Notes

An Alkoxo−Hydroxo-Bridged Octanuclear Copper(II) Complex with a Hydrophobic Exterior and a Hydrophilic Metallamacrobicyclic Core Showing Selective Hydrogen-Bonding Interactions

Kannappan Geetha, Munirathinam Nethaji, and Akhil R. Chakravarty*

Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore-560 012, India

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Introduction

Selective binding of a substrate to a molecular receptor system leads to the formation of a supramolecular entity by the process of molecular recognition.[1] Organic macrocyclic compounds having binding sites suitable for noncovalent interactions are the key systems in supramolecular chemistry.[1,2] It is envisaged that the metallamacrocyclic transition-metal complexes could be potential "inorganic analogues" of the organic macrocyclic receptor systems.[3−5] The presence of metal ions in the metallamacrocyclic framework is expected to fine-tune the receptor capabilities of the available binding sites for noncovalent interactions with other molecular species. Recent reports have shown that a new class of complexes, viz. metallacrowns and metallacryptates, show novel physicochemical properties that are distinctly different from those of their organic analogues.[4]

Herein, we report the isolation of the octanuclear metallamacrobicyclic copper(II) complex $[Cu_8L_4(OH)_3](ClO_4)\cdot 3H_2O\cdot C_7H_{12}$, exemplifying a new supramolecular entity with a hydrophilic polar core and an outer hydrophobic environment showing chemically significant noncovalent interactions (L = the trianion of a pentadentate Schiff-base ligand). Although a few octanuclear copper(II) complexes are reported[6−11] in the literature, there is only one structurally characterized complex, $[Cu_8(dmpz)_8(OH)_8]\cdot 2C_6H_5NO_2$, that has a core cavity clatharating two nitrobenzene molecules (Hdmpz = 3,5-dimethylpyrazole).[6] The present complex shows a new structural motif involved in noncovalent interactions.

Experimental Section

The Schiff-base ligand 2-hydroxy-1,3-propanediylbis(acetylacetone imine) (H_3L) was prepared according to the literature procedure.[12]

Preparation of $[Cu_8L_4(OH)_3](ClO_4)$, 1. To a solution of $Cu(ClO_4)_2\cdot 6H_2O$ (741 mg; 2.0 mmol) in methanol (30 mL) were added H_3L (254 mg; 1.0 mmol) and KOH (224 mg; 4.0 mmol). The solution was magnetically stirred for 2 h at room temperature. The resulting green solution was filtered, and the filtrate on slow evaporation gave **1** in 60% yield. Anal. Calcd for $C_{52}H_{79}N_8O_{19}ClCu_8$: C, 37.53; H, 4.75; N, 6.74. Found: C, 37.32; H, 5.21; N, 6.84. λ_{max}, nm (ϵ, M^{-1} cm^{-1}) in CH_2Cl_2: 615 (830). $\chi_M^{cor} = 4.79 \times 10^{-4}$ cm^3 mol^{-1} at 295 K. $\mu_{eff} = 1.06$ μ_B/Cu at 295 K. IR data (cm^{-1}): 3545 (br), 2918 (w), 1601 (s), 1514 (s), 1403 (s), 1269 (m), 1200 (w), 1140 (vs, ClO_4^-), 939 (m), 778 (m), 625 (s), 454 (m) (vs = very strong; s = strong; m = medium; w = weak; br = broad).

Safety Note. Perchlorate salts of metal complexes with organic ligands are potentially explosive and should be prepared in small quantities and handled with great caution.

Measurements. Elemental analyses were performed using a Heraeus CHN-O Rapid instrument. Electronic and IR spectra were recorded on Hitachi U3400 and Bio-Rad FTS-7 spectrometers, respectively. Room-temperature magnetic susceptibility data were obtained on polycrystalline samples from a George Associates model 300 Lewis-coil-force magnetometer using $Hg[Co(NCS)_4]$ as calibrant. The X-ray intensity data were collected at 294 K with an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo Kα radiation.

