Synthesis of a Heteroditopic Cryptand Capable of Imposing a Distorted Coordination Geometry onto Cu(II): Crystal Structures of the Cryptand (L), [Cu(L)(CN)](picrate), and [Cu(L)(NCS)](picrate) and Spectroscopic Studies of the Cu(II) Complexes

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The synthesis of a new macrobicyclic cryptand (**L**) with heteroditopic receptor sites has been achieved in good yields by the [1 + 1] Schiff base condensation of tris(2-aminoethyl)amine (tren) with the tripodal trialdehyde, tris{[2-(3-(oxomethyl)phenyl)oxy]ethyl}amine at 5 °C temperature. The crystal structure of **L** ($P2_1/c$, $a = 10.756$ (5) Å, $b = 27.407(9)$ Å, $c = 12.000(2)$ Å, $\beta = 116.22(3)°$, $Z = 4$, $R = 0.060$, $R_w = 0.058$) shows a pseudo-3-fold symmetry axis passing through the two bridgehead nitrogens. This symmetry is maintained in chloroform solution also, as indicated from its ^{1}H-NMR spectral data. The cryptand readily forms inclusion complexes with the Cu(II) ion at the tren end of the cavity. The tetracoordinated Cu(II) cryptate (**1**) thus formed with Cu(picrate)$_2$ exhibits a very small A_{II} value (60×10^{-4} cm^{-1}) in its EPR spectrum and low-energy ligand field bands in its electronic spectrum in MeCN at room temperature. The bound Cu(II) ion readily accepts the anions CN$^-$, SCN$^-$, or N$_3$$^-$, forming distorted trigonal bipyramidal complexes (**2**−**4**). The crystal structure of [Cu(L)(CN)](picrate) (**2**) ($P2_1/C$, $a = 13.099(1)$ Å, $b = 11.847(8)$ Å, $c = 25.844(7)$ Å, $\beta = 91.22(1)°$, $Z = 4$, $R = 0.056$, $R_w = 0.054$) has been determined. The equatorial coordination is provided by the three secondary amino N atoms of the tren unit in **L**, while the two axial positions are occupied by the bridgehead N of the tren unit and the C atom of the cyanide group. One of the equatorial Cu−N bond distances is 2.339(6) Å, which is longer than normal values. The crystal structure of [Cu(L)(NCS)](picrate) (**3**) ($C2/c$, $a = 47.889(10)$ Å, $b = 10.467(5)$ Å, $c = 16.922(2)$ Å, $\beta = 93.90(2)°$, $Z = 8$, $R = 0.054$, $R_w = 0.055$) shows the coordination geometry around the Cu(II) ion to be very similar to that in the case of **2**. The electronic spectral and EPR spectral data obtained on **2**−**4** are characteristic of trigonal bipyramidal Cu(II) complexes. The three meta-substituted benzene rings present in **L** makes the donor atom somewhat rigid in nature which enforces a distorted geometry around the Cu(II) ion.

Introduction

Cryptands as ligands for transition metal ions are of considerable current interest.[1−4] In a cryptand, the donor atoms' topology as well as their rigidity can be varied via ligand design. Therefore, with these molecules imposition of a desired geometry onto a coordinating metal ion can be achieved.[5] Imposition of an unusual coordination geometry in turn will lead to new electronic structure and bonding of the metal complex formed. A heteroditopic cryptand can be designed so that a metal ion can recognize only one receptor site, leaving the other side empty. It will be possible for an inorganic/organic group to occupy this vacant site, thereby forming cascade complexes. These type of complexes are formed via a sequential double selection process, (a) binding of the cation by the ligand's donor atoms and (b) selection of the substrate controlled by the nature and arrangement of the complexed cation. In literature there are a few examples[1,6−9] of binuclear metal cryptates, which bind the substrates of compatible size between both of the complexed metal ions in a cascade fashion, while such complexes of mononuclear cryptates are very rare.[10] The present ligand has been synthesized by keeping all these aspects in mind. Herein, we report our first results in this area. The new macrobicyclic heteroditopic cryptand (**L**) was synthesized by [1 + 1] condensation of a new tripodal trialdehyde with tris(2-aminoethyl)amine (tren). We and others have described the synthesis of macrobicyclic molecules using alkali/alkaline earth metal ions as templates.[11−13] Recently, a macrobicyclic cryptand has been synthesized[14] by [2 + 3] condensation of tren with glyoxal at low temperature. The present cryptand **L** has been synthesized in multigram scale at low temperature without using any templating metal ions. The cryptand is well-suited to accommodate a transition metal ion at the tren end of the cavity, leaving an empty space to enable inorganic anions to enter and get bonded to the metal ion.

The aim of the present work is to probe whether the donor atom in the cryptand can impose a distorted geometry onto Cu(II) and whether simple inorganic anions like CN$^-$, SCN$^-$, and N$_3$$^-$ can add onto the metal ion inside the cavity. Herein

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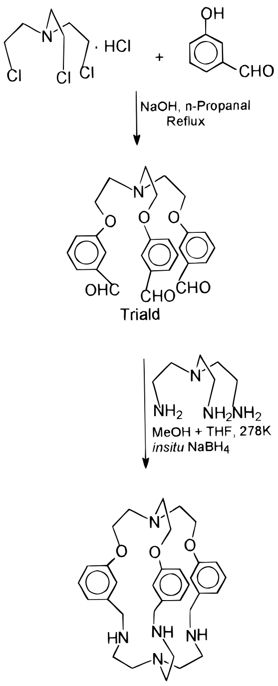
Scheme 1. Synthesis of the Cryptand **L**



we report the synthesis of **L** and its ligating characteristics toward the Cu(II) ion.

Experimental Section

Materials. Reagent grade tris(2-aminoethyl)amine, 3-hydroxybenzaldehyde (Aldrich), and triethanolamine (Glaxo) were used as received. Thionyl chloride and all of the solvents (SD Fine Chemicals) were purified prior to use by following standard procedures.[15]

Synthesis. Tris{[2-(3-(oxomethyl)phenyl)oxy]ethyl}amine, Triald. To a solution of 3-hydroxybenzaldehyde (7.33 g; 60 mmol) in propanol (200 cm^3) was added crushed NaOH (3.2 g, 80 mmol) and stirred at 303 K for 30 min. To the resulting brown solution, solid tris(2-chloroethyl)amine hydrochloride[16] (4.8 g; 20 mmol) was added at once, and the mixture was heated under reflux for 4 h. After this period, the brown solution was allowed to cool to room temperature and poured into 200 cm^3 of cold water. Triald was extracted from this mixture with 3 × 50 cm^3 of $CHCl_3$. The organic layer was washed several times with water, then dried over anhydrous Na_2SO_4, and finally treated with activated charcoal. Triald was obtained by evaporating the organic layer as a pale yellow semisolid; yield, 80%. IR (KBr pellet, cm^{-1}): ν_{max} 1690 s. ^{1}H-NMR (80 MHz, $CDCl_3$): δ 3.2 (t, 6H), 4.2 (t, 6H), 7.3 (m, 12H), 10.0 (s, 3H).

