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Synthesis, Crystal Structure, and Magnetic Properties of a Dimeric Quinoline Adduct of Copper(II) Trifluoroacetate

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Abstract: Further synthetic investigations of the copper(II) trifluoroacetate-quinoline system have led to the isolation and characterization of two new products, in addition to the two previously reported. A hygroscopic green crystalline material has been shown by a crystal structure analysis to be the dimeric quinoline adduct $[Cu(O_2CCF_3)_2(quinoline)]_2$. This material hydrolyzes readily to monomeric blue $Cu(O_2CCF_3)_2(quinoline)(H_2O)$. The dimeric complex crystallizes in space group $C\,2/c$ with a = 14.886 (24) Å, b = 16.707 (29) Å, c = 13.694 (23) Å, and β = 111.26 (5) °. Observed and calculated densities are 1.74 (2) and 1.76 g/cm^3, respectively. The structure determination was based upon 1555 independent counter data; anisotropic full-matrix least-squares refinement converged to a conventional R factor of 0.062. The centrosymmetric diquinolinetetra-μ-trifluoroacetato(*O,O'*)-dicopper(II) molecule has the familiar bridged dimeric copper(II) acetate structure with an unusually long Cu-Cu distance of 2.886 (4) Å. Magnetic susceptibility data (85-340°K) conform to the usual dimer equation, with a singlet-triplet energy separation of $2J = -310$ cm^{-1}. The electron paramagnetic resonance spectrum of a polycrystalline sample of the dimer shows a triplet pattern much like that of copper(II) acetate hydrate. The unexpectedly close similarity of the magnetic properties of the acetate and trifluoroacetate adducts forces a reexamination of the hypothesis that the magnitude of metal-metal interaction in these dimers is determined by the strength of the parent carboxylic acid.

A vast number of dimeric copper(II) carboxylate monoadducts, $[Cu(O_2CR)_2L]_2$, have been investigated in an effort to determine the factors influencing the magnitude of the intramolecular magnetic exchange interaction which occurs between the two Cu^{2+} ions in these compounds.[1] One frequently advanced relationship is that between the basicity of the bridging carboxylate anion, as measured by the pK_a of its parent acid, and the magnitude of the exchange coupling constant $2J$.[1,2] Although there is some experimental support for such a correlation, there also exist exceptions[10] to the postulated dependence of $2J$ upon pK_a, and the entire situation must still be regarded as ill-defined. The situation is further complicated by the general disinclination toward formation of the bridged dimeric structure by copper(II) complexes of the stronger carboxylic acids. Thus, the anhydrous copper(II) carboxylates $Cu(O_2CR)_2$ with R = $CHCl_2$, CCl_3, and CF_3 are probably not dimeric[11-13] and these carboxylates tend to form monomeric, magnetically dilute adducts, $Cu(O_2CR)_2L_2$, with most bases.[14-16] For this reason dimeric copper(II) trichloroacetates or trifluoroacetates, which could potentially be important in clarifying the relationship between pK and $2J$, have not been available until very recently.

We have recently shown that the copper(II) trifluoroacetate adduct initially formulated as $Cu(O_2CCF_3)_2(quin)$[15] (where quin = quinoline) is in fact the tetranuclear basic carboxylate $[Cu_2OH(O_2CCF_3)_3(quin)_2]_2$.[17] However, in the course of our synthetic investigations of the copper(II) trifluoroacetate–quinoline system, three new products in addition to the tetranuclear carboxylate and the well-known bis adduct $Cu(O_2CCF_3)_2(quin)_2$[15,16] were isolated. One of these products proves to be the dimeric adduct $[Cu(O_2CCF_3)_2(quin)]_2$; in this paper we report the details of its preparation, crystal structure, and magnetic behavior. Portions of these results have previously been communicated in preliminary form.[18]

Experimental Section

Preparation of the Complex. The violet bisquinoline adduct of Cu(II) trifluoroacetate was heated in an evaporating dish at 80°. The complex eventually became light green in color. Crystals suitable for X-ray study were obtained from the green powder by Soxhlet extraction and recrystallization from hot benzene. The resulting light green crystals were extremely hygroscopic, turning to a light blue powder on exposure to air. C, H, and N analyses of both the green product and the blue decomposition product were performed by Chemalytics, Inc., of Tempe, Ariz. *Anal.* Calcd for (green) $CuC_{13}H_7NO_4F_6$: C, 37.28; H, 1.68; N, 3.34. Found: C, 39.05; H, 1.68; N, 3.44. Calcd for (blue) $CuC_{13}H_9NO_5F_6$: C, 35.91; H, 1.62; N, 3.22. Found: C, 35.63; H, 1.68; N, 2.94. The instability of the green product led to difficulty in obtaining reproducible analytical results and presumably accounts for the poor agreement between observed and calculated analyses for this material.

