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Contribution from the Department of Chemistry, Case Western Reserve University,
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Structure and Electron Paramagnetic Resonance Spectrum of the Product of the Reaction of Aqueous Pyridine with Copper(II) Hexafluoroacetylacetonate. Tetrakis(pyridine)bis(trifluoroacetato)copper(II)

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Relationships between structure and EPR spectroscopic parameters for copper(II) coordination are of interest due to the diversity of coordination geometries found with this ion. Often EPR parameters are the only available spectroscopic information concerning the ion, especially in proteins. Tetragonal CuN_4O_2 coordination in the title compound for a copper-doped zinc sample produces high $g_{\parallel}$ (2.288) and $A_{\parallel}$ (169×10^{-4} cm^{-1}) values. The sample is obtained by decomposition of copper(II) and zinc(II) hexafluoroacetylacetonate complexes in aqueous pyridine. Single-crystal X-ray analysis was used to identify the product as tetrakis(pyridine)bis(trifluoroacetato)copper(II), $Cu(py)_4(CF_3CO_2)_2$, a compound first encountered as a byproduct during the synthesis of copper(II)-doped $Zn(F_6acac)_2(py)_2$ and subsequently prepared by reaction of pyridine with copper(II) trifluoroacetate. The title compound crystallizes in the triclinic space group $P\bar{1}$ with $a = 9.528$ (6) Å, $b = 9.218$ (5) Å, $c = 18.471$ (10) Å, $\alpha = 104.57$ (5)°, $\beta = 98.50$ (6)°, and $\gamma = 118.65$ (4)°. Least-squares refinement of 3126 reflections resulted in a final conventional R factor of 0.067. The molecule contains a tetragonally elongated CuN_4O_2 geometry with an average Cu–N bond distance of 2.046 (6) Å and an average Cu–O bond distance of 2.367 (7) Å. The four pyridine molecules occupy the equatorial positions, and the two monodentate trifluoroacetate ligands occupy the axial positions. The tetragonality parameter T is larger (0.86) than for any CuN_4O_2 complex previously reported.

Introduction

Systematic studies of the stereochemistry of copper(II) complexes have been pursued by Hathaway and co-workers[1] and others[2]. The copper(II) ion has an [Ar]3d^9 electron configuration which leads to a Jahn–Teller electronic degeneracy in complexes of high symmetry.[3] Bersuker[2a] has attempted to systematize the stereochemical features observed in copper(II) complexes containing CuO_6, CuN_6, and CuN_4O_2 coordination. The metal–ligand equatorial, R_S, and axial, R_L, distances appear to be correlated,[4] and the tetragonality parameter $T = R_S/R_L$ for CuN_4O_2 geometries is less than 0.81 for all complexes heretofore reported.[1,2] Interest in copper(II) coordination stems, in part, from the prevalence of this ion in several metalloenzyme systems[5,6a] and industrially important catalytic reactions.[6b]

Our own group has presented results of magnetic and crystallographic studies[7] wherein certain complexes with a CuO_4N_2 coordination geometry are fluxional in the solid state at temperatures down to 70 K and below. These studies involved complexes containing the 1,1,1,5,5,5-hexafluoro-2,4-pentanedionato ligand (F_6acac) and pyridine (py). During attempts to synthesize copper-doped $Zn(F_6acac)_2(py)_2$ with excess pyridine, blue crystals were isolated which appeared from IR studies to contain uncoordinated carbonyl[8] and from electron paramagnetic resonance (EPR) studies, four equivalent nitrogen atoms. A monodentate F_6acac coordination was postulated.[9] Structural studies[10] revealed that the correct stoichiometry for this material is $Cu(py)_4(O_2CCF_3)_2$. The hexafluoroacetylacetonate ligand apparently hydrolyzes with C–C bond rupture under the conditions of the synthesis, a somewhat surprising result since anhydrous hexafluoroacetylacetonate is usually dried (it is a dihydrate when moist) by distillation from sulfuric acid. Subsequent studies by one of us[10b] (J.P.S.) have shown that the hydrolysis to trifluoroacetate is catalyzed by both Cu(II) and Zn(II).

Experimental Section

Synthesis. A pyridine solution of $Cu(F_6acac)_2$ in contact with the atmosphere for several weeks produces blue crystals of $Cu(py)_4(CF_3CO_2)_2$ along with some green crystals of $Cu(F_6acac)_2(py)_2$.

