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 $[Cu_4(\text{thiolate})_6]^{2-}$ 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 × 0.20 × 0.20 mm. A total of 2638 unique reflexions were collected with a Syntex $P2_1$ four circle diffractometer (2θ–θ 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.]

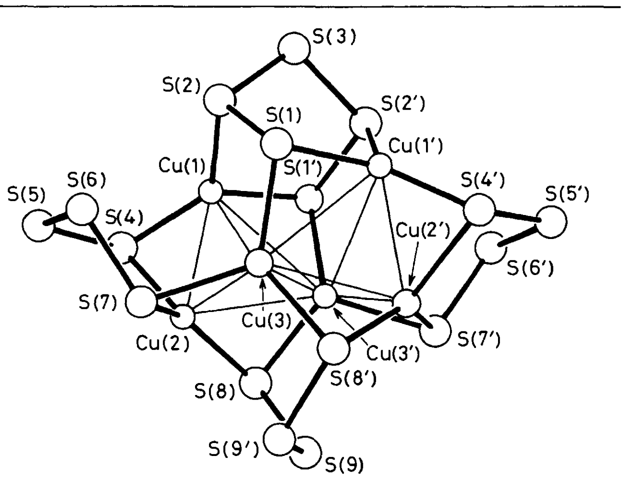

Figure 1. Structure of the polycyclic $[Cu_6(S_4)_3S_5]^{2-}$ anion (**1**); the primed atoms are related to the unprimed ones by a twofold axis which passes through S(3) and bisects the S(9)–S(9′) bond.

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

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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 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.

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