Basicity Properties of a Novel Azaparacyclophane Receptor and its Acyclic Precursor: a Thermodynamic and Structural Approach

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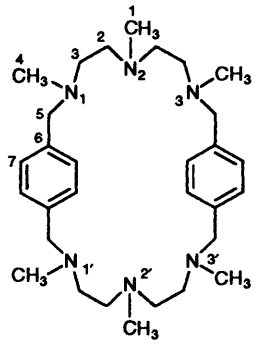
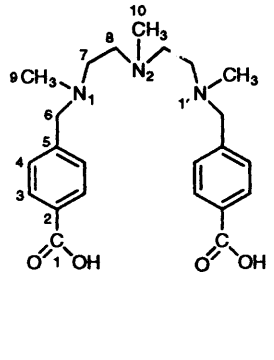
The protonation behaviour of the aza-*p*-cyclophane receptor 1,4,7,16,19,22-hexamethyl-1,4,7,16,19,22-hexaaza[9.9]paracyclophane (**L1**) and its acyclic precursor 4,4'-*N*-methyliminobis(ethylene-*N*-methyliminomethylene)dibenzoic acid (H_2**L2**) has been studied in aqueous solution by means of potentiometric, calorimetric and ^{1}H and ^{13}C NMR techniques. **L1** behaves as a pentaprotic base. NMR experiments have allowed the determination of the stepwise protonation sites. Considering the $[H_4L1]^{4+}$ species, the acidic protons occupy alternate positions in the macrocycle, separated by an unprotonated amino group. The crystal structure of $[H_4L1](ClO_4)_4$ (space group *Pbca*, a = 16.103(6), b = 22.34(2), c = 23.625(8) Å; V = 8499(9) Å^3, Z = 8, R = 0.0637) confirms the NMR data, showing the four protons located on the amino groups adjacent to the aromatic rings. Two ClO_4^- anions interact, *via* hydrogen bonds, with the protonated nitrogens of the macrocycle. **L1** is characterized by two N_3 binding subunits, each of them interacting with one perchlorate ion. As far as H_2**L2** is concerned, calorimetric and NMR data allow the proton sites to be determined. In the H_2**L2** species two protons are located on two amino groups, while the two carboxylate groups are unprotonated, giving rise to an ionic structure.

In the past few years the design of polyammonium receptors has received much attention, with the aim being to study the molecular recognition of anionic species.[1] Structural factors, besides simple charge–charge interactions, have been shown to play significant roles in determining the strength of the interactions between the polyammonium receptor and the anionic guest.[2–4] In this context, the introduction into the molecular framework of structural features that impart high selectivity in the recognition of different guests is one of the goals in the design of synthetic receptors. Aromatic subunits are often introduced as integral parts of the host molecules. In particular, great effort has been devoted to the synthesis of macrocyclic or macropolycyclic receptors containing 1,4-phenylene subunits as rigid spacers to link two binding moieties, such as polyamine chains or polyaza-crown structures, to form ditopic macrocycles or cryptands.[5–10] In these compounds, the aromatic rings and the donor atoms can converge in the cavity and the aromatic rings act as rigid spacers between the two binding moieties.

With this aim, we synthesized the novel receptor 1,4,7,16,19,22-hexamethyl-1,4,7,16,19,22-hexaaza[9.9]paracyclophane (**L1**), which shows two equal N_3 binding subunits separated by two aromatic spacers, together with its acyclic precursor 4,4'-*N*-methyliminobis(ethylene-*N*-methyliminomethylene)dibenzoic acid (H_2**L2**).[11]



L1



H_2**L2**

In fact, the co-ordination of anionic guests can be achieved by using, as host species, polyprotonated forms of *p*-azacyclophanes. The basic properties of such receptors are strictly correlated with their binding features and the study of their proton transfer behaviour is a key step in the analysis of the binding characteristics towards anionic species.[5,12]

As a consequence, the stepwise protonation equilibria of **L1**, together with those of H_2**L2**, have been studied in aqueous solution by means of potentiometric, calorimetric and ^{1}H and ^{13}C NMR techniques and the results are herein reported. The crystal structure of the $[H_4L1](ClO_4)_4$ salt adds further information on the protonation behaviour of **L1**.