Upon addition of water to a pyridine solution of $Cu(F_6acac)_2$, a blue phase is produced which separates from a green phase. When the blue solution is mixed with an equal amount of benzene, blue crystals of $Cu(py)_4(CF_3CO_2)_2$ are obtained upon slow evaporation in air.

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Table I. Electron Spin Resonance Data for $Cu(py)_4(CF_3CO_2)_2$

compd	$g_{\|}$	$10^4A_{\|}$, cm^{-1}	$g_{\perp}$	$A^N_{\|}$, G	$A^N_{\perp}$, G
powder sample of $Cu:Zn(py)_4$-$(CF_3CO_2)_2$	2.288	169	2.051	9	13
glass sample of $Cu(py)_4$-$(CF_3CO_2)_2$	2.281	169.2	2.054	...	...

Table II. Summary of Crystal Data for $Cu(py)_4(CF_3CO_2)_2$

molecular formula	$Cu(C_5H_5N)_4(F_3CO_2)_2$
fw	601.944
d_{calcd}, g/cm^3	1.529
d_{obsd}, g/cm^3	1.51 (3)
Z	2
μ, cm^{-1}	9.57
λ(Mo Kα), Å	0.710 69
crystal dimensions, mm^3	0.12 × 0.2 × 0.17
systematic absences	no conditions
space group	C_i^1-$P\bar{1}$ (No. 2), triclinic
cell constants[a]	
a, Å	9.528 (6)
b, Å	9.218 (5)
c, Å	18.471 (10)
α, deg	104.57 (5)
β, deg	98.50 (6)
γ, deg	118.65 (4)
V, Å^3	1307.24 (144)
$F(000)$	606

[a] At 25 °C ambient temperature; least-squares fit of 15 reflections; $2\theta_{av} = 15.82°$.

Table III. Summary of Final Refinement for $Cu(py)_4(CF_3CO_2)_2$

data used	$I/\sigma(I) \geqslant 3.0$
no. of reflections (not corrected for absorption)	3126
no. of varied parameters (nonhydrogen) per cycle	247
(no. of reflections)/(no. of varied parameters)	12.7
final R $[R_1 = \Sigma \|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|]$	0.067
final R_w $[R_w = \{\Sigma w(\|F_o\| - \|F_c\|)^2/\Sigma w\|F_o\|^2\}^{1/2}$	0.076
final weighting scheme	$w_i = 1/\sigma_i^2$

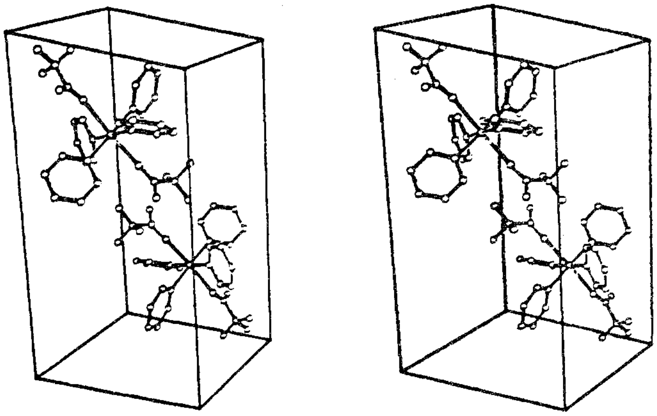

Figure 1. Stereoscopic view of the unit cell of $Cu(py)_4(CF_3CO_2)_2$.

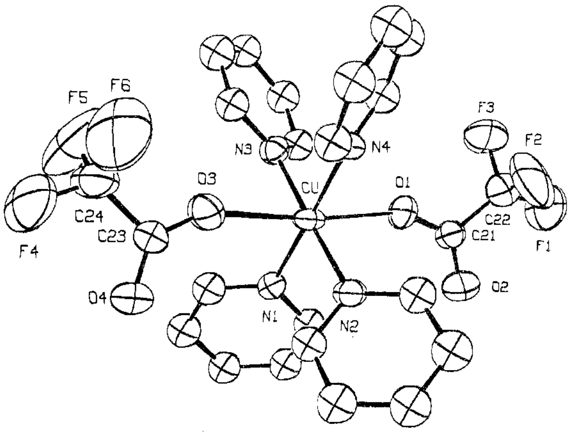

Figure 2. ORTEP thermal ellipsoid projected view (50% probability) of the $Cu(py)_4(CF_3CO_2)_2$ molecule.

