Metal-ion controlled Helicity of an 18-membered Hexaaza Tetraamine Macrocycle

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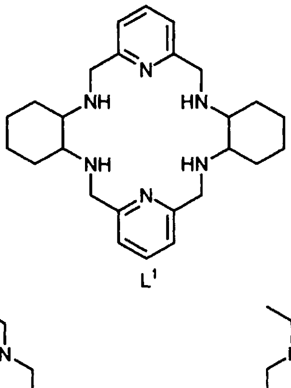
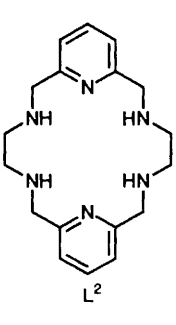
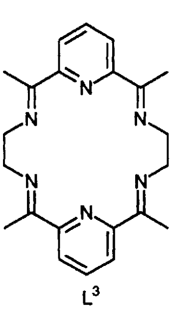
Complexes of Zn^{II}, Cd^{II} and La^{III} with a novel hexadentate tetraamine macrocycle L^1 are prepared and their X-ray structure analyses demonstrate the helicity of the tetraamine macrocycle is controlled by the metal ion size and its prefered coordination.

Molecular helicity in inorganic complexes has attracted considerable interest in recent years with single-, double-, and triple-helical arrays being produced by ligands containing pyridine groups in their framework.[1] While much attention has been focussed on open-chain systems, the deployment of macrocyclic ligands in deliberate syntheses of this type remain limited to only a few examples.[2,3] We report here the synthesis of a new 18-membered N_6 macrocycle L^1, and the crystal structure of the first lanthanide complex of a hexaaza tetraamine macrocycle, [LaL^1(NO$_3$)$_3$], which has a 'twist-fold' conformation of the macrocycle.† The essential role of metal ion size in controlling the conformation of this type of macrocycle has been demonstrated by the synthesis and X-ray structure analysis of the analogous d-block complexes [ZnL^1]$^{2+}$ and [CdL^1]$^{2+}$ where there is no folding and the 'twist-wrap' conformation is sufficient to produce a macrocyclic helicate. It has previously been shown that the related hexaaza tetraamine L^2 has the ability to adopt a helical chiral structure with the very small ion Zn^{II},[3] but the effect of increasing metal ion diameter has not previously been demonstrated. The present work shows high macrocycle helicity is induced by the very small ion Zn^{II}, lower helicity by the larger ion Cd^{II}, but with the very large La^{III} ions an alternative 'twist-fold' conformation is observed.

The new macrocyclic ligand L^1 was obtained in a one-step synthesis by reducing the corresponding tetraimine[4] with NaBH$_4$ *in situ*, and purifying the brown-yellow oily product by column chromatography. The absence of the ν(C=N) at 1650 cm^{-1} and the presence of a medium sharp ν(NH) stretch at 3305 cm^{-1} for L^1 confirms the successful synthesis of the tetraamine compounds. Both ^{13}C and ^{1}H NMR results indicate D_2 symmetry in solution.‡ Complexation of L^1 was carried out by refluxing a solution of the ligand L^1 in dichloromethane and a solution of nitrate or perchlorate salts in acetonitrile. ^{1}H NMR spectra of the complexes of Zn^{II} and Cd^{II} again indicate D_2 symmetry in solution,§ but the spectra of the complex of La^{III} is complicated, indicating the macrocyclic ligand has an asymmetric conformation.


L^1


L^2


L^3

Although complexes of hexaaza tetraimine macrocycle are well known for a range of lanthanide metals, and have proved to be of considerable potential in a range of applications,[4] the eleven coordinate complex [LaL^1(NO$_3$)$_3$] is the first example of a f-block complex of the hexaaza tetraamine class of macrocycle to have been isolated (Fig. 1).¶ Despite the more flexible backbone of the tetraamine the overall structure of [LaL^1(NO$_3$)$_3$] has many features in common with the well established tetraimine class of lanthanide macrocycles. In the present tetraamine structure the addition of hydrogens at the amino carbon atoms breaks the conjugation, present in the tetraimine, and the two nitrogens are no longer coplanar with the pyridine ring. A slight twist is still apparent in the conformation of the macrocycle but it is dominated by the folding of the macrocycle (dihedral angle between pyridine groups 51.8°) away from the two nitrate ligands towards the third. The conformation of the tetraamine is surprisingly similar to the arrangement observed in the less flexible tetraimine structures. For example the fold angle is comparable to that of 59.0° which arises in the only other eleven coordinate hexaaza macrocyclic complex to have been reported, the tetraimine [CeL^3(NO$_3$)$_2$MeOH]$^+$.[5]

