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Synthesis, characterization and complexation properties of a heteroditopic cryptand L towards Cu^{II} and Zn^{II}: crystal structures of $L\cdot3H_2O$ and $[ZnL][ClO_4]_2\cdot2H_2O$ †

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A new heteroditopic cryptand (L) has been synthesized in high yields, at 5 °C and in absence of any templating metal ion, by tripod–tripod Schiff-base condensation of tris(3-aminopropyl)amine and 2,2′,2″-nitrilotris-(ethyleneoxy)tris(benzaldehyde) followed by reduction *in situ* with $NaBH_4$. The molecule has an *endo-endo* conformation with a distance of 5.291 Å between the two bridgehead nitrogens. The cryptand forms mononuclear cryptates of the general formula $[ML][ClO_4]_2$ with copper(II) and zinc(II) perchlorates. The crystal structure of $[ZnL][ClO_4]_2\cdot2H_2O$ was determined. The Zn^{II} occupies the N_4 end of the cavity in an almost ideal tetrahedral geometry. The blue copper(II) cryptate exhibits ligand-field bands at 875 and 745 nm and a ligand-to-metal charge transfer at 275 nm in acetonitrile solution at 298 K indicative of pseudo-tetrahedral CuN_4 co-ordination. However, its EPR spectral characteristics in the solid state or in solution are typical of a magnetically concentrated complex.

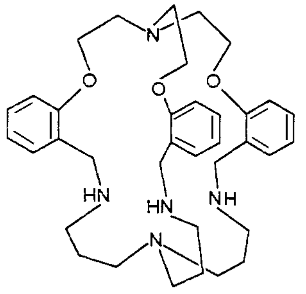
Macrobicyclic cryptands as ligands for transition-metal ions have attracted attention from a number of chemists.[1–10] This is because such metal cryptates hold enormous potential[11] in diverse areas of chemistry, biochemistry and materials research. Cryptands as ligands possess several desirable features[12] such as donor atom topology, binding-site rigidity, layer effects, *etc.* which determine the stability, selectivity and properties of the metal cryptates formed. The magnitude of steric strain of the ligand is an important parameter which to a large extent determines the complexation process. If the ligand donor set is pre-organized to impart a co-ordination geometry preferable to a particular metal ion then the complexation process will be facile. On the other hand, a cryptand with a flexible binding site can show poor chemoselectivity. We have been engaged in the synthesis of a number of heteroditopic cryptands incorporating two distinct binding sites.[13–15] These molecules have derivatizable secondary amino groups in the ligand architecture. It has been possible to derivatize the cryptands with long alkyl chains to give new generation amphiphiles.[16] Again, when derivatized with fluorphoric group(s), these systems become potential molecular photonic devices.[17] Herein, we present a new heteroditopic macrobicyclic cryptand that is designed to have a flexible binding site. We are interested in probing this cryptand as a ligand for a variety of transition-/inner-transition-metal ions with the ultimate goal of obtaining new molecular photonic devices. In the present paper we describe a low-temperature synthesis of the cryptand which was achieved in high yields without using any templating metal ions. The crystal structures of the cryptand L and its zinc(II) complex are also described along with spectral characteristics of the copper(II) cryptate.

Experimental

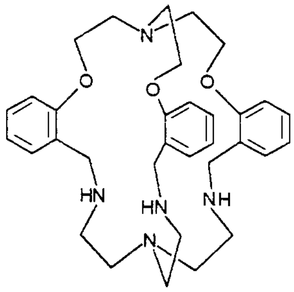
All reagent-grade chemicals were from Aldrich Chemical Co. except tris(3-aminopropyl)amine which was from Strem Chemicals. They were used as received. All the solvents (S.D. Fine Chemicals, India) were purified prior to use.

