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Synthetic, Spectroscopic, and Solution Studies of Imidazolate-Bridged Dicopper(II) Complexes

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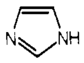
The synthesis and spectroscopic characterization of discrete, water soluble, imidazolate-bridged copper(II) complexes are reported. Binuclear imidazolate-bridged complexes were crystallized from basic aqueous or methanolic solutions of $Cu(pip)^{2+}$, pip = 2-[(2-(2-pyridyl)ethylimino)methyl]pyridine, or $Cu(PMDT)^{2+}$, PMDT = 1,1,4,7,7-pentamethyldiethylenetriamine, and various substituted imidazoles. The condensation of imidazole-4,5-dicarboxaldehyde with (2-(2-aminoethyl)-pyridine)copper(II) afforded the Cu_2bpim^{3+} cation, where bpim is 4,5-bis[(2-(2-pyridyl)ethylimino)methyl]imidazolate. Addition of imidazole and sodium hydroxide to aqueous solutions of this cation yielded the tetranuclear complex $[Cu_2bpim(im)]_2(NO_3)_4{\cdot}4H_2O$ (im = imidazolate). Potentiometric titrations and solution electron spin resonance spectroscopic studies showed that the integrity of the imidazolate bridge in the Cu_2bpim^{3+} cation is maintained in the range 3.5 < pH < 11.5. Similar studies of the $[Cu(pip)]_2im^{3+}$ complex revealed that the bridge is broken both by protonation of the imidazolate group at low pH and by competition with hydroxide ions at high pH. Four protons are reversibly titrated in solutions of $[Cu_2bpim(im)]_2^{4+}$ corresponding to protonation of the imidazolate rings that link the two Cu_2bpim^{3+} units in this complex to form 2 equiv of imidazolium ion.

Introduction

The imidazolate (im) anion, the deprotonated form of im-


imidazole, imH


imidazolate, im

idazole (imH), can serve as a bridging ligand between transition-metal ions.[1-9] Such complexes are of interest as models for histidine-bridged bimetallic centers in metalloproteins.[10] They also provide an opportunity to probe further the electronic and magnetic exchange interactions mediated by polyatomic bridging ligands, especially nitrogen heterocycles.[11] Physical and chemical studies of imidazolate-bridged complexes will also contribute to our general understanding of ligand-bridged metal clusters.

Our studies in this area have focused on imidazolate-bridged complexes of copper(II) because they have well-understood magnetic and spectroscopic behavior and because an active form of bovine erythrocyte superoxide dismutase (BESOD) has been prepared that contains a histidine-bridged dicopper(II) active site.[12] The following requirements for an imidazolate-bridged complex were established at the outset of our work. It should be crystalline in order to guarantee analytical purity, to permit verification of the imidazolate-bridged unit by X-ray crystallography, and to facilitate the interpretation of magnetic susceptibility data. It should be soluble in polar solvents such as water in order to permit examination of its chemical reactivity, solution behavior, and spectroscopic and magnetic properties under biologically relevant conditions. On dissolution the integrity of the metal–imidazolate–metal unit should be maintained. Finally, the complex should be nonpolymeric in order to facilitate interpretation of the behavior that results from the indirect metal–metal interactions.

This paper is the first of a series and reports the results of synthetic, spectroscopic, and solution studies of the imidazolate-bridged di- and tetranuclear complexes **1**–**7** (Figure 1). Two subsequent papers will describe the crystal and molecular structures of **2**, **3**, **5**, and **6** (the structure of **1** has already been described[1b]) and a quantitative interpretation of the magnetic superexchange interactions mediated by the bridging imidazolate ligand in **1**–**7**.[13] Some of the results have already appeared in preliminary form.[1a,2]

Experimental Section

Materials and Methods. All compounds were prepared from commercially available reagents. Before use benzimidazole, imidazole, and 2-methylbenzimidazole were recrystallized successively from water, toluene and water to yield compounds having melting points in satisfactory agreement with the literature values. Other reagents were used without further purification. Microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn. NMR spectra were recorded on a Varian A-60 spectrometer, and the shifts are reported with respect to tetramethylsilane, which was used as an internal standard. Solution electronic spectra were recorded with a Cary 118C spectrophotometer using 1-cm matched quartz cells. Electronic spectra of the finely ground powders were recorded as mineral oil mulls dispersed on filter paper with use of the same instrument. X-ray diffraction photographs were obtained with a precession camera using Ni-filtered Cu$K\alpha$ radiation (λ 1.5418 Å) and an Enraf-Nonius Diffractis Model 581 generator. Frozen-solution electron spin resonance spectra were recorded as described previously.[3]

Syntheses. *Warning!* Several of the compounds reported here were isolated as the perchlorate salts. Although these compounds seem to be stable to shock and heat, and we have worked with these compounds in a number of organic solvents without incident, the unpredictable behavior of perchlorate salts[14] necessitates extreme caution in their handling.

Dimethyl Imidazole-4,5-dicarboxylate (9). A 500-mL three-necked round-bottom flask was fitted with a mechanical stirrer and a reflux

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(1) (a) Kolks, G.; Frihart, C. R.; Rabinowitz, H. N.; Lippard, S. J. *J. Am. Chem. Soc.* **1976**, *98*, 5720–5721. (b) Dewan, J. C.; Lippard, S. J. *Inorg. Chem.* **1980**, *19*, 2079–2082.

(2) Kolks, G.; Lippard, S. J. *J. Am. Chem. Soc.* **1977**, *99*, 5804–5806 and references cited therein.

(3) O'Young, C.-L.; Dewan, J. C.; Lilienthal, H. R.; Lippard, S. J. *J. Am. Chem. Soc.* **1978**, *100*, 7291–7300.

(4) (a) Coughlin, P. K.; Dewan, J. C.; Lippard, S. J.; Watanabe, E.-i.; Lehn, J. M. *J. Am. Chem. Soc.* **1979**, *101*, 265–266. (b) Coughlin, P. K.; Lippard, S. J.; Martin, A. E.; Bulkowski, J. E. *Ibid.* **1980**, *102*, 7616–7617.

(5) (a) Haddad, M. S.; Hendrickson, D. N. *Inorg. Chem.* **1978**, *17*, 2622–2630. (b) Haddad, M. S.; Duesler, E. N.; Hendrickson, D. N. *Ibid.* **1979**, *18*, 141–148.

(6) (a) Mori, W.; Nakahara, A.; Nakav, Y. *Inorg. Chim. Acta* **1979**, *37*, L507–L508. (b) Hendricks, H. M. J.; Reedjik, J. *Ibid.* **1979**, *37*, L509–L510.

(7) (a) Landrum, J. T.; Reed, C. A.; Hatana, K.; Scheidt, W. R. *J. Am. Chem. Soc.* **1978**, *100*, 3232–3234. (b) Landrum, J. T.; Hatano, K.; Scheidt, W. R.; Reed, C. A. *Ibid.* **1980**, 6729–6735.

(8) Evans, C. A.; Rabenstein, D. L.; Geier, G.; Erni, I. W. *J. Am. Chem. Soc.* **1977**, *99*, 8106–8108.

(9) Isied, S. S.; Kuehn, C. G. *J. Am. Chem. Soc.* **1978**, *100*, 6754–6756.

(10) Ibers, J. A.; Holm, R. H. *Science (Washington, D.C.)* **1980**, *209*, 223–235.

(11) Inoue, M.; Kubo, M. *Coord. Chem. Rev.* **1976**, *21*, 1–27.

(12) Fee, J. A.; Briggs, R. G. *Biochim. Biophys. Acta* **1975**, *400*, 439–450.

(13) Kolks, G.; Lippard, S. J., to be submitted for publication.

(14) Everett, K.; Graf, F. A., Jr. In "CRC Handbook of Laboratory Safety", 2nd ed.; Steere, N. V., Ed.; Chemical Rubber Publishing Co.: Cleveland, Ohio, 1971.

