

binations Y-Ru,⁴² Sc-Co,⁴³ Zr-Mn, Zr-Fe,⁴⁴ and Zr-P.⁴⁵ Compounds in the sequence $ZrZ_n-Zr_5Sb_3Z-Zr_6(Z)X_{12+n}$ involve the progressive oxidation of zirconium, and we imagine that the parallel removal of conduction band (or other) electrons that shield the bonding between Zr and Z is responsible for the inverse distance trend. It is evident that an unusual chemistry is operable in these systems.

Summary

The Zr_5Sb_3 example of the Mn_5Si_3 structure type exhibits a remarkable versatility in the variety of interstitial heteroatoms Z that may be bound within the confacial octahedra ${}_6[Zr_{6/2}Sb_{6/2}]$, for example, all elements in the fourth period from cobalt through selenium. The principal dimensional change taking place during these processes is the expansion of the zirconium octahedra within this chain, while the Zr-Sb distances show

minimal variations. Electronically, the process of bonding Z within Zr_5Sb_3 converts some of the 11 approximately nonbonding electrons (per formula unit) and some Zr-Zr bonding states in the large conduction band into six strong Zr-Z interactions. This is accompanied by the partial loss of nine weaker Zr-Zr interactions in the octahedral chain, but with negligible alteration of the broad Zr-Sb-based valence band and the strong bonding of the Zr_5Sb_3 host reflected thereby. Each Zr_5Sb_3Z product is naturally thermodynamically stable with respect to the binary ZrZ_n phases that also exist for all examples of Z.

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Supplementary Material Available: Tables of parameters for the single-crystal studies and the anisotropic atom displacement parameters in Zr_5Sb_3Si and Zr_5Sb_3Zn (2 pages); listings of observed and calculated structure factors for the same compounds (2 pages). Ordering information is given on any current masthead page.

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Selective Lithium Encapsulation in Aqueous Solution by the New Cage 4,10-Dimethyl-1,4,7,10,15-pentaazabicyclo[5.5.5]heptadecane (L). Synthesis, Characterization, and Structural Aspects. Crystal Structures of $[LiL][ClO_4]$ and $[CuL]Br_2 \cdot 3H_2O$

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Synthesis and characterization of the new azamacrobicycle 4,10-dimethyl-1,4,7,10,15-pentaazabicyclo[5.5.5]heptadecane (L) are reported. The stepwise basicity constants have been determined by potentiometry (25 °C, 0.15 mol dm⁻³ NaCl). The azacage L behaves as a strong base (log $K_1 = 12.48$) in the first protonation step, as a much weaker base in the second step (log $K_2 = 9.05$), and as a very weak base in the last step (log $K_3 < 1$). The cage selectively encapsulates Li⁺, and the inclusion $[LiL]^+$ complex formation equilibrium has been investigated by potentiometry (log $K = 4.8$) and ⁷Li NMR techniques. The molecular structure of the complex $[LiL][ClO_4]$ 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 $a = 15.046$ (11) Å, $b = 8.893$ (4) Å, $c = 15.305$ (8) Å, and $\beta = 113.58$ (4)°, with $Z = 4$. Least-squares refinement converged at $R = 0.065$ for 1385 observed reflections of $I > 3\sigma(I)$. Li⁺ is wholly enclosed in the cage cavity and adopts a five-coordinate geometry, with a short Li-N mean distance of 2.04 Å. The molecular structure of the complex $[CuL][Br_2] \cdot 3H_2O$ has been determined by single-crystal X-ray analysis. The compound crystallizes in an orthorhombic unit cell (space group $Cmc2_1$) with lattice constants $a = 11.629$ (1) Å, $b = 13.031$ (1) Å, and $c = 14.702$ (1) Å, with $Z = 4$. Least-squares refinement converged at $R = 0.068$ for 542 observed reflections of $I > 3\sigma(I)$. The Cu²⁺ is enclosed by the cage and is five-coordinated, adopting a trigonal-bipyramidal coordination geometry. The electronic spectra of the copper complex show essentially the same features in the solid state and in solution and are diagnostic of five-coordinate trigonal-bipyramidal structures.

