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Synthesis, Crystal Structure, and Magnetic Properties of an Alkoxo–Hydroxo-Bridged Octanuclear Copper(II) Complex Showing Chemically Significant Hydrogen-Bonding Interactions Involving a Metallamacrocyclic Core

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A novel 16-member metallamacrocyclic octanuclear copper(II) complex of formulation $[Cu_8L_4(OH)_4]$ (**1**) has been prepared from a reaction of $[Cu_2L(O_2CMe)]$ and NaOH in methanol, where L is a pentadentate trianionic Schiff base ligand *N*,*N*′-(2-hydroxypropane-1,3-diyl)bis(salicylaldimine). The complex has been characterized by analytical, structural, and spectral methods. It crystallizes in the monoclinic space group *C*2/*c* with the following unit cell dimensions: $a = 30.365(3)$ Å; $b = 14.320(2)$ Å; $c = 19.019(2)$ Å; $\beta = 125.33(2)°$; $V = 6746.7(13)$ Å^3; $Z = 4$. A total of 4589 unique data with $I > 2\sigma(I)$ were used to refine the structure to $R1(F_o) = 0.0525$ and $wR2 = 0.1156$. The structure consists of four binuclear $\{Cu_2L\}^+$ units linked covalently by four hydroxide ligands to form an octanuclear core which is stabilized by strong hydrogen-bonding interactions involving the hydroxide ligands. Each binuclear unit has a pentadentate ligand L showing N_2O_3 coordination with an endogenous alkoxide bridging atom. The magnetic susceptibility data of **1**, obtained in the temperature range 14–306 K, show the presence of antiferromagnetic exchange interactions between adjacent spin-1/2 Cu(II) ions. The μ_{eff} values are 1.54 and 0.26 μ_B (per copper) at 295 and 15 K, respectively. The magnetic data have been theoretically fitted using a Heisenberg spin-1/2 Hamiltonian with nearest-neighbor antiferromagnetic interactions. The spin coupling in the metallamacrocyclic ring has been modeled using four different coupling constants (*J*) on the basis of the structural parameters of the octanuclear core. The coupling constants obtained are $J_1 = -318.8$, $J_2 = -293.3$, $J_3 = -111.6$, and $J_4 = -63.8$ cm^{-1}. The theoretical modeling of the susceptibility data gives a higher magnitude of the antiferromagnetic interaction within the binuclear $\{Cu_2L\}^+$ unit compared to those involving adjacent dimeric units.

Introduction

High-nuclearity transition-metal complexes are of current importance as new nanometric materials and single molecule magnets (SMM) and for modeling the structural and functional aspects of several multimetal active sites of metalloproteins.[2−6] Such complexes also provide an important link between the chemistry of discrete low-nuclearity complexes and that of extended 1−3-dimensional solids. An assembly of a large number of metal ions having d^n ($n = 1-9$) electronic configuration in a single molecule generates unusual magnetic, optical, and electronic properties. The polymetallic complexes, generally formed by "self-assembly" of mono- or dimeric precursors, display "unique" structural

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features that are susceptible to change on minor variation of the ligand structure and the reaction conditions. Besides, different types of intra- and intermolecular noncovalent interactions, the key aspects of the supramolecular chemistry, play a significant role in stabilizing a polymetallic cage structure.[7−10]

This work stems from our earlier report of an octanuclear copper(II) complex $[Cu_8L'_4(OH)_3](ClO_4)\cdot 3H_2O\cdot C_7H_{12}$.[11] This complex was prepared from a reaction of copper(II) perchlorate hexahydrate with a trianionic pentadentate Schiff base, *N*,*N*′-(2-hydroxypropane-1,3-diyl)bis(acetylacetoneimine) (H_3L'), and KOH in MeOH. It has a metallamacrobicyclic core which is formed from the self-assembly of four $\{Cu_2L'\}^+$ units bonded through two μ_3-OH and one μ_2-OH ligands. The cationic complex has a hydrophilic core in which three water molecules are hydrogen-bonded in the interior cavity while the outer hydrophobic exterior shows noncovalent interaction with a hydrocarbon lattice molecule. We have probed this chemistry further using an analogous pentadentate Schiff base, *N*,*N*′-(2-hydroxypropane-1,3-diyl)-bis(salicylaldimine) (H_3L), under similar reaction conditions. Interestingly, we have again observed the formation of a discrete alkoxo−hydroxo-bridged octanuclear copper(II) complex, $[Cu_8L_4(OH)_4]$ (**1**), but with a significantly different core structure. Unlike the previous one, complex **1** has four hydroxide ligands displaying μ_2-binding mode. A significant observation in **1** is the presence of strong intramolecular hydrogen-bonding interactions involving four hydroxide ligands thus stabilizing the core structure and exemplifying a new structural motif. Herein, we present the synthesis, crystal structure, and magnetic properties of **1**. Isolation of **1** with a Cu_8 core is of interest in the chemistry[12−16] of asymmetrically dibridged dicopper(II) complexes as this pentadentate ligand in combination with OH^- is known[15] to form a discrete binuclear copper(II) species $[Cu_2L(OH)]$ with an endogenous alkoxide and an exogenous hydroxide ligand showing ferromagnetic behavior ($J = +17$ cm^{-1}). This work also demonstrates the utility of such dinuclear precursors having multidentate Schiff base ligands in the formation of discrete polymetallic cores showing novel magneto−structural properties.

