Tetranuclear, Hexanuclear, and Octanuclear Copper(II) Complexes of a Series of Novel Dendritic Poly(phthalazine) Ligands

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A series of new branched, dendritic, polynucleating, poly(aminophthalazine) ligands involving two (N_8) (**O-P**, **C-P**), three (N_{12}) (G-P), and four (N_{16}) (**P-P**) connected phthalazine groups has been synthesized and their copper coordination chemistry investigated. 6,6′-(1,2-phenylenedioxy)bis[1,4-bis(2′-pyridylamino)phthalazine] (**C-P**) and 6,6′-oxybis[1,4-bis(2′-pyridylamino)phthalazine] (**O-P**) bind four copper(II) centers in two well-separated dinuclear copper pairs in one molecular entity in the derivatives [Cu_4(**C-P**)(μ_2-OH)$_2$(μ_2-NO$_3$)$_2$(H$_2$O)$_2$(NO$_3$)$_2$](NO$_3$)$_2$·4H$_2$O (**1**), {[Cu_4(**O-P**)(μ_2-OH)$_2$(μ_2-NO$_3$)$_2$(H$_2$O)$_7$]$_2$(μ_2-NO$_3$)}(NO$_3$)$_7$·6H$_2$O (**2**). Variable-temperature magnetic studies indicate strong local antiferromagnetic coupling in these hydroxide-bridged compounds, with nonexistent coupling across the ligand framework itself. The crystal and molecular structure for **1** and **2** are reported. **1** crystallizes in the monoclinic system, space group $P2_1/c$ (No. 14), with a = 13.346(4) Å, b = 37.71(1) Å, c = 21.519(6) Å, β = 91.04(2)°, and Z = 4. The structure was refined to R = 0.063 and R_w = 0.058 for 5958 unique reflections with $I > 2.50\sigma(I)$. **2** crystallizes in the monoclinic system, space group $C2/c$, with a = 31.948(5) Å, b = 30.900(8) Å, c = 12.683(6) Å, β = 96.22(2)°, and Z = 8. A poorer structural refinement gave R = 0.121 and R_w = 0.137 for 5634 unique reflections with $I > 2.00\sigma(I)$. In **1** two chemically identical, but structurally slightly different, tetranuclear species exist per unit cell. Pairs of square-pyramidal copper centers are bridged equatorially by hydroxides and phthalazine diazine units with Cu–OH–Cu angles in the range 110.4–116.7°, and Cu–Cu separations in the range 3.122–3.188 Å. In **2** pairs of six-coordinate copper centers are bridged equatorially by hydroxides and phthalazine groups with comparable dinuclear center dimensions to **1**. Two tetranuclear complexes are linked by a bidentate nitrate bridge to form an associated octanuclear species. External dimensions for both complexes are very large, bringing them well into the nanometer size range. Other polynuclear complexes involving three and four hydroxide-bridged copper(II) pairs have been synthesized and will be discussed in terms of their structural and magnetic properties.

Introduction

Most coordination complexes studied today fall into a relatively low molecular weight regime and involve one metal center per molecule. Binding two metal centers requires some special feature on the part of an organic ligand, which is usually a bidentate, bridging group, e.g. N_2 diazine (phthalazine, pyridazine, pyrazole, pyrazine, imidazole), alkoxide, phenoxide, etc., and is quite common. Extension beyond two metals provides more of a challenge, and frequently requires the use of "templating" techniques, where simple molecular fragments are organized prior to a series of condensation steps. Tetranuclear and octanuclear [(Cu$_4$)$_2$], and hexanuclear and even dodecanuclear [(Cu$_6$)$_2$] species can be achieved in this manner.[1–8] These systems involve a single, macrocyclic ligand encompassing four and six metals respectively. In the case of the dodecanuclear species[8] two hexanuclear macrocyclic halves are held together by μ_3-hydroxide bridges, forming a molecule with a molecular weight of about 2700, which would fit into a cylinder with a diameter of approximately 19 Å and a height of approximately 9.7 Å.

A recent surge of interest in "supramolecular species" with dimensions in the nanometer size range, and in particular those with high nuclearity, indicates that a certain degree of synthetic ingenuity is required to build such systems. Recent reports outline a novel approach to Ru$_{13}$ and Ru$_{22}$ dendrimeric systems involving a technique of combining a metal complex as a metal with a metal complex as a ligand (bridging ligand 2,3-bis(2-pyridyl)pyrazine).[9,10] However creating a single ligand, using organic techniques, with the capacity to accommodate large numbers of metals is a special challenge and relies, in part, on the availability of suitable, repeating building blocks. We have been successful in this regard by extending 1,2,4,5-tetracyanobenzene via the intermediate tetrasubstituted benzodipyrrole to produce 1,2,4,5-tetrakis(2-pyridyl(R)amino)benzodipyridazines (R = H, Me), which bind four copper(II) centers in two antiferromagnetically coupled pairs.[11,12] Each half of the molecule compares closely to the familiar dinuclear complexes of open chain, tetradentate hydrazinophthalazine (DHPH) and (pyridylamino)phthalazine (PAPR) ligands.[13–48]

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High nuclearity, polynuclear complexes, in which a single ligand can bind multiples of essentially identical, spin-coupled dinuclear centers attracted our interest because (a) they have the potential to act as novel multielectron-transfer catalysts, in particular if the individual units have demonstrated catalytic activity in corresponding monomeric species and (b) they could generate new magnetic materials or "polymagnets" if the coupled dinuclear centers orient themselves appropriately in the crystal lattice or could be connected appropriately within the lattice.

The coordination chemistry of mono(phthalazine) ligands is well developed,[13-48] and the hydroxide-bridged dinuclear copper(II) complexes are strongly antiferromagnetically coupled due to spin communication between the two copper centers through hydroxide and diazine bridges. In some instances quite high, positive reduction potentials have also been reported[32,33,37-39] and catalytic activity, e.g., for the aerial oxidation of catechols, has been demonstrated.[33,49] In the present work we report the synthesis of a series of novel, branched poly((pyridylamino)-phthalazines) with two, three, and four bis(pyridylamino)-phthalazine subunits attached to polyalcoholic substrates (Figure 1 a,b). Reaction with copper(II) salts produces tetranuclear, hexanuclear, and octanuclear derivatives with what is effectively a repeating three dimensional array of spin-coupled dinuclear centers. These complexes are discussed in terms of their structural, spectral, and magnetic properties. A preliminary report of the structure and some properties of **1** has already been published.[50]

Experimental Section

Physical Measurements. NMR spectra were recorded with a GE300 spectrometer (SiMe$_4$ internal standard); mass spectra were obtained with a VG micromass 7070 HS spectrometer with a direct insertion probe (EI) and a Kratos MS50TC ultra high resolution spectrometer (FABS with NOBA as matrix material). Electronic spectra were obtained with a Cary 5E spectrometer. C, H, N, analyses were carried out by Canadian Microanalytical Service, Delta, Canada, and copper analysis were carried out by EDTA titration. Variable-temperature magnetic susceptibility data were obtained in the range 5−305 K using an Oxford Instruments superconducting Faraday magnetic susceptibility system with a Sartorius 4432 microbalance. A main solenoid field of 1.5 T and a gradient field of 10 T m^{-1} were employed. Calibration data were obtained using HgCo(NCS)$_4$.

