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Three Different Modes of Bonding by 1-Methylpyrimidine-2-thione in the Crystal Structure of a Novel Copper(I)–Sulphur Cluster Compound

D. M. L. GOODGAME, G. A. LEACH, A. C. SKAPSKI and K. A. WOODE

Chemical Crystallography and Inorganic Chemistry Laboratories, Imperial College, London SW7 2AY, U.K.

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During the extension of our work on the coordination of pyrimidine-2-thiones to metal ions [1–4] we have observed that 1-methylpyrimidine-2-thione (L) reacts with copper(II) perchlorate or tetrafluoroborate to form dark red complexes of stoichiometry $Cu_2L_3X_2$ (X = ClO_4 or BF_4). The compounds are diamagnetic, give no e.p.r. signal, and have no bands in their electronic spectra assignable as d–d transitions of copper(II). It appeared that the thione ligand had reduced the copper to copper(I), which is known to form various types of cluster compounds with sulphur donor ligands.

The usual geometries for clusters containing a Cu^I:S ratio of 2:3 are either a tetrahedron of copper atoms bridged along each edge by a sulphur atom [5–8] or a cube of copper atoms similarly bridged [9, 10]. As pyrimidinethiones are quite versatile in their coordination behaviour we have carried out an X-ray structural study on $Cu_4L_6(BF_4)_4$ to establish the mode of bonding of the ligand and the arrangement of the copper atoms.

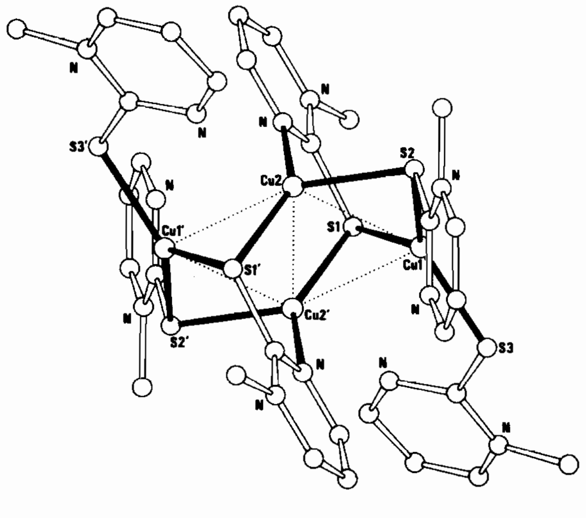

Figure 1. Centrosymmetric structure of the $[Cu_4(1\text{-methylpyrimidine-2-thione})_6]^{4+}$ cation (all unlabelled atoms are carbon).

Crystals suitable for X-ray study were obtained as follows. Hexaquocopper(II) tetrafluoroborate (1 mmol) was dissolved in a few drops of water and the solution was made up to 10 cm^3 with acetone. This was added, with stirring, to a warm solution (*ca.* 40 °C) of the ligand in acetone (1.5 mmol in 30 cm^3). The resulting deep green solution was left in a stoppered flask in a refrigerator for 3 - 4 days. Red, needle-like crystals formed and the supernantant liquid became pale yellow. The crystals were filtered off, washed with a little acetone and diethyl ether, and air dried. Micro-analytical results were: Found; C, 26.4; H, 2.8; N, 12.2. Calc. for $Cu_4(C_5H_6N_2S)_6(BF_4)_4$: C, 26.5; H, 2.7; N, 12.4%.

The red needles are monoclinic, with unit-cell dimensions a = 7.730(1), b = 24.845(1), c = 12.834(1) Å, β = 104.48(1)°, U = 2386.5 Å^3 (at 11 °C), space group $P2_1/c$ and Z = 2. Using CuKα radiation the intensity data were collected on a Siemens automatic four-circle diffractometer. A total of 3002 independent reflections were measured (to θ = 55°), of which 295 were judged to be 'unobserved'. The structure was solved by Patterson and Fourier methods, and least-squares refinement has reached R = 0.036.

The structure of the cation (Figure 1) comprises a planar centrosymmetric array of four copper atoms which form a parallelogram consisting of two nearly equilateral triangles. Sides of the parallelogram have Cu...Cu distances of 2.713(1) and 2.824(1) Å, while a Cu...Cu separation of 2.839(1) Å forms its short diagonal. This Cu_4 cluster is encompassed by six thione ligands which bind in three different ways: type I, which bridge a pair of copper atoms via sulphur and a third copper atom by means of the non-methylated nitrogen atom; type II, which bridge two copper atoms via sulphur; type III, which are bonded terminally through sulphur.

