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Characterization of metal complexes of 2,6-diacetylpyridinebis(imines). Preparation and crystal structure of tetrafluoroborato-2,2′-bipyridyl-{2,6-bis[1-(*p*-ethylphenylimino)ethyl]pyridine}-copper(II) tetrafluoroborate

ELMER C. ALYEA, GEORGE FERGUSON,*
MARY NAHUIS, and BARBARA L. RUHL
Department of Chemistry and Biochemistry
University of Guelph, Guelph, Ontario
Canada N1G 2W1

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Abstract

X-ray analysis has established the "semicoordination" bonding mode for one tetrafluoroborate anion in tetrafluoroborato-2,2′-bipyridyl{2,6-bis[1-(*p*-ethylphenylimino)ethyl]pyridine}copper(II) tetrafluoroborate, [Cu(bipy)($C_{25}H_{27}N_3$)(FBF_3)]BF_4. Crystals of the title compound are monoclinic, space group $P2_1/n$ with four molecules in the unit cell of $a = 14.991(3)$, $b = 14.989(3)$, $c = 16.933(4)$ Å, $\beta = 109.33(2)°$. The structure was solved by the heavy-atom method and refined by blocked full-matrix least squares calculations with anisotropic thermal parameters for nonhydrogen atoms to $R = 0.049$ and $R_w = 0.051$ for 3311 reflections with $I > 3\sigma(I)$. The copper atom coordination is pseudo-octahedral, with one nitrogen atom of the bipyridyl ligand [Cu—N(2) 1.985(4) Å] and three nitrogen atoms of the terdentate NNN donor ligand [Cu—N(3) 1.923(4), Cu—N(4) 2.073(4), Cu—N(5) 2.073(4) Å] forming the equatorial plane. The axial sites are occupied by the second nitrogen atom of the bipyridyl ligand [Cu—N(1) 2.186(5) Å] and a loosely bound fluorine atom [Cu—F(21) 2.692(5) Å] of the "semicoordinated" tetrafluoroborate group. The other BF_4^- anion is ionic. Electronic and vibrational spectral data for the complex are discussed in terms of the geometry of the cation.

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Introduction

Terdentate NNN donor ligands (L) readily obtained from 2,6-diacetylpyridine and substituted anilines by Schiff-base condensation have coordinating abilities that are comparable with the well-known terpyridine ligand (Alyea and Merrell, 1978). Crystallographic studies in our laboratories on the 2,6-diacetylpyridinebis(anil) derivatives $LM(NO_3)_2$ [M = Ni(II) (Alyea *et al.*, 1975), Cu(II) (Ferguson and Restivo, 1976)] confirmed the near planarity of the NNN donor set. More recently (Merrell *et al.*, 1982), our characterization of two pseudo-octahedral metal complexes of the type $[MLL'(NO_3)]Y$ [M(II) = Ni, Zn; L' = bidentate ligand; Y = noncoordinating anion] led us to attempt the synthesis of the potentially pentacoordinate mixed ligand complexes $[MLL']Y_2$ [M(II) = Co, Ni, Cu, Zn, Cd] (E.C. Alyea, L. Ecott, C. Maltby, and M. Nahuis, unpublished work). The present paper describes the synthesis and single crystal X-ray analysis of $[Cu(bipy)(C_{25}H_{27}N_3)(FBF_3)]BF_4$, wherein a "semicoordinated" tetrafluoroborate group fills the sixth site of a distorted octahedron around Cu.

Experimental

Preparation of $[Cu(bipy)(C_{25}H_{27}N_3)(FBF_3)]BF_4$

2,2′-Bipyridyl (0.20 g, 1.3 mmol) dissolved in absolute ethanol (10 ml) was added to an ethanolic solution (10 ml) of $Cu(NO_3)_2 \cdot 3H_2O$ (0.32 g. 1.3 mmol) and the blue solution was warmed and stirred. The color became dark green when a warm ethanolic solution (10 ml) of the terdentate NNN ligand (0.48 g, 1.3 mmol) was added. No precipitation occurred when $NaBF_4$ (0.29 g, 2.6 mmol) is aqueous ethanol (15 ml) was added, but refrigeration gave dark green crystals. The solution was reduced in volume and the product collected, washed with absolute ethanol and ether, recrystallized from dichloromethane, and dried *in vacuo* in 100° for 3 h. Yield, 91%. Decomp. >235°. Anal. Found: C, 55.8; H, 4.67; N, 9.19. Calcd. for $C_{35}H_{35}N_5B_2CuF_8$: C, 55.1; H, 4.62; N, 9.18. Λ_M (10^{-3} M, CH_3NO_2), 204.2 Ω^{-1} cm^2 mol^{-1}. μ_{eff}, 2.05 B.M. (Evans method (Evans, 1959; Crawford and Swanson, 1971) CH_2Cl_2 solution). λ_{max}, 668 nm (CH_2Cl_2 solution). *Crystal Data*: $C_{35}H_{35}N_5B_2CuF_8$, M_r = 762.8, monoclinic, a = 14.991(3), b = 14.989(3), c = 16.933(4) Å, β = 109.33(2)°, U = 3590.6 Å^3, Z = 4, D_c = 1.41 g cm^{-3}, λ(Mo $K\alpha$) = 0.70926 Å, μ(Mo $K\alpha$) = 7.1 cm^{-1}. Space group $P2_1/n$ (alternative setting of C_{2h}^5, No. 14) from systematic absences ($h0l$ absent for $h + l = 2n + 1$; $0k0$ absent for $k = 2n + 1$).

