Inorg. Chem. **1992**, *31*, 4635–4642

Dinuclear Copper(II) and Polymeric Tetranuclear Copper(II) and Copper(II)–Copper(I) Complexes of Macrocyclic Ligands Capable of Forming Endogenous Alkoxide and Phenoxide Bridges. Structural, Magnetic, and Electrochemical Studies

Santokh S. Tandon,[1a] Laurence K. Thompson,*,[1a] John N. Bridson,[1a] Vickie McKee,[1b] and Alison J. Downard[1b]

Departments of Chemistry, Memorial University of Newfoundland, St. John's, Newfoundland, Canada A1B 3X7, and University of Canterbury, Christchurch-1, New Zealand

Received April 6, 1992

Template condensation of 2,6-diformyl-4-R-phenols with 1,3-diamino-2-hydroxypropane in methanol or ethanol, in the presence of copper(II) salts, produced the 20-membered macrocyclic complexes $[Cu_2(H_2L1)(CH_3OH)(ClO_4)][ClO_4]$ (I), $[Cu_2(H_2L1)X_2]\cdot 2H_2O$ ($X = NO_3$ (II); X = Cl (III)), $[Cu_2(H_2L1)(NCS)_2]$ (IV), $[Cu_2(H_2L2)(H_2O)_2][ClO_4]_2$ (VI), and $[Cu_2(H_2L2)(NO_3)_2]\cdot H_2O$ (VII) (H_4L1, R = Me; H_4L2, R = tBu). Template condensation in the presence of copper(II) acetate and excess azide produced the polymeric complexes $[Cu_2(H_2L)][Cu_2(N_3)_6]$ (L = L1 (VIII); L = L2 (IX)), while template condensation in the presence of CuCl produced an unusual, mixed-oxidation-state species $[Cu_2(H_2L1)][Cu_2Cl_4]$ containing the unique $Cu_2Cl_4^{2-}$ anion, which has a dinuclear, chloro-bridged triangular structure. The crystal and molecular structures of $[Cu_2(H_2L1)(CH_3OH)(ClO_4)][ClO_4]$ (I), $[Cu_2(H_2L1)][Cu_2Cl_4]$ (V), and $[Cu_2(H_2L2)][Cu_2(N_3)_6]$ (IX) are reported. I crystallized in the monoclinic system, space group $P2_1/c$, with $a = 12.139$ (6) Å, $b = 17.051$ (4) Å, $c = 14.457$ (3) Å, $\beta = 93.51$ (2)°, and four formula units per unit cell. Refinement by full-matrix least-squares procedures gave final residuals of $R = 0.060$ and $R_w = 0.050$. V crystallized in the triclinic system, space group $P\bar{1}$, with $a = 8.940$ (4) Å, $b = 10.371$ (3) Å, $c = 8.018$ (5) Å, $\alpha = 95.59$ (4)°, $\beta = 106.62$ (4)°, $\gamma = 101.86$ (3)°, and one formula unit per unit cell. Refinement by full-matrix least-squares procedures gave final residuals of $R = 0.053$ and $R_w = 0.049$. IX crystallized in the triclinic system, space group $P\bar{1}$, with $a = 11.064$ (3) Å, $b = 12.154$ (4) Å, $c = 8.439$ (4) Å, $\alpha = 108.42$ (3)°, $\beta = 90.85$ (3)°, $\gamma = 109.80$ (2)°, and two formula units per unit cell. Refinement by full-matrix least-squares procedures gave final residuals of $R = 0.045$ and $R_w = 0.036$. I involves an almost planar, dinuclear macrocyclic cation with no secondary alkoxide coordination. A similar cation exists in V and IX, but with the bridging anions linking cations in an unusual axial, polymeric structure. Low room-temperature magnetic moments and variable-temperature magnetic studies indicate strong intradimer antiferromagnetic exchange ($-2J = 675$–$902\ cm^{-1}$) and also extended exchange in the azide anion bridged polymers. Electrochemical properties of the dinuclear cations show sequential one-electron-transfer steps at negative potentials ($E_{1/2}{}^1 = -0.93$ to -0.96 V; $E_{1/2}{}^2 = -1.32$ to -1.35 V (vs Fc^+/Fc) due to the formation of Cu(II)–Cu(I) and Cu(I)–Cu(I) species.

Introduction

2:2 macrocyclic dicopper(II) complexes derived from 2,6-diformyl- and 2,6-diacetyl-(4-substituted) phenols and simple aliphatic and aromatic diamines have been studied extensively from the standpoint of their interesting structural, electrochemical, magnetic, and EPR properties and also because of their relevance as dinuclear copper metalloprotein model compounds.[2-20] The dinuclear copper(II) centers generally exhibit strong antiferromagnetic exchange and one-electron reduction steps at negative potentials.[4,8,10-12,14,15,18] The endogenous phenolate group bridges the copper pairs in these complexes and is primarily responsible for spin coupling. The versatility of this group of ligands can be greatly enhanced by the incorporation of both alcoholic and phenolic residues in the same molecule, which could lead to the formation of both alkoxide and phenoxide bridges within the same polynuclear complex. This can be achieved by the template condensation of 2,6-diformyl-4-alkylphenols with e.g. 1,3-diamino-2-hydroxypropane (H_4L1, H_4L2; Figure 1) and 1,5-diamino-3-hydroxypentane (H_4L3, H_4L4; Figure 1). All of these ligands have the potential to bind four metal centers, with proton loss at all hydroxyl groups. In earlier studies we have reported the synthesis and structural characterization of complexes of H_4L1, H_4L3, and H_4L4 with Ba(II), Pb(II), Cd(II), Mn(II), Ni(II), Co(II), and Zn(II) salts.[21-27] The Ba(II) ion forms only

---

* To whom correspondence should be addressed.

(1) (a) Memorial University of Newfoundland. (b) University of Canterbury.

(2) Pilkington, N. H.; Robson, R. *Aust. J. Chem.* **1970**, *23*, 2225.

(3) Okawa, H.; Kida, S. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 1759.

(4) Addison, A. W. *Inorg. Nucl. Chem. Lett.* **1976**, *12*, 899.

(5) Hoskins, B. F.; McLeod, N. J.; Schaap, H. A. *Aust. J. Chem.* **1976**, *29*, 515.

(6) Gagné, R. R.; Koval, C. A.; Smith, T. J. *J. Am. Chem. Soc.* **1977**, *99*, 8367.

(7) Lambert, S. L.; Hendrickson, D. N. *Inorg. Chem.* **1979**, *18*, 2683.

(8) Gagné, R. R.; Koval, C. A.; Smith, T. J.; Cimolino, M. C. *J. Am. Chem. Soc.* **1979**, *101*, 4571.

(9) Gagné, R. R.; Henling, L. M.; Kistenmacher, T. J. *Inorg. Chem.* **1980**, *19*, 1226.

(10) Mandal, S. K.; Nag, K. J. *J. Chem. Soc., Dalton Trans.* **1983**, 2429.

(11) Long, R. S.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1983**, *105*, 1513.

(12) Mandal, S. K.; Nag, K. J. *J. Chem. Soc., Dalton Trans.* **1984**, 2141.

(13) Carlisle, W. D.; Fenton, D. E.; Roberts, P. B.; Casellato, U.; Vigato, P. A.; Graziani, R. *Transition Met. Chem.* (*London*) **1986**, *11*, 292.

(14) Mandal, S. K.; Thompson, L. K.; Nag, K.; Charland, J.-P.; Gabe, E. J. *Inorg. Chem.* **1987**, *26*, 1391.

(15) Mandal, S. K.; Thompson, L. K.; Nag, K.; Charland, J.-P.; Gabe, E. J. *Can. J. Chem.* **1987**, *65*, 2815.

(16) Mandal, S. K.; Thompson, L. K.; Nag, K. *Inorg. Chim. Acta* **1988**, *149*, 247.

(17) Lacroix, P.; Kahn, O.; Gleizes, A.; Valade, L.; Cassoux, P. *Nouv. J. Chim.* **1984**, *8*, 643.

(18) Lacroix, P.; Kahn, O.; Theobald, F.; Leroy, J.; Wakselman, C. *Inorg. Chim. Acta* **1988**, *142*, 129.

