Macrocyclic Ligands designed to impose Tetrahedral Coordination: [1-(3-Dimethylaminopropyl)-1,5,9-triazacyclododecane], L1, [1{2-(Pyrrolidin-1-yl)ethyl}-1,5,9-triazacyclododecane], L2, and their Zinc(II) Complexes

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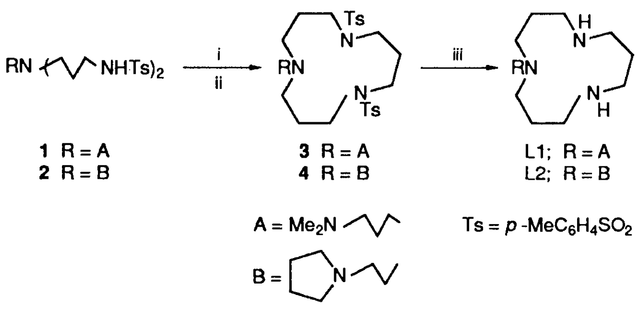
The all-propyl-linked pendent-arm triazamacrocycle 1-(3-dimethylaminopropyl)-1,5,9-triazacyclododecane encapsulates zinc(II) to give a tetrahedral complex.

For most simple ligands, the stability of complexes formed with the first-row transition-metal dications follows the Irving–Williams sequence (Mn < Fe < Co < Ni < Cu > Zn).[1] This order arises from the interplay of size (ionic radius decreases monotonically from Mn to Zn) and ligand field effects (LFSE in high-spin octahedral environment peaks at d^8, but d^9 can acquire extra stabilisation through Jahn–Teller distortion). Although stability data for multidentate and macrocyclic ligands are patchy, these ligands also generally manifest the Irving–Williams sequence; most anomalies may be attributed to structural dislocations as the 3d block is traversed. However, the available data largely pertain to ligands and conditions (dilute aqueous solutions) which give rise to octahedral complexes. In an attempt to generate novel patterns of selectivity among the first-row transition metal cations, we considered the use of a ligand which forms tetrahedral complexes with all the first-row transition metal ions. In particular, complexes of Co^{II} might be favoured relative to Ni^{II} and Cu^{II} (the reverse of the Irving–Williams sequence) because the d^7 electron configuration gives rise to maximal ligand-field stabilisation in a tetrahedral environment.

Although a simple tetradentate ligand which enforces tetrahedral coordination has not previously been reported, several factors led us to believe that a pendent-arm ligand based on 1,5,9-triazacyclododecane ([12]aneN_3) might achieve the goal. The presence of a macrocycle within the ligand serves particularly to enhance the stability of the complexes (the macrocyclic effect). The ligand [12]aneN_3 itself has been shown to supply a basal plane of three nitrogen donors in the tetrahedral complex $[([12]aneN_3)ZnBr]^+$ ($Zn–N_{av}$ = 2.04 Å, $N–Zn–N_{av}$ = 105°).[2] Similarly, the sulphur analogue 1,5,9-trithiacyclododecane ([12]aneS_3) forms $[Cu_2([12]aneS_3)_3]^{2+}$, which contains two tetrahedral Cu^I centres.[3] Whilst suitable for tetrahedral geometry, these 12-membered rings are not easily incorporated in octahedral complexes. [12]aneS_3 forms octahedral bis complexes $[M([12]aneS_3)_2]^{n+}$ only reluctantly while [12]aneN_3 apparently forms $[([12]aneN_3)CoX_3]$,[4] but not $[M([12]aneN_3)_2]^{n+}$ (M = Co, n = 3; M = Ni, n = 2).[5] These observations suggested that the ligands L1 and L2 (Scheme 1) might form stable tetrahedral complexes in which the [12]aneN_3 moiety supplies a basal plane of three nitrogen donors while the pendent arm affords an apical donor. We synthesised the ligands by standard methods and undertook crystal structures of their Zn^{II} complexes to ascertain the optimum length of pendent arm required to complete tetrahedral coordination.

The ligands were prepared by a modified Richman–Atkins method (Scheme 1): Reaction of the sodium salts of the sulphonamides $RN(CH_2CH_2CH_2NHTs)_2$ (Ts = p-$MeC_6H_4SO_2$) (**1** and **2**; prepared as described†) with $TsOCH_2CH_2CH_2OTs$ in dimethylformamide (DMF) at



Scheme 1 *Reagents*: i, NaH–DMF: ii, $TsO(CH_2)_3OTs$; iii, H_2SO_4 (conc.) or Na-naphthalene

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† The starting amines were obtained from the reaction of two moles of acrylonitrile with XNH_2 (X = A or B; Scheme 1) in presence of acetic acid, followed by reduction of the products $X(NCH_2CH_2CN)_2$ with $NaBH_4$–Raney Ni (R. A. Egli, *Helv. Chim. Acta*, 1970, **53**, 47). The amines were tosylated by standard methods.

