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Proton inclusion properties of a new azamacrocycle. Synthesis, characterization and crystal structure of $[H_3L][Cl]_3 \cdot 2H_2O$ (L = 4,10-dimethyl-1,4,7,10-tetraazabicyclo [5.5.2] tetradecane)

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Proton inclusion properties of a new azamacrocycle. Synthesis, characterization and crystal structure of $[H_3L][Cl]_3 \cdot 2H_2O$ (L = 4,10-dimethyl-1,4,7,10-tetraazabicyclo[5.5.2]tetradecane)

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INTRODUCTION

Macrocyclic compounds have been extensively investigated, the interest for this huge class of compounds spans from fundamental research to specific industrial applications.[1–8] We have recently published a few papers on small macrocycles having cage-like molecular topology.[9–19] They present special proton-transfer properties and in few cases they are strong, selective lithium binders in aqueous solution.[14,15,17] The three-dimensional cavity present in these compounds is achieved by connecting two secondary nitrogen atoms of a tetraazamacrocycle with different bridging groups (see Fig 1). Molecular topology and nature of donor atoms are the most important elements influencing the chemical properties of this class of compounds. For these reasons we are continuing our investigations on these compounds by systematically changing the bridging unit; we report here the synthesis and chemical properties of the new cage 4,10-dimethyl-1,4,7,10-tetraazabicyclo[5.5.2]-tetradecane, abbreviated as L.

EXPERIMENTAL

Synthesis

The reaction sequence to obtain L is reported in Fig 1, the starting macrocyclic compound 1,7-dimethyl-1,4,7,10-tetraazacyclododecane (**1**) was prepared as already described.[20]

Bicyclic diamide 2. A sample (4.0 g, 0.02 mol) of the tetraazamacrocycle **1** and triethylamine (8 cm^3) in dry benzene (500 cm^3) and oxalyl chloride (2.54 g, 0.02 mol) in dry benzene (500 cm^3) were added simultaneously, with vigorous stirring, over a period of ca. 7 h at room temperature. The reaction mixture was filtered and then evaporated to dryness on a rotary evaporator. The crude product was extracted in hot cyclohexane and the resulting solution was concentrated; on cooling a white solid separated (yield 1.47 g, 29%). Anal. Calcd for $C_{12}H_{22}N_4O_2$: C, 56.67; H, 8.72; N, 22.03. Found: C, 56.5; H, 8.7; N, 22.0.

4,10-Dimethyl-1,4,7,10-tetraazabicyclo[5.5.2]tetradecane bis(hydrochloride). $[H_2L][Cl]_2$. BH_3THF adduct (100 cm^3, 1 mol dm^{-3}) was added dropwise, under nitrogen atmosphere, to a solution of (**2**) (1.98 g, 7.8 mmol) in dry THF (30 cm^3) cooled to ice temperature. After the addition the cooling bath was removed and the reaction mixture was allowed to warm to room temperature and then refluxed for 3 h. The solution was cooled and the excess of diborane was destroyed with a little water. The solution was then evaporated to dryness, the white residue was dissolved in $HCl/H_2O/MeOH$ (6:9:30) mixture and refluxed for 4 h. The resulting solution was evaporated to dryness