Results and Discussion

Protonation.—The protonation equilibria of **L1** and **L2** have been studied in 0.15 mol dm^{-3} NaCl solution at 298.1 ± 0.1 K by potentiometric pH ($-\log [H^+]$) measurements and microcalorimetry. The thermodynamic parameters for their protonation reactions are reported in Table 1. The distribution diagrams for the species present in solution as a function of pH for the systems **L1**–H^+ and $\mathbf{L2}^{2-}$–H^+ are reported in Figs. 1(*a*) and (*b*), respectively.

As far as **L1** is concerned, it behaves as a pentaprotic base, at least in the pH range investigated (2–11). The first four basicity constants range between 8.93 and 6.44 log units, while the fifth is less than 2 log units and the sixth protonation step is not detectable by potentiometry in aqueous solution. This behaviour can be rationalized by minimizing the electrostatic repulsion between positive charges in protonated species of polyaza macrocycles. In other words, the first four protons can occupy alternate positions in the macrocycle, while in the pentaprotonated receptor three or more protonated nitrogens are necessarily contiguous. These considerations are supported by the NMR study in aqueous solution and the crystal structure of the $[H_4L1]^{4+}$ cation, which shows the four protons located on the N-1, N-3, N-1' and N-3' nitrogen atoms (*vide infra*).

The values of the basicity constants of **L1** are lower than those reported for the corresponding protonation steps of the

Table 1 Protonation constants and thermodynamic parameters (kJ mol^{-1}) for the protonation of **L1** and $\mathbf{L2}^{2-}$ in aqueous solution (298.1 K, NaCl 0.15 mol dm^{-3})

Reaction	Log K	$-\Delta G°$	$-\Delta H°$	$T\Delta S°$
$\mathbf{L1} + H^+ = [\mathbf{HL1}]^+$	8.93(1)[a]	50.90(6)	26.4(3)	24.5(4)
$[\mathbf{HL1}]^+ + H^+ = [\mathbf{H_2L1}]^{2+}$	8.22(1)	46.86(6)	28.4(3)	18.5(4)
$[\mathbf{H_2L1}]^{2+} + H^+ = [\mathbf{H_3L1}]^{3+}$	7.35(1)	41.90(6)	42.5(3)	−0.6(4)
$[\mathbf{H_3L1}]^{3+} + H^+ = [\mathbf{H_4L1}]^{4+}$	6.44(1)	36.71(6)	49.0(3)	−12.3(4)
$[\mathbf{H_4L1}]^{4+} + H^+ = [\mathbf{H_5L1}]^{5+}$	1.5(1)[b]	8.4(6)		
$\mathbf{L2}^{2-} + H^+ = [\mathbf{HL2}]^-$	8.25(2)[a]	47.0(1)	24.1(2)	22.9(3)
$[\mathbf{HL2}]^- + H^+ = [\mathbf{H_2L2}]$	6.89(2)	39.3(1)	36.3(2)	3.0(3)
$[\mathbf{H_2L2}] + H^+ = [\mathbf{H_3L2}]^+$	3.70(2)	21.1(1)	2.8(3)	18.3(4)
$[\mathbf{H_3L2}]^+ + H^+ = [\mathbf{H_4L2}]^{2+}$	3.19(2)	18.2(1)	3.3(3)	14.9(4)
$[\mathbf{H_4L2}]^{2+} + H^+ = [\mathbf{H_5L2}]^{3+}$	1.64(5)[b]	9.3(3)		

[a] Values in parentheses are standard deviations on the last significant figure. [b] The values of the fifth protonation constant are too low to determine confidently the enthalpic contribution.

