures are formed, in which each Cu atom carries just one terminal halogen atom, and the resulting complex anions can be regarded as MS_4^{2-} with bridging Cu*X* molecular units. As the number of Cu*X* units is increased from two (Sécheresse *et al.*, 1986; Hosaini Sadr *et al.*, 2003), through three (Manoli *et al.*, 1982; Clegg *et al.*, 1983; Potvin *et al.*, 1984; Müller *et al.*, 1989; Bernès *et al.*, 1992), to four (Nicholson *et al.*, 1983; Clegg *et al.*, 1987; Sécheresse *et al.*, 1991), a planar arrangement of the metal atoms is maintained, so that no S-atom bridges more than three metal atoms. The central MS_4 tetrahedron remains close to its ideal geometry, with a small increase in *M*—S bond lengths and only minor changes to bond angles. Cu usually adopts a trigonal planar coordination, attached to two S atoms and a terminal halogen atom, though bridging of Cu atoms by halogens occurs for some of the $[MS_4(CuX)_4]^{2-}$ anions, leading to dimers or chain polymers.

In the new polymorph, the discrete anion (Figs. 1 and 2) lies on a position with crystallographic fourfold rotation symmetry, and the S atoms are disordered equally over two sets of positions. Tetrahedral coordination of Mo by four S atoms involves selection of two atoms from one set of equivalent positions and two from the other. This coordination is hardly distorted from ideal, with S—Mo—S angles deviating only slightly from the normal tetrahedral angle of 109.5° (Table 1). The four Cu-bridged S⋯S edges of the MoS_4 tetrahedron are shorter than the two unbridged edges. Coordination of Cu by two S and one halogen atom is trigonal planar, with a reduced angle between the two Cu—S bonds as a result of geometric constraints of the central MoS_4 tetrahedron; this feature is normal for MoS_4 and WS_4 tetrahedra with edges bridged by Cu^I atoms. The metal and halogen atoms of the anion are essentially coplanar, with the S atoms above and below this plane. Bond lengths are normal for this type of complex ion. Allowing for the disorder, the anion has essentially the same structure as in the first polymorph, where it has crystallographic $\overline{4}$ symmetry and is ordered.

The two crystallographically independent cations lie on positions of $\overline{4}$ point symmetry, each having four symmetry-equivalent *n*-butyl groups; a similar arrangement is found in the first polymorph. Bond lengths and angles are normal. Torsion angles for the *n*-butyl groups (Table 1) show that one cation has fully extended chains, while the other has one *trans* and one *gauche* arrangement for each chain.

The cations and anions are arranged in layers (Fig. 3), the anions being well separated from each other, with no bridging by the halogen atoms.

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Experimental

To a dry acetone suspension (80 ml) of $(NH_4)_2[MoS_4]$ (0.26 g, 1.0 mmol), solid $(N^nBu_4)Br$ (0.65 g, 2.0 mmol) and CuCl (0.40 g, 4.0 mmol) were added under an atmosphere of purified nitrogen. After vigorous stirring for 12 h, the resulting red–violet solution was filtered and the filtrate was concentrated to about 10 ml. The product was precipitated as a powder by addition of diethyl ether and the supernatant solution was removed. The dark red precipitate was washed with *n*-hexane (3 × 20 ml) and dried *in vacuo*. It was dissolved in dichloromethane, to which diethyl ether was added until the solution became slightly turbid. Single crystals were obtained after 48 h. They were washed several times with diethyl ether. IR (KBr, cm^{-1}): ν(Mo–S) 455 (*s*). Electronic spectrum [DMF, λ nm (absorbance)]: 408.3 (0.541), 314.4 (1.661), 265 (1.364), 258 (1.314), 255.4 (1.185). ^{1}H NMR (DMSO-d_6, δ): 0.930 [*t*, ^3J(HH) = 0.183 Hz, 3H, $-CH_3$], 1.306 (*m*, 2H, $-CH_2CH_3$), 1.563 (*m*, 2H, $-CH_2-$), 3.155 (*m*, 2H, $-CH_2N$). ^{13}C NMR (DMSO-d_6, δ): 13.524 ($-CH_3$), 19.237 ($-CH_2CH_3$), 23.085 ($-CH_2-$), 57.562 ($-CH_2N$).