Copper trifluoroacetate and pyridine in a 1:4 ratio are dissolved in ether. The solution is cooled to 0 °C, from which blue crystals precipitate. The melting point of $Cu(py)_4(CF_3CO_2)_2$ is 116–117 °C. While the compound loses pyridine when exposed to the open air, it is stable under a pyridine atmosphere.

$Cu:Zn(py)_4(CF_3CO_2)_2$. To a pyridine solution of $Cu(F_6acac)_2$ and $Zn(F_6acac)_2$ ([Cu]:[Zn] = 1:20) is added excess water. Pale blue crystals, mp 97–98 °C, are obtained after slow evaporation.

Physical Measurements. EPR spectra of the Cu-doped (~5%) Zn complex as a powder and the pure copper complex as a glass (CH_3Cl/toluene, 50:50) were measured with a Varian Model E-3 X-band spectrometer at 133 K. The data are presented in Table I. Diphenylpicrylhydrazyl, DPPH, was used as g marker.

The visible and far-IR absorption spectra in the 350–1300-nm region were obtained with a Cary 14 spectrometer. Spectrograde pyridine and chloroform were used as solvents without purification.

IR spectra from 4000 to 300 cm^{-1} were taken with Beckman IR-10 and Perkin-Elmer 257 spectrophotometers. Samples were pressed into KBr disks.

Crystallographic Parameters. Crystals suitable for the structure determination were grown from a benzene–pyridine solution. They were thin plates which had to be cut in order to be sealed in a quartz capillary. The crystal used for the actual structure determination had the approximate dimensions 0.12 × 0.2 × 0.17 mm. It was found to belong to the triclinic space group $P\bar{1}$-C_i^1. Lattice parameters were deduced (at an ambient temperature of 25 °C) from the angular settings of 15 well-centered reflections ($2\theta_{av} = 15.8°$) by using graphite-crystal-monochromated Mo Kα radiation. A listing of crystal data is given in Table II. A total of 4881 reflections (hkl, $hk\bar{l}$, $h\bar{k}l$, $h\bar{k}\bar{l}$ with $2\theta \leq 50°$) were collected on a Syntex $P2_1$ diffractometer with three standard reflections monitored every 50 reflections. The number of reduced data which had $I/\sigma(I) > 3.0$ was 3126. Absorption corrections were deemed unnecessary (μ = 9.5 cm^{-1}).

Solution and Refinement. Both direct methods (MULTAN) and Patterson syntheses revealed the same Cu atom positions along with a number of false peaks. Refinement with the Cu atom positions alone gave a residual R (Table III) of 0.45 for 891 data. Several trial-and-error Fourier syntheses produced all nonhydrogen atom positions. Full-matrix isotropic refinement of 39 atoms produced an R of 0.10 for 1537 data. At this stage, it was determined that the correct stoichiometry was $Cu(py)_4(CF_3CO_2)_2$. Several cycles of least-squares refinement with 19 atoms (1 Cu, 4 N, 6 F, 4 O, 4 C) anisotropic and 20 atoms (20 C) isotropic resulted in a final conventional R factor of 0.067 for the full set of 3126 data. A summary of the final refinement is given in Table III. Final coordinates are presented in Table IV, and significant bond lengths and angles are given in Tables V and VI, respectively. Computer programs used in the refinement have been described elsewhere.[10a] Neutral atomic scattering factors were taken from Cromer and Waber.[11] Thermal parameters and structure factors are available as supplementary material.

Results and Discussion

Description of the Structure. The unit cell of $Cu(py)_4$-$(CF_3CO_2)_2$ (see Figure 1) contains two molecules that are mirror images of each other. A single molecule is shown in Figure 2. The structure is a classic example of a tetragonally elongated octahedral Cu(II) complex. Even though the overall crystallographic symmetry for each molecule is only C_1 with all atoms in general positions, the CuN_4O_2 coordination comes very close to D_{4h} symmetry. Four pyridine molecules occupy the equatorial positions. The axial positions are taken by oxygen atoms of two trifluoroacetate ligands which are clearly monodentate, with uncoordinated Cu–O distances of 4.152 (9) and 4.154 (9) Å. Cu–O bond distances are 2.365 (7) and 2.369 (7) Å, whereas the Cu–N bonds vary between 2.043 (7)

