Heteroditopic Cryptands of Tunable Cavity Size: Imposition of Distorted Geometry onto Copper(II) and Nickel(II) and Molecular Recognition of Water Molecules

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Complexation behavior of a previously described heteroditopic cryptand $\mathbf{L^1}$ and a newly synthesized cryptand $\mathbf{L^2}$ toward transition metal ions is described. The cryptands readily accept a transition metal ion like Cu(II) or Ni(II) at the N_4 end of the cavity forming mononuclear cryptates. The Cu(II)-cryptate of $\mathbf{L^1}$ further accepts a water molecule to form $[Cu(\mathbf{L^1})(OH_2)]\cdot(picrate)_2\cdot(H_2O)$, i.e., $C_{45}H_{53}N_{11}O_{19}Cu$. This molecule crystallizes in the monoclinic space group $C2/c$ with $a = 34.199(8)$ Å, $b = 12.286(5)$ Å, $c = 23.289(7)$ Å, $\beta = 93.12(4)°$, $Z = 8$. The O atom of the water molecule is strongly bonded to the Cu(II) ion, while its H atoms are H-bonded to the nearest benzene rings. The UV−vis spectral and magnetic studies of the complexes are consistent with the mononuclear nature of the cryptates. Cryptand $\mathbf{L^1}$ undergoes diprotonation upon treatment with a mineral acid like HCl or $HClO_4$. This diprotonated cryptand is found to be a good host for two molecules of water inside the cavity. The diperchlorate salt, $[H_2\mathbf{L^1}\subset(H_2O)_{1.5}]\cdot(ClO_4)_2\cdot(H_2O)_{0.75}$, i.e., $C_{33}H_{51.5}Cl_2N_5O_{13.25}$, crystallizes in the monoclinic space group $P2_1/c$ with $a = 12.204(1)$ Å, $b = 11.465(1)$ Å, $c = 28.537(3)$ Å, $\beta = 91.98(2)°$, $Z = 4$. The cryptand has an ellipsoidal cavity with both the bridgehead N atoms adopting an endo-endo conformation in the solid state. The water O atoms O(1w) and O(2w) lie in the pseudo 3-fold axis joining the two bridgehead N atoms. Occupancy of O(2w) is found to be 0.5 while that of O(1w) is unity. The water molecules are held inside the cavity through H-bonding with an ice-like structure. The FAB-mass spectral data and the bond distances involving the water oxygens suggest that both the water molecules are tightly held inside the cavity. The present cryptate is the first X-ray crystallographically characterized complex with two water molecules inside the cavity of a cryptand.

Introduction

Cryptands as complexing agents for transition metal ions[1] and as hosts for organic/inorganic[2−4] cations, anions, and neutral molecules are subjects of considerable current interest. We have been involved in using heteroditopic cryptands for the complexation of transition as well as nontransition metal ions[5,6] and molecular recognition of planar neutral molecules[7] with the aim(s) of using such cryptates for developing further chemistry.[8−10] These cryptands possess several desirable properties as ligands such as donor atoms' topology and recognition characteristics of the different binding sites inside the cavity, which can be manipulated via design. A heteroditopic cryptand can be designed to bind to a metal ion at one end of the cavity leaving the other end empty. This remaining space inside the cavity can be made use of in homogeneous catalytic reactions.[8] Also, molecules or ionic fragments can enter the cavity and bond to the metal ion and at the same time can be involved in hydrogen bonding[6] to the cryptand.

In addition, these cryptands have amino nitrogens, which upon protonation,[7] can become good hosts for water molecules through H bonds. The underlying principle of hydrogen bonding is that the strongest H-bond acceptor tends to pair up with the strongest H-bond donor. With aromatic groups acting as acceptors, a donor molecule usually forms π-facial H bonding.[11] However, when such H-bond requirements cannot be satisfied due to structural constraints, novel H-bonding modes can be observed. Hydrogen bonding involving aromatic groups is of fundamental importance[12] in chemical as well as in biological systems as this can direct self-assembly and recognition processes in vivo. Also, natural antibiotics, when not complexed with metal ions, bind water molecules through hydrogen bonding. This complexation with water interacts with influences the hydration shell of the metal ion which is believed[13] to assist