Crystal data

$(C_{16}H_{36}N)_2[MoS_4(CuCl)_4]$
$M_r = 1119.51$
Tetragonal, $P4/n$
$a = 13.3356$ (6) Å
$c = 13.6495$ (9) Å
$V = 2427.4$ (2) Å^3
$Z = 2$
$D_x = 1.532$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 86 reflections
$\theta = 2.5$–$25.0°$
$\mu = 2.64$ mm^{-1}
$T = 150$ (2) K
Plate, purple
0.40 × 0.40 × 0.05 mm

Data collection

Nonius KappaCCD diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2002)
$T_{min} = 0.701$, $T_{max} = 0.876$
19584 measured reflections
2796 independent reflections

2191 reflections with $I > 2\sigma(I)$
$R_{int} = 0.031$
$\theta_{max} = 27.5°$
$h = -17 \rightarrow 17$
$k = -15 \rightarrow 17$
$l = -17 \rightarrow 17$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.024$
$wR(F^2) = 0.058$
$S = 1.09$
2796 reflections
119 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0191P)^2 + 1.5691P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.46$ e Å^{-3}
$\Delta\rho_{min} = -0.36$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Mo—S	2.2406 (10)	Cu—S^{i}	2.2159 (11)
Mo—S′	2.2556 (10)	Cu—S′	2.2768 (10)
Cu—Cl	2.1563 (5)	Cu—S′^{i}	2.2783 (10)
Cu—S	2.2134 (10)		
S—Mo—S^{ii}	109.78 (6)	S^{i}—Cu—S′	108.67 (4)
S—Mo—S′^{iii}	108.56 (4)	S—Cu—S′^{i}	108.68 (4)
S—Mo—S′^{i}	108.53 (4)	Mo—S—Cu	72.12 (3)
S′—Mo—S′^{ii}	112.85 (5)	Mo—S—Cu^{iii}	72.08 (3)
Cl—Cu—S	123.75 (3)	Cu—S—Cu^{iii}	113.61 (5)
Cl—Cu—S^{i}	123.93 (3)	Mo—S′—Cu	70.69 (3)
Cl—Cu—S′	127.36 (3)	Mo—S′—Cu^{iii}	70.66 (3)
Cl—Cu—S′^{i}	127.53 (3)	Cu—S′—Cu^{iii}	108.91 (4)
N1—C1—C2—C3	−174.11 (15)	N2—C5—C6—C7	−173.47 (16)
C1—C2—C3—C4	−172.65 (19)	C5—C6—C7—C8	74.8 (3)

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

The space group $P4/n$ was determined unambiguously from the systematic absences and confirmed by successful refinement; there is pseudo-body-centring, reflections with $h + k + l = 2n + 1$ having an average intensity approximately 40% of that for reflections with $h + k + l = 2n$. Mo lies on a crystallographic fourfold rotation axis (4 or C_4), while the two N atoms lie at improper fourfold rotation sites ($\bar{4}$ or S_4); thus the asymmetric unit of the structure consists of one-quarter of the anion and two separate quarters of cations. The structure is affected by two types of disorder. The S atoms are disordered equally over two independent sets of equivalent positions, generating eight positions around the central Mo atom; each anion contains two S atoms from one set (*S*) and two from the other (S′). The chlorine atoms are partially substituted by bromine (derived from the tetra-*n*-butylammonium bromide reagent); the refined proportion of Br is 8.2 (2)%, which is too low to allow independent refinement of separate positions for Cl and Br, so they were constrained to the same site with identical displacement parameters. H atoms were placed geometrically (C—H = 0.98–0.99 Å) and refined with a riding model; U_{iso}(H) was constrained to be 1.2 (1.5 for methyl groups) times U_{eq} of the carrier atom.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *EvalCCD* (Duisenberg *et al.*, 2003); data reduction: *EvalCCD*; 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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