(19) Mandal, S. K.; Thompson, L. K.; Newlands, M. J.; Gabe, E. J. *Inorg. Chem.* **1989**, *28*, 3707.

(20) Mandal, S. K.; Thompson, L. K.; Newlands, M. J.; Gabe, E. J. *Inorg. Chem.* **1990**, *29*, 1324.

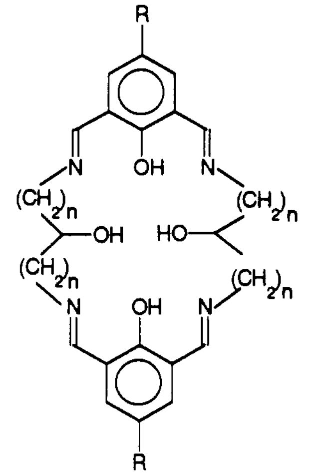
(21) Mckee, V.; Tandon, S. S. *J. Chem. Soc., Chem. Commun.* **1988**, 385.

(22) Mckee, V.; Tandon, S. S. *J. Chem. Soc., Chem. Commun.* **1988**, 1334.

(23) Tandon, S. S.; Mckee, V. *J. Chem. Soc., Dalton Trans.* **1989**, 19.

(24) Mckee, V.; Tandon, S. S. *Inorg. Chem.* **1989**, *28*, 2901.

0020-1669/92/1331-4635\$03.00/0



H_4L1, R= CH_3; H_4L2, R= tBu (n=1)

H_4L3, R= CH_3; H_4L4, R= tBu (n=2)

Figure 1. Macrocyclic ligands.

mononuclear compounds with H_4L1, in which the metal ion is coordinated to all of the oxygen donors and two diagonally related imine nitrogen atoms.[23] Pb(II) reacts with H_4L1 to form mononuclear $[Pb(H_4L1)][ClO_4]_2$ and dinuclear $[Pb_2(H_2L1)][ClO_4]_2$ complexes.[23] Mn(II), Ni(II), Co(II), Zn(II), and Cd(II) ions react with H_4L1 to form dinuclear complexes where the macrocycle acts as a hexadentate (N_4O_2) ligand, in which the phenolic groups are deprotonated and act as bridges between the metal centers.[23,24,27] The secondary alcohol ligand groups remain protonated and do not coordinate. The macrocycles H_4L3 and H_4L4 react with Cu(II), Co(II), Ni(II), Mn(II), and Zn(II) to form tetranuclear complexes, and in some cases with Cu(II), octanuclear species are formed by a dimeric association of two tetranuclear complexes.[21,22,24,26,27] Recently, Robson et al. reported the synthesis and structural characterization of tetranuclear Zn(II) and Ni(II)[28,29] complexes and hexanuclear Cu(II) complexes with related ligands.[30] Sufficient flexibility associated with the hydroxypentanediimine bridges in H_4L3 and H_4L4, upon the formation of six-membered chelate rings, clearly allows for the accommodation of four metal centers by these ligands. However, with H_4L1 and H_4L2, the smaller, five-membered chelate rings inevitably lead to increased ring strain, such that four metal ions cannot be accommodated.

The present study deals with a series of dinuclear and polymeric copper(II) complexes of H_4L1 and H_4L2, in which the secondary alcohol groups remain uncoordinated in all cases. Single-crystal X-ray studies of a dinuclear copper(II) complex, $[Cu_2(H_2L1)(CH_3OH)(ClO_4)][ClO_4]$ (I), a polymeric copper(II) complex, $[Cu_2(H_2L2)][Cu_2(N_3)_6]$ (IX), and a polymeric, mixed-oxidation-state complex, $[Cu^{II}_2(H_2L1)][Cu^{I}_2Cl_4]$ (V) are reported. The electrochemical, variable-temperature magnetic (5–300 K), and other spectral properties are also discussed.

Experimental Section

Physical Measurements. Infrared spectra were recorded as KBr disks using a Pye Unicam SP3-300 spectrometer or as Nujol mulls using a Mattson Polaris FT-IR instrument. Electronic spectra of solids and solutions (DMF) were recorded using Beckman DK-2A, Cary 17, and Varian DMS 100 spectrometers. Room-temperature magnetic moments were measured using a Cahn 7600 Faraday magnetic balance or a Newport Instruments Gouy balance. Variable-temperature magnetic data (5–300 K) were obtained using an Oxford Instruments superconducting Faraday susceptometer with a Sartorius 4432 microbalance. A main solenoid field of 1.5 T and a gradient field of 10 T m^{-1} were employed.

Electrochemical measurements were made using a Princeton Applied Research (PAR) Model 173 potentiostat–galvanostat, with a PAR 175 universal programmer and a Graphtec WX 1200 X-Y recorder and with a BAS CV-27 voltammograph and a Houston Omnigraph 2000 X-Y recorder. The electrochemical cell consisted of a Pt-wire auxiliary electrode, a Ag-wire pseudoreference electrode or SCE reference electrode, and a platinum- or glassy-carbon-disk working electrode. All measurements were carried out in DMF (0.1 M TEAP) under a nitrogen atmosphere with 1 mM complex concentrations. Potentials were recorded versus the ferrocenium/ferrocene (Fc^+/Fc) couple or SCE.

Syntheses of Complexes. (a) $[Cu_2(H_2L1)(CH_3OH)(ClO_4)][ClO_4]$ (I). Copper acetate (4 mmol), 2,6-diformyl-4-methylphenol (2 mmol) and 1,3-diamino-2-hydroxypropane (2 mmol) were refluxed in methanol (100 mL) for 24 h to give a dark green solution. To it was added a solution of $NaClO_4$ (excess) in methanol. A green solid separated, which was filtered off and washed with methanol (2 × 3 mL). A sample suitable for X-ray analysis was obtained by slow diffusion of ether solvent into a solution of the complex in a mixture of DMF/MeOH (1:1).

(b) $[Cu_2(H_2L1)(NO_3)_2]\cdot 2H_2O$ (II). Copper(II) nitrate trihydrate (2 mmol) and 2,6-diformyl-4-methylphenol (2 mmol) were dissolved in hot methanol (30 mL) to give a yellowish green solution, which was refluxed for 10 min. 1,3-Diamino-2-hydroxypropane (2 mmol), dissolved in methanol (10 mL), was added dropwise over a period of 5 min. The color of the solution changed to dark green. It was refluxed for ca. 6 h, and a green solid separated, which was filtered off, washed with ethanol, and dried in vacuo at 60 °C for 3 h. Yield: 80%. Anal. Calcd for $C_{24}H_{30}N_6O_{12}Cu_2$: C, 39.94; H, 4.16; N, 11.65; Cu, 17.61. Found: C, 40.03; H, 4.03; N, 11.15; Cu, 17.49.

(c) $[Cu_2(H_2L1)Cl_2]\cdot 2H_2O$ (III). This was obtained through a transmetalation reaction by heating $[Pb_2(H_2L1)][ClO_4]_2$ (1 mmol) with $CuCl_2\cdot H_2O$ (excess) in methanol solution. After refluxing for ca. 2 h, the mixture was filtered hot and the filtrate was concentrated to ca. 20 mL. When the solution was allowed to stand at ambient temperature, a green solid separated, which was filtered off, washed with methanol (3 × 5 mL), and recrystallized from methanol. Yield: 40%. Anal. Calcd for $C_{24}H_{30}N_4O_6Cu_2$: C, 43.11; H, 4.49; Cu, 19.01. Found: C, 42.75; H, 4.39; Cu, 18.76.

(d) $[Cu_2(H_2L1)(NCS)_2]$ (IV). This was prepared by reacting I (1 mmol), dissolved in hot methanol, with $Mn(NCS)_2$ (2 mmol) in the same solvent. The green solid that separated was filtered off, washed with methanol (3 × 3 mL), and dried in vacuo at 65 °C for 6 h. Yield: 60%. Anal. Calcd for $C_{26}H_{26}N_6O_4Cu_2S_2$: C, 46.07; H, 3.87; N, 12.40; Cu, 18.75. Found: C, 45.97; H, 3.82; N, 12.32; Cu, 18.63.