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the metal complexation process of the antibiotics. Inclusion of water inside the cavity of crown ethers and oxazamacrocycles has been reported.[14] Some of these have been characterized in the solid state by X-ray crystallography. In the case of macrobicyclic molecules, only a handful of examples are available[7,15−18] where a water molecule is included inside the cavity. However, no report is available to date where more than one water molecule is included inside the cavity of a macrobicyclic host. Such systems are available only with macrocycles.[19,20] However, if the cavity size can be tuned properly, it should be possible to put more than one water molecules inside the cavity of a cryptand. Any such study has the ultimate goal of putting several water molecules inside the cavity to have water clusters. Studies on water clusters are of considerable current interest as they have been implicated in several contemporary problems.[21]

Herein, we describe the structures of $[\mathrm{Cu}(\mathbf{L}^1)(\mathrm{OH_2})]\cdot(\mathrm{picrate})_2\cdot(\mathrm{H_2O})$, **1a**, and $[\mathrm{H_2}\mathbf{L}^1\subset(\mathrm{H_2O})_{1.5}]\cdot(\mathrm{ClO_4})_2\cdot(\mathrm{H_2O})_{0.75}$, **5**, of a previously synthesized[5] heteroditopic cryptand $\mathbf{L}^1$. In case of **1a**, the oxygen of the water molecule makes a strong bond with the Cu(II) ion inside the cavity while its H atoms are involved in H-bonding with two of the benzene rings of the cryptand. This cryptand readily becomes diprotonated on treatment with a mineral acid and binds two water molecules inside the cavity forming **5**. The binding modes of the water molecules in **5** are different from each other, as shown by the X-ray structural study.

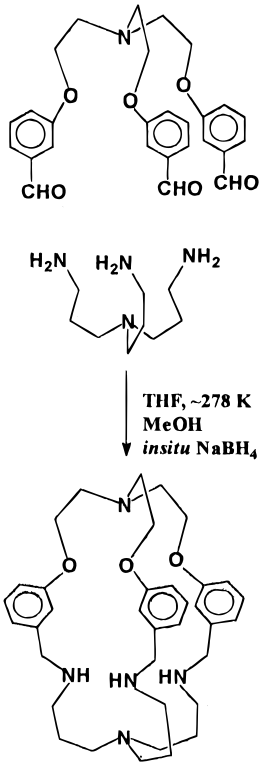
Experimental Section

Materials. Reagent-grade chemicals (Aldrich) were used as received. All the solvents (SD Fine Chemicals, India) were purified prior to use. Spectroscopic and analytical data for the complexes were collected as described earlier.[5]

Synthesis. Cryptand $\mathbf{L}^1$. The cryptand $\mathbf{L}^1$ was prepared as described earlier[5] by [1+1] Schiff base condensation of the tripodal triamine, tris(2-aminoethyl)amine with the tripodal trialdehyde, tris{[2-(3-benzaldehyde)oxo]ethyl}amine followed by reduction with $\mathrm{NaBH_4}$.

Cryptand $\mathbf{L}^2$. This cryptand was synthesized by modifying our earlier scheme (Scheme 1). Tris{[2-(3-benzaldehyde)oxo]ethyl}amine (0.46 g, 1 mmol) was taken in 100 cm^3 of THF, in a 500 cm^3 round-bottomed flask at 278 K. To this solution was added, with continuous stirring, a solution of tris(3-aminopropyl)amine (0.19 g, 1 mmol) in 100 cm^3 of THF over a period of 2 h maintaining the temperature at 278 ± 1 K. The addition was adjusted so as to disperse each drop before another fell into the reaction mixture. At the end of the addition, the reaction was stirred at room temperature for a period of 12 h. Reduction of the Schiff base thus formed was achieved by hydrogenating it with an excess of $\mathrm{NaBH_4}$ (~0.3 g), with prior addition of 50 cm^3 of MeOH, at room temperature for 2 h followed by refluxing for another 2 h. The solvent was evaporated until it was almost dry, and the residue was treated with 20 cm^3 of cold water. The desired cryptand $\mathbf{L}^2$ was extracted with 3 × 10 cm^3 of $\mathrm{CHCl_3}$. The organic layer was dried over anhydrous $\mathrm{Na_2SO_4}$ and evaporated to obtain a pale yellow semisolid. Yield 45%. ^{1}H NMR (80 MHz, $\mathrm{CDCl_3}$): δ 1.6 (m, 6H), 2.6 (m, 12H), 3.2 (t, 6H), 3.7 (s, 6H), 4.1 (t, 6H), 7.1 (m, 12H). FAB-MS, *m/z*: 600 (40) $[\mathrm{M}-2]^+$.

