Inorg. Chem. 1982, 21, 969-977

Contribution from the Department of Chemistry and the Materials Research Center,
Northwestern University, Evanston, Illinois 60201

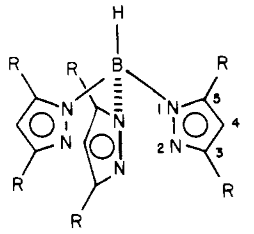
Metal Ion Binding Sites Composed of Multiple Nitrogenous Heterocycles. Synthesis and Spectral and Structural Study of Bis(2,2′,2′′-tripyridylamine)copper(II) Bis(trifluoromethanesulfonate) and Its Bis(acetonitrile) Adduct

PATRICIA L. DEDERT, JEFFERY S. THOMPSON, JAMES A. IBERS,* and TOBIN J. MARKS*

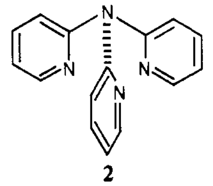
Received June 8, 1981

The copper complex $[Cu(N(py)_3)_2(CH_3CN)_2][SO_3CF_3]_2$, $N(py)_3$ = 2,2′,2′′-tripyridylamine, can be prepared by the reaction of $Cu(SO_3CF_3)_2$ with $N(py)_3$ in acetonitrile. The complex $Cu(N(py)_3)_2(SO_3CF_3)_2$ can be prepared from $Cu(SO_3CF_3)_2$ and $N(py)_3$ in methanol or by recrystallizing the bis(acetonitrile) complex from acetone/ether. The bis(acetonitrile) complex crystallizes in the monoclinic space group C_{2h}^5-$P2_1/n$ with two molecules in a unit cell of dimensions a = 11.825 (2) Å, b = 14.774 (3) Å, c = 11.516 (2) Å, and β = 97.699 (4)°. Least-squares refinement of the 193 variables led to a value of the conventional R index (on F) of 0.070 for 1669 reflections having $F_o^2 > 3\sigma(F_o^2)$. The geometry about the cupric ion is tetragonally distorted octahedral (crystallographically imposed symmetry $\bar{1}$) with two pyridyl rings from each *bidentate* $N(py)_3$ ligand defining the equatorial coordination. The Cu(II) ion and four nitrogen atoms are rigorously coplanar, with an average Cu–N distance of 2.020 (3) Å. The acetonitrile ligands occupy axial ligation positions with a Cu–N distance of 2.526 (8) Å. The above complexes have been studied by infrared, optical, and EPR spectroscopy. The vibrational spectroscopic results in the $N(py)_3$ and SO_3CF_3 skeletal regions are in accord with bidentate $N(py)_3$ coordination in both compounds. For $Cu(N(py)_3)_2(SO_3CF_3)_2$, axial triflate coordination is indicated. The optical and EPR spectral data are also in accord with these structural conclusions. For $[Cu(N(py)_3)_2(CH_3CN)_2][SO_3CF_3]_2$, the ^{14}N superhyperfine coupling shows the pyridyl and acetonitrile donors to be magnetically indistinguishable.

In recent years, research in this laboratory has focused on the synthesis and characterization of metal complexes of multidentate heterocyclic nitrogenous bases to serve as active site approximations for a number of copper proteins.[1,2] Studies on native systems have implicated the imidazole (histidine) residues as copper ligands in many of these metalloproteins.[3-5] However, the synthesis of accurate model compounds has been hampered at least in part by the paucity of structurally variable chelating ligands with two or more imidazole groups.[6] Consequently, our approach has been to substitute other nitrogenous heterocyclic bases for imidazole, in order to assemble copper binding environments that would serve as approximations or representations of the protein active sites. Such ligands have been chosen not only because of the chemical and structural similarities to imidazole (pK_a and mode of coordination to metal ions) but also because of the possibility that these ligands might constrain the copper(II) ion to unusual coordination geometries such as that demonstrated for the type I copper ion of the blue copper proteins.[4,5,7] Without the constraints imposed by a relatively rigid, multidentate ligand, copper(II) will adopt the familiar tetragonal (4 + 2) or square-pyramidal (4 + 1) coordination polyhedron.[8] As an example of the constraints that can be imposed, we have previously shown that pseudotetrahedral Cu(II) complexes with very high degrees of trigonal distortion can be prepared with the tripodlike poly(pyrazolyl)borate series of ligands **1**.[1,2]



1, R = H or CH_3



2

Another multidentate ligand composed of heterocyclic nitrogenous bases, 2,2′,2′′-tripyridylamine ($N(py)_3$) (**2**) seemed worthy of investigation because the ligand appears capable of forming rigidly nontetragonal copper complexes by coordination through the three pyridyl nitrogen atoms.[9] We also anticipated that this ligand might more closely approximate the active-site ligands of copper proteins than do the poly(pyrazolyl)borates because the pK_a values of pyridine and imidazole are more comparable than are the pK_a values of various pyrazoles and imidazole.[10] Although copper(II) complexes of **2** have been known for a number of years,[11-13]

---

(1) (a) Arcus, C. S.; Wilkinson, J. L.; Mealli, C.; Marks, T. J.; Ibers, J. A. *J. Am. Chem. Soc.* **1974**, *96*, 7564-7565. (b) Mealli, C.; Arcus, C. S.; Wilkinson, J. L.; Marks, T. J.; Ibers, J. A. *Ibid.* **1976**, *98*, 711-718.

(2) (a) Thompson, J. S.; Marks, T. J.; Ibers, J. A. *Proc. Natl. Acad. Sci. U.S.A.* **1977**, *74*, 3114-3118. (b) Thompson, J. S.; Marks, T. J.; Ibers, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 4180-4192. (c) Thompson, J. S.; Sorrell, T.; Marks, T. J.; Ibers, J. A. *Ibid.* **1979**, *101*, 4193-4200. (d) Thompson, J. S.; Zitzmann, J. L.; Marks, T. J.; Ibers, J. A. *Inorg. Chim. Acta* **1980**, *46*, L101-L105. (e) Marks, T. J. *Fundam. Res. Homogeneous Catal.* **1978**, *2*, 285-300.

(3) (a) Colman, P. M.; Freeman, H. C.; Guss, J. M.; Murata, M.; Norris, V. A.; Ramshaw, J. A. M.; Venkatappa, M. P. *Nature (London)*, **1978**, *272*, 319-324. (b) Adman, E. T.; Stenkamp, R. E.; Sieker, L. C.; Jensen, L. H. *J. Mol. Biol.* **1978**, *123*, 35-47.

(4) (a) Salvato, B.; Zatta, P.; Ghiretti-Magaldi, A.; Ghiretti, F. *FEBS Lett.* **1973**, *32*, 35-36. (b) Wood, E. J.; Bannister, W. H. *Biochim. Biophys. Acta* **1968**, *154*, 10-16. (c) Van Holde, K. E. *Biochemistry* **1967**, *6*, 93-99.

(5) (a) Solomon, E. I.; Hare, J. W.; Gray, H. B. *Proc. Natl. Acad. Sci. U.S.A.* **1976**, *73*, 1389-1393. (b) Siiman, O.; Young, N. M.; Carey, P. R. *J. Am. Chem. Soc.* **1976**, *98*, 744-748. (c) Bereman, R. D.; Kosman, D. J. *Ibid.* **1977**, *99*, 7322-7325.

(6) Tang, C. C.; Davalian, D.; Huang, P.; Breslow, R. *J. Am. Chem. Soc.* **1978**, *100*, 3918-3922.

(7) Miskowski, V.; Tang, S. P. W.; Spiro, T. G.; Shapiro, E.; Moss, T. H. *Biochemistry* **1975**, *14*, 1244-1250.

(8) (a) Cotton, F. A.; Wilkinson, G. W. "Advanced Inorganic Chemistry", 4th ed.; Interscience: New York, 1980; pp 811-818. (b) Freeman, H. C. In "The Biochemistry of Copper"; Peisach, J., Aisen, P., Blumberg, W. E., Eds.; Academic Press: New York, 1966, pp 77-113. (c) Freeman, H. C. In "Inorganic Biochemistry"; Eichhorn, G. L., Ed.; Elsevier: Amsterdam, 1973; Vol. 1, pp 121-166. (d) Freeman, H. C. *Adv. Protein Chem.* **1967**, *22*, 257-424. (e) Buckingham, D. In "Inorganic Biochemistry"; Eichhorn, G. L., Ed.; Elsevier: Amsterdam, 1973; Vol. 1, pp 3-62. (f) Wells, A. F. "Structural Inorganic Chemistry", 3rd ed.; Oxford University Press: London, 1967; pp 856-886. (g) Osterberg, R. *Coord. Chem. Rev.* **1974**, *12*, 309-347.

(9) McWhinnie, W. R. *Coord. Chem. Rev.* **1970**, *5*, 293-311.

(10) Rappoport, Z., Ed. "CRC Handbook of Tables for Organic Compound Identification", 3rd ed.; Chemical Rubber Co: Cleveland, Ohio, 1967. The pK_a values of the conjugate acids (BH^+) of the bases imidazole, pyridine, 3,5-dimethylpyrazole, and pyrazole are 6.95, 5.25, 4.38, and 2.48, respectively.

(11) McWhinnie, W. R.; Kulasingam, G. C.; Draper, J. C. *J. Chem. Soc. A* **1966**, 1199-1203.

(12) Kulasingam, G. C.; McWhinnie, W. R. *J. Chem. Soc. A* **1967**, 1253-1255.

