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Metal Binding Characteristics of a Laterally Nonsymmetric Aza Cryptand upon Functionalization with a π-Acceptor Group

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The laterally nonsymmetric aza cryptand synthesized by condensing tris(2-aminoethyl)amine (tren) with tris{[2-(3-(oxomethyl)phenyl)oxy]ethyl}amine readily forms mononuclear inclusion complexes with both transition and main-group metal ions. In these complexes, the metal ion occupies the tren-end of the cavity making bonds with the three secondary amino and the bridgehead N atoms. When a strong π-acceptor group such as 2,4-dinitrobenzene is attached to one of the secondary amines, the binding property of the cryptand changes drastically. When perchlorate or tetrafluoroborate salts of Ni(II), Cu(II), Zn(II), or Cd(II) are used, the metal ion enters the cavity which can be monitored by the hypsochromic shift of the intramolecular charge-transfer transition from the donor amino N atom to the acceptor dinitrobenzene. However, in the presence of coordinating ions such as Cl^-, N_3^-, and SCN^-, the metal ion comes out of the cavity and binds the cryptand outside the cavity at a site away from the dinitrobenzene moiety. Four such complexes are characterized by X-ray crystallography. Thus, a metal ion can translocate between inside and outside of the cryptand cavity depending upon the nature of the counter anion.

Introduction

Macrobicyclic cryptands occupy an important position in supramolecular chemistry due to the enormous potential[1,2] these molecules offer in diverse areas of chemistry, biochemistry, and materials research. Cryptands incorporating nitrogen atoms placed at strategic positions in the three bridges can readily complex transition metal ions. We have been particularly interested in using laterally nonsymmetric aza cryptands for complexation of transition[3] as well as main-group[4] metal ions and molecular recognition of neutral molecules[5] with the goal of using such cryptates for further applications.[6] In all these complexes, the metal ion is included inside the cryptand as it forms stable complexes. The extra stability of these metal inclusion complexes is termed the cryptate effect.[7] However, binding of a cryptand from outside is reported for Ag(I) ion with an octaazamacrobicyclic cryptand.[8] Translocation of a metal ion inside and outside a cryptand cavity has not been reported in the literature to date. Such translocation, if possible, could lead to a new class of molecular machines[9−11] adding a new dimension to the kinetic, thermodynamic, photophysical, electron-transfer, and multitude of other properties in these molecules. A pertinent

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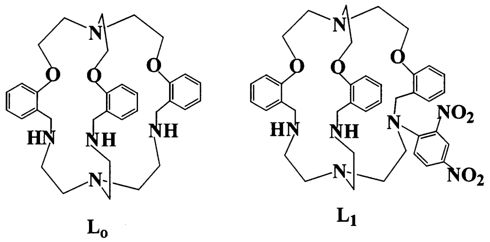

L_o L_1

Figure 1. Laterally nonsymmetric cryptand and its monoderivative.

question in this regard is the following: When can such a cryptand be forced to bind a metal ion from outside? The easiest way this can be achieved would be to alter the donor characteristics of an amino nitrogen by attaching an electron withdrawing group to it. This way, less electron density will be available for binding the metal ion inside the cryptand and coaxing it to bind from outside. The ultimate aim will be having cryptands where donor properties can be tuned to effect translocation of a metal ion inside and outside the cavity depending on various factors such as counteranions, dielectric constant of the solvent, temperature, and so on.

In our initial attempt in this direction, we present here a laterally nonsymmetric aza cryptand (Figure 1),[12] which is monosubstituted with the π-accepting 2,4-dinitrobenzene group. This transformation causes the lone-pair of the amino N atom to be in conjugation with the π-acceptor reducing its availability inside the cryptand. The coordination properties of this π-A functionalized cryptand $\mathbf{L_1}$ toward metal ions such as Cu(II), Zn(II) and Cd(II) are described.

Experimental Section

Materials. Reagent grade tris(2-aminoethyl)amine (Aldrich), salicylaldehyde, triethanolamine, and 2,4-dinitrochlorobenzene (SD Fine Chemicals) were used as received. All the solvents (SD Fine Chemicals) were purified prior to use following standard procedures. For chromatographic separation, 100−200 mesh silica gel (Acme Synthetic Chemicals) was used.