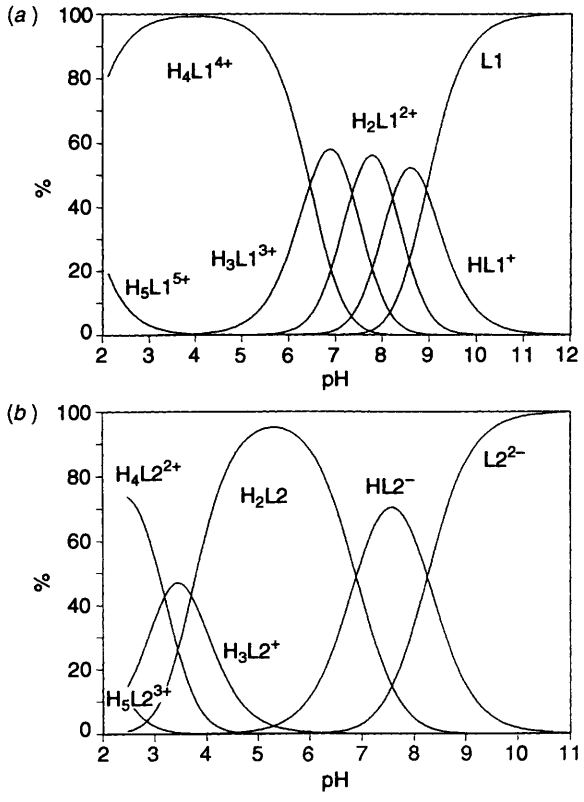


Fig. 1 Distributions diagrams of the protonated species formed by (*a*) **L1** and (*b*) $\mathbf{L2}^{2-}$ as a function of pH ([**L1**] = [$\mathbf{H_2L2}$] = 1 × 10^{-2} mol dm^{-3}) at 298 °C

dimensionally analogous 1,4,7,16,19,22-hexaaza[9.9]metacyclophane,[13] in which all the donors are secondary amino groups. As reported for other macrocyclic polyamines, this effect can be ascribed mainly to the methylation of the amino groups.[14]

Note that the enthalpy changes of the first two protonation steps are similar to each other and far lower than those observed in the third and fourth steps. In other words, the enthalpic contribution to the stepwise protonation of **L1** becomes more favourable with the increasing degree of protonation. On the other hand, the entropic term is favourable in the first and in the second protonation steps, negligible in the third and weakly unfavourable in the fourth one. These features can be explained by considering the increasing amount of positive charges on the ligand with successive protonation to produce a strong organization of solvent molecules beyond the protonated receptor leading to an evident decrease in translational entropy. The increasingly favourable enthalpic contribution to the successive protonation steps is mainly determined by a balance between an unfavourable term due to the electrostatic repulsion between positive charges and a predominantly favourable term due to the hydration of the protonated receptor.

However, the remarkably higher enthalpic contributions of the third and the fourth protonation steps, with respect to those found for the first two steps, cannot be explained only in terms of hydration of the polyammonium cation. The crystal structure of the $[\mathbf{H_4L1}]^{4+}$ ion shows the presence, in each N_3 subunit, of an hydrogen bond network involving two protonated nitrogens and the unprotonated one (*vide infra*). It seems that such interactions can contribute to the markedly favourable enthalpic changes in the third and fourth protonations.

The similarity between the thermodynamic parameters for the first and the second steps suggests that, in the diprotonated species, the two protons are far from each other, and are most likely to be located in separated N_3 binding subunits of the macrocycle.

As far as $\mathbf{L2}^{2-}$ is concerned, the two first protonation steps are characterized by an exothermic enthalpic contribution. Furthermore, the entropic term is remarkably favourable in the first step, but is negligible in the second one. As reported above, this trend is due to the protonation of amino groups. In other words, the $\mathbf{H_2L2}$ species is characterized by an ionic structure, with two protonated nitrogens and two anionic carboxylate groups.

The third and the fourth protonation steps exhibit different thermodynamic characteristics. The enthalpic contribution is negligible, while the entropic change is somewhat favourable. These features can be ascribed to protonation of the two carboxylate groups that leads to charge neutralization and a consequent remarkable desolvation. As a consequence, the protonation of such groups is characterized by a more favourable entropic contribution with respect to that found for amino groups. The desolvation effect explains the almost negligible enthalpic contribution. Concluding, these thermodynamic data indicate that the N_3 binding subunit is the preferred lodging for the first two protons, while the third and the fourth protonations take place on the carboxylate groups.

The folded conformation of the $[\mathbf{H_4L1}]^{4+}$ cation is most likely related to its cyclic framework. As $\mathbf{H_2L2}$ is an open chain receptor, we believe that a folded conformation is improbable. Such a conformation does not allow for minimization of the electrostatic repulsion in the $\mathbf{H_2L2}$ species, which presents an ionic structure. However, at present we do not have reliable information on the possible conformations of the acyclic precursor $\mathbf{H_2L2}$ in solution. We are undertaking molecular modelling studies on such a molecule.

