

Use of Ligand Design To Provide Coordination Asymmetry in a Binuclear Metalloprotein Model System: Ligand Synthesis, Coordination Chemistry with Copper, and Demonstration of Site-Directed Reactivity

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The synthesis and coordination chemistry of a new asymmetric multidentate ligand designed for modeling coordination number asymmetry at metal sites in binuclear metalloproteins are described. A binuclear copper complex of this ligand demonstrates proof-of-concept for inducing coordinative unsaturation at one metal of the binuclear pair, and subsequent reaction with azide illustrates site-directed reactivity. The ligand *N,N,N'*-tris(*N*-methyl-2-benzimidazolyl)methyl)-*N'*-methyl-1,3-diamino-2-propanol (HBMDP) was prepared in good yield by a five-step procedure. HBMDP reacts with the copper(II) ion in methanol to produce a mononuclear copper complex, [CuHBMDP](ClO₄)₂·CH₃CN, that crystallizes in the triclinic space group *P*1̄ with unit cell dimensions *a* = 10.833(3) Å, *b* = 12.457(3) Å, *c* = 15.214(3) Å, α = 78.28(2)°, β = 79.26(2)°, and γ = 68.10(2)°. A single-crystal X-ray structure shows that the copper ion is coordinated to the five nitrogen donor atoms in a distorted trigonal bipyramid. The hydroxo oxygen of the ligand does not participate in metal coordination. On the other hand, the reaction of HBMDP with 2 equiv each of copper(II) ion and acetate in methanol produces the binuclear copper complex [Cu₂BMDP(OAc)](ClO₄)₂·2H₂O, which crystallizes in the monoclinic space group *C*2/*m* with unit cell dimensions *a* = 19.934(4) Å, *b* = 23.460(9) Å, *c* = 20.039(4) Å, and β = 110.65(2)°. A single-crystal X-ray structure reveals that the two copper ions are coordinated to the aromatic and aliphatic nitrogens as well as being bridged by the acetate anion and the alkoxide oxygen of the ligand. As a result of the inherent asymmetry of the ligand, one copper ion is five-coordinate (distorted trigonal bipyramidal) while the other copper ion is four-coordinate (distorted square planar). The crystal structure also reveals that in the solid state an oxygen from one of the perchlorate counterions is weakly bound to the four-coordinate copper (~2.6 Å), suggesting that a vacant coordination site exists at this formally four-coordinate copper center. The potential for site-directed reactivity at this lower coordinated copper center was demonstrated by adding 0.5 equiv of azide ion to the binuclear copper complex in acetonitrile. The resulting azido-bridged complex, {[Cu₂BMDP(OAc)]₂N₃}(ClO₄)₃·8.5H₂O, crystallizes in the orthorhombic space group *Cmca* with unit cell dimensions *a* = 22.603(3) Å, *b* = 19.565(3) Å, and *c* = 36.965(3) Å. A single-crystal X-ray structure shows that the two copper ions within the binuclear unit are still coordinated by the ligand nitrogens, the acetate, and the ligand alkoxy oxygen. In addition, the copper ion that was four-coordinate in the binuclear complex is now bridged by azide to its companion four-coordinate copper in a separate binuclear unit. As a result, both coppers within the binuclear unit are now five-coordinate, one remaining distorted trigonal bipyramidal while the other adopts square pyramidal geometry. In this reaction, azide specifically fills the vacant coordination site of the four-coordinate copper ion in the binuclear complex. Although these two binuclear paramagnetic copper(II) complexes are magnetically weakly coupled, their ¹H NMR spectra show relatively sharp lines that provide solution assignments consistent with the solid state structures. To our knowledge this is the first example of a binuclear copper complex to exhibit both coordination number asymmetry and directed reactivity at one metal center by virtue of ligand design.

Introduction

Binuclear centers containing transition elements such as iron and copper are common among metalloproteins.¹ These centers often function by binding and activating substrate(s). The individual metal ions found at the binuclear center, however, may have quite distinct roles in the overall function. Examples of this role separation include the active sites in erythrocyte superoxide dismutase (SOD) and alkaline phosphatase where one metal binds to the substrate while the other metal is responsible for maintaining the structural integrity of the active site or regulates activity, respectively.² In such cases, it is often

found that the binuclear site of the metalloenzyme situates its metal ions in chemically distinct environments. From the perspective of the metal, four distinct environments can be

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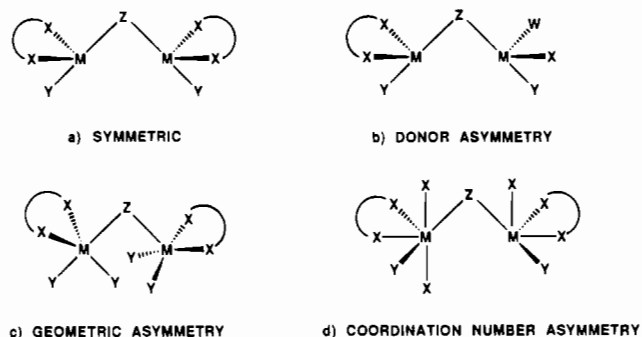


Figure 1. Classification of metal coordination environments found in metalloproteins containing multinuclear metal centers. M is a general transition metal and W, X, Y, and Z represent heteroatom donors (e.g. N, O, S, etc.).

readily identified: (1) symmetric, identical donor atoms (type and number) bound to each metal in similar geometries; (2) donor asymmetry, different types of donor atoms bound to each metal; (3) geometrical asymmetry, inequivalent geometrical/spatial arrangement of the donor atoms about each metal; and/or (4) coordination number asymmetry, an unequal number of donor atoms coordinated to each metal. Figure 1 presents a schematic representation of examples of each type of environment.

The individual metals of binuclear centers have been found to possess donor asymmetry in, for example, cobalt-based methionine aminopeptidase,³ bovine SOD,⁴ and the trizinc enzyme phospholipase C.⁵ Geometric asymmetry of metalloprotein binuclear sites has also been reported for the B2 protein active iron site of ribonucleotide reductase⁶ and certain adducts of the dicopper site of hemocyanin.⁷⁻⁹ There are several examples of binuclear metalloproteins where coordination number asymmetry is known or proposed. These include some copper-containing tyrosinases,¹⁰ hemerythrin,¹¹ uteroferrin,¹² and the hydroxylase component of soluble methane monooxygenase.^{13,14}

It is also possible that any combination of these types of asymmetry may occur in a single binuclear enzyme, as demonstrated by several of the cited examples. However, for this work we are primarily concerned with coordination number asymmetry. Coordination number asymmetry in metalloenzymes presents the possibility of "open" coordination sites for direct interaction of one metal center with substrate. It is becoming apparent that coordination number asymmetry exists

in a number of metalloproteins and may be responsible for imparting unique reactivity.¹⁵⁻¹⁷

Model complexes have been developed and used to describe various aspects of the structure and function of binuclear centers found in naturally occurring metalloproteins.¹⁸ In particular, the use of model systems to understand the spectroscopic signatures of metalloenzymes has been shown to be of considerable utility.^{1b} The most typical model system is symmetric (Figure 1a) and possesses a uniform donor set with similar metal geometries resulting on complexation. An example of such a model is the binuclear copper complex of the ethylated tetrakis-(benzimidazolymethyl)-1,3-diaminopropanol ligand reported by Reed.¹⁹ A model system for donor asymmetry has also been reported.⁸ However, the effects that geometric or coordination number asymmetry have on the physical properties and function of binuclear sites are much less studied. The reason for this appears to stem from a lack of suitable model systems. A few complexes have been reported that unexpectedly formed with geometric^{20a,b} or coordination number asymmetry,^{20c,d} but these examples are rare and not conducive to strict synthetic control. The rational design of ligands that can induce coordination number asymmetry in binuclear complexes is a desirable target for developing a more complete description of spectroscopic and chemical reactivity properties related to metalloenzyme systems.

In a preliminary report, we outlined the synthesis of a prototype chelating ligand, containing a metal-bridging hydroxo group, that was designed to induce coordination number

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asymmetry in a binuclear complex and described its complexation chemistry with copper(II).²¹ A subsequent communication by Jameson describes a structurally related ligand, but with a metal-bridging phenolato group, and its coordination to copper(II) that now provides a second example of a model designed to produce coordination number asymmetry in binuclear complexes.²² We report here the complete details on the preparation of our new ligand and the synthesis, characterization, and structure of three copper complexes. The present work demonstrates both the formation of binuclear complexes with different coordination numbers at each metal ion and, importantly, metal-specific reactivity. Such complexes are relevant to the development of model systems for the active sites of binuclear metalloproteins.²³

Experimental Section

General Procedures. All starting materials were purchased from commercial sources and used without further purification unless otherwise noted. Melting points were determined with a MEL-TEMP melting point apparatus and are uncorrected. ¹H, ²H, and ¹³C NMR spectra were recorded with either a Nicolet NT 200 MHz or a Bruker MSL 300 MHz spectrometer. Proton or deuterium NMR spectra of the paramagnetic copper complexes were obtained using standard acquisition parameters and a recycle delay of 10 ms (20 000 transients, ~2 h) for routine spectra or a 1.5 s recycle delay (20 000 transients, ~12 h) for integrals. The carrier frequency was set at several different positions within the spectra to ensure the validity of the integrals. Infrared measurements were obtained on KBr pellets using a Bio-Rad FTS-40 instrument. UV-vis measurements were recorded on a Perkin-Elmer Lambda 9 spectrometer. Mass spectroscopy was carried out using a Millipore/Extrel GC-LC-MS spectrometer (methanol/water, 1:1, 70 eV EI). Solvates were determined by thermogravimetric analysis (TGA) with a Perkin-Elmer 7 series thermal analysis system (room temperature to 600 °C at 10 °C/min under flowing argon). Microanalytical analyses were performed at the Lawrence Livermore National Laboratory or by a commercial vendor (Schwarzkopf Microanalytical). [Caution: While none of these perchlorate complexes has proved to be shock sensitive, care is recommended!²⁴]

(Benzalamino)-3-chloro-2-propanol (1). This product was prepared by modification of a literature procedure.²⁵ To a solution of benzaldehyde (106 g, 1 mol) in 500 mL of ethanol was added concentrated aqueous ammonium hydroxide (100 mL, 1.5 mol). Under stirring, epichlorohydrin (92.5 g, 1 mol) was added to this solution continuously over a period of 5 min. After stirring at room temperature overnight, the solution was heated in a water bath at 50 °C for 1 h and then concentrated to an oil by rotary evaporation at 60 °C. The oil was added to 200 mL of ice-cold water and maintained at 0 °C with occasional stirring (~2 h) until a solid mass developed. The solid mass was ground to a powder, washed once with cold water, and dried in a vacuum oven at 40 °C overnight. This product was then dissolved in 2400 mL of hot hexanes to produce a clear solution and a yellow oil (thoroughly drying the solid prior to dissolving in hot hexanes minimizes the formation of the yellow oil). The hot hexanes solution was decanted from the oil, and the solution was allowed to cool to room temperature. White needles of the product formed on cooling (yields for this first crop of crystalline product varied between 20 and 30%; yields up to 60% were obtained by combining all crystallization crops): mp 76–78 °C (lit.²⁵ mp 81–83 °C); ¹H NMR (300.13 MHz, CDCl₃) δ 3.67 (m, 2H), 3.81 (m, 2H), 4.10 (q, 1H), 7.44 (m, 3H), 7.74 (m, 2H), 8.35 (s, 1H); ¹³C{¹H} NMR (75.4 MHz, CH₂Cl₂) δ 164.1, 136.4, 131.5, 129.2, 128.7, 71.5, 64.0, 48.0.

