

the method of Golding for analysis of the temperature dependence of  $\Delta E$  for  $[\text{Fe}(\text{terpy})_2](\text{ClO}_4)_3$  was somewhat less successful and no discussion of this type is presented here.

**Orbital Ground States.** A study of the literature for low-spin ferric complexes shows that where detailed investigations have been performed, nondegenerate orbital ground terms seem to be generally favored. Thus for instance in addition to  $[\text{Fe}(\text{terpy})_2](\text{ClO}_4)_3$  considered here and for which the ground term is  ${}^2\text{B}$ , nitrogen systems<sup>8,10</sup> such as  $[\text{Fe}(\text{phen})_3](\text{ClO}_4)_3$ ,  $[\text{Fe}(\text{bipy})_3](\text{ClO}_4)_3$ , and the corresponding dicyano bisdiimine complexes<sup>29</sup> all have nondegenerate ( ${}^2\text{A}$ ) ground terms. These observations extend to sulfur compounds, e.g.,  $[\text{Fe}(\text{dithioacetylacetonate})_3]$ ,<sup>30</sup>  $[(\text{phenyl})_4\text{P}]_3[\text{Fe}(\text{S}_2\text{C}_2(\text{CCN})_2)_3]$ —a tris dithiolene,<sup>31</sup> and the persulfides<sup>32</sup>  $[\text{Fe}(\text{ttd})_2(\text{dtt})]$  and  $[\text{Fe}(\text{ttd})(\text{dtt})_2]$  where ttd is trithioperoxy-*p*-toluate and dtt is dithio-*p*-toluate. For  $[\text{Fe}(\text{dtt})_3]$ ,  $V_{zz}$  is positive and Hill, *et al.*,<sup>32</sup> assign the hole in the  $t_{2g}$  manifold equally to  $d_{zz}$  and  $d_{yz}$  or thus a doubly degenerate ground term. However, the probable near  $D_3$  symmetry of this complex suggests threefold quantization and hence  $V_{zz} > 0$  corresponds to a hole in  $d_{zz}$  or once again an orbitally nondegenerate ground term. Finally it is interesting to point out that

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the trans dichloroarsenic system  $[\text{Fe}(o\text{-phenylenebis}(\text{dimethylarsine}))_2\text{Cl}_2]\text{BF}_4$  also exhibits a nondegenerate ground term on the basis of perturbed Mössbauer and esr results.<sup>33</sup>

The foregoing observations for a variety of systems may be rationalized from two points of view. The most obvious is that a nondegenerate ground term allows avoidance of Jahn-Teller distortion which although not usually large for  $t_{2g}$  configurations would still have to occur for a  ${}^2\text{E}$  ground term. The second point deals with reduction of the ferric ion charge by ligand to metal  $\pi$  bonding. For low-spin  $d^5$ , a nondegenerate ground term readily results when there is destabilization of a single metal orbital ( $d_{xy}$  in the present case) by strong ligand to metal  $\pi$  bonding and concomitant metal charge reduction.

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## Preparation, Structure, and Magnetism of a Tetranuclear Basic Quinoline Adduct of Copper(II) Trifluoroacetate

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**Abstract:** The basic copper(II) trifluoroacetate adduct  $[\text{Cu}_2\text{OH}(\text{O}_2\text{CCF}_3)_3(\text{quinoline})_2]_2$  has been prepared and shown by a crystal structure analysis to have a novel tetranuclear structure. This complex crystallizes in the triclinic space group  $P\bar{1}$  with  $a = 10.401$  (16) Å,  $b = 12.773$  (20) Å,  $c = 15.237$  (24) Å,  $\alpha = 58.07$  (5)°,  $\beta = 124.22$  (4)°,  $\gamma = 113.81$  (4)°. Observed and calculated densities are 1.73 (2) and 1.76 g/cm<sup>3</sup>, respectively. The structure determination was based upon 3332 data collected by counter methods; full-matrix least-squares refinement converged to a conventional  $R$  factor of 0.073. The crystal structure is comprised of centrosymmetric tetranuclear molecules in which copper atoms are linked by carboxylate bridges and by triply bridging  $\text{OH}^-$  ions. Each of the two crystallographically independent  $\text{Cu}^{2+}$  ions is coordinated to four oxygen atoms and a quinoline nitrogen atom in a distorted square pyramidal configuration. Two of the three independent carboxylate groups form bridges from an apical coordination site of one copper atom to a basal site of another; the third trifluoroacetate group is monodentate. Magnetic susceptibility measurements clearly demonstrate the presence of substantial Cu-Cu interaction. Consideration of various models for this interaction leads to the conclusion that it must involve all four metal atoms and must be transmitted, at least in part, by the triply bridging hydroxo group.

Copper(II) trifluoroacetate differs in a number of important respects from copper(II) acetate and its higher homologs. Magnetic studies have shown anhydrous  $\text{Cu}(\text{O}_2\text{CCF}_3)_2$  to possess a room-temperature effective magnetic moment of  $\sim 1.8$  BM and to exhibit molar magnetic susceptibilities in conformity with the Curie-Weiss expression over the temperature range 94–

297°K.<sup>1</sup> These results may be contrasted with the room-temperature  $\mu_{\text{eff}}$  of 1.4 BM and the antiferromagnetic  $\chi_M$  vs.  $T$  behavior exhibited by anhydrous copper(II) acetate.<sup>2</sup> It has been suggested that this

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substantial difference in magnetic properties could be a consequence of the weaker basicity of the trifluoroacetate ion in comparison to that of the acetate group.<sup>3</sup> On the presumption that the two salts are isostructural, the magnetic data could then be accounted for by variations in the degree of electron donation to the metal ion by the carboxylate group. This explanation finds some support in magnetic data on chloro-substituted acetates;<sup>3,4</sup> however, other attempts to correlate the basicity of various carboxylate groups with the magnetic properties of the corresponding copper(II) salts have met with mixed results.<sup>3,5-11</sup> One obvious problem with correlations of this sort is their dependence upon the isostructural nature of the compounds under comparison. Though the dimeric copper(II) acetate structure is adopted by many other copper(II) carboxylates, it is by no means clear that the trifluoroacetate possesses this structure. It has in fact been proposed, on the basis of magnetic susceptibility and infrared spectral data, that the dimeric structure is *not* adopted by anhydrous copper(II) trifluoroacetate.<sup>1</sup>

A further point of difference between copper(II) trifluoroacetate and the copper(II) alkanoates involves the type of adducts formed with nitrogen bases. Bis adducts,  $\text{Cu}(\text{O}_2\text{CCF}_3)_2\text{L}_2$ , are the products most frequently obtained from the addition of donor ligands L to  $\text{Cu}(\text{O}_2\text{CCF}_3)_2$ ;<sup>12-15</sup> monoadducts,  $\text{Cu}(\text{O}_2\text{CCF}_3)_2\text{L}$ , of the sort commonly formed by the unsubstituted alkanoates have only rarely been reported.<sup>12,13</sup> The bis adducts usually possess room-temperature magnetic moments  $\geq 1.8$  BM and are presumably monomeric. To date, there has been no well-documented instance of a substantial metal-metal interaction (as evidenced by a room-temperature magnetic moment significantly lower than 1.8 BM) in a copper(II) trifluoroacetate adduct.

