DALTON

Template synthesis of helicates of a [2 + 2] tetraimine macrocycle: crystal structure of the lead(II) perchlorate complex

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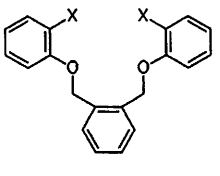
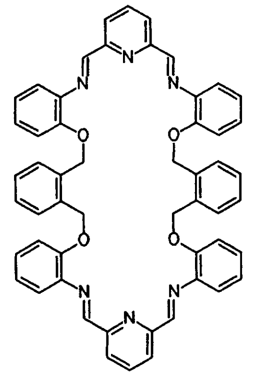
The Schiff-base condensation of α,α′-bis(2-aminophenoxy)-*o*-xylene and pyridine-2,6-dicarbaldehyde produced mononuclear complexes of the same [2 + 2] cyclocondensation product L^1 in the presence of divalent metal ions ranging in size from Mn^{II} to Ba^{II}. The origin of the apparent insensitivity of the synthesis to the metal-ion size lies in the ability of the resulting 34-membered macrocycle to adopt either of two distinct co-ordination modes featuring double helical configurations stabilised by intramolecular π–π interactions. The crystal structure of $[PbL^1][ClO_4]_2\cdot 4MeCN$ [trigonal, space group $P\bar{3}c1$, $a = b = 20.557(3)$, $c = 23.843(3)$ Å, $R = 0.0499$, $R' = 0.0440$] shows the metal ion co-ordinated by the N_6O_4 donor set of the macrocycle within a full double helical ligand array stabilised by five separate aromatic π–π interactions. Proton NMR studies of the diamagnetic complexes of L^1, assisted by detailed assignments of aromatic subspectra, provided evidence for retention of molecular helicity in solution; an interesting example of T_1-spin decoupling of ^{207}Pb is noted in the field-dependent spectra of $[PbL^1][ClO_4]_2$ in CD_3CN.

Metal ions show remarkable versatility in assembling materials with defined three-dimensional structures. Notable examples include the self-assembly syntheses of molecular double and triple helices,[1] molecular cylinders, boxes and knots,[1,2] and the preorientation/activation of reactants in template syntheses of macrocycles and cryptands.[3] Metal-templated condensation reactions between α,ω-diamines and dialdehydes or diketones provide effective routes to many novel imine macrocyclic complexes and, indeed, Schiff-base condensations of this type featured in some of the earliest syntheses of macrocyclic complexes.[4] Heterocyclic dicarbonyls and diketones have found particular application in this field and underpin an important class of Schiff-base macrocyclic complex,[5] a feature of which is the occurrence of higher-order condensation products yielding [2 + 2] and in some cases larger rings. These larger macrocycles are often obtained with larger metal-ion templates, *e.g.* Ag^I, Pb^{II}, Ba^{II} and lanthanide ions.[5,6] The occurrence of the higher-order condensation products is often rationalised in terms of a size match between the cavity of the resulting macrocycle and the templating device, although Constable *et al.*[7] have demonstrated the fallibility of a synthetic approach using only this concept within flexible systems.

As part of a wider study into metal-ion discrimination in semi-rigid, mixed-donor macrocyclic complexes, we have synthesised the aromatic diamine 1,2-bis[(2-aminophenoxy)-methyl]benzene **2** to act as a precursor to macrocycles that complement the established series of alkyl-bridged [1 + 1] N_3O_2 macrocycles.[8] Remarkably, the condensation of this diamine with pyridine-2,6-dicarbaldehyde in the presence of s-, p- and d-block metals ranging in size from Mn^{II} to Ba^{II} yields the same 34-membered [2 + 2] ligand L^1. The structural chemistry of the resulting complexes has implications for the design of selective complexing agents and suggests a cause of the unusual insensitivity of the template reaction to the character of the metal ion in these reactions. We have established complexes of Co^{II}, Ni^{II} and Zn^{II} of L^1 as the first macrocyclic helicates[9] and have communicated the crystal structure of $[PbL^1][ClO_4]_2\cdot 4MeCN$.[10]



1 X = NO_2
2 X = NH_2



L^1

Experimental

Reagents

Starting materials were obtained from Aldrich Chemical Company and used without further purification. General-purpose-grade solvents were used as supplied, with the exception of 1,4-dioxane which was dried over sodium metal using the method described by Loewenthal.[11] Pyridine-2,6-dicarbaldehyde was obtained by SeO_2 oxidation of pyridine-2,6-dimethanol in dry dioxane using the method of Jerchel *et al.*[12]

Physical measurements

Proton NMR spectra were obtained using a Bruker AM250 spectrometer operating at 250.134 MHz at ambient temperature (300 K); a ^2D field–frequency lock was used in all cases. Saturated solutions of samples were prepared in deuteriated solvents containing $SiMe_4$ as the reference standard. Infrared spectra in the range 4000–500 cm^{-1} were obtained on a Bio-Rad FTS40 spectrophotometer linked to a 3240–SPC data station, with samples supported in pressed KBr microdiscs (3 mm diameter) containing *ca.* 1% (w/w) sample. Analyses for carbon, hydrogen and nitrogen content were obtained using a Carlo Erba 1106 elemental analyser. Electron-impact (EI) mass spectra were obtained for organic compounds using an AEI MS-9, or a Kratos Profile, spectrometer operating in positive-ion mode. Positive-ion, fast atom bombardment (FAB) mass spectra were obtained for metal complexes in 2-nitrobenzyl alcohol matrices.

Preparation of α,α′-bis(2-nitrophenoxy)-*o*-xylene 1

The preparative method employed was adapted from that described by Cannon *et al.*[13] for synthesis of 1,2-bis(2-nitrophenoxy)ethane.