The coordination about each copper atom is distorted trigonal planar with an S_3 donor atom set in the case of Cu(1) and bond angles S(1)–Cu(1)–S(3) 112.0(1)°, S(1)–Cu(1)–S(2) 120.2(1)° and S(2)–Cu(1)–S(3) 127.8(1)°, but with an S_2N set around Cu(2) with greater distortion from trigonal symmetry (angles: S(1')–Cu(2)–S(2) 113.7(1)°, S(1')–Cu(2)–N 142.6(1)°, S(2)–Cu(2)–N 103.6(1)°). Despite this distortion, however, the coordinations about both copper atoms are closely planar, with the metal atom less than 0.03 Å from the least-squares plane through the four atoms.

All the metal–sulphur bond lengths, the terminal Cu(1)–S(3) 2.241(1) Å and the bridging Cu–S distances 2.264(1)–2.356(1) Å, are in the range previously reported for Cu^I–sulphur cluster compounds [5–17]. The Cu–N bond length is 2.035(3) Å.

Several features of the structure of $[Cu_4L_6]^{4+}$ merit comment. A planar Cu_4 array is very unusual for a Cu^I–sulphur donor cluster, although it may be present in $[Cu_4(ethylenethiourea)_9]^{4+}$ (the report [18] is not explicit on this point and planarity of the Cu_4 unit is not required by the C_2 symmetry of the cation). A planar copper atom array is, however, found in a number of tertiary phosphine [19] or diphosphine [20] complexes containing a halogen-bridged Cu_4 unit, and also in the carbon-bridged cluster $[Cu(CH_2SiMe_3)]_4$ [21].

The question of Cu–Cu bonding in Cu^I clusters has been a matter of appreciable debate. The presence of such bonding has been proposed [10, 15, 22] in a variety of clusters involving sulphur donors with Cu...Cu separations of *ca.* 2.7–2.9 Å, but much shorter Cu^I...Cu^I distances (*ca.* 2.4 Å) are present in some carbon-bridged clusters for which Cu–Cu bonding is not advocated [21, 23]. In the present structure, there is essentially trigonal planar coordination geometry about each copper, and we can see no reason for invoking any significant Cu–Cu bonding.

The bonding of the terminal thione ligands (type III) is straightforward. The thiones of type II are bonded in a manner rather similar to that observed by Amma and co-workers [14, 24] for the bridging ligands in some dimeric and tetrameric copper(I)–thiourea complexes, at least with respect to the inequivalence of the Cu–S bonds in the bridge (S(2)–Cu(1) 2.264(1) Å, S(2)–Cu(2) 2.356(1) Å) and also the orientation of the pyrimidine ring relative to the Cu–S bonds (S(2)–Cu(1) approximately coplanar with ring).

It was proposed [14, 24] that the two electron pairs used by the sulphur atom in such bridges were in essentially sp^2 hybrid and $p\pi$ orbitals for the shorter and the longer Cu–S bonds respectively. However, in the present structure both Cu–S bonds involving a type II thione ligand are significantly shorter than the analogous bonds in the thiourea complexes (2.26 Å compared with 2.33–2.37 Å, and 2.36 Å compared with 2.43–2.46 Å). Moreover, the angle C–S(2)–Cu(1) (105.2(1)°) is smaller than and the C–S(2)–Cu(2) angle (107.8(1)°) larger than the corresponding angles in the thiourea complexes (107.4–108.1° and 101.3–105.7° respectively). These differences, particularly of bond length, may well be due to changes in electron density at sulphur because of its bonding to the pyrimidine ring, as compared with sulphur in thiourea.

In the type I thione ligand the additional Cu–N bonding causes the plane of the pyrimidine ring to swing round between the Cu–S bonds. This change appears to reduce somewhat the asymmetry of the Cu–S bonds (S(1)–Cu(2′) 2.265(1) Å, S(1)–Cu(1) 2.312(1) Å) as compared with the type II bridge but, apart from this, there is no apparently significant alteration in the relevant bond lengths and angles within the bridge.

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