0020-1669/82/1321-0969$01.25/0 © 1982 American Chemical Society

little is known about the molecular structures of these compounds. Indeed, the structures of 2,2′-dipyridylamine, 2,2′,2″-tripyridylamine,[9,14-16] 2,2′-dipyridyl sulfide,[17] and 2,2′,2″-tripyridylphosphine[18] complexes have been inferred largely on the basis of infrared spectroscopic correlations. Recent diffraction results on a 2,2′-dipyridylamine Cu(II) complex casts some doubt on the reliability of such spectral correlations.[19,20] For these reasons, we initiated a synthetic, spectroscopic, and X-ray diffraction structural investigation of the properties of (tripyridylamine)copper(II) complexes.

In the course of our investigations with **2**, a crystalline complex was isolated that contained two $N(py)_3$ ligands per copper ion. The presence of acetonitrile could be detected by elemental and infrared analysis, but the coordination of the acetonitrile could not be unambiguously established by these methods. Coordination of acetonitrile would appear to require the ligand $N(py)_3$ to act as a bidentate ligand.

We report here the crystal and molecular structure of $[Cu(N(py)_3)_2(CH_3CN)_2][SO_3CF_3]_2$ (**3**). When the diffraction results are correlated with vibrational, electronic, and EPR data, ligational as well as structure–spectra criteria emerge that should be useful in assessing chelation modes of Cu(II) ions by $N(py)_3$ and related ligands, as well as by triflate.

Experimental Section

Analytical and Physical Measurements. All elemental analyses were performed by Miss H. Beck of the Analytical Services Laboratory of Northwestern University.

Electronic spectra were recorded on a Cary 17D spectrophotometer. The copper(II) complexes were examined in CH_3CN or CH_2Cl_2 solution or as Nujol mulls between quartz windows. Some solution spectra were recorded at −78 °C with the use of a low-temperature cell. Infrared spectra of Nujol or Fluorolube mulls between KBr windows were recorded on a Perkin-Elmer 267 or 283 spectrophotometer. A Varian E-4 X-band EPR spectrometer was used to obtain spectra of frozen glasses or polycrystalline samples at 77 K and at room temperature. Samples were studied in quartz capillary tubes fitted with Schlenk connections. EPR spectra were calibrated with diphenylpicrylhydrazyl or a Varian strong-pitch sample.

Reagents and Syntheses. Solvents were distilled under an N_2 atmosphere from an appropriate drying agent. Trifluoromethanesulfonic acid was purchased from the Aldrich Chemical Co. and was subjected to vacuum trap-to-trap distillation before use.

Standard Schlenk techniques were employed to prepare the starting material, cupric triflate, $Cu(SO_3CF_3)_2$.[21] It was thoroughly dried by heating in vacuo until a granular white powder was obtained. Unless it is handled in a dry atmosphere, this compound is rapidly hydrated to become pale blue. The ligand, $N(py)_3$, was prepared by a literature procedure[22] and was recrystallized from hot water to obtain a product with a satisfactory elemental analysis and melting point.

Preparation of $[Cu(N(py)_3)_2(CH_3CN)_2][SO_3CF_3]_2$ (3). Cupric triflate (0.20 g, 0.55 mmol) was mixed with 2 equiv of solid $N(py)_3$ (0.27 g, 1.1 mmol) in an atmosphere of prepurified nitrogen. Next, 5 mL of CH_3CN was added to the flask by syringe. A blue solution resulted, which rapidly turned a clear, dark green. After 20 min of stirring, a light-colored solid precipitated. The green supernatant was removed by syringe, and the remaining gray-green powder was washed with ether and then dried in vacuo until the C–N stretch of CH_3CN was no longer visible in the infrared region. This crude product represented an approximately 60% yield, based on copper.

Table I. Crystal Data for $[Cu(N(py)_3)_2(CH_3CN)_2][SO_3CF_3]_2$

mol formula	$C_{36}H_{30}CuF_6N_{10}O_6S_2$
mol wt	940.37
a, Å	11.825 (2)
b, Å	14.774 (3)
c, Å	11.516 (2)
β, deg	97.699 (4)
V, Å^3	1994
Z	2
ρ_c, g/cm^3	1.566
space group	$C_{2h}^5 - P2_1/n$
cryst faces	{010}, {$\bar{1}$01}, {100}, {001}, $V = 0.0027$ mm^3
radiation	Cu Kα_1 (λ(Cu Kα_1) 1.540 562 Å), Ni filtered
scan speed, deg/min	2 in 2θ
scan range	0.9° below Kα_1 to 0.9° above Kα_2
2θ limits	$5° \leq 2\theta \leq 110°$
receiving aperture	5.5 mm wide × 3.5 mm high, 32 cm from crystal
bkgd counting time, s	20 with rescan option[a]
temp, °C	24
abs coeff, cm^{-1}	24.85
transmission coeff	0.622–0.766
unique data used ($F_o^2 > 3\sigma(F_o^2)$)	1669
no. of variables	193
R	0.070
R_w	0.072

[a] The diffractometer was operated under the disk-oriented Vanderbilt system: Lenhert, P. G. *J. Appl. Crystallogr.* 1975, *8*, 568–570.

Very dark green, almost black, air-stable crystals were obtained by dissolving the crude product in hot CH_3CN under an N_2 atmosphere, followed by slow cooling to freezer temperature (−15 °C). Anal. Calcd for $C_{36}H_{30}CuF_6N_{10}O_6S_2$: C, 45.98; H, 3.22; N, 14.90. Found: C, 45.55; H, 3.27; N, 14.62.

Complete IR data (Nujol mull): 3097 w, 3068 w, 2300 w, 2270 m, 1660 vw, 1609 s, 1592 s, 1570 s, 1490 s, 1478 vs, 1440 vs, 1430 vs, 1332 s, 1270 vs, br, 1223 s, 1158 vs, 1122 m, 1060 m, 1030 vs, 993 m, 958 w, 938 w, 922 vw, 798 s, 782 sh, 777 m, 761 m, 754 w, 749 vw, 741 m, 664 m, 658 m, 649 s, 633 vs, 619 w, 572 m, 550 m, 518 s, 462 w, 448 m, 408 w cm^{-1}.

In connection with experiments to be described elsewhere,[23] another, less direct synthesis of the complex $[Cu(N(py)_3)_2(CH_3CN)_2]$-$[SO_3CF_3]_2$ was achieved by the injection of molecular oxygen (in 0.5-mol quantities) into the N_2 atmosphere above a solution of the cuprous complex $Cu(N(py)_3)(SO_3CF_3)$[23] in CH_3CN. After prolonged standing at −15 °C with no product crystallizing from the solution, ether was carefully layered atop the solution. A few days later, a small amount of crystalline product was isolated. The product appeared to be a mixture of green and lavender crystals, but under appropriate lighting the lavender crystals also appeared green. One of these lavender crystals was chosen for X-ray analysis. This indirect synthesis is not strictly reproducible, as the formation of $[Cu_4(OH)_4$-$(SO_3CF_3)_2(N(py)_3)_4][SO_3CF_3]_2$[23] usually interferes with the isolation of the small yield of $[Cu(N(py)_3)_2(CH_3CN)_2][SO_3CF_3]_2$.

Preparation of $Cu(N(py)_3)_2(SO_3CF_3)_2$ (4). The crude product isolated from CH_3CN (vide supra) was dissolved in acetone in the presence of air. Addition of ether induced the formation of shiny green crystals, which did not contain either acetone or acetonitrile. Anal. Calcd for $C_{32}H_{24}CuF_6N_8O_6S_2$: C, 44.78; H, 2.82; N, 13.06. Found: C, 44.03; H, 2.84; N, 12.84.

Complete IR data (Nujol mull): 3103 vw, 3057 vw, 1602 s, 1590 s, 1564 s, 1485 s, 1472 vs, 1462 vs, 1437 vs, 1428 vs, 1329 s, 1290 vs, 1286 sh, 1268 vw, 1242 vs, 1223 s, 1158 vs, 1142 sh, 1126 vw, 1120 vw, 1058 w, 1028 vs, 998 w, 967 vw, 952 w, 933 w, 882 w, 782 m, 772 s, 753 s, 747 m, 741 w, 737 w, 667 vw, 661 vw, 654 vw, 643 w, 633 s, 618 w, 572 m, 547 m, 517 m, 470 w, br, 460 w, 442 m, 432 w, 417 w, 407 w cm^{-1}.

Green crystals of $Cu(N(py)_3)_2(SO_3CF_3)_2$ were also isolated when cupric triflate was reacted with 2 equiv of $N(py)_3$ in methanol, as

---

(13) Kulasingam, G. C.; McWhinnie, W. R. *J. Chem. Soc A* **1968**, 254–258.
(14) Kulasingam, G. C.; Lancaster, J. C.; McWhinnie, W. R.; Watts, J. B. *Spectrochim. Acta, Part A* **1970**, *26A*, 835–839.
(15) Lancaster, J. C.; McWhinnie, W. R.; Welham, P. L. *J. Chem. Soc. A* **1971**, 1742–1746.
(16) McWhinnie, W. R. *J. Chem. Soc. A* **1964**, 5165–5169.
(17) Driver, R.; Walker, W. R. *Aust. J. Chem.* **1968**, *21*, 331–337.
(18) Boggess, R. K.; Zatko, D. A. *J. Coord. Chem.* **1975**, *4*, 217–224.
(19) Johnson, J. E.; Jacobson, R. A. *J. Chem. Soc., Dalton Trans.* **1973**, 580–584.
(20) Johnson, J. E.; Beineke, T. A.; Jacobson, R. A. *J. Chem. Soc. A* **1971**, 1371–1374.
(21) Jenkins, C. L.; Kochi, J. K. *J. Am. Chem. Soc.* **1972**, *94*, 843–855.
(22) Wibaut, J. P.; LaBastide, G. L. C. *Recl. Trav. Chim. Pays-Bas* **1933**, *52*, 493–498.
(23) Dedert, P. L.; Sorrell, T.; Marks, T. J.; Ibers, J. A., submitted for publication.