Scheme 1. Synthesis of the Cryptand $\mathbf{L}^2$



$[\mathrm{Cu}(\mathbf{L}^1)]\cdot(\mathrm{picrate})_2$, 1. To $\mathbf{L}^1$ (0.056 g, 0.1 mmol) dissolved in 5 cm^3 of dry MeOH was added Cu(II) picrate (0.052 g, 0.1 mmol) dissolved in 5 cm^3 of dry MeOH. A green solid separated immediately which was collected by filtration, washed with dry MeOH, and dried in vacuo at 40 °C. Yield 90%. Anal. Calcd for $\mathrm{C_{45}H_{49}N_{11}O_{17}Cu}$: C, 50.07; H, 4.58; N, 14.27. Found: C, 49.83; H, 4.72; N, 14.08. FAB-MS, *m/z*: 622 (100) [M − 2 picrates]. The solid, upon recrystalization from moist MeCN, at room temperature, afforded dark green crystals of $[\mathrm{Cu}(\mathbf{L}^1)(\mathrm{OH_2})]\cdot(\mathrm{picrate})_2\cdot(\mathrm{H_2O})$ (**1a**) in 80% overall yield. FAB-MS, *m/z*: 1113 (15) $[\mathrm{M}-2]^+$ and 622 (20) $[\mathrm{M}-2\mathrm{H_2O}-2\ \text{picrates}]^+$.

$[\mathrm{Ni}(\mathbf{L}^1)]\cdot(\mathrm{picrate})_2$, 2. This cryptate was prepared following the procedure adopted for **1** except that Ni(II) picrate was used instead of Cu(II) picrate. A brownish solid separated immediately which was collected by filtration, washed with dry MeOH, and dried in vacuo at 40 °C. Yield 85%. Anal. Calcd for $\mathrm{C_{45}H_{49}N_{11}O_{17}Ni}$: C, 50.30; H, 4.60; N, 14.34. Found: C, 50.40; H, 4.45; N, 14.50.

$[\mathrm{Cu}(\mathbf{L}^2)]\cdot(\mathrm{picrate})_2$, 3. To $\mathbf{L}^2$ (0.060 g, 0.1 mmol) dissolved in 5 cm^3 of dry MeOH was added Cu(II) picrate (0.052 g, 0.1 mmol) dissolved in 5 cm^3 of dry MeOH. A green solid separated immediately which was collected by filtration, washed with dry MeOH, and dried in vacuo. Yield 75%. Anal. Calcd for $\mathrm{C_{48}H_{55}N_{11}O_{17}Cu}$: C, 51.40; H, 4.94; N, 13.74. Found: C, 51.26; H, 5.10; N, 13.59.

$[\mathrm{Ni}(\mathbf{L}^2)]\cdot(\mathrm{picrate})_2$, 4. This complex was isolated in a similar way as for **3** except that Ni(II) picrate was used instead of the Cu(II) salt to obtain a brownish solid. Yield 80%. Anal. Calcd for $\mathrm{C_{48}H_{55}N_{11}O_{17}Ni}$: C, 51.63; H, 4.96; N, 13.80. Found: C, 51.78; H, 4.805; N, 14.00.

$[\mathrm{H_2}\mathbf{L}^1\subset(\mathrm{H_2O})_{1.5}]\cdot(\mathrm{ClO_4})_2\cdot(\mathrm{H_2O})_{0.75}$, 5. To a stirred solution of $\mathbf{L}^1$ (0.056 g, 0.1 mmol) in methanol (5 cm^3) was added 2 equiv of aqueous perchloric acid at 5 °C whereupon a white solid precipitated. The solid was filtered and recrystallized from MeCN at room temperature by slow evaporation to obtain colorless crystals in 80% yield, mp 115−116 °C. Anal. Calcd for $\mathrm{C_{33}H_{51.5}Cl_2N_5O_{13.25}}$: C, 47.57; H, 6.66; N, 8.40. Found: C, 46.78; H, 6.805; N, 7.51.

