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Tris(tetraethylammonium) tris(μ_3-sulfido)-bis[bromocopper(I)][dibromocopper(I)]-oxomolybdate(VI) acetone solvate

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The title compound, $(NEt_4)_3[(MoOS_3)(CuBr)_2(CuBr_2)]\cdot(CH_3)_2CO$, contains a central pseudo-tetrahedral $MoOS_3^{2-}$ unit with Cu atoms bridging all three S$\cdots$S edges while the Mo=O bond remains terminal. The Mo, 3 Cu and three triply bridging S atoms occupy seven of the vertices of a distorted cube, the vertex opposite Mo being vacant. Two of the Cu atoms carry one terminal halogen atom each and have distorted trigonal planar coordination, while the third carries two and has distorted tetrahedral coordination. One of these two halogen atoms on the third Cu atom has a secondary interaction with one of the other Cu atoms, so it may be considered as semi-bridging. Three of the four halogen sites show disorder as a result of minor substitution of Cl for Br, the semi-bridging halogen atom being purely or essentially Br. This semi-bridging type of halogen is unprecedented in $MOS_3Cu_3X_n$ cluster anions.

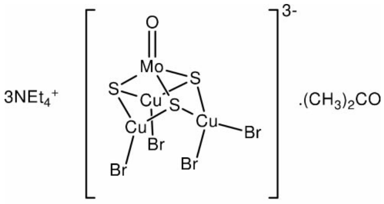
Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.020 Å
Disorder in main residue
R factor = 0.053
wR factor = 0.128
Data-to-parameter ratio = 13.5

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 obtained as an unexpected decomposition product during an attempt to prepare complexes of molybdenum-copper-sulfur clusters with nitrogen heterocyclic ligands. Although the structure determination was hampered by problems of twinning and disorder, the result is of interest as a new variant of halocopper(I)-bridged complexes of the pseudo-tetrahedral $MoOS_3^{2-}$ core.



(I)

The cations (two of which are disordered) and acetone solvent molecule are of unexceptional geometry. The structure of the anion is shown in Fig. 1, with selected geometric parameters in Table 1. This also shows some disorder, in that three of the four halogen sites are occupied predominantly by Br atoms [refined occupation factors of 0.849 (9), 0.696 (9) and 0.870 (9)], with a minor component of Cl; Br arises from the counterion in the tetraethylammonium bromide reagent, and Cl from copper(I) chloride. The fourth halogen site appears to be essentially or completely occupied by Br (Br4).

The central core of the anion is an incomplete cubane-like arrangement of Mo, 3Cu and three triply bridging sulfides; the eighth vertex of the distorted cube, opposite Mo, is vacant. The $MoOS_3$ unit, recognisable from the $[MoOS_3]^{2-}$ reagent, retains its approximate tetrahedral geometry and deviates only slightly from ideal C_{3v} symmetry; the three S—Mo—S angles are smaller than the three O—Mo—S angles, as expected, because each S···S edge is bridged by a Cu atom, while the terminal bond to oxygen is formally a double bond. Two of the Cu atoms carry a terminal halogen atom each, while the third, Cu3, is bonded to two halogen atoms, disrupting the threefold symmetry of the anion. The Cu—Br bond to Br4 is markedly longer than the others. There is a secondary intermolecular interaction of Br4 with Cu1, with a length of 2.996 (2) Å, such that Br4 may be considered as semi-bridging. Thus, the primary coordination of Cu1 and Cu2 is distorted trigonal planar (the secondary interaction of Cu1 with Br4 having little impact on this geometry), while that of Cu3 is distorted tetrahedral. The three-coordinate Cu atoms form shorter Cu—S bonds than the four-coordinate Cu3, as expected.