Collection and Reduction of the X-Ray Data. Precession photographs ($h0l$, $h1l$, $0kl$, $1kl$) displayed monoclinic symmetry with systematic absences (hkl, $h + k \neq 2n$; $h0l$, $l \neq 2n$; $0k0$, $k \neq 2n$) consistent with either space group Cc or $C2/c$. Satisfactory solution and refinement of the structure were achieved in the latter, centrosymmetric space group, which was also indicated by the distribution statistics for normalized structure factors.[19] Lattice parameters were obtained by least-squares refinement of the setting angles of 13 reflections which had been accurately centered on a Picker four-circle X-ray diffractometer. The unit cell constants (21°, λ (Mo $K\alpha_1$) 0.70926 Å) obtained in this manner are a = 14.866 (24) Å, b = 16.707 (29) Å, c = 13.694 (23) Å, and β = 111.26 (5)°. The numbers in parentheses are the standard deviations obtained from least-squares refinement of the setting angles. The density of 1.76 g/cm³ calculated on the basis of eight formula units (four dimeric molecules) per unit cell agrees well with a density of 1.74 (2) g/cm³ obtained by flotation in a CH_2Br_2-CH_2Cl_2 solution.

Intensity data were collected from a green, nearly octahedral crystal of dimensions 0.37 × 0.47 × 0.40 mm. The bounding planes of the crystal were of the $\{\bar{1}11\}$, $\{110\}$, $\{11\bar{1}\}$, and $\{1\bar{1}0\}$ forms. The crystal was mounted under nitrogen on a glass fiber approximately along the crystallographic c axis. It was then sprayed with an acrylic coating because of its instability in air. This proved to be a more effective means of preserving the crystal than mounting in a capillary, though decomposition still occurred over a period of weeks. Narrow-source open-counter ω scans through several reflections displayed an average full width at half-maximum of 0.14°, indicative of an acceptably low mosaic spread. The data were collected by the use of procedures described previously.[20] A takeoff angle of 1.5° was employed. The diffracted beam was filtered through 3.0 mil Nb foil. The counter aperture was 5 × 5 mm and was positioned 30.0 mm from the crystal. The pulse height analyzer was set to admit ~95% of the Mo $K\alpha$ peak. Data were collected by the θ-2θ scan method. A symmetric scan range of ±0.80° from the calculated scattering angle was used. The intensities of all independent reflections with $2\theta \leq 44°$ were collected. The scan rate was 1°/min, and stationary background counts of 20 sec were taken at each end of the scan range. Copper foil attenuators were automatically inserted whenever the count rate exceeded ~10,000 counts/sec; only 11 reflections required attenuation. Four standard reflections, chosen to lie in widely separated regions of reciprocal space, were monitored after every 100 reflections throughout the data collection. The intensity of these standards decreased an average of 30% by the end of the data collection. The decay was linear with time and equivalent for all four standards. The observed intensities were scaled to compensate for the change in intensity of the standards.

Previously described methods were employed in processing the data.[20] The p factor in the expression for the standard deviation of the observed intensities was given the value of 0.05. Of the 1975 independent reflections collected, 1555 were above background by three or more standard deviations.

Solution and Refinement of the Crystal Structure. The coordinates of the single copper atom in the asymmetric unit of space group $C2/c$ were determined from a three-dimensional Patterson map. The positions of the remaining nonhydrogen atoms were determined from Fourier difference maps. Initial refinement of all nonhydrogen atoms with individual isotropic temperature factors converged to discrepancy factors

$$R_1 = \Sigma\big||F_o| - |F_c|\big|/\Sigma F_o = 0.215$$

and

$$R_2 = [\Sigma w(|F_o| - |F_c|)^2/w|F_o|^2]^{1/2} = 0.256$$

based on the 1555 reflections with $F_o \geq 3\sigma(F_o)$. At this point it was noted on a difference Fourier map that there was a great deal of thermal motion and/or disorder of the CF_3 groups. Further refinement employed anisotropic thermal parameters for all nonhydrogen atoms. Because of the large number of parameters involved, the anisotropic refinement was carried out in blocks. The first block included the scale factor, the metal atom, and the trifluoroacetate ligands. The second block was comprised of the scale factor, the Cu atom, and the quinoline ligand. Hydrogen atoms of the quinoline were included as fixed contributions in the refinement. New hydrogen positions were calculated after each pair of cycles. An absorption correction was applied to the observed intensities. Based upon a linear absorption coefficient of 14.52 cm⁻¹, the calculated transmission factors ranged from 0.57 to 0.70. Final anisotropic refinement converged to R_1 = 0.062 and R_2 = 0.087. A final difference map had no peaks greater than 1 e/Å³; the largest of these residual peaks were in the vicinity of the fluorine atoms. The largest parameter shift in the last cycle was $<0.1\sigma$.