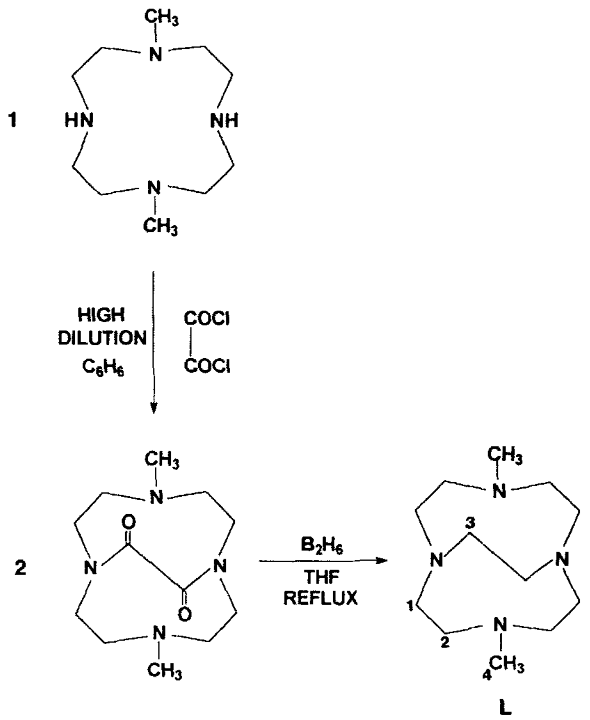

Figure 1 Reaction sequence for the synthesis of L. Atoms labelling used in NMR experiments.

and then the residue was dissolved in 5 cm^3 of water. The solution was made alkaline by addition of concentrated aqueous NaOH and extratced with chloroform (4 x 50 cm^3). The combined extracts were evaporated to dryness under reduced pressure to afford an oil, which was dissolved in ethanol (15 cm^3). By addition of hydrochloric acid the dichloridrate salt separated, which was filtered and recrystallized from ethanol-water (yield 1.52 g, 65%). Anal. Calcd for $C_{12}H_{28}N_4Cl_2$: C, 48.16; H, 9.43; N, 18.72. Found: C, 48,2; H, 9.5; N, 18.6.

Preparation of $[H_3L][Cl]_3{\cdot}2H_2O$. Crystals of $[H_3L][Cl]_3{\cdot}2H_2O$ suitable for X-ray analysis were obtained by slow cooling and evaporation at room temperature of a methanolic solution containing **L** and hydrochloric acid in stoichiometric amount.

Reagents

NaCl (Merck Suprapur) was used as ionic medium. Standardized CO_2-free solutions of NaOH were prepared according to the procedure already described.[21]

Potentiometric measurements

The potentiometric titrations were carried out with a fully automatic apparatus, as described in ref. 22. Two titration curves (100 data points) were used to determine the protonation constants of **L**. The computer program SUPERQUAD[23] was used to process the potentionetric data and calculate the protonation and stability constants.

NMR spectroscopy

A 200 MHz Bruker Ac-200 instrument was used to record the ^1H and ^{13}C spectra at an operating frequency of 50.32 MHz.

X-ray structure analysis

Colourless crystal of $[H_3L][Cl]_3{\cdot}2H_2O$ of approximate dimensions 0.3 × 0.2 × 0.1 mm was mounted on an Enraf-Nonius CAD4 X-ray diffractometer and used for data collection at room temperature with graphite-monochromatized Cu-Kα radiation. A summary of the crystallographic data is reported in Table 1. Cell parameters were determined by least-squares refinement of diffractometer setting angles for 25 carefully centred reflections. Crystals belong to the monoclinic family, space group Pa. Intensity data were corrected for Lorentz and polarization effects, an absorption correction was applied once the structure had been solved by using the Walker and Stuart method.[24]

The structure was solved by direct methods of SIR88[25] and subsequently refined by a full-matrix least-squares technique by using 1493 reflections having $I > 2\sigma(I)$. The function minimized was $\sum w(|F_o| - |F_c|)^2$, with $w = a/(\sigma^2(F) + 0.0006F^2)$, where a is an adjustable parameter. An isotropic extinction parameter refined to $0.01261{\cdot}10^{-4}$ was used during

Table 1 Crystal data and intensity collection parameters for $[H_3L][Cl]_3{\cdot}2H_2O$

Formula	$C_{12}H_{33}N_4Cl_3O_2$
M	371.8
Space group	Pa
a/Å	13.512(8)
b/Å	7.088(2)
c/Å	10.391(3)
β	109.14(5)°
U/Å^3	940(1)
Z	2
D_cg cm^{-3}	1.31
F(000)	400
μ(Cu-Kα) cm^{-1}	45.88
T	Ambient
Scan rate/° min^{-1}	4
Scan mode	$\theta - 2\theta$
Scan width/°	$0.7 + 0.15\,\mathrm{tg}\theta$
2θ range/°	5–150
No of reflections collected	1850
Unique obs. reflections [$I > 2.0\sigma(I)$]	1493
Refined parameters	218
R[a]	0.079
R_w[b]	0.084

[a] $R = \sum ||F_o| - |F_c|| / \sum |F_o|$.
[b] $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2}$.