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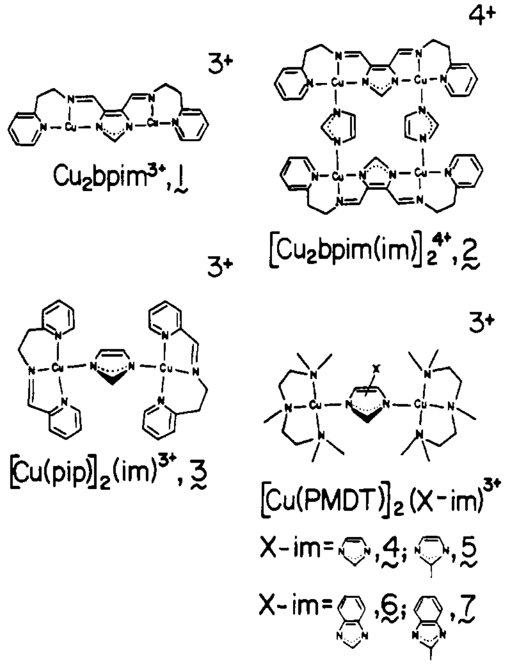

Figure 1. Imidazolate-bridged complexes studied in this work.

condenser. It was charged with 300 mL of methanol and 31 g (0.2 mol) of imidazole-4,5-dicarboxylic acid, **8**, obtained from Eastman Chemicals. Anhydrous hydrogen chloride, introduced via the third neck of the flask, was bubbled through the well-stirred suspension until no solid remained. By this time the methanol had ceased refluxing. The solution was stirred for another 3 h, and then the methanol was removed by rotary evaporation under reduced pressure. The white solid that remained was dissolved in 200 mL of water, and this solution was neutralized by the addition of solid sodium hydroxide, thus precipitating the crude diester **9**, which was collected by filtration (25.1 g, 68%). Concentration and cooling of the filtrate yielded an additional 6.1 g (17%). NMR ($CDCl_3$–5% Me_2SO-d_6): δ 3.80 (s, 6 H), 7.75 (s, 1 H). A small amount was recrystallized from water (1 g/10 mL) and had a melting point of 199–200 °C (sealed capillary, uncorrected).

4,5-Bis(hydroxymethyl)imidazole (10). This compound was made by a literature procedure,[15] details for which are as follows. A 500-mL three-necked round-bottom flask was fitted with a mechanical stirrer and reflux condenser and charged with 300 mL of tetrahydrofuran from a freshly opened bottle and 10 g (0.26 mol) of lithium aluminum hydride. The crude diester **9** (10.5 g, 0.05 mol) was slowly added to the well-stirred suspension, and the reaction mixture was refluxed with stirring for 24 h. The mixture was then allowed to come to room temperature. The reaction vessel and contents were then cooled in an ice bath, and a stream of nitrogen gas was passed over the surface of the mixture while 100 mL of water was added dropwise, with vigorous stirring. The resulting suspension was then stirred overnight at room temperature. The solid aluminum hydroxide salts were then collected by centrifugation and washed with 200 mL of hot methanol. The combined washings and filtrate were taken to dryness under reduced pressure. After the remaining solid was dissolved in absolute ethanol, dry ice (10 g) was added and the mixture was stirred overnight. The resulting precipitate was removed by centrifugation, and the filtrate was evaporated to dryness to yield 4.2 g (65%) of crude dialcohol **10**. NMR (Me_2SO-d_6): δ 3.10 (s, 3 H), 4.73 (s, 4 H), 7.76 (s, 1 H).

Imidazole-4,5-dicarboxaldehyde (11). A mixture of crude dialcohol **10**, (3.0 g, 0.023 mol), activated manganese dioxide[16] (30 g, 0.34 mol), and *N,N*-dimethylacetamide (DMA, 150 mL) was stirred at room temperature for 6 days. The MnO_2 was collected by centrifugation and washed with two 50-mL portions of DMA. The combined supernatant and washings along with 6 g of silica gel were evaporated to dryness under reduced pressure at 40 °C. The remaining solid was placed on the top of a silica gel column (2 cm × 38 cm) packed in $CHCl_3$. After the column was washed with $CHCl_3$, the dialdehyde **11** (1.08 g, 37%) was eluted with $CHCl_3$–methanol (9.5:0.5, v/v). Stirring the recovered MnO_2 in DMA for 6 days yielded, after a similar workup, an additional 0.38 g (13%) of dialdehyde **11**, mp 235 °C (sealed capillary; lit.[15] mp 237 °C). NMR (Me_2SO-d_6): δ 7.92 (s, 1 H), 9.90 (s, 2 H).

$[Cu_2bpim](NO_3)_3 \cdot 2H_2O$ (1). Crude imidazole-4,5-dicarboxaldehyde (0.62 g, 5 mmol) dissolved in 50 mL of 0.10 N aqueous sodium hydroxide solution was added dropwise to a well-stirred solution of 2-(2-aminoethyl)pyridine (1.22 g, 10 mmol) and $Cu(NO_3)_2 \cdot 3H_2O$ (2.42 g, 10 mmol) in 100 mL of ethanol. The solution was stirred overnight at 50 °C and filtered to remove the small amount of brown solid that invariably formed, and the filtrate was evaporated to dryness under reduced pressure at 45 °C. The resulting friable solid was dissolved in 30 mL of boiling ethanol and then cooled slowly to room temperature. A blue precipitate (1.63 g, 48%) was collected by filtration, washed with cold ethanol, and air-dried. Although chemical analyses of this compound are consistent with the formulation given above, where bpim is the ligand 4,5-bis[(2-(2-pyridyl)ethylimino)-methyl]imidazolate (Figure 1), magnetic susceptibility studies showed that it was contaminated with up to 10 mol % of a monomeric copper impurity. Thin-layer chromatography on silica gel using ethanol as the eluant showed that the precipitate consisted mostly of a green-blue component but also contained a violet-blue impurity, which was probably the monomeric copper compound, and often a yellow impurity. Thus, the above formulation is only approximate, and this material was used only as a crude intermediate.

$[Cu_2bpim(NO_3)_2](ClO_4) \cdot$(solvent). Crude $Cu_2bpim(NO_3)_3 \cdot 2H_2O$ (663 mg, 0.97 mmol), prepared as above, was dissolved in boiling methanol (25 mL) and then added to a beaker containing $NaClO_4 \cdot H_2O$ (150 mg, 1.07 mmol) dissolved in 2 mL of methanol. The beaker was covered with a piece of filter paper. Several crops of large, well-formed dark blue crystals were collected over the next several days (290 mg total, 41%). Although crystallographic studies[1b] indicated that the compound contains one coordinated water molecule and one lattice water molecule per Cu_2bpim^{3+} unit, chemical analyses suggested that the bulk material contains one water molecule and one molecule of methanol.

Anal. Calcd for $[Cu_2bpim(NO_3)_2](ClO_4) \cdot H_2O \cdot MeOH$, $C_{20}H_{25}N_8O_{12}ClCu_2$: C 32.82; H, 3.44; N, 15.31; O, 26.23; Cl, 4.84; Cu, 17.36. Calcd for $[Cu_2bpim(NO_3)_2](ClO_4) \cdot 2H_2O$, $C_{19}H_{23}N_8O_{12}ClCu_2$: C, 31.79; H, 3.23; N, 15.61; O, 26.74; Cl, 4.94; Cu, 17.70. Found: C, 32.78; H, 3.22; N, 15.35; O (by difference), 26.30; Cl, 4.92; Cu, 17.43.

$[Cu_2bpim(im)]_2(NO_3)_4 \cdot 4H_2O$ (2). A solution of crude $Cu_2bpim(NO_3)_3 \cdot 2H_2O$ (680 mg, 1.0 mmol) in water (8.0 mL) was brought to boiling. Imidazole (68 mg, 1.0 mmol) dissolved in 1.00 mL of 1.00 M aqueous sodium hydroxide was added dropwise to the well-stirred boiling solution. When the gray-green gelatinous mass that formed upon the addition of the imidazole/NaOH solution was fully dissolved, the dark blue solution was filtered through a hot funnel into a small vial and capped. Crystals began forming immediately and were collected the next day (485 mg, 71%). The crystals grow as dark blue, tetragonal bipyramids compressed along the fourfold axis.

Anal. Calcd for $[Cu_2bpim(im)]_2(NO_3)_4 \cdot 4H_2O$, $C_{44}H_{52}N_{20}O_{16}Cu_4$: C, 38.54; H, 3.82; N, 20.43; O, 18.67; Cu, 18.54. Found (two preparations): C, 38.62, 38.63; H, 3.94, 3.89; N, 20.45, 20.34; O (by difference), 18.96, 18.87; Cu, 18.03, 18.27.

[2-[(2-(2-Pyridyl)ethylimino)methyl]pyridine]copper(II) Nitrate Hydrate, $Cu(pip)(NO_3)_2 \cdot H_2O$. Pyridine-2-carboxaldehyde (1.07 g, 10 mmol) was added slowly and with vigorous stirring to a solution of 2-(2-aminoethyl)pyridine (1.22 g, 10 mmol) and $Cu(NO_3)_2 \cdot 2.5H_2O$ (2.32 g, 10 mmol) in methanol (15 mL). Very small crystals (3.33 g, 80%) began to form almost immediately after the addition was complete, and they were separated from the green-blue supernatant by filtration after an additional 20 min.

Anal. Calcd for $Cu(pip)(NO_3)_2 \cdot H_2O$, $C_{13}H_{15}N_5O_7Cu$: C, 37.46; H, 3.63; N, 16.80. Found: C, 37.35; H, 3.62; N, 16.51.

