Varying Coordination Modes and Magnetic Properties of Copper(II) Complexes with Diazamesocyclic Ligands by Altering Additional Donor Pendants on 1,5-Diazacyclooctane

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Received January 28, 2000

A series of new diazamesocyclic ligands based on a diazamesocycle, l,5-diazacyclooctane (DACO), functionalized by additional donor groups—1,5-bis(*N*-1-methylimidazol-2-ylmethyl)-1,5-diazacyclooctane ($\mathbf{L^1}$), 1-(2-hydroxybenzyl)-1,5-diazacyclooctane ($\mathbf{HL^2}$), 1,5-bis(2-hydroxybenzyl)-1,5-diazacyclooctane ($\mathbf{H_2L^3}$), and 1-(*N*-1-methylimidazol-2-ylmethyl)-1,5-diazacyclooctane ($\mathbf{L^4}$)—and their Cu(II) complexes have been synthesized and characterized. Single-crystal X-ray diffraction analysis of the four Cu(II) complexes revealed that $\mathbf{L^1}$ forms a five-coordinate mononuclear complex, $\mathbf{HL^2}$ a N_3^- μ-bridged binuclear complex, $\mathbf{H_2L^3}$ an oxygen μ-bridged trinuclear complex, and $\mathbf{L^4}$ a one-dimensional zigzag coordination polymeric complex with Cu(II). $[Cu\mathbf{L^1}ClO_4](ClO_4)$ (**I**): $a = 12.194(2)$ Å, $b = 13.351(3)$ Å, $c = 14.473(3)$ Å, $\beta = 107.10(3)°$, $Z = 4$. $[Cu\mathbf{L^2}(N_3)]_2$ (**II**): $a = 8.1864(6)$ Å, $b = 18.141(2)$ Å, $c = 9.3307(7)$ Å, $\beta = 103.662(6)°$, $Z = 2$. $[Cu_3(\mathbf{L^3})_2Cl_2]$ (**III**): $a = 10.7296(13)$ Å, $b = 13.7707(17)$ Å, $c = 13.5523(17)$ Å, $\beta = 106.350(3)°$, $Z = 2$. $\{[Cu\mathbf{L^4}Cl]_2ClO_4\}_\infty$ (**IV**): $a = 7.279(1)$ Å, $b = 23.695(5)$ Å, $c = 19.308(4)$ Å, $\beta = 100.28(3)°$, $Z = 8$. All four complexes crystallize in the monoclinic crystal system with the $P2_1/c$ space group, and each Cu(II) center coordinated with DACO is pentacoordinated with a distorted square-pyramidal or trigonal-bipyrimidal coordination environment. In complex **IV**, the binuclear cation unit $[Cu\mathbf{L^4}Cl]_2^{2+}$ constitutes the fundamental building block of an infinite alternating zigzag chain structure, and the binuclear unit contains two types of geometries around the Cu(II) centers: the Cu(1) center is a distorted square-pyramidal environment, while the Cu(2) is a distorted trigonal-bipyramidal coordination environment. To the best of our knowledge, this is the first Cu(II) complex of a diazamesocyclic ligand with an infinite polymeric structure. The magnetic properties of complexes **II**, **III**, and **IV** have been investigated by variable-temperature magnetic susceptibility measurements in the solid state. The obtained parameters are $2J = 2.06$ cm^{-1} (**II**), -345.56 cm^{-1} (**III**), and -2.60 cm^{-1} (**IV**), which differ greatly from ferromagnetic to weak and strong antiferromagnetic coupling. These results unequivocally indicate that the nature of the pendant arms is a key factor governing the structure and properties of the complexes; therefore, the coordination modes and properties of the metal complexes of a diazamesocycle can be controlled by altering the pendant donors on it. Magneto−structural correlation has been precisely analyzed, and the solution properties of these complexes have also been described.

Introduction

Macrocyclic polyamines and their metal complexes have been the subject of extensive studies for several decades.[1−5] Special attention and great efforts have been devoted to the studies of macrocyclic tri- and tetraamines, e.g., 1,5,9-triazacyclododecane ([12]aneN_3),[4] 1,4,8,11-tetraazacyclotetradecane (cyclam),[5] etc.

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(1) For examples, see: (a) Kimura, E. *Pure Appl. Chem.* **1989**, *61*, 823. (b) Kimura, E.; Koike, T.; Shionoya, M. *Struct. Bonding (Berlin)* **1997**, *89*, 1. (c) Kimura, E.; Shionoya, M. In *Transition Metal Ions in Supramolecular Chemistry*; NATO ASI Series; Kluwer: Norweil, MA, 1994; p 245. (d) Busch, D. H. In *Transition Metal Ions in Supramolecular Chemistry*; NATO ASI Series; Kluwer: Norweil, MA, 1994; p 55. (e) De Santis, G.; Di Casa, M.; Fabbrizzi, L.; Licchelli, M.; Mangano, C.; Pallavicini, P.; Perotti, A.; Poggi, A.; Sacchi, D.; Taglietti, A. In *Transition Metal Ions in Supramolecular Chemistry*; NATO ASI Series; Kluwer: Norweil, MA, 1994; p 133. (f) Kaden, T. A. In *Transition Metal Ions in Supramolecular Chemistry*; NATO ASI Series; Kluwer: Norweil, MA, 1994; p 211. (g) Bencini, A.; Bianchi, A.; Paoletti, P.; Espana, E. G. In *Transition Metal Ions in Supramolecular Chemistry*; NATO ASI Series; Kluwer: Norweil, MA, 1994, p 309.

(2) For examples, see: (a) Lehn, J.-M. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1304. (b) Martel, A. E.; Hancock, R. D. *Comments Inorg. Chem.* **1988**, *6*, 237. (c) Lindoy, L. F. *The Chemistry of Macrocyclic Ligand Complexes*; Cambridge University Press: Cambridge, 1989.

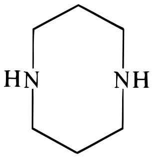
(3) For examples, see: (a) Fabbrizzi, L.; Perotti, A.; Profumo, A.; Soldi, T. *Inorg. Chem.* **1986**, *25*, 4256. (b) Santis, G. D.; Fabbrizzi, L.; Licchelli, M.; Pallavicini, P. *Coord. Chem. Rev.* **1992**, *120*, 237, and references therein.

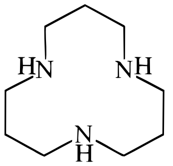
(4) For examples, see: (a) Kimura, E.; Shiota, T.; Koike, T.; Shiro, M.; Kodama, M. *J. Am. Chem. Soc.* **1990**, *112*, 5805. (b) Kimura, E., Karlin, K. D., Eds.; *Progress in Inorganic Chemistry*; Wiley: New York, 1993; p 443. (c) Snodin, M. D.; Beer, P. D.; Drew, M. G. B. *J. Chem. Soc., Dalton Trans.* **1997**, 3407.

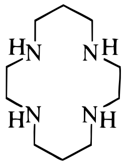
(5) For examples, see: (a) Kimura, E. *Tetrahedron* **1992**, *48*, 6175, and references therein. (b) Bernhardt, P. V.; Lawrence, G. A. *Coord. Chem. Rev.* **1990**, *104*, 297, and references therein. (c) Kimura, E.; Bu, X. H.; Shionoya, M.; Wada, S.; Maruyama, S. *Inorg. Chem.* **1992**, *31*, 4542. (d) Bu, X. H.; An, D. L.; Cao, X. C.; Zhang, R. H.; Clifford, T.; Kimura, E. *J. Chem. Soc., Dalton Trans.* **1998**, 2247.

10.1021/ic000094d CCC: $19.00

Such ligands can form stable complexes with transition metal ions, and interesting features and important functions were found in these complexes.[1−5]


DACO

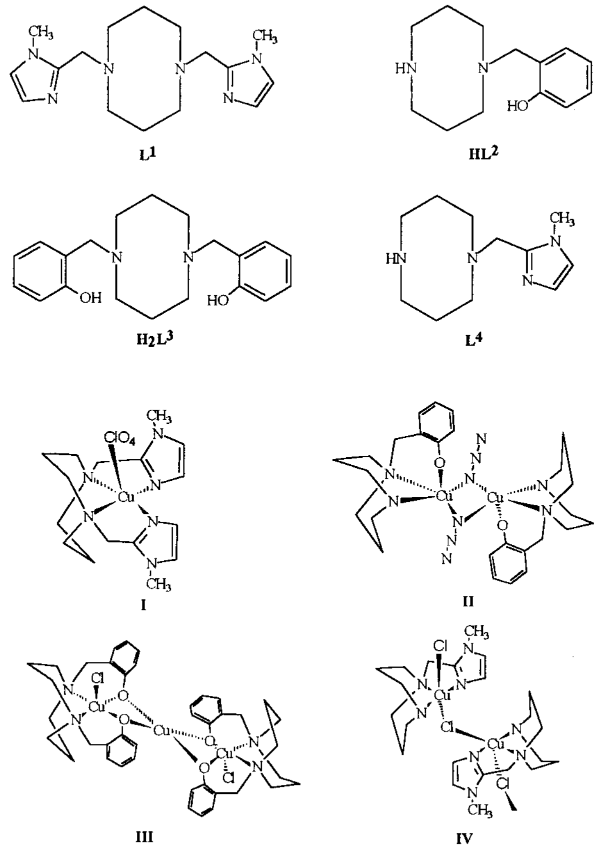

[12]aneN$_3$


Cyclam

Mesocyclic diamines, such as 1,5-diazacyclooctane (DACO), are some of the smallest members of the family of cyclic polyamines. Although the syntheses of these compounds were reported several decades ago,[6] compared to the rich chemistry and the remarkable efforts made in the functionalization of saturated macrocyclic tri- and tetraamines, studies of the medium-sized cyclic diamines have remained relatively limited.[7] To date, some examples of diazamesocycles bearing functional pendant groups have been reported,[8] but those bearing only one heterocyclic group as the functional pendant have never been reported. Diazamesocyclic compounds have two nitrogen donor atoms with potential bidentate chelating ability. Since they have only two nitrogen donors, two or more of these ligands are required for the formation of one metal center. However, the incorporation of one or two functional donor groups onto the nitrogen atom(s) on such compounds could lead to a rational design of ligands with well-defined structures as well as tailored functions.[8,9]