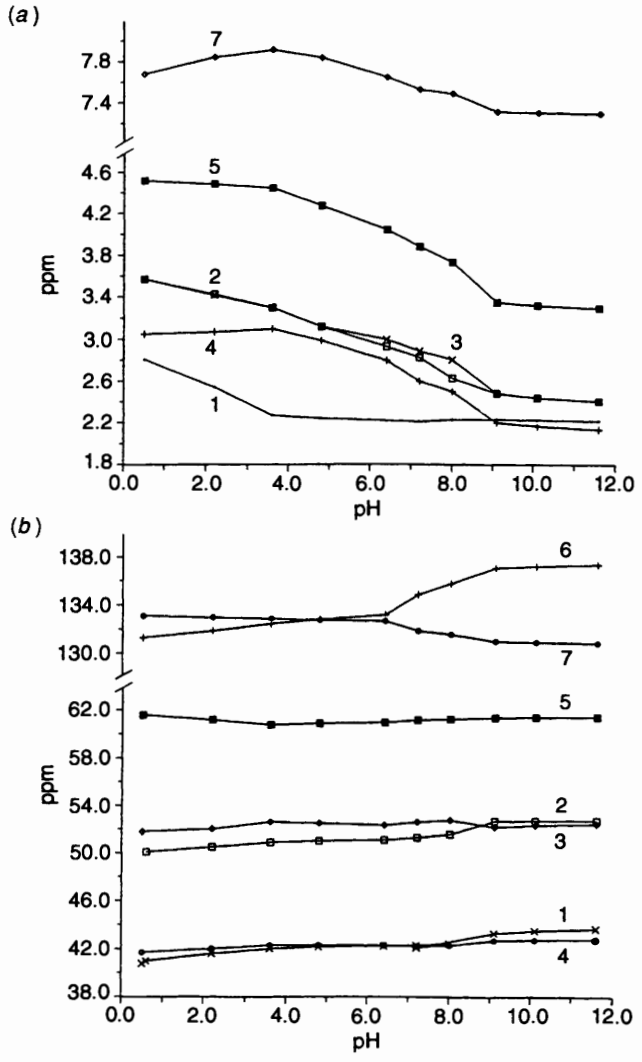


Fig. 2 Experimental (*a*) ^{1}H and (*b*) ^{13}C NMR chemical shifts of **L1** as a function of pH

NMR Analysis.—In order to shed further light on the protonation mechanism of such polyamines, ^{1}H and ^{13}C NMR spectra in aqueous solution have been recorded at various pH values. All the assignments have been made on the basis of ^{1}H–^{1}H homonuclear and ^{1}H–^{13}C heteronuclear correlation experiments at the different pH values studied.

The ^{13}C spectrum of **L1** at pH 11.6, where the unprotonated amine predominates in solution [see Fig. 1(*a*)], exhibits seven peaks, at 42.8 (C-4),† 43.7 (C-1), 52.4 (C-3), 52.7 (C-2), 61.5 (C-5), 130.9 (C-7) and 137.4 (C-6). The ^{1}H spectrum shows two singlets at 2.16 and 2.22 ppm (attributed to the hydrogens of the methyl groups C-4 and C-1, respectively), a multiplet at 2.41 ppm (the hydrogen atoms of the ethylenic chain), a singlet at 3.30 ppm (the hydrogens of C-5) and a singlet at 2.30 ppm (the protons of the aromatic rings). These spectral features indicate a D_{2h} time-averaged symmetry. This symmetry is preserved throughout the pH range investigated.

Figs. 2(*a*) and (*b*) show, respectively, the ^{1}H and ^{13}C NMR chemical shifts of **L1** as a function of pH.