$[Cu(pip)(NO_3)](NO_3)$. Recrystallization of $Cu(pip)(NO_3)_2 \cdot H_2O$ from boiling water (1 g/mL) yielded light blue, monoclinic prisms suitable for single-crystal studies. The compound crystallizes in space group $P2_1/c$. Cell constants obtained from uncalibrated films with Cu Kα radiation are as follows: *a*, 8.565 (8) Å; *b*, 14.72 (1) Å; *c*, 12.321 (8) Å; *β*, 96.5 (1)°. The observed density of 1.70 g cm^{-3} obtained by flotation in CCl_4–$CHBr_3$ is in agreement with the cal-

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(15) Schubert, H.; Rudorf, W. D. *Z. Chem.* **1971**, *11*, 175–176.

(16) Goldman, J. C. *J. Org. Chem.* **1969**, *34*, 1979–1981.

culated density of 1.72 g cm^{-3} for $Z = 4$.

Anal. Calcd for [Cu(pip)(NO_3)](NO_3), $C_{13}H_{13}N_5O_6Cu$: C, 39.15; H, 3.29; N, 17.56. Found: C, 39.39; H, 3.62; N, 17.34.

Cu(pip)(ClO_4)$_2$·H_2O. Pyridine-2-carboxaldehyde (10.7 g, 0.1 mol) was added to a well-stirred solution of Cu(ClO_4)$_2$·6H_2O (37.1 g, 0.1 mol) and 2-(2-aminoethyl)pyridine (12.2 g, 0.1 mol) in 100 mL of warm (60 °C) water. The solution was allowed to stand uncovered for a few days, after which time small blue monoclinic prisms formed, which were collected by filtration, washed with cold mother liquor, and air-dried (34 g, 69%).

Anal. Calcd for Cu(pip)(ClO_4)$_2$·H_2O, $C_{13}H_{15}N_3O_9Cl_2Cu$: C, 31.75; H, 3.07; N, 8.55; Cl, 14.42. Found: C, 31.81; H, 3.02; N, 8.41; Cl, 14.50.

Zn(pip)(NO_3)$_2$. Pyridine-2-carboxaldehyde (2.14 g, 20 mmol) and 2-(2-aminoethyl)pyridine (2.44 g, 20 mmol) were mixed together in methanol (5.0 mL) and added with vigorous stirring to a solution of Zn(NO_3)$_2$·6H_2O (5.94 g, 20 mmol) in 30 mL of methanol. A beige to light yellow microcrystalline precipitate formed immediately and was collected by filtration (6.2 g, 77%). Recrystallization from boiling water afforded colorless monoclinic crystals.

Anal. Calcd for Zn(pip)(NO_3)$_2$, $C_{13}H_{13}N_5O_6Zn$: C, 38.97; H, 3.27; N, 17.48; O, 23.96; Zn, 16.32. Found: C, 39.12; H, 3.38; N, 17.34; O (by difference) 23.61; Zn, 16.55.

[Cu(pip)(1-MeIm)](ClO_4)$_2$. The addition of 1-methylimidazole (0.21 g, 2.5 mmol) to a warm solution of Cu(pip)(ClO_4)$_2$·H_2O (1.23 g, 2.5 mmol) in methanol (30 mL) caused the immediate precipitation of very small, fine, blue needles, which were collected by filtration after slowly cooling to room temperature (1.04 g, 75%).

Anal. Calcd for [Cu(pip)(1-MeIm)](ClO_4)$_2$, $C_{17}H_{19}N_5O_8Cl_2Cu$: C, 36.74; H, 3.45; N, 12.60. Found: C, 37.01; H, 3.65; N, 12.27.

[Cu(pip)]$_2$(im)(NO_3)$_3$·2.5H_2O (3). Cu(pip)(NO_3)$_2$·H_2O (1.05 g, 2.5 mmol) was dissolved in boiling water (5.0 mL). To this solution was added imidazole (85 mg, 1.25 mmol). Aqueous sodium hydroxide (1.25 mL of a 1.00 M solution, 1.25 mmol) was slowly added to the still boiling solution. The solution was stirred only enough to dissolve the gray-blue gelatinous precipitate that formed both upon the addition of the imidazole and of the sodium hydroxide. The solution was then removed from the heat, the beaker was covered with a piece of filter paper, and the solution was allowed to cool slowly to room temperature. Fine blue monoclinic prisms of the complex grew by evaporation over the next few days and were collected by filtration (533 mg, 50%). Care must be taken to minimize the amount of dissolved atmospheric carbon dioxide in the reaction mixture, which leads to the formation of blue hexagonal bipyramidal crystals of the carbonate-bridged complex [Cu(pip)(H_2O)]$_3$$CO_3$($NO_3$)$_4$.[17] Thus the water used was boiled prior to use, and stirring was kept to a minimum.

Anal. Calcd for [Cu(pip)]$_2$(im)(NO_3)$_3$·2.5H_2O, $C_{29}H_{34}N_{11}O_{11.5}Cu_2$: C, 41.09; H, 4.04; N, 18.17; O, 21.70; Cu, 14.99; H_2O, 5.31. Found: C, 40.84; H, 4.14; N, 18.02; O (by difference), 22.03; Cu, 14.97; H_2O (by Karl Fischer titration), 5.06.

(1,1,4,7,7-Pentamethyldiethylenetriamine)copper(II) Perchlorate–2-Acetonitrile, Cu(PMDT)(ClO_4)$_2$·2CH_3CN. Cu(ClO_4)$_2$·6H_2O (11.13 g, 30 mmol) and 1,1,4,7,7-pentamethyldiethylenetriamine (5.19 g, 30 mmol) were dissolved in methanol (45 mL) and stirred vigorously while acetonitrile (18 mL) was added dropwise. The lavender precipitate that began to form after 10 mL of CH_3CN was added was collected by filtration upon completion of the addition and dissolved in 80 mL of hot CH_3CN. Cooling of the solution to room temperature produced 6.55 g of blue-violet monoclinic prisms. Concentration of the filtrate and cooling to 4 °C yielded another 5.0 g (11.55 g total, 74%). The compound is moisture sensitive and should be stored in a sealed bottle.

Anal. Calcd for Cu(PMDT)(ClO_4)$_2$·2CH_3CN, $C_{13}H_{29}N_5O_8Cl_2Cu$: C, 30.15; H, 5.65; N, 13.52; Cl, 13.69. Found: C, 29.98; H, 5.77; N, 13.57; Cl, 13.83.

(μ-Imidazolato)-bis(1,1,4,7,7-pentamethyldiethylenetriamine)copper(II)) Perchlorate, [Cu(PMDT)]$_2$(im)(ClO_4)$_3$ (4). Aqueous sodium hydroxide solution (1.00 mL, 1.00 M) was added to a boiling solution of Cu(PMDT)(ClO_4)$_2$·2CH_3CN (1.03 g, 2.0 mmol) and imidazole (68 mg, 1.0 mmol) in methanol (20 mL). When the solution was cooled to room temperature, small, violet-blue tetragonal platelets formed, which were collected by filtration (0.67 g, 79%). Analytical data show that the compound may be formulated equally well as the hemihydrate or as the anhydrate.

Table I. Analytical Data (Percent) for [(PMDT)Cu]$_2$(BzIm)(ClO_4)$_3$·(solvent)

	calcd for solvent		found for prepn		
	H_2O	$H_2O\cdot$MeOH	I[a]	II[b]	III[a]
C	33.10	33.18	32.89, 32.96	33.29	33.16, 33.17
H	5.89	6.32	5.94, 6.17	5.77	6.15, 6.10
N	12.35	11.90	12.01	11.92	12.14
O	22.93	23.80	24.16[f]	23.78[f]	22.79[f]
Cl	11.72	11.30	11.36	12.14	11.85
Cu	14.01	13.50	13.64	13.10	13.94
water[c]	1.99	1.91	1.12	e	1.66
density[d]	1.48	1.53	1.48 (1)	1.48 (1)	1.52 (1)

[a] C and H analyses were repeated for these preparations using duplicate samples of the same batch. [b] The crystal structure was determined by using a crystal from this batch.[13] [c] Analyzed by the Karl Fischer method. [d] Determined by neutral buoyancy in $CHCl_3$–$CHBr_3$ solutions; in g cm^{-3}. [e] Not determined. [f] By difference.

Anal. Calcd for [Cu(PMDT)]$_2$(im)(ClO_4)$_3$·0.5H_2O, $C_{21}H_{50}N_8O_{12.5}Cl_3Cu_2$: C, 29.74; H, 5.94; N, 13.21; O, 23.58; Cl, 12.54; Cu, 14.98. Calcd for the anhydrate, $C_{21}H_{49}N_8O_{12}Cl_3Cu_2$: C, 30.05; H, 5.89; N, 13.37; O, 22.88; Cl, 12.68; Cu, 15.16. Found (two preparations): C, 29.80, 29.79; H, 5.85, 6.32; N, 13.18, 13.09; O (by difference), 23.53; Cl, 12.77, 12.55; Cu, 14.87 (one determination only).

