Synthesis and *X*-Ray Crystal Structure of $[Cu(SC_6H_2Pr^i_3)]_8$

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The cluster $[Cu(SC_6H_2Pr^i_3)]_8$ contains a twisted 16-membered cyclic aggregate of alternating copper and sulphur atoms; the sulphur atoms are doubly bridging and each copper atom exhibits linear two-co-ordination.

As part of a systematic investigation on steric control of aggregation in neutral d^{10}-metal thiolates, the brownish-yellow copper–thiolate complex $[Cu(SC_6H_2Pr^i_3)]_8$ has been synthesized and structurally characterized.

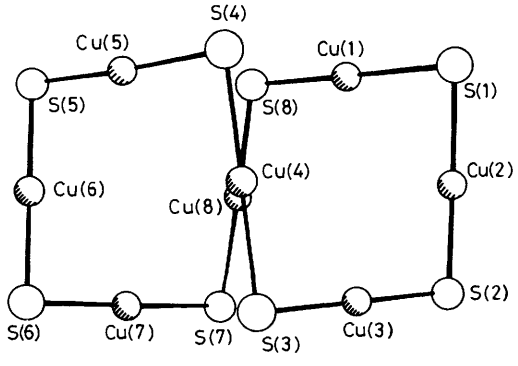

Figure 1. The structure of the Cu_8S_8 core.

The complex was prepared by refluxing CuCl (43 mg) with 4.5 equiv. of 2,4,6-tri-isopropylthiophenol (490 mg) in MeCN (1.5 ml)–EtOH (3 ml) in the presence of trimethylamine (33% solution, 0.5 ml) for 3 h. Yellow crystals formed from the reaction mixture after it was left to stand at room temperature. Recrystallization from hot ethanol gave brownish-yellow rhomboid crystals.

The structure of the Cu_8S_8 core in crystalline $[Cu(SC_6H_2Pr^i_3)]_8$ is shown in Figure 1.† The core is a twisted 16-membered ring of alternating copper and sulphur atoms

† *Crystal data:* $a = 17.174(4)$, $b = 52.981(4)$, $c = 14.918(3)$ Å, $\beta = 108.00(2)°$; space group $P2_1/a$, $Z = 4$, 6242 diffractometer observed reflections $[I_o \geqslant 2\sigma(I_o)]$. With anisotropic thermal parameters for Cu, S atoms and isotropic thermal parameters for C atoms, H atoms not included, $R = 0.103$. Because of the unusually long b-axis (52.981 Å), a longer crystal-to-detector distance (400 mm) and a strong *X*-ray source from a rotating anode tube were used during data collection. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

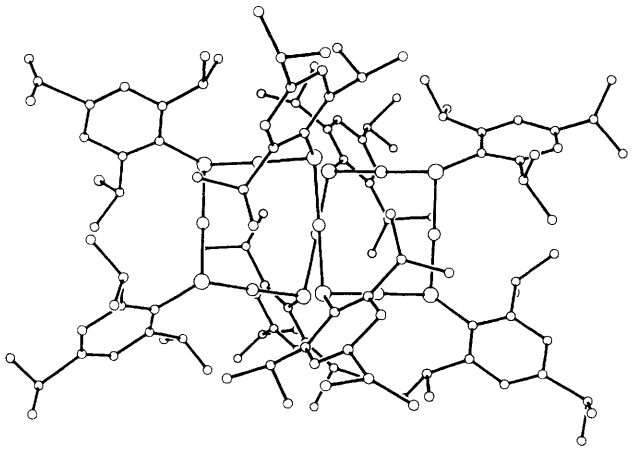

Figure 2. The molecular structure of $[Cu(SC_6H_2Pr^i_3)]_8$.

with the S atoms at the eight corners. The twisted centre of the 16-membered ring is located between Cu(4) and Cu(8). All the thiolate ligands are doubly-bridging, forming the 16-membered Cu–S ring in which each of the eight two-co-ordinate copper atoms are almost linearly co-ordinated (S–Cu–S average 177.5°). The array of Cu atoms can be considered as two Cu_5 polyhedrons connected by sharing the edge Cu(4)–Cu(8). Each Cu_5 polyhedron consists of a distorted tetrahedron with an additional Cu atom over its longest edge. The Cu_5 geometry is comparable with that observed in $[Cu_5(SPh)_7]^{2-}$.[1] In Figure 1 one can recognize the two distorted tetrahedra and also the two additional Cu atoms, Cu(2) and Cu(6), respectively over their longest edges Cu(1)–Cu(3) and Cu(5)–Cu(7).

In the Cu_8S_8 cluster the copper co-ordination is linear instead of the usually preferred trigonal planar co-ordination for Cu(I) thiolates.[1—7] The reduced co-ordination at the bridged metal centres is attributed to the steric and electronic effect of the $SC_6H_2Pr^i_3$ ligand.

Another structural feature is the short distance, 3.146 Å, between the unbridged copper atoms Cu(4) and Cu(8). This leads to an increase in the distances between Cu(4) or Cu(8) and the contiguous bridged atoms Cu(3), Cu(5) or Cu(1), Cu(7) (3.107 Å on average) over the distances Cu(1)–Cu(2), Cu(2)–Cu(3), Cu(5)–Cu(6), and Cu(6)–Cu(7) (2.705 Å on average), and the corresponding bond angles Cu–S–Cu increase from 77.2° to 92.5°. The distances between the two Cu atoms may suggest that they are involved in very weak Cu–Cu bonding. The average Cu–S bond length, 2.162 Å, is similar to the Cu–S distance in $[Cu_5(SPh)_7]^{2-}$ and $[Cu_5(SBu^t)_6]^-$, 2.160 and 2.17 Å respectively.[1,2]

The molecular structure of $[Cu(SC_6H_2Pr^i_3)]_8$ is shown in Figure 2.

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