Experimental Section

Materials and Measurements. Solvents and reagents used for the preparative procedures were obtained from commercial sources. The Schiff base *N*,*N*′-(2-hydroxypropane-1,3-diyl)bis(salicylaldimine) (H_3L) and the precursor copper(II) complex $[CuL(\mu\text{-}O_2CMe)]$ were prepared by literature methods.[13] The elemental analysis was done using a Heraeus CHN-O rapid instrument. The electronic and infrared spectral data were obtained from Hitachi U-3400 and Bruker Equinox 55, respectively. Variable-temperature magnetic susceptibility data in the temperature range 14−306 K for a polycrystalline sample of **1** were measured using model 300 Lewis Coil Force magnetometer (George Associates Inc., Berkeley, CA) equipped with a closed cycle cryostat (Air products) and a Cahn balance. $Hg[Co(NCS)_4]$ was used as a calibrant. Experimental susceptibility data were corrected for diamagnetic contributions ($\chi_{dia} = -95.3 \times 10^{-6}$ cm^3 M^{-1}/copper atom). The magnetic moments at various temperatures were calculated in μ_B units ($\mu_B \approx 9.274 \times 10^{-24}$ J T^{-1}).

Preparation of $[Cu_8L_4(OH)_4]$, 1. To a solution of $[Cu_2L(\mu\text{-}O_2CMe)]$ (0.3 g, 0.62 mmol) in 10 mL of methanol was added sodium hydroxide (0.05 g, 1.23 mmol) in 10 mL of methanol under stirring condition for 2 h at 25 °C. A green solid thus formed was filtered off, washed with cold methanol, and finally dried in a vacuum over P_4O_{10} (yield: 0.17 g, 63%). The complex was crystallized by a diffusion technique using a CH_2Cl_2 solution of **1** and hexane. Anal. Calcd for $C_{68}H_{64}N_8O_{16}Cu_8$: C, 46.47; H, 3.67; N, 6.38. Found: C, 46.62; H, 3.88; N, 6.46. IR data (cm^{-1}) in KBr phase: 3394 (br), 2904 (w), 1635 (s), 1597 (m), 1538 (m), 1471 (m), 1450 (s), 1397 (w), 1338 (m), 1316 (m), 1189 (m), 1145 (m), 1130 (m), 1056 (w), 1035 (w), 974 (w), 894 (w), 863 (w), 760 (m), 671 (w), 566 (w), 463 (w) (s, strong; m, medium; w, weak; br, broad). λ_{max}, nm (ϵ/Cu_8, M^{-1} cm^{-1}) in CH_2Cl_2: 626 (850), 368 (35 000), 272 (78 100). χ_M^{corr}/Cu: 1.01×10^{-3} cm^3 M^{-1} at 295 K and 0.30×10^{-3} cm^3 M^{-1} at 15 K. μ_{eff}/Cu: 1.54 μ_B at 295 K; 0.26 μ_B at 15 K.

Solubility and Stability. Complex **1** is soluble in DMSO, DMF, $CHCl_3$, and CH_2Cl_2, less soluble in alcohols, and insoluble in hydrocarbons and water. The complex is stable in the solid and solution phases.

X-ray Crystallographic Procedures for $[Cu_8L_4(OH)_4]$, 1. Green colored single crystals of **1** were grown by a diffusion technique in which hexane was layered on the top of a CH_2Cl_2 solution of **1** in a Schlenk tube. A crystal of approximate size 0.43 × 0.28 × 0.05 mm was mounted on a glass fiber with epoxy cement. All the X-ray diffraction data were measured in frames with increasing ω (width of 0.3 deg/frame) and with a scan speed at 12 s/frame on a Bruker SMART APEX CCD diffractometer, equipped with a fine-focus 1.75 kW sealed-tube X-ray source. Empirical absorption corrections were carried out using SADABS program.[17a] The structure was solved by the heavy atom method and refined by full matrix least-squares using SHELX system of programs.[17b] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms attached to carbon atoms in the complex were generated and assigned isotropic thermal parameters, riding on their parent carbon atoms, and used for structure factor calculation only.

