for complex **3** that it converts from totally valence trapped in phase I through a region where the third valence-detrapped doublet is present (phase II?) eventually to a region (phase III?) where all Fe_3O complexes are valence detrapped. These same types of changes in Mössbauer spectra were seen for the undoped Fe_3O complex **1**. Thus, in contrast to the predictions of Figure 12, it appears that the $x = 0.5$ complex does access the ferrodistortive phase I. A larger concentration of cocrystallized Fe_2CoO complexes is needed in order to avoid the apparently ferrodistortively ordered phase I. It will take considerable additional experiments before the critical concentration x_c can be evaluated. DTA results[7h] indicated that the lowest temperature thermal effect (84.5 K for $x = 0.50$) could not be seen for a solid with $x = 0.60$. However, as can be seen in Figure 5, the various thermal effects become quite broad and difficult to detect as x increases. Perhaps Mössbauer data will be more useful in determining x_c.

There is one other aspect of the experimental data that should be noted. There is a phase transition at 148.5 K in the undoped Fe_2CoO complex **2**. From the heat capacity and solid-state ^2H NMR data this phase transition primarily involves the onset of motion of the pyridine solvate molecules. There is enough communication between a given solvate molecule in one lattice site with its neighboring solvate molecules that there is a somewhat cooperative onset of each solvate molecule reorienting about the C_3 axis even though there is no direct contact between pairs of pyridine solvate molecules. Solvate–solvate intermolecular interactions must be propagated via py···Fe_2CoO···py pathways. Thus, the interaction between a given Fe_2CoO complex and the two nearby solvate molecules must be appreciable. The influence of solvate molecules on the phase transitions in these complexes needs to be included in a theory developed for the phase transitions in these complexes. In this sense it is important to remember that $[Fe_3O(O_2CCH_3)_6(py)_3]$, a complex without solvate molecules, has been reported[7f] to remain completely valence trapped up to the highest temperature (315 K) at which it has been examined.

Acknowledgment. We are grateful for support from National Institutes of Health Grant HL13652 (D.N.H.) and National Science Foundation Grants DMB-8606358 (R.J.W.).

Supplementary Material Available: Tables 11, 21, 31, 41, 51, 12, 22, 32, 42, 52, and 72, listing atom coordinates, bond distances, bond angles, anisotropic thermal parameters, hydrogen atom coordinates, and complete crystallographic data for $[Fe_3O(O_2CCH_3)_6(py)_3](py)$ (**1**) and for $[Fe_2CoO(O_2CCH_3)_6(py)_3](py)$ (**2**) (6 pages); Table 61 and 62, listing structure factors for complexes **1** and **2** (15 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry, Memorial University of Newfoundland, St. John's, Newfoundland, Canada A1B 3X7, and National Research Council, Ottawa, Ontario, Canada K1A 0R6

Binuclear Metallacyclic Copper(II) Complexes with a Large Unoccupied Cavity Derived from a Tetradentate, Nonmacrocyclic Polyhydroimidazole Ligand[†]

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The potentially tetradentate ligand 1,2,4,5-tetrakis(4,5-dihydroimidazol-2-yl)benzene (BTIM) forms bischelating binuclear square-pyramidal copper(II) complexes in which two ligands and two metals form a metallacyclic structure with a very large, unoccupied cavity. The cavity is defined by a large copper–copper separation (Cu–Cu = 7.610 Å in $[Cu_2(BTIM)_2Cl_2]Cl_2\cdot7H_2O$ (I); Cu–Cu = 7.30 and 7.42 Å in $[Cu_2(BTIM)_2(N_3)_2](N_3)_2\cdot5H_2O$ (II)) and a large separation between the two parallel, eclipsed benzene rings (3.93 Å (I), 4.4 and 4.3 Å (II)). Variable-temperature magnetism and ESR spectra support the presence of very weak antiferromagnetic exchange between the copper (II) centers in I and II. The crystal and molecular structure of the complex $[Cu(LP)_2](ClO_4)_2$ (IV) (LP = 1,2-bis(4,5-dihydroimidazol-2-yl)benzene) is also reported. LP represents half of the ligand BTIM. IV crystallized in the monoclinic system, space group $P2_1/n$, with $a = 10.4569$ (5) Å, $b = 11.1376$ (8) Å, $c = 12.6854$ (7) Å, $\beta = 98.500$ (10)°, and two formula units per unit cell. Refinement by full-matrix least squares gave final residuals of $R = 0.060$ and $R_w = 0.067$. The mononuclear copper center in IV is square planar, involving two bidentate ligands.

Introduction

Polyfunctional ligands involving benzimidazole, benzothiazole, and hydroimidazole functional groups (and derivatives thereof) can be synthesized simply by condensation of appropriate nitriles with *o*-phenylenediamine, (*o*-aminobenzene)thiol, and ethylenediamine, respectively (or derivatives thereof). Examples of such bidentate ligands and their cobalt(II), nickel(II), copper(II), and zinc(II) complexes have already been reported.[2-5] These ligands were derived from phthalonitrile, and the complexes were found to be mostly mononuclear. Our interest in polynuclear complexes led us to investigate similar derivatives obtained from the tetranitrile 1,2,4,5-tetracyanobenzene, and in the present study copper(II) complexes of the ligand 1,2,4,5-tetrakis(4,5-dihydroimidazol-2-yl)benzene (BTIM) (Figure 1) are reported. The juxtaposition of the hydroimidazole rings would suggest a preference for the formation of binuclear derivatives, and this has been demonstrated for the complexes $[Cu_2(BTIM)_2X_2]X_2\cdot yH_2O$ (X = Cl, $y = 7$ (I); X = N_3, $y = 5$ (II)). However, contrary to what was expected, the structures involve two essentially parallel ligands bridging the two copper centers, which create a large, empty cavity with a large copper–copper separation (>7.3 Å). Binuclear coordination complexes involving cavity structures, with essentially isolated metal centers separated by large distances (>5 Å), usually involve large, macromonocyclic and -polycyclic ligands, which essentially encapsulate the two metals.[6,7] Macropolycyclic cryptand ligands involving nitrogen and sulfur donors generate binuclear copper(II) derivatives of this sort, in which the copper centers display reversible monoelectronic, simultaneous reduction at identical, positive potentials. The ligand 1,7,13,19-tetraaza-4,16-dioxa-10,22,27,32-tetrathiatricyclo[17.5.5.5^{7,13}]tetratriacontane forms a binuclear copper(II) complex that exhibits a single reduction wave at $E_{1/2} = 0.200$ (5) V vs SCE[8-11] and involves

