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Lithium Binder in Aqueous Solution. Synthesis and Characterization of the New Cage 4,10,15-Trimethyl-1,4,7,10,15-pentaazabicyclo[5.5.5]heptadecane (L). Protonation and Lithium Complex Formation. Crystal Structures of [HL][BPh$_4$] and [LiL][BPh$_4$]

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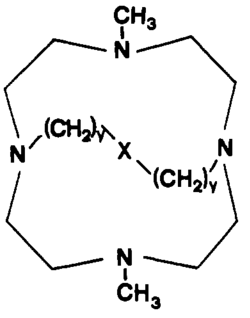
The synthesis and characterization of the new azamacrocycle 4,10,15-trimethyl-1,4,7,10,15-pentaazabicyclo[5.5.5]heptadecane (L) are reported. The stepwise basicity constants have been determined by potentiometry (25 °C, NaCl 0.15 mol dm^{-3}). L behaves as biprotic base: log K_1 = 11.8; log K_2 = 10.0. The molecular structure of the monoprotonated salt [HL][BPh$_4$] has been determined by single-crystal X-ray analysis. The compound crystallizes in a monoclinic unit cell (space group $P2_1/n$) with lattice constants a = 9.92 (1) Å, b = 23.07 (1) Å, c = 15.769 (5) Å, and β = 96.31 (5)°, with Z = 4. Least-squares refinement converged at R = 0.096 (R_w = 0.061) for 1497 unique reflections of $I > 3\sigma(I)$. The structure of [HL]$^+$ shows the five nitrogen atoms in endo configuration, indicating that the proton is inside the cage cavity. Geometrical considerations indicate that the proton is bound to the bridgehead nitrogen atom N(2). The cage L selectively encapsulates Li$^+$, and the equilibrium for the formation of the inclusion complex [LiL]$^+$ has been investigated by potentiometry (log K = 5.5) and ^{7}Li NMR techniques. The molecular structure of the complex [LiL][BPh$_4$] has been determined by single-crystal X-ray analysis. The compound crystallizes in a monoclinic unit cell (space group $P2_1/c$) with lattice constants a = 14.483 (4) Å, b = 12.762 (8) Å, c = 19.22 (3) Å, and β = 93.42 (7)°, with Z = 4. Least-squares refinement converged at R = 0.075 (R_w = 0.054) for 2681 unique reflections with $I > 3\sigma(I)$. Li$^+$ is wholly enclosed in the cage cavity adopting a regular bipyramidal geometry with the Li–N distances in the 2.01–2.08-Å range. Cu(II) is also encapsulated by L; the electronic spectra of the complex show essentially the same features in the solid state and in solution and are diagnostic of a five-coordinate trigonal-bipyramidal structure.

Introduction

Continuing our systematic study on the ligational properties of a series of small azamacrocycles of general formula I, we have



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synthesized the macrobicyclic cage 4,10,15-trimethyl-1,4,7,10,15-pentaazabicyclo[5.5.5]heptadecane (hereafter abbreviated as L). Common characteristics to all these cages are both their high molecular preorganization, which confers unusual basicity behavior, and the presence of small cavities, which allows selective encapsulation of metal ions of appropriate size.[2-7] The ability of selectively binding Li$^+$ in aqueous solution is another remarkable feature of some of these compounds. The present study is therefore dedicated to the enhancement of the Li$^+$ binding capability in aqueous solution by these azacages.

Experimental Section

Synthesis of 4,10,15-Trimethyl-1,4,7,10,15-pentaazabicyclo[5.5.5]heptadecane (L). The complete reaction sequence to obtain (L) is reported in Figure 1. The tetraazamacrocycle 1,7-dimethyl-1,4,7,10-tetraazacyclododecane (**1**) and the bis(2-chloroethyl)methylamine (**2**) were prepared as described in ref 8; the last compound was used as the hydrochloride.

4,10,15-Trimethyl-1,4,7,10,15-pentaazabicyclo[5.5.5]heptadecane (L). To a refluxing suspension of 4 g (0.02 mol) of **1** and 7.4 g of Li$_2$CO$_3$ in 500 cm^3 of acetonitrile was added, over a period of ca. 7 h, a solution of **2** (3.84 g, 0.02 mol) in 250 cm^3 of acetonitrile. The reaction mixture was maintained at reflux for 1 h and then filtered and evaporated to dryness on a rotary evaporator. The crude product obtained was dissolved in CHCl$_3$ (50 cm^3); the resulting solution was filtered and chromatographed over a Al$_2$O$_3$ (neutral, activity I) column (diameter 4 cm, length 30 cm) with CHCl$_3$. The eluted solution was evaporated under reduced pressure, and the white solid obtained was then dissolved in ethanol (30 cm^3). To the resulting solution was dropwise added concentrated HClO$_4$ up to acid pH. When this was allowed to stand, a white solid separated, which was filtered, washed with ethanol and diethyl ether, and then dried in vacuo. Anal. Calcd for C$_{15}$H$_{33}$N$_5$·3HClO$_4$: C, 30.80; H, 6.20; N, 11.97. Found: C, 30.6; H, 6.3; N, 12.1. The monoprotonated derivative [HL][ClO$_4$] was prepared by dissolving the previous trihydroperchlorate salt in water and treating with NaOH to reach alkaline pH. When this was allowed to stand, a white product precipitated, which was washed with cold water and dried in vacuo. Anal. Calcd for C$_{15}$H$_{33}$N$_5$·HClO$_4$: C, 46.92; H, 8.93; N, 18.24. Found: C, 47.1; H, 8.9; N, 18.2.