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Table 1. Crystallographic Data for [$Cu_8L_4(OH)_4$] (**1**)

empirical formula	$C_{68}H_{64}Cu_8N_8O_{16}$
fw	1757.59
cryst size, mm	0.43 × 0.28 × 0.05
cryst system	monoclinic
space group (No.)	*C2/c* (15)
a, Å	30.365(3)
b, Å	14.320(2)
c, Å	19.019(2)
β, deg	125.33(2)
V, Å^3	6746.7(13)
Z	4
μ(Mo Kα), cm^{-1}	25.46
ρ_{calc}, g cm^{-3}	1.730
λ, Å	0.710 73
T, K	293(2)
R1^a [R1 (all data)]	0.0525 [0.0969]
wR2^b [wR2 (all data)]	0.1156 [0.1289]

[a] $R1 = \sum|F_o| - |F_c|/\sum|F_o|$. [b] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2/\sum[w(F_o^2)^2]\}^{1/2}$. $w = 1/[\sigma^2(F_o^2) + (0.0536P)^2 + 0.0P]$, where $P = [\max(F_o^2, 0) + 2F_c^2]/3$.

The hydrogen atoms of the hydroxo ligands were located from the difference Fourier maps, and they were refined two cycles isotropically at the initial stage. At the final stage of refinement, their thermal parameters were only refined isotropically. The crystallographic data are summarized in Table 1. The goodness-of-fit was 0.86. The maximum shift/esd was 0.001. The highest peak after final refinement showed an electron density of 1.16 e/Å^3, and the peak was located at ~0.9 Å from the Cu(4) atom.

Results and Discussion

Synthesis and Crystal Structure. The precursor complex [$Cu_2L(O_2CMe)$] has a dicopper(II) unit bridged by the endogenous alkoxide oxygen of the trianionic pentadentate Schiff base (L) and a triatomic bridging acetate.[13] Such asymmetrically dibridged complexes with a $\{Cu_2(\mu\text{-}OR)(\mu\text{-}O_2CR)\}^{2+}$ core are of interest as they show reduced magnitude of $-2J$ due to "countercomplimentary" effect of the spin exchange phenomena involving the bridging ligands.[12−16] The carboxylate ligand is labile and can be substituted with a variety of anionic ligands to form binuclear complexes showing novel magneto−structural properties.[12] Earlier report shows that, in the presence of potassium hydroxide in methanol, cupric bromide hydrate reacts with H_3L to form [$Cu_2L(\mu\text{-}OH)$]. This discrete binuclear alkoxo−hydroxo-bridged complex exhibits a ferromagnetic exchange coupling with a J value of $+17$ cm^{-1}.[15] Using a different precursor complex we have observed the formation of an octanuclear copper(II) complex [$Cu_8L_4(OH)_4$] (**1**) in high yield (eq 1). The octanuclear core displays different structural and magnetic properties in comparison to its binuclear analogue. Complex **1** exhibits a d−d band at 626 nm in CH_2Cl_2.

$$4[Cu_2L(O_2CMe)] + 4NaOH \xrightarrow{MeOH} [Cu_8L_4(OH)_4] + 4NaO_2CMe \quad (1)$$

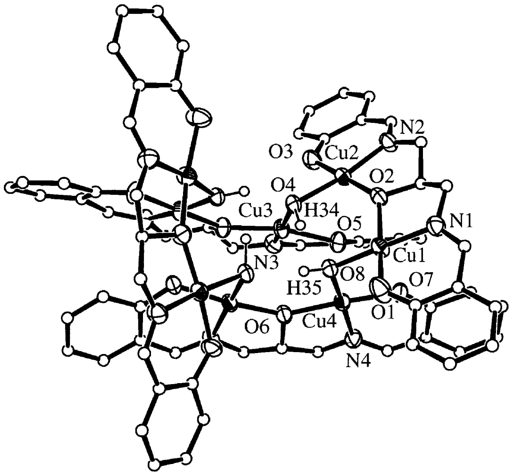

Figure 1. ORTEP view of [$Cu_8L_4(OH)_4$] showing the atom-labeling scheme for the coordination spheres and the 50% probability thermal ellipsoids for the metal and the heteroatoms. The carbon atoms and the hydroxo hydrogen atoms are shown as small spheres. Weak axial bonds involving the phenoxo oxygen atoms are not shown for clarity.

