# Synthesis and Structure of $[Ph_4P]_2[Cu_6(S_4)_3S_5]$, a Polycyclic Hexanuclear Copper(I) Cluster with Complete Sulphur Co-ordination

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The reaction of a methanolic $Cu^I$–thiolate solution with elemental sulphur yields deep-red $[Cu_6(S_4)_3S_5]^{2-}$ which is the first hexanuclear $Cu^I$ cluster with the complete sulphur co-ordination; the polycyclic anion can be regarded as an inorganic analogue of a corresponding mixed thiolate-sulphide complex and thus can serve as a possible model for $Cu^I$–thiolate sites in biological systems.



Besides iron the element copper is one of the most frequently observed transition metals in biological systems.[1] The occurrence of metal–thiolate bonds has now been established for different metallothioneins including the copper containing species.[2] As the cysteine:copper ratios of these proteins which range from 1.2—6.2[2] indicate the existence of $Cu^I$–thiolate sites different from that observed in yeast Cu-thionein[3] the synthesis of polynuclear copper–sulphur centres which reflect structural characteristics of protein sites is of special importance.

We have previously shown that tetra- and penta-sulphido ligands form tetranuclear complexes with $Cu^I$ which are closely related to the analogous $[Cu_4(thiolate)_6]^{2-}$ clusters[4] which proves the potential value of polysulphide complexes as suitable model compounds for $Cu^I$–thiolate sites.[5] In this communication we report the preparation and structure of the anion $[Cu_6(S_4)_3S_5]^{2-}$ (**1**) which not only represents the first hexanuclear $Cu^I$ cluster with complete sulphur co-ordination but is also the only isolated binary $Cu^I$–sulphur complex presently known besides $[Cu_{12}S_8]^{4-}$ and $[Cu_4(S_4)_3]^{2-}$.[5] The reaction of $CuCl_2{\cdot}2H_2O$ with a threefold excess of NaSR (R = Et, $CH_2Ph$) in MeOH under an $N_2$ atmosphere led to soluble $Cu^I$–thiolates[6] and insoluble polymeric $(CuSR)_n$. The pale yellow filtrate reacted with elemental sulphur to give deep-red solutions from which orange $[Ph_4P]_2[Cu_6(S_4)_3S_5]$ (**2**) precipitated on addition of $Ph_4PBr$. The structure of (**2**) was determined by *X*-ray crystallography.

$$[Ph_4P]_2[Cu_6(S_4)_3S_5]$$
(**2**)

*Crystal data*: $C_{48}H_{40}P_2S_{17}Cu_6$, $M = 1605.1$, monoclinic, $a = 20.069(5)$, $b = 11.546(2)$, $c = 27.202(7)$ Å, $\beta = 115.09(2)°$, space group $C2/c$, $Z = 4$, $T = 150$ K, $D_c = 1.867$ g cm$^{-3}$, $\mu(\text{Mo-}K_\alpha) = 29.6$ cm$^{-1}$, crystal dimensions *ca.* $0.25 \times 0.20 \times 0.20$ mm. A total of 2638 unique reflexions were collected with a Syntex $P2_1$ four circle diffractometer ($2\theta$–$\theta$ scan, $2\theta_{max} = 40°$) equipped with a scintillation counter and a graphite monochromator. The structure was solved by direct methods and refined [full-matrix least-squares, anisotropic temperature factors for all non-H atoms, H atoms fixed at their calculated positions, 2294 reflexions with $I > 1.96\sigma(I)$] to $R = 0.027$ and $R_w = 0.030$, respectively.† In crystals of (**2**) isolated anions (**1**) are separated by $Ph_4P^+$ cations which do not show any unusual features. The structure of (**1**) is given in Figure 1. The hexanuclear metal frame is held together by the unusual and unprecedented co-ordinating properties of three tetrasulphido groups and an additional pentasulphido ligand. Anion (**1**) is located on a twofold axis which passes through S(3) and bisects the S(9)–S(9′) bond. The architecture of the Cu framework can be described in terms of two distorted metal tetrahedra (indicated by single lines in Figure 1) which share the edge Cu(3)· · ·Cu(3′). The two $S_4^{2-}$ groups related by symmetry [S(4) to S(7) and S(4′) to S(7′)] define five-membered $CuS_4$ cycles with Cu(2) and Cu(2′), respectively. In this respect they are different from the third one [S(8) to S(8′)] which does not act as a chelating ligand. Each terminal sulphur atom of the bidentate $S_4^{2-}$ ligands bridges two adjacent Cu atoms resulting in short Cu· · ·Cu contacts for the chelating [Cu(1)· · ·Cu(2) 2.695(1), Cu(2)· · ·Cu(3) 2.790(1) Å] and significantly longer ones for the non-chelating ligand [Cu(2)· · ·Cu(3′) 2.928(1) Å.]

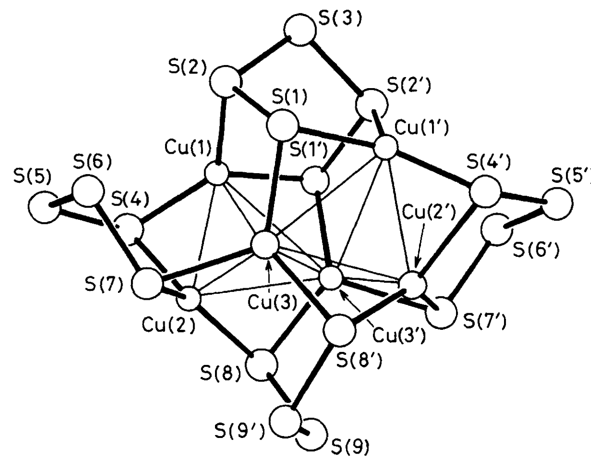


**Figure 1.** Structure of the polycyclic $[Cu_6(S_4)_3S_5]^{2-}$ anion (**1**); the primed atoms are related to the unprimed ones by a twofold axis which passes through S(3) and bisects the S(9)–S(9′) bond.

Another novel co-ordination principle is realized by four of the five sulphur atoms of the tetradentate $S_5^{2-}$ ligand which form a total of 6 S–Cu bonds. The most interesting structural feature is the bond between the β–S atom S(2) and Cu(1) which results in the formation of $CuS_4$ chelate rings [Cu(1), S(2), S(3), S(2′), S(1′)] different from those formed by the $S_4^{2-}$ groups. In addition, both terminal S atoms bridge opposite edges of two fused metal triangles resulting in Cu· · ·Cu separations [Cu(1)· · ·Cu(3′) 3.079(1) Å] comparable to those between atoms bridged by the non-chelating $S_4^{2-}$ ligand but significantly shorter than those which are not associated with a sulphur bridge [Cu(3)· · ·Cu(3′) 3.265(1), Cu(1)· · ·Cu(3) 3.409(1) Å].

The arrangement of the tetra- and penta-sulphido ligands results in a distorted trigonal-planar sulphur co-ordination for each Cu atom with Cu–S distances ranging from 2.180(2)—2.309(2) Å. From the architecture of the $[Cu_6(\alpha\text{–}S)_8(\beta\text{–}S)_2]^{2-}$ core of (**1**) a structurally related Cu–S frame with thiolate (replacing α–S atoms) or mixed thiolate–sulphide ligands

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

(replacing β-S atoms) can be derived that might reflect structural characteristics of Cu–S centres in proteins.

*Received, 25th November 1983; Com. 1543*

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