Preparation of [HL][BPh$_4$]. Colorless crystals of [HL][BPh$_4$], suitable for X-ray analysis, were collected by slow evaporation at room temperature of a solution obtained by dissolving 38 mg (0.1 mmol) of [HL]-[ClO$_4$] and 34 mg (0.1 mmol) of NaBPh$_4$ in 10 cm^3 of methanol. A 10 cm^3 aliquot of *n*-butanol was then added to form the final mixed-solvent solution.

Preparation of [LiL][ClO$_4$]·1.5H$_2$O. To a boiling solution of 0.58 g (1.5 mmol) of [HL][ClO$_4$] in 50 cm^3 of methanol was added a solution of 0.36 g (15 mmol) of LiOH and 0.84 g (6 mmol) of NaClO$_4$·H$_2$O in 70 cm^3 of methanol. The resulting solution was boiled for 1 h and then rotaevaporated to dryness. The white residue was dissolved in CHCl$_3$ (40 cm^3) and the suspension filtered. When cyclohexane (80 cm^3) was added, a colorless solid precipitated, which was filtered and dried under vacuo;

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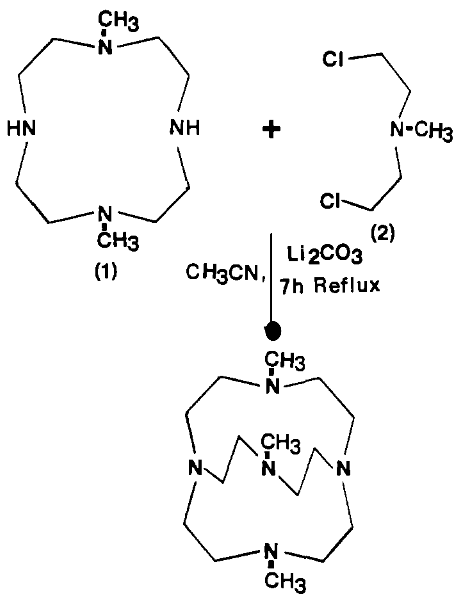

(L)

Figure 1. Reaction scheme for the synthesis of L.

yield 0.42 g (67%). Anal. Calcd for $C_{15}H_{36}N_5O_{5.5}ClLi$: C, 43.21; H. 8.70; N, 16.79. Found: C, 43.0; H, 8.7; N, 16.7.

Preparation of [LiL][BPh$_4$]. Colorless crystals of [LiL][BPh$_4$], suitable for X-ray analysis, were collected by slow evaporation at room temperature of a solution obtained by dissolving 41.7 mg (0.1 mmol) of [LiL][ClO$_4$]·1.5H$_2$O and 34 mg (0.1 mmol) of NaBPh$_4$ in 10 cm^3 of methanol. A 10 cm^3 aliquot of *n*-butanol was then added to form the final mixed-solvent solution.

Preparation of [CuL][ClO$_4$]$_2$. A solution of $Cu(ClO_4)_2{\cdot}6H_2O$ (0.105 g, 0.28 mmol) in methanol (50 cm^3) was added to a solution of L·HClO$_4$ (0.11 g, 0.28 mmol) in methanol (50 cm^3). To the resulting solution was added 10 cm^3 of a 1 mol dm^{-3} NaOH solution in methanol. The reaction mixture was heated to reflux for 120 h. The hot suspension was filtered and then evaporated to 25 cm^3. On cooling, blue crystals separated, which were filtered out and dried in a desiccator. (*Caution! Perchlorate salts of metal complexes can be explosive and must be handled with care. Compounds should not be heated as solids.*) Anal. Calcd for $C_{15}H_{33}N_5O_8Cl_2Cu$: C, 33.00; H, 6.09; N, 12.80. Found: C, 33.1; H, 6.1; N, 12.7.

Materials. All potentiometric measurements were carried out at constant ionic strength $I = 0.15$ mol dm^{-3}. The ionic medium was prepared with NaCl (Merck Suprapur). Standardized CO$_2$-free solutions of NaOH, used in the potentiometric measurements, were prepared according to standard procedures.[9] The standard potential of the cell, $E°$, was determined by the Gran method.[10]

Protonation and Complex Formation Constant. The potentiometric titrations were carried out with a fully automatic apparatus, as described in ref 11. Two titration curves (130 data points) were used to determine the basicity constants of L. Due to the long time required for chemical equilibrium to be attained in the reaction between Li$^+$ and L, a batchwise potentiometric procedure was used to determine the stability constant of the complex [LiL]$^+$. This procedure and its application to macrocyclic complexes have been described in ref 12. Ten aqueous solutions of the ionic medium (NaCl), containing different amounts of the complex [LiL][ClO$_4$] (concentration range (1-3) × 10^{-3} mol dm^{-3}) and NaOH, were prepared in separate bottles. The solutions were maintained at 25 °C, and the value of $-\log [H^+]$ for each solution was measured periodically until a constant value was reached. The computer program SUPERQUAD[13] was used to process the potentiometric data and calculate the basicity and stability constants.

