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Preparation and Crystal Structure of the Unusual Double-Helical Copper(I) Complex Bis(2,6-bis(1-methylbenzimidazol-2-yl)pyridine)dicopper(I) Naphthalene-1,5-disulfonate

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From solutions containing copper(I) and the tridentate ligand 2,6-bis(1-methylbenzimidazol-2-yl)pyridine (diMeBIP) the dinuclear complex [Cu_2(diMeBIP)$_2$] naphthalene-1,5-disulfonate may be isolated. The crystal structure of this compound ($C_{52}H_{40}N_{10}Cu_2O_6S_2$, a = 27.376 (9) Å, b = 7.6688 (16) Å, c = 23.925 (7) Å, β = 115.8 (2)°, monoclinic, Cc, Z = 4) shows an unusual double helical structure in which each copper is essentially linearly coordinated by a benzimidazole group of each ligand and experiences a weak interaction with a bridging pyridine group. The complex shows an intramolecular stacking interaction between benzimidazole groups. UV–visible spectra and ^{1}H NMR spectra show the dimer to be unstable in solution: in propylene carbonate (PC), tetramethylurea (TMU), dimethylformamide (DMF), nitromethane ($MeNO_2$), and dimethyl sulfoxide (DMSO), diMeBIP coordinates to Cu(I) as a planar tridentate ligand, but in acetonitrile (MeCN) it is bidentate, with exchange on the NMR time scale between free and coordinated benzimidazole.

Introduction

There is currently a considerable interest in systems in which a number of molecular units can be made to assemble into a structured supramolecular entity[1] such as the double helix well-known for nucleic acids. In coordination chemistry such a system may be constructed by the use of catenated multidentate ligands to form the strands of the helix that twist around the helical axis along which are disposed the metal ions to which the ligands coordinate. Many such systems have been reported in the literature for dimetallic systems containing iron(III),[2] copper(I),[3] zinc,[4] silver(I),[5] and mercury(II).[6] More recently, planned syntheses of double-helical systems have been reported for copper(II) with a quinquepyridyl ligand,[7] and Lehn and his collaborators have used oligobipyridyl ligands to form double helical complexes containing up to five copper(I) ions disposed along the helical axis.[8,9] In the course of our studies of the chemistry of copper with the planar tridentate nitrogen ligand 2,6-bis(1-methylbenzimidazol-2-yl)pyridine (diMeBIP, **1**) we have isolated a dimetallic double-helical copper(I) salt that shows both an unusually low coordination number for the metal ions and the existence of an intramolecular stacking interaction as found in the nucleic acids. The crystal structure of this salt and the relevant solution chemistry of the complex are reported in this paper.

Experimental Section

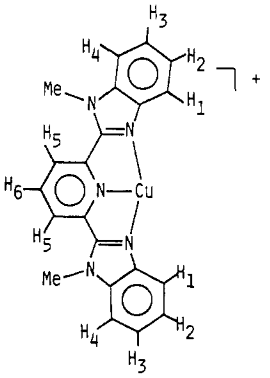
Solvents and Starting Materials were purchased from Fluka and used without further purification, unless otherwise stated.

Preparation of Cu(diMeBIP)(X)$\cdot{}^1/_2H_2O$ (X = ClO_4 (2); X = PF_6 (3)). All manipulations were performed under N_2 by using Schlenk techniques. 2,6-Bis(1-methylbenzimidazol-2-yl)pyridine (diMeBIP),[10] Cu(MeCN)$_4$(ClO_4),[11] and Cu(MeCN)$_4$(PF_6)[12] were prepared according to literature methods. A 0.5-g sample of diMeBIP (1.48 mmol) was dissolved in 80 mL of MeCN. Then, 0.48 g of freshly crystallized Cu(MeCN)$_4$(ClO_4) (1.48 mmol) was dissolved in 20 mL MeCN and then transferred to the ligand solution with vigorous magnetic stirring. After a short time, orange crystals were collected and the mother liquor was concentrated to give a second and a third portion of product. We obtained 0.67 g (1.31 mmol) of orange Cu(diMeBIP)(ClO_4)$\cdot{}^1/_2H_2O$ (**2**) (yield = 89%). Anal. Calcd for $CuC_{21}H_{17}N_5ClO_4\cdot 0.5H_2O$: Cu, 12.43; C, 49.32; N, 13.70; H, 3.52.; Found: Cu, 12.0; C, 49.08; N, 13.73; H, 3.56.

The same procedure was used to prepare orange Cu(diMeBIP)(PF_6)$\cdot{}^1/_2H_2O$ (yield = 88%) from Cu(MeCN)$_4$(PF_6). Anal. Calcd for $CuC_{21}H_{17}N_5PF_6\cdot 0.5H_2O$: C, 45.28; N, 12.58; H, 3.23. Found: C, 45.65; N, 12.56; H, 3.23. Reproducible results for the copper analysis were obtained with some difficulty as a result of precipitation after mineralization.

Preparation of Bis(tetrabutylammonium) Naphthalene-1,5-disulfonate. A 3.22-g sample of disodium naphthalene-1,5-disulfonate (Na_2NDS) (10 mmol) and 5.62 g of tetrabutylammonium chloride monohydrate (19.0 mmol) were dissolved in 100 mL of distilled water. This mixture was extracted with three 30-mL portions of dichloromethane. The organic layer was dried over cellulose and the solvent removed under vacuum. The white powder was recrystallized from CH_2Cl_2/heptane to give 5.7 g of $(NBu_4)_2$NDS (7.4 mmol; yield = 78%). This compound did not contain chloride ($AgNO_3$ test) or sulfate ($BaCl_2$ test), and gave the expected IR and ^{1}H NMR spectra. ^{1}H NMR in $CDCl_3$: 9.15 (2 H, d, J^3 = 9 Hz), 8.20 (2 H, d, J^3 = 8 Hz), 7.30 (2 H, pseudo-t, J^3 = 8.5 Hz), 2.9 (16 H, m), 0.8–1.5 (56 H, m).