Table II. Positional and Thermal Parameters for the Nongroup Atoms of $[Cu(N(py)_3)_2(CH_3CN)_2][SO_3CF_3]_2$

ATOM	X[A]	Y	Z	B11[B]	B22	B33	B12	B13	B23
CU	1/2	0	-1/2	71.1(15)	36.09(88)	77.1(15)	-10.9(11)	10.9(11)	-1.4(11)
S	0.19054(26)	0.13706(20)	-0.17743(25)	132.8(31)	66.4(17)	108.0(28)	3.5(20)	14.5(24)	-4.6(19)
O(1)	0.22050(68)	0.21556(49)	-0.10434(66)	201.(10)	65.6(46)	188.(10)	-28.0(56)	-3.0(78)	-41.3(58)
O(2)	0.27649(61)	0.06670(53)	-0.17085(60)	134.8(80)	108.2(60)	145.0(85)	52.7(59)	14.3(63)	-13.2(56)
O(3)	0.13314(56)	0.15454(43)	-0.29092(53)	145.5(76)	69.4(45)	93.7(62)	-3.5(47)	-10.5(57)	12.3(44)
F(1)	0.03750(59)	0.01473(44)	-0.16938(60)	211.6(89)	67.8(43)	193.3(84)	-30.7(51)	12.0(67)	0.2(51)
F(2)	-0.00269(59)	0.14347(54)	-0.09730(62)	148.8(76)	139.7(62)	213.2(93)	37.9(57)	64.5(68)	-28.9(62)
F(3)	0.12107(59)	0.05695(55)	-0.00077(58)	187.5(88)	184.9(74)	123.9(72)	-9.4(64)	16.3(63)	59.4(61)
N(4)	0.14350(51)	0.40806(40)	0.20564(52)	76.0(63)	25.9(34)	70.0(59)	9.4(37)	13.1(47)	1.7(38)
N(5)	0.42305(68)	0.15193(53)	-0.44734(70)	106.8(87)	47.5(48)	119.7(87)	-6.9(53)	1.3(67)	-14.6(55)
C(16)	0.0822(11)	0.08404(82)	-0.1076(10)	147.(14)	68.1(75)	116.(12)	0.1(87)	0.(10)	-10.1(82)
C(17)	0.38755(83)	0.21606(70)	-0.41658(89)	97.(10)	45.2(57)	135.(12)	-15.1(66)	20.0(85)	-15.5(71)
C(18)	0.3426(10)	0.30030(71)	-0.3731(11)	155.(14)	48.3(64)	266.(19)	-6.7(79)	63.(13)	-21.3(93)
N(3)	0.09881(88)	0.31759(52)	0.35767(80)	266.(15)	38.7(48)	151.(11)	-18.5(68)	113.(10)	-5.2(59)
C(11)	0.13968(72)	0.32209(57)	0.25874(74)	78.9(84)	41.1(52)	72.9(79)	-5.5(53)	13.5(66)	2.4(53)
C(12)	0.17283(82)	0.24546(67)	0.20695(93)	127.(11)	46.7(59)	177.(13)	31.2(66)	89.4(99)	34.7(73)
C(13)	0.16646(93)	0.16310(67)	0.2586(11)	151.(13)	45.0(62)	195.(15)	32.7(71)	66.(11)	41.7(82)
C(14)	0.1259(10)	0.15884(67)	0.36319(98)	185.(15)	37.1(59)	133.(12)	3.3(75)	27.(11)	20.4(74)
C(15)	0.0920(13)	0.23381(76)	0.4063(10)	365.(24)	45.1(68)	142.(14)	-39.(11)	134.(15)	11.1(80)

[a] Estimated standard deviations in the least significant figure(s) are given in parentheses in this and all subsequent tables. [b] The form of the anisotropic thermal ellipsoid is as follows: $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)]$. The quantities given in the table are the thermal coefficients × 10^4.

Table III. Derived Parameters for the Rigid-Group Atoms of $[Cu(N(py)_3)_2(CH_3CN)_2][SO_3CF_3]_2$

ATOM	X	Y	Z	B, A^2	ATOM	X	Y	Z	B, A^2
N(1)	0.46620(39)	0.03907(32)	0.33099(29)	3.59(14)	N(2)	0.16455(29)	0.45915(30)	0.01554(40)	3.62(14)
C(1)	0.40563(39)	-0.01412(26)	0.25041(40)	3.29(15)	C(6)	0.21216(39)	0.41957(33)	0.11563(34)	3.48(16)
C(2)	0.38516(42)	0.01085(35)	0.13266(36)	4.12(17)	C(7)	0.32647(41)	0.39326(35)	0.13193(36)	4.88(18)
C(3)	0.42863(47)	0.09188(38)	0.10014(32)	5.00(20)	C(8)	0.39034(30)	0.40876(36)	0.04261(47)	4.48(19)
C(4)	0.49026(48)	0.14643(29)	0.18121(47)	4.82(20)	C(9)	0.34290(39)	0.44890(37)	-0.05941(39)	4.37(18)
C(5)	0.50782(42)	0.11772(30)	0.29762(40)	4.38(19)	C(10)	0.22814(40)	0.47367(32)	-0.07042(32)	4.02(18)

RIGID GROUP PARAMETERS

GROUP	X_C[A]	Y_C	Z_C	DELTA[B]	EPSILON	ETA
PY1	0.44742(27)	0.06548(24)	0.21556(29)	-0.5512(33)	-2.9761(29)	-1.8599(31)
PY2	0.27745(28)	0.43395(20)	0.02907(28)	-0.2301(78)	1.9328(33)	-0.0472(79)

[a] x_c, y_c and z_c are the fractional coordinates of the origin of the rigid group. [b] The rigid-group orientation angles (in radians) have been defined previously: La Placa, S. J.; Ibers, J. A. *Acta Crystallogr.* 1965, *18*, 511–519.

in the above preparation of $[Cu(N(py)_3)_2(CH_3CN)_2][SO_3CF_3]_2$. The infrared spectrum of this product was identical with that of the aforementioned product crystallized from acetone.

X-ray Data Collection for $[Cu(N(py)_3)_2(CH_3CN)_2][SO_3CF_3]_2$ (3). The lavendar crystal chosen for data collection was grown from an acetonitrile solution of $Cu(N(py)_3)(SO_3CF_3)$ and molecular oxygen at −15 °C. The crystal was mounted in a glass capillary under an inert atmosphere. Examination of the crystal by Weissenberg and precession methods established that it belongs to the monoclinic system. The space group C_{2h}^5–$P2_1/n$, deduced from the systematic absences, was confirmed ultimately by successful refinement of the structure. With two molecules in the unit cell, a center of inversion is imposed on the cation. The lattice constants were determined by a least-squares analysis[24] of the angle settings of 17 hand-centered reflections in the range 45° > 2θ > 31° with Cu Kα radiation. The refined cell constants and other relevant crystal data are given in Table I.

Intensity data were collected by the standard θ–2θ technique with Ni-filtered Cu Kα radiation at a takeoff angle of 3.0°. During the data collection, 6 standard reflections were collected after every 100 reflections. There was no significant variation of these standard reflections during data collection. The intensity data were processed as previously described,[24] with the parameter p chosen as 0.04. Of the 2639 unique reflections collected, 1669 independent reflections were found with intensity greater than $3\sigma(I_0)$ and were used in the subsequent solution and refinement of the structure.

Solution and Refinement of the Structure. The structure was solved by direct methods. The copper, sulfur, and copper-bonded pyridine nitrogen atoms were found in the first Fourier map and the remaining nonhydrogen atoms in subsequent maps. The three pyridine rings in the asymmetric unit were refined initially as rigid bodies.[25] Scattering factors and anomalous dispersion terms for the copper and sulfur atoms were taken from the usual sources.[26] On the final cycle all atoms but the two coordinated pyridine rings were refined anisotropically. These two rings were refined as rigid bodies. All hydrogen atoms were included at their idealized positions as fixed contributions. This final cycle with 1669 independent reflections and 193 variables converged to values of R and R_w of 0.070 and 0.072. The largest peaks in the final difference Fourier map were approximately of height 0.4 e Å^{-3}.

The final positional and thermal parameters for the nongroup atoms along with their estimated standard deviations are given in Table II. Table III lists the derived parameters for the atoms belonging to the two rigid groups. The root-mean-square amplitudes of vibrations for the anisotropic atoms are listed in Table IV.[27] Table V lists the idealized positions of the hydrogen atoms.[27] Table VI is a listing of $10|F_o|$ and $10|F_c|$.[27]

Results and Discussion

Synthesis and Properties. The copper(II) complex of formula $[Cu(N(py)_3)_2(CH_3CN)_2][SO_3CF_3]_2$ (3) can be synthesized in good yield via the route of eq 1 and can also be produced (albeit less directly, and in much smaller yield) by the reaction of molecular oxygen with the $N(py)_3$ complex of

---

(24) Doedens, R. J.; Ibers, J. A. *Inorg. Chem.* **1967**, *6*, 204–210.