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) Including the Hydrogen-Bonding Interactions in [$Cu_8L_4(OH)_4$] (**1**)

Cu(1)···Cu(2)	3.652(1)	Cu(3)−O(3)	2.561(4)
Cu(1)···Cu(4)	3.125(1)	Cu(3)−O(4)	1.929(3)
Cu(2)···Cu(3)	2.908(1)	Cu(3)−O(5)	1.944(3)
Cu(3)···Cu(4′)^a	3.461(1)	Cu(3)−O(6′)^a	1.961(3)
Cu(1)−O(1)	1.939(3)	Cu(3)−N(3)	1.942(4)
Cu(1)−O(2)	1.996(3)	Cu(4)−O(5)	2.538(4)
Cu(1)−O(7)	2.499(4)	Cu(4)−O(6)	1.988(3)
Cu(1)−O(8)	1.895(3)	Cu(4)−O(7)	1.928(3)
Cu(1)−N(1)	1.932(4)	Cu(4)−O(8)	1.908(3)
Cu(2)−O(2)	1.947(3)	Cu(4)−N(4)	1.931(4)
Cu(2)−O(3)	1.925(3)	O(4)···O(8)	2.696(3)
Cu(2)−O(4)	1.926(3)	O(4)···O(8′)^a	2.693(6)
Cu(2)−O(5)	2.543(3)	O(8)−H(35)	0.924(4)
Cu(2)−N(2)	1.933(4)	O(4)−H(34)	1.102(3)
Cu(1)−O(2)−Cu(2)	135.63(16)	O(4)−Cu(3)−N(3)	169.97(15)
Cu(1)−O(7)−Cu(4)	88.82(13)	O(5)−Cu(3)−O(6′)^a	167.69(14)
Cu(1)−O(8)−Cu(4)	110.53(14)	O(5)−Cu(3)−N(3)	91.16(15)
Cu(2)−O(3)−Cu(3)	79.45(13)	O(6′)^a−Cu(3)−N(3)	84.54(15)
Cu(2)−O(4)−Cu(3)	97.93(15)	O(6)−Cu(4)−O(7)	176.76(13)
Cu(2)−O(5)−Cu(3)	79.59(12)	O(6)−Cu(4)−O(8)	94.80(12)
Cu(2)−O(5)−Cu(4)	108.71(12)	O(6)−Cu(4)−N(4)	84.45(14)
Cu(3)−O(5)−Cu(4)	100.26(13)	O(7)−Cu(4)−O(8)	87.70(13)
Cu(3′)^a−O(6)−Cu(4)	136.38(17)	O(7)−Cu(4)−N(4)	92.87(15)
O(1)−Cu(1)−O(2)	167.05(16)	O(8)−Cu(4)−N(4)	174.69(15)
O(1)−Cu(1)−O(8)	93.38(14)	Cu(1)−O(8)···O(4)	106.50(15)
O(1)−Cu(1)−N(1)	91.79(16)	Cu(1)−O(8)···O(4′)^a	141.2(2)
O(2)−Cu(1)−O(8)	92.59(14)	Cu(2)−O(4)···O(8)	97.60(13)
O(2)−Cu(1)−N(1)	83.51(15)	Cu(2)−O(4)···O(8′)^a	146.3(2)
O(8)−Cu(1)−N(1)	172.33(16)	Cu(3)−O(4)···O(8)	100.87(13)
O(2)−Cu(2)−O(3)	175.08(14)	Cu(3)−O(4)···O(8′)^a	101.39(15)
O(2)−Cu(2)−O(4)	96.74(13)	Cu(4)−O(8)···O(4)	100.62(14)
O(2)−Cu(2)−N(2)	85.32(15)	Cu(4)−O(8)···O(4′)^a	107.69(17)
O(3)−Cu(2)−O(4)	85.71(13)	O(4)···O(8)···O(4′)^a	71.92 (13)
O(3)−Cu(2)−N(2)	92.85(16)	O(8)···O(4)···O(8′)^a	105.44(16)
O(4)−Cu(2)−N(2)	171.73(16)	O(4)−H(34)···O(8)	143.50(18)
O(4)−Cu(3)−O(5)	87.08(13)	O(8)−H(35)···O(4′)^a	152.0(3)
O(4)−Cu(3)−O(6′)^a	99.11(12)		

[a] Symmetry transformations used to generate equivalent atoms: $2 - x$, $+y$, $3/2 - z$.