1-Amino-3-chloro-2-propanol Hydrochloride (2). This product was prepared by a literature-reported hydrolysis of 1 in >95% yield:²⁶ mp 102–103 °C (lit.²⁶ mp 103–104 °C); ¹H NMR (300.13 MHz, D₂O) δ 3.08 (dd, 1H), 3.27 (dd, 1H), 3.65 (dd, 1H), 3.72 (dd, 1H), 4.17 (m, 1H); ¹³C NMR (75.4 MHz, D₂O) δ 41.4 (t), 45.5 (t), 66.5 (d).

N-Methyl-1,3-diamino-2-propanol (3). The hydrochloride salt 2 (47.54 g, 0.326 mol) was dissolved in 150 mL of water. Aqueous methylamine (280 mL of 40%, 101 g, 3.26 mol) was then slowly added, and the solution was stirred at room temperature overnight. Solid NaOH (26.08 g, 0.652 mol) was added, and after it had dissolved, the solution was concentrated by rotary evaporation at 70–80 °C to a salt/oil mixture. The mixture was suspended in a minimal volume of 2-propanol and filtered through a sintered glass frit to remove NaCl. The alcohol filtrate was concentrated by rotary evaporation at 80 °C to a viscous oil, and the oil was then dissolved in chloroform and shaken with sodium sulfate. Removal of the chloroform by rotary evaporation resulted in a slightly yellow, viscous oil. The dried oil was distilled through a short-path distillation apparatus at 300 mTorr and the colorless fraction between 83 and 90 °C was collected (25.30 g, 74.6% yield): ¹H NMR (200.08 MHz, D₂O) δ 2.25 (s, 3H), 2.53 (m, 4H), 3.64 (m, 1H); ¹³C NMR (50.3 MHz, D₂O) δ 69.7 (d), 52.5 (t), 43.3 (t), 33.4 (q). Anal. Calcd for C₄H₁₂N₂O (3): C, 46.13; H, 11.61; N, 26.90. Found: C, 46.12; H, 11.67; N, 27.06.

N-Methyl-1,3-diamino-2-propanol-N,N'-triacetic Acid (4). This compound was prepared by a modification of the method described by Martell.²⁷ An aqueous NaCN solution (17.15 g, 0.35 mol, of NaCN and 1 g of NaOH in 50 mL of distilled water) was added to an aqueous solution of 3 (10.4 g, 0.1 mol in 25 mL of distilled water). The resulting solution was placed in a 250 mL three-neck flask equipped with a reflux condenser, an addition funnel, and a gas dispersion tube. The solution was heated to 80 °C with stirring under a nitrogen purge (~4 L/min), and aqueous formaldehyde (29.6 mL of 39.6% in water, 0.37 mol) was added dropwise over a period of not less than 8 h. The reaction vessel was maintained at 80 °C and purged until the evolution of ammonia could no longer be detected above the condenser with moist pH paper. The total reaction time varied from 20 to 30 h depending on the purge rate.

Purification Procedure A. The cooled reaction mixture was acidified to pH < 1.2 with concentrated sulfuric acid and refluxed for 3 h to remove any unreacted cyanide. [Caution: Work in a well-ventilated hood, as poisonous HCN may be liberated during this step!] After cooling, the flask contents were passed through a 4 × 30 cm cation exchange column (Amberlite IR-120, H⁺ form) and washed with distilled water to remove H₂SO₄ and nitrilotriacetic acid.²⁸ The product was then eluted with 15 L of 0.1 N NaOH, and the eluent was reduced in volume to ~400 mL by rotary evaporation. The addition of 200 mL of absolute ethanol to the concentrated eluent resulted in a turbid solution that became clear and homogeneous when heated. Additional ethanol was added, and heating was continued until a total of 800 mL of the alcohol had been added. At this point the solution was boiling and permanently turbid. Another 800 mL of ethanol was then added with stirring, and the solution was allowed to cool. The precipitate was recovered by filtration and dried under vacuum to yield 16.1 g of a white, hygroscopic salt (yield 35.6%): ¹H NMR (200.08 MHz, D₂O) δ 2.38 (s, 3H), 2.61 (m, 4H), 3.17 (s, 2H), 3.29 (s, 4H), 3.89 (q, 1H); ¹³C{¹H} NMR (75.4 MHz, D₂O) δ 176.9, 170.1, 169.6, 61.2, 59.8, 58.8, 58.0, 57.6, 50.3, 48.9.

Purification Procedure B. Subsequent preparations of 4 were monitored by NMR and shown to contain no nitrilotriacetic acid using these reaction conditions. It was found that the initial reaction solution could be acidified with concentrated HCl, refluxed for 3 h to remove unreacted NaCN, and used directly in the preparation of HBMDP. [Caution: Work in a well-ventilated hood, as poisonous HCN may be liberated during this step!] The acidified, refluxed reaction solution was then concentrated to an oil/salt mixture by rotary evaporation. An aliquot was weighed out and added to 0.5 mL of a 0.1 N NaOD/D₂O solution containing a known amount of TSP.²⁹ The integral of the

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aliphatic methyl singlet (3H) was compared to the area of the TSP singlet (9H) and used to calculate moles of triacid per weight of oil/salt mixture.

***N,N,N'*-Tris(*N*-methyl-2-benzimidazolyl)methyl)-*N'*-methyl-1,3-diamino-2-propanol Hydrate, HBMDP (5).** This condensation reaction³⁰ was performed using an appropriate weight of the oil/salt mixture obtained as described in purification procedure B for **4** (0.1 mol of triacid **4**). The oil/salt mixture was dissolved in 150 mL of 6 N HCl, and solid *N*-methyl-1,2-diaminobenzene dihydrochloride (56.1 g, 0.285 mol) was added. The solution was refluxed for 24 h, during which time the color changed from pink to dark green. After the solution was cooled to 0 °C, concentrated NH₄OH was added slowly while the temperature was maintained below 15 °C. At pH ~7 a white flocculent precipitate began to develop. The NH₄OH addition was continued until no more precipitation occurred (pH ~9). During this time, the precipitate converted to a green-brown oil. The supernatant was decanted from the oil, water was added, and the oil was triturated using a glass rod with slight warming (≤40 °C) until a tan powder resulted. The powder was collected on a sintered-glass frit, washed twice with water, and vacuum-dried to yield 33.9 g (63.2% based on **3**) of crude ligand.

The crude product was recrystallized from acetonitrile/water (1:2): Crude HBMDP (6 g) was dissolved in 500 mL of acetonitrile, and the solution was filtered to remove any insolubles. Water was then added (~1100 mL) until the solution became cloudy. The solution was warmed (<40 °C) until homogeneous, covered, and cooled at -20 °C overnight. The off-white crystalline material was collected on a sintered-glass frit, washed with acetonitrile/water (1:1), and vacuum-dried (82% recovery): ¹H NMR (300 MHz, CDCl₃) δ 2.23 (m, 1H), 2.28 (s, 3H), 2.49 (m, 1H), 2.76 (m, 2H), 3.49 (s, 6H), 3.69 (s, 3H), 3.76 (s, 3H), 4.02 (s, 4H), 7.2 (m, 9H), 7.7 (m, 3H); ¹³C-{¹H} NMR (DEPT) NMR (75.4 MHz, CDCl₃) δ 153.4 (C*, 1C), 153.1 (C*, 2C), 142.3 (C*, 3C), 137.3 (C*, 1C), 137.1 (C*, 2C), 124.2 (CH, 2C), 124.0 (CH, 1C), 123.5 (CH, 2C), 123.3 (CH, 1C), 119.4 (CH, 3C), 111.0 (CH, 3C), 68.7 (CH, 1C), 63.0 (CH₂, 1C), 60.3 (CH₂, 1C), 55.9 (CH₂, 1C), 53.1 (CH₂, 2C), 43.5 (CH₃, 1C), 30.3 (CH₃, 1C), 30.2 (CH₃, 2C); MS *m/e* (assignment, relative intensity) 537 (MH⁺, 2), 536 (M⁺, 3), 348 (100). Anal. Calcd for C₃₁H₃₆N₈O₉·H₂O: C, 67.13; H, 6.91; N, 20.20. Found: C, 67.27; H, 6.85; N, 20.17.

(*N,N,N'*-Tris(*N*-methyl-2-benzimidazolyl)methyl)-*N'*-methyl-1,3-diamino-2-propionato)copper(II) Perchlorate, [CuHBMDP](ClO₄)₂·CH₃CN (6**).** A solution of Cu(ClO₄)₂·xH₂O (17.2% Cu, 0.688 g, 1.86 mmol) in 15 mL of methanol was added to a solution of HBMDP (1.00 g, 1.86 mmol) in 15 mL of methanol with stirring. A precipitate formed immediately on addition of the copper solution, and the mixture was stirred at room temperature for 10 min and then cooled at -20 °C for ~1 h. The resulting blue-green solid was collected on a glass frit, washed with 3 × 5 mL portions of cold methanol, and dried under vacuum at 25 °C. The dried solid was dissolved in 75 mL of hot acetonitrile to produce a dark green solution, which was filtered hot and cooled to room temperature. Dark green crystals obtained by vapor diffusion of ether into this solution were collected on a sintered-glass frit and air-dried to give 1.23 g of **6** (81% yield). Anal. Calcd for C₃₁H₃₆Cl₂CuN₈O₉·CH₃CN (**6**): C, 47.18; H, 4.68; N, 15.00; Cu, 7.56; Cl, 8.44. Calcd for C₃₁H₃₆Cl₂CuN₈O₉·CH₃CN·H₂O: C, 46.19; H, 4.82; N, 14.69; Cu, 7.4; Cl, 8.26. Found: C, 46.06; H, 4.74; N, 14.36; Cu, 7.42; Cl, 8.30. Weight loss by thermogravimetric analysis: calcd, 4.9% for CH₃CN; calcd, 6.9% for CH₃CN and H₂O; found, 4.9% weight loss. (We have found that these copper complexes can readily gain and lose H₂O.)

Diffraction-quality crystals were obtained by vapor diffusion of ether into an acetonitrile solution prepared as above. Although the crystals appeared to be moderately stable upon removal from solvent, a single crystal of **6** was transferred along with the mother liquor into a light hydrocarbon oil; the mixture was placed in a capillary tube, which was immediately sealed for X-ray analysis.

(*μ*-Acetato-*O,O'*)(*N,N,N'*-tris(*N*-methyl-2-benzimidazolyl)methyl)-*N'*-methyl-1,3-diamino-2-propionato)dicationicopper(II) Perchlorate, [Cu₂BMDP(OAc)](ClO₄)₂·5.5H₂O (7**).** **Procedure A.** A solution of Cu(ClO₄)₂·xH₂O (17.2% Cu, 1.377 g, 3.72 mmol) in 15 mL of methanol was added to a solution of HBMDP (1.00 g, 1.86 mmol) and sodium acetate trihydrate (0.507 g, 3.72 mmol) in 15 mL of methanol with stirring. A light blue precipitate formed initially and was quickly replaced (~30 s) by a deep blue solid. The mixture was stirred for 30 min at room temperature and then cooled at -20 °C overnight. The solid was collected on a sintered-glass frit, washed with 10 mL of cold methanol, and air-dried to yield a blue powder. Vapor diffusion of ether into an acetonitrile solution (50 mL) of this product gave dark blue, moderately hygroscopic crystals. These were collected on a sintered-glass frit and air-dried to give 1.55 g of **7** (84% yield). Samples for microanalysis and magnetic susceptibility measurements were recrystallized twice by ether diffusion into an acetonitrile solution of the product. Anal. Calcd for C₃₃H₃₈Cl₂Cu₂N₈O₁₁·5.5H₂O (**7**): C, 38.87; H, 4.84; N, 10.99; Cu, 12.46; Cl, 6.95. Found: C, 38.88; H, 4.87; N, 10.86; Cu, 12.57; Cl, 6.62. IR (KBr, cm⁻¹): ν_{asym}(COO) 1560; ν_{sym}(COO) 1496. Weight loss by thermogravimetric analysis: calcd, 9.7%; found, 9.3%, which corresponds to 5.3 H₂O.

