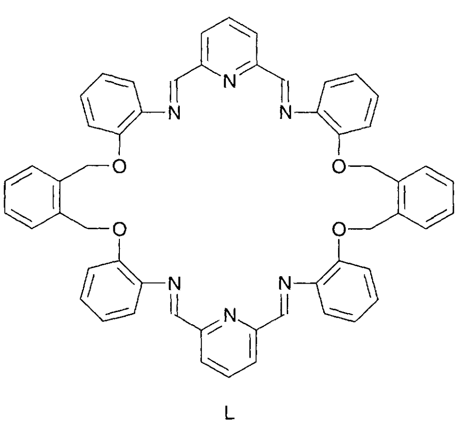
Ambidentate binding in macrocyclic helicates: towards tuning secondary structure

Ray W. Matthews, Mary McPartlin and Ian J. Scowen*

School of Applied Chemistry, University of North London, Holloway Road, London, UK N7 8DB

X-Ray analysis of new helicates of Cd^{II} and Pb^{II} derived from a tetraimine macrocyclic ligand shows that the compression of the double-helical array as the size of the metal ion increases corresponds with a change in coordination mode of the ligand.

The drive to produce materials with defined three-dimensional structures has led to elegant syntheses of molecular helices, catenates, knots and boxes where metal ions play a crucial role in organizing ligand substrates.[1] The widespread interest in molecular helicity has recently led to the exploitation of pyridine-based macrocycles as helicating ligands[2] and we described the propensity of the macrocycle L to form fully twisted double helicates with first-row divalent transition metals.[3] In this paper, we report the structural chemistry of new complexes of Cd^{II} and Pb^{II} with L and show that the presence of weakly binding phenoxy ether donors in the macrocycle allows the ligand to adapt its metal-binding domain to accommodate metals with higher coordination numbers while retaining its double-helical configuration. Remarkably, the encapsulation of these larger metals in the macrocycle compresses the double-helicate structure of the complexes (Fig. 1).



L

The new complexes of L were obtained from contrasting routes:† the complex $[PbL][ClO_4]_2$ was prepared *via* the metal-templated Schiff-base condensation of pyridine-2,6-dicarbaldehyde and α,α′-bis(2-aminophenoxy)-*o*-xylene in methanol, while $[CdL][ClO_4]_2$ was obtained by the transmetallation of $[Ag_2L][ClO_4]_2$[3] with a five-fold excess of $Cd(ClO_4)_2$ in acetonitrile solution. As crystals suitable for X-ray analysis were unobtainable from samples of $[CdL][ClO_4]_2$, metathesis of the anion was attempted by treating the transmetallation solution with excess aqueous LiSCN. The reaction yielded yellow crystals which were subsequently characterised as $\{[CdL][Cd(NCS)_6Ag_2]\}_x$ by single-crystal X-ray analysis.

The crystal structure of $\{[CdL][Cd(NCS)_6Ag_2]\}_x$‡ shows discrete, helically chiral $[CdL]^{2+}$ cations within an anionic superlattice derived from ribbons of thiocyanate-bridged metals, propagating parallel to the *c*-axis. The repeat unit of each anionic ribbon comprises two silver atoms in S_4-tetrahedral and one cadmium in N_6-octahedral coordination environments linked *via* four μ- and two μ_3-bridging thiocyanates.

In $[CdL]^{2+}$, the metal is coordinated by all the nitrogen donors of the ligand at the centre of the double helical array [Fig. 1(*b*)]. The cadmium coordination geometry is distinctly irregular and although it is best described as distorted octahedral, there appears to be significant interaction with the phenoxy ether donors of the ligand. The metal–oxygen