Caution! *Care must be taken while treating organic compounds with metal picrates or perchloric acid as potentially explosive mixtures may be formed.*

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Table 1. Crystallographic and Experimental Data for $[Cu(\mathbf{L^1})(OH_2)]\cdot(picrate)_2\cdot(H_2O)$ (**1a**) and $[H_2\mathbf{L^1}\subset(H_2O)_{1.5}]\cdot(ClO_4)_2\cdot(H_2O)_{0.75}$ (**5**)

	1a	**5**
empirical formula	$C_{45}H_{53}N_{11}O_{19}Cu$	$C_{33}H_{51.5}N_5O_{13.25}Cl_2$
MW	1115.517	833.26
temp, °C	25	25
diffractometer	CAD4-mach	CAD4-mach
radiation, graphite monochromated	Mo Kα	Mo Kα
λ, Å	0.710 73	0.710 73
cryst syst	monoclinic	monoclinic
space group	$C2/c$	$P2_1/c$
a, Å	34.199(8)	12.204(1)
b, Å	12.286(5)	11.465(1)
c, Å	23.289(7)	28.537(3)
β, deg	93.12(4)	91.98(2)
V, Å^3	9770(7)	3990.5(6)
Z	8	4
D_{calcd}, g/cm^3	1.514	1.334
μ, cm^{-1}	5.3	2.3
cryst size, mm^3	0.20 × 0.20 × 0.40	0.10 × 0.20 × 0.40
transm (max, min)	0.8538, 0.7293	0.9661, 0.8716
decay	<0.9%	<0.4%
no. of unique reflns	8269	7769
no. of reflns used ($I > 2\sigma(I)$)	4251	2357
no. of variables	685	515
R^a	0.060	0.088
R$_w$^{b}	0.071	0.088
goodness of fit	3.209	3.299

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = [\sum\omega(|F_o| - |F_c|)^2/\sum\omega(F_o)^2]^{1/2}$, $\omega = 1/\sigma(F)$.

X-ray Structural Studies. Crystallographic data for **1a** and **5** are listed in Table 1. In each case, a crystal of suitable size was mounted at the end of a glass fiber with epoxy cement. The cell parameters in each case were determined by least-squares refinement of diffractometer setting angles for 25 centered reflections that were in the range $20 \leq 2\theta \leq 30°$. Intensity data were corrected for Lorentz and polarization effects; analytical absorption corrections were applied. The XTAL 3.2 program package[22] was used in absorption and all subsequent calculations using a 486-DX personal computer (PCL, India) operating at 66 MHz under MS-DOS version 5. The linear absorption coefficients, scattering factors for the atoms, and the anomalous-dispersion corrections were taken from the *International Tables for X-ray Crystallography*.[23] The structures were solved by the direct methods[24] and completed by successive difference Fourier syntheses. The refinement was done by the full-matrix least-squares technique using anisotropic thermal parameters for all non-hydrogen atoms. Some of the H atoms could be located in the difference maps for either cryptates, the rest were calculated assuming ideal geometries of the atoms concerned. For the water molecule inside the cavity in **1a** both the hydrogens were located in the difference map. In the case of **5**, however, the hydrogens of only one water molecule could be located in the difference map. The H atom positions or thermal parameters were not refined. All the atoms were included, however, in the final structure factor calculations.

Results and Discussion

The cryptand $\mathbf{L^1}$ was prepared as reported earlier[5] in the solvent system THF/MeOH (1:10 ratio by volume). The cryptand $\mathbf{L^2}$ could not be isolated in the above-mentioned solvent system where polymers of indefinite compositions are formed. Although many THF/MeOH solvent systems were examined, pure THF gave the best result for the Schiff base condensation step. After the condensation was complete, MeOH was added in order to facilitate the hydrogenation reaction with $NaBH_4$.

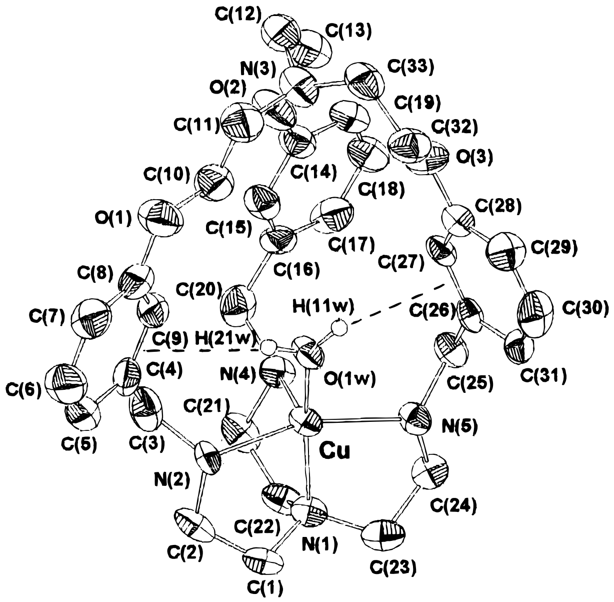

Figure 1. ORTEP[32] drawing of the cation of **1a** showing the thermal ellipsoids and the atomic numbering scheme. Hydrogen atoms are omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $\{[Cu(\mathbf{L^1})(OH_2)\}(picrate)_2(H_2O)$ (**1a**) (Esd's in Parentheses)