Spectroscopic and microanalytical data for the complexes were collected as described earlier.[18]

Preparations



L



L′

Cryptand L. This cryptand was synthesized following our earlier scheme.[10] 2,2′,2″-Nitrilotris(ethyleneoxy)tris(benzaldehyde) (1.84 g, 4 mmol) was taken in tetrahydrofuran (thf)–MeOH (1 : 40 v/v, 300 cm^3), in a 1000 cm^3 round-bottomed flask at 278 K. To this solution was added, with continuous stirring, a solution of tris(3-aminopropyl)amine (0.75 g, 4 mmol) in MeOH (300 cm^3) over 8 h maintaining the temperature at 5 ± 1 °C. The addition was adjusted to as to disperse a drop before another drop fell into the reaction mixture. At the end of the addition the mixture was stirred at room temperature for 4 h. Reduction of the Schiff base thus formed was achieved by hydrogenating it with an excess of $NaBH_4$ (≈1.0 g) at room temperature for 2 h followed by refluxing for 2 h. The solvent was evaporated almost to dryness, and the residue treated with cold water (50 cm^3). The desired cryptand L was extracted with $CHCl_3$ (3 × 40 cm^3). The organic layer was dried over anhydrous Na_2SO_4 and evaporated to obtain a pale yellow semi-solid. This was dissolved in hot moist MeCN (40 cm^3) and kept at 5 °C to afford colourless single crystals of X-ray diffraction quality. On exposure to air the crystals slowly turned to a white powder. Yield 56%, m.p. 101 °C (Found: C, 71.63; H, 8.59; N, 11.91. Calc. for $C_{36}H_{51}N_5O_3$: C, 71.85; H, 8.54; N, 11.64%). FAB mass spectrum: *m/z* (%) 602 (100), M^+; ^1H NMR (80 MHz, $CDCl_3$, 25 °C, $SiMe_4$ reference): δ 1.6 (m, 6 H), 2.0 (br s, 3 H), 2.3 (t, 6 H), 2.6 (t, 6 H), 3.3 (t, 6 H), 3.8 (s, 6 H), 4.1 (t, 6 H) and 6.7–7.4 (m, 12 H).

$[ZnL][ClO_4]_2$ 1. A solution of $[Zn(H_2O)_6][ClO_4]_2$ (0.18 g, 0.5 mmol) in MeOH (15 cm^3) was added to a stirred solution of L (0.30 g, 0.5 mmol) dissolved in MeOH (15 cm^3) at room temperature. A white solid precipitated immediately, was filtered

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† *Non-SI unit employed*: $\mu_B \approx 9.27 \times 10^{-24}$ J T^{-1}.

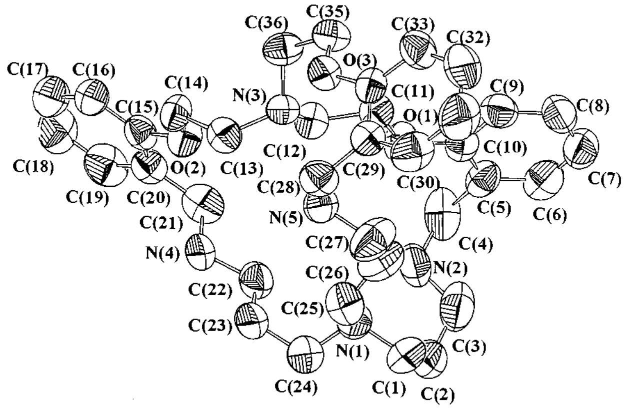

Fig. 1 An ORTEP[21] drawing of cryptand L showing the thermal ellipsoids and the atomic numbering scheme. Hydrogen atoms are omitted for clarity

