both the large positive value of ΔS determined for the dynamic process as well as the ^{13}C NMR results. However, this possibility seemed unlikely due to the high thermal stability that has been observed[5] for monometallic complexes containing pyS ligands. In order to establish whether the predominant species at elevated temperatures is a di- or monometallic species, we performed molecular weight determinations by measuring the elevation of the boiling point of carbon tetrachloride into which **1** was dissolved. The molecular weight of 303 ± 43 determined by these studies demonstrates that the species dominating the equilibrium at elevated temperatures is a monopalladium complex. Thus it appears that the observed dynamic process is rapid equilibrium between **1** and a monomeric PdCl(pyS)(PMe_3) complex.

Conclusion

Our studies indicate that in solution the dipalladium pyS complex **1** is in rapid equilibrium with a monomeric PdCl(η^2-pyS)(PMe_3) complex, clearly establishing that such species can rapidly interconvert at ambient conditions. Therefore, the interconversion of di- and monometallic η^2-pyS complexes should be considered along with the mechanisms proposed previously by Deeming[2] and Oro[3] for the fluxional behavior of dimetallic μ-η^2-pyS complexes.

Acknowledgment. We thank the University of Hawaii Research Council for the support of this research. The assistance of Mr. M. Mediati and Prof. R. E. Cramer in the X-ray diffraction study as well as helpful discussions with Prof. T. T. Bopp and Dr. Walter Niemczura is gratefully acknowledged.

Supplementary Material Available: Tables and plots of variable-temperature NMR data, a table of calculations of energetics, and tables of anisotropic thermal parameters, bond distances, bond angles, and hydrogen atom coordinates and isotropic thermal parameters for $Pd_2(\mu\text{-}N\text{-}S\text{-}\eta^2\text{-pyS})_2Cl_2(PMe_3)_2\cdot EtOH$ (7 pages); a table of structure factors (5 pages). Ordering information is given on any current masthead page.

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Synthesis and Characterization of Dinuclear Copper(II) Complexes of the Dinucleating Ligand 2,6-Bis[(bis((1-methylimidazol-2-yl)methyl)amino)methyl]-4-methylphenol

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Received December 14, 1989

The synthesis, crystal structures, and magnetic and spectroscopic properties are reported for a series of dinuclear copper(II) complexes of the novel dinucleating polyimidazole ligand 2,6-bis[(bis((1-methylimidazol-2-yl)methyl)amino)methyl]-4-methylphenol (Hbimp). The copper complexes have both "open" ($[Cu_2(bimp)(H_2O)_2](ClO_4)_3$ (**2**) and $[Cu_2(bimp)(CH_3OH)_2](ClO_4)_3$ (**3**)) and "closed" ($[Cu_2(bimp)(OCH_3)](ClO_4)_2$ (**4**) and $[Cu_2(bimp)(N_3)](ClO_4)_2$ (**5**)) type structures. X-ray crystal structures of complexes **3** and **4** were determined with Mo Kα radiation. Crystal data: **3**, $C_{31}H_{45}N_{10}Cu_2Cl_3O_{15}$, monoclinic, $P2_1/n$, $a = 17.855$ (3) Å, $b = 13.377$ (3) Å, $c = 18.054$ (4) Å, $\beta = 105.78$ (2)°, $Z = 4$, $R(F) = 0.051$ for 5074 independent data [$I \geq 3\sigma(I)$]; **4**, $C_{32}H_{48}N_{10}Cu_2Cl_2O_{12}$, monoclinic, $C2/c$, $a = 23.221$ (3) Å, $b = 12.903$ (2) Å, $c = 17.681$ (3) Å, $\beta = 125.34$ (1)°, $Z = 4$, $R(F) = 0.054$ for 2439 independent data [$I \geq 3\sigma(I)$]. In complex **3**, the copper ions are pentacoordinate, bonded to two imidazoles, a tertiary amine nitrogen, a methanol oxygen atom, and the bridging phenolate oxygen atom. The dinuclear complex has a Cu(1)–O(1)–Cu(2) angle of 142.9 (2)° and a Cu–Cu separation of 4.090 (1) Å. In complex **4**, the copper ions also are pentacoordinate, bridged both by the phenolate oxygen atom and by a methoxide ion. The Cu–Cu′ separation is 3.026 (1) Å with a Cu–O(1)–Cu′ angle of 98.7 (1)°. Magnetic susceptibility measurements reveal that there is no appreciable exchange interaction between the copper ions in complexes **2** and **5** ($|J| \leq 0.3$ cm^{-1}), over the temperature range 2–300 K. In complex **4**, magnetic data indicate that the copper ions are involved in a moderate antiferromagnetic exchange interaction ($J = -47$ cm^{-1}) over the temperature range 5–300 K. Differences in the strength of the magnetic exchange interactions are rationalized by using a magnetic orbital approach. UV–visible electronic spectral and EPR spectral data are presented for each complex.

Introduction

The synthesis of binuclear complexes containing histidyl imidazole functionalities as analogues of the ligating sites of complex metalloproteins is of current interest. This "synthetic analogue approach"[1] has been applied to modeling the active sites of the type III copper proteins hemocyanin (Hc) and tyrosinase (Ty).[2] Hemocyanin functions as an oxygen-transport protein in the hemolymph of several species of anthropods and mollusks, while tyrosinase is a monooxygenase enzyme. X-ray crystallographic data on deoxy-Hc indicate that the two Cu(I) ions are separated by 3.8 ± 0.4 Å, with each copper bonded to two histidine residues at 2.0 Å and a third at 2.7 Å.[3] Results from EXAFS[4] and other spectroscopic studies[2,5,6] indicate that when oxygen binds to deoxy-Hc, the histidine ligands remain coordinated and the Cu–Cu separation is reduced to approximately 3.6 Å. In oxy-Hc, the Cu(II) ions are thought to be bridged by an oxygen molecule, in

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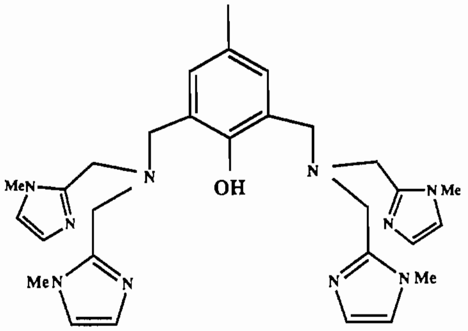
0020-1669/91/1330-1357$02.50/0

the form of a peroxide ion, as well as by a single endogenous ligand. Presently, the endogenous ligand is thought to be either a water molecule or a hydroxide ion[7] that provides a major pathway for spin exchange between Cu(II) centers. At room temperature, oxy-Hc is essentially diamagnetic as a result of strong antiferromagnetic exchange coupling ($|J| > 500$ cm^{-1}).[8] Interestingly, a similar dinuclear unit may be present in the trinuclear portion of the multicopper center of ascorbate oxidase from zucchini studied recently by X-ray crystallography.[9]

In previous studies modeling the active sites of Hc and Ty, a variety of ligands have been used to hold the two copper centers in close proximity.[10] Several of the polypodal ligands[11] contain a bridging phenolate oxygen atom, since tyrosine was initially thought to be a possible candidate for the endogenous bridging ligand.[7a,12,13] In addition, these ligands contain pendant pyridine,[14-17] pyrazole,[18,19] and benzimidazole[20] groups as analogues of the histidine binding sites. Polypodal ligands also are known to stabilize Cu(I) complexes that in certain instances bind oxygen reversibly.[21,22] However, the Cu–Cu separations in these complexes typically are less than 3.1 Å.

As part of a systematic study of the structural and magnetic properties of complexes derived from the tridentate bis(imidazole) ligand bis((1-methylimidazol-2-yl)methyl)amine (bmima),[23] we describe herein the synthesis and characterization of a new polypodal ligand, 2,6-bis[(bis((1-methylimidazol-2-yl)methyl)amino)methyl]-4-methylphenol (Hbimp (**1**)). Compounds such as **1** are of interest because they provide two 5-5-6 tripodal coordination sites that can stabilize "open" type coordination environments[15,17] as well as 1,2- or 1,3-bridged structures with large Cu–Cu separations. The term "open" type structure refers to complexes studied previously by Suzuki[15] and Maloney et al.[17] and is mentioned to describe a less constrained and more relaxed bridging mode of the dinucleating ligand. In addition, compound **1** is the first example of a phenolate-containing polypodal ligand having the biologically relevant imidazole pendant functionalities. Reed et al.[24] have reported a polybenzimidazole complex that contains two 5-5-5 tripodal coordination sites for binding Cu(II) ions. The resulting 1,3-bridged azide polybenzimidazole complex is diamagnetic and has a Cu–Cu separation of 3.615 (3) Å. Similarly, a diamagnetic 1,3-bridged azide complex with a Cu–Cu separation of 3.75 Å has been reported by Sorrell et al.[19] using a polypyrazole ligand. Both of these complexes are good models for the active site of azidomethemocyanin.