(μ-(2-Methylimidazolato))-bis((1,1,4,7,7-pentamethyldiethylenetriamine)copper(II)) Perchlorate, [Cu(PMDT)]$_2$(2-MeIm)(ClO_4)$_3$ (5). 2-Methylimidazole (0.41 g, 5 mmol) and Cu(PMDT)(ClO_4)$_2$·2CH_3CN (2.59 g, 5 mmol) were dissolved in boiling methanol (100 mL). When the solution was cooled to room temperature, red-brown, orthorhombic prismatic crystals formed, which were collected by filtration (1.78 g, 83%).

Anal. Calcd for [Cu(PMDT)]$_2$(2-MeIm)(ClO_4)$_3$, $C_{22}H_{51}N_8O_{12}Cl_3Cu_2$: C, 30.97; H, 6.03; N, 13.13; Cl, 12.47. Found: C, 31.06; H, 6.12; N, 13.13; Cl, 12.44.

(μ-Benzimidazolato)-bis((1,1,4,7,7-pentamethyldiethylenetriamine)copper(II)) Perchlorate–Solvent, [Cu(PMDT)]$_2$(BzIm)(ClO_4)$_3$·(solvent) (6). A solution of Cu(PMDT)(ClO_4)$_2$·2CH_3CN (1.04 g, 2 mmol), benzimidazole (235 mg, 2 mmol), and water (200 μL) in methanol (40 mL) was refluxed for 24 h. The clusters of small, orange-brown, orthorhombic prisms that formed were collected by filtration of the hot solution (450 mg, 49%). Chemical analyses of several preparations of this compound as well as density measurements indicate that the solvent composition is variable either with water or with water and methanol of crystallization being present. Analysis of the crystal structure[13] suggests that variable solvent content is possible. Powder X-ray photographs of the several batches of crystals were virtually identical. Table I presents the analytical data for three batches of crystals and compares the results to the two theoretical formulations.

(μ-(2-Methylbenzimidazolato))-bis((1,1,4,7,7-pentamethyldiethylenetriamine)copper(II)) Perchlorate–Methanol, [Cu(PMDT)]$_2$(2-MeBzIm)(ClO_4)$_3$·MeOH (7). A solution of Cu(PMDT)(ClO_4)$_2$·2CH_3CN (0.52 g, 1 mmol), 2-methylbenzimidazole (132 mg, 1 mmol), and water (100 μL) in boiling methanol (17 mL) was cooled slowly to room temperature. The small but well-formed parallelepipeds that deposited were collected by filtration (224 mg, 48%). The crystals are lavender when viewed perpendicular to the largest face via transmitted light and orange-brown when viewed at a more acute angle. The crystals are lavender by reflected light.

Anal. Calcd for [Cu(PMDT)]$_2$(2-MeBzIm)(ClO_4)$_3$·MeOH, $C_{26}H_{57}N_8O_{13}Cl_3Cu_2$: C, 34.68; H, 6.14; N, 11.98; O, 22.24; Cl, 11.37; Cu, 13.59. Found: C, 34.32; H, 5.86; N, 11.91; O (by difference) 22.82; Cl, 11.52; Cu, 13.57.

Potentiometric Titrations. Hydrogen ion concentrations were measured with a combination glass microelectrode and a Radiometer TTT-1C pH meter. The pH meter, graduated to 0.1 pH unit and read to 0.01 pH unit, was calibrated at pH 7 with use of a commercially prepared buffer (Fisher Scientific) and at pH 4.01 with use of 0.1000 M potassium hydrogen phthalate solution. All titrations were carried

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[17] Kolks, G.; Lippard, S. J.; Waszczak, J. V. *J. Am. Chem. Soc.* **1980**, *102*, 4832–4833.

out in water-jacketed reaction vessels with the temperature maintained at 25.0 ± 0.1 °C.

Water used for the titrations was distilled and deionized. The ionic strength of all solutions was maintained at 0.16 with use of potassium nitrate. Carbonate-free standard sodium hydroxide solution (~0.1 M) was prepared in the usual way,[18] standardized against potassium hydrogen phthalate, and protected from atmospheric CO_2 during storage. Decinormal nitric acid was prepared from the concentrate and standardized with the sodium hydroxide solution. Both standardizations were repeated periodically.

Typically, the solution to be titrated was ~3 mM in Cu(II) (6–12 mg of compound in a 5-mL solution), and 3.00 mL of this solution was transferred to the titration vessel. The pH of the solution was then adjusted to 5.5 with standard acid, and nitrogen gas was bubbled through the solution for 10 min in order to purge the solution of dissolved CO_2. The nitrogen gas that was used for the titrations was passed first through an 8 in. long column of Ascarite, to free it of CO_2, and then through a 0.16 M aqueous solution of potassium nitrate, to adjust the activity of the gas. Upon completion of the purging cycle, the nitrogen bubbler was removed and the titrating vessel was sealed in a "Zip-lock" plastic bag. The water hoses from the temperature bath, the combination electrode, and the microburet (Gilson Micrometer buret, 2 mL) were inserted into the titrating vessel through small holes in the plastic bag. Nitrogen gas introduced through the "Zip-lock" opening maintained a CO_2-free atmosphere over the reaction vessel during the titration. During the titration the solution was constantly stirred with a magnetic stirrer and stirring bar. The stirring apparently had no effect on the performance of the buret (viz., it did not promote leaking via capillary flow) nor did it affect the readings of the pH electrode. During the titration the tip of the buret was kept just below the surface of the solution.

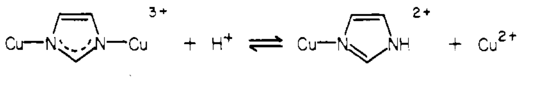
The solutions were titrated first with base to a pH of about 11.5, then with acid to pH of 3.5, and then with base to the original pH of the solution (~5.5) in order to check the reversibility of the titration. The proton number, $\bar{p}$, is defined as the average number of titratable protons remaining on the molecule being studied at a given pH.[18] It is initially given the arbitrary value of zero. At any other pH the new proton number can be calculated by knowing the number of hydroxide or hydronium ions that have been added in a given aliquot of titrant and the change in the number of these ions in the reaction solution upon addition of the aliquot. The difference between these two values is respectively the number of protons removed from or added to the compound being titrated. The proton number, $\bar{p}$, is then equal to this difference divided by the number of molecules of complex in solution.

The free hydronium or hydroxide ion concentration is calculated from the measured pH. Several samples of water were titrated with either standard acid or base, and the pH of the solution after the addition of each aliquot was measured. By assuming total dissociation of the nitric acid and the sodium hydroxide in solution, it is possible to calculate the true concentrations of the solution at a given pH. Conversely, by referral to the experimentally obtained plot of true H^+ or OH^- concentration vs. pH, a measurement of the pH can be made to yield the H^+ or OH^- concentration in solution, which are the desired quantities.

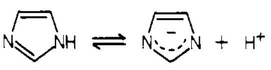
After completion of the titration the scale of $\bar{p}$ was adjusted so that the value of the end point at the highest pH was zero and $\bar{p}$ increased as pH decreased. Most of the titrations were repeated twice, and the agreement between the two sets of data was good.

Results and Discussion

Syntheses. In the first synthesis of a soluble, nonpolymeric imidazolate-bridged dicopper(II) complex the imidazolate ring was incorporated into the chelating bpim ligand (Figure 1).[1a] It was anticipated that in protic solvents such as water the chelate effect of the ligand would stabilize the $Cu_2(im)^{3+}$ unit against protonation (eq 1), thus permitting spectroscopic and chemical reactivity studies of the bridged complex to be carried out in the physiological pH range. The pK_a of the pyrrole hydrogen of the imidazole ring of histidine is 14.4[19] (eq 2).



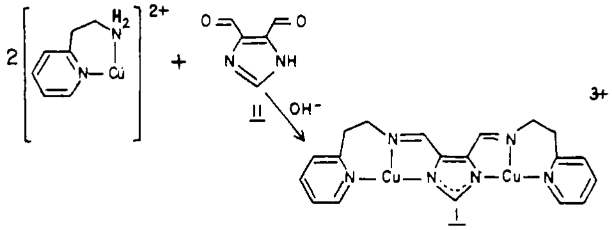
(1)



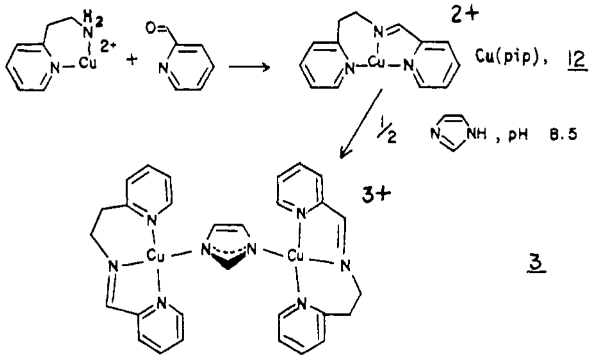
(2)

Coordination of a copper atom at the pyridine nitrogen, as in Cu(L-his)$_2$,[20] reduces this pK_a to 11.7 while substitution of the hydrogen atom by copper(II) as in eq 1 occurs at pH 9.6[21] in solutions of neutral complexes of Cu(glycyl-L-histidine). It was likely, then, that the copper atoms in the Cu_2bpim^{3+} unit, **1**, would remain bridged down to pH 7 or 8.

