Synthesis and Characterisation of an Octaazamacrobicyclic Ligand using Alkali-metal Ions as Templates; Characterisation of a Dicopper Complex as the Perchlorate Salt†

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A polyazamacrobicyclic compound (cryptand) has been synthesised in good yield from tris(2-aminoethyl)amine and glyoxal as a [2 + 3] condensation product in the presence of rubidium or caesium ion as a template. On reduction by $NaBH_4$ this gives a potentially multidentate ligand $N(CH_2CH_2NHCH_2CH_2NHCH_2CH_2)_3N$ (L) for transition-metal ions. A dicopper complex $[Cu_2L(ClO_4)][ClO_4]_3$ has been isolated in the solid state as the perchlorate salt and characterised by elemental analysis, electrochemistry, room-temperature magnetic susceptibility, IR, electronic and EPR spectroscopy.

The use of macrobicyclic compounds as ligands for transition-metal ions is of considerable current interest.[1–12] As ligands they possess several desirable features[13] such as their donor atom topology, binding site rigidity, layer effects *etc.* that determine stability, selectivity and properties of their complexes with metal ions. In complex formation reactions, the magnitude of steric strain of the ligand is an important parameter that determines to a large extent the ease of complexation. If the ligand donor set is preorganised to impart a preferable co-ordination geometry for a particular metal ion the complex formation will be facile. An investigation of metal-ion selectivity *vs.* steric strain of the ligand can provide much needed clues to biological metal selection processes. A wide scope exists for achieving desired topologies for donor sets in cryptands through ligand design. Another property of cryptands which is of enormous importance is their ability to impose unusual co-ordination geometries on metal ions owing to the neoplastic nature of the donor atoms.[13] In the same way that a protein matrix can impose a co-ordination geometry to a metal ion (or ions) in an intrinsic active site, the donor atoms in a suitably designed cryptand should be able to stabilize a particular co-ordination geometry for a metal ion that is not possible with a simple ligand. By this means attempts can be made to mimic the entatic state of an active site.[14] Moreover, co-operativity between multimetal centres is possible if they are held in the cavity of a cryptand so that they can converge onto a substrate. In order to probe these aspects of cryptands as ligands to transition-metal ions, we have initiated a research programme to synthesise a variety of cryptands for use as ligands. In this paper, the synthesis of an octaazamacrobicyclic Schiff base by use of an alkali-metal (Rb^+ or Cs^+) template reaction is described. Reduction of the Schiff base by $NaBH_4$ gives $N(CH_2CH_2NHCH_2CH_2NHCH_2CH_2)_3N$ (L), a nitrogen analogue of cryptand-222, and its complexation behaviour towards copper and zinc is discussed. This all-nitrogen cryptand, synthesised previously by Lehn and co-workers[15] using high-dilution methods, acts as an anion receptor upon protonation. Hunter *et al.*[3] have previously synthesised the corresponding Schiff base by use of strontium ion as the template and have probed its ligating abilities towards transition-metal ions.

Experimental

Chemicals and Starting Materials.—All the solvents and reagents, tris(2-aminoethyl)amine (tren), copper(II) perchlorate hexahydrate, glyoxal, RbCl and CsCl were from commercial sources. While the reagents were used as received, the solvents were purified prior to use by applying standard procedures.[16] Tetrabutylammonium perchlorate was prepared from tetrabutylammonium bromide (Aldrich) and 70% aqueous perchloric acid and was recrystallised from ethanol and dried *in vacuo*.

Measurements.—Solution electrical conductivity was measured with a model CM-82T Elico conductivity bridge (Hyderabad, India) with solute concentrations of *ca.* 1×10^{-3} mol dm^{-3}. Spectroscopic data were collected as follows: IR (KBr disc, 4000–200 cm^{-1}), Perkin-Elmer model 580; ^1H NMR, Bruker 400 MHz spectrometer; electronic absorption spectra [room temperature, acetonitrile or dimethylformamide (dmf)], Perkin-Elmer Lambda-2; magnetic susceptibility {room temperature, $[CoHg(SCN)_4]$ standard}, Cahn Faraday magnetic balance; EPR [X band, solid and solution, diphenylpicrylhydrazyl (dpph) standard], Varian E-109 with solute concentrations of *ca.* 1×10^{-3} mol dm^{-3} in acetonitrile or dmf at room temperature as well as at liquid-nitrogen temperature (77 K). Cyclic voltammetric measurements were performed on a PAR model 370-4 electrochemistry system: 174A, polarographic analyser; 175, universal programmer; and RE 0074, x–y recorder. Potentials are recorded in acetonitrile at room temperature relative to a saturated calomel reference electrode (SCE) and are uncorrected for liquid junction potentials. The working electrode was platinum and the supporting electrolyte was tetrabutylammonium perchlorate. The set-up described by Ray *et al.*[17] was used and all measurements were made under a dry dinitrogen atmosphere. The potential of the ferrocene-ferrocenium couple was used for calibration.[17] Microanalyses were obtained at the microanalytical laboratory at Indian Institute of Technology, Kanpur and at the Central Drug Research Institute, Lucknow, India.

