Synthesis and Crystal Structure of $[PPh_4]_2[MoS_4(CuBr)_4]\cdot Me_2CO$; the Assembly of Four Copper(I) Centres about a Tetrathiomolybdate(VI) Moiety

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Reaction of $[MoS_4]^{2-}$ with CuX (1:4) in acetone produces the mixed-metal–sulphur complex anions $[MoS_4(CuX)_4]^{2-}$ (X = Cl or Br); a crystal structure determination for $[PPh_4]_2[MoS_4(CuBr)_4]\cdot Me_2CO$ shows that four edges of the tetrahedral MoS_4 core are bridged by Cu^I atoms, giving an aggregate of approximate D_{2d} symmetry, with μ_2-Br bridges linking these aggregates to form a one-dimensional polymeric anion.

The characterisation of discrete Cu–Mo–S aggregates is currently undergoing significant developments.[1–6] The intrinsic chemical interest in these systems is stimulated by the need to improve the chemical basis for the interpretation of Cu–Mo–S interactions in biological systems, especially the molybdenum-induced copper deficiency in ruminant animals.[7,8]

Herein, we report that $[PPh_4]_2[MoS_4]$ reacts with CuX (X = Cl or Br) (1:4) in acetone, to afford the corresponding $[PPh_4]_2[MoS_4(CuX)_4]$ salt as the major reaction product. Crystals of $[PPh_4]_2[MoS_4(CuBr)_4]\cdot Me_2CO$ from the preparation were suitable for *X*-ray crystallographic study.

Crystal data: $C_{51}H_{46}Br_4Cu_4MoOP_2S_4$, $M_r = 1534.85$, triclinic, $P\bar{1}$, $a = 12.478(2)$, $b = 16.783(2)$, $c = 27.461(3)$ Å, $\alpha = 79.35(1)$, $\beta = 88.84(1)$, $\gamma = 82.00(1)°$, $U = 5596.7$ Å^3, $Z = 4$, $D_c = 1.82$, $D_m = 1.8$ g cm^{-3}, $F(000) = 3008$, Mo-K_α radiation, $\lambda = 0.71069$ Å, $\mu = 47.79$ cm^{-1}. Data were collected to $2\theta_{max} = 45°$ on a Stoe–Siemens diffractometer; of 14546 reflections, 8352 with $F > 4\sigma(F)$ were used for structure determination by Patterson and Fourier methods. Least-squares refinement with anisotropic thermal parameters for heavy atoms, isotropic for C and O, no H atoms, and phenyl rings constrained as ideal hexagons of side 1.395 Å, gave a final R of 0.079; $R_w = [\Sigma_w(F_o - F_c)^2/\Sigma_w F_o^2]^{1/2} = 0.065$, with $w^{-1} = \sigma^2(F) + 0.00009(F)^2$. Data were corrected for absorption by a semi-empirical method.†

The structure contains, as crystallographically independent units, four $[PPh_4]^+$ cations, two acetone molecules, and two $[MoS_4(CuBr)_4]^{2-}$ anions. Each molybdenum atom of the structure (Figure 1) is at the centre of an essentially tetrahedral MoS_4 unit, in which the mean Mo–S bond length is 2.235(6) Å [maximum 2.242(6), minimum 2.227(5) Å], and the S–Mo–S angles lie between 108.3(1) and 111.1(1)°. Four copper atoms are bound to the MoS_4 core: each is symmetrically attached to one edge of the tetrahedron. The overall arrangement involves each sulphur atom bonding to two copper atoms with Cu–S bond lengths ranging from 2.237(5) to 2.305(5) Å, so that the MoS_4Cu_4 aggregate approximates to D_{2d} symmetry. The 4:1 copper to molybdenum stoicheiometry is the