Table 2 Atomic coordinates ($\times 10^4$) of $[H_3L][Cl]_3 \cdot 2H_2O$, with estimated standard deviations in parentheses

Atom	*x/a*	*y/b*	*z/c*
Cl(1)	1389	3376(3)	8176
Cl(2)	4910(3)	784(3)	11430(3)
Cl(3)	2990(3)	3373(4)	4578(4)
N(1)	2795(5)	8280(8)	11433(7)
C(1)	2824(7)	9304(12)	12665(9)
C(2)	3602(8)	8576(12)	13965(10)
N(2)	4702(5)	8490(9)	13907(7)
C(3)	5045(8)	6425(11)	13885(10)
C(4)	5239(8)	5895(12)	12590(10)
N(3)	4314(6)	6169(8)	11369(8)
C(5)	4657(8)	5991(12)	10135(10)
C(6)	3845(11)	6628(11)	8829(10)
N(4)	3425(8)	8598(10)	8882(8)
C(7)	2313(7)	8530(12)	8907(9)
C(8)	2211(8)	9326(12)	10172(9)
C(9)	3528(10)	9838(14)	7775(10)
C(10)	5456(9)	9532(13)	15036(10)
C(11)	3387(7)	4957(10)	11347(10)
C(12)	2501(6)	6253(9)	11439(10)
O(1)	1959(7)	6515(11)	5791(10)
O(2)	5029(9)	3080(11)	7145(13)

the refinement. A ΔF map calculated in the final stage of the refinement showed unambiguously the three hydrogen atoms bound to N1, N2, and N4 nitrogen atoms. All the hydrogen atoms of the tripotonated ligand were introduced in calculated positions and treated isotropically with their coordinates refined in agreement with those of the linked atoms. Anisotropic thermal parameters were used for all the non-hydrogen atoms. The final agreement factor was $R = 0.079$ for 218 refined parameters; residual electron density ranges from -0.59 to $0.68\,e/Å^3$. Table 2 shows the final co-ordinates with estimated standard deviations.

All calculations, carried out on an IBM PS/2 computer model 80, were performed with the SHELX-76 set of programs[26] which use the analytical approximation for the atomic scattering factors and anomalous dispersion corrections for all the atoms from the International Tables for Crystallography.[27] The molecular plots were produced by the ORTEP program.[28]

RESULTS AND DISCUSSION

Solution studies

Because of the shortness of the two carbons bridging unit it is still possible to speak in terms of three-dimensional cavity? Are the chemical properties typical of these aza-cages retained? To answer these questions we have carried out potentiometric and NMR spectroscopic studies on protonation equilibria.

In aqueous solution **L** behaves as triprotic base, although only the equilibrium constant for the second step of protonation has been accurately measured ($\log K_2 = 5.95 \pm 0.01$), being the first and the third protonation constants respectively too high ($\log K_1 > 13$) and too low ($\log K_3 < 2$) to be measured in the chosen experimental conditions. However, although the first basicity constant is very high, the unprotonated **L** is achievable by extracting with $CHCl_3$ its strong alkaline aqueous solution. The most protonated specie H_3L^{3+} is instead obtained by treating **L** with concentrated hydrochloric acid solution (see experimental section). **L** shows a remarkable decrease of basicity as its degree of protonation increases: the difference between $\log K_1$ and $\log K_2$ can be estimated greater than 7 log units, $\log K_2$–$\log K_3$ is similar, and although more inaccurate indicates that the successive addition of positive charges causes, in a rigid molecular framework, strong repulsions which much reduce the stability of more protonated species.