Synthesis of $N(CH_2CH_2NHCH_2CH_2NHCH_2CH_2)_3N$ (L).—The Schiff-base precursor to this ligand was synthesised by a [2 + 3] Schiff-base condensation of tren with glyoxal in presence of Rb^+ or Cs^+ ions; tren (0.73 g, 5 mmol) in methanol (500 cm^3) containing RbCl (0.3 g, 2.5 mmol) or CsCl (0.42 g, 2.5 mmol) under argon was allowed to warm to 50 °C. To this

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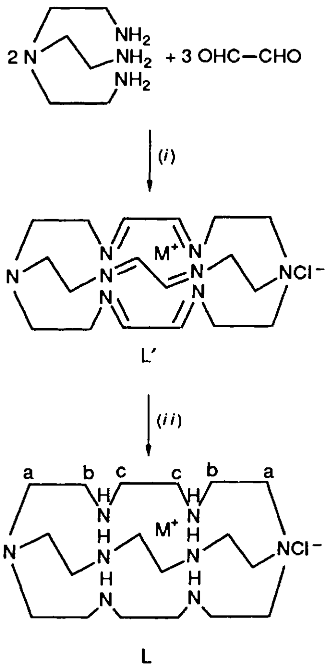

Scheme 1 (*i*) RbCl or CsCl in MeOH, (*ii*) NaBH$_4$

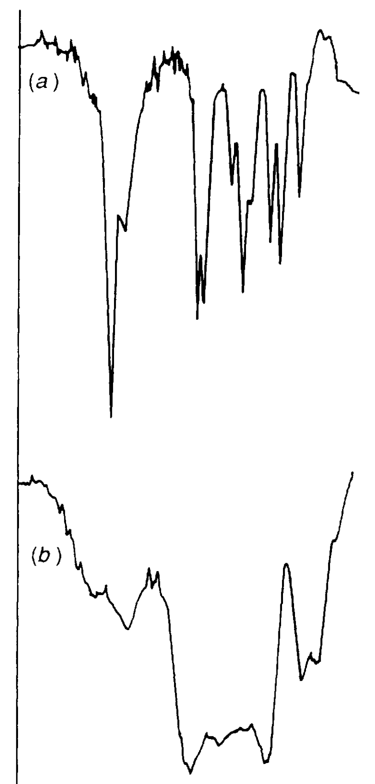

Fig. 1 Infrared spectrum in the range, 1200–1800 cm^{-1}: (*a*) for the Schiff base, (*b*) for the reduced cryptand

colourless solution was added dropwise a 40% aqueous glyoxal solution (0.44 g, 7.5 mmol) in methanol (200 cm^3) with constant stirring over 2 h. After the addition was complete, the resulting solution was allowed to reflux for 8 h. The resulting light yellow solution was cooled to room temperature, decolourised with activated charcoal and reduced in volume to 10 cm^3 in a rotary evaporator. On keeping the solution in a desiccator over

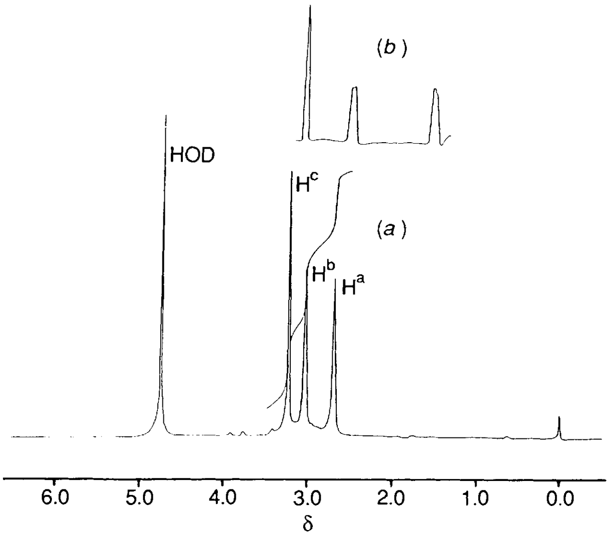

Fig. 2 (*a*) 400 MHz proton NMR spectrum in D$_2$O of [RbL]PF$_6$, (*b*) resonance enhanced spectrum in the region δ 2.6–3.6