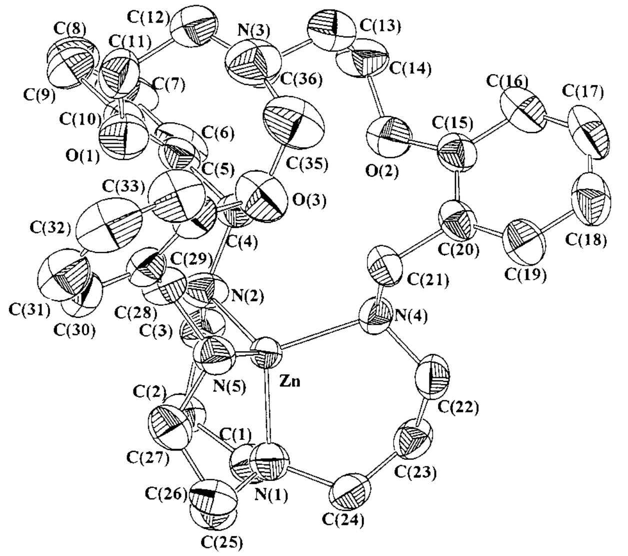

Fig. 2 An ORTEP[21] drawing of complex **1** showing the thermal ellipsoids and the atomic numbering scheme. Hydrogen atoms are omitted for clarity

off, washed with MeOH and dried *in vacuo*. Yield 79%. X-Ray-quality colourless crystals were grown from moist MeCN solution upon slow evaporation at room temperature.

[CuL][ClO$_4$]$_2$ 2. A solution of [Cu(H$_2$O)$_6$][ClO$_4$]$_2$ (0.18 g, 0.5 mmol) in MeOH (15 cm^3) was added to a stirred solution of L (0.30 g, 0.5 mmol) dissolved in MeOH (15 cm^3) at room temperature. A blue solid precipitated immediately which was filtered off, washed with MeOH and dried *in vacuo*. Yield 85% (Found: C, 50.63; H, 6.09; N, 7.96. $C_{36}H_{51}Cl_2CuN_5O_{11}$ requires C, 50.02; H, 5.95; N, 8.10%).

[CuL][BF$_4$]$_2$ 3. Complex **3** was isolated when copper(II) tetrafluoroborate was used instead of perchlorate in the same molar ratio at room temperature in MeOH. The blue solid was washed with MeOH and dried *in vacuo*. Yield 80% (Found: C, 51.84; H, 6.07; N, 8.21. $C_{36}H_{51}B_2CuF_8N_5O_3$ requires C, 51.53; H, 6.13; N, 8.35%). Crystals suitable for X-ray crystallographic studies could not be grown from either **2** or **3**.

CAUTION: care must be taken while treating organic compounds with metal perchlorates as potentially explosive mixtures may be formed.

X-Ray crystallography

Crystallographic data for the cryptand and complex **1** are listed in Table 1. The crystals of L become brittle on exposure to air in about an hour. Therefore, a crystal of suitable size was mounted inside a Lindemann glass capillary containing a small volume of the mother-liquor. For **1**, however, a crystal was mounted at the end of a glass fibre with epoxy cement. Cell parameters and reflection intensities were measured at 298 K on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.710\,73$ Å). The structures were solved by direct methods and completed by successive Fourier-difference syntheses. The crystal of L did not diffract very well and data could be collected only up to 2θ 45°. For both structures, all non-hydrogen atoms were anisotropically refined on F by full-matrix least-squares calculations. In each case a few H atoms could be located in the Fourier-difference maps while others were added at calculated positions. The H atoms of the water molecules were located in the difference maps. However, in each case, H atoms attached to O(2w) could not be located from the difference map and they were not calculated either. Hydrogen atoms were given a fixed U_{eq} (0.2 Å^2 for L, 0.1 Å^2 for **1**). Their positions and thermal parameters were not refined. Computations were made with the XTAL 3.2 program package[19] on a 486-DX personal computer (IBM compatible, PCL, India). Selected bond lengths and angles for both structures are collected in Table 2.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/561.

Results and Discussion

The cryptand L forms easily by tripod–tripod Schiff-base condensation of one tripodal triamine and one tripodal trialdehyde unit. The condensation reaction goes smoothly at 5 °C without being assisted by a templating metal ion. We believe that at this temperature the conformational degrees of freedom of the two units are restricted. The yield is quite high possibly due to the size of one unit matching that of the other and the product is thermodynamically stable under the reaction conditions. The best solvent system found by trial and error was thf–MeOH in the ratio 1:40 (v/v). The tris(3-aminopropyl)amine moiety is well suited to accept a metal ion like Cu^{II}, Zn^{II}, *etc.* inside the cavity forming MN$_4$ chromophores. Both copper and zinc-cryptates are stable in air and soluble in common organic solvents like MeCN, acetone, *etc.* The molecular conductivity for compounds **1**–**3** in MeCN (*ca.* 1×10^{-3} M) at 25 °C was found to be 188, 209 and 214 Ω^{-1} cm^2 mol^{-1} respectively, corresponding[20] to 1:2 electrolytes.