(e) $[Cu_2(H_2L1)][Cu_2Cl_4]$ (V). CuCl (2 mmol) was added to a solution of 2,6-diformyl-4-methylphenol (1 mmol) in acetonitrile (30 mL) under nitrogen and the mixture stirred at room temperature for 30 min. A solution of 1,3-diamino-2-hydroxypropane (1 mmol) in a mixture of acetonitrile and dichloromethane (20 mL/20 mL) was added with continued stirring. The reaction mixture was left for 2 d exposed to air, and a dark brown crystalline solid formed, which was filtered off, washed with acetonitrile, and dried under vacuum. Yield: 30%.

(f) $[Cu_2(H_2L2)(H_2O)_2][ClO_4]_2$ (VI). $Cu(ClO_4)_2\cdot 6H_2O$ (2 mmol) and 2,6-diformyl-4-*tert*-butylphenol (2 mmol) were dissolved in hot, dry ethanol (30 mL), and the reddish brown solution obtained was refluxed for ca. 10 min. A solution of 1,3-diamino-2-hydroxypropane (2 mmol) in dry ethanol (10 mL) was added dropwise over ca. 5 min. The color of the reaction mixture immediately changed to dark green. It was refluxed for ca. 20 h and concentrated, under reduced pressure, to ca. 10 mL. It was then warmed on a steam bath, ether solvent was added till a turbidity appeared, and the resultant mixture was kept at room temperature overnight. A dark green crystalline solid separated, which was filtered off, washed with ether, and dried in a desiccator under reduced pressure. Yield: 60%. Anal. Calcd for $C_{30}H_{42}N_4O_{14}Cu_2Cl_2$: C, 40.91; H, 4.77; Cu, 14.43. Found: C, 40.63; H, 5.21; Cu, 13.95.

(g) $[Cu_2(H_2L2)(NO_3)_2]\cdot H_2O$ (VII). VII was prepared by the same procedure as VI using $Cu(NO_3)_2\cdot 3H_2O$. Yield: 50%. Anal. Calcd for $C_{30}H_{40}N_6O_{11}Cu_2$: C, 45.71; H, 5.08; N, 10.67; Cu, 16.12. Found: C, 45.46; H, 4.79; N, 10.38; Cu, 15.93.

---

(25) Downard, A. J.; Mckee, V.; Tandon, S. S. *Inorg. Chim. Acta* **1990**, *173*, 181.

(26) Tandon, S. S.; Mckee, V. *J. Chem. Soc., Dalton Trans.* **1991**, 221.

(27) Tandon, S. S.; Mckee, V. Unpublished results.

(28) Bell, M.; Edwards, A. J.; Hoskins, B. F.; Kachab, E. H.; Robson, R. *J. Am. Chem. Soc.* **1989**, *111*, 3603.

(29) Grannas, M. J.; Hoskins, B. F.; Robson, R. *J. Chem. Soc., Chem. Commun.* **1990**, 1644.

(30) Hoskins, B. F.; Robson, R.; Smith, P. *J. Chem. Soc., Chem. Commun.* **1990**, 488.

Table I. Summary of Crystal, Intensity Collection, and Structure Refinement Data for I, V, and IX

	I	V	IX
formula	$Cu_2C_{25}H_{32}Cl_2N_4O_{13}$	$Cu_4C_{24}H_{26}Cl_4N_4O_4$	$Cu_2C_{15}H_{19}N_{11}O_2$
cryst color, habit	green, irregular	dark brown, irregular	yellow, irregular plate
fw	794.54	830.49	512.48
cryst syst	monoclinic	triclinic	triclinic
space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a (Å)	12.139 (6)	8.940 (4)	11.064 (3)
b (Å)	17.051 (4)	10.371 (3)	12.154 (4)
c (Å)	14.457 (3)	8.018 (5)	8.439 (4)
α (deg)		95.59 (4)	108.42 (3)
β (deg)	93.51 (2)	106.62 (4)	90.85 (3)
γ (deg)		101.86 (3)	109.80 (2)
V (Å^3)	2987 (1)	687.4 (6)	1003.6 (7)
d_{calcd} (g cm^{-3})	1.767	2.006	1.696
Z	4	1	2
abs coeff, μ (cm^{-1})	16.79	34.96	21.62
radiation, λ (Å)	Mo Kα, 0.710 69	Mo Kα, 0.710 69	Mo Kα, 0.710 69
T (°C)	25	25	25
F_{000}	1624	414	520
scan rate (deg min^{-1})	8.0	8.0	8.0
$2\theta_{max}$ (deg)	50.0	50.1	50.0
no. of data collected	5746	2607	3722
no. of unique data	2461 ($I > 2.5\sigma(I)$)	1487 ($I > 3.5\sigma(I)$)	1913 ($I > 3.0\sigma(I)$)
no. of variables	424	189	272
goodness of fit	2.09	2.66	1.57
R	0.060	0.053	0.045
R_w	0.050	0.049	0.036

(h) $[Cu_2(H_2L1)][Cu_2(N_3)_6]\cdot 1.5MeOH$ (VIII). 2,6-Diformyl-4-methylphenol (2 mmol) dissolved in hot methanol (50 mL) was added to a solution of copper acetate (2 mmol) in methanol (200 mL). The resulting green solution was refluxed for ca. 20 min, and to it was added dropwise over a period of 10 min a solution of 1,3-diamino-2-hydroxypropane (2 mmol) in 30 mL of methanol containing KOH (2 mmol). A dark green solution formed, which was refluxed for 24 h and filtered. A solution of NaN_3 (4 mmol) in 40 mL of hot methanol was then added to the filtrate. The resulting mixture was refluxed for 5 min and left at ambient temperature overnight. A brownish-green crystalline product formed, which was filtered off, washed with methanol (3 × 10 mL), and dried in vacuo at room temperature for 24 h. Yield: 45%. Anal. Calcd for $C_{25.5}H_{32}N_{22}O_{5.5}Cu_4$: C, 30.97; H, 3.24; N, 31.17; Cu, 25.71. Found: C, 31.08; H, 2.94; N, 30.89; Cu, 26.38.

(i) $[Cu_2(H_2L2)][Cu_2(N_3)_6]$ (IX). This was prepared by the same procedure used for VII with 2,6-diformyl-4-*tert*-butylphenol and obtained as yellow-brown crystals. Yield: 40%. Anal. Calcd for $C_{30}H_{38}N_{22}O_4Cu_4$: C, 35.16; H, 3.71; N, 30.08; Cu, 24.80. Found: C, 34.98; H, 3.67; N, 29.53; Cu, 24.58.

C, H, and N analyses were carried out by the Microanalytical Unit, University of Otago, and by Canadian Microanalytical Service, Delta. Copper was analyzed by EDTA titration.

Safety Note. Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of material should be prepared, and these should be handled with caution. The complexes described in this report have, so far, been found to be safe when used in small quantities.

Crystallographic Data Collections and Refinements of the Structures. (a) $[Cu_2(H_2L1)(CH_3OH)(ClO_4)][ClO_4]$ (I). The crystals of I are green. The diffraction intensities of an approximately 0.35 × 0.25 × 0.10 mm crystal were collected with graphite-monochromatized Mo Kα radiation using a Rigaku AFC6S diffractometer at 25 °C and the ω–2θ scan technique to a $2\theta_{max}$ value of 50.0°. A total of 5746 reflections were measured, of which 5476 (R_{int} = 0.075) were unique and 2461 were considered significant with $I_{net} > 2.5\sigma(I_{net})$. An empirical absorption correction was applied, after a full isotropic refinement, using the program DIFABS,[31] which resulted in transmission factors ranging from 0.81 to 1.22. The data were corrected for Lorentz and polarization effects. The cell parameters were obtained from the least-squares refinement of the setting angles of 20 carefully centered reflections with 2θ in the range 34.39–41.44°.

The structure was solved by direct methods.[32,33] The non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on 2461 observed reflections ($I > 2.50\sigma(I)$) and 424 variable parameters and converged with unweighted and weighted agreement factors of $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.060$ and $R_w = [(\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2} = 0.050$. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.65 and −0.57 electron/Å^3 and have no chemical significance. Neutral-atom scattering factors[34] and anomalous-dispersion terms[35,36] were taken from the usual sources. All calculations were performed using the TEXSAN[37] crystallographic software package and a VAX 3100 workstation. Hydrogen atoms were located in a difference map in all cases except those of the secondary alcohol groups but were not refined. Disorder was observed in the secondary alcohol groups. Crystal and other data are listed in Table I.