Accurate unit cell dimensions were obtained by a least-squares procedure applied to the setting angles for 25 general reflections, with $10 < \theta < 20°$, measured on an Enraf-Nonius CAD-4 diffractometer. The intensities of the unique reflections with $2 < \theta < 27°$ were surveyed; of the 8409 unique reflections measured, the 3311 with $I > 3\sigma(I)$ were labelled observed, and after correction for Lorentz, polarization effects, and absorption (maximum and minimum transmission coefficients were 0.884 and 0.859 respectively) were used in all subsequent calculations. There were very few reflections with $\theta > 20°$, hence the relatively low (39%) (observed/total) reflection ratio.

Structure solution and refinement

The structure was solved by the heavy-atom method from phases originally derived from the coordinates of the copper atom whose position was deduced from a three-dimensional Patterson synthesis. Structure refinement was begun with the N.R.C. system (Larson and Gabe, 1978) but completed using the SHELX program (Sheldrick, 1976) because of the large number of parameters involved. The structure was refined initially with isotropic and then with anisotropic thermal parameters for nonhydrogen atoms, by blocked full-matrix least-squares calculations. Cu, dipyridyl, N(3), N(4), N(5), C(1), C(2), C(3), C(4), C(41), and C(51) were included in all refinement cycles. One *p*-ethylphenyl group and one BF_4 group were placed in each of two blocks to be refined in alternate cycles. A difference Fourier synthesis revealed the positions of all the hydrogen atoms close to those expected on geometrical grounds. These were then positioned geometrically (C—H 0.95 Å) and included but not refined in the final rounds of refinement. Refinement converged with $R = 0.049$ and $R_w = (\Sigma w\Delta^2/\Sigma F_o^2)^{1/2} = 0.051$. Scattering factors were calculated (Cromer and Mann, 1968; Stewart *et al.*, 1965) using an analytical approximation, and anomalous dispersion corrections were made (Cromer and Liberman, 1970). In the least-squares calculations, the weights were based on counting statistics and a final difference map showed no peaks greater than 0.45 e Å^{-3}.

Final atomic coordinates of all nonhydrogen atoms are given in Table 1. Interatomic distances and angles are given in Tables 2 and 3. Figure 1 is a stereoview of the cation with our numbering scheme. Figure 2 shows the immediate coordination geometry of the Cu atom.

Discussion

Interest in the varied stereochemistries of copper(II) complexes, particularly those involving five-coordination, has continued for many years (Muetterties and Schunn, 1966; Hathaway and Billing, 1970; Foley *et al.*, 1984). X-ray crystallographic data are extensive for certain classes of compounds (e.g., 34 $[Cu(bipy)_2X]Y$ type complexes) (Foley *et al.*, 1984), but examples are more limited for five-coordinate CuN_5 complexes (Ray and Hathaway, 1978; Duggan *et al.*, 1980; Ray *et al.*, 1981). The present mixed ligand complex was synthesized as part of our studies (Alyea and Merrell, 1978; Alyea *et al.*, 1975; Fer-