Synthesis of Ligands. A reaction scheme for the synthesis of the ligands and their isoindoline intermediates is shown in Figure 1a,b. Figure 1a outlines the synthetic sequence to the catechol-bridged bis-(phthalazine) **C-P**, while Figure 1b depicts a general synthesis of the other ligands and their precursors. Ligand and precursor abbreviations are assigned according to the branched substrate and isoindoline (**I**) or phthalazine (**P**) (Figure 1): *o*-catechol isoindoline (**C-I**), *o*-catechol phthalazine (**C-P**); glycerol isoindoline (**G-I**), glycerol phthalazine (**G-P**), pentaerythritol isoindoline (**P-I**), and pentaerythritol phthalazine (**P-P**).

a. 5,5′-Oxybis[1,3-bis(2′-pyridylimino)isoindoline] (O-I) 4,4′-Oxybis[1,2-dicyanobenzene][51] (2.5 g, 9.3 mmol) and a large excess of 2-aminopyridine were mixed and heated under N$_2$ at 170 °C for about 24 h, cooled to room temperature, and then refluxed with 100 mL diethyl ether, the mixture was filtered, and the solid residue was washed with diethyl ether and acetone to remove unreacted starting materials and byproducts and dried under vacuum to give a dark yellow solid. The yellow solid was dissolved in CHCl$_3$ (100 mL) and the solution refluxed with activated charcoal for 0.5 h, filtered, and concentrated to about 30 mL. MeOH (150 mL) was then added and the mixture allowed to stand overnight. Yellow microcrystals were obtained, which were filtered off, washed with MeOH and diethyl ether, and dried under vacuum. (Yield: 1.7 g; 29.7%.) Mp: 234−236 °C. Anal. Calcd for C$_{36}$H$_{24}$N$_{10}$O: C, 70.58; H, 3.95; N, 22.86. Found: C, 70.52; H, 4.10; N, 22.54. Mass spectrum, major mass peaks in *m/z* (relative intensity) corresponding to the molecular ion and reasonable degradation fragments: 613 (87), 612 (P) (100), 611 (30), 534 (35), 517 (20), 440 (79), 363 (13), 267 (1.4), 78 (100).

b. 6,6′Oxybis[1,4-bis(2′-pyridylamino)phthalazine] (O-P). O-I (1.82g, 2.97 mmol) was dissolved in a hot CHCl$_3$/MeOH mixture (25 mL), a solution of 5 mL of 85% hydrazine hydrate in 125 mL of MeOH added, and the mixture refluxed for 48 h. When this mixture was allowed to stand overnight, a pale yellow solid appeared, which was filtered off, washed with MeOH and diethyl ether, and dried under vacuum. Yield: 1.4 g; 73.3%. Mp: 283−285 °C. Anal. Calcd for C$_{36}$H$_{26}$N$_{12}$O.1.5CH$_3$OH: C, 65.21; H, 4.38; N, 24.34. Found: C, 65.65; H, 4.33; N, 24.06. Mass spectrum, major mass peaks in *m/z* (relative intensity): 643 (22), 642 (P) (65), 550 (14), 548 (13), 455 (22), 320 (9), 94 (24), 78 (100).

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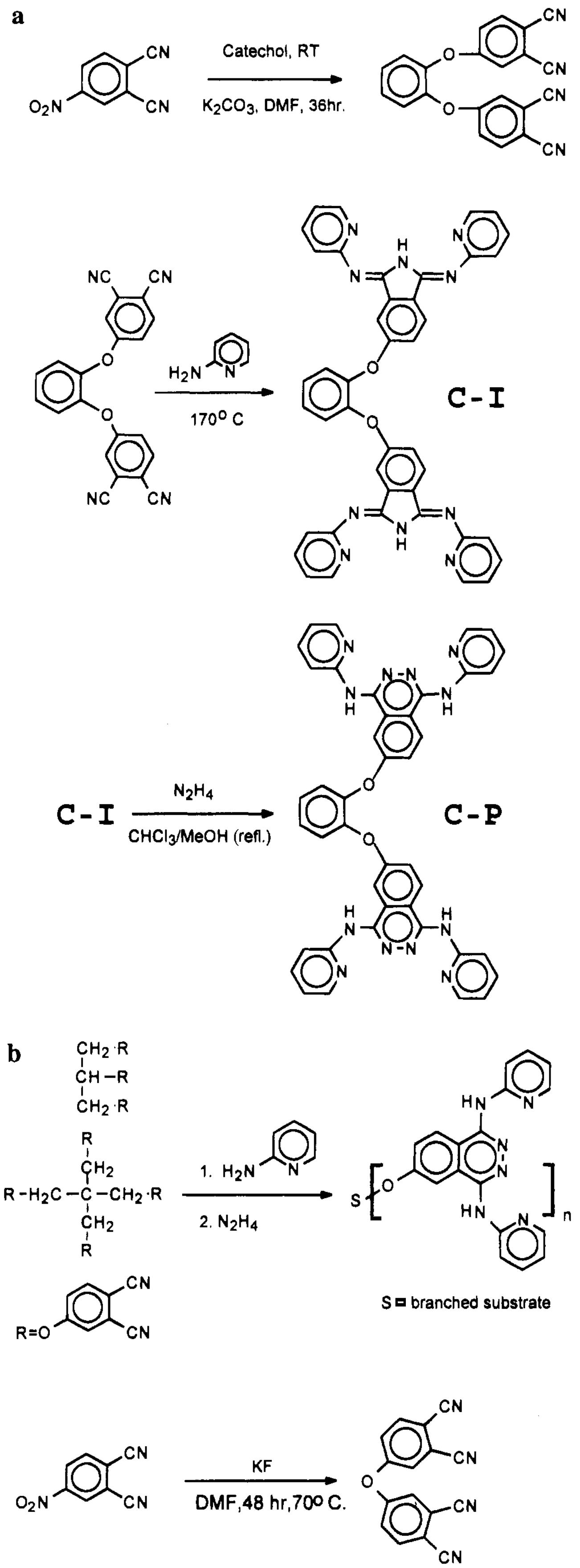

Figure 1. (a) Reaction scheme for synthesis of **C-P**. (b) General reaction scheme for synthesis of the ligands.

C-I was prepared in the same manner from 1,2-bis(3,4-dicyanophenoxy)benzene,[52] and **C-P** was prepared by a similar reaction of the isoindoline intermediate with hydrazine. **C-I** (yield: 25.7%): mp 268–271 °C. Anal. Calcd for $C_{42}H_{28}N_{10}O_2\cdot 2CH_3OH$: C, 68.75; H, 4.72; N, 18.22. Found: C, 68.60; H, 4.03; N, 18.01. Mass spectrum, major mass peaks in *m/z* (relative intensity): 626 (P − Py) (12), 609 (5), 532 (29), 455 (3), 440 (2), 352 (7), 313 (3), 170 (3), 155 (2), 94 (3), 78 (100). **C-P** (yield: 45%): mp 241–244 °C. Anal. Calcd for $C_{42}H_{30}N_{12}O_2$: C,68.66; H, 4.12; N, 22.88. Found: C, 68.55; H, 4.49; N, 22.89. Mass spectrum, major mass peaks in *m/z* (relative intensity): 641 (M − NH − Py) (30), 624 (15), 547 (46), 532 (7), 519 (2), 455 (8), 422 (4), 403 (3), 367 (17), 311 (5), 194 (3), 155 (3), 95 (13), 78 (100).

c. 1,2,3-Tris(3,4-dicyanophenoxy)propane (G-CN). 4-Nitrophthalonitrile[53,54] (6.93 g, 0.04 mol), K_2CO_3 (17.0 g), and glycerol (1.26 g, 0.014 mol) were stirred in DMF (80 mL) for 72 h at room temperature and the mixture poured into 1 L of water. A pale yellow solid formed, which was filtered off, washed with water, and dried under vacuum. Yield: 5.7 g; 91%. Mp: 214–218 °C.