(25) La Placa, S. J.; Ibers, J. A. *Acta Crystallogr.* **1965**, *18*, 511–519.

(26) Cromer, D. T.; Waber, J. T. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, Tables 2.2A and 2.3.1.

(27) Supplementary material.

$$\mathrm{Cu(SO_3CF_3)_2 + 2N(py)_3 \xrightarrow{CH_3CN} [Cu(N(py)_3)_2(CH_3CN)_2][SO_3CF_3]_2} \quad (1)$$

Cu(I), as described in the Experimental Section. The product of these syntheses is usually green, but on occasion a mixture of green and lavender crystals is produced. The two types of crystals are analytically identical and display indistinguishable infrared spectra. In addition, some product crystals appear either green or lavender depending on the illumination. A unit cell determination of one of the green crystals showed it to display qualitatively the same intensities and unit cell constants as the lavender crystal used in the full structure determination. Thus, the green and lavender forms of complex **3** are rather similar, and any differences appear at most to reflect the type of "distortion isomerism" common to Cu(II) complexes.[28] Such effects are also evident in the thermochromism displayed by **3** (vide infra).

The complex $\mathrm{Cu(N(py)_3)_2(SO_3CF_3)_2}$ (**4**) is readily prepared in several polar solvents (eq 2), and spectral studies as well as analytical data show that solvent is not present either coordinated to the copper ion or uncoordinated in the structure. Unlike compound **3**, this complex is invariably green in color. Both **3** and **4** are stable in air at room temperature.

$$\mathrm{Cu(SO_3CF_3)_2 + 2N(py)_3 \xrightarrow{methanol} Cu(N(py)_3)_2(SO_3CF_3)_2} \quad (2)$$

Description of the Structure of $\mathrm{[Cu(N(py)_3)_2(CH_3CN)_2][SO_3CF_3]_2}$, (3). The overall crystal structure of the complex $\mathrm{[Cu(N(py)_3)_2(CH_3CN)_2][SO_3CF_3]_2}$ is apparent in the stereoscopic drawing of the unit cell shown in Figure 1. The structure consists of monomeric $\mathrm{[Cu(N(py)_3)_2(CH_3CN)_2]^{2+}}$ cations and associated $\mathrm{SO_3CF_3^-}$ anions. Shown in Figure 2 is the structure of the cation. The geometry of the copper coordination sphere is elongated tetragonal, which is typical of six-coordinate copper(II) complexes.[8,29-31] Two acetonitrile molecules are coordinated to the copper ion in the axial positions. Each $\mathrm{N(py)_3}$ ligand coordinates equatorially through the pyridine nitrogen atoms of two (rings 1 and 2) of the three pyridyl rings. Because the copper ion occupies a crystallographic inversion center, the coordinated pyridyl nitrogen atoms and the copper ion are rigorously coplanar. The bidentate nature of the $\mathrm{N(py)_3}$ ligand contrasts with its mode of bonding in the $\mathrm{Fe(N(py)_3)_2^{2+}}$ and $\mathrm{Co(N(py)_3)_2^{2+}}$ perchlorate salts where each $\mathrm{N(py)_3}$ acts as a rigorously tridentate ligand.[32]

The elongated tetragonal symmetry can be seen more clearly in Figure 3, which diagrams the copper inner-coordination sphere. The equatorial ligands do not form a square plane; rather, the geometry is typical of bis-chelating ligands in that the interligand N–N distance (N(1)–N(2)′ = 2.947 (5) Å) is longer than the intraligand N–N distance (N(1)–N(2) = 2.764 (6) Å).[33] A rectangular rather than a square basal plane is the result. Note also that the acetonitrile ligand is not perpendicular to the equatorial plane. With the bond angles of N(5)–Cu–N(1) = 86.9 (2)° and N(5)–Cu–N(2) = 85.0 (2)°, each $\mathrm{CH_3CN}$ ligand slants slightly toward an uncoordinated pyridine ring.

Table VII. Selected Bond Distances (Å) and Angles (Deg) for $\mathrm{[Cu(N(py)_3)_2(CH_3CN)_2][SO_3CF_3]_2}$

	Copper Inner Coordination Sphere		
Cu-N(1)	2.018 (3)	N(1)-Cu-N(2)	86.3 (2)
Cu-N(2)	2.022 (4)	N(1)-Cu-N(5)	86.9 (2)
Cu-N(5)	2.526 (8)	N(2)-Cu-N(5)	85.0 (2)
	Amine Nitrogen Atom		
N(4)-C(1)	1.412 (7)	C(1)-N(4)-C(6)	118.1 (5)
N(4)-C(6)	1.410 (8)	C(1)-N(4)-C(11)	122.6 (6)
N(4)-C(11)	1.413 (9)	C(6)-N(4)-C(11)	118.8 (6)
	Ring 3[a]		
N(3)-C(11)	1.300 (10)	C(11)-N(3)-C(15)	117.1 (9)
C(11)-C(12)	1.362 (11)	C(12)-C(11)-N(3)	120.3 (9)
C(12)-C(13)	1.361 (12)	C(12)-C(11)-N(4)	122.0 (8)
C(13)-C(14)	1.356 (13)	N(3)-C(11)-N(4)	117.6 (8)
C(14)-C(15)	1.299 (14)	C(11)-C(12)-C(13)	121.1 (9)
C(15)-N(3)	1.365 (12)	C(12)-C(13)-C(14)	118.5 (10)
		C(13)-C(14)-C(15)	117.6 (10)
		C(14)-C(15)-N(3)	125.4 (11)
	Trifluoromethanesulfonate Anion		
S-O(1)	1.449 (7)	O(1)-S-O(2)	115.4 (5)
S-O(2)	1.449 (7)	O(1)-S-O(3)	116.1 (5)
S-O(3)	1.413 (6)	O(2)-S-O(3)	115.2 (4)
S-C(16)	1.782 (12)	O(1)-S-C(16)	103.0 (5)
C(16)-F(1)	1.317 (11)	O(2)-S-C(16)	101.7 (5)
C(16)-F(2)	1.351 (12)	O(3)-S-C(16)	102.3 (5)
C(16)-F(3)	1.317 (11)	F(1)-C(16)-F(2)	107.7 (10)
		F(1)-C(16)-F(3)	109.5 (10)
		F(2)-C(16)-F(3)	106.6 (10)
		F(1)-C(16)-S	111.1 (9)
		F(2)-C(16)-S	110.0 (8)
		F(3)-C(16)-S	111.9 (9)
	Acetonitrile Group		
N(5)-C(17)	1.113 (11)	C(17)-N(5)-Cu	174.8 (9)
C(17)-C(18)	1.467 (13)	N(5)-C(17)-C(18)	178.5 (12)

[a] Rings 1 and 2 were refined as rigid bodies based on the following bond distances and angles, starting at N, around the ring: 1.35, 1.39, 1.38, 1.37, 1.39, 1.34 Å; 119, 122, 118, 121, 118, 122°.

Selected bond distances and angles are presented in Table VII. The average in-plane Cu–N distance of 2.020 (3) Å is equal to that found in nearly all Cu(II) complexes of this geometry, regardless of whether the nitrogen is sp^3 or sp^2 hybridized.[29] Elongated tetragonal complexes of copper show a large variation in the out-of-plane bond lengths. This parameter is greater than 2.6 Å in some of the complexes of copper with nonaromatic nitrogen ligands,[34] and as low as 2.2 Å in the tris(bipyridyl)copper(II) complex.[35] The present value of 2.526 (8) Å is within this range, and the value of 0.80 for the tetragonality factor R_S/R_L[36] (R_S = short copper–ligand distance, R_L = long copper–ligand distance) is also typical of elongated tetragonal complexes of copper(II).[36,37]

Although the metal ion coordination geometry in $\mathrm{[Cu(N(py)_3)_2(CH_3CN)_2][SO_3CF_3]_2}$ is typical of six-coordinate copper(II) complexes, the *bidentate* manner in which the $\mathrm{N(py)_3}$ ligands coordinate to the copper ion is unprecedented. The expected mode of coordination is the tridentate configuration found in the aforementioned $\mathrm{[M(N(py)_3)_2][ClO_4]_2}$ complexes, where M = Fe, Co.[32]

The present structure is also unusual in that the coordinated heterocyclic nitrogen atoms rigorously define a plane about the copper ion, in a traditional tetragonally distorted octahedral coordination sphere. In contrast, when two 2,2′-bipyridyl

---

(28) Gažo, J.; Bersuker, I. B.; Garaj, J.; Kabešová, M.; Kohout, J.; Langfelderová, H.; Melnik, M.; Serator, M.; Valach, F. *Coord. Chem. Rev.* **1976**, *19*, 253–297.

(29) Hathaway, B. J.; Hodgson, P. G. *J. Inorg. Nucl. Chem.* **1973**, *35*, 4071–4081.

(30) Holm, R. H.; Everett, G. W.; Chakravorty, A. *Prog. Inorg. Chem.* **1964**, *7*, 83–214.

(31) Holm, R. H.; O'Connor, M. J. *Prog. Inorg. Chem.* **1971**, *14*, 241–401.

(32) (a) Kucharski, E. S.; McWhinnie, W. R.; White, A. H. *Aust. J. Chem.* **1978**, *31*, 53–56. (b) *Ibid.* **1978**, *31*, 2647–2650.