Chart I. diMeBIP (**1**) Acting as a Tridentate Ligand, Showing the Proton-Numbering Scheme



Preparation of [Cu(diMeBIP)]$_2$NDS (4). A 50-mg sample of Cu(MeCN)$_4$(ClO_4) (0.15 mmol) and 51.9 mg of diMeBIP (0.15 mmol) were dissolved in 25 mL of MeCN under N_2 in a Schlenk tube. The mixture was stirred until a clear red solution was obtained. A solution of 173 mg of $(NBu_4)_2$NDS (0.22 mmol) in a minimum of the same solvent was slowly added. Thin orange needles precipitated rapidly but were transformed into red lozenges after standing in contact with the solution for 10 days at room temperature. We obtained 70 mg of [Cu(diMeBIP)]$_2$NDS (0.064 mmol; yield = 86%), which was characterized by its IR spectrum and X-ray diffraction analysis.

Preparation of Zn(diMeBIP)$_2$(ClO_4)$_2\cdot{}^3/_2H_2O$ (5). A 1.0-g sample of

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Table I. Summary of Crystal Data, Intensity Measurements, and Structure Refinement for [Cu_2(diMeBIP)$_2$]NDS (4)

formula	$Cu_2(C_{21}H_{17}N_5)_2(C_{10}H_6O_6S_2)$
mol wt	1092.2
cryst syst	monoclinic
space group	*Cc*
a, Å	27.376 (9)
b, Å	7.6688 (16)
c, Å	23.925 (7)
β, deg	115.8 (2)
V, Å^3	4522 (8)
Z	4
ρ_{obs}, g cm^{-3}	1.58
ρ_{calc} g cm^{-3}	1.60
radiation	Mo Kα (λ = 0.71069 Å)
μ, mm^{-1}	1.095
$((\sin\theta)/\lambda)_{max}$, Å^{-1}	0.505
hkl range	-24 to 24, 0 to 7, 0 to 21
temp, °C	20
no. of measd reflcns	2676
no. of obsd reflcns	2065
criterion for obsd reflcns	$\lvert F_o\rvert > 4\sigma(F_o)$ and $\lvert F_o\rvert > 8$
R ($=R_w$; w = 1))	0.047

diMeBIP (2.95 mmol) was dissolved in 50 mL of absolute ethanol at 50 °C. A solution of 1.099 g of $Zn(ClO_4)_2 \cdot 6H_2O$ (2.95 mmol; prepared by metathesis of $ZnCO_3$ with $HClO_4$) in the same solvent was added. A white precipitate was obtained, which was maintained at 50 °C for 30 min. The precipitate was then filtered, washed with ethanol and ether, and dried in vacuo. We obtained 1.3 g of white microcrystalline Zn(diMeBIP)$_2$(ClO_4)$_2$·$^3/_2H_2O$ (1.34 mmol; yield = 91% calculated from diMeBIP). Anal. Calcd for $ZnC_{42}H_{34}N_{10}Cl_2O_8 \cdot 1.5H_2O$: Zn, 6.75; C, 51.99; N, 14.44; H, 3.82. Found: Zn, 6.76; C, 52.24; N, 14.35; H, 3.80.

Caution! Perchlorate salts with organic ligands are potentially explosive and should be handled with the necessary precautions.[13]

Crystal Structure Determination for [Cu_2(diMeBIP)$_2$]NDS (4). Crystal data and details of intensity measurement and refinement are given in Table I. Intensities were measured at room temperature on a Philips PW1100 diffractometer with graphite-monochromated Mo Kα radiation, $\omega/2\theta$ scans, scan width 1.2°, and scan speed 0.03°/s; two reference reflections measured every 90 min showed variations less than $2.2\sigma(I)$. The normalized structure factors showed an intensity distribution typical of an acentric space group. Data were corrected for Lorentz and polarization effects but not for absorption. The structure was solved by direct methods using MULTAN 80;[14] all other calculations used a local version of the XRAY 76 system[15] and ORTEP II[16] programs. Atomic scattering factors and anomalous dispersion terms (for Cu, S, O, and N) were taken from ref 17. Blocked-matrix (four blocks) least-squares refinement based on *F* using unit weights gave final values of $R = R_w = 0.047$ for 361 variables and 2065 contributing reflections. Hydrogen atoms were placed in calculated positions. Cu, S, and N were refined with anisotropic displacement parameters, and C and O were refined with isotropic displacement parameters. The final Fourier difference synthesis showed a maximum of +0.52 and a minimum of -0.37 e Å^{-3}.

Physical Measurements. Electronic spectra in the UV–visible range were recorded in solution with a Perkin-Elmer Lambda 5 spectrophotometer at 20 °C using quartz cells of 1-, and 0.1-, and 0.01-cm path length. ^{1}H NMR spectra were recorded on Varian EM 360A (60 MHz) and Varian XL 200 (200 MHz) spectrometers. IR spectra were obtained from KBr pellets with a Perkin-Elmer IR 597 spectrophotometer. Cyclic voltammograms were recorded by using a Tacussel PRGE-DEC potentiostat connected to a function generator and a XY plotter. A three-electrode system consisting of a stationary platinum disk working electrode, a platinum counter electrode and a nonaqueous Ag/Ag$^+$ reference electrode was used. The reference potential was standardized against the known complex $Ru(bpy)_3(ClO_4)_2$.[18] The scan speed used was 0.2 V/s, and voltammograms were analyzed according to established procedures.[18] A 0.1 M solution of tetrabutylammonium perchlorate (TBAP) served as inert electrolyte. Propylene carbonate (PC)[19] and nitromethane ($MeNO_2$)[20] were purified according to the literature. Acetonitrile was distilled from P_2O_5 and then passed through an Alox column (pH = 9.5). All other solvents used were distilled under reduced pressure (10^{-2} Torr): DMSO from CaH_2, TMU from NaH, and DMF from Alox. Elemental analyses (C, H, N) were performed by Dr. H. Eder of the Microchemical laboratory of the University of Geneva. Copper was determined by atomic absorption (Pye Unicam SP9) and zinc by complexometric EDTA titration after acidic oxidative mineralization of the complex.