Table 1. Final fractional coordinates (Cu × 10^5, remainder × 10^4) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Cu	16444(4)	11402(4)	33677(4)
N(1)	1401(3)	94(3)	4172(3)
N(2)	250(3)	1196(3)	3078(2)
N(3)	2975(3)	1137(3)	3523(2)
N(4)	1699(3)	223(3)	2469(2)
N(5)	2122(3)	2137(3)	4257(2)
C(1)	2522(4)	58(4)	2445(3)
C(2)	2765(4)	-573(4)	1866(4)
C(3)	3030(4)	2244(3)	4516(3)
C(4)	3584(4)	2904(4)	5146(3)
C(12)	477(4)	-92(3)	3965(3)
C(13)	171(5)	-805(4)	4321(4)
C(14)	804(6)	-1315(4)	4900(4)
C(15)	1750(5)	-1112(5)	5117(4)
C(16)	2018(4)	-409(4)	4730(4)
C(22)	-163(3)	523(4)	3358(3)
C(23)	-1137(4)	453(5)	3099(4)
C(24)	-1691(4)	1092(5)	2595(4)
C(25)	-1273(4)	1795(5)	2343(4)
C(26)	-296(4)	1820(4)	2582(3)
C(32)	3294(4)	542(4)	3076(3)
C(33)	4259(4)	461(4)	3256(4)
C(34)	4862(4)	977(5)	3880(4)
C(35)	4513(4)	1585(4)	4309(4)
C(36)	3544(3)	1650(4)	4114(3)
C(41)	877(4)	-282(3)	1974(3)
C(42)	760(4)	-1122(4)	2236(4)
C(43)	-63(6)	-1562(5)	1833(5)
C(44)	-776(5)	-1210(5)	1172(4)
C(45)	-615(4)	-369(5)	915(4)
C(46)	214(4)	100(4)	1320(4)
C(47)	-1699(5)	-1677(6)	760(6)
C(48)	-2333(7)	-1571(7)	1221(7)
C(51)	1555(3)	2596(3)	4664(3)
C(52)	849(4)	3160(4)	4219(4)
C(53)	299(4)	3587(4)	4614(5)
C(54)	434(5)	3456(4)	5449(5)
C(55)	1126(4)	2869(4)	5880(4)
C(56)	1681(4)	2432(4)	5495(3)
C(57)	-165(6)	3976(7)	5872(6)
C(58)	-650(7)	3449(7)	6262(6)
B(1)	6410(5)	9383(6)	3116(5)
F(11)	7191(3)	9005(5)	3026(3)
F(12)	6333(3)	9106(3)	3874(3)
F(13)	6478(3)	10284(3)	3149(3)
F(14)	5610(3)	9131(3)	2514(3)
B(2)	1665(6)	2531(8)	1499(6)
F(21)	1561(3)	2464(3)	2271(3)
F(22)	1831(5)	3336(4)	1300(3)
F(23)	940(4)	2179(4)	931(3)
F(24)	2407(4)	2032(6)	1561(4)

Table 2. Bond lengths (Å)

Cu—N(1)	2.186(5)	C(25)—C(26)	1.385(8)
Cu—N(2)	1.985(4)	C(32)—C(33)	1.381(8)
Cu—N(3)	1.923(4)	C(33)—C(34)	1.378(8)
Cu—N(4)	2.073(4)	C(34)—C(35)	1.372(10)
Cu—N(5)	2.073(4)	C(35)—C(36)	1.383(8)
Cu—F(21)	2.692(5)	C(41)—C(42)	1.368(8)
N(1)—C(12)	1.342(7)	C(41)—C(46)	1.354(7)
N(1)—C(16)	1.318(7)	C(42)—C(43)	1.366(9)
N(2)—C(22)	1.351(7)	C(43)—C(44)	1.372(9)
N(2)—C(26)	1.339(6)	C(44)—C(45)	1.379(11)
N(3)—C(32)	1.356(8)	C(45)—C(46)	1.395(9)
N(3)—C(36)	1.325(6)	C(44)—C(47)	1.501(10)
N(4)—C(1)	1.273(8)	C(47)—C(48)	1.426(16)
N(4)—C(41)	1.443(6)	C(51)—C(52)	1.368(7)
N(5)—C(3)	1.295(6)	C(51)—C(56)	1.378(8)
N(5)—C(51)	1.436(7)	C(52)—C(53)	1.379(10)
C(1)—C(2)	1.492(9)	C(53)—C(54)	1.375(11)
C(1)—C(32)	1.478(7)	C(54)—C(55)	1.372(9)
C(3)—C(4)	1.489(7)	C(55)—C(56)	1.379(10)
C(3)—C(36)	1.483(3)	C(54)—C(57)	1.533(14)
C(12)—C(13)	1.378(9)	C(57)—C(58)	1.380(16)
C(12)—C(22)	1.474(7)	B(1)—F(11)	1.354(10)
C(13)—C(14)	1.352(8)	B(1)—F(12)	1.390(11)
C(14)—C(15)	1.377(11)	B(1)—F(13)	1.353(9)
C(15)—C(16)	1.368(10)	B(1)—F(14)	1.346(8)
C(22)—C(23)	1.382(7)	B(2)—F(21)	1.371(11)
C(23)—C(24)	1.365(9)	B(2)—F(22)	1.298(13)
C(24)—C(25)	1.365(10)	B(2)—F(23)	1.301(10)
		B(2)—F(24)	1.315(13)