Cu−N(1)	2.031(8)	Cu−N(5)	2.085(7)
Cu−N(2)	2.094(8)	Cu−O(1w)	1.975(6)
Cu−N(4)	2.321(6)		
N(1)−Cu−N(2)	85.7(3)	O(1w)−Cu−N(1)	163.2(3)
N(1)−Cu−N(4)	82.92(2)	O(1w)−Cu−N(2)	89.5(3)
N(1)−Cu−N(5)	85.2(3)	O(1w)−Cu−N(4)	113.85(3)
N(2)−Cu−N(4)	102.84(4)	O(1w)−Cu−N(5)	93.4(3)
N(2)−Cu−N(5)	157.8(3)	Cu−O(1w)−H(11w)	131.2(5)
N(4)−Cu−N(5)	96.13(3)	Cu−O(1w)−H(21w)	117.1(5)

Both the cryptands readily form mononuclear inclusion complexes with Cu(II) and Ni(II) salts giving green and brown precipitates, respectively. When the Cu(II) salt of $\mathbf{L^1}$ is allowed to crystallize in moist CH_3CN the metal ion accepts a molecule of water inside the cavity forming a pentacoordinated complex. With $\mathbf{L^2}$, however, crystals suitable for X-ray crystallography could not be grown. The perchlorate salts of both the cryptates are found to be hygroscopic. Therefore, only picrate salts were subjected to spectral studies.

Description of the Structures. $[Cu(L^1)(OH_2)]\cdot(picrate)_2\cdot(H_2O)$, 1a. A perspective view of the molecule giving the atom numbering scheme is shown in Figure 1. Selected bond distances and angles are collected in Table 2. The molecular structure consists of discrete $[Cu(\mathbf{L^1})(OH_2)]^{2+}$ cations and two picrate anions. In addition, one molecule of water is present in the crystal lattice. The Cu(II) ion is coordinated to four N atoms of the tren unit at one end of the cavity. The coordination geometry around the metal ion is almost square-pyramidal where the basal plane is comprised of two secondary N atoms, N(2) and N(4), which are trans to each other; similarly the bridgehead atom N(1) and the water O(1w) are trans to each other. The atom N(4) is axially coordinated. However, the geometry has a very small trigonal-bipyramidal component[25] with $\tau = 0.09$. For a perfect trigonal bipyramidal coordination geometry, the

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Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) for $[H_2\mathbf{L}^1\subset(H_2O)_{1.5}]\cdot(ClO_4)_2\cdot(H_2O)_{0.75}$ (**5**) for the Hydrogen Bonding Scheme (Esd's in Parentheses)

O(1w)−O(2w)	2.70(2)	N(5)−H(1O1)	2.04(1)
O(1w)−N(2)	2.71(2)	O(2w)−H(2O1)	1.66(2)
O(1w)−N(4)	2.71(2)	O(2w)−O(1)	2.86(3)
O(1w)−N(5)	2.75(1)	O(2w)−O(2)	2.84(3)
O(1w)−H(2N(a))	1.603(9)	O(2w)−O(3)	2.83(3)
O(1w)−H(4N(a))	1.582(9)		
O(1w)−H(1O1)−N(5)	170.8(9)	H(2O1)−O(1w)−H(2N(a))	112.2(7)
O(1w)−H(4N(a))−N(4)	168.8(7)	H(2O1)−O(1w)−H(4N(a))	122.8(7)
O(1w)−H(2N(a))−N(2)	154.6(7)	H(1O1)−O(1w)−H(2N(a))	91.8(8)
O(1w)−H(2O1)−O(2w)	178.4(9)	H(1O1)−O(1w)−H(4N(a))	106.3(8)
H(2O1)−O(1w)−H(1O1)	113.7(9)	H(2N(a))−O(1w)−H(4N(a))	105.4(4)

