$[Cu_6S_{17}]^{2-}$, a Novel Binary Discrete Polynuclear Cu^I Complex with Several Interesting Structural Features: The Arrangement of the Metal Atoms and Co-ordination of Ligands

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The structure of $[PPh_4]_2[Cu_6S_{17}]$, obtained from Cu(acac)$_2$ (Hacac = acetylacetone) and PPh_4Br in an ethanol solution of polysulphide, contains an unusual arrangement of metal atoms (which can only approximately be described as two distorted Cu tetrahedra sharing one edge) and novel ligand co-ordination of polysulphide (S_4^{2-} and S_5^{2-}) ions.

Only a few mononuclear homoleptic $\{[Pt(S_5)_3]^{2-}$ [1]$\}$ and polynuclear $\{(Fe_2S_2(S_5)_2]^{2-}$ [2]$\}$ discrete polysulphido complexes have been reported. However, owing to the presence of different S_x^{2-} ions in polysulphide solutions and the ability of the ions to co-ordinate in various ways, it should be possible to stabilize a variety of different transition metal aggregates.

The novel compound $[PPh_4]_2[Cu_6S_{17}]$ (**1**) was obtained by the reaction of a mixture of Cu(acac)$_2$ (1 g) (Hacac = acetylacetone), PPh_4Br (0.5 g), and dimethylformamide (50 ml) with an ethanol solution of polysulphide (6 ml).† The mixture was heated quickly to 75 °C and filtered. A mixture of acetone (15 ml) and n-pentane (35 ml) was added at room temperature and after 1 week red–brown crystals (0.34 g) of (**1**) were obtained.

$$[PPh_4]_2[Cu_6S_{17}]$$
(**1**)

The crystal structure of (**1**) has been determined from a single crystal structure analysis.‡ The molecular structure of the discrete $[Cu_6S_{17}]^{2-}$ ion in crystalline (**1**) is shown in Figure 1 (including bond lengths and angles). There is a twofold axis through the non-co-ordinating sulphur atom of the S_5^{2-} ligand [S(1)] and the centre of the S(9)–S(9′) bond of the opposite S_4^{2-} ligand.

The anion contains a novel aggregate of six Cu^I ions, which can only very approximately be described as two greatly distorted tetrahedra [Cu(1) Cu(2) Cu(2′) Cu(3) and Cu(1′) Cu(2) Cu(2′) and Cu(3′)] sharing one edge [Cu(2) Cu(2′)]. The Cu–Cu distances within the Cu tetrahedra vary between 2.695(2) and 3.408(2) Å and the distances between the vertices are 4.561(2) [Cu(1)–Cu(1′)] and 3.888(2) Å [Cu(3)–Cu(3′)]. {A tetrahedral Cu_4 core, but not as distorted, with bridging sulphur ligands is found in $[Cu_4(\mu_2\text{-}SPh)_6]^{2-}$ [3]}. The shortest metal to metal distance in the aggregate [Cu(1)–Cu(3) 2.695(2) Å] is slightly longer than in Cu metal (2.551 Å). However, as our knowledge about closed shell Cu^I–Cu^I interactions is limited a discussion is difficult. In general the distances seem to be strongly influenced by the stereochemical demands of the ligands.[4]