Table IV. Positional Parameters and Estimated Standard Deviations for $Cu(py)_4(CF_3CO_2)_2$

atom	*x*	*y*	*z*
Cu	0.1943 (1)	0.5577 (1)	0.2575 (1)
O(1)	0.2801 (6)	0.4513 (6)	0.3477 (3)
C(21)	0.2475 (8)	0.3427 (9)	0.3805 (4)
O(2)	0.1281 (7)	0.2697 (8)	0.4037 (4)
C(22)	0.3756 (11)	0.2914 (12)	0.3917 (6)
F(1)	0.3664 (8)	0.2056 (9)	0.4386 (5)
F(2)	0.3500 (9)	0.1747 (10)	0.3232 (5)
F(3)	0.5317 (6)	0.4233 (8)	0.4130 (5)
O(3)	0.1424 (6)	0.6787 (7)	0.1654 (3)
C(23)	0.0543 (9)	0.7099 (9)	0.1241 (4)
O(4)	−0.0927 (7)	0.6630 (8)	0.1128 (4)
C(24)	0.1499 (11)	0.8344 (6)	0.0842 (6)
F(4)	0.0652 (8)	0.8718 (10)	0.0390 (4)
F(5)	0.2737 (10)	0.9889 (11)	0.1336 (5)
F(6)	0.2234 (15)	0.7815 (16)	0.0438 (7)
N(1)	0.0681 (6)	0.6306 (7)	0.3233 (3)
C(1)	−0.0037 (8)	0.5402 (9)	0.3682 (4)
C(2)	−0.0888 (9)	0.5895 (9)	0.4142 (4)
C(3)	−0.1017 (9)	0.7330 (9)	0.4142 (4)
C(4)	−0.0280 (9)	0.8272 (10)	0.3683 (4)
C(5)	0.0563 (9)	0.7698 (9)	0.3221 (4)
N(2)	−0.0201 (6)	0.3112 (7)	0.1950 (3)
C(6)	−0.0234 (9)	0.1616 (10)	0.1905 (4)
C(7)	−0.1713 (10)	−0.0100 (10)	0.1512 (5)
C(8)	−0.3158 (10)	−0.0221 (10)	0.1146 (5)
C(9)	−0.3127 (9)	0.1318 (10)	0.1182 (5)
C(10)	−0.1621 (9)	0.2978 (9)	0.1583 (4)
N(3)	−0.4122 (6)	0.7998 (7)	0.3204 (3)
C(11)	0.4877 (9)	0.8448 (9)	0.3970 (4)
C(12)	0.6491 (9)	0.9956 (10)	0.4388 (4)
C(13)	0.7359 (9)	1.1020 (9)	0.3995 (4)
C(14)	0.6575 (10)	1.0596 (10)	0.3213 (5)
C(15)	0.4939 (9)	0.9073 (9)	0.2833 (4)
N(4)	0.3238 (6)	0.4911 (7)	0.1914 (3)
C(16)	0.2674 (9)	0.4357 (9)	0.1126 (4)
C(17)	0.3600 (10)	0.4057 (10)	0.0652 (5)
C(18)	0.5158 (10)	0.4357 (10)	0.1006 (5)
C(19)	0.5722 (10)	0.4906 (10)	0.1832 (5)
C(20)	0.4712 (9)	0.5162 (9)	0.2261 (4)

Table V. Significant Interatomic Distances for $Cu(py)_4(CF_3CO_2)_2$ (Å)