Hbimp

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In this study, we will report the synthesis and properties of several Cu$^{II}_2$ complexes of **1**. These include the "open" complexes [Cu_2(bimp)(H_2O)$_2$](ClO_4)$_3$ (**2**) and [Cu_2(bimp)(CH_3OH)$_2$](ClO_4)$_3$ (**3**) as well as the "closed" complexes [Cu_2(bimp)(X)](ClO_4)$_2$, where X represents monoatom-exogenous bridging ligands: methoxide (**4**) and azide (**5**). The X-ray structures and spectroscopic and magnetic properties of these complexes will be discussed.

Experimental Section

Reagent grade chemicals were used in all experiments. Solvents were dried by standard procedures prior to use. The characterization and purity of compound **1** were determined by ^{1}H and ^{13}C NMR spectroscopies. Melting points were obtained by using a Fisher-Johns melting point apparatus and are uncorrected. All elemental analyses were performed by Desert Analytics Organic Microanalysis, Tuscon, AZ 85717. ^{1}H and ^{13}C NMR spectra were recorded on a Varian XL-300 spectrometer. Infrared spectra were recorded as DRIFTS on a Nicolet 9000 FT-IR spectrophotometer using KCl as a diluting matrix. Visible electronic absorption spectra were recorded with a Shimadzu UV-160 spectrophotometer. EPR spectra were obtained by using a Varian E-109 spectrometer equipped with an Oxford Instruments Inc. cryostat and calibrated by using diphenylpicrylhydrazyl (DPPH) as a standard. Bmima was prepared by a previously published procedure,[23] and 2,6-bis(chloromethyl)-*p*-cresol was prepared by following the procedure of Berends and Stephan.[20a]

Variable-temperature magnetic susceptibility data on complexes **4** and **5** were obtained by using a Series 800 VTS-50 SQUID susceptometer (SHE Corp.) operating at 10 kG, whereas data on complex **2** were obtained on a SQUID susceptometer (Quantum Design MPMS) operating at 0.5 T. All data have been corrected for diamagnetism by using Pascal's constants and are reported as molar paramagnetic susceptibility values. These molar susceptibilities were fit to the appropriate theoretical expressions by means of a least-squares-fitting computer program.[25] The *R* index for compound **2** was determined to be 4.9×10^{-7} on the basis

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Table I. Crystallographic Data for the Complexes

	3	**4**
chem formula	$C_{31}N_{45}N_{10}Cu_2Cl_3O_{15}$	$C_{32}H_{48}N_{10}Cu_2Cl_2O_{12}$
fw	1031.20	960.77
space group	$P2_1/n$ (No. 14)	$C2/c$ (No. 15)
a, Å	17.855 (3)	23.221 (3)
b, Å	13.377 (3)	12.903 (2)
c, Å	18.054 (4)	17.681 (3)
β, deg	105.78 (2)	125.34 (2)
V, Å^3	4149.6	4321.4
Z	4	4
T, °C	23	23
radiation (λ, Å)	Mo Kα (0.709 26)	Mo Kα (0.709 26)
ρ_{calcd}, g cm^{-3}	1.65	1.48
ρ_{obsd}, g cm^{-3}	1.63	1.50
μ, cm^{-1}	13.0	11.8
$R(F_o)$	0.051	0.054
$R_w(F_o)$	0.057	0.060

of the following formula: $R = \sum[(\chi T)_{exp} - (\chi T)_{cal}]^2/N\sum[(\chi T)_{exp}]^2$, where N = number of measurements (81).

Synthesis of Ligand and Copper(II) Complexes. 2,6-Bis[(bis((1-methylimidazol-2-yl)methyl)amino)methyl]-4-methylphenol (1). A solution of 2,6-bis(chloromethyl)-*p*-cresol (0.51 g, 2.5 mmol)[20a] in 50 mL of tetrahydrofuran (THF) was added slowly to a solution of bmima (1.03 g, 5.0 mmol)[23] and triethylamine (0.8 g, 8.0 mmol) in 100 mL of THF. The resulting solution was allowed to stir for 4 h, after which the precipitate was filtered out and washed with 10 mL of THF. The filtrate and washings were taken to dryness under reduced pressure, and the crude solid was recrystallized from THF/hexane, yielding 1.11 g (82%) of **1**. Mp: 182 °C. Anal. Calcd (found) for $C_{29}H_{38}N_{10}O$: C, 64.18 (63.89); H, 7.06 (7.27); N, 25.81 (25.78). ^1H NMR ($CDCl_3$, δ): 2.20 (s, 3 H), 3.30 (s, 12 H), 3.69 (s, 4 H), 3.70 (s, 8 H), 6.76 (s, 4 H), 6.83 (s, 2 H), 6.90 (s, 4 H). ^{13}C NMR ($CDCl_3$, δ): 20.4 (Ar-CH_3), 32.3 (Im N-CH_3), 49.4 (Im CH_2), 54.8 (benzylic CH_2), 121.4 and 126.8 (Im CH), 123.7 (benzylic C), 126.7 (Ar C), 131.6 (Ar CH), 145.4 (Im C), 154.1 (phenolate C).

$[Cu_2(bimp)(H_2O)_2](ClO_4)_3\cdot3H_2O$ (2). Compound **1** (0.454 g, 0.8 mmol) was dissolved in 10 mL of methanol, and the solution was added with stirring to a 20-mL methanol solution of $[Cu(H_2O)_6](ClO_4)_2$ (0.619 g, 1.7 mmol). The solution was allowed to stir for 2 h at room temperature and then cooled to −20 °C overnight, yielding 0.71 g (82%) of complex **2** as a light green powder. Anal. Calcd (found) for $C_{29}H_{47}N_{10}Cu_2O_{18}Cl_3$: C, 32.95 (33.11); H, 4.48 (4.39); N, 13.25 (12.96).

$[Cu_2(bimp)(CH_3OH)_2](ClO_4)_3$ (3). Complex **3** was prepared by dissolving 0.100 g of complex **2** in 20 mL of methanol. Over the period of 2 weeks, crystals of complex **3** (0.05 g) (50%) precipitated from solution and were collected by filtration.

$[Cu_2(bimp)(\mu\text{-}OCH_3)](ClO_4)_2\cdot2CH_3OH$ (4). Compound **1** (0.543 g, 1 mmol) was dissolved in 20 mL of methanol, and the solution was added to a 20-mL methanol solution of $[Cu(H_2O)_6](ClO_4)_2$ (0.741 g, 2 mmol). The mixture was allowed to stir at 50 °C for 1 h. A suspension of sodium imidazolate (0.09 g, 1 mmol) in 10 mL of methanol was added to the resulting solution. The solution was then allowed to stir for an additional 0.5 h at 60 °C. The resulting precipitate was filtered out and washed with 10 mL of warm methanol, yielding 0.70 g (78%) of **4** as a light green powder.[26]

$[Cu_2(bimp)(\mu\text{-}1,1\text{-}N_3)](ClO_4)_2$ (5). A 20-mL methanol solution of **1** (0.543 g, 1 mmol) was added with stirring to a 20-mL methanol solution containing $[Cu(H_2O)_6](ClO_4)_2$ (0.741 g, 2 mmol). NaN_3 (0.073 g, 1 mmol) was added to the resulting solution, and the mixture was warmed to 50 °C for several minutes and filtered. Upon overnight standing at 25 °C, a reddish brown microcrystalline solid deposited and was collected by filtration, yielding 0.65 g (72%) of **5**. Anal. Calcd (found) for $C_{29}H_{37}N_{13}Cu_2O_9Cl_2$: C, 38.29 (38.57); H, 4.10 (4.01); N, 20.02 (19.55).

Warning! Even though the perchlorate complexes isolated in this study were not found to be shock sensitive, care is recommended in their handling.

X-ray Crystallography. Green crystals of complexes **3** and **4** suitable for X-ray structural determination were obtained by slow cooling of methanol solutions containing $[Cu_2(bimp)(H_2O)_2](ClO_4)_3$ and $[Cu_2(bimp)(OCH_3)](ClO_4)_2$. Due to the gradual loss of methanol solvate molecules, a dark green parallelepiped-shaped crystal of **4** (0.30 × 0.38 × 0.45 mm^3) was sealed in a capillary tube prior to data collection. A block-shaped crystal of **3** (0.30 × 0.35 × 0.48 mm^3) was mounted and covered with an epoxy resin prior to data collection. Cell constants and orientation matrices were determined by least-squares refinement of 25 accurately centered reflections; these are reported in Table I along with other experimental parameters associated with the data collections. The choice of space groups ($P2_1/n$ (**3**) and $C2/c$ (**4**)) were confirmed by the program TRACER[27] and by successful solution of the structures. Intensity data were collected on an Enraf-Nonius CAD-4 diffractometer (Mo Kα, λ = 0.709 26 Å, graphite monochromator in incident beam) by using the ω–2θ scan technique to maximum 2θ values of 45° (**3**) and 50° (**4**). As a check of crystal and electronic stability, three representative reflections were measured every hour of exposure time. The intensities of these reflections decreased throughout the data collection for both complexes (−6.6% for **3**, −3.1% for **4**), and linear decay corrections were applied. All data were corrected for Lorentz and polarization effects, and an empirical absorption correction based on a series of ψ scans was applied. Relative transmission coefficients ranged from 0.863 to 0.990 for complex **3** and from 0.896 to 1.000 for **4**. All data were processed and the crystal structures solved by using the SDP package.[27] Scattering factors were taken from Cromer and Waber,[28] and anomalous dispersion effects were included in F_c.[29] Values for $\Delta f'$ and $\Delta f''$ used in this study were those of Cromer.[30]

The positions of the copper atoms were obtained by using direct method (MULTAN).[27] The remaining non-hydrogen atoms were located from a series of difference Fourier maps. For compound **4**, at least one hydrogen of each methyl group was located from the difference Fourier maps. The remaining hydrogen atom positions were calculated (C–H = 0.97 Å) and added to the structure factor calculations with $B_{iso} = 1.2B_{iso}$ of the bonded atom. Hydrogen atom positions were not refined in either structure. Both structures were refined by full-matrix least-squares techniques using anisotropic thermal parameters for indicated atoms.