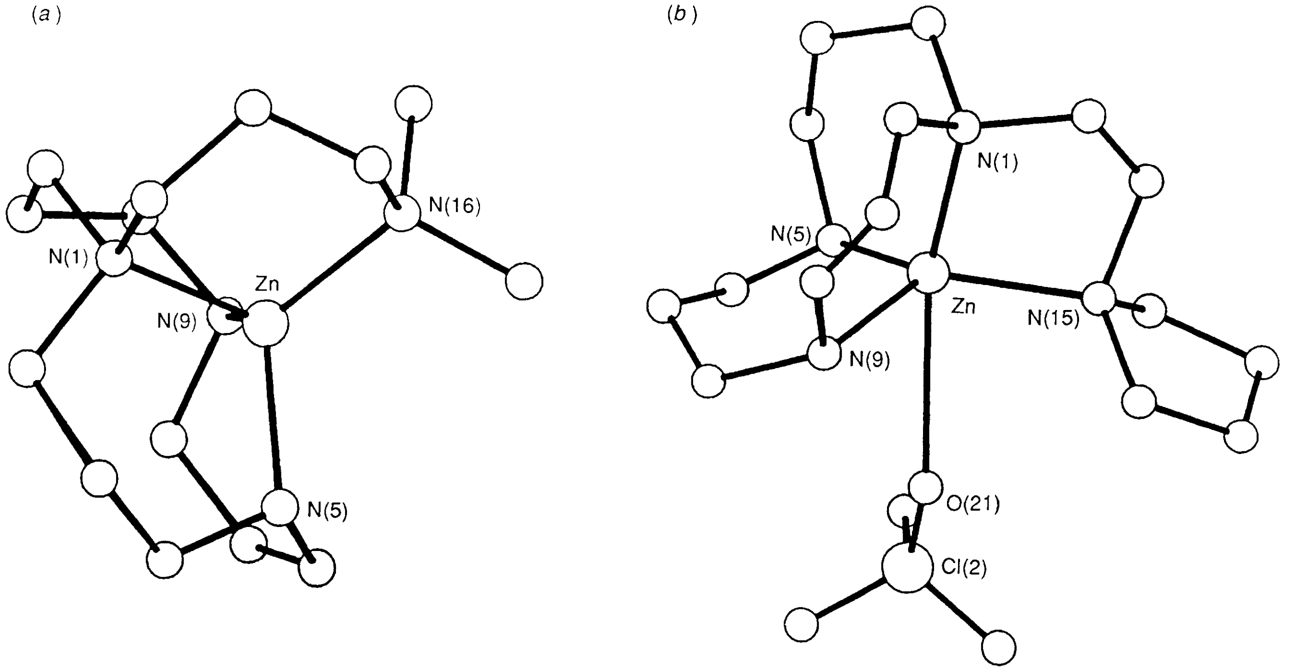

Fig. 1 Crystal Structures of (*a*) $[Zn(L1)]^{2+}$ and (*b*) $[Zn(L2)(OClO_3)]^{+}$. Atoms are numbered sequentially around the macrocyclic ring [N(1), C(2), C(3), C(4), N(5), *etc.*].

100 °C yielded the cyclic ditosylates (**3** and **4**). These were deprotected with concentrated sulphuric acid or sodium-naphthalene.[6] The Zn^{II} complexes were prepared from molar equivalents of the ligands and $[Zn(Me_2SO)_4](ClO_4)_2$[7] in nitromethane solution, and recrystallised from nitromethane–ethanol.‡ The perchlorate salts pose a potential explosion hazard; although no problems were encountered, it is advisable that only *small-scale* preparations of these materials be attempted.

The tetradentate ligand L1 encapsulates the Zn^{II} ion (Fig. 1), affording approximately tetrahedral coordination geometry with $Zn–N_{av}$ = 2.00 Å (there is very little deviation amongst the individual Zn–N distances). The 12-membered ring provides a basal plane of three nitrogen donors, whilst the pendent arm provides the apex. Although the fragment C(4)–N(5)–C(6) is rather disordered, the chelate rings in the macrocyclic part of the ligand clearly adopt chair, twist-boat and flattened chair conformations.§ The pendent arm chelates in the chair conformation.

The propyl linkages in L1 are unable to subtend the full tetrahedral angle of 109.5°; the chelating N–Zn–N angles average 104.8°. Consequently, the non-chelating angles expand to an average of 118.2°, generating a distinct cleft in the $[Zn(L1)]^{2+}$ cation. Oxygen atoms from the perchlorate counterions protrude into the cleft, but interact only weakly with the central zinc ion [Zn–O(11) = 3.87 Å, Zn–O(22A) = 4.12 Å]. The Zn^{II} complex of the related ligand 1-{3-(pyrrolidin-1-yl)propyl}-1,5,9-triazacyclododecane shows a similar structure.[8]

In $[Zn(L2)](ClO_4)_2$, however, the pyrrolidinylethyl pendent arm allows a chelate angle of only 87.8°. Thus, although the remaining (propyl-linked) chelates of the macrocylic moiety maintain an average chelate angle of 105.6° {*cf.* 104.8° in $[Zn(L1)]^{2+}$} the non-chelating N–Zn–N angles increase to an average of 123.1° {*cf.* 118.2° in $[Zn(L1)]^{2+}$}. Correspondingly, the cleft in the $[Zn(L2)]^{2+}$ cation expands to allow a strong interaction with a perchlorate counterion [Zn–O(21) = 2.71 Å]. Indeed, the Zn ion is best considered 5-coordinate, with the bridgehead N atom [N(1)] and the perchlorate anion comprising the apices of a distorted trigonal bipyramid (Fig. 1). Because of the increased coordination number, Zn–N

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‡ L1 and L2 were characterised by electron impact mass spectra and ^1H and ^{13}C NMR, and the Zn^{II} complexes of formula $[Zn(L)][ClO_4]_2$ (L = L1 and L2) by fast atom bombardment mass spectra, ^1H and ^{13}C NMR and C, H, N analyses.