Cryptand, L. Triald (3.68 g, 8 mmol) was taken in 400 cm^3 of the mixed solvent system THF:MeOH (1:10 ratio by volume), in a 2000 cm^3 round bottomed flask at 278 K. To this solution was added a solution of tris(2-aminoethyl)amine (1.17 g, 8 mmol) in 300 cm^3 of MeOH over a period of 12 h, while the temperature was maintained at 278 ± 1 K and the mixture was stirred continuously. The addition was adjusted so as to disperse a drop before another drop can fall into the reaction mixture. At the end of the addition, the reaction was carried out simply by stirring 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 $NaBH_4$ (~1.6 g) 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 40 cm^3 of cold water. The desired cryptand **L** was extracted with 4 × 50 cm^3 of $CHCl_3$. The organic layer was dried over anhydrous Na_2SO_4 and evaporated to obtain a pale yellow solid. The solid washed with 50 cm^3 of MeCN and dried in air; yield, 39% (mp, 125 °C). ^{1}H-NMR (80 MHz, $CDCl_3$): δ 1.9 (s, 3H), 2.65 (s, 12H), 3.05 (t, 6H), 3.6 (s, 6H), 4.0 (t, 6H), 6.9 (m, 12H). ^{13}C-NMR (20.1 MHz, $CDCl_3$): δ 48.10, 54.00, 55.90, 56.41, 68.03, 113.20, 114.63, 120.70, 129.17, 142.40, 159.75. FAB-MS: *m/z* 560 (M + 1)$^+$. Anal. Calcd. for $C_{33}H_{45}N_5O_3$: C, 70.81; H, 8.10; N, 12.51. Found: C, 70.27; H, 8.31; N, 12.42. Crystals of this compound suitable for X-ray analysis were grown by slow evaporation of a dilute solution with the mixed MeOH:MeCN solvent (1:1 by volume) at room temperature.

[Cu(L)](picrate)$_2$, 1. To **L** (0.056 g, 0.1 mmol) dissolved in 5 cm^3 of MeOH was added Cu(picrate)$_2$ (0.052 g, 0.1 mmol) dissolved in 5 cm^3 of MeOH. A green solid separated immediately that was collected by filtration, washed with MeOH and air-dried. The solid, upon recrystallization from MeCN, afforded a green crystalline solid in 90% overall yield which was dried under vacuum at 40 °C (mp (dec.), 150 °C). Anal. Calcd for $C_{45}H_{49}N_{11}O_{17}Cu$: C, 50.07; H, 4.58; N, 14.27. Found: C, 49.83; H, 4.72; N, 14.08.

[Cu(L)(CN)](picrate), 2. Complex **1** (0.109 g, 0.1 mmol) was dissolved in 10 cm^3 of MeCN and treated with NaCN (0.005 g, 0.1mmol) dissolved in 2 cm^3 of MeOH with warming at 50 °C. Upon addition of NaCN, the color of the solution became dark green. The solution was filtered and allowed to evaporate slowly at room

Table 1. Crystallographic and Experimental Data for **L**, {[Cu(CN)]**L**}(picrate) (**2**) and {[Cu(NCS)]**L**}(picrate) (**3**)

	L	(**2**)	(**3**)
formula	$C_{33}H_{45}N_5O_3$	$C_{40}H_{47}N_9O_{10}Cu$	$C_{40}H_{47}N_9O_{10}SCu$
MW	559.758	878.049	910.113
temp, °C	25	25	25
radiation, graphite monochromated	Mo Kα	Mo Kα	Mo Kα
λ, Å	0.71073	0.71073	0.71073
cryst sys	monoclinic	monoclinic	monoclinic
space group	$P2_1/C$	$P2_1/C$	$C2/c$
a,Å	10.756(5)	13.099(1)	47.889(10)
b, Å	27.407(9)	11.847(8)	10.467(5)
c,Å	12.000(2)	25.844(7)	16.922(2)
β, deg	116.22(3)	91.22(1)	93.90(2)
V, Å^3	3174.5(2)	4009.8(5)	8464.0(4)
Z	4	4	8
F(000), electrons	500	699	715
D_{calcd}, g/cm^3	1.269	1.453	1.427
μ, mm^{-1}	0.08	0.62	0.64
cryst size, mm^3	0.20 × 0.30 × 0.50	0.20 × 0.30 × 0.30	0.15 × 0.20 × 0.40
transmn (max, min)	0.9757, 0.9406	0.8323, 0.7614	0.8664, 0.6845
no. of unique reflcns	5570	7362	7445
no. of reflcns used ($I > 2\sigma(I)$)	2368	4482	3605
no. of variables	370	541	550
R^a	0.060	0.056	0.054
$R_w{}^b$	0.058	0.054	0.055
goodness of fit	2.169	2.917	1.702

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

Table 2. Non-Hydrogen Positional and Equivalent Isotropic Displacement Parameters (Å^2) for **L** (Esds in Parentheses)

atom	*x/a*	*y/b*	*z/c*	*U*(eq)
O(1)	− 0.2274(6)	0.6215(2)	0.1187(6)	0.084(4)
O(2)	−0.0170(6)	0.5151(3)	0.1239(6)	0.087(4)
O(3)	−0.0747(7)	0.5430(2)	0.3838(6)	0.083(4)
N(1)	0.5714(8)	0.7215(3)	0.4850(8)	0.080(5)
N(2)	0.2776(8)	0.7435(3)	0.3376(7)	0.076(4)
N(3)	−0.2765(8)	0.5178(3)	0.1388(8)	0.073(4)
N(4)	0.4900(8)	0.6390(3)	0.3169(7)	0.087(5)
N(5)	0.4408(9)	0.6589(3)	0.6015(8)	0.097(5)
C(1)	0.517(1)	0.7712(4)	0.4519(9)	0.091(6)
C(2)	0.368(1)	0.7744(4)	0.4384(9)	0.083(6)
C(3)	0.140(1)	0.7378(3)	0.3307(8)	0.075(5)
C(4)	0.0477(9)	0.7113(3)	0.2133(9)	0.062(5)
C(5)	0.053(1)	0.7197(4)	0.101(1)	0.082(6)
C(6)	−0.035(1)	0.6953(4)	−0.0050(9)	0.102(6)
C(7)	−0.1305(9)	0.6614(4)	−0.0027(9)	0.088(6)
C(8)	−0.1355(9)	0.6535(4)	0.108(1)	0.068(5)
C(9)	−0.047(1)	0.6777(3)	0.2151(9)	0.063(5)
C(10)	−0.307)1)	0.5911(4)	0.0151(9)	0.086(5)
C(11)	−0.377(1)	0.5524(4)	0.0583(9)	0.085(6)
C(12)	−0.235(1)	0.4798(4)	0.0799(9)	0.088(6)
C(13)	−0.077(1)	0.4719(4)	0.1454(9)	0.088(6)
C(14)	0.123(1)	0.5205(4)	0.1890(9)	0.070(6)
C(15)	0.176(1)	0.5646(4)	0.1734(8)	0.073(6)
C(16)	0.318(1)	0.5739(4)	0.2341(9)	0.073(6)
C(17)	0.404(1)	0.5390(4)	0.313(1)	0.089(6)
C(18)	0.352(1)	0.4957(4)	0.328(10	0.096(6)
C(19)	0.209(1)	0.4847(4)	0.265(1)	0.083(6)
C(20)	0.373(1)	0.6205(4)	0.2071(9)	0.085(6)
C(21)	0.556(1)	0.6815(4)	0.2940(9)	0.092(6)
C(22)	0.6514(9)	0.7050(4)	0.419(1)	0.097(6)
C(23)	0.635(1)	0.7106(4)	0.618(1)	0.105(6)
C(24)	0.590(1)	0.6599(4)	0.6402(9)	0.102(6)
C(25)	0.387(1)	0.6107(4)	0.6025(9)	0.091(6)
C(26)	0.236(1)	0.6121(4)	0.5752(9)	0.083(7)
C(27)	0.142(1)	0.5805(4)	0.4898(9)	0.075(6)
C(28)	0.004(1)	0.5770(4)	0.4674(9)	0.072(6)
C(29)	−0.043(1)	0.6079(4)	0.531(1)	0.094(6)
C(30)	0.051(1)	0.6399(4)	0.617(1)	0.117(7)
C(31)	0.189(1)	0.6428(4)	0.639(1)	0.105(7)
C(32)	−0.218(1)	0.5421(4)	0.3526(9)	0.087(6)
C(33)	−0.2840(9)	0.5040(4)	0.2515(9)	0.082(6)