Table 3. Bond angles (deg)

N(1)—Cu—N(2)	78.8(2)	N(1)—C(12)—C(13)	120.7(5)
N(1)—Cu—N(3)	107.0(2)	N(1)—C(12)—C(22)	115.5(5)
N(1)—Cu—N(4)	92.1(2)	C(13)—C(12)—C(22)	123.8(5)
N(1)—Cu—N(5)	98.8(2)	C(12)—C(13)—C(14)	120.0(6)
N(1)—Cu—F(21)	168.4(2)	C(13)—C(14)—C(15)	118.8(7)
N(2)—Cu—N(3)	173.4(2)	C(14)—C(15)—C(16)	118.8(6)
N(2)—Cu—N(4)	98.1(2)	C(15)—C(16)—N(1)	122.5(6)
N(2)—Cu—N(5)	103.4(2)	N(2)—C(22)—C(23)	120.2(5)
N(2)—Cu—F(21)	89.6(2)	N(2)—C(22)—C(12)	116.4(4)
N(3)—Cu—N(4)	78.9(2)	C(23)—C(22)—C(12)	123.4(5)
N(3)—Cu—N(5)	79.0(2)	C(22)—C(23)—C(24)	120.4(6)
N(3)—Cu—F(21)	84.6(2)	C(23)—C(24)—C(25)	119.3(6)
N(4)—Cu—N(5)	157.4(2)	C(24)—C(25)—C(26)	118.7(6)
N(4)—Cu—F(21)	89.2(2)	C(25)—C(26)—N(2)	122.1(6)
N(5)—Cu—F(21)	84.0(2)	N(3)—C(32)—C(33)	118.1(5)
Cu—N(1)—C(12)	110.9(3)	N(3)—C(32)—C(1)	113.0(5)
Cu—N(1)—C(16)	129.5(4)	C(33)—C(32)—C(1)	129.0(6)
C(12)—N(1)—C(16)	119.1(5)	C(32)—C(33)—C(34)	119.6(6)
Cu—N(2)—C(22)	116.7(3)	C(33)—C(34)—C(35)	120.7(6)

Table 3. Continued

Cu—N(2)—C(26)	124.0(4)	C(34)—C(35)—C(36)	118.3(5)
C(22)—N(2)—C(26)	119.1(4)	C(35)—C(36)—N(3)	120.2(6)
Cu—N(3)—C(32)	117.8(3)	C(35)—C(36)—C(3)	126.6(5)
Cu—N(3)—C(36)	118.8(4)	N(3)—C(36)—C(3)	113.1(4)
C(32)—N(3)—C(36)	123.1(4)	N(4)—C(41)—C(42)	118.4(4)
Cu—N(4)—C(1)	115.2(3)	N(4)—C(41)—C(46)	120.6(5)
Cu—N(4)—C(41)	122.9(4)	C(42)—C(41)—C(46)	120.6(5)
C(1)—N(4)—C(41)	121.4(5)	C(41)—C(42)—C(43)	118.8(5)
Cu—N(5)—C(3)	114.1(4)	C(43)—C(44)—C(47)	123.2(7)
Cu—N(5)—C(51)	125.3(3)	C(45)—C(44)—C(47)	120.7(6)
C(3)—N(5)—C(51)	120.0(4)	C(44)—C(45)—C(46)	121.8(6)
N(4)—C(1)—C(2)	126.4(5)	C(45)—C(46)—C(41)	119.3(6)
N(4)—C(1)—C(32)	114.7(5)	C(44)—C(47)—C(48)	111.9(8)
C(2)—C(1)—C(32)	118.9(5)	N(5)—C(51)—C(52)	120.3(5)
N(5)—C(3)—C(4)	126.8(5)	N(5)—C(51)—C(56)	120.1(4)
N(5)—C(3)—C(36)	114.6(4)	F(11)—B(1)—F(12)	108.5(6)
C(4)—C(3)—C(36)	118.5(5)	F(11)—B(1)—F(13)	111.5(6)
C(52)—C(51)—C(56)	119.5(6)	F(11)—B(1)—F(14)	112.6(7)
C(51)—C(52)—C(53)	119.8(6)	F(12)—B(1)—F(13)	106.8(7)
C(52)—C(53)—C(54)	121.7(6)	F(12)—B(1)—F(14)	106.8(7)
C(53)—C(54)—C(55)	117.7(7)	F(13)—B(1)—F(14)	110.3(6)
C(53)—C(54)—C(57)	119.9(6)	F(21)—B(2)—F(22)	114.1(8)
C(55)—C(54)—C(57)	122.4(7)	F(21)—B(2)—F(23)	110.1(8)
C(54)—C(55)—C(56)	121.5(6)	F(21)—B(2)—F(24)	103.9(7)
C(55)—C(56)—C(51)	119.8(5)	F(22)—B(2)—F(23)	111.8(7)
C(54)—C(57)—C(58)	114.5(9)	F(22)—B(2)—F(24)	108.7(9)
C(42)—C(43)—C(44)	123.5(7)	F(23)—B(2)—F(24)	107.8(9)
C(43)—C(44)—C(45)	116.0(6)		