The compound **L** forms in aqueous solution a stable Cu(II) complex; in the solid state a complex with stechiometry $[CuL][ClO_4]_2$ can be isolated. This complex is immediately destroyed in aqueous solution by the addition of a strong acid solution, showing a very different behaviour from that found for Cu(II) complexes of the other aza-cages, which are instead extremely inert toward the acidic decomposition.[9,11,14,17,29] This remarkable chemical difference can be explained admitting that, while in the other aza-cages there is a tridimensional cavity in which the metal ion is encapsulated, in the case of **L** the tridimensional cavity does not exist and the metal ion is externally bound.

NMR studies

The ^1H spectrum of the free **L** in $CDCl_3$ is reported in Fig 2a, the assignment were made by ^1H-^1H homonuclear and ^1H-^{13}C heteronuclear correlations. The spectrum shows a singlet at 3.3 ppm (six protons), two multiplets at 3.1 ppm (eight protons) and 2.9 ppm (eight protons) and a singlet at 2.4 ppm (eight protons). By addition of one equivalent of CF_3COOH to the $CDCl_3$ solution of **L** we obtain the spectrum reported in Fig 2b, which can be considered that one of the monoprotonated species $[HL]^+$; this spectrum is also very similar to that obtained in D_2O at $pD = 10$ in which the monoprotonated species is predominant. The spectrum presents a broad signal at 10 ppm (integrating one proton), due to the ammonium proton $\text{-N-H}^+\cdots\text{N}$. The deshielding of the proton, found in other aza-cages,[9,13,18,19] indicates the formation of an internal hydrogen bond which stabilizes the mono-