Potassium carbonate (27.6 g, 0.20 mol) was added portionwise to 2-nitrophenol (31.9 g, 0.195 mol assuming 15% water impurity) in hot dimethylformamide (250 cm^3). α,α′-Dibromo-*o*-xylene (26.4 g, 0.10 mol) was added to the refluxing mixture over 40 min and refluxing was continued for 2 h. The reaction mixture was cooled, concentrated under reduced pressure and poured into cold water (600 cm^3). After cooling at 4 °C for 24 h, a white precipitate was isolated at the pump. Concentration of the filtrate under reduced pressure yielded more white solid on cooling. The crops were combined, washed with portions of methanol (3 × 50 cm^3) and recrystallised from hot acetone. The resulting white flocculent solid was isolated at the pump, washed with chilled acetone (4 × 5 cm^3) and desiccated *in vacuo* over phosphorus pentaoxide for 24 h. Yield 23.7 g (62%). M.p. = 135.7–136.4 °C (Found: C, 63.3; H, 4.2; N, 7.4. Calc. for $C_{20}H_{16}N_2O_6$: C, 63.2; H, 4.2; N, 7.4%). FTIR (KBr, 3 mm disc): $\tilde{\nu}_{max}$/cm^{-1} 3117w (aromatic), 3070w (aromatic), 1616s (aromatic), 1581m (aromatic), 1521s (NO_2), 1454m, 1345s (NO_2), 1316m, 1274s, 1250m, 1168m, 1019m, 985m, 865m, 858m, 752m and 738s (aromatic). EI mass spectrum (positive ion): *m/z* 242 (11, $[M - C_6H_4NO_3]^+$), 196 {100, $[M - (C_6H_4NO_3 + NO_2)]^+$} and 104 (29%, $[M - 2C_6H_4NO_3]^+$). ^{1}H NMR ($CDCl_3$): δ 7.81 [H^{31}, dd, $^3J(H^{31}–H^{32})$ = 8.2, $^4J(H^{31}–H^{42})$ = 1.7], *ca.* 7.6–7.45 (H^{42} and H^{62} or H^{61}, m), *ca.* 7.4 (H^{61} or H^{62}, m), 7.23 [H^{41}, dd, $^3J(H^{41}–H^{42})$ = 8.3, $^4J(H^{41}–H^{32})$ = 0.9], 7.01 [H^{32}, ddd, $^3J(H^{32}–H^{42})$ ≈ 8 Hz] and 5.39 (H^5, s).

Preparation of α,α′-bis(2-aminophenoxy)-*o*-xylene 2

Compound 1 was reduced using a method adapted from that described by Fenton *et al.*[8b] for reduction of 2,6-bis(2-nitrophenoxymethyl)pyridine. α,α′-Bis(2-nitrophenoxy)-*o*-xylene (9.5 g, 0.025 mol) was slurried in ethanol–water (3:2 v/v, 500 cm^3) containing iron filings (14.0 g, 0.25 mol) and brought to reflux. Glacial acetic acid (15 cm^3) was added over 30 min and refluxing was continued for 18 h. The reaction mixture was filtered whilst hot through cellulose floc (Whatman Ashless Floc) at the pump and refrigerated at 4 °C for 12 h. Beige crystals separated from the filtrate during storage and were collected at the pump. Concentration of the filtrate under reduced pressure yielded more product. The crops of crystals were combined and recrystallised twice from propan-2-ol containing decolourising charcoal. Soft, beige, plate-like crystals were isolated at the pump after several days and washed with portions of chilled methanol (2 × 5 cm^3) before desiccation *in vacuo* over P_2O_5 for 24 h. Yield = 3.60 g (45%). M.p. = 98.0–98.7 °C (Found: C, 75.6; H, 6.4; N, 8.8. Calc. for $C_{20}H_{20}N_2O_2$: C, 75.0; H, 6.3; N, 8.7%). FTIR (KBr, 3 mm disc): $\tilde{\nu}_{max}$/cm^{-1} 3480s (NH_2), 3380s (NH_2), 2940w, 2880w, 1620s (aromatic), 1590m (aromatic), 1510s (aromatic), 1460m, 1380m, 1300s, 1230s, 1215s, 1140m, 1050m, 1020m and 760s (aromatic). EI mass spectrum (positive ion): *m/z* 320 (15, $[M]^+$), 212 (83, $[M - C_6H_4NH_2O]^+$), 108 (51, $[C_6H_4NH_2O]^+$), 104 (36, $[M - 2C_6H_4NH_2O]^+$) and 80 (100%). ^{1}H NMR ($CDCl_3$): δ *ca.* 7.52 (H^{61}, m), *ca.* 7.38 (H^{62}, m), 6.86 [H^{41}, dd, $^3J(H^{41}–H^{42})$ = 7.6, $^4J(H^{41}–H^{32})$ = 1.4], 6.81 [H^{32}, ddd, $^3J(H^{32}–H^{31})$ = 7.8, $^3J(H^{32}–H^{42})$ = 7.1], 6.72 [H^{31}, dd, $^4J(H^{31}–H^{42})$ = 2.0], 6.69 (H^{42}, ddd), 5.19 (H^5, s) and 3.79 (NH_2, br).

Metal-template syntheses

Metal-template syntheses were adapted from the method described by Fenton *et al.*[8b] In each case, diperchlorate complexes of $[ML^1]^{2+}$ were obtained from [2 + 2] condensation of diamine 2 with pyridine-2,6-dicarbaldehyde in the presence of the appropriate hydrated metal perchlorate; characterisation data for the complexes are presented in Table 1. **CAUTION**: perchlorates are potentially explosive and should be treated with extreme care.