Scheme I



Scheme II



The Cu_2bpim^{3+} cation **1** is a simple Schiff base complex that is synthesized from (2-(2-aminoethyl)pyridine)copper(II) and imidazole-4,5-dicarboxaldehyde (**11**) in the presence of base as shown in Scheme I. The synthesis of the dialdehyde **11** was effected by using a modification (see Experimental Section) of a literature procedure.[16] During attempts to isolate **1** with imidazole in the fourth equatorial site, it was interesting to find that, under the relatively mild conditions employed (pH 8–9), the imidazole groups acted as their own base, became deprotonated, and served to bridge two Cu_2bpim^{3+} units, yielding **2** (Figure 1). This result suggested that simple imidazolate-bridged dicopper species such as **3** could be prepared by adding imidazole to basic solutions of copper(II) complexes having tridentate amine ligands. By analogy to the synthesis of Cu_2bpim^{3+}, salts of Cu(pip)$^{2+}$, **12**, were obtained by the condensation of 2-(2-aminoethyl)pyridine and pyridine-2-carboxaldehyde in the presence of copper(II) (Scheme II). The imidazolate-bridged species **3** was obtained by evaporation of a mildly alkaline aqueous solution of Cu(pip)$^{2+}$ and imidazole (Scheme II). The reaction is completely general and has been used to synthesize [Cu(triamine)]$_2$(im)(ClO_4)$_3$ compounds[3,4] and the heterobinuclear complex [(PMDT)Cu(im)Co(NH_3)$_5$](ClO_4)$_4$.[22] A number of substituted imidazolates and benzimidazolates may be used to bridge the two copper(II) centers as evidenced by the syntheses of compounds **5**–**7**. In these cases the solvent of choice is methanol and

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(18) Anderegg, G. In "Coordination Chemistry"; Martell, A. E., Ed.; Van Nostrand-Reinhold: New York, 1971; Vol. I.

(19) Yagil, G. *Tetrahedron* **1967**, *23*, 2855–2861.

(20) Morris, P. J.; Martin, R. B. *J. Am. Chem. Soc.* **1970**, *92*, 1543–1550.

(21) Morris, P. J.; Martin, R. B. *J. Inorg. Nucl. Chem.* **1971**, *33*, 2913–2918.

(22) Davis, W. M.; Dewan, J. C.; Lippard, S. J. *Inorg. Chem.* **1981**, *20*, 2928.

Table II. Summary of Spectroscopic and Solution Data

compd	solid λ_{max},[a] nm	soln λ_{max},[b] nm	soln ϵ[c]	pH[d]	ESR[e]
$[Cu_2bpim(NO_3)_2(ClO_4)(H_2O)]\cdot H_2O$ (1)	622	653	65	6.43	axial, $g = 2.212, 2.072$
$[Cu_2bpim(im)]_2(NO_3)_4\cdot 4H_2O$ (2)	616	605	87	8.5	isotropic, $g = 2.10$, $\Delta M = \pm 2$, $g = 4.23$ (100×)
$Cu(pip)(NO_3)_2\cdot H_2O$	683	668, 379	55, 50	6.0	rhombic, $g_1 = 2.18$, $g_2 = 2.10$, $g_3 = 2.04$
$Cu(pip)(NO_3)_2$	655	668, 379	56, 70	5.9	rhombic, $g_1 = 2.20$, $g_2 = 2.10$, $g_3 = 2.05$
$Cu(pip)(ClO_4)_2\cdot H_2O$	649	663	63, 58	6.1	axial, $g = 2.22, 2.06$
$Cu(pip)(1\text{-}MeIm)(ClO_4)_2$	612	637	63	7.9	isotropic, $g = 2.08$
$[Cu(pip)]_2(im)(NO_3)_3\cdot 2.5H_2O$ (3)	637	637, 377	68	9.1	isotropic, $g = 2.11$, $\Delta M = \pm 2$, $g = 4.27$ (50×)
$[Cu(PMDT)](ClO_4)_2\cdot 2CH_3CN$	628	659	225	6.8	rhombic, $g_1 = 2.16$, $g_2 = 2.11$, $g_3 = 2.05$
$[(PMDT)Cu]_2(im)(ClO_4)_3$ (4)	565, 610 (pr)	643	196	9.2	isotropic, $g = 2.09$
$[(PMDT)Cu]_2(2\text{-}MeIm)(ClO_4)_3$ (5)	493, 600	647	194	9.1	isotropic, $g = 2.09$, $\Delta M = \pm 2$, weak
$[(PMDT)Cu]_2BzIm(ClO_4)_3\cdot H_2O$ (6)	500, 565 (sh)			9.0	isotropic, $g = 2.09$, $\Delta M = \pm 2$, weak
$[(PMDT)Cu]_2(2\text{-}MeBzIm)(ClO_4)_3\cdot MeOH$ (7)	483, 615				isotropic, $g = 2.09$, $\Delta M = \pm 2$, weak

[a] Measured as a Nujol mull of the ground powder. Abbreviations: pr = poorly resolved, sh = shoulder. [b] Measured for an aqueous solution of the sample, which is 0.01 ± 0.001 M copper. [c] Extinction coefficient measured in L (mol of Cu)$^{-1}$ cm^{-1}. If two absorbances are given, then the extinction coefficients are listed in the same order as are the absorbances. [d] pH of a carbonate-free solution of the compound in 0.16 M aqueous sodium nitrate, which is 0.01 ± 0.001 M in copper. [e] ESR parameters for finely ground samples measured at X band (~9.5 GHz) and at 80 K. The number in parentheses indicates the increase in gain required to make the $\Delta M = \pm 2$ transition amplitude equal to about half that of the signal at $g = 2.1$.

equimolar quantities of the triaminecopper(II) salt and imidazole are used. The imidazole acts as its own base in these cases. The small amounts of water that are added during the preparations of **6** and **7** facilitate the growth of X-ray-quality crystals, probably by increasing the solubility of the bridged complexes in the mother liquor and retarding the rate of crystallization. Extended refluxing of the solutions of **6** is required in order to obtain crystals of suitable size for crystallographic studies. Simple addition of benzimidazole to hot solutions of $Cu(PMDT)(ClO_4)_2\cdot 2CH_3CN$ yields, on cooling, very thin lavender platelets.

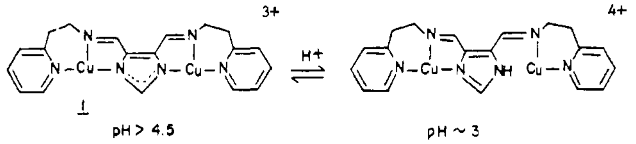
The apparent variability in the solvent composition of compounds **1** and **6** is of no consequence. Crystallographic studies[1b,13] of both of these compounds verify the existence of the imidazolate-bridged species. The procedures given in the Experimental Section repeatedly yield homogeneous crystalline products, which optical goniometric studies show to be identical from batch to batch. Furthermore, X-ray powder photographs of the various preparations are identical with each other, within the limits of the technique. Examination of the crystal structure of **6** reveals that there are channels that could accommodate extra solvent. In fact, crystals of this compound have been found in which the *b* axis is 0.19 Å (>11σ) longer than in the crystal used for the X-ray studies. This result suggests that a larger solvent molecule, i.e., methanol, has been included. Similarly, one molecule of water in **1** is not coordinated to the copper atoms and exhibits large thermal motion. It is not impossible that methanol could replace this water molecule. The evidence therefore indicates conclusively that the differences in the analyses are due to solvent composition. These differences, however, produce quite small changes in the molecular weights of the compounds and therefore introduce only minor uncertainties into experiments in which the mass of the compound used is important. In particular, the interpretation of the magnetic susceptibility results[13] is not sensitive to the solvent composition of **1** or **6**.

Solution and Spectroscopic Studies. Table II summarizes salient features of the visible and solid-state X-band electron spin resonance spectra of the compounds prepared in this study. Also included is qualitative information pertaining to the behavior of the various complexes upon dissolution in water.