DACO is a simple example of a diazamesocycle, showing an interesting "boat/chair" configuration in transition metal coordination complexes. Such configuration inhibits axial coordination at the metal center, preventing the formation of a hexacoordinate complex. So far, some derivatives of DACO bearing donor pendants, such as $-CH_2CO_2^-$, $-CH_2CH_2SH$, and $-CH_2$-pyridyl, and their metal complexes have been reported.[8,9] The metal complexes with such functionalized ligands were shown by Darensbourg et al.[8,9] to have very interesting properties and functions. However, until now, most of the studies in this field have focused on Ni(II) complexes, and studies on Cu(II) complexes are comparatively rare.[8c,d,g]

Chart 1



The coordinating abilities of DACO could be adjusted through the attachment of donor pendants. This interesting chemistry promoted our investigation on the chemical modification of DACO by introducing functional groups to clarify their essential roles in the structures and properties of their metal complexes. On the basis of previous studies of DACO and its derivatives, we synthesized a series of new DACO ligands bearing one or two functional groups. These tri- and tetradentate ligands can form stable mononuclear, binuclear, trinuclear, or polynuclear complexes with Cu(II) by altering the pendant arms.

We report herein the syntheses of four novel DACO ligands and their Cu(II) complexes (see Chart 1). The influences of the functional pendant groups on the structure and magnetic properties of Cu(II) complexes have been studied, and the X-ray crystal structures have been determined in detail. We found that the nature of the pendant arms is a determining factor governing the structure and properties of the complexes.

Experimental Section

Materials and General Methods. Most of the starting materials and solvents for syntheses were obtained commercially and purified prior to use. The starting compounds, DACO·2HBr, l-methyl-2-chloromethylimidazole hydrochloride, and 2-bromomethyl phenyl acetate were prepared according to the literature methods.[6,10,11] All other reagents for syntheses and analyses were of analytical grade. FT-IR spectra were taken on a FT-IR 170SX (Nicolet) spectrometer. Elemental analyses were carried out on a Perkin-Elmer 240C analyzer. ^{1}H NMR spectra

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(6) (a) Buhle, E. L.; Moore, A. M.; Wiseloge, F. G. *J. Am. Chem. Soc.* **1943**, *65*, 29. (b) Billman, J. H.; Dorman, L. C. *J. Org. Chem*. **1962**, *27*, 2419.

(7) Musker, W. K. *Coord. Chem. Rev.* **1992,** *117*, 133, and references therein.

(8) (a) Legg, J. I.; Nielson, D. O.; Smith, D. L.; Larson, M. L. *J. Am. Chem. Soc.* **1968**, *90*, 5030. (b) Nielson, D. O.; Larsen, M. L.; Willett, R. D.; Legg, J. I. *J. Am. Chem. Soc.* **1971**, *93*, 5079. (c) West, M. H.; Legg, J. I. *J. Chem. Soc.* **1976**, *98*, 6945. (d) Mills, D. K.; Reibenspies, J. H.; Darensbourg, M. Y. *Inorg. Chem.* **1990**, *29*, 4364. (e) Darensbourg, M. Y.; Font, I.; Mills, D. K.; Pala, M.; Reibenspies, J. H. *Inorg. Chem.* **1992**, *31*, 4965. (f) Bu, X. H.; Fang, Y. Y.; Shang, Z. L.; Zhang, R. H.; Zhu, H. P.; Liu, Q. T. *Acta Crystallogr*. **1999**, *C55*, 39. (g) Bu, X. H.; Shang, Z. L.; Weng, W.; Zhang, R. H.; Zhu, H. P.; Liu, Q. T. *Acta Chem. Scand.* **1999**, *53*, 295.

(9) (a) Farmer, P. J.; Solouki, T.; Mills, D. K.; Soma, T.; Russell, D. H.; Reibenspies, J. H.; Darensbourg, M. Y. *J. Am. Chem. Soc.* **1992**, *114*, 4601. (b) Farmer, P. J.; Solouki, T.; Soma, T.; Russell, D. H.; Darensbourg, M. Y. *Inorg. Chem.* **1993**, *32*, 4171. (c) Font, I.; Buonomo, R.; Reibenspies, J. H.; Darensbourg, M. Y. *Inorg. Chem.* **1993**, *32*, 5898. (d) Buonomo, R. M.; Font, I.; Maguire, M. J.; Reibenspies, J. H.; Tuntulani, T.; Darensbourg, M. Y. *J. Am. Chem. Soc.* **1995**, *117*, 963. (e) Goodman, D. C.; Farmer, P. J.; Darensbourg, M. Y.; Reibenspies, J. H. *Inorg. Chem.* **1996**, *35*, 4989. (f) Musie, G.; Reibenspies, J. H.; Darensbourg, M. Y. *Inorg. Chem.* **1998**, *37*, 302. (g) Lyon, E. J.; Musie, G.; Reibenspies, J. H.; Darensbourg, M. Y. *Inorg. Chem*. **1998**, *37*, 6942. (h) Grapperhaus, C. A.; Darensbourg, M. Y. *Acc. Chem. Res.* **1998**, *31*, 451, and references therein. (i) Grapperhaus, C. A.; Bellefeuille, J. A.; Reibenspies, J. H.; Darensbourg, M. Y. *Inorg. Chem.* **1999**, *38*, 3698.

(10) Turner, R. A.; Huebner, C. F.; Scholz, C. R. J. *J. Am. Chem. Soc.* **1949**, *71*, 2801.

(11) Range, R. *Tetrahedron* **1971**, *27*, 1499.

were recorded on a Bruker AC-P 200 spectrometer (200 MHz) at 25 °C with tetramethylsilane as the internal reference. Electronic absorption spectra were taken on a Shimadzu UV-260 spectrophotometer.

Syntheses of Ligands. 1,5-Bis(*N*-1-methylimidazol-2-ylmethyl)-1,5-diazacyclooctane tetrahydrochloride monohydrate (L^1·4HCl·H_2O). A solution of DACO·2HBr (1.63 g, 6.0 mmol) and KOH (0.67 g, 12.0 mmol) in anhydrous ethanol (40 mL) was stirred for 4 h at room temperature. Then l-methyl-2-chloromethylimidazole hydrochloride (2.52 g, 15.1 mmol) and triethylamine (2.09 g, 15.0 mmol) in anhydrous ethanol (20 mL) were added dropwise to the mixture over 2 h with stirring. After the addition was complete, triethylamine (5 mL) was further added to the reaction mixture, and stirring was continued for ca. 48 h at room temperature. The solvent was then removed under reduced pressure, and the residue was dissolved in water (15 mL); the pH of the new mixture was adjusted to ca. 10 with K_2CO_3, and then it was extracted with $CHCl_3$ (100 mL × 5). The combined organic phases were evaporated under vacuum, and the crude product was purified by silica gel column chromatography (CH_2Cl_2:MeOH:NH_3·H_2O = 10:10:l) to obtain acid-free ligand as a colorless oil. The ligand was further purified by conversion to the HCl salts to obtain colorless crystalline material (yield: 1.66 g, 60% based on DACO). ^{1}H NMR (D_2O): δ 1.97−1.99 (4H, m), 3.14 (8H, t, J = 5.8 Hz), 3.83 (6H, s), 4.42 (4H, s), 7.42 (4H, s). IR (KBr pellet): 2977, 1623, 1597, 1560, 1527, 1478, 1462, 994, 740 cm^{-1}. Anal. Calcd for $C_{16}H_{26}N_6$·4HCl·H_2O: C, 41.21; H, 6.92; N, 18.03. Found: C, 41.18; H, 6.98; N, 18.37.

1-(2-Hydroxybenzyl)-1,5-diazacyclooctane (HL^2). A solution of DACO·2HBr (3.14 g, 11.5 mmol) and KOH (1.27 g, 22.7 mmol) in anhydrous methanol (40 mL) was stirred for 5 h, and a solution of 2-bromomethyl phenyl acetate (1.11 g, 4.8 mmol) in anhydrous methanol (15 mL) was added dropwise over 1.5 h. The resulting mixture was heated at reflux for 2.5 h and then stirred at room temperature for 72 h. The solvent was evaporated under reduced pressure, the residue was dissolved in water (30 mL) and basified with KOH (0.3 g, 5.4 mmol), and the resulting mixture was heated at reflux for 2 h. The mixture was extracted with CH_2Cl_2 (100 mL × 3), the combined CH_2Cl_2 layers were dried over $MgSO_4$, the solvent was evaporated, and the residue was purified by silica gel column chromatography (CH_2Cl_2:MeOH:NH_3·H_2O from 10:10:1 to 5:5:l). The final product was obtained as a white solid (yield: 0.69 g, 65% based on 2-bromomethyl phenyl acetate). ^{1}H NMR ($CDCl_3$): δ 1.65−1.71 (4H, m), 2.77 (4H, t, J = 5.5 Hz), 2.90 (4H, t, J = 5.8 Hz), 3.75 (2H, s), 6.30−6.93 (4H, m), 7.22−7.26 (1H, m). IR (KBr pellet): 2939, 2669, 2600, 1594, 1458, 1347, 1277, 1248, 929, 750 cm^{-1}. Anal. Calcd for $C_{13}H_{20}N_2O$: C, 70.87; H, 9.15; N, 12.72. Found: C, 70.42; H, 9.13; N, 12.87.

