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Crystal and Molecular Structure of Bis(6,6'-dimethyl-2,2'-bipyridyl)copper(I) Tetrafluoroborate

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The crystal data for the title compound are space group $P2_1/c$, $Z = 4$, $a = 12.147$ (4) Å, $b = 21.984$ (7) Å, $c = 9.018$ (5) Å, $\beta = 95.326$ (5)°, $V = 2398.1$ Å³, and $R = 6.9\%$ for 1771 reflections. The anions are uncoordinated and the copper(I) environment (CuN_4) is pseudotetrahedral with a dihedral angle of 80.9° between the planes defined by the copper center and each set of bipyridyl nitrogens. The deviation from tetrahedral symmetry about copper is therefore larger than has sometimes been assumed. Attempts to measure the EPR spectrum of Cu(II) centers in the lattice after γ irradiating the Cu(I) system failed. Possible reasons for the failure are discussed. Isolating a salt of the Cu(I) complex and then extracting the ligand from a solution of the complex provide a method of separating the ligand from the organic mixture that results from the ligand synthesis.

Introduction

Distorted tetrahedral metal binding sites have been found in a number of copper-containing proteins. In the two "blue" proteins plastocyanin¹ and azurin² the sites involve two imine nitrogens from histidine residues, a thioether sulfur from a methionine residue, and a thiolate sulfur from a cysteine residue. In superoxide dismutase, four imine nitrogens from histidines form the donor set.³ Stimulated by our interest in copper proteins⁴ and in photoinduced electron-transfer reactions of copper(I) complexes,^{5,6} we have been interested in determining the structure of copper complexes of sterically demanding ligands which might favor a tetrahedral environment about the metal irrespective of the oxidation state. Substituted derivatives of 2,2'-bipyridine and 1,10-phenanthroline are of interest in this regard since even complexes of the type $\text{M}(\text{bpy})_2^{n+}$ and $\text{M}(\text{phen})_2^{n+}$ are unable to adopt a square-planar configuration because of steric interactions between hydrogen atoms α to the nitrogens.⁷ Complexes of copper(II) with the unsubstituted ligands are generally found to be five-⁸⁻¹⁶ or six-coordinate;¹⁷⁻¹⁹ it has been suggested, however, that $[\text{Cu}(\text{dmp})_2](\text{ClO}_4)_2$ ($\text{dmp} = 2,9$ -dimethyl-1,10-phenanthroline)²⁰ and $[\text{Cu}(\text{tmbp})_2](\text{ClO}_4)_2$

Table I. Crystal Data for $\text{Cu}(\text{dmbp})_2\text{BF}_4^a$

$a = 12.147$ (4) Å	mol wt = 518.9
$b = 21.984$ (7) Å	$\rho_{\text{calcd}} = 1.44$ g cm ⁻³
$c = 9.018$ (5) Å	$\rho_{\text{measd}} = 1.42$ g cm ⁻³ by flotation in
$\beta = 95.326$ (5)°	$\text{CCl}_4/\text{benzene}$
$V = 2398.1$ Å ³	$Z = 4$
	$\lambda(\text{Mo K}\alpha) = 0.71069$ Å

^a Space group $P2_1/C$ (monoclinic).

($\text{tmbp} = 4,4',6,6'$ -tetramethyl-2,2'-bipyridine)²¹ may exhibit pseudotetrahedral geometries, although direct structural evidence is lacking. The analogous copper(I) complexes with phenanthroline, bipyridine, and their substituted derivatives are often assumed to have nearly regular tetrahedral geometries,²² but until now almost no direct structural information has been available. Here we report the crystal and molecular structure of bis(6,6'-dimethyl-2,2'-bipyridine)copper(I) tetrafluoroborate, $[\text{Cu}(\text{dmbp})_2]\text{BF}_4$, which represents the first structural report of a bis(bipyridine) complex of copper(I). In contrast to what is often assumed,²² we find that the complex exhibits an appreciably distorted tetrahedral geometry, at least in the solid state. During the course of this work the structure of the related phenanthroline complex $[\text{Cu}(\text{dmp})_2]\text{NO}_3$ was reported.²³