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[†] This paper assigned NRCC Contribution No. 31247.

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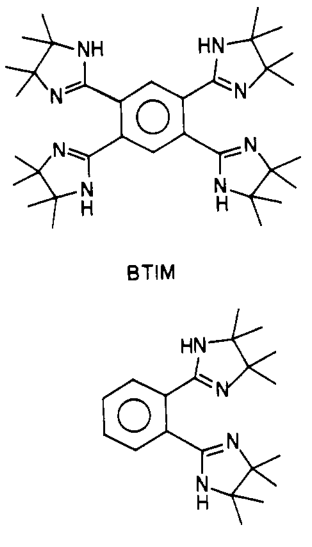

BTIM

LP

Figure 1. Structures of the ligands.

relatively weak antiferromagnetic exchange between the metal centers ($-J$ = 54.5 cm^{-1}),[12] which are separated by 5.62 Å. Systems of this sort can generate inclusion complexes involving monatomic (e.g. Br, NCS),[13,14] diatomic (e.g. pyrazolate),[15] and triatomic (e.g. azide)[16] bridges, which provide an internal linkage between the metal centers. The complexes described in the present study appear to be very weakly antiferromagnetically coupled and have resisted, so far, attempts to insert small ligands into the molecular cavity.

The structure, and some properties, of the complex [Cu(LP)$_2$](ClO$_4$)$_2$ (LP = 1,2-bis(4,5-dihydroimidazol-2-yl)benzene (Figure 1), involving a ligand which is effectively half of BTIM, are also reported. A preliminary report of the structure and some properties of [Cu$_2$(BTIM)$_2$Cl$_2$]Cl$_2$·7H$_2$O has already been published.[17]

Experimental Section

Synthesis of Ligands and Copper Complexes. BTIM. Tetracyanobenzene[18] (10.7 g; 70 mmol) was added in portions over a period of 30 min to cold (0 °C) ethylenediamine (30 mL), and a catalytic amount of P_2S_5 was added. The mixture was stirred at room temperature for 6–7 h and then refluxed for 2 days. The mixture was cooled to room temperature and water (200 mL) added. A solid brown product formed, which was filtered off, washed several times with water, and recrystallized from a boiling chloroform/methanol (50/50) mixture (yield 3.4 g, 14%; mp 270–300 °C dec). Anal. Calcd for $C_{18}H_{22}N_8$·0.5H$_2$O: C, 60.15; H, 6.45; N, 31.17. Found: C, 60.28; H, 5.98; N, 30.98.

[Cu$_2$(BTIM)$_2$Cl$_2$]Cl$_2$·7H$_2$O (I). BTIM (0.70 g; 2.0 mmol) was dissolved in boiling methanol (300 mL) and the solution filtered. An aqueous solution (50 mL) of CuCl$_2$·2H$_2$O (0.35 g, 2.0 mmol) was added with stirring and the resulting solution allowed to evaporate slowly. Blue crystals were obtained, and the product was recrystallized from a water/methanol mixture (yield 0.60 g). Anal. Calcd for [Cu$_2$(C$_{18}$H$_{22}$N$_8$)$_2$Cl$_2$]Cl$_2$·7H$_2$O: C, 39.45; H, 5.30; N, 20.46; Cl, 12.96. Found: C, 39.55; H, 4.95; N, 20.49; Cl, 12.94.

Table I. Crystallographic Data for [Cu(LP)$_2$](ClO$_4$)$_2$ (IV)

chem formula CuC$_{24}$H$_{28}$Cl$_2$N$_8$O$_8$
fw 690.98
a = 10.4569 (5) Å
b = 11.1376 (8) Å
c = 12.6854 (7) Å
β = 98.500 (10)°
V = 1461.17 Å^3
Z = 2

space group $P2_1/n$
T = 22 °C
λ = 0.709 30 Å
ρ_{calcd} = 1.571 g cm^{-3}
μ = 1.98 mm^{-1}
R = 0.060
R_w = 0.067

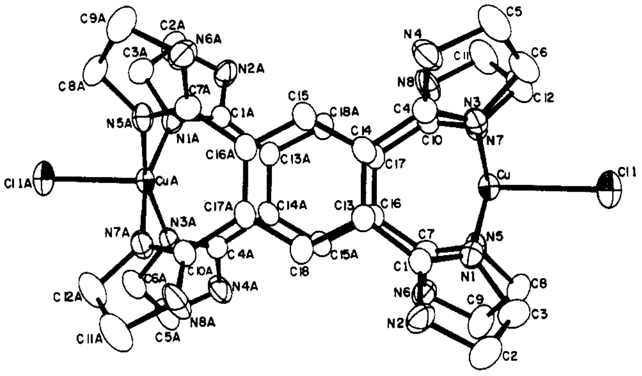

Figure 2. Structural representation of [Cu$_2$(BTIM)$_2$Cl$_2$]$^{2+}$ (I^{2+}) with hydrogen atoms omitted.