temperature. Overnight, dark green plates appeared which were collected by filtration and air-dried. A further crop was obtained on further evaporation of the solvent at room temperature; yield 86% (mp (dec.) 200 °C) Anal. Calcd for $C_{40}H_{47}N_9O_{10}Cu$: C, 54.72; H, 5.40; N, 14.43. Found: C, 54.19; H, 5.87; N, 14.23.

[Cu(L)(NCS)](picrate), 3. This complex was isolated following the procedure adopted for **2** except that NH_4SCN (0.008 g, 0.1 mmol) was used instead of NaCN. Dark green rectangular parallelepipeds were isolated in 80% yield (mp (dec.) 200 °C). Anal. Calcd for $C_{40}H_{47}N_9O_{10}SCu$: C, 52.80; H, 5.20; N, 13.92. Found: C, 52.45; H, 5.31; N, 13.81.

[Cu(L)(N$_3$)](picrate), 4. Dark green thin plates of **4** were isolated as above in 88% yield (mp (dec.) 175 °C). Anal. Calcd for $C_{39}H_{47}N_{11}O_{10}$ Cu: C, 52.43; H, 5.30; N, 17.24. Found: C, 52.21; H, 5.12; N, 16.98.

***Caution*!** The picrate salts must be handled with care as they are potential explosives.

Measurements. Spectroscopic data were collected as follows: IR (KBr disk, 400−4000 cm^{-1}), Perkin-Elmer Model 1320; electronic absorption spectra (at 298 K, freshly distilled MeCN as solvent), JASCO V-570 UV−vis−near-IR spectrophotometer, proton and carbon NMR (80 and 20.1 MHz, respectively, $CDCl_3$, TMS), Bruker WP-80FT instrument, FAB mass spectrometry ($CHCl_3$ as solvent, argon as the carrier gas), JEOL Model SX 102/DA-6000; EPR (X-band at 298 and 77 K, solid and solution), Varian E-109 with solute concentration of ca. 1 × 10^{-3} M in MeCN. Microanalyses were obtained at CDRI, Lucknow, India. Reported melting points are uncorrected.

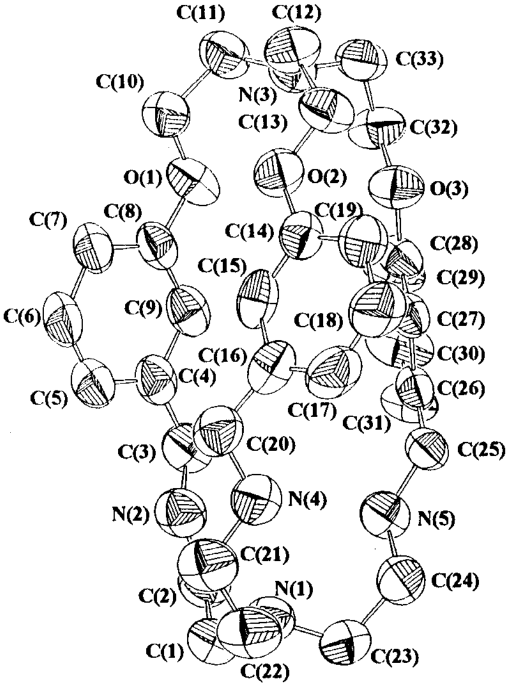


Figure 1. ORTEP[21] drawing of **L** showing the thermal ellipsoids and the atomic numbering scheme. Hydrogen atoms are omitted for clarity.

X-ray Structural Studies. X-ray quality crystals were obtained only with **L**, **2**, and **3**. Single crystal X-ray data on them were collected at room temperature on an Enraf-Nonius CAD4-Mach diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.710\ 73$ Å). The cell parameters in each case were determined by least-squares refinement of the diffractometer setting angles for 25 centered reflections that were in the range 22° $\leq 2\theta \leq$ 25°. Systematic absences were consistent with the space group $P2_1/c$ for both **L** and **2**. For **3**, the systematic absences were consistent with the space groups *Cc* and *C*2/*c*. The structure was solved and successfully refined in the space group *C*2/*c*. Three standard reflections were measured at every hour to monitor instrument and crystal stability. The maximum corrections of intensity based on the standard reflections were less than 1% for each. Intensity data were corrected for Lorentz and polarization effects; analytical absorption corrections were applied. The XTAL 3.2 program package[17] was used in absorption and all subsequent calculations, utilizing 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-disperson corrections were taken from the *International Tables for X-ray Crystallography*.[18] The structures were solved by the direct method[19] and successive difference Fourier syntheses. The refinement was done by 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 in each case, the rest were calculated assuming ideal geometries of the atom concerned. H atom positions or thermal parameters were not refined.