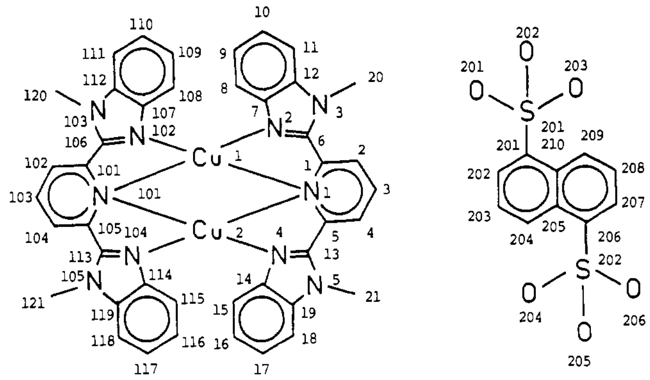

Figure 1. Atomic numbering scheme for **4**.

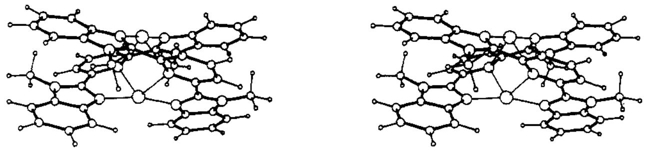

Figure 2. ORTEP[16] stereoscopic view of the cationic dimer in **4** perpendicular to the Cu–Cu axis.

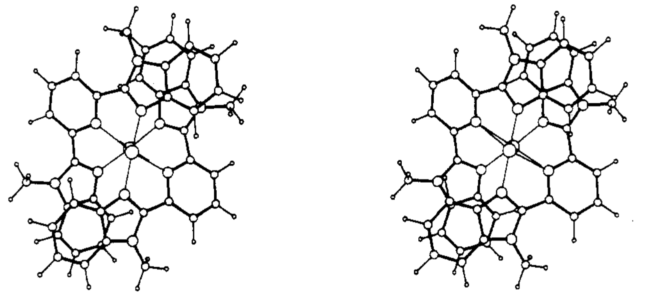

Figure 3. ORTEP[16] stereoscopic view of the cationic dimer in **4** looking roughly down the Cu–Cu axis, and showing the superimposition of the benzimidazole groups.

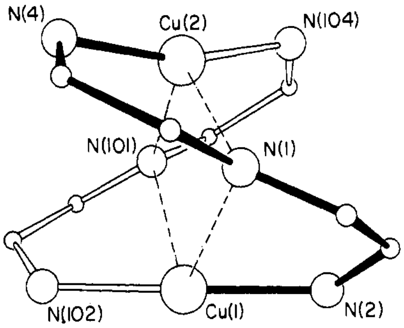

Figure 4. Atomic numbering of the coordination shell of the copper in **4**, showing the strands of the double helix.

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Table II. Fractional Atomic Coordinates with Esd's in Parentheses for **4**