(33) An explanation of the numbering scheme is required. Atoms belonging to the pyridyl rings are assigned as follows: ring 1, N(1) and C(1)–C(5); ring 2, N(2) and C(6)–C(10); ring 3, N(3) and C(11)–C(15). The numbering scheme for the acetonitrile group is shown in Figures 1 and 2. The atom C(16) is the trifluoromethanesulfonate carbon atom, which is bonded to the sulfur atom and the three fluorine atoms. The amine nitrogen atom, N(4), is bonded to C(1), C(6), and C(11).

(34) Hathaway, B. J.; Tomlinson, A. G. *Coord. Chem. Rev.* **1970**, *5*, 1–43.

(35) Anderson, O. P. *J. Chem. Soc., Dalton Trans.* **1972**, 2597–2601.

(36) Hathaway, B. J. *Struct. Bonding (Berlin)* **1973**, *14*, 49–67.

(37) Hathaway, B. J. *J. Chem. Soc., Dalton Trans.* **1972**, 1196–1199.

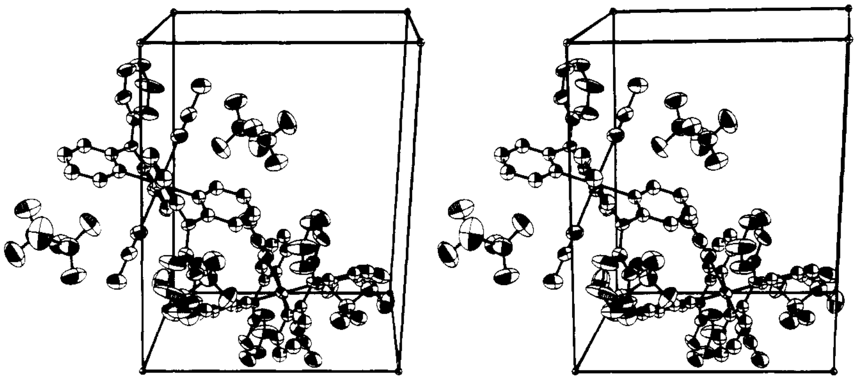


Figure 1. Stereoview of the unit cell of $[Cu(N(py)_3)_2(CH_3CN)_2][SO_3CF_3]_2$. The *y* axis is almost vertical and the *x* axis horizontal and to the right. Vibrational ellipsoids are drawn at the 40% probability level.

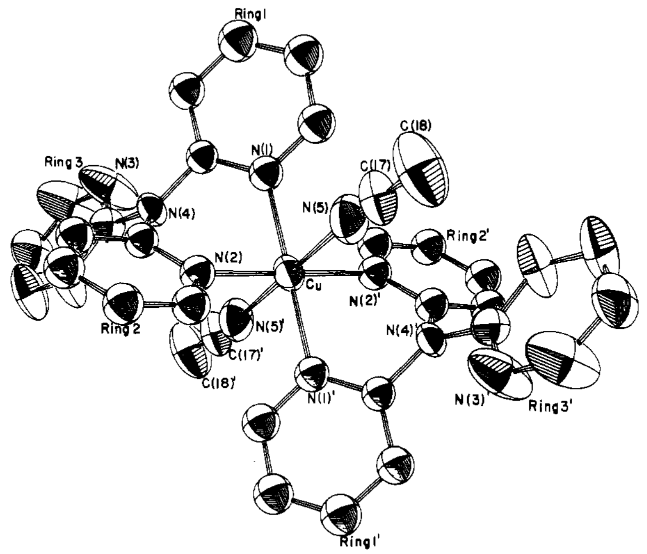


Figure 2. Molecular structure of $[Cu(N(py)_3)_2(CH_3CN)_2]^{2+}$, with H atoms omitted. The 40% probability thermal ellipsoids are shown.

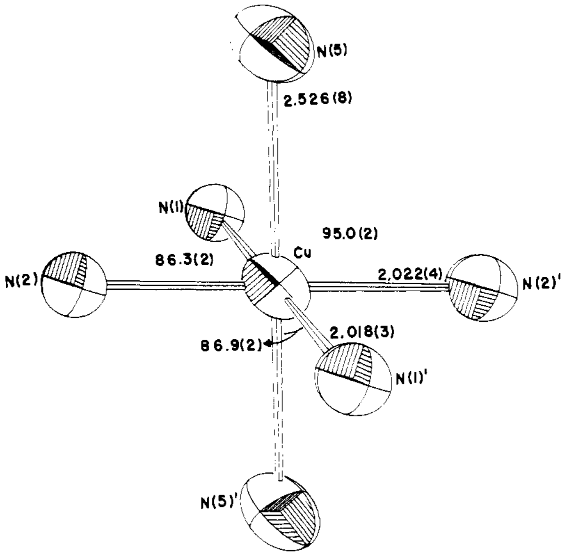


Figure 3. View of the coordination sphere about the copper ion in $[Cu(N(py)_3)_2(CH_3CN)_2]^{2+}$.

molecules coordinate to a cupric ion, no such coplanar arrangement is observed, as in such a disposition there would be severe steric interference between the 6- and 6′-hydrogen atoms of the bipyridyl ligand.[38,39] In several other cases of biscoordination of 2,2′-bipyridyl to Cu(II), the environment around the metal ion has been found to be trigonal bipyramidal, with only two bipyridyl nitrogen atoms in the equatorial plane.[38,40,41] In the closest known example of coplanar coordination of two 2,2′-bipyridyl ligands,[39] $[Cu(ClO_4)(bpy)_2][ClO_4]$, the four nitrogen atoms are arranged in a flattened tetrahedral manner, the copper coordination sphere approximating a tetragonally distorted octahedron with bridging perchlorate ions in the axial positions. The dihedral angle between the two Cu–bipyridyl planes is 37°.

The ligand 2,2′-dipyridylamine ($NH(py)_2$) is more closely analogous to the bidentate form of $N(py)_3$ than is bipyridyl. Some investigators have concluded[42,43] that, as for bipyridyl, steric interactions prevent two $NH(py)_2$ ligands or two $N(py)_2^-$ ligands from being coplanar in a copper(II) complex. In structural studies of copper(II) complexes with two $NH(py)_2$ ligands,[19,20] such a planar arrangement of the ligands has never been observed. Instead, a pseudotetrahedral Cu(II) environment was found in the structure of $[Cu(NH(py)_2)_2][ClO_4]_2$,[20] and the complex $[Cu(NH(py)_2)_2I]I$ was found[19] to have trigonal-bipyramidal coordination about the cupric ion, as in $[Cu(bpy)_2I]I$.[38] The bis complexes of Cu(II) with deprotonated 3,3′-dimethyl-2,2′-dipyridylamine, deprotonated dipyridylamine, and 2-pyridyl-2-pyrimidylamine also display pseudotetrahedral coordination geometries.[43–45] The structural results for **3** demonstrate that two $N(py)_3^-$ ligands can coordinate in the basal plane of a copper(II) complex, just as two $N(py)_2^-$ ligands form a square-planar complex with palladium(II).[46]

In the present structure, there is a 56.3° dihedral angle between the two coordinated pyridyl rings of each $N(py)_3$ ligand. In the two pseudotetrahedral structures of Cu(II) with $NH(py)_2$,[19,20] corresponding dihedral angles of 9.6 and ca. 35° were observed. The greater dihedral angle found in the present complex appears to allow the two ligands to assume a planar configuration about copper. In square-planar $Pd(N(py)_2)_2$, the dihedral angle between the coordinated pyridine rings is 38.2°.[46] Figure 2 shows that, because of the bending of the ligand about the amine nitrogen atom in **3**, there is no steric interference between the hydrogen atoms attached to atoms C(10) and C(5)′, or those attached to C(5) and C(10)′.[33] It

---

(38) Barclay, G. A.; Hoskins, B. F.; Kennard, C. H. L. *J. Chem. Soc.* **1963**, 5691–5699.

(39) Nakai, H. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 2412–2415.

(40) Stephens, F. S. *J. Chem. Soc., Dalton Trans.* **1972**, 1350–1353.

(41) Stephens, F. S.; Tucker, P. A. *J. Chem. Soc., Dalton Trans.* **1973**, 2293–2297.

(42) Gouge, E. M.; Geldara, J. F. *Inorg. Chem.* **1978**, *17*, 270–275.

(43) Rodig, O. R.; Brueckner, T.; Hurlburt, B. K.; Schlatzer, R. K.; Venable, L.; Sinn, E. *J. Chem. Soc., Dalton Trans.* **1981**, 196–199.

(44) Baxter, C. E.; Rodig, O. R.; Schlatzer, R. K.; Sinn, E. *Inorg. Chem.* **1979**, *18*, 1918–1921.

(45) Gouge, E. M.; Geldard, J. F.; Sinn, E. *Inorg. Chem.* **1980**, *19*, 3356–3359.

(46) Freeman, H. C.; Snow, M. R. *Acta Crystallogr.* **1965**, *18*, 843–850.

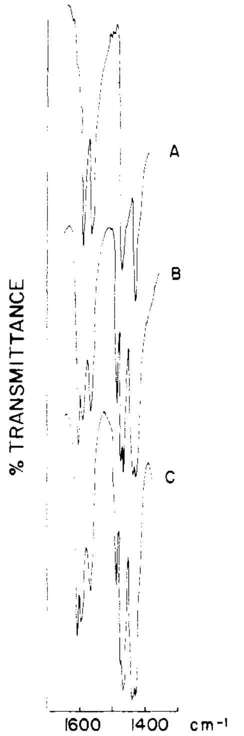


Figure 4. Infrared spectra of Fluorolube mulls of selected compounds in the region 1650–1400 cm^{-1}, showing the $\nu_{C=C}$ and $\nu_{C=N}$ skeletal vibrations in complexes of 2,2′,2″-tripyridylamine and in the free ligand: A, 2,2′,2″-tripyridylamine; B, $[Cu(N(py)_3)_2(CH_3CN)_2][SO_3CF_3]_2$ (**3**); C, $Cu(N(py)_3)_2(SO_3CF_3)_2$ (**4**).