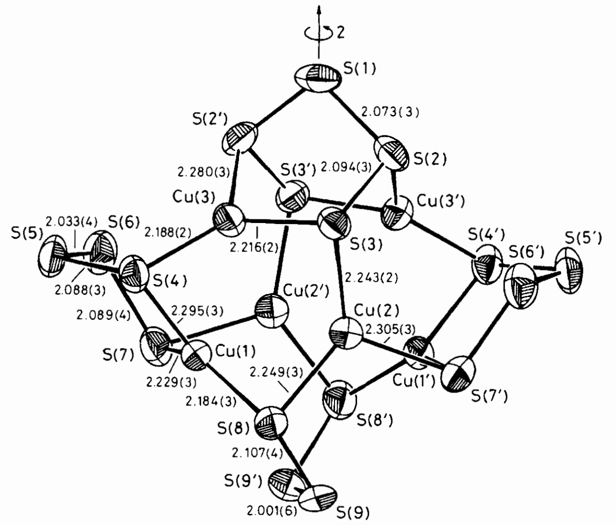

Figure 1. Structure of the $[Cu_6S_{17}]^{2-}$ anion. Distances shown are given in Å. Distances [all e.s.d.s are (2)]: Cu(1) $\cdots$ Cu(2), 2.959; Cu(1) $\cdots$ Cu(2′), 2.800; Cu(1) $\cdots$ Cu(3), 2.695; Cu(2) $\cdots$ Cu(2′), 3.301; Cu(2) $\cdots$ Cu(3), 3.094; Cu(2′) $\cdots$ Cu(3), 3.408; Cu(1) $\cdots$ Cu(1′), 4.561; Cu(3) $\cdots$ Cu(3′), 3.888 Å. Bond angles [all e.s.d.s. are (1) unless otherwise stated]: S(4)–Cu(1)–S(7), 106.0; S(4)–Cu(1)–S(8), 118.4; S(7)–Cu(1)–S(8), 135.5; S(3)–Cu(2)–S(7′), 117.6; S(3)–Cu(2)–S(8), 125.7; S(7′)–Cu(2)–S(8) 110.6; S(2′)–Cu(3)–S(3), 104.3; S(2′)–Cu(3)–S(4), 128.3; S(3)–Cu(3)–S(4), 127.1; S(2)–S(1)–S(2′), 102.2(2); Cu(3′)–S(2)–S(1), 98.3; Cu(3′)–S(2)–S(3), 101.1; S(1)–S(2)–S(3), 104.0(2); Cu(2)–S(3)–Cu(3), 87.8; Cu(2)–S(3)–S(2), 109.6; Cu(3)–S(3)–S(2), 102.3; Cu(1)–S(4)–Cu(3), 73.9; Cu(1)–S(4)–S(5), 98.7; Cu(3)–S(4)–S(5), 110.1; S(4)–S(5)–S(6), 104.5(2); S(5)–S(6)–S(7), 105.2(2); Cu(1)–S(7)–Cu(2′), 76.2; Cu(1)–S(7)–S(6), 99.8; Cu(2′)–S(7)–S(6), 104.2; Cu(1)–S(8)–Cu(2), 83.7; Cu(1)–S(8)–S(9), 112.8; Cu(2)–S(8)–S(9), 99.4; S(8)–S(9)–S(9′), 111.4(2)°.

The complex also contains novel types of ligand co-ordination. Whereas only the two terminal S atoms of the three S_4^{2-} ligands are bonded to copper atoms, co-ordination of four S atoms of the S_5^{2-} ligand [S(3)–S(2)–S(1)–S(2′)–S(3′)] is found. Each of the two equivalent S_4^{2-} ions [S(4)–S(5)–S(6)–S(7) and S(4′)–S(5′)–S(6′)–S(7′)] acts as a bridging and chelating ligand for the two Cu tetrahedra with co-ordination to three different Cu atoms. S(4) and S(7) [correspondingly S(4′) and S(7′)] are bonded to the same atom Cu(1) [Cu(1′)] and also to Cu(3) and Cu(2′) [Cu(3′) and Cu(2)], respectively. The other S_4^{2-} [S(8)–S(9)–S(9′)–S(8′)]

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† Preparation of the polysulphide solution: NH_3 was passed through cooled ethanol (400 ml) for 45 min. After the addition of sulphur (S_8) (40 g) a stream of H_2S was passed through the suspension for *ca.* 2 min.

‡ *Crystal data*: $C_{48}H_{40}Cu_6P_2S_{17}$, $M = 1605.1$, monoclinic, space group $C2/c$, $a = 20.270(7)$, $b = 11.605(5)$, $c = 26.331(9)$ Å, $\beta = 109.68(4)°$, $U = 5832(4)$ Å^3, $D_c = 1.83$ g cm^{-3}, $Z = 4$, $\mu(\text{Mo-}K_\alpha) = 27.32$ cm^{-1}. Diffraction data were collected using a Syntex $P2_1$-diffractometer (ω-scan, at 21 °C). The structure was solved by conventional heavy-atom methods. Least-squares refinements (with the phenyl rings refined as regular hexagons; C–C = 1.395 Å) converged at an R value of 0.063 for 3562 independent reflections [$F_o > 3.92\sigma(F_o)$; $4° < 2\theta < 48°$]. 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.

and the S_5^{2-} ligand are responsible for the connection of the tetrahedra. Both ligands show co-ordination to 4 different Cu atoms.

The results, in particular the number of co-ordination sites of the polysuphido ligands, prove that soft metal aggregates can be nicely 'glued' by S_x^{2-} ions.

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