Mass spectrum, major mass peaks in *m/z* (relative intensity): 470 (P) (12), 183 (57), 158 (12), 157 (100), 155 (16), 144 (43), 129 (13), 127 (40), 116 (11), 100 (10). ^1H NMR (302 K, DMSO-d_6), δ (relative intensity): 4.61 (4) (doublet, CH_2), 5.52 (1) (multiplet, CH), 7.50 (3) (multiplet, H_6), 7.85 (3) (multiplet, H_5), 8.05 (3) (doublet, H_2).

d. Preparation of G-I and G-P. G-I was prepared as above from **G-CN**, and **G-P** by reaction of **G-I** with hydrazine as described previously. **G-I**: yield: 54%; mp 209–212 °C. Anal. Calcd for $C_{57}H_{41}N_{15}O_3\cdot 2.5H_2O$: C, 66.53; H, 4.51; N, 20.42. Found: C, 66.43; H, 4.53; N, 20.49. Mass spectrum, major mass peaks in *m/z* (relative intensity) (FABS): 984 (P) (2), 983 (5), 982 (6), 906 (1), 304 (4), 260 (8), 238 (2), 216 (11), 194 (14), 176 (4), 172 (16), 154 (16), 150 (100), 136 (14).

G-P: yield: 98%; mp 188–194 °C. Anal. Calcd for $C_{57}H_{44}N_{18}O_3\cdot 4H_2O$ C, 62.17; H, 4.76; N, 22.90. Found: C, 61.93; H, 4.88; N, 22.75. Mass spectrum, major mass peaks in *m/z* (relative intensity) (FABS): 1028 (P) (4), 1027 (4), 514 (1), 371 (3), 331 (6), 330 (4), 329 (9), 314 (2), 308 (4), 289 (10), 273 (4), 237 (2), 155 (24), 153 (7), 139 (11).

e. Preparation of P-I and P-P. P-I was prepared from tetrakis-[(3,4-dicyanophenoxy)methyl]methane,[55] and the ring was expanded in the usual way to produce **P-P**.

P-I: yield: 98%; mp >300 °C. Anal. Calcd for $C_{77}H_{56}N_{20}O_4\cdot 1.5H_2O$: C, 68.38; H, 4.40; N, 20.71. Found: C, 67.91; H, 5.05; N, 21.16. Mass spectrum, major mass peaks in *m/z* (relative intensity) (FABS): 1326 (P + H)(5), 1324 (0.3), 1249 (5), 1173 (2), 482 (7), 460 (15), 329 (61), 309 (6), 307 (100).

P-P: yield: 55%; mp 225–230 °C. Anal. Calcd for $C_{77}H_{60}N_{24}O_4\cdot 3H_2O$: C, 64.24; H, 4.62; N, 23.36. Found: C, 64.79; H, 4.67; N, 22.88. Mass spectrum, major mass peaks in *m/z* (relative intensity) (FABS): 1386 (P) (4), 1384 (16), 1307 (9), 1197 (2), 979 (1), 329 (64), 237 (42), 154 (100).

Synthesis of the Complexes. $[Cu_4(C\text{-}P)(\mu_2\text{-}OH)_2(\mu_2\text{-}NO_3)_2(H_2O)_2(NO_3)_2](NO_3)_2\cdot 2H_2O$ (1), $\{[Cu_4(O\text{-}P)(\mu_2\text{-}OH)_2(\mu_2\text{-}NO_3)_2(H_2O)_7]_2(\mu_2\text{-}NO_3)\}(NO_3)_7\cdot 6H_2O$ (2). C-P (0.1 g, 0.14 mmol) was added to an aqueous solution of excess $Cu(NO_3)_2\cdot 3H_2O$, and the mixture was refluxed for 24 h. The green solution was filtered to remove unreacted ligand and concentrated to about 10 mL. Green crystals formed on standing by adding a small amount of ethanol; these were filtered, washed with EtOH, and dried under vacuum. Anal. Calcd for $C_{42}H_{40}N_{18}O_{26}Cu_4$ (**1**): C, 34.39; H, 2.75; N, 17.19. Found: C, 34.42; H, 2.67; N, 17.34. The crystals crumble readily on drying, losing lattice solvent. An X-ray sample was kept in contact with the mother liquid prior to crystallographic analysis. **2** was prepared similarly by reacting **O-P** with $Cu(NO_3)_2$. Solid $NaNO_3$ was added to a concentrated aqueous solution of the initial green reaction product and the solution concentrated on a steam bath. Green crystals suitable for X-ray analysis were obtained after allowing the concentrated aqueous solution to stand for several days and were kept in contact with the mother liquor because

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of solvent loss on exposure to air. Elemental analysis on this sample indicates the presence of approximately 10 water molecules. Anal. Calcd for $C_{36}H_{48}N_{18}O_{31}Cu_4$ (**2**): C, 29.16; H, 3.24; N, 17.01; Cu, 17.04. Found: C, 28.63; H, 2.96; N, 17.57; Cu, 17.01.

[Cu$_4$(C-P)(OH)$_2$(SO$_4$)$_2$]SO$_4$·4H$_2$O (3). Excess aqueous sodium sulfate was added to an aqueous solution of **1** and the mixture heated on a steam bath for a few minutes. A green solid formed, which was filtered off, washed with water and ethyl alcohol, and dried under vacuum. Anal. Calcd for $C_{46}H_{40}N_{12}O_{20}S_3Cu_4$: C, 36.48; H, 3.47; N, 12.16; Found: C, 36.33; H, 3.01; N, 12.54.

[Cu$_6$(G-P)(OH)$_3$Cl$_9$]·4H$_2$O (4), and [Cu$_6$(G-P)(OH)$_3$Br$_9$]·6H$_2$O (5). **G-P** (0.2 g, 0.19 mmol) was added to an aqueous solution (15 mL) of $CuCl_2 \cdot 2H_2O$ (0.6 g, 3.5 mmol), and the mixture refluxed for 24 h. An insoluble green solid formed, which was filtered off, washed with water, methanol, and ether, and dried under vacuum. Yield: 0.2 g. Anal. Calcd for $C_{57}H_{55}N_{18}O_{10}Cl_9Cu_6$ (**4**): C, 36.95; H, 2.97; N, 13.61; Cu, 20.61; Found: C, 37.00; H, 3.16; N, 13.50; Cu, 19.86. **5** was obtained in a similar fashion as a dark green solid. Anal. Calcd for $C_{57}H_{59}N_{18}O_{12}Br_9Cu_6$: C, 29.90; H, 2.64; N, 11.01; Cu, 16.64; Found: C, 30.49; H, 2.40; N, 11.09; Cu, 15.94.

[Cu$_6$(G-P)(OH)$_3$(NO$_3$)$_9$]·12H$_2$O (6). **G-P** (0.25g, 0.24 mmol) was suspended in ethanol (30 mL) and an aqueous solution (30 mL), of $Cu(NO_3)_2 \cdot 3H_2O$ (1.0 g, 4.1 mmol) was added and the mixture refluxed for 72 h, forming a deep green solution. The volume of the solution was reduced to about 20 mL with the formation of a yellow green solid, which was filtered off, washed with ethanol, and dried under vacuum. Yield: 0.40 g. Anal. Calcd for $C_{57}H_{71}N_{27}O_{45}Cu_6$: C, 30.62; H, 3.20; N, 16.92; Cu, 17.06: Found: C, 30.07; H, 2.46; N, 17.45; Cu, 16.82.