In the solid state, cryptand L has a pronounced *endo-endo* conformation (Fig. 1) with a distance of 5.291(14) Å between the two bridgehead nitrogens. The corresponding distance in the cryptand L′ with the unit tris(2-aminoethyl)amine (tren) in place of tris(3-aminopropyl)amine (trpn) was found[10] to be 6.249(5) Å. The shrinkage of the cavity is due to the more flexible nature of the trpn unit. The bond distances and angles in the molecule lie within normal values.[9,10] The distances between any two of the secondary amino nitrogens (Table 2) are very different from one another; the same is true for the ether oxygens. This means the three-fold symmetry about the axis passing through the two bridgehead nitrogens is lost in the solid state. The cryptand crystallizes with three water molecules in the lattice. None of the water molecules, however, lies inside the cavity.

The structure of complex **1** consists of the cation [ZnL]$^{2+}$ (Fig. 2) and two perchlorate anions. In addition, two molecules of water are also present in the lattice. One of the perchlorate anions is severely disordered. As the trpn unit is somewhat flexible it arranges itself around the Zn^{II} in an almost ideal tetrahedral geometry. As a result the cavity enlarges with the

Table 1 Crystallographic and refinement data for cryptand L·3H$_2$O and complex **1***

	L·3H$_2$O	**1**
Formula	$C_{36}H_{51}N_5O_3 \cdot 3H_2O$	$C_{36}H_{51}Cl_2N_5O_{11}Zn \cdot 2H_2O$
M	655.862	901.725
Crystal system	Monoclinic	Triclinic
Space group	$C2/c$	$P\bar{1}$
a/Å	15.398(12)	9.987(3)
b/Å	20.062(6)	10.640(6)
c/Å	25.207(3)	19.944(10)
α/°		80.86(4)
β/°	103.80(2)	86.86(11)
γ/°		77.65(11)
U/Å^3	7561.0(6)	2043.5(70)
Z	8	2
D_c, D_m/g cm^{-3}	1.152, 1.16	1.466, 1.43
μ/mm^{-1}	0.08	0.80
Crystal size/mm	0.4 × 0.2 × 0.2	0.4 × 0.3 × 0.2
Transmission (maximum, minimum)	0.9763, 0.9533	0.7890, 0.6233
2θ Range/°	2–45	2–50
Total reflections measured	5924	7810
No. unique reflections	5161	7636
No. reflections used [$I > 3\sigma(I)$]	2293	4030
No. variables	425	550
R	0.088	0.064
R'	0.123	0.069
Goodness of fit	7.671	2.223
Largest and mean shift/e.s.d.	0.004, 0.0008	0.0003, 0.0001
Minimum, maximum peak in Fourier-difference map/e Å^{-3}	−0.61, +0.49	−0.97, +1.21

* Details in common: θ–2θ scans, range 0.80 + 0.35 tan θ; $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R' = [(\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2]^{\frac{1}{2}}$, $w = 1/\sigma(F)$.

Table 2 Selected bond lengths (Å), angles (°) and non-bonded distances (Å)

Complex **1**

Zn−N(1)	2.025(7)	Zn−N(4)	2.021(7)
Zn−N(2)	2.033(6)	Zn−N(5)	2.008(8)
N(1)−Zn−N(2)	106.5(3)	N(2)−Zn−N(4)	111.0(3)
N(1)−Zn−N(4)	107.8(3)	N(2)−Zn−N(5)	112.0(3)
N(1)−Zn−N(5)	107.6(3)	N(4)−Zn−N(5)	111.7(3)