Results and Discussion

The cryptand **L** can be easily synthesized via tripod−tripod Schiff base condensation of one triamine and one trialdehyde

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Table 3. Bond Lengths (Å) and Angles (deg) for **L** (Esds in parentheses)

O(1)−C(8)	1.37(1)	C(6)−C(7)	1.39(2)
O(1)−C(10)	1.42(1)	C(7)−C(8)	1.37(2)
O(2)−C(13)	1.43(1)	C(8)−C(9)	1.39(1)
O(2)−C(14)	1.37(1)	C(10)−C(11)	1.52(2)
O(3)−C(28)	1.36(1)	C(12)−C(13)	1.54(1)
O(3)−C(32)	1.42(1)	C(14)−C(15)	1.39(2)
N(1)−C(1)	1.47(1)	C(14)−C(19)	1.38(1)
N(1)−C(22)	1.48(2)	C(15)−C(16)	1.39(1)
N(1)−C(23)	1.46(1)	C(16)−C(17)	1.38(1)
N(2)−C(2)	1.44(1)	C(16)−C(20)	1.50(2)
N(2)−C(3)	1.45(1)	C(17)−C(18)	1.36(2)
N(3)−C(11)	1.44(1)	C(18)−C(19)	1.41(1)
N(3)−C(12)	1.44(1)	C(21)−C(22)	1.53(1)
N(3)−C(33)	1.44(2)	C(23)−C(24)	1.53(2)
N(4)−C(20)	1.45(1)	C(25)−C(26)	1.51(2)
N(4)−C(21)	1.45(1)	C(26)−C(27)	1.38(1)
N(5)−C(24)	1.46(1)	C(26)−C(31)	1.38(2)
N(5)−C(25)	1.44(1)	C(27)−C(28)	1.39(2)
C(1)−C(2)	1.53(2)	C(28)−C(29)	1.38(2)
C(3)−C(4)	1.50(1)	C(29)−C(30)	1.39(1)
C(4)−C(5)	1.39(2)	C(30)−C(31)	1.39(2)
C(4)−C(9)	1.38(2)	C(32)−C(33)	1.52(1)
C(5)−C(6)	1.38(1)		
C(8)−O(1)−C(10)	118.1(9)	O(2)−C(14)−C(15)	115.6(9)
C(13)−O(2)−C(14)	117.4(8)	O(2)−C(14)−C(19)	123.0(1)
C(28)−O(3)−C(32)	117.1(9)	C(15)−C(14)−C(19)	120.9(9)
C(1)−N(1)−C(22)	113.4(9)	C(14)−C(15)−C(16)	120.8(9)
C(1)−N(1)−C(23)	115.0(9)	C(15)−C(16)−C(17)	119.0(1)
C(22)−N(1)−C(23)	114.9(8)	C(15)−C(16)−C(20)	119.3(9)
C(2)−N(2)−C(3)	113.8(9)	C(17)−C(16)−C(20)	121.6(9)
C(11)−N(3)−C(12)	116.8(8)	C(16)−C(17)−C(18)	120.0(9)
C(11)−N(3)−C(33)	117.8(9)	C(17)−C(18)−C(19)	122.3(9)
C(12)−N(3)−C(33)	115.5(8)	C(14)−C(19)−C(18)	117.0(1)
C(20)−N(4)−C(21)	114.1(8)	N(4)−C(20)−C(16)	111.6(8)
C(24)−N(5)−C(25)	113.7(8)	N(4)−C(21)−C(22)	109.0(9)
N(1)−C(1)−C(2)	110.8(9)	N(1)−C(22)−C(21)	110.7(8)
N(2)−C(3)−C(4)	109.8(9)	N(1)−C(23)−C(24)	110.2(8)
C(3)−C(4)−C(5)	122.3(9)	N(5)−C(24)−C(23)	110.4(8)
C(3)−C(4)−C(9)	120.0(1)	N(5)−C(25)−C(26)	111.7(9)
C(5)−C(4)−C(9)	118.1(8)	C(25)−C(26)−C(27)	121.0(1)
C(4)−C(5)−C(6)	121.0(1)	C(25)−C(26)−C(31)	121.6(9)
C(5)−C(6)−C(7)	121.0(1)	C(27)−C(26)−C(31)	118.0(1)
C(6)−C(7)−C(8)	118.0(9)	C(26)−C(27)−C(28)	124.0(1)
O(1)−C(8)−C(7)	122.3(8)	O(3)−C(28)−C(27)	117.0(1)
O(1)−C(8)−C(9)	116.0(1)	O(3)−C(28)−C(29)	125.0(1)
C(7)−C(8)−C(9)	121.0(1)	C(27)−C(28)−C(29)	118.1(9)
C(4)−C(9)−C(8)	121.0(1)	C(28)−C(29)−C(30)	118.0(1)
O(1)−C(10)−C(11)	108.0(9)	C(29)−C(30)−C(31)	123.0(1)
N(3)−C(11)−C(10)	110.7(8)	C(26)−C(31)−C(30)	119.0(1)
N(3)−C(12)−C(13)	111.3(7)	O(3)−C(32)−C(33)	107.0(9)
O(2)−C(13)−C(12)	106.1(8)	N(3)−C(33)−C(32)	111.7(9)

units, as shown in Scheme 1. The condensation reaction goes smoothly at the temperature range of 278−298 K without using any templating metal ion. We have tried many solvents; the mixed solvent system of THF + MeOH gives the best results. The temperature for the reaction was kept at (278 ± 1 K) to restrict the conformational degrees of freedom of the two tripodal units. The high yield of the desired product shows that it is thermodynamically very stable. The same cryptand can be synthesized at elevated temperature (313 K) in presence of Cs(I) as the templating ion in comparable yields. The tren end of the cavity is well-suited to form inclusion complexes with transition metal ions, and the presence of three meta-substituted benzene rings makes the N donor atoms in **L** somewhat rigid. The cryptand readily forms mononuclear complexes with the Cu(II) ion when it is treated in one molar ratio with copper(II) perchlorate hexahydrate or copper(II) picrate salts. The perchlorate complex was found to be very hygroscopoic, and we did not proceed any further with this complex. The picrate complex can be isolated in the solid state without any difficulty, and it readily takes up anions like CN^-, SCN^-, and N_3^-, forming pentacoordinated complexes.

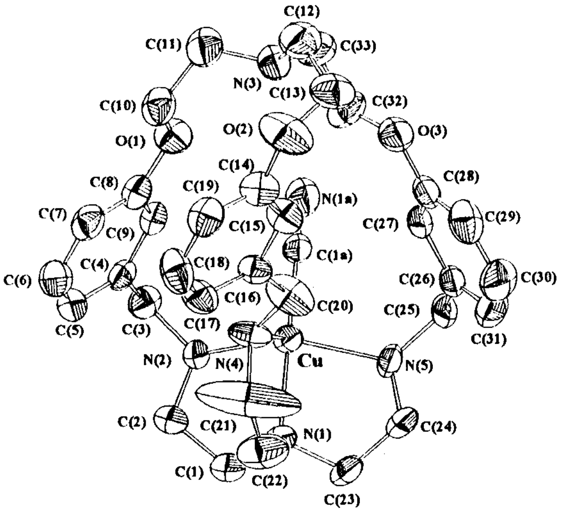

Figure 2. ORTEP[21] drawing of the cation of **2** showing the thermal ellipsoids and the atomic numbering scheme. Hydrogen atoms are omitted for clarity.

All of the complexes are stable in air and soluble in common organic solvents such as MeCN and chloroform. Molecular conductivity studies for **1−4** in MeCN (ca. 1×10^{-3} M) have been carried out at 298 K. Λ_M for **1** is 221 Ω^{-1} cm^2 mol^{-1}. This value corresponds[20] to a 1:2 electrolyte. For **2−4**, the Λ_M values range within 131−149 Ω^{-1} cm^2 mol^{-1}, corresponding[20] to 1:1 electrolytes.