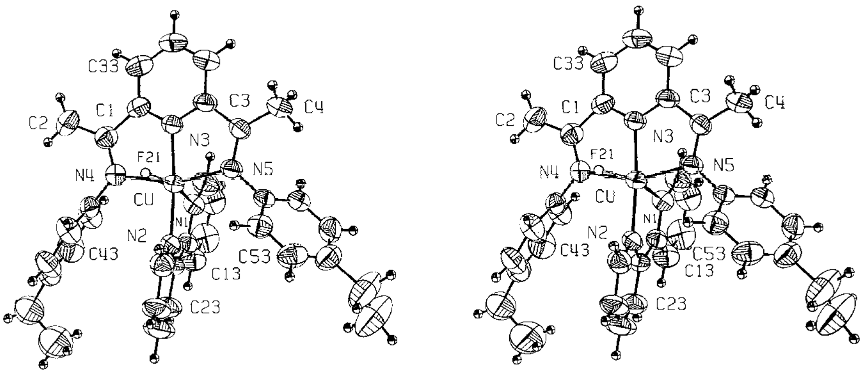


Fig. 1. A stereoview of the $[Cu(bipy)(C_{25}H_{27}N_3)(FBF_3)]^+$ cation with the crystallographic numbering scheme. For clarity, only the fluorine [F(21)] of the semicoordinated BF_4^- moiety is shown.

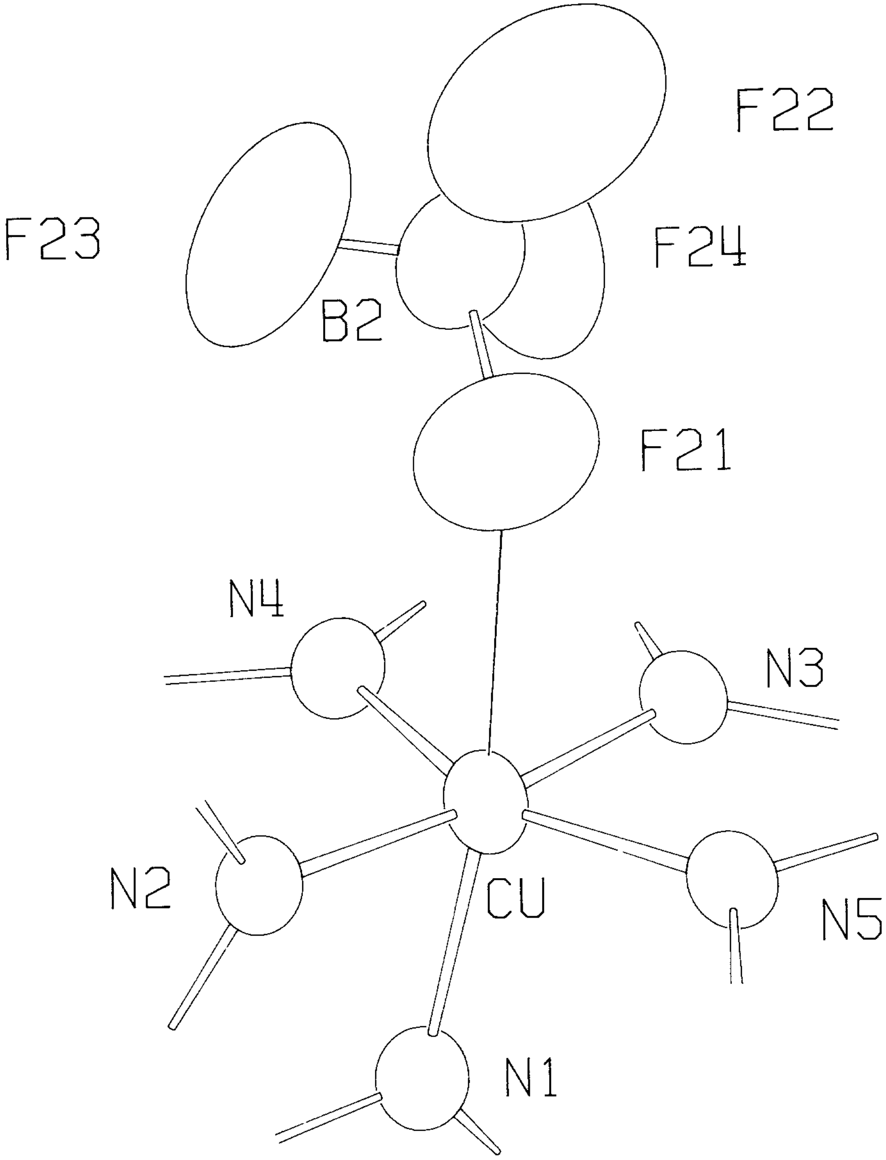
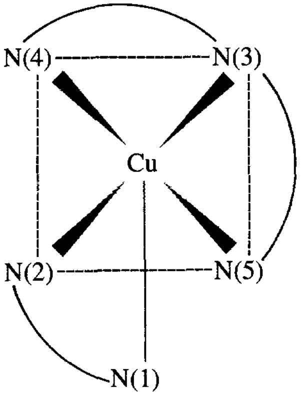