Cu–O(1)	2.365 (7)	C(2)–C(3)	1.387 (14)
Cu–O(3)	2.369 (7)	C(3)–C(4)	1.388 (12)
Cu–N(1)	2.043 (7)	C(4)–C(5)	1.426 (13)
Cu–N(2)	2.050 (4)	N(2)–C(6)	1.345 (12)
Cu–N(3)	2.044 (4)	N(2)–C(10)	1.345 (11)
Cu–N(4)	2.046 (7)	C(6)–C(7)	1.413 (9)
O(1)–C(21)	1.237 (11)	C(7)–C(8)	1.380 (14)
O(3)–C(23)	1.234 (11)	C(8)–C(9)	1.389 (15)
C(21)–O(2)	1.219 (10)	C(9)–C(10)	1.399 (8)
C(23)–O(4)	1.216 (10)	N(3)–C(11)	1.344 (9)
C(21)–C(22)	1.511 (16)	N(3)–C(15)	1.349 (10)
C(23)–C(24)	1.521 (14)	C(11)–C(12)	1.397 (8)
C(22)–F(1)	1.298 (15)	C(12)–C(13)	1.389 (12)
C(22)–F(2)	1.337 (13)	C(13)–C(14)	1.384 (11)
C(22)–F(3)	1.303 (9)	C(14)–C(15)	1.405 (8)
C(24)–F(4)	1.296 (16)	N(4)–C(16)	1.341 (9)
C(24)–F(5)	1.292 (10)	N(4)–C(20)	1.336 (11)
C(24)–F(6)	1.257 (20)	C(16)–C(17)	1.401 (13)
N(1)–C(1)	1.348 (10)	C(17)–C(18)	1.391 (13)
N(1)–C(5)	1.347 (12)	C(18)–C(19)	1.409 (11)
C(1)–C(2)	1.396 (13)	C(19)–C(20)	1.399 (13)
	Bite Distances		
O(1)–O(2)	2.228 (9)	O(3)–O(4)	2.226 (10)
	Nonbonded Distances		
Cu–O(2)	4.152 (9)	Cu–O(4)	4.154 (9)

Table VI. Important Interatomic Angles in $Cu(py)_4(CF_3CO_2)_2$ (deg)

O(1)–Cu–N(1)	93.3 (3)	C(23)–C(24)–F(4)	117.1 (8)
–N(2)	91.4 (3)	–F(5)	113.1 (8)
–N(3)	87.1 (3)	–F(6)	113.3 (9)
–N(4)	87.7 (3)	F(4)–C(24)–F(5)	103.5 (7)
–O(3)	172.9 (3)	–F(6)	106.2 (8)
N(1)–Cu–N(2)	91.0 (3)	F(5)–C(24)–F(6)	102.0 (8)
–N(3)	90.1 (3)	N(1)–C(1)–C(2)	121.2 (6)
–N(4)	178.5 (3)	C(1)–C(2)–C(3)	120.2 (6)
–O(3)	92.2 (3)	C(2)–C(3)–C(4)	119.1 (7)
N(2)–Cu–N(3)	178.2 (3)	C(3)–C(4)–C(5)	118.2 (7)
–N(4)	90.1 (3)	C(4)–C(5)–N(1)	121.7 (6)
–O(3)	93.0 (3)	C(5)–N(1)–C(1)	119.6 (5)
N(3)–Cu–N(4)	88.8 (3)	N(2)–C(6)–C(7)	122.7 (6)
–O(3)	88.4 (3)	C(6)–C(7)–C(8)	117.8 (7)
N(4)–Cu–O(3)	86.8 (3)	C(7)–C(8)–C(9)	118.8 (7)
O(1)–C(21)–O(2)	130.2 (6)	C(8)–C(9)–C(10)	119.6 (6)
–C(22)	114.0 (6)	C(9)–C(10)–N(2)	121.1 (6)
O(2)–C(21)–C(22)	115.8 (6)	C(10)–N(2)–C(6)	119.1 (5)
O(3)–C(23)–O(4)	130.6 (6)	N(3)–C(11)–C(12)	122.6 (6)
–C(24)	113.6 (6)	C(11)–C(12)–C(13)	118.8 (7)
O(4)–C(23)–C(24)	115.7 (6)	C(12)–C(13)–C(14)	119.1 (7)
C(21)–C(22)–F(1)	116.6 (7)	C(13)–C(14)–C(15)	119.0 (7)
–F(2)	109.2 (7)	C(14)–C(15)–N(3)	121.9 (6)
–F(3)	114.4 (7)		
F(1)–C(22)–F(2)	102.1 (7)		
F(1)–C(22)–F(3)	107.5 (7)		
F(2)–C(22)–F(3)	105.8 (7)		
C(15)–N(3)–C(11)	118.5 (6)	C(18)–C(19)–C(20)	118.7 (7)
N(4)–C(16)–C(17)	121.9 (6)	C(19)–C(20)–N(4)	122.2 (6)
C(16)–C(17)–C(18)	119.3 (7)	C(20)–N(4)–C(16)	119.6 (5)
C(17)–C(18)–C(19)	118.3 (7)		

and 2.050 (4) Å, with an average value of 2.046 Å.

