Formation and *X*-Ray Structure of the Hexa(t-butylthiolato)pentacuprate(I) Monoanion

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Summary The $[Cu_5(\mu_2\text{-}SBu^t)_6]^-$ cluster contains a metal–metal bonded trigonal bipyramid of copper(I) atoms enclosed within a distorted octahedron of doubly-bridging thiolate ligands.

Although copper-thiolate (RS^-) compounds have been known for many years,[1] and have recently been studied owing to their biological occurrence[2] and chemotherapeutic value,[3] definitive structural information for copper co-ordination by monothiolate ligands is still virtually non-existent.[4] Three classes of structure are anticipated: (i) extensively non-molecular insoluble compounds $[CuSR]_n$; (ii) monometallic complexes $[Cu(SR)_x]^{1-x}$; (iii) molecular cluster complexes with intermediate RS^-:Cu ratios. We now report the formation and stereochemistry of a new copper(I)-t-butylthiolate cluster complex.

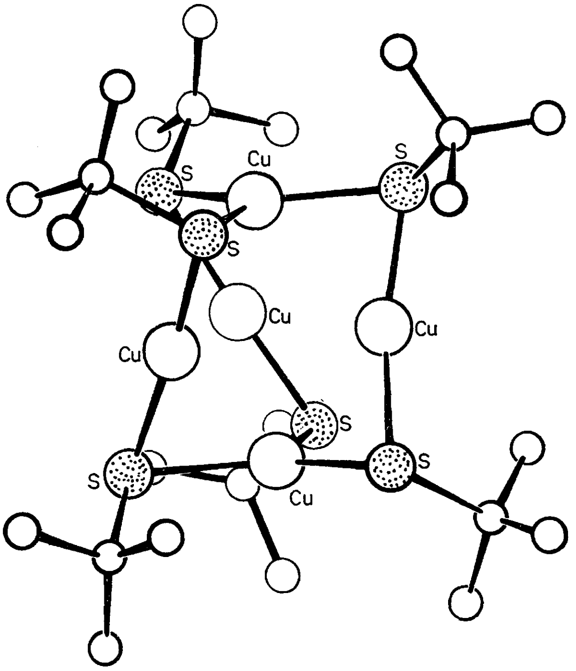

Figure 1. The $[Cu_5(\mu_2\text{-}SBu^t)_6]^-$ cluster.

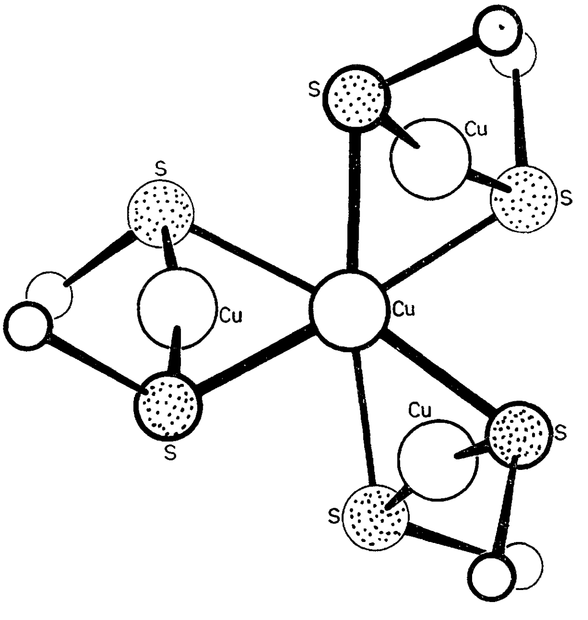

Figure 2. View of the $Cu_5(\mu_2\text{-}SBu^t)_6$ cluster (excluding terminal carbon atoms) along the pseudo-threefold Cu_{trig}–Cu_{trig} axis, showing the 49° twist of the trigonal co-ordination planes and the 0·4 Å displacement of each Cu_{dig} towards the cluster centroid.

