X-Ray Crystal Structure of $[Cu_2OH(O_2CCF_3)_3(quinoline)_2]_2$, A Tetranuclear Basic Copper(II) Carboxylate Adduct with Significant Metal–Metal Interaction

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Summary The basic copper(II) carboxylate adduct, $[Cu_2OH(O_2CCF_3)_3(quinoline)_2]_2$, has been shown by an X-ray structural analysis to have a novel tetranuclear structure; magnetic susceptibility data show that substantial Cu–Cu interaction is present in this compound.

Recently Ablov *et al.* described a green crystalline quinoline adduct of copper(II) trifluoroacetate which they formulated as $Cu(O_2CCF_3)_2(quin)$.[1] These workers interpreted the results of an e.s.r. investigation as implying strong magnetic coupling between Cu^{II} ions in this compound and suggested the possibility of a dimeric structure analogous to that of copper(II) acetate monohydrate.[2] Previous investigations of copper(II) trifluoroacetate and its adducts with various donor ligands[3–5] have yielded no well-documented instances of substantial metal–metal interactions. Thus anhydrous copper(II) trifluoroacetate exhibits a normal room-temperature magnetic moment and its magnetic susceptibility conforms to the Curie–Weiss law between 94 and 297 K.[2] Most adducts of copper(II) trifluoroacetate studied so far possess two or more addend molecules per copper atom and have been presumed not to have the dimeric structure.[1,4–6] Because of these observations and as a part of our continuing studies of structure and metal–metal interactions in copper(II) complexes,[7] we investigated the copper(II) trifluoroacetate–quinoline system.

A green crystalline product was obtained from a cooled solution of anhydrous $Cu(O_2CCF_3)_2$ (3·2 g) and quinoline (1·0 g) in 95% ethanol (40 ml). The deep blue-green solution first deposited purple crystals, presumably $Cu(O_2CCF_3)_2(quin)_2$; however, repeated filtration and concentration of the mother liquor eventually led to crystallization of the green material. Subsequent work has shown that minor variations of this procedure result in the isolation of other crystalline products. Magnetic susceptibility data (μ_{eff} = 1·59 B.M. per Cu at 300 K; 1·14 B.M. per Cu at 85 K) indicate the presence of significant copper–copper interaction. Analytical results (Cu, C, H, N) did not correspond to the expected formulation as a mono-quinoline adduct, but were in agreement with the stoicheiometry established by the structural analysis.

The green prismatic crystals of $[Cu_2(O_2CCF_3)_3(quin)_2OH]_2$ have triclinic symmetry with reduced cell constants a = 10·401(16), b = 12·773(20), c = 15·237(24) Å, α = 58·07(5),

$\beta = 124{\cdot}22(4)$, and $113{\cdot}81(4)°$; $Z = 1$, $D_c = 1{\cdot}76$, $D_m = 1{\cdot}73(2)$ g cm^{-3}. The structure determination was based upon 3332 independent non-zero reflections collected on a Picker diffractometer by the θ—2θ scan technique. An absorption correction ($\mu = 16{\cdot}51$ cm^{-1}) was applied to the observed intensities. The structure was solved on the assumption of space group $P\bar{1}$ by Patterson and Fourier methods. Least-squares refinement with anisotropic thermal parameters assigned to the Cu atoms and to the atoms of the CF_3 groups and with the quinoline molecules treated as rigid groups converged to a conventional discrepancy factor $R = 0{\cdot}073$.

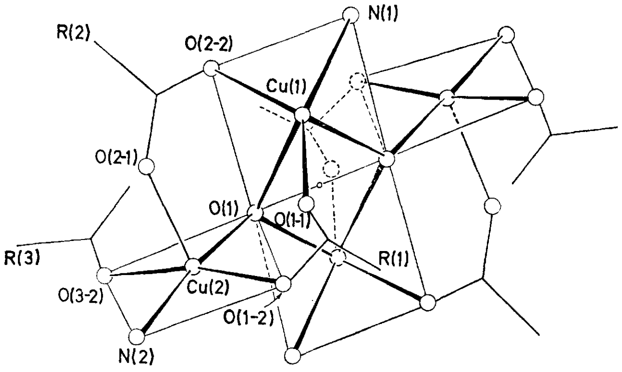

FIGURE. *A view of the molecular structure of* $[Cu_2OH(O_2CCF_3)_3(quin)_2]_2$. *Quinoline rings are not shown and* CF_3 *groups are represented as* R(1), R(2), *and* R(3). *Major bond lengths not mentioned in the text include:* Cu(1)–O(1) = 1·964(6), Cu(1)–O(1′) = 1·990(6), Cu(1)–N(1) = 1·989(7), Cu(1)–O(2-2) = 1·936(7), Cu(1)–O(1-1) = 2·174(6), Cu(2)–O(1) = 1·963(6), Cu(2)–N(2) = 2·004(7), Cu(2)–O(1-2) = 1·968(7), Cu(2)–O(3-2) = 1·990(6), Cu(2)–O(2-1) = 2·200(7) Å.

The discrete centrosymmetric $[Cu_2OH(O_2CCF_3)_3(quin)_2]_2$ molecule, illustrated in the Figure, contains two crystallographically independent copper atoms, each bound to four oxygen atoms and a quinoline nitrogen atom in a distorted square pyramidal configuration. Three independent carboxylate groups are present; of these two form bridges from the apical position of one copper atom to a basal site of a second metal atom. The third trifluoroacetate group is bound as a monodentate ligand in the basal plane of Cu(2). The remaining positions in the metal co-ordination spheres are occupied by one quinoline nitrogen atom per copper and the triply bridging atom O(1). Since hydrogen atoms were not located in this study, the identity of O(1) as the oxygen atom of a hydroxo-group must rest on other evidence: (i) The configuration about O(1) [∠Cu(1)–O(1)–Cu(1′) = 98·6(2)°, ∠Cu(1)–O(1)–Cu(2) = 116·9(3)°, ∠Cu(1′)–O(1)–Cu(2) = 124·9(3)°; O(1) 0·51 Å out of Cu(1)–Cu(1′)–Cu(2) plane†] suggests a distorted tetrahedral geometry. (ii) The short contact of 2·55(1) Å between O(1) and the unco-ordinated oxygen atom of the monodentate carboxylate groups is presumed to stem from an O · · · H–O hydrogen bond. A broad absorption occurs in the i.r. spectrum in the region expected (*ca.* 2900 cm^{-1}) for such a hydrogen bond.

The origin of the observed magnetic interaction is of interest. Direct Cu–Cu interaction is made unlikely by the metal–metal distances, Cu(1)–Cu(1′) = 2·996(4) Å, Cu(1)–Cu(2) = 3·347(5) Å, and by the relative orientations of the copper co-ordination polyhedra. Copper(II) ions are linked by apical-to-basal trifluoroacetate bridges and by triply bridging OH$^-$ groups. Neither of these types of bridging linkage has previously been demonstrated to be associated with substantial magnetic interaction.‡

This work was supported by the National Science Foundation. We thank Dr. Michael Lawson for his help with the magnetic measurements.

(*Received*, 11*th November* 1971; *Com.* 1958.)

† Primes denote atoms related to those in the asymmetric unit by the crystallographic centre of symmetry.

‡ A possible exception is the trinuclear basic salt $Cu_3L_3OH(SO_4){\cdot}xH_2O$ (L = deprotonated pyridine-2-aldehyde oxime) in which coupling of two of the three unpaired spins per cluster leads to Curie law behaviour with $\mu_{eff} = 1{\cdot}00$ B.M. per copper(II) ion.[8]

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