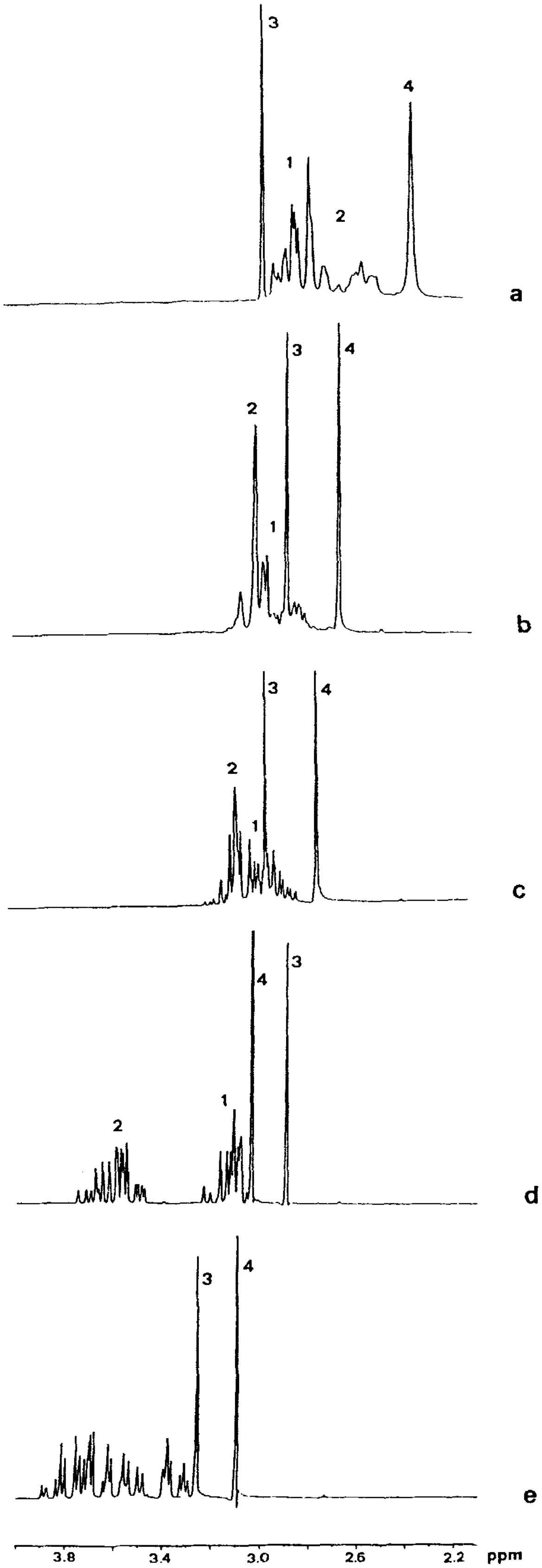

Figure 2 ^1H NMR spectra of L: a) L in $CDCl_3$; b) HL in $CDCl_3$; c) pH = 10; d) pH = 3.8; e) pH < 1.

protonated species. On addition of H_2O or MeOH to the $[HL]^+$ solution the signal at 10 ppm disappears indicating a fast exchange with the protons of the bulk. The downfield shifts experienced by the signals of the protons on C2 and C4 indicate that the first protonation mainly involves the methylated nitrogens. Furthermore, the ^{13}C spectrum of $[HL]^+$ in $CDCl_3$ consists of four signals (52.8 ppm C1, 49.4 ppm C2, 47.9 ppm C3, 43.4 ppm C4) typical of an averaged molecular C_{2v} symmetry, indicating that the proton is rapidly exchanged between the methylated nitrogens. In Fig 2d, the ^1H spectrum of **L** is reported at $pH = 3.8$, which can be considered the spectrum of the diprotonated species $[H_2L]^{2+}$. There is a clear downfield shift of the signals of the protons bound to the carbon atoms C2 and C4, while those relative to the protons of C3 and C1 are rather insensitive. All this indicates that also in the second protonation a methylated nitrogen is mainly involved. To complete the series of the ^1H spectra, the spectrum of the triprotonated species $[H_3L]^{3+}$, recorded at $pH < 0.5$, has been reported in Fig 2e. Having three protons over four protonation sites close to each other, it is likely that delocalization occurs between the bridgehead nitrogen atoms.

Crystal structure

The structure of the compound consists of discrete $[H_3L]^{3+}$ cations, chloride anions and crystallization water molecules. The overall molecular shape adopted by the macrocycle is a clamp-like, with the N-CH_3 groups as arms, quite different from those adopted by other aza-cages.[10,13,14,15,17,18,19] Figure 3a shows an ORTEP drawing of the cation with the atomic labelling. Bond lengths and angles of the macrocyclic ligand are reported in Table 3. The macrocycle is protonated on the two methylated nitrogen atoms N2 and N4, with the third proton bound to N1 (see Fig 3a). The latter hydrogen atom forms a very strong hydrogen-bond with the other bridgehead nitrogen atom N3 (N1-H1···N3, 1.762(9) Å). This unprotonated nitrogen also interacts with the other two protons, but the distances N2-H2···N3 and N4-H4···N3 are significantly longer that those usually considered for an hydrogen bond (2.650(9) and 2.649(9), respectively). The last two hydrogen atoms, on the contrary, form strong interactions with the chlorine anion Cl2: N2-H2···Cl2 2.067(8) and N4-H4···Cl2 2.085(7) Å; while the contact distance between H1 and Cl2 is significantly longer: N1-H1···Cl2 2.546(7) Å (see Fig 3b). Furthermore in the crystal lattice there are some interactions involving the chlorine ions Cl1 and Cl3 with the water molecules.

