Molybdenum–Copper–Sulphur-containing Cage System and its Bioinorganic Relevance. Preparation and *X*-Ray Crystal Structure of $(Cu_3MoS_3Cl)(PPh_3)_3S$ with an Interesting Stereochemistry of Non-equivalent Cu Atoms

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Summary The preparation and structural characterization of $(Cu_3MoS_3Cl)(PPh_3)_3S$, which has a molybdenum–copper–sulphur-containing pseudo-cubane type cage structure and which is a model for Cu–Mo–S interactions in biochemical processes, is reported; the stereochemistry of the three non-equivalent Cu atoms is unusual with the co-ordination of copper ranging from strongly distorted tetrahedral to pseudo-trigonal planar.

The biological importance of several transition metal–sulphur clusters and cage systems is well known. Compounds containing different biometals are also important although these are in general much more difficult to prepare. Corresponding species containing molybdenum and copper should be interesting because of the inter-relation between these metals in numerous biological processes[1–5] (the so-called 'Mo–Cu antagonism;' *e.g.* where the Mo concentration in the forage is low, an excess of Cu accumulates in the liver of ruminants[1]). Cu–Mo–S interactions have been reported to be responsible for this type of inter-relation in different processes.[2–4] Here we report a Cu–Mo–S-containing compound having a strongly distorted cubane-like structure together with a possible reason for this inter-relation.

Red diamagnetic crystals of $(Cu_3MoS_3Cl)(PPh_3)_3S$ were prepared by extracting an aqueous solution of $(NH_4)_2MoS_4$ with a solution of $CuCl_2{\cdot}2H_2O$ and PPh_3 in CH_2Cl_2 and then crystallizing the compound by vapour diffusion. (A tube containing the organic phase was kept for 2—3 days in a closed beaker containing diethyl ether.) A characteristic i.r. absorption doublet (solid, KBr pellet) due to the $\nu(Mo{-}S)_{br}$ vibration was found at 441 and 447 cm^{-1}.

Crystal data: $C_{54}H_{45}ClCu_3MoP_3S_4$, $M = 1237{\cdot}2$, orthorhombic, space group $P2_12_12_1$, $a = 12{\cdot}991(2)$, $b = 17{\cdot}833(2)$, $c = 22{\cdot}674(3)$ Å, $U = 5253{\cdot}1$ Å^3, $Z = 4$, $D_c = 1{\cdot}56$ g cm^{-3}, $\mu = 18{\cdot}0$ cm^{-1} for Mo-K_α ($\lambda = 0{\cdot}71069$ Å). The structure was solved by conventional heavy atom methods. Anisotropic (except for the carbon atoms) least-squares refinements converged at $R = 0{\cdot}063$ for 3537 independent