Experimental Section

The ligand dmbp was obtained in an impure form by the treatment of α -picoline with W7-J Raney nickel catalyst as described in the literature.²⁴ The title compound was prepared by dissolving the impure ligand in a methanol-water mixture (1:1) and adding $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ followed by excess NaBF_4 . Reduction with a slight excess of ascorbate and concentration by rotary evaporation gave deep red crystals of the complex. A crystal suitable for structure determination was obtained by slow evaporation of an ethanol solution of the complex.

Electron spin resonance spectra were obtained by using a Varian Associates E-109 spectrometer. The γ -irradiation experiments were performed at liquid-nitrogen temperature by using a ⁶⁰Co source (~ 7500 Ci).

If an alcohol/water solution of the complex was oxidized and ethylene diamine added, the ligand could be extracted from the (basic) solution into a volatile organic solvent. Evaporation of solvent and

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Table II. Final Positional and Thermal Parameters for Nonhydrogen Atoms

atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	0.20587 (11)	0.12507 (6)	0.09428 (18)	0.00798 (11)	0.00248 (4)	0.01726 (24)	0.00017 (7)	0.00346 (13)	0.00006 (12)
N(1)	0.1739 (9)	0.3957 (4)	0.8078 (17)	0.0084 (10)	0.0023 (3)	0.0168 (19)	-0.0001 (4)	0.0021 (11)	0.0002 (6)
N(2)	0.0461 (8)	0.3487 (4)	0.5808 (12)	0.0100 (10)	0.0018 (3)	0.0134 (18)	0.0002 (4)	0.0018 (12)	-0.0003 (6)
N(3)	0.3303 (7)	0.3239 (4)	0.5254 (10)	0.0079 (9)	0.0023 (3)	0.0138 (17)	-0.0007 (4)	0.0004 (10)	0.0001 (6)
N(4)	0.2811 (7)	0.4415 (4)	0.4822 (10)	0.0060 (8)	0.0022 (2)	0.0167 (18)	0.0003 (4)	0.0010 (10)	-0.0004 (6)
C(1)	0.3593 (11)	0.4360 (6)	0.8735 (18)	0.0090 (13)	0.0046 (5)	0.0339 (36)	-0.0017 (8)	0.0009 (18)	-0.0006 (11)
C(2)	0.2416 (13)	0.4260 (6)	0.9104 (17)	0.0141 (16)	0.0019 (3)	0.0172 (28)	0.0000 (6)	-0.0029 (19)	-0.0005 (8)
C(3)	0.1982 (15)	0.4485 (6)	1.0430 (16)	0.0186 (19)	0.0032 (4)	0.0160 (29)	0.0008 (8)	0.0004 (21)	-0.0009 (8)
C(4)	0.0878 (15)	0.4395 (7)	1.0067 (17)	0.0151 (18)	0.0053 (6)	0.0172 (30)	0.0008 (8)	0.0020 (21)	0.0009 (11)
C(5)	0.0178 (13)	0.4065 (7)	0.9632 (18)	0.0179 (19)	0.0036 (4)	0.0157 (18)	0.0014 (7)	0.0055 (20)	-0.0001 (9)
C(6)	0.0655 (10)	0.3862 (5)	0.8316 (16)	0.0096 (12)	0.0019 (3)	0.0196 (26)	0.0004 (5)	0.0025 (16)	0.0012 (8)
C(7)	-0.0015 (10)	0.3544 (4)	0.7105 (17)	0.0071 (11)	0.0016 (3)	0.0198 (27)	0.0004 (4)	-0.0006 (15)	0.0003 (7)