Diffraction-quality crystals were obtained by vapor diffusion of ether into an acetonitrile solution prepared as above. The crystals were friable upon removal from solvent; therefore a single crystal of **7** was transferred along with the mother liquor into a light hydrocarbon oil, and the mixture was placed in a capillary tube, which was immediately sealed for X-ray analysis. X-ray analysis reveals 2 mol of H₂O/mol of **7** while elemental analysis and TGA show 5.5 mol of H₂O. The difference reflects the hygroscopic nature of this complex.

Procedure B. Alternatively, the mononuclear complex **6** could be converted to the binuclear complex **7** by the addition of 1 equiv of copper(II) and 2 equiv of acetate. Thus, 0.1000 g (0.119 mmol) of **6** was placed in 10 mL of methanol to produce a pale blue-green suspension. The solids Cu(ClO₄)₂·xH₂O (17.2% Cu, 0.044 g, 0.119 mmol) and sodium acetate trihydrate (0.032 g, 0.238 mmol) were added sequentially to this suspension. The mixture was warmed to 50 °C and stirred for 30 min. The resulting solid was collected, washed with cold methanol, recrystallized by vapor diffusion of ether into an acetonitrile solution of this solid, and air-dried to yield 0.092 g of dark blue crystals of **7** (75% yield). These crystals were shown to be identical (UV-vis, IR, ¹H NMR) to those obtained in procedure A.

Bis(*μ*-acetato-*O,O'*)(*N,N,N'*-tris(*N*-methyl-2-benzimidazolyl)methyl)-*N'*-methyl-1,3-diamino-2-propionato)dicationicopper(II) *μ*-1,3-Azide Perchlorate, {[Cu₂BMDP(OAc)]₂N₃}(ClO₄)₂·8.5H₂O (8**).** A solution of **7** (0.100 g, 0.098 mmol) in 10 mL of acetonitrile was treated with a 10 mL acetonitrile solution of bis(triphenylphosphoranylidene)ammonium (PPN) azide (0.0285 g, 0.049 mmol). The mixture was stirred for 4 h at room temperature, during which the solution changed from deep blue to emerald green. When diethyl ether was added to the solution, green and white solids were precipitated; the white solid was tentatively identified as (PPN)ClO₄ by IR. The desired product was selectively crystallized by vapor diffusion of ether (1-2 days) into the original reaction mixture. During this time, green crystals of the product formed and the solution became pale green. (Longer crystallization times resulted in the solution turning colorless and in the deposition of white crystals of (PPN)ClO₄ on top of the desired product.) The product was collected on a sintered-glass frit and washed with ether to afford 0.848 g of emerald green crystals of **8** (89.2% yield). Anal. Calcd for C₆₆H₇₆Cl₃Cu₂N₁₉O₁₈·8.5H₂O (**8**): C, 40.92; H, 4.84; N, 13.74; Cu, 13.12; Cl, 5.49. Found: C, 40.83; H, 4.92; N, 13.31; Cu, 13.08; Cl, 5.60. IR (KBr, cm⁻¹): ν_{asym}(COO) 1559; ν_{sym}(COO) 1498; ν_{asym}(N₃) 2064. Weight loss by thermogravimetric analysis: calcd, 7.9%; found, 7.4%, corresponding to 8 H₂O.

Diffraction-quality crystals were obtained by vapor diffusion of ether into an acetonitrile solution as prepared above. The crystals appeared to be moderately stable upon removal from solvent. Thus, the mother

(29) Abbreviations used: HBMDP = *N,N,N'*-tris(*N*-methyl-2-benzimidazolyl)methyl)-*N'*-methyl-1,3-diamino-2-propanol; (PPN)₃ = bis(triphenylphosphoranylidene)ammonium azide; HL-Et = *N,N,N',N'*-tetrakis(2-((1-ethylbenzimidazolyl)methyl))-2-hydroxy-1,3-diaminopropane; N₃O(H)N₂-B = 2-[[bis(2-benzimidazolyl)methyl]amino]methyl-4-methyl-6-[[((2-benzimidazolyl)methyl)benzylamino]methyl]phenol; OAc = acetate; OBz = benzoate; EAEP = 2-(2-(ethylamino)ethyl)pyridine; DMAEP = 2-(2-(dimethylamino)ethyl)pyridine; TAEH = 1,5,9,13-tetraazacyclohexadecane; TSP = 3-(trimethylsilyl)propionic-2,2,3,3-*d*-acid, sodium salt; ImH = imidazole; *N*-Melm = *N*-methylimidazole; Hc = hemocyanin.

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Table 1. Crystal Data for Complexes 6–8

	6	7	8
formula	C ₃₁ H ₃₆ ClCuN ₈ O ₅ ·CH ₃ CN	C ₃₃ H ₃₈ Cl ₂ Cu ₂ N ₈ O ₁₁ ·2H ₂ O	C ₆₆ H ₇₆ Cl ₃ Cu ₄ N ₁₉ O ₁₈ ·8.5H ₂ O
fw	840.2	961.7	1919.97
cryst syst	triclinic	monoclinic	orthorhombic
a, Å	10.833(3)	19.934(4)	22.603
b, Å	12.457(3)	23.460(9)	19.565
c, Å	15.214(3)	20.034(4)	36.965
α, deg	78.28(2)		
β, deg	79.26(2)	110.65(2)	
γ, deg	68.10(2)		
V, Å ³	1851(2)	8770(4)	16347
space group	P1	C2/m	Cmca
Z	2	8	8
density (calc), g cm ⁻³	1.507	1.457	1.368
T, K	292	292	125
no. of obsd data	3405	2349	3337
no. of params	400	217	567
R	0.057	0.107	0.076 ^a
R _w	0.068	0.133	
goodness-of-fit	2.07	3.89	1.03

^a Value given is $R1 = \sum |F_o| - |F_c| / \sum |F_o|$.

liquor was removed from the crystals, which were then transferred into a light hydrocarbon oil. A suitable crystal was mounted on a glass fiber and immediately placed in a liquid nitrogen stream for low-temperature X-ray analysis.

Single-Crystal X-ray Structure Determinations. Diffraction data for 6 and 7 were obtained with a Rigaku AFC6R diffractometer (ambient temperature) at Oregon State University; data for 8, with a Siemens P4RA diffractometer (−148 °C) at the University of California, Davis. Selected crystal data and parameters for the three structure determinations are given in Table 1. Complete tables containing details of data collection and refinement are included in the supplementary material.

A. [CuHBMDP](ClO₄)₂·CH₃CN (6). A well-formed tablet of dimensions 0.35 × 0.35 × 0.08 mm was mounted on a glass fiber. The orientation matrix and cell dimensions were determined from the setting angles for 25 centered reflections in the range 10.9° ≤ 2θ ≤ 13.4°. The crystal diffracted sharply but weakly, and data collection was halted in the middle of the last shell (45° ≤ 2θ ≤ 50°), where the fraction of observed reflections [$I \geq 3\sigma(I)$] was only ca. 30%.

The Cu atom was located from the Patterson function, and the other non-hydrogen atoms, including those of a CH₃CN molecule, from DIRDIF.³¹ The ClO₄[−] groups did not refine cleanly. Difference syntheses at all stages showed residual electron density peaks at 1.3–1.6 e Å^{−3} from Cl atoms, but no clear model for alternative orientations was apparent. Refinements of the anions as rigid groups with standard dimensions, or with the oxygen atoms constrained so as to define tetrahedra, were not satisfactory. However, refinement with no constraints led to large values of the shift-to-error ratio in each cycle for the oxygen x, y, z, and U_{ij} parameters and rather short Cl–O bond lengths. Consequently the ClO₄[−] oxygen parameters were fixed in the last cycles, and convergence was reached at R = 0.057, R_w = 0.068, and S = 2.07 for 400 parameters and 3405 observed independent reflections. Hydrogen atoms of the complex cation were included at “riding” positions. The TEXSAN program suite³² was used in all calculations. Selected bond distances/angles and atomic coordinates for the cation of 6 are given in Tables 2 and 3, respectively.

B. [Cu₂BMDP(OAc)](ClO₄)₂·2H₂O (7). A crystal of dimensions 0.10 × 0.25 × 0.58 mm was sealed in a glass capillary and mounted on the diffractometer. The cell dimensions and orientation matrix were

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Complexes 6–8

Complex 6			
Cu–N1	2.077(5)	Cu–N2	2.263(5)
Cu–N3	1.979(5)	Cu–N5	2.006(5)
Cu–N7	1.950(5)	N1–Cu–N2	99.2(2)
N1–Cu–N3	83.0(2)	N1–Cu–N5	81.6(2)
N1–Cu–N7	175.0(2)	N2–Cu–N3	100.9(2)
N2–Cu–N5	107.8(2)	N2–Cu–N7	79.2(2)
N3–Cu–N5	149.2(2)	N3–Cu–N7	101.9(2)
N5–Cu–N7	94.4(2)		
Complex 7			
Cu1···Cu2	3.55		
Cu1–O1	1.94(1)	Cu2–O1	1.88(1)
Cu1–O2	1.92(2)	Cu2–O3	1.95(2)
Cu1–N1	2.10(2)	Cu2–N2	2.07(2)
Cu1–N3	2.04(2)	Cu2–N7	1.98(2)
Cu1–N5	2.13(2)	Cu2–O4	2.57(2)
Cu1–O1–Cu2	126.5(8)	N1–Cu1–N3	82.9(7)
N1–Cu1–N5	81.7(8)	N1–Cu1–O1	80.9(6)
N1–Cu1–O2	176.0(7)	N2–Cu2–O1	83.0(7)
N2–Cu2–N7	82.9(7)	N2–Cu2–O3	178.8(7)
Complex 8			
Cu1···Cu2	3.41		
Cu1–O1	1.923(5)	Cu2–O1	1.896(5)
Cu1–O2	1.941(6)	Cu2–O3	1.979(6)
Cu1–N4	2.112(7)	Cu2–N2	1.990(6)
Cu1–N5	2.005(7)	Cu2–N3	2.098(7)
Cu1–N7	2.151(7)	Cu2–N9	2.215(8)
Cu1–O1–Cu2	126.6(3)	N4–Cu1–N5	81.0(3)
N4–Cu1–N7	81.0(3)	N4–Cu1–O1	83.1(3)
N4–Cu1–O2	175.9(3)	O1–Cu1–O2	97.7(2)
N2–Cu2–N3	81.8(3)	N2–Cu2–N9	108.1(3)
N2–Cu2–O1	153.0(3)	N2–Cu2–O3	95.7(3)
O3–Cu2–N3	170.2(3)	O1–Cu2–O3	94.4(2)

obtained from the setting angles for 25 centered reflections in the range 20° ≤ 2θ ≤ 27°. The cell found was C-centered monoclinic, and the Laue symmetry was confirmed to be 2/m. The crystal diffracted only weakly, and data collection was halted in the middle of the shell, 40° ≤ 2θ ≤ 45°, when the incidence of observed reflections [$I \geq 3\sigma(I)$] had fallen below 1 in 10.