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

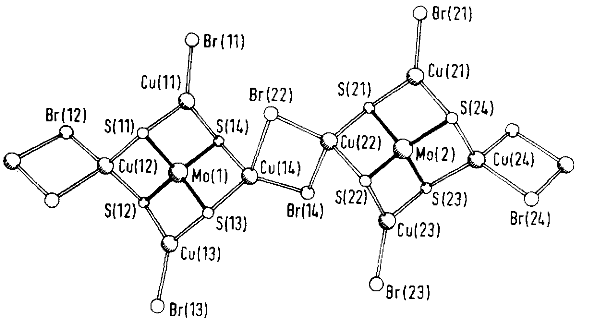

Figure 1. The crystallographically independent anions in $[PPh_4]_2[MoS_4(CuBr)_4]\cdot Me_2CO$, showing the atom labelling and the linkages forming a polymeric chain. Key bond lengths: Cu(12)–S(11) 2.296(5), Cu(12)–S(12) 2.286(5), Cu(24)–S(23) 2.305(5), Cu(24)–S(24) 2.297(5), other Cu–S mean 2.254(11), Cu(12)–Br(12) 2.442(3), Cu(12)–Br(24′) 2.551(3), Cu(24)–Br(24) 2.473(3), Cu(24)–Br(12″) 2.537(3), Cu(14)–Br(14) 2.320(3), Cu(14)–Br(22) 2.927(3), Cu(22)–Br(22) 2.333(3), Cu(22)–Br(14) 2.787(3), other Cu–Br mean 2.281(3) Å. Single and double primes indicate atoms translated by +1 and —1 respectively along the crystallographic *b* axis; this axis runs horizontally in the figure.

largest metal uptake so far obtained in a metal-sulphide cluster based on MoS_4. Therefore, this compound provides a further illustration of a possible mechanism for the depletion of the available copper, in biological systems when $[MoS_4]^{2-}$ is generated or ingested.

The approximate D_{2d} symmetry of the metal-sulphide core is the highest yet identified for this type of system. The lengthening of the Mo–S bonds, from 2.178 Å in $[MoS_4]^{2-}$,[9] to 2.235(6) Å, is normal[1–6] for copper(I) co-ordination and is reflected in the change in the ν(Mo–S) i.r. stretching frequency from 472 to 458 cm^{-1}. The Mo · · · Cu distances [2.618(3) to 2.685(3) Å] are typical of the corresponding separations observed in other copper(I)–molybdenum(VI)–sulphur clusters,[1–6] and the approach is sufficiently close to permit a direct metal–metal interaction.

In $[PPh_4]_2[MoS_4(CuBr)_4]\cdot Me_2CO$, two mutually *trans* copper atoms of each MoS_4Cu_4 aggregate have their co-ordination completed by a bromine atom [mean Cu–Br = 2.281(3) Å], to produce an essentially trigonal planar S_2CuBr arrangement. The other two copper atoms possess a distorted tetrahedral co-ordination geometry involving two bromine atoms, each of which serves as a bridging ligand between different MoS_4Cu_4 aggregates. Two types of $Cu(\mu_2\text{-}Br)_2Cu$ linkages occur, one involving four Cu–Br bonds of a comparable length [2.442(3), 2.550(3); 2.473(3), 2.536(3) Å], and the other comprising a disparate collection of Cu–Br bonds [2.330(3), 2.927(3); 2.333(3), 2.787(3) Å]. Thus, the latter linkage hardly affects the bonding of the relevant copper atoms [Cu(14) and Cu(22)] to the MoS_4 cores, the long Cu–Br bond being approximately perpendicular to the otherwise trigonal S_2Br co-ordination of the copper atoms. The former linkage, however, weakens the attachment of Cu(12) and Cu(24) to the MoS_4 cores, giving significantly longer Cu–S and Cu · · · Mo distances. These *trans* associations of the metal sulphide aggregates produce an anionic polymeric chain (Figure 1). Therefore, the bulk properties of $[PPh_4]_2[MoS_4(CuBr)_4]\cdot Me_2CO$ are potentially interesting, and these are currently under investigation.

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References

1 S. R. Acott, C. D. Garner, J. R. Nicholson, and W. Clegg, *J. Chem. Soc., Dalton Trans.*, 1983, 713.
2 S. F. Gheller, P. A. Gazzana, A. F. Masters, R. T. C. Brownlee, M. J. O'Connor, A. G. Wedd, J. R. Rodgers, and M. R. Snow, *Inorg. Chim. Acta*, 1981, **54**, L131.
3 A. Müller, M. Dartmann, C. Römer, W. Clegg, and G. M. Sheldrick, *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 1060.
4 A. Müller, H. Bögge, H. G. Tolle, R. Jostes, U. Schimanski, and M. Dartmann, *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 654; A. Müller, H. Bögge, and U. Schimanski, *Inorg. Chim. Acta*, 1983, **69**, 5.
5 A. Müller, U. Schimanski, and J. Schimanski, *Inorg. Chim. Acta*, 1983, **76**, L245.
6 C. D. Garner, J. R. Nicholson, and W. Clegg, *Acta Crystallogr., Sect. C*, 1983, **39**, 552.
7 C. F. Mills, *Philos. Trans. R. Soc., London, Ser. B*, 1979, **288**, 51.
8 I. Bremner, C. F. Mills, and B. W. Young, *J. Inorg. Biochem.*, 1982, **16**, 109.
9 A. Müller, E. Diemann, R. Jostes, and H. Bögge, *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 934 and references therein.