concentrated H$_2$SO$_4$, the Schiff base L′ was obtained (Scheme 1) as a colourless microcrystalline solid. Yield 60%; ν_{max}(imine) 1650s cm^{-1} (KBr). The Schiff base turned yellow in air in two days and decomposed slowly. Upon reduction by refluxing with NaBH$_4$ in methanol for 4 h the desired cryptand L could be isolated in 85% yield (based on L′). The reduced product did not show any IR absorptions due to imine (Fig. 1). The PF$_6^-$ salt of the rubidium cryptate could be isolated as a colourless microcrystalline solid when solid NH$_4$PF$_6$ was added in slight excess to a concentrated solution of the chloride in water. This complex was purified by recrystallisation twice from acetonitrile; m.p. 125–127 °C (Found: C, 35.25; H, 7.20; N, 19.05. C$_{18}$H$_{42}$F$_6$N$_8$PRb requires C, 35.95; H, 7.05; N, 18.65%); ν_{max}(PF$_6$) 850s and 565s cm^{-1} (KBr);[18] δ_H(400 MHz; solvent D$_2$O) 4.8 [s br, HOD], 3.21 [12 H, s, H^c], 3.02 [12 H, s br, H^b] and 2.70 [12 H, s br, H^a] (Fig. 2). (For designation of the protons refer to Scheme 1.) Neither the ^{1}H NMR or IR data of the cryptand L or its corresponding Schiff base L′ have been published previously.

Synthesis of the Zinc Complex (Zn$_2$L[NO$_3$]$_4$).—Synthesis of the zinc complex of cryptand L was undertaken to observe possible shifts in proton NMR signals upon complexation. It was prepared by refluxing a methanolic solution containing Zn(NO$_3$)$_2$·6H$_2$O and [RbL]PF$_6$ in a 2:1 molar ratio for 30 min. The solution was then allowed to cool to room temperature and was filtered. The zinc complex (Zn$_2$L[NO$_3$]$_4$) separated as a colourless microcrystalline solid upon concentration of the solution over concentrated H$_2$SO$_4$ in a desiccator. The solid was collected and purified by recrystallisation from acetonitrile. Yield 35% (Found: C, 28.60; H, 5.70; N, 21.95. C$_{18}$H$_{42}$N$_{12}$O$_{12}$Zn$_2$ requires C, 28.85; H, 5.65; N, 22.4%).

As complexes of zinc(II) do not have diagnostic electronic spectral bands, it is not possible in the absence of a single-crystal diffraction study to establish firmly whether the metal ions are inside or outside the cavity of the cryptand. We have not been able to grow suitable single crystals of this compound but in the X-ray crystal structure of a related mixed dinuclear copper(II)–zinc(II) complex [19] Zn^{II} is bound to four nitrogens of a tren ligand. Also, solution studies of Zn^{II}–tren systems indicate [20] that Zn^{II} may be co-ordinated to the four nitrogens of the tren ligand. If the two Zn^{II} ions are inside the cavity and each is bound to four nitrogens, then the proton NMR spectrum of the complex should be quite similar to that of the rubidium complex. This is found to be so, with a slight downfield shifting of the three peaks being observed: δ_H(400 MHz, solvent D$_2$O) 4.8 (s br, HOD), 3.59 (12 H, s, H^c), 3.30 (12 H, br s, H^b), and 2.85 (12 H, br s, H^a). The corresponding perchlorate salt is very hygroscopic and difficult to handle.

Table 1 Electronic absorption data of the complexes in MeCN

Compound	λ_{max}/nm	$\tilde{\nu}$/cm^{-1}	ε_{max}/dm^3 mol^{-1} cm^{-1}
$[Cu_2L(ClO_4)_4$	750	13 260	880
	630	15 920	590
	280	35 740	5 570
$Cu_2L(ClO_4)_4$	680 (br)	14 705	500
$+6NaN_3$*	380	26 315	2 150
	280	35 740	3 820

* Spectrum recorded 4 h after addition of NaN_3.