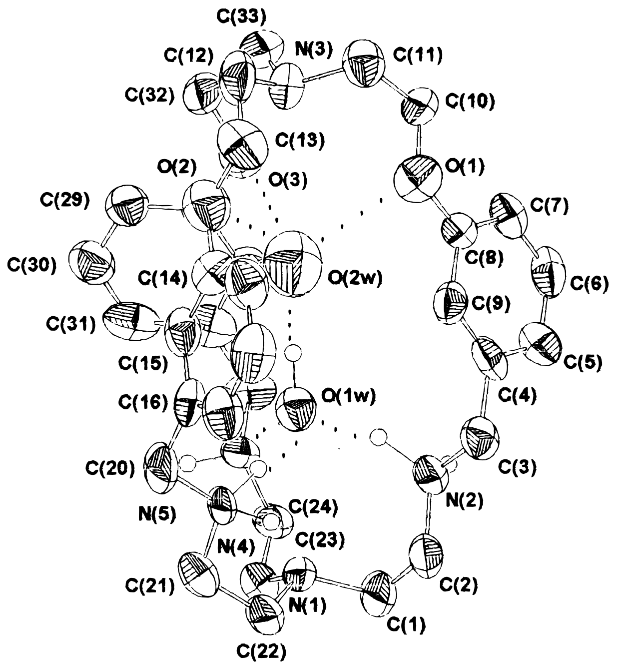

Figure 2. ORTEP[32] drawing of the cation of **5** showing the thermal ellipsoids and the atomic numbering scheme. Only those H atoms which are found in the difference map and are involved in H bonding are shown. Hydrogen atoms of O(2w) could not be located in the difference map. For clarity, some of the atoms are not labeled.

value of τ should be 1. The cavity above the tren binding site undergoes reorganization as compared to the free cryptand but not as severely as in the case where anions such as CN^- or SCN^- occupies the position of bound water.[5] The ligand maintains the endo-endo conformation where the two bridgehead N atoms have come closer to each other by about 0.78 Å compared to that in the uncomplexed $\mathbf{L}^1$. The water molecule is strongly bound as evident from the distance of 1.975(6) Å for Cu−O(1w). The Cu−N(4) bond length of 2.321(6) Å is significantly longer than the average of the other three (2.070(8) Å) due to the rigidity imposed on the cryptand by the three meta substituted benzene rings.

The entrapped water molecule exhibits interesting H-bonding characteristics. The distance from O(1w) to the centroid of the benzene rings described by C(4)−C(9), C(26)−C(31), and C(14)−C(19) are 4.138(3), 3.650(2), and 4.561(3) Å, respectively. The two H atoms of the water molecule are H-bonded to two of the benzene rings. The atom H(11w) and H(21w) are at distances of 2.907(2) and 3.264(2) Å, respectively, from their closest benzene rings. Thus, the H-bonding interactions with the benzene rings are not very strong as the theoretically predicted ideal distance is 3.11 Å.[26] However, the distances from the midpoint of C(4)−C(9) and C(26)−C(27) bonds to O(1w) are 3.258(2) and 3.125(2) Å, respectively. The distances to H(21w) and H(11w) are 2.447(2) and 2.482(2) Å, respectively signifying strong H-bonding interactions between the water hydrogens and the corresponding π bonds of the benzene rings. The corresponding bond angles are 151.85 and 138.00°, respectively. The underlying principle of hydrogen bonding is that the strongest acceptor tends to pair up with the strongest[27] donor. With a H atom donor, benzene rings tend to pair up in a π-facial manner. However, due to structural constraints, the H atoms of the water molecule in **1a** are not able to make π-facial hydrogen bonding to the center of the benzene rings. In the crystal structure of 4-nitro-2,6-diphenylphenol similar H-bonding mode has been observed[28] with OH---π hydrogen bond distances of 2.44 and 2.79 Å.

$[H_2\mathbf{L}^1\subset(H_2O)_{1.5}]\cdot(ClO_4)_2\cdot(H_2O)_{0.75}$, 5. A view of the complex cation is shown in Figure 2. The relevant bond distances and angles are collected in Table 3. The molecule consists of the cation $[H_2(\mathbf{L}^1)(H_2O)_{1.5}]^{2+}$, two perchlorate anions, and one lattice water. Occupancy of one of the water molecules O(2w) inside the cavity is less than 1. We have tried various occupancy factors and 0.5 provided the best result. Likewise, occupancy of the lattice water O(3w) is determined to be 0.75. The cryptand $\mathbf{L}^1$ shows abnormal protonation behavior which results from a cooperativity effect[7,16] mediated by the water molecule O(1w). The atoms N(2) and N(4) are protonated. The coordination of O(1w) consists of two H atoms from N(4) and N(5) and its own two H atoms which are bonded to O(2w) and the unprotonated N(5). The coordination of O(2w) consists of one H atom of O(1w) and its own two H atoms which are H-bonded to the three ethereal O atoms. The bond angles around O(1w) are nearly tetrahedral. Both the water oxygens lie in the pseudo 3-fold axis joining the two bridge head nitrogens.The atom O(1w) is 1.27(6) Å above the plane described by N(2), N(4), and N(5) while the atom O(2w) is moved toward O(1w) being 1.57(5) Å below the plane described by O(1), O(2) and O(3). The short O(1w)−N, O(1w)−O(2w), and O(2w)−O distances observed (range, 2.70(2)−2.86(3) Å) signify strong H-bonding interactions present in the cryptate. The bridgehead atoms N(1) and N(3) do not participate significantly in H bonding and lie at a distance of 3.07(5) and 3.28(6) Å, respectively from the nearest O atom of the water molecules even though the distance between N(1) and N(3) decreased to 9.05(2) Å from 9.904(7) Å in the free cryptand. Earlier we reported[7] that the cryptand $\mathbf{L}^3$ (Figure 3) accommodated one water molecule in its cavity. In this cryptand,