X-ray Crystallographic Procedure. Green rectangular crystals of composition $\mathbf{1}\cdot 3H_2O\cdot C_7H_{12}$ were obtained by the diffusion technique using a dichloromethane solution of **1** and petroleum ether. The sources of water and 3-methyl-1,4-hexadiene (C_7H_{12}) were the commercially available solvents used for crystallization. The crystal structure was determined using procedures reported earlier.[13] The crystallographic data are presented in Table 1. The positional parameters for selected atoms are given in Table 2. The intensity data collected in the range $2 \leq 2\theta \leq 50°$ by the ω-scan technique were corrected for Lorentz, polarization, and absorption[14] effects. There were 13 441 unique reflections, of which 8528 unique data with $I > 2\sigma(I)$ were used for structure solving and refinement with the Patterson method and full-matrix least-squares techniques. All calculations were carried out using an IBM computer and the SHELX system of programs[15] with scattering

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Table 1. Crystallographic Data for $[Cu_8L_4(OH)_3](ClO_4)\cdot 3H_2O\cdot C_7H_{12}$

empirical formula	$C_{59}H_{97}N_8O_{22}ClCu_8$
fw	1814.22
cryst size, mm	0.23 × 0.3 × 0.18
cryst system	triclinic
space group (No.)	$P\bar{1}$ (2)
a, Å	12.202(5)
b, Å	14.852(4)
c, Å	23.362(5)
α, deg	74.73(2)
β, deg	84.73(2)
γ, deg	69.42(3)
V, Å^3	3823(2)
Z	2
T, K	294
λ, Å	0.7107
ρ_{calc}, g cm^{-3}	1.58
μ(Mo Kα), cm^{-1}	22.89
R1[a]	0.0577
wR2[b]	0.1391

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$. $w = [\sigma^2(F_o^2) + (0.0831P)^2 + 8.93P]^{-1}$ where $P = [\max(F_o^2,0) + 2F_c^2]/3$.

Table 2. Positional Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for Selected Atoms in $[Cu_8L_4(OH)_3](ClO_4)\cdot 3H_2O\cdot C_7H_{12}$

atom	x	y	z	U(eq)[a]
Cu(1)	2372(1)	1960(1)	4167(1)	50(1)
Cu(2)	1985(1)	4492(1)	4199(1)	44(1)
Cu(3)	3524(1)	5108(1)	3256(1)	46(1)
Cu(4)	2636(1)	5437(1)	1793(1)	59(1)
Cu(5)	4503(1)	3157(1)	2129(1)	50(1)
Cu(6)	2854(1)	1707(1)	2871(1)	47(1)
Cu(7)	1897(1)	3582(1)	1816(1)	49(1)
Cu(8)	345(1)	3057(1)	3110(1)	46(1)
O(1)	3080(5)	795(4)	3872(2)	56(1)
O(2)	1947(5)	3155(4)	4470(2)	47(1)
O(3)	1898(5)	5858(4)	3920(2)	57(1)
O(4)	4210(5)	4192(4)	3985(2)	52(1)
O(5)	3187(5)	5752(4)	2437(2)	60(2)
O(6)	1787(6)	5237(4)	1223(2)	66(2)
O(7)	4788(5)	4275(4)	1597(3)	63(2)
O(8)	4286(5)	2054(4)	2758(2)	50(1)
O(9)	1370(5)	1541(4)	2839(2)	57(1)
O(10)	3306(5)	3054(5)	1393(3)	61(2)
O(11)	518(4)	3942(4)	2328(2)	50(1)
O(12)	146(5)	2290(4)	3885(2)	55(1)
O(13)	2000(4)	2719(3)	3326(2)	42(1)
O(14)	2333(4)	4446(3)	3348(2)	42(1)
O(15)	2878(4)	4038(4)	2229(2)	45(1)
N(1)	2458(7)	1233(5)	4984(3)	59(2)
N(2)	1651(5)	4573(5)	5011(3)	48(2)
N(3)	4479(6)	5915(5)	3203(3)	52(2)
N(4)	2785(7)	6657(5)	1312(3)	63(2)
N(5)	6060(6)	2266(5)	2055(3)	55(2)
N(6)	3637(6)	734(5)	2421(3)	56(2)
N(7)	970(6)	3082(5)	1435(3)	57(2)
N(8)	−1279(6)	3492(5)	2896(3)	52(2)
O(20)	537(6)	5709(5)	2556(4)	92(2)
O(21)	4499(6)	2229(5)	3924(3)	80(2)