1,5-Bis(2-hydroxybenzyl)-1,5-diazacyclooctane (H_2L^3). A solution of DACO·2HBr (2.28 g, 8.3 mmol) and KOH (2.53 g, 45.1 mmol) in toluene (50 mL) was stirred for 2 h at 70 °C, and a solution of 2-bromomethyl phenyl acetate (4.60 g, 20.1 mmol) in toluene (20 mL) was added dropwise over 1.5 h. The resulting mixture was heated at reflux for 2.5 h and then stirred at room temperature for 12 h. The solvent was evaporated under reduced pressure, and the residue was dissolved in water (50 mL); KOH (5.0 g, 89 mmol) was added, and then the resulting mixture was heated at reflux for 2 h. The mixture was extracted with CH_2Cl_2 (100 mL × 5), and the combined CH_2Cl_2 layers were dried over $MgSO_4$ and evaporated. The residue was purified by recrystallization from methanol. The final product was obtained below 0 °C as a white solid (yield: 2.17 g, 80% based on DACO). ^{1}H NMR ($CDCl_3$): δ 1.84−1.87 (4H, m), 2.81 (8H, t, J = 5.9 Hz), 3.81 (4H, s), 6.76−6.98 (8H, m), 7.16−7.24 (2H, m). IR (KBr pellet): 2939, 2669, 2600, 1614, 1581, 1492, 1461, 1216, 1168, 769 cm^{-1}. Anal. Calcd for $C_{20}H_{26}N_2O_2$: C, 73.58; H, 8.03; N, 8.58. Found: C, 73.60; H, 7.67; N, 8.77.

1-(*N*-1-Methylimidazol-2-ylmethyl)-1,5-diazacyclooctane Trihydrochloride Monohydrate (L^4·3HCl·H_2O). A solution of DACO·2HBr (8.3 g, 30 mmol) and KOH (3.3 g, 58.8 mmol) in anhydrous methanol (40 mL) was stirred for 4 h. Then a solution of l-methyl-2-chloromethylimidazole hydrochloride (1.26 g, 7.5 mmol) in anhydrous methanol (15 mL) was added dropwise, and the resulting mixture was heated at reflux for 1 h, followed by stirring at room temperature for 48 h. The solvent was evaporated under reduced pressure, and the residue was dissolved in water (20 mL); the pH of the new mixture was adjusted to ca. 10 with Na_2CO_3, and then it was extracted with $CHCl_3$ (100 mL × 3). The combined $CHCl_3$ layers were dried over $MgSO_4$ and evaporated, and the residue was purified by silica gel column chromatography (CH_2Cl_2:MeOH:NH_3·H_2O = 5:5:l) to yield a colorless oil. The ligand was further purified by conversion to the HCl salts by acidification of the free base with HCl gas. The HCl salts were obtained as a pale cream solid (yield: 1.52 g, 60% based on l-methyl-2-chloromethylimidazole hydrochloride). ^{1}H NMR (D_2O): δ 1.88−1.93 (4H, m), 2.88 (4H, t, J = 5.5 Hz), 3.23 (4H, t, J = 5.1 Hz), 3.78 (3H, s), 4.08 (2H, s), 7.30−7.42 (2H, m). IR (KBr pellet): 2956, 1607, 1566, 1536, 1490, 1466, 789 cm^{-1}. Anal. Calcd for $C_{11}H_{20}N_4$·3HCl·H_2O: C, 39.35; H, 7.51; N, 16.69. Found: C, 39.08; H, 7.69; N, 16.37.

Syntheses of Cu(II) Complexes. [CuL^1ClO_4](ClO_4) (I). The pH value of a solution containing equimolar amounts of $Cu(ClO_4)_2$·$6H_2O$ (37 mg, 0.1 mmol) in methanol (5 mL) and **L^1**·4HCl·H_2O (47 mg, 0.1 mmol) in H_2O (5 mL) was adjusted to ca. 6−7 with 0.1 M NaOH aqueous solution. The blue solution was filtered and left to stand at room temperature. Single crystals suitable for X-ray analysis were obtained by slow evaporation of the solvent. Yield: 36 mg (65%). IR (KBr pellet): 2957, 1614, 1556, 1507, 1445, 1082, 623 cm^{-1}. Anal. Calcd for $C_{16}H_{26}Cl_2CuN_6O_8$: C, 34.02; H, 4.64; N, 14.88. Found: C, 33.88; H, 4.32; N, 14.52.

[CuL^2(N_3)]$_2$ (II). Complex **II** was prepared by mixing equimolar amounts of $Cu(ClO_4)_2$·$6H_2O$ (73 mg, 0.2 mmol) and **HL^2** (42 mg, 0.2 mmol) in a mixed solution of acetone and water (v:v = 1:1), followed by the addition of an equimolar amount of NaN_3 (14 mg, 0.2 mmol). The reaction mixture was filtered, and green single crystals suitable for X-ray analysis were obtained by the slow evaporation of the solvent. Yield: 25 mg (40%). IR (KBr pellet): 2954, 2044, 1594, 1476, 1432, 1287, 983, 719 cm^{-1}. Anal. Calcd for $C_{26}H_{38}Cu_2N_{10}O_2$: C, 48.06; H, 5.90; N, 21.56. Found: C, 47.97; H, 5.96; N, 21.50.

[Cu_3(L^3)$_2$$Cl_2$] (III). Complex **III** was prepared by mixing $CuCl_2$·$2H_2O$ (47 mg, 0.3 mmol) and **H_2L^3** (59 mg, 0.2 mmol) in a mixed solution of acetone and methanol (v:v = 1:1). The dark green solution was then filtered and left to stand at room temperature. Single crystals suitable for X-ray analysis were obtained by the slow evaporation of the solvent. Yield: 41 mg (50%). IR (KBr pellet): 2969, 1596, 1486, 1455, 1340, 1270, 1125, 1115, 1080, 988, 756 cm^{-1}. Anal. Calcd for $C_{40}H_{48}Cl_2Cu_3N_4O_4$: C, 52.77; H, 5.32; N, 6.16. Found: C, 52.69; H, 5.21; N, 6.50.

$\{$**[CuL^4Cl]$_2$ClO_4**$\}_\infty$ **(IV).** The pH value of the solution containing equimolar amounts of $Cu(ClO_4)_2$·$6H_2O$ (54 mg, 0.15 mmol) in methanol (5 mL) and **L^4**·3HCl·H_2O (50 mg, 0.15 mmol) in H_2O (5 mL) was slowly adjusted to ca. 6−7 with 0.1 M NaOH aqueous solution. The blue solution was filtered and left to stand at room temperature. Single crystals suitable for X-ray analysis were obtained by the slow evaporation of the solvent. Yield: 28 mg (45%). IR (KBr pellet): 2957, 1635, 1558, 1516, 1446, 1122, 1089, 623 cm^{-1}. Anal. Calcd for $C_{11}H_{20}ClCuN_4$·ClO_4: C, 32.48; H, 4.96; N, 13.78. Found: C, 32.26; H, 4.65; N, 14.10.

Caution. While we have experienced no problems with the perchlorate and azide compounds in this study, these should be handled with great caution due to their potential for explosion.

Magnetic Studies. The variable-temperature magnetic susceptibilities were measured on a model CF-l magnetometer (for **II**, **IV**) or a SQUID (for **III**) apparatus in 4.2−300 K temperature range. The susceptibilities were corrected for diamagnetism with Pascal's constants for all the constituent atoms, and magnetic moments were calculated by the equation $\mu_{\mathrm{eff}} = 2.828(\chi_{\mathrm{M}}T)^{1/2}$.