[Cu$_2$(BTIM)$_2$(N$_3$)$_2$](N$_3$)$_2$·5H$_2$O (II) and [Cu$_2$(BTIM)$_2$(H$_2$O)$_2$](ClO$_4$)$_4$·2H$_2$O (III). The azide derivative (II) was obtained as buff crystals from an aqueous solution of I, to which an excess of aqueous sodium azide had been added. Anal. Calcd for [Cu$_2$(C$_{18}$H$_{22}$N$_8$)$_2$(N$_3$)$_2$](N$_3$)$_2$·5H$_2$O: C, 39.82; H, 5.01; N, 36.10. Found: C, 39.64; H, 4.94; N, 35.64. Compound III was prepared similarly to compound I by reaction of the ligand, BTIM, with copper perchlorate in aqueous methanol and obtained as blue crystals. Anal. Calcd for [Cu$_2$(C$_{18}$H$_{22}$N$_8$)$_2$(H$_2$O)$_2$](ClO$_4$)$_4$·2H$_2$O: C, 33.30; H, 4.01; N, 17.27. Found: C, 33.54; H, 3.97; N, 17.23.

[Cu(LP)$_2$](ClO$_4$)$_2$ (IV) was prepared as described previously.[5]

Physical Measurements. The electrochemical experiments were performed at room temperature in acetonitrile (spectroscopic grade, dried over molecular sieves) under O$_2$-free conditions by using a BAS CV27 voltammograph and a Hewlett-Packard XY recorder. A three-electrode system was used (cyclic voltammetry) in which the working electrode was either glassy carbon or platinum and the counter electrode platinum with a standard calomel (SCE) electrode as reference. For coulometry measurements a three-electrode system was employed, consisting of a platinum-mesh-flag working electrode, a platinum-mesh counter electrode, and a SCE reference electrode. The supporting electrolyte was tetrabutylammonium perchlorate (TBAP) (0.1 M), and all solutions were 10^{-3}–10^{-4} M in complex. The best combination of experimental conditions (working electrode, scan rates, solvent, etc.) was determined by preliminary experiment. Room-temperature magnetic moments were measured by the Faraday method using a Cahn 7600 Faraday magnetic susceptibility system. Variable-temperature magnetic susceptibility data were obtained in the range 5–300 K (compounds I and II) by using an Oxford Instruments superconducting Faraday magnetic susceptibility system with a Sartorius 4432 microbalance. A main solenoid field of 1.5 T and a gradient field of 10 T m^{-1} were employed.

Infrared spectra were recorded by using a Perkin-Elmer 283 instrument and electronic spectra with a Cary 17 spectrometer. EPR spectra were recorded with a Bruker ESP 300 X-band spectrometer at room temperature and 77 K. Microanalyses were carried out by the Canadian Microanalytical Service, Vancouver, Canada.

Crystallographic Data Collection and Refinement of the Structure for [Cu(LP)$_2$](ClO$_4$)$_2$ (IV). Crystals of IV are brown. The diffraction intensities of an approximately 0.12 × 0.15 × 0.20 mm crystal were collected with graphite-monochromatized Mo Kα radiation by using a Nonius diffractometer and the $\theta/2\theta$ scan mode, with profile analysis.[19]

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Table II. Final Atomic Positional Parameters and Equivalent Isotropic Debye–Waller Temperature Factors (Esd's) for $[Cu(LP)_2](ClO_4)_2$ (IV)

	x	y	z	B_{iso},[a] Å^2
Cu	0	$^1/_2$	$^1/_2$	3.18 (6)
Cl	0.21954 (21)	0.27464 (20)	0.05266 (19)	4.20 (9)
O1	0.2849 (6)	0.3735 (6)	0.0134 (6)	6.3 (4)
O2	0.2409 (7)	0.2733 (7)	0.1642 (5)	6.8 (4)
O3	0.0874 (7)	0.2899 (8)	0.0161 (7)	9.4 (5)
O4	0.2654 (10)	0.1661 (7)	0.0120 (6)	8.7 (6)
N1	0.0201 (5)	0.4914 (6)	0.6565 (4)	3.4 (3)
N2	0.1032 (6)	0.4688 (7)	0.8268 (5)	3.0 (3)
N3	0.1144 (6)	0.3591 (6)	0.5001 (5)	3.3 (3)
N4	0.2863 (7)	0.2392 (7)	0.5224 (6)	3.1 (3)
C1	−0.0901 (7)	0.4932 (9)	0.7164 (6)	4.2 (4)
C2	−0.0348 (9)	0.4455 (9)	0.8265 (7)	6.8 (5)
C3	0.1231 (6)	0.4806 (7)	0.7252 (6)	3.1 (3)
C4	0.2585 (7)	0.4890 (8)	0.7017 (5)	3.4 (3)
C5	0.3398 (8)	0.5645 (9)	0.7698 (7)	4.8 (4)
C6	0.4660 (9)	0.5802 (11)	0.7579 (8)	6.2 (6)
C7	0.5158 (8)	0.5173 (12)	0.6798 (9)	6.5 (6)
C8	0.4379 (8)	0.4415 (9)	0.6117 (8)	4.8 (4)
C9	0.3074 (7)	0.4271 (7)	0.6212 (6)	3.2 (3)
C10	0.2321 (7)	0.3426 (7)	0.5466 (6)	3.4 (3)
C11	0.2026 (10)	0.1830 (9)	0.4380 (9)	7.9 (6)
C12	0.0735 (9)	0.2487 (8)	0.4358 (7)	4.5 (4)
HN2	0.176	0.475	0.897	3.7
HN4	0.3706 (10)	0.2401 (9)	0.5566 (9)	3.2 (5)
H1A	−0.1177 (10)	0.5800 (9)	0.7321 (9)	3.2 (5)
H1B	−0.1671 (10)	0.4625 (9)	0.6933 (9)	3.2 (5)
H2A	−0.0603 (10)	0.3319 (9)	0.8268 (9)	3.2 (5)
H2B	−0.0375 (10)	0.5052 (9)	0.9063 (9)	3.2 (5)
H5	0.301	0.612	0.834	5.6
H6	0.5361 (10)	0.6458 (9)	0.8043 (9)	3.2 (5)
H7	0.6144 (10)	0.5108 (9)	0.6635 (9)	3.2 (5)
H8	0.4810 (10)	0.3848 (9)	0.5540 (9)	3.2 (5)
H11A	0.2375 (10)	0.0858 (9)	0.4479 (9)	3.2 (5)
H11B	0.2125 (10)	0.2271 (9)	0.3438 (9)	3.2 (5)
H12A	0.0267 (10)	0.2734 (9)	0.3553 (9)	3.2 (5)
H12B	0.0241 (10)	0.2168 (9)	0.4906 (9)	3.2 (5)