[a] Equivalent isotropic U(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

factors taken from ref 16. All non-hydrogen atoms were refined anisotropically except those of one water molecule and the organic solvent molecule. The hydrogen atoms attached to carbon atoms in the cationic complex were generated and assigned isotropic thermal parameters, riding on their parent carbon atoms, and used for structure factor (F_o^2) calculations only. The solvent molecule C_7H_{12} was successfully modeled by applying geometrical restraints using the DFIX provision available on SHELXL-93. The goodness-of-fit was 1.067. The final difference Fourier map was featureless, showing the highest peak of 0.987 e Å^{-3} situated 1.7 Å from the chlorine atom.

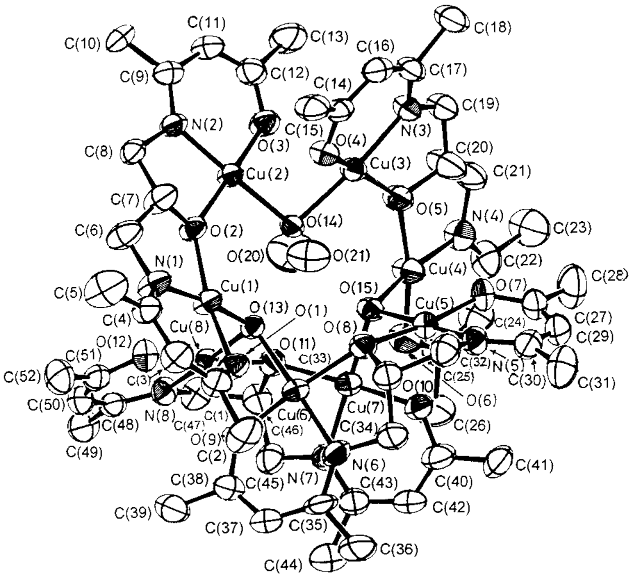

Figure 1. ORTEP view of the cationic complex $[Cu_8L_4(OH)_3]^+$ along with two water molecules in **1**$\cdot 3H_2O\cdot C_7H_{12}$.

Results and Discussion

The reaction of copper(II) perchlorate hexahydrate with a Schiff base (H_3L) in the presence of KOH in methanolic medium leads to the self-assembly of the octanuclear core in high yield (eq 1). An ORTEP[17] view of the cationic complex along with

$$8Cu(ClO_4)_2\cdot 6H_2O + 4H_3L + 15KOH \xrightarrow{\text{MeOH}} \underset{\mathbf{1}}{[Cu_8L_4(OH)_3](ClO_4)} + 60H_2O + 15KClO_4 \quad (1)$$

two water molecules is shown in Figure 1. Selected bond distances and angles in the cationic complex are given in Table 3, and significant hydrogen-bonding data are given in Table 4. The octanuclear complex consists of four alkoxo-bridged dinuclear units $\{Cu_2L\}^+$ that are covalently linked by one μ_2-OH and two μ_3-OH ligands to form the octacopper(II) core. Each copper atom in **1** is in an axially elongated square-pyramidal NO_4 coordination environment with the axial positions being occupied by the oxygen atom of the pentadentate ligand, giving a Cu···O distance in the range 2.3−2.7 Å. The Cu(1) and Cu(4) atoms display an additional weak axial ligation by water molecules.

The Cu···Cu distances lie in the range 2.93−3.65 Å. The Cu···Cu distances in the $\{Cu_2L\}^+$ units are significantly different from each other. The Cu(1)···Cu(2) and Cu(3)···Cu(4) distances are considerably longer than the Cu(5)···Cu(6) and Cu(7)···Cu(8) distances. This could be due to the significantly higher Cu(1)−O(2)−Cu(2) and Cu(3)−O(5)−Cu(4) angles (135−138°) compared to Cu(5)−O(8)−Cu(6) and Cu(7)−O(11)−Cu(7) (127−125°). The Cu···Cu distances between two nearest $\{Cu_2L\}^+$ units are shorter than the same distances within the dinuclear units. The Cu(2)−O(14)−Cu(3) angle of 94.3(2)° is the smallest. Consequently, the alkoxy bridge angles in the $\{Cu_2L\}^+$ units involved in the μ_2-OH bonding are the largest. The other Cu−OH−Cu angles lie