Introduction

Only in recent years attention has been paid to the coordination chemistry of alkali metals with nitrogen donor ligands.^{2,3} Recently, we have synthesized a series of small azamacrobicycles, types of compounds that are highly preorganized molecules showing unusual basicity and complexing properties.⁴⁻⁹ One of

the interesting properties of some of these compounds is the selective Li⁺ binding in aqueous solution, even in the presence of Na⁺ excess.^{4,6,8} With the aim of enhancing the Li⁺ binding

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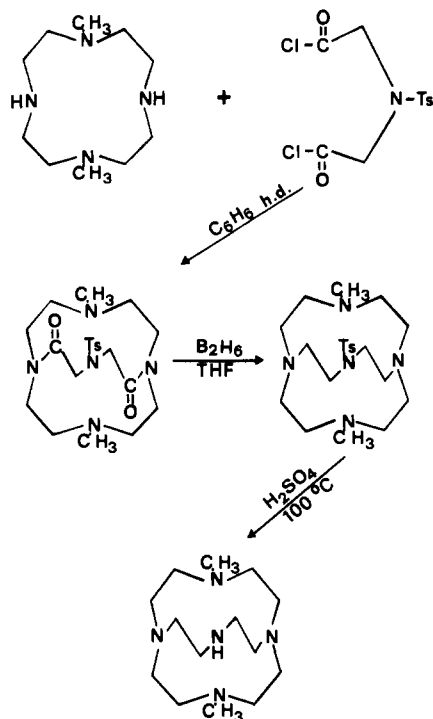


Figure 1. Reaction pathway for the synthesis of cage L.

capability of such kinds of ligands, we have synthesized the macrobicyclic cage 4,10-dimethyl-1,4,7,10,15-pentaazabicyclo[5.5.5]heptadecane (hereafter abbreviated as L). Indeed, this macrobicyclic cage is able to selectively encapsulate a lithium ion, forming a very stable complex in aqueous solution.

Experimental Section

The reaction sequence for the synthesis of 4,10-dimethyl-1,4,7,10,15-pentaazabicyclo[5.5.5]heptadecane (L) is reported in Figure 1. The tetraazamacrocyclic 1,7-dimethyl-1,4,7,10-tetraazacyclododecane (**1**) was prepared as described.¹⁰

N-Tosyliminodiacetyl Dichloride (2). To a solution of 40 g (0.3 mol) of iminodiacetic acid and 40 g of NaOH (1 mol) in 400 cm³ of H₂O was added, over a period of ca. 2 h, a solution of *p*-toluenesulfonyl chloride (57 g, 0.3 mol) in diethyl ether (300 cm³). The reaction mixture was then stirred overnight, the nonaqueous phase separated, and the aqueous layer evaporated to small volume. To this residue was added 90 cm³ of concentrated HCl (37%), and the white solid separated was filtered off, washed with water, and recrystallized from water. Yield: 41.7 g (48.3%). Mp 198–200 °C. Anal. Calcd for C₁₁H₁₃N₂SO₄: C, 45.99; H, 4.56; N, 4.88. Found: C, 45.5; H, 4.4; N, 4.6.

N-tosyliminodiacetyl dichloride (2) was obtained by treating a sample of the above compound (4.5 g, 0.016 mol) with SOCl₂ (35.7 g, 0.3 mol) at 50 °C for 20 h. The unreacted SOCl₂ was removed under reduced pressure, the residue was dissolved in dry benzene (50 cm³), and the solvent was evaporated under reduced pressure. The last operation was repeated two times, and the white solid obtained was used without further purification.

Bicyclic Diamide (3). A 3.93-g (0.019-mol) sample of the trans-dimethylated tetraazamacrocyclic **1** and 4 g (0.44 mol) of triethylamine in 500 cm³ of dry benzene and 6.3 g (0.019 mol) of *N*-tosyliminodiacetyl acid chloride (**2**) in 500 cm³ of dry benzene were added simultaneously to 1 dm³ of dry benzene, under vigorous stirring, over a period of ca. 7 h at room temperature. The reaction mixture was then evaporated to dryness on a rotary evaporator. The crude yellowish product obtained was dissolved in CHCl₃ and chromatographed over a Al₂O₃ (basic, 7–230 mesh, activity II–III) column (diameter 3 cm, length 20 cm) with CHCl₃. The eluted solution was evaporated under reduced pressure, and the white solid obtained was recrystallized from CHCl₃/hexane mixture. Yield: 1.6 g (18%). Mp: 206–208 °C. IR (Nujol) (cm⁻¹): 1635 w (C=O). Anal. Calcd for C₂₁H₃₃N₅SO₄: C, 58.85; H, 7.37; N, 15.51. Found: C, 58.7; H, 7.6; N, 15.3.