[a] B_{iso} is the mean of the principal axes of the thermal ellipsoid.

A total of 4184 reflections were measured, of which 2517 were unique and 1589 were considered significant with $I_{net} > 2.5\sigma(I_{net})$. Lorentz and polarization factors were applied, but no correction was made for absorption The cell parameters were obtained by the least-squares refinement of the setting angles of 25 reflections with 2θ in the range 35–40°.

The structure was solved by direct and difference Fourier methods using the NRCVAX crystal structure programs[20] and refined by full-matrix least-squares methods to final residuals of R and R_w of 0.060 and 0.067, respectively ($R = \sum(|F_o| - |F_c|)/\sum(|F_o|)$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(|F_o|)^2]^{1/2}$), with unit weights. The final difference map had no peaks greater than 0.62 e/A^3. All hydrogen atoms, with the exception of H2B and HN2 were obtained from difference maps, but none were refined. Scattering factors for neutral species were taken from ref 21. A summary of crystal data is given in Table I, and atomic coordinates are given in Table II. Anisotropic thermal parameters (Table SI) and a listing of structure factors are included as supplementary material.

Results

Description of the Structures of $[Cu_2(BTIM)_2Cl_2]Cl_2 \cdot 7H_2O$ (I), $[Cu_2(BTIM)_2(N_3)_2](N_3)_2 \cdot 5H_2O$ (II), and $[Cu(LP)_2](ClO_4)_2$ (IV). Details of the structure of $[Cu_2(BTIM)_2Cl_2]Cl_2 \cdot 7H_2O$ (I) have already been reported.[17] However, for comparison with compounds II and IV, some details of the structure are reproduced in this report. The structure of the cation of I is shown in Figures 2 and 3, and bond lengths and bond angles relevant to the copper coordination spheres are given in Table III. The structure consists of a most unusual arrangement of two binucleating tetradentate ligands enclosing the two copper(II) centers in such a way as to create a large, unoccupied cavity between the two metal centers. Each copper atom has a slightly distorted square-pyramidal structure with a long apical distance (2.505 (4) Å) to a chlorine and with the copper center displaced by 0.287 (5) Å from the mean N_4 plane toward the chlorine. The two copper atoms are separated by 7.610 (2) Å. The planar benzene rings are parallel to each other (dihedral angle 0.1 (6)° between rings) and eclipse each other and are separated by 3.93 Å on average, which is somewhat larger than the layer separation in graphite (3.35 Å). The molecular cation is highly symmetric with a center of inversion at the center of the cavity. Intermolecular contacts in the crystal (Figure 3) are considered to be insignificant, with the shortest distance between bound chlorine atoms being 6.03 Å.

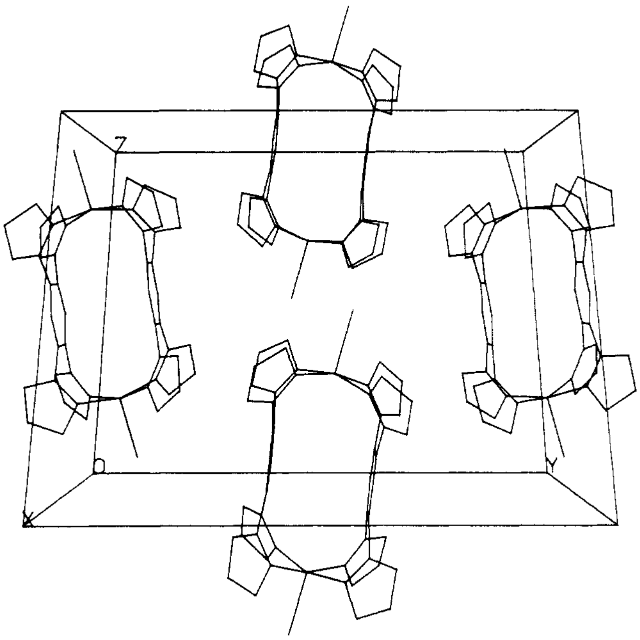

Figure 3. Packing diagram for $[Cu_2(BTIM)_2Cl_2]^{2+}$ (I^{2+}).