[Cu$_8$(P-P)(OH)$_4$Cl$_{12}$]·10H$_2$O (7), [Cu$_8$(P-P)(OH)$_4$Br$_{12}$]·8H$_2$O (8). **P-P** (0.15g, 0.11 mmol) was added to a solution of $CuCl_2 \cdot 2H_2O$ (0.5 g, 2.9 mmol) dissolved in methanol (50 mL) and the mixture refluxed for 36 h. A green solid formed, which was filtered off, washed with methanol and diethyl ether, and dried under vacuum. Yield: 0.22 g. Anal. Calcd for $C_{77}H_{84}N_{24}O_{18}Cl_{12}Cu_8$: C, 36.02; H, 3.12; N, 13.09; Cu, 20.08: Found: C, 35.96; H, 2.84; N, 12.96; Cu, 20.72. **8** was prepared in a similar manner. Anal. Calcd for $C_{77}H_{80}N_{24}O_{16}Br_{12}Cu_8$: C, 30.18; H, 2.63; N, 10.97; Cu, 16.59: Found: C, 30.45; H, 2.41; N, 10.89; Cu, 15.93.

Crystallographic Data Collection and Refinement of the Structures. [Cu$_4$(C-P)(μ_2-OH)$_2$(μ_2-NO$_3$)$_2$(NO$_3$)$_2$(H$_2$O)$_2$](NO$_3$)$_2$·4H$_2$O (1). Crystals of **1** are green hexagonal plates. The diffraction intensities of an approximately 0.40 × 0.30 × 0.05 mm crystal, were collected with graphite-monochromatized Mo Kα radiation using the ω-2θ scan mode to $2\theta_{max} = 44.9°$ on a Rigaku AFC6S diffractometer at −80(1) °C. Of a total of 10 911 measured reflections, 10 338 were unique and 5958 reflections were observed with $I_{net} > 2.5\sigma(I_{net})$. Data were corrected for Lorentz−polarization effects. The cell parameters were obtained by the least-squares refinement of the setting angles of 24 reflections with $2\theta = 9.12-11.23°$. An empirical absorption correction was applied, using the program DIFABS,[56] which resulted in transmission factors ranging from 0.74 to 1.00.

Table 1. Summary of Crystallographic Data for [Cu$_4$(**C-P**)(μ_2-OH)$_2$(μ_2-NO$_3$)$_2$(H$_2$O)$_2$(NO$_3$)$_2$](NO$_3$)$_2$·4H$_2$O (**1**) and {[Cu$_4$(**O-P**)(μ_2-OH)$_2$(μ_2-NO$_3$)$_2$(H$_2$O)$_7$]$_2$(μ_2-NO$_3$)}(NO$_3$)$_7$·6H$_2$O (**2**)

	1	**2**
empirical formula	$C_{84}H_{69}O_{52}N_{36}Cu_8$	$C_{36}H_{26}O_{33.5}N_{18}Cu_4$
fw	2923.05	1500.89
space group	$P2_1/c$	$C2/c$
a (Å)	13.346(4)	31.948(5)
b (Å)	37.71(1)	30.900(8)
c (Å)	21.519(6)	12.683(6)
β (deg)	91.04(2)	96.22(2)
V (Å)^3	10829(6)	12446(6)
Z	4	8
ρ_{calcd} (g cm^{-3})	1.793	1.602
μ (cm^{-1})	16.56	14.51
λ (Å)	0.710 69	0.710 69
GOF	1.96	5.54
T (°C)	−80	−90
R^a	0.063	0.121
$R_w{}^b$	0.058	0.137

^{a} $R = \Sigma(|F_o| - |F_c|)/\Sigma(|F_o|)$. ^{b} $R_w = [(\Sigma w(|F_o| - |F_c|)^2/\Sigma w(|F_o|)^2]^{1/2}$.

The structure was solved by direct methods[57,58] and only the copper atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on 5958 reflections and 762 variables and converged with $R = 0.063$ and $R_w = 0.049$, with weights based on counting statistics. The maximum and minimum peaks on the final difference map corresponded to +1.09 and −0.84 e$^-$/Å^3 respectively. Neutral atom scattering factors[59] and anomalous dispersion terms[60,61] were taken from the usual sources. All calculations were performed with the TEXSAN[62] crystallographic software package using a VAX 3100 work station. A summary of crystal and other data is given in Table 1. Atomic coordinates (Table S1), thermal parameters (Table S2), a full listing of bond distances and angles (Table S3), and least-squares planes data (Table S4) are included as Supporting Information.

{[Cu$_4$(O-P)(μ_2-OH)$_2$(μ_2-NO$_3$)$_2$(H$_2$O)$_7$]$_2$(μ_2-NO$_3$)}(NO$_3$)$_7$·6H$_2$O (2). Structural data were collected for a green irregular plate-like crystal of **2** with approximate dimensions 0.40 × 0.25 × 0.15 mm at −90(1) °C by the same procedure outlined for **1**. The structure was solved by direct methods,[57,58] clearly revealing the main complex fragments and some hydrogen-bonded water molecules. No further improvement of the modelling of the structure could be made, and additional lattice water molecules, which were expected to be present in partially occupied sites, could not be adequately identified, thus preventing a reasonable overall structural refinement. Attempts to refine C, N, and O atoms anisotropically led to unrealistic ellipsoids, and the inclusion of additional solvent atoms and/or the refinement of solvent site occupancies, while lowering the R values, resulted in nonconvergence. The irregular shape of the crystal precluded analytical corrections such as AGNOST, and DIFABS was considered inappropriate since the contents of the cell have not been fully included in the model. However the octanuclear complex fragment has been fully described, albeit with limited precision.

A summary of crystal and other data is given in Table 1. Atomic coordinates (Table S5), thermal parameters (Table S6), and a full listing of bond distances and angles (Table S7) are included as supplementary material.

Results and Discussion

The synthesis of polynucleating ligands and especially polynuclear complexes is a challenge, due in large measure to the limitations associated with providing a repeating arrangement of donor groups appropriately placed within the ligand structure. 4-Nitrophthalonitrile condenses conveniently with hydroxyl groups in the presence of base (K_2CO_3/DMF) to produce aliphatic and aromatic dicyano ethers[51−54]. These polyphthalonitriles have been converted to their corresponding isoindolines and cyclized to produce poly(metallophthalocyanines),[52,54,55] with, so far, up to four phthalocyanine units. A simple extension of these poly(phthalonitriles) to poly((dipyridylimino)isoindolines), followed by ring expansion with hydrazine (Figure 1a,b) leads to a series of "dendritic" poly(aminophthalazines), with a capacity for up to eight metals in the case of **P-P**, which is based on pentaerythritol as the polyalcoholic substrate.

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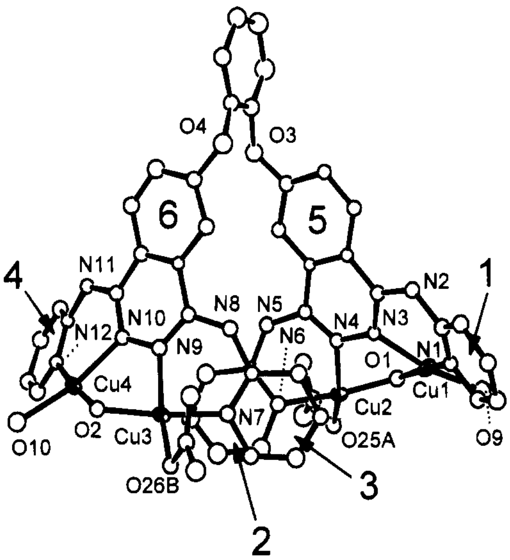

Figure 2. Structural representation of $[Cu_4(\mathbf{C\text{-}P})(\mu_2\text{-}OH)_2(\mu_2\text{-}NO_3)_2(H_2O)_2(NO_3)_2]\ (NO_3)_2\cdot 4H_2O$ (**1**).