$[Cu_2(bimp)(CH_3OH)_2](ClO_4)_3$ (3). The weighting function applied in the final cycles was that of Killean and Lawrence[31] with $w = [\sigma(F)^1 + (0.02F)^2 + 2.0]^{-1}$. Final agreement factors are $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.051$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.057$ for 551 parameters and 5074 ($I > 3\sigma(I)$) reflections. The highest peak in the final difference Fourier map was found to be 0.89 (10) e/Å^3, associated with Cu(2).

$[Cu_2(bimp)(OCH_3)](ClO_4)_2\cdot2CH_3OH$ (4). The anion and solvate molecules are severely disordered. The perchlorate was modeled by using a common Cl atom and two tetrahedral O_4 units having occupancies of 0.6 and 0.4. The solvate molecule was found to occupy two sites having total occupancies of 0.6 and 0.4. At each solvate site, the methanol unit was found to be further disordered, having relative site occupancies of 0.2, 0.2, 0.3, and 0.3, respectively. The atoms of the disordered perchlorate were refined anisotropically, while the atoms of the disordered solvate were refined with fixed isotropic thermal parameters. The weighting function applied in the final least-squares cycles of refinement was $w = 1/(\sigma(F))^2$. Final agreement factors were found to be $R = 0.054$ and $R_w = 0.060$ for 315 parameters and 2439 ($I > 3\sigma(I)$) reflections. The highest peak on the final difference Fourier map was found to be 0.57 (8) e/Å^3, associated with Cu(1). Thermal parameters for the atoms of the cation are well-behaved, while those of the anion and solvate molecules are large. Attempts to improve the model were unsatisfactory and were abandoned. Final atomic coordinates of compounds **3** and **4** are listed in Tables II and III, respectively.

Results and Discussion

(I) Compound Synthesis. Imidazoles are known to be present at the active site of hemocyanin and many other metalloproteins.[32,33] Imidazole compounds, however, are generally considered to be difficult to prepare due to their enhanced water solubility[34] and rather tedious methods of preparation.[35]

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(26) Attempts to synthesize **2** more efficiently by reacting Hbimp with $[Cu(H_2O)_6](ClO_4)_2$ and sodium methoxide repeatedly resulted in isolation of a substantial quantity of a monomer species.

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Table II. Positional Parameters and Their Estimated Standard Deviations for Complex **3**

atom	*x*/*a*	*y*/*b*	*z*/*c*
Cu(1)	0.54447 (3)	0.08995 (5)	0.63628 (4)
Cu(2)	0.53841 (3)	0.00656 (4)	0.85250 (3)
Cl(1)	0.74071 (7)	0.3593 (1)	0.45228 (8)
Cl(2)	0.73619 (9)	0.5096 (1)	0.1231 (1)
Cl(3)	0.36843 (9)	0.3597 (1)	0.3403 (1)
O(1)	0.5394 (2)	0.0975 (2)	0.7542 (2)
O(2)	0.6369 (2)	−0.0699 (3)	0.8619 (2)
O(3)	0.4760 (3)	−0.0323 (3)	0.6279 (3)
O(11)	0.7527 (3)	0.4630 (4)	0.4699 (4)
O(12)	0.8002 (3)	0.3077 (5)	0.5106 (3)
O(13)	0.6667 (2)	0.3284 (4)	0.4546 (3)
O(14)	0.7523 (3)	0.3418 (5)	0.3804 (3)
O(21)	0.6866 (3)	0.5891 (5)	0.1001 (4)
O(22)	0.8143 (3)	0.5369 (5)	0.1406 (5)
O(23)	0.7299 (5)	0.4759 (7)	0.1950 (5)
O(24)	0.7221 (5)	0.4361 (5)	0.0719 (5)
O(31)	0.3553 (5)	0.3070 (6)	0.2718 (4)
O(32)	0.3086 (3)	0.3312 (5)	0.3736 (4)
O(33)	0.4394 (4)	0.3283 (6)	0.3889 (5)
O(34)	0.3674 (4)	0.4608 (4)	0.3295 (5)
N(1)	0.6171 (2)	0.2157 (3)	0.6439 (2)
N(2)	0.6373 (3)	0.0187 (3)	0.6302 (3)
N(3)	0.7551 (3)	0.0236 (4)	0.6129 (3)
N(4)	0.4615 (2)	0.1855 (3)	0.5925 (3)
N(5)	0.4305 (2)	0.3445 (4)	0.5750 (3)
N(6)	0.4329 (2)	0.0653 (3)	0.8649 (2)
N(7)	0.4730 (2)	−0.1073 (3)	0.8110 (3)
N(8)	0.3603 (3)	−0.1833 (3)	0.7896 (3)
N(9)	0.5835 (2)	0.1067 (3)	0.9305 (2)
N(10)	0.5621 (3)	0.2397 (4)	0.9929 (3)
C(1)	0.5234 (3)	0.1927 (4)	0.7681 (3)
C(2)	0.5710 (3)	0.2710 (4)	0.7559 (3)
C(3)	0.5525 (3)	0.3686 (4)	0.7684 (3)
C(4)	0.4863 (3)	0.3922 (4)	0.7915 (3)
C(5)	0.4394 (3)	0.3151 (4)	0.8034 (3)
C(6)	0.4567 (3)	0.2158 (4)	0.7914 (3)
C(7)	0.4656 (4)	0.5004 (5)	0.8028 (5)
C(8)	0.6397 (3)	0.2455 (4)	0.7270 (3)
C(9)	0.6884 (3)	0.1886 (4)	0.6207 (3)
C(10)	0.6945 (3)	0.0767 (4)	0.6224 (3)
C(11)	0.6623 (4)	−0.0797 (5)	0.6251 (4)
C(12)	0.7343 (4)	−0.0758 (5)	0.6151 (4)
C(13)	0.8268 (3)	0.0650 (6)	0.6011 (4)
C(14)	0.5720 (3)	0.2962 (4)	0.5952 (3)
C(15)	0.4877 (3)	0.2776 (4)	0.5875 (3)
C(16)	0.3825 (3)	0.1953 (5)	0.5828 (4)
C(17)	0.3624 (3)	0.2925 (6)	0.5714 (4)
C(18)	0.4370 (4)	0.4520 (5)	0.5676 (5)
C(19)	0.4015 (3)	0.1322 (4)	0.7971 (3)
C(20)	0.3765 (3)	−0.0193 (4)	0.8616 (3)
C(21)	0.4018 (3)	−0.1031 (4)	0.8208 (3)
C(22)	0.4769 (3)	−0.1948 (4)	0.7712 (4)
C(23)	0.4074 (4)	−0.2411 (5)	0.7573 (4)
C(24)	0.2788 (3)	−0.2036 (5)	0.7867 (4)
C(25)	0.4487 (3)	0.1217 (4)	0.9375 (3)
C(26)	0.5308 (3)	0.1573 (4)	0.9548 (3)
C(27)	0.6517 (3)	0.1610 (4)	0.9542 (3)
C(28)	0.6395 (3)	0.2414 (5)	0.9932 (4)
C(29)	0.5208 (4)	0.3152 (5)	1.0259 (4)
C(32)	0.6940 (4)	−0.0526 (7)	0.8257 (4)
C(33)	0.4518 (5)	−0.1017 (6)	0.5678 (5)

Therefore, it was our objective to develop general methods for preparing polyimidazole ligands. The ligand Hbimp (**1**) is prepared by the reaction of 2,6-bis(chloromethyl)-*p*-cresol and bmima in THF containing an excess of triethylamine. The resulting triethylamine hydrochloride can be removed by filtration and the THF and excess triethylamine removed in vacuo, giving a crude oil of **1**. The resulting oil crystallizes from THF/hexane, giving complex **1** as a solid.