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Table 3. Selected Bond Distances (Å) and Bond Angles (deg) in $[Cu_8L_4(OH)_3](ClO_4)\cdot 3H_2O\cdot C_7H_{12}$

Bond Distances (Å)							
Cu(1)···Cu(2)	3.642(2)	Cu(1)−O(2)	1.965(5)	Cu(4)−O(5)	1.927(5)	Cu(6)−O(1)	2.359(5)
Cu(1)···Cu(6)	3.125(2)	Cu(1)−O(12)	2.696(6)	Cu(4)−N(4)	1.923(7)	Cu(6)−O(13)	2.002(5)
Cu(1)···Cu(8)	3.323(2)	Cu(1)−O(13)	1.994(5)	Cu(4)−O(6)	1.901(6)	Cu(7)−O(10)	1.921(6)
Cu(2)···Cu(3)	2.932(2)	Cu(2)−O(2)	1.935(5)	Cu(4)−O(7)	2.663(6)	Cu(7)−N(7)	1.935(6)
Cu(3)···Cu(4)	3.540(2)	Cu(2)−N(2)	1.931(6)	Cu(4)−O(15)	1.987(5)	Cu(7)−O(11)	1.972(5)
Cu(4)···Cu(5)	3.283(2)	Cu(2)−O(3)	1.927(5)	Cu(5)−O(7)	1.914(6)	Cu(7)−O(6)	2.446(6)
Cu(4)···Cu(7)	3.173(2)	Cu(2)−O(4)	2.614(5)	Cu(5)−N(5)	1.919(7)	Cu(7)−O(15)	1.988(5)
Cu(5)···Cu(6)	3.483(2)	Cu(2)−O(14)	2.008(5)	Cu(5)−O(8)	1.969(5)	Cu(8)−O(11)	1.991(5)
Cu(5)···Cu(7)	3.133(2)	Cu(3)−O(4)	1.920(5)	Cu(5)−O(10)	2.423(5)	Cu(8)−N(8)	1.925(6)
Cu(6)···Cu(8)	3.107(2)	Cu(3)−N(3)	1.921(6)	Cu(5)−O(15)	1.987(5)	Cu(8)−O(12)	1.915(5)
Cu(7)···Cu(8)	3.475(2)	Cu(3)−O(5)	1.911(5)	Cu(6)−O(8)	1.966(5)	Cu(8)−O(9)	2.379(5)
Cu(1)−O(1)	1.919(5)	Cu(3)−O(3)	2.524(6)	Cu(6)−N(6)	1.937(6)	Cu(8)−O(13)	1.981(5)
Cu(1)−N(1)	1.921(7)	Cu(3)−O(14)	1.990(5)	Cu(6)−O(9)	1.922(6)		
Bond Angles (deg)							
O(1)−Cu(1)−N(1)	94.3(3)	O(5)−Cu(3)−O(14)	94.6(2)	O(8)−Cu(5)−O(15)	91.8(2)	N(8)−Cu(8)−O(13)	175.6(2)
O(1)−Cu(1)−O(2)	169.3(2)	N(3)−Cu(3)−O(14)	171.0(2)	O(7)−Cu(5)−O(10)	91.1(2)	O(12)−Cu(8)−O(11)	175.8(2)
N(1)−Cu(1)−O(2)	86.3(2)	O(4)−Cu(3)−O(14)	87.6(2)	N(5)−Cu(5)−O(10)	107.1(3)	N(8)−Cu(8)−O(11)	85.3(2)
O(1)−Cu(1)−O(13)	87.1(2)	O(5)−Cu(3)−O(3)	111.9(2)	O(8)−Cu(5)−O(10)	96.1(2)	O(13)−Cu(8)−O(11)	92.5(2)
N(1)−Cu(1)−O(13)	170.2(3)	N(3)−Cu(3)−O(3)	100.8(2)	O(15)−Cu(5)−O(10)	73.0(2)	O(12)−Cu(8)−O(9)	88.2(2)
O(2)−Cu(1)−O(13)	94.2(2)	O(4)−Cu(3)−O(3)	84.2(2)	O(9)−Cu(6)−N(6)	93.0(3)	N(8)−Cu(8)−O(9)	109.3(2)
O(1)−Cu(1)−O(12)	96.8(2)	O(14)−Cu(3)−O(3)	70.8(2)	O(9)−Cu(6)−O(8)	169.3(2)	O(13)−Cu(8)−O(9)	74.7(2)