In contrast, with softer metals of lower coordination requirements, the new hexaaza tetraamine ligand adopts a distorted octahedral arrangement of the six nitrogen donor atoms giving the rare helical chiral macrocyclic complexes [ZnL^1]$^{2+}$ (Fig. 2) and [CdL^1]$^{2+}$.§ For the smaller ion, Zn^{II}, the dihedral angle between the two sets of meridional N$_3$ donor is 103.4° but, as the size of the metal increases, unwrapping of the helix occurs and in [CdL^1]$^{2+}$ the smaller value of 69.0° is observed. This type of 'twist-wrap' helical macrocyclic conformation has been observed once before in related hexaaza tetraamine macrocycle [ZnL^2]$^{2+}$ but at that time it was not possible to deduce the effect of increasing metal size on helicity.[3] This work provides evidence that as size increases the 'twist wrap' nature reduces, giving way to a 'twist-fold' as the coordination number exceeds six (Fig. 3). The 'planar'

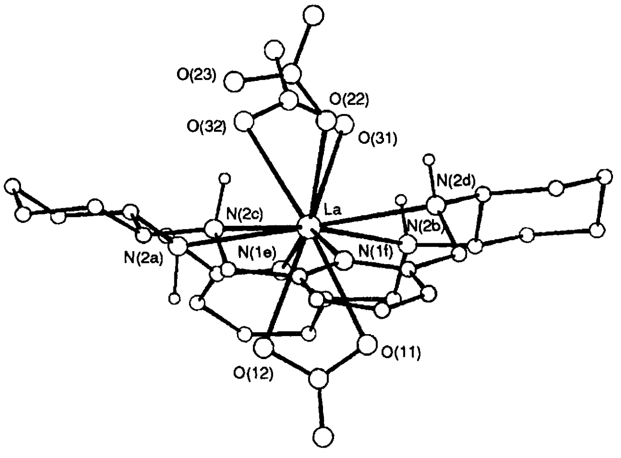


Fig. 1 The structure of the eleven-coordinate complex [LaL^1(NO$_3$)$_3$] showing the 'twist-fold' conformation of the macrocycle. Selected bond lengths (Å) are: La–O(11) 2.649(12), La–O(12) 2.644(13), La–O(22) 2.574(14), La–O(31) 2.812(18), La–O(32) 2.695(16), La–N(2a) 2.770(10), La–N(2b) 2.771(11), La–N(2c) 2.729(10), La–N(2d) 2.719(11), La–N(1e) 2.730(11), La–N(1f) 2.696(11), La···O(21) 3.54.