At pH 8, where the H_2L1^{2+} species prevails in solution, the resonances of the hydrogens of C-3 and C-5, as well as those of the methyl group C-4 in an α-position with respect to the N-1, bear a downfield shift with respect to the ^{13}C spectrum at pH 11.6, while the signal of the hydrogens of the methyl group C-1 does not shift appreciably [see Fig. 2(*a*)]. This suggests that the first two protons binding the macrocycle are shared, respectively, by the N-1, N-3 and N-1′, N-3′ couples of nitrogen atoms. This hypothesis is confirmed by the ^{13}C spectrum recorded at this pH that shows the signals of the carbon atoms C-2 and C-6 shift upfield [Fig. 2(*b*)], in good agreement with the β-shift reported for protonation of polyamines.[15]

The same trend is shown by the ^{1}H and ^{13}C NMR spectra recorded at pH 7.2, where the triprotonated species $[H_3L1]^{3+}$ is present in solution, until pH 3.6, where the only species present in solution is the tetraprotonated $[H_4L1]^{4+}$ [Fig. 1(*a*)]. In other words, in the pH range 11.6–3.6, the first four protonation steps involve only the four nitrogen atoms N-1, N-1′, N-3 and N-3′. Since the protons occupy alternate positions, separated from each other either by the aromatic rings or the unprotonated N-2 or N-2′ nitrogens, such a disposition would mean a minimum in electrostatic repulsions. It is of interest that the benzylic nitrogens of **L1** seem to display a higher basicity than the N-2 or N-2′ amino groups. A π-ammonium interaction, *i.e.*, a stabilizing effect of the π-cloud of the aromatic rings, could be invoked to explain such behaviour.[12]

The molecular topology of the two receptors is remarkably different. While **L1** is a macrocyclic molecule, H_2L2 is an open chain polyamine. As a consequence, the crystal structure of the $[H_4L1]^{4+}$ polycharged macrocycle cannot be used to make hypotheses on the possible conformations of the H_2L2 receptor in aqueous solution. However, we believe that a geometry involving an N–H directed into the face of the π-cloud is not the only factor determining the basicity of benzylic amino groups. In fact, the basicity of amino groups depends also on their solvation, which can be influenced by the adjacent π-cloud.

Obviously, the fifth protonation takes place on the nitrogens N-2 and N-2′, as confirmed by the sharp downfield shift experienced by the hydrogen atoms of C-1 and C-2 in the ^{1}H spectrum at pH 1 [see Fig. 2(*a*)].

Considering the amino acid H_2L2, the ^{13}C NMR spectrum at pH 11.6, where the $L2^{2-}$ dicarboxylate anion is present in solution, shows nine signals, at 43.1 (C-9 and C-10), 53.9 and 54.5 (the carbon atoms of the ethylenic chain), 62.2 (C-6), 130.4 and 131.1 (C-4 and C-3) and 136.9 (C-2), 141.6 (C-5) and 176.5 ppm (C-1).

As far as the ^{13}C NMR spectra are concerned, in the pH range investigated, the number of signals does not exceed half of the overall carbon atoms of this molecule indicating a C_{2v} time-averaged symmetry.

The ^{1}H NMR spectrum at pH 11.6 exhibits a singlet at 2.16 ppm (attributed to the hydrogens of C-9 and C-10), a multiplet at 2.47 (the hydrogens of the ethylenic chain), a singlet at 3.53 (C-6) and two doublets at 7.37 and 7.85 (C-4 and C-3, respectively).

The ^{1}H and ^{13}C NMR chemical shifts of $L2^{2-}$ as a function of pH are reported in Figs. 3(*a*) and (*b*), respectively.

In the pH range 11–5 two protons bind the $L2^{2-}$ dianion and originate the uncharged H_2L2 species [see Fig. 1(*b*)]. In this range the resonances of the hydrogens of C-6, C-7 and C-9, in the α-position with respect to the nitrogens N-1 and N-1′ bear a remarkable downfield shift [Fig. 3(*a*)]. This trend indicates that the first two protons binding the $L2^{2-}$ species as located on the nitrogen atoms N-1 and N-1′. The ^{13}C spectra recorded in the same pH range [Fig. 3(*b*)] show an upfield shift of the signals of C-5, in the β-position with respect to N-1 and N-1′, supporting the proposed lodgings for the two protons.[15] These NMR data confirm the ionic structure for the H_2L2 species proposed on the basis of the thermodynamic data.

In the pH range 5–3, the signal of the carbons of the

† The numbering of the carbon atoms in the labelled drawings does not correspond to systematic numbering and is not related to the atom labelling of the ORTEP drawings in Fig. 4.