Cu_2bpim^{3+} (1). On dissolution of **1** in water the nitrate groups, which occupy the fourth equatorial coordination sites of either copper atom,[1b] are replaced by water molecules, weakening the crystal field as judged by the increase in λ_{max} from 622 to 653 nm (Table II). The small drop in the pH of the solution from 7.0 to 6.43 indicates ionization of the coordinated water molecules as shown in eq 3. Had the imidazolate bridge broken in solution, the resulting pH would be expected to be greater than 7 as suggested by eq 1.

$$[Cu_2bpim(H_2O)_2]^{3+} \rightleftharpoons [Cu_2bpim(H_2O)(OH)]^{2+} + H^+ \rightleftharpoons [Cu_2bpim(OH)_2]^+ + 2H^+ \quad (3)$$

Potentiometric and pH-dependent ESR spectroscopic titrations substantiate this interpretation of the solution behavior of **1**. Between pH 5.7 and 10.7 two protons may be reversibly titrated from the $[Cu_2bpim(H_2O)_2]^{3+}$ moiety, corresponding to eq 3. The ESR spectrum of **1** in frozen solution consists of a single broad asymmetric signal at $g = 2.1$ and a much weaker signal at $g = 4.2$; this result is consistent with the imidazolate-bridged dicopper(II) unit remaining intact.[3,23] Magnetic susceptibility studies[13] indicate that the two copper atoms are strongly antiferromagnetically coupled. No change in the ESR spectrum is observed between pH 12 and 4.5, but by pH 3.05 the features are typical of monomeric Cu(II) species. This result indicates that the imidazolate bridge has finally become protonated with concomitant disruption of the superexchange pathway (eq 4). It is not possible to identify



(4)

the monomeric species, but examination of the $g_{\parallel}$ region suggests that there are at least two compounds in solution at very low pH.

The stability of the imidazolate-bridged unit **1** to attack by either protons or hydroxide ions is unprecedented (cf. ref 3, 4) and is no doubt due to the chelating properties of the bpim ligand.

$[Cu_2bpim(im)]_2^{4+}$ (2). The visible spectrum of **2** remains unchanged on dissolution in water, and the pH of the resulting solution is 8.5. This result suggests that at least one of the imidazolate bridges that join the Cu_2bpim^{3+} halves of **2** is being broken and that free hydroxide ions are being formed according to eq 5. As shown in Figure 2, four protons are reversibly titrated between pH 4.25 and 9.5 with the midpoint of the titration being 7.0. We attribute this behavior to the complete protonation of the imidazolate groups that join the Cu_2bpim^{3+} halves as shown in eq 6. Note in Table III that at low pH the λ_{max} values for the Cu_2bpim^{3+} and $[Cu_2bpim(im)]_2^{4+}$ systems are identical, indicating that in both systems

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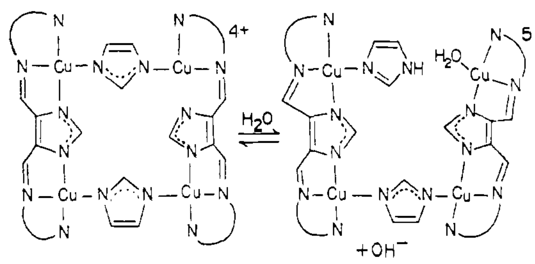
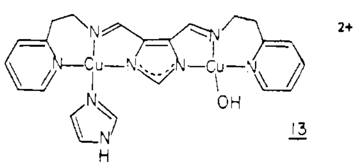
(23) Smith, T. D.; Pilbrow, J. R. *Coord. Chem. Rev.* **1974**, *13*, 173–278.



(5)

$$2 + 4H^+ \rightleftharpoons 2(\mathbf{1}) + 2(imH_2)^+ \qquad (6)$$

the low pH species are the same, namely, $[Cu_2bpim(H_2O)_2]^{3+}$. When the pH is increased, λ_{max} shifts to higher energy in both cases but the spectrophotometric titration is complete at lower pH for the $[Cu_2bpim(im)]_2^{4+}$ system, in parallel with the results of the potentiometric titration. The different behavior exhibited by the two systems suggests that at high pH dinuclear species like **13** do not occur to any great extent in the



13

$[Cu_2bpim(im)]_2^{4+}$ system. It would be expected that the pK_a's of the imidazolium and coordinated water molecules that are titrated to form **13** would be approximately 7[24] and 9,[25] respectively. Hence, at pH 8.9 the titration of the hydroxide groups would be only half complete, and thus the overall titration would be three-fourths complete. Yet, both the spectrophotometric and potentiometric titrations show quite clearly that the titration of $[Cu_2bpim(im)]_2^{4+}$ is 95% complete by pH 9. Thus eq 6 is reasonable. It is impossible to derive any accurate pK_a values from the titration curve without recourse to curve fitting, but we can obtain an upper bound for the pK_a of the substitution of the imidazole proton by copper(II) (eq 5). This pK_a is ≤8.4, considerably lower than that observed for the Cu(glycyl-L-histidine) case mentioned previously.[2] This result suggests that some sort of "super chelate effect" stabilizes the formation of the $[Cu_2bpim(im)]_2^{4+}$ unit, facilitating formation of the imidazolate bridge.

The behavior of the ESR spectrum of **2** as a function of pH is identical with that observed for **1**. Although the copper atoms also interact with each other through the imidazolate groups that link the Cu_2bpim^{3+} halves of **2**,[2,13] the interaction is smaller than that within the Cu_2bpim^{3+} units and apparently this internal interaction dominates the ESR spectrum.

$[Cu(pip)(H_2O)]^{2+}$ (12). This species does not behave unexpectedly. On dissolution the d → d transitions of $Cu(pip)(NO_3)_2$ and $Cu(pip)(ClO_4)_2 \cdot H_2O$ shift to lower energy (Table II), suggesting that the fourth equatorial ligand of these complexes is different in the crystalline and solution states. In solution the three $Cu(pip)^{2+}$ salts have identical spectra, indicating that the same species is present in the three solutions, as expected. The transition at ~380 nm is probably an internal ligand transition since it occurs in the zinc complex (Experimental Section) at the same position and with the same extinction coefficient as in the copper complexes. The acidic pH values measured for solutions of these three compounds are due to the deprotonation of the coordinated water molecule as indicated by eq 7. Titration of **12**, shown in Figure 3,

$$[Cu(pip)(H_2O)]^{2+} \rightleftharpoons [Cu(pip)OH]^+ + H^+ \qquad (7)$$

reveals that one proton is titrated between pH 4.5 and 10.5.

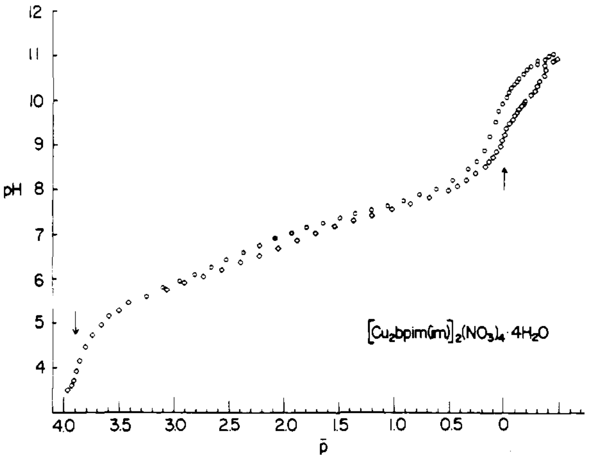


Figure 2. Potentiometric titration for $[Cu_2bpim(im)]_2^{4+}$. The titration with base (○) was begun at pH ~5.7 and terminated at pH 11. The return titration with acid (◇) was concluded at pH 3.5. Arrows mark the apparent end points.

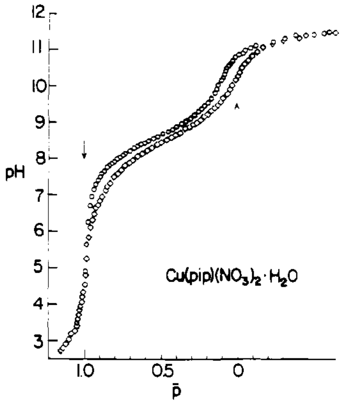


Figure 3. Potentiometric titration for $Cu(pip)(NO_3)_2$. The titration with base (○) was begun at pH 4.5 and concluded at pH 11.5. The return titration with acid (◇) was stopped at pH 2.75. Arrows mark the apparent end points.

Table III. Visible Absorption Spectra in Aqueous Solutions of $[Cu_2bpim](NO_3)_2ClO_4 \cdot 2H_2O$ and $[Cu_2bpim(im)]_2(NO_3)_4 \cdot 4H_2O$ as a Function of pH

$[Cu_2bpim]$-$(NO_3)_2ClO_4 \cdot 2H_2O$		$[Cu_2bpim(im)]_2$-$(NO_3)_4 \cdot 4H_2O$	
pH	λ_{max},[a] nm	pH	λ_{max},[a] nm
3.14	650	3.43	652
4.15	650	4.08	650
5.40	648	5.14	646
7.18	641	5.48	643
8.05	635	6.09	633
9.40	625	6.64	625
10.81	619	7.60	615
11.76	619	8.37	607
12.3	613	11.73	608

[a] The uncertainty in the wavelength is ±3 nm.