Table III. Positional Parameters and Their Estimated Standard Deviations for Complex **4**

atom	*x*/*a*	*y*/*b*	*z*/*c*
Cu	0.93057 (3)	0.09213 (4)	0.15496 (3)
Cl	0.7966 (1)	0.3225 (2)	0.3752 (1)
O(1)	1.000	−0.0086 (3)	0.250
O(2)	1.000	0.1814 (4)	0.250
O(3)	0.8447 (4)	0.2842 (8)	0.3678 (5)
O(4)	0.766 (1)	0.391 (1)	0.3210 (9)
O(5)	0.8135 (8)	0.339 (2)	0.4555 (8)
O(6)	0.756 (1)	0.228 (1)	0.359 (2)
O(7)	0.7870 (5)	0.282 (1)	0.4396 (6)
O(8)	0.7308 (8)	0.310 (1)	0.2799 (9)
O(9)	0.7794 (6)	0.4279 (9)	0.3682 (9)
O(10)	0.8610 (7)	0.287 (2)	0.398 (1)
O(21)	0.8350 (9)	0.490 (2)	0.232 (1)
O(22)	0.7839 (8)	0.483 (1)	0.204 (1)
N(1)	0.8650 (2)	−0.0245 (3)	0.0695 (2)
N(2)	0.8417 (2)	0.1500 (3)	0.1322 (2)
N(3)	0.7263 (2)	0.1374 (4)	0.0502 (3)
N(4)	0.9376 (2)	0.1144 (3)	0.0414 (2)
N(5)	0.9100 (2)	0.0471 (4)	−0.0905 (2)
C(1)	1.000	−0.1107 (4)	0.250
C(2)	0.9372 (2)	−0.1657 (4)	0.1890 (3)
C(3)	0.9384 (3)	−0.2721 (4)	0.1890 (4)
C(4)	1.000	−0.3276 (6)	0.250
C(5)	1.000	−0.4461 (8)	0.250
C(6)	0.8667 (2)	−0.1141 (4)	0.1256 (3)
C(7)	0.7919 (2)	0.0182 (4)	0.0113 (3)
C(8)	0.7856 (2)	0.1003 (4)	0.0636 (3)
C(9)	0.8164 (3)	0.2223 (5)	0.1646 (3)
C(10)	0.7458 (3)	0.2151 (5)	0.1136 (4)
C(11)	0.6535 (3)	0.1037 (6)	−0.0211 (5)
C(12)	0.8867 (2)	−0.0595 (4)	0.0087 (3)
C(13)	0.9109 (2)	0.0339 (4)	−0.0138 (3)
C(14)	0.9554 (2)	0.1847 (4)	−0.0020 (3)
C(15)	0.9381 (3)	0.1423 (5)	−0.0824 (3)
C(16)	0.8836 (3)	−0.0273 (5)	−0.1668 (3)
C(17)	1.000	0.2895 (7)	0.250
C(21)	0.830 (1)	0.572 (2)	0.260 (2)
C(22)	0.814 (1)	0.569 (3)	0.213 (2)
O(23)	0.991 (3)	0.519 (5)	0.471 (3)
O(24)	1.023 (2)	0.573 (3)	0.577 (2)
C(23)	1.004 (3)	0.451 (4)	0.471 (3)
C(24)	1.019 (3)	0.556 (5)	0.488 (4)

In previous studies, it was shown that manganese and iron form stable triply bridged complexes of **1** with metal–metal separations of 3.5 Å.[36,37] More recently, we have found that **1** reacts with $[Cu(H_2O)_6](ClO_4)_2$, forming an open type structure (compound **2**). Attempts to crystallize **2** from methanol, however, result in the isolation of $[Cu_2(bimp)(CH_3OH)_2](ClO_4)_3$ (**3**). The water molecules bound to the copper ions in **2** are susceptible to exchange in coordinating solvents as well as in the presence of potential ligands. Compound **3** also has an open type structure in which the copper ions are separated by 4.090 (1) Å. Addition of sodium azide or sodium imidazolate to a solution containing **2**, on the other hand, results in the formation of monoatom-bridged complexes containing bridging azide and methoxide ions, respectively. These results are in contrast to the open type complexes reported by Suzuki et al.[15] with H(bpmp), a pyridine containing ligand that is structurally similar to **1**. They report that the addition of excess sodium azide to a solution containing $[Cu(H_2O)_6](ClO_4)_2$ and Hbpmp results in the formation of a complex containing one azide bound to each copper ion. Addition of sodium methoxide and imidazole to a solution containing $[Cu(H_2O)_6](ClO_4)_2$ and Hbpmp reportedly results in the formation of a complex formulated as having an imidazole bridge. However, Maloney et al.[17] report isolating monoatom-bridged Cu_2bpmp complexes under similar conditions. Results from our studies with **1**, described below, are

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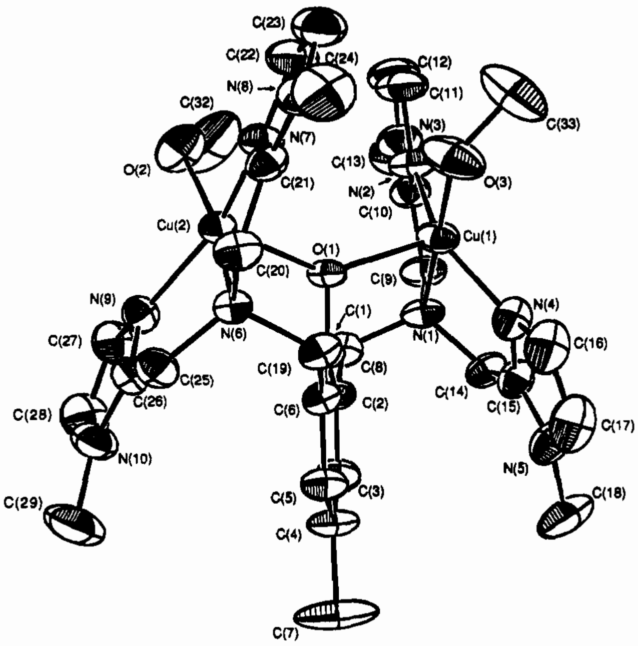

Figure 1. ORTEP plot of the $[Cu_2(bimp)(CH_3OH)_2]^{3+}$ cation in complex 3. Hydrogens are omitted for clarity. Ellipsoids are drawn at the 50% probability level.

Table IV. Selected Bond Lengths (Å) and Angles (deg) for Complex 3

Cu(1)–O(1)	2.157 (3)	Cu(2)–O(1)	2.156 (3)
Cu(1)–O(3)	2.022 (4)	Cu(2)–O(2)	2.002 (4)
Cu(1)–N(1)	2.105 (4)	Cu(2)–N(6)	2.109 (4)
Cu(1)–N(2)	1.941 (5)	Cu(2)–N(7)	1.941 (5)
Cu(1)–N(4)	1.954 (4)	Cu(2)–N(9)	1.951 (5)
Cu(1)–Cu(2)	4.09 (2)	Cu(1)–O(1)–Cu(2)	142.9 (2)
O(1)–Cu(1)–O(3)	85.7 (2)	O(1)–Cu(2)–O(2)	98.8 (2)
O(1)–Cu(1)–N(1)	95.0 (1)	O(1)–Cu(2)–N(6)	95.0 (1)
O(1)–Cu(1)–N(2)	110.2 (2)	O(1)–Cu(2)–N(7)	105.3 (2)
O(1)–Cu(1)–N(4)	97.9 (2)	O(1)–Cu(2)–N(9)	96.5 (2)
N(1)–Cu(1)–N(2)	82.9 (2)	N(6)–Cu(2)–N(9)	82.7 (2)
N(1)–Cu(1)–O(3)	178.9 (2)	N(6)–Cu(2)–O(2)	166.2 (2)
N(2)–Cu(1)–O(3)	96.2 (2)	N(9)–Cu(2)–O(2)	96.3 (2)
O(3)–Cu(1)–N(4)	97.0 (2)	O(2)–Cu(2)–N(7)	93.1 (2)
N(4)–Cu(1)–N(1)	83.6 (2)	N(7)–Cu(2)–N(6)	82.6 (2)
N(4)–Cu(1)–N(2)	149.8 (3)	N(7)–Cu(2)–N(9)	154.6 (2)

more consistent with the monoatom-bridged complexes reported by Maloney et al.[17] with Hbpmp.

(II) Description of the X-ray Structures. $[Cu_2(bimp)(CH_3OH)_2](ClO_4)_3$ (3). Compound 3 crystallizes in the monoclinic space group $P2_1/n$. An ORTEP view of the cation of complex 3 is shown in Figure 1, and selected bond lengths and angles are given in Table IV. Each cupric ion is bound to two imidazole ring nitrogen atoms, one amine nitrogen atom, the phenolate oxygen atom, and a methanol oxygen atom. The complex is one of only a few examples of an open coordination environment in which the Cu(II) ions are bridged by a phenolate ion and no other group.[16,20] The geometry around each Cu(II) ion is best described as distorted square pyramidal with the phenolate oxygen atom occupying the apical position of each pyramid (Figure 2). Analysis of the shape-determining angles using the approach of Muetterties and Guggenberger[38] yields e_3 values of 24.40 and 7.32° for Cu(1) and Cu(2), respectively. In this approach, a quantitative measure of the shape of the molecule is obtained from the dihedral angles e_1, e_1, and e_3. The most important shape-determining angle is e_3, which varies from 0.0°, for an idealized tetragonal pyramid, to 53.1°, for an idealized trigonal bipyramid. Therefore, the e_3 value of 24.4° for Cu(1) indicates that the geometry around this copper is distorted toward a trigonal bipyramid, while the geometry around the Cu(2) center is best described as square pyramidal.