In all structure factor calculations, the atomic scattering factors of Cromer and Waber[21] were used for Cu and F. Values for O, N, and C were from ref 22 and those of Stewart, *et al.*,[23] were used for H. The $\Delta f'$ and $\Delta f''$ values of Cromer[24] were employed in correction of the F_c values for anomalous scattering by the copper atoms. The quantity minimized in the least-squares refinement was $\Sigma w(|F_o| - |F_c|)^2$, where $w = 4F_o^2/\sigma^2(F_o^2)$. The final standard deviation of an observation of unit weight was 2.7. Calculation of mean $w(\Delta F)^2$ values as functions of F_o, uncorrected intensity, and Bragg angles revealed no significant trends. Calculation of structure factors for data with $F_o < 3\sigma(F_o)$ showed 33 reflections for which F_c exceeded the 3σ cutoff by as much as three standard deviations.

Final atomic positional and thermal parameters are given in Tables I and II. Bond distances and angles are listed in Tables III and IV, respectively. Principal amplitudes of thermal motion for atoms refined anisotropically are tabulated in Table V. Results of least-squares plane calculations are summarized in Table VI. A table of observed and calculated structure factors is available.[25]

Magnetic Susceptibility Measurements. Magnetic susceptibilities were measured by the Faraday method by use of 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. Measurements were made at a field strength of *ca.* 8000 G on a powdered sample under nitrogen. The calibrant employed was $HgCo(NCS)_4$, the magnetic susceptibility of which was taken as 16.44 × 10⁻⁶ cgs units at 20°. A diamagnetic correction of −169.38 × 10⁻⁶ cgs units was calculated from Pascal's constants. The effective magnetic moment was calculated from the equation

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

where $N\alpha$ was given the value of 60 × 10⁻⁶ cgs units. The observed magnetic susceptibility data were fitted to the usual expression for exchange coupled dimers.[26] In the fitting procedure, all experimentally observed susceptibilities were equally weighted and

Table I. Atomic Positional and Thermal Parameters for $[Cu(O_2CCF_3)_2(C_9H_7N)]_2$[a]

	x	y	z	β_{11}[b]	β_{22}	β_{33}	β_{12}	β_{12}	β_{23}
Cu	0.31705 (6)	0.31575 (5)	0.53459 (7)	59.7 (6)	38.2 (4)	64.3 (7)	−15.9 (4)	21.5 (5)	−3.3 (4)
O1	0.3907 (4)	0.2464 (4)	0.4742 (4)	77 (4)	52 (3)	86 (5)	−10 (3)	33 (4)	−15 (3)
O2	0.2147 (5)	0.3546 (4)	0.5804 (5)	106 (5)	43 (2)	116 (6)	−2 (3)	66 (4)	−3 (3)
O3	0.3635 (5)	0.2505 (4)	0.6651 (4)	77 (4)	70 (3)	64 (4)	−17 (3)	16 (3)	16 (3)
O4	0.2424 (5)	0.3508 (4)	0.3901 (4)	83 (4)	57 (3)	66 (4)	−14 (3)	14 (4)	−1 (3)
C1	0.3636 (7)	0.1826 (6)	0.4318 (7)	70 (6)	55 (5)	72 (6)	−1 (4)	30 (5)	7 (4)
C2	0.4264 (10)	0.1419 (8)	0.3837 (11)	134 (11)	60 (6)	146(12)	−17 (6)	90 (9)	−31 (6)
C3	0.1752 (7)	0.3131 (6)	0.3254 (7)	73 (6)	59 (4)	64 (6)	6 (5)	26 (5)	15 (5)
C4	0.1366 (11)	0.3502 (10)	0.2188 (8)	116 (10)	120 (9)	66 (8)	−53 (8)	9 (8)	16 (7)
F1	0.5110 (7)	0.1714 (5)	0.4057 (8)	141 (7)	121 (5)	310 (13)	−18 (5)	146 (8)	−68 (7)
F2	0.4403 (11)	0.0706 (6)	0.4023 (17)	342 (18)	79 (5)	765 (39)	−25 (7)	435 (24)	−79 (10)
F3	0.3921 (8)	0.1421 (13)	0.2887 (8)	201 (11)	432 (21)	123 (8)	115 (12)	75 (8)	−60 (10)
F4	0.0511 (6)	0.3417 (7)	0.1678 (6)	118 (6)	191 (8)	129 (7)	−28 (6)	−13 (6)	80 (6)
F5	0.1728 (7)	0.4129 (5)	0.2037 (6)	212 (9)	111 (5)	140 (7)	−59 (6)	−7 (6)	63 (5)
F6	0.1661 (14)	0.3023 (9)	0.1550 (8)	432 (25)	210 (11)	124 (9)	59 (13)	125 (12)	58 (8)
N	0.4192 (5)	0.4091 (4)	0.5840 (4)	71 (5)	39 (3)	50 (4)	−15 (3)	28 (4)	−3 (3)
C5	0.5095 (5)	0.3836 (5)	0.6303 (5)	46 (5)	54 (4)	56 (5)	−7 (4)	10 (4)	5 (4)
C6	0.5888 (6)	0.4377 (6)	0.6707 (6)	56 (5)	88 (6)	57 (6)	−18 (5)	14 (4)	0 (5)
C7	0.5702 (8)	0.5189 (5)	0.6604 (6)	101 (8)	50 (4)	69 (6)	−29 (5)	41 (6)	−7 (4)
C8	0.4775 (6)	0.5438 (5)	0.6126 (6)	77 (6)	38 (3)	59 (5)	−20 (4)	33 (4)	−5 (3)
C9	0.4513 (9)	0.6280 (6)	0.6004 (8)	127 (9)	48 (5)	111 (8)	−28 (5)	71 (8)	−13 (5)
C10	0.3624 (10)	0.6515 (6)	0.5539 (9)	121 (9)	44 (4)	160 (12)	0 (6)	82 (9)	4 (6)
C11	0.2880 (8)	0.5958 (6)	0.5164 (9)	107 (8)	47 (5)	146 (10)	8 (5)	73 (7)	9 (5)
C12	0.3061 (6)	0.5164 (5)	0.5261 (7)	67 (6)	42 (4)	105 (7)	−2 (4)	40 (5)	1 (4)
C13	0.4013 (6)	0.4886 (4)	0.5745 (6)	76 (6)	34 (3)	59 (5)	−13 (3)	38 (4)	−7 (3)