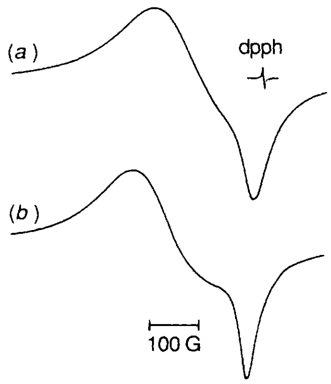

Fig. 3 EPR spectra of the solid dicopper complex at (*a*) room temperature, (*b*) liquid-nitrogen temperature

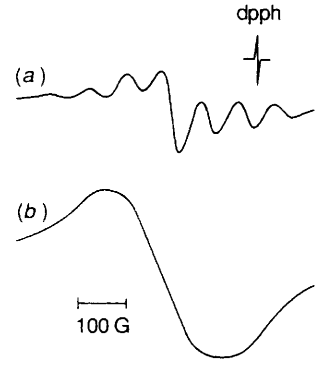

Fig. 4 EPR spectra of the dicopper complex in MeCN at (*a*) room temperature, (*b*) liquid-nitrogen temperature

Synthesis of the Dicopper Complex $[Cu_2L(ClO_4)][ClO_4]_3$.—Copper(II) perchlorate hexahydrate (1.1 g, 3 mmol) dissolved in methanol (50 cm^3) was added dropwise to a warm solution (40 °C) of $[RbL]PF_6$ (0.6 g, 1 mmol) in methanol (250 cm^3). After addition was complete, the resulting blue solution was allowed to reflux for 0.5 h and then cooled to room temperature. A blue microcrystalline solid separated out which was collected by filtration and air-dried. Yield 72% (Found: C, 23.95; H, 4.65; N, 12.60. $C_{18}H_{42}Cl_4Cu_2N_8O_{16}$ requires C, 24.15; H, 4.75; N, 12.50%).

Hunter *et al.*[3] have reported the isolation of a dicopper complex of the corresponding Schiff-base L′ which they have suggested to exist as a Cu^{II}–Cu^{I} mixed-valence species in solution based on EPR data (see below). However, their elemental analysis suggests that in the solid state it exists as $Cu_2L'(ClO_4)_4$ with both coppers in +2 oxidation state.

Results and Discussion

The dicopper complex $[Cu_2L(ClO_4)][ClO_4]_3$ is stable in air and soluble in common organic solvents as well as water. The molar conductivity of the copper complex in acetonitrile is found to be 370 ohm^{-1} cm^2 mol^{-1} at room temperature. While only a few conductivity data are available for compounds other than 1:1 electrolytes in acetonitrile,[21] a value of 380 ohm^{-1} cm^2 mol^{-1} has been attributed as the average value for 1:3 electrolytes. In this case, the dicopper complex can thus be formulated as $[Cu_2L(ClO_4)]^{3+}3ClO_4^-$ with one perchlorate co-ordinated to copper(s) in acetonitrile solution.

In the infrared spectrum of the complex, strong signals appear at 1143, 1116 and 1090 cm^{-1} besides moderately strong peaks at 1011, 996 and 818 cm^{-1}. The alkali-metal complex of the ligand with chloride as counter ion does not absorb appreciably at these positions. It can be suggested, based on literature data[22,23] that both co-ordinated and unco-ordinated perchlorates are present.

Two ligand-field and one ligand-to-metal charge-transfer (l.m.c.t.) transitions are observed in the electronic absorption spectra of the complex in acetonitrile at room temperature (Table 1). The shape and position of the ligand-field bands remain almost unchanged in dmf at room temperature. The spectra in the solid state though not well resolved indicate that the complex ion does not disintegrate in solution. The strong band at 280 nm is attributed to an N→Cu^{II} l.m.c.t. transition.[24] For the two ligand-field bands, the stronger one appears at 750 nm while the weaker one is at higher energy at 630 nm. A regular trigonal-bipyramidal CuN_5 chromophore usually gives two ligand-field transitions in this region with greater absorption intensity for the lower energy transition[25] although exceptions to this general observation are known.[26] The shapes of the ligand-field bands agree well (Table 1) with the complexes $[Cu(tren)X]^{n+}$ ($X = NCS^-$ or NH_3, $n = 1$ or 2) where the co-ordination geometry around copper is trigonal bipyramidal.[27] The present macrobicyclic ligand may be considered as consisting of two tren units separated by two carbon spacers (Scheme 1). Two copper ions can be easily fitted into the macrobicycle and the fifth co-ordination site is possibly provided by a bridged perchlorate. For trigonal-bipyramidal geometry the ground state orbital is d_{z^2}.[25,27] The absorption at 750 nm is then due to the transition $d_{xy},d_{x^2-y^2} \longrightarrow d_{z^2}$ which is allowed in C_3 or D_{3h} local symmetry and the less intense one at 630 nm is due to the $d_{xz},d_{yz} \longrightarrow d_{z^2}$ transition which is allowed in C_3 local symmetry only. The relative intensities of the two bands are not very different which suggests[27a] the effective local symmetry is lower than D_{3h}. The ligand-field bands are well separated from the charge-transfer band so that the high intensities of these transitions cannot be due to an intensity stealing mechanism.[28] However, if both the coppers are in a +2 oxidation state, the intensities are within the range found for trigonal-bipyramidal copper(II) complexes. When this perchlorate complex is treated with 6 equivalents of sodium azide, the colour of the solution slowly changes to green. After 4 h the two ligand-field bands are replaced by a very broad signal similar to that for $[Ag\{Cu(NH_3)_2(SCN)_3\}]$ in which the co-ordination geometry around Cu^{II} is trigonal bipyramidal.[29c] Also a new band appears at 380 nm suggestive of azide co-ordination.[29a,b]