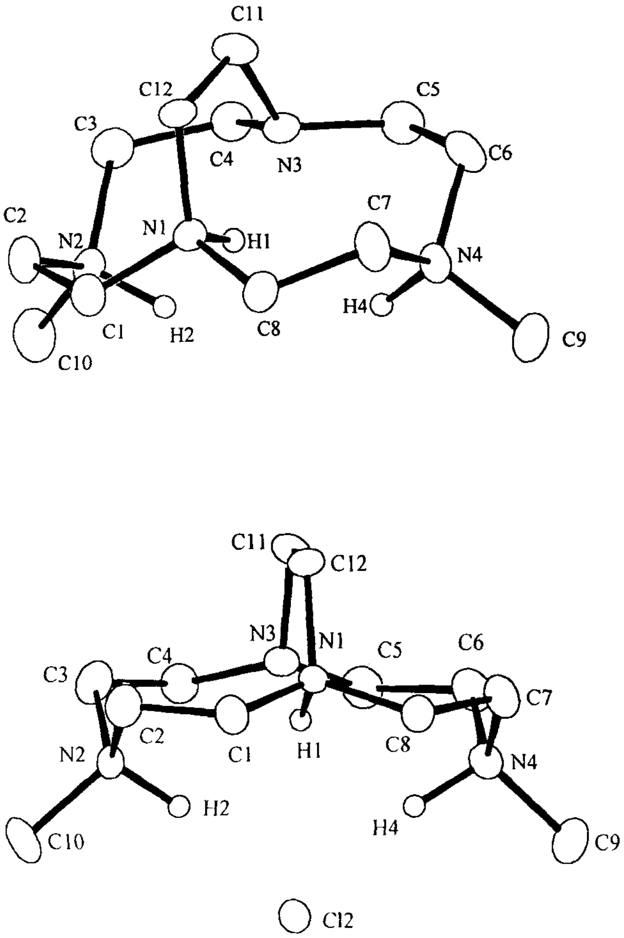

Figure 3 a) ORTEP drawing of the $[H_3L]^{3+}$ cation; b) side view of the same cation and Cl2 anion.

Table 3 Selected bond distances/Å and angles/° of $[H^3L][Cl)_3 \cdot 2H_2O$, with estimated standard deviation in parentheses

N(1)-C(1)	1.46(1)	N(1)-C(8)	1.49(1)
N(1)-C(12)	1.49(1)	C(1)-C(2)	1.51(1)
C(2)-N(2)	1.51(1)	N(2)-C(3)	1.54(1)
N(2)-C(10)	1.48(1)	C(3)-C(4)	1.50(2)
C(4)-N(3)	1.47(1)	N(3)-C(5)	1.50(1)
N(3)-C(11)	1.51(1)	C(5)-C(6)	1.51(1)
C(6)-N(4)	1.51(1)	N(4)-C(7)	1.51(1)
N(4)-C(9)	1.49(2)	C(7)-C(8)	1.48(1)
C(11)-C(12)	1.54(1)		
C(8)-N(1)-C(12)	114.8(7)	C(1)-N(1)-C(12)	113.9(7)
C(1)-N(1)-C(8)	112.2(6)	N(1)-C(1)-C(2)	115.2(7)
C(1)-C(2)-N(2)	112.7(8)	C(2)-N(2)-C(10)	112.4(7)
C(2)-N(2)-C(3)	110.2(6)	C(3)-N(2)-C(10)	110.8(7)
N(2)-C(3)-C(4)	113.2(7)	C(3)-C(4)-N(3)	113.1(9)
C(4)-N(3)-C(11)	113.7(7)	C(4)-N(3)-C(5)	108.2(8)
C(5)-N(3)-C(11)	115.1(7)	N(3)-C(5)-C(6)	113.9(8)
C(5)-C(6)-N(4)	114.5(8)	C(6)-N(4)-C(9)	112.6(7)
C(6)-N(4)-C(7)	110.9(7)	C(7)-N(4)-C(9)	112.2(8)
N(4)-C(7)-C(8)	112.7(8)	N(1)-C(8)-C(7)	114.6(7)
N(3)-C(11)-C(12)	108.5(6)	N(1)-C(12)-C(11)	111.2(6)

CONCLUSIONS

The ligational properties of the studied compound **L** are different from other aza-cages because of the lack of a true tridimensional cavity; thus the metal ion encapsulation is not possible. However, **L** is still a highly preorganized molecule and its proton-transfer properties are influenced by the formation of a hydrogen bonds network.[30,31] The convergently arranged positive charges in the most protonated $[H_3L]^{3+}$ species build up a high positive charge concentration and allow the coordination of the spherical chloride anion.[32]

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