Fig. 2. The immediate coordination sphere of Cu in $[Cu(bipy)(C_{25}H_{27}N_3)(FBF_3)]^+$. Atoms N(1) and N(2) are from the bipyridyl ligand, and N(3), N(4), and N(5) are from the terdentate ligand described in the text.

guson and Restivo, 1976; Merrell *et al.*, 1982) of the coordinating ability of a series of neutral terdentate NNN donor Schiff base ligands derived from 2,6-diacetylpyridine and aromatic amines. Consideration of the expected (Alyea *et al.*, 1975; Ferguson and Restivo, 1976) planarity of the terdentate NNN donor set and the known structures for $[CuLL']Y_2$ type complexes containing terdentate and bidentate ligands (Ray and Hathaway, 1978) led us to anticipate a square-pyramidal geometry, as shown below:



The behavior of the product as a 1:2 electrolyte (Geary, 1971) in nitromethane ($\Lambda_M = 204\ \Omega^{-1}\ cm^2\ mol^{-1}$) and the position ($\lambda_{max} = 14{,}970\ cm^{-1}$) and profile (no high-frequency shoulder indicative of considerable distortion toward a trigonal bipyramidal stereochemistry) (Foley *et al.*, 1984; Duggan *et al.*, 1980; Ray *et al.*, 1981) of the visible band were compatible with that expectation, at least in solution. Application of the infrared spectral criterion (Procter *et al.*, 1968) for tetrafluoroborate coordination, for which several examples were recently discussed (Foley *et al.*, 1984), did not appear feasible due to the many ligand bands in the region of the characteristic vibrational modes of the BF_4^- anion. Infrared spectroscopy and elemental analyses indicated the absence of water that could occupy a copper coordination site. Our X-ray structural determination of the title complex has established not only the (principally) square-pyramidal CuN_5 core of the mixed ligand complex but also the presence of a "semicoordinated" tetrafluoroborate group in the sixth coordination site.

The structure consists of discrete $[Cu(bipy)(C_{25}H_{27}N_3)(FBF_3)]^+$ cations (Figs. 1 and 2) and BF_4^- anions. The stereochemistry of the cation is pseudo-octahedral, with the CuN_5F core corresponding to a 4 + 1 + 1* geometry in the Hathaway nomenclature (Hathaway, 1973). The principal feature of the stereochemistry is a square-pyramidal copper coordination, with the terdenate NNN donor ligand occupying three in-plane bonding positions N(3—5) (meridional positions of octahedral coordination) and the bidentate bipyridyl ligand bonding in the plane, N(2), and in an axial site, N(1). The atoms of the NNN terdentate donor set [N(3), N(4), N(5), C(1), C(2), C(3), C(4), C(32), C(33), C(34), C(35), C(36), C(41), C(51)] are planar to within 0.13 Å and the two phenyl rings are twisted out of this coordination plane through angles of 75 and 188°. The terdentate ligand has the expected (Alyea *et al.*, 1975; Ferguson and Restivo, 1976) conformation; i.e., it is analogous to terpyridine (Masku *et al.*, 1974; Anderson *et al.*, 1976) rather than diethylenetriamine (dien), which can also adopt a bent conformation in its copper complexes (Druhan and Hathaway, 1979; Bew *et al.*, 1972). The individual pyridine rings of the bipy ligand are planar (0.023 Å), but are twisted about the C(12)—C(22) bond through an angle of 7.1° within the range normally found (Ray and Hathaway, 1978; Stephens, 1972; Anderson, 1972).