An ORTEP view of the complex is shown in Figure 1. Selected bond distances and bond angles and significant hydrogen-bonding interactions are given in Table 2. The octanuclear complex consists of four binulcear $\{Cu_2L\}^+$ units that are covalently bonded through four μ_2-OH ligands. In the $\{Cu_2L\}^+$ unit, the trianionic ligand displays N_2O_3-pentadentate coordination mode with the alkoxide oxygen acting as the endogenous bridging ligand. Each copper in **1** shows an essentially square-pyramidal (4 + 1) coordination geometry in which the basal plane has the imino nitrogen,

Table 3. Deviation of Copper from the Basal Planes (*d*), Dihedral Angles between Two Basal Planes (φ), and the Geometric Parameter (τ) for the Coordination Geometries in $[Cu_8L_4(OH)_4]$ (**1**)

	d Values (Å)		
Cu(1)	0.0505(7)	Cu(3)	0.0311(6)
Cu(2)	0.0192(6)	Cu(4)	0.0585(6)
	τ Value		
Cu(1)	0.09	Cu(3)	0.04
Cu(2)	0.07	Cu(4)	0.04
	Dihedral Angles (φ, deg)[a]		
plane 1−plane 2	18.0(1)	plane 1−plane 4	88.7(1)
plane 2−plane 3	63.3(1)	plane 3−plane 4	17.7(1)

[a] Basal planes 1−4 contain Cu(1)−Cu(4), respectively.

the alkoxo oxygen, the phenoxo oxygen of the salicylaldimine moiety, and the hydroxo oxygen atoms. The phenoxo oxygen atom of the salicylaldimine moeity displays axial−equatorial bonding. The Cu−N and Cu−O (basal plane) bond distances lie in the range 1.931(4)−1.942(4) and 1.895(3)−1.996(3) Å, respectively. The axial Cu···O distances vary from 2.499(3) to 2.561(4) Å. The Cu···Cu separations within the $\{Cu_2L\}^+$ units, viz. Cu(1)···Cu(2) and Cu(3)···Cu(4′), are 3.652(1) and 3.461(1) Å. The Cu(1)···Cu(4) and Cu(2)···Cu(3) distances involving metal centers belonging to different $\{Cu_2L\}^+$ moieties are 3.125(1) and 2.908(1) Å. The shorter interunit Cu···Cu distances are due to lower value of the Cu−OH−Cu angles in comparison with the alkoxo bridge angles. While the hydroxo bridge angles Cu(2)−O(4)−Cu(3) and Cu(1)−O(8)−Cu(4) are 97.9 and 110.5°, the alkoxo bridge angles Cu(1)−O(2)−Cu(2) and Cu(3)−O(6)−Cu(4′) are ~136°.

The crystal structure gives τ values in the range 0.04−0.09 indicating an essentially square-pyramidal (4 + 1) coordination geometry of the metal in **1** (Table 3).[18] The dihedral angles (φ) between the basal planes are 17.7 and 18° within the $\{Cu_2L\}^+$ moiety (Table 3). This suggests a near planarity of the two planes which could be related to the larger Cu−OR−Cu alkoxo bridge angle. Such a planar orientation is expected to promote stronger antiferromagnetic exchange interaction between the metal centers. The dihedral angles between two interunit basal planes having hydroxide bridging ligands are 63 and 89°. The near-perpendicular orientation of the planes may reduce the magnitude of the exchange coupling considerably.

Complex **1** has a 16-member metallamacrocyclic core (Figure 2). A hydrogen-bonding network involving four bridging hydroxide ligands stabilizes the core conformation. The O(4)···O(8) and O(4)···O(8′) distances of ~2.69 Å with respective O−H···O angle of ~144 and ~153° indicate the presence of strong hydrogen-bonding interactions. The O(4) and O(8) atoms have a distorted tetrahedral geometry. In each hydroxide ligand, two lone pairs are used for bridging two copper centers. The remaining lone pair and the hydrogen atom are involved in the hydrogen bonding. The deviation of some angles around the oxygen from an idealized tetrahedral geometry could be due to the steric constraints imposed by the metal ions. A plane calculation using four hydroxide oxygen atoms in **1** shows that while the O(4) and O(4′) atoms are 0.2 Å above the plane, the O(8) and O(8′) atoms lie 0.2 Å below the plane. The three-dimensional packing of **1** reveals the formation of channels along the *c*-axis of the crystal lattice (Figure 3). While the square-shaped channel (~5 Å^2) has a polar environment due to the presence of metal and the heteroatoms, the strawberry-shaped channel has essentially a hydrophobic environment due to the presence of carbon and hydrogen atoms.