In light of these generalizations, we viewed with interest a report by Ablov, *et al.*,<sup>13</sup> of the synthesis and epr investigation of pyridine, substituted pyridine, and quinoline adducts of various copper(II) carboxylates. In particular, these workers found that two products were obtained from the addition of quinoline (in an alcoholic solution) to aqueous copper(II) trifluoroacetate. With an excess of quinoline, violet crystals were formed for which elemental analyses (C, H, N) were consistent with a  $\text{Cu}(\text{O}_2\text{CCF}_3)_2(\text{quin})_2$  (quin = quinoline) stoichiometry. On the other hand, use of a

deficiency of quinoline was reported to yield a green crystalline product formulated as  $\text{Cu}(\text{O}_2\text{CCF}_3)_2(\text{quin})$ . The epr spectra of polycrystalline samples of these two materials were measured; for the violet complex, a spectrum indicative of magnetically isolated Cu(II) ions was obtained. However, the green product was reported to yield no signals typical of molecules with either  $S = 1/2$  or  $S = 1$ . It was suggested that this observation could stem from the presence of dimeric molecules with a Cu-Cu interaction so strong that no appreciable population of any triplet state occurs at room temperature. It was also noted, however, that the possibility of a more complex structure could not be excluded.<sup>13</sup>

Our synthetic, structural, and magnetic investigations of the copper(II) trifluoroacetate-quinoline system were motivated by the lack of structural information on  $\text{Cu}(\text{O}_2\text{CCF}_3)_2$  and its adducts, by the possible existence of novel structural types, and by the potential pertinence of the results to the general problem of the interrelations between structure and magnetic interaction in dinuclear and polynuclear copper(II) complexes. In the present paper we report the structural and magnetic characterization of the basic quinoline adduct,  $[\text{Cu}_2\text{OH}(\text{O}_2\text{CCF}_3)_3(\text{quin})_2]_2$ , obtained by a procedure similar to that of Ablov, *et al.* The structural results for this complex have previously been reported in a preliminary fashion.<sup>16</sup>

## Experimental Section

**Preparation of the Complex.** Anhydrous  $\text{Cu}(\text{O}_2\text{CCF}_3)_2$  (3.2 g) was dissolved in 95% ethanol and filtered. An ethanolic solution of 1.0 g of quinoline was added. The resulting deep blue-green solution was concentrated over  $\text{P}_2\text{O}_5$ . The solution initially deposited purple crystals (presumably  $\text{Cu}(\text{O}_2\text{CCF}_3)_2(\text{quin})_2$ ); after repeated fractional crystallizations from the mother liquor, crystals of a green material were obtained. Analyses were performed by Chemalytics, Inc. of Tempe, Ariz. *Anal.* Calcd for  $\text{Cu}_2\text{C}_{24}\text{H}_{15}\text{N}_2\text{O}_7\text{F}_6$ : C, 38.87; N, 3.8; H, 1.9. Calcd for  $\text{Cu}_2\text{C}_{13}\text{H}_7\text{NO}_4\text{F}_6$ : C, 37.28; N, 3.35; H, 1.68. Found: C, 39.0; N, 3.9; H, 1.9.

**Collection and Reduction of the X-Ray Data.** Precession photographs of the green crystals revealed no evidence of monoclinic or higher symmetry; a Delaunay reduction confirmed the assignment of this material to the triclinic crystal system. Solution of the structure was successfully achieved in the centrosymmetric space group  $P\bar{1}$ . Lattice parameters ( $21^\circ$ ,  $\lambda(\text{Mo K}\alpha_1)$  0.70926 Å), obtained from least-squares refinement of the setting angles of 15 reflections which had been carefully centered on a Picker four-circle X-ray diffractometer, were  $a = 10.401$  (16) Å,  $b = 12.773$  (20) Å,  $c = 15.237$  (24) Å,  $\alpha = 58.07$  (5)°,  $\beta = 124.22$  (4)°, and  $\gamma = 113.81$  (4)°. The three shortest noncoplanar cell translations define a reduced cell with  $a = 10.401$  Å,  $b = 12.731$  Å,  $c = 12.773$  Å,  $\alpha = 107.65^\circ$ ,  $\beta = 113.81^\circ$ , and  $\gamma = 98.27^\circ$ . All results are reported in terms of the nonreduced cell; the transformation matrix from the data cell to the reduced cell is

$$\begin{pmatrix} 1 & 0 & 0 \\ -1 & 0 & -1 \\ 0 & 1 & 0 \end{pmatrix}$$

Observed (floatation in  $\text{CCl}_4\text{-CH}_2\text{Br}_2$  solutions) and calculated ( $Z =$  one tetranuclear molecule per cell) densities are 1.73 (2) and 1.76  $\text{g/cm}^3$ , respectively. Satisfactory agreement of observed and calculated densities could not be obtained on the basis of the initial presumption of  $\text{Cu}(\text{O}_2\text{CCF}_3)_2(\text{quin})$  stoichiometry.

Intensity data were collected from a well-formed green centrosymmetric crystal of dimensions  $0.53 \times 0.46 \times 0.33$  mm. The crystal was mounted in a thin-walled glass capillary approximately about the 120 direction. Bounding planes of the crystal belonged

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**Table I.** Positional and Thermal Parameters for  $[\text{Cu}_2\text{OH}(\text{O}_2\text{CCF}_3)_2(\text{C}_9\text{H}_7\text{N})_2]_2$ 

Atom	x	y	z	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
Cu(1)	0.14821 (12) <sup>a</sup>	0.09067 (8)	0.02863 (8)	177.1 (2.0) <sup>b</sup>	61.3 (1.0)	67.2 (0.9)	34.6 (1.0)	51.1 (1.1)	-13.8 (0.7)
Cu(2)	0.20412 (12)	-0.20772 (8)	0.19508 (8)	160.3 (1.8)	63.9 (1.0)	67.9 (0.9)	36.6 (1.0)	53.5 (1.0)	-11.5 (0.7)
O(1)	0.0639 (6)	-0.0828 (5)	0.1031 (5)	3.79 (10) <sup>c</sup>					
O(1-1)	0.2492 (7)	0.0328 (5)	-0.0281 (5)	4.68 (12)					
O(1-2)	0.2137 (7)	-0.1763 (5)	0.0576 (5)	4.53 (12)					
O(2-1)	0.4104 (8)	-0.0812 (6)	0.2668 (6)	5.55 (14)					
O(2-2)	0.3287 (7)	0.1027 (6)	0.1698 (6)	5.67 (14)					
O(3-1)	0.0585 (9)	-0.1203 (7)	0.2829 (7)	7.57 (18)					
O(3-2)	0.1617 (7)	-0.2758 (5)	0.3294 (5)	4.38 (12)					
C(1-1)	0.2424 (9)	-0.0726 (8)	-0.0152 (7)	3.96 (16)					
C(1-2)	0.2706 (15)	-0.0807 (9)	-0.0998 (10)	340 (24)	90 (10)	163 (12)	-4 (13)	176 (15)	-53 (10)
C(2-1)	0.4209 (11)	0.0254 (9)	0.2511 (8)	4.83 (19)					
C(2-2)	0.5678 (18)	0.0696 (10)	0.3393 (12)	363 (31)	66 (10)	104 (14)	5 (15)	20 (18)	-29 (11)
C(3-1)	0.1071 (10)	-0.2238 (8)	0.3462 (8)	4.55 (18)					
C(3-2)	0.0996 (12)	-0.2881 (9)	0.4605 (8)	207 (18)	119 (11)	82 (8)	55 (12)	69 (11)	-24 (8)
F(1-1)	0.3865 (9)	-0.1433 (7)	-0.0440 (7)	356 (15)	218 (10)	256 (11)	48 (10)	197 (11)	-117 (9)
F(1-2)	0.1484 (9)	-0.1448 (7)	-0.1575 (6)	397 (17)	244 (11)	150 (8)	-10 (11)	136 (10)	-121 (8)
F(1-3)	0.3030 (11)	0.0272 (5)	-0.1714 (6)	800 (25)	99 (6)	261 (9)	3 (10)	410 (14)	-26 (6)
F(2-1)	0.6627 (11)	0.1512 (10)	0.2976 (9)	356 (20)	302 (15)	219 (12)	-128 (15)	119 (13)	-134 (12)
F(2-2)	0.5376 (12)	0.1493 (12)	0.3552 (10)	451 (24)	405 (22)	285 (16)	63 (18)	4 (16)	-271 (17)
F(2-3)	0.6306 (9)	-0.0043 (5)	0.4337 (4)	619 (19)	120 (6)	113 (4)	56 (9)	-127 (8)	-13 (4)
F(3-1)	0.0835 (9)	-0.2157 (7)	0.4890 (6)	521 (19)	234 (10)	122 (7)	144 (11)	142 (9)	-50 (7)
F(3-2)	0.2109 (9)	-0.3473 (7)	0.5459 (5)	407 (16)	328 (11)	75 (5)	25 (12)	85 (8)	15 (6)
F(3-3)	-0.0322 (9)	-0.3721 (8)	0.4485 (7)	349 (17)	231 (12)	200 (10)	-31 (12)	183 (11)	-59 (9)
Group parameters <sup>d</sup>									
Group	$x_0$	$y_0$	$z_0$	$\phi$	$\theta$	$\rho$			
Quin 1	0.24640 (35)	0.42429 (28)	-0.04697 (26)	13.3113 (24)	-136.7448 (18)	-58.8804 (32)			
Quin 2	0.32972 (41)	-0.51323 (32)	0.34589 (29)	121.2683 (22)	-154.8032 (21)	163.5506 (32)			