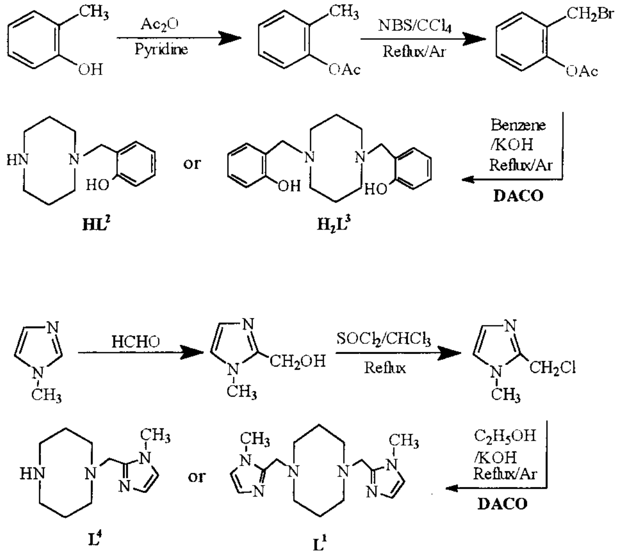
Crystallographic Studies. Single-crystal X-ray diffraction measurements were carried out with an Enraf-Nonius CAD-4 diffractometer (for **I, IV**), a Siemens P4 diffractometer (for **II**), or a Bruker Smart 1000 CCD diffractometer (for **III**). Each of the diffractometers is equipped with a graphite crystal monochromator situated in the incident beam for data collection. The determination of unit cell parameters and data collections were performed with Mo Kα radiation (λ = 0.71073 Å). Unit cell dimensions were obtained with least-squares refinements analyses of 25 (for **I**), 3648 (for **II**), 9854 (for **III**), and 25 (for **IV**) reflections. All the structures were solved by direct methods,

Table 1. Crystallographic Data and Structure Refinement Summary for Complexes **I**−**IV**

	I	**II**	**III**	**IV**
chemical formula	$C_{16}H_{26}ClCuN_6O_4{\cdot}ClO_4$	$C_{26}H_{38}Cu_2N_{10}O_2$	$C_{40}H_{48}Cl_2Cu_3N_4O_4$	$C_{11}H_{20}ClCuN_4{\cdot}ClO_4$
formula weight	564.87	649.76	910.34	406.75
space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
T (K)	299 ± 1	293 ± 2	293 ± 2	299 ± 1
a (Å)	12.194(2)	8.1864(6)	10.7296(13)	7.279(1)
b (Å)	13.351(3)	18.141(2)	13.7707(17)	23.695(5)
c (Å)	14.473(3)	9.3307(7)	13.5523(17)	19.308(4)
β (deg)	107.10(3)	103.662(6)	106.350(3)	100.28(3)
V (Å^3)	2252(1)	1346.5(2)	1921.4(4)	3277(1)
ρ_{calcd} (g cm^3)	1.666	1.588	1.573	1.649
Z	4	2	2	8
μ (cm^{-1})	12.642	16.25	18.31	16.850
R^a	0.073	0.0408	0.0401	0.055
R_w	0.077^b	0.0901^c	0.1058^d	0.062^b

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}$. $w^{-1} = \sigma^2(F) + 0.0001F^2$. [c] $R_w = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2]^{1/2}$. $w^{-1} = s^2(F_o^2) + (0.0564P)^2 + 0.3041P$, where $P = (F_o^2 + 2F_c^2)/3$. [d] $R_w = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2]^{1/2}$. $w^{-1} = s^2(F_o^2) + (0.1000P)^2 + 0.000P$, where $P = (F_o^2 + 2F_c^2)/3$.

Scheme 1



and empirical (for **I** and **IV**) and semiempirical (for **II** and **III**) absorption corrections were applied. Cu atoms in each complex were located from the *E*-maps. The other non-hydrogen atoms were located in successive difference Fourier syntheses. The final refinement was performed by full-matrix least-squares methods with anisotropic thermal parameters for non-hydrogen atoms on *F* (for **I**, **IV**) or F^2 (for **II**, **III**). The hydrogen atoms were added theoretically onto the specific atoms and refined with fixed thermal factors. Crystallographic data and experimental details for structural analyses are summarized in Table 1. Preliminary results of the crystal structure for **II** were published recently.[12]

Results and Discussion

Syntheses of Ligands. The new ligands were prepared according to Scheme 1. An excess of DACO was used to obtain the monoalkylated products **HL^2** and **L^4**, which were purified by silica gel column chromatography. **HL^2** could be obtained directly as a colorless solid after column chromatography, but acid-free **L^4** can only be isolated as an oil, so we converted it to the HCl salts to obtain a white solid. The doubly substituted ligands **L^1** and **H$_2$L^3** were prepared by using an excess of l-methyl-2-chloromethylimidazole hydrochloride or 2-bromomethyl phenyl acetate. **L^1** was also purified by silica gel column chromatography, whereas **HL^3** could be obtained directly as a white solid by recrystallization from methanol solution. Acid-free **L^1** can only be obtained as an oil, so it was also converted to the HCl salts to obtain a crystalline solid. The yields for all the syntheses were greater than 60%. All analytical and spectral data are in good agreement with the theoretical requirements for all the new ligands.

Syntheses of Complexes and General Characterizations. The syntheses of complexes **I** and **IV** were achieved by the reaction of the corresponding acid-free ligand (**L^1** or **L^4**) with $Cu(ClO_4)_2{\cdot}6H_2O$. Since the corresponding ligands are the HCl salts, they must be neutralized with NaOH aqueous solution prior to complexation. Complexes **II** and **III** were synthesized by the reaction of the corresponding free ligands (**HL^2** and **H$_2$L^3**) with $Cu(ClO_4)_2{\cdot}6H_2O$ (including NaN_3 when preparing complex **II**) or $CuCl_2{\cdot}2H_2O$. Since **HL^2** and **H$_2$L^3** are deprotonated when forming complexes with Cu(II) and the coordinating anions (N_3^- or Cl^-), **II** and **III** are both neutral complexes. The uncharged nature of **III** resulted in its very low solubility in many general solvents, including H_2O and methanol. The results of elemental analyses for all the four complexes were in good agreement with the theoretical requirements of their compositions. The IR spectra of complexes **I** and **IV** showed absorption bands resulting from the skeletal vibrations of imidazole ring in the 1400−1600 cm^{-1} region. In addition, the bands of ClO_4^- appeared at the 1089−1075 and 625−623 cm^{-1} regions for **I** and **IV**, respectively, in their IR spectra.

Description of the Crystal Structures. The Mononuclear Complex I. The ORTEP structure of complex **I** with atom labeling is shown in Figure 1, and the selected bond distances and angles are given in Table 2.

The structure of complex **I** consists of a discrete [Cu**L^1**(ClO$_4$)]$^+$ cation and a perchlorate anion. The coordination geometry around Cu(II) can be described as a near-ideal square-pyramid stereochemistry ($\tau = 0.06$).[13] All the nitrogen donors of **L^1** occupy equatorial positions. It is somewhat to our surprise that an oxygen from one perchlorate ion, not water or Cl$^-$, coordinated to the central Cu(II) from an apical position, although the crystal was obtained from water solution in the presence of Cl$^-$. For the ligand, the two nitrogen atoms of the imidazole pendant groups and the two nitrogen atoms of the diazamesocyclic ring are in cis positions at the coordination polyhedron. The Cu(II) ion deviates from the mean equatorial plane of the square pyramid toward the apical O(11) by ca. 0.27 Å. In this complex, the ligand adopts a boat/chair configuration

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(12) Bu, W. M.; Ye, L.; Xu, Q.; Bu, X. H.; Yang, G. D.; Fan, Y. G. *Acta Crystallogr., Sect. C* **1999**, *55*, 44.

(13) Addison, A. W.; Rao, T. N.; Reedijk, J.; Rijn, V. J.; Verschoor, G. C. *J. Chem. Soc., Dalton Trans.* **1984**, 1349.

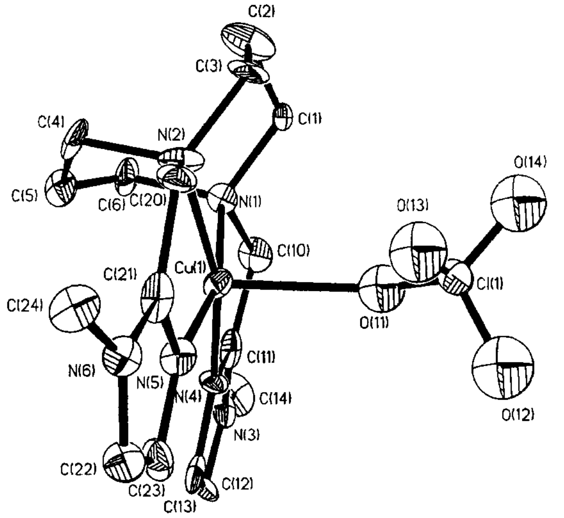

Figure 1. ORTEP structure of complex **I** with 30% thermal ellipsoid probability.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Complex **I**

Bond Lengths (Å)			
Cu(1)−N(1)	2.073(14)	Cu(1)−N(2)	2.043(15)
Cu(1)−N(4)	1.981(14)	Cu(1)−N(5)	1.951(14)
Cu(1)−O(11)	2.332(18)		
Bond Angles (deg)			
N(1)−Cu(1)−N(2)	87.8(6)	N(1)−Cu(1)−N(4)	82.7(6)
N(2)−Cu(1)−N(4)	160.9(7)	N(1)−Cu(1)−N(5)	164.7(7)
N(2)−Cu(1)−N(5)	83.1(6)	N(4)−Cu(1)−N(5)	102.3(6)
N(1)−Cu(1)−O(11)	90.7(6)	N(2)−Cu(1)−O(11)	105.6(6)
N(4)−Cu(1)−O(11)	91.1(6)	N(5)−Cu(1)−O(11)	103.6(6)

with two five-membered chelate rings [N(1)−C(10)−C(11)−N(4)−Cu(1) and N(2)−C(20)−C(21)−N(5)−Cu(1)], forming a N(1)−Cu(1)−N(4) angle of 82.7(6)° and a N(2)−Cu(1)−N(5) angle of 83.1(6)°.