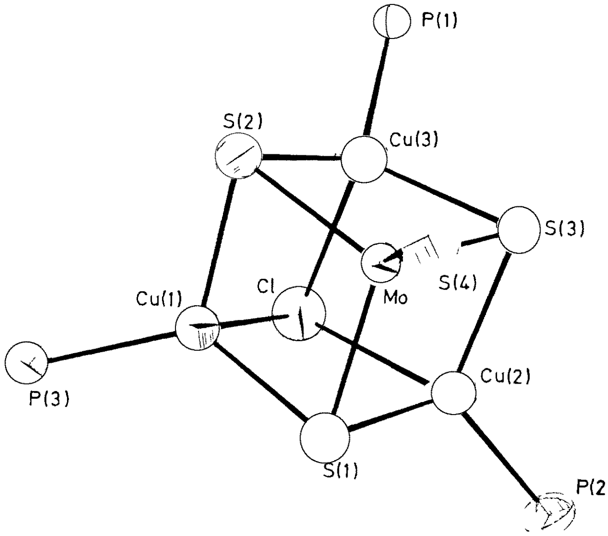

Figure 1. Molecular structure of (Cu_3MoS_3Cl) $(PPh_3)_3S$. The phenyl rings have been omitted for clarity. Bond distances: Mo–S(1) 2·269(4), Mo–S(2) 2·253(4), Mo–S(3) 2·241(3), Mo–S(4) 2·118(4), Mo . . . Cu(1) 2·678(2), Mo . . . Cu(2) 2·702(2), Mo . . . Cu(3) 2·720(2), Cu(1)–S(1) 2·266(4), Cu(1)–S(2) 2·281(4), Cu(1)–P(3) 2·224(4), Cu(1)–Cl 2·764(4), Cu(2)–S(1) 2·293(4), Cu(2)–S(3) 2·287(4), Cu(2)–P(2) 2·225(4), Cu(2)–Cl 2·723(4), Cu(3)–S(2) 2·318(4), Cu(3)–S(3) 2·332(4), Cu(3)–P(1) 2·225(4), Cu(3)–Cl 2·471(4) Å.

reflections [$4{\cdot}0 < 2\theta < 48^\circ$, $I \geqslant 1{\cdot}96\sigma(I)$] measured on a Syntex P2$_1$ four-circle diffractometer.†

The molecular structure is illustrated in Figure 1. It can be described as a highly distorted cube, in which four of the corners are formed by the terdentate MoS$_4^{2-}$ ligand. {The co-ordination polyhedron of the Mo atom is found to be a slightly distorted tetrahedron [S–Mo–S angles 107·34(13)—111·99(15)°]}. The remaining positions are occupied by one chlorine and three copper atoms, each of the metals having a terminal PPh$_3$ ligand. The co-ordination variability of Cu is very interesting and ranges from a strongly distorted tetrahedron [angles about Cu(3): 102·43(14)—126·46(15)°] to a nearly trigonal planar co-ordination {with a very weak Cu–Cl interaction roughly perpendicular to the plane formed by the two sulphur and the phosphorus atoms [Cu(1): 95·14(13)—130·57(15)°]; see Figure 2}.

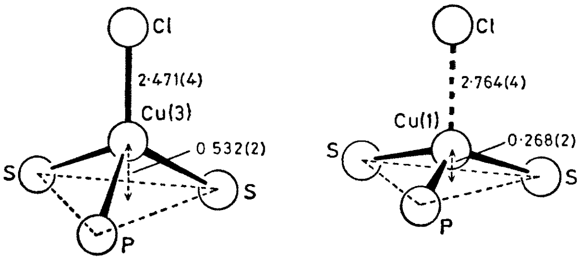

FIGURE 2. Schematic drawing of the co-ordination polyhedra of Cu(1) and Cu(3). The co-ordination polyhedron of Cu(2) is in between those of Cu(1) and Cu(3).

Our investigations showed that thiometallates like MoS$_4^{2-}$ can be used to generate unusual transition metal ring and cage systems.[6] This is especially interesting because the Cu–Mo–S inter-relation just mentioned has been postulated to be due to the reaction of thiomolybdate (formed from molybdate, *e.g.* in the rumen after reduction of sulphate to sulphide) with Cu^{2+} to give CuMoS$_4$.[2]‡ The formation of Cu complexes with thiomolybdate ions as ligands in several biological processes may well be responsible for the Cu–Mo inter-relation, considering the fact that the MoS$_4^{2-}$ ions have a high tendency to form complexes with transition metal cations,[8] especially soft ones.[6] (Nitrogenase in its native state should also contain a thiomolybdate ligand.)[9]

It is probable that Cu–Mo–S inter-relationships play a key role not only in different biological processes in plants and animals but also in Wilson's disease of humans.[1] For most individuals the rate of elimination of the amount of Mo is proportional to that of Cu but for patients with Wilson's disease the elimination rate for both metals is much higher.

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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.

‡ This is definitely incorrect as Cu^{2+} is reduced in the presence of thiometallates like WS$_4^{2-}$ or MoS$_4^{2-}$.[7]

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