<sup>a</sup> Numbers in parentheses in all tables and in the text are estimated standard deviations in the least significant figures. <sup>b</sup> The form of the anisotropic thermal ellipsoid is  $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ . Tabulated  $\beta$  values are  $\times 10^4$ . <sup>c</sup> For atoms refined isotropically, the isotropic thermal parameter (in  $\text{\AA}^2$ ) is tabulated under  $\beta_{11}$ . <sup>d</sup> The coordinates  $x_0$ ,  $y_0$ , and  $z_0$  are the fractional coordinates of the origin of the group coordinate system (taken at the midpoints of the C-C bond common to both rings); the angles  $\phi$ ,  $\theta$ , and  $\rho$  are the orientation angles defined in ref 19.

to the  $\{001\}$ ,  $\{011\}$ ,  $\{10\bar{1}\}$ ,  $\{1\bar{1}\bar{1}\}$ , and  $\{112\}$  forms. Narrow-source open-counter  $\omega$ -scans of several reflections from the crystal used for data collection showed well-formed profiles with an average full-width at half-maximum of  $0.12^\circ$ . This was in contrast to some previously examined crystals which had been discarded because of broad and multiple peaked profiles. Data were collected with Mo  $K\alpha$  radiation by the  $\theta$ - $2\theta$  scan technique; general aspects of the procedures used have been described previously.<sup>17</sup> Reflections were scanned at a rate of  $1^\circ/\text{min}$  and 10-sec stationary background counts were taken at each end of the scan. The scan range extended from  $-0.55$  to  $+0.75^\circ$  in  $2\theta$  from the calculated scattering angle. The takeoff angle was  $1.5^\circ$ . The counter aperture measured  $5 \times 5$  mm and was situated 29 cm from the crystal. The pulse-height analyzer was set to admit  $\sim 90\%$  of the Mo  $K\alpha$  peak. The intensities of four standard reflections were measured at regular intervals; no systematic variations in intensity were observed. Data were collected for all independent reflections with  $2\theta \leq 48^\circ$ .

Processing of the data was accomplished by previously described methods.<sup>17,18</sup> The  $p$  factor in the expression for the standard deviations was given a value of 0.03. Of the 4366 independent reflections measured, 3332 had  $F^2 \geq 3\sigma(F^2)$ ; these data were employed in the solution and refinement of the structure. Absorption corrections were applied; based upon a linear absorption coefficient of  $16.51 \text{ cm}^{-1}$ , calculated transmission factors ranged from 0.55 to 0.69.

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(18) Programs employed in this structural analysis included local versions of PICK (J. A. Ibers) for cell refinement and generation of diffractometer settings, PICKOUT (R. J. Doedens, J. A. Ibers) for data processing, GONO (W. C. Hamilton) for absorption correction, FORDAP (A. Zalkin) for Fourier summations, UCIGLS (derived from Busing, Martin, and Levy's ORFLS) for structure factor calculations and least-squares refinement, ORFFE (Busing, Martin, and Levy) for function and error calculations, PLANET (D. L. Smith) for least-squares plane calculations, DANFIG (R. J. Dellaca, W. T. Robinson) and ORTEP (C. K. Johnson) for preparation of figures, and RSCAN (R. J. Doedens) for evaluation of the weighting scheme. All computations were carried out on the local PDP-10 computer.

**Solution and Refinement of the Structure.** Elemental analysis and unit cell data (*vide infra*) were inconsistent with the  $\text{Cu}(\text{O}_2\text{C}-\text{CF}_3)_2(\text{quin})$  stoichiometry; the correct formulation was established by the crystal structure analysis. The coordinates of the two copper atoms in the asymmetric unit were obtained from a three-dimensional Patterson map and the remaining 42 nonhydrogen atoms were located by difference Fourier methods. In refinement of the structure, the two independent quinoline molecules were treated as rigid groups.<sup>19</sup> In the absence of precise structural data for free quinoline, the heterocyclic ring was presumed to have the dimensions of free pyridine<sup>20</sup> and the remainder of the molecule was given the distances and angles of a phenyl ring ( $\text{C}-\text{C} = 1.395 \text{ \AA}$ ,  $\angle \text{C}-\text{C}-\text{C} = 120^\circ$ ). Hydrogen atoms were included in the groups. Refinement with individual isotropic thermal parameters assigned to all nonhydrogen atoms (including group atoms) converged to discrepancy factors  $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.135$  and  $R_2 = [\sum w(F_o - |F_c|)^2 / \sum w|F_o|^2]^{1/2} = 0.170$ , based on the 3332 reflections with  $F_o \geq 3\sigma(F_o)$ . Further refinement with anisotropic thermal parameters assigned to the copper atoms resulted in  $R_1 = 0.106$  and  $R_2 = 0.136$ . At this point it was observed that the atoms of the  $\text{CF}_3$  groups had high isotropic thermal parameters and that the C-F bond distances showed greater variations than would ordinarily be expected. These observations, together with anomalous peak shapes on previous difference maps, were taken as evidence for substantial anisotropy in the thermal motion of the  $\text{CF}_3$  groups. Hence the final refinement employed anisotropic thermal parameters for the atoms of these groups as well as for the metal atoms. This refinement converged to  $R_1 = 0.073$  and  $R_2 = 0.094$ . A final difference map revealed no residual electron density greater than  $1.0 \text{ e/\AA}^3$ , compared with peak heights of  $1.3$ - $2.7 \text{ e/\AA}^3$  for carbon and oxygen atoms on previous difference maps. The largest residual electron densities were in the immediate vicinities of atoms O(3-1), O(2-2), C(14), and C(15); these residuals may be accounted for in terms of anisotropic thermal motion or an inadequate description of

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the quinoline molecule. Full anisotropic refinement would undoubtedly have improved this situation, but, since the goals of the study had already been achieved, such refinement was not considered a worthwhile investment of limited computing funds. No convincing evidence for the hydrogen atom presumed to be bound to O(1) (*vide infra*) was found on this map.

In all structure factor calculations, the atomic scattering factors tabulated in ref 21 were used for Cu, F, O, and C and those of Stewart, *et al.*,<sup>22</sup> were used for H. The  $\Delta f'$  and  $\Delta f''$  values of Cromer<sup>23</sup> were employed in correction of the  $F_o$  values for anomalous scattering by the copper atoms. The quantity minimized in the least-squares refinements was  $\sum w(|F_o| - |F_c|)^2$ , where  $w = 4F_o^2/\sigma^2(F_o^2)$ . The final standard deviation of an observation of unit weight was 4.0. Calculation of mean  $w(\Delta F)^2$  values as functions of  $F_o$ , uncorrected intensity, and Bragg angle revealed no significant trends. Calculation of structure factors for data with  $F_o < 3\sigma(F_o)$  showed only six reflections for which  $F_o$  exceeded the  $3\sigma$  cutoff by as much as three standard deviations.