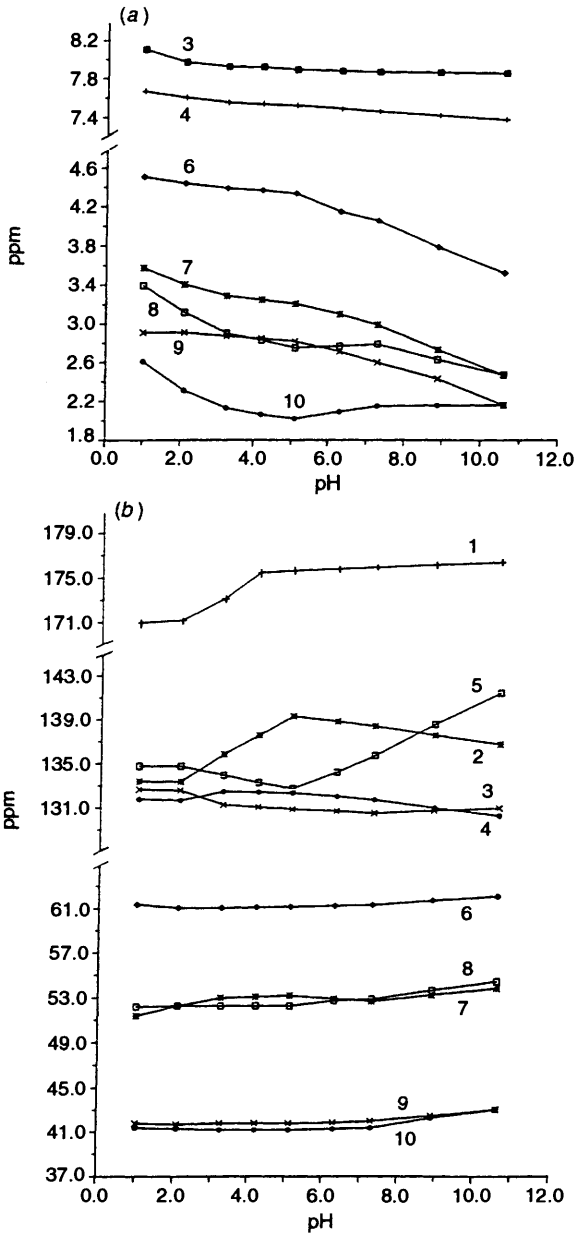


Fig. 3 Experimental (*a*) ^1H and (*b*) ^{13}C NMR chemical shifts of $L2^{2-}$ as a function of pH

carboxylate groups (C–1), as well as that of C-2 shift upfield. No other significant shift is observed in either the ^1H or the ^{13}C spectra. These features indicate that the third and fourth protonation steps involve the carboxylate groups.

Finally, the fifth protonation occurs on the N-2 nitrogen and gives rise, in the ^1H NMR spectra recorded below pH 2, to the downfield shift of the signals of the hydrogens of C-8 and C-10, in the α-position with respect to N-2 [Fig. 3(*a*)].

Description of the Molecular Structure of $[H_4L1](ClO_4)_4$.—The molecular structure consists of $[H_4L1]^{4+}$ cations and perchlorate anions. An ORTEP[16] drawing of the $[H_4L1]^{4+}$ cation and two perchlorate ions, interacting *via* hydrogen bonds with the macrocycle, is shown in Fig. 4(*a*), while a top stereoscopic view is reported in Fig. 4(*b*).

The overall conformation of the macrocycle is boat-shaped and shows an approximate C_{2v} symmetry. The aromatic rings are not coplanar, forming a dihedral angle of 105.8(4)°.

The six nitrogen atoms are in an *endo* conformation and the acidic protons are localized on the N(1), N(3), N(4) and