Table I. Crystallographic Data for [HL][BPh$_4$] and [LiL][BPh$_4$]

	[HL][BPh$_4$]	[LiL][BPh$_4$]
mol formula	$C_{39}H_{54}BN_5$	$C_{39}H_{53}BLiN_5$
mol wt	602.69	609.63
space group	$P2_1/n$	$P2_1/c$
a, Å	9.92 (1)	14.483 (4)
b, Å	23.07 (1)	12.762 (8)
c, Å	15.769 (5)	19.22 (3)
β, deg	96.31 (5)	93.42 (7)
V, Å^3	3588 (6)	3546 (6)
Z	4	4
$F(000)$	1312	1320
μ, cm^{-1}	0.34	0.62
D_C, g cm^{-1}	1.12	1.14
radiation	graphite-monochromated Mo Kα ($\lambda = 0.7107$ Å)	
T	298	298
w	$1/\sigma^2(F_o)$	$1/\sigma^2(F_o)$
R^a	0.096	0.075
$R_w{}^b$	0.061	0.054

[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 II. Positional Parameters (×10^4) for $C_{39}H_{53}BLiN_5$ with Their Esd's Given in Parentheses

atom	x/a	y/b	z/c
Li	2406 (8)	3069 (10)	853 (7)
N(1)	2178 (4)	1521 (5)	948 (3)
N(2)	2665 (4)	3168 (5)	1927 (3)
N(3)	2632 (5)	4620 (5)	761 (4)
N(4)	1085 (4)	3257 (5)	404 (3)
N(5)	3498 (4)	2768 (5)	228 (3)
C(1)	2227 (6)	1336 (7)	1708 (4)
C(2)	2000 (5)	2368 (6)	2084 (4)
C(3)	3502 (5)	3058 (7)	2362 (4)
C(4)	2295 (6)	4219 (6)	1983 (5)
C(5)	2769 (6)	4979 (7)	1497 (4)
C(6)	1786 (5)	5035 (7)	394 (4)
C(7)	1333 (6)	4137 (6)	−46 (4)
C(8)	204 (5)	3468 (7)	732 (4)
C(9)	1055 (6)	2229 (6)	55 (4)
C(10)	1251 (5)	1349 (7)	596 (4)
C(11)	2939 (5)	1037 (6)	579 (4)
C(12)	3778 (5)	1773 (6)	584 (4)
C(13)	3518 (5)	2635 (7)	−537 (4)
C(14)	4049 (6)	3690 (7)	470 (5)
C(15)	3470 (5)	4691 (7)	364 (4)
B	2611 (6)	8203 (7)	−1128 (5)
C(16)	1718 (5)	8790 (6)	−1517 (4)
C(17)	1442 (5)	9758 (6)	−1278 (4)
C(18)	706 (5)	10334 (7)	−1594 (4)
C(19)	230 (6)	9924 (7)	−2178 (4)
C(20)	487 (5)	8999 (7)	−2449 (5)
C(21)	1239 (5)	8424 (7)	−2128 (4)
C(22)	3516 (5)	8887 (5)	−1351 (4)
C(23)	3970 (4)	9631 (5)	−928 (4)
C(24)	4736 (5)	10195 (6)	−1141 (4)
C(25)	5068 (5)	10016 (6)	−1789 (4)
C(26)	4633 (5)	9277 (6)	−2217 (4)
C(27)	3864 (5)	8725 (6)	−2012 (4)
C(28)	2563 (5)	8166 (5)	−269 (3)
C(29)	3338 (5)	7893 (5)	165 (4)
C(30)	3330 (6)	7827 (6)	890 (4)
C(31)	2516 (5)	8030 (6)	1204 (5)
C(32)	1730 (6)	8284 (6)	809 (4)
C(33)	1757 (6)	8346 (6)	77 (4)
C(34)	2726 (5)	6966 (5)	−1353 (3)
C(35)	1990 (5)	6277 (6)	−1474 (4)
C(36)	2131 (5)	5231 (7)	−1646 (4)
C(37)	2998 (5)	4842 (7)	−1692 (4)
C(38)	3743 (6)	5472 (6)	−1551 (4)
C(39)	3617 (5)	6520 (6)	−1388 (4)

Spectroscopy. A 300-MHz Varian VXR-300 instrument was used to record the ^{13}C spectra at an operating frequency of 75.43 MHz and ^{7}Li spectra at 116.59 MHz.