	L·3H$_2$O	**1**
N(1) · · · N(3)	5.291	7.263
N(2) · · · N(4)	4.960	3.342
N(2) · · · N(5)	6.526	3.350
N(4) · · · N(5)	6.410	3.336
O(1) · · · O(2)	4.974	4.589
O(1) · · · O(3)	5.321	4.309
O(2) · · · O(3)	5.805	4.346

distance between the two bridgehead N atoms becoming 7.263(10) Å while still maintaining the *endo-endo* conformation. The cryptand assumes a pseudo-three-fold symmetry about the axis passing through the two bridgehead nitrogens (Table 2). This shows that the cavity in L is quite flexible. The Zn−N bond distances are somewhat shorter compared to those found in other zinc-cryptates.[2–4]

Two ligand-field (LF) and one ligand-to-metal charge-transfer (LMCT) transitions are observed in the electronic spectra of complexes **2** and **3** in acetonitrile at room temperature. Dichloromethane, chloroform or methanol cannot be used as solvent due to solubility problems. In the LF region the two bands appear at λ_{max} 875 (ε 375) and 745 nm (235 dm^3 mol^{-1} cm^{-1}) while in the LMCT region the strong band appears at λ_{max} 275 nm (9350 dm^3 mol^{-1} cm^{-1}). The low energy of the LF bands are attributable to a pseudo-tetrahedral CuN$_4$ chromophore[22] while the intense band at 275 nm is due to a secondary N→Cu^{II} LMCT transition.[23]

The effective magnetic moments (μ_{eff}/μ_B) for the copper(II) complexes **2** and **3** after diamagnetic corrections were found to be 1.97 and 2.01 at 297 K consistent[24] with discrete, mononuclear complexes. The complexes display an asymmetric broad EPR signal in the solid state at 298 K which becomes symmetric and broad at 77 K without revealing any fine structure. Thus, although the EPR signal is not indicative of the stereochemistry it is likely that a structural change takes place upon cooling. In acetonitrile solution (*ca.* 1 × 10^{-3} M) at 298 K each complex exhibits an axial spectrum which changes to a broad signal at 77 K similar to the one obtained in the solid state at the same temperature.

Cyclic voltammetry of complexes **2** and **3** at 298 K in MeCN (*ca.* 1 × 10^{-3} M) does not show any response in the region +1.0 to −1.0 V. When scanned first at negative potentials an ill defined peak was observed in each case that disappeared in the reverse scan. This means that spatial rearrangements upon oxidation/reduction of the metal–ligand ensemble are not facile.

Conclusion

We have shown here that the cryptand L forms a collapsible cavity. When a metal ion enters the cavity enlarges and the cryptand assumes a pseudo-three-fold symmetry about the axis passing through the bridgehead nitrogens. The metal ion occupies the N$_4$ end of the cavity leaving the other end vacant. With Zn^{II} an almost ideal tetrahedral co-ordination geometry is formed. Copper(II) possibly binds to the N$_4$ end in a pseudo-tetrahedral fashion. Efforts are underway to probe the ligational behaviour of L towards inner-transition metal ions.

Acknowledgements

Financial support from the Department of Science and Technology (DST), New Delhi, India (No. SP/S1/F-13/91) is gratefully acknowledged. The structural studies were made at the National Facility on Single Crystal X-Ray Diffraction at the Department of Chemistry, Indian Institute of Technology Kanpur. P. K. B. thanks the DST for funding the facility (under the IRHPA Programme; No. 6P/S1/F-47/89).