Synthesis. Cryptand $\mathbf{L_1}$. To a suspension of the cryptand $\mathbf{L_o}$[12] (0.56 g; 1 mmol) in dry EtOH (40 mL) was added anhydrous K_2CO_3 (0.44 g; 2 mmol), and the reaction mixture was stirred for 10 min. Subsequently, a solution of 2,4-dinitrochlorobenzene (0.65 g; 1.8 mmol) in dry EtOH (10 mL) was added dropwise over a period of 15 min, and the reaction mixture was allowed to stir at RT for 2 h when the solution became yellow-orange in color. For completion of the reaction, the mixture was allowed to reflux for 4 h. After cooling to RT, the solvent was removed under vacuo, and the yellow solid product obtained was repeatedly washed with water (5 × 100 mL). This product contains a mixture of all the three derivatives. The tris and the bis derivatives were removed by column chromatography in silica gel with chloroform/methanol mixed solvent with 99.5:0.5 v/v and 98.5:1.5 v/v, respectively, as the eluent. The desired mono derivative ($\mathbf{L_1}$) was eluted out finally using a chloroform/methanol ratio of 95.5:4.5 (v/v). This product was isolated as a bright yellow crystalline solid upon evaporation of the solvent. Yield 32%. Mp 145 °C. ^{1}H NMR: δ 2.42−2.51 (m, 4H), 2.64−2.75 (m, 4H), 2.89−2.94 (m, 2H), 3.23−3.26 (m, 4H), 3.35−3.41 (m, 4H), 3.62 (d, $J = 13$ Hz, 2H), 3.91 (d, $J = 13$ Hz, 2H), 4.23−4.26 (m, 6H), 4.48 (s, 2H), 5.33 (br, 2H), 6.82−6.99 (m, 8H), 7.1 (d, $J = 9.4$ Hz, 1H), 7.22−7.28 (m, 4H), 8.07 (dd, $J = 9.4$ Hz, $J = 2$ Hz, 1H), 8.54 (d, $J = 2$ Hz, 1H). FAB-MS (*m/z*) 726 (100%). Anal. Calcd for $C_{39}H_{47}N_7O_7$: C, 64.54; H, 6.53; N, 13.51. Found: C, 64.62; H, 6.61; N, 13.42.

$[Cu(L_1)Cl(ClO_4)]\cdot H_2O$, 1. To $\mathbf{L_1}$ (0.073 g, 0.1 mmol) dissolved in 10 mL of MeOH was added $Cu(H_2O)_6\cdot 2ClO_4$ (0.037 g, 0.1 mmol) dissolved in 5 mL of MeOH with gentle heating at 50 °C. On addition of NaCl (0.1 mmol), a dark green solid separated in ∼30 min which was filtered off, washed with MeOH, and dried in vacuo. X-ray quality crystals were grown from MeOH solution upon slow evaporation at RT in 85% overall yield. Anal. Calcd for $C_{39}H_{49}N_7O_{12}Cl_2Cu$: C, 49.71; H, 5.24; N, 10.41. Found: C, 49.84; H, 5.30; N, 10.32.

$[Cu(L_1)Cl](BF_4)$, 2. To $\mathbf{L_1}$ (0.073 g, 0.1 mmol) dissolved in 10 mL of MeOH was added $Cu(BF_4)_2\cdot xH_2O$ (0.024 g, 0.1 mmol) dissolved in 5 mL of MeOH, and the solution was heated gently for 10 min at 50 °C. A dark green solid separated overnight on addition of NaCl (0.1 mmol) which was collected by filtration, washed with MeOH, and air-dried. X-ray quality crystals were grown from MeCN solution upon slow evaporation at RT in 90% overall yield. Anal. Calcd for $C_{39}H_{47}N_7O_7BF_4ClCu$: C, 51.38; H, 5.19; N, 10.75. Found: C, 51.48; H, 5.25; N, 10.62.

$[Zn(L_1)N_3)_2]$, 3. To $\mathbf{L_1}$ (0.073 g, 0.1 mmol) dissolved in 10 mL of MeOH was added $[Zn(H_2O)_6][ClO_4]_2$ (0.037 g, 0.1 mmol) dissolved in 5 mL of MeOH with gentle heating at 50 °C. Upon addition of 2 equiv of NaN_3, the solution became yellowish-orange in color. After the solution stood overnight, orange crystalline solids were isolated which were collected by filtration and air-dried. Crystals suitable for X-ray diffraction were grown by slow evaporation of MeCN solution. Yield 88%. Anal. Calcd for $C_{39}H_{47}N_{13}O_7Zn$: C, 53.51; H, 5.41; N, 20.80. Found: C, 53.61; H, 5.47; N, 20.72.