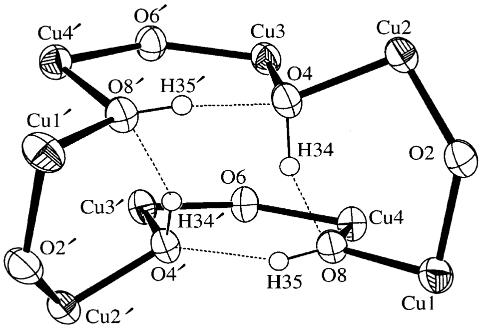

Figure 2. View of the 16-member metallamacrocyclic core in $[Cu_8L_4(OH)_4]$ showing the hydrogen-bonding network involving four hydroxide ligands.

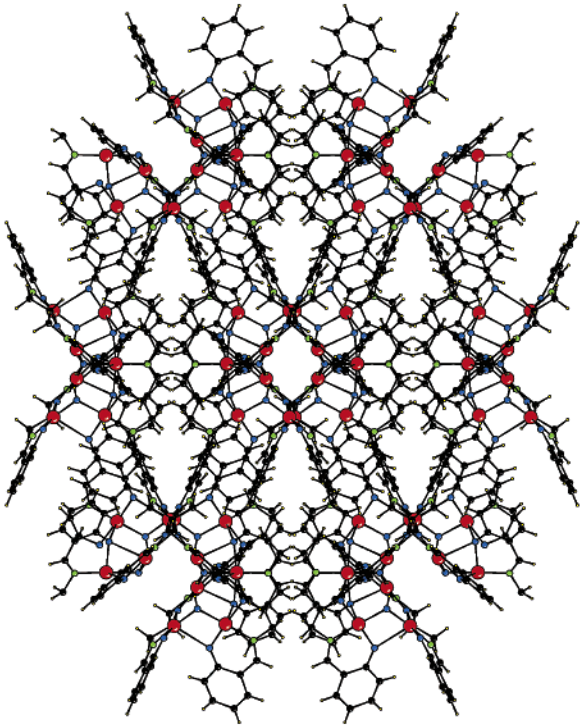

Figure 3. View of the packing of discrete octanuclear copper(II) species $[Cu_8L_4(OH)_4]$ along the *c* axis showing channels of different polarities.

The core structure in 1 is considerably different from that of $[Cu_8L'_4(OH)_3](ClO_4)\cdot 3H_2O\cdot C_7H_{12}$.[11] This could be due to the greater steric bulk of H_3L in comparison to H_3L'. While **1** has a metallamacrocyclic core, its analogue has a metallamacrobicyclic core. There are four hydroxo ligands in **1** of μ_2-type. The other species has two μ_3-OH and one μ_2-OH ligands. The crystal structure of **1** is of importance as structurally characterized discrete molecular octanuclear

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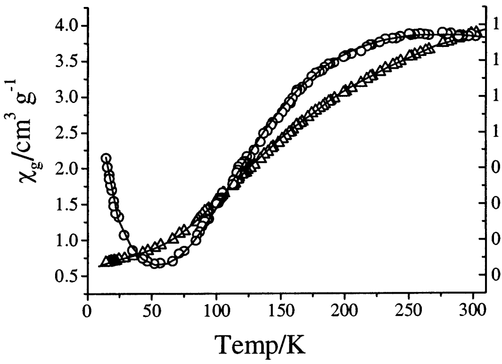

Figure 4. Magnetic susceptibility χ (○) and magnetic moment μ_{eff} (△) (per copper) vs temperature plots for [$Cu_8L_4(OH)_4$]. The solid lines are the theoretical fittings of the experimental data.

copper(II) complexes are limited in number.[11,19−30] Again, the diversity of the core structures in these high-nuclearity copper(II) complexes makes any meaningful comparison difficult. Besides **1**, the other example of an octanuclear copper(II) complex having a 16-member metallamacrocyclic core is [$Cu_8(dmpz)_8(OH)_8$], where dmpz is 3,5-dimethylpyrazole.[19] Again, there are only three reports in which four binuclear copper(II) units are linked together to form the Cu_8 cores, but these structures have no similarity with the core structure of **1**.[11,24,25] Complex **1**, showing a novel intramolecular hydrogen-bonding network like calixarene,[31,32] presents a new structural motif in the supramolecular chemistry.