N(1)−Cu(1)−O(12)	101.9(3)	O(6)−Cu(4)−N(4)	95.8(3)	N(6)−Cu(6)−O(8)	86.2(3)	O(11)−Cu(8)−O(9)	95.9(2)
O(2)−Cu(1)−O(12)	93.6(2)	O(6)−Cu(4)−O(5)	168.4(3)	O(9)−Cu(6)−O(13)	85.5(2)	Cu(1)−O(1)−Cu(6)	93.3(2)
O(13)−Cu(1)−O(12)	68.3(2)	N(4)−Cu(4)−O(5)	85.8(3)	N(6)−Cu(6)−O(13)	178.4(3)	Cu(2)−O(2)−Cu(1)	138.0(3)
O(1)−Cu(1)−O(21)	85.0(2)	O(6)−Cu(4)−O(15)	87.0(2)	O(8)−Cu(6)−O(13)	95.2(2)	Cu(2)−O(3)−Cu(3)	81.2(2)
N(1)−Cu(1)−O(21)	105.4(3)	N(4)−Cu(4)−O(15)	166.2(3)	O(9)−Cu(6)−O(1)	90.2(2)	Cu(3)−O(4)−Cu(2)	78.9(2)
O(2)−Cu(1)−O(21)	84.5(2)	O(5)−Cu(4)−O(15)	94.1(2)	N(6)−Cu(6)−O(1)	104.8(2)	Cu(3)−O(5)−Cu(4)	134.6(3)
O(13)−Cu(1)−O(21)	84.4(2)	O(6)−Cu(4)−O(7)	100.0(2)	O(8)−Cu(6)−O(1)	100.4(2)	Cu(4)−O(6)−Cu(7)	92.9(2)
O(12)−Cu(1)−O(21)	152.4(2)	N(4)−Cu(4)−O(7)	96.3(3)	O(13)−Cu(6)−O(1)	75.9(2)	Cu(5)−O(7)−Cu(4)	90.1(2)
O(3)−Cu(2)−N(2)	93.8(2)	O(5)−Cu(4)−O(7)	91.2(2)	O(10)−Cu(7)−N(7)	94.4(3)	Cu(6)−O(8)−Cu(5)	124.5(3)
O(3)−Cu(2)−O(2)	175.7(2)	O(15)−Cu(4)−O(7)	69.9(2)	O(10)−Cu(7)−O(11)	172.1(2)	Cu(6)−O(9)−Cu(8)	91.9(2)
N(2)−Cu(2)−O(2)	86.0(2)	O(6)−Cu(4)−O(20)	88.5(2)	N(7)−Cu(7)−O(11)	85.2(3)	Cu(7)−O(10)−Cu(5)	91.6(2)
O(3)−Cu(2)−O(14)	84.7(2)	N(4)−Cu(4)−O(20)	114.1(3)	O(10)−Cu(7)−O(15)	85.2(2)	Cu(7)−O(11)−Cu(8)	122.6(3)
N(2)−Cu(2)−O(14)	178.5(2)	O(5)−Cu(4)−O(20)	80.3(2)	N(7)−Cu(7)−O(15)	177.6(3)	Cu(8)−O(12)−Cu(1)	90.6(2)
O(2)−Cu(2)−O(14)	95.5(2)	O(15)−Cu(4)−O(20)	79.5(2)	O(11)−Cu(7)−O(15)	95.0(2)	Cu(8)−O(13)−Cu(1)	113.4(2)
O(3)−Cu(2)−O(4)	81.6(2)	O(7)−Cu(4)−O(20)	147.5(2)	O(10)−Cu(7)−O(6)	87.9(2)	Cu(8)−O(13)−Cu(6)	102.6(2)
N(2)−Cu(2)−O(4)	109.4(2)	O(7)−Cu(5)−N(5)	93.7(3)	N(7)−Cu(7)−O(6)	108.9(3)	Cu(1)−O(13)−Cu(6)	102.9(2)
O(2)−Cu(2)−O(4)	102.5(2)	O(7)−Cu(5)−O(8)	172.5(2)	O(11)−Cu(7)−O(6)	99.8(2)	Cu(3)−O(14)−Cu(2)	94.3(2)
O(14)−Cu(2)−O(4)	70.3(2)	N(5)−Cu(5)−O(8)	86.0(3)	O(15)−Cu(7)−O(6)	73.5(2)	Cu(5)−O(15)−Cu(4)	111.4(2)
O(5)−Cu(3)−N(3)	85.5(3)	O(7)−Cu(5)−O(15)	88.4(2)	O(12)−Cu(8)−N(8)	94.3(3)	Cu(5)−O(15)−Cu(7)	104.1(2)
O(5)−Cu(3)−O(4)	163.6(2)	N(5)−Cu(5)−O(15)	177.9(3)	O(12)−Cu(8)−O(13)	87.5(2)	Cu(4)−O(15)−Cu(7)	105.9(2)
N(3)−Cu(3)−O(4)	94.9(3)						