No systematic absences were observed other than those required by the C lattice. The space group was assumed to be C2/m, as implied by the centric distribution of intensities, and not C2 or Cm. The PHASE subprogram of DIRDIF gave the positions of the two independent Cu atoms, while a SHELXS³³ E map showed the Cu atoms at the same positions and also Cl1 and the oxygen atom. The C and N atoms of the organic ligand were located via DIRDIF, and the other ClO₄[−] groups, from difference syntheses. It proved possible to refine the parameters for all atoms of the complex (including the anion ClO₄[−], which lies on a crystal diad axis and is coordinated to Cu2). However, the other three independent anions, centered on Cl2,3,4 at sites of symmetry m, did not refine satisfactorily although appearing initially to have acceptable tetrahedral geometry. Unconstrained refinement led to some improbable bond lengths and angles and large thermal parameters, but when the ClO₄[−] groups were constrained as tetrahedra, a difference synthesis following the refinement showed considerable (ca. 3 e Å^{−3}) residual electron density. The anomalies persisted after an empirical absorption correction (DIFABS³⁴) was applied. The results suggested that each of the ill-behaved anions was disordered over two or more positions in each of which the Cl atom lay near but not on the crystallographic mirror plane, although a model for refinement could not be identified. Structure solution and refinement in space groups C2 and Cm gave similar results; moreover, corresponding parameters for many pairs of atoms that would be symmetry-related in C2/m showed strong correlation coefficients, and the values of B for such pairs of atoms often became improbably different. In the end, Cl2,3,4 were refined freely and the attached O atoms were fixed at the sites

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Table 3. Selected Atomic Coordinates and Isotropic Thermal Parameters (\AA^2) for **6**

atom	x	y	z	B_{eq}^a
Cu1	0.67271(8)	0.71528(7)	0.28640(5)	3.20(6)
O1	0.2748(5)	0.9900(5)	0.4060(4)	6.5(5)
N1	0.6409(5)	0.8663(4)	0.3387(3)	3.3(4)
N2	0.4659(5)	0.7029(4)	0.3264(3)	3.2(4)
N3	0.7555(5)	0.6375(4)	0.3988(3)	3.1(4)
N4	0.7898(5)	0.6555(5)	0.5344(3)	3.6(5)
N5	0.6696(5)	0.8245(5)	0.1695(3)	3.6(5)
N6	0.7199(6)	0.9813(5)	0.1012(4)	4.2(5)
N7	0.6926(6)	0.5821(5)	0.2293(3)	3.7(5)
N8	0.6017(7)	0.4969(5)	0.1594(4)	4.7(6)
C1	0.8079(6)	0.5259(6)	0.4468(4)	3.4(6)
C2	0.8298(6)	0.5357(6)	0.5321(5)	3.6(6)
C3	0.8805(7)	0.4404(7)	0.5963(5)	4.5(6)
C4	0.9097(7)	0.3326(7)	0.5712(5)	4.7(7)
C5	0.8874(7)	0.3202(6)	0.4876(5)	4.5(6)
C6	0.8366(7)	0.4160(6)	0.4241(5)	3.9(6)
C7	0.7469(6)	0.7115(6)	0.4541(4)	3.2(5)
C8	0.7903(7)	0.7095(7)	0.6110(5)	4.8(7)
C9	0.6889(7)	0.8398(6)	0.4283(5)	4.3(6)
C10	0.6980(7)	0.9320(6)	0.0336(5)	4.1(6)
C11	0.6655(7)	0.8349(6)	0.0772(4)	3.7(6)
C12	0.6341(8)	0.7695(7)	0.0271(5)	4.8(7)
C13	0.6382(8)	0.8046(8)	-0.0649(5)	5.4(7)
C14	0.6724(8)	0.9000(8)	-0.1071(5)	5.6(7)
C15	0.7037(8)	0.9668(7)	-0.0587(5)	5.4(7)
C16	0.7025(7)	0.9129(6)	0.1791(5)	3.7(6)
C17	0.7627(9)	1.0813(7)	0.0879(6)	6.5(8)
C18	0.7217(7)	0.9274(6)	0.2699(5)	4.2(6)
C19	0.4962(7)	0.9440(6)	0.3424(5)	4.2(6)
C20	0.3927(7)	0.8914(6)	0.3888(5)	4.7(6)
C21	0.3587(7)	0.8170(6)	0.3373(5)	4.2(6)
C22	0.7393(10)	0.4513(7)	0.1339(5)	5.2(7)
C23	0.7948(8)	0.5054(6)	0.1780(5)	4.4(6)
C24	0.9320(9)	0.4826(7)	0.1665(5)	6.0(8)
C25	1.0086(10)	0.4023(9)	0.1087(7)	8(1)
C26	0.9494(14)	0.3474(9)	0.0673(7)	8(1)
C27	0.8159(12)	0.3709(8)	0.0766(6)	7(1)
C28	0.5808(8)	0.5738(6)	0.2160(4)	3.8(6)
C29	0.4966(10)	0.4710(7)	0.1288(6)	7.0(9)
C30	0.4477(7)	0.6520(6)	0.2533(5)	4.5(7)
C31	0.4679(7)	0.6190(6)	0.4113(5)	4.2(6)

$$^a B_{\text{eq}} = (8\pi^2/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$$

originally located with $B(\text{O})$ held at $1.2B(\text{Cl})$. The Cu atoms and C11 were refined anisotropically in the last cycles, and H atoms were included at calculated "riding" positions with $B(\text{H})$ equal to $1.2B(\text{C})$. The strongest peaks in the final difference synthesis were all close to the crystallographic mirror plane in the voids between the complex cations, but those peaks not in the vicinity of ClO_4^- groups could not be convincingly identified as atoms of solvent molecules. The TEXSAN program system, incorporating standard atomic scattering factors,³⁵ was used in all calculations. Selected bond distances/angles and atomic coordinates for the cation of **7** are given in Tables 2 and 4, respectively.

C. $\{[\text{Cu}_2\text{BMDP}(\text{OAc})_2\text{N}_3](\text{ClO}_4)_3 \cdot 8.5\text{H}_2\text{O} (\mathbf{8})\}$. An emerald green prism of dimensions $0.35 \times 0.08 \times 0.08$ mm was coated with a light hydrocarbon oil and mounted in the 125 K nitrogen stream of the diffractometer equipped with a locally modified LT-2 low-temperature apparatus. Intensity data were collected using Ni-filtered Cu $K\alpha$ radiation from a rotating anode operating at 15 kW. The data were corrected for Lorentz and polarization effects. The orientation matrix and cell dimensions were determined from the setting angles of the diffractometer for 25 centered reflections and data collected by using ω scans with $0^\circ \leq 2\theta \leq 108.5^\circ$ at a scan rate of $20^\circ \text{ min}^{-1}$. The crystal stability was monitored by recording two standard reflections every 200 reflections; no significant variation was observed. The positions of the copper atoms were obtained from the Patterson function, and the remaining non-hydrogen atoms, including those of solvent

Table 4. Selected Atomic Coordinates and Isotropic Thermal Parameters (\AA^2) for **7**

atom	x	y	z	B_{eq}^a
Cu1	0.67080(13)	0.27627(13)	0.26724(15)	3.4(1)
Cu2	0.49254(14)	0.28092(14)	0.16688(15)	3.6(1)
O1	0.5806(7)	0.3151(6)	0.2204(8)	3.4(3)
O2	0.6420(8)	0.2009(7)	0.2303(8)	4.7(4)
O3	0.5196(8)	0.2028(7)	0.1978(8)	3.9(4)
N1	0.7030(9)	0.3599(8)	0.3008(10)	3.8(4)
N2	0.4632(9)	0.3641(8)	0.1359(10)	3.6(4)
N3	0.7747(9)	0.2684(8)	0.2733(9)	3.5(4)
N4	0.8743(9)	0.3154(8)	0.2916(9)	3.1(4)
N5	0.6788(9)	0.2678(9)	0.3758(10)	3.8(4)
N6	0.6824(10)	0.3229(9)	0.4703(11)	4.7(5)
N7	0.3881(9)	0.2677(8)	0.1249(9)	3.3(4)
N8	0.2803(10)	0.3034(9)	0.1009(10)	3.6(4)
C1	0.8295(11)	0.2298(12)	0.2897(12)	3.8(5)
C2	0.8922(11)	0.2605(9)	0.3009(11)	2.5(5)
C3	0.9555(11)	0.2300(11)	0.3190(12)	4.0(6)
C4	0.9532(12)	0.1739(11)	0.3274(13)	4.0(6)
C5	0.8920(14)	0.1434(12)	0.3183(14)	5.6(7)
C6	0.8266(13)	0.1711(12)	0.2941(13)	4.6(6)
C7	0.8047(11)	0.3192(10)	0.2788(12)	2.8(5)
C8	0.9238(13)	0.3609(11)	0.2963(13)	5.0(6)
C9	0.7609(12)	0.3721(11)	0.2708(13)	4.5(6)
C10	0.6501(12)	0.2729(12)	0.4754(13)	4.2(6)
C11	0.6473(12)	0.2368(11)	0.4169(13)	3.8(6)
C12	0.6211(12)	0.1820(11)	0.4109(14)	4.6(6)
C13	0.5951(14)	0.1631(13)	0.4638(17)	6.5(8)
C14	0.5944(14)	0.2012(13)	0.5159(16)	6.1(7)
C15	0.6191(14)	0.2548(13)	0.5262(15)	5.8(7)
C16	0.6972(12)	0.3172(11)	0.4062(14)	4.4(6)
C17	0.6964(14)	0.3748(13)	0.5162(15)	6.3(7)
C18	0.7356(13)	0.3613(12)	0.3787(14)	5.4(7)
C19	0.6417(12)	0.3965(11)	0.2750(12)	4.1(6)
C20	0.5880(11)	0.3720(10)	0.2065(12)	3.1(5)
C21	0.5137(11)	0.4002(10)	0.1872(12)	3.2(5)
C22	0.2731(12)	0.2473(11)	0.0971(13)	3.7(6)
C23	0.3397(12)	0.2225(12)	0.1122(12)	4.1(6)
C24	0.3485(12)	0.1659(11)	0.1085(13)	4.1(6)
C25	0.2902(14)	0.1301(12)	0.0918(14)	5.8(7)
C26	0.2234(14)	0.1593(13)	0.0788(14)	5.4(7)
C27	0.2117(12)	0.2107(12)	0.0817(13)	4.5(6)
C28	0.3512(13)	0.3149(11)	0.1185(13)	4.5(6)
C29	0.2287(14)	0.3472(13)	0.0969(15)	6.7(8)
C30	0.3877(13)	0.3716(12)	0.1345(13)	5.1(6)
C31	0.4659(13)	0.3741(12)	0.0631(5)	6.4(7)
C32	0.5780(15)	0.1805(11)	0.2069(14)	5.2(7)
C33	0.5765(15)	0.1148(14)	0.1965(15)	7.7(9)

$$^a B_{\text{eq}} = (8\pi^2/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$$

molecules, by direct methods using SHELXS-92. Scattering factors and correction for anomalous dispersion were taken from a standard source,³⁵ and an absorption correction was applied.³⁶ Refinements were made by full-matrix least squares on F^2 (SHELXL-92), and convergence was reached at $R1 = 0.077$. Selected bond distances/angles and atomic coordinates for the cation of **8** are given in Tables 2 and 5, respectively.

Magnetic Susceptibility and Electrochemical Measurements. Solid state magnetic susceptibility measurements were obtained at applied fields of 0.5 and 1 kOe on an SHE SQUID magnetometer operating between 6 and 300 K. Measurements of the magnetic moment at 6 K as a function of field between 0.1 and 55 kOe demonstrated the lack of saturation effects. Determinations were made on finely ground crystalline samples loaded into gelatin capsules. Diamagnetic corrections for the capsules were made by direct measurement, while correction for the ligand HBMDP was calculated by use of Pascal's constants.³⁷ Calibration of the instrument was performed

(36) The method obtains an empirical absorption tensor from an expression relating F_o and F_c ; Moezzi, B. Ph.D. Thesis, University of California, Davis, CA, 1987.