Table III. Interatomic Distances (Å) and Angles (deg) Relevant to the Copper Coordination Spheres in $[Cu_2(BTIM)Cl_2]Cl_2 \cdot 7H_2O$ (I) and $[Cu_2(BTIM)(N_3)_2](N_3)_2 \cdot 5H_2O$ (II)

	Complex I		
Cu–Cl(1)	2.504 (3)	Cl(1)–Cu–N5	96.0 (3)
Cu–N1	1.994 (9)	Cl(1)–Cu–N7	97.08 (24)
Cu–N3	1.995 9)	N1–Cu–N3	86.2 (4)
Cu–N5	1.991 (9)	N1–Cu–N5	164.4 (3)
Cu–N7	1.991 (9)	N1–Cu–N7	89.6 (4)
Cu–CuA	7.610 (3)	N3–Cu–N5	91.1 (4)
Cl(1)–Cu–N1	99.56 (24)	N3–Cu–N7	162.4 (3)
Cl(1)–Cu–N3	100.5 (3)	N5–Cu–N7	88.3 (4)
	Complex II		
Cu1–N1	1.989 (24)	N1–Cu1–N3	87.4 (10)
Cu1–N3	1.94 (3)	N1–Cu1–N5	169.1 (11)
Cu1–N5	2.01 (3)	N1–Cu1–N8	92.2 (10)
Cu1–N8	2.05 (3)	N1–Cu1–N9	94.3 (10)
Cu1–N9	2.27 (3)	N3–Cu1–N5	89.5 (11)
		N3–Cu1–N8	164.5 (11)
Cu1–Cu1′	7.297 (15)	N3–Cu1–N9	97.9 (10)
		N5–Cu1–N8	88.1 (11)
		N5–Cu1–N9	96.6 (11)
		N8–Cu1–N9	97.6 (10)

An X-ray structural investigation has been carried out on the azide derivative, II, but the low level of refinement prevents publication of full details of the structure at this time.[22] Two crystallographically independent half-molecules comprise the asymmetric unit. Each has a structure similar to the cation of II (Figure 4). Some dimensions associated with the copper

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(22) Monoclinic, space group $P2_1/a$, a = 18.349 (3) Å, b = 12.7667 (13) Å, c = 20.488 (3) Å, β = 115.816 (12)°, V = 4658.86 Å^3, Z = 4, fw 1063.96, R = 0.178.

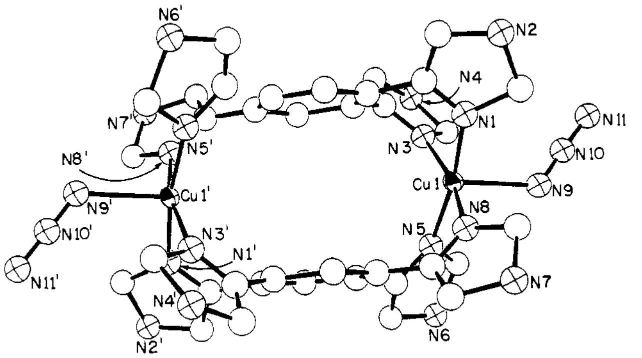

Figure 4. Structural representation of $[Cu_2(BTIM)_2(N_3)_2]^{2+}$ (II^{2+}) with hydrogen atoms omitted.

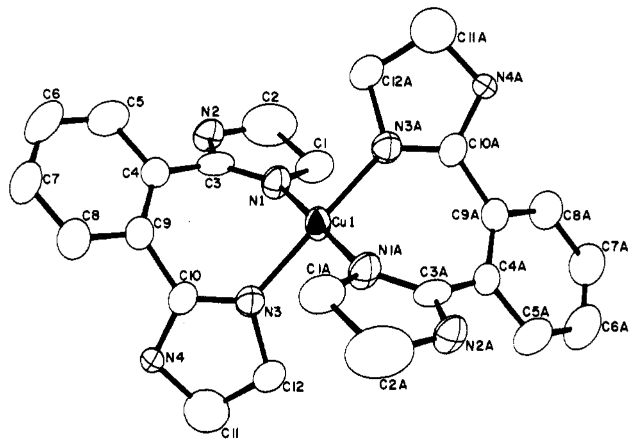

Figure 5. Structural representation of $[Cu(LP)_2]^{2+}$ (IV^{2+}) with hydrogen atoms omitted.

Table IV. Interatomic Distances (Å) and Angles (deg) Relevant to the Copper Coordination Sphere in $[Cu(LP)_2](ClO_4)_2$ (IV)

Cu-N1	1.967 (6)	N1-Cu-N1A	180.0
Cu-N1A	1.967 (6)	N1-Cu-N3	89.2 (3)
Cu-N3	1.973 (6)	N1-Cu-N3A	90.8 (3)
Cu-N3A	1.973 (6)	N1A-Cu-N3	90.8 (3)
		N1A-Cu-N3A	89.2 (3)
		N3-Cu-N3A	180.0

coordination spheres in this compound are given in Table III. The empty cavity in this structure is similar in size to that found in I with copper-copper separations of 7.30 and 7.42 Å and a benzene ring separation of 4.3 or 4.4 Å. Each copper atom is square pyramidal with a terminal, bent azide as an apical ligand (Cu-N = 2.18 (3), 2.27 (3) Å; Cu-N-N = 125.3 (22), 126.1 (25)°).

The structure of the cation of $[Cu(LP)_2](ClO_4)_2$ (IV) is illustrated in Figure 5, and bond distances and angles relevant to the copper coordination sphere are given in Table IV. The bidentate bis(hydroimidazole) ligand, LP, form a trans structure about the square-planar copper(II) center, with the hydroimidazole rings canted by 109.4 (4)° to each other and by 130.2 (3) and 39.1 (3)° with respect to the benzene ring. The canting of the five-membered rings is, of necessity, a result of the formation of a seven-membered chelate ring. The CuN_4 chromophore is rigidly square planar, with no net displacement of any of the five atoms by more than 0.001 Å from the CuN_4 mean plane. Within the CuN_4 plane, N-Cu-N angles are very close to 90° (89.2, 90.8°) and Cu-N distances are 1.967 (Cu-N1) and 1.973 Å (Cu-N3).