Final positional and thermal parameters for nongroup atoms are given in Table I, as are final group positional and orientational parameters. Derived coordinates for the group atoms are listed in Table II and bond distances and angles are given in Tables III and IV, respectively. Principal amplitudes of thermal motion for

**Table II.** Positional and Thermal Parameters of Group Atoms

	x	y	z	B
N(1)	0.2060 (7) <sup>a</sup>	0.2732 (3)	-0.0498 (4)	4.14 (14)
C(2) <sup>b</sup>	0.2580 (7)	0.3098 (4)	-0.1270 (4)	4.93 (19)
C(3)	0.3192 (5)	0.4304 (5)	-0.1781 (4)	6.13 (24)
C(4)	0.3293 (6)	0.5216 (4)	-0.1500 (4)	5.81 (21)
C(5)	0.2829 (8)	0.5731 (3)	-0.0380 (5)	6.28 (24)
C(6)	0.2288 (8)	0.5344 (5)	0.0418 (5)	6.71 (25)
C(7)	0.1685 (6)	0.4094 (5)	0.0891 (4)	6.34 (23)
C(8)	0.1622 (6)	0.3231 (4)	0.0566 (4)	4.87 (19)
C(9)	0.2162 (4)	0.3618 (3)	-0.0233 (3)	3.96 (16)
C(10)	0.2766 (5)	0.4868 (3)	-0.0706 (3)	4.83 (19)
N(2)	0.3290 (5)	-0.3459 (4)	0.2805 (5)	4.18 (14)
C(12)	0.4830 (6)	-0.3076 (4)	0.3059 (5)	5.63 (21)
C(13)	0.5891 (4)	-0.3871 (5)	0.3647 (5)	7.15 (27)
C(14)	0.5372 (5)	-0.5149 (5)	0.4009 (5)	7.36 (28)
C(15)	0.3182 (7)	-0.6844 (3)	0.4096 (6)	7.55 (30)
C(16)	0.1588 (7)	-0.7231 (4)	0.3829 (6)	7.73 (29)
C(17)	0.0602 (5)	-0.6348 (5)	0.3226 (5)	6.84 (26)
C(18)	0.1210 (4)	-0.5077 (4)	0.2891 (4)	4.92 (19)
C(19)	0.2804 (4)	-0.4691 (3)	0.3158 (3)	4.24 (16)
C(20)	0.3790 (5)	-0.5574 (3)	0.3760 (4)	5.92 (22)
H(2) <sup>c</sup>	0.2509	0.2400	-0.1497	d
H(3)	0.3590	0.4541	-0.2393	
H(4)	0.3769	0.6173	-0.1888	
H(5)	0.3296	0.6699	-0.0747	
H(6)	0.2338	0.6013	0.0670	
H(7)	0.1266	0.3794	0.1509	
H(8)	0.1154	0.2263	0.0932	
H(12)	0.5251	-0.2085	0.2784	
H(13)	0.7110	-0.3510	0.3826	
H(14)	0.6178	-0.5799	0.4474	
H(15)	0.3946	-0.7527	0.4562	
H(16)	0.1120	-0.8213	0.4089	
H(17)	-0.0630	-0.6646	0.3019	
H(18)	0.0447	-0.4393	0.2425	

<sup>a</sup> Standard deviations of group atomic coordinates are estimated from the errors of the group parameters and may be meaningfully used only to estimate errors in distances between group and nongroup atoms or between atoms in *different* groups. <sup>b</sup> Carbon atoms of the first group are numbered in the conventional manner for the carbon atoms of a quinoline molecule; those in the second group are denoted by a number greater by 10 than this conventional designation. <sup>c</sup> The numbering of the hydrogen atoms corresponds to that of the carbon atoms; *e.g.*, H(2) is bound to C(2), etc. <sup>d</sup> Hydrogen atoms were assigned thermal parameters one unit greater than those of the corresponding carbon atoms.

(21) "International Tables for X-Ray Crystallography," Vol. 3, The Kynoch Press, Birmingham, England, 1962.

(22) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

(23) D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).

**Table III.** Intramolecular Distances (Å)

(a) Copper Coordination Spheres			
Cu(1)-O(1)	1.964 (6)	Cu(2)-O(1)	1.963 (6)
Cu(1)-O(1) <sup>a</sup>	1.990 (6)	Cu(2)-O(1-2)	1.968 (7)
Cu(1)-O(2-2)	1.936 (7)	Cu(2)-O(3-2)	1.990 (6)
Cu(1)-N(1)	1.989 (4)	Cu(2)-N(2)	2.004 (6)
Cu(1)-O(1-1)	2.174 (6)	Cu(2)-O(2-1)	2.200 (7)
(b) Trifluoroacetate Groups			
O(1-1)-C(1-1)	1.230 (10)	C(2-2)-F(2-1)	1.280 (16)
C(1-1)-O(1-2)	1.254 (9)	C(2-2)-F(2-2)	1.339 (16)
C(1-1)-C(1-2)	1.534 (13)	C(2-2)-F(2-3)	1.181 (13)
C(1-2)-F(1-1)	1.312 (13)	O(3-1)-C(3-1)	1.256 (11)
C(1-2)-F(1-2)	1.312 (12)	C(3-1)-O(3-2)	1.215 (10)
C(1-2)-F(1-3)	1.285 (11)	C(3-1)-C(3-2)	1.516 (12)
O(2-1)-C(2-1)	1.220 (10)	C(3-2)-F(3-1)	1.305 (11)
C(2-1)-O(2-2)	1.250 (10)	C(3-2)-F(3-2)	1.256 (10)
C(2-1)-C(2-2)	1.501 (15)	C(3-2)-F(3-3)	1.342 (12)
(c) Nonbonded Contacts			
Cu(1)···Cu(1)'	2.996 (4)	O(1)···O(1)'	2.579 (11)
Cu(1)···Cu(2)	3.347 (5)	O(1)···O(3-1)	2.550 (10)
Cu(1)···Cu(2)'	3.502 (5)		

<sup>a</sup> Primes denote atoms related to those in the asymmetric unit by the crystallographic center of symmetry.

atoms refined anisotropically are tabulated in Table V. A table of observed and calculated structure factors is available.<sup>24</sup>

**Magnetic Susceptibility Measurements.** Magnetic susceptibilities were measured between 80 and 300°K by the Faraday method on a powdered sample under nitrogen at a field strength of *ca.* 8000 G. The calibrant used was HgCo(SCN)<sub>4</sub>, whose magnetic susceptibility was taken as  $16.44 \times 10^{-6}$  cgsu at 20°. Measurements were made on an Alpha Model 1402 magnetic susceptibility system equipped with an Alpha/Ainsworth Model 1071 electronic balance and an Alpha Model 1424 variable temperature accessory system. The data were corrected for the diamagnetism of the sample holder and for the temperature independent paramagnetism of the copper atoms ( $60 \times 10^{-6}$  cgsu per copper). The correction for the diamagnetism of the constituent atoms was calculated by use of Pascal's constants and found to be  $-161.78 \times 10^{-6}$  cgsu per copper. The effective magnetic moment was calculated from the equation

$$\mu_{\text{eff}} = 2.83[(\chi_M' - N\alpha)T]^{1/2}$$

The magnetic data are presented in Table VI.

### Description of the Structure

This structural analysis has shown the green crystalline material obtained under the conditions described to be composed of discrete, centrosymmetric [Cu<sub>2</sub>OH-(O<sub>2</sub>CCF<sub>3</sub>)<sub>2</sub>(quin)<sub>2</sub>]<sub>2</sub> molecules. The elemental analysis (*vide supra*) is consistent with this stoichiometry and not with the initial formulation of the complex as Cu-(O<sub>2</sub>CCF<sub>3</sub>)<sub>2</sub>(quin). A schematic view of the structure of one tetranuclear molecule is shown in Figure 1. A second view of the molecular structure, designed to illustrate the carboxylate groups and the triply bridging oxygen atom, is presented in Figure 2. The two crystallographically independent copper atoms are each bound to four oxygen atoms and a quinoline nitrogen atom in a distorted square pyramidal configuration. Three independent carboxylate groups are present; two of these (designated as groups 1 and 2 in Figure 1) form bridges from the apical position of one copper atom to the basal site of a second metal atom. The third trifluoroacetate group (designated as group 3) is bound as a monodentate ligand in the basal plane of Cu(2). The remaining two basal positions in each copper coordination sphere are occupied by one quinoline nitrogen atom per copper and the triply bridging

(24) See paragraph at end of paper regarding supplementary material.