Description of the Structures. Cryptand, L. The structure of **L** was confirmed by crystallographic analysis. A perspective view of the molecule showing the atom numbering scheme is given in Figure 1, while the bond distances and angles are collected in Table 3. The molecule has an endo−endo conformation, at least in the solid state, where the distance between the two bridgehead nitrogens is found to be 9.904(7) Å. The distances between any two secondary amino N atoms are similar; the same is true in the case of the ethereal O atoms or the corresponding C atoms of the three aromatic rings (Table 7). The bridgehead nitrogen and the secondary amino N atoms are also quite close to one another (range, 2.894(7)−2.933(9) Å); similarly, at the other end of the cavity, the distance between any one ethereal O atom and the bridgehead N spans the range, 2.860(5)−2.919(7) Å. Thus, the molecule has a pseudo-3-fold symmetry axis passing through the bridgehead nitrogens in the solid state. Both the ^{1}H- and ^{13}C-NMR data are also consistent with a 3-fold symmetry in the molecule in chloroform solution. The distances and angles involving the bonded atoms of the molecule lie within normal statistical values (Table 3).

[Cu(L)(CN)](picrate), 2. A perspective view of the molecule giving the atom numbering scheme is shown in Figure 2. The molecular structure consists of discrete $[Cu(L)(CN)]^+$ cations and picrate anions. The Cu(II) ion is coordinated to four N atoms of the tren unit at one end of the cavity. The fifth coordination site is occupied by a CN^- group. The cavity above the tren binding site undergoes reorganization upon binding of the cyanide group. The top of the cavity is skewed away from the metal center and the cyanide group. So, the pseudo-3-fold symmetry present in **L** is lost, and the cyanide group resides mostly outside the cavity. However, the ligand maintains the endo−endo conformation where the two bridgehead N atoms

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(21) Johnson, C. K. *ORTEP*. Report ORNL- 3794; Oak Ridge National Laboratory: Oak Ridge, TN, 1971.

Table 4. Non-Hydrogen Positional and Equivalent Isotropic Displacement Parameters (Å^2) for {[Cu(CN)]**L**}(picrate) (**2**) (Esds in parentheses)

atom	*x/a*	*y/b*	*z/c*	*U*(eq)
Cu	0.24559(5)	0.85770(6)	0.28364(2)	0.0352(2)
N(1a)	0.2377(4)	1.1110(5)	0.2595(2)	0.065(2)
C(1a)	0.2406(4)	1.0174(5)	0.2669(2)	0.042(2)
O(1)	0.4332(3)	1.0317(4)	0.1248(1)	0.053(2)
O(2)	0.2503(4)	0.8434(5)	−0.0226(2)	0.089(2)
O(3)	0.0905(3)	1.0204(4)	0.0963(1)	0.057(2)
O(4)	0.1904(3)	0.5742(4)	−0.1031(1)	0.063(2)
O(5)	0.0111(3)	0.6783(5)	−0.0844(2)	0.085(2)
O(6)	−0.0024(4)	0.7363(5)	−0.0075(2)	0.117(3)
O(7)	0.1296(5)	0.5248(6)	0.1329(2)	0.134(4)
O(8)	0.2547(6)	0.4118(6)	0.1228(2)	0.140(4)
O(9)	0.3245(4)	0.2966(5)	−0.0563(2)	0.120(3)
O(10)	0.3640(4)	0.4468(5)	−0.0964(2)	0.124(30
N(1)	0.2486(3)	0.6961(4)	0.3136(2)	0.039(2)
N(2)	0.3869(3)	0.8740(4)	0.3256(2)	0.040(2)
N(3)	0.2810(4)	1.0716(4)	0.0388(2)	0.049(2)
N(4)	0.2990(4)	0.7599(40	0.2104(2)	0.047(2)
N(5)	0.0889(3)	0.8490(4)	0.3012(2)	0.044(2)
N(6)	0.0367(4)	0.6769(5)	−0.0395(2)	0.069(3)
N(7)	0.1887(7)	0.4752(7)	0.1060(30	0.099(4)
N(8)	0.3148(5)	0.3971(6)	−0.0649(2)	0.074(3)
C(1)	0.3282(4)	0.6929(5)	0.3560(2)	0.052(2)
C(2)	0.4196(4)	0.7615(5)	0.3409(2)	0.054(2)
C(3)	0.4703(4)	0.9479(5)	0.3069(2)	0.045(2)
C(4)	0.5037(4)	0.9226(5)	0.2515(2)	0.039(2)
C(5)	0.5756(4)	0.8395(5)	0.2397(2)	0.051(2)
C(6)	0.6000(4)	0.8197(5)	0.1888(2)	0.056(3)
C(7)	0.5546(4)	0.8813(5)	0.1491(2)	0.052(2)
C(8)	0.4845(4)	0.9641(5)	0.1604(2)	0.044(2)
C(9)	0.4598(4)	0.9848(5)	0.2114(2)	0.040(2)
C(10)	0.4548(4)	1.0163(6)	0.0721(2)	0.057(3)
C(11)	0.3891(5)	1.0981(6)	0.0406(2)	0.064(3)
C(12)	0.2400(5)	1.0486(7)	−0.0123(3)	0.071(3)
C(13)	0.1847(5)	0.9392(7)	−0.0192(2)	0.068(3)
C(14)	0.2875(5)	0.7911(5)	0.0217(2)	0.052(2)
C(15)	0.2496(4)	0.8075(5)	0.0704(2)	0.050(2)
C(16)	0.2918(4)	0.7559(5)	0.1129(2)	0.041(2)
C(17)	0.3726(4)	0.6845(5)	0.1059(2)	0.052(2)
C(18)	0.4073(4)	0.6642(6)	0.0564(2)	0.065(3)
C(19)	0.3661(5)	0.7184(6)	0.0144(2)	0.056(3)
C(20)	0.2392(5)	0.7777(6)	0.1632(2)	0.069(3)
C(21)	0.295(1)	0.6492(7)	0.2251(3)	0.193(7)
C(22)	0.2710(5)	0.6126(5)	0.2724(3)	0.076(3)
C(23)	0.1455(4)	0.6719(5)	0.3363(2)	0.053(2)
C(24)	0.0632(4)	0.7302(5)	0.3042(20	0.052(2)
C(25)	0.0089(4)	0.9205(5)	0.2757(2)	0.050(2)
C(26)	−0.0041(4)	0.9010(5)	0.2179(2)	0.039(2)
C(27)	0.0497(4)	0.9700(5)	0.1844(2)	0.040(2)
C(28)	0.0389(4)	0.9574(5)	0.1315(2)	0.044(2)
C(29)	−0.0260(5)	0.8741(7)	0.1119(2)	0.062(3)
C(30)	−0.0803(5)	0.8069(6)	0.1447(3)	0.071(3)
C(31)	−0.0695(4)	0.8217(6)	0.1975(3)	0.062(3)
C(32)	0.1703(5)	1.0929(6)	0.1158(2)	0.061(3)
C(33)	0.2212(5)	1.1486(6)	0.0706(3)	0.075(3)
C(34)	0.1827(4)	0.5462(5)	−0.0575(2)	0.047(2)
C(35)	0.1120(5)	0.5941(6)	−0.0210(2)	0.054(3)
C(36)	0.1153(5)	0.5714(6)	0.0310(3)	0.062(3)
C(37)	0.1829(6)	0.4942(6)	0.0507(3)	0.069(3)
C(38)	0.2471(5)	0.4372(6)	0.0187(3)	0.064(3)
C(39)	0.2455(5)	0.4619(5)	−0.0329(2)	0.051(2)