	x	*y*	*z*
Cu(1)	0.49584 (8)	−0.24131 (21)	0.49975 (16)
Cu(2)	0.50228 (8)	0.13019 (21)	0.50099 (16)
N(1)	0.5060 (4)	−0.0474 (14)	0.4189 (5)
N(2)	0.4264 (4)	−0.2336 (14)	0.4307 (4)
N(3)	0.3657 (4)	−0.1314 (13)	0.3419 (4)
N(4)	0.5777 (3)	0.1388 (14)	0.5177 (5)
N(5)	0.6482 (4)	0.0690 (14)	0.4987 (5)
N(101)	0.4826 (4)	−0.0243 (13)	0.5768 (4)
N(102)	0.5632 (4)	−0.2460 (14)	0.5722 (4)
N(103)	0.6188 (4)	−0.1670 (15)	0.6675 (4)
N(104)	0.4276 (4)	0.1825 (13)	0.4817 (4)
N(105)	0.3484 (4)	0.1582 (14)	0.4879 (5)
S(201)	1.14662 (14)	−0.0953 (5)	0.8334 3(19)
S(202)	0.86917 (14)	0.0106 (5)	0.6702 0(17)
C(1)	0.4654 (5)	−0.1111 (16)	0.3672 (5)
C(2)	0.4698 (5)	−0.1335 (18)	0.3125 (6)
C(3)	0.5193 (5)	−0.0932 (17)	0.3116 (6)
C(4)	0.5619 (5)	−0.0294 (17)	0.3638 (6)
C(5)	0.5539 (5)	−0.0051 (16)	0.4179 (5)
C(6)	0.4187 (5)	−0.1586 (16)	0.3780 (6)
C(7)	0.3753 (5)	−0.2522 (18)	0.4307 (6)
C(8)	0.3614 (5)	−0.3172 (18)	0.4747 (6)
C(9)	0.3067 (6)	−0.3088 (21)	0.4607 (7)
C(10)	0.2686 (6)	−0.2415 (21)	0.4062 (7)
C(11)	0.2817 (5)	−0.1809 (18)	0.3605 (6)
C(12)	0.3377 (5)	−0.1857 (18)	0.3733 (6)
C(13)	0.5927 (4)	0.0672 (16)	0.4753 (5)
C(14)	0.6234 (4)	0.1845 (15)	0.5683 (5)
C(15)	0.6302 (5)	0.2609 (18)	0.6238 (6)
C(16)	0.6837 (5)	0.2902 (19)	0.6683 (6)
C(17)	0.7285 (5)	0.2455 (20)	0.6576 (6)
C(18)	0.7224 (5)	0.1739 (17)	0.6023 (6)
C(19)	0.6683 (5)	0.1459 (17)	0.5560 (5)
C(20)	0.3405 (5)	−0.0466 (19)	0.2798 (6)
C(21)	0.6823 (5)	0.0004 (18)	0.4702 (6)
C(101)	0.5178 (5)	−0.1064 (18)	0.6281 (6)
C(102)	0.5050 (5)	−0.1353 (19)	0.6785 (6)
C(103)	0.4554 (5)	−0.0830 (19)	0.6721 (6)
C(104)	0.4203 (5)	0.0049 (19)	0.6203 (6)
C(105)	0.4357 (4)	0.0307 (16)	0.5742 (5)
C(106)	0.5656 (5)	−0.1749 (16)	0.6240 (5)
C(107)	0.6148 (5)	−0.2856 (17)	0.5818 (6)
C(108)	0.6353 (6)	−0.3529 (20)	0.5420 (7)
C(109)	0.6910 (6)	−0.3655 (21)	0.5633 (7)
C(110)	0.7256 (6)	−0.3053 (22)	0.6230 (7)
C(111)	0.7072 (6)	−0.2421 (22)	0.6623 (7)
C(112)	0.6502 (5)	−0.2319 (17)	0.6405 (6)
C(113)	0.4032 (5)	0.1230 (17)	0.5146 (6)
C(114)	0.3861 (4)	0.2552 (16)	0.4279 (5)
C(115)	0.3891 (5)	0.3303 (18)	0.3757 (6)
C(116)	0.3403 (5)	0.3912 (19)	0.3284 (7)
C(117)	0.2914 (6)	0.3686 (19)	0.3335 (7)
C(118)	0.2883 (5)	0.2953 (19)	0.3833 (6)
C(119)	0.3373 (5)	0.2378 (17)	0.4319 (6)
C(120)	0.6393 (6)	−0.0896 (20)	0.7297 (6)
C(121)	0.3085 (6)	0.1227 (21)	0.5106 (7)
O(201)	1.1633 (4)	0.0128 (13)	0.7946 (4)
O(202)	1.1774 (4)	−0.0709 (13)	0.8991 (5)
O(203)	1.1407 (4)	−0.2760 (14)	0.8155 (5)
O(204)	0.8609 (4)	−0.1216 (15)	0.7084 (5)
O(205)	0.8641 (4)	0.1851 (14)	0.6901 (5)
O(206)	0.8376 (4)	−0.0199 (14)	0.6037 (5)
C(201)	1.0796 (5)	−0.0249 (17)	0.8173 (5)
C(202)	1.0684 (5)	0.0339 (18)	0.8637 (6)
C(203)	1.0157 (6)	0.0787 (20)	0.8545 (7)
C(204)	0.9728 (5)	0.0651 (19)	0.7971 (7)
C(205)	0.9818 (4)	0.0049 (18)	0.7464 (6)
C(206)	0.9384 (5)	−0.0161 (17)	0.6841 (6)
C(207)	0.9500 (5)	−0.0605 (18)	0.6356 (6)
C(208)	1.0020 (5)	−0.0911 (18)	0.6441 (7)
C(209)	1.0454 (5)	−0.0849 (18)	0.7022 (6)
C(210)	1.0357 (5)	−0.0338 (18)	0.7548 (6)

Table III. Selected Bond Length (Å) and Angle (deg) Data for $[Cu_2(diMeBIP)_2]NDS$ (**4**)

Cu(1)–N(1)	2.548 (12)	Cu(2)–N(1)	2.427 (12)
Cu(1)–N(2)	1.901 (8)	Cu(2)–N(4)	1.925 (10)
Cu(1)–N(101)	2.622 (11)	Cu(2)–N(101)	2.415 (12)
Cu(1)–N(102)	1.903 (8)	Cu(2)–N(104)	1.933 (10)
Cu(1)–Cu(2)	2.854 (2)		

N(2)–Cu(1)–N(102)	176.4 (6)	N(4)–Cu(2)–N(104)	165.9 (4)
N(1)–Cu(1)–N(101)	104.9 (3)	N(1)–Cu(2)–N(101)	115.7 (4)

Table IV. Least-Squares Plane Data for $[Cu_2(diMeBIP)_2]NDS$ (**4**)

		deviations, Å	
plane	description	rms	max
1	pyridine, N(1)	0.009	0.011
2	benzimidazole, N(2), N(3)	0.025	0.039
3	benzimidazole, N(4), N(5)	0.019	0.043
4	pyridine, N(101)	0.014	0.021
5	benzimidazole, N(102), N(103)	0.034	0.047
6	benzimidazole, N(104), N(105)	0.018	0.033
7	naphthalene	0.040	0.062

Interplane Angles (deg)

	2	3	4	5	6	7
1	41.8	22.6	50.1	25.3	44.1	27.5
2		49.1	19.2	47.8	2.3	39.2
3			47.3	3.9	50.9	13.1
4				44.6	18.4	34.5
5					49.5	10.1
6						40.7

Results

Preparation of Compounds. The Cu(I) complexes are prepared simply by addition of $[Cu(CH_3CN)_4]^+$ to a solution of the ligand in the absence of oxygen. An orange red solution is formed from which the perchlorate (**2**) and hexafluorophosphate (**3**) salts may be isolated. The Cu(I) complex may also be obtained by hydrazine reduction of a DMF solution of the Cu(II) complex $Cu(diMeBIP)(ClO_4)_2 \cdot 2DMF$.[10] Addition of a solution of naphthalene-1,5-disulfonate to a MeCN solution of **2** gives an immediate fine yellow precipitate and leaves the supernatant colorless, but if the solution is left for several days, orange lozenges of salt **4** are formed. With zinc perchlorate we were unable to isolate a 1:1 zinc–diMeBIP complex, but obtained a high yield of the 1:2 complex.