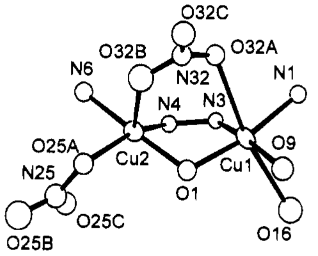

Figure 3. Structural representation of one dinuclear center in **1**.

Table 2. Bond Distances (Å) and Angles (deg) Relevant to the Copper Coordination Spheres in $[Cu_4(\mathbf{C\text{-}P})(\mu_2\text{-}OH)_2(\mu_2\text{-}NO_3)_2(H_2O)_2(NO_3)_2](NO_3)_2\cdot 4H_2O$ (**1**)

Cu(1)−O(1)	1.904(9)	Cu(2)−O(32B)	2.26(1)
Cu(1)−O(9)	1.99(1)	Cu(3)−O(2)	1.906(9)
Cu(1)−N(1)	1.96(1)	Cu(3)−O(26B)	2.038(9)
Cu(1)−N(3)	2.00(1)	Cu(3)−N(7)	1.98(1)
Cu(1)−O(32A)	2.589(9)	Cu(3)−N(9)	2.00(1)
Cu(1)−O(16)	2.57(1)	Cu(3)−O(29C)	2.30(1)
Cu(2)−O(1)	1.897(9)	Cu(4)−O(2)	1.897(9)
Cu(2)−O(25A)	2.053(9)	Cu(4)−O(10)	1.99(1)
Cu(2)−O(32B)	2.26(1)	Cu(4)−N(10)	2.01(1)
Cu(2)−N(4)	2.02(1)	Cu(4)−N(12)	1.96(1)
Cu(2)−N(6)	1.97(1)	Cu(4)−O(29A)	2.48(1)
Cu(1)−Cu(2)	3.163(3)	Cu(5)−Cu(6)	3.122(3)
Cu(3)−Cu(4)	3.122(3)	Cu(7)−Cu(8)	3.188(3)
O(1)−Cu(1)−O(9)	92.5(4)	O(32B)−Cu(2)−N(6)	95.1(4)
O(1)−Cu(1)−N(1)	169.5(4)	N(4)−Cu(2)−N(6)	87.7(5)
O(1)−Cu(1)−N(3)	88.0(4)	O(2)−Cu(3)−O(26B)	96.9(4)
O(9)−Cu(1)−N(1)	93.7(4)	N(7)−Cu(3)−N(9)	87.8(5)
O(9)−Cu(1)−N(3)	169.7(4)	O(2)−Cu(3)−N(7)	173.2(4)
N(1)−Cu(1)−N(3)	87.4(4)	O(2)−Cu(3)−N(9)	85.5(4)
O(1)−Cu(2)−O(25A)	95.4(4)	O(26B)−Cu(3)−N(7)	89.7(4)
O(1)−Cu(2)−O(32B)	89.2(4)	O(26B)−Cu(3)−N(9)	153.3(4)
O(1)−Cu(2)−N(4)	85.8(4)	N(10)−Cu(4)−N(12)	87.9(5)
O(1)−Cu(2)−N(6)	173.5(4)	O(2)−Cu(4)−O(10)	91.9(4)
O(25A)−Cu(2)−O(32B)	77.9(4)	O(2)−Cu(4)−N(10)	87.5(4)
O(25A)−Cu(2)−N(4)	156.8(4)	O(10)−Cu(4)−N(12)	93.4(4)
O(25A)−Cu(2)−N(6)	90.3(4)	O(10)−Cu(4)−N(10)	165.9(4)
O(32B)−Cu(2)−N(4)	125.4(4)	O(2)−Cu(4)−N(12)	174.2(4)
Cu(1)−O(1)−Cu(2)	112.6(5)	Cu(5)−O(5)−Cu(6)	111.4(5)
Cu(3)−O(2)−Cu(4)	110.4(4)	Cu(7)−O(6)−Cu(8)	116.7(5)

Description of the Structures. The structure of **1** is shown in Figures 2 and 3, and interatomic distances and angles relevant to the copper coordination spheres are given in Table 2. There are two chemically equivalent, but structurally slightly different and not symmetry related tetranuclear copper(II) complexes present in the unit cell, and one of these (**1**) is illustrated in Figure 2 (molecule 1 Cu(1)Cu(2)Cu(3)Cu(4); molecule 2 Cu(5)Cu(6)Cu(7)Cu(8); axial contacts have been omitted for clarity; distances and angles for molecule 2 are found in Supporting Information Table S3). The basic structure represents a unique arrangement in which four copper(II) centers are grouped into two pairs on each side of the catechol group, and within each dinuclear unit the coppers are bridged equatorially by the diazine N_2 group and by a hydroxide and axially by a bidentate nitrate (Figure 3 illustrates one dinuclear center showing the axial contacts). The dinuclear center Cu(1)−Cu(2) differs slightly from the rest in that Cu(1) is considered to be six-coordinate with a long axial contact to a water molecule (Cu(1)−O(16) = 2.57(1) Å). The other dinuclear centers involve square-pyramidal copper atoms with additional basal sites occupied by monodentate nitrates and water molecules. Equatorial copper−ligand donor distances fall in the range 1.866(9)−2.053(7) Å, and compare closely with those in related monomeric dinuclear complexes. The shortest equatorial distances involve the hydroxide bridges (1.866(9)−1.906(9) Å). Much longer axial distances are found to the bidentate bridging nitrates, which are bound in an asymmetric fashion with a relatively long and short copper−oxygen contact in all cases. The long Cu(1)−O(32A) distance (2.589(9) Å) is a reflection on the presence of a second axial ligand ($H_2O(16)$) bound to Cu(1) (Figure 3). Intradinuclear copper-copper separations fall in the range 3.122(3)−3.188(3) Å, with large Cu−OH−Cu bridge angles in the range 110.4(4)−116.7(5)° (average 112.8(5)°). **1** is structurally similar to the binuclear Cu(II) (pyridylamino)phthalazine complexes $[Cu_2(PAP4Me)(\mu_2\text{-}OH)(H_2O)_2(\mu_2\text{-}NO_3)(NO_3)]NO_3$ and $[Cu_2(PAP)(\mu_2\text{-}OH)(\mu_2\text{-}SO_4)Cl]\cdot 2H_2O$,[29] which involve square-pyramidal copper(II) centers bridged equatorially by the phthalazine-diazine (N_2) and a hydroxy group and axially by a bidentate anion. The pendant pyridine rings in **1** are twisted with respect to the phthalazine groups (dihedral angles (1−5) 38.4°, (2−5) 28.3°, (3−6) 32.0°, and (4−6) 41.5° for molecule 1 (Figure 2): comparable dihedral angles for molecule 2 are 28.3°, 34.2°, 36.4°, 33.1°) in a *syn* conformation, with a twist angle similar to those found in the monomeric PAP4Me complex.[29] As is usual in complexes of this sort, the dinuclear centers are folded along the Cu−Cu axes, with fold angles between the Cu_2N_2 and Cu(OH)Cu least squares planes of 129.9 and 125.9° for molecule 1 and 132.1 and 138.0° for molecule 2.

The two dinuclear centers do not lie close enough to each other for any direct interaction between them, and the distance between the extreme copper atoms is around 10 Å (Cu(1)−Cu(4) 10.475(3) Å). However the folding of the ligand around the connecting 1,2-catecholyl residue does cause some overlay of the two dinuclear centers, with the closest approach associated with two pyridine rings (Figure 2; 2,3). These rings are essentially parallel (dihedral angles 5.4° (molecule 1), 4.8° (molecule 2) between the pyridine mean planes) and quite closely spaced (distances expressed from pyridine nitrogen to adjacent pyridine mean plane: N(7)−pyr(N(6)) 3.76 Å; N(6)−pyr(N(7)) 3.68 Å; N(19)−pyr(N(18)) 4.35 Å; N(18)−pyr(N(19)) 4.35 Å).