[a] Numbers in parentheses in tables and in the text are estimated standard deviations in the least significant figures. [b] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. Anisotropic thermal parameters tabulated are multiplied by 10^4.

Table II. Hydrogen Atom Positional Parameters[a]

Atom	x	y	z
H5	0.5223	0.3247	0.6371
H6	0.6561	0.4173	0.7057
H7	0.6239	0.5586	0.6877
H9	0.5032	0.6692	0.6287
H10	0.3474	0.7100	0.5450
H11	0.2201	0.6150	0.4818
H12	0.2518	0.4774	0.4989

[a] Hydrogen atoms are numbered according to the carbon atom to which they are bound. Coordinates are based upon trigonal geometry about the carbon atoms with C–H = 1.0 Å. All hydrogen atoms were assigned isotropic thermal parameters of 7.0 Å^2.

Table III. Intramolecular Distances, Å

Cu···Cu′[a]	2.886 (4)	C4–F4	1.216 (14)
Cu–N	2.109 (6)	C4–F5	1.230 (13)
Cu–O1	1.970 (6)	C4–F6	1.369 (20)
Cu–O2	1.956 (7)	N–C5	1.330 (9)
Cu–O3	1.990 (6)	N–C13	1.352 (10)
Cu–O4	1.973 (6)	C5–C6	1.428 (11)
C1–O1	1.211 (10)	C6–C7	1.382 (13)
C1–O2′	1.276 (10)	C7–C8	1.360 (12)
C3–O3′	1.239 (10)	C8–C9	1.453 (13)
C3–O4	1.240 (10)	C8–C13	1.406 (10)
C1–C2	1.488 (14)	C9–C10	1.303 (15)
C3–C4	1.495 (14)	C10–C11	1.393 (15)
C2–F1	1.281 (13)	C11–C12	1.351 (13)
C2–F2	1.221 (16)	C12–C13	1.407 (11)
C2–F3	1.213 (15)		

[a] Primes refer to atoms related to those in the crystallographic asymmetric unit by a center of symmetry.

Table IV. Intramolecular Angles (deg)