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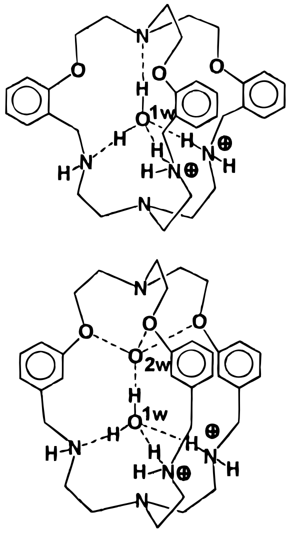

Figure 3. Chemical structures of the cations of the water cryptates $[H_2\mathbf{L^3}\subset(H_2O)]^{2+}$ (above) and $[H_2\mathbf{L^1}\subset(H_2O)_{1.5}]^{2+}$ (below). The cryptand $\mathbf{L^3}$ is from ref 7.

Table 4. Selected Nonbonded Distances (Å) for $\mathbf{L^1}$, $[Cu(\mathbf{L^1})(OH_2)]\cdot(picrate)_2\cdot(H_2O)$ (**1a**), and $[H_2\mathbf{L^1}\subset(H_2O)_{1.5}]\cdot(ClO_4)_2\cdot(H_2O)_{0.75}$ (**5**)

	$\mathbf{L^1}$	**1a**	**5**
N(1)···N(3)	9.904(7)	9.22(1)	9.05(2)
N(2)···N(4)	3.738(7)	3.45(1)	4.14(2)
N(2)···N(5)	3.684(7)	4.10(1)	4.24(2)
N(4)···N(5)	3.717(9)	3.28(1)	4.18(2)
N(1)···N(2)	2.923(6)	2.81(1)	3.06(2)
N(1)···N(4)	2.894(7)	2.89(1)	3.00(2)
N(1)···N(5)	2.933(9)	2.79(1)	3.00(2)
O(1)···O(2)	3.672(6)	4.49(1)	4.10(2)
O(1)···O(3)	3.579(5)	5.33(1)	4.15(1)
O(2)···O(3)	3.520(7)	3.63(1)	4.15(2)
N(3)···O(1)	2.919(7)	3.66(1)	2.92(2)
N(3)···O(2)	2.873(7)	2.82(1)	3.01(2)
N(3)···O(3)	2.860(5)	2.85(1)	2.91(2)
C(9)···C(15)	4.09(1)	4.28(1)	5.08(2)
C(9)···C(27)	4.022(8)	5.69(1)	5.20(2)
C(15)···C(27)	4.00(1)	4.02(1)	5.19(2)

two of the secondary N atoms present in the bridging chains get protonated on treatment with a mineral acid which then encapsulates a water molecule. This abnormal protonation behavior is believed[7,16] to be the result of a cooperativity effect mediated by the water molecule. Proton binding characteristics of these compounds are strongly influenced by molecular topology and unfavorable electrostatic repulsive effects.[29] The oxygen atom of the water molecule is tetrahedrally coordinated through H bonding with two protonated amines, the third unprotonated amine and the bridgehead N of the NO_3 site. In the solid state, free $\mathbf{L^3}$ has an endo-endo conformation with a distance of 6.249(5) Å between the bridgehead nitrogens. In case of free $\mathbf{L^1}$, this distance is[5] substantially larger (9.904(7) Å) and therefore, the larger cavity accepts two water molecules.

The selected nonbonding distances for $\mathbf{L^1}$, **1a**, and **5** are noted in Table 4. A comparison of the structures reveals that the cryptand is pre-organized and did not distort severely upon complexation.