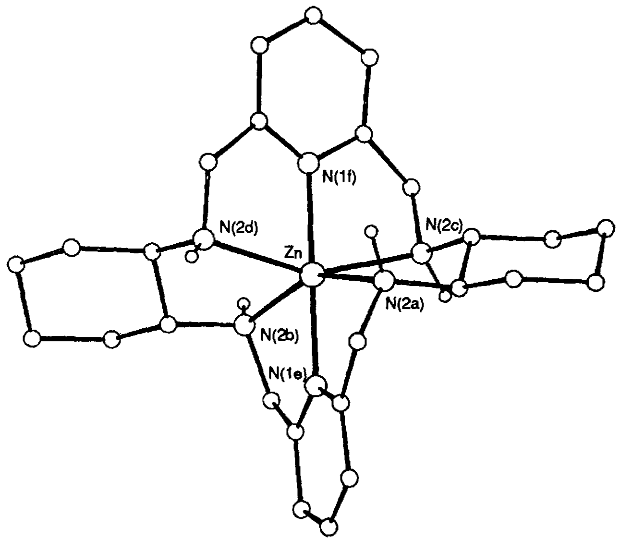


Fig. 2 The distorted octahedral conformation of the complex $[ZnL^1]^{2+}$. Selected bond lengths (Å) and angles (°) are {the numbers in square parenthesis are the parameters of the Cd^{II} analogue $[CdL^1]^{2+}$}: Zn–N(2a) 2.266(11) [2.369(5)], Zn–N(2b) 2.175(10) [2.396(5)], Zn–N(2c) 2.210(10) [2.361(5)], Zn–N(2d) 2.220(11) [2.378(6)], Zn–N(1e) 2.096(11) [2.263(6)], Zn–N(1f) 2.066(11) [2.261(6)], N(2a)–Zn–N(2b) 151.7(4) [143.3(2)], N(2c)–Zn–N(2d) 152.7(4) [146.4(2)], N(1e)–Zn–N(1f) 178.1(4) [174.8(2)].

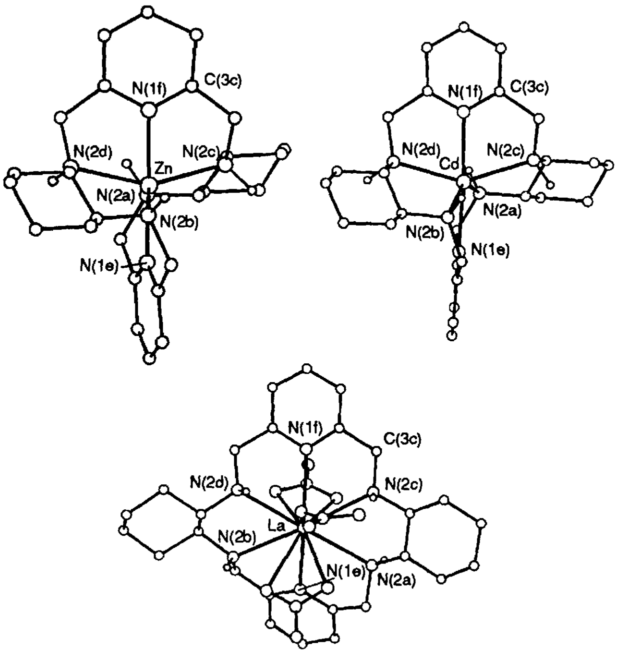


Fig. 3 The structure of the complexes $[ZnL^1]^{2+}$, $[CdL^1]^{2+}$ and $[LaL^1(NO_3)_3]$, each viewed perpendicular to the pyridine ring C(3c)–N(1f), showing how the ligand 'unwraps' as the size of the cation increases

limiting conformation proposed[6] earlier appears to be ruled out in this case by the *S,S* chair conformation of the backbone cyclohexyl groups.

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Footnotes

† Two types of conformation are observed for this type of hexaaza macrocyclic ligand, which may be defined relative to a hypothetical planar arrangement. In a 'twist-wrap' conformation, the ligand wraps round the metal ion by a twisting of the two pyridyl bridge-head units relative to each other, eventually giving a helical conformation in which they are approximately orthogonal. In a 'twist-fold' conformation a slight twisting of the two bridge-heads is accompanied by an overall folding of the great ring of the macrocycle so that the pyridine nitrogen atoms and the metal ion are no longer virtually linear.

‡ L^1: ^1H NMR (250.1 MHz, $CDCl_3$, $SiMe_4$) δ 1.08, 1.14, 1.72, 2.15, 2.20 (5H, m, cyclohexyl), 2.93 (1H, m, NH), 3.88 (2H, dd, ^2J = 13.7 Hz, pyridyl CH_2), 7.03 (2H, d, ^3J = 7.65 Hz, 2 pyridine CH), 7.53 (1H, t, ^3J = 7.65 Hz, pyridine CH). ^{13}C NMR (67.9 MHz, $CDCl_3$, $SiMe_4$) δ 25.02, 30.72, 59.83 (cyclohexyl), 51.22 (pyridyl CH_2), 120.96, 136.42, 159.44 (pyridine). LSIMS [liquid secondary ion mass spectrum *m*-noba (*meta*-nitrobenzyl alcohol) matrix]: *m/z* 435 (100%, $[M + H]^+$), 218 (26%, $[M/2 + H]^+$).