C(8)	-0.1084 (10)	0.3337 (6)	0.7341 (17)	0.0072 (12)	0.0026 (4)	0.0303 (35)	-0.0005 (5)	-0.0015 (17)	0.0018 (9)
C(9)	-0.1692 (11)	0.3066 (6)	0.6160 (22)	0.0092 (14)	0.0023 (4)	0.0328 (40)	0.0006 (6)	0.0031 (20)	0.0020 (10)
C(10)	-0.1242 (11)	0.3009 (5)	0.4799 (18)	0.0081 (13)	0.0020 (4)	0.0308 (36)	-0.0002 (5)	-0.0008 (17)	0.0002 (9)
C(11)	-0.0144 (11)	0.3213 (5)	0.4633 (18)	0.0097 (13)	0.0016 (3)	0.0248 (32)	-0.0001 (5)	-0.0014 (18)	0.0001 (8)
C(12)	0.0396 (11)	0.3153 (7)	0.3218 (16)	0.0155 (15)	0.0049 (5)	0.0171 (26)	-0.0012 (7)	0.0080 (17)	-0.0017 (10)
C(13)	0.2656 (10)	0.2310 (5)	0.6319 (16)	0.0135 (14)	0.0026 (4)	0.0249 (29)	-0.0012 (6)	0.0049 (18)	0.0019 (9)
C(14)	0.3501 (11)	0.2639 (5)	0.5514 (14)	0.0132 (15)	0.0017 (4)	0.0164 (25)	0.0008 (6)	-0.0002 (15)	0.0000 (8)
C(15)	0.4456 (11)	0.2357 (6)	0.5047 (16)	0.0106 (13)	0.0030 (4)	0.0213 (29)	0.0012 (6)	0.0025 (16)	0.0012 (9)
C(16)	0.5207 (11)	0.2699 (7)	0.4282 (17)	0.0118 (14)	0.0035 (5)	0.0225 (31)	0.0010 (7)	0.0009 (17)	-0.0013 (10)
C(17)	0.5011 (10)	0.3326 (6)	0.3946 (14)	0.0091 (12)	0.0029 (4)	0.0217 (26)	0.0012 (5)	0.0007 (14)	-0.0011 (9)
C(18)	0.4035 (9)	0.3569 (5)	0.4486 (13)	0.0067 (10)	0.0026 (4)	0.0113 (20)	0.0005 (5)	-0.0011 (11)	-0.0007 (7)
C(19)	0.3738 (9)	0.4231 (5)	0.4183 (13)	0.0070 (10)	0.0019 (3)	0.0143 (22)	0.0001 (5)	-0.0001 (13)	-0.0001 (7)
C(20)	0.4390 (10)	0.4597 (6)	0.3363 (14)	0.0118 (13)	0.0027 (4)	0.0155 (24)	-0.0022 (6)	0.0004 (14)	0.0014 (8)
C(21)	0.4045 (10)	0.5214 (7)	0.3200 (15)	0.0092 (12)	0.0034 (4)	0.0205 (28)	-0.0014 (6)	0.0003 (15)	0.0004 (9)
C(22)	0.3118 (11)	0.5415 (6)	0.3814 (15)	0.0102 (14)	0.0032 (4)	0.0176 (26)	-0.0018 (6)	0.0007 (15)	0.0003 (9)
C(23)	0.2511 (11)	0.5013 (5)	0.4674 (15)	0.0100 (13)	0.0020 (4)	0.0197 (26)	-0.0003 (6)	-0.0014 (15)	0.0002 (8)
C(24)	0.1487 (10)	0.5207 (6)	0.5402 (17)	0.0101 (12)	0.0034 (4)	0.0357 (35)	0.0013 (6)	0.0082 (17)	0.0001 (10)
B ^a	0.3033	0.8736	0.4279	B = 18.0 Å ²					
F(1)	0.2994 (9)	0.8248 (6)	0.3421 (15)	0.0249 (13)	0.0080 (5)	0.0655 (39)	-0.0029 (7)	-0.0015 (19)	-0.0053 (11)
F(2)	0.3894 (8)	0.9036 (5)	0.3995 (15)	0.0256 (14)	0.0069 (4)	0.0755 (38)	-0.0036 (6)	0.0271 (19)	-0.0048 (10)
F(3)	0.3103 (11)	0.8563 (7)	0.5610 (15)	0.0391 (14)	0.0129 (7)	0.0459 (34)	0.0064 (10)	0.0191 (22)	0.0035 (14)
F(4)	0.2139 (4)	0.9072 (5)	0.4083 (18)	0.0245 (14)	0.0089 (5)	0.0968 (51)	0.0074 (7)	0.0227 (23)	0.0098 (14)

^a As explained in the text the parameters for B were interpolated.