The structure of IV is very similar to the recently reported structure of the complex $Cu(L)_2(ClO_4)_2{\cdot}4H_2O$, where L is the bis(imidazole) analogue of LP (1,2-bis(imidazol-2-yl)benzene).[23] In this complex the two ligands are bound similarly to the square-planar copper center in a trans fashion with similar canting of the imidazole rings. Slightly longer Cu-N bond lengths occur in this compound (1.996 Å), and two water molecules are bound weakly at the axial sites (Cu-O = 2.624 Å).

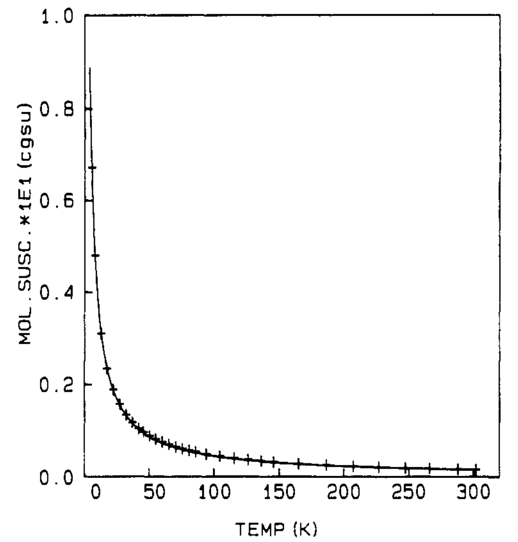

Figure 6. Magnetic data for $[Cu_2(BTIM)_2Cl_2]Cl_2{\cdot}7H_2O$ (I). The solid line was calculated from eq 1 with $g = 2.149$ (8) and $-2J = 1.8$ (1) cm^{-1}.

Spectral, Magnetic, and Electrochemical Properties. Infrared spectra of compounds I-III are similar in regions associated with ligand vibrations, indicating an overall structural similarity of the three compounds. In the far-infrared region a prominent absorption in I at 298 cm^{-1}, which is absent in II and III, is associated with the terminal copper-chlorine stretch. Compound II exhibits one major azide band, which appears to have two components at 2020 and 2035 cm^{-1}, which are tentatively assigned to ionic and coordinated azide,[24] and the perchlorate derivative, III, has a strong, broad adsorption at 1100 cm^{-1}, indicating the presence of ionic perchlorate. All three compounds have broad absorptions around 3500 cm^{-1}, associated with water, and lower energy bands (3180 cm^{-1} (I), 3200 cm^{-1} (II), 3350 cm^{-1} (III)) that can be assigned to NH vibrations in the hydroimidazole rings. A particularly sharp, strong band is observed for III, which might indicate the involvement of the NH proton in this compound in hydrogen bonding. The spectral properties of IV have already been described.[5]

Electronic spectral data in the solid state (Table V) for compounds I-III are characterized by the presence of two prominent bands, one in the range 17900-19100 cm^{-1}, clearly d-d in origin, with a higher intensity band around 31000 cm^{-1}, associated with a charge-transfer transition. The intensities of equivalent bands in aqueous solution support these assignments. The high-energy visible band observed for III, both in the solid state and in solution, suggests that water is a ligand, and the lower energy bands observed for I and II are consistent with chloride and azide as ligands in these complexes. The similarity in absorpion energies in aqueous solution for all three compounds suggests the presence of the same hydrated species in each case in this solvent, which presumably involves axially coordinated water.

Infrared and electronic spectral data indicate a close similarity in the structures of I-III and suggest that for compound III a cavity structure similar to that found in I and II exists and that coordinated water occupies the axial position of the square-pyramidal copper centers.

All of the binuclear complexes have room-temperature magnetic moments in excess of 1.8 μ_B, suggesting that, if the copper centers are spin coupled, exchange is likely to be weak. Variable-temperature magnetic studies were carried out on powdered samples of I and II in the temperature range 5-300 K. Magnetic moments (μ_{eff}) are roughly constant above 100 K (1.91 μ_B (104.5 K), 1.93 μ_B (301.8 K) for I; 1.94 μ_B (104.3 K), 1.98 μ_B (301.8 K) for II)

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Table V. Electronic Spectral and Magnetic Data

		UV/vis, cm^{-1} (ϵ)	μ_{eff}, μ_B (room temp)	g	$-2J$, cm^{-1}
I	$[Cu_2(BTIM)_2Cl_2]Cl_2\cdot7H_2O$	17 900, 31 100^a	1.93	2.149 (8)	1.8 (1)^c
		18 500 (144), 32 800 (6020), 36 400 (6700)^b		2.148 (8)	1.7 (1)^d
II	$[Cu_2(BTIM)_2(N_3)_2](N_3)_2\cdot5H_2O$	18 200^a	1.98	2.172 (9)	1.9 (1)^c
		18 900 (166), 33 300 (7200), 36 400 (7900)^b		2.172 (9)	1.8 (1)^d
III	$[Cu_2(BTIM)_2(H_2O)_2](ClO_4)_4\cdot2H_2O$	19 050, 30 800^a	1.83		
		19 050 (143), 32 800 (6150), 36 400 (7300)^b			
IV	$[Cu(LP)_2](ClO_4)_2$	16 100, 20 800^a	1.77		

^{a} Mull transmittance. ^{b} Aqueous solution (ϵ per Cu). ^{c} Bleaney–Bowers expression. ^{d} Magnetization expression.