Cu′–Cu–O1	80.65 (22)	C1–C2–F1	116.1 (10)
Cu′–Cu–O2	80.39 (22)	C1–C2–F2	116.0 (11)
Cu′–Cu–O3	81.45 (20)	C1–C2–F3	112.8 (13)
Cu′–Cu–O4	80.00 (20)	C3–C4–F4	117.7 (11)
Cu′–Cu–N	177.74 (18)	C3–C4–F5	118.7 (10)
O1–Cu–O3	89.5 (3)	C3–C4–F6	106.4 (14)
O1–Cu–O4	87.1 (3)	F1–C2–F2	104.4 (14)
O2–Cu–O3	87.1 (3)	F1–C2–F3	104.3 (13)
O2–Cu–O4	90.2 (3)	F2–C2–F3	101.6 (14)
O1–Cu–O2	161.0 (3)	F4–C4–F5	115.6 (14)
O3–Cu–O4	161.4 (2)	F4–C4–F6	94.3 (13)
N–Cu–O1	97.1 (3)	F5–C4–F6	97.4 (12)
N–Cu–O2	101.8 (3)	C5–N–C13	119.3 (7)
N–Cu–O3	98.1 (3)	N–C5–C6	122.1 (8)
N–Cu–O4	100.4 (3)	C5–C6–C7	118.4 (8)
Cu–O1–C1	125.5 (6)	C6–C7–C8	118.6 (8)
Cu–O2–C1′	125.1 (6)	C7–C8–C13	121.2 (8)
Cu–O3–C3′	122.8 (6)	C7–C8–C9	122.2 (8)
Cu–O4–C3	125.5 (6)	C13–C8–C9	116.6 (9)
Cu–N–C5	113.7 (5)	C8–C9–C10	122.0 (9)
Cu–N–C13	127.0 (5)	C9–C10–C11	120.5 (10)
O1–C1–O2′	128.4 (9)	C10–C11–C12	121.1 (10)
O4–C3–O3′	130.2 (8)	C11–C12–C13	120.1 (8)
O1–C1–C2	117.5 (9)	C12–C13–C8	119.6 (7)
O2′–C1–C2	114.1 (9)	N–C13–C8	120.4 (8)
O3′–C3–C4	115.4 (9)	N–C13–C12	120.0 (7)
O4–C3–C4	114.4 (9)		

the "best" values of g and $2J$ were taken to be those which minimized $\Sigma[\chi_M'(\text{obsd}) - \chi_M'(\text{calcd})]^2$. The magnetic data are given in Table VII and are represented graphically in Figure 1.

Electron Paramagnetic Resonance Measurements. The epr spectrum was taken at room temperature with a Varian E-3 X-band spectrometer on a powdered sample sealed under nitrogen. The instrument was equipped with 100-KHz modulation. The operating frequency was 9.164-GHz. The spectrum shown in Figure 2 was interpreted according to published methods.[27,28]

Description of the Structure

The structure of diquinolinetetra-μ-trifluoroacetato(O,O')-dicopper(II), shown in Figure 3, is of the familiar dimeric copper(II) acetate type. The most remarkable aspect of the structure is the Cu–Cu distance of 2.886 (4) Å, a full 0.272 Å longer than is found in cupric acetate monohydrate.[29,30] Structural changes accompanying this longer Cu–Cu distance include a small increase in the mean Cu–O–C angle to 124.7 (6)°, a significant increase to 129.3 (9)° in the mean O–C–O angle, and a larger Cu-basal plane distance of 0.32 Å. Corresponding parameters in copper(II) acetate hydrate are mean Cu–O–C = 123.1 (3)°, mean O–C–O = 124.8 (4)°, and Cu-basal plane = 0.19 Å.

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

Atom	Shortest	Intermediate	Longest
Cu	0.1928 (14)	0.2307 (13)	0.2748 (13)
O1	0.237 (8)	0.263 (7)	0.302 (7)
O2	0.245 (7)	0.252 (8)	0.341 (8)
O3	0.215 (8)	0.253 (8)	0.352 (8)
O4	0.228 (8)	0.263 (7)	0.325 (8)
C1	0.228 (11)	0.261 (11)	0.284 (12)
C2	0.241 (14)	0.290 (14)	0.406 (14)
C3	0.214 (12)	0.265 (11)	0.300 (12)
C4	0.228 (14)	0.274 (14)	0.478 (17)
F1	0.268 (8)	0.374 (9)	0.551 (12)
F2	0.266 (10)	0.356 (10)	0.836 (21)
F3	0.240 (11)	0.406 (11)	0.821 (20)
F4	0.248 (8)	0.356 (9)	0.588 (12)
F5	0.250 (8)	0.348 (8)	0.590 (12)
F6	0.266 (11)	0.530 (14)	0.672 (19)
N	0.191 (9)	0.210 (8)	0.285 (8)
C5	0.199 (10)	0.227 (10)	0.287 (10)
C6	0.212 (10)	0.235 (11)	0.362 (12)
C7	0.209 (12)	0.232 (11)	0.348 (12)
C8	0.191 (11)	0.212 (10)	0.299 (11)
C9	0.224 (12)	0.261 (12)	0.380 (13)
C10	0.247 (12)	0.284 (12)	0.383 (14)
C11	0.254 (12)	0.269 (12)	0.366 (12)
C12	0.234 (11)	0.249 (11)	0.296 (11)
C13	0.192 (10)	0.203 (11)	0.288 (10)

Table VI. Least-Squares Planes[a]

1. Plane containing: O1, O2, O3, O4
   Equation of plane: $-0.5689X - 0.7674Y - 0.2959Z = -6.9162$
   Distances to plane (Å)