$[Cd(L_1)(NCS)_2]\cdot 1/2MeOH\cdot 1/2MeCN\cdot 2H_2O$, 4. To $\mathbf{L_1}$ (0.073 g, 0.1 mmol) dissolved in 10 mL of MeOH was added $[Cd(NO_3)_2]$ (0.031 g, 0.1 mmol) dissolved in 5 mL of MeOH with gentle heating at 50 °C. Upon addition of 2 equiv of KSCN, the solution became bright yellow which afforded a yellow solid within 1 h. The solid was washed with methanol and then dissolved in 100 mL of MeCN. Crystals suitable for X-ray diffraction were grown by slow evaporation of this MeCN solution. Yield 72%. Anal. Calcd for $C_{42.5}H_{51.5}N_{9.5}O_{9.5}S_2Cd$: C, 51.46; H, 5.23; N, 13.42. Found: C, 51.51; H, 5.37; N, 13.62.

All attempts to grow single crystals of $\mathbf{L_1}$ with perchlorate, triflate, or picrate salts of the aforementioned metal ions remained unsuccessful.

Caution! Care must be taken while performing complexation of organic compounds with metal perchlorates as potentially explosive mixtures may be formed.

Measurements. Spectroscopic data were collected as follows: IR (KBr disk, 400−4000 cm^{-1}) Perkin-Elmer model 1320, electronic absorption spectra (at 295 K, freshly distilled MeCN as solvent) JASCO V-570 UV−vis−NIR spectrophotometer, ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 298 K) JEOL JNM-LA400 FT instrument, FAB mass spectrometry ($CHCl_3$ solvent, argon carrier gas, 298 K) JEOL SX 102/DA-6000, EPR (X-band, 298 and 77 K, solid and solution in MeCN) Varian E-109 with DPPH as the external standard. Melting points were determined with an electrical melting point apparatus by PERFIT, India, and were uncorrected. Microanalyses were obtained either from IIT Kanpur or from CDRI, Lucknow.

X-ray Structural Studies. Single-crystal X-ray data on **1**−**3** were collected at room temperature on a P4 Bruker X-ray diffractometer using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The data for **4** were collected on a Nonius Kappa

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Table 1. Crystal Data and Structure Refinement for **1**, **2**, **3**, and **4**

empirical formula	$C_{39}H_{49}N_7O_{12}Cl_2Cu$	$C_{39}H_{47}N_7O_7BF_4ClCu$	$C_{39}H_{47}N_{13}O_7Zn$	$C_{42.5}H_{51.5}N_{9.5}O_{9.5}CdS_2$
fw	942.29	911.64	875.27	1023.95
T	293(2) K	293(2) K	293(2) K	173(2) K
wavelength	0.71073 Å	0.71073 Å	0.71073 Å	0.71073 Å
cryst syst	monoclinic	monoclinic	triclinic	triclinic
space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a, Å	8.649 (11)	17.290 (5)	10.907(10)	12.430(3)
b, Å	16.927 (2)	13.170 (5)	12.089(10)	13.771(3)
c, Å	29.394 (4)	18.210 (5)	17.099(2)	16.613(5)
α (deg)	90	90	108.160(10)	66.672(10)
β (deg)	87.304 (2)	97.00 (5)	100.460(10)	77.723(10)
γ (deg)	90	90	95.770(10)	70.084(10)
V, Å^3	4299 (10)	4116 (2)	2076.7(4)	2411.5(11)
Z	4	4	2	2
ρ_{calcd} Mg/m^3	1.440	1.471	1.400	1.410
μ, mm^{-1}	0.703	0.672	0.657	0.602
F(000)	1964	1892	916	1058
reflns collected	7372	8740	8328	15799
ndep reflns	4085	7223	7099	9038
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
data/params	7372/554	7223/540	7099/534	9038/581
GOF	1.024	0.943	0.848	1.027
final R indices [$I > 2\sigma(I)$]	R1 = 0.0753 wR2 = 0.1644	R1 = 0.0833 wR2 = 0.2272	R1 = 0.0723 wR2= 0.1945	R1 = 0.0554 wR2= 0.1311
R indices (all data)	R1 = 0.1442 wR2 = 0.2024	R1 = 0.1299 wR2 = 0.2915	R1 = 0.1026 wR2 = 0.2295	R1 = 0.0919 wR2 = 0.1480