(b) V and IX. The same procedures were used for these compounds. Crystal and other data are listed in Table I.

Results and Discussion

Synthesis and Spectroscopic Characterization. The template condensation of 2,6-diformyl-4-methylphenol (DFMP) or 2,6-diformyl-4-*tert*-butylphenol (DFTBP) with 1,3-diamino-2-hydroxypropane (DAHP) in the presence of copper(II) salts in methanol/ethanol produced dinuclear copper(II) complexes of the 20-membered, potentially octadentate macrocyclic ligands H_4L1 and H_4L2. These 2:2 ligands do not involve endogenous alkoxide and phenoxide bridges simultaneously and do not accommodate four metal centers, unlike the 24-membered macrocycles derived from 1,5-diamino-3-hydroxypentane (H_4L3, H_4L4; Figure 1).[21,22,24,26,27] This is undoubtedly associated with the small cavity size in H_4L1 and H_4L2. These dinuclear complexes can also be prepared by transmetalation techniques reacting Pb(II) or Ba(II) complexes of the macrocycles with appropriate copper(II) salts. The simultaneous involvement of both alkoxide and phenoxide bridges with macrocyclic ligands derived from DAHP can however be effected by template condensation of DFMP and DFTBP with DAHP in the presence of copper(II) salts and base (e.g. Et_3N), but in this case 3:3

---

(31) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158.

(32) Gilmore, C. J. *J. Appl. Crystallogr.* **1984**, *17*, 42.

(33) Beurskens, P. T. DIRDIF. Technical Report 1984/1; Crystallography Laboratory: Toernooiveld, 6525 Ed Nijmegen, The Netherlands, 1984.

(34) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, U.K., 1974; Vol. IV, Table 2.2A.

(35) Ibers, J. A.; Hamilton, W. C. *Acta Crystallogr.* **1974**, *17*, 781.

(36) Cromer, D. T. *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, U.K., 1974; Vol. IV, Table 2.3.1.

(37) Texan-Texray Structure Analysis Package, Molecular Structure Corp., 1985.

macrocyclic ligands form, which accommodate six metals.[38] The expansion of the macrocyclic ring clearly relieves the strain inherent in the 2:2 condensed ligands.

The use of copper(II) chloride as templating agent in the above condensation reactions resulted in the formation of a polymeric product of undefined composition. With copper(II) thiocyanate as templating agent, the protonated ligand salt $[H_6L1][NCS]_2\cdot 2H_2O$ was produced, rather than a copper(II) complex. In an earlier study, we reported[23] the formation and the X-ray crystal structure of an analogous compound $[(H_6L1)(H_2O)_2][ClO_4]_2$, which was formed along with monolead and dilead complexes of H_4L1, in the template condensation of DFMP and DAMP in the presence of $Pb(ClO_4)_2$. Thus the complexes $[Cu_2(H_2L1)Cl_2]\cdot 2H_2O$ (III) and $[Cu_2(H_2L1)(NCS)_2]$ (IV) were prepared by reacting $[Pb_2(H_2L1)][ClO_4]_2$ and $[Cu_2(H_2L1)(H_2O)_2][ClO_4]_2$ with excess copper(II) chloride and manganese(II) thiocyanate, respectively. Template condensation of DFMP and DFTBP with DAHP in the presence of copper(II) acetate and excess azide ions in methanol produced the polymeric copper(II) complexes $[Cu_2(H_2L1)][Cu_2(N_3)_6]\cdot 1.5MeOH$ (VIII) and $[Cu_2(H_2L2)][Cu_2(N_3)_6]$ (IX). Complex V, $[Cu_2(H_2L1)][Cu_2Cl_4]$, was derived by template condensation of DFMP and DAPH in the presence of copper(I) chloride but clearly involves an oxidation to give the mixed-oxidation-state species. Extraneous anions are not required, and since the reaction mixture was exposed to air, the oxidation of copper(I) must involve molecular oxygen. This complex was isolated in low yield, which is consistent with the 2:1 metal:ligand stoichiometry used in the reaction. Dinuclear copper(II) macrocyclic species like III are, no doubt, present in small amounts in the mother liquor but will remain in solution.

Infrared spectra indicate that cyclization has occurred in these complexes by the disappearance of bands associated with carbonyl and amine groups and the appearance of bands in the region 1628–1638 cm^{-1} associated with imine stretching. For all compounds, a broad band of medium to strong intensity at 3375–3445 cm^{-1} is associated with O–H stretch of uncoordinated, pendant, secondary alcohol groups and in some cases water. The $\nu_3(ClO_4)$ vibration in I shows significant splitting (1140 vs, 1105 vs, 1080 vs cm^{-1}), suggesting the presence of a low-symmetry perchlorate, possibly acting as a ligand. The X-ray structure determination for I shows the presence of monodentate perchlorate. An intense, broad band at 1100 cm^{-1} observed for VI suggests the presence of ionic perchlorate. Fundamental nitrate bands for II and VII were not informative concerning the possible coordination of nitrate. However a FAB mass spectrum for VII shows clearly the presence of the ion $[Cu_2(H_2L2)(NO_3)]^+$, indicating monodentate coordination of at least one nitrate group. A strong thiocyanate (ν(CN)) stretching absorption at 2040 cm^{-1} suggests axial coordination of isothiocyanate ligands in IV. Strong bands associated with asymmetric azide stretch were observed for VIII and IX in the ranges 2069–2054 and 2059–2036 cm^{-1}, respectively. Comparable bands for $[PPh_4]_2[Cu_2(N_3)_6]$, which contains the same anion, occur at 2072 and 2030 cm^{-1}.[39]

Electronic spectra of DMF solutions of compounds I–IV, VI, and VII exhibit three main bands at 609–649 nm (ϵ = 103–141 L mol^{-1} cm^{-1}), 350–360 nm (ϵ = 8450–12 840 L mol^{-1} cm^{-1}), and 269–271 nm (ϵ = 34 900–50 000 L mol^{-1} cm^{-1}). The lower energy, asymmetric band, which does not occur in the corresponding dinuclear zinc(II) complexes,[40] is assigned to a d–d transition. In the solid state, the d–d band is observed at approximately the same wavelength (550–675 nm), suggesting that similar structures exist both in the solid state and in solution. Comparable solid-state d–d bands associated with the macrocyclic cations are observed for V, VIII, and IX in the range 625–630 nm. Broad asymmetric peaks at approximately 600 nm, with a low-energy shoulder, have been observed for related macrocyclic dicopper(II) complexes with square-planar or square-pyramidal geometries.[8,10,41] The intense bands observed in solution in the range 350–360 nm are also observed in the solid state at 350–365 nm and are associated with intraligand and ligand-to-metal charge-transfer transitions, while the higher energy, very intense bands are undoubtedly $\pi^* \leftarrow \pi$ in nature. The azide complexes VIII and IX exhibit four visible absorptions in the solid state, with additional bands at 570, 420 nm (VIII) and 560, 420 nm (IX), which are reasonably associated with the anion $Cu_2(N_3)_6^{2-}$.

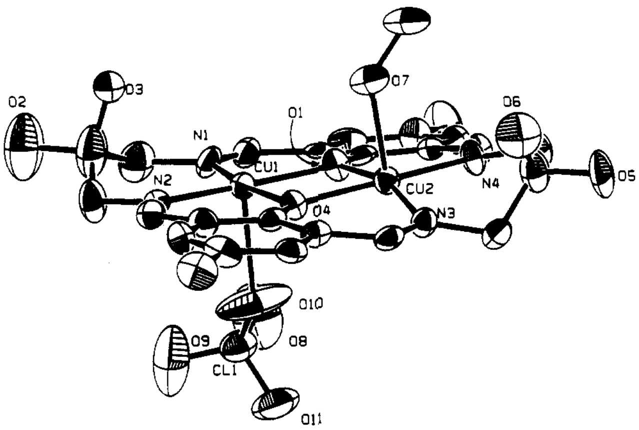


Figure 2. Structural representation of $[Cu_2(H_2L1)(CH_3OH)(ClO_4)]^+$ (cation of I) with hydrogen atoms omitted (40% probability thermal ellipsoids).