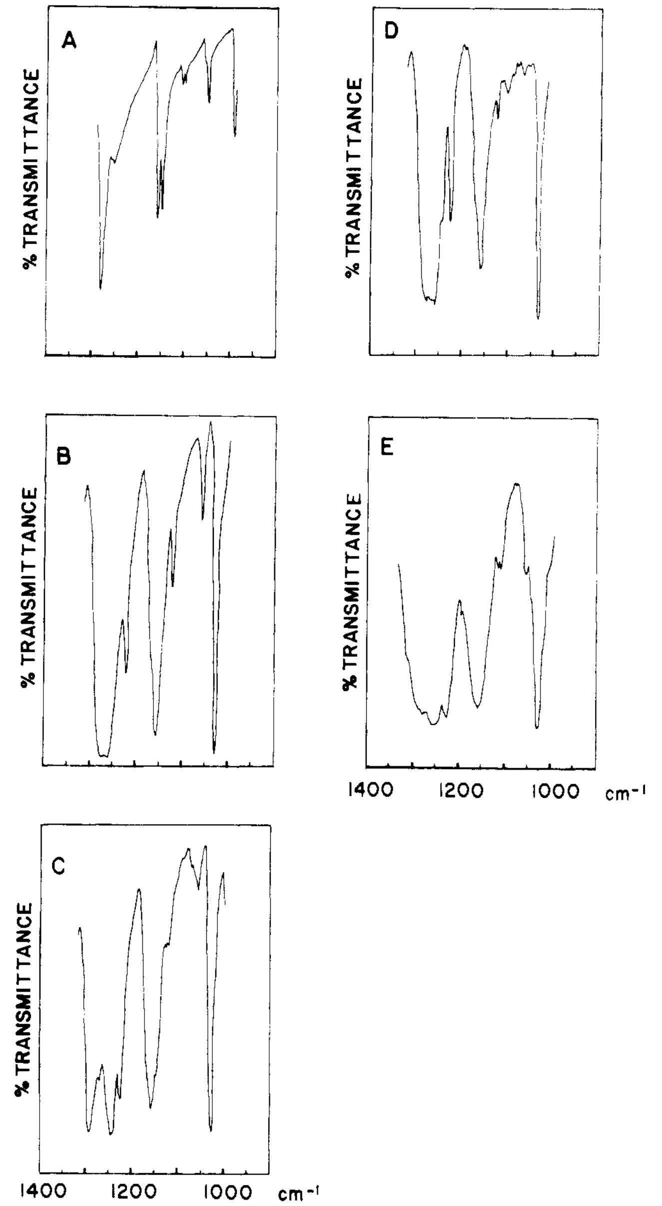


Figure 5. Infrared spectra of Nujol mulls of selected compounds in the 1300–1000-cm^{-1} region, where stretching vibrations of the $SO_3CF_3^-$ anion appear: A, 2,2′,2″-tripyridylamine; B, $[Cu(N(py)_3)_2(CH_3CN)_2][SO_3CF_3]_2$ (**3**); C, $Cu(N(py)_3)_2(SO_3CF_3)_2$ (**4**); D, $[Cu_4(OH)_4(SO_3CF_3)_2(N(py)_3)_4][SO_3CF_3]_2$;[23] E, A copper(II) ditriflate complex[52] of a ligand prepared from the condensation of 1,2,4,5-tetraaminomethylbenzene and 4 mol of pyridinecarboxaldehyde.

has already been noted that such steric interactions prevent two 2,2′-bipyridyl ligands from being coplanar.[38,39]

Infrared Spectral Studies. The relevant portions of representative infrared spectra of complexes **3** and **4**, as well as two related species of interest, are presented in Figures 4 and 5. Figure 4 shows the region from 1600 to 1400 cm^{-1}, of particular interest in terms of the mode of $N(py)_3$ coordination. It can be seen that the four $\nu_{C=C}$ and $\nu_{C=N}$ skeletal vibrations of the free ligand[18,47] (Figure 4A) are split into at least eight bands upon complexation of $N(py)_3$ to the cupric ion in complexes **3** and **4**. This region of the infrared spectrum has been used in the past[18,47] to demonstrate the equivalence or nonequivalence of all three pyridyl rings in the ligand 2,2′,2″-tripyridylphosphine oxide (TPPO). In the spectrum of the complex $[Cu(TPPO)_2][ClO_4]_2$, the presence of only four bands in the $\nu_{C=C}$, $\nu_{C=N}$ region was taken to indicate tridentate coordination of the ligand, with all three pyridine rings equivalent. The IR spectrum of an isomer of the same material showed at least eight bands in the 1400–1600-cm^{-1} region and was presumed to have the TPPO ligand coordinating in a bidentate fashion and hence have nonequivalence of the three pyridyl rings. This conclusion was supported by IR evidence for perchlorate coordination in the second isomer. For complexes **3** and **4**, with $N(py)_3$ as the ligand, the eight bands of Figure 4B,C would also suggest nonequivalence of the three pyridyl rings of the $N(py)_3$ molecule. The present diffraction results for **3** now render such correlations more tenable. In addition, the similarity of parts B and C of Figure 4 indicates that $N(py)_3$ acts as a bidentate ligand in **4** also, in which there is no solvent present to act as an axial ligand.

Figure 5 presents infrared spectra in the region 1000–1300 cm^{-1}, one of the areas where evidence of triflate ion coordination appears.[48-50] Notice that the strong bands in the 1000–1200-cm^{-1} region appear very similar in Figure 5B–D. There is, however, a significant variation in the three spectra in the vicinity of 1250 cm^{-1}. In the spectrum of **3** (Figure 5B), the broad absorption encompassing both the asymmetric (E under C_{3v} symmetry) S–O stretching region of the uncoordinated triflate anion (1270–1280 cm^{-1})[48,49] and the $N(py)_3$ vibration at 1280 cm^{-1}[51] is centered to the high-energy side of 1250 cm^{-1}. In the spectrum of **4** (Figure 5C), the $N(py)_3$ mode remains to the high-energy side of 1250 cm^{-1}, but the S–O stretch has now split, with the lower energy component falling below 1250 cm^{-1}. Splitting of the ν_{S-O}(asym) band has been reported previously[48] for $Cu(SO_3CF_3)_2$ where coordina-

---

(47) Boggess, R. K.; Boberg, S. J. *J. Inorg. Nucl. Chem.* **1980**, *42*, 21–26.

(48) Arduini, A. L.; Garnett, M.; Thompson, R. C.; Wong, T. C. T. *Can. J. Chem.* **1975**, *53*, 3812–3819.

(49) Gramstad, T.; Haszeldine, R. N. *J. Chem. Soc.* **1956**, 173–180.

(50) Dalziel, J. R.; Klett, R. D.; Yeats, P. A.; Aubke, F. *Can. J. Chem.* **1974**, *52*, 231–239.

(51) The strong band appearing at 1280 cm^{-1} in the free ligand is assumed to be present in the broad 1270-cm^{-1} transition of the cupric complex.

Table VIII. Electronic Absorption Bands of Complexes $[Cu(N(py)_3)_2(CH_3CN)_2][SO_3CF_3]_2$ (3) and $Cu(N(py)_3)_2(SO_3CF_3)_2$ (4) in Solution and as Nujol Mulls

complex	solvent	λ, nm (ε, M^{-1} cm^{-1})
3	CH_3CN	408 (107), 577 (60)
4	CH_3CN	410, 577
3	CH_2Cl_2	410 (114), 593 (79)
4	CH_2Cl_2	410 (130), 593 (85)
3	mull	383, 528 sh
4	mull	385, 540 sh

tion of the triflate anion to Cu(II) was proposed. Such splitting arises from coordination of the anion as a unidentate or bidentate ligand, lowering the symmetry to C_s. If the anion were to coordinate in a tridentate fashion, the symmetry would not necessarily be lowered from C_{3v}, but the change in force constants should lead to a shift in the S–O stretching mode. Such tridentate coordination by the anion has been proposed for the compound $Co(SO_3CF_3)_2$,[48] because ν_{S-O}(asym) does not split but does shift to significantly lower energy.