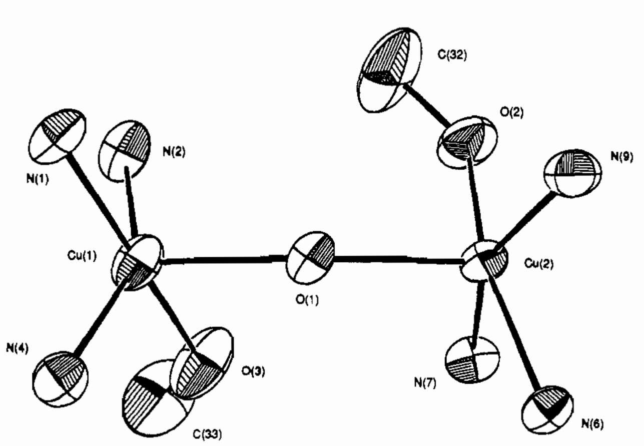

Figure 2. Inner coordination spheres of the copper ions in the $[Cu_2(bimp)(CH_3OH)_2]^{3+}$ cation.

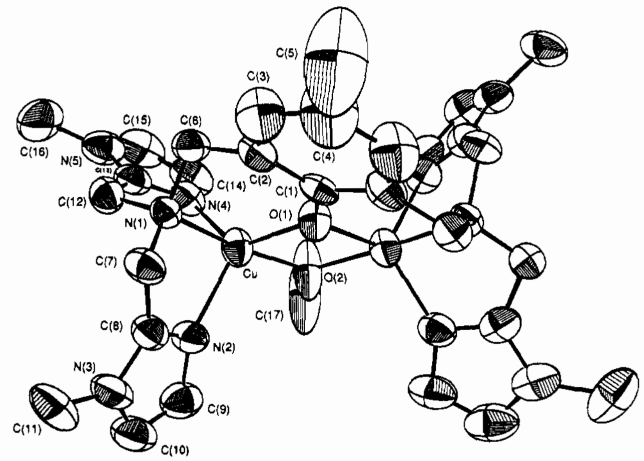

Figure 3. ORTEP plot of the $[Cu_2(bimp)(CH_3O)]^{2+}$ cation in complex 4. Hydrogens are omitted for clarity. Ellipsoids are drawn at the 50% probability level.

The Cu–O and Cu–N bond distances in 3 are typical of other copper(II) complexes.[39,40] The apical Cu(1)–O(1) and Cu(2)–O(1) bond distances are equivalent, with values of 2.157 (3) and 2.156 (3) Å, respectively. This is in contrast with the results reported by Berends and Stephan[20] for a phenolate-bridged polybenzimidazole complex, where large differences in the Cu–O(phenolate) bond distances are observed (1.92 (1) vs 2.28 (1) Å) resulting from the binding of the phenolate ion in the equatorial position of one square pyramid and in the apical position of the other. Berends and Stephan[20] also report a Cu–Cu separation for the benzimidazole complex of 3.875 Å. The Cu–Cu separation in complex 3 is 4.090 (1) Å, and is one of the largest metal–metal separations reported for complexes containing this type of polypodal ligand.[14-20] Nishida et al.,[16] on the other hand, have prepared an open type dinuclear Cu(II) complex in which the copper ions are separated by 4.128 (3) Å. The phenolate oxygen atom in this complex occupies a bridging apical position of two square pyramids, resulting in longer Cu–O(phenolate) bond distances (2.20 Å average), consistent with the bond distances observed for complex 3.

In complex 3, the basal planes of the square pyramids form a dihedral angle of 33.48 (13)°, resulting in a Cu(1)–O(1)–Cu(2) angle of 142.9 (2)°. The metal ion positions deviate substantially from the planes defined by their four basal ligand atoms, with Cu(1) deviating by 0.233 Å and Cu(2) by 0.309 Å. The cop-

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Table V. Selected Bond Lengths (Å) and Angles (deg) for Complex **4**

Cu–Cu′	3.026 (1)	N(1)–Cu–O(1)	92.2 (2)
Cu–N(1)	2.050 (3)	N(1)–Cu–O(2)	169.9 (1)
Cu–N(2)	2.004 (3)	N(1)–Cu–N(2)	83.5 (1)
Cu–N(4)	2.128 (4)	N(1)–Cu–N(4)	80.4 (1)
Cu–O(1)	1.994 (2)	N(2)–Cu–O(1)	130.4 (1)
Cu–O(2)	1.901 (2)	N(2)–Cu–O(2)	101.5 (2)
Cu–O(1)–Cu′	98.7 (1)	N(2)–Cu–N(4)	113.1 (1)
Cu–O(2)–Cu′	105.4 (1)	N(4)–Cu–O(1)	114.7 (1)
O(1)–Cu–O(2)	77.9 (1)	N(4)–Cu–O(2)	105.3 (1)

per–amine bond distances are slightly longer than the average copper–imidazole distances (2.107 vs 1.947 Å average), reflecting in part the constraining nature of the five-membered chelate rings of the bmima pendants. The long copper–amine distances also contribute to the large Cu(1)–Cu(2) separation observed in **3**. The coordination sphere of each copper ion is completed by a methanol molecule that occupies an equatorial position of the basal plane. The Cu–O(methanol) bond distances average 2.012 Å, somewhat longer than the distances reported by Nishida and Kida[41] for an unusual hydrogen-bonded methoxide/methanol-bridged complex (1.915 Å average) but similar to the Cu–O(water) bond distances (2.01 Å average) reported by Berends and Stephan.[20]

$[Cu_2(bimp)(OCH_3)](ClO_4)_2 \cdot 2CH_3OH$ (4). Complex **4** crystallizes in the monoclinic space group *C*2/*c*. An ORTEP view of the cation of complex **4** is shown in Figure 3, and selected bond lengths and angles are given in Table V. The structure contains a $[Cu_2(bimp)(OCH_3)]^{2+}$ cation, disordered perchlorate anions, and two molecules of methanol incorporated as lattice solvate molecules. Each copper is pentacoordinate, bonded to two imidazole ring nitrogen atoms, a tertiary amine nitrogen atom, an endogenous phenolate oxygen atom, and an exogenous methoxide bridging group. The cation lies on a crystallographically imposed 2-fold axis bisecting the phenolate and exogenous bridging groups. The geometry about each copper ion is described best as a distorted trigonal bipyramid with the phenolate oxygen (O(1)) and the imidazole nitrogen atoms (N(2) and N(4)) lying in the equatorial plane. Bond angles in this plane deviate slightly from the expected 120°, with the largest deviation being 10.4 (1)° for the N(2)–Cu–O(1) angle. Analysis of the shape-determining angles[38] yields a value for e_3 of 41.50°. This indicates that the copper atoms in **4** are distorted only slightly toward square-pyramidal geometry. The two Cu–N(imidazole) bond distances, on the other hand, differ by more than 0.12 Å (Cu–N(2) = 2.004 (3) Å; Cu–N(4) = 2.127 (4) Å). These distances are much longer than the Cu–N(imidazole) lengths reported for complex **3**, as well as for other Cu(II) complexes,[40,42–44] reflecting the strain imposed on the copper coordination environment in this closed arrangement. A similar structure has been reported recently for $[Cu_2(bpmp)(OCH_3)]^{2+}$.[17] The Cu–N(pyridine) bond distances are similar to Cu–N(imidazole) distances found in complex **4**. This indicates that the molecular distortions required to form the closed structure in **4** are larger, since Cu–N(imidazole) bond distances are usually shorter than Cu–N(pyridine) distances. In addition, apical distances (2.11 (1)–2.28 (1) Å) typically exceed basal distances (1.913 (7)–2.07 (2) Å) in tetragonal-pyramidal copper(II) complexes containing imidazole ligation.[20,24b,45] In complex **4**, the longer Cu–N(4) length (2.127 (4) Å) suggests that N(4) could be occupying an apical position of a highly distorted square pyramid, while N(1), N(2), O(1), and O(2) lie in the basal plane. Overall, however, the geometry around the copper ions appears to be closer to trigonal bipyramidal than square pyramidal.

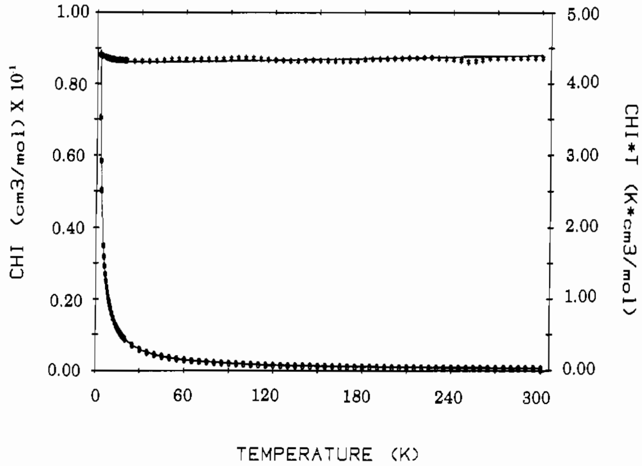

Figure 4. Plot of the magnetic susceptibility data (χ) vs T (lower) as well as χT (upper) for $[Cu_2(bimp)(H_2O)_2](ClO_4)_3$ (**2**). The solid lines represent the best least-squares fitting of the data.