The structural solution for **2** was hampered by our inability to completely resolve what appear to be localized groups of water molecules in the lattice. However, the main molecular fragment is clearly identified, and consists of a dimeric unit in which two tetranuclear complexes are linked by two axial interactions at Cu(2) to a nitrate bridge (N(17) to form an octanuclear complex (Figure 4). Bond distances and angles relevant to the copper coordination spheres are given in Table

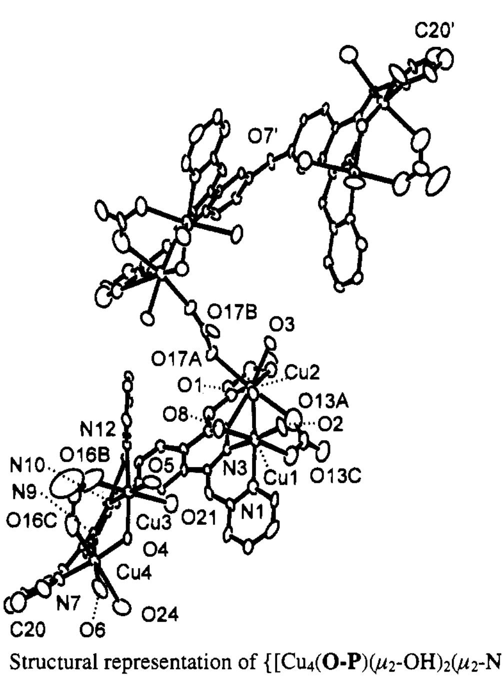

Figure 4. Structural representation of $\{[Cu_4(\mathbf{O\text{-}P})(\mu_2\text{-}OH)_2(\mu_2\text{-}NO_3)_2(H_2O)_7]_2(\mu_2\text{-}NO_3)\}(NO_3)_7{\cdot}6H_2O$ (**2**).

Table 3. Bond Distances (Å) and Angles (deg) Relevant to the Copper Coordination Spheres in $\{[Cu_4(O\text{-}P)(\mu_2\text{-}OH)_2(\mu_2\text{-}NO_3)_2(H_2O)_7]_2(\mu_2\text{-}NO_3)\}(NO_3)_7{\cdot}6H_2O$ (**2**)

Cu(1)−O(1)	1.89(2)	Cu(3)−O(5)	2.02(2)
Cu(1)−O(2)	2.02(2)	Cu(3)−N(10)	2.01(2)
Cu(1)−N(1)	1.95(2)	Cu(3)−N(12)	1.95(2)
Cu(1)−N(3)	2.01(2)	Cu(3)−O(16B)	2.50(3)
Cu(1)−O(13C)	2.46(2)	Cu(3)−O(21)	2.62(2)
Cu(1)−O(8)	2.58(2)	Cu(4)−O(4)	1.92(1)
Cu(2)−O(1)	1.88(2)	Cu(4)−O(6)	1.99(2)
Cu(2)−O(3)	2.02(2)	Cu(4)−N(7)	1.98(2)
Cu(2)−N(4)	2.05(2)	Cu(4)−N(9)	2.05(2)
Cu(2)−N(6)	1.92(2)	Cu(4)−O(16C)	2.48(3)
Cu(2)−O(17A)'	2.48(2)	Cu(4)−O(24)	2.56(2)
Cu(2)−O(13A)	2.53(3)	Cu(1)−Cu(2)	3.138(4)
Cu(3)−O(4)	1.89(1)	Cu(3)−Cu(4)	3.206(4)
O(1)−Cu(1)−O(2)	89.4(7)	O(4)−Cu(3)−N(10)	89.2(6)
O(1)−Cu(1)−N(1)	174.8(7)	O(4)−Cu(3)−N(12)	174.5(7)
O(1)−Cu(1)−N(3)	87.6(7)	O(5)−Cu(3)−N(10)	172.5(7)
O(2)−Cu(1)−N(1)	93.2(7)	O(5)−Cu(3)−N(12)	92.8(7)
O(2)−Cu(1)−N(3)	176.5(7)	N(10)−Cu(3)−N(12)	88.8(7)
N(1)−Cu(1)−N(3)	89.7(7)	O(4)−Cu(4)−O(6)	88.6(7)
O(1)−Cu(2)−O(3)	91.2(7)	O(4)−Cu(4)−N(7)	174.7(7)
O(1)−Cu(2)−N(4)	89.5(7)	O(4)−Cu(4)−N(9)	88.0(6)
O(1)−Cu(2)−N(6)	175.9(8)	O(6)−Cu(4)−N(7)	94.6(8)
O(3)−Cu(2)−N(4)	170.9(7)	O(6)−Cu(4)−N(9)	173.9(7)
O(3)−Cu(2)−N(6)	91.2(7)	N(7)−Cu(4)−N(9)	89.1(7)
N(4)−Cu(2)−N(6)	88.8(7)	Cu(1)−O(1)−Cu(2)	112.9(8)
O(4)−Cu(3)−O(5)	89.8(7)	Cu(3)−O(4)−Cu(4)	114.7(7)

3. A 2-fold rotational axis along the N(17)−O(17B) bond, relates the halves of the molecule. The six-coordinate copper(II) centers in each dinuclear fragment are bridged by phthalazine (N_2) and hydroxide groups in the equatorial plane and by an axial nitrate. Other coordination sites are occupied by water molecules, with the exception of O(17A), bound to Cu(2), which is part of the bridging nitrate. Intra-dinuclear copper-copper separations (Cu(1)−Cu(2) 3.138(4) Å, Cu(3)−Cu(4) 3.206(4) Å), and Cu−(OH)−Cu angles (Cu(1)−O(1)−Cu(2) 112.9(8)°, Cu(3)−O(4)−Cu(4) 114.7(7)°) are comparable with those in **1**. In plane copper−ligand distances are all 2.05 Å, or less, with contacts to the bridging hydroxide which are substantially shorter than the others (Cu(1)−O(1) 1.89(2) Å, Cu(2)−O(1) 1.88(2) Å, Cu(3)−O(4) 1.89(1) Å, Cu(4)−O(4) 1.92(1) Å). The axial copper−oxygen distances fall in the range 2.46−2.62 Å, typical for tetragonal, six-coordinate copper. Cu(2) is bound to an intramolecular nitrate bridge (Cu(2)−O(13A) 2.53(3) Å) and an intermolecular nitrate bridge (Cu(2)−O(17A) 2.48(2) Å).

Each half of the tetranuclear species is twisted about the oxygen (O(7)) atom connecting the two phthalazine subunits in such a way that the two dinuclear centers do not approach each other closely enough for any possible contact between the copper atoms, thus creating a complex with large external dimensions. Within the same tetranuclear entity inter-dinuclear copper−copper separations are quite long (8.8−13.3 Å), and the length of the tetranuclear species is estimated to be about 20 Å (C(20)−C(16) 19.9 Å), placing it squarely in the nanometer scale range. The dimeric, octanuclear complex cation is even longer, with a length of approximately 32 Å (C(20)−C(20)[65602] 31.5 Å).