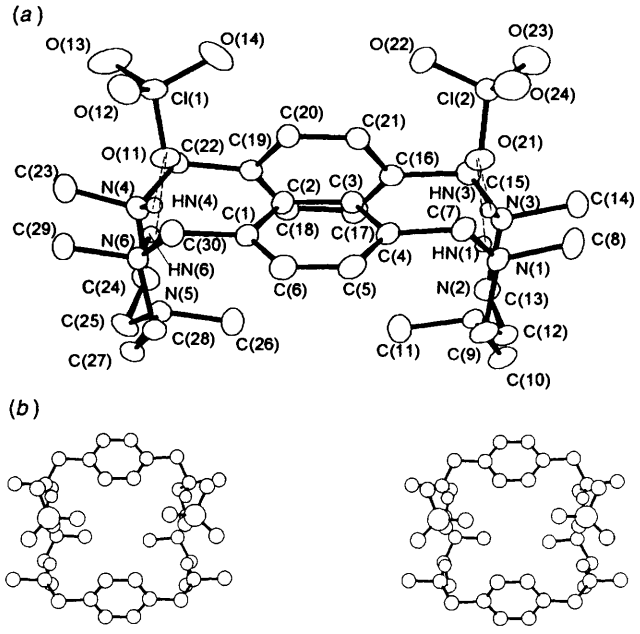


Fig. 4 ORTEP drawing showing the $[H_4L1]^{4+}$ cation and two perchlorate ions, interacting *via* an hydrogen bond with the macrocycle: (*a*) side view; (*b*) top stereoscopic view

N(6) atoms. As a consequence of the *endo* conformation, strong intramolecular contacts are present between the protons and the two unprotonated nitrogen atoms [N(2)···HN(1) 2.46(3), N(2)···HN(3) 2.58(2) and N(5)···HN(4) 2.48(3), N(5)···HN(6) 2.53(3) Å]. Molecular strain is shown by almost all the macrocyclic bond angles (mean value 112.4°) and particularly by those involving the benzylic carbon atoms [C(19)–C(22)–N(4) 114.4(2)°, N(3)–C(15)–C(16) 113.4(2)°, C(4)–C(7)–N(1) 113.7(2)° and C(1)–C(30)–N(6) 113.8(3)°].

The tetraprotonated macrocycle interacts *via* a hydrogen bond with the two perchlorate anions, as shown in Fig. 4(*a*). As reported above, **L1** consists of two N_3 binding subunits, separated by two rigid spacers. Each of these N_3 moieties interacts, *via* hydrogen bonds, with one perchlorate anion. In particular, a couple of acidic protons are localized on each N_3 subunit. The two couples of protons, HN(1), HN(3) and HN(4), HN(6), give rise to an hydrogen bond network involving, respectively, the oxygen atoms O(21) and O(11), with interatomic distances HN(1)···O(21) 2.25(3) Å, HN(3)···O(21) 2.12(2) Å, HN(4)···O(11) 2.14(2) Å and HN(6)···O(11) 2.09(3) Å. The two perchlorate ions are *cis* with respect to the macrocycle and the O(14) and O(22) oxygen atoms are 4.126(4) Å apart from each other.

The presence of these two N_3 binding subunits, each of them interacting with one perchlorate ion, suggests this macrocycle is a promising ditopic receptor for dianionic substrate.

Experimental

Synthesis of **L1** *and* H_2L2.—Compounds **L1** and H_2L2 were obtained as reported in ref. 11. Both **L1**·6HCl·1.5H_2O and H_2L2·3$HClO_4$ had satisfactory elemental analysis.

Crystals of $[H_4L1](ClO_4)_4$, suitable for X-ray analysis, were obtained, in almost quantitative yield, by cooling at room temperature a hot aqueous solution (5 cm^3) containing **L1**·6HCl·1.5H_2O (15 mg, 0.02 mmol) and $NaClO_4$·H_2O (17 mg, 0.12 mmol).

EMF Measurements.—All the potentiometric measurements were carried out in 0.15 mol dm^{-3} NaCl at 298.1 ± 0.1 K, in the pH range 2.5–11, by using the equipment that has already been

described.[17] The reference electrode was an Ag/AgCl electrode in saturated KCl solution. The glass electrode was calibrated as a hydrogen concentration probe by titrating known amounts of HCl with CO_2-free NaOH solutions and determining the equivalent point by the Gran's method[18] which allows the standard potential E° and the ionic product of water (pK_w = 13.73 ± 0.01 to be determined). Solutions were prepared from **L1**·6HCl·1.5H_2O and H_2**L2**·3$HClO_4$. At least three measurements (about 100 experimental points each) were performed for each system. The computer program SUPERQUAD[19] was used to calculate the protonation from emf data. The titration curves for each system were treated either as a single set or as separate entities without significant variations in the values of the basicity constants.‡

NMR Spectroscopy.—200.0 MHz ^1H and 50.32 MHz ^{13}C NMR spectra in D_2O solutions at different pH values were recorded at 298 K on a Bruker AC-200 spectrometer. The ^1H NMR spectra peak positions are reported relative to HOD at 4.75 ppm. Dioxane was used as a reference standard in ^{13}C NMR spectra (δ = 67.4 ppm). Small amounts of 0.01 mol dm^{-3} NaOD or DCl solutions were added to a solution of **L1**·6HCl·1.5H_2O or H_2**L2**·3$HClO_4$ to adjust the pD. The pH was calculated from the measured pD values using the following relationship[20] pH = pD − 0.40.