The two terminal nitrogen atoms of the terdentate ligand form bonds of equal length to the copper(II) ion [Cu—N(4) and Cu—N(5) 2.073(4) Å]. The nitrogen atom of the central pyridine ring is bonded to Cu at a significantly shorter distance [Cu—N(3) 1.923(4) Å] as a result of the constrained ligand geometry. This distortion is doubtless at least partially a consequence of the small bite angles [79.0(2)° mean] of this chelating terdentate NNN ligand. An exactly analogous situation was found previously for 2,6-diacetylpyridine-bis(anil) complexes [e.g., M—N differences of 0.13 Å for Ni (Alyea *et al.*, 1975) and 0.13 Å for Cu (Ferguson and Restivo, 1976)] and for terpyridyl complexes [e.g., M—N differences of 0.21 Å for Co (Masku *et al.*, 1974), and 0.11 Å for Cu (Anderson *et al.*, 1976)]. The four equatorial Cu—N distances [1.923–2.073(4) Å] are normal for strong Cu—N(pyridine) type bonding to copper(II); for example, equatorial Cu—N distances are 2.00–2.07(1) Å in tris(1,10-phenanthroline)copper(II) perchlorate (Teo *et al.*, 1975), 1.985(II) Å in $[Cu(bipy)_2X]X$ ($X = BF_4$, ClO_4) (Foley *et al.*, 1984), and 1.913-2.046(3) Å in dinitrato {2,6-bis[1-(phenylimino)ethyl]pyridine}copper(II) (Ferguson and Restivo, 1976). The long axial Cu—N(1) bond distance, 2.186(5) Å, is typical for square-pyramidal copper(II) complexes (Hathaway and Billing, 1970); axial Cu—N distances are 2.169(5) Å in [Cu(dien)(bipyam)] $ClO_4 \cdot H_2O$ (bipyam = di-2-pyridylamine) (Ray *et al.*, 1981), 2.218(17) Å in $[Cu(bpa)(bipy)](NO_3)_2$ [bpa = bis(3-aminopropyl)amine] (Ray and Hathaway, 1978), and 2.193(22) Å in $K[Cu(NH_3)_5][PF_6]_3$ (Duggan *et al.*, 1980). The latter complex, which is the most symmetrical square-pyramidal complex of copper(II) involving five equivalent σ bonding ligands known to date (Duggan *et al.*, 1980), has a tetragonality (defined as the ratio of the mean in-plane and out-of-plane Cu—N distances) of 0.925. The tetragonality of our complex is 0.92, which is also comparable to values for other square-pyramidal copper(II) complexes containing both terdentate and bidentate ligands (Ray and Hathaway, 1978; Duggan *et al.*, 1980; Ray *et al.*, 1981). By contrast, some six-coordinate CuN_4O_2 species have tetragonality values of *ca.* 0.75 (Foley *et al.*, 1984). Not surprisingly, in agreement with results found for analogous complexes (Ray and Hathaway, 1978; Duggan *et al.*, 1980; Ray *et al.*, 1981), the copper(II) ion is lifted out of the plane of the four in-plane N atoms, N(2)—N(5), by 0.10 Å toward the axial nitrogen atom N(1). This results in out-of-plane angles N(1)—Cu—N(3), N(1)—Cu—N(4), and N(1)—Cu—N(5) of 107.0(2), 92.1(2), and 98.8(2)°, respectively. The corresponding basal angles N(2)—Cu—N(3) [173.4(2)° = α_4] and N(4)—Cu—N(5) [157.4(2)° = α_3] do not differ markedly from the corresponding angles of 167.2(8) and 163.8(10)° found (Duggan *et al.*, 1980) in the highly symmetric square-pyramidal $[Cu(NH_3)_5]^{2+}$ ion [160–164° are predicted for a d^9 σ-bonding system] (Rossi and Hoffmann, 1975). The angular distortion in the basal angles represents a small tendency toward trigonal bipyramidal stereochemistry, with α_4 representing the trigonal axis (i.e., nearly linear) and α_3 the trigonal angle. The ($\alpha_4 - \alpha_3$) difference of 16.0(2)° reflects a moderate distortion in the flexible stereochemistry (Hathaway and Billing, 1970; Hathaway, 1973) (or "plasticity effect") (Gazo *et al.*, 1976) of the copper(II) ion in which CuN_5 species are known to adopt intermediate geometries along the structural pathway (Dunitz, 1979; Burgi, 1975; Reinen and Friebel, 1984) from square-pyramidal to trigonal bipyramidal stereochemistry. The analogous mixed ligands [Cu(bpa)(bipy)]/$(NO_3)_2$ and $[Cu(dien)(bipyam)](ClO_4)_2 \cdot H_2O$ have ($\alpha_4 - \alpha_3$) differences of 25.8(7) (Ray and Hathaway, 1978) and 15.9(2)° (Ray *et al.*, 1981), representing similar significant trigonal distortions from their square-pyramidal stereochemistry. The considerable variation of ($\alpha_4 - \alpha_3$) with anion for the latter cation distortion isomer demonstrates that subtle forces such as lattice packing forces may influence the degree of distortion along the structural pathway linking the two idealized geometries. An obvious contribution to the distortion from square-pyramidal stereochemistry comes from the small bite angle of the bipy ligand [78.8(2)°]. Hathaway (Ray and Hathaway, 1978) has shown by comparing two related mixed ligand copper(II) complexes that the angular distortion is considerably reduced when a six-membered ring ligand rather than a five-membered ring ligand spans the axial-equatorial positions of the square pyramid. Specifically, di-2-pyridylamine (dpyam) with a bite angle of 89.2° gave $\alpha_4 - \alpha_3 =$ 8.7° whereas bipy with a bite angle of 77.0 gave $\alpha_4 - \alpha_3 = 25.8°$. The shorter bite of the bipy ligand also is expected (Ray *et al.*, 1981) to contribute to the tetragonality of the complex [i.e., a long Cu—N(1) distance, 2.186(5) Å], and to the inequality of the N(1)—Cu—N(3) angle [107.0(2)°] as compared to the N(1)—Cu—N(4,5) angles [92.1(2) and 98.8(2)°, respectively]. The monodentate ligands in the symmetrical $[Cu(NH_3)_5]^{2+}$ ion (Duggan *et al.*, 1980) allow nearly equal out-of-plane angles of 97.2 and 98.0°.