have come closer to each other by about 1.5 Å (distance 8.397(7) Å) compared to that in the uncomplexed **L**. The coordination geometry around the metal ion is close to trigonal bipyramidal, where the bridgehead nitrogen N(1) and the atom C(1a) of the cyanide occupy the axial positions. The metal ion is 0.278(4) Å out of the trigonal plane described by the three secondary amino N atoms (N(2), N(4), and N(5)) in the direction away from the bridgehead atom N(1). Equatorial Cu−N bond lengths are significantly longer than the axial one (Table 6). An imporatnt fact about this structure is that the equatorial Cu−N(4) bond length (2.339(6) Å) is appreciably long for a Cu−N bond.[22] The Cu−N(1) (bridgehead N)[22] as well as the Cu−C (CN^-)[23] bond distances are within the normal ranges. The long Cu−N(4) distance is due to the ligand architecture which does not allow the N(4) atom to come closer to the Cu(II) ion. We propose that it is due to the presence of three meta-substituted benzene rings which make the N donor atoms somewhat rigid. The relationship of the Cu−N bond lengths in trigonal-bipyramidal CuN_4X complexes has been the subject of investigation by different groups.[24] The Cu−C(1a)−N(1a) angle is almost linear 175.9(5)°. The distance between the N atom of the CN^- group and N(3) is 5.761(7) Å.

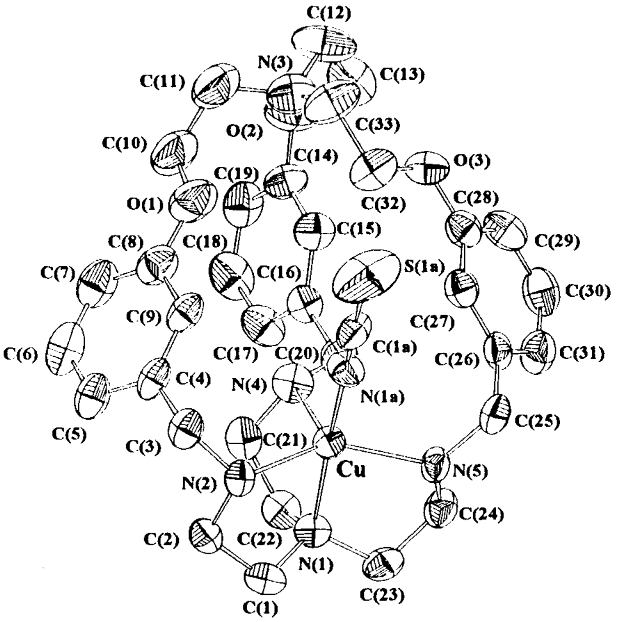

Figure 3. ORTEP[21] drawing of the cation of **3** showing the thermal ellipsoids and the atomic numbering scheme. Hydrogen atoms are omitted for clarity.

[Cu(L)(NCS)](picrate), 3. A perspective view of the molecule showing the atom numbering scheme is given in Figure 3. The molecular structure consists of $[Cu(L)(NCS)]^+$ cations and picrate anions. In this case, also, the cryptand has an endo−endo conformation where the distance between the two bridgehead N atoms is 8.225(5) Å, which is very similar to that found in **2**. As in the case of **2**, the Cu(II) ion is coordinated to four N atoms at the tren end of the cavity. The fifth coordination site is occupied by the N atom of the SCN^- group. The coordination geometry around Cu(II) is quite similar to that found in the case of **2**. The Cu−N(4) bond distance (2.384(5) Å) is again much longer than normal,[22] whereas the other Cu−N distances range within 1.939(5)−2.094(5) Å, the length of the axial Cu−N(1a) bond being the lowest. The Cu(II) ion is 0.230(4) Å above the plane described by the equatorially bonded N(2), N(4), and N(5) atoms. The coordination geometry around the Cu(II) ion is thus quite similar to that found in **2**. Upon binding of the thiocyanate group, the top of the cavity is skewed away from the metal center more than that in case of **2**. This has increased the nonbonding distance between N(3) and S(1a) to 6.223(3) Å.

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Table 5. Non-Hydrogen Positional and Equivalent Isotropic Displacement Parameters (Å^2) for {[Cu(NCS)]**L**}(picrate) (**3**) (Esds in parentheses)