The Cu−N distances of the macrocyclic ring lie in the range of 1.951(14)−2.073(14) Å, all being normal lengths for Cu−N coordination bonds; however, the bonds of the nitrogen atoms of the diazamesocycle that coordinate with Cu(II) (Cu−N(1) = 2.073(14) Å and Cu−N(2) = 2.043(15) Å) are longer than the Cu−N bonds of the imidazole groups (Cu−N(4) = 1.981(14) Å and Cu−N(5) = 1.951(14) Å), indicating weaker coordination of N(1) and N(2) compared with N(4) and N(5). The Cu−O distance of 2.332(18) Å is greater than normal Cu−O bond distance,[3b,5d] indicating weak coordination of the perchlorate ion, probably due to the Jahn−Teller effect or steric constraints between the larger perchlorate ion and $\mathbf{L^1}$. The weak coordination of the perchlorate ion makes it possible that stronger donor atoms can replace it, and this is important in the further application of this complex as a potential catalyst or a functional building block for the construction of larger functional architectures.

The Binuclear Complex II. The ORTEP view of complex **II**, including the atomic numbering scheme, is given in Figure 2. Relevant bond distances and angles have been listed in Table 3. The structure of the azido complex consists of neutral binuclear entities. Each complex results from the pairing of two mononuclear units related by a crystallographic center of symmetry. The two Cu(II) centers are bridged equivalently by two end-on azido anions. The bridging azido anions are bound asymmetrically to Cu(II) at distances of 2.174(3) and 2.215(3) Å, and the Cu−N$_3$−Cu angle (90.93(10)°) is the smallest one observed in similar complexes. The Cu···Cu intramolecular distance is 3.129(4) Å, which is rather large compared to that observed in binuclear Cu(II) complexes with azido anions bridging in an end-on fashion at the two equatorial positions (3.045−3.162 Å).[14]

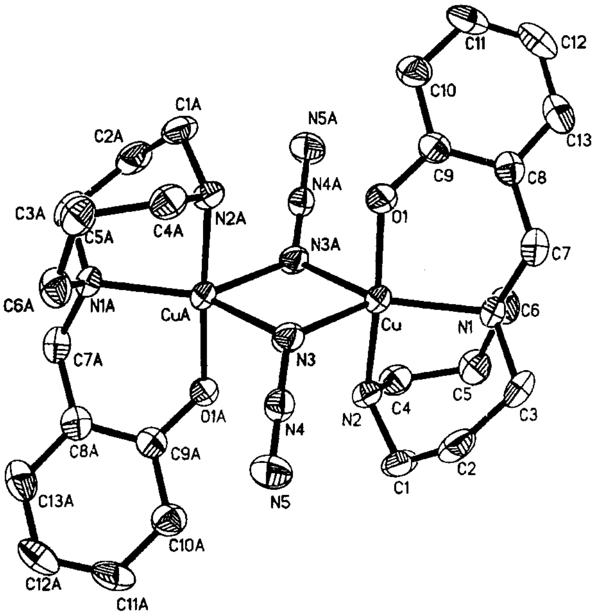

Figure 2. ORTEP structure of complex **II** with 50% thermal ellipsoid probability.

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

Bond Lengths (Å)			
Cu−O(1)	1.911(2)	Cu−N(2)	1.996(3)
Cu−N(1)	2.067(3)	Cu−N(3)	2.174(3)
Cu−N(3A)	2.215(3)		
Bond Angles (deg)			
O(1)−Cu−N(2)	173.54(11)	O(1)−Cu−N(1)	96.50(10)
N(2)−Cu−N(1)	87.25(11)	O(1)−Cu−N(3)	89.99(10)
N(2)−Cu−N(3)	91.02(11)	N(1)−Cu−N(3)	135.32(11)
O(1)−Cu−N(3A)	89.61(10)	N(2)−Cu−N(3A)	84.03(11)
N(1)−Cu−N(3A)	134.93(10)	N(3)−Cu−N(3A)	89.07(10)
Cu−N(3)−Cu(A)	90.93(10)		

Each Cu(II) atom in complex **II** is bound by five donor atoms occupying the vertexes of a distorted trigonal bipyramid with $\tau = 0.637$.[13] Two bridging azido molecules and a nitrogen donor of the DACO ring of $\mathbf{L^2}$ comprise the basal plane, and the axial coordination sites are occupied by one oxygen atom of the deprotonated pendant phenol group and the remaining nitrogen atom of DACO. The Cu−N bond (basal plane) distances fall in the expected range.[15]

The end-on azido bridge is almost linear with a N(3)−N(4)−N(5) bond angle of 178.4(4)°. The N(3)−N(4) and N(4)−N(5) bond lengths (1.200(4) and 1.150(4) Å, respectively) are approximately equal to each other, and the longer bond involving the nitrogen atom is linked to the metal. This is consistent with the structural results obtained with the other end-on bridging azido complexes.[14a,16]

The Trinuclear Complex III. The ORTEP structure of complex **III** is shown in Figure 3, and the selected bond lengths

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(14) (a) Kahn, O.; Sikorav, S.; Gouteron, J.; Jeannin, S.; Jeannin, Y. *Inorg. Chem.* **1983**, *22*, 2877. (b) Sikorav, S.; Bkouche-Waksman, I.; Kahn, O. *Inorg. Chem.* **1984**, *23*, 490. (c) Boillot, M. L.; Journaux, Y.; Bencini, A.; Gatteschi, D.; Kahn, O. *Inorg. Chem.* **1985**, *24*, 263. (d) Costes, J. P.; Dahan, F.; Ruiz, J.; Laurent, J. P. *Inorg. Chim. Acta* **1995**, *239*, 53.

(15) Thompson, L. K.; Tandon, S. S.; Manuel, M. E. *Inorg. Chem.* **1995**, *34*, 2356.

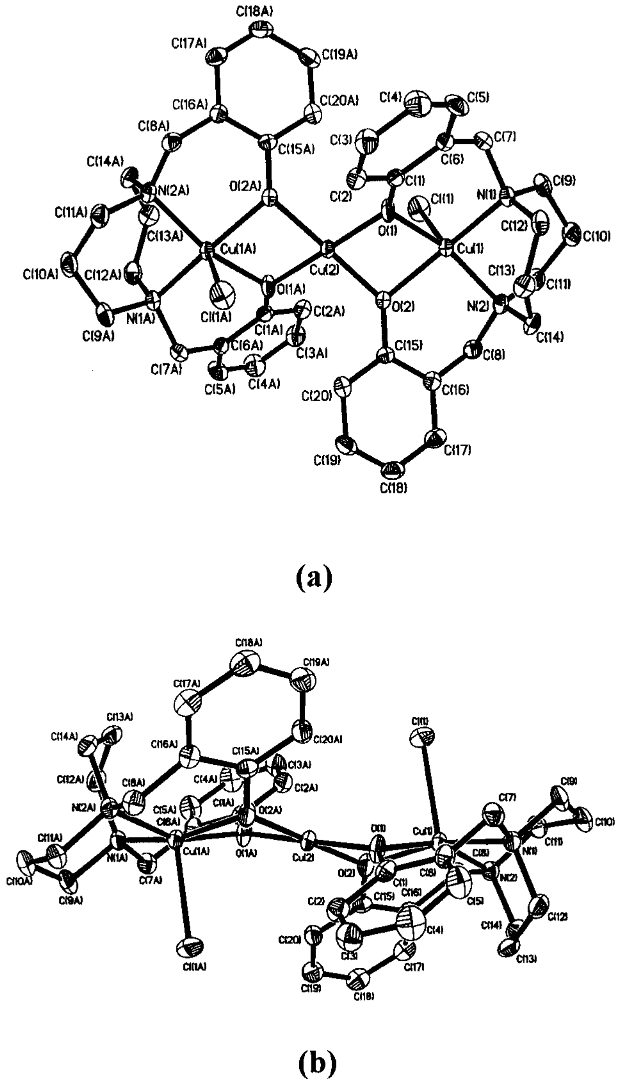

Figure 3. (a) Top view and (b) side view of ORTEP structure of complex **III** with 30% thermal ellipsoid probability.

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

Bond Lengths (Å)			
Cu(1)−O(1)	1.986(3)	Cu(1)−O(2)	2.005(3)
Cu(1)−N(2)	2.023(3)	Cu(1)−N(1)	2.028(3)
Cu(1)−Cl(1)	2.4493(13)	Cu(1)−Cu(2)	2.9389(5)
Cu(2)−O(1)	1.900(3)	Cu(2)−O(2)	1.922(3)
Bond Angles (deg)			
O(1)−Cu(1)−O(2)	76.48(13)	O(1)−Cu(1)−N(2)	156.36(15)
O(2)−Cu(1)−N(2)	94.03(13)	O(1)−Cu(1)−N(1)	93.03(13)
O(2)−Cu(1)−N(1)	162.11(14)	N(2)−Cu(1)−N(1)	90.01(14)

and angles are listed in Table 4. Like complex **II**, **III** is also a neutral complex in which each ligand is doubly deprotonated. The asymmetric unit is formed by half a molecule of the complex, which shows inversion in the center of the rhombus plane (Cu(2) is just on this center). The Cu(1) and Cu(1A) atoms, which occupy the general positions, are centrosymmetrically related to one another; hence, Cu(1), Cu(2), and Cu(1A) lie in a straight line. They are bound to the ligands by two oxygen atoms of the pendant groups and a pair of nitrogen donors of the macrocyclic ring. Chloride anions complete the coordination polyhedron around the two Cu(II) centers. The Cu(1) atom is pentacoordinated with a N_2O_2Cl donor set, and the coordination polyhedron may be best described as a real square pyramid with $\tau = 0.1$.[13] The Cu(2) atom is bridged by four oxygen donors of the phenol groups of the two ligands into flanking units, and due to its position on the inversion center, the structure is entirely symmetric. The folding angle between the perfect square-planar [Cu(2), O(1), O(2), O(1A), and O(2A)] and the best plane calculated for [N(1), N(2), O(1), and O(2)] is 15.02°. The dihedral angle between the two planes of the phenol rings of the ligand is 62.93°. The Cu(1) atom is 0.3185 Å above the mean plane formed by [N(1), N(2), O(1), and O(2)] toward the apical Cl^- ion. The apical position is occupied by a Cl^- donor with an axial [Cu(1)−Cl(1)] bond of 2.4493(13) Å, which is longer than normal, probably due to the Jahn−Teller effect. The weak coordination of Cl^- also reserves this position as an active site for further applications or reactions. The Cu(1)···Cu(2) distance in the dimer is 2.9389(5) Å, which is rather short and raises the possibility of Cu−Cu bonding between adjacent Cu(II) centers. This suggests that there might be some cluster character in this complex.