X-ray Crystal Structure of $[Cu_2(diMeBIP)_2]NDS$ (4). Atomic coordinates are given in Table II, selected bond lengths and angles in Table III, and selected least squares plane data in Table IV. Figure 1 shows the atomic numbering scheme. Figure 2 and 3 give ORTEP[16] stereoviews of the complex, and Figure 4 shows the atoms in the immediate vicinity of the copper.

The crystal structure determination shows compound **4** to be composed of a dimeric cation $[Cu_2(diMeBIP)_2]^{2+}$ and an uncoordinated naphthalene-1,5-disulfonate anion. The anion shows no features of interest, but the cation has a double-helical structure in which the two diMeBIP ligands are twisted around the Cu(1)–Cu(2) axis. Each copper atom is approximately linearly coordinated by two benzimidazole nitrogen atoms, one from each diMeBIP strand. The pyridine groups of the ligands lie in between the two copper atoms, and each pyridine binds weakly to both copper atoms. The diMeBIP ligand may be described as bridging the two copper ions, with each benzimidazole bound strongly to one copper and the pyridine bound weakly to both copper ions.

The sites of the two copper ions are not identical. Cu(1) forms two short Cu–N(benzimidazole) bonds (average Cu–N distance 1.902 Å) that are nearly linear (N(2)–Cu(1)–N(102) = 176.4 (6)°) and has two much longer Cu–N(pyridine) bonds (average Cu–N distance 2.585 Å). For Cu(2) the Cu–N(benzimidazole) bonds are longer (average 1.929 Å) and less colinear (N(4)–Cu(2)–N(104) = 165.9 (4)°), and the Cu–N(pyridine) bonds are shorter (average 2.421 Å). The copper atoms may be described as linearly coordinated by benzimidazoles, with a slight distortion toward a tetrahedral structure resulting from the weak interaction with the pyridines, this distortion being more pronounced for Cu(2). The Cu–N(benzimidazole) distances are close to those in other Cu(I) complexes.[21]

The bridging pyridine ligand is unusual, and we are aware of only two other examples, both in double-helical systems, the dimeric Zn(II) complex $[Zn_2(dapp)_2]$,[4] and another Cu(I) complex, $[Cu_2L^2_2]$ (L^2 = 2,6-bis(2-((methoxyethyl)imino)ethyl)-pyridine).[3] The Cu–pyridine distances found in **4** (2.421 Å) are close to the Zn–μ-pyridine distances in $[Zn_2(dapp)_2]$ (2.590 (10) and 2.390 (10)Å), although the Zn–Zn distance found by Wester and Palenik (3.503 Å) is appreciably greater than the Cu–Cu distance found here (2.854 (2) Å). In $[Cu_2L^2_2]$ the two copper atoms have very different coordination spheres, and the bridging pyridines are more strongly bound to the four-coordinate Cu (Cu–N = 2.21 Å) than to the six-coordinate Cu (Cu–N = 2.68 Å). The Cu–Cu distance in this compound (2.626 (1) Å), which the authors take as evidence for the existence of a Cu–Cu bond,[3] is shorter than in **4**. The stereochemistry of the copper atoms in **4** may reasonably be explained on the basis of two copper(I) ions brought close together by the bridging pyridines, and since the Cu–Cu distance, although short, is still greater than twice the metallic radius of copper,[22] we do not consider it necessary to postulate the existence of a Cu–Cu bond. A recent study of a system showing a much shorter Cu(I)–Cu(I) bond (2.497 (2) Å) concluded that no Cu–Cu bond was present.[23]

Compound **4** exhibits a number of novel features for a double-helical coordination compound. First, it is the first such complex in which the metal ions are essentially two-coordinate, with the coordinate bonds roughly perpendicular to the helical axis, as is found for the hydrogen bond between base pairs in nucleic acids.[24] As a result of this, a double-helical structure is formed with a ligand with only three binding sites—all other helical complexes contain four-, five-, or six-coordinate ions, and thus require ligands of higher denticity. Second, the least-squares plane data in Table IV show that the benzimidazole and pyridine rings of the ligand remain essentially planar, and the distortions necessary to form the helix are limited to torsional rotation about the bonds joining the rings. A feature of particular interest is that pairs of benzimidazoles that are constrained by the helical structure to lie close to each other (planes 2 and 6 and planes 3 and 5) are very nearly parallel, with interplane angles of 2.3 and 3.9°, respectively. The observation of several short nonbonded interatomic distances between the superimposed benzimidazole groups (Figure 3) allows us to estimate a stacking distance of about 3.4 Å, close to that found between base pairs in DNA.[24]

Examination of the crystal packing shows the dimer to pack with the Cu–Cu (helical) axis parallel to the short crystallographic *b* axis. The naphthalene-1,5-disulfonate anions lie in between the columns of dimer cations and are roughly parallel to the overlapping benzimidazole planes 3 and 5 and tilted at about 17° with respect to the *a*–*c* plane. The disparity in length of the crystallographic axes is explained by the parallel packing of tabular cations and anions.