X-ray Structure Analysis. Crystals of [HL][BPh$_4$] and [LiL][BPh$_4$] were mounted on a Enraf-Nonius CAD4 automatic diffractometer and

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Table III. Positional Parameters ($\times 10^4$) for $C_{39}H_{54}BN_5$ with Their Esd's Given in Parentheses

atom	*x*/*a*	*y*/*b*	*z*/*c*
N(1)	5470 (13)	1521 (8)	6609 (10)
N(2)	8107 (15)	1583 (6)	7058 (9)
N(3)	8919 (17)	976 (9)	5741 (9)
N(4)	6838 (17)	418 (5)	6581 (10)
N(5)	8352 (18)	709 (7)	8288 (8)
C(1)	6101 (22)	2087 (7)	6425 (11)
C(2)	7585 (20)	2020 (7)	6416 (11)
C(3)	9652 (18)	1539 (8)	7010 (13)
C(4)	9842 (20)	1380 (10)	6118 (14)
C(5)	8952 (21)	373 (9)	6093 (13)
C(6)	7556 (24)	128 (9)	6028 (15)
C(7)	5390 (19)	527 (8)	6259 (10)
C(8)	5228 (18)	1116 (9)	5934 (10)
C(9)	7910 (19)	1736 (7)	7930 (12)
C(10)	8494 (18)	1300 (9)	8570 (11)
C(11)	7001 (18)	484 (9)	8186 (11)
C(12)	6927 (19)	90 (7)	7429 (14)
C(13)	4288 (17)	1645 (7)	6961 (10)
C(14)	8881 (15)	987 (7)	4871 (10)
C(15)	9243 (13)	350 (6)	8826 (9)
B(1)	−2516 (13)	1329 (6)	1752 (9)
C(20)	−839 (10)	1410 (4)	1836 (7)
C(21)	−120 (11)	1308 (5)	1134 (7)
C(22)	1307 (12)	1322 (5)	1201 (8)
C(23)	2040 (13)	1425 (5)	1974 (8)
C(24)	1381 (12)	1517 (4)	2684 (7)
C(25)	−38 (11)	1499 (4)	2625 (7)
C(26)	−3262 (11)	1702 (5)	928 (7)
C(27)	−2654 (12)	2126 (5)	477 (7)
C(28)	−3313 (12)	2445 (5)	−196 (8)
C(29)	−4659 (13)	2339 (5)	−410 (8)
C(30)	−5349 (13)	1932 (5)	8 (8)
C(31)	−4648 (12)	1611 (5)	677 (7)
C(32)	−2738 (11)	634 (5)	1617 (8)
C(33)	−2324 (11)	242 (5)	2284 (8)
C(34)	−2425 (11)	−352 (6)	2219 (8)
C(35)	−2977 (12)	−593 (5)	1462 (8)
C(36)	−3355 (11)	−242 (6)	778 (8)
C(37)	−3250 (11)	366 (5)	845 (8)
C(38)	−3154 (11)	1599 (5)	2564 (7)
C(39)	−4139 (12)	1284 (5)	2966 (7)
C(40)	−4778 (12)	1540 (6)	3642 (8)
C(41)	−4448 (12)	2088 (5)	3900 (7)
C(42)	−3494 (12)	2405 (6)	3544 (8)
C(43)	−2863 (11)	2158 (5)	2875 (7)

used for data collection. A summary of the crystallographic data is reported in Table I. Unit cell dimensions were determined from angular setting of 25 carefully centred reflections. Three standard reflections were monitored periodically for stability control during data collections. Intensities were corrected for Lorentz and polarization effects. All calculations were performed on a IBM Personal System/2 Model 80 computer with the SHELX-76 set of programs[14] that uses the analytical approximation for the atomic scattering factors and anomalous dispersion corrections for all the atoms from ref 15. Tables II and III report the list of the final atomic coordinates for non-hydrogen atoms. Tables IV and V contain selected bond distances and angles. The molecular plots were performed by the program ORTEP.[16]

[HL][BPh$_4$]. The structure was solved by the direct-methods technique, with the use of MULTAN-78 program,[17] which gives all the nonhydrogen atoms. Finally, the atomic positions were refined by means of the full-matrix least-squares methods.

[LiL][BPh$_4$]. The structure was solved by using the direct-methods of MULTAN-78 and successive Fourier syntheses. Anisotropic thermal parameters were used for all non-hydrogen atoms of the complex cation, while the atoms in the counterion were refined isotropically. All the hydrogen atoms were introduced in calculated positions with isotropic temperature factors.