Table 4. Chemically Significant Hydrogen-Bonding Interactions in $[Cu_8L_4(OH)_3](ClO_4)\cdot 3H_2O\cdot C_7H_{12}$

Contacts (Å)			
O(20)···O(14)	2.79	O(21)···O(4)	2.85
O(20)···O(22)	3.29	O(21)···O(8)	2.85
O(20)···O(11)	2.78		
Angles (deg)			
Cu(4)−O(20)···O(14)	77.2	O(11)···O(20)···O(22)	165.4
Cu(4)−O(20)···O(22)	80.6	Cu(1)−O(21)···O(4)	107.7
Cu(4)−O(20)···O(11)	86.1	Cu(1)−O(21)···O(8)	87.0
O(14)···O(20)···O(11)	82.7	O(4)···O(21)···O(8)	114.2
O(14)···O(20)···O(22)	99.9		

in the range 102−114°. The alkoxo bridge angle in related[12] discrete dicopper(II) complexes having similar pentadentate Schiff-base ligands is ∼135°.

The assembly of four $\{Cu_2L\}^+$ units gives an unusual lateral-type metallamacrobicyclic core[2,5] in **1** with a small inner cavity that consists of O(13), O(14), and O(15) atoms whose interatomic distances range between 2.8 and 3.2 Å (Figure 2). In the crystal lattice, it forms a channel that is nearly parallel to the *b* axis (∼16° inclined) and is nearly perpendicular to the 101 plane (∼77°). The geometry at the bridging alkoxy atoms O(2) and O(5) is planar, as the sum of the Cu−O−Cu and two Cu−O−Cu angles for these atoms in the $\{Cu_2L\}^+$ units is ∼355°. The geometry of the other alkoxy bridging atoms O(8) and O(11) is, however, pyramidal, the sum of the angles being ∼337°. The core is thus unique in showing the presence of both planar and pyramidal alkoxy oxygen atoms.

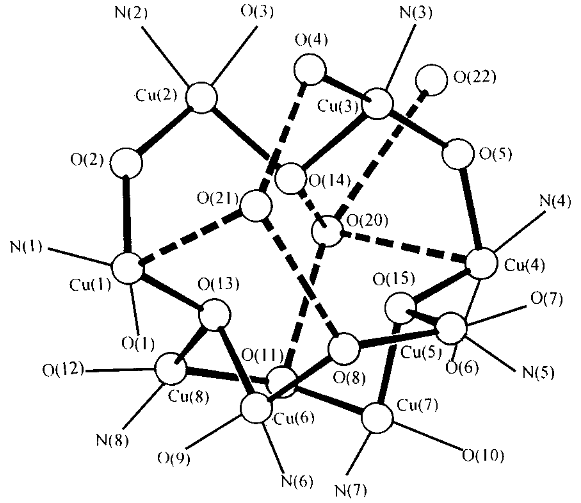

Figure 2. View of the lateral-type metallamacrobicyclic core in the cationic complex showing the spatial arrangement of three water molecules in the polar core and their possible contacts.