Synthetic experiments involved the addition of copper(II) nitrate in EtOH to *ca.* 0·1M Bu^tSH (with equimolar triethylamine) in acetone or acetonitrile, with exclusion of dioxygen. A dark coloured species forms initially, but disappears within one second, after which only copper(I) complexes are present. At $[RS^-]:[Cu^I]$ ratios >10 the intensely yellow equilibrium species are probably the co-ordinatively saturated complexes $[Cu(SBu^t)_x]^{1-x}$, while $[CuSBu^t]_n$ precipitates when $[RS^-]:[Cu^I] < 1\cdot8$. Addition of $Et_4N^+Br^-$ in EtOH to solutions with $[RS^-]:[Cu^I]$ *ca.* 3 readily gives large bright yellow crystals of $Et_4N^+[Cu_5(SBu^t)_6]^-$. During approximately ten hours exposure to diffuse sunlight these crystals darken through orange to brown, and eventually fragment.

The structure of the $[Cu_5(SBu^t)_6]^-$ cluster in the crystalline state† is illustrated in Figure 1. Five copper atoms are arrayed as a regular trigonal bipyramid, Cu_{ax}–Cu_{eq} = 2·72 ± 0·01 Å, Cu_{eq}–Cu_{eq} = 3·23 ± 0·04 Å.‡ Each of the six thiolate sulphur atoms bridges an axial-equatorial pair of copper atoms such that the two copper atoms axial in the trigonal bipyramid possess trigonal planar co-ordination (Cu_{trig}) and the three equatorial copper atoms possess approximately linear digonal co-ordination (Cu_{dig}). Two notable geometrical properties are: (i) the average copper co-ordination number (2·4) is less than the value of 2·8 found[4] with the less basic PhS^- ligand in $[Cu_5(\mu_2\text{-}SPh)_7]^{2-}$, and (ii) the Cu_{dig}–S bond length (2·17 ± 0·01 Å) is significantly shorter than Cu_{trig}–S (2·27 ± 0·02 Å).‡

There is significant geometrical evidence for substantial intracluster copper-copper bonding. Figure 2, which views the Cu_5S_6 core along the pseudo-threefold axis common to both Cu_{trig} atoms, emphasises two systematic distortions which carry all copper atoms towards the centroid of the cluster without decreasing copper–sulphur distances. The S–Cu_{dig}–S angles are decreased below 180° to 170 ± 1°, and the S_6 prism is twisted 49° about the threefold axis. The resulting contraction of the Cu_5 core within the S_6 ligand polyhedron is apparent in the following significantly decreased distances (compared with the idealized undistorted distances in parentheses): centroid–Cu_{trig}, 1·98 Å (2·17 Å); centroid–Cu_{dig}, 1·90, 1·86, 1·84 Å (2·27 Å); Cu_{dig}–Cu_{trig}, 2·72 Å (3·14 Å); Cu_{dig}–Cu_{dig}, 3·23 Å (3·93 Å). This prominent structural feature, observed also in chelated $[Cu_8(S\text{-}S)_6]^{4-}$ cluster structures,[5] reveals multicentre attractive interactions between the copper atoms.

(*Received*, 10*th November* 1975; *Com.* 1248.)

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† $Et_4NCu_5(SCMe_3)_6$, bright yellow truncated pyramids, space group *C*2/*c*, *a* = 45·500, *b* = 11·805, *c* = 20·168 Å, *β* = 117·81°. Diffractometer data (3965 reflections) were corrected *via* a reference reflection for deterioration in diffraction quality due to irradiation (Cu-K_α) induced crystal fragmentation: normal precision levels cannot be attained in this structure determination. At isotropic refinement of all non-hydrogen atoms *R* = 0·12.

‡ Average derivations from the mean.

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[4] The structure of $[Cu_5(\mu_2\text{-}SPh)_7]^{2-}$ has been determined; I. G. Dance, *J.C.S. Chem. Comm.*, 1976, in the press.

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