(37) (a) Carlin, R. L. *Magnetochemistry*; Springer-Verlag: Berlin, 1986; pp 2-4. (b) Earnshaw, A. *Introduction to Magnetochemistry*; Academic Press: London, 1968; pp 4-8.

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Table 5. Selected Atomic Coordinates and Isotropic Thermal Parameters (\AA^2) for **8**

atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq) ^a
Cu1	0.2274(1)	0.2552(1)	0.3830(1)	0.042(1)
Cu2	0.2278(1)	0.1208(1)	0.3241(1)	0.043(1)
O1	0.1899(3)	0.1837(3)	0.3556(2)	0.047(2)
O2	0.3078(3)	0.2401(3)	0.3664(2)	0.050(2)
O3	0.3070(3)	0.1336(3)	0.3459(2)	0.047(2)
N1	0.2064(4)	-0.0766(4)	0.2998(2)	0.048(2)
N2	0.2433(3)	0.0273(3)	0.3053(2)	0.042(2)
N3	0.1411(3)	0.0961(4)	0.3086(2)	0.047(2)
N4	0.1395(3)	0.2777(3)	0.3984(2)	0.045(2)
N5	0.2341(3)	0.3571(3)	0.3873(2)	0.042(2)
N6	0.1861(3)	0.4557(3)	0.3927(2)	0.041(2)
N7	0.2306(3)	0.2194(3)	0.4380(2)	0.044(2)
N8	0.1739(4)	0.1918(4)	0.4845(2)	0.049(2)
N9	0.2532(4)	0.1952(4)	0.2817(2)	0.056(2)
N10	0.25	0.1949(5)	0.25	0.047(3)
C1	0.1630(5)	-0.1341(5)	0.3018(3)	0.055(2)
C2	0.2668(4)	-0.0838(4)	0.2977(2)	0.045(2)
C3	0.3026(5)	-0.1402(5)	0.2923(2)	0.056(3)
C4	0.3624(5)	-0.1284(4)	0.2904(2)	0.053(2)
C5	0.3866(5)	-0.0635(5)	0.2937(2)	0.056(3)
C6	0.3501(4)	-0.0072(5)	0.2996(2)	0.048(2)
C7	0.2900(4)	-0.0180(4)	0.3010(2)	0.044(2)
C8	0.1942(4)	-0.0094(4)	0.3046(2)	0.040(2)
C9	0.1358(4)	0.0197(5)	0.3099(3)	0.054(2)
C10	0.1307(4)	0.1216(5)	0.2716(2)	0.055(2)
C11	0.1018(4)	0.1303(5)	0.3352(3)	0.053(2)
C12	0.1305(4)	0.1956(4)	0.3480(2)	0.044(2)
C13	0.1012(4)	0.2230(4)	0.3823(2)	0.048(2)
C14	0.1254(4)	0.3468(5)	0.3842(3)	0.052(2)
C15	0.1818(4)	0.3876(4)	0.3879(2)	0.041(2)
C16	0.1374(4)	0.5046(4)	0.3952(3)	0.053(2)
C17	0.2456(4)	0.4697(4)	0.3970(2)	0.043(2)
C18	0.2760(5)	0.5305(5)	0.4048(2)	0.054(2)
C19	0.3355(5)	0.5255(5)	0.4103(3)	0.055(2)
C20	0.3659(4)	0.4626(5)	0.4065(2)	0.053(2)
C21	0.3366(4)	0.4042(5)	0.3978(2)	0.044(2)
C22	0.2754(4)	0.4077(4)	0.3933(2)	0.043(2)
C23	0.1342(4)	0.2763(4)	0.4385(2)	0.047(2)
C24	0.1799(4)	0.2277(4)	0.4535(2)	0.047(2)
C25	0.1245(5)	0.1892(5)	0.5096(2)	0.059(3)
C26	0.2270(4)	0.1568(4)	0.4885(2)	0.047(2)
C27	0.2451(5)	0.1103(5)	0.5151(2)	0.060(3)
C28	0.3021(6)	0.0860(5)	0.5112(3)	0.065(3)
C29	0.3390(5)	0.1059(5)	0.4829(3)	0.061(3)
C30	0.3194(5)	0.1499(5)	0.4570(2)	0.053(2)
C31	0.2618(4)	0.1756(4)	0.4597(2)	0.044(2)
C32	0.3326(4)	0.1877(5)	0.3543(2)	0.047(2)
C33	0.3984(4)	0.1908(5)	0.3505(3)	0.064(3)

^a *U*(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

using $\text{HgCo}(\text{SCN})_4$.³⁸ Solution magnetic susceptibilities were obtained in methanol using the modified Evans method.³⁹

Cyclic voltammetry electrochemical measurements were carried out using a Bioanalytical Sciences system (BAS 100A voltammograph) with a 3 mm glassy carbon working electrode encased in KEL-F, a platinum wire counter electrode, and a $\text{Ag}/\text{AgNO}_3/\text{CH}_3\text{CN}$ reference electrode. Measurements were obtained at room temperature for acetonitrile solutions containing 1 mM complex and 0.1 M tetra-*n*-butylammonium perchlorate (TBAP) as the supporting electrolyte. The $\text{Fe}(0/+)$ couple of ferrocene ($E^\circ = 0.400$ V vs NHE) was used as an internal standard.⁴⁰

Results and Discussion

Ligand Synthesis. The synthetic strategy for preparing HBMDP centers on producing the unsymmetrical aliphatic

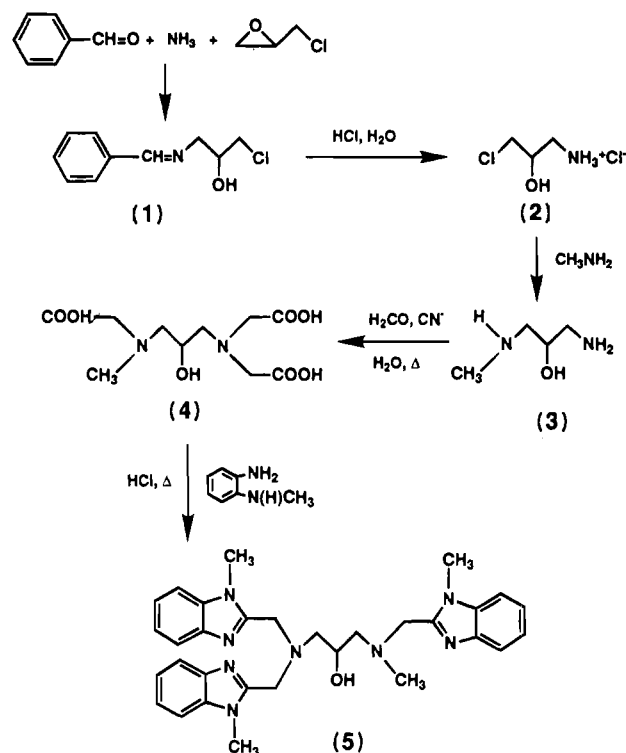


Figure 2. Summary of the synthetic route producing the asymmetric chelating ligand HBMDP.

backbone *N*-methyl-1,3-diamino-2-propanol. This diamine is then converted to the tris(*N*-carboxymethyl) compound and following condensation with *N*-methylphenylenediamine yields the desired ligand. Figure 2 outlines the synthetic route for the prototype binuclear chelating ligand, HBMDP. Synthesis of **1** involves the initial formation of benzalimine by the reaction of benzaldehyde with excess aqueous ammonia. The imine is reacted *in situ* with epichlorohydrin to undergo an epoxide ring opening reaction. Compound **1** is then hydrolyzed with aqueous HCl to yield the salt **2** in nearly quantitative yield. The salt can be neutralized and efficiently alkylated at room temperature by the addition of a 10-fold excess of aqueous methylamine to give **3**. This alkylation step produces **3** in ~50% yield based on epichlorohydrin. The preparation of compound **3** has been reported elsewhere as a two-step synthesis involving the direct reaction of methylamine with epichlorohydrin followed by ammonolysis with aqueous ammonia, producing **3** in a reported yield of 14.7% (based on epichlorohydrin).⁴¹ Our synthetic route not only offers the advantage of an improved yield but also avoids formation of the symmetric *N,N*-dimethyl-1,3-diamino-2-propanol, which was found to be present in significant quantity when methylamine was reacted directly with epichlorohydrin.

The conversion of **3** to the triacid **4** used a modification of a method by Martell.²⁷ This reaction is a classic Strecker α -amino acid synthesis and produces the trinitrile that is then hydrolyzed to the triacid salt. By elimination of *tert*-butyl alcohol as a cosolvent (used to maintain a constant temperature in the literature procedure) and provision of a high purge rate exiting through the condenser, ammonia generated during the reaction can be swept away rapidly. This avoids contamination of **4** with the salts of glycine, iminodiacetate, and nitrilotriacetate that are formed when ammonia competes with amine **3** as a nucleophile for formaldehyde. The condensation reaction to

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(41) Nagarajan, K.; Shenoy, S. J.; Sen, H. G.; Deb, B. N. *Indian J. Pharm. Sci.* **1986**, *48*, 125.

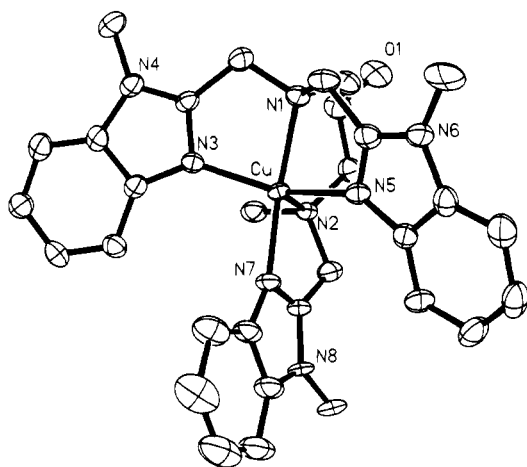


Figure 3. Structure of the cation part of the mononuclear copper(II) complex $[\text{CuHBMDP}](\text{ClO}_4)_2 \cdot \text{CH}_3\text{CN}$ (**6**), with partial atom labels and numbering scheme. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 30% level.

produce the tris(benzimidazole) **5** could, therefore, proceed directly without isolation of triacid **4**. This condensation reaction proceeds cleanly in dilute hydrochloric acid with *N*-methyl-1,2-diaminobenzene and the triacid; ring closure and elimination of water provide the driving force. The use of *N*-methyl-1,2-diaminobenzene directly gives the *N*-methylbenzimidazole compound on condensation and eliminates a subsequent reaction to alkylate one of the benzimidazole nitrogens. Attempts to perform this condensation by a direct fusion of *N*-methyl-1,2-diaminobenzene and isolated triacid (in a melt reaction) led to excessive decomposition and lower yields.

Coordination Chemistry. As a ligand, HBMDP possesses a hydroxy functionality that can potentially serve as a bridging alkoxo group in addition to aliphatic and aromatic nitrogen donor atoms. Using the C–OH bond as a bisecting line in this molecule, it is clear that the ligand has the potential to coordinate two metal ions in different environments (see Figure 2, compound **5**). One half of the ligand provides three coordination sites: an aliphatic tertiary amine nitrogen, a benzimidazole nitrogen, and a bridging oxygen. The other half provides four coordination sites: one tertiary amine, two benzimidazole nitrogens, and a bridging oxygen. Reactions with copper ion demonstrate that the ligand is a potent chelating agent. Blue or blue-green complexes are formed rapidly in the presence of copper(II) by stoichiometric reactions in methanol using hydrated metal salts. Characterization by elemental analysis and single-crystal X-ray crystallography shows that either mononuclear or binuclear complexes are obtained.