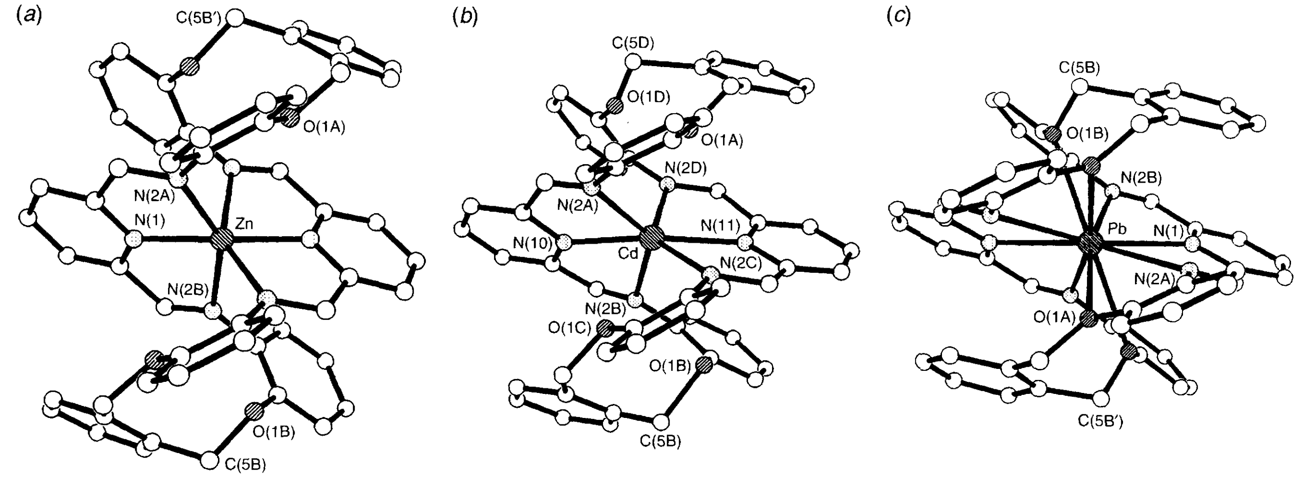


Fig. 1 Helicates derived from the macrocycle L showing the compression of the molecular helix [characterized by the distance between bridgehead methylenes, C(5b)···C5(d) or C5(b′)] as metal size increases. (*a*) $[ZnL]^{2+}$, C(5b)···C(5b′) 10.4 Å, N(1)–Zn–N(1′) 146.3, dihedral angle between pyridyldiimine planes 75.5°.[3] (*b*) $[CdL]^{2+}$ C(5b)···C(5d) 8.8 Å, Cd–N(10) 2.237(15), Cd–N(2a) 2.37(2), Cd–N(2b) 2.57(2), Cd–N(2c) 2.40(2), Cd–N(2d) 2.43(2), Cd–N(11) 2.356(17), Cd···O(1a) 3.06, Cd···O(1b) 3.37, Cd···O(1c) 2.90, Cd···O(1d) 3.45 Å, N(10)–Cd–N(11) 147.6(6), dihedral angle 57.9°. (*c*) $[PbL]^{2+}$ C(5b)···C(5d) 7.5 Å; Pb–N(1) 2.714(8), Pb–N(2a) 2.846(9), Pb–N(2b) 2.673(9), Pb–O(1a) 2.955(7), Pb–O(1b) 2.855(7) Å, N(1)–Pb–N(1′) 135.6, dihedral angle 28.8°.

distances in the complex are noticeably shorter than those of the first-row transition metal helicates derived from L {M = Co^{II}, Ni^{II}, Zn^{II}; $[ZnL]^{2+}$ is presented as an example of this isostructural series in Fig. 1(*a*)}[3] and, significantly the shortest metal–oxygen distances in the complex, Cd–O(1a) 3.05 and Cd–O(1c) 2.90 Å, are comparable with Cd–O bonds in eight-coordinate cadmium(II) complexes of crowns and aza-crowns.[4]

X-Ray analysis of $[PbL][ClO_4]_2 \cdot 4MeCN$§ showed the presence of discrete complex cations with crystallographic two-fold symmetry, the metal atom being coincident with the rotation axis. In the complex cation [Fig. 1(*c*)], the ligand L deploys all its potential donors and coordinates to the metal in an N_6O_4 environment unique among the relatively few ten-coordinate lead(II) complexes structurally characterized to date.[5] The ligand encapsulates the metal at the centre of its double-helical array and computed space filling models indicate no stereochemical role for the lone pair of Pb^{II}.

Despite the considerable differences in metal ion sizes, the lead(II) and cadmium(II) complexes show features in common with the other helicates derived from L:[3] the complex cations show idealised two-fold symmetry with the rotation axis lying perpendicular to the helix axis. The double-helical configurations of each complex are stabilized by five intra-ligand π–π interactions: two iminophenoxy rings lie in offset face-to-face dispositions to one side of each complex, while each pyridyl ring is sandwiched between an *o*-xylenyl unit and an iminophenoxy ring. The repetition of these features in complexes of metals of such different characteristics reiterates the remarkable propensity of L for helicate formation.

However, while the phenoxy ether donors of L are extruded well away from the N_6 metal coordination sphere in $[ZnL]^{2+}$, in $[PbL]^{2+}$ they effectively 'swing-in' to complete the ten-coordinate, N_6O_4 coordination sphere, causing the compression of the double helix. The structure of the cadmium(II) helicate lies between these two 'extremes' with the consequence that its helical pitch lies between that of the other two complexes. The accommodation of ions of different size within the double-helical ligand array is analogous to stretching and squashing a spring to, respectively, reduce or enlarge its cross-section. Notably, the influence of metal ion size in these systems contrasts with that observed in smaller N_6 macrocyclic complexes,[2] where the pitch of the molecular helix reduces as the ligands wrap more tightly around smaller metal ions. The difference clearly originates in the ambidentate properties of L and its ability to enlarge its metal-binding cavity by compressing the double-helical array; in these examples a smooth variation in the secondary structure of the helicate results.