While the observed Cu–N bond distances are about normal, the observed Cu–O bond distances are shorter than expected for tetragonally elongated CuN_4O_2 complexes, resulting in a comparatively small tetragonal elongation. The tetragonality parameter[1,12] *T* has a value of 0.86. That is very much closer to unity than the values of 0.72, 0.78, 0.78, 0.80, and 0.81 reported for the related CuN_4O_2 complexes $Cu(dimen)_2(F_6acac)_2$,[8] $Cu(en)_2(NO_3)_2$,[13] $Cu(en)_2(ClO_4)_2$,[14] $Cu(dps)_2(H_2O)_2(ClO_4)_2$,[15] and $Cu(tn)_2(NO_3)_2$.[16]

A somewhat unexpected structural result is the small difference between coordinated and uncoordinated C–O bond distances in the monodentate trifluoroacetate ligands. Bond distances between carbon atoms and oxygen atoms coordinated to Cu are 1.237 (11) and 1.234 (11) Å, whereas C–O bond distances involving uncoordinated oxygen atoms (1.219 (10) and 1.216 (10) Å) are shorter by less than 0.02 Å. This result contrasts with film data reported for monodentate acetate ions in lithium acetate dihydrate,[17] where the difference between coordinated (1.33 Å) and uncoordinated C–O bonds (1.22 Å) was found to be 0.11 Å. Monodentate,[17] bidentate,[18] and bridge[19] coordination is known for acetate ligands.

The relative shortness of the axial Cu–O bonds and the comparatively small tetragonal elongation of the CuN_4O_2 octahedron indicate that the axial Cu–O bonds in the title compound are stronger than axial bonds in related CuN_4O_2 complexes.[8,13–16] The small difference between coordinated and uncoordinated C–O bond distances, however, suggests that the trifluoroacetate binds rather ionically to the $Cu(py)_4^{2+}$ cation.

The remaining structural features of the title compound appear to be normal. All pyridine rings and the trifluoroacetate anions (excluding the F atoms) are planar within the limits of error. C–N and C–C bond distances within the pyridine rings are normal as are the C–C bonds in the trifluoroacetate anions. Average values are 1.345, 1.396, and 1.516 Å, respectively. Variations in the C–F bond distances (1.257–1.337 Å) should not be considered statistically significant. The large anisotropic temperature factors displayed by the fluorine atoms (Table A1, supplementary material) and the direction of this anisotropy (Figure 2) suggest some rotational disorder in the CF_3 group.[20]

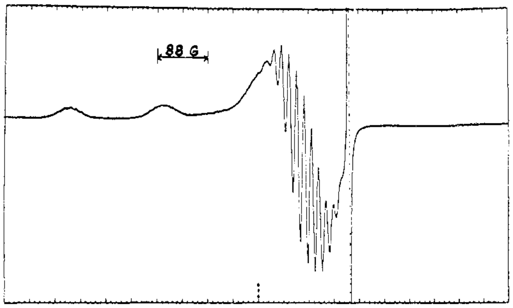

Figure 3. EPR powder spectrum for Cu:Zn(py)$_4$(CF$_3$CO$_2$)$_2$ (1:50::[Cu]:[Zn]) at −180 °C (modulation amplitude 0.8 G, microwave frequency 9.168 GHz.

Synthesis and Spectroscopic Studies. Hexafluoroacetylacetone has been made by condensing ethyl trifluoroacetate with trifluoroacetone in the presence of sodium.[21] The decomposition of the ligand under mild conditions has not been reported previously. We have found this reaction to occur with water, pyridine, and copper(II) or zinc(II), although the specific role of metal ion is not clear. It is well-known that OH$^-$ reacts with fluoroketones.[22]

The blue crystals obtained from pyridine solutions of Cu(F$_6$acac)$_2$ or Cu:Zn(F$_6$acac)$_2$ in contact with the atmosphere for several weeks show a strong C–O bond at 1675 cm^{-1} with a shoulder at 1690 cm^{-1}. This suggested to us that the diketone ligand was no longer chelated to the metal. The X-ray structure subsequently confirmed the fact that the C–C bond had ruptured and that the carbonyl-containing ligand was the trifluoroacetate anion.