Table IV. Selected Distances (Å) and Angles (deg) for $C_{39}H_{54}BN_5$

Distances			
N(1)–C(1)	1.49 (3)	N(1)–C(8)	1.42 (2)
N(1)–C(13)	1.38 (2)	N(2)–C(2)	1.48 (2)
N(2)–C(3)	1.55 (2)	N(2)–C(9)	1.45 (2)
N(3)–C(4)	1.39 (3)	N(3)–C(5)	1.50 (3)
N(3)–C(14)	1.37 (2)	N(4)–C(6)	1.36 (3)
N(4)–C(7)	1.49 (2)	N(4)–C(12)	1.53 (3)
N(5)–C(10)	1.44 (3)	N(5)–C(11)	1.43 (2)
N(5)–C(15)	1.42 (2)	C(1)–C(2)	1.48 (3)
C(3)–C(4)	1.49 (3)	C(5)–C(6)	1.49 (3)
C(7)–C(8)	1.45 (3)	C(9)–C(10)	1.50 (2)
C(11)–C(12)	1.50 (3)		
Angles			
C(8)–N(1)–C(13)	111 (1)	C(1)–N(1)–C(13)	107 (1)
C(1)–N(1)–C(8)	118 (1)	C(3)–N(2)–C(9)	107 (1)
C(2)–N(2)–C(9)	114 (1)	C(2)–N(2)–C(3)	107 (1)
C(5)–N(3)–C(14)	113 (2)	C(4)–N(3)–C(14)	111 (2)
C(4)–N(3)–C(5)	118 (2)	C(7)–N(4)–C(12)	110 (1)
C(6)–N(4)–C(12)	109 (1)	C(6)–N(4)–C(7)	115 (2)
C(11)–N(5)–C(15)	112 (1)	C(10)–N(5)–C(15)	110 (1)
C(10)–N(5)–C(11)	116 (1)	N(1)–C(1)–C(2)	111 (1)
N(2)–C(2)–C(1)	110 (1)	N(2)–C(3)–C(4)	107 (1)
N(3)–C(4)–C(3)	115 (2)	N(3)–C(5)–C(6)	110 (2)
N(4)–C(6)–C(5)	109 (1)	N(4)–C(7)–C(8)	110 (1)
N(1)–C(8)–C(7)	110 (1)	N(2)–C(9)–C(10)	113 (1)
N(5)–C(10)–C(9)	114 (2)	N(5)–C(11)–C(12)	106 (1)
N(4)–C(12)–C(11)	113 (1)		

Table V. Selected Distances (Å) and Angles (deg) for $C_{39}H_{54}BLiN_5$

Distances			
Li–N(1)	2.013 (1)	Li–N(2)	2.080 (3)
Li–N(3)	2.016 (1)	Li–N(4)	2.066 (1)
Li–N(5)	2.077 (2)	N(1)–C(1)	1.477 (2)
N(1)–C(10)	1.483 (1)	N(1)–C(11)	1.481 (1)
N(2)–C(2)	1.449 (1)	N(2)–C(3)	1.438 (1)
N(2)–C(4)	1.450 (1)	N(3)–C(5)	1.488 (2)
N(3)–C(6)	1.476 (1)	N(3)–C(15)	1.474 (1)
N(4)–C(7)	1.476 (1)	N(4)–C(8)	1.481 (1)
N(4)–C(9)	1.473 (1)	N(5)–C(12)	1.488 (1)
N(5)–C(13)	1.482 (2)	N(5)–C(14)	1.482 (1)
C(1)–C(2)	1.547 (1)	C(4)–C(5)	1.536 (1)
C(6)–C(7)	1.548 (1)	C(9)–C(10)	1.545 (1)
C(11)–C(12)	1.536 (1)	C(14)–C(15)	1.535 (1)
Angles			
N(4)–Li–N(5)	119.9 (2)	Li–N(2)–C(3)	131.9 (2)
N(3)–Li–N(5)	89.9 (2)	Li–N(2)–C(2)	94.6 (2)
N(3)–Li–N(4)	90.1 (1)	C(3)–N(2)–C(4)	110.5 (2)
N(2)–Li–N(5)	119.1 (2)	C(2)–N(2)–C(4)	112.6 (2)
N(2)–Li–N(4)	121.0 (2)	C(2)–N(2)–C(3)	111.0 (2)
N(2)–Li–N(3)	90.4 (2)	Li–N(3)–C(15)	104.4 (2)
N(1)–Li–N(5)	90.3 (1)	Li–N(3)–C(6)	105.0 (2)
N(1)–Li–N(4)	89.9 (2)	Li–N(3)–C(5)	103.4 (2)
N(1)–Li–N(3)	179.8 (2)	C(6)–N(3)–C(15)	114.6 (3)
N(1)–Li–N(2)	89.5 (2)	C(5)–N(3)–C(15)	114.0 (3)
Li–N(1)–C(11)	103.6 (2)	C(5)–N(3)–C(6)	113.8 (2)
Li–N(1)–C(10)	104.7 (2)	Li–N(4)–C(9)	95.0 (2)
Li–N(1)–C(1)	104.4 (2)	Li–N(4)–C(8)	130.1 (3)
C(10)–N(1)–C(11)	113.6 (3)	Li–N(4)–C(7)	94.7 (2)
C(1)–N(1)–C(11)	114.4 (3)	C(8)–N(4)–C(9)	110.7 (2)
C(1)–N(1)–C(10)	114.5 (3)	C(7)–N(4)–C(9)	114.3 (3)
Li–N(2)–C(4)	94.9 (2)	C(7)–N(4)–C(8)	110.9 (2)
Li–N(5)–C(14)	94.9 (2)	Li–N(5)–C(13)	131.0 (2)
Li–N(5)–C(12)	95.1 (2)	C(13)–N(5)–C(14)	111.1 (3)
C(12)–N(5)–C(14)	114.0 (2)	C(12)–N(5)–C(13)	109.7 (2)
N(1)–C(1)–C(2)	109.1 (2)	N(2)–C(2)–C(1)	109.9 (2)
N(2)–C(4)–C(5)	111.0 (2)	N(3)–C(5)–C(4)	110.2 (2)
N(3)–C(6)–C(7)	108.0 (2)	N(4)–C(7)–C(6)	110.7 (2)
N(4)–C(9)–C(10)	110.0 (2)	N(1)–C(10)–C(9)	108.8 (2)
N(1)–C(11)–C(12)	110.7 (2)	N(5)–C(12)–C(11)	109.0 (2)
N(5)–C(14)–C(15)	109.8 (2)	N(3)–C(15)–C(14)	109.9 (2)