CCD diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 173 K. The cell parameters in each case were determined by least-squares refinement of the diffractometer setting angles from 25 centered reflections that were in the range $20° \leq 2\theta \leq 25°$. Three standard reflections were measured every hour to monitor instrument and crystal stability. The linear absorption coefficients, scattering factors for the atoms, and the anomalous dispersion corrections were taken from the International Tables for X-ray Crystallography.[13] The structures were solved by the direct method using SIR92[14] and were refined on F^2 by full-matrix least-squares technique using the SHELXL-97[15] program package. In each case, some of the H atoms could be located in the difference maps while the rest were calculated assuming ideal geometries of the atoms concerned. The H atom positions or thermal parameters were not refined but included in the structure factor calculations. The crystal data for the four structures are collected in Table 1.

Results and Discussion

The unsubstituted cryptand (**L₀**) has three derivatizable secondary amino groups in the three bridges. With the pK_a values[16] for these being different, selective functionalization of the cryptand can be made. It has been empirically found that upon reacting 1.8 equiv of 2,4-dinitrochlorobenzene with the unsubstituted cryptand (**L₀**), mono, bis, and tris derivatives are formed in almost equal amounts. The mono π-A functionalized cryptand (**L₁**) can be separated by column chromatography from the tris and the bis derivatives. Thus, by utilizing this simple and straightforward strategy we can avoid the hassles of multistep protection and deprotection of amines and isolate the compounds in good yields.

All the metal complexes are isolated in high yields. The crystals, once formed, become sparingly soluble in common organic solvents such as alcohol, acetonitrile, acetone, chloroform, and THF but are soluble in DMF and DMSO.

Spectral and Magnetic Studies. The unsubstituted cryptand (**L₀**) does not absorb to any significant extent at energies lower than 250 nm. The mono substituted cryptand **L₁** exhibits an intense absorption band centered at 380 nm ($\epsilon_{max} = 17180$ M^{-1} cm^{-1}) attributable[17] to the intramolecular charge transfer (ICT) transition from the donor N atom to the acceptor dinitrobenzene moiety which can accept electron density into its available π-symmetry orbital. The metal inclusion complexes of the unsubstituted cryptand do not absorb in the range 300−450 nm, to any noticeable extent. Therefore, the ICT transition can be utilized to monitor the inclusion of a metal ion inside the cryptand as the bound metal ion will modulate the donor ability of the N atom attached to the dinitrobenzene moiety. The alkali or alkaline-earth metal ions do not exhibit any changes in the absorption spectra since these ions occupy the upper deck of the cryptand and, hence, are not able to communicate with the D−π−A chromophore unit. Addition of a metal ion such as Ni(II), Cu(II), Zn(II), or Cd(II) as the perchlorate or tetrafluoroborate salt induces a blue-shift[17] with concomitant lowering of intensity of the ICT band (Figure 2) as these metal ions enter and occupy the tren-end of the cavity and become directly involved with the D−π−A chromophore

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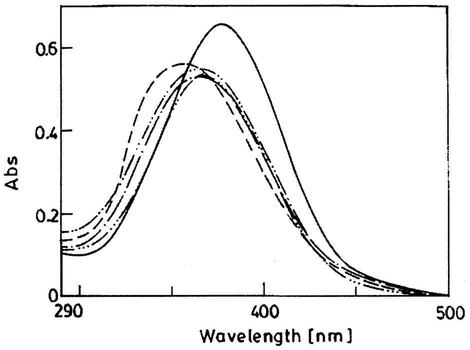

Figure 2. Effect of addition of metal perchlorates on the ICT band of $\mathbf{L_1}$: (—) metal free $\mathbf{L_1}$; (— —) upon addition of Cu(II); (— • • • —) upon addition of Cd(II) added; (— • —) upon addition of Ni (II); (— • • • —) upon addition of Zn(II). Concentration of $\mathbf{L_1}$ was 5 × 10^{-4} M and that of the metal perchlorates was 5 × 10^{-3} M.