but decrease significantly below 100 K and drop below 1.8 μ_B at temperatures <15 K. Magnetic susceptibility data are plotted as a function of temperature for I in Figure 6. The temperature variation of inverse susceptibility was analyzed for both compounds by using the Curie–Weiss law, giving g values of 2.16 (I) and 2.17 (II) and Θ values of −0.92 (I) and −0.98 K (II). Clearly, exchange coupling is very small for both compounds. The variable-temperature susceptibility data were fitted to the Bleaney–Bowers expression (eq 1)[25] by using the isotropic (Heisenberg) exchange

$$\chi_m = (N\beta^2g^2/3kT)[1 + \tfrac{1}{3}\exp(-2J/kT)]^{-1} + N\alpha \quad (1)$$

Hamiltonian ($\mathcal{H} = -2Js_1\cdot s_2$) for two interacting $S = {}^1/_2$ centers (χ_m is expressed per mole of copper atoms and $N\alpha$ is the temperature-independent paramagnetism, set at 60×10^{-6} cgsu). A nonlinear regression analysis was employed with g and J as variables,[26] and the results are presented in Table V. The results of the fit are shown as the solid line for I in Figure 6 (a similar fit was obtained for compound II) and indicate the presence of very weak antiferromagnetic exchange between the copper(II) centers in both compounds. Since the singlet–triplet splitting in both cases is comparable with the Zeeman energy, $g\beta H$, the data were also fitted to the magnetization expression (eqs 2 and 3).[27,28]

$$M = \frac{Ng\beta \sinh (g\beta H/kT)}{\exp(-2J/kT) + 2 \cosh (g\beta H/kT) + 1} \quad (2)$$

$$\chi_m = M/H + N\alpha \quad (3)$$

Values of g and J obtained from this analysis (Table V) are essentially the same as those obtained from the Bleaney–Bowers expression. The average g values compare reasonably well with those obtained from ESR measurements. The X-ray structural data indicate that there are no significant intermolecular contacts that could reasonably contribute a significant interdimer coupling interaction, and so no molecular field correction was applied. The absence of a maximum in the plots of χ_m verus T for both compounds and the lower temperature limit of 5.7 K for the susceptibility data question somewhat the assessment of the very weak spin coupling for these compounds on the basis of magnetic measurements alone. Clearly, lower temperature data are desirable.

The X-band ESR spectra of polycrystalline, undoped, powdered samples of I and II were obtained at 295 and 77 K. The spectra, which are very similar, do not show any detectable half-field absorption associated with a $\Delta M_s = \pm2$ transition but exhibit two main features (Figure 7), corresponding to the triplet $\Delta M_s = \pm1$ transitions, associated with an axial **g** tensor. Estimates of g values gave $g_\parallel = 2.240$ and $g_\perp = 2.040$ for I and $g_\parallel = 2.215$ and $g_\perp = 2.052$ for II at room temperature, with very little change in the spectrum or g values on cooling to 77 K. Compound III exhibits a very broad, single resonance in the solid state at room temperature centered at $g = 2.09$. In solution (DMF/toluene, nitromethane, acetonitrile) the room-temperature ESR spectra of compounds I–III are characterized by the presence of a very broad, single resonance in the range $g = 2.09$–2.10. However, when solutions of I and III in DMF/toluene, DMF/H_2O, and nitromethane are cooled to 77 K, essentially identical spectra are obtained with a rich hyperfine splitting in the $g_\parallel$ region, in addition to resolution in the $g_\perp$ region (Figure 8). For a copper(II) dimer with weak exchange and axial symmetry, two $\Delta M_s = \pm1$ features might be expected: a $g_\parallel$ feature, zero-field-split into two resonances, and a zero-field-split $g_\perp$ feature, giving two resonances. Six hyperfine lines are clearly resolved in the $g_\parallel$ region, with an average hyperfine splitting of 86 G, which is roughly half that

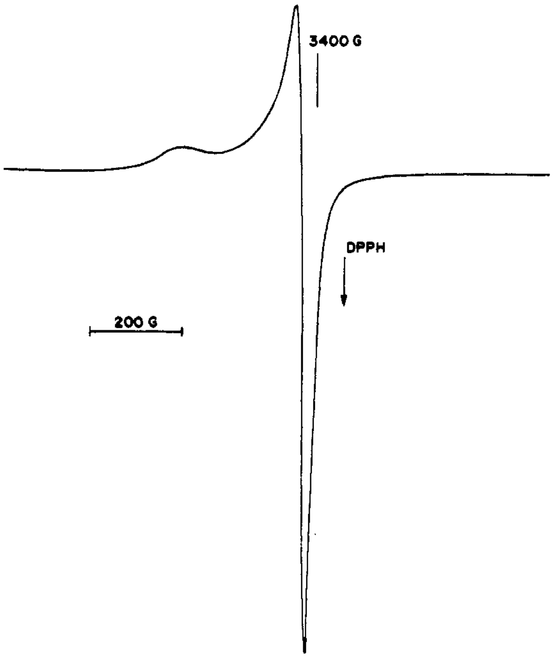

Figure 7. X-Band EPR spectrum for $[Cu_2(BTIM)_2(N_3)_2](N_3)_2\cdot5H_2O$ (II) at room temperature (9.73 GHz).