Results and Discussion

Protonation. In discussing the proton-transfer properties of (L), comparison with related cages of the series must be made. As

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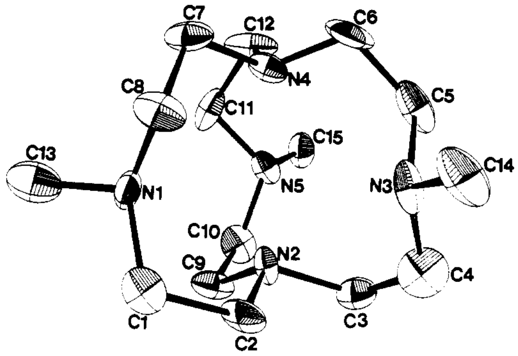

Figure 2. ORTEP drawing of the monoprotonated species $[HL]^+$.

we have already stated in the introduction, these cages are highly preorganized molecules with similar molecular topology. However, in spite of this similarity, only the precursor of the series, i.e., 12,17-dimethyl-1,5,9,12,17-pentaazabicyclo[7.5.5]nonadecane (L1) ($Y = 2$, X = NH in structure I) and the oxygen derivative 12,17-dimethyl-5-oxa-1,9,12,17-tetraazabicyclo[7.5.5]nonadecane (L2) ($Y = 2$, X = O in the structure I) behave as "*fast proton sponges*" in the first protonation step, their basicity being too high to be measured in aqueous solution.[2,18,19] The change either of the nature of the "apical" group or of the length of the hydrocarbon chains disposed around the apical group will not reproduce these special protonation features, which are due to the presence of a hydrogen-bond network in the molecular framework. In aqueous solution, L behaves as a biprotic base, being a relatively strong base in both protonation steps: $\log K_1 = 11.8 \pm 0.1$, and $\log K_2 = 10.0 \pm 0.1$. The third protonation constant is not appreciable under the experimental conditions employed in the potentiometric measurements, although the triprotonated salt (see Experimental Section) can be isolated in the solid state.

Figure 2 reports the ORTEP drawing of the $[HL]^+$ cation. The five nitrogen atoms of $[HL]^+$ are in the endo configuration, indicating that the proton is encapsulated by L. They lie at the vertices of a slightly distorted trigonal bipyramid. The three methyl groups on the basal nitrogens assume the head-to-tail configuration, the symmetry of the whole $[HL]^+$ ion being roughly C_3 (see Figure 2). The N(2)–N(4) distance (3.03 Å, see Table IV) between the bridgehead nitrogens is the shortest among those found for our protonated azacages (3.70–4.70 Å), and it is even shorter than that found for $[H(111)]^+$, i.e., 3.60 Å.[20] Such a distance is not short enough to support the occurrence of a H^+ symmetrically located between the bridgehead nitrogens. This situation was instead claimed to occur for the monoprotonated form of 1,6-diazabicyclo[4.4.4]tetradecane (N–N distance of 2.53 Å) and of other bicyclic amines.[21] However the short N(2)–N(4) distance seems to be indicative of the presence of a hydrogen atom bound to one of these bridgehead nitrogen atoms. A geometrical study, carried out to identify the most likely proton site, shows the N(2) atom. This nitrogen is indeed closer to the equatorial plane (1.31 (1) Å, defined by the three methylated nitrogens, than N(4) (1.71 (1) Å), thus allowing closer N–H···N(equatorial) contacts.

Copper Complex. The electronic spectra of the $[CuL]^{2+}$ complex in aqueous solution (11 800 ($\epsilon = 230$), 15 200 ($\epsilon = 392$), 32 500 cm^{-1}) and in the solid state (11 700, 15 000 cm^{-1}) are the same and are diagnostic of a five-coordinated, bipyramidal complex.[22] As already found for the related Cu(II) cage complexes,[2,4,6,23] $[CuL]^{2+}$ is very inert toward acid solutions: $[CuL]^{2+}$ in 0.1–1 mol dm^{-3} HCl for 60 days shows no detectable decomposition. These findings suggest the encapsulation of the Cu(II) ion within the cage cavity.

