Synthesis, *X*-Ray Crystal Structure, and Magnetic and Spectroscopic Properties of a Novel Copper(I)–Copper(II) Cluster

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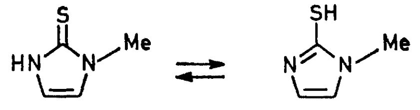
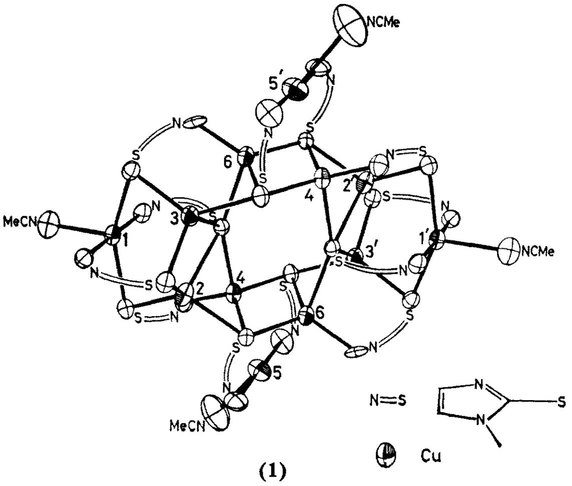
Summary The cluster $[Cu^{I}_{10}Cu^{II}_{2}(C_4H_5N_2S)_{12}(MeCN)_4][BPh_4]_2(MeCN)_4$, where $C_4H_5N_2S$ is the mercaptide anion of 1-methyl-2-mercaptoimidazole, presents a novel polynuclear arrangement of copper(I); the copper(II) centres of this compound display spectroscopic features similar to those observed for the copper(II) site in the blue copper proteins.

MIXED valence copper(I)–copper(II) clusters with thiol group-containing ligands such as penicillamine, mercaptoisobutyric acid, and cysteamine have been described recently.[1,2] With 1-methyl-2-mercaptoimidazole, $C_4H_6N_2S$, we have now prepared the mixed valence complex $[Cu_{12}(C_4H_5N_2S)_{12}(MeCN)_4][BPh_4]_2(MeCN)_4$ (**1**) by mixing $[Cu^I(MeCN)_4(ClO_4)]$, $[Cu^{II}(MeCO_2)_2(H_2O)]_2$, and $C_4H_6N_2S$ in a



1 : 1 MeCN–MeOH solution, the dark blue precipitate was dissolved in MeCN and $NaBPh_4$ was then added. Compound (**1**) was crystallized by slow evaporation after addition of acrylonitrile.[3]



(**1**)

Crystal data: $[Cu_{12}(C_4H_5N_2S)_{12}(MeCN)_4][BPh_4]_2(MeCN)_4$, $M = 3065.70$, triclinic, space group $P\bar{1}$, $a = 16.400$, $b = 14.630$, $c = 14.680$ Å, $\alpha = 76.80$, $\beta = 105.57$, $\gamma = 95.23°$, $Z = 1$. Anisotropic thermal parameters were used for all non-hydrogen atoms, and least-squares refinement yielded a standard residual $R = 0.078$ [Philips PW1100 diffractometer, Cu-K_α radiation, 5736 independent reflections used with $\sigma(I) < 0.3I$].†

The stereochemistry of the cluster cation present in (**1**) is shown in Figure 1. It is located on a crystallographic centre of symmetry its actual symmetry is close to $2/m$ (C_{2h}). Eight tetrahedrally co-ordinated copper atoms Cu(2), Cu(3), Cu(4), and Cu(6) and their centrosymmetric counterparts Cu(2′), Cu(3′), Cu(4′) and Cu(6′) form a 'ring cluster'. For each of these copper atoms the donor atom sets are either S_4 [Cu(2) and Cu(3)] or NS_3 [Cu(4) and Cu(6)], with fourteen independent Cu–S bond distances ranging from 2.280(2) to 2.645(2) Å and two independent Cu–N distances of 1.977(4) and 1.984(4) Å. These eight copper atoms are each two-by-two *doubly bridged* by two sulphur atoms, the Cu_2S_2 rings so formed are alternatively planar or bent about the Cu···Cu axes. The Cu···Cu distances between these eight atoms, which range from 2.547(1) to 2.724(1) Å, together with the magnetic properties of (**1**), indicate that all these atoms are in the Cu^I state.