Table II. Interatomic Distances (Å) and Angles (deg) Relevant to the Copper Coordination Spheres in $[Cu_2(H_2L1)(CH_3OH)(ClO_4)][ClO_4]$ (I)

Cu(1)–O(1)	1.969 (7)	O(1)–Cu(1)–O(4)	75.8 (3)
Cu(1)–O(4)	1.946 (7)	O(1)–Cu(1)–N(1)	93.0 (3)
Cu(1)–N(1)	1.949 (9)	O(1)–Cu(1)–N(2)	167.9 (4)
Cu(1)–N(2)	1.950 (9)	O(4)–Cu(1)–N(1)	168.7 (3)
Cu(2)–O(1)	1.956 (7)	O(4)–Cu(1)–N(2)	92.9 (3)
Cu(2)–O(4)	1.960 (7)	N(1)–Cu(1)–N(2)	98.3 (4)
Cu(2)–N(3)	1.929 (9)	O(1)–Cu(2)–O(4)	75.8 (3)
Cu(2)–N(4)	1.947 (8)	O(1)–Cu(2)–N(3)	162.1 (4)
Cu(1)–O(10)	2.440 (9)	O(1)–Cu(2)–N(4)	94.2 (4)
Cu(2)–O(7)	2.311 (9)	O(4)–Cu(2)–N(3)	93.7 (4)
Cu(1)–Cu(2)	3.089 (2)	O(4)–Cu(2)–N(4)	169.7 (4)
		N(3)–Cu(2)–N(4)	95.5 (4)
		Cu(1)–O(1)–Cu(2)	103.8 (3)

X-ray Crystal Structures. (a) $[Cu_2(H_2L1)(CH_3OH)(ClO_4)][ClO_4]$ (I). A perspective view of I is shown in Figure 2, and selected bond distances and angles relevant to the copper coordination species are given in Table II. Each copper ion is five-coordinate, bonded to two imine nitrogen atoms and two endogenous phenolate oxygen bridges in the basal plane, with a methanol oxygen (Cu(2)) or perchlorate oxygen (Cu(1)) occupying the fifth, axial positions. The geometry around each copper is slightly distorted square-pyramidal, with the copper centers displaced by 0.044 Å (Cu(1)) and 0.160 Å (Cu(2)) toward the axial ligands from the mean plane of the six basal donor atoms (N_4O_2). The copper-copper separation is 3.089 (2) Å, and the phenoxide bridge angles are 103.8 (3)° (O(1)) and 104.5 (3)° (O(4)). The copper–oxygen and copper–nitrogen bond contacts are comparable with those reported for complexes with related ligands.[5,9,14,18] The axial contacts to the coordinated perchlorate (2.440 (9) Å) and to the coordinated methanol (2.331 (9) Å) are somewhat longer and typical of five-coordinate structures of this sort.

Oxygens of the secondary alcohols appear at both quasi-equatorial and axial positions in the approximate ratio of 4:1 at

---

(38) Tandon, S. S.; Thompson, L. K.; Bridson, N. J. *J. Chem. Soc., Chem. Commun.* **1992**, 911.

(39) Fenske, D.; Steiner, K.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1987**, *553*, 57.

(40) McKee, V.; Tandon, S. S. Unpublished results.

(41) Mandal, S. K.; Adhikary, B.; Nag, K. *J. Chem. Soc., Dalton Trans.* **1986**, 1175.

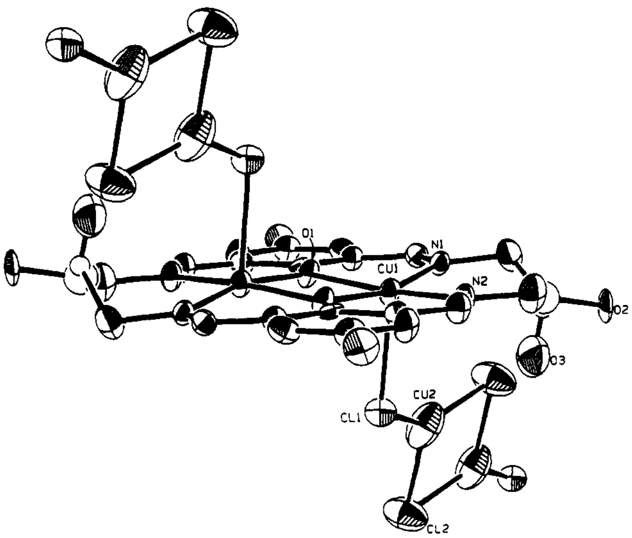


Figure 3. Structural representation of a fragment of $\{[Cu_2(H_2L1)][Cu_2Cl_4]\}_n$ (V) with hydrogen atoms omitted (40% probability thermal ellipsoids).

Table III. Interatomic Distances (Å) and Angles (deg) Relevant to the Copper Coordination Spheres in $[Cu_2(H_2L1)][Cu_2Cl_4]$ (V)

Cu(1)–O(1)	1.981 (6)	O(1)–Cu(1)–O(1)	76.5 (2)
Cu(1)–O(1)	1.970 (6)	O(1)–Cu(1)–N(1)	92.7 (3)
Cu(1)–N(1)	1.950 (7)	O(1)–Cu(1)–N(2)	166.6 (3)
Cu(1)–N(2)	1.984 (7)	O(1)–Cu(1)–N(1)	165.3 (3)
Cu(2)–Cl(1)	2.139 (3)	O(1)–Cu(1)–N(2)	92.7 (3)
Cu(2)–Cl(2)	2.382 (4)	N(1)–Cu(1)–N(2)	96.4 (3)
Cu(2)–Cl(2)	2.242 (4)	Cl(1)–Cu(2)–Cl(2)	120.7 (1)
Cu(1)–Cl(1)	2.654 (4)	Cl(1)–Cu(2)–Cl(2)	138.2 (2)
Cu(1)–Cu(1)	3.103 (3)	Cl(2)–Cu(2)–Cl(2)	101.0 (1)
Cu(2)–Cu(2)	2.944 (4)	Cu(2)–Cl(2)–Cu(2)	79.0 (1)
		Cu(1)–O(1)–Cu(1)	103.5 (2)

both sites. Occupancies were not refined, but optimized in a series of trials. The phenomenon can be interpreted as conformational disorder and/or the presence of both cis and trans ligands in appropriate fractional occupancies.

(b) $[Cu_2(H_2L1)][Cu_2Cl_4]$ (V). A perspective view of a fragment of V is shown in Figure 3, and selected bond distances and angles relevant to the copper coordination spheres are given in Table III. The structure is polymeric with a fairly flat macrocyclic cation, involving two square-pyramidal copper(II) ions bridged, as in I, by phenoxide oxygen atoms. The cations are in turn bridged in a trans-axial fashion by the unique, unusual, flat, $Cu_2Cl_4^{2-}$ anion, which involves two copper(I) ions. Within the macrocyclic cation, the copper–oxygen and copper–nitrogen distances compare closely with those observed for I. The two copper(II) centers are displaced slightly by 0.225 Å from the mean plane of the equatorial donors toward the "terminal" chlorines of the $Cu_2Cl_4^{2-}$ ion. The contact Cu(1)–Cl(1), although quite long (2.654 (4) Å), can be considered as a significant axial bonding interaction. The $Cu_2Cl_4^{2-}$ anion is asymmetric with a short copper–chlorine distance involving the chlorine (Cl(1)) linking the two dinuclear ions and longer internal copper–chlorine distances involving Cl(2) (2.242 (4), 2.382 (4) Å). Although the angles around Cu(2) are quite different, with a rather small internal angle Cl(2)–Cu(2)–Cl(2) of 101.0 (1)°, the sum of the angles around Cu(2) indicates the three copper–chlorine bonds to be close to coplanar. Disorder at the secondary alcohol groups, similar to that observed for I, was again evident. In this case, the carbon atom is displaced as well as the attached oxygen.