$[ML^1][ClO_4]_2 \cdot nH_2O$ (M = Ca or Sr, *n* = 1; M = Ba or Mn, *n* = 2). Diamine 2 (3.2 g, 0.01 mol in 50 cm^3 methanol) was added dropwise to a warm solution of pyridine-2,6-dicarbaldehyde (1.35 g, 0.01 mol) and the appropriate metal perchlorate (0.005 mol in 250 cm^3 methanol). Within *ca.* 1 min yellow or orange microcrystalline products precipitated. They were isolated at the pump, washed with chilled methanol and dried under suction. Yields *ca.* 90%.

$[PbL^1][ClO_4]_2 \cdot H_2O$. Diamine 2 (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). A microcrystalline yellow solid precipitated on addition of the diamine. Refluxing was terminated after the dropwise addition of the diamine had been completed. After cooling, the solid was isolated at the pump and then dissolved in hot acetonitrile (25 cm^3). The solution was allowed to cool and diethyl ether (*ca.* 3 cm^3) added. Yellow, efflorescent plates were isolated after 48 h, washed with chilled methanol (2 × 5 cm^3) and diethyl ether (1 × *ca.* 2 cm^3), and dried *in vacuo* over P_2O_5 for 24 h. Yield = 8.40 g (67%).

Crystallography

Crystal data. $[PbL^1][ClO_4]_2 \cdot 4MeCN$, $C_{62}H_{54}Cl_2N_{10}O_{12}Pb$, *M* = 1409.3, trigonal, space group $P\bar{3}c1$ (no. 165), *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) = 0.710 69 Å.

Data collection. A yellow crystal with dimensions 0.50 × 0.50 × 0.48 mm was obtained by slow evaporation of a saturated acetonitrile solution of $[PbL^1][ClO_4]_2 \cdot H_2O$. It was mounted over its mother-liquor and supported in silicone grease in a sealed Lindemann tube for data collection. Data were collected on a Philips PW1100 four-circle diffractometer in the θ range 3–25° using a scan width of 0.9° and a speed of 0.05° s^{-1} with the method described previously.[14] Data were corrected for Lorentz-polarisation factors and equivalent reflections were merged in space group $P\bar{3}c1$ (R_{int} = 0.0426) to give 2497 unique reflections with $I/\sigma(I) > 3$.

Structure solution and refinement.[15] The position of the metal atom was located from a Patterson synthesis and the remaining non-hydrogen atoms were located from a series of Fourier and Fourier-difference syntheses. A Fourier-difference synthesis calculated using low-angle data (sin θ < 0.35) revealed the positions of all methylene hydrogen atoms of the macrocycle for which a common isotropic thermal parameter refined to 0.09 Å^2. The remaining hydrogen atoms were included in idealised positions (C–H 1.08 Å) and assigned a fixed thermal

Table 1 Elemental analytical, selected mass and infrared spectral data for complexes of L^1

	Analysis (%)[a]			Mass spectrum[b]			Infrared spectrum[c]		
Complex	C	H	N	*m/z*	%	Assignment	ν(C=N)	$\nu_3(ClO_4)$	$\nu_4(ClO_4)$
$[MnL^1][ClO_4]_2\cdot 2H_2O$	57.2	4.4	7.2	993	100	$[MnL^1(ClO_4)]^+$	1620m	1095vs	622s
	(57.5)	(4.1)	(7.4)	894	58	$[MnL^1]^+$			
$[CaL^1][ClO_4]_2\cdot H_2O$	59.7	4.1	7.9	977	100	$[CaL^1(ClO_4)]^+$	1635m	1100vs	625s
	(59.2)	(4.0)	(7.7)	878	33	$[CaL^1]^+$			
				775	6	$[Ca(L^1 - C_8H_8)]^+$			
				670	10	$[Ca(L^1 - 2C_8H_8)]^+$			
$[SrL^1][ClO_4]_2\cdot H_2O$	56.8	4.0	7.5	1025	100	$[SrL^1(ClO_4)]^+$	1630m	1090vs	625s
	(56.7)	(3.9)	(7.4)	926	48	$[SrL^1]^+$			
				821	11	$[Sr(L^1 - C_8H_8)]^+$			
				718	14	$[Sr(L^1 - 2C_8H_8)]^+$			
$[BaL^1][ClO_4]_2\cdot 2H_2O$	53.6	3.8	6.9	1075	100	$[BaL^1(ClO_4)]^+$	1630m	1095vs	625s
	(53.6)	(3.9)	(6.8)	976	38	$[BaL^1]^+$			
				873	8	$[Ba(L^1 - C_8H_8)]^+$			
				767	6	$[Ba(L^1 - 2C_8H_8)]^+$			
$[PbL^1][ClO_4]_2\cdot H_2O$	51.7	3.3	6.7	1145	29	$[PbL^1(ClO_4)]^+$	1632m	1095vs	624s
	(51.4)	(3.5)	(6.7)	1046	11	$[PbL^1]^+$			
				507	100				

[a] Required values in parentheses. [b] Positive-ion FAB in 2-nitrobenzyl alcohol matrix. [c] As KBr discs.

parameter (0.08 Å^2). Extended regions of electron density were observed around the perchlorate counter ion; while one oxygen was assigned a site of full occupancy, two were disordered over two sites of equal population and one over three sites in the ratio 5:3:2. Residual electron density was assigned to two acetonitrile molecules, one lying along the crystallographic three-fold axis and the other in a general position. The latter was refined using a disorder model corresponding to an interchange of terminal nitrogen and carbon positions. Absorption corrections[16] (maximum 1.107, minimum 0.949) were applied after refinement on F with isotropic thermal parameters for all non-hydrogen atoms (before correction $R = 0.0690$, after 0.0644). Individual weights of $1/\sigma^2(F)$ were assigned to each reflection and in the final cycles of least-squares refinement on F anisotropic thermal parameters were assigned to the metal, the chlorine and to the atoms of the inner great ring of the macrocycle. Refinement converged at $R = 0.0499$ and $R' = 0.0440$ for 286 parameters. The final Fourier map showed maximum residual electron density of *ca.* 0.7 e Å^{-3}.