There are eleven structures in the Cambridge Structural Database (version 5.25, November 2003; Allen, 2002) containing an MOS$_3$Cu$_3$ core with halogen atoms X attached to the copper atoms (M = Mo or W). Of these, six with X:M = 3 have just three halogen atoms, which are terminally bonded, giving anions of approximate C_{3v} symmetry [Müller *et al.*, 1989; Clegg, Garner *et al.*, 1983; Clegg, Scattergood & Garner, 1988; Jeannin *et al.*, 1992 (two isomorphous structures); Hou *et al.*, 1995]. Two with X:M = 3 have dimeric anions with two unsymmetrical halogen bridges between Cu atoms (Hou *et al.*, 1994; Hou, Long *et al.*, 1996). One has an extra iodine atom (X:M = 4) bridging all three Cu atoms (Hoggard *et al.*, 1996). The other two, with X:M = 4, contain one bridging halogen, but this is a symmetrical bridge (Hou, Liang *et al.*, 1996; Shi *et al.*, 1995). The highly unsymmetrical bridge in the title compound is thus unprecedented in this family of complexes. The previous structure with a symmetrical Br bridge (Shi *et al.*, 1995) has Cu—Br bonds of length 2.871 Å, intermediate between the primary [2.603 (2) Å] and secondary [2.996 (2) Å] bond lengths for Br4 in the title compound.

Experimental

In an attempt to prepare a complex of the MoOS$_3$Cu$_3$ core with 1-methyl-imidazoline-2(3*H*)-thione (Hmimt), (NH$_4$)$_2$[MoO$_2$S$_2$] (0.24 g, 1 mmol) was mixed with Et$_4$NBr (0.42 g, 2 mmol), CuCl (0.21 g, 2.1 mmol) and Hmimt (0.46 g, 4 mmol) in acetone (30 ml). The red solution, believed to contain the desired product (UV–vis λ_{max} = 500 nm; IR ν(Mo—S) = 445 cm^{-1}, ν(Mo—O) = 911 cm^{-1}), was allowed to stand at 278 K for 24 h after addition of a small amount of petroleum ether to aid crystallization. The resultant small crystals of the title compound, however, represent a decomposition product.

Crystal data

$(C_8H_{20}N)_3[(MoOS_3)(CuBr)_2$-
$(CuBr_2)]\cdot C_3H_6O$
M_r = 1141.42
Monoclinic, $P2_1/n$
a = 14.2654 (10) Å
b = 17.8039 (18) Å
c = 17.288 (2) Å
β = 93.224 (9)°
V = 4383.9 (7) Å^3
Z = 4
D_x = 1.729 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 6309
reflections
θ = 2.5–23.4°
μ = 5.04 mm^{-1}
T = 150 (2) K
Block, red
0.30 × 0.16 × 0.10 mm

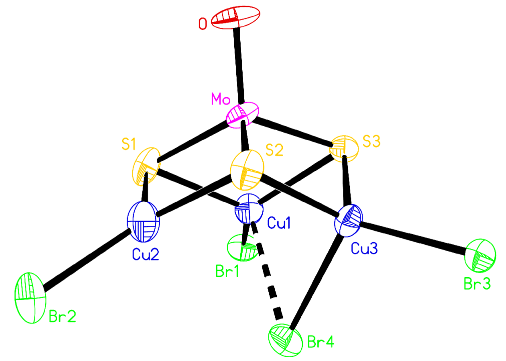


Figure 1
The structure of the anion, with atom labels and 50% probability ellipsoids for non-H atoms. Minor disorder components (Cl substitution for Br) are omitted. The secondary Cu3···Br4 interaction is shown dashed.