Spectral and Magnetic Properties. The infrared spectra of the (polyaminophthalazine) ligands exhibit bands around 990 cm^{-1}, which are associated with a pyridine ring breathing mode of vibration, and are typically shifted to higher energy by 20−30 cm^{-1} on coordination.[16] The infrared spectra of all the complexes are similar in this region, with a pyridine ring breathing band in excess of 1000 cm^{-1} (Table 4) indicating coordination of all the pyridine residues. Infrared spectra of all the complexes have characteristic absorptions around 3500 cm^{-1} or above, associated with the bridging OH group, and coordinated water. Far-infrared spectra for the complexes are very complex and difficult to assign, but internal comparisons of **4** and **5** and **7** and **8** and with other derivatives, indicate the presence of coordinated halogen. The nitrate complexes **1** and **2** exhibit complex nitrate combination bands ($\nu_1 + \nu_4$)[63] in the range 1720−1790 cm^{-1}. Four bands are identified for **1** (Table 4) associated with ionic and bidentate bridging nitrate groups. Unequivocal assignment of these bands is difficult, but the complex absorption pattern is certainly consistent with the different nitrates indicated by the X-ray structure. Six nitrate combination bands are clearly defined for **2** (Table 4) in the range 1787−1726 cm^{-1}. The X-ray structure reveals two different bridging nitrates and ionic nitrates are present in the lattice, which would be consistent with such a complicated spectral pattern. **6** has a much simpler spectrum in this region, and the bands at 1759 and 1714 cm^{-1} are reasonably assigned to bidentate nitrate, while the band at 1736 cm^{-1} is consistent with ionic nitrate. The sulfate complex (**3**) exhibits a ν_3 sulfate vibration which is split into several components with major peaks at 1180, 1110, and 1060 cm^{-1}. This suggests the presence of low symmetry sulfates and the likelihood of axial sulfato bridges, similar to the situation in $[Cu_2(PAP)(\mu_2\text{-}OH)Cl(\mu_2\text{-}SO_4)]{\cdot}2H_2O$.[29]

Solid-state, mull transmittance spectra for all of the complexes are characterized by the presence of an intense charge transfer absorption in the range 300−480 nm, with a lower energy, less intense, shoulder in the range 640−700 nm, which is assigned to a d−d transition (Table 4). The intense charge transfer absorptions observed for these complexes are likely to be $\pi-\pi^*$ in nature, in keeping with the assignments for dinuclear copper(II) complexes of typical mono(bispyridylamino)phthalazine) ligands.[16] For these systems low energy $\pi-\pi^*$ bands (>450 nm) are associated with the presence of anionic ligand fragments, but given the analytical data and the presence of infrared bands that are associated with hydroxide, the ligands appear to be neutral in the current complexes. The visible d−d absorptions are similar for all complexes and would reasonably suggest five- or six-coordination in complexes **3**-**8**.

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Table 4. Spectral and Magnetic Data

complex	infrared (cm^{-1})[a]	λ_{max} (nm)[c]	μ_{eff}(room temperature) (μ_B)
$[Cu_4(\mathbf{C\text{-}P})(\mu_2OH)_2(\mu_2\text{-}NO_3)_2(H_2O)_2(NO_3)_2](NO_3)_2\cdot 4H_2O$ (**1**)	1025 1776, 1764, 1755, 1731[b]	650	0.98
$\{[Cu_4(\mathbf{O\text{-}P})(\mu_2\text{-}OH)_2(\mu_2\text{-}NO_3)_2(H_2O)_7]_2(\mu_2\text{-}NO_3)\}(NO_3)_7\cdot 6H_2O$ (**2**)	1024 1787, 1776, 1764, 1754, 1748, 1726[b]	660	1.04
$[Cu_4(\mathbf{C\text{-}P})(OH)_2(SO_4)_2]SO_4\cdot 4H_2O$ (**3**)	1029	670	0.74
$[Cu_6(\mathbf{G\text{-}P})(OH)_3Cl_9]\cdot 4H_2O$ (**4**)	1023	690	1.32
$[Cu_6)(\mathbf{G\text{-}P})(OH)_3Br_9]\cdot 6H_2O$ (**5**)	1024	700	1.27
$[Cu_6(\mathbf{G\text{-}P})(OH)_3(NO_3)_9]\cdot 12H_2O$ (**6**)	1028 1759, 1730, 1714[b]	650	1.10
$[Cu_8(\mathbf{P\text{-}P})(OH)_4Cl_{12}]\cdot 10H_2O$ (**7**)	1023	640	0.72
$[Cu_8(\mathbf{P\text{-}P})(OH)_4Br_{12}]\cdot 8H_2O$ (**8**)	1022	650	0.59

[a] Pyridine. [b] $\nu_1 + \nu_4$ (NO_3). [c] Mull transmittance.

On the basis of the two structures (**1** and **2**), and the spectral evidence, including similarities with known dinuclear complexes of simple tetradentate (pyridylamino)phthalazine ligands, complexes **3** and **6** contain dendritic arrays of hydroxide bridged dinuclear copper(II) complex entities, involving tetradentate phthalazine ligand fragments, with axially bound anions. The copper ion stereochemistries are likely to be five or six-coordinate with additional coordination sites occupied by water molecules. The halide complexes **4, 5, 7,** and **8** have hydroxide bridged dinuclear centers, but the low room temperature magnetic moments (Table 4) are indicative of structures different from those of the parent complexes $[Cu_2(PAP)(\mu_2\text{-}OH)X_3]\cdot 1.5H_2O$[16] (1.66 μ_B (X = Cl), 1.60 μ_B (X = Br)). The simple dinuclear species have triply bridged structures, involving phthalazine and hydroxide as equatorial bridges and an axial halogen bridge. The substantially lower magnetic moments for **4** and **5** and very low moments for **7** and **8** suggest much larger hydroxide bridge angles, which would rule out any axial bridging. These complexes are therefore suggested to be dendritic species involving three (**4** and **5**) and four (**7** and **8**) pendant dinuclear complex fragments with the two copper centers bridged just by the hydroxide and diazine groups. Such an arrangement has been shown to exist in a series of tetranuclear copper(II) complexes of a group of tetrakis(pyridylamino)benzodipyridazine ligands, which have hydroxide bridge angles of ≈116° and exhibit strong antiferromagnetic coupling (magnetic moment (room temperature) 0.7–1.3 μ_B).[12] Equatorial coordination sites in **4**–**8** are likely to be occupied by halogens with the possibility of halogens and waters in axial positions.

Variable temperature magnetic studies were performed on dried, powdered samples of **1** and **2** in the temperature range 5–300 K. Fitting of the magnetic data for **1** to the Bleaney–Bowers equation[64] (eq 1) for a copper dimer gave best fit

$$\chi_m = \frac{N\beta^2 g^2}{3k(T-\Theta)}([1 + {}^1/_3 \exp(-2J/kT)]^{-1})(1-\varrho) + \frac{[N\beta^2 g^2]\,\varrho}{4kT} + N\alpha \quad (1)$$

parameters $g = 2.05(2)$, $-2J = 537(7)$ cm^{-1}, $\rho = 0.02$, $N\alpha = 58 \times 10^{-6}$ emu, and $\Theta = 0$ K ($10^2R = 1.1$; $R = [\Sigma(\chi_{obs} - \chi_{calc})^2/\Sigma(\chi_{obs})_2]^{1/2}$) ($\Theta$ is a corrective, Weiss-like term for possible intermolecular magnetic interactions,[65,66] and ρ is the fraction of a mononuclear paramagnetic impurity species; other terms have their usual meaning). Figure 5 illustrates a plot of χ_m vs temperature for **1**, with the solid line corresponding to the derived parameters quoted above. The exchange integral for **1** is entirely consistent with that observed for the complex $[Cu_2(PAP4Me)(\mu_2\text{-}OH)(\mu\text{-}NO_3)(NO_3)(H_2O)_2]\cdot NO_3$ $-2J = 497$ cm^{-1}), which has a comparable hydroxide bridge angle of 115.3(1)°.[29] The rise in χ_m at low temperature is indicative of the presence of a small amount of paramagnetic impurity. The Θ value of 0 K indicates no interdinuclear spin interactions, and indicates that there is no magnetic connection through the catechol bridge linking the halves of the molecule together. This is supported by an analysis of the variable temperature magnetic data for the catechol–bis(isoindoline) derivative $[Cu_2(\mathbf{C\text{-}I})Br_4]\cdot CH_3OH$ ($g = 2.147(6)$, $-2J = 1.4(4)$ cm^{-1}) (Figure 1a).[67] In the absence of structural details for this compound it is not clear how the weak exchange is propagated, but on the assumption that it might occur through the catechol bridge, it is extremely small.