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.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/132

Results and Discussion

Synthesis of precursors

The dinitro compound **1** was obtained in 62% yield using a Williamson ether synthesis from 2-nitrophenol and α,α'-dibromo-*o*-xylene in dimethylformamide. Some difficulty was encountered in obtaining an efficient reduction of **1** to give the macrocycle precursor diamine **2**. In these experiments $LiAlH_4$ and $NaBH_4$ proved ineffective while hydrazine hydrate and palladium on activated charcoal resulted in the recovery of 2-aminophenol, the required reduction of the NO_2 functions being accompanied by reduction of the CH_2O phenoxy ether linkages. (Notably, the reactivity of these phenoxy linkages in both **1** and **2** is reflected in their electron-impact mass spectra where molecular ions are, respectively, absent and very weak, and the spectra are dominated by fragmentation species corresponding to cleavage of PhO–CH_2 bonds.) The diamine was successfully obtained *via* reduction of **1** with metallic iron, although prolonged refluxing (> 12 h) was required. Separation of **2** from the reaction mixture was difficult requiring at least two recrystallisations from propan-2-ol and activated charcoal; these difficulties are reflected in the mediocre yield of 45%.

Schiff-base macrocyclic complexes

Metal complexes (M = Mn^{II}, Ca^{II}, Sr^{II}, Ba^{II} or Pb^{II}) of the 34-membered macrocyclic ligand L^1 were prepared using *in situ* metal-template condensations of pyridine-2,6-dicarbaldehyde with the diamine **2**. Condensation reactions attempted at normal and high dilutions in the absence of metal ions resulted in the recovery of off-white solids of indeterminate composition presumably containing a range of oligo- and poly-meric species. In metal-template reactions addition of the diamine (as a methanolic solution) to pyridine-2,6-dicarbaldehyde and the appropriate metal perchlorate in methanol was accompanied by the development of an intense yellow colouration in the solution; in the case of Pb^{II} the complex appeared as a microcrystalline precipitate before the addition of diamine was completed. The yellow or orange colour of the complexes is characteristic of Schiff-base complexes derived from 'spectroscopically silent' metal ions and the IR spectrum of each shows a medium-intensity peak at *ca.* 1630 cm^{-1} attributable to the imine stretching mode which, together with the absence of peaks due to carbonyl and amine functions, confirms the presence of the Schiff-base product. Peaks at *ca.* 1100 and *ca.* 625 cm^{-1} (respectively very strong and strong) correspond to the ν_3 and ν_4 modes of the tetrahedral perchlorate ion[17] and confirm, in the first instance, the presence of metal complex species. The unsplit nature of these bands indicates that the anions are not co-ordinated although some broadening of the ν_3 band in the aquated samples indicates a lowering of the degeneracy of the stretching mode in the solid state, possibly arising from hydrogen-bonded associations in the crystal lattice. In spectra of the complexes broad peaks at *ca.* 3500 cm^{-1} correspond to the presence of lattice water and are consistent with the formulations proposed from elemental analyses.

Positive-ion FAB mass spectrometry provides key evidence for the formation of the [2 + 2] cyclocondensation compound L^1 as the sole product of reactions involving each metal ion. The highest-mass peak in each case corresponds to the general formulation $[ML^1(ClO_4)]^+$ and, as is common with complexes of this type,[8,18,19] a characteristic fragmentation pattern resulting from stepwise loss of perchlorate from the neutral parent complexes is observed. Species corresponding to fragmentation of diperchlorate complexes of the corresponding [1 + 1] ligand are notably absent from the spectra. With the exception of the lead complex, base peaks in the FAB$^+$ spectra correspond with the $[ML^1]^+$ ion and minor fragmentation products appear to correspond to cleavage of phenoxy ether linkages in the ligand, mirroring the behaviour of the dinitro and the diamine precursor compounds. Ligand fragmentation in the lead complex evidently occurs by a different pathway.

Proton NMR spectra of the diamagnetic (Ca^{II}, Sr^{II}, Ba^{II} and Pb^{II}) complexes of L^1 (Table 2) show four-fold equivalence for ligand environments in solution and several common features. In each the prochiral methylene protons of L^1 give AB subspectra indicating that the complexes are chiral in solution. In the light of the double helicate structures observed in the solid state for complexes of first-row transition metals,[9] Cd^{II}[9] and Pb^{II} (this work) with L^1 it seems likely that helical D_2 structures are adopted by the complexes in solution. Clearly the higher symmetry observed in solution is the result of a fast exchange process which interchanges ligand environments but retains the chirality of the complex.