The pK_a of ~8.4 is typical for a (triamine)copper(II) complex.[25] ESR spectra of centimolar solutions of the three $Cu(pip)^{2+}$ complexes in 1:1 water–methanol solutions at liquid nitrogen temperatures are identical. The signal is somewhat distorted from pure axial symmetry with $g_{\parallel} = 2.27$, $g_{\perp} = 2.07$, and $A_{\parallel} = 173$ G.

$[Cu(pip)(1\text{-}MeIm)]^{2+}$. The ESR spectrum of this species, collected under conditions identical with those used for $[Cu(pip)(H_2O)]^{2+}$, is very similar to that of **12**. As expected there is very little distortion from axial symmetry, and at least four nitrogen hyperfine lines appear on the perpendicular compo-

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[24] (a) Sundberg, R. J.; Martin, R. B. *Chem. Rev.* **1974**, *74*, 471–517. (b) *Spec. Publ.-Chem. Soc.* **1974**, *No. 17*.

[25] Allison, J. W.; Angelici, R. J. *Inorg. Chem.* **1971**, *10*, 2233–2238.

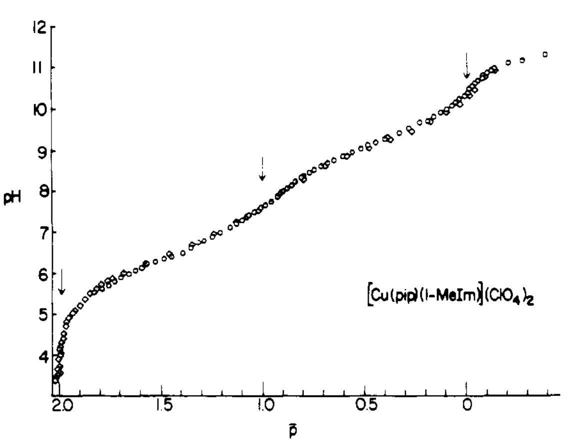


Figure 4. Potentiometric titration for $[Cu(pip)(1\text{-}MeIm)]^{2+}$. The titration with base (○) was begun at pH 5.5 and stopped at pH 11.5. The return titration with acid (◇) was stopped at pH 3.5. Arrows mark the apparent end points.

Table IV. Visible Absorption Spectra in Aqueous Solutions of $Cu(pip)(NO_3)_2$ and $[Cu(pip)]_2(im)(NO_3)_3 \cdot 2.5H_2O$

$Cu(pip)(NO_3)_2$		$[Cu(pip)]_2(im)(NO_3)_3 \cdot 2.5H_2O$			
pH	λ_{max},[a] nm	pH	λ_{max},[a] nm	pH	λ_{max},[a] nm
4.0, 6.4	666	3.7	665	9.4	637
8.4	651	6.0	661	9.6	636
10.7	635	7.2	651	10.0	635
		8.1	641	11.2	633
		8.5	641		

[a] The uncertainty in the wavelength is ±3 nm.

nent: $g_\parallel = 2.25$, $g_\perp = 2.06$, $A_\parallel = 173$ G, $A_\perp(N) = 13$ G. When this complex is dissolved in water, the λ_{max} shifts to lower energy and the resulting solution is basic, suggesting that the 1-methylimidazole ring dissociates from the copper complex as indicated in eq 8. Accordingly, one might expect to be able

$$[Cu(pip)(1\text{-}MeIm)]^{2+} \rightleftharpoons [Cu(pip)(H_2O)]^{2+} + OH^- + 1\text{-}MeImH^+ \quad (8)$$

to titrate one proton for this system, corresponding to 1-methylimidazolium going to coordinated 1-methylimidazole, with a pK_a of about 7.[24] Potentiometric titrations (Figure 4) indicate, however, that the complex reversibly titrates two protons between pH 4 and 11 with pK_a's of 6.45 and 9.05. Two schemes are consistent with this titration, eq 9a and 9b.

$$\begin{array}{c} [Cu(pip)(H_2O)]^{2+} \\ + \\ 1\text{-}MeImH^+ \\ (pH < 4) \end{array} \rightleftharpoons \begin{array}{c} [Cu(pip)(H_2O)]^{2+} \\ + \\ 1\text{-}MeIm \\ (pH\ 7.5) \end{array} \rightleftharpoons \begin{array}{c} [Cu(pip)(OH)]^{+} \\ + \\ 1\text{-}MeIm \\ (pH > 11) \end{array} \quad (9a)$$

$$\begin{array}{c} [Cu(pip)(H_2O)]^{2+} \\ + \\ 1\text{-}MeImH^+ \end{array} \rightleftharpoons [Cu(pip)(1\text{-}MeIm)]^{2+} \rightleftharpoons \begin{array}{c} [Cu(pip)(OH)]^{+} \\ + \\ 1\text{-}MeIm \end{array} \quad (9b)$$

Equation 9a is wrong since it predicts the following, by analogy with the above studies of **12**: (i) the two observed pK_a's would be 7[24] for the 1-MeImH$^+$ group and 8.4 for the coordinated water molecule, not 6.45 and 9.05, as observed; (ii) the EPR spectrum should exhibit no superhyperfine coupling, contrary to what is observed; (iii) the λ_{max} would be greater than 650 nm at pH 7.9 and not the value of 637 nm, which is observed (Tables II and IV). Hence we conclude that eq 9b describes the titration and that the copper–imidazole bond is split at low pH by protons and at high pH by the competitive binding of the hydroxide group. The lowering of the pK_a of the 1-methylimidazolium cation suggests that the coordination of the copper ion facilitates the deprotonation of this group in much the same way that the pK_a of the pyrrole proton of coordinated imidazole is decreased when deprotonation of the ring is accompanied by coordination of a metal ion. Using the known pK_a (7.06) of the 1-methylimidazolium cation[24] and the concentration (3 mM) of $Cu(pip)^{2+}$ in this particular titration, we computed the formation constant for $[Cu(pip)(1\text{-}MeIm)]^{2+}$ to be $10^{3.2}$. This value is of the correct magnitude for copper(II)–imidazole interactions.[24] Splitting of the imidazolate bridge between two copper(II) centers by hydroxide ion has been previously established for $[(TMDT)_2Cu(im)(ClO_4)_2](ClO_4)$.[3]

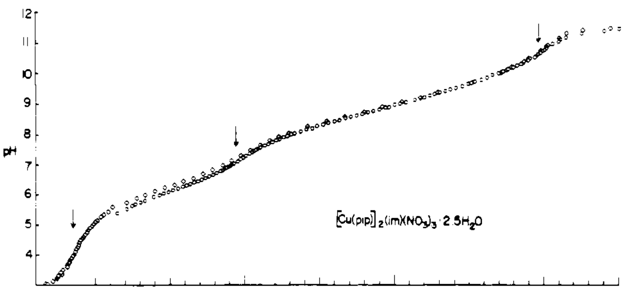
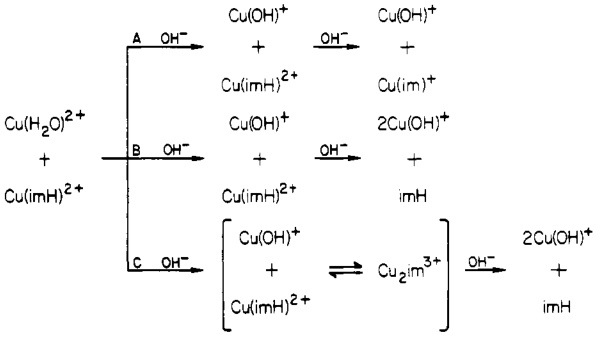


Figure 5. Potentiometric titration for $[Cu(pip)]_2(im)^{3+}$. The titration with base (○) was begun at pH 5.3 and stopped at pH 11.5. The return titration with acid (◇) was terminated at pH 3. Arrows mark the apparent end points.