The Polymeric Complex IV. The polymeric complex, $\{[Cu\mathbf{L}^4Cl]_2(ClO_4)_2\}_\infty$ (**IV**), is composed of $[Cu_2(\mathbf{L}^4)_2Cl_2]^+$ cation units and perchlorate anions. The ORTEP structure of binuclear cation unit of **IV** is shown in Figure 4a, and the selected bond distances and angles are listed in Table 5. The structure of this complex is interesting because there are two kinds of coordination geometry, and therefore, the complex has an alternating zigzag chain structure. The binuclear cation unit $[Cu_2(\mathbf{L}^4)_2Cl_2]^+$ constitutes the fundamental building block of the infinite zigzag chain structure, and the adjacent Cu(II) atoms are linked by Cl^- anions. Each Cu(II) center is five-coordinated with three nitrogen atoms of the ligand ($\mathbf{L}^4$) and two chloride anions. The binuclear unit contains two types of geometries around Cu(II) centers: the Cu(1) center has a nearly perfect square-pyramidal coordination environment ($\tau = 0.05$)[13] generated by the least-squares plane of N(1)−N(11)−N(12)−Cl(3) and the apical Cl(4) anion, and it is displaced from the mean equatorial plane of the square pyramid toward the apical Cl(4) by ca. 0.38 Å, whereas Cu(2) is in a distorted trigonal-bipyramidal coordination environment ($\tau = 0.81$)[13] with two Cl^- anions and a N(14) atom in the equatorial plane and two N atoms [N(3) and N(13)] in the axial positions. The N(3)−Cu(2)−N(13) angle of 165.2(2)° is smaller than the ideal angle of 180°, whereas the sum of angles in the equatorial plane is 360° [Cl(4b)−Cu(2)−N(14) = 117.0(2)°, Cl(3)−Cu(2)−N(14) = 137.5(2)°, and Cl(3)−Cu(2)−Cl(4b) = 105.5(1)°]. Diazamesocycles and their derivatives usually form metal complexes with square-planar or square-pyramidal geometry, and such complexes, having both trigonal-bipyramidal and square-pyramidal coordination environments, are very rare and may provide an excellent example for the study of an alternating chain structure. To the best of our knowledge, this is the first example of Cu(II) complexes which have alternating chain structures with diazamesocyclic ligands and their derivatives.

The Cu(1)−Cl(3) (basal plane) is normal as a Cu−Cl bond but shorter than the Cu(1)−Cl (apex) bond probably due to the Jahn−Teller effect. Therefore, there are also two kinds of Cl^- bridges in the complex. The least intramolecular Cu(1)···Cu(2) and Cu(1)···Cu(2a) nonbonded distances are 4.571(6) and 4.425(4) Å, respectively, which are comparable

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(16) (a) Fehlhammer, W. P.; Dahl, L. F. *J. Am. Chem. Soc.* **1972**, *94*, 3377. (b) Comarmond, J.; Plumere, P.; Lehn, J.-M.; Agnus, Y.; Louis, R.; Weiss, R.; Kahn, O.; Morgenstern-Badarau, I. *J. Am. Chem. Soc.* **1982**, *104*, 6330.

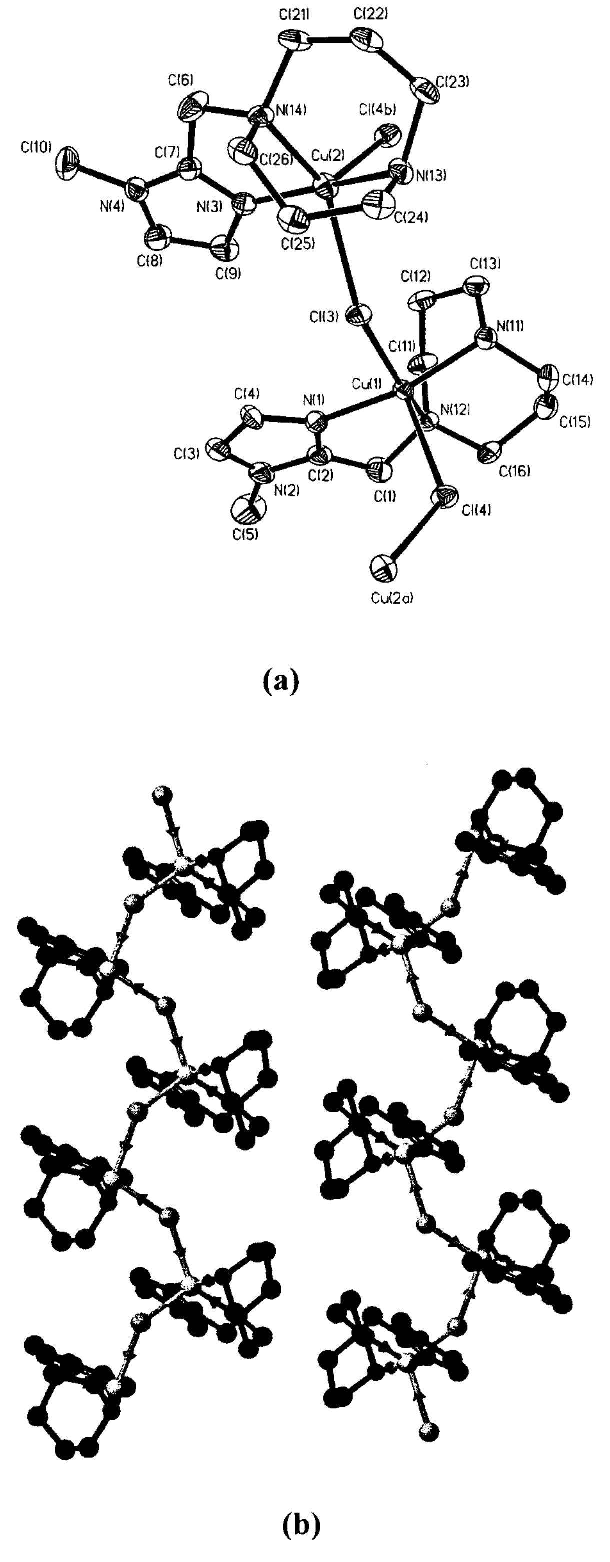

Figure 4. (a) ORTEP structure of a binuclear unit in the polymeric chain complex **IV**; (b) view of the one-dimensional infinite zigzag chains in the unit cell of complex **IV**.

to Cu···Cu distances found in the μ-chloro-bridged Cu(II) chain compounds.[17]

Table 5. Selected Bond Lengths (Å) and Angles (deg) for Complex **IV**

Bond Lengths (Å)			
Cu(1)−Cl(3)	2.329(2)	Cu(2)−N(3)	1.932(6)
Cu(1)−Cl(4)	2.541(2)	Cu(2)−N(13)	1.978(5)
Cu(1)−N(1)	1.955(5)	Cu(2)−N(14)	2.110(6)
Cu(1)−N(11)	1.980(5)	Cu(2)−Cl(3)	2.523(2)
Cu(1)−N(12)	2.100(6)	Cu(2)−Cl(4b)	2.401(2)
Cl(4)−Cu(2a)	2.401(2)		
Bond Angles (deg)			
Cl(3)−Cu(2)−N(13)	87.4(2)	Cl(3)−Cu(1)−N(1)	92.8(2)
N(3)−Cu(2)−N(13)	165.2(2)	Cl(4)−Cu(1)−N(1)	99.0(2)
Cl(3)−Cu(2)−N(14)	137.5(2)	Cl(3)−Cu(1)−N(11)	90.5(2)
N(3)−Cu(2)−N(14)	83.6(2)	Cl(4)−Cu(1)−N(11)	99.2(2)
N(13)−Cu(2)−N(14)	86.4(2)	N(1)−Cu(1)−N(11)	159.9(2)
Cl(3)−Cu(1)−N(12)	157.2(2)	Cl(4)−Cu(1)−N(12)	96.9(2)
N(1)−Cu(1)−N(12)	82.7(2)	N(11)−Cu(1)−N(12)	86.6(2)
Cu(1)−Cl(3)−Cu(2)	140.8(1)	Cl(3)−Cu(2)−N(3)	92.7(2)
Cu(1)−Cl(4)−Cu(2a)	127.1(1)		

Table 6. UV−vis Spectra Data for the Four Complexes (**I**−**IV**)

complex	$\lambda_{\max}$, nm ($\epsilon_{\max} \times 10^{-3}$)^a		
I	600 (0.16)	259 (4.91)	193 (16.3)
II	629 (0.51)	278 (16.2)	231 (16.7)
III	607 (0.25)	260 (7.67)	209 (15.0)
IV	640 (0.38)	295 (17.6)	260 (7.87)

^{a} In water solution (for complexes **I**, **II**, and **IV**) or DMF solution (for complex **III**).