Table VI. Stabilities (Logarithms) of Lithium Complexes in Aqueous Solution as a Function of the Apical Group (X) and Length of the Hydrocarbon Chains Disposed around It (Structure I)

	L1[a]	L3[b]	L4[c]	L[d]
apical group (X)	NH	*N*-CH_3	NH	*N*-CH_3
chains	$X[(-CH_2)_{3}-]_2$	$X[(-CH_2)_{3}-]_2$	$X[(-CH_2)_{2}-]_2$	$X[(-CH_2)_{2}-]_2$
log *K*	very low	3.2	4.8	5.5

[a] Basicity constants for L1: $\log K_1 > 14$; $\log K_2 = 8.41$.[2] [b] Basicity constants for L3: $\log K_1 = 11.83$; $\log K_2 = 9.53$; $\log K_3 = 3.43$.[4] [c] Basicity constants for L4: $\log K_1 = 12.48$; $\log K_2 = 9.05$; $\log K_3 < 1$.[6] [d] Basicity constants for L: $\log K_1 = 11.8$; $\log K_2 = 10.0$; this work.

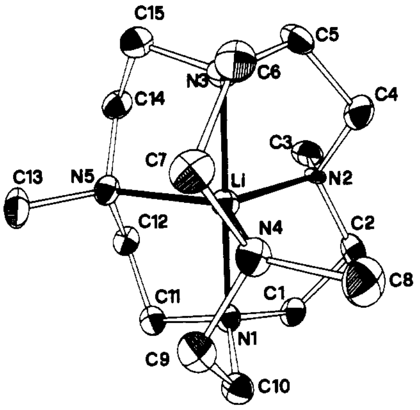

Figure 3. ORTEP drawing of the $[LiL]^+$ cation.

Lithium Complex. The encapsulation of small cations into the cavity of these cages with a high degree of selectivity[3-6] is one of their most important characteristics. The present cage (L) has been synthesized with the purpose of enhancing the lithium binding capability. Indeed L is a very strong lithium binder, the value of the equilibrium constant for reaction 1 is exceptionally high

$$Li^+(aq) + L(aq) \rightleftharpoons [LiL]^+(aq) \qquad (1)$$

($\log K = 5.5 \pm 0.1$), which is probably the highest value for a lithium complex with azamacrocycles in aqueous solution. The Li^+ encapsulation is also documented by the ^{13}C and ^7Li spectra of the complex. The ^{13}C NMR spectrum of $[LiL][ClO_4]$ in $CDCl_3$ solution consists of six sharp signals at room temperature [δ_C 40.0 (q), 42.8 (q), 44.1 (t), 54.3 (t), 54.7 (t), 58.7 (t) ppm], indicative of time-averaged C_{2v} symmetry with two nonequivalent types of methyl groups and the lithium atom lying in the symmetry plane. The ^7Li spectrum of an aqueous solution containing a mixture of $[LiL][ClO_4]$ and LiCl exhibits two sharp peaks, one for the free lithium and one for the complexed, highly deshielded, Li^+ ($\delta = +2.88$ ppm), indicating a slow exchange between the two species on the NMR time scale. The recorded chemical shift is independent of the solvent, indicating that no solvent molecules have close approach to the tightly encapsulated Li^+.[24] The stable $[LiL]^+$ complex is also quite inert toward acid dissociation, a few days being necessary to completely destroy it in an acidic solution, buffered at pH = 4.

The four cages of the series having the nitrogen atom in the apical position are able to encapsulate Li^+ although with very different strengths (see Table VI). Methylation of the secondary amino group in the apical position (X = *N*-CH_3) and shortening of the hydrocarbon chains disposed around the apical group ($Y = 1$) are the two molecular modifications that enhance very much the lithium complex stability. The methylation of the secondary nitrogen in the apical position lowers the basicity strength in the

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first protonation step, making the proton less competitive. The difference is particularly evident between L1 and L3 where the introduction of a methyl group suppresses the protonic sponge behavior, making the basicity strength of L3 a few orders of magnitude smaller than that of L1. The consequence on the lithium complex stability is of the same order of magnitude (see Table VI). A similar trend is observed for L and its unmethylated derivative L4, where coupled to a reduced basicity of L with respect to L4 there is an enhancement of the lithium complex stability, which goes from log $K = 4.8$ for $[LiL4]^+$ up to log $K = 5.5$ for $[LiL]^+$ (see Table VI). The shortening of the hydrocarbon chains disposed around the apical group, which produces a smaller cage cavity, is the other important molecular parameter influencing the lithium complex stability: the $[LiL]^+$ complex is ca. 20 times more stable than $[LiL3]^+$ (see Table VI). That the Li^+ cation fits better into the smaller cavity of L, with respect to that present in L3, is also demonstrated by the X-ray analysis that has been carried out on $[LiL][BPh_4]$. In Figure 3, the ORTEP drawing of the $[LiL]^+$ complex cation is reported. The lithium atom is enclosed inside the cage cavity, adopting a fairly regular bipyramidal geometry with the Li–N distances in the 2.01–2.08 Å range. These distances, which are similar to those found for the unmethylated derivative $[LiL4]^+$,[6] are instead much shorter than those found in the Li^+ complexes either of the (211) cryptand (2.29 Å)[25] or of the related larger cage 5,12,17-trimethyl-1,5,9,12,17-pentaazabicyclo[7.5.5]nonadecane L3 (2.14–2.45 Å).[4]