Scheme III



$[Cu(pip)]_2(im)^{3+}$ (3). The titration of this compound also proceeds in an interesting manner. The potentiometric titration (Figure 5) indicates that three protons are titrated reversibly between pH 4 and 11, one with a pK_a of 6.2 and two, where the midpoint of the titration occurs, at pK_a 8.9. By analogy with $[Cu(pip)(1\text{-}MeIm)]^{2+}$, the first p$K_a$ is that of free imidazolium ion going to coordinated imidazole (eq 10). The

$$[Cu(pip)(H_2O)]^{2+} + imH_2^+ \rightleftharpoons [Cu(pip)(imH)]^{2+} + H^+ \quad (10)$$

pK_a of 6.2 is lower than the value of 6.45 found for the 1-methylimidazole complex because of the higher $Cu(pip)^{2+}$ to imidazole ratio (2:1 vs. 1:1) in this case. From the known pK_a of imidazole[24] and the value of the $Cu(pip)^{2+}$ concentration (5.2×10^{-3} M) used in this titration a formation constant of $10^{3.3}$ is calculated for $[Cu(pip)(imH)]^{2+}$. This result is in good agreement with the value obtained from the titration of $[Cu(pip)(1\text{-}MeIm)]^{2+}$.

The titration of the remaining two protons may be explained in several ways summarized in Scheme III. The species Cu(pip) has been written simply as Cu in this scheme. Without recourse to curve fitting, the potentiometric titration data are unable to distinguish among the three possibilities A, B, and C. Other experiments, however, can help us.

If A is the correct reaction route, then we would expect to see two separate pK_a's, one at 8.4 due to the deprotonation of the coordinated water and one at 11.7 due to deprotonation

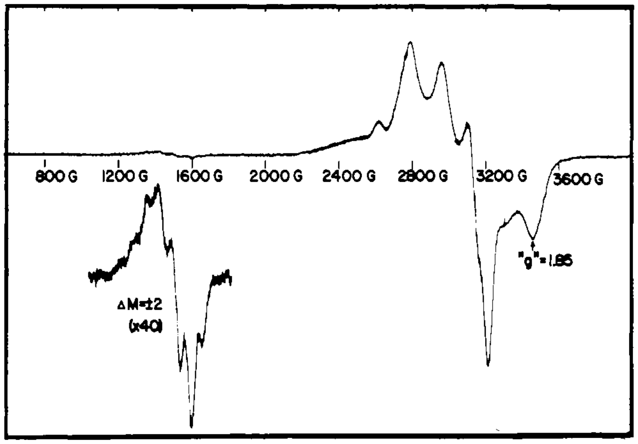


Figure 6. Electron spin resonance spectrum of a frozen 10 mM solution of $[Cu(pip)]_2(im)(NO_3)_3 \cdot 2.5H_2O$ in Me_2SO-H_2O (1:1, v/v) at 77 K. The pH of the aqueous solution before addition of the Me_2SO was 8.9. Spectrometer settings: 9.108-GHz irradiating frequency, 10-mW microwave power, receiver gain of 800 (32 000 for the half-field transitions), modulation frequency of 100 kHz, modulation amplitude of 5 G, scan rate of 4.2 G/s, and a time constant of 0.3 s.

of the imidazole. The first value is obtained from the titration of $[Cu(pip)(H_2O)]^{2+}$, while the latter pK_a is that for the deprotonation of the imidazole ring in $Cu(L\text{-}his)_2$.[20] There is no reason to believe that these values should be much different in path A. Since the titration is complete by a pH of 10.7, however, we can rule out path A.

The composition of the solutions at high pH is the same whether path B or path C is followed. The prediction of $Cu(OH)^+$ in this pH region is supported by the spectrophotometric titrations of $Cu(pip)(NO_3)_2$ and $[Cu(pip)]_2(im)(NO_3)_3 \cdot 2.5H_2O$ (Table IV). At pH ~10.3 λ_{max} in the visible region is ~635 nm for both compounds. Paths B and C differ only in that C assigns the imidazolate-bridged dicopper(II) species $[Cu(pip)]_2(im)^{3+}$ in solution. This species can be detected by ESR spectroscopy. Figure 6 is the ESR spectrum of a frozen 5 mM solution of **3** in 1:1 Me_2SO–water. The pH of the solution before addition of the Me_2SO was 8.9. The $\Delta M = \pm 2$ transition at 1520 G is strong evidence for the existence of a bridged species in solution.[23] The seven-line hyperfine pattern with an average spacing of 65 G is due to the interaction of the two copper nuclei ($I_{Cu} = {}^3/_2$, $2S_I + 1 = 7$). The interpretation of the spectrum in the region of $g = 2$ is complicated by the large (-26 cm^{-1}) coupling between the copper atoms, which is mediated by the imidazolate bridge. Still, the pattern in the $g_\parallel$ region and especially the feature at 3460 G are typical of a bridged species.[3] The "g value" of this signal is 1.85, which is not a value that can be attributed to a monomeric copper species. The experimental evidence thus permits us unequivocally to eliminate schemes A and B and to confirm that only C is consistent with the data.

Another reaction route consistent with the titration data would involve deprotonation of the imidazolium ion to form free imidazole followed by the deprotonation of 2 equiv of coordinated water molecules. The electronic and ESR spectral results absolutely rule out this possibility.

The important point of this and the 1-methylimidazole titration studies is that the imidazolate bridge is unstable at both high and low pH. The imidazolate bridge is attacked by protons to yield imidazole and imidazolium at low pH while at high pH competition with hydroxide ions severs the copper–imidazolate and copper–imidazole bonds. The results of the $Cu(pip)(H_2O)^{2+}$ and $Cu(pip)(1\text{-}MeIm)^{2+}$ titrations suggest that $[Cu(pip)]_2(im)^{3+}$ should be most stable in the pH range from 8.4 (the pK_a for the formation of the hydroxo complex, eq 7) to 9.1 (the pK_a for the replacement of 1-methylimidazole by hydroxide ion, eq 9b). This estimate is in agreement with detailed ESR titrations of a related dicopper(II) imidazolate-bridged compound.[3] The present work reveals, however, that the monocopper(II)–imidazolate species $Cu(TMDT)(im)^+$, postulated to exist at pH ~11, would be most unlikely to occur at such a low pH. Equation 7 of ref 3 should therefore be rewritten as scheme C.

Thermodynamic studies of the CH_3Hg^+–imH system[8] in water reach parallel conclusions to those drawn from the titrations reported here. The implications of these findings to the pH dependence of the redox potential of BESOD have been previously discussed.[3] Only when the Cu_2im^{3+} moiety is incorporated into a chelate such as bpim (**1**) or a binucleating macrocycle[4] is the bridge stable over a very wide pH range.

Pentamethyldiethylenetriamine Complexes. The changes in the visible spectra of the $Cu(PMDT)^{2+}$ imidazolate-bridged complexes upon dissolution in water (two d → d transitions in the solid state but only one, at lower frequency, in solution, Table II) are probably due to the alteration of the coordination spheres in solution. First, the strong-field ligand imidazolate is replaced by the weaker field ligand water (by analogy with the above work on **3**) in the equatorial plane. Second, in the solid state[13] both copper atoms of **5** and one copper atom of **6** are strictly four-coordinate. Coordination of water to the axial sites of the copper atoms (in solution) could change the visible spectrum by altering the energy levels of the d_{z^2}, d_{xz}, and d_{yz} orbitals. The coordination of axial-site ligands also seems to reduce the tetrahedral distortion of the copper atoms (cf. the structure of **6**),[13] and this might be another contributing factor.[26]

Transitions in the UV region of several copper–imidazole and copper–imidazolate complexes have recently been assigned as imidazole-to-copper charge-transfer bands.[27] The solid-state UV spectra for the compounds reported here have not yet been examined. In solution, no change is observed in the UV spectra of **1**, **2**, or **3** as a function of pH. This result may be due, however, to interference from the rich absorption spectrum of the bpim and pip ligands. Interference from ligand absorption bands in the infrared region similarly rendered this technique useless in the present work.

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Registry No. **1**, 73611-43-5; **2**, 73906-04-4; **3**, 64254-63-3; **4**, 78003-94-8; **5**, 78003-96-0; **6**, 78003-98-2; **7**, 78018-26-5; **8**, 570-22-9; **9**, 3304-70-9; **10**, 33457-48-6; **11**, 33457-11-3; $Cu(pip)(NO_3)_2 \cdot H_2O$, 78004-00-9; $Cu(pip)(NO_3)_2$, 78004-02-1; $Cu(pip)(ClO_4)_2 \cdot H_2O$, 78004-03-2; $Cu(pip)(1\text{-}MeIm)(ClO_4)_2$, 78004-05-4; $[Cu(PMDT)](ClO_4)_2 \cdot 2CH_3CN$, 74911-61-8; $[Cu_2bpim](NO_3)_3 \cdot 2H_2O$, 60764-98-9; $Zn(pip)(NO_3)_2$, 78004-07-6; pyridine-2-carboxaldehyde, 1121-60-4; 2-(2-aminoethyl)pyridine, 2706-56-1.

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(26) Furlani, C.; Morpurgio, G. *Theor. Chim. Acta* **1963**, *1*, 102–115.

(27) Fawcett, T. G.; Bernaducci, E. E.; Krogh-Jesperson, K.; Schugar, H. J. *J. Am. Chem. Soc.* **1980**, *102*, 2598–2604.