(a) Mononuclear Complex 6. Reaction at a metal-to-ligand ratio of 1:1 produces a mononuclear complex. In fact, the addition of copper in all proportions produces only the mononuclear complex. This behavior is dissimilar from the symmetric tetrabenzimidazole analog HL-Et and the asymmetric N3O(H)N2-B, both of which produce a binuclear complex in the presence of 2 equiv of copper ion.^{19,22}

The X-ray crystal structure of $[\text{CuHBMDP}](\text{ClO}_4)_2 \cdot \text{CH}_3\text{CN}$ consists of discrete cations and anions with two molecules per unit cell. A perspective view of the cation is displayed in Figure 3 along with a selected atom-numbering scheme. The potentially ligating 2-hydroxy group (O1) of the 1,3-diaminopropane backbone of HBMDP is located remote from the copper center and does not participate in metal coordination. Instead, it hydrogen bonds to an acetonitrile molecule that is included in the asymmetric unit.

The copper atom is five-coordinate with ligation by the three benzimidazole and two tertiary amines, the latter being bound in a cis configuration in distorted trigonal bipyramidal geometry. The three angles for the equatorial nitrogen donors sum to 358° , consistent with a small displacement of the copper atom from the trigonal plane (0.156 \AA). The largest deviation of angle from the expected 120° occurs between the two benzimidazoles N3 and N5, connected to a common amine nitrogen (N3–Cu–N5: 149°). This probably arises from the constraint of the formation of a six-membered chelate ring from the N1 (apical) and N2 (equatorial) backbone amines, which forces a “butterfly” opening of the two planar benzimidazole moieties. Because of this interplay, the Cu–N2 bond is substantially longer ($2.263(5) \text{ \AA}$) than the other four donor atom bonds, which average 2.01 \AA , while the axial angle (N1–Cu–N7) is perturbed only slightly to 175° .

The UV–vis spectrum of complex **6** in acetonitrile exhibits absorption maxima at 820 nm ($\epsilon = 165 \text{ M}^{-1} \text{ cm}^{-1}$) and 463 nm ($\epsilon = 96 \text{ M}^{-1} \text{ cm}^{-1}$) along with a shoulder at $\sim 485 \text{ nm}$ in the visible region. By comparison, there are two bands reported at 862 nm ($\epsilon = 129 \text{ M}^{-1} \text{ cm}^{-1}$) and 680 nm ($\epsilon = 93 \text{ M}^{-1} \text{ cm}^{-1}$) for $[\text{Cu}(\text{L}_1)\text{ImH}](\text{ClO}_4)_2$ in DMF, where L_1 is the tripodal ligand tris(2-benzimidazolylmethyl)amine and ImH is imidazole.^{42a}

Magnetic susceptibility measurement of the mononuclear complex exhibits expected Curie behavior from 6 to 300 K (151 data points). The linear plot for $1/\chi$ vs T ($R = 0.9998$) shows a near-zero intercept of -0.6 K , and from the Curie constant, a g value of 2.05 is calculated. The effective moment, μ_{eff} , at 300 K is $1.80 \mu_{\text{B}}$ for the solid state, while acetonitrile solution Evans method measurement of μ_{eff} yields $1.91 \mu_{\text{B}}$ at 297 K.

(b) Binuclear Complex 7. (i) Synthesis by Direct Reaction. Reaction at a metal-to-ligand ratio of 2:1 and in the presence of 2 equiv of sodium acetate produces the asymmetric binuclear complex **7**. It is also observed that a similar reaction with a metal-to-ligand ratio of 2:1 but with only 1 equiv of sodium acetate does not cleanly give the binuclear complex (a mixture of the mononuclear and binuclear complex appears to be formed). The fact that the binuclear complex is not formed by reaction with Cu(II) alone and requires 2 equiv of acetate ion may indicate the necessity for a base to assist in deprotonation of the hydroxy group, enabling formation of the binuclear complex.

The X-ray crystal structure of $[\text{Cu}_2\text{BMDP}(\text{OAc})](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ reveals that each crystallographic asymmetric unit consists of a binuclear copper cation and two perchlorate ions. Both copper atoms are linked by the ligand-derived alkoxide and by an exogenous acetate ion, leading to a copper–copper separation of 3.55 \AA (see Table 2).

A perspective view of the cation is displayed in Figure 4A along with the atom-numbering scheme. The asymmetry of the ligand leads to two distinct copper centers; the inner coordination sphere of both can be seen more clearly in Figure 4B. Cu1 is five-coordinate with ligation by two benzimidazoles and a tertiary amine nitrogen as well as oxygen donation from the alkoxo and acetato groups. The geometry lies between distorted trigonal bipyramidal and square pyramidal. When the geometry is viewed as trigonal bipyramidal, the tertiary amine N1 and the acetate oxygen O2 occupy axial positions (N1–Cu1–O2 = 176°) with bond lengths of 2.10 and 1.92 \AA , respectively. Benzimidazole N5, N3 and alkoxo O1 donors occupy the equatorial positions, the respective bond lengths being 2.13,

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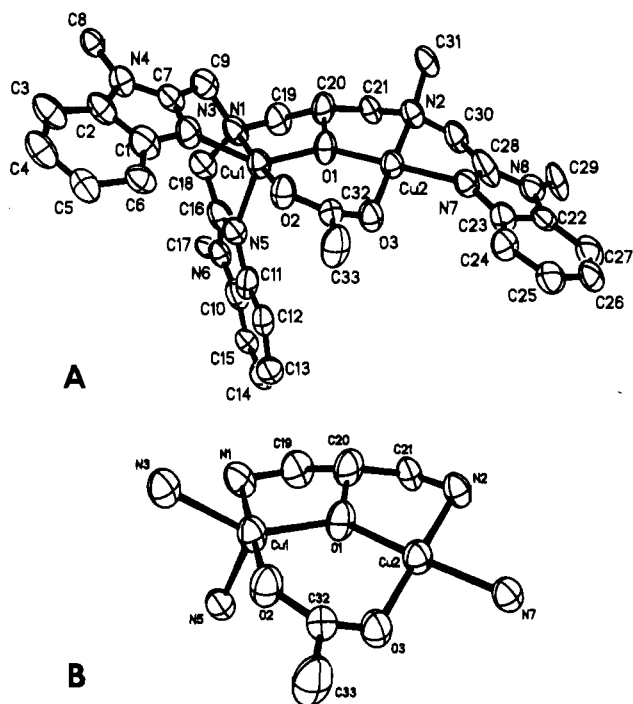


Figure 4. (A) Structure of the cation part of the binuclear copper(II) complex $[\text{Cu}_2\text{BMDP}(\text{OAc})](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ (**7**), with atom labels and numbering scheme. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 50% level. (B) Inner coordination sphere of **7** showing aliphatic backbone and acetate carbons to locate alkoxo and acetate oxygens, respectively. Pendant nitrogens are from benzimidazole. Coordination number asymmetry at the copper centers is clearly demonstrated where Cu1 is five-coordinate with geometry between trigonal bipyramidal and square pyramidal and Cu2 is four-coordinate and approximately square planar.

2.04, and 1.94 Å. These angles and lengths are similar to those found in $[\text{Cu}_2\text{L-Et}(\text{OAc})](\text{ClO}_4)_2$ (the symmetric analog of HBMDP) in which both copper ions reside in five-coordinate trigonal bipyramidal geometry with identical donor atoms.¹⁹

Cu2, on the other hand, is nominally four-coordinate square planar with two cis oxygen atoms and two nitrogen donors. The Cu–O distances are 1.95 and 1.88 Å for the acetate and alkoxide, and the Cu–N distances for the benzimidazole and the amine are 1.98 and 2.07 Å, respectively; all these distances are typical. In the solid state there appears to be an interaction with an oxygen atom of one of the perchlorate anions at a longer distance of 2.57(2) Å. This counterion lies on a crystal diad axis in space group $C2/m$ and as such lies between two identical copper atoms of two binuclear molecules.

Previous examples of perchlorate binding in the solid state include the binuclear copper aminopyridine complex $[\text{Cu}(\text{EAEP})\text{OH}]_2(\text{ClO}_4)_2$ in which the perchlorate occupies an axial position ~ 2.6 Å from one copper ion but does not bridge intermolecularly to a second molecule.⁴³ An example of intramolecular perchlorate bridging to copper can be found in the crystal structure of the related copper (dimethylamino)pyridine complex $\alpha\text{-}[\text{Cu}(\text{DMAEP})\text{OH}]_2(\text{ClO}_4)_2$.⁴⁴ In this system

two Cu–O(perchlorate) bonds occupy trans positions in the octahedral CuN_2O_4 core and the bond distances are slightly longer (2.78 and 2.72 Å).

The ^1H NMR spectrum of **7** in acetonitrile- d_3 (Figure 5A) displays relatively sharp and well-defined resonances spread over a 270 ppm range.⁴⁵ The line widths at half-height for these peaks range from 22 to 1280 Hz. The observation of this spectrum is of interest since, in general, there appear to be few reports of paramagnetic copper(II) ^1H NMR signals sharp enough to allow for peak assignments.⁴⁶ This is especially true for binuclear copper(II) complexes that are magnetically weakly coupled, as is complex **7** (see following section on magnetic properties). As expected, a room-temperature ESR signal was not observed for complex **7**. This behavior is unlike that reported by Jameson for the chloride-bridged binuclear copper(II) complex of the N3O(H)N2-B ligand, where a room-temperature ESR signal was observed and a ^1H NMR spectrum was absent.²²

The type of proton represented by each resonance for complex **7** was assigned by integration of peaks and deuteration of the ligand. Deuterated HBMDP was prepared by converting the *N*-methyl-diaminopropanol (**3**) to the triacid- d_6 using formaldehyde- d_2 in D_2O , followed by condensation with *N*-methylphenylenediamine in 6 N DCl. Because of the ease of exchange of protons of the aromatic diamine under acidic reflux, the resulting benzimidazole groups are also deuterium-exchanged, leading to HBMDP- d_{18} .⁴⁷

The methyl group resonances are readily identified by integration. Thus the three peaks at -0.34 , 1.12, 2.15 ppm and the peak at 119.8 ppm are assigned as CH_3 groups, the downfield resonance presumably belonging to the aliphatic methyl group. The CH_3 protons of the acetate group are found at 26.4 ppm and are easily assigned by their disappearance in the ^1H spectrum (and appearance in ^2H spectrum) when the binuclear complex was prepared using NaOAc- d_3 . When deuterated HBMDP- d_{18} was used to prepare **7**, the peaks labeled with asterisks in Figure 5A are absent in the ^1H spectrum. The ^2H NMR spectrum of the deuterated complex verifies the chemical shift assignments of these resonances and complements integration information. The five resonances due to the two CH_2 and the CH backbone protons are seen at 18, 19.6, 22, 240, and 260 ppm and are unaffected by deuteration. Since they all integrate as single protons, no further interpretation based on areas is possible. The ^1H NMR spectrum is consistent with the solid state representation of the binuclear complex **7**.