Examples of simple tetraalkylammonium and trialkylarylammonium salts containing the trigonal-planar dimeric copper(I) anions $Cu_2Br_4^{2-}$ and $Cu_2I_4^{2-}$ are well-known.[42-44] The anion $Cu_2Br_4^{2-}$ has also been reported in combination with a dinuclear copper(II) cation,[45,46] where it is reputed to result from dimerization of $CuBr_2^-$, produced when Br^- is oxidized to Br_2. Although a similar chemical reduction was reported in an earlier study involving the reaction of a phosphazene ring with anhydrous copper(II) chloride in ethyl methyl ketone, only the linear $CuCl_2^-$ anion was produced.[47] The tendency for dimerization of such an anion was predicted to be similar to that of $CuBr_2^-$,[42] but we are not aware of any previous reports on the dimeric $Cu_2Cl_4^{2-}$ anion. In the present study, the $Cu_2Cl_4^{2-}$ anion has apparently formed by oxidation of copper(I) chloride and acts as a bidentate ligand.

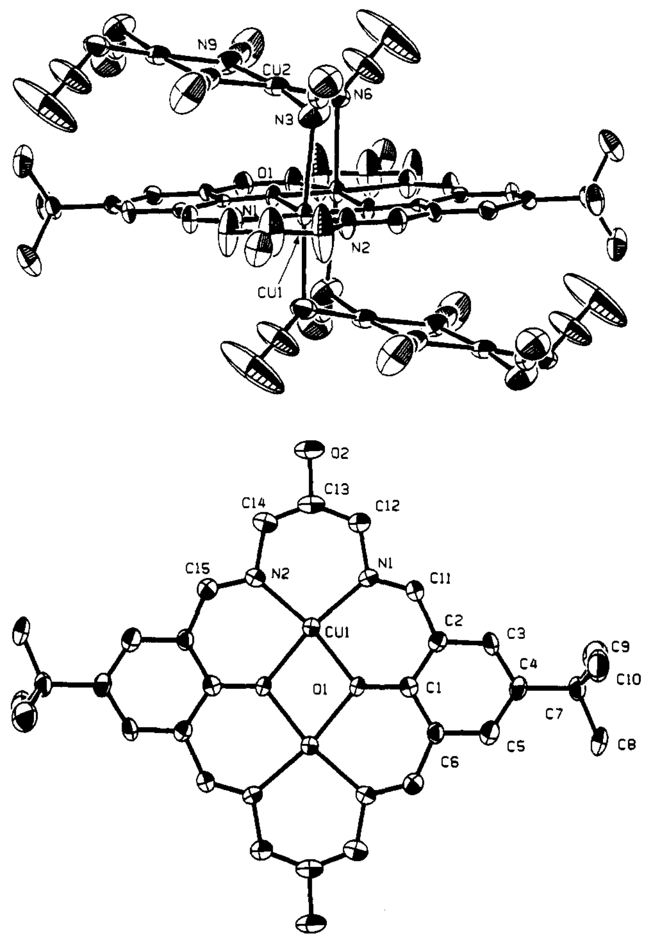


Figure 4. (a, Top) Structural representation of a fragment of $\{[Cu_2(H_2L2)][Cu_2(N_3)_6]\}_n$ (IX) with hydrogen atoms omitted (40% probability thermal ellipsoids). (b, Bottom) Structural representation of the macrocyclic cation in $\{[Cu_2(H_2L2)][Cu_2(N_3)_6]\}_n$ (IX) with hydrogen atoms omitted (40% probability thermal ellipsoids).

(c) $[Cu_2(H_2L2)][Cu_2(N_3)_6]$ (IX). A perspective view of a fragment of IX is shown in Figure 4a (Figure 4b illustrates the macrocyclic cation), and selected bond distances and angles relevant to the copper coordination spheres are given in Table IV. The structure is polymeric and closely related to V. The binuclear cation is typical of these macrocyclic systems, with the two copper(II) centers bridged internally by phenoxide oxygen atoms (Cu(1)–O(1)–Cu(1) = 102.9 (2)°) and no coordination of the secondary alcohol groups. Each copper center is six-coordinate, with nitrogen atoms from terminal azide groups on the $Cu_2(N_3)_6^{2-}$ anion acting as axial ligands (Cu(1)–N(3)–2.562 (8) Å, Cu(1)–N(6) = 2.449 (8) Å). The structure consists of an alternating,

---

[42] Asplund, M.; Jagner, S. *Acta Chem. Scand.* **1984**, *A38*, 135.

[43] Asplund, M.; Jagner, S.; Nillson, M. *Acta Chem. Scand.* **1982**, *A36*, 751.

[44] Anderson, S.; Jagner, S. *Acta Chem. Scand.* **1985**, *A39*, 423.

[45] Adams, H.; Candeland, G.; Crane, J. D.; Fenton, D. E.; Smith, A. J. *J. Chem. Soc., Chem. Commun.* **1990**, 93.

[46] Crane, J. D.; Fenton, D. E.; Latour, J. M.; Smith, A. J. *J. Chem. Soc., Dalton Trans.* **1991**, 2979.

[47] Marsh, W. C.; Trotter, J. *J. Chem. Soc. A* **1971**, 1482.

Table IV. Interatomic Distances (Å) and Angles (deg) Relevant to the Copper Coordination Spheres in $[Cu_2(H_2L2)][Cu_2(N_3)_6]$ (IX)

Cu(1)–N(2)	1.945 (6)	Cu(1)–N(3)	2.562 (8)
Cu(1)–O(1)	1.973 (4)	Cu(2)–N(3)	1.931 (8)
Cu(1)–N(1)	1.987 (6)	Cu(2)–N(6)	1.947 (7)
Cu(1)–O(1)	1.998 (4)	Cu(2)–N(9)	1.975 (7)
Cu(1)–N(6)	2.449 (8)	Cu(2)–N(9)	1.982 (7)
Cu(1)–Cu(1)	3.106 (2)	Cu(2)–Cu(2)	3.121 (2)
N(2)–Cu(1)–O(1)	168.4 (2)	N(1)–Cu(1)–N(3)	97.1 (3)
N(2)–Cu(1)–N(1)	97.2 (2)	O(1)–Cu(1)–N(6)	86.4 (2)
N(2)–Cu(1)–O(1)	93.1 (2)	O(1)–Cu(1)–N(3)	85.9 (2)
N(2)–Cu(1)–N(6)	93.8 (3)	N(6)–Cu(1)–N(3)	172.2 (2)
N(2)–Cu(1)–N(3)	87.8 (3)	N(3)–Cu(2)–N(6)	92.8 (3)
O(1)–Cu(1)–N(1)	92.9 (2)	N(3)–Cu(2)–N(9)	171.4 (3)
O(1)–Cu(1)–O(1)	77.1 (2)	N(3)–Cu(2)–N(9)	96.3 (3)
O(1)–Cu(1)–N(6)	91.8 (2)	N(6)–Cu(2)–N(9)	94.6 (3)
O(1)–Cu(1)–N(3)	85.3 (2)	N(6)–Cu(2)–N(9)	169.2 (3)
N(1)–Cu(1)–O(1)	169.3 (2)	N(9)–Cu(2)–N(9)	75.9 (3)
N(1)–Cu(1)–N(6)	90.3 (3)		
Cu(2)–N(9)–Cu(2)	104.1 (3)	Cu(1)–O(1)–Cu(1)	102.9 (2)

stepped, chain of interconnected dinuclear macrocyclic cations $[Cu_2(H_2L2)]^{2+}$ bridged axially through 1,1-azide interactions to the dinuclear $Cu_2(N_3)_6^{2-}$ anions. The basal donor set (N_4O_2) of the macrocyclic cation is very close to planar, with displacements of the copper centers from this plane of less than 0.03 Å. Much larger displacements are observed for I and V, consistent with their five-coordinate geometries. The unusual hexaazido anion, which has a chair conformation in this structure, is not unique and has been reported previously in the centrosymmetric compound $[PPh_4]_2[Cu_2(N_3)_6]$.[39] However, the polymeric 1,1-azide bridging interaction displayed by the anion in IX is novel and we are not aware of its being reported previously.