In other words, we have prepared and structurally characterized two cupric complexes that contain coordinated triflate ions.[23] The IR spectra of these compounds, presented in Figure 5D,E, are an aid in interpreting Figure 5C and in testing the triflate structure–spectra criteria advanced previously. The complex exhibiting spectrum Figure 5D is $[Cu_4(OH)_4(SO_3CF_3)_2(N(py)_3)_4][SO_3CF_3]_2$, in which equal numbers of triflate units exist as coordinated and noncoordinated counterions.[23] The coordinated triflate ligands are bidentate and bridge two cupric ions. The IR spectrum of this tetrameric complex displays a well-defined shoulder just below 1250 cm^{-1}, while part of the antisymmetric S–O stretch appears as a broad band above 1250 cm^{-1}. This result is consistent with the presence of both coordinated and uncoordinated triflate ions. Figure 5E is the spectrum of a cupric complex in which each triflate ion present is shown by X-ray diffraction[52] to be axially coordinated through one oxygen atom. The spectrum of this complex shows ν_{S-O}(asym) to be a broad band centered at 1250 cm^{-1}. Thus, the spectra shown in Figure 5D,E confirm that coordination of a triflate ion to a cupric ion leads to the appearance of a transition at or below 1250 cm^{-1}.[48,50,53,54]

We therefore conclude that the position of the antisymmetric S–O stretching mode of complex **4** (Figure 5C) indicates that the triflate ions are coordinated to the cupric ion. Because the electronic and EPR data (vide infra) indicate that the cupric ion in complex **4** retains a tetragonally distorted octahedral coordination sphere, these triflate ions must coordinate axially, filling the sites occupied by CH_3CN in complex **3**. The similarity of the IR spectra of **3** and **4** in the region 1600–1400 cm^{-1} (Figure 4B,C) argue that the uncoordinated pyridine rings of the $N(py)_3$ ligands remain uncoordinated when acetonitrile is not present. Although triflate was originally chosen as a counterion for these studies because it was thought to be a relatively noncoordinating anion, these results[23,52] demonstrate that triflate is not clearly so reluctant to coordinate to a metal ion as was previously supposed.[55]

It should be noted that in the past there has been some controversy[48-50,53,54] as to whether the triflate band assigned to the antisymmetric S–O stretching mode might have considerable (or even predominant) C–F stretching character. The results presented here support the assignment of the 1270-cm^{-1} band to a transition with predominant S–O stretching, as it is the only band that undergoes a significant shift upon coordination of the anion to copper(II) (Figure 5). Because the mode of triflate coordination is through the oxygen atoms,[23,52] it is reasonable that the S–O band would be the one most affected by coordination to the metal ion.

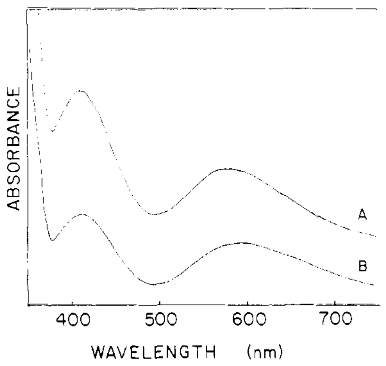


Figure 6. Electronic spectra of $[Cu(N(py)_3)_2(CH_3CN)_2][SO_3CF_3]_2$ (3) as a solution: A, in acetonitrile; B, in CH_2Cl_2.

Electronic Spectral Studies. The optical spectra of acetonitrile and dichloromethane solutions of **3** are shown in Figure 6. Table VIII summarizes the data derived from solution and mull spectra for both **3** and **4**. The spectra of **3** and **4** are fairly similar in the two solvents, and essentially identical in the same solvent. This implies that there is substantial acetonitrile dissociation in methylene chloride solutions of **3** at room temperature (vide infra). In both solvents, **3** and **4** exhibit two transitions in the 600–350-nm region. The lower energy band is always broad, flat-topped, and unsymmetrical, with an absorptivity of approximately 75 M^{-1} cm^{-1}. The higher energy band is always more intense, with ε ca. 115 M^{-1} cm^{-1}. In mull spectra of **3** and **4**, the low-energy band found in solution appears as a very broad, ill-defined shoulder. The higher energy band also appears as a shoulder, but it is more intense and better defined.

The transition in the region 625–530 nm is very typical of tetragonally distorted octahedral copper(II) complexes with nitrogenous ligands.[34,36,37,56-58] Complexes of the type CuL_2X_2, where L = a bidentate ethylenediamine (en) derivative, usually exhibit a multicomponent band in the region 625–550 nm.[56,57] A computer-aided deconvolution of the electronic spectra of seven $(en)_2Cu^{II}$ complexes[57] showed that the asymmetric band in the visible spectrum could most probably be resolved into three closely spaced bands. As support, the single-crystal electronic spectra of tetragonally distorted octahedral complexes $Cu(NH_3)_4X_2$ show three transitions between 750 and 500 nm.[34] The asymmetry observed in the visible band in the $(en)_2Cu^{II}$ complexes resembles the asymmetry noted in the 590-nm band of complexes **3** and **4**.

The position of the low-energy band in solution spectra of **3** and **4** falls within the range of 650–540 nm assigned by Hathaway[37] to the d–d transitions of elongated tetragonal CuN_6 compounds with a tetragonality factor[59] T of 0.8. In fact, according to this analysis, all d–d bands for CuN_6 complexes of any geometry should appear at wavelengths greater than 500 nm. We thus conclude that the more intense, higher energy band observed in the spectra of **3** and **4** is a manifestation of a low-lying py(π) → Cu(II) charge-transfer transition. A high-energy band in the vicinity of 400 nm is commonly observed in spectra of copper(II) coordinated to aro-

---

(52) Jason, M.; Sorrell, T.; Ibers, J. A.; Marks, T. J., manuscript in preparation.

(53) Yeats, P. A.; Sams, J. R.; Aubke, F. *Inorg. Chem.* **1971**, *10*, 1877–1881.

(54) Miles, M. G.; Doyle, G.; Cooney, R. P.; Tobias, R. S. *Spectrochim. Acta, Part A* **1969**, *25A*, 1515–1526.

(55) Rosenthal, M. R. *J. Chem. Educ.* **1973**, *50*, 331–335.

(56) Zimmerman, D. N.; Hall, J. L. *Inorg. Chem.* **1973**, *12*, 2616–2620.

(57) Procter, I. M.; Hathaway, B. J.; Nicholls, P. *J. Chem. Soc. A* **1968**, 1678–1684.

(58) Hecht, H. G.; Kerns, R. C. *J. Inorg. Nucl. Chem.* **1969**, *31*, 1983–1992 and references cited therein.

(59) As defined by Hathaway in ref 29 and 36, the tetragonality factor, T, is the ratio of the short, in-plane bond distances (R_S) to the longer, out-of-plane bond distances (R_L). Therefore $T = R_S/R_L$.

Table IX. EPR Data for Powders and Frozen Glasses of $[Cu(N(py)_3)_2(CH_3CN)_2][SO_3CF_3]_2$ (3) and $Cu(N(py)_3)_2(SO_3CF_3)_2$ (4)

complex	solvent	$g_\parallel$ major component	$g_\parallel$ minor component	$g_\perp$	$A_\parallel$, G	$A'_\parallel$, G	$A_N^\parallel$, G	$A_N^\perp$, G
3	CH_3CN	2.237	*a*	2.069	185			
3	MeOH	2.237	*a*	2.070	191			
3	CH_2Cl_2	2.235	. . .	2.050[b]	187.5		11	13
3	powder	2.235	. . .	2.060	184			
4	MeOH	2.241	2.294	2.064	185	165		
4	EtOH	2.282	2.238	2.069	160	187.5		
4	CH_2Cl_2	2.227	. . .	2.049[b]	187.5		10	14
4	powder	2.218	. . .	2.063	. . .			

[a] Several minor components present. [b] This value of $g_\perp$ is approximate owing to broadening of the signal by the $M_I = -{}^3/_2$ hyperfine line.

matic nitrogenous bases, including imidazole.[11,14,16,42,60]

The similarity of the spectra of solutions of **3** and **4** indicates similar structures, and the position of the d–d transition indicates that the cupric ion geometry in solution is elongated tetragonal, as in the solid state. The spectra of **3** and **4** in the solid state are also very similar. However, the higher energy of the d–d absorption of **4** indicates a slightly higher degree of tetragonal distortion in this complex.[36-38] If triflate ions are acting as the axial ligands in **4** as suspected (vide supra), weaker out-of-plane coordination is expected in **4** as compared with **3**, because triflate is a weaker coordinating ligand than CH_3CN. This would lead to a greater degree of tetragonal distortion in **4**.

Temperature Dependence of the Electronic Spectra. When polycrystalline samples of **3** are cooled to −196 °C, a dramatic color change from green to lavender is observed. This change is reversed upon returning the temperature to ambient. The EPR spin Hamiltonian parameters (vide infra) do not measurably change through the transition. Such thermochromic behavior is not unusual in Cu(II) coordination chemistry and usually reflects a temperature dependence in the degree of tetragonal distortion.[28,60-68] Energy shifts in the visible region d–d transition of 1×10^3 cm^{-1} in response to the increasing tetragonality at low temperature are not uncommon. Interestingly, related complex **4** is not thermochromic. This appears to reflect, among other factors, pronounced weakness of the triflate ligation, noted in the previous discussion of the optical spectra (vide supra).

The electronic spectrum of **3** in methylene chloride solution is also temperature dependent, with the d–d transition shifting from 593 to 566 nm when the temperature is lowered from +25 to −95 °C. These changes may reflect the temperature dependence of the equilibrium constant for acetonitrile dissociation and/or solution-state structural changes similar to those observed in the solid-state studies.