unit. On gradual addition of the perchlorate salts, the absorption spectra show[6d] a well-defined isosbestic point suggesting a 1:1 stoichiometry with $\mathbf{L_1}$. Compound $\mathbf{L_1}$ exhibits a maximum blue-shift in the presence of cupric perchlorate (21 nm with regard to free $\mathbf{L_1}$). However, when the chloride salts of these metal ions are used, no shift or change of intensity of the ICT band is observed. Also, when Cl^-, SCN^-, or N_3^- ion is added to the metal perchlorate and $\mathbf{L_1}$ mixture, the ICT band position and intensity slowly change (~24 h) to the values obtained on free $\mathbf{L_1}$. These results lead us to the suggestion that, in the presence of a coordinating anion like chloride, azide, etc., the metal ion has a strong preference to bind the cryptand from outside.

The effective magnetic moment values ($\mu_{\mathrm{eff}}/\mu_{\mathrm{B}}$) for the Cu(II) complexes after diamagnetic corrections lie in the range 1.94−2.01 at 295 K, consistent[18] with the discrete, mononuclear formulation of the complexes. The EPR spectral studies of the Cu(II) complexes were carried out in the solid state and in dry DMF as the solvent. In the solid state, a broad signal with $g_{\mathrm{av}} \approx 2.05$ is observed in each case at ambient temperature; the signal sharpens somewhat at 77 K. These pure solids are not magnetically dilute enough to yield ESR spectra indicative of the solid-state stereochemistry. On the other hand, in DMF solution at 298 K, a typical four-line signal ($g_{\mathrm{av}} = 2.14$ for **1** and 2.11 for **2**) is observed in each case. At 77 K, the signal changes to an axial one with $g_{\parallel} = 2.22$ and $g_{\perp} = 2.02$ for **1** and $g_{\parallel} = 2.30$ and $g_{\perp} = 2.04$ for **2**. The $A_{\parallel}$ values for **1** and **2** are 170 × 10^{-4} and 175 × 10^{-4} cm^{-1}, respectively. It follows, therefore, from the ESR results that the stereochemistry in solution is also most likely to be square pyramidal as in the solid-state X-ray structure.

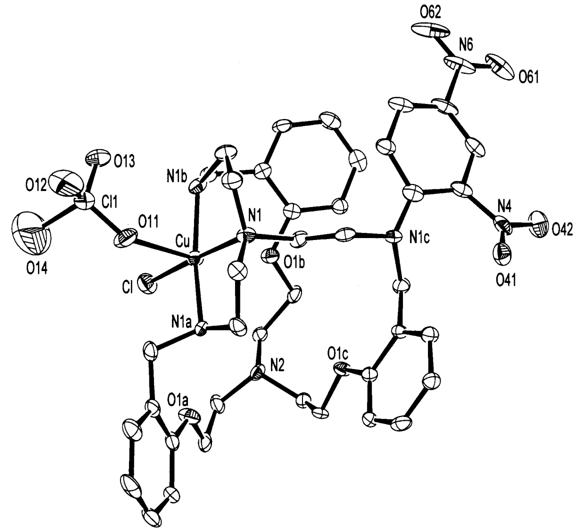

Figure 3. Crystal structure of **1**.