Infrared Spectra. We have recorded the infrared spectra of **2**–**4** in the solid state. The spectra show vibrations associated with the diMeBIP ligand in the range 1600–1500 cm^{-1} which are shifted to lower energy by 5–10 cm^{-1} in comparison with values for copper(II) complexes of this ligand.[10] A weak absorption band at 1520 cm^{-1}, present in copper(II) complexes, is absent in the copper(I) complexes and serves as a useful indicator of the copper oxidation state. The perchlorate, hexafluorophosphate, and naphthalene-1,5-disulfonate anions show symmetric absorptions with no indication of coordination to copper. Water of crystallization absorbs at 3450 cm^{-1} (broad) in **2** and gives two narrow bands (possibly resulting from hydrogen bonding) at 3660 and 3580 cm^{-1} in **3**. With the exception of the bands due to the anions, the spectra of **2**–**4** are essentially identical, and there is no difference between the initial precipitate of **4** and the crystals formed after some days. It is therefore possible that the dimer exists in all three compounds, although the absence of strong bands due to Cu–N vibrations in the 600–200-cm^{-1} region, which would be expected to be most sensitive to the dimer–monomer change, leaves some uncertainty.

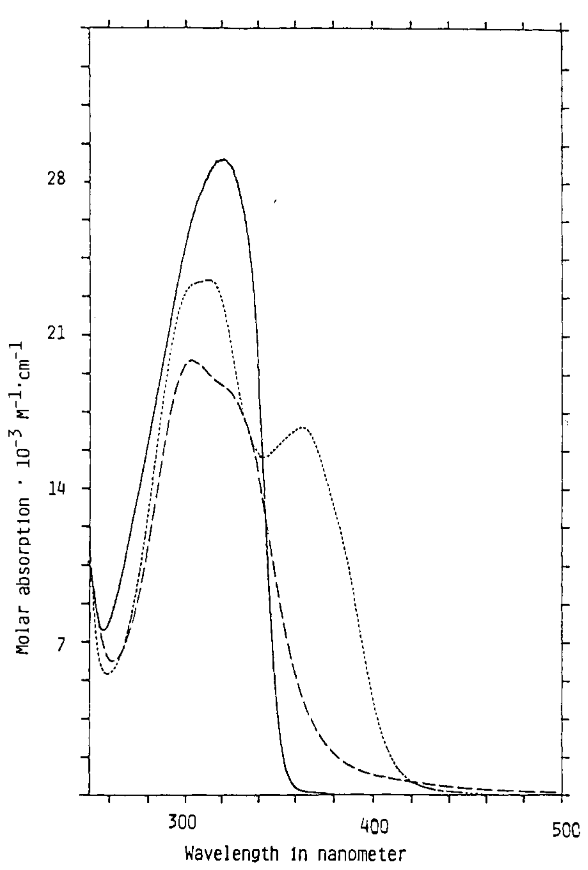

Figure 5. Electronic spectrum of the ligand diMeBIP (full line), $[Cu(diMeBIP)]^{2+}$ (dotted line), and $[Cu(diMeBIP)]^{+}$ (dashed line).

Table V. Electronic Spectral Data for $[Cu(diMeBIP)](ClO_4)$ in Polar Aprotic Solvents at 20 °C

solvent	$\pi_1{}^a \rightarrow \pi^*$	$\pi_1{}^b \rightarrow \pi^*$
PC	33 000 (20 000)[a]	31 050 (18 900) sh
TMU	32 800 (19 000)	30 770 (18 000) sh
DMF	32 570 (19 400)	31 450 (19 000) sh
DMSO	32 680 (22 500)	31 150 (21 500) sh
MeCN	33 000 (25 800) sh	31 450 (27 500)

[a] Molar absorption coefficients (ε) in parentheses in M^{-1} cm^{-1}; sh = shoulder.

Structure in Solution. We have studied the UV-visible and ^1H NMR spectra of solutions of **2** in a variety of solvents to investigate the possible formation of the dimer in solution.

1. UV-Visible Spectra. Compound **2** is soluble in polar aprotic solvents such as DMSO, DMF, TMU, PC, MeCN, and $MeNO_2$ to give intense orange-red solutions whose UV spectra show an intense absorption around 31 000 cm^{-1} (ε = 20 000–25 000 M^{-1} cm^{-1}) attributed to $\pi \rightarrow \pi^*$ by analogy with copper(II) and zinc(II) complexes of the same ligand.[10] The splitting of this transition into two components $\pi_1{}^a$, $\pi_1{}^b \rightarrow \pi^*$ is less important for **2** (2000 cm^{-1} in PC) than for the analogous copper(II) complex $[Cu(diMeBIP)]^{2+}$ (4000 cm^{-1} in PC), but its observation in the copper(I) complex strongly indicates coordination of the ligand in solution.[10] A careful examination of Figure 5 shows a greater absorbance for **2** in the range 23 500–20 000 cm^{-1} compared to the data for corresponding copper(II) complex, possibly due to Cu(I) → π^*(ligand) MLCT in this region.

The intense $\pi_1{}^a$, $\pi_1{}^b \rightarrow \pi^*$ transitions observed for compound **2** (35 000–25 000 cm^{-1}) probably mask weaker MLCT bands expected to appear around 25 000 cm^{-1} for T-shaped copper(I) complexes of heterocyclic nitrogen bases.[25,26] The electronic

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Table VI. ^1H NMR Shifts (TMS) for Complexes **2** and **5** in Polar Aprotic Solvents[a]

compd	solvent	H_1–H_4	H_2–H_3	H_5	H_6	Me
diMeBIP	$CDCl_3$	7.3–7.9 (m)		8.42 (d)	8.05 (t)	4.25 (s)
2	CD_3NO_2	6.94 (d), 7.15 (d)	7.30 (t), 7.40 (t)	8.35 (d)	8.55 (t)	3.66 (s)
2	DMSO-d_6	6.90 (d), 7.15–7.40 (m)		8.50 (d)	8.60 (t)	3.65 (s)
2	CD_3CN	7.25 (broad s)		8.6 (broad s)		3.60 (s)
5	DMSO-d_6	6.85 (d), 7.78 (d)	7.16 (t), 7.35 (t)	8.85 [AB_2]		4.38 (s)
5	CD_3CN	6.45 (d), 7.00 (d)	7.23 (t), 7.55 (t)	8.85 [AB_2]		4.30 (s)