Data collection

Nonius KappaCCD diffractometer
φ and ω scans
Absorption correction: multi-scan
(*SADABS*; Sheldrick, 2002)
T_{min} = 0.297, T_{max} = 0.601
6309 measured reflections
6309 independent reflections
5046 reflections with $I > 2\sigma(I)$
θ_{max} = 23.4°
h = −15 → 15
k = −19 → 19
l = −19 → 19

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.053
$wR(F^2)$ = 0.128
S = 1.08
6309 reflections
468 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0173P)^2$
$+ 40P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 1.06 e Å^{-3}
$\Delta\rho_{min}$ = −0.97 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Mo—O	1.708 (6)	Cu1—S3	2.275 (3)
Mo—Cu1	2.6728 (14)	Cu2—Br2	2.2822 (19)
Mo—Cu2	2.6461 (16)	Cu2—S1	2.243 (3)
Mo—Cu3	2.6869 (14)	Cu2—S2	2.249 (3)
Mo—S1	2.266 (3)	Cu3—Br3	2.3432 (16)
Mo—S2	2.278 (3)	Cu3—Br4	2.6035 (15)
Mo—S3	2.265 (3)	Cu3—S2	2.300 (3)
Cu1—Br1	2.3130 (16)	Cu3—S3	2.309 (3)
Cu1—S1	2.264 (3)		
O—Mo—S1	111.7 (3)	Br3—Cu3—S3	116.79 (8)
O—Mo—S2	111.8 (3)	Br4—Cu3—S2	102.93 (8)
O—Mo—S3	109.8 (3)	Br4—Cu3—S3	97.68 (7)
S1—Mo—S2	107.39 (10)	S2—Cu3—S3	106.29 (10)
S1—Mo—S3	107.37 (10)	Mo—S1—Cu1	72.32 (8)
S2—Mo—S3	108.59 (9)	Mo—S1—Cu2	71.87 (8)
Br1—Cu1—S1	118.66 (9)	Cu1—S1—Cu2	101.22 (11)
Br1—Cu1—S3	126.61 (9)	Mo—S2—Cu2	71.54 (8)
S1—Cu1—S3	107.09 (10)	Mo—S2—Cu3	71.87 (8)
Br2—Cu2—S1	118.94 (10)	Cu2—S2—Cu3	99.41 (10)
Br2—Cu2—S2	130.27 (9)	Mo—S3—Cu1	72.14 (8)
S1—Cu2—S2	109.20 (11)	Mo—S3—Cu3	71.94 (8)
Br3—Cu3—Br4	108.94 (6)	Cu1—S3—Cu3	92.54 (9)
Br3—Cu3—S2	120.86 (8)		

The crystal was non-merohedrally twinned; the two components of the twinning were identified and resolved with the program *ROTWIN* (Pink & Young, 2000). Because of the overlap of inequivalent reflections from the two components, merging of symmetry-equivalent reflections before refinement was not possible. Intensity data were truncated at a resolution of 0.9 Å, higher-angle data being weak and having poor internal agreement statistics. The structure was

m232 Beheshti *et al.* • $(C_8H_{20}N)_3[(MoOS_3)(CuBr)_2(CuBr_2)]\cdot C_3H_6O$ *Acta Cryst.* (2004). E**60**, m231–m233

found to suffer from two types of disorder. Two of the three cations are disordered, and each was modelled with two alternative arrangements of the ethyl groups; the atoms of the minor disorder components were refined with isotropic displacement parameters, and similarity restraints were applied to geometry and displacement parameters in these disordered cations. Three of the four halogen sites were modelled as largely Br with a minor substitution by Cl (both halogens being present in the reaction components), the exception being Br4, which refined acceptably as exclusively bromine; it was not possible to distinguish separate sites for Cl and Br, despite the expected difference in bond lengths to Cu, and a common site was used in each case, together with common displacement parameters. We found and modelled a similar Br/Cl disorder in another complex of this type recently (Brooks *et al.*, 2004).

H atoms were placed geometrically and refined with a riding model, with C—H = 0.98 Å, and with $U_{\rm iso}$ constrained to be $1.5U_{\rm eq}$(C). The largest features of the final difference synthesis lie approximately 1 Å from heavy atoms (Mo and Br).

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *EvalCCD* (Duisenberg *et al.*, 2003); data reduction: *EvalCCD* and *ROTWIN* (Pink & Young, 2000); 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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