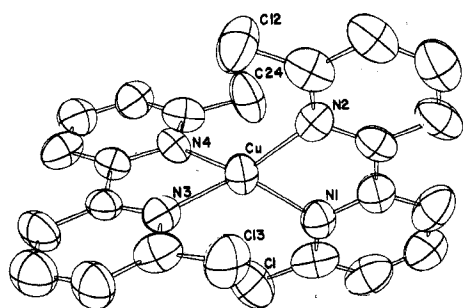


Figure 1. ORTEP diagram of $[\text{Cu}(\text{dmbp})_2]^+$ showing 50% probability ellipsoids. The carbons are numbered consecutively about the ligands.

sublimation yielded the pure ligand.

Crystallographic Data

A rotation photograph of a chunky crystal with an average radius of ~ 0.3 mm and a survey of reciprocal space on the diffractometer showed the space group to be $P2_1/c$. Lattice parameters (Table I) were determined from a least-squares refinement of the 2θ values of 69 reflections measured at positive and negative 2θ ($40^\circ < 2\theta < 48^\circ$) using an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated $\text{Mo K}\alpha$ radiation. All reflections were collected from a hemisphere of reciprocal space with $2\theta < 50^\circ$. The θ - 2θ scanning technique with a variable speed was used with a 2θ range of $2^\circ + 0.2 \tan \theta$ centered about the averaged peak position. The aperture was set at 4 mm. Each reflection was scanned twice at a rate varying from 1 to $6.7^\circ \text{ min}^{-1}$ depending on its intensity as determined by a rapid prescan of the peak. In no case were the results of the two scans statistically different. Background counts were made for one-fourth of the scan time at both ends of both scans. Three control reflections monitored after each 120 reflections did not change significantly during the course of data collection. Integrated intensities, I , were calculated by using the expression $I = C - 2B$ where C is the total number of counts collected during the two slow scans and B is the sum of the backgrounds. The standard deviation was assigned as $\sigma(I) = (I + 4B)^{1/2}$. The data were corrected for Lorentz-polarization effects but not absorption, and then equivalent reflections were averaged, giving 1771 strong independent reflections with $I > \sigma(I)$.

The structure was solved by using conventional heavy-atom methods; the positions of Cu and two of the N atoms were obtained from a Patterson synthesis, and other nonhydrogen atoms were located from several Fourier maps. The positions of copper and all nonhydrogen atoms of the dmbp ligands were then refined, assuming isotropic thermal parameters. Addition of boron and fluorine atoms at this point did not lead to a satisfactory refinement, so the boron atom was omitted and all other nonhydrogen atoms were refined, first using isotropic and then anisotropic thermal parameters. The position of boron was then calculated from the fluorine positions and the value assumed for the isotropic thermal parameter of boron was taken as the average of those of the F atoms. Including these values, the final calculated R factor was 0.069. Atomic scattering factors with real and imaginary anomalous scattering corrections for Cu, N, and C were taken from ref 25. Positional and thermal parameters for nonhydrogen atoms are given in Table II.

Results and Discussion

The structure consists of monomeric $\text{Cu}(\text{dmbp})_2^+$ cations and uncoordinated tetrafluoroborate anions with a closest approach of 3.14 Å between F(4) and C(5). A view of the cation, including the atom numbering scheme, is shown in Figure 1. Interatomic bond distances and angles for the molecule are given in Tables III and IV, respectively. Packing within the unit cell is shown in Figure 2.