EPR Studies. EPR spectroscopy of **3** and **4** as a function of solvent and added ligands provides information on the ligational tendencies of Cu(II) in a binding environment composed of multiple nitrogenous heterocycles and readily displaceable axial ligands. X-Band spectra of **3** and **4** in frozen solutions are shown in Figure 7. Spin Hamiltonian data are compiled in Table IX. Spectra of **3** are best resolved in CH_2Cl_2 (Figure 7B), and spin Hamiltonian parameters ($g_\parallel$, $g_\perp$, $A_\parallel(^{63/65}Cu)$) are typical of tetragonal Cu(II) complexes[69-71] as well as type 2 copper proteins, which exhibit "normal" EPR spectra.[50,72] The nitrogen-14 superhyperfine structure indicates the coordination of 6 approximately equivalent nitrogen atoms (12 of the 13 expected lines are resolved in the parallel $M_I = {}^3/_2$ region). The derived constants $A_N^\parallel$ = 11 G and $A_N^\perp$ = 13 G agree favorably with nitrogen superhyperfine splittings observed in both type 2[5,72] and type 1[2] copper proteins. Interestingly, the present results indicate nearly identical couplings to the equatorial pyridyl and axial acetonitrile nitrogen nuclei. Complementary experiments with **4** in CH_2Cl_2 (vide infra) argue that the CH_3CN units have not been replaced by the third pyridyl ligands of each $N(py)_3$ group. The EPR spectra of **3** in methanol (Figure 7A) as well as of **4** in

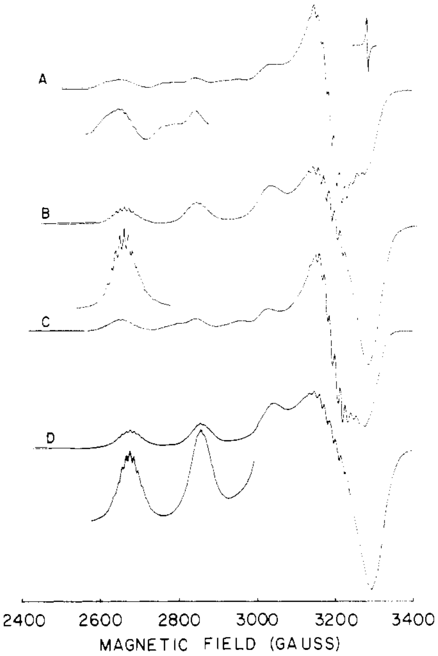


Figure 7. Representative X-band EPR spectra of $[Cu(N(py)_3)_2(CH_3CN)_2][SO_3CF_3]_2$ (3) and $Cu(N(py)_3)_2(SO_3CF_3)_2$ (4) in frozen solution at 77 K: A, 3 in CH_3OH; B, 3 in CH_2Cl_2; C, 4 in CH_3OH; D, 4 in CH_2Cl_2.

---

(60) Bernarducci, E.; Schwindinger, W. F.; Hughey, J. L., IV; Krogh-Jespersen, K.; Schugar, H. J. *J. Am. Chem. Soc.* **1981**, *103*, 1686–1691.

(61) Yokoi, H.; Sai, M.; Isobe, T. *Chem. Lett.* **1972**, 25–28.

(62) Yokoi, H.; Sai, M.; Isobe, T. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 2232–2238 and references cited therein.

(63) Lever, A. B. P.; Mantovani, E.; Donini, J. C. *Inorg. Chem.* **1971**, *10*, 2424–2427.

(64) Kennedy, B. P.; Lever, A. B. P. *J. Am. Chem. Soc.* **1973**, *95*, 6907–6913.

(65) Fabbrizzi, L.; Micheloni, M.; Paoletti, P. *Inorg. Chem.* **1974**, *13*, 3019–3021.

(66) Ferraro, J. R.; Basile, L. J.; Garcia-Ineguez, L. R.; Paoletti, P.; Fabbrizzi, L. *Inorg. Chem.* **1976**, *15*, 2342–2345.

(67) Ferraro, J. R.; Fabbrizzi, L.; Paoletti, P. *Inorg. Chem.* **1977**, *16*, 2127–2129.

(68) Andino, M. M.; Curet, J. D.; Muir, M. M. *Acta Crystallogr., Sect. B* **1976**, *B32*, 3185–3190.

(69) Abragam, A.; Bleaney, B. "Electron Paramagnetic Resonance of Transition Ions"; Clarendon Press: Oxford, 1970; pp 52–60.

(70) Goodman, B. A.; Raynor, J. B. *Adv. Inorg. Chem. Radiochem.* **1970**, *13*, 135–362.

(71) The true value of $g_\parallel$ could be more reliably determined by carrying out computer simulation studies.

(72) (a) Malmström, B. G.; Reinhammar, B.; Vänngård, T. *Biochim. Biophys. Acta* **1968**, 156, 67–76. (b) Holwerda, R. A.; gray, H. B. *J. Am. Chem. Soc.* **1974**, *96*, 6008–6022.

methanol (Figure 7C) or ethanol evidence the presence of more than one Cu(II) species. For **3**, a second species in addition to the starting complex is observed, suggesting at least partial replacement of acetonitrile by alcohol is possible. For **4** in alcohols, two species, neither of which appears to be the starting complex, are observed. The spectrum of **4** in CH_2Cl_2 (Figure 7D) is well resolved and is significantly different from that of **3** in CH_2Cl_2. Thus, $g_{\parallel}$ is lower for **4** as expected, since the degree of tetragonal distortion is approaching a square-planar environment.[69,70] The nine-line superhyperfine pattern expected from four-coordinated pyridyl nitrogen nuclei is also evident. The A_N values are comparable with those in **3**; again, the magnitude of $A_N^{\parallel}$ is less than that of $A_N^{\perp}$.

Fluoride ion produces distinctive effects on the EPR spectra of the type 2 copper sites present in fungal laccase, lacquer tree laccase, ceruloplasmin, and galactose oxidase.[5c,73] In all cases, evidence for 1:1 or, in the case of fungal laccase[73a] and galactose oxidase,[73d] also 2:1 fluoride:copper binding at the type 2 site is observed. Fluorine-19 superhyperfine coupling on the order of 40–55 G in the parallel direction (larger in the perpendicular direction) is detected, $A_{\parallel}$ decreases, and $g_{\parallel}$ increases. Although there is evidence that at least two nitrogenous bases (possibly imidazole) are copper ligands in several of the above proteins, little else is known about the structure of the binding site. The affinity of **4** for fluoride ion was investigated in CH_2Cl_2 and ethanol, with use of KF solubilized with dicyclohexano-18-crown-6. Curiously, incremental addition of KF up to a ca. 10-fold excess had almost no effect on the EPR spectral parameters. If fluoride can compete with triflate for sites on the copper ion, a plausible explanation for this spectral insensitivity may be that the fluoride ion binds in an equatorial rather than axial site in the proteins. Here, interaction with the unpaired electron in the copper $d_{x^2-y^2}$ orbital would be considerably greater. There is already evidence from EPR studies that fluoride binds in an equatorial site in galactose oxidase[73d] and that it replaces an equatorial rather than axial $^{17}OH_2$ molecule in fungal laccase.[74] The effects of fluoride ion on the EPR spectra of the present complexes are under further investigation.

The powder spectrum of **3** yields the spin Hamiltonian parameters compiled in Table IX. These are rather similar to those obtained for **3** in frozen CH_3CN, as expected. Because of the relatively large metal–metal distances in the crystal structure of **3** (10–11 Å), the system displays a significant degree of magnetic dilution, and it was possible to resolve the $^{63/65}Cu$ hyperfine coupling in the parallel direction ($A_{\parallel}$). The powder spectrum of **4** is more typical of Cu(II) powder spectra in a tetragonally distorted octahedral ligand field.[70] The parameter $A_{\parallel}$ is not resolved, and the low value of $g_{\parallel}$ evidences a large degree of distortion.

Conclusions

This study provides new unexpected information on well-known and supposedly well-understood ligands. In regard to 2,2′,2″-tripyridylamine, there is now incontrovertible proof that it can function as a bidentate ligand. Furthermore, ligands as weak as acetonitrile or the supposedly "innocent" triflate anion can occupy coordination sites in preference to the third pyridyl ligand of $N(py)_3$. In terms of understanding copper ion coordination in multi-imidazole binding sites, the present results underscore the very rigorous stereochemical demands that must be satisfied before residues (even those that are excellent donors and in close proximity) can be coordinated to the metal ion. In regard to copper protein structure–spectra criteria, the present results indicate that it is incorrect to assume that nonequivalent nitrogenous ligands will give rise to magnetically nonequivalent superhyperfine interactions. Also, binding and superhyperfine interactions with exogenous ligands such as fluoride will be a sensitive function of the coordination geometry and the types of vacant coordination sites available.

Acknowledgments. We thank the National Institutes of Health (J.A.I., Grant No. HL 13157), the National Science Foundation (T.J.M., Grant No. CHE8009060), and the NSF-MRL program through the Materials Research Center of Northwestern University (Grant DMR 79-23573) for generous support of the research. P.L.D. thanks the American Association of University Women for a fellowship.

Registry No. **2**, 79991-89-2; **4**, 79991-90-5; $Cu(N(py)_3)(SO_3CF_3)$, 79991-91-6; $N(py)_3$, 10428-50-9.

Supplementary Material Available: Root-mean-square amplitudes of vibration (Table IV), idealized hydrogen positions (Table V), and structure amplitudes (Table VI) for $[Cu(N(py)_3)_2(CH_3CN)_2]$-$[SO_3CF_3]_2$ (8 pages). Ordering information is given on any current masthead page.

---

(73) (a) Malkin, R.; Malmström, B. G.; Vänngård, T. *FEBS Lett.* **1968**, *1*, 50–54. (b) Brändén, R.; Malmström, B. G.; Vänngård, T. *Eur. J. Biochem.* **1973**, *36*, 195–200. (c) Malkin, R.; Malmström, B. G. *Adv. Enzymol. Relat. Areas Mol. Biol.* **1970**, *33*, 177–244. (d) Marwedel, B. J.; Kosman, D. J.; Bereman, R. D.; Kurland, R. J. *J. Am. Chem. Soc.* **1981**, *103*, 2842–2847 and references therein.

(74) Deinum, J. S. E.; Vänngård, T. *FEBS Lett.* **1975**, *58*, 62–65.