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) of the Complexes

$[Cu(L_1)(Cl)(ClO_4)]\cdot H_2O$, **1**			
Cu−N1	2.055(5)	Cu−N1b	2.045(5)
Cu−N1	2.055(5)	Cu−Cl	2.280(19)
Cu−O11	2.391(5)		
N1a−Cu−N1b	168.1(2)	N1−Cu−N1a	84.4(2)
N1−Cu−N1b	83.7(2)	N1−Cu−Cl	174.6(2)
N1a−Cu−O11	89.7(2)	N1−Cu−O11	89.2(2)
N1b−Cu−Cl	95.9 (1)	N1b−Cu−O11	88.9(2)
Cl−Cu−O11	96.1(1)		
$[Cu(L_1)(Cl)](BF_4)$, **2**			
Cu−N1a	2.012(7)	Cu−N1	2.073(6)
Cu−O1a	2.48 (6)	Cu−N1b	2.010(6)
Cu−Cl	2.264(5)		
N1a−Cu−N1b	165.5(3)	N1b−Cu−O1a	94.1(2)
N1−Cu−Cl	175.9(2)	N1−Cu−O1a	98.26(2)
N1a−Cu−O1a	84.24(2)	N1a−Cu−N1	84.2(3)
N1b−Cu−N1	85.5(2)	N1a−Cu−Cl	95.4(2)
N1b−Cu−O1a	107.37(2)		
$[Zn(L_1)(N_3)_2]$, **3**			
Zn−N1a	2.089(4)	Zn−N1b	2.050(4)
Zn−N1z	1.943(7)	Zn−N4z	1.989(8)
N1a−Zn−N1b	110.7(2)	N1a−Zn−N1z	108.8(3)
N1a−Zn−N4z	105.5(3)	N1b−Zn−N1z	106.7(2)
N1b−Zn−N4z	111.2(3)	N1z−Zn−N4z	113.9(3)
$[Cd(L_1)(NCS)_2]\cdot 1/2MeOH\cdot 1/2MeCN\cdot 2H_2O$, **4**			
Cd−N1	2.416(3)	Cd−N11	2.228(4)
Cd−N1a	2.408(4)	Cd−N12	2.444(4)
Cd−N1b	2.362(4)	Cd−N12′	2.499(4)
N11−Cd−N1b	93.54(16)	N11−Cd−N1a	91.98(16)
N1b−Cd−N1a	107.27(14)	N11−Cd−N1	162.25(15)
N1b−Cd−N1	77.50(13)	N1a−Cd−N1	76.45(13)
N11−Cd−N12	96.89(16)	N1b−Cd−N12	86.91(14)
N1a−Cd−N12	162.81(13)	N1−Cd−N12	97.88(12)
N11−Cd−N12	99.53(15)	N1b−Cd−N12	161.44(13)
N1a−Cd−N12	85.50(14)	N1−Cd−N12	93.02(12)
N12−Cd−N12	78.54(17)		

Description of the Structures. $[Cu(L_1)(Cl)(ClO_4)]\cdot H_2O$, 1. The structure of **1** consists of discrete, neutral $[Cu(L_1)(Cl)(ClO_4)]$ units and water molecules. A perspective view of the molecule showing the atom numbering scheme is given in Figure 3 while the bond distances and angles are collected in Table 2. The Cu(II) ion is bonded to the two secondary amino N atoms and the bridgehead N atom at the tren-end, in an unprecedented fashion outside the cavity. The other two coordination sites are occupied by one chloride ion and one oxygen of a perchlorate ion. The dinitrobenzene moiety remains furthest from the metal ion. As a result of this binding mode, the cryptand has undergone a significant conformational change. The two bridgehead N atoms have

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[18] Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley: New York, 1988; p 768.

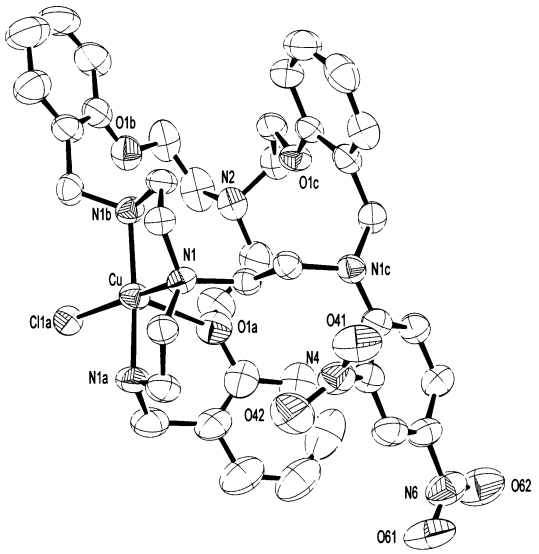

Figure 4. Crystal structure of **2**.

come much closer at 5.281 Å from the distance of 6.249 Å in **L₀**.[3c] The metal ion has pulled the three N donors of the cryptand moiety toward itself causing these three atoms to be inverted with their lone-pairs directed at the metal ion. Thus, the cryptand has changed to an endo−exo conformation upon metal binding. All the bond distances and angles in the cryptand moiety are, however, within normal statistical errors.