The arrangement of the 1-methyl-2-mercaptoimidazole anions around the eight copper(I) atoms of the ring cluster is such that it creates two other types of metal sites. (i) One type corresponds to Cu(5) and its centrosymmetric counterpart Cu(5′). Each of these two atoms is linearly σ-bonded by two nitrogens with Cu–N bond distances of 1.867(8) and 1.885(8) Å and an N–Cu–N angle of 179.2(5) Å. An acetonitrile molecule interacts very weakly with these copper atoms Cu(5)···N = 2.92(2) Å. These structural features together with the spectroscopic properties of (**1**) (*vide infra*) are again entirely consistent with Cu(5) and Cu(5′) being Cu^I species. (ii) The second type of metal site is occupied by Cu(1) and its centrosymmetric counterpart Cu(1′). These metal atoms are co-ordinated to a *trans*-N_2S_2 donor set with Cu–N bond distances of 1.960(5) and 1.934(5) Å and Cu–S bond distances of 2.464(3) and 2.466(2) Å. The values of the N–Cu(1)–N and S–Cu(1)–S bond angles are 175.4(3) and 150.9(1)°, respectively. This environment is completed by a nitrogen atom from an acetonitrile molecule with a large Cu(1)···N bond distance of 2.295(8) Å. Consequently, the co-ordination polyhedron

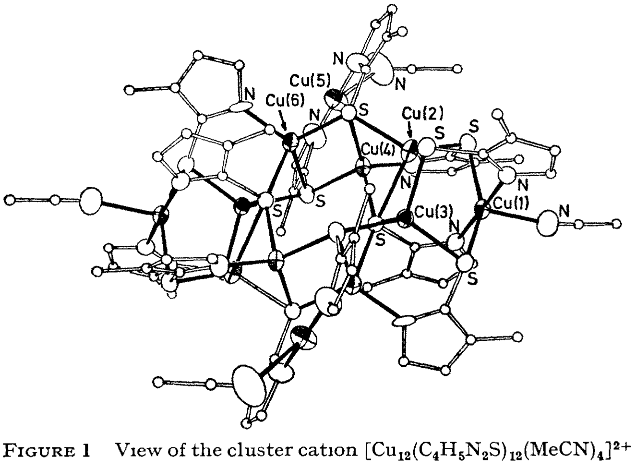


Figure 1 View of the cluster cation $[Cu_{12}(C_4H_5N_2S)_{12}(MeCN)_4]^{2+}$

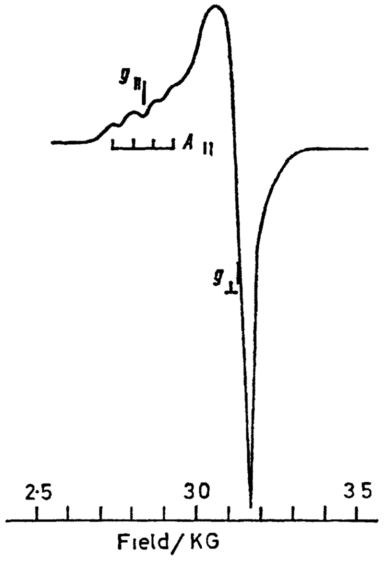


Figure 2 E.s.r. spectrum (8.902 GHz) of a powdered sample of $[Cu_{12}(C_4H_5N_2S)_{12}(MeCN)_4][BPh_4]_2(MeCN)_4$ at 150 K.

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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 Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

around these atoms is best described as a distorted square pyramid with the N_2S_2 donor set in the slightly distorted equatorial plane. The stoicheiometry of (**1**), the structural features already seen, and the magnetic properties indicated below show clearly that Cu(1) and Cu(1′) are the two Cu^{II} ions present in (**1**).

The magnetic susceptibility of a powdered sample of (**1**), determined by the Faraday method over the temperature range 4·2—300 K, shows that (**1**) follows the Curie law with a Curie constant C = 0·990 cm^3 mol^{-1} K and μ_{eff} = 2·0 B.M. per Cu^{II}. This behaviour is typical for a copper(II) centre isolated from all magnetic interactions. The e.s.r. spectra of powdered samples obtained between 4·2 and 300 K contain four hyperfine lines in the $g_{\|}$ region and one strong signal in the $g_{\perp}$ region (Figure 2); the spin Hamiltonian parameter values are $g_{\perp}$ = 2·04, $g_{\|}$ = 2·24, $A_{\perp}$ = 0, and $A_{\|}$ = 62 G. The reflectance (Nujol) and transmittance (MeCN) electronic spectra of (**1**) show a large and intense band at 635 nm (ϵ = 3·800 l mol^{-1} cm^{-1} per Cu^{II}) and two less intense absorptions at 410 (ϵ = 1200) and 880 nm (ϵ = 1800) (Figure 3).