As shown in Figure 4, in the zigzag chain structure of complex **IV**, the odd and even Cu(II) centers can be visualized to arrange separately in each zigzag chain, and the odd and even Cl$^-$ anions also lie separately in an individual straight line. The four visualized lines limit the extension of the chain in the *a*-orientation (Figure 4b). The repeated arrangement of the binuclear units in the chain is limited by the angles of Cu−Cl−Cu (140.8(1)° and 127.1(1)°) and Cl−Cu−Cl (105.5(1)° and 105.9(1)°). They are in the range of the Cu−Cl−Cu angles (114−145°) reported for similar chain complexes.[17] The chain extension is along the *b*-direction. The corresponding interchain separation is the *a*-axis. The position of each ligand ($\mathbf{L}^4$) around each Cu(II) center in a chain is opposed to those in adjacent chains.

In all four complexes, the 1,5-diazacyclooctane mesocyclic rings of the ligands take the boat/chair configuration, and this configuration inhibits axial coordination at the metal center, preventing the formation of a hexacoordinate complex.[18] Although the four ligands bear different pendant arms, their Cu(II) complexes all have approximately the same $\mathrm{Cu-N_{DACO}}$ bond distances (2.058 Å for **I**, 2.032 Å for **II**, 2.031 Å for **III**, and 2.040 and 2.044 Å for **IV**). This indicates that the influences of the pendant groups on the $\mathrm{Cu-N_{DACO}}$ bond lengths are small, possibly negligible. However, the nature of the pendant arms is the determining factor controlling the coordination geometry of Cu(II) in forming mononuclear, binuclear, trinuclear, or polynuclear complexes.

Electronic Spectra. The UV−vis spectra of the four complexes in water (for complexes **I**, **II**, and **IV**) or DMF solution (for complex **III**) have absorption maxima in the range of 600−640 nm (Table 6). For pentacoordinate Cu(II) complexes, this spectral feature is typical for Cu(II) complexes with square-pyramidal or distorted square-pyramidal geometry, which generally exhibits a band in the 550−660 nm range (d_{xz}, $d_{yz} \rightarrow d_{x^2-y^2}$).[8b] The polynuclear (**IV**) and binuclear complexes (**II**) display slightly higher $\lambda_{\max}$'s (640 and 629 nm, respectively),

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(17) Cortes, R.; Lezama, L.; Ruiz de Larramendi, J. I.; Maddariaga, G.; Mesa, J. L.; Zuniga, F. J.; Rojo, T. *Inorg. Chem.* **1995**, *34*, 778.

(18) (a) Bereman, R.; Churchill, M.; Schaber, P.; Winkler, M. *Inorg. Chem.* **1979**, *18*, 3122. (b) Haidar, R.; Ipek, M.; Dasgupta, B.; Yousat, M.; Zompa, L. *Inorg. Chem.* **1997**, *36*, 3125.

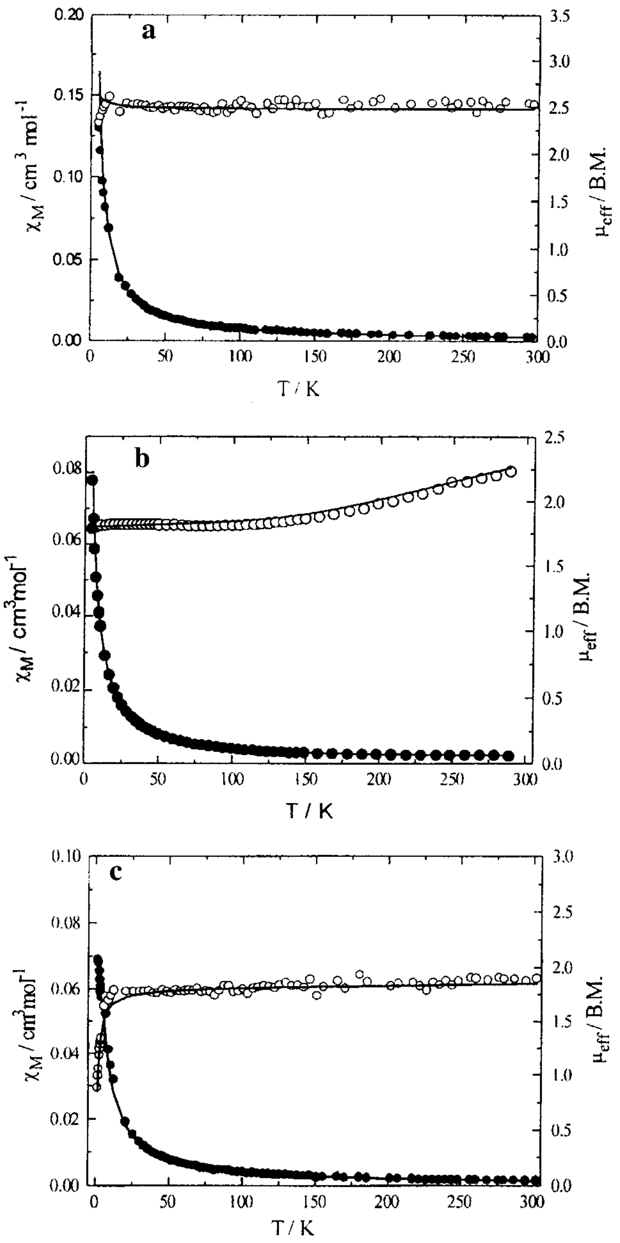

Figure 5. Magnetic coupling diagram of complexes (a) **II**, (b) **III**, and (c) **IV**.

indicating that their geometries are distorted more toward the trigonal bipyramid than those of the trinuclear and mononuclear complexes because **IV** and **II** already contain a distorted trigonal-bipyramidal geometry in their units.[19] The spectral data are consistent with the degree of distortion from the square-pyramidal geometry found in the X-ray structural analysis. In addition, the solution spectra of the complexes in the 200−350 nm range also show $\pi \rightarrow \pi^*$ ligand transitions.

Magnetic Properties. The temperature dependence of the susceptibility and magnetic moment for complexes **II**−**IV** are shown in Figure 5, and the magnetic parameters are summarized in Table 7.

Table 7. Magnetic Parameters of Complexes **II**−**IV**

complex	g	$2J$ (cm^{-1})	F^a
II	2.02	2.06	1.40×10^{-3}
III	2.08	−345.56	4.68×10^{-6}
IV	2.10	−2.60	2.60×10^{-4}

^{a} $F = \Sigma(\chi_{obs} - \chi_{calc})^2/\Sigma(\chi_{obs})^2$.

For complex **II**, we can see from Figure 5a that the χ_M value and μ_{eff} value increase as the temperature decreases. The μ_{eff} reaches a maximum (2.61 μ_B) at T = 12 K, then goes down sharply. The expected value of μ_{eff} (2.83 μ_B) for a $S = 1$ spin ground state is not reached, which is indicative of intramolecular ferromagnetic interactions and intermolecular antiferromagnetic interactions in the ground state. The singlet−triplet energy gap ($2J$) was deduced from the least-squares fit of the experimental data to the temperature for isotropic exchange by using a Bleaney−Bowers equation ($H = -2JS_1S_2$, $N\alpha = 120 \times 10^{-6}$ cm^{-1})

$$\chi_M = 2Ng^2\beta^2(KT)^{-1}[3 + \exp(-2J/KT)]^{-1} + N\alpha \quad (1)$$

We have not analyzed the data at temperatures below 12 K because the zero-field splitting and intermolecular interaction become significant and are no longer negligible. The best fitness parameters are shown in Table 7.

The ferromagnetic interactions in complex **II** could be interpreted on the basis of the DFT calculation[15,20] and spin-polarization effect.[21] Experimental observation and theoretical analysis show that there is a critical bridging angle (Cu−N−Cu) of about 108.5°. The smaller angles lead to accidental orthogonality of the magnetic orbital, resulting in the ferromagnetic interaction between Cu(II) atoms, while an antiferromagnetic exchange interaction is expected with a large angle.[20] When our data are compared with the results shown in Table 8, it is found that the Cu−N−Cu angle is the smallest in all bis(end-on) azide-bridged Cu(II) complexes. The small J value could be interpreted as follows: the electronegative phenoxo atom lowers the HOMO energy, and the coordination geometry around Cu(II) ion is an intermediate between the ideal square-pyramidal and trigonal-bipyramidal geometries other than the ideal square-pyramid geometry on which the DFT calculation[15,20] was based; therefore, the magnetic orbital is contributed not only by $d_{x^2-y^2}$ but also by d_{z^2}, which leads to a weak ferromagnetic interaction.