The Cu–Cu′ separation in **4** is 3.026 (1) Å, approximately 0.03 Å longer than the length reported for $[Cu_2(bpmp)(OCH_3)]^{2+}$ [17] but consistent with other doubly bridged dinuclear Cu(II) complexes containing polypodal phenolate ligands.[17,18,46] The Cu–O(1)–Cu′ bond angle is 98.7 (1)°, while the Cu–O(2)–Cu′ angle is 105.4 (1)°. In order for **4** to adopt a closed doubly bridged arrangement, the phenolate ring has twisted 18.0 (5)° out of the plane defined by the Cu_2O_2 core. This distortion is different from the distortion observed for $[Cu_2(bpmp)(OCH_3)]^{2+}$,[17] where the Cu_2O_2 core is bent relative to the phenolate ring, forming a dihedral angle of 27°. Similar twisting of phenolate ligand has been observed in the structures of two related mixed-valence complexes: $[Fe_2(bpmp)(\mu\text{-}OPr)_2]^{2+}$ [47] and $[Fe_2(bimp)(\mu\text{-}OBz)_2]^{2+}$.[37] In contrast, planar arrangements are usually observed for complexes that do not contain sterically constraining pendant ligands[14,18] or for compounds with open type structures.[16,20] In complex **4**, the bmima pendants offer constraining five-membered chelate rings that result in N(1)–Cu–N(2) and N(1)–Cu–N(4) angles of 83.5 (1) and 80.4 (1)°, respectively. As a result, the N(2)–Cu–O(1) angle opens to 130.4 (1)°.

(III) Electronic Spectra. The electronic absorption spectra (supplementary material) for complexes **2**–**5** in acetonitrile solutions show distinct maxima between 200 and 750 nm. Transitions below 300 nm are assigned to ligand $\pi \rightarrow \pi^*$ transitions of the Hbimp ligand, which occur at 204 nm (ϵ = 51 000 M^{-1} cm^{-1}) and 290 nm (ϵ = 3375 M^{-1} cm^{-1}), respectively. These complexes also exhibit other ligand-to-metal charge transfer (LMCT) transitions. For example, complex **2** exhibits a phenolate–Cu(II) LMCT band at 478 nm (ϵ = 184 M^{-1} cm^{-1}) and a band at 672 nm (ϵ = 188 M^{-1} cm^{-1}), tentatively assigned as a d–d transition. These transitions shift slightly to 495 nm (ϵ = 178 M^{-1} cm^{-1}) and 672 nm (ϵ = 192 M^{-1} cm^{-1}) for complex **3**, where methanol ligands have replaced coordinated water molecules. The phenolate–Cu(II) LMCT bands of **4** and **5**, on the other hand, occur at 435 nm (ϵ = 382 M^{-1} cm^{-1}) and 482 nm (ϵ = 220 M^{-1} cm^{-1}), whereas the d–d transitions occur at much lower energy, at 742 nm (ϵ = 228 M^{-1} cm^{-1}) and 718 nm (ϵ = 187 M^{-1} cm^{-1}), respectively. Since the copper ion coordination geometries of **4** and **5** are best described as distorted trigonal bipyramids, overlap between the phenolate oxygen and the d_{z^2} orbital should be small, resulting in weak phenolate–Cu(II) LMCT transitions. Maloney et al.[17] have found that an open type structure results when the Cu_2O_2 core found in $[Cu_2(bpmp)(OH)]^{2+}$ is ruptured in basic solutions. They argue that the shift in the d–d transitions from 710 nm (ϵ = 250 M^{-1} cm^{-1}) to 690 nm (ϵ = 757 M^{-1} cm^{-1}), concomitant with an increase in the intensity of the phenolate–Cu(II) LMCT band, results from an increased overlap of the bridging phenolate p

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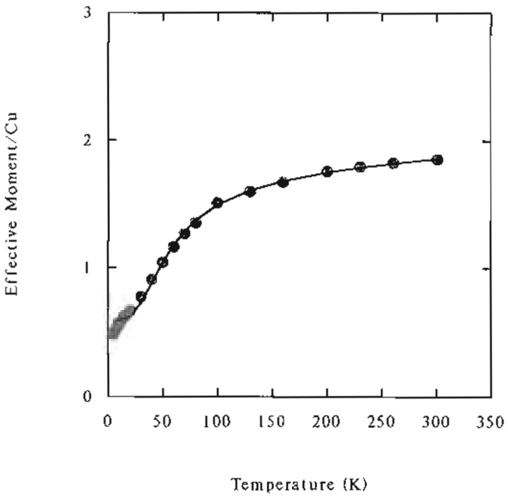

Figure 5. Effective magnetic moment per copper ion vs temperature (T) for $[Cu_2(bimp)(CH_3O)](ClO_4)_2$ (**4**). The solid line represents the best least-squares fit of the data.

orbitals with the metal $d_{x^2-y^2}$ orbitals. The phenolate–Cu(II) charge-transfer transition is more intense when the phenolate oxygen atom overlaps with the copper $d_{x^2-y^2}$ orbital.[19,20] In complexes **2** and **3**, there is a large shift in the positions of the d–d transitions to lower energies compared to those of complexes **4** and **5**, consistent with a more open type structure in solution.[17] The geometries around the Cu(II) ions in complexes **2** and **3** remain essentially square pyramidal with apically bonded phenolate oxygen atoms that result in weak phenolate–Cu(II) LMCT transitions.

(IV) Magnetic Properties. Variable-temperature magnetic susceptibility data for complexes **2**, **4**, and **5** were collected over a temperature range of 2–300 K. No significant exchange coupling in complex **2** is detected from the plot of the susceptibility data (Figure 4). Simulation of the data using the Bleaney–Bowers equation[48a] consistently gives an extremely weak ferromagnetic exchange interaction, in agreement with the slight increase in χT near helium temperatures. The best fit of the data gives $J = 0.27$ cm^{-1}, with $g = 2.14$ and TIP fixed at 80×10^{-6} cm^3 mol^{-1}. The absence of significant exchange coupling obviously is due to the fact that the bridging phenolate oxygen atom is apical to the two tetragonal Cu atoms. In this situation, there is no significant overlap of the metal $d_{x^2-y^2}$ magnetic orbitals and therefore no exchange interaction.

A plot of effective magnetic moment (μ_{eff}) per copper ion versus temperature for complex **4** is illustrated in Figure 5. The value of μ_{eff}/Cu gradually decreases from 1.85 μ_B at 300.9 K to 1.04 μ_B at 50.0 K and eventually drops to 0.49 μ_B at 5.0 K. The data were least-squares-fit to the Bleaney–Bowers equation.[48a] The temperature-independent paramagnetism (TIP) was held fixed at 500×10^{-6} cm^3 mol^{-1} for the dinuclear complex. Least-squares fitting[48b] of the data with variations of the magnetic exchange parameter $J(H = -2JS_1 \cdot S_2)$ and the g value gives values of $J = -47$ cm^{-1} and $g = 2.05$. TIP and $\chi_{impurity}$ were fixed at 500×10^{-6} cm^3 mol^{-1} and 7.5%, respectively. Considerable effort was made to improve the fitting of the data below 50 K, by adjusting TIP and $\chi_{impurity}$; however, this only resulted in a few wavenumber differences in the value of J.

The magneto behavior of the azide complex (**5**) is similar to that of compound **2** (supplementary material). The μ_{eff}/Cu is nearly constant and equal to 2.16 (2) μB over the entire 5–300 K temperature range. Although there is no evidence of any significant exchange interaction in **5**, EPR studies (vide infra) confirm that the copper centers are coupled, having an estimated $|J|$ value of ≤ 0.3 cm^{-1}.[49]

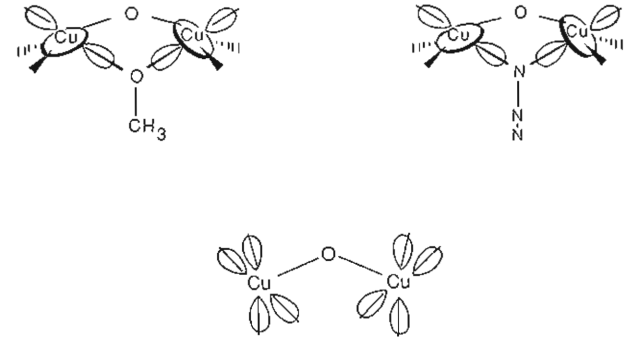

Figure 6. Schematic representations of the orbital orientations in complexes **3** (middle), **4** (left), and **5** (right).