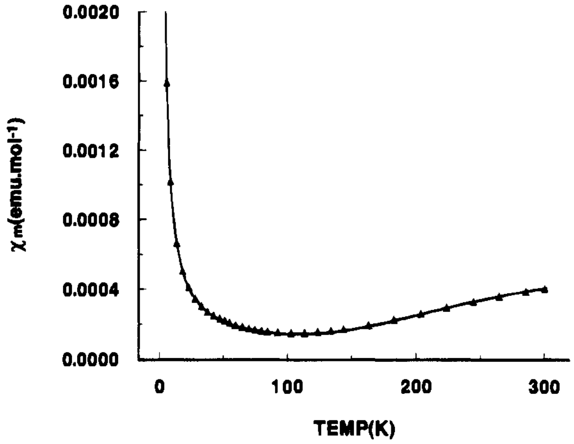

Figure 5. Magnetic data for $[Cu_4(\mathbf{C\text{-}P})(\mu_2\text{-}OH)_2(\mu_2\text{-}NO_3)_2(H_2O)_2(NO_3)_2](NO_3)_2\cdot 4H_2O$ (**1**). The solid line was calculated from eq 1, with $g = 2.05(2)$, $-2J = 537(7)$ cm^{-1}, $\rho = 0.02$, $N\alpha = 58 \times 10^{-6}$emu, $\Theta = 0$ K.

Variable temperature magnetic data for **2** are quite different from those for **1**. A maximum in the χ_m vs temperature plot occurs at about 225K (Figure 6), in contrast to **1**, which has a maximum in excess of 300 K. Dimensions at each dinuclear center in **2** are similar to those in **1**, in particular with respect to comparable hydroxide bridge angles (Cu–OH–Cu(av) 112.8°(**1**), 113.8°(**2**)) and dinuclear center fold angles, which would suggest a comparable exchange integral. A meaningful fit of the data for **2** cannot be achieved using the Bleaney–Bowers equation for a simple dinuclear species, and after we tested a variety of models, the only one that gave a reasonable data fit involved two different dinuclear centers in equal

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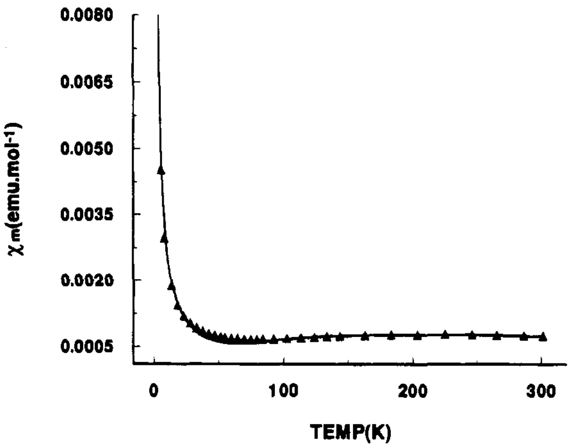

Figure 6. Magnetic data for $\{[Cu_4(\mathbf{O\text{-}P})(\mu_2\text{-}OH)_2(\mu_2\text{-}NO_3)_2(H_2O)_7]_2(\mu_2\text{-}NO_3)\}(NO_3)_7 \cdot 6H_2O$ (**2**). The solid line was calculated using a modified form of eq 1 ($\chi_T = \chi f(2J_1) + \chi f(2J_2)$), assuming a single averaged g value ($g_{av} = 2.04(3)$, $-2J_1 = 509(25)$ cm^{-1}, $-2J_2 = 198(10)$ cm^{-1}, $\rho = 0.065$, $N\alpha = 60 \times 10^{-6}$ emu, $\Theta = -4$ K).

proportions, with different exchange integrals, and adjusted for a significant paramagnetic impurity correction ($g_{ave} = 2.04(3)$, $-2J_1 = 509(25)$ cm^{-1}, $-2J_2 = 198(10)$ cm^{-1}, $\rho = 0.065$). The solid line in Figure 6 is calculated using the parameters derived above ($N\alpha = 60 \times 10^{-6}$ emu, $\Theta = -4$K, $10^2R = 2.6$). To rationalize such a magnetic difference between dinuclear centers would require some rather more marked structural differences than are apparent in the overall structure of **2**. Both bridging hydroxide oxygens are hydrogen bonded, with close contacts to lattice water molecules (O(1)−O(9) 2.42(2) Å, O(4)−O(10) 2.48(2) Å), but this would not be expected to significantly affect intramolecular antiferromagnetic exchange, and certainly not to lead to two very different coupling constants. The difference in Cu−OH−Cu bridge angles, a sensitive probe of exchange coupling in systems of this sort,[40] would only lead to a difference of 40−50 cm^{-1} between the two dinuclear centers. However, the significant axial bridging nitrate contact, which links the Cu(2) atoms (Cu(2)−O(17A) 2.48(2)Å), and is unique to the Cu(1)−Cu(2) dinuclear centers, could lead to a ferromagnetic interaction, which would significantly alter the spin exchange between Cu(1) and Cu(2) through the diazine and hydroxide bridges, leading to a reduction in the expected antiferromagnetic term. This and the smaller Cu−OH−Cu bridge angle for the Cu(1)−Cu)2) dinuclear center are the most likely factors leading to reduced antiferromagnetic coupling. The Θ correction could possibly be associated with interdinuclear exchange via hydrogen-bonding interactions.

Conclusion

The generation of dendritic, polypodal ligands with the capacity to coordinate large numbers of metal centers and produce nanometer-sized complexes has been demonstrated using a simple condensation reaction involving poly(alcoholic) substrates and 4-nitro-1,2-dicyanobenzene to give poly(phthalonitriles), which are further functionalized to produce polyisoindolines and poly(aminophthalazines). The poly(aminophthalazine) ligands produce tetranuclear, hexanuclear, and octanuclear copper(II) complexes, which contain repeating arrays of spin-coupled, dinuclear centers. In principle the synthesis of comparable higher order ligands with even greater metal ion capacity will only be limited by the availability of suitable polyalcoholic substrates. With appropriate modification of the geometric features of the dinucleating centers, e.g. ligand bite, and the use of bridging groups, e.g., azide, capable of generating ferromagnetic coupling,[68,69] the potential exists for the synthesis of high nuclearity ferromagnetic complexes. The intermolecular extension of the exchange coupling to create a supramolecular magnetic material is much more of a challenge. However recent results[70,71] indicate that both azide and hydroxide groups can produce tetranuclear dimers, involving both intramolecular and intermolecular azide and hydroxide bridges, with PAP and PTPH (1,4-bis(2′-pyridylthio)phthalazine) respectively, thus suggesting the possibility of similar interactions with the dendritic systems. We are presently exploring this approach.

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Supporting Information Available: Tables listing detailed full crystallographic data, hydrogen atom positional parameters, anisotropic thermal parameters, bond length and angles and least-squares planes for **1** (61 pages). Ordering information is given on any current masthead page.

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