References

1 M. G. B. Drew, C. J. Harding, V. McKee, G. G. Morgan and J. Nelson, *J. Chem. Soc., Chem. Commun.*, 1995, 1035; M. G. B. Drew, O. W. Howarth, G. G. Morgan and J. Nelson, *J. Chem. Soc., Dalton Trans.*, 1994, 3149.
2 J.-L. Pierre, P. Chautemps, S. M. Refaif, C. G. Beguin, A. El-Marzouki, G. Serratrice, E. Saint-Aman and P. Rey, *J. Am. Chem. Soc.*, 1995, **117**, 1965; J.-L. Pierre, P. Chautemps, S. M. Refaif, C. G. Beguin, A. El-Marzouki, G. Serratrice, P. Rey and J. Laugier, *J. Chem. Soc., Chem. Commun.*, 1994, 1117.
3 C. Bazzicalupi, A. Bencini, V. Fusi, L. Mazzanti, P. Paoletti and B. Valtancoli, *Inorg. Chem.*, 1995, **34**, 3003.
4 C. Bazzicalupi, A. Bencini, V. Fusi, L. Mazzanti, P. Paoletti and B. Valtancoli, *J. Chem. Soc., Chem. Commun.*, 1994, 881.
5 Y. S. Yan, L. Q. Hui and S. M. Chang, *Inorg. Chem.*, 1994, **34**, 1251.
6 K. G. Ragunathan and P. K. Bharadwaj, *J. Chem. Soc., Dalton Trans.*, 1992, 1653.
7 J. de Mendoza, E. Mesa, J.-C. Rodriguez-Ubis, P. Vázquez, F. Vögtle, P.-M. Windscheif, K. Rissanen, J.-M. Lehn, D. Lilienbaum and R. Ziessel, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 1331.
8 R. Menif, J. Reibenspies and A. E. Martell, *Inorg. Chem.*, 1991, **30**, 3446; R. J. Motekaitis, A. E. Martell, I. Murase, J.-M. Lehn and M. W. Hosseini, *Inorg. Chem.*, 1988, **27**, 3630.
9 D. K. Chand and P. K. Bharadwaj, *Inorg. Chem.*, 1996, **35**, 3380.
10 P. Ghosh, S. Sengupta and P. K. Bharadwaj, *J. Chem. Soc., Dalton Trans.*, 1997, 935.
11 J. M. Lehn, *Supramolecular Chemistry—Concepts and Perspectives*, VCH, Weinheim, 1995, ch. 4 and 8; R. M. Izatt, K. Pawlak, J. S. Bradshaw and R. L. Bruening, *Chem. Rev.*, 1995, **95**, 2529; J.-M. Lehn, in *Perspective in Coordination Chemistry*, eds. A. F. Williams, C. Floriani and A. F. Merbach, VCH, New York, 1992, p. 447; P. K. Bharadwaj, *J. Sci. Ind. Res.* (*India*), 1993, **52**, 533.
12 J. M. Lehn, *Struct. Bonding* (*Berlin*), 1973, **16**, 1.
13 K. G. Raghunathan and P. K. Bharadwaj, *Tetrahedron Lett.*, 1992, 7581.
14 P. Ghosh, R. Shukla, D. K. Chand and P. K. Bharadwaj, *Tetrahedron*, 1995, **51**, 3265.
15 D. K. Chand and P. K. Bharadwaj, *Tetrahedron Lett.*, 1996, 8443.
16 P. Ghosh, T. K. Khan and P. K. Bharadwaj, *Chem. Commun.*, 1996, 189.
17 P. Ghosh, P. K. Bharadwaj, S. Mandal and S. Ghosh, *J. Am. Chem. Soc.*, 1996, **118**, 1553.
18 S. Mandal and P. K. Bharadwaj, *Polyhedron*, 1992, **11**, 1037.
19 S. R. Hall, J. M. Stewart and H. B. Flack, *The XTAL 3.2 Reference Manual*, Universities of Western Australia and Maryland, 1993.
20 W. J. Grey, *Coord. Chem. Rev.*, 1971, **7**, 81.
21 C. K. Johnson, ORTEP, Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, TN, 1971.
22 S. Knapp, T. P. Keenan, X. Zhang, R. Fikar, J. A. Potenza and H. J. Schugar, *J. Am. Chem. Soc.*, 1990, **112**, 3452 and refs. therein.
23 V. M. Miskowski, J. A. Thich, R. Solomon and H. J. Schugar, *J. Am. Chem. Soc.*, 1976, **98**, 8344.
24 F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 5th edn., Wiley, New York, 1988, p. 768.

Received 11*th March* 1997; *Paper* 7/01692A