The effective magnetic moment value for the dicopper complex is found to be 1.61 μ_B at 303 K per copper which is lower than for discrete monomeric copper(II) complexes[29] and can be attributed to the existence of a weak antiferromagnetic interaction between the two coppers in the complex. The EPR spectrum in the solid state displays a broad signal centred near $g = 2$ at room temperature with a very weak signal at $g = 4$. The signal near $g = 2$ becomes more asymmetric upon cooling to liquid-nitrogen temperature (77 K) as shown in Fig. 3. The solid-state spectrum is typical of magnetically concentrated copper(II) dimeric complexes[25a] and is not indicative of the solid-state stereochemistry. In the solution phase, the shape of the spectrum depends upon the solvent. At room temperature in acetonitrile a seven-line spectrum centred at $g = 2$ is observed which changes to a symmetric absorption at 77 K (Fig. 4). A seven-line spectrum at room temperature near $g = 2$ is also observed in dmf. However, the shape of the spectrum in this solvent does not change upon cooling to 77 K. The weak signal at $g = 4$ is not observed in solution. We can explain the EPR data as follows: both the coppers are in a +2 oxidation state and owing to poor superexchange only a very weak interaction ($2J \longrightarrow 0$) exists between the two ions. In this situation, the dominant mechanism that perturbs the EPR spectrum is the dipolar interaction[30] between the two Cu^{II} ions. This splits the $\Delta M_s = \pm 1$ transition at $g = 2$ and the $\Delta M_s = \pm 2$ transition at $g = 4$ appears as a weak signal. In acetonitrile solution the seven-line spectrum is replaced by a broad signal at $g = 2$ at low temperature apparently due to structural changes upon cooling. Hunter *et al.*[3] reported a seven-line spectrum for the dicopper Schiff-base complex $Cu_2L'(ClO_4)_4$ in dmf as due to the presence of a single electron delocalised over the two copper centres. This would suggest a mixed-valence Cu^ICu^{II} species despite the formulation of the complex as $[Cu_2L'(ClO_4)_4]$. These authors do not report any signal near $g = 4$, nor do they report the spectra in acetonitrile solution. Reports are available describing multi-line EPR spectra and a six-line spectrum was obtained[26] for the complex $[Cu(ntb)I]BF_4{\cdot}2MeOH{\cdot}4H_2O$ [ntb = tris(2-benzimidazolylmethyl)amine] at 77 K. A similar observation[31] was made in case of polycrystalline $[Cu\{N(CH_2CH_2NMe_2)_3\}I]I$ doped into the isomorphous zinc salt where the shape of the spectrum persists up to 133 K. The spectra were rationalised by presuming some overlap of two sets of resonances from two Cu^{II} centres with slightly different stereochemistries. It is obvious, however, that only an X-ray structural analysis of our dicopper complex can provide a clearer picture.

Cyclic voltammetry of this complex at 298 K in acetonitrile (1×10^{-3} mol dm^{-3}) show two anodic responses at +1.2 and at +1.3 V but no cathodic peak is found on scan reversal. When the voltage scan on the negative side is probed, two cathodic peaks, at −0.6 and at −1.6 V are observed. However, on scan reversal, only a broad peak appears at about −0.2 V attributable to the oxidation of copper deposited on the electrode. Similar observations have been made on related systems.[32] An analysis of the cyclic voltametric study is complicated due to the irreversibility of the electrode processes.

Conclusion

It is shown that the all-nitrogen cryptand L can be easily synthesised in high yields using alkali-metal ions as templates without applying high-dilution techniques. The cryptand forms a dicopper complex having interesting magnetic interactions. Complete understanding of the structure and bonding requires knowledge of its crystal and molecular structures. Efforts are underway to grow X-ray quality single crystals of the complex. Structural results along with variable-temperature magnetic susceptibility data and simulation of EPR spectra will be discussed in another study.

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