O1	0.002	O4	−0.002
O2	0.002	Cu	−0.321
O3	−0.002		

2. Plane containing: O1, O2′, C1
   Equation of plane: $-0.1385X + 0.4674Y - 0.8731Z = -3.8379$
   Distances to plane

C2	0.057	Cu	0.062

3. Plane containing: O3′, O4, C3
   Equation of plane: $0.8139X - 0.5087Y - 0.2807Z = -3.0220$
   Distances to plane

C4	0.030	Cu	0.099

4. Plane containing: N, C5, C6, C7, C8, C9, C10, C11, C12, C13
   Equation of plane: $0.4670X - 0.0029Y - 0.8843Z = -5.0554$
   Distances to plane

N	0.000	C9	−0.011
C5	−0.002	C10	0.004
C6	−0.004	C11	0.000
C7	0.004	C12	−0.002
C8	0.010	C13	0.002

Dihedral Angles between These Planes

Planes	Angle, deg	Planes	Angle, deg
1-2	91.24	2-3	96.05
1-3	89.41	2-4	45.08
1-4	90.10	3-4	50.97

[a] 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 $A \times B$.

Most other features of the structure are unremarkable. The average Cu-O and C-O distances of 1.972 (6) and 1.241 (10) Å, respectively, fall within the range of values previously reported for analogous complexes.[9] The variation in C-F distances from 1.213 (15) to 1.369 (20) Å is greater than would ordinarily have been expected and is undoubtedly related to an incomplete description of the thermal motion of the CF_3 groups. This problem was not pursued further; clearly one should not attach too much significance to the individual C-F distances. Similar problems have been reported in other trifluoroacetate complexes.[17,31,32] The quinoline ligand is staggered with respect to the planes of the bridging carboxylates, forming dihedral angles of 45.1° with the O1-C1-O2′ plane and 51.0° with the O3′-C3-O4 plane. The mean C-C distance within the quinoline molecule is 1.387 (13) Å. The closest intramolecular contacts between the hydrogen atoms of the quinoline and the carboxylate oxygen atoms are O2···H12 = 2.49 Å and O4···H12 = 2.56 Å. The Cu-N distance is 2.109 (6) Å, toward the short end of the range of analogous distances previously observed.

Table VII. Magnetic Susceptibility Data[a]

T, °K	χ_M' (obsd)	χ_M' (calcd)[b]	μeff
85	178	177	0.28
105	322	311	0.47
125	449	461	0.62
145	588	599	0.78
178	775	771	1.01
213	891	875	1.19
242	918	917	1.29
252	942	923	1.33
277	921	931	1.38
290	924	930	1.42
302	918	927	1.44
322	912	918	1.48
340	903	906	1.51

[a] Observed and calculated susceptibility values listed are molar paramagnetic susceptibilities per copper ion in cgs units × 10^6. [b] These values are the best fit values obtained from the dimer equation with fitting parameters $g = 2.27$ and $2J = 310$ cm^{-1}.

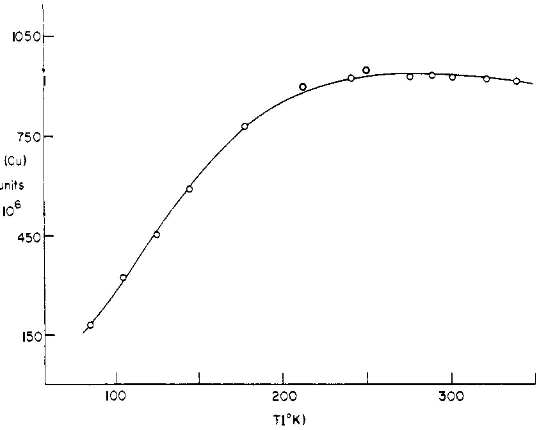

Figure 1. Magnetic susceptibility of $[Cu(O_2CCF_3)_2(quin)]_2$. The solid line is calculated from the dimer equation with best fit parameters $g = 2.27$ and $2J = -310$ cm^{-1}.

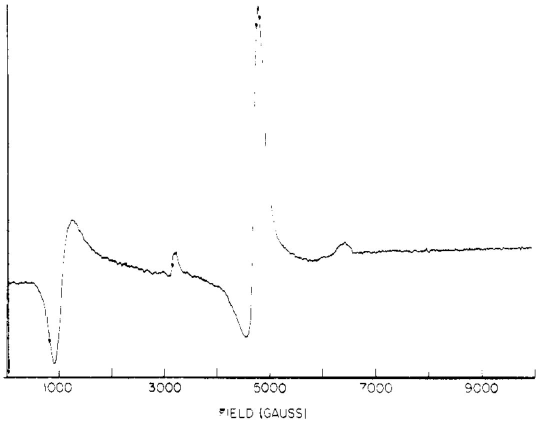

Figure 2. The electron paramagnetic resonance spectrum of a polycrystalline sample of $[Cu(O_2CCF_3)_2(quin)]_2$. See text for experimental conditions and assignment of resonances.