The electronic spectrum of Cu(py)$_4$(CF$_3$CO$_2$)$_2$ consists of one very broad peak in the visible region. The band position in pyridine is different from the position in chloroform, 645 nm (15 500 cm^{-1}) and 670 nm (14 000 cm^{-1}), respectively. The difference presumably arises from partial dissociation of the Cu(py)$_4$(CF$_3$CO$_2$)$_2$ in solution. The effective solid-state symmetry about the copper ion in Cu(py)$_4$(CF$_3$CO$_2$)$_2$ is D_{4h}. This implies that three transitions ($^2B_{1g} \rightarrow {}^2A_{1g}$, $^2B_{1g} \rightarrow {}^2E_g$, $^2B_{1g} \rightarrow {}^2B_{2g}$) are contained in the broad band, as often observed in tetragonally distorted octahedral complexes[23,24] of copper(II).

The EPR spectrum of Cu:Zn(py)$_4$(CF$_3$CO$_2$)$_2$ is presented in Figure 3. Nitrogen hyperfine structure in the perpendicular band shows nine lines equally spaced at 13 G. These lines are produced by the four equivalent nitrogen atoms (total spin $I = 4$) which are coordinated on the equatorial plane, giving rise to the $2I + 1 = 9$ transitions. The $g_\parallel$ (2.288), $g_\perp$ (2.051), and $A_\parallel$ (169 × 10^{-4} cm^{-1}) tensors fall within the range expected for tetragonal CuN$_4$O$_2$ coordination. The nitrogen superhyperfine component $A^N{}_\parallel$ is 9 G. If the Cu(py)$_4{}^{2+}$ cation had contained a pseudotetrahedral coordination, $A_\parallel$ would be substantially reduced[24,15] from 169 × 10^{-4} cm^{-1}. Spectra obtained in a frozen chloroform/toluene glass suggest that the tetragonal coordination is maintained in solution.

Flattened pseudotetrahedral Cu^{II}N$_4$ coordination is found[25] in Cu(Cu^{II})(CH$_3$CN)$_4$(ClO$_4$) and CuHg(SCN)$_4$, where g is 2.32–2.44 and $A_\parallel$ is (80–92) × 10^{-4} cm^{-1}. Attanasio and Tomlinson[26] recently reported that bis[4-phenyl-2-(phenylimino)pent-3-enato-*N*,*N*′]copper(II), a CuN$_4$ complex, has features similar to the most important spectral features of the "blue proteins", with $g_\parallel = 2.218$, $g_\perp = 2.070$, and $A_{zz} = 107 \times 10^{-4}$ cm^{-1}. However, in the proteins,[5] $A_\parallel$ values are closer to 60 × 10^{-4} cm^{-1}. As will be reported elsewhere,[15] a change in the dihedral angle between NCuN planes toward 90° brings $A_\parallel$ down to ~80 × 10^{-4} cm^{-1} as a minimum value. Sulfur atom coordination also generally reduces[28] $g_\parallel$. Furthermore, the A_{max} value is reduced[7] in trigonal-bipyramidal CuO$_5$ coordination to ~63 × 10^{-4} cm^{-1} with $g_{max} \sim 2.26$. With square-pyramidal, CuO$_4$P, five-coordination,[27] however, $A_\parallel$ is large at ~140 × 10^{-4} cm^{-1}. Thus, we suggest that both pseudotetrahedral four-coordination with soft ligand atoms such as sulfur and distorted trigonal-bipyramidal five-coordination with O (or N) ligand atom coordination can approximate the EPR parameters of the "blue proteins" but that neither "tetrahedral" CuO$_x$N$_{4-x}$ nor "square-pyramidal" CuO$_x$N$_{4-x}$S (x = 1–4) coordination will match the EPR results for the protein.

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Registry No. Cu(py)$_4$(CF$_3$CO$_2$)$_2$, 23852-16-6; Zn(py)$_4$(CF$_3$CO$_2$)$_2$, 71697-20-6; Cu(F$_6$acac)$_2$, 14781-45-4; Zn(F$_6$acac)$_2$, 14949-70-3.

Supplementary Material Available: A listing of anisotropic thermal parameters is contained in Table AI and structure factor amplitudes are given in Table AII (15 pages). Ordering information is given on any current masthead page.

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