Magnetic Properties. The variable-temperature magnetic susceptibility data within 306−14 K show an antiferromagnetic behavior of **1** (Figure 4). The μ_{eff} values are 1.54 and 0.26 μ_B (per copper) at 295 and 15 K, respectively. A theoretical fit of the magnetic data for the octanuclear core has been done using a Heisenberg spin-1/2 Hamiltonian with nearest neighbor antiferromagnetic interactions.[3a] The alkoxo bridge angles are ~136°, while the hydroxo bridge angles are 98 and 110°. In cases where the Cu−O−Cu bond angles are less than 90°, at least one Cu−O distance is too large to support any superexchange interaction. A strong antiferromagnetic interaction is expected when the bridging angle is close to 180°, whereas for angles close to 90° the interaction is expected to be either ferromagnetic or weakly antiferromagnetic. On the basis of the structural observations, we have assumed four different coupling constants (J) for this metallamacrocyclic ring having eight spin-1/2 copper(II) centers (Figure 5).

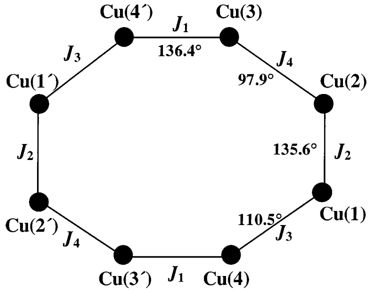

Figure 5. Schematic diagram showing the coupling scheme in [$Cu_8L_4(OH)_4$] (**1**). Four different Cu−O−Cu bond angles are shown.

The strongest antiferromagnetic coupling is between spins of Cu(3)−Cu(4′) and Cu(3′)−Cu(4), since the Cu−O−Cu bond angle is ~136° and the Cu−Cu distance is 3.461 Å. Next strongest antiferromagnetic coupling is between spins of Cu(1)−Cu(2) and Cu(1′)−Cu(2′), where although the bond angles are still ~136° the Cu−Cu distance is slightly longer at 3.652 Å. The exchange interactions between spins at Cu(1)−Cu(4) and Cu(2)−Cu(3) are weaker because of smaller Cu−O−Cu bond angles. Thus, although the Cu−O−Cu bond angle is smaller for the Cu(2)−Cu(3) interaction, the shorter Cu(2)−Cu(3) distance leads to a stronger antiferromagnetic interaction than in the case of Cu(1)−Cu(4). Since we are basing on exchange interactions on a superexchange mechanism, the only bond angles relevant to our case are those in which oxygen is bridging two copper ions. On the basis of the structural data, the spin Hamiltonian for the octanuclear copper(II) core can be written as

$$\hat{H} = -J_1(S_3S_{4'} + S_{4'}S_3) - J_2(S_1S_2 + S_{1'}S_{2'}) - J_3(S_1S_4 + S_{1'}S_{4'}) - J_4(S_2S_3 + S_{2'}S_{3'}) \quad (2)$$

where negative J values correspond to antiferromagnetic interactions with $|J_1| > |J_2| > |J_3| > |J_4|$. At first sight it may appear that we need to include interaction between other pairs of copper ions such as Cu(1)−Cu(3) and Cu(2)−Cu(4). However, we note from the structure that they are not connected by oxygen bridges but rather by hydrogen bonds. Superexchange through hydrogen bonds would be extremely weak and negligible because the intermediate or virtual states have very high energies and the hopping integral between a hydrogen-bonded hydrogen atom and the copper ion is also very small. All the energy levels of the spin Hamiltonian (eq 2) can be obtained by setting up the Hamiltonian matrix in the constant total M_s basis and diagonalizing the matrix.[33]

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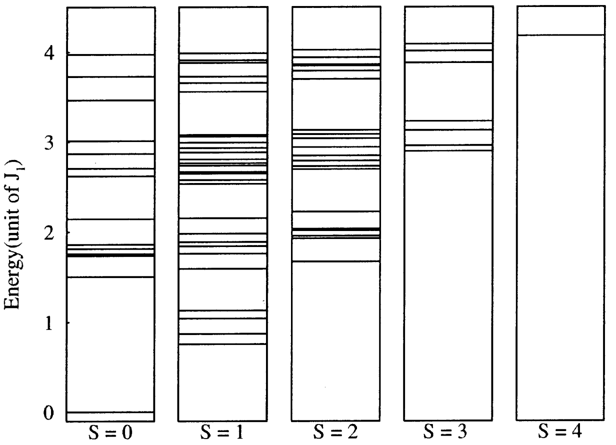

Figure 6. Energy levels of $[Cu_8L_4(OH)_4]$ (**1**) with the degeneracy of each spin state as $2S + 1$.

From the spin−spin correlation function computed in each of the states, the expectation value of the $\hat{S}_{\text{total}}^2$ operator was calculated, and the total spin of each eigenstate was thereby identified.[34] The ground state of this octanuclear cluster is a singlet, and the first excited state is a triplet. Figure 6 displays the energy levels of the cluster.