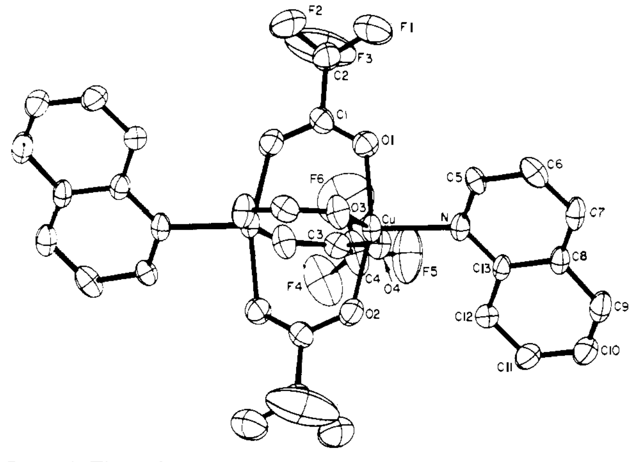

Figure 3. The molecular structure of the quinoline monoadduct of copper(II) trifluoroacetate. Thermal ellipsoids are drawn at the 25% probability level. One CF_3 group is omitted for clarity.

While this compound represents the first definitive example of a dimeric copper(II) trifluoroacetate adduct, similar trifluoroacetate-bridged dimers have been found with other metal ions. The structures of both anhydrous $Mo_2(O_2CCF_3)_4$[32a] and its pyridine adduct[32b] are known; both of these species have very short metal-metal distances (2.090 Å for the anhydrous carboxylate and 2.129 Å for the pyridine adduct) and presumably very strong Mo-Mo bonds. It is interesting to note that in the pyridine adduct the six-membered ring lies nearly in the plane of one pair of bridging carboxylate groups in contrast to the staggered orientation we observe. The cyclopentadienyl vanadium trifluoroacetate dimer $[\pi\text{-}C_5H_5V(O_2CCF_3)_2]_2$ also possesses four bridging trifluoroacetate ligands but in this molecule the metal-metal distance is a very long 3.70 Å.[33] As is evident from the data tabulated in Table VIII, the major change in ligand geometry accompanying the increasing metal-metal distance is an increase in the M-O-C angle from 115.2° in the Mo dimer to 124.7° in our copper complex and to 134° in the cyclopentadienyl vanadium trifluoroacetate. Clearly, the bridging trifluoroacetate group is flexible enough in its steric requirements to enable it to span a considerable range of metal-metal distances.

Discussion

The Cu-Cu distance of 2.886 (4) Å is, by a significant margin, the longest such distance observed in any bridged dimeric copper(II) carboxylate. The next longest Cu-Cu separation of 2.747 (3) Å occurs in the α-picoline adduct of copper(II) chloroacetate.[34] In 11 other neutral dimeric copper(II) carboxylates, this separation ranges from 2.565 to 2.657 Å.[9] It appears that the longer distance we observe is a consequence of the identity of the bridging carboxylate group rather than of the terminal ligand L. This conclusion follows from the fact that the quinoline adduct of copper(II) acetate displays a normal Cu-Cu distance of 2.642 Å.[35] In view of the trends observed in Cu-Cu distance, one is tempted to suggest a correlation between the strength of the parent carboxylic acid and the Cu-Cu separation in these dimers. However, the available data are probably insufficient to firmly establish such a correlation. It is interesting to note that the principal structural change accompanying the longer metal-metal distances is the movement of the Cu^{2+} ion further out of its basal coordination plane.

The magnetic susceptibility behavior of $[Cu(O_2CCF_3)_2(quin)]_2$ is clearly of interest because of its status as the first documented example of a dimeric copper(II) trifluoroacetate adduct and because of the relationship which has been postulated for these dimers between $2J$ and the pK_a of the parent carboxylic acid.[1,2] The best fit of the magnetic data to the usual expression for the molar susceptibility of an isolated pair of interacting ions of spin $\frac{1}{2}$[26] was obtained for $g = 2.27$ and $2J = -310$ cm^{-1}. As is evident from the observed and calculated susceptibility curves shown in Figure 1, the magnetic data in the range 85–340°K are satisfactorily represented by the dimer equation. The magnetic behavior of our trifluoroacetate dimer is thus qualitatively very similar to that of copper(II) acetate monohydrate; quantitatively, our $2J$ value of -310 cm^{-1} is slightly greater in magnitude than that of -284 cm^{-1} found for the acetate adduct.[36] This is contrary to the frequently expressed view that $|2J|$ should decrease as the electron withdrawing properties of R increase.