For each complex the spectra [*e.g.* Fig. 1(*a*)] confirm the integrity of the ligand in acetonitrile solution; imine resonances appear as characteristic downfield singlets and resonances attributable to aldehydic and amino functions are noticeably absent. The β- and γ-protons of the 2,6-disubstituted pyridines give rise to AB$_2$ subspectra while the protons of the xylene rings produce characteristic AA'BB' subspectra typical[20] of symmetrically 1,2-disubstituted aromatic rings. Iminophenoxy subspectra were assigned on a first-order basis although, where ambiguities arose (*e.g.* proton sites *ortho* to ring substituents each give rise to a doublet of doublets), preferred assignments were obtained from substituent shift parameters derived from a range of model compounds.[21]

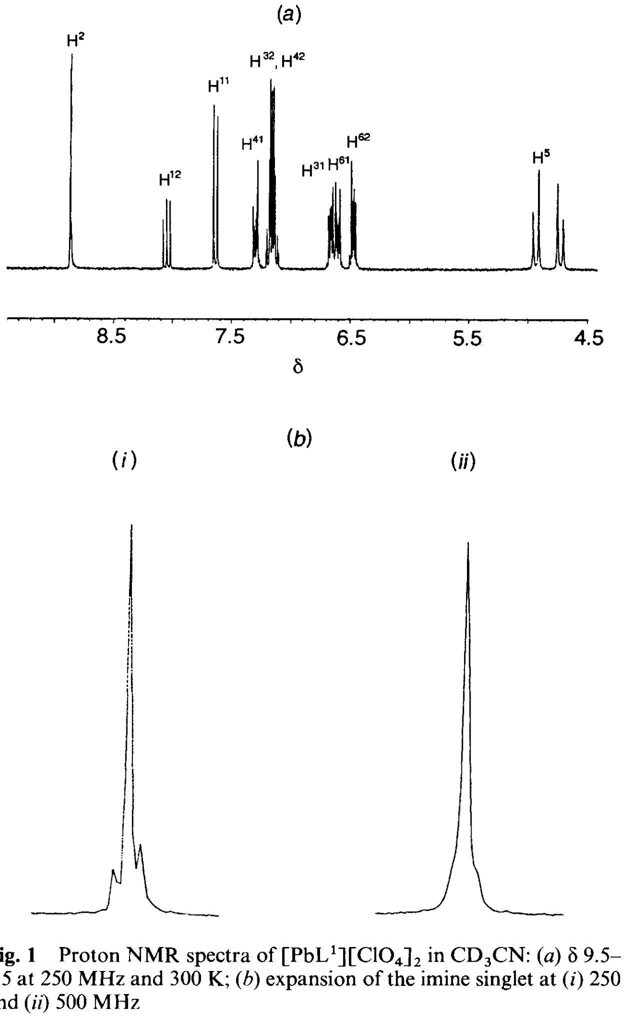
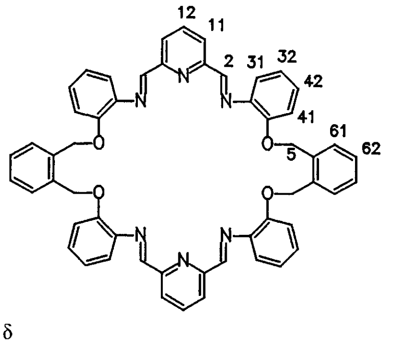


Fig. 1 Proton NMR spectra of $[PbL^1][ClO_4]_2$ in CD_3CN: (*a*) δ 9.5–4.5 at 250 MHz and 300 K; (*b*) expansion of the imine singlet at (*i*) 250 and (*ii*) 500 MHz

A noteworthy feature of the 250 MHz spectra of the lead complex is the satellites which flank the imine singlet [Fig. 1(*b*)]; the lack of a dependence of the separation of the satellites on the sample spinning rate precludes their assignment as spinning side-bands. Coupling to $I = \frac{1}{2}$ metal nuclei is an emerging feature of both proton and carbon-13 NMR spectra of complexes containing the pyridine-2,6-diimine unit[19,21,22] and is indicative of complexes inert to metal exchange on the NMR time-scale; in this case the observations are consistent with coupling to ^{207}Pb and indicate considerable interaction between the metal and the nitrogen donors of the ligand. This appears to be only the second report of ^{207}Pb–^1H coupling in compounds of this type and the $^3J(^{207}Pb–H_{imine})$ coupling constant of 4.3 Hz is somewhat smaller than those recently reported for lead complexes of 18-membered N_4S_2 macrocycles.[19] Comparison of proton spectra of $[PbL^1][ClO_4]_2$ obtained at 250 and 500 MHz shows an interesting paradox; at the higher frequency, as might be expected, the second-order character of the aromatic region is largely resolved although the ^{207}Pb coupling satellites observed at 250 MHz are so broadened that they appear only as shoulders on the imine singlet [Fig. 1(*b*)]. The broadening is attributed to the dominance of chemical shift anisotropy relaxation for the heavy nucleus at the higher field,[23] and thus provides an interesting example of T_1-spin decoupling for ^{207}Pb.

In summary, the characterisation data presented show that mononuclear complexes of the [2 + 2] compound L^1 are formed exclusively. Substantial twisting of the 34-membered macrocyclic ring is anticipated as it presents appropriate donor atoms to the single ions. The manganese(II) complex is expected to adopt the double helicate dication structure observed[9] for the isostructural series $[CoL^1]^{2+}$, $[NiL^1]^{2+}$ and $[ZnL^1]^{2+}$.

Table 2 Proton NMR parameters for $[ML^1][ClO_4]_2$ (M = Ca^{II}, Sr^{II}, Ba^{II} or Pb^{II})[a]



Proton[b]	δ $[CaL^1]^{2+}$	$[SrL^1]^{2+}$	$[BaL^1]^{2+}$	$[PbL^1]^{2+}$[c]
H^2	8.04 (s)	8.23 (s)	8.34 (s)	8.85 (s)[d]
H^{12}	8.06 (m)	7.96 (m)	7.96 (m)	8.03 (t)
H^{11}	7.60 (d)	7.54 (d)	7.56 (d)	7.62 (d)
H^{41}	6.97 (dd)	7.28 (m)	7.38 (m)	7.29 (dd)
H^{32}	7.15 (ddd)	7.15 (ddd)	7.22 (ddd)	7.16 (ddd)
H^{42}	7.02 (td)	7.10 (ddd)	7.17 (ddd)	7.13 (ddd)
H^{31}	6.74 (dd)	6.56 (m)	6.65 (m)	6.59 (dd)
H^{61} (H^{62})	6.77 (m)	6.64–6.53 (m)	6.56 (m)	6.45 (m)
H^{62} (H^{61})	6.26 (m)		6.82 (m)	6.65 (m)
H^5[e]	4.95 (d) 4.67 (d)	4.99 (d) 4.68 (d)	5.03 (d) 4.73 (d)	4.92 (d) 4.72 (d)