[a] Key: s, singlet; d, doublet; t, triplet; m, multiplet.

spectrum of $[Cu(terpy)]^+$ (formed in situ by mixing stoechiometric quantities of 2,2′:6′,2″-terpyridyl (terpy) and $Cu(MeCN)_4(ClO_4)$ in PC solution shows the two expected $\pi_1^a, \pi_1^b \rightarrow \pi^*$ transitions (35 340 cm^{-1}, ϵ = 13 100 M^{-1} cm^{-1}; 31 060 cm^{-1}, ϵ = 15 400 M^{-1} cm^{-1}) but no resolved MLCT band confirming Crumbliss' results for $[Cu(terpy)]^+$ in aqueous acetonitrile.[26] With the exception of MeCN solutions, the electronic $\pi_1^a, \pi_1^b \rightarrow \pi^*$ transitions of **2** are slightly solvent dependent (Table V) but always have a similar form with a main absorption near 33 000 cm^{-1} and a low-energy shoulder. For MeCN the reverse is found (main absorption 31 450 cm^{-1}, high-energy shoulder), and the spectrum is very similar to that of the free ligand (maximum absorption 31 250 cm^{-1}, ϵ = 29 500 M^{-1} cm^{-1}), which suggests a different coordination in this solvent.

2. NMR Spectra. Solutions of **2** in DMSO-d_6 and CD_3NO_2 show similar ^1H NMR spectra with an AB_2 spin system for the pyridine protons and a pseudo-first-order spectrum with two triplets (H_2, H_3) and two doublets (H_1, H_4) for the phenylene groups. The equivalence of the two benzimidazole groups implies a plane of symmetry bisecting the pyridine moiety perpendicular to the plane of the ligand and is not consistent with the dimeric structure found in the solid state. The ^1H NMR spectrum of the dimer would be expected to be quite different from that observed for complexes where diMeBIP acts as a normal, nonbridging tridentate ligand, since the benzimidazole groups bind more strongly and the pyrindine groups less strongly to the copper. The dimer is chiral by virtue of its helicity, and the symmetry of the ligand is destroyed by the twisting of the benzimidazole groups relative to the pyridine. It is difficult to reconcile the observed NMR spectra with the presence of a significant proportion of dimer in solution.

In CD_3NO_2 the H_5 pyridine signal is shifted little compared to the free ligand, but the H_6 signal moves 0.50 ppm downfield. This parallels the behavior of the pyridinium ion,[27] where the equivalent proton moves 1.15 ppm downfield, and of a Schiff base derived from 2,6-diformylpyridine where H_6 is moved by 0.22 ppm and H_5 only 0.16 ppm downfield when coordination to copper(I) occurs in MeCN.[3] The two triplets (H_2, H_3) at 7.3–7.4 ppm and the two doublets (H_1, H_4) of the benzimidazole moieties are shifted slightly upfield in contrast to the change observed for the benzimidazolium ion.[28]

For the purpose of comparison, we have synthesized the zinc complex $Zn(diMeBIP)_2(ClO_4)_2\cdot{}^3/_2H_2O$ (**5**) whose ^1H NMR spectrum in DMSO-d_6 shows two equivalent diMeBIP ligands probably coordinated to Zn(II) in a pseudooctahedral fashion. As for the copper(I) complex **2**, coordination of diMeBIP to zinc results in a downfield shift of H_6 (+0.8 ppm) and a shift upfield of the benzimidazole protons (H_1–H_4). Although the ligand proton resonances are shifted more in the Zn(II) complex than in the Cu(I) complex, the ^1H NMR characteristics of **2** and **5** are very similar and strongly indicate an identical structure for diMeBIP around the metal atom. A meridional tridentate coordination of diMeBIP (Chart I) around Cu(I) (in $MeNO_2$ and DMSO) and Zn(II) (DMSO and MeCN) in solution is consistent with NMR results, and such a structure has already been proposed for a Schiff base derived from 2,6-diacetylpyridine around copper(I)[29] and for the binuclear tridentate ligand TPEN in $[Cu_2(TPEN)]^{2+}$ in MeCN.[30]

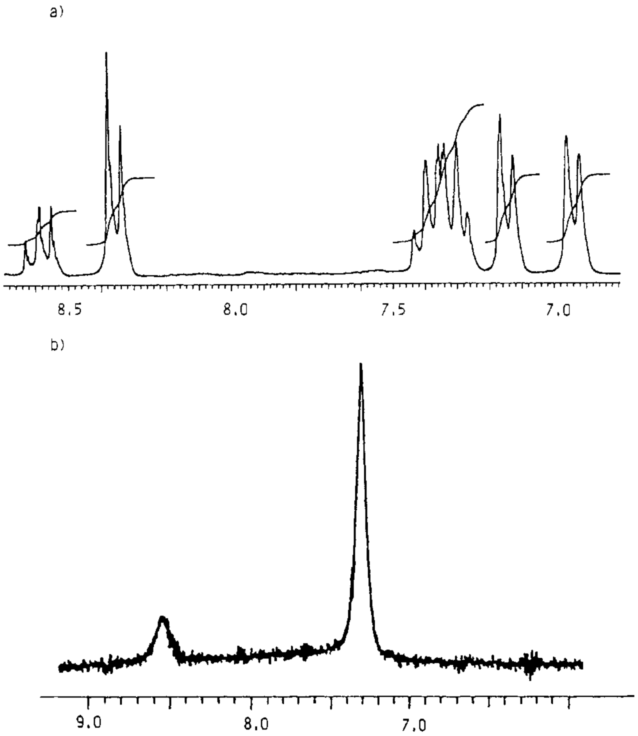

Figure 6. 200-MHz ^1H NMR spectrum of $[Cu(diMeBIP)]^+$ in $MeNO_2$-d_3 (a) and CD_3CN (b).