The semicoordinated BF_4^- ion has a bond length Cu—F(21) 2.692(5) Å. The occurrence of metal coordination by the BF_4^- anion is uncommon, though crystallographic data are available for a few examples (Foley *et al.*, 1983). The

Cu—F bond is variously described as "strong," 2.12(1) Å in $[Ni(en)_2(OH_2)/(FBF_3)]BF_4$ (Tomlinson *et al.*, 1972), "weak," 2.339(9) and 2.261(9) Å, in $Cu(FBF_3)(P(C_6H_5)_3)_3$ (Goughan *et al.*, 1974), or "semicoordinated," 2.56 Å in $[Cu(en)_2(FBF_3)_2]$ (Procter *et al.*, 1968). A unique example of a bridging "semicoordinated" $F_2BF_2^-$ ion having Cu—F distances 2.531(5) and 2.693(2) Å was recently reported (Velthuizen *et al.*, 1983). Our complex may therefore be categorized as containing a "semicoordinated" BF_4^- anion. This anion exhibits nearly tetrahedral geometry (F—B—F 103.9(7)-114.1(8)°, mean 109.4°], with the B—F bond distance [1.371(11) Å] of the "semicoordinated" fluorine atom being longer than the other three B—F distances [1.298-1.315(13) Å, mean 1.305 Å]. The ionic BF_4^- ion also has angles close to tetrahedral (F—B—F 106.8-112.6(7)°, mean 109.4°] but no short B—F distances [B—F 1.346-1.390(11) Å, mean 1.361 Å]. The presence of a Cu—F interaction is not unexpected because some related square-pyramidal CuN_5 cores involving similar bidentate and terdentate ligands (Ray and Hathaway, 1978; Duggan *et al.*, 1980; Ray *et al.*, 1981) show some tendency {$[Cu(dien)(bipyam)](ClO_4)_2 \cdot H_2O$ has a $Cu—O(OClO_3)$ bond distance of 2.56(7) Å in agreement with "semicoordination"} to coordinate an atom in the sixth position. It is worth noting that "semicoordination" does not occur for square-pyramidal CuN_5 complexes involving only σ-bonding ligands {$K[Cu(NH_3)_5](PF_6)_3$} (Duggan *et al.*, 1980) and $[Cu(en)_2(NH_3)](BF_4)_2$ (Ray, 1976). One may also deduce that tetragonal CuN_4 systems (Foley *et al.*, 1983) tend to "semicoordinate" anions (with either σ- or π-bonding N ligands) but may (BF_4^-) (Foley *et al.*, 1983) or may not (PF_6^-) (Foley *et al.*, 1984), depending on the anion. The predictability of "semicoordination" by BF_4^- or other normally ionic anions thus remains rather elusive.

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