[a] Obtained at 250 MHz for saturated solutions in CD_3CN at 298 K unless otherwise noted. Shifts are relative to internal $SiMe_4$. Multiplicities in parentheses: s = singlet, dd = doublet of doublets, ddd = doublet of doublets of doublets, m = multiplet. [b] Possible alternative assignments are given in parentheses. [c] At 500 MHz. [d] Satellites present at 250 MHz, $^3J(^{207}Pb–H^2) = 4.3$ Hz. [e] AB multiplets, ^2J = 11.8 (Ca^{II}), 11.5 (Sr^{II}), 11.3 (Ba^{II}), 11.4 Hz (Pb^{II}).

This structure arises from convergence of the planar N_3 'head units' of the ligand to present a distorted-octahedral N_6-donor environment. However, inspection of models indicates that a second co-ordination mode that retains similar molecular helicity is available for mononuclear complexes of L^1. 'Flattening' the disposition of the pyridine-2,6-diimine head units to their attached iminophenoxy aromatic rings brings the phenoxy ether donors into a position suitable for metal co-ordination and creates a larger, 10-co-ordinate cavity in the macrocycle derived from 'crossed' N_3O_2 units. Given the larger size of Ca^{II}, Sr^{II}, Ba^{II} and Pb^{II}, allied to their established affinity for 'hard' oxygen donors, it seems reasonable to suggest that their complexes feature this second double helicate mode. The availability of crystals of the lead complex allowed us to investigate the mode adopted by the ligand in accommodating a relatively large metal ion.

Crystal structure

Slow evaporation of a saturated acetonitrile solution of $[PbL^1][ClO_4]_2{\cdot}H_2O$ over a period of several months yielded yellow efflorescent blocks which, after mounting over mother-liquor in sealed Lindemann tubes, proved suitable for X-ray analysis. The structure determination showed the presence of discrete complex cations, perchlorate anions and molecules of acetonitrile solvate in the crystal lattice corresponding to the formulation $[PbL^1][ClO_4]_2{\cdot}4MeCN$. The $[PbL^1]^{2+}$ cation is helically chiral and both enantiomers are present in equal proportions in the crystal. The structure of the *P* enantiomer[24] is shown in Fig. 2 and a computed space-filling representation in Fig. 3. Selected bond lengths and angles are given in Table 3.

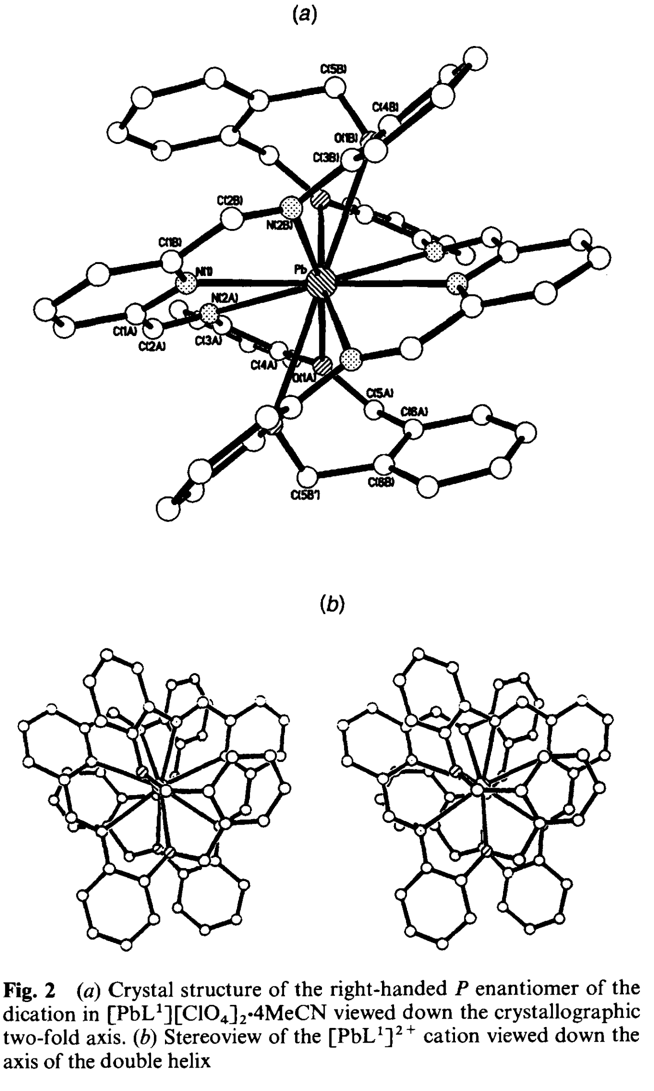


Fig. 2 (*a*) Crystal structure of the right-handed *P* enantiomer of the dication in $[PbL^1][ClO_4]_2{\cdot}4MeCN$ viewed down the crystallographic two-fold axis. (*b*) Stereoview of the $[PbL^1]^{2+}$ cation viewed down the axis of the double helix