The coordination geometry around the metal ion is square pyramidal where the three N and the Cl$^-$ occupy the basal plane with the O atom at the axial position. The coordination geometry has a very small trigonal bipyramidal component[19] with $\tau = 0.1$. For a perfect square pyramidal geometry, this value should be 0. The Cu(II) ion is only 0.045 Å above the least-squares plane described by the four basal atoms and toward the axial O atom. All Cu−N bond distances are within the normal range,[20] and the Cu−Cl distance is also within the normal range found in other compounds. The ClO$_4^-$ anion is tightly held to the metal ion as the Cu−O bond is shorter[21] compared to other perchlorate bound Cu complexes.

[Cu(L$_1$)Cl](BF$_4$), 2. The X-ray structure of **2** consists of discrete [Cu(L$_1$)Cl]$^+$ cations and BF$_4^-$ anions. As in **1**, the metal ion is bound to the cryptand from outside the cavity (Figure 4) although there is a significant difference in the mode of binding in the two cases. In **2**, the metal ion is again square pyramidal with two amino and one bridgehead N atoms and the Cl$^-$ ion forming the basal plane, and the axial site is occupied by an ethereal O atom of the cryptand moiety.

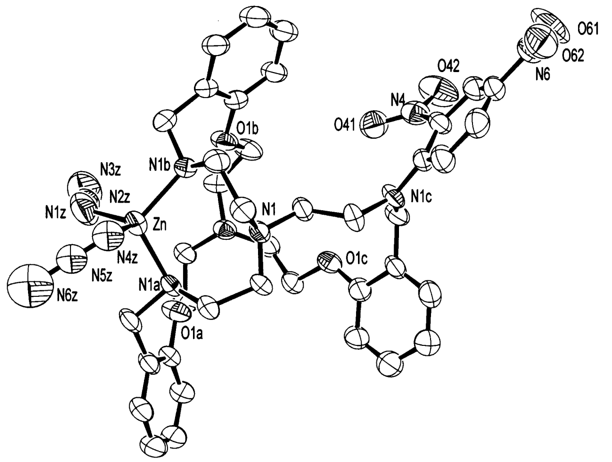

Figure 5. Crystal structure of **3**.

The difference in the binding mode is due to the less coordinating nature of BF$_4^-$ compared to that of the ClO$_4^-$ anion. The coordination geometry ($\tau = 0.17$) is also more distorted from an ideal square pyramid[19] compared to **1**, and the metal ion is situated 0.221 Å above the least-squares plane described by the four atoms in the basal plane and toward the axial O atom. All the Cu−N and the Cu−Cl bond distances are, however, within normal ranges.[20] The axial Cu−O(ethereal) bond is significantly long, as otherwise the cryptand moiety would have undergone severe distortion. The two bridgehead N atoms are closer at 4.952 Å compared to that in **1** in the overall endo−exo conformation. The bond distances and angles within the cryptand moiety are normal. The Cl$^-$ ion shows positional disorder in the structure.

[Zn(L$_1$)(N$_3$)$_2$], 3. The X-ray structure of **3** reveals a slightly different binding mode to **L$_1$**. Here, the Zn(II) ion is bonded to the cryptand through two secondary amino N atoms (the bridgehead N atom remains uncoordinated) while the other two coordination sites are occupied by two azide anions forming an almost ideal tetrahedral coordination geometry (Figure 5). One of the azide groups is disordered. All the Zn(II)−N bond distances are normal.[22] The metal ion has pulled the two amino N atoms away from the cryptand causing severe conformational distortion, and as a result, the two bridgehead N atoms are much closer compared to **1** and **2** at 4.652 Å. All the bond distances and angles within the cryptand are again normal. The packing diagram of this complex shows that the metal-bound N atom of one of the azide groups makes a C−H···N intermolecular hydrogen bonding interaction (C···N, 3.308 Å) with an aromatic proton of the neighboring cryptand forming an infinite supramolecular linear array in the crystal lattice (Figure 6).