The UV–vis spectrum of **7** in acetonitrile exhibits a single absorption maximum occurring at 692 nm ($\epsilon = 103 \text{ M}^{-1} \text{ cm}^{-1}$). Although shifted in energy, a single band is also reported by Nakao for the symmetric tetrakis(benzimidazole) analog $[\text{Cu}_2\text{-L-Et}(\text{OAc})](\text{ClO}_4)_2$ (776 nm; $\epsilon = 61 \text{ M}^{-1} \text{ cm}^{-1}$; in DMF solution).⁴⁸

Magnetic susceptibility of the binuclear complex **7** from 6 to 200 K (40 data points) is displayed as a Curie plot in Figure 6. The linear plot ($R = 0.99968$) shows a near-zero intercept of +3.5 K, and from the Curie constant, a g value of 2.15 is calculated. The effective moment per copper ($\mu_{\text{eff}}/\text{Cu}$) is 1.90 μ_{B} at 302 K in the solid state, while acetonitrile solution Evans method measurement yields $\mu_{\text{eff}}/\text{Cu}$ of 1.93 μ_{B} at 295 K. Least-squares fitting of all solid state data assuming Curie–Weiss behavior was also performed. Minimizing g and Θ with a fixed TIP of $60 \times 10^{-6} \text{ cm}^3/\text{mol}$ gives $g = 2.11$ and a Weiss correction of +4.9 K with $R = 0.99963$.⁴⁹ The magnetic data

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(45) Solution ^1H NMR of **6** in acetonitrile- d_3 shows only broad resonances with chemical shifts in the 0–10 ppm range.

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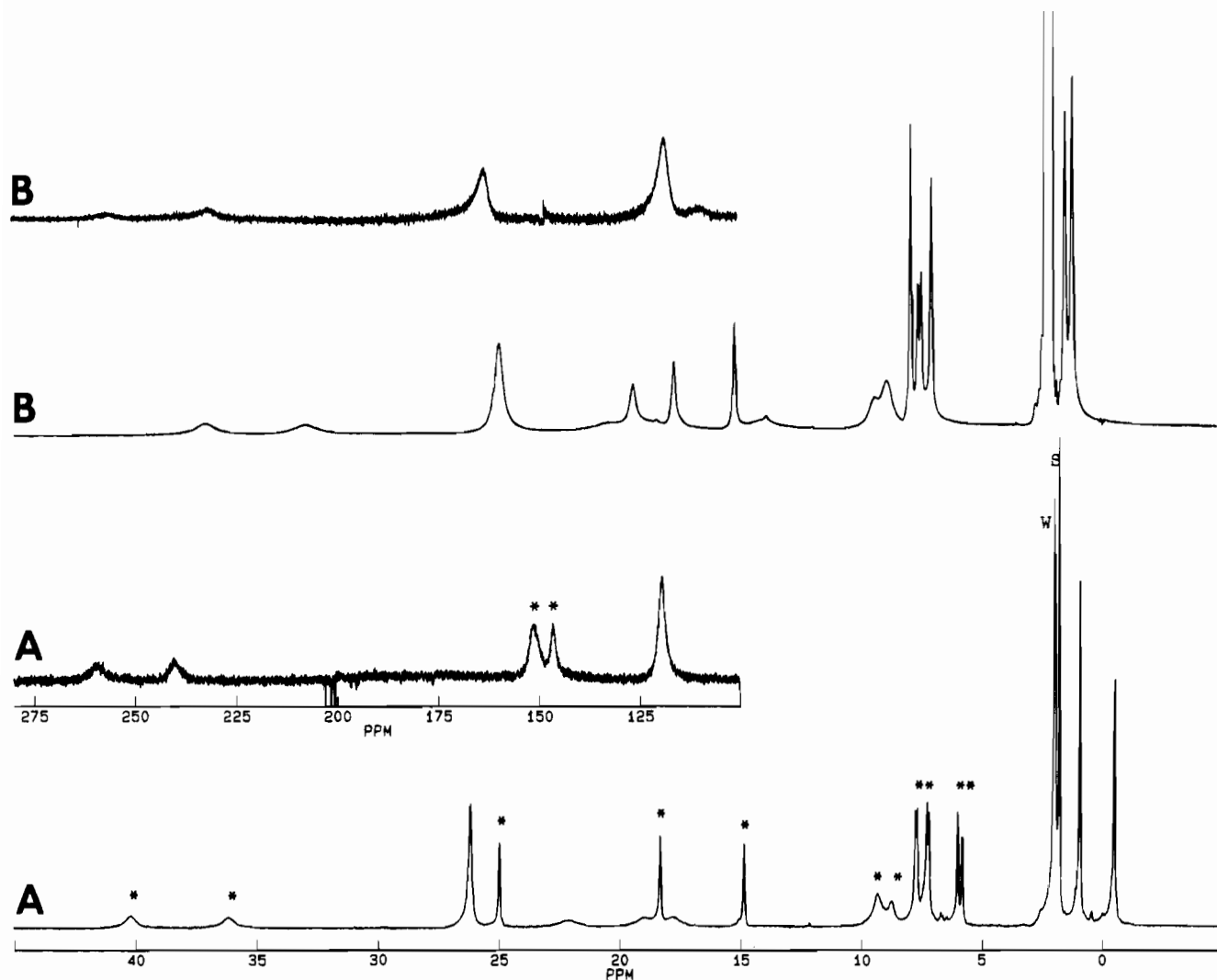


Figure 5. (A) ^1H NMR spectrum (-5 to $+45$ ppm and inset for 100 – 280 ppm) of the paramagnetic binuclear copper(II) complex **7** in CD_3CN . Peaks labeled with an asterisk are resonances that are removed on deuteration; S and W designate solvent and water resonances, respectively. (B) ^1H NMR spectrum (-5 to $+45$ ppm and inset for 100 – 280 ppm) of the paramagnetic azide-bridged binuclear copper(II) complex **8** in CD_3CN .

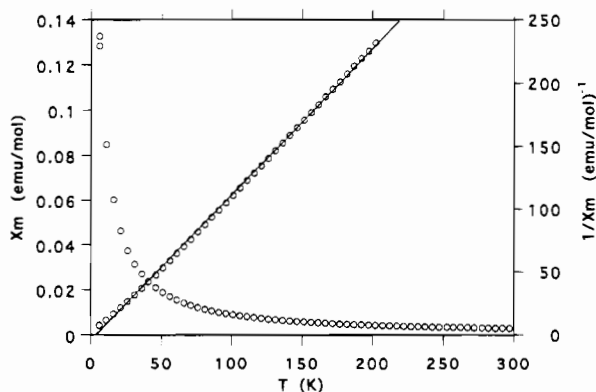


Figure 6. Temperature dependence of the corrected molar susceptibility of $[\text{Cu}_2\text{BMDP}(\text{OAc})](\text{ClO}_4)_2 \cdot 5\text{H}_2\text{O}$ (**7**) (6 – 300 K). Solid line represents linear least-squares fitting of the 6 – 200 K solid state data assuming Curie behavior.

for this asymmetric binuclear copper complex suggest that the copper ions are essentially independent centers or, at best, very weakly coupled. For comparison, the symmetric analog $[\text{Cu}_2\text{L-Et}(\text{OAc})](\text{ClO}_4)_2$ is reported to exhibit a weak ferromagnetic coupling of approximately $+13 \text{ cm}^{-1}$ (estimated from Curie–Weiss fitting),¹⁹ while the asymmetric binuclear copper(II) complex of $\text{N}_3\text{O}(\text{H})\text{N}_2\text{-B}$ is characterized as showing no significant ferro- or antiferromagnetic coupling.²²

(ii) Synthesis from the Mononuclear Complex. We have observed that the presence of the acetate anion regulates formation of the binuclear complex. It is interesting to note that when an additional equivalent of $\text{Cu}(\text{II})$ ion and 2 equiv of acetate are added to a methanol suspension of the mononuclear $[\text{CuHBMDP}]^{2+}$ complex at 50°C , a change from pale blue-green to the deep blue color characteristic of the binuclear complex is observed. The binuclear copper complex is subsequently isolated from this blue suspension.

The facile conversion of the mononuclear complex to the binuclear system suggests the potential for producing hetero-

(49) Attempts were also made to model this data by the Bleaney–Bowers equation (1) and its modification using the molecular field approximation (eq 2, accounting for interdimer effects):³⁸

$$C = (2Ng^2\mu_B^2/3kT)[1 + \frac{1}{3} \exp(-2J/kT)]^{-1} \quad (1)$$

$$C' = C/[1 - (2zJ'/Ng^2\mu_B^2)C] + \text{TIP} \quad (2)$$

In eq 2, J is the intradimer coupling and zJ' corresponds to the interdimer exchange interaction; all other symbols have their usual meaning. Fitting of the data for the Bleaney–Bowers equation yields the parameters $J = -0.6 \text{ cm}^{-1}$ with $R = 0.9967$ using a fixed g of 2.15 (from Curie plot) and a fixed TIP correction of $60 \times 10^{-6} \text{ cm}^3/\text{mol}$. Fitting of the data for the Bleaney–Bowers/molecular field approximation yields the parameters $J = -2.1 \text{ cm}^{-1}$, $zJ' = +0.2 \text{ cm}^{-1}$ with $R = 0.9968$ using a fixed g of 2.15 (from Curie plot), and a fixed TIP correction of $60 \times 10^{-6} \text{ cm}^3/\text{mol}$. This modeling also indicates very weak coupling between copper centers (either intra- or interdimer).

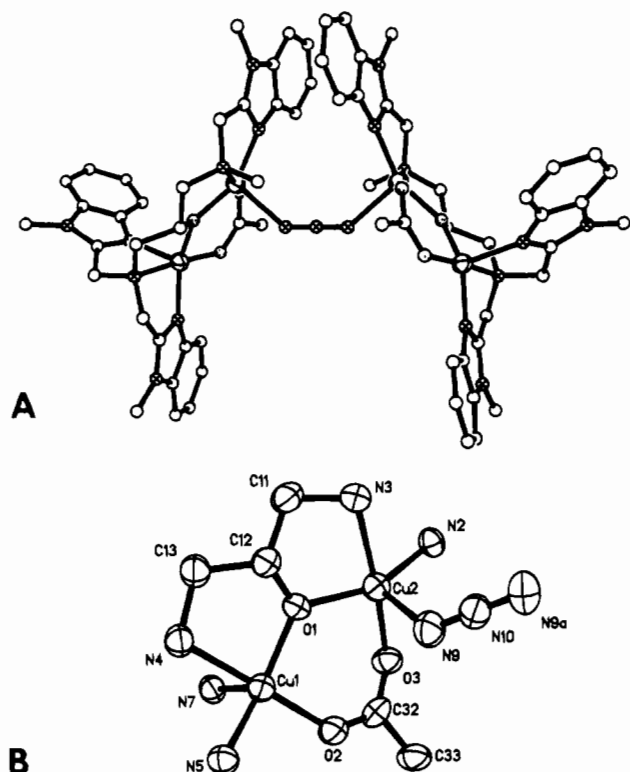


Figure 7. (A) Structure of the azide-bridged binuclear copper(II) complex $\{[\text{Cu}_2\text{BMDP}(\text{OAc})_2\text{N}_3](\text{ClO}_4)_3 \cdot 8.5\text{H}_2\text{O}\}$ (**8**). Atom types: copper, thermal ellipsoids; carbon, open circles; nitrogen, cross-hatched circles; oxygen, dotted circles. Hydrogen atoms are omitted for clarity. (B) Inner coordination sphere of one binuclear unit of **8** showing aliphatic backbone and acetate carbons to locate alkoxy and acetate oxygens, respectively. Pendant nitrogens are from benzimidazole, and N9–N10–N9a is the azide bridge. Cu2 is now distorted square pyramidal by virtue of azide binding; Cu1 remains trigonal bipyramidal. (The symmetry-related binuclear copper core that binds to N9a of the azide bridge is omitted for clarity.)

nuclear bimetallic species in a similar fashion. Such reactions are currently being explored with other first-row transition metals with the prospect not only of generating heteronuclear species but also of controlling what metal resides at which particular site of the bimetallic complex.