The spectrum of **5** is not greatly changed in CD_3CN, but that of **2** changes considerably. Two broad singlet signals only are observed in the aromatic domain corresponding respectively to pyridine protons H_5–H_6 at 8.6 ppm and benzimidazole protons at 7.25 ppm. The line shapes are typical of exchange at a moderate rate on a NMR time scale. A titration of a DMSO-d_6 solution of **2** with CD_3CN results in a progressive broadening of the initial resonance signals accompanied by shift of H_5 downfield (toward H_6) and coalescence of the H_1–H_4 signals at an intermediate δ value to give eventually the same spectrum as in pure acetonitrile. This change is consistent with an exchange mechanism in acetonitrile where the benzimidazole side arms are rapidly decomplexed from copper(I). The pyridine nucleus, which remains complexed, is thereby more affected by the positive charge localized on copper(I), and this may explain the greater downfield H_5 shift as observed for **3** with the doubly charged zinc(II). A similar titration of **2** in DMSO + 0.1 M TBAP by MeCN (ratio 1/0 to 1/1) was followed by cyclic voltammetry. The reduction wave attributed to Cu(II)/Cu(I) is progressively moved from +0.35 to +0.38 V vs NHE, which indicates solvent participation in the exchange mechanism since MeCN is well-known to stabilize Cu(I) with respect to Cu(II).[31] From these results (electronic, NMR spectroscopy, and cyclic voltammetry), we conclude that $[Cu(diMeBIP)]^+$ adopts a T-shaped structure in all solvents used

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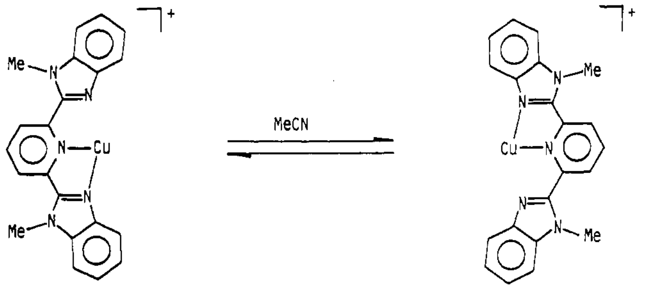
Scheme I. Postulated Mechanism for Benzimidazole Exchange for **2** in MeCN Solution



(PC, DMSO, TMU, DMF, $MeNO_2$) except for MeCN where rapid exchange of a benzimidazole side arm with solvent is proposed (Scheme I). Such solvent participation has already been reported for the very similar ligand terpy: the kinetic data for the dioxygen oxidation of $[Cu(terpy)_2]^+$ led Crumbliss[26] to propose equilibria with the solvent in aqueous acetonitrile:

$$[Cu(terpy)_2]^+ + MeCN \rightleftarrows [Cu(terpy)_2(MeCN)]^+ \quad (1)$$

$$[Cu(terpy)_2(MeCN)]^+ + MeCN \rightleftarrows [Cu(terpy)(MeCN)_2]^+ + terpy \quad (2)$$

The solid-state X-ray structure of $[Cu(diMeBIP)_2](ClO_4)_2{\cdot}H_2O$[32] shows one diMeBIP meridionally tricoordinated to copper(II), but the other is coordinated in a bidentate fashion with one of the benzimidazoles turned away from the copper, and the sixth position of the pseudooctahedral complex is occupied by a water molecule. The adoption of such a bidentate mode of coordination by $[Cu(diMeBIP)]^+$ in acetonitrile, accompanied by exchange between coordinated and noncoordinated benzimidazole groups would explain the NMR and electronic spectra.

Conclusions

Although the formation of the double-helical compound **4** was fortuitous, the structural results show that it is possible to use metal ions with a coordination number of 2 (e.g. Cu(I), Ag(I), Au(I), Hg(II)) as a basis for the helix; this has three advantages—the ligand requires fewer binding sites and will be easier to prepare, the simpler coordination sphere will be easier to fit into a helical structure, and, finally, if planar aromatic groups are used to bind the cations, they will be in an orientation favorable for intramolecular stacking interactions. The spectroscopic data suggest that the dimer does not exist in solution: **4** was isolated both from MeCN and DMF solutions although ^1H NMR and UV–visible spectra show the structures in solution to be different. The naphthalene-1,5-disulfonate salt **4** is virtually insoluble, and the addition of a dianion offers an efficient means of precipitating the dicationic dimer from solution.

Note Added in Proof. Professor U. Burger has kindly pointed out that the magnetic equivalence of the benzimidazole protons in the ^1H NMR spectrum of **2** in DMSO-d_6 and CD_3NO_2 does not exclude the existence of the dimer if there is a 2-fold symmetry axis passing through H_6 and the pyridine nitrogen. The symmetry argument presented is thus invalid, but the proton chemical shift values rule out the presence of the dimer.

Registry No. **2**, 120966-43-0; **3**, 120989-85-7; **4**, 120966-45-2; **5**, 120966-47-4; $Cu(MeCN)_4(ClO_4)$, 14057-91-1; $Cu(MeCN)_4(PF_6)$, 64443-05-6; Na_2NDS, 1655-29-4; $[Cu(terpy)]^+$, 120966-48-5; bis(tetrabutylammonium) naphthalene-1,5-disulfonate, 109203-14-7; tetrabutylammonium chloride, 1112-67-0.

Supplementary Material Available: A full table of bond distances and angles (Table SI), a listing of the calculated least-squares planes (Table SII), a listing of all atomic coordinates, thermal displacement parameters, and observed structure factors in the format of the Standard Crystallographic Data File[33] (Table SIII) and a summary of the experimental details of the X-ray structure determination (Table SIV) (36 pages). Ordering information is given on any current masthead page.

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