Electrochemistry. The electrochemical properties of complexes I–IV, VI, and VII are very similar in dimethylformamide (DMF). Typically, two reduction waves occur at negative potentials (vs Fc^+/Fc) associated with two one-electron reduction steps. The narrow peak-to-peak separation for these waves (60–80 mV at 100 mV s^{-1}), which only changes slightly as a function of scan speed, indicates a high degree of chemical reversibility for these redox steps. $E_1{}^{\circ\prime}$ and $E_2{}^{\circ\prime}$ occur in the ranges –0.93 to –0.96 and –1.32 and –1.35 V (vs Fc^+/Fc), respectively, and these processes are associated with stepwise one-electron transfers, typical of systems of this sort (see ref 14 and references therein). The mixed-valence (Cu(II)–Cu(I)) species have K_{con} values in the range 1.3×10^7–2.7×10^6, indicating significant stability of these species, comparable with those associated with related macrocyclic complexes (in DMSO) having just propane residues between the imine ligand centers.[14] The complex $[Zn_2(H_2L2)(NCS)_2]$ was examined in the range –2.0 to 0 V (vs Fc^+/Fc) and displayed no significant redox waves, indicating that in all cases the redox processes are metal based. The electrochemical behavior of these dinuclear, macrocyclic complexes shows that the potentials for the first and second reduction steps remain essentially unchanged throughout the series. This suggests that the coordination environments at the dinuclear copper center are very similar, indicating the likelihood of solvent coordination at the axial copper sites.

The electrochemical behaviors of VIII and IX are very similar. The cyclic voltammograms exhibited by VIII are shown in Figure 5. Two quasi-reversible reduction steps are observed at negative potentials ($E_1{}^{\circ\prime}$ = 0.47–0.49 V, $E_2{}^{\circ\prime}$ = 0.86–0.89 V (vs SCE)), each associated with a one-electron reduction process in the macrocyclic dinuclear cation, indicating that the polymeric structure observed in the solid state is unlikely to exist in solution in DMF. Another wave at $E^{\circ\prime}$ = +0.095 V (vs SCE) (VIII) (+0.10 V (IX)) is associated with a two-electron quasi-reversible redox process, on the basis of current height measurements, involving the redox couple $Cu^{II}{}_2/Cu^{I}{}_2$ and is associated with the $Cu_2(N_3)_6{}^{2-}$ anion.

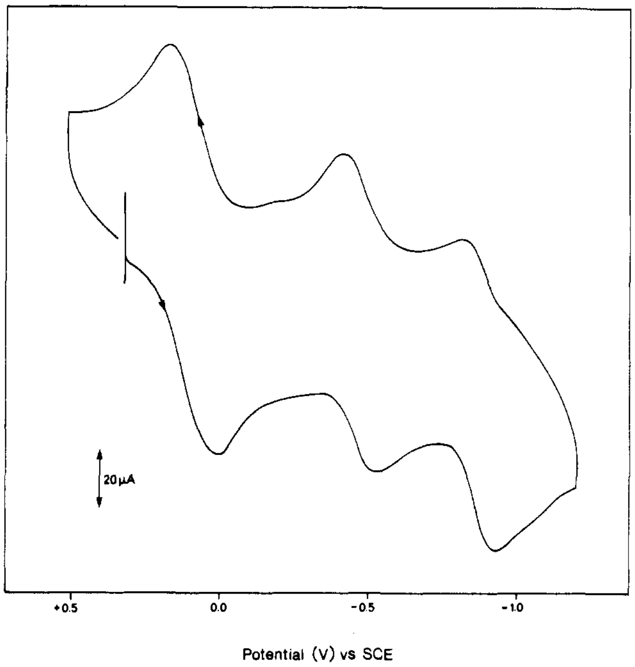


Figure 5. Cyclic voltammogram for $[Cu_2(H_2L1)][Cu(N_3)_6]$ (VIII) (DMF, 0.1 M TEAP, GC; scan rate 200 mV s^{-1}).

Magnetic Properties. Compounds I, II, and V–VII have room-temperature magnetic moments in the range 0.49–0.90 μ_B (Table V), indicating strong antiferromagnetic exchange between the copper(II) centers. Compounds VIII and IX have significantly larger room-temperature magnetic moments (μ_{eff} = 1.39 and 1.28 μ_B, respectively), indicating somewhat weaker net antiferromagnetism. Variable-temperature (5–300 K) magnetic data were obtained for compounds I, V, VIII, and IX. A plot of the experimental data for I is given in Figure 6. A rise in susceptibility at high temperatures, with the Néel point clearly far above room temperature, indicates the presence of very strong exchange. The data were fitted to the Bleaney–Bowers expression (eq 1),[48] using

$$\chi_m = \frac{N\beta^2 g^2}{3K(T-\Theta)}\left[1 + \frac{1}{3}\exp(-2J/kT)\right]^{-1}(1-\rho) + \left[\frac{N\beta^2 g^2}{4kT}\right]\rho + N\alpha \quad (1)$$

the isotropic (Heisenberg) exchange Hamiltonian ($H = -2JS_1S_2$) for two interacting $S = {}^1/_2$ centers (χ_m is expressed per mole of copper atoms, $N\alpha$ is the temperature-independent paramagnetism, ρ is the fraction of monomeric impurity, and Θ is the corrective term to account for interdimer interactions[49,50]). A nonlinear regression analysis was carried out with ρ and Θ as floating parameters. The best fit line is shown in Figure 6 for $-2J$ = 828 (10) cm^{-1}, g = 2.06 (5), and Θ = 0 (Table V). The very large value of $-2J$ indicates very strong antiferromagnetic coupling between the copper(II) centers, which occurs via a superexchange mechanism through the phenoxide bridges. The major factor which contributes to exchange in flat dinuclear oxygen-bridged cations of this sort appears to be the angle at the oxygen bridge. The average angle for I (104.2°) places this compound firmly in a group of related macrocyclic derivatives with comparable ligands, which have $-2J$ values in the range 816–857 cm^{-1} and Cu–O–Cu angles in the range 101.6–104.2°.[15,19,20]

---

(48) Bleaney, B.; Bowers, K. D. *Proc. R. Soc. London, A* **1952**, *214*, 451.

(49) McGregor, K. T.; Barnes, J. A.; Hatfield, W. E. *J. Am. Chem. Soc.* **1973**, *95*, 7993.

(50) Sikorav, S.; Bkouche-Waksman, I.; Kahn, O. *Inorg. Chem.* **1984**, *23*, 490.

Table V. Magnetic Data[a]

compound	g	$-2J$ (cm^{-1})	TIP (10^{-6} cgsu)	ρ	Θ (K)	R
$[Cu_2(H_2L1)(CH_3OH)(ClO_4)][ClO_4]$ (I)	2.06 (5)	828 (10)	63	0	0	0.75
$[Cu_2(H_2L1)][Cu_2Cl_4]$ (V)	2.071 (4)	902 (3)	150	0.034	0	0.76
$[Cu_2(H_2L1)][Cu_2(N_3)_6]\cdot 1.5MeOH$ (VIII)	2.03 (19) 2.047 (8)	696 (5) −19 (5)	60	0.01	−12	1.40
$[Cu_2(H_2L2)][Cu_2(N_3)_6]$ (IX)	2.07 (4) 2.014 (12)	675 (3) 84 (3)	60	0.056	−12	0.88

[a] $R = [\sum(\chi_{obx} - \chi_{calc})^2/\sum(\chi_{obs})^2]^{1/2} \times 10^2$. Magnetic moments (per Cu) (μ_{eff}, μ_B (300 K)): (I) 0.49; (II) 0.89; (V) 0.69; (VI) 0.53; (VII) 0.80; (VIII) 1.39; (IX) 1.28.

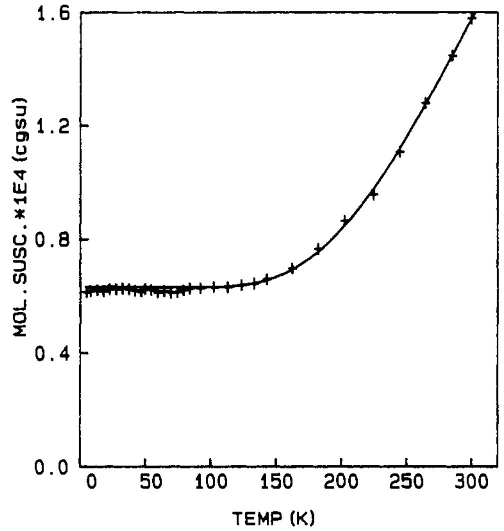


Figure 6. Magnetic data for $[Cu_2(H_2L1)(CH_3OH)(ClO_4)][ClO_4]$ (I). The solid line was calculated from eq 1 with $g = 2.06$ (5), $-2J = 828$ (10) cm^{-1}, $\rho = 0$, and $N\alpha = 63 \times 10^{-6}$ cgsu ($R = 0.81$).