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Footnotes

† $[PbL][ClO_4]_2 \cdot H_2O$: α,α′-Bis(2-aminophenoxy)-*o*-xylene (3.2 g, 0.01 mol; in 50 cm^3 methanol) was added over *ca.* 40 min to a refluxing solution of lead(II) perchlorate trihydrate (4.6 g, 0.01 mol) and pyridine-2,6-dicarbaldehyde (1.3 g, 0.01 mol) in methanol (200 cm^3). The resulting microcrystalline yellow precipitate was recrystallised from acetonitrile, yielding yellow efflorescent crystals. MS (FAB, positive ion): *m/z* 1145 {29%, $[PbL(ClO_4)]^+$}, 1046 {11, $[PbL]^+$}, 507 (100). A second recrystallisation from acetonitrile yielded crystals of $[PbL][ClO_4]_2 \cdot 4MeCN$ suitable for X-ray analysis.

$[CdL][ClO_4]_2 \cdot MeCN \cdot H_2O$: Treatment of $[Ag_2L][ClO_4]_2$ (0.1257 g, 0.10 mmol) with $Cd(ClO_4)_2 \cdot 6H_2O$ (0.2058 g, 0.49 mmol) in MeCN yielded pale yellow, efflorescent crystalline plates. MS (FAB, positive ion): *m/z* 1051 {81%, $[CdL(ClO_4)]^+$}, 952 {34, $[CdL]^+$}, 476 {29, $[CdL]^+$}, 428 {100, $[Cd(L - C_{35}H_{29}N_3O_2)]^+$}.

$\{[CdL][Cd(NCS)_6Ag_2]\}_x$: $[Ag_2L][ClO_4]_2$ (0.1242 g, 0.10 mmol) and $Cd(ClO_4)_2 \cdot 6H_2O$ (0.2242 g, 0.50 mmol) in MeCN (25 cm^3) was treated with 4 drops of saturated aqueous Li(SCN). Pale yellow crystalline blocks appeared on standing.

All compounds gave satisfactory analyses for C, H and N.

‡ *Crystal data* for $\{[CdL][Cd(NCS)_6Ag_2]\}_x$, $C_{60}H_{42}Ag_2Cd_2N_{12}O_4S_6$, M = 1628.0, monoclinic, space group *Cc*, a = 13.442(2), b = 22.223(3), c = 20.912(3) Å, U = 6228.65 Å^3, Z = 4, $F(000)$ = 3216, D_c = 1.736 g cm^{-3}, μ(Mo-Kα) = 1.45 mm^{-1}, λ(Mo-Kα) = 0.71069 Å. Data were collected on a Philips PW1100 four-circle diffractometer in the θ range 3–25° with the method described previously.[6] The structure was solved by the Patterson method.[7] Non-hydrogen atoms were located by difference-Fourier syntheses. After refinement with isotropic thermal parameters for all non-hydrogen atoms, an empirical absorption correction[8] was applied. Anisotropic thermal parameters were assigned to all metal and sulfur atoms in the structure. Refinement converged at R = 0.0739 and R_w = 0.0683 for a total of 333 parameters and 2351 unique reflections [$I/\sigma(I) > 2$].

§ *Crystal data* for $[PbL][ClO_4]_2 \cdot 4MeCN$, $C_{62}H_{54}Cl_2N_{10}O_{12}Pb$, M = 1409.3, trigonal, space group $P\bar{3}c1$, $a = b$ = 20.557(3), c = 23.843(3) Å, U = 8725.91 Å^3, Z = 6, $F(000)$ = 4248, D_c = 1.609 g cm^{-3}, μ(Mo-Kα) = 2.96 mm^{-1}, λ(Mo-Kα) = 0.71069 Å. Data were collected on a Philips PW1100 four-circle diffractometer in the θ range 3–25° with the method described previously.[6] The metal atom was located from a Patterson synthesis and the remaining non-hydrogen atoms were located from a series of Fourier and difference-Fourier syntheses.[7] Absorption corrections[8] were applied after refinement with isotropic thermal parameters for all non-hydrogen atoms. Anisotropic thermal parameters were assigned to the metal and chlorine atoms and those of the inner great ring of the macrocycle and refinement converged at R = 0.0499 and R_w = 0.0440 for a total of 286 parameters and 2497 unique reflections [$I/\sigma(I) > 3$].

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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