Microcalorimetry.—The enthalpies of protonation of the ligands have been determined in 0.15 mol dm^{-3} NaCl at 298.15 ± 0.01 K. The automated system as well as the calibration procedure have been fully described elsewhere.[21] The calorimeter stability is within 0.0002 K. In a typical experiment an NaOH (0.15 mol dm^{-3}, addition volumes of 15 μl) (1 μl = 1 mm^3) solution was added to 1.5 cm^3 of **L1**·6HCl·1.5H_2O or H_2**L2**·3$HClO_4$ ($0.01–5 \times 10^{-3}$ mol dm^{-3}). Corrections for the heat of dilution were applied. Under the reaction conditions and employing the determined equilibrium constants, the concentration of each species present in solution before and after each addition was calculated and the corresponding enthalpies of reaction were determined by means of the KK88 program.[22] At least three measurements were performed. The titration curves for each system were treated either as a single set or as separate entities without significant variations in the values of the enthalpy changes.

Crystal Data.—$C_{30}H_{54}Cl_4N_6O_{16}$, M = 896.59. Orthorhombic, a = 16.103(6), b = 22.34(2), c = 23.625(8) Å, V = 8499(9) $Å^3$ (by least-squares refinement of diffractometer angles of 25 carefully centred reflections, λ = 0.710 69 Å), space group *Pbca*, Z = 8, D_c = 1.401 g cm^{-3}. Prismatic colourless crystal. Approximate crystal dimensions 0.4 × 0.4 × 0.3 mm, μ(Mo-Kα) = 0.351 mm^{-1}.

Data Collection and Processing.[23]—Enraf–Nonius CAD4 X-ray diffractometer, θ–2θ scan mode with θ scan width = 0.8 + 0.35 tgθ, θ speed = 4.1 deg min^{-1}, graphite monochromatized Mo-Kα radiation; 9240 reflections measured (2θ range = 5.02–53.92°, h, k, l). Two standard reflections monitored: no loss of intensity observed. Lorentz and polarization effects correction applied.

Structure Analysis and Refinement.§—Direct method. Absorption correction applied after structure resolution. Full-matrix least-squares refinement with all the non-hydrogen atoms anisotropic; methylic, methylenic and aromatic hydrogen atoms in calculated positions with fixed thermal parameters (U = 0.093, 0.061 and 0.059 $Å^2$, respectively). High degree of disorder found for the oxygen atoms bound to Cl(3) and Cl(4). No reliable model for these perchlorates was found. Introduced 14, around Cl(3), and nine, around Cl(4), oxygen atoms. Their population parameters were refined and then fixed in such a way the sum was four for each perchlorate. All the acidic hydrogen atoms localized by ΔF map and isotropically refined. Function minimized: $\Sigma w(|F_o|^2 - |F_c|^2)^2$, with the weighting scheme calculated in agreement to the resolution program (weighting factors 0.0721 and 7.93). 665 refined parameters. Final agreement factors: R = 0.0637 (5210 unique reflections with $I > 2\sigma(I)$) and wR^2 = 0.21. Programs used and source of atomic scattering factors and anomalous dispersion corrections are given in ref. 23. Details of positional and thermal parameters, atomic coordinates, bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.¶

Acknowledgements

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‡ On the basis of a critical evaluation of the least-squares results and of the statistical analysis of the weighted residuals supplied by the SUPERQUAD program, we have considered acceptable only the models for which the value of the variance of the residuals σ^2 is not greater than nine (estimated errors of 0.2 mV on the emf readings and 0.002 cm^3 on the titrant volume).

§ Computer used: DEX-486 DX.

¶ For details of the deposition scheme see Instructions for Authors, *J. Chem. Soc., Perkin Trans. 2*, 1995, Issue 1.

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