Site-Directed Reactivity. An important aspect of developing binuclear metal complexes containing coordination number asymmetry is the introduction of an open coordination site(s) at one metal. The crystal structure of **7** reveals that in the solid state an oxygen from one of the perchlorate counterions is weakly bound to the four-coordinate copper, suggesting that a vacant coordination site exists at this formally four-coordinate copper center. We sought to demonstrate that this site was a viable coordinating position on copper with a simple model reaction using azide ion. The addition of 0.5 equiv of (PPN)-N₃ to an acetonitrile solution of **7** results in the production of the isolable solid **8**. The X-ray crystal structure of $\{[\text{Cu}_2\text{BMDP}(\text{OAc})_2\text{N}_3](\text{ClO}_4)_3\}$ reveals that each asymmetric unit consists of 1 binuclear copper cation, 0.5 of an azide ion, and 1.5 perchlorate anions. Figure 7A presents an overall perspective view of the cation, and a detailed view of the inner coordination sphere of the copper centers is shown in Figure 7B.

The ligation about the coppers as described for **7** (including an exogenous acetate and ligand-derived alkoxy bridge) remains intact (see Table 2 for a comparison of distances and angles). Cu1 is still five-coordinate, and the geometry is now slightly closer to trigonal bipyramidal. Importantly, Cu2 is now formally five-coordinate square pyramidal with the bridging azide donor occupying the apical site with a bond distance of 2.215(8) Å.

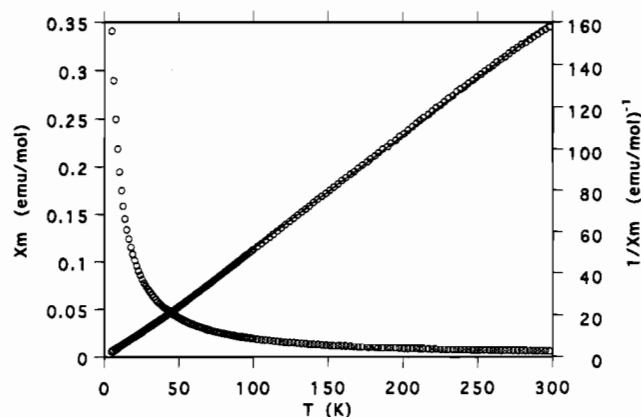


Figure 8. Temperature dependence of the corrected molar susceptibility of $[\text{Cu}_2\text{BMDP}(\text{OAc})_2(\text{ClO}_4)_3 \cdot 8.5\text{H}_2\text{O}$ (**8**) (6–300 K). Solid line represents linear least-squares fitting of all solid state data assuming Curie behavior.

The copper–copper separation within the binuclear unit has been shortened slightly to 3.41 Å and the Cu1–O1–Cu2 angle is unchanged at 126.6°. The formerly four-coordinate Cu atom of one binuclear unit is linked through the linear azide bridge in a cis arrangement to an identical Cu atom of a second binuclear molecule; the dihedral angle is 49.6°. Although the cis azido linkage was recently reported for a nickel(II) chain structure,⁵⁰ this cis bridging is apparently unprecedented for *intermolecular* binuclear copper(II) complexes containing only a single linking azide with no other supporting atoms.

The ¹H NMR spectrum of **8** (Figure 5B) displays relatively sharp and well-defined resonances spread over a 270 ppm range with line widths at half-height ranging from 22 to 1320 Hz.⁵¹ The spectra of complexes **7** and **8** are similar but not identical. On the basis of the similarities (chemical shifts, number of peaks, integrations), the spectrum of **8** is consistent with a single type of binuclear unit. The chemical shift changes, as compared to the binuclear starting material, are presumably due to the influence of the bound azide. The ¹H NMR spectrum of complex **8** confirms that there is no binuclear starting material present in solution, is consistent with a single type of binuclear HBMDP ligand coordinated to copper, and shows coordination of the bridging acetate. The NMR spectrum suggests that the solid state structure of the azide complex is maintained in solution.

Absorption maxima for **8** are observed at 349 nm ($\epsilon = 809 \text{ M}^{-1} \text{ cm}^{-1}$), 745 nm ($\epsilon = 190 \text{ M}^{-1} \text{ cm}^{-1}$), and 961 nm ($\epsilon = 161 \text{ M}^{-1} \text{ cm}^{-1}$). These maxima are similar to the bands reported by Reed at 364 nm ($\epsilon = 2520 \text{ M}^{-1} \text{ cm}^{-1}$), 705 nm ($\epsilon = 201 \text{ M}^{-1} \text{ cm}^{-1}$), and 975 nm ($\epsilon = 149 \text{ M}^{-1} \text{ cm}^{-1}$) for the azide complex $[\text{Cu}_2\text{L-Et}(\text{N}_3)](\text{ClO}_4)_2$.¹⁹ In the symmetric complex, the azide spans the copper ions within the binuclear unit. By comparison with bands of similar energy for metHc(N₃) (*Busycon canaliculatum*) at 360 nm ($\epsilon = 1500 \text{ M}^{-1} \text{ cm}^{-1}$) and 710 nm ($\epsilon = \sim 200 \text{ M}^{-1} \text{ cm}^{-1}$), the maxima at 349 and 745 nm for **8** are assigned to azide LMCT and d–d transitions, respectively.⁵²

Magnetic susceptibility of the binuclear complex **8** from 6 to 300 K (150 data points) is displayed as a Curie plot in Figure 8. The linear plot ($R = 0.99982$) shows a near-zero intercept of +4.2 K, and from the Curie constant, a g value of 2.21 is

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(51) As expected, a room-temperature ESR signal was not observed for complex **8**.

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calculated. The $\mu_{\text{eff}}/\text{Cu}$ is $1.94 \mu_{\text{B}}$ at 300 K in the solid state, while acetonitrile solution Evans method measurement yields $\mu_{\text{eff}}/\text{Cu}$ of $1.94 \mu_{\text{B}}$ at 297 K. Least-squares fitting of all solid state data assuming Curie–Weiss behavior was also performed. Minimizing g and Θ with a fixed TIP of $60 \times 10^{-6} \text{ cm}^3/\text{mol}$ gives $g = 2.17$ and a Weiss correction of $+5.7 \text{ K}$ with $R = 0.99974$.⁵³ The lack of significant coupling between copper centers mediated by azide can be rationalized on the basis of overlap. The major σ pathway for the interaction of the two copper ions is via their d_{z^2} orbitals through the azide. The nearly square pyramidal geometry of d^9 copper atoms suggests they have $(d_{x^2-y^2})^1$ ground states; therefore, the unpaired electrons localized in the basal planes cannot effectively couple. In addition, the effect of altering the local geometry of the azide-bound copper from square planar to square pyramidal shows no appreciable change in the exchange interaction mediated via the carboxylate and/or alkoxo bridges as shown by the comparable $\mu_{\text{eff}}/\text{Cu}$ values for **7** and **8**.

The feature of interest in the infrared spectra of **8** is $\nu_{\text{asym}}(\text{N}_3)$, which appears at 2064 cm^{-1} in KBr as compared to 2042 cm^{-1} reported for $\text{metHc}(\text{N}_3)$ from *Busycon*.⁵⁴ Vibrational spectra for intramolecular *cis*-(μ -1,3-azido)dicationic copper complexes supported by alkoxo and hydroxo bridges show $\nu_{\text{asym}}(\text{N}_3)$ at 2020 and 2028 cm^{-1} , respectively.^{19,55} In the binuclear copper complex $[\text{Cu}_2(\text{TAEH})(\text{ClO}_4)_3]$, although the macrocycle (TAEH) forms a backbone to maintain structural integrity, an intramolecular *cis* μ -1,3-azido bridge is formed between the two copper atoms with no other direct bridging atoms.⁵⁶ In this complex $\nu_{\text{asym}}(\text{N}_3)$ appears at 2068 cm^{-1} . Thus, the increase in energy for the asymmetric stretch may be indicative of unsupported *cis* azide bridge formation.

Electrochemistry. Cyclic voltammetry (CV) experiments in acetonitrile for the metal complexes over the range $+1.00$ to -1.00 V vs SCE were performed. For complex **6** a reversible reduction occurred at $E^{\circ'} = -135 \text{ mV}$ with $i_a/i_c = 0.91$ at a scan rate of 100 mV/s . ΔE_p values varied between 80 and 120 mV at differing scan rates. Repetitive CV scans of **6** over the scan range show that the redox couple is maintained with no significant decrease in either cathodic or anodic waves. Comparable reduction potentials have been noted for $[\text{Cu}(\text{L}_2)(\text{N-MeIm})(\text{ClO}_4)_2]$ ($E^{\circ'} = -103 \text{ mV}$, DMF) and $[\text{Cu}(\text{L}_1)\text{ImH}](\text{ClO}_4)_2$ ($E^{\circ'} = -110 \text{ mV}$, DMF), where L_2 is the tripodal ligand tris(*N*-methyl-2-benzimidazolyl)methylamine and L_1 is the nonmethylated compound.⁴² These reductions have been shown to be derived from the $\text{Cu}(\text{II})/\text{Cu}(\text{I})$ redox couple and not from ligand or electrolyte.⁵⁷ Cyclic voltammetry of **7** and **8** showed

only ill-defined reductions at potentials more negative than that of **6** and at high scan rates ($1\text{--}5 \text{ V/s}$).

Conclusions

A binuclear, asymmetric coordinating ligand that is an effective metal chelator has been designed and prepared. The new ligand reacts rapidly with copper(II), forming a variety of copper coordination complexes. A mononuclear complex is formed by reaction of copper with the ligand. A binuclear complex where the metals possess different coordination numbers is produced either by the direct reaction of copper and acetate with the ligand or indirectly by conversion of the mononuclear complex. An exogenous anion (azide) added to the binuclear complex is found to bind at an open coordination site of one metal, created by virtue of ligand asymmetry.

The binuclear complex **7** is of significant interest since it represents proof-of-principle for the development of coordination number asymmetry in binuclear metal chelates used to probe metalloenzyme sites. In particular, **7** allows for a direct comparison of spectroscopic properties such as UV–vis and IR and magnetic susceptibility with those of a symmetric analog, and in this case, only minor differences are observed. Since these techniques are among those used to deduce the coordination environments in metalloproteins, it is clear that a variety of well-defined models are needed to interpret such spectroscopic measurements with confidence.

Of equal importance is the manner in which the asymmetric complex **7** reacts with an exogenous ion such as azide. The production of **8** without significant alteration of geometry establishes the feasibility for developing multinuclear complexes with directed activity at a specific metal. Although this structural type of chelator (coordination number asymmetry) now appears to be common in biological systems, it is not well described for inorganic coordination chemistry. It is anticipated that metal complexes of ligands designed for coordination number asymmetry will play an important role in the development of models that aim to mimic metalloenzymes that function by substrate interaction at a specific metal of a multinuclear site.

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Supplementary Material Available: A computer-generated drawing (50% probability level) of **8** along with a partial atom labeling scheme and, for complexes **6–8**, full tables of structural parameters and refinement data, atom coordinates, bond distances and angles, hydrogen coordinates, and anisotropic thermal parameters (40 pages). Ordering information is given on any current masthead page.

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(53) A Bleaney–Bowers/molecular field approximation model of these data gave $J = -2.5 \text{ cm}^{-1}$ and $zJ' = +0.53 \text{ cm}^{-1}$ for the case of g and TIP fixed at 2.19 and $60 \times 10^{-6} \text{ cm}^3/\text{mol}$, respectively. This modeling also indicates very weak coupling between copper centers (either intra- or interdimer).

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