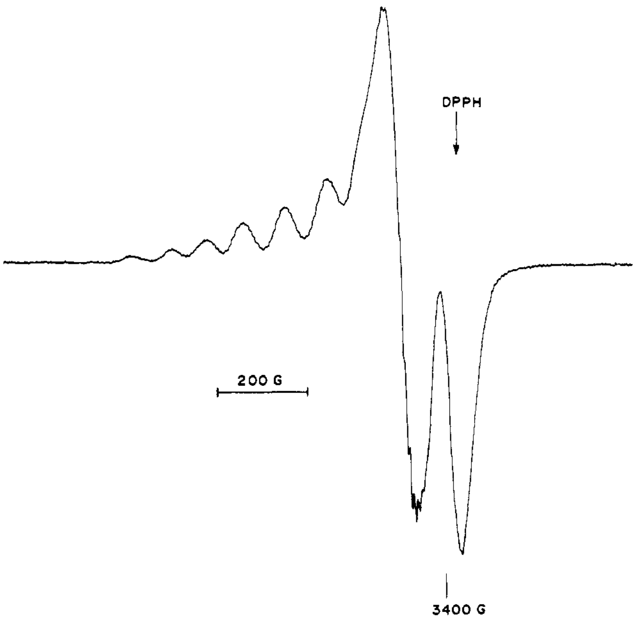

Figure 8. X-Band EPR spectrum of a frozen solution (77 K) of $[Cu_2(BTIM)_2(H_2O)_2](ClO_4)_4\cdot2H_2O$ in DMF/toluene (9.52 GHz).

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of the analogous copper(II) monomer $[Cu(LP)_2](ClO_4)_2$.[5] The seventh line is overlapped with a major peak at 3300 G. The appearance of seven low-field hyperfine lines with a splitting of 86 G is typical of a system with a weak exchange interaction,[29–32] but contrary to what might be expected, no discernible hyperfine lines were observed on the high-field side of the $g_\perp$ transitions. Typically, such lines are weak, but because of small zero-field splitting, they may simply be buried under the $g_\perp$ resonance in this case. Assigning values to D, the zero-field splitting, and $g_\parallel$ is thus difficult. No $\Delta M_s = \pm 2$ transition was observed at 77 K.

Resolution of the copper(II) hyperfine structure in the frozen glass prompted us to "dilute" the binuclear copper cation in the solid state by preparing the tetraphenylborate salt, $[Cu_2(BTIM)_2(H_2O)_2](BPh_4)_4 \cdot 6H_2O$, by reaction of I with excess $NaBPh_4$ in aqueous methanol (satisfactory elemental analysis was obtained for this compound, and infrared and electronic spectra indicate the presence of the same binuclear cation as found in III). This technique has been employed successfully by other workers.[32] The same low-field, seven-line copper hyperfine feature was observed in the solid state at both room temperature and 77 K (average hyperfine splitting 86 G), for the BPh_4 complex, but again no high-field lines were observed. The frozen-glass spectrum of this compound (DMF/toluene, 77 K) was identical with the seven-line spectra obtained for I and III under the same conditions. The presence of large, bulky tetraphenylborate anions clearly separates the paramagnetic cations, leading to a substantial degree of magnetic dilution beween dimers. Interdimer magnetic effects can therefore be considered to be very small or insignificant, and so more credibility can be given to the magnetic analysis, which suggests the presence of very weak antiferromagnetic intradimer coupling for I and II, which have the same, basic, binuclear cavity structure. Also, because a seven-line spectral feature was observed for $[Cu_2(BTIM)_2(H_2O)_2](BPh_4)_4 \cdot 6H_2O$ at room temperature, dipole–dipole interactions seen unlikely to be the source of exchange.

The spin–spin interaction between the copper(II) centers in I and II can therefore be considered to occur only via a superexchange mechanisn involving the ligand itself. The large metal–metal separation and the long molecular pathway between the copper centers are certainly consistent with very weak exchange. Such weak exchange is typified by compounds in which the two copper(II) centers are separated by large distances with intervening 1,2,4,5-tetrasubtituted benzene rings.[33,34] The binuclear copper(II) acetate complex of the double isoindoline ligand derived by condensation of 1,2,4,5-tetracyanobenzene and 2-amino-4-*sec*-butylpyridine involves an essentially equivalent intramolecular spin-exchange pathway and is very weakly coupled with $J = -1$ cm^{-1}.[34]

Electrochemical studies were carried out on I and III in acetonitrile (Pt/TBAP/SCE). The cyclic voltammograms obtained for both compounds are not well resolved and depict irreversible redox processes. Waves at $E^1/_2 = -0.38$ V for I and at $E_{1/2} = -0.48$ V for III have peak-to-peak separations in excess of 230 mV and are considered to involve a one-electron reduction step at each copper(II) center. The nonreversible nature of the waves suggests that a factor inhibiting reduction would rest with the rigidity of the cavity structural arrangement and the inability of the ligand donor groups to accommodate geometrical changes that would be likely to accompany the reduction process. Molecular models indicate that this is the case and also show that a tetrahedral arrangement of donors about each copper could not occur if the molecular integrity was maintained. It seems likely, therefore, that significant molecular rearrangement accompanies the reduction process, possibly involving the rupture of the metallacycle and the formation of mononuclear copper(I) fragments.

The electrochemical properties of $[Cu(LP)_2](ClO_4)_2$ (IV) are in complete contrast to those of the binuclear derivatives. In acetonitrile very clean cyclic voltammograms are observed ($E_{1/2} = -0.33$ V), with peak-to-peak separation varying very slightly as a function of scan rate ($\Delta E_p = 110$ mV at 200 mV s^{-1}), suggesting a quasi-reversible redox process. Controlled-potential electrolysis at −0.2 V requires the passage of 1 equiv of charge, accompanied by discharge of the purple color of the solution, indicating a one-electron reduction process. The ligand, LP, gave no electrochemical response in the range $-0.8 \rightarrow +1.2$ V (vs SCE).

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Supplementary Material Available: Anisotropic thermal parameters and bond length and angle data for IV (Tables SI and SII, respectively) (4 pages); a listing of observed and calculated structure factors for IV (17 pages). Ordering information is given on any current masthead page.

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