Table IV. Bond Angles (deg)

(a) Copper Coordination Spheres			
O(1)-Cu(1)-O(1)'	81.4 (2)	O(1)-Cu(2)-O(1-2)	91.5 (2)
O(1)-Cu(1)-O(2-2)	95.7 (3)	O(1)-Cu(2)-O(3-2)	92.0 (2)
O(1)-Cu(1)-N(1)	171.2 (4)	O(1)-Cu(2)-N(2)	174.2 (2)
O(1)-Cu(1)-O(1-1)	91.5 (2)	O(1)-Cu(2)-O(2-1)	92.7 (3)
O(2-2)-Cu(1)-N(1)	87.0 (2)	O(1-2)-Cu(2)-N(2)	86.4 (3)
O(2-2)-Cu(1)-O(1)'	166.7 (2)	O(1-2)-Cu(2)-O(3-2)	166.6 (2)
O(2-2)-Cu(1)-O(1-1)	100.6 (3)	O(1-2)-Cu(2)-O(2-1)	102.4 (3)
O(1)'-Cu(1)-N(1)	94.0 (2)	O(3-2)-Cu(2)-N(2)	88.8 (3)
O(1)'-Cu(1)-O(1-1)	92.4 (3)	O(3-2)-Cu(2)-O(2-1)	90.4 (3)
N(1)-Cu(1)-O(1-1)	96.3 (3)	N(2)-Cu(2)-O(2-1)	93.1 (3)
(b) Trifluoroacetate Groups			
Cu(1)-O(1-1)-C(1-1)	129.1 (6)	Cu(2)-O(2-1)-C(2-1)	130.0 (6)
O(1-1)-C(1-1)-O(1-2)	129.1 (8)	O(2-1)-C(2-1)-O(2-2)	128.5 (9)
O(1-1)-C(1-1)-C(1-2)	116.6 (8)	O(2-1)-C(2-1)-C(2-2)	114.9 (9)
O(1-2)-C(1-1)-C(1-2)	114.3 (8)	O(2-2)-C(2-1)-C(2-2)	116.6 (9)
Cu(2)-O(1-2)-C(1-1)	127.2 (6)	Cu(1)-O(2-2)-C(2-1)	128.6 (6)
C(1-1)-C(1-2)-F(1-1)	110.9 (9)	C(2-1)-C(2-2)-F(2-1)	112.2 (12)
C(1-1)-C(1-2)-F(1-2)	110.9 (8)	C(2-1)-C(2-2)-F(2-2)	110.1 (12)
C(1-1)-C(1-2)-F(1-3)	112.6 (9)	C(2-1)-C(2-2)-F(2-3)	119.1 (10)
F(1-1)-C(1-2)-F(1-2)	104.5 (9)	F(2-1)-C(2-2)-F(2-2)	94.4 (10)
F(1-1)-C(1-2)-F(1-3)	108.2 (9)	F(2-1)-C(2-2)-F(2-3)	113.6 (15)
F(1-2)-C(1-2)-F(1-3)	109.4 (10)	F(2-2)-C(2-2)-F(2-3)	104.2 (14)
Cu(2)-O(3-2)-C(3-1)	126.4 (6)	F(3-1)-C(3-2)-F(3-2)	108.1 (9)
O(3-2)-C(3-1)-O(3-1)	129.0 (9)	F(3-1)-C(3-2)-F(3-3)	103.9 (8)
O(3-1)-C(3-1)-C(3-2)	113.6 (8)	F(3-2)-C(3-2)-F(3-3)	106.3 (9)
O(3-2)-C(3-1)-C(3-2)	117.3 (8)		
C(3-1)-C(3-2)-F(3-1)	114.7 (8)		
C(3-1)-C(3-2)-F(3-2)	115.5 (8)		
C(3-1)-C(3-2)-F(3-3)	107.4 (8)		
(c) Triply Bridging Oxygen Atom			
Cu(1)-O(1)-Cu(1)'	98.6 (2)	Cu(1)-O(1)···O(3-1)	112.2 (3)
Cu(1)-O(1)-Cu(2)	116.9 (3)	Cu(1)'-O(1)···O(3-1)	113.9 (3)
Cu(1)-O(1)-Cu(2)'	124.8 (3)	Cu(2)-O(1)···O(3-1)	91.2 (3)
		C(3-1)-O(3-1)···O(1)	97.3 (6)

Table V. Principal Root-Mean-Square Amplitudes of Thermal Motion, Å

Atom	Minimum	Intermediate	Maximum
Cu(1)	0.179 (2)	0.222 (2)	0.257 (2)
Cu(2)	0.178 (2)	0.214 (2)	0.251 (1)
C(1-2)	0.208 (16)	0.234 (13)	0.378 (13)
C(2-2)	0.194 (15)	0.256 (18)	0.469 (15)
C(3-2)	0.219 (13)	0.235 (12)	0.297 (12)
F(1-1)	0.201 (9)	0.360 (8)	0.424 (9)
F(1-2)	0.231 (8)	0.351 (8)	0.418 (9)
F(1-3)	0.198 (8)	0.264 (8)	0.565 (8)
F(2-1)	0.276 (11)	0.390 (10)	0.546 (12)
F(2-2)	0.264 (11)	0.447 (13)	0.572 (15)
F(2-3)	0.190 (6)	0.290 (8)	0.722 (11)
F(3-1)	0.219 (8)	0.326 (8)	0.456 (8)
F(3-2)	0.214 (6)	0.272 (8)	0.516 (8)
F(3-3)	0.264 (9)	0.391 (9)	0.431 (10)

atom O(1). This latter atom is believed to be the oxygen atom of a hydroxo group (*vide infra*). The square pyramidal coordination polyhedra of Cu(1) and its centrosymmetric equivalent Cu(1)' share a basal edge, while Cu(2) and Cu(2)' each share a single basal coordination site with the two "central" metal atoms. The basal coordination planes of Cu(1) and Cu(1)' are parallel (as required by the molecular center of symmetry); the dihedral angle between the Cu(1) and Cu(2) basal planes is 87.9°.

Since hydrogen atoms were not located in this study, identification of the triply bridging atom O(1) as the oxygen atom of a hydroxo group rests on indirect evidence. The Cu-O-Cu angles about O(1), taken together with the fact that O(1) is out of the Cu(1)-Cu(1)'-Cu(2) plane by 0.51 Å, are consistent with a

Table VI. Magnetic Susceptibility Data<sup>a</sup>

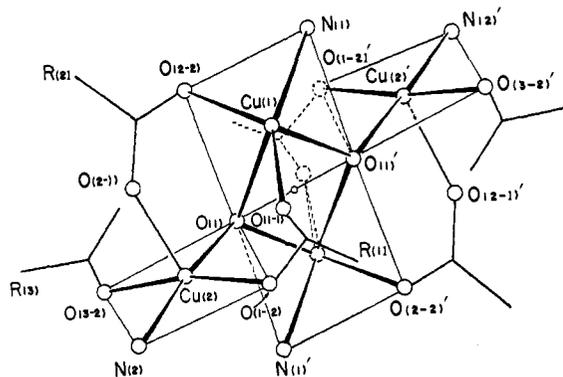
T, °K	$\chi_M'$ (obsd)	$\chi_M'$ (calcd)	$\mu_{eff}$
82.5	1733	1726	1.05
102.5	1693	1699	1.16
123	1653	1646	1.25
141	1572	1587	1.31
161	1532	1522	1.38
181	1471	1457	1.43
201	1391	1394	1.46
221	1330	1334	1.50
241	1270	1276	1.53
260	1230	1225	1.56
280	1169	1174	1.58
300	1129	1126	1.60

<sup>a</sup> Observed and calculated susceptibility values listed are molar paramagnetic susceptibilities per copper ion in cgs units  $\times 10^6$ . Calculated susceptibilities are based upon the four-center model described in the text.

distorted tetrahedral geometry. Furthermore, the uncoordinated oxygen atom of the monodentate carboxylate group, O(3-1), is involved in a short contact of 2.550(10) Å with O(1). This contact is indicative of an O···H-O hydrogen bond; it is distinctly shorter than twice the van der Waals' radius of an oxygen atom but within the usual range of hydrogen-bonded O···H-O contacts.<sup>25</sup> Two broad absorptions occur in the infrared spectrum in the region expected (2700-2900  $\text{cm}^{-1}$ ) for such a hydrogen bond. We see no alternative interpretation of O(1) which is both chemically feasible and consistent with the structural results.

The square pyramidal configurations of the two

(25) W. C. Hamilton and J. A. Ibers, "Hydrogen Bonding in Solids," W. A. Benjamin, New York, N. Y., 1968, pp 14-16.