Crystal data for $[Zn(L1)](ClO_4)_2$; $C_{14}H_{32}N_4ZnCl_2O_8$; M_r = 520.7; orthorhombic; *Pcab*; *a* = 15.054(8); *b* = 15.34(1); *c* = 19.25(1) Å; *V* = 4444 Å^3; *Z* = 8; D_c = 1.56 g cm^{-3}. Mo-Kα radiation (λ = 0.71073 Å). μ(Mo-Kα) = 14.2 cm^{-1}. *T* = 290 K. *R* = 7.50% for 1488 unique reflections with $I > 2\sigma(I)$.

Crystal data for $[Zn(L2)](ClO_4)_2$; $C_{15}H_{32}N_4ZnCl_2O_8$; M_r = 532.8; orthorhombic; $Pn2_1a$; *a* = 13.875(13); *b* = 9.811(6); *c* = 16.186(9) Å; *V* = 2203 Å^3; *Z* = 4; D_c = 1.61 g cm^{-3}. Mo-Kα radiation (λ = 0.71073 Å). μ(Mo-Kα) = 14.3 cm^{-1}. *T* = 293 K. *R* = 5.70% for 1224 unique reflections with $I > 2\sigma(I)$.

Data were collected with a Nicolet $P2_1$ four circle diffractometer in the ω–2θ mode; backgrounds were measured at each end of the scan for 0.25 of the scan time. Three standard reflections were monitored every 200 reflections, and the data were rescaled to correct for any decay. Reflections were processed using profile analysis, and corrected for Lorentz, polarisation and absorption effects (by the Gaussian method). Heavy-atoms were located by the Patterson interpretation section of SHELXTL, and light-atoms then found on successive Fourier syntheses. Anisotropic temperature factors were used for all non-H atoms, except as noted. Hydrogen atoms were given fixed isotropic temperature factors, *U* = 0.07 Å^2. Those defined by the molecular geometry were inserted at calculated positions and not refined; methyl groups were treated as CH_3 units, with their initial orientation taken from the strongest H-atom peaks on a difference Fourier synthesis. Final refinement was on *F* by least-squares methods refining 268 and 245 parameters respectively. Weighting schemes of the form $W = 1/[\sigma^2(F) + gF^2]$ (with *g* = 0.0008 and 0.001 respectively) were used, and shown to be satisfactory by a weight analysis. For the complex of L2, the uncoordinated ClO_4 was held as a rigid group; C(2) was disordered [refined occupancies of C(2a) and C(2b) 60:40]; C(1)–C(3) and C(14) were unstable when refined anisotropically and were held isotropic.

Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

§ The conformation of the macrocyclic part of the ring thus parallels that observed in $[12]aneS_3$ complexes of octahedral metal ions in which dilation of the coordination sphere is also observed: S. R. Cooper, S. C. Rawle, J. R. Hartman, E. J. Hintsa and G. A. Admans, *Inorg. Chem.*, 1988, **27**, 1209; S. C. Rawle, T. J. Sewell and S. R. Cooper; *Inorg. Chem.*, 1987, **26**, 3769.

distances (average 2.04 Å) in $[(L2)Zn(OClO_3)]^+$ significantly exceed those in $[Zn(L1)]^{2+}$.

The structure determinations show that only the all-propyl-linked ligand L1 supports tetrahedral coordination, whilst L2, containing a pyrrolidinylethyl pendent arm, admits further ligands into the coordination sphere. However, the profusion of propyl chelates in L1 severely reduces the stability of its complexes. Although the analogous 1-(3-dimethylamino-propyl)-[9]aneN_3 ([9]aneN_3 = 1,4,7-triazacyclononane) could be expected to form more stable complexes than L1, the tighter macrocyclic ring cannot readily accommodate a tetrahedral geometry (N–metal–N bond angles in complexes of [9]aneN_3 are usually less than 90°), and there are no known tetrahedral complexes of [9]aneN_3. Since the Ni^{II} and Co^{II} complexes of L1 and related ligands have been found to accept additional ligands (to form 5- and 6-coordinate complexes),[9] we are presently investigating ligands derived from L1 by alkylation, changing donor atoms, and introducing negative charge (whilst retaining the proven backbone). These changes should enhance the stability of the complexes and extend the range of tetrahedral complexation to metals other than Zn^{II}. The results of these studies will be reported fully at a later date.

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