atom	*x/a*	*y/b*	*z/c*	*U*(eq)
Cu	0.59568(2)	0.83961(8)	0.34814(4)	0.0382(3)
S(1a)	0.62312(7)	0.6345(3)	0.5875(1)	0.121(1)
N(1a)	0.6094(1)	0.7554(6)	0.4461(3)	0.049(2)
C(1a)	0.6148(2)	0.7055(7)	0.5049(4)	0.051(3)
O(1)	0.6654(1)	1.1013(5)	0.5366(3)	0.081(2)
O(2)	0.7436(1)	1.1338(6)	0.3861(3)	0.089(3)
O(3)	0.70925(9)	0.7648(5)	0.4345(3)	0.060(2)
O(4)	0.54442(9)	0.6562(5)	0.3362(2)	0.052(2)
O(5)	0.5623(1)	0.4836(6)	0.2340(3)	0.089(3)
O(6)	0.5576(2)	0.2915(7)	0.2701(4)	0.124(4)
O(7)	0.4764(1)	0.1611(7)	0..3896(4)	0.102(3)
O(8)	0.4555(1)	0.2954(6)	0.4656(4)	0.091(3)
O(9)	0.4773(1)	0.7364(5)	0.4613(3)	0.073(2)
O(10)	0.5014(1)	0.8101(5)	0.3699(4)	0.085(3)
N(1)	0.5752(1)	0.9091(5)	0.2469(3)	0.041(2)
N(2)	0.5637(1)	0.9275(5)	0.4055(3)	0.040(2)
N(3)	0.7215(1)	1.0012(7)	0.5251(4)	0.075(3)
N(4)	0.6296(1)	0.9921(5)	0.3165(3)	0.049(2)
N(5)	0.6027(1)	0.6786(5)	0.2792(3)	0.042(2)
N(6)	0.5521(1)	0.4015(7)	0.2770(4)	0.062(3)
N(7)	0.4721(2)	0.2682(8)	0.4162(4)	0.071(3)
N(8)	0.4931(1)	0.7202(7)	0.4081(4)	0.053(2)
C(1)	0.5466(1)	0.9438(7)	0.2679(4)	0.050(3)
C(2)	0.5479(1)	1.0110(6)	0.3482(4)	0.045(2)
C(3)	0.5687(1)	0.9891(7)	0.4848(3)	0.049(3)
C(4)	0.5909(2)	1.0904(7)	0.4879(4)	0.046(3)
C(5)	0.5847(2)	1.2175(8)	0.4711(4)	0.058(3)
C(6)	0.6059(2)	1.3078(8)	0.4738(4)	0.072(4)
C(7)	0.6332(2)	1.2736(9)	0.4935(5)	0.068(3)
C(8)	0.6392(2)	1.1473(9)	0.5128(4)	0.060(3)
C(9)	0.6183(2)	1.0574(7)	0.5093(4)	0.049(3)
C(10)	0.6887(2)	1.1821(9)	0.5326(5)	0.090(4)
C(11)	0.7137(2)	1.114(1)	0.5686(6)	0.100(5)
C(12)	0.7531(2)	1.0079(8)	0.4160(5)	0.078(4)
C(13)	0.7511(2)	1.000(1)	0.5019(5)	0.086(4)
C(14)	0.7201(1)	1.1451(8)	0.3377(4)	0.057(3)
C(15)	0.6989(1)	1.0551(7)	0.3300(4)	0.053(3)
C(16)	0.6759(1)	1.0734(7)	0.2775(4)	0.046(3)
C(17)	0.6738(2)	1.1872(8)	0.2346(4)	0.061(3)
C(18)	0.6942(2)	1.2791(8)	0.2450(5)	0.071(3)
C(19)	0.7171(2)	1.2583(8)	0.2962(5)	0.062(3)
C(20)	0.6536(1)	0.9708(7)	0.2685(4)	0.054(3)
C(21)	0.6096(1)	1.0856(7)	0.2813(4)	0.053(3)
C(22)	0.5907(1)	1.0216(7)	0.2170(4)	0.049(3)
C(23)	0.5742(1)	0.8036(7)	0.1873(3)	0.051(3)
C(24)	0.6002(1)	0.7229(7)	0.1959(3)	0.051(3)
C(25)	0.6244(1)	0.5800(6)	0.2966(4)	0.049(3)
C(26)	0.6543(1)	0.6243(6)	0.2973(4)	0.044(2)
C(27)	0.6677(1)	0.6711(7)	0.3672(3)	0.047(2)
C(28)	0.6950(1)	0.7113(7)	0.3700(4)	0.048(3)
C(29)	0.7101(1)	0.6998(8)	0.3028(5)	0.063(3)
C(30)	0.6970(2)	0.6538(8)	0.2340(4)	0.064(3)
C(31)	0.6693(2)	0.6165(7)	0.2303(4)	0.058(3)
C(32)	0.6933(2)	0.8023(8)	0.4982(4)	0.066(3)
C(33)	0.7132(2)	0.8795(9)	0.5556(4)	0.082(4)
C(34)	0.5268(1)	0.5722(7)	0.3466(3)	0.041(2)
C(35)	0.5295(1)	0.4397(7)	0.3243(4)	0.045(3)
C(36)	0.5120(2)	0.3434(7)	0.3462(4)	0.056(3)
C(37)	0.4898(1)	0.3719(7)	0.3905(4)	0.049(3)
C(38)	0.4839(1)	0.4963(8)	0.4100(4)	0.048(3)
C(39)	0.5012(1)	0.5919(7)	0.3871(3)	0.042(2)

The nonbonding distances between the three equatorially coordinated N atoms are similar in **2** as well as in **3** and are slightly different compared to the corresponding distances found in **L** (Table 7). A comparison of the structures of **2** and **3** with that of **L** reveals that the tren end is quite rigid and the N donor atoms at this end do not move tremendously upon metal binding. In another words, the donor atoms enforce the distorted coordination geometry on to the Cu(II) ion in both of the structures.

Table 6. Selected Bond Lengths (Å) and Angles (deg) for {[Cu(CN)]**L**}(picrate) (**2**) and {[Cu(NCS)]**L**}(picrate) (**3**) (Esds in Parentheses)

	2	**3**
Bond Lengths		
Cu−N(1)	2.055(5)	2.058(5)
Cu−N(2)	2.134(5)	2.094(5)
Cu−N(4)	2.339(6)	2.384(5)
Cu−N(5)	2.114(5)	2.067(5)
Cu−C(1a)	1.942(6)	
Cu−N(1a)		1.939(5)
Bond Angles		
N(1)−Cu−N(2)	83.4(4)	84.2(2)
N(1)−Cu−N(4)	80.8(5)	81.7(2)
N(1)−Cu−N(5)	83.4(4)	84.9(2)
N(2)−Cu−N(4)	100.5(5)	109.1(3)
N(2)−Cu−N(5)	136.9(4)	140.9(2)
N(4)−Cu−N(5)	117.2(8)	105.3(3)
C(1a)−Cu−N(1)	170.8(2)	
C(1a)−Cu−N(2)	92.8(3)	
C(1a)−Cu−N(4)	108.1(5)	
C(1a)−Cu−N(5)	93.8(4)	
Cu−C(1a)−N(1a)	175.9(5)	
N(1a)−Cu−N(1)		171.0(2)
N(1a)−Cu−N(2)		91.1(2)
N(1a)−Cu−N(4)		107.2(3)
N(1a)−Cu−N(5)		94.1(2)
Cu−N(1a)−C(1a)		173.3(6)

Table 7. Selected Nonbonded Distances (Å) for **L**, {[Cu(CN)]**L**}(picrate) (**2**) and {[Cu(NCS)]**L**}(picrate) (**3**)

	L	**2**	**3**
N(1)···N(3)	9.904(7)	8.397(7)	8.225(5)
N(2)···N(4)	3.738(7)	3.445(6)	3.551(2)
N(2)···N(5)	3.684(7)	3.951(6)	3.922(1)
N(4)···N(5)	3.717(9)	3.804(6)	3.555(1)
N(1)···N(2)	2.923(6)	2.793(6)	2.782(2)
N(1)···N(4)	2.894(7)	2.862(6)	2.915(5)
N(1)···N(5)	2.933(9)	2.779(6)	2.785(2)
O(1)···O(2)	3.672(6)	4.982(6)	4.582(5)
O(1)···O(3)	3.579(5)	4.535(6)	4.505(4)
O(2)···O(3)	3.520(7)	4.302(6)	4.298(9)
N(3)···O(1)	2.919(7)	2.990(6)	2.903(7)
N(3)···O(2)	2.873(7)	3.156(7)	2.985(2)
N(3)···O(3)	2.860(5)	2.993(6)	2.949(2)
C(9)···C(15)	4.09(1)	4.984(8)	5.071(6)
C(9)···C(27)	4.022(8)	5.406(7)	5.339(4)
C(15)···C(27)	4.00(1)	4.424(8)	4.350(2)

Spectral and Magnetic Studies. In the UV−vis−near-IR spectral studies, **1**−**4** show two broad ligand field bands in the region, 9500−16 000 cm^{-1}. At energies higher than 22 000 cm^{-1}, the picrate anion shows intense absorption[25] obscuring LMCT transitions involving the metal ion and the ligating donor atoms. At energies lower that 7200 cm^{-1}, sharp peaks due to vibrational overtones appear. Spectra in the solid state, though not well-resolved, indicate that the complex ions retain their identity in solutions. The ligand field bands do not change shape or position upon changing the solvent from MeCN to DMF. For a regular trigonal-bipyramidal Cu(II) complex, usually two ligand field bands appear[26] in the region, 9500−16 000 cm^{-1} with greater absorption intensity for the lower energy transition, although exceptions[27] to this general observation are known. The general shape and band positions (Table 8) in the spectra of **2**−**4**, are quite similar to those observed for trigonal-