**Figure 1.** A schematic view of the molecular structure of  $[\text{Cu}_2\text{OH}(\text{O}_2\text{CCF}_3)_2(\text{quin})_2]$ . For clarity, quinoline rings are not shown and  $\text{CF}_3$  groups are represented as R(1), R(2), and R(3). The lighter lines denote the basal planes of the four square pyramidal copper(II) coordination polyhedra.

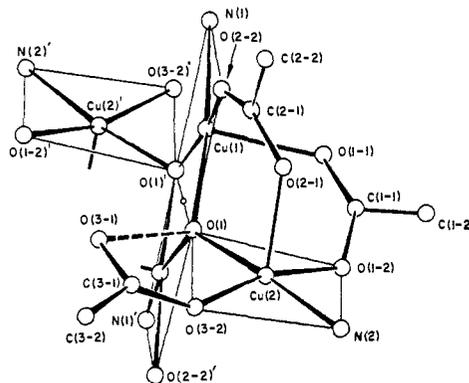
independent copper atoms are quite similar. The displacements of Cu(1) and Cu(2) from their basal coordination planes are 0.174 and 0.151 Å, respectively. As is evident from data tabulated in Table VII, the

**Table VII.** Least-Squares Planes<sup>a</sup>

1. Plane containing O(1), O(1)', N(1), and O(2-2) <sup>b</sup> Equation of plane: $0.8816X - 0.3890Y - 0.2673Z = -0.0001$ Distance to plane (Å)	O(1) 0.040	O(2-2) -0.059	
	O(1)' -0.039	Cu(1) 0.174	
	N(1) 0.032		
2. Plane containing O(1), N(2), O(1-2), and O(3-2) <sup>b</sup> Equation of plane: $-0.4655X - 0.8337Y - 0.2969Z = -0.0204$ Distances to plane	O(1) -0.055	O(3-2) 0.066	
	N(2) -0.052	Cu(2) -0.151	
	O(1-2) 0.071		
3. Plane containing O(1-1), O(1-2), C(1-1), and C(1-2) Equation of plane: $-0.7198X - 0.2990Y - 0.6265Z = -1.7877$ Distances to plane	O(1-1) 0.001	C(1-1) -0.004	
	O(1-2) 0.001	C(1-2) 0.001	
4. Plane containing O(2-1), O(2-2), C(2-1), and C(2-2) Equation of plane: $0.8324X + 0.1193Y - 0.5413Z = 0.3724$ Distances to plane	O(2-1) 0.005	C(2-1) -0.013	
	O(2-2) 0.005	C(2-2) 0.003	
5. Plane containing O(3-1), O(3-2), C(3-1), and C(3-2) Equation of plane: $-0.5851X - 0.6905Y - 0.4253Z = -0.6989$ Distances to plane	O(3-1) -0.003	C(3-1) 0.011	
	O(3-2) -0.002	C(3-2) -0.003	

<sup>a</sup> Unit weights were employed in the calculation of all planes. The equations of the planes are expressed with respect to coordinates (X, Y, Z) referred to an orthogonal system (A, B, C) oriented with respect to the crystallographic axes such that A is parallel to a, B is parallel to  $c^* \times a$ , and C is parallel to  $A \times B$ . <sup>b</sup> These groupings of atoms are not in fact coplanar. Information concerning the "best" basal planes is included for comparison with other square pyramidal structures.

atoms occupying the four basal sites of each metal atom are not strictly coplanar. The principal distortion of



**Figure 2.** An alternative view of the molecular structure, chosen to illustrate the configurations of the bridging groups. Only selected atoms lying outside the crystallographic asymmetric unit are shown.

the Cu(1) coordination polyhedron is a compression of the O(1)-Cu-O(1)' angle to 81.4 (2)°; for Cu(2) the major distortions are reflected in the N(2)-Cu(2)-O(1-2) angle of 86.4 (3)° and in the angles O(2-1)-Cu(2)-O(3-2) = 90.4 (3)° and O(2-1)-Cu(2)-O(1-2) = 102.4 (3)°. The Cu-O and Cu-N bond distances are well within the normal ranges observed for square pyramidal copper(II). The three Cu-O(1) distances range only from 1.963 (6) to 1.990 (6) Å and the Cu-N distances of 1.989 (4) and 2.004 (6) Å are equal within experimental error. Basal Cu-O (carboxylate) distances range from 1.936 (7) to 1.990 (6) Å; the apical Cu-O distances are Cu(1)-O(1-1) = 2.174 (6) Å and Cu(2)-O(2-1) = 2.200 (7) Å.

The metal-bridging configuration of the two bidentate carboxylate groups differs somewhat from the conventional geometry found in most dimeric copper(II) carboxylates. The CuOC(C)OCu grouping is not coplanar; rather the metal atoms are displaced by 0.29–0.62 Å from the plane defined by the carboxylate carbon and oxygen atoms (see Table VII). As is most clearly evident in Figure 2, the bridging trifluoroacetate groups have the syn,syn configuration. The C-O distances range from 1.220 (10) to 1.254 (9) Å. A similar range is observed in the acid salt  $\text{KH}(\text{O}_2\text{CCF}_3)_2$  and its deuterated analog,<sup>26</sup> in  $\text{NH}_4\text{O}_2\text{CCF}_3$ , the C...O distances are equal within experimental error, with a mean value of 1.269 (5) Å.<sup>27</sup> In both of the bridging carboxylate groups, the longer C-O distance involves the oxygen atom coordinated in a basal copper coordination site, though the differences are only marginally significant on a statistical basis. The C-CF<sub>3</sub> distances do not differ significantly and have a mean value of 1.517 (13) Å. The CF<sub>3</sub> groups display a relatively high degree of anisotropic thermal motion. This problem is particularly severe for the group designated as R(2) and is indicative of high-amplitude torsion motion and/or rotational disorder for these groups. This situation has been observed in other structures containing CF<sub>3</sub> groups.<sup>28,29</sup> One of the C-F distances, C(2-2)-F(2-3),

(26) Lj. Golič and J. C. Speakman, *J. Chem. Soc.*, 2530 (1965); A. L. Macdonald, J. C. Speakman, and D. Hadzi, *J. Chem. Soc., Perkin Trans. 2*, 825 (1972).

(27) D. W. J. Cruickshank, D. W. Jones, and G. Walker, *J. Chem. Soc.*, 1303 (1964).

(28) R. A. Lalancette, M. Cefola, W. C. Hamilton, and S. J. La Placa, *Inorg. Chem.*, 6, 2127 (1967).

(29) F. A. Cotton and J. G. Norman, Jr., *J. Coord. Chem.*, 1, 161 (1972); *J. Amer. Chem. Soc.*, 94, 5697 (1972).

has an unreasonably short value of 1.181 (13) Å. This distance is certainly not to be taken seriously; it is undoubtedly related to the high degree of anisotropy of the thermal motion of F(2-3). The other eight C-F distances range from 1.256 (10) to 1.339 (16) Å, with an average value of 1.304 (13) Å.

## Discussion

**Structural Aspects.** The structure of  $[\text{Cu}_2\text{OH}(\text{O}_2\text{C}-\text{CF}_3)(\text{quin})_2]_2$ , as determined by this study, displays several unusual features and is, as a whole, completely unprecedented. Basic carboxylates of Cu(II) are known, but none of the previous examples of such salts showed stoichiometry or magnetic properties resembling those of this complex.<sup>6,30</sup> The central portion of the molecule (*i.e.*, Cu(1), Cu(1)', and the inner coordination spheres of these two atoms) bears a strong resemblance to certain oxygen-bridged square-pyramidal copper(II) dimers. These include, for example, di- $\mu$ -methoxy-bis[chloro(2-methylpyridine)copper(II)],<sup>31</sup> di- $\mu$ -hydroxo-bis[2-(2-ethylaminoethyl)pyridinecopper(II)] perchlorate,<sup>32</sup> and di- $\mu$ -hydroxo-bis[bipyridylcopper(II)] nitrate.<sup>33</sup> It is, however, important to note that the bridging hydroxide ion in our trifluoroacetate adduct is tetracoordinate, while in the three bridged dimers mentioned above the oxygen atom is tricoordinate. This difference is reflected in the longer Cu(1)-OH distances we observe (1.964 (6) Å and 1.990 (6) Å) in comparison to the mean value of 1.92 Å found for the corresponding distance in each of the bridged dimers. The Cu(1)-Cu(1)' distance of 2.996 (4) Å is toward the long end of the range of 2.85-3.02 Å observed in the three dimers.