The complex cation has a crystallograpic two-fold axis coincident with the metal and perpendicular to the helix axis of the ligand [close to the line joining the methylene carbons C(5B) and C(5B′)]. The lead atom is in a 10-co-ordinate N_6O_4 environment and is bound by all the potential donors of the macrocycle, a unique donor environment within the small group of 10-co-ordinate lead species structurally characterised to date.[25,26] The metal interacts most strongly with the nitrogen donors of each pyridine-2,6-diimine unit of the ligand, although its co-ordination is strongly asymmetrical within each of these 'head units'. Unusually for complexes containing head units of this type,[5,6] the shortest metal–nitrogen bonds are to imine donors [Pb–N(2B) 2.673(9) Å] and are comparable with the corresponding Pb–N_{py} bond lengths [Pb–N(1) 2.714(8) Å]; co-ordination bonds to the other 'pair' of imine donors are significantly longer [Pb–N(2A) 2.846(9) Å]. The 10-co-ordinate metal sphere is completed with the four phenoxy ether oxygens of the ligand [Pb–O(1A) 2.955(7), Pb–O(1B) 2.855(7) Å]. These Pb–O distances are towards the upper end of the range observed in 10-co-ordinate crown, azacrown and cryptand complexes[25] and are thus consistent with predominantly electrostatic metal–

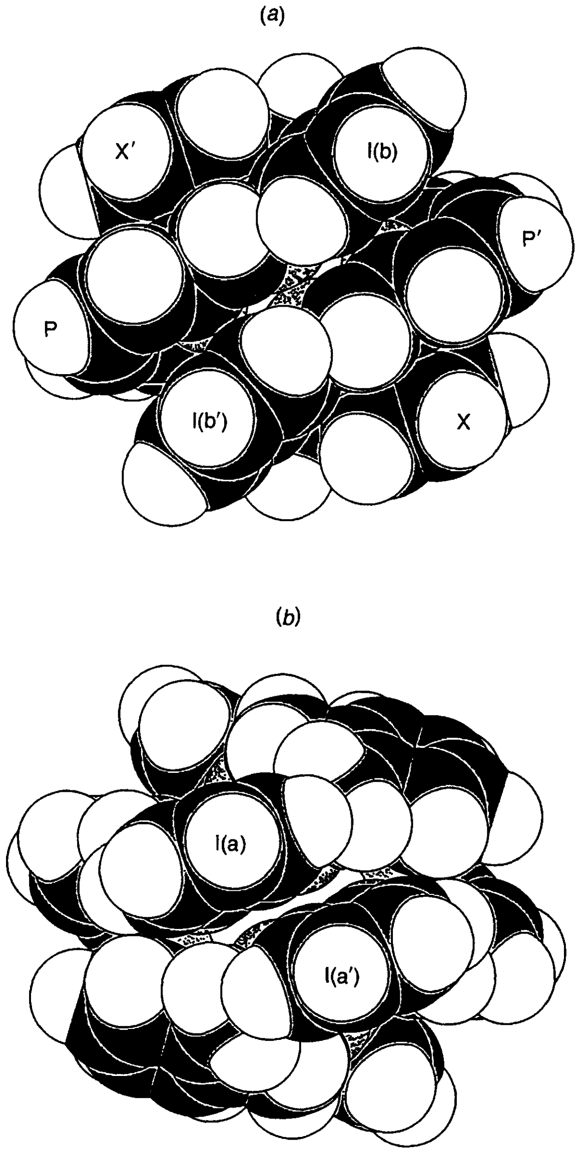
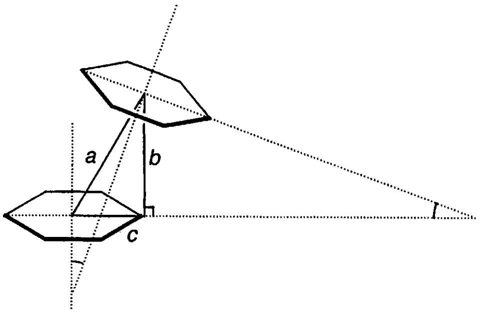


Fig. 3 Computed space-filling diagrams of the $[PbL^1]^{2+}$ cation showing the full encapsulation of the metal by the ligand. (*a*) A view of the two three-tier π–π stacks consisting of xylene (X), pyridine (P) and iminophenoxy [I(b)] aromatic rings. (*b*) A view of the 'opposite' side of the complex cation showing the pair of π–π interacting iminophenoxy rings [I(a)]

Table 3 Selected bond lengths (Å) and angles (°) for $[PbL^1][ClO_4]_2\cdot 4MeCN$

Pb–N(1)	2.714(8)	Pb–N(2B)	2.673(9)
Pb–O(1B)	2.855(7)	Pb–N(2A)	2.846(9)
Pb–O(1A)	2.955(7)	N(1)–C(1B)	1.346(12)
N(1)–C(1A)	1.358(12)	C(1B)–C(2B)	1.474(13)
C(2B)–N(2B)	1.249(12)	N(2B)–C(3B)	1.423(12)
C(3B)–C(4B)	1.361(14)	C(4B)–O(1B)	1.359(12)
O(1B)–C(5B)	1.461(12)	C(6B)–C(6A)	1.413(14)
C(1A)–C(2A)	1.433(14)	C(2A)–N(2A)	1.267(13)
N(2A)–C(3A)	1.395(13)	C(3A)–C(4A)	1.385(15)
C(4A)–O(1A)	1.405(12)	O(1A)–C(5A)	1.459(12)
C(5A)–C(6A)	1.492(14)		
N(2B)–Pb–N(1)	59.9(3)	O(1B)–Pb–N(1)	104.0(2)
O(1B)–Pb–N(2B)	57.5(2)	N(2A)–Pb–N(1)	58.4(3)
N(2A)–Pb–N(2B)	115.3(3)	N(2A)–Pb–O(1B)	123.7(2)
O(1A)–Pb–N(1)	108.3(2)	O(1A)–Pb–N(2B)	168.1(2)
O(1A)–Pb–O(1B)	131.8(2)	O(1A)–Pb–N(2A)	54.4(2)
N(1′)–Pb–N(1)	135.6	N(1′)–Pb–N(2B)	82.3
N(2B′)–Pb–N(1)	82.3	N(2B′)–Pb–N(1′)	59.9
N(2B′)–Pb–N(2B)	65.8	N(1′)–Pb–N(2A)	161.8
N(2B′)–Pb–N(2A)	121.3	N(2A′)–Pb–N(2B′)	115.3
N(2A′)–Pb–N(2A)	111.5		