Each dmbp ligand coordinates in a bidentate manner via the pyridine nitrogen atoms providing a distorted tetrahedral environment about copper. The dihedral angle between the planes defined by the copper center and each set of bipyridyl nitrogens is 80.9° and is appreciably smaller than expected

Table III. Interatomic Distances (Å) within $\text{Cu}(\text{dmbp})_2\text{BF}_4^a$

Cu-N(1)	2.052 (1)	Cu-N(3)	2.024 (1)
Cu-N(2)	2.018 (1)	Cu-N(4)	2.040 (1)
C(1)-C(2)	1.514 (10)	C(13)-C(14)	1.499 (10)
C(2)-C(3)	1.438 (9)	C(14)-C(15)	1.413 (5)
C(3)-C(4)	1.391 (6)	C(15)-C(16)	1.411 (4)
C(4)-C(5)	1.405 (2)	C(16)-C(17)	1.426 (2)
C(5)-C(6)	1.439 (4)	C(17)-C(18)	1.427 (10)
C(6)-N(1)	1.369 (4)	C(18)-N(3)	1.381 (2)
C(6)-C(7)	1.476 (4)	C(18)-C(19)	1.519 (2)
C(7)-C(8)	1.411 (10)	C(19)-C(20)	1.389 (10)
C(8)-C(9)	1.374 (10)	C(20)-C(21)	1.422 (10)
C(9)-C(10)	1.395 (10)	C(21)-C(22)	1.372 (10)
C(10)-C(11)	1.428 (5)	C(22)-C(23)	1.425 (4)
C(11)-C(12)	1.493 (10)	C(23)-C(24)	1.520 (10)
C(11)-N(2)	1.372 (10)	C(23)-N(4)	1.368 (7)
N(2)-C(7)	1.357 (4)	N(4)-C(19)	1.372 (5)
B-F(1)	1.32 (1)	B-F(3)	1.25 (1)
B-F(2)	1.28 (1)	B-F(4)	1.31 (1)

^a Estimated standard deviations are given in parentheses.

for regular tetrahedral geometry, consistent with the values reported for the analogous copper(II) complexes $[\text{Cu}(\text{dmp})_2]\text{NO}_3^{23}$ and $[\text{Cu}(\text{dmp})_2]\text{NO}_3 \cdot 2\text{H}_2\text{O}^{26}$ (80.27° and 85° , respectively). At the present time the factor(s) responsible for the deviation of the dihedral angle from the tetrahedral value of 90° cannot be identified. However, in view of the large deviations observed in the two different dmp structures^{23,26} and in the dmbp structure reported herein, it seems unlikely that the effect is attributable to crystal packing forces. The implication is that the "flattened" structures are likely to persist in solution as well.

The dmbp ligands are nonplanar and are slightly twisted about the 2,2' carbon bond (12.3 and 4.4° for the ligands defined by N1N2 and N3N4, respectively). However, the individual pyridine moieties are planar within 0.02 Å. Least-squares planes for each of the four pyridine rings are given in Table V. The authors are not aware of structural studies involving the dmbp ligand, but for comparison's sake, it can be noted that the bond distances and bond angles of the dmbp molecule are comparable with values previously reported for 2,2'-bipyridine²⁸ and its copper(II) complexes.⁸⁻¹³

The Cu-N distances for the two nitrogens of the same dmbp ligand are not equal. The differences seem to correlate with the degree of twist about the carbon-carbon bond joining the rings. Thus the difference between the Cu-N1 and Cu-N2 distances is somewhat larger than that observed between the Cu-N3 and Cu-N4 distances, and the twist is also greater in the N1N2 ligand system. Interestingly, the average Cu-N bond distance (2.03 Å) lies within the range (1.97–2.04 Å) previously found for (five-coordinate) copper(II) complexes with 2,2'-bipyridine.⁸⁻¹³ It therefore seemed reasonable to assume that the metal-binding sites in the lattice could as well accommodate copper(II). In an effort to observe the EPR spectrum of the Cu(II) system we irradiated several samples containing $\text{Cu}(\text{dmbp})_2^+$ with γ rays, a technique previously used to create copper sites in the copper(I) lattices of $\text{Cu}(\text{CH}_3\text{CN})_4^+$ and $\text{Cu}(\text{CH}_3\text{CSNH}_2)_4^+$.²⁹⁻³¹ An irradiated quartz tube containing microcrystalline $[\text{Cu}(\text{dmbp})_2]\text{BF}_4$ gave an intense EPR signal at $g \sim 2$, but a similar signal was obtained by irradiating an empty sample tube. The interfering signals could be removed by transferring the sample to another