The triply bridging configuration of the OH<sup>-</sup> ion is unusual though not unprecedented.<sup>34</sup> Another copper(II) complex in which such a configuration has been demonstrated crystallographically is the trinuclear species  $\text{Cu}_3\text{L}_3(\text{OH})\text{SO}_4 \cdot 16.3\text{H}_2\text{O}$  (L = deprotonated pyridine-2-carbaldehyde oxime).<sup>35,36</sup> In this molecule, the hydroxide ion lies on a crystallographic threefold axis, thus forming a symmetric triple bridge with a Cu-O-Cu angle of 108.2 (4)°. Other compounds in which a single OH<sup>-</sup> ion has been shown to simultaneously bridge three metal ions include  $[\text{Ni}_3(\text{tfacac})_3\text{OH}(\text{H}_2\text{O})]_2$  (tfacac = 1,1,1-trifluoropentane-2,4 dionate),<sup>37</sup>  $[(\text{CH}_3)_3\text{Pt}(\text{OH})]_4$ ,<sup>38</sup> and  $\text{Pb}_6\text{O}(\text{OH})_6(\text{ClO}_4)_4 \cdot \text{H}_2\text{O}$ .<sup>39</sup> Methoxide ion has also been demonstrated to adopt a triply bridging configuration in several tetranuclear cluster compounds of cobalt and nickel.<sup>40-42</sup>

The range of metal-oxygen-metal angles about these triply bridging OH<sup>-</sup> and OMe<sup>-</sup> ions is 88-118°. Two of the three Cu-O-Cu angles we observe (Cu(1)-O(1)-Cu(1)' = 98.6 (2)° and Cu(1)-O(1)-Cu(2) = 116.9 (3)°) fall within this range, while the third (Cu(1)-O(1)'/Cu(2)' = 124.8 (3)°) is somewhat larger.

It is of some interest to speculate as to the reasons for adoption of this unusual structure and its relationship to other products obtained from the copper(II) trifluoroacetate-quinoline system. Our preparative procedure is qualitatively consistent with that employed by Ablov, *et al.*,<sup>13</sup> and, though some discrepancies exist, it is likely that our green product is identical with theirs. The Russian workers reported that an epr investigation "failed to reveal signals due either to molecules with  $S = 1$  or with  $S = 1/2$ ." We find that a polycrystalline sample of our green product does display an epr spectrum (X-band, Varian E3 esr spectrometer, operating frequency of 9.167 GHz, 100-KHz modulation) but that, apart from a line at ~3200 G which we attribute to a small amount of mononuclear impurity, the spectrum is weak and ill-defined. Results of the elemental analyses of Ablov, *et al.*,<sup>13</sup> are also somewhat ambiguous, though only Cu and N analyses are reported. The matter is further complicated by the fact that experimental work in our laboratory subsequent to that reported above has resulted in the isolation and characterization of two additional products from the copper trifluoroacetate-quinoline system.<sup>43</sup> These include a very hygroscopic light green material, shown by X-ray structural analysis to be  $[\text{Cu}(\text{O}_2\text{CCF}_3)_2(\text{quin})]_2$ , and a blue product believed to be  $\text{Cu}(\text{O}_2\text{CCF}_3)_2(\text{quin}) \cdot \text{H}_2\text{O}$ . These two products exhibit distinct epr spectra; full details of their characterization and properties will be reported in due course. We may summarize by stating that, of the four products we have obtained from this system, the tetranuclear basic trifluoroacetate is most nearly consistent with the green product described by Ablov, *et al.*

It is worthy of note that the potential sixth coordination site of each copper atom is effectively blocked. This blockage is achieved for Cu(1) by the CF<sub>3</sub> group designated as R(1) and for Cu(2) by the quinoline molecule of which N(1) is the metal-bound atom. The hindrance of approach of potential ligands from the sixth octahedral coordination site of the metal atoms may well be of importance in stabilizing this unusual structure. Finally, we point out that application of the usual rules for estimation of the *formal* oxidation states of the two metal ions leads to nonintegral oxidation states which differ for the two independent copper ions, namely 1<sup>2</sup>/<sub>3</sub> for Cu(1) and 2<sup>1</sup>/<sub>3</sub> for Cu(2).

**Magnetic Results.** The magnetic susceptibility data of Table VI are represented graphically in Figure 3. It is clear from the shape of this curve and from the temperature variation of  $\mu_{\text{eff}}$  that substantial copper-copper interaction exists in this compound. This interaction cannot be satisfactorily represented by a simple Curie-Weiss expression, as is evident from the reciprocal susceptibility *vs.* *T* plot of Figure 4. The susceptibility

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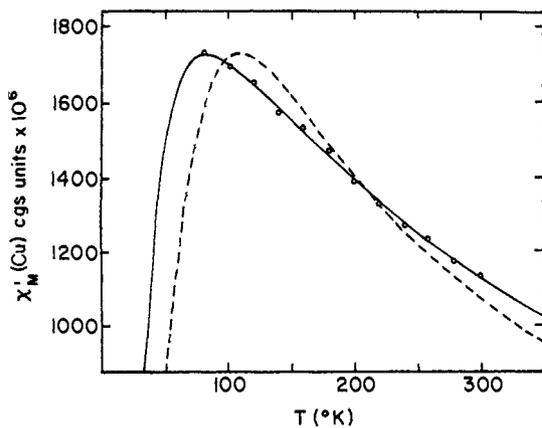


Figure 3. Magnetic susceptibility of  $[\text{Cu}_2\text{OH}(\text{O}_2\text{CCF}_3)_3(\text{quin})_2]_2$ . The dashed curve is the "best" fit to the dimer equation and the solid susceptibility curve is calculated from the four-center model described in the text.

results, together with the discrete nature of the tetranuclear molecules, are consistent with a predominantly intramolecular magnetic interaction. As usual, one cannot rigorously exclude the possibility of intermolecular coupling terms, though these are likely to be small.

In attempting to construct a model for the magnetic coupling, initial consideration was focused upon simple schemes whereby the interaction could be represented as one which involves only magnetically isolated copper(II) ions and/or metal atoms interacting in a pairwise fashion. In the first such model investigated, the interaction was presumed to be a pairwise coupling between the nonequivalent copper ions Cu(1) and Cu(2) and, by symmetry, between Cu(1)' and Cu(2)'. This model might be expected to be valid if the interaction were transmitted solely through the bridging trifluoroacetate ligands. If this were the case, one would expect to be able to represent the susceptibility curve by the usual equation for an isolated pair of interacting ions of spin  $1/2$ .<sup>44</sup> The "best" least-squares fit to this equation is indicated by the dashed curve of Figure 3; it is obvious that this curve does not satisfactorily reproduce the experimental data. Furthermore, the  $g$  value of 1.97 obtained by fitting the observed data to this equation is unreasonable. Clearly, this model for the magnetic interaction is unsatisfactory.

The second simple model investigated for the magnetic coupling was one in which the interaction was solely between Cu(1) and Cu(1)', with Cu(2) and Cu(2)' exhibiting Curie law behavior. This model would give rise to an overall susceptibility per copper ion which may be expressed as

$$\chi_M'(\text{Cu}) = \frac{1}{2}(\chi(1) + \chi(2))$$

where  $\chi(1)$  is the contribution of Cu(1) (and of Cu(1)') calculated by the dimer equation or some variant thereof and  $\chi(2)$  stems from the noninteracting atoms Cu(2) and Cu(2)'. Assumptions of Curie law form for  $\chi(2)$  and of a  $\mu_{\text{eff}}$  value of 1.80 BM for Cu(2) and Cu(2)' yields a contribution from this term alone which is greater than the experimental susceptibility at low temperatures. For example, at 82.5°K,  $\frac{1}{2}\chi(2) =$

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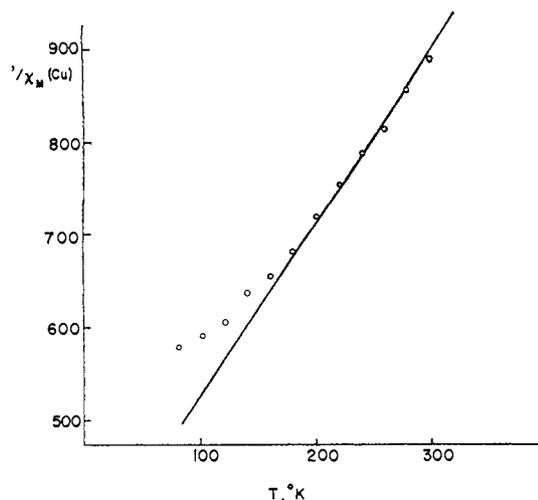
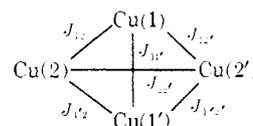


Figure 4. Curie-Weiss plot of reciprocal susceptibility vs. temperature.

