Dimeric Quinoline Adduct of Copper(II) Trifluoroacetate: Preparation, Structure, and Magnetism

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Summary The dimeric quinoline adduct of copper(II) trifluoroacetate has been shown to have a long Cu-Cu distance of 2.886 Å and magnetic properties similar to those of copper(II) acetate monohydrate.

Considerable difference exists between the magnetic properties of anhydrous copper(II) acetate and those of the corresponding anhydrous trifluoroacetate. In contrast to the depressed effective magnetic moment at 295 K of 1.4 B.M. per Cu²⁺ ion and the antiferromagnetic behaviour for copper (II) acetate,¹ the trifluoroacetate displays a normal room-temperature moment of 1.81 B.M. and a magnetic susceptibility which conforms to the Curie-Weiss law between 94 and 297 K.² The variation in magnetic behaviour has been attributed to differences in basicity between the trifluoroacetate group and the acetate ion.³ This explanation, however, becomes untenable if the anhydrous carboxylates are not in fact isostructural. No definitive evidence of the dimeric structure exists for copper(II) trifluoroacetate; it has been suggested on the basis of magnetic susceptibility and i.r. spectral data that anhydrous copper(II) trifluoroacetate does not adopt the copper(II) acetate structure.³ This situation is further complicated by the general disinclination of copper(I) complexes of this type to form mono-adducts of the Cu(O,CR)₂⁻L stoichiometry typically found for the acetate and many other carboxylates.⁴ We now report the preparation and characterization by crystallographic, magnetic susceptibility, and e.s.r. methods of the first definitive example of a copper(II) trifluoroacetate adduct of the Cu(O₃CR)₂⁻L stoichiometry and the copper(II) acetate structure.

A light green solid material was obtained by heating the violet bisquinoline adduct Cu(O₃CCF₃)₂(quinoline)₄⁵⁶ in hot benzene. The crystals are highly hygroscopic, forming a blue product in air. Crystals of bis[quinoline-bis-(μ-trifluoroacetato-OO‘)-copper(II)] have been obtained from the susceptibility data. Three conclusions can be made: (i) Since replacement of acetate by trifluoroacetate in the bridged dimeric copper carboxylate structure has relatively little effect upon the

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magnitude of the Cu-Cu interaction, the pKa of the parent carboxylic acid cannot be a major factor in determining the strength of the interaction. (ii) The substantial difference between the magnetic properties of anhydrous copper-(t) trifluoroacetate and those of the dimeric quinoline adduct supports the view\(^2\) that the anhydrous salt does not have the bridged dimeric structure. (iii) The large difference in Cu-Cu separation between the magnetically similar acetate and trifluoroacetate adducts demonstrates that the metal–metal distance in these dimers is not an important factor in determining the strength of the Cu-Cu interaction. This point has previously been made in other contexts.\(^10\)

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