The asymmetric unit of the unit cell contains three water molecules and one C_7H_{12} molecule in addition to the cationic complex and the perchlorate anion. Two water molecules show significant interactions with the cationic complex. A space-

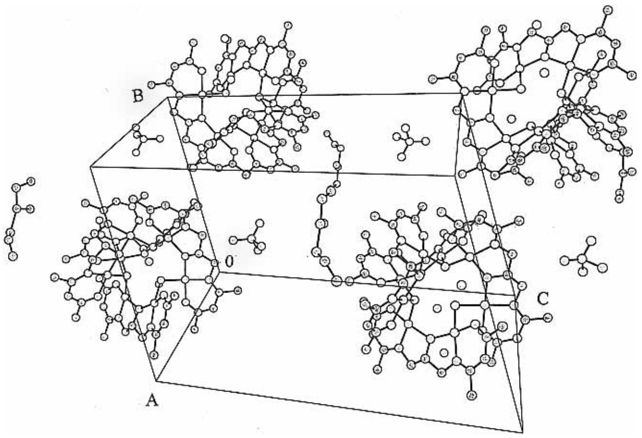

Figure 3. Unit cell packing diagram of $[Cu_8L_4(OH)_3](ClO_4)\cdot 3H_2O\cdot C_7H_{12}$ showing the presence of three water molecules in the polar interior and the C_7H_{12} molecule near the hydrophobic exterior region of the complex cation.

filling model shows the presence of a small inner cavity in the core. The water molecules, viz. the O(20) and O(21) atoms, lie above and below the plane formed by three hydroxo oxygen atoms. The water molecules occupy the elongated axial sites of the Cu(4) and Cu(1) atoms giving a 4+2 geometry at the metal center [O(21)−Cu(1)−O(12) = 157.4(2)°; O(20)−Cu(4)−O(7) = 147.5(2)°]. While O(20) shows significant hydrogen-bonding interactions with O(14) and O(11), atom O(21) is involved in a similar type of interaction with O(4) and O(8). Figure 2 shows the significant hydrogen-bonding interactions between the polar core and the water molecules. Atom O(20) is also involved in a weak hydrogen-bonding interaction with O(22). The water molecule oxygens O(20) and O(21) have hydrogen-bonding interactions with the μ_2-OH group, one terminal oxygen atom of the ligand and two alkoxo oxygen atoms having pyramidal geometry. The planar alkoxo oxygen atoms and the μ_3-OH groups do not show any chemically significant interactions with the water molecules. The axial ligation of O(20) and O(21) to Cu(4) and Cu(1) involve the lone-pair electrons on the oxygen atoms. The hydrogen atoms of O(21) form hydrogen bonds with O(4) and O(8), leaving one lone pair of electrons on O(21). The hydrogen atom of O(20) is bonded to O(11). The situation is not clear for the hydrogen bonding of O(22) and O(14) with O(20), as the atoms have both the lone pair(s) and hydrogen atom(s) available for interaction.

The cationic complex has a hydrophilic core and an outer hydrophobic exterior (Figure 3). The C_7H_{12} molecule, which lies along a channel made by the octanuclear cationic species in the crystal lattice, is in the hydrophobic environment created by the methyl groups of the pentadentate ligands. The perchlorate anion occupies the relatively less hydrophobic region in the crystal lattice. The water molecules are in the polar interior region of the metallamacrobicyclic core and display preferential selection of binding sites for noncovalent interactions.

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Supporting Information Available: Figures showing an additional ORTEP diagram and a space-filling model (2 pages). An X-ray crystallographic file, in CIF format, for the complex **1**$\cdot 3H_2O\cdot C_7H_{12}$ is available on the Internet only. Ordering and access information is given on any current masthead page.

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