$2594 \times 10^{-6}$  cgsu under these assumptions and the experimental susceptibility at this temperature is  $1733 \times 10^{-6}$  cgsu. Reasonable modifications of the assumptions made do not significantly improve this situation; hence this model is also rejected.

We may summarize the discussion to this point by stating that all three of the models considered (Curie-Weiss, dimer, and dimer + Curie law) have been clearly demonstrated to be qualitatively incapable of agreement with the experimental susceptibility curve for any reasonable choice of parameters. We are thus led, by elimination, to the conclusion that all four of the metal ions must be involved in the magnetic interaction.<sup>45-48</sup> The most general four-center model for such an interaction would involve six coupling constants whose function may be represented schematically as shown in Scheme I. In this particular case, symmetry

#### Scheme I



imposes the constraints  $J_{12} = J_{12'}$  and  $J_{11'} = J_{12'}$ . Furthermore it is reasonable to presume that  $J_{22'}$  should be small, since Cu(2) and Cu(2)' are relatively remote from each other and are not directly linked by any bridging ligands. Finally, it is evident that the susceptibility curve can provide no basis for separation of the interactions represented by  $J_{12}$  and  $J_{12'}$ .<sup>49</sup> Hence one may arbitrarily set one of these two constants equal to zero and use the other one to represent the sum of the interactions of Cu(2) with Cu(1) and Cu(1)'. The

(45) In reaching this conclusion, it has been implicitly presumed that the assumptions commonly made in treating magnetic exchange in Cu(II) systems are valid for this complex. These assumptions are outlined in detail in several recent review articles.<sup>46-48</sup>

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(47) E. Sinn, *Coord. Chem. Rev.*, **5**, 313 (1970).

(48) A. P. Ginsberg, *Inorg. Chim. Acta Rev.*, **5**, 45 (1971).

(49) Although the pathways represented by  $J_{12}$  and  $J_{12'}$  are physically distinct, they enter into the susceptibility expression in a fashion which does not permit their separation by any sort of fitting process. This degeneracy has been verified by calculation and can perhaps best be rationalized by recognizing that  $J_{12}$  and  $J_{12'}$  each represent an interaction of Cu(2) with the Cu(1)-Cu(1)' couple.

general four-center coupling model thus reduces to one in which only  $J_{12}$ ,  $J_{11'}$ , and  $J_{1'2'}$  are nonzero and  $J_{12} = J_{1'2'}$ . The coupling model is thus mathematically equivalent to that for a symmetrical four atom chain and contains only two independently variable  $J$  values.

The constraints enumerated above were applied in attempts to fit the experimental susceptibility curve by use of a general computer program for calculation of magnetic susceptibilities for multicenter arrays of interacting paramagnetic centers.<sup>50</sup> In this process, only contributions of spin terms to the calculated susceptibility were explicitly considered and the  $g$  values of both metal atoms were constrained to reasonable values of 2.17. A least-squares fit to the observed susceptibility curve was achieved with  $J_{11'} = -90 \text{ cm}^{-1}$  and  $J_{12} = -70 \text{ cm}^{-1}$ ; this calculated curve is indicated by the solid line of Figure 3. The agreement over the temperature range covered is good and the calculated curve suggests that the susceptibility passes through a maximum in the vicinity of liquid nitrogen temperature. The existence of this maximum was confirmed by approximate measurements of susceptibilities at lower temperatures. It should be emphasized that the  $J$  values quoted are likely to be subject to substantial uncertainty and are at best only crude estimates. Also, it should be noted that  $J_{12}$  represents the sum of the two distinct interactions represented by  $J_{12}$  and  $J_{1'2'}$  in the general four-center model.

In view of these limitations, it is inadvisable to attempt to ascribe any significance to the actual  $J$  values obtained. Nonetheless, some qualitative comments concerning the possible modes of interaction may be made. On the presumption that the pathway for the observed Cu-Cu coupling is an indirect one involving the bridging ligands, two sorts of bridges must be considered as possible contributors to the interaction. A pair of triatomic carboxylate bridges links Cu(1) and Cu(2). These bridges are like those found in copper(II) acetate and related species, though they differ qualitatively from most previous examples of such bridges in that they link an apical coordination site of one square pyramidal metal ion with a basal site of a second copper(II) ion. In general, the strongest Cu-Cu interactions are observed when bridging groups link basal coordination sites of pairs of copper atoms; however, no good precedent exists for the sort of triatomic apical-to-basal bridge we have found. One can, however, infer from our magnetic data that the interaction cannot occur *exclusively via* the carboxylate bridges. This inference is possible because the trifluoroacetates link the metal ions in pairs, with no carboxylate bridging between Cu(1) or Cu(2) and their centrosymmetric equivalents. Thus one would expect the magnetic behavior of a dimer if the trifluoroacetate bridges provided the sole pathway for interaction. As discussed above, the observed susceptibility curve deviates substantially from that expected for a dimer.

This line of reasoning forces us to conclude that at

(50) This program was generously supplied by Professor E. Sinn of the University of Virginia. It was written by R. A. Palmer at the University of Wellington and employs the general methods outlined in ref 47.

least part of the pathway for the observed magnetic interaction must involve the bridging oxygen atom. As mentioned above, the only structural precedent for a triply bridging hydroxide ion in a complex of copper(II) occurs in the trinuclear species  $\text{Cu}_3\text{L}_3\text{OH}(\text{SO}_4) \cdot 16.3\text{H}_2\text{O}$ , where L = deprotonated pyridine-2-carbaldehyde oxime.<sup>35, 36</sup> In this molecule the three metal ions adopt an equilateral triangular configuration with a Cu-Cu separation of 3.21 Å. Triply bridging  $\text{OH}^-$  and  $\text{SO}_4^{2-}$  groups link the metal atoms on opposite sides of their plane and aldoximate groups bridge pairs of metal atoms. The bridging hydroxo group fulfills a function qualitatively similar to that which we observe in the tetranuclear basic trifluoroacetate, though the configuration about the oxygen atom in the trinuclear molecule approaches much more closely to that of a regular tetrahedron.

The  $\text{Cu}_3\text{L}_3\text{OH}(\text{SO}_4)$  cluster also displays magnetic properties which imply substantial Cu-Cu interaction. In fact, its magnetic susceptibility follows the Curie law over the temperature range 105–405°K, with a magnetic moment indicative of one unpaired electron per three copper atoms. It has been proposed that the magnetic interaction implied by these data occurs *via* a pathway involving the bridging hydroxo group. A qualitative molecular orbital model for a four-center delocalized interaction in the  $\text{Cu}_3\text{O}$  tetrahedron has been put forward as consistent with the magnetic data; however, a localized superexchange mechanism, presumably also involving the oxygen atom of the  $\text{OH}^-$  bridge, could not be ruled out.<sup>35</sup> Although our  $\text{OH}^-$  bridge is considerably less symmetric than that in the trinuclear copper cluster compound, the same sort of *qualitative* rationale employed by Beckett, *et al.*, could be used for our system.

The existence of this precedent for magnetic interaction among three  $\text{Cu}^{2+}$  ions through a triply bridging hydroxo group is encouraging, since we have already concluded that the  $\text{OH}^-$  bridge in our basic trifluoroacetate adduct must constitute at least part of the pathway for the observed Cu-Cu interaction. Further speculation on the detailed nature of the magnetic interaction seems unwarranted at this stage.

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**Supplementary Material Available.** A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$4.00 for photocopy or \$2.00 for microfiche, referring to code number JACS-74-3834.