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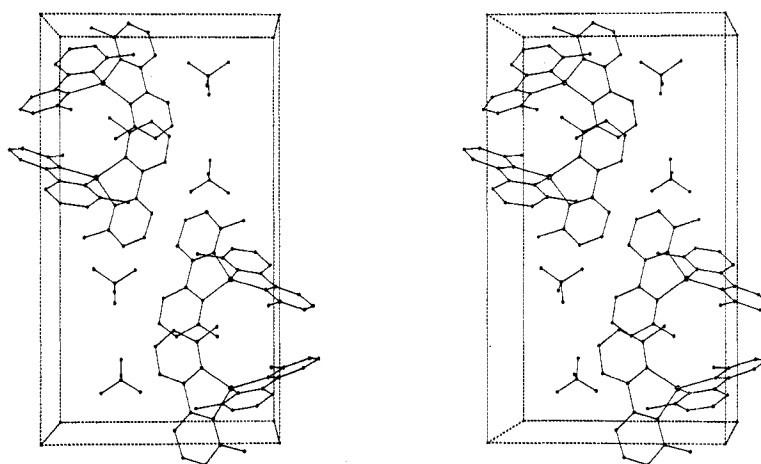


Figure 2. Stereopair view of packing in the unit cell of $[\text{Cu}(\text{dmbp})_2]\text{BF}_4$ as seen from the ab face.

Table IV. Bond Angles (Deg) within $\text{Cu}(\text{dmbp})_2\text{BF}_4$

N(1)-Cu-N(2)	81.66 (6)	C(9)-C(10)-C(11)	120.74 (30)	C(17)-C(18)-C(19)	119.19 (51)
N(3)-Cu-N(4)	82.21 (2)	C(10)-C(11)-C(12)	123.32 (25)	C(19)-C(20)-C(21)	115.43 (28)
N(1)-Cu-N(3)	128.46 (4)	N(2)-C(11)-C(10)	119.65 (25)	C(20)-C(21)-C(22)	120.68 (12)
N(1)-Cu-N(4)	115.95 (3)	N(2)-C(11)-C(12)	116.93 (27)	C(21)-C(22)-C(23)	120.37 (28)
N(2)-Cu-N(3)	124.41 (12)	C(11)-N(2)-C(7)	117.75 (5)	C(22)-C(23)-C(24)	123.22 (95)
N(2)-Cu-N(4)	130.33 (7)	Cu-N(3)-C(14)	127.72 (2)	N(4)-C(23)-C(22)	120.07 (23)
Cu-N(1)-C(2)	126.45 (2)	Cu-N(3)-C(18)	113.32 (1)	N(4)-C(23)-C(24)	116.64 (100)
Cu-N(1)-C(6)	112.37 (19)	Cu-N(4)-C(23)	127.56 (1)	C(23)-N(4)-C(19)	117.65 (17)
Cu-N(2)-C(11)	126.92 (6)	F(1)-B-F(2)	106.6 (5)	N(2)-C(7)-C(6)	115.54 (31)
Cu-N(2)-C(7)	113.96 (5)	F(1)-B-F(3)	108.1 (6)	C(6)-C(7)-C(8)	119.53 (21)
N(1)-C(2)-C(1)	116.62 (28)	F(1)-B-F(4)	113.2 (2)	C(6)-N(1)-C(2)	120.09 (14)
N(1)-C(2)-C(3)	119.34 (30)	Cu-N(4)-C(19)	114.98 (2)	C(18)-N(3)-C(14)	118.88 (16)
C(1)-C(2)-C(3)	124.02 (17)	N(3)-C(14)-C(13)	115.72 (20)	N(2)-C(7)-C(8)	124.91 (30)
C(2)-C(3)-C(4)	120.82 (11)	N(3)-C(14)-C(15)	120.91 (32)	N(4)-C(19)-C(18)	113.38 (24)
C(3)-C(4)-C(5)	120.20 (19)	C(13)-C(14)-C(15)	123.36 (31)	N(4)-C(19)-C(20)	125.71 (23)
C(4)-C(5)-C(6)	116.33 (21)	C(14)-C(15)-C(16)	119.73 (19)	C(18)-C(19)-C(20)	120.88 (18)
N(1)-C(6)-C(5)	123.15 (24)	C(15)-C(16)-C(17)	121.15 (26)	F(2)-B-F(3)	109.9 (5)
N(1)-C(6)-C(7)	115.45 (11)	C(16)-C(17)-C(18)	114.56 (34)	F(2)-B-F(4)	111.3 (6)
C(5)-C(6)-C(7)	121.39 (25)	N(3)-C(18)-C(17)	124.71 (33)	F(3)-B-F(4)	107.6 (6)
C(7)-C(8)-C(9)	117.27 (20)	N(3)-C(18)-C(19)	116.09 (29)	F(1)-B-F(4)	113.2 (2)
C(8)-C(9)-C(10)	119.63 (20)				