(V) Magnetostructural Correlations. The magnitude of the magnetic exchange interactions between copper ions in dinuclear complexes is dependent upon the orbital ground-state configuration of the copper(II) ions. Strong magnetic exchange interactions require both good σ-bonding orientation of the magnetic orbitals (e.g., the orbitals that contain the unpaired electrons) and good superexchange pathways provided by the bridging atom orbitals.[50,51] Magnetic susceptibility data obtained on the proposed open structure of complex **2** show a slight ferromagnetic exchange interaction with $J = 0.27$ cm^{-1}, in agreement with the structure observed for complex **3**. Since the copper ions have distorted square-pyramidal coordination geometries and $d_{x^2-y^2}$ ground states, significant exchange coupling is not expected through the apical bonded phenolate oxygen atom. Nishida et al.[16] observed no exchange coupling in $[Cu_2(bpmp)Cl_2]^+$, which has a similar open type structure. The crystal structure of **3** does show a significant distortion of the environment around Cu(1). However, in the trigonal-bipyramidal limiting geometry, the phenolate bridge would be in the equatorial plane and would overlap poorly with the torus lobe of the d_{z^2} magnetic orbital, thus leading to a weak antiferromagnetic exchange interaction. So the distortion toward trigonal-bipyramidal geometry is not expected to give rise to a significant exchange interaction either.

The coordination geometry about each copper ion in **4** is approximately trigonal bipyramidal, which leads to a d_{z^2} ground state. The major lobes of the magnetic orbitals are oriented along the axial direction of the trigonal bipyramid toward the bridging methoxide ligand (short σ-bonding pathway), as shown in Figure 6. By virtue of the 2-fold symmetry of the complex ($C2/c$ space group), the magnetic orbitals associated with each metal ion interact identically with the bridging methoxide orbitals. Magnetic susceptibility data for the methoxide bridged complex indicate that the copper(II) ions are moderately coupled antiferromagnetically with $J = -47$ cm^{-1}. Bridging alkoxide ions are known to facilitate antiferromagnetic exchange coupling.[24,51b] In light of the absence of a significant exchange interaction in compound **2**, it seems plausible that the methoxide ion is mediating the exchange interaction in compound **4**. In the latter complex, the phenolate oxygen atom overlaps with the torus lobe of the d_{z^2} magnetic orbitals, resulting in long Cu–O distances (1.994 Å) and an acute Cu–O(1)–Cu′ angle of 98.7°. The shorter Cu–O(2) (methoxide ion) distance (1.901 Å) and larger Cu–O(2)–Cu′ angle of 105.4° provide a better pathway for antiferromagnetic exchange coupling.[54]

The magnetic data on complex **5**, on the other hand, indicate that the Cu(II) ions are essentially uncoupled ($|J| \leq 0.3$ cm^{-1}). Since the coordination environment of the copper ions in **5**[52] is

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Table VI. EPR and Magnetic Susceptibility Parameters

complex	temp, K[a]	g values	D, cm^{-1}	J, cm^{-1}
2	4	$g_x = g_y = 2.08$ $g_z = 2.09$	0.04	0.27
3	4	$g_x = g_y = 2.09$ $g_z = 2.20$, $g = 4.40$	0.05	
4	4	$g_x = g_y = 2.08$ $g_z = 2.25$, $g = 4.29$	0.04	−48.4
5		$g_x = g_y = 2.08$		$<\cong 0.3$
2	298	$g_x = g_y = 2.08$ $g_z = 2.20$, $g = 4.31$	0.04	
3	298	$g = 2.11$, $g = 4.25$		
4	298	$g = 2.08$, $g = 4.50$		
5	298	$g = 2.09$		

[a] The g values reported at 298 K were taken from powdered spectra, whereas those reported at 4 K were taken from frozen acetonitrile/toluene/methanol solution spectra.

similar to that of complex **4**, the difference in magnetic behavior between the complexes must result from differences in orbital overlap of the bridging exogeneous ligands.[53] Apparently, neither the phenolate oxygen atom nor the azide ion effectively mediate exchange coupling in **5**, due most likely to poor overlap with bridging ligand orbitals. 1,1-Bridged azides are known to facilitate strong ferromagnetic exchange coupling in dinuclear copper complexes,[54] but in light of the apparent absence of exchange coupling in **4**, this is not always the case.[14a,55]

(VI) Electron Paramagnetic Resonance. The X-band EPR spectra of powdered samples and frozen acetonitrile/methanol/toluene (1:1:1) solutions of complexes **2–5** have been recorded and are shown in Figure 7. Spectral parameters for each complex are given in Table VI. The powder spectrum of complex **2** (Figure 7a) is very broad and displays evidence of zero-field splitting. The spectral line positions have been fit by using a modified version of the line-fitting program developed by Wasserman et al.[56,57] The g values ($g_\parallel$ (g_z) = 2.20, $g_\perp$ (g_x, g_y) = 2.08) and the zero-field-splitting parameter, D (0.04 cm^{-1}), are consistent with other dinuclear Cu(II) complexes.[57] The powder spectrum of complex **3**, on the other hand, displays an isotropic signal with $g = 2.11$ at 298 K and a weak transition at 1525 G, tentatively assigned to the $\Delta M_S = 2$ transition expected for a magnetically coupled dinuclear copper(II) complex. The powder spectra of complexes **4** and **5** are much broader and not well resolved, due presumably to dipolar broadening.

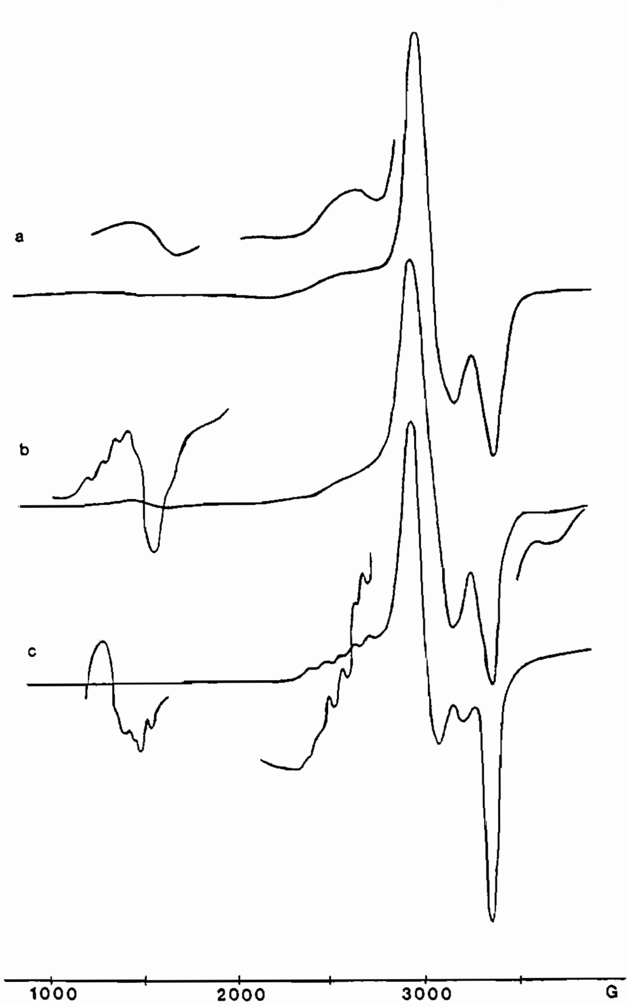

Figure 7. X-band EPR spectra: (a) spectrum for a polycrystalline sample of **2** at 298 K; (b) frozen acetonitrile/methanol/toluene solution spectrum of complex **3** at 4 K; (c) frozen acetonitrile/methanol/toluene solution spectrum of complex **4** at 4 K.

The frozen-solution spectra of all four compounds are very similar and typical of magnetically coupled dinuclear Cu(II) complexes.[57] The frozen-solution spectrum and powder spectrum of complex **2** are similar, having nearly identical g values and zero-field-splitting parameters. The frozen-solution spectrum of complex **3** is shown in Figure 7b. Analysis of the spectrum gives $g_\parallel = 2.20$, $g_\perp = 2.08$, and $D = 0.04$ cm^{-1}. Since the spectrum of **3** is nearly identical with the spectrum of **2**, we conclude that the two compounds are isostructural and display similar magnetic properties. Six poorly resolved copper hyperfine lines appear on the low-field side of the $\Delta M_S = 1$ transitions in the frozen-solution spectrum of **3**, corroborating the presence of a dinuclear structure in solution. The presence of copper hyperfine splitting ($A_\parallel$) of 75 G also is consistent with retention of a dinuclear structure in solution. In addition, on the "half-field" $\Delta M_S = 2$ (1460 G) signal, there are seven clearly resolved copper hyperfine lines with an average spacing of 75 G.