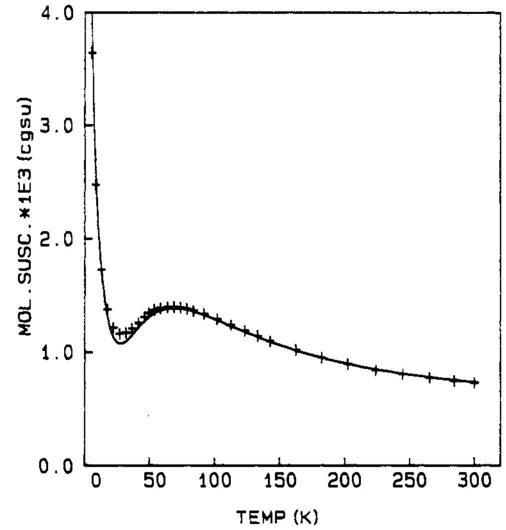


Figure 7. Magnetic data for $[Cu_2(H_2L2)][Cu_2(N_3)_6]$ (IX). The solid line was calculated from eq 2 with $g_1 = 2.07$ (4), $g_2 = 2.014$ (12), $-2J_1 = 675$ (3) cm^{-1}, $-2J_2 = 84$ (3) cm^{-1}, $\rho = 0.056$, $\Theta = -12$ K, and $N\alpha = 60 \times 10^{-6}$ cgsu ($R = 0.88$).

The mixed-oxidation-state complex V contains a diamagnetic dinuclear copper(I) anion and a paramagnetic dinuclear copper(II) cation. The very low room-temperature magnetic moment ($\mu_{eff} = 0.69\ \mu_B$) indicates very strong coupling within the dinuclear cation comparable with that in I. Variable-temperature magnetic data indicate the presence of a small amount of paramagnetic impurity, and a nonlinear regression analysis of the data using eq 1 gives $g = 2.071$ (4), $-2J = 902$ (3) cm^{-1}, and $\Theta = 0$ (Table V). An unusually high TIP was required to fit these data successfully, especially when compared with the case of other related systems for which TIP values around 60×10^{-6} cgsu were appropriate. This cannot be associated with errors in the diamagnetic corrections of the ligand atoms and, in view of the good fit of the data, raises the question as to whether the additional TIP could be associated with the copper(I) anion. Considering the Cu–O–Cu angle (103.5 (2)°) in the dinuclear cation, the high value of $-2J$ is entirely consistent with other related systems. A good data fit was obtained without an interdimer correction, indicating the absence of intermolecular associative effects propagated through the anion bridge framework.

The polymeric complexes (VIII, IX) have low room-temperature magnetic moments (<1.4 μ_B), indicating the presence of net antiferromagnetism. However, these values are much larger than those observed for the complexes with just a dinuclear cation. Variable-temperature magnetic data for IX are illustrated in Figure 7. A maximum in the susceptibility/temperature profile is observed at approximately 70 K, with a sharp rise at temperatures <25 K. Such a profile is not typical of a very strongly coupled species (e.g. I), and considering the Cu–O–Cu angle within the cation (102.9 (2)°), a large value of $-2J$ would be anticipated. Rather, the profile appears to be the sum of two dominant paramagnetic components, and considering its shape, they are both antiferromagnetic in nature. In the analysis of the data, the two dinuclear centers are assumed to behave as independent and equal contributors to the total susceptibility.

$$\chi^1_{m(Cu)} = f(g_1, J_1, (T - \Theta)) \times 0.5$$

$$\chi^2_{m(Cu)} = f(g_2, J_2, (T - \Theta)) \times 0.5$$

$$\chi^T_{m(Cu)} = (\chi^1_m + \chi^2_m)(1 - \rho) + \frac{N\beta^2((g_1 + g_2)/2)^2}{4kT}\rho + N\alpha \quad (2)$$

Equation 2 represents an adaptation of the Bleaney–Bowers expression incorporating two independent, spin-coupled dinuclear species with different g and J values, corrected for paramagnetic impurity and including an interdimer correction. A poor fit of the data was obtained in the absence of a Θ correction. However, with an interdimer correction of −12 K, a good fit of the data was obtained for $g_1 = 2.07$ (4), $g_2 = 2.015$ (12), $-2J_1 = 675$ (3) cm^{-1}, $-2J_2 = 84$ (3) cm^{-1}, and $\rho = 0.056$ (theoretical line, Figure 7). J_1 is clearly associated with the macrocyclic cation, and such a large negative value is typical of such systems. The azide anion is also antiferromagnetically coupled, though much less strongly. 1,1-Azide bridged dinuclear copper(II) complexes have been shown to order ferromagnetically,[50] especially with relatively small azide bridge angles, and this phenomenon has been attributed to a spin-polarization effect.[51] However, with increasing bridge angle, J would be expected to decrease with the eventual onset of antiferromagnetic coupling.[51] The large internal 1,1-azide bridge angle in IX (104.1 (3)°), coupled with the fact that copper azide itself has a polymeric chain structure involving both intramolecular and intermolecular 1,1-azide bridges, comparable with the structure of IX, and is itself antiferromagnetically ordered,[50] is consistent with the negative J_2 value. The significant Θ correction (−12 K) indicates the presence of weak antiferromagnetic coupling between the dinuclear cation and anion, which

---

(51) Kahn, O.; Mallah, T.; Gouteron, J.; Jeannin, S.; Jeannin, Y. *J. Chem. Soc., Dalton Trans.* **1989**, 1117.

is perhaps surprising in view of the nominally orthogonal nature of the bridging interaction. Attempts to fit the magnetic data to theoretical equations involving three different J values have, so far, been unsuccessful.

Variable-temperature magnetic data for VIII exhibit a profile rather different from that of IX, with a steady rise of χ_m with decreasing temperature and no low-temperature maximum in the susceptibility. However, a plot of $\chi_m T$ versus T decreases with decreasing temperature, signaling the presence of a dominant antiferromagnetic component. Treatment of the data using eq 2 does not give as good a fit as that for IX (Table V) but shows again the strong antiferromagnetic coupling associated with the dinuclear macrocyclic cation. However, exchange within the anion appears to be ferromagnetic in this case, perhaps signifying some structural changes within the anion itself, in particular with regard to the internal azide bridge angle. In other respects, VIII and IX appear to have similar structures, with similar, apparent interdimer antiferromagnetic components in both cases.

Conclusions

The template condensation of 2,6-diformylphenols and 1,3-diamino-2-hydroxypropane with copper(II) salts produces only dinuclear, phenoxide-bridged macrocyclic complexes in which the secondary alcohol groups do not act as ligands. The inability to form tetranuclear complexes is viewed as a consequence of the small macrocyclic ring size. The structural and magnetic properties of the dinuclear macrocyclic cations are comparable with those of similar derivatives involving non-alcoholic bridge groups. Three most unusual polymeric derivatives were produced involving dinuclear macrocyclic cations bridged axially by the anions $Cu_2Cl_4^{2-}$ and $Cu_2(N_3)_6^{2-}$. Extended magnetic interactions were observed for the azide derivatives in which intra-ring antiferromagnetic exchange and independent exchange within the anion are accompanied by extended, antiferromagnetic interdimer exchange.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada (L.K.T., S.S.T., J.N.B.) and the New Zealand University Grants Committee (V.M., A.J.D., S.S.T.) for financial support of this study.

Supplementary Material Available: Tables of atomic coordinates and isotropic thermal parameters, bond lengths, bond angles, anisotropic thermal parameters, least-squares planes, and electronic spectral and electrochemical data and two fully labeled structural diagrams for I and V (37 pages). Ordering information is given on any current masthead page.