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 Cu^{2+} ion and the antiferromagnetic χ_M *vs.* T 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.[2] This situation is further complicated by the general disinclination of copper(II) trifluoroacetate to form mono-adducts of the $Cu(O_2CR)_2{\cdot}L$ stoicheiometry 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 $Cu(O_2CR)_2{\cdot}L$ stoicheiometry and the copper(II) acetate structure.

A light green solid material was obtained by heating the violet bisquinoline adduct $Cu(O_2CCF_3)_2(quinoline)_2$.[4b,c,5] A crystalline sample was obtained by Soxhlet extraction and recrystallization from hot benzene. The crystals are highly hygroscopic, forming a blue product in air. Crystals of bis[quinoline-bis-(μ-trifluoroacetato-*OO′*)-copper(II)] are monoclinic with $a = 14{\cdot}866(24)$, $b = 16{\cdot}707(29)$, $c = 13{\cdot}694(23)$ Å, and $\beta = 111{\cdot}26(5)°$. Calculated ($Z = 4$) and observed densities are 1·76 and 1·74(2) g cm^{-3}, respectively. The structure analysis was based on 1555 independent non-zero reflections collected by the θ–2θ scan technique with Mo-K_α radiation on a Picker diffractometer. The structure was solved in space group $C2/c$ by Patterson and Fourier methods. Full-matrix anisotropic least-squares refinement for all non-hydrogen atoms, with hydrogen atoms included as fixed contributions, converged to a conventional R factor of 0·062. The molecular structure (Figure) is of the familiar dimeric copper acetate hydrate type. The Cu–Cu distance is 2·886(2) Å, a full 0·272 Å longer than the corresponding distance in copper(II) acetate monohydrate.[6] Other structure parameters are unremarkable; the thermal parameters of the CF_3 groups display considerable anisotropy.

Magnetic susceptibility measurements were made from 80—300 K by the Faraday method on an Alpha/Ainsworth susceptibility system. Corrections for diamagnetic and temperature-independent paramagnetic contributions were applied. The susceptibility data were satisfactorily fitted to the usual expression for an isolated pair of interacting ions of spin 1/2.[7] The best fit was obtained for $g = 2{\cdot}27$ and $2J = -310$ cm^{-1}. The effective magnetic moment at 300 K is 1·42 B.M. per Cu^{2+} ion. This susceptibility behaviour is similar to that of copper(II) acetate monohydrate [μ_{eff} (295 K) = 1·40 B.M., $2J = -284$ cm^{-1}].[1] The e.s.r. spectrum of a powdered sample was taken on a Varian E-3, X-band spectrometer. The e.s.r. spectrum is qualitatively identical to that of copper(II) acetate monohydrate.[8a] Analysis of this triplet spectrum by publishing methods[8] yields $g_{\parallel} = 2{\cdot}44$, $g_{\perp} = 2{\cdot}17$, $D = 0{\cdot}425$ cm^{-1}, and $\bar{g} = 2{\cdot}26$. The average g-value, though on the large side for copper(II) complexes of this structure type,[9] agrees well with the value independently obtained from the susceptibility data.

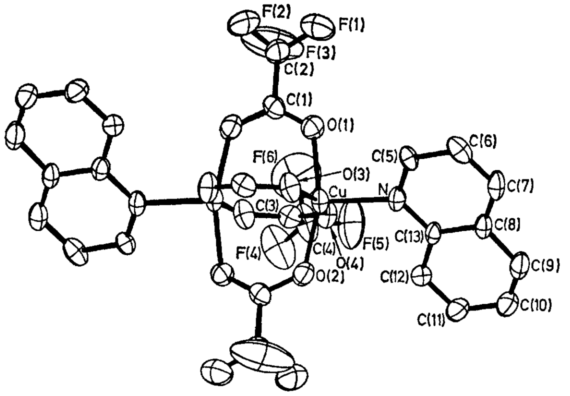

Figure. The molecular structure of $[Cu(O_2CCF_3)_2(quinoline)]_2$ Thermal ellipsoids are drawn at the 25% probability level. One of the CF_3 groups has been omitted for clarity. Bond distances within the copper co-ordination sphere are: Cu–O(**1**) = **1·970(7)**, Cu–O(2) = 1·954(8), Cu–O(3) = **1·991(6)**, Cu–O(**4**) = **1·972(5)**, Cu–N = **2·107(6)** Å.

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 magnitude of the Cu–Cu interaction, the pK_a 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(II) 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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[1] B. N. Figgis and R. L. Martin, *J. Chem. Soc.*, 1956, 3837.

[2] R. C. Thompson and D. B. W. Yawney, *Canad. J. Chem.*, 1965, **43**, 1240.

[3] M. Kato, H. B. Jonassen, and J. C. Fanning, *Chem. Rev.*, 1964, **64**, 99.

[4] (a) S. F. A. Kettle and A. J. P. Pioli, *J. Chem. Soc.* (*A*), 1968, 1243; (b) A. V. Ablov, L. N. Milkova, and Yu. V. Yablokov, *Russ. J. Inorg. Chem.*, 1969, **14**, 358; (c) C. A. Agambar and K. G. Orrell, *J. Chem. Soc.* (*A*), 1969, 897; (d) L. K. Thompson, V. T. Chacko, J. A. Elvidge, A. B. P. Lever, and R. V. Parish, *Canad. J. Chem.*, 1969, **47**, 4141.

[5] R. G. Little, D. B. W. Yawney, and R. J. Doedens, *J.C.S. Chem. Comm.*, 1972, 228.

[6] J. N. van Niekerk and F. R. L. Schoening, *Acta Cryst.*, 1953, **6**, 227; R. Chidambarum and G. M. Brown, Abstract D3, American Crystallographic Association Meeting, Gatlinburg, Tenn., June 1965.

[7] B. Bleaney and K. D. Bowers, *Proc. Roy. Soc.* (*A*), 1952, **214**, 451.

[8] (a) J. R. Wasson, C.-I. Shyr, and C. Trapp, *Inorg. Chem.*, 1968, **7**, 469; (b) E. Wasserman, L. C. Snyder, and W. A. Yager, *J. Chem. Phys.*, 1964, **41**, 1763.

[9] For a tabulation, see R. W. Jotham, S. F. A. Kettle, and J. A. Marks, *J.C.S. Dalton*, 1972, 428.

[10] D. M. L. Goodgame, N. J. Hill, D. F. Marsham, A. C. Skapski, M. L. Smart, and P. G. H. Troughton, *Chem. Comm.*, 1970, 629; D. B. W. Yawney and R. J. Doedens, *Inorg. Chem.*, 1970, **9**, 1626; T. Asakawa, M. Inoue, K. Hara, and M. Kubo, *Bull. Chem. Soc. Japan*, 1970, **45**, 1054.