The room-temperature magnetic moment μ_{eff} (2.23 μ_B) for complex **III** is considerably smaller than the expected value (3 μ_B) for three coupled Cu(II) ions, and it decreases gradually upon the cooling of complex **III**. This is characteristic of significant antiferromagnetic interactions between Cu(II) ions within the trinuclear complex. The magnetic analysis was carried out within the susceptibility equation based on $H = -2J(S_1S_2 + S_2S_3)$

$$\chi_M = (Ng^2\beta^2/4KT)[1 + \exp(-2J/KT) + 10\exp(J/KT)]/[1 + \exp(-2J/KT) + 2\exp(J/KT)] + N\alpha \quad (2)$$

where χ_M denotes the susceptibility per trinuclear complex and $N\alpha$ is the temperature-independent paramagnetism (180×10^{-6} cm^3 mol^{-1}). As shown in Figure 5b, the results indicate that there is a strong antiferromagnetic spin−exchange interaction among the nearest Cu(II) ions within each molecule.

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(19) McLachlan, G. A.; Fallon, G. D.; Martin, R. L.; Spiccia, L. *Inorg. Chem.* **1995**, *34*, 254.

(20) (a) Ruiz, E.; Alemany, P.; Aloarez, S.; Cano, J. *J. Am. Chem. Soc.* **1997**, *119*, 1297. (b) Escuer, A.; Vicente, R.; Mautner, F. A.; Goher, M. A. S. *Inorg. Chem.* **1997**, *36*, 1233. (c) Tandon, S. S.; Thompson, L. K.; Manuel, M. E.; Bridson, J. N. *Inorg. Chem.* **1994**, *33*, 5555.

(21) Charlot, M. F.; Kahn, O.; Chaillet, M.; Larrien, C. *J. Am. Chem. Soc.* **1986**, *108*, 2574, and references therein.

Table 8. Comparison of the Structural Data and Magnetic Properties for Some Bis(μ-N_3)$_2$ Binuclear Cu(II) Complexes

complex	θ (deg)	Cu−N (Å)[a]	Cu−Cu (Å)	J_{exp} (cm^{-1})	refs
$[Cu(terpy)(N_3)(H_2O)]_2(PF_6)_2$	95.7	1.927, 2.851	3.595	−2.9	22a
$[Cu(tbz)(N_3)_2]_2(CH_3OH)_2$	104.66	2.037, 2.059	3.2422	23	22b
$[Cu_2(t\text{-}Bupy)_4(N_3)_2](ClO_4)_2$	100.5	1.99, 1.97	3.042	105	22c
$Cu_2(n\text{-}N_3)_2(N_3)_2([24]ane\text{-}N_2O_6)$	101.65, 105.46	1.990, 2.043	3.162	70	16b
$[Cu_2(L^2)_2(N_3)_2]$ (**II**)	90.93	2.174, 2.215	3.129	1.03	this work

[a] Azide bridge.

The study of magneto−structural correlation has been performed in di-phenoxo-bridged Cu(II) complexes.[23] Recently, Thompson and co-workers[24] derived the magneto−structural relationship for bis(phenoxide)-bridged binuclear Cu(II) complexes, $-J = 31.95\alpha - 2462$ cm^{-1}, where α is defined as the Cu−O(phenol)−Cu angle. In complex **III**, the α angle is 98.26°, and the $-J$ value predicted by the above equation should be 677.4 cm^{-1}, which is much higher than in the experimental data mainly because the dihedral angle (165°) is defined by the two planes Cu(1)−O(1)−O(2) and Cu(2)−O(1)−O(2). To date, di-phenoxo-bridged Cu(II) complexes with a small α angle (α < 77°), in which a crossover from antiferromagnetism to ferromagnetism could be reached, are still not known.[24] To synthesize such complexes with a small α angle is still an unresolved problem.

The μ_{eff} value of complex **IV** is approximately constant in the range of 300−70 K (see Figure 5c), which is close to the value expected for uncoupled Cu(II) ion, but below 30 K, it decreases slightly, reaching a value of 1.38 μ_B at 4 K. This behavior indicates a slightly antiferromagnetically coupled one-dimensional compound. The magnetic analysis was carried out with the susceptibility equation[25] of isotropically coupled $S = {}^1/_2$ ions in antiferromagnetic linear chains

$$\chi_M = (Ng^2\beta^2/KT)[(A + BX + CX^2)/(1 + DX + EX^2 + FX^3)] \quad (3)$$

where χ_M denotes the susceptibility per Cu(II) complex, $X = |J|/KT$, $A = 0.25$, $B = 0.14995$, $C = 0.30094$, $D = 1.9862$, $E = 0.68854$, and $F = 6.0626$.

As shown in Figure 5c, least-squares fitting leads to $J = -1.30$ cm^{-1}, which is rather small. This small value may be related to the two adjacent Cu(II) environments of complex **IV**, in which Cu(1) ion adopts a distorted square-pyramidal coordination environment with the nearest neighbors in the basal plane of N(1)−N(11)−N(12)−Cl(3) and, eventually, a Cl(4) in the apical position. The unpaired electron is mainly described by a d_{xy}-type orbital pointing from Cu(1) toward the nearest neighbors in an antibonding fashion. However, owing to the slight distortion toward the trigonal bipyramid, the unpaired electron should be described by a ($d_{xy} + \lambda d_{z^2}$)-type orbital with residual spin density on the apical sites Cl(4). On other side of the bridge, the Cu(2) ion is in a distorted trigonal-bipyramidal coordination environment with residual spin density in the equatorial plane and residual spin density on the axial positions. Owing to some $d_z{}^2$ character of Cu(2), usually a weak magnetic interaction is possible. The result is in good agreement with the extended Hükel calculation.[17]

Conclusions and Comments

A series of new diazamesocyclic ligands functionalized by additional donor pendants have been synthesized and characterized. The interesting coordination modes of the four Cu(II) complexes with these ligands (**I**−**IV**) have been elucidated by X-ray structural analyses, and the magneto−structural correlations were investigated for complexes **II**−**V**. The following points were reached:

(1) By attaching one or two methylimidazole or phenol donor pendants to the framework of DACO, we obtained a series of new polydentate ligands, and the formation of mononuclear, binuclear, trinuclear, and alternating zigzag chain Cu(II) complexes has been achieved. Namely, the variation of the coordination modes of Cu(II) with DACO has been achieved here by the attachment of different pendant donor groups on its framework. We therefore conclude that the nature of the pendant donor groups on DACO is a determining factor governing the structure and properties of their metal complexes. This is an important point for the rational design and control of metal complexes with different structures and properties, which might be required for different applications. From the structures of our complexes and other reported metal complexes[9] with DACO ligands, we can conclude that DACO derivatives are good model ligands for the formation of metal complexes whose coordination geometries cannot be more than five-coordinated due to the stereochemical effect (boat/chair configuration of DACO) and whose pendant arms can provide bridging functionality. The first example of a unique alternating zigzag chain Cu(II) complex has been achieved by using a DACO ligand, which might provide a good example for the study of alternating chain complexes.

(2) With respect to the magnetic properties for the three complexes (**II**−**IV**), very different magnetic interactions were found to exist from weak ferromagnetic to weak antiferromagnetic and strong antiferromagnetic interactions. The bis(end-on) azido-bridged Cu(II) complex (**II**) shows both ferromagnetic and antiferromagnetic coupled interactions in different temperature ranges, while the trinuclear complex **III** shows strong antiferromagnetic interactions, and the chain complex **IV** shows weak antiferromagnetic coupled interactions. This indicates that the rational design of metal complexes having different magnetic properties might be achieved by selecting the proper functional donor groups. Furthermore, from our study on the binuclear complex, it may be concluded that the magnitude of the coupling interaction is not only governed by the θ angle but also dominated by a spin delocalization in the complexes. The study on the magnetic properties for the zigzag arrangement successfully confirmed the results based on the extended Hükel MO calculation.

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(22) (a) Cortes, R.; Urtiaga, M. K.; Lezama, L.; Larramendi, J. I. R.; Arriortua, M. I.; Rojo, T. *J. Chem. Soc., Dalton Trans.* **1993**, 3685. (b) Albada, G. A. V.; Lakin, M. T.; Veldman, N.; Spek, A. L.; Reedijk, J. *Inorg. Chem.* **1995**, *34*, 4910. (c) Aebersold, M. A.; Gillon, B.; Plantevin, O.; Pardi, L.; Kahn, O.; Bergerat, P.; Seggern, I. V.; Tuczek, F.; Ohrstriom, L.; Grand, A.; Lelievre-Berna, E. *J. Am. Chem. Soc.* **1998**, *120*, 5238.

(23) (a) Kahn, O. *Molecular Magnetism*; VCH: Weinheim, Germany, 1993; Chapter 8. (b) Charlot, M. F.; Jeannin, S.; Jeannin, Y.; Kahn, O.; Lucrece-Abaul, J.; Frere, M. J. *Inorg. Chem.* **1979**, *18*, 1675. (c) Chiari, B.; Piovesana, O.; Tarantelli, T.; Zanazzi, P. F. *Inorg. Chem.* **1987**, *26*, 952.

(24) Thompson, L. K.; Mandal, S. K.; Tandon, S. S.; Bridson, J. N.; Park, M. K. *Inorg. Chem.* **1996**, *35*, 3117.

(25) Ojima, H.; Nomoyama, K. *Coord. Chem. Rev.* **1988**, *92*, 85.

Acknowledgment. This work was financially supported by the National Natural Science Foundation of China (Grants 29771022 and 29971019) and the Trans-Century Talents Training Program Foundation from the State Education Ministry of China.

Supporting Information Available: Listings of the anisotropic thermal parameters, bond lengths, and angles for complexes **I**−**IV**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC000094D