Analysis of the frozen-solution spectrum of complex **4** (Figure 7c) gives $g_\parallel = 2.25$, $g_\perp = 2.08$, and $D = 0.04$ cm^{-1}. Six of the seven expected copper hyperfine lines are well resolved on the $g_\parallel$ portion of the triplet signal. As with complex **3**, the copper hyperfine lines have an average spacing ($A_\parallel$(Cu)) of 75 G, which is approximately half the value observed for monomeric Cu(II) complexes.[26,58] A weak $\Delta M_S = 2$ transition is observed in the

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(52) Compound analyzes correctly for proposed structure (sample pumped on overnight under vacuum prior to analysis). Anal. Calcd (found) for $C_{29}H_{37}N_{13}Cu_2O_9Cl_2$: C, 38.29 (38.57); H, 4.10 (4.01); N, 20.02 (19.55). X-ray analysis on $[Cu_2(bimp)(\mu\text{-}N_3)](ClO_4)_2\cdot 2CH_3OH$ indicates a highly disordered cation, a μ-1,1-azide-bridged structure, and approximate trigonal-bipyramidal geometries for the copper(II) ions. A PLUTO view of the cation is deposited in the supplementary material. The compound crystallizes in the monoclinic space group $C2/c$ with a = 23.465 (6) Å, b = 12.407 (4) Å, c = 18.177 (6) Å, β = 131.46 (2)°, V = 3966.13 Å^3, ρ_{obsd} = 1.52 (1) g cm^{-3}, ρ_{calcd} = 1.522 g cm^{-3}, and Z = 4. With the use of 1401 unique reflections ($F_o > 3\sigma(F_o)$) at 293 (1) K with Mo Kα (λ = 0.709 26 Å) radiation out to 2θ = 40° on a single-crystal X-ray diffractometer, the structure was solved by standard direct (MULTAN) and difference Fourier methods and refined with 258 variables to a current value of the discrepancy index of $R(F)$ = 0.067: Cu–O(1) = 1.999 (6) Å, Cu–N(1) = 1.900 (8) Å, Cu–N(5) = 2.053 (9) Å, Cu–N(6) = 2.00 (2) Å, Cu–N(8) = 2.097 (6) Å, N(1)–N(2) = 1.19 (4) Å, O(1)–Cu–N(1) = 79.4 (4)°, O(1)–Cu–N(5) = 91.6 (3)°, O(1)–Cu–N(6) = 126.3 (2)°, O(1)–Cu–N(8) = 112.9 (3)°, N(1)–Cu–N(5) = 170.9 (4)°, N(1)–Cu–N(6) = 100.9 (3)°, N(1)–Cu–N(8) = 103.9 ⇄3)°, N(5)–Cu–N(6) = 83.2 (4)°, N(5)–Cu–N(8) = 80.7 (4)°, N(6)–Cu–N(8) = 118.8 (3)°, Cu–N(1)–N(2) = 122 (3)°, Cu–O(1)–C(1) = 131.5 (3)°, Cu–N(1)–Cu′ = 97.3 (3)°, Cu–O(1)–Cu′ = 103.8 (3)°. The severity of the disorder and weakness of the data collected do not allow for unambiguous identification of the azide ligand. Evidence for the presence of μ-1,1-azide is based on analysis and spectral data.

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spectrum of **4** at 1500 G. There are four copper hyperfine lines resolved on this signal with an average spacing of 75 G, as well. The only significant difference among the spectra of compounds **2**–**4** is the resolution of a very weak transition at 3640 G ($H(Z)_2$ signal[56]) in compound **3**. Since the frozen-solution spectrum of compound **2** is similar to its powder spectrum, it appears that the open structure present in the solid state persists as well in solution. The spectral parameters of **4** ($g_\parallel > 2.1$) indicate that the copper(II) ions are distorted toward square-pyramidal geometry[59] rather than toward the trigonal-bipyramidal geometry observed in the crystal structure. This may indicate that the strained geometry observed in the solid state (twisting of the phenol ring relative to the Cu_2O_2 plane) may be relaxed in the frozen acetonitrile/toluene/methanol solution and that the Cu(II) centers may be in environments that resemble square-pyramidal geometries.

The frozen-solution spectrum of complex **5** (supplementary material) is very similar to the spectra of complexes **2**–**4**, but much broader. The $g_\parallel$ signal is very broad, trailing into the $\Delta M_S = 2$ region and essentially obscuring this signal. The overall shape of the spectrum indicates that the Cu(II) centers also may be in square-pyramidal environments. It is important to note, however, that the method used to determine *g* values in this study is not very accurate,[56,57] so an exact ground-state configuration for these complexes in solution is not obtainable at the present time.

Conclusions

New open type dinuclear polyimidazole copper(II) complexes (**2** and **3**) have been synthesized and used to prepare two doubly bridged dinuclear Cu(II) complexes (**4** and **5**). Complexes **3** and **4** have been characterized by X-ray crystallography and shown to have copper centers with square-pyramidal and distorted trigonal-bipyramidal geometries, respectively. Magnetic susceptibility data presented for complexes **2** and **5** (supplementary material) demonstrate that the Cu(II) ions are essentially uncoupled magnetically. The exchange interaction is much stronger in compound **4** and is antiferromagnetic. Both the electronic spectral and frozen-solution (acetonitrile/toluene/methanol) EPR spectral data of compounds **2** and **3** are consistent with the open type structure observed in the crystal structure of **3**. The electronic spectral data for complexes **4** and **5** in acetonitrile solution are consistent with the closed structures observed by X-ray crystallography. In frozen acetonitrile/toluene/methanol solution, however, the EPR spectra of complexes **4** and **5** are more consistent with dinuclear Cu(II) complexes having square-pyramidal geometries, in contrast with their solid-state structures. It appears then that the constraining nature of the Hbimp ligand is influenced by the physical state of the samples.

Acknowledgment. This work was supported by National Institutes of Health Grant HL13652 (D.N.H.), National Science Foundation Grant RII-8610671, and the Commonwealth of Kentucky through the Kentucky EPSCoR program (R.M.B.).

Supplementary Material Available: Tables of crystallographic data, non-hydrogen positional parameters and general anisotropic displacement parameters, non-hydrogen bond distances and angles, hydrogen positional and thermal parameters, and hydrogen bond distances and angles for **3** and **4**, a perspective view (PLUTO) of the disordered $[Cu_2bimp(\mu\text{-}N_3)]^{2+}$ cation, electronic absorption spectra of the complexes, tables of magnetic data for **2**, **4**, and **5**, a plot of μ_{eff} vs *T* data for **5**, a frozen-solution EPR spectrum of **5**, and powder EPR spectra of **2**–**5** (40 pages); listings of structure factors for **3** and **4** (32 pages). Ordering information is given on any current masthead page.

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Synthesis of 3- and 4-Coordinate Coinage Metal $[ML_3][X]$, $[MXL_3]$, and $[ML_4][X]$ Complexes: Crystal Structures of $[Cu\{P(p\text{-}C_6H_4OMe)_3\}_3][ClO_4]$ and $[Cu\{Sb(p\text{-}C_6H_4F)_3\}_4][BF_4]$

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Received July 6, 1990

Forty-nine complexes of the type $[M\{Z(Ph)_m(p\text{-}C_6H_4Y)_{3-m}\}_n][X]$ (M = Cu, Ag; X = BF_4, ClO_4; Z = P, As, Sb; Y = Cl, F, Me, OMe; $n = 3, 4$; $m = 0$–2) have been prepared and characterized with the intent of demonstrating electronic control of their stereochemistry. With electron-withdrawing substituents (Y = Cl, F), primarily $n = 3$ complexes are formed. IR spectra are, however, characteristic of coordinated anions, indicating the existence of 4-coordinate complexes. In a few instances, where M = Cu, Z = Sb, and Y = F, $n = 4$ complexes are isolated. For electron-donating substituents (Y = Me, OMe), both $n = 3$ and $n = 4$ complexes are obtained, with $n = 3$ preferred for Cu and $n = 4$ dominating for Ag. Coordination of the anions is generally not anticipated for the $n = 3$ complexes, based on the IR spectra. One Ag complex with $n = 2$ was isolated. Crystals of $[Cu\{P(p\text{-}C_6H_4OMe)_3\}_3][ClO_4]$ are in the rhombohedral space group $R\bar{3}$, with $a = 19.423$ (7) Å, $c = 27.616$ (18) Å, and $Z = 6$ at $T = -120$ °C. The structural refinement converged to $R = 0.098$. The structure consists of isolated $[CuL_3]^+$ cations and $[ClO_4]^-$ anions. The Cu atom is 3-coordinate, with the Cu atom lying only 0.23 Å out of the plane of the three phosphorus atoms. The $[Cu\{Sb(p\text{-}C_6H_4F)_3\}_4][BF_4]$ salt is trigonal, space group $P31c$, with $a = 13.489$ (1) Å, $c = 23.327$ (3) Å, and $Z = 2$ at 22 °C. The structure refined to $R = 0.052$. The 4-coordinate Cu atom is located at a site of C_3 symmetry, with three Sb atoms at 2.556 (1) Å and one at 2.547 (1) Å.

Introduction

In previous papers[1,2] we have attempted to define more precisely the steric limits by group VB ligands, of 2-, 3-, and 4-coordinate univalent coinage metal cations. While it was apparent that the ZPh_3 ligands normally form $[ML_4][X]$ (X = ClO_4, BF_4) complexes, the complex $\{Cu(FBF_3)(PPh_3)_3\}$[3] and the salts $[M(PPh_3)_2][BF_4]$ (M = Ag,[4] Au[5]) have previously been isolated. Thus, the isolation of complexes containing less than four neutral

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