[Cd(L$_1$)(NCS)$_2$]·1/2MeOH·1/2MeCN·2H$_2$O, 4. In the asymmetric unit, a Cd(II) ion is bonded to the cryptand through its two secondary amines and two thiocyanate anions. The molecular structure (Figure 7) reveals a dimeric unit, where two Cd(II) ions are bonded to two bridging thiocyanate anions, and in addition, each metal ion is bonded to one **L$_1$** and one terminal thiocyanate anion. The crystal lattice also

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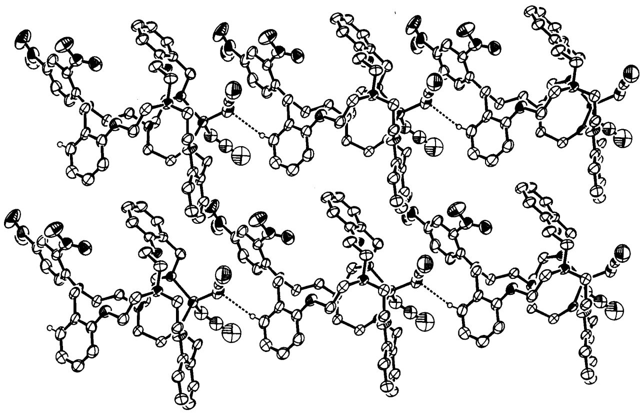

Figure 6. Packing of **3** in the crystal lattice showing an infinite supramolecular array.

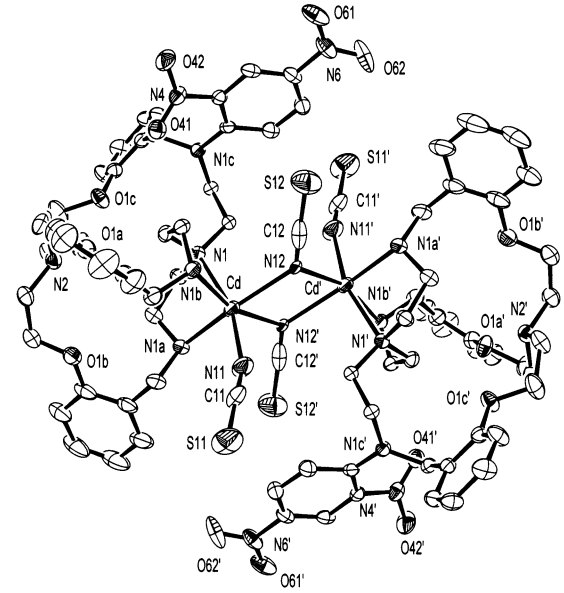

Figure 7. Crystal structure of **4**.

contains disordered solvent molecules such as methanol, acetonitrile, and water. Each Cd(II) ion is bonded to six N atoms in a distorted octahedral environment (Table 2): two secondary amino N atoms, the bridgehead N at the tren-end of the cryptand moiety, a terminal thiocyanate, and two bridging thiocyanates.

All the Cd(II)−N bond distances are within the normal range found in other complexes[23] of Cd(II). The two bridgehead N atoms have come much closer (4.523 Å) compared to other complexes in the series. Thus, the cryptand moiety in **4** has undergone maximum distortion from its pseudo-3-fold symmetry. Although thiocyanate anions are known[23] to bind Cd(II) through both S and N atoms, none of the S atoms here are bonded to the metal ions. The Cd(II)−N bond distances involving the bridging thiocyanates are significantly longer compared to the known structures[24] due to the steric hindrance provided by the dinitrobenzene moiety.

Conclusion

The present study shows that it is possible to bind a metal ion outside the cavity of a cryptand if it is modified suitably. More interestingly, a metal ion bound inside the cavity can be forced outside by changing the counteranions. The cryptand is not very rigid and can distort to a different extent for optimum binding of a metal ion outside the cavity. It will be of interest to probe if a cryptand which is much more rigid compared to the present one can translocate a metal ion in a similar fashion. This result is significant because this offers a possibility of controlling any property of the metal cryptate in a reversible manner simply by changing the counteranion. It is thus possible, in principle, to attach fluorophoric groups to such cryptand derivatives for signaling the presence of transition metal ions inside the cavity. As the metal ion can be forced out by coordinating anions, these fluorescent signaling systems can be made reversible. Besides, the metal ions bound to the cryptand from outside can be utilized to have metal assembled giant structures with cryptands. We are presently working along these lines.

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Supporting Information Available: Additional figures, table, and crystallographic information. This material is available free of charge via the Internet at http://pubs.acs.org.

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