§ $[ZnL^1][ClO_4]_2\cdot MeOH$: ^1H NMR (250.1 MHz, CD_3CN, $SiMe_4$) δ 1.06, 1.67, 1.78, 2.29 (5H, m, cyclohexyl), 2.93 (1H, m, NH), 4.17 (2H, s, pyridyl CH_2), 7.47 (2H, d, ^3J = 7.80 Hz, 2 pyridine CH), 8.05 (1H, t, ^3J = 7.80 Hz, pyridine CH). LSIMS in *m*-noba matrix: *m/z* 597 (100%, $[M + H]^+ - HClO_4$), 497 (49%, $[M + H]^+ - 2HClO_4$). $[CdL^1][ClO_4]_2$: ^1H NMR (250.1 MHz, CD_3CN, $SiMe_4$) δ 1.00, 1.16, 1.72, 1.93, 2.43 (5H, m, cyclohexyl), 2.87 (1H, m, NH), 4.20 (2H, m, pyridyl CH_2), 7.42 (2H, d, ^3J = 7.80 Hz, 2 pyridine CH), 7.98 (1H, t, ^3J = 7.80 Hz, pyridine CH). LSIMS (*m*-noba): *m/z* 647 (100%, $[M + H]^+ - HClO_4$), 547 (44%, $[M + H]^+ - 2HClO_4$). $[LaL^1(NO_3)_3]\cdot CH_3CN$: LSIMS (*m*-noba) *m/z* 801 (31%, $[M + H]^+$), 697 (100%, $[M + H]^+ - MeCN - HNO_3$). All compounds gave satisfactory analyses for C, H, N.

¶ *Crystal data* for $[ZnL^1][ClO_4]_2\cdot MeOH$: $C_{27}H_{42}Cl_2N_6O_9Zn$, M = 730.95, colourless crystal (0.25 × 0.25 × 0.30 mm^3), monoclinic, space group $P2_1/c$, a = 8.945(2), b = 24.183(5), c = 15.189(3) Å, β = 100.27(2)°, U = 3233.0 Å^3, Z = 4, $F(000)$ = 1528, D_c = 1.502 g cm^{-3}, μ(Mo-Kα) = 9.6 cm^{-1}. R = 0.0699 (R' = 0.0675) for 2028 unique reflections having $I/\sigma(I) \geqslant 3.0$ and 271 variables. For $[CdL^1][ClO_4]_2$: $C_{26}H_{38}CdCl_2N_6O_8$, M = 745.93, colourless crystal (0.22 × 0.32 × 0.11 mm^3), monoclinic, space group $C2/c$, a = 23.519(5), b = 11.090(3), c = 25.305(5) Å, β = 111.05(2)°, U = 6159.7 Å^3, Z = 8, $F(000)$ = 3056, D_c = 1.609 g cm^{-3}, μ(Mo-Kα) = 8.9 cm^{-1}. R = 0.0444 (R' = 0.0450) for 3120 unique reflections having $I/\sigma(I) \geqslant 3.0$ and 388 variables. For $[LaL^1(NO_3)_3]\cdot MeCN$: $C_{28}H_{41}LaN_{10}O_9$, M = 800.60, colourless crystal (0.11 × 0.19 × 0.23 mm^3), monoclinic space group $P2_1/c$, a = 12.169(3), b = 20.126(3), c = 15.017(3) Å, β = 114.76(2)°, U = 3339.78 Å^3, Z = 4, $F(000)$ = 1632, D_c = 1.592 g cm^{-3}, μ(Mo-Kα) = 12.7 cm^{-1}, R = 0.0585 (R' = 0.04569) for 2252 unique reflections having $I/\sigma(I) \geqslant 3.0$ and 258 variables.

Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at The Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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