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Table 8. Ligand Field Bands (cm^{-1}) and Magnetic and EPR Spectral Data for **1**−**4**

compound	d−d[a]	μ/μ_B[b]	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}$ ($\times10^4$ cm^{-1})	ref
1	9500(95)	1.94	2.07(g_{av})[c]			this work
	11000(115)		2.14[d]	2.06	60	
	14200(210)		2.18[e]	2.05	91	
2	11400(145)	2.01	2.09(g_{av})[c]			this work
	15100(215)		2.03[d]	2.12	65	
			2.03[e]	2.21	70	
3	11300(150)	1.98	2.08(g_{av})[c]			this work
	14800(180)		2.04[d]	2.14	70	
			2.03[e]	2.24	75	
4	11400(170)	2.03	2.06(g_{av})[c]			this work
	15200(220)		2.03	2.13	70	
			2.02	2.21	85	
$[Cu(NTB)(N_3)]^{1+}$	9700(119)		2.00	2.21	69	27
	13150(100)					
$[Cu(NTB)(NCS)]^{1+}$	9500(212)		2.01	2.22	69	27
	12500(235)					
$[Cu(tren)(OH)]^{1+}$			2.00	2.21	68	28
$[Cu(tren)Br]Br$	11200		2.00	2.21	67	28
	13800					
$[Cu(tren)(NH_3)]^{2+}$	11400		2.21	2.18	84	28
	15200					

[a] Electronic spectra of **1**−**4** at 298 K in MeCN; molar extinction coefficient is in parentheses. [b] 298 K. [c] Solid sample at 298 K. [d] In MeCN at 298 K. [e] In MeCN at 77 K.

bipyramidal $[Cu(tren)X]^{n+}$ ($X = Br^-$, NH_3; $n = 1,2$)[28] and $[Cu(NTB)X]^{1+}$ (NTB = tris(2-benzimidazolylmethyl)amine; X = SCN^- and N_3^-)[27] complexes. For **1**, which will be tetracoordinated with ligation from four N donors of **L**, the ligand field bands are slightly red-shifted and three bands can be located (Table 8). We have seen that the cryptand enforces a distorted trigonal-pyramidal geometry onto the Cu(II) ion in both **2** and **3**. It is quite reasonable to assume that in **1**, also, the coordination geometry around Cu(II) will be distorted trigonal pyramidal. Therefore, we propose that the ligand field bands in **1** correspond to a distorted trigonal-pyramidal CuN_4 chromophore which is unique in the literature. However, it is possible that MeCN or DMF might be weakly coordinated to the metal ion in **1**.

The effective magnetic moment values for **1**−**4** lie within 1.94−2.03 μ_B at 298 K, which are well within the normal range observed[29] for discrete Cu(II) complexes. The EPR spectral data of the complexes are collected in Table 8. Complex **1** displays interesting EPR spectral characteristics. It shows a broad signal with $g_{av} = 2.07$ in the solid state at 298 K, which sharpens somewhat on cooling to 77 K. Thus, the pure solid sample is not magnetically dilute to exhibit resolved EPR spectrum indicative of its stereochemistry. However, in MeCN solution at 298 K, it shows an axial spectrum (Figure 4). Changing the solvent to $CHCl_3$, which is less coordinating, gives an identical spectrum. The $g_{\parallel}$ value of 2.14 obtained with **1** is smaller compared to typical pseudotetrahedral CuN_4 complexes, where the $g_{\parallel}$ values have been found[30] to be equal to or above 2.24. If we can assume that in **1** the four N donors impose a geometry similar to that in **2** and **3**, then this geometry will be distorted trigonal pyramidal, where the Cu(II) ion will be above the equatorial plane and away from the bridgehead N atom. Also, one of the equatorial bonds will be appreciably longer (like Cu−N(4) bond in **2** and **3**) leading to a low ligand field strength. In MeCN glass (77 K), the signal is still axial (Figure 4), and the *g* values change slightly. This is attributable to the conformational changes in the ligand superstructure upon cooling, which will enforce changes in the coordination geometry or to the solvent coordination at low temperature. Complexes **2**−**4** show broad signals near g = 2.05 in the solid state at 298 or 77 K. In MeCN each exhibits a significantly rhombic signal (Table 8) at 298 K, which sharpens at 77 K. The *g* and *A* values are quite different from those obtained in **1** and agrees well with trigonal-bipyramidal $[Cu(NTB)X]^{1+}$ (X = NCS^- and N_3^-)[27] and $[Cu(tren)(OH)]^{1+}$ and $Cu(tren)Br_2$[28] complexes.

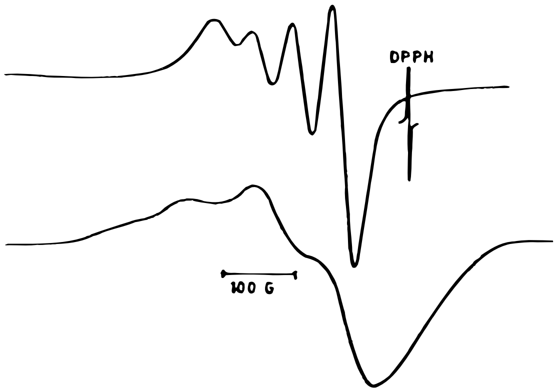

Figure 4. EPR spectra of **1** in MeCN at 298 K (top) and at 77 K (bottom).

Electrochemistry. Electron transfer properties of the complexes were probed by cyclic voltammetry at 298 K on dinitrogen flushed solutions in MeCN. None of the complexes show any cyclic responses in the region, +1.0 to −1.0 V. Only ill-defined peaks are found in the forward scans which disappear in the reverse scans. Rigidity of the N_4-donor set does not allow its spatial rearrangements upon reduction/oxidation of the metal−ligand ensemble, leading to irreversibility of the cyclic redox processes.

Conclusion. The three meta-substituted benzene rings present in the cryptand **L** makes the donor atoms somewhat rigid in nature. Therefore, the cryptand can enforce a distorted trigonal-pyramidal geometry onto the Cu(II) ion. When the fifth coordination site is empty, the geometry around the Cu(II) ion becomes distorted trigonal pyramidal. This gives an interesting EPR spectrum. Once the crystal structure of **1** is available, the preorganization of the ligand structure and the spectral char-

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acteristics of **1** can be probed quantitatively. To test the rigidity of the binding site, it is also important to have Ni(II) or Pt(II) cryptates with **L**. Efforts are on to reach these goals.

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Supporting Information Available: Tables of crystallographic data, hydrogen positional parameters, anisotropic thermal factors for **L**, **2**, and **3** and all of the bond distances and angles for **2** and **3** and figures of the packing diagrams for **L**, **2**, and **3** (16 pages). Ordering information is given on any current masthead page.

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