Conclusions. The aim of this work was to synthesize an azacage with elevated binding capability toward Li^+ in aqueous solution. Previous experiences with other cages of the series have led to L, which is indeed the best lithium binder of the series. The high stability constant and the very regular coordination geometry, coupled with short Li-N bonds, are all good indications of an extremely good match between the cation radius and the cavity hole.

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Registry No. **1**, 90281-17-7; **2**·HCl, 55-86-7; $[H_3L][ClO_4]_3$, 135365-48-9; $[HL][BPh_4]$, 135365-49-0; $[LiL][ClO_4]$, 135393-35-0; $[LiL][BPh_4]$, 135501-17-6; $[CuL][ClO_4]_2$, 135393-37-2; $[HL][ClO_4]$, 135365-50-3.

Supplementary Material Available: Tables of complete positional and isotropic thermal parameters, hydrogen atom parameters, anisotropic thermal parameters, and bond lengths and angles (10 pages); listings of observed and calculated structure factors (21 pages). Ordering information is given on any current masthead page.

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Tetradentate Macrocyclic Complexes of Platinum. X-ray Crystal Structures and Redox Behavior of Complexes Containing Nitrogen or Sulfur Donor Atoms[1]

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Several complexes of platinum containing aliphatic tetradentate (N or S donors) macrocyclic (12–16-membered rings) ligands have been prepared and characterized. The most thoroughly examined of these complexes were those containing 14-membered macrocyclic ligands. In this series of complexes, the half-wave potential of the $Pt(MCL)^{2+}/Pt(MCL)Cl_2^{2+}$ couple (in 1 M NaCl) increased in a regular manner as secondary amine donors were successively replaced by thioether donors (MCL = a macrocyclic ligand). This pattern of behavior was correlated with changes of interligand repulsions (between axial Cl^- and the equatorially coordinated macrocycle) that accompany the change of ligand conformation from the axially unrestricted endo conformation of coordinated 1,4,7,11-tetraazacyclotetradecane ($[14]aneN_4$) to the somewhat restricted exo conformation adopted by 1,4,7,11-tetrathiacyclotetradecane ($[14]aneS_4$). Related shifts in potentials were found in methyl-substituted tetraazacyclotetradecane complexes. $[Pt([14]aneN_4)Cl_2]Cl_2{\cdot}HCl{\cdot}H_2O$, $PtN_4C_{10}H_{23}Cl_5O$, crystallizes in the monoclinic space group $P2_1/n$ with $Z = 1$ and $a = 7.5059$ (9) Å, $b = 18.812$ (5) Å, $c = 7.669$ (2) Å, and $\beta = 99.09$ (2)°. The structure refined to $R = 0.050$ and $R_w = 0.062$ for 1592 reflections. $[Pt(\textit{ms}\text{-}(5,12)\text{-}Me_6[14]aneN_4)](ClO_4)_2{\cdot}2H_2O$, $PtN_4C_{16}H_{40}Cl_2O_{10}$ ($\textit{ms}\text{-}(5,12)\text{-}Me_6[14]aneN_4$ = *meso*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane), crystallizes in the monoclinic space group $P2_1/c$ with $Z = 2$ and $a = 10.0331$ (9) Å, $b = 16.198$ (3) Å, $c = 8.660$ (1) Å, and $\beta = 107.48$ (1)°. The structure refined to $R = 0.035$ and $R_w = 0.024$ for 1526 reflections. $[Pt([14]aneS_4)](ClO_4)_2$, $PtS_4C_{10}H_{20}Cl_2O_8$, crystallizes in the monoclinic space group $P2_1/n$ with $Z = 4$ and $a = 12.098$ (1) Å, $c = 12.557$ (2) Å, and $\beta = 98.69$ (1)°. The structure refined to $R = 0.043$ and $R_w = 0.042$ for 2703 reflections.

Introduction

Transition-metal complexes with macrocyclic ligands have been useful in the study of metal oxidation–reduction behavior in well-defined coordination environments and often for generating metals in relatively rare oxidation states.[3-6] We have long had an interest in the chemical behavior of complexes with the relatively rare[7,8] low-spin d^7 electronic configuration.[9] While low-spin d^7 cobalt(II)[3-5,9b-d] and nickel(III)[4,5,9c,10-12] complexes can often be isolated and fully characterized, the rhodium(II)[9a] and platinum(III)[13] analogues are usually encountered as short-lived, transient species.

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