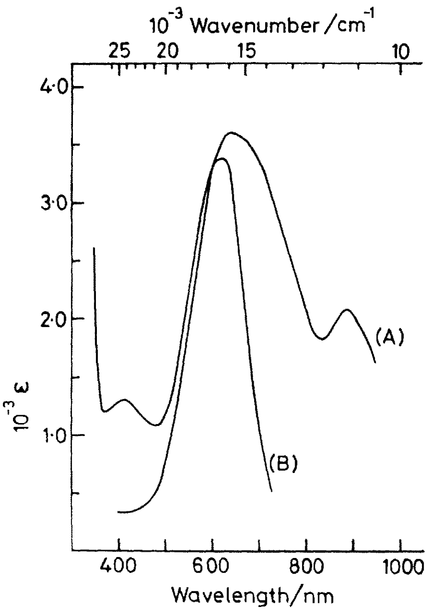

FIGURE 3. Electronic spectra of: (**1**) in acetonitrile solution (curve A); *Pseudomonas aeruginosa* azurin (curve B).

The electrochemical reduction of (**1**) in acetonitrile solutions on a rotating platinum disk electrode indicates the transfer of two electrons at −205 ± 5 mV with regard to a saturated calomel electrode (μ = 0·1 M, tetraethylammonium perchlorate); the complete disappearance of the colour during this reduction is followed by regeneration of the same colour and of the identical electronic spectrum under air or oxygen.

Thus (**1**) displays two of the spectroscopic properties which are usually associated with the 'type 1' copper site in blue copper proteins,[4] *i.e.* a large and intense band at 635 nm and an e.s.r. spectrum with a small $A_{\|}$ hyperfine coupling constant. However, the co-ordination geometry of copper(II) and (**1**) is not a distorted tetrahedron as in the blue copper proteins, but a distorted square pyramid.[5]

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[1] Y. Sugiura and H. Tanaka, *Chem. Pharm. Bull.*, 1970, **18**, 368; J. R. Wright and E. Frieden, *Bioinorg. Chem.*, 1975, **4**, 163; W. G. Musker and C. H. Neagley, *Inorg. Chem.*, 1975, **14**, 1728.

[2] H. J. Schugar, C. Ou, J. A. Thich, J. A. Potenza, R. A. Lalancette, and W. Furey, *J. Am. Chem. Soc.*, 1976, **98**, 3047; P. J. M. W. L. Birker and H. C. Freeman, *ibid.*, 1977, **99**, 6890; P. J. M. W. L. Birker, *Inorg. Chem.*, 1979, **18**, 3502.

[3] A similar complex, ill defined in composition and properties has been reported (A. Dobry-Duclaux and P. Perichon, *J. Chim. Phys.*, 1976, **73**, 1058).

[4] J. A. Fee, *Struct. Bonding (Berlin)*, 1975, **23**, 1; P. M. Colman, H. C. Freeman, J. M. Guss, M. Murata, V. A. Norris, J. A. M. Ramshaw, and M. P. Venkatappa, *Nature (London)*, 1978, **272**, 319; E. T. Adman, R. E. Stenkamp, L. C. Sieker, and L. H. Jensen, *J. Mol. Biol.*, 1978, **123**, 35; T. D. Tullius, P. Frank, and K. O. Hodgson, *Proc. Natl. Acad. Sci. USA*, 1978, **75**, 4069.

[5] J. S. Thompson, T. J. Marks, and J. A. Ibers, *Proc. Natl. Acad. Sci. USA*, 1977, **74**, 3114; *J. Am. Chem. Soc.*, 1979, **101**, 4180; B. J. Hathaway and D. E. Billing, *Coord. Chem. Rev.*, 1970, **5**, 168; R. Barbucci, A. Mastroianni, and M. J. M. Campbell, *Inorg. Chim. Acta*, 1978, **27**, 109; M. Scharnoff and C. W. Renian, *J. Chem. Phys.*, 1965, **43**, 2998; J. E. Roberts, T. G. Brown, B. M. Hoffman, and J. Peisach, *J. Am. Chem. Soc.*, 1978, **102**, 825; A. R. Amundsen, J. Whelan, and B. Bosnich, *ibid.*, 1977, **99**, 6730; M. B. Robin and P. Day, *Adv. Inorg. Radiochem.*, 1967, **10**, 247.