Table V. Least-Squares Planes

atom	deviation	atom	deviation	atom	deviation
N1 Ring					
N(1)	0.002	C(2)	0.01	C(4)	-0.01
C(1)	-0.01	C(3)	0.008	C(5)	0.009
C(6)	0.008				
$2.622x - 1.887y + 3.999z = -3.7802$					
N2 Ring					
N(2)	0.005	C(8)	-0.009	C(10)	0.017
C(7)	0.006	C(9)	-0.007	C(11)	-0.002
C(12)	-0.009				
$-4.170x + 1.959y - 2.371z = 5.2599$					
N3 Ring					
N(3)	0.02	C(14)	-0.001	C(16)	0.009
C(13)	-0.01	C(15)	0.006	C(17)	-0.02
C(18)	-0.004				
$5.239x + 5.211y + 7.455z = 7.3189$					
N4 Ring					
N(4)	-0.01	C(20)	0.007	C(22)	-0.02
C(19)	0.003	C(21)	0.005	C(23)	0.01
C(24)	0.006				
$6.064x + 5.223y + 7.065z = 7.4311$					
Angle N1 Ring-N2 Ring = 12.3°					
Angle N3 Ring-N4 Ring = 4.4°					

tube while the temperature was maintained at ca. -125°C with a methylcyclohexane slush bath; however, no EPR signal from the sample was detected. In an attempt to retard the recombination of ejected electrons (vide infra), γ irradiation was carried out on samples of $[\text{Cu}(\text{dmbp})_2]\text{BF}_4$ in a frozen

CH_2Cl_2 glass and on samples bound to an SP Sephadex C-25 ion-exchange resin. In the former case no EPR signal was detected. In the latter an apparently axial copper(II) EPR spectrum was observed, but the same signal was observed in resin-bound samples which had *not* been γ irradiated, suggesting that oxidation had occurred during sample preparation. As we have no information regarding the structure of the oxidized complex the analysis of this signal has not been pursued.

Our results indicate that γ irradiation may not be a general method for generating the copper(II) analogues of structurally characterized copper(I) systems. It is possible that in our system the delocalized π systems of the dmbp ligands facilitate the recombination of the copper(II) centers with the electrons which we presume are "ionized" by the γ rays. Alternatively, other, unsuspected secondary chemical reactions could have led to the formation of EPR nondetectable products.

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Registry No. $\text{Cu}(\text{dmbp})_2\text{BF}_4$, 73017-54-6.

Supplementary Material Available: Listing of observed and calculated structure factors (18 pages). Ordering information is given on any current masthead page.