Spectral, Magnetic, and Electrochemical Studies. A freshly prepared Cu(II) cryptate **1** exhibits three ligand field bands in chloroform or acetonitrile medium (concentrated $\sim 1 \times 10^{-2}$ M). A prominent band appears at 670 nm ($\epsilon_{max} = 210$ M^{-1} cm^{-1}) and two shoulders at about 900 and 1000 nm. At energies higher than 500 nm, the picrate anion shows strong absorption[17] obscuring LMCT transitions involving the Cu(II) ion and the nitrogen donor atoms. At energies lower than 1200 nm, sharp peaks appear which are vibrational overtones. Spectra in the solid state, though not well-resolved, indicate that the complex ion retain its identity in solution. The coordination geometry around the metal ion is proposed to be distorted trigonal pyramidal[5] although it might be possible that solvent molecules are weakly coordinated. When a few drops of water is added to the acetonitrile solution (enough to saturate all Cu(II) sites), the color of the solution turns darker and a distinctive change can be observed in the electronic spectrum. The 670 nm band becomes much broader and shifts to 715 nm ($\epsilon_{max} =$ 200 M^{-1} cm^{-1}) while one shoulder can be seen around 1000 nm. Complex **1a** shows a spectrum which is almost identical to the one obtained with water added. With **3**, two distinct ligand field bands are observed at 660 and 910 nm. Upon addition of water to the complex, no change is observed in its spectral characteristics. Two ligand field bands at 600 and 970 nm with intensities of 30 and 20 M^{-1} cm^{-1}, respectively, can be observed for the Ni(II) cryptate **2** in acetonitrile medium; for the complex **4** the two bands appear at 600 and 1020 nm with intensities of 30 and 15 M^{-1} cm^{-1} in acetonitrile. The band positions are similar to the ones observed earlier with a closely related cryptand[6] although in absence of a crystal structure no conclusion can be drawn about the coordination geometry.

The effective magnetic moment values (μ_{eff}/μ_B) for the Cu(II) cryptates after diamagnetic corrections lie in the range, 1.91−2.03 at 300 K consistent with[30] the discrete, mononuclear formulation of the complexes. For the Ni(II) cryptates, the magnetic moment values at 300 K are found to be within the range 3.01−3.04. The magnetic moment values of the Ni(II) cryptates are not indicative of the coordination geometry as both four- and five-coordinated Ni(II) complexes show[31] magnetic moment values in the same range. The EPR spectral studies carried out on the cupric complexes both in the solid state and in freshly prepared solutions. In MeCN solution at 298 K, an axial spectra is observed for both the Cu(II) cryptates **1** and **1a**. In MeCN glass (77 K), the signal is still axial although the g and A_{II} values change slightly. In the case of **3**, only broad signals are observed and not indicative of its stereochemistry.

Electron-transfer properties of the cryptates probed by cyclic voltammetry (298 K, dinitrogen flushed MeCN solution, concentrated $\sim 1.0 \times 10^{-3}$ M, glassy carbon working electrode, TBAP as the supporting electrolyte) do not exhibit any cyclic response in the region, +1.0 to −1.0 V. Only ill-defined peaks are observed in the forward scans which disappear in the reversed scans.

Conclusion. The cryptands accept a transition metal ion like Cu(II) and Ni(II) at the end of the cavity that provides four nitrogen donors. The X-ray structure of **1a** reveals that the cryptand $\mathbf{L^1}$ is mostly preorganized before the inclusion of a

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Cu(II) ion and a water molecule in the cavity. The water molecule is held inside the cavity by a combination of metal coordination and hydrogen bonding to benzene rings. Due to structural constraints, the H atoms of the water molecule are not able to make π-facial hydrogen bonding to the center of the benzene rings. However, they make strong H bonding to the midpoint of the nearest C−C linkage of the benzene moieties. We have also shown here that, if the cavity is large enough in a cryptand with strategic location of the heteroatoms capable of forming H bonds, then more than one water molecule can be included. The binding mode of the water molecules beautifully demonstrates the heteroditopic nature of the cryptand. Following this lead, it might be possible to design cryptands with large enough cavity to hold more than two water molecules inside forming water clusters. Efforts are underway in our laboratory to meet this goal.

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Supporting Information Available: Tables of crystallographic data, non-hydrogen positional, hydrogen positional, and atomic displacement parameters, bond lengths and bond angles, and packing diagrams are available (22 pages). Ordering information is given on any current masthead page.

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