The susceptibility was calculated by obtaining the magnetization in an applied field H by using the expression

$$M = [\textstyle\sum_i M_I \exp(-E_i(H)/k_BT)]/[\textstyle\sum_i \exp(-E_i(H)/k_BT)] \quad (3)$$

where $E_i(H) = E_i^{(0)} + gM_iH$. $E_i^{(0)}$ is the eigenvalue of eq 2, obtained from exact diagonalization, and M_i is the z-component of the spin in the eigenstate "i". The g value is 2.10, and H is the magnitude of the magnetic field. The applied magnetic field is taken to be 0.5 T as per the experimental conditions. To account for the small concentration of paramagnetic impurity present in the sample we have assumed an additional Curie-like contribution to the susceptibility of the form C/T, where C is a constant. The impurity contribution becomes significant at low temperatures, and a divergent behavior of susceptibility is observed below 40 K. The theoretical susceptibility data agree well with the experimental values (Figure 4). The error (R) calculated as $R = \sum_i[(\chi_{\text{obs}}(T_i) - \chi_{\text{cal}}(T_i))^2/\chi_{\text{obs}}(T_i)^2]$ is 1.86×10^{-4}. The impurity concentration is 0.03 free spin/octameric ring. From the theoretical fit we get the values of the coupling constants as $J_1 = -318.8$, $J_2 = -293.3$, $J_3 = -111.6$, and $J_4 = -63.8$ cm^{-1}. If we assume that the Heisenberg exchange constants have a $(\cos\theta)/r$ dependence, where θ is the Cu−O−Cu bond angle and r is the Cu−Cu distance, then we expect the ratio of J_1, J_2, J_3, and J_4 to be 1:0.95:0.52:0.23. The slight discrepancy between the ratios of the fitted J values and that from the empirical formula could be attributed to multiple exchange pathways between pair of copper ions. The ratio between the exchange constants obtained from the fit of the experimental susceptibility data is 1:0.92:0.35:0.20. We have tried fitting the experimental data by using wide but reasonable variations in J_1, J_2, J_3, and J_4, and the best fit corresponds to the J values quoted above. Besides the ratios of the J values that provide the best fit, the J values can also be justified to some extent on the basis of an empirical form of superexchange parameter. The gap between ground-state singlet and the first excited-state triplet is proportional to the magnitude of the exchange constant. So a complex with a higher J value (i.e. larger spin gap) will exhibit a maxima in susceptibility at a higher temperature. Thus, a strong antiferromagnetic interaction (J_1) is in accordance with the susceptibility maximum, observed around 300 K. It is interesting to note that, in the model that best fits the experimental magnetic susceptibility data, the strongest interaction is indeed the interdimer interaction. In the isolated dimer the exchange interaction is ferromagnetic. In the octanuclear complex, the intradimer interaction is antiferromagnetic, as seen from the structural data and the best fit model parameters.

Conclusions

A new discrete octanuclear copper(II) complex $[Cu_8L_4(OH)_4]$ (**1**), having four pentadentate Schiff base *N,N′*-(2-hydoxypropane-1,3-diyl)bis(salicylaldimine) and four hydroxide ligands, has been prepared and structurally characterized. The crystal structure of the complex shows the presence of a 16-member metallamacrocylic core formed by the covalent linkage of four $\{Cu_2L\}^+$ units by μ_2-OH ligands. The core structure is stabilized by strong intramolecular hydrogen-bonding interactions involving the hydroxide ligands. The magnetic properties of **1** show the presence of four different types of exchange coupling interactions within the core. The magnitudes of the antiferromagnetic (AF) interactions vary considerably. While the AF interaction is very strong within the $\{Cu_2L\}^+$ unit due to large alkoxo bridge angle (∼136°), a lower magnitude is observed for the exchange interaction involving two adjacent units linked by hydroxide ligands (angles, 98 and 110.5°). Complex **1** with a macrocyclic ring, which is stabilized by novel intramolecular hydrogen-bonding interactions similar to that of calixarene, presents a new structural motif in the chemistry of high-nuclearity transition-metal complexes. The association of four ferromagnetically coupled $[Cu_2^{II}L(OH)]$ units ($J = +17$ cm^{-1}) into **1** has resulted in the formation of an antiferromagnetically coupled octanuclear core. The results are of significance toward assembling discrete molecular copper(II) clusters of larger dimensions for their use in the chemistry of nanoclusters.

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Supporting Information Available: A unit cell packing diagram (Figure S1), a table of magnetic susceptibility data at various temperatures, and the crystallographic data in CIF format for **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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