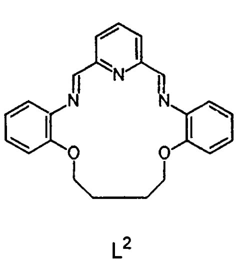
Table 4 Dispositions of interacting aromatic rings in $[PbL^1][ClO_4]_2\cdot 4MeCN$



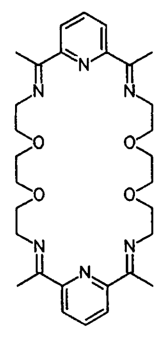
	Interplanar angle/°	Centroid–centroid distance (*a*)/Å	Mean height above plane (*b*)/Å	Offset (*c*)/Å
P • • • I(b′)	22.1	3.75	3.59	1.08
P • • • X′	7.7	4.12	3.28	2.51
I(a) • • • I(a′)	11.5	4.39	3.56	2.57

phenoxy ether interactions. The asymmetry of the metal co-ordination in $[PbL^1]^{2+}$ mirrors the distorted co-ordination geometries observed in other complexes of L^1, and appears to originate in the dominance of stereochemical demands of the ligand in determining the gross structure of the complex. Thus it appears that the metal occupies the most favourable position within the double helical ligand array.

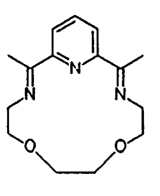
The complexes have a double helical structure which results from the twisting induced in the ligand by the convergence of the head units in co-ordinating to the single ion. The double helical configuration adopted by L^1 in the lead complex is broadly similar to that of the N_6-co-ordinated first-row transition-metal complexes of L^1.[9] In the lead case however, the involvement of the phenoxy ether donors in the co-ordination sphere compresses the double helical array; the helical pitch of *ca.* 7.5 Å in the $[PbL^1]^{2+}$ cation (estimated as the distance between the bridgehead methylenes) is noticeably shorter than helical pitches in excess of 10 Å observed in the series $[CoL^1]^{2+}$, $[NiL^1]^{2+}$ and $[ZnL^1]^{2+}$.[10] Oxygen co-ordination in $[PbL^1]^{2+}$ flattens the disposition of the iminophenoxy rings with respect to the pyridylimine head units, effectively 'swinging-in' the oxygen atoms from the N_6-only binding mode in the small-ion complexes, and producing a metal co-ordination environment consisting of two 'crossed' N_3O_2 units. As for the complexes of the smaller ions, two deviations from an idealised D_{2h} '*trans*-orthogonal' arrangement of the ligand head units around the metal ion are apparent in $[PbL^1]^{2+}$; the N_3 arrays of the essentially planar pyridine-2,6-diimine head units intersect at a dihedral angle of 28.8° and the *trans* N_{py}–M–$N_{py'}$ angle is substantially smaller than 180° [N(1)–Pb–N(1′) 135.6°]. While the latter angle is only somewhat reduced from the corresponding angle in the complexes of Co^{II}, Ni^{II} and Zn^{II} with L^1 [146.3(5)–158.5(3)°], the dihedral angle is dramatically altered compared to those in the small-ion complexes (75.7–84.2°). These deviations, representing a 'drawing together' of the N_3 units of the ligand to one side of the metal, produce offset, face-to-face π–π interactions between each co-ordinated pyridyl ring and the iminophenoxy ring from the opposite head unit [*i.e.* P with I(b′) and P′ with I(b)]. The juxtaposition of a xylene ring with each pyridyl ring (X with P′ and X′ with P) completes the two three-tier π stacks that lie to one side of the complex [Fig. 3(*a*)]. The opposite side of the molecule features the remaining iminophenoxy rings [I(a) and I(a′)] in a further offset, face-to-face π–π interaction [Fig. 3(*b*)]. The dispositions of each pair of rings in these intramolecular π–π interactions are summarised in Table 4. Computed space-filling diagrams show the metal to be completely encapsulated by the macrocycle and thus there appears to be no stereochemical role for the lone pair of electrons of Pb^{II} in the complex.



L^2



L^3



L^4

These findings show that the incorporation of aromatic units to stiffen precursor diamines can have a profound effect on the identity and the co-ordination chemistry of the resultant macrocyclic products. More flexible analogues of the diamine **2** produce significantly different types of template product with pyridine dicarbonyls (*e.g.* mononucleating [1 + 1] compounds L^2 and L^4, and the mono- and di-nucleating [2 + 2] compound L^3)[8,27,28] suggesting that the specificity of the template reaction reported here originates in the unique properties of the macrocyclic product. The [2 + 2] product L^1, by adapting its donor cavity, is able to accommodate a range of metal ions of differing size and character while maintaining a double helix which facilitates the occurrence of stabilising π–π interactions on the periphery of the macrocycle. These findings support the inadvisability of predicting the chemistry of flexible or semi-rigid macrocycles on ring-size considerations alone. We are currently further investigating how systematic changes in the ligand backbone and donor type control the rich co-ordination chemistry of macrocyclic frameworks of this type.

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