Table VIII. Structural Comparison of Trifluoroacetate-Bridged Dimers

	$[V(tfa)_2C_5H_5]_2$	$[Cu(tfa)_2(C_9H_7N)]_2$	$[Mo(tfa)_2C_5H_5N]_2$
M–M	3.70 Å	2.886 (4) Å	2.129 (2) Å
M–O	2.05 Å	1.972 (6) Å	2.116 (6) Å
O–C	1.26 Å	1.242 (10) Å	1.26 (1) Å
M–O–C	134°	124.7 (6)°	115.2 (6)°
O–C–O	124°	129.3 (8)°	126.1 (10)°
Ref	33	This work	32b

The electron paramagnetic resonance spectrum of a powdered sample, shown in Figure 2, is also qualitatively much like the epr spectrum of copper(II) acetate hydrate. This similarity immediately suggested assignment of the lines as follows: 1050 G = low field parallel line, 3200 G = monomeric impurity, 4675 G = perpendicular line, 6425 G = high field parallel line.[28] Based upon these assignments, analysis of the spectrum by published methods[27,28] yields $g_{\parallel} = 2.44$, $g_{\perp} = 2.17$, $D = 0.425$ cm^{-1}, and $g = 2.26$. The average g value obtained is high for a copper(II) complex, though it agrees well with the best fit value obtained from the susceptibility data. Confirmation of the assignment of the impurity band was made by opening the sample tube to the air and taking successive epr spectra over a period of time. As the green powder gradually turned blue, the signal at 3200 G increased in intensity while the triplet spectrum decayed and ultimately vanished. This behavior, together with the elemental analysis, identifies the blue decomposition product as monomeric $Cu(O_2CCF_3)_2(quin)(H_2O)$.

From these results we are forced to conclude that the differing base strengths of the acetate and trifluoroacetate anions are not dominant factors in determining the relative magnitudes of the Cu-Cu interaction in dimeric copper(II) complexes of these ligands. At this point it is unclear whether this lack of dependence of $2J$ upon pK_a of the parent acid is a general phenomenon or if the trifluoroacetate complex is merely a special case. Though some apparent trends exist among other copper(II) carboxylate dimers, the number of exceptions to the postulated correlation of $2J$ with pK_a is sufficiently great as to render its validity (or at least its generality) seriously questionable. It should also be noted that the magnetic properties of the quinoline and water monoadducts of copper(II) acetate are similar ($2J = -284$ cm^{-1} for L = H_2O[36] and -320 cm^{-1} for L = quin);[37] this suggests that the quinoline addend has no major effect upon the value of $2J$ in these dimers.

Other conclusions are less surprising. These results reinforce the observation that there is no simple correlation between the Cu-Cu distance and the magnitude of $2J$ in the bridged copper(II) dimers, a point which has previously been made in other contexts.[34,38-40] The mounting evidence for this insensitivity of $2J$ even to fairly large variations in Cu-Cu distance weighs against the importance of direct Cu-Cu interactions in accounting for the magnetic coupling in these systems. Also, the substantial difference in magnetic properties between this adduct and anhydrous copper(II) trifluoroacetate[12] reinforces the view[11-13] that the anhydrous material does not possess the bridged dimeric structure.

Finally, we note that the general difficulty of preparing dimeric copper(II) trifluoroacetate adducts and the strong tendency of this complex to undergo hydrolysis are consistent with the observation that the bridged dimeric structure tends to be destabilized as the strength of the parent carboxylic acid increases. This appears to be a well-established trend and may be rationalized in a number of ways. The great lability of $[Cu(O_2CCF_3)_2(quin)]_2$ to hydrolysis suggests that it could be of interest to investigate its reactions with other ligands in the absence of water. It is conceivable that such reactions could afford a route for preparation of novel bridged dimeric species which are not readily obtainable from the more stable copper(II) acetate dimers.

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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-75-508.

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Synthesis of Structurally Unusual Fluorocarbons by Direct Fluorination

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Abstract: The reaction of elemental fluorine with structurally unusual hydrocarbon starting materials has been carefully controlled so that structurally analogous perfluorocarbons have been successfully obtained. The syntheses by direct fluorination of perfluoroneopentane, perfluorohexamethylethane, perfluoronorbornane, 1-hydroundecafluoronorbornane, perfluorocyclooctane, and monohydropentadecafluorocylcooctane are reported.

New techniques for controlling the reactions of elemental fluorine[2] have recently been discovered which are of significant utility in both inorganic[3-5] and organic[3,6] synthesis. Hydrocarbons, hydrocarbon polymers,[7] and other hydrocarbon derivations with functional groups, particularly those containing oxygen,[8] have been previously studied in this laboratory. The synthesis of structurally unusual (see Figure 1) fluorocarbons in our laboratory was undertaken because the delicate structures were a challenge to the technique and because many of the perfluorocarbons prepared are also of interest. This task has led to the development of new techniques and apparatus[3,8] to overcome difficulties as-

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