4,10-Dimethyl-4-tosyl-1,4,7,10,15-pentaazabicyclo[5.5.5]heptadecane (4). The reduction of **3** to L was carried out with diborane in dry THF;

0.05 mol of diborane in 50 cm³ of dry THF was added dropwise under inert atmosphere to a cooled suspension (20 cm³) of dry THF containing 1.4 g (0.003 mol) of **3**, over a period of 30 min. After removal of the cooling bath the reaction mixture was allowed to warm up to room temperature and then refluxed for 6 h. The solution was then cooled to 0 °C, and the excess of diborane was destroyed with water. The white solid obtained was dissolved in an HCl/H₂O/MeOH mixture (3/9/30 cm³) and refluxed for 4 h. The reaction mixture was evaporated to dryness on a rotary evaporator. The residue was treated with 15 cm³ of water, and the resulting solution was made strongly alkaline with sodium hydroxide. This solution was extracted with CHCl₃ (4 × 20 cm³), and the combined extracts were dried over sodium sulfate. The CHCl₃ was removed under reduced pressure and the residue recrystallized from hexane. Yield: 0.6 g of **4** (46%). Mp: 126–128 °C. Anal. Calcd for C₂₁H₃₇N₅SO₂: C, 59.54; H, 8.80; N, 16.53. Found: C, 59.1; H, 8.9; N, 16.1.

4,10-Dimethyl-1,4,7,10,15-pentaazabicyclo[5.5.5]heptadecane (L). A 1.9-g (0.0045-mol) sample of the tosyl derivative **4** was dissolved in concentrated H₂SO₄ (4 cm³, 96%), and the solution was heated to 100 °C for 60 h. Ethanol (10 cm³) was then carefully added to the ice-cold solution while it was stirring. Dropwise addition of diethyl ether (20 cm³) precipitated the crude sulfate of L, which was washed with cold diethyl ether and dried in vacuo. This product was dissolved in water (10 cm³) and 4 cm³ of NaOH solution (2 g) added. The resulting solution was extracted with CHCl₃ (4 × 50 cm³), and the combined extracts were dried over Na₂SO₄ and then evaporated to dryness under reduced pressure, affording a yellowish residue, which was sublimed. Yield: 0.75 g (66.4%). Mp: 115–117 °C. Anal. Calcd for C₁₄H₃₁N₅: C, 62.39; H, 11.60; N, 25.99. Found: C, 62.1; H, 11.7; N, 25.8. MS: *m/z* 269.4. ¹³C NMR (CDCl₃): δ 40.8, 48.3, 53.4, 53.6, 59.6.

L·4HBr. The tetrahydrobromide salt was obtained by adding concentrated HBr to an ethanolic solution containing the free amine L. The hydrobromide salt was filtered off, washed with ethanol, and dried in vacuum. Anal. Calcd for C₁₄H₃₅N₅Br₄: C, 28.35; H, 5.95; N, 11.81. Found: C, 28.4; H, 5.9; N, 11.7.

Metal Complexes. **[CuL]Br₂·3H₂O.** A solution of CuBr₂ (0.090 g, 0.4 mmol) in ethanol (10 cm³) was added to a neutralized solution of L·4HBr (0.24 g, 0.4 mmol). The resulting blue solution was kept at 60 °C for 1 h and then filtered. On cooling, blue crystals separated, which were filtered off and dried in a desiccator. Anal. Calcd for C₁₄H₃₇N₅O₃Br₂Cu: C, 34.12; H, 6.34; N, 14.21. Found: C, 34.0; H, 6.3; N, 14.0.

[LiL][ClO₄]. A solution of LiOH (0.1 g, 4.18 mmol) and NaClO₄ (26 mg, 0.19 mmol) in MeOH (20 cm³) was slowly added to a boiling solution of L (50 mg, 0.19 mmol). The mixture was refluxed for 30 min and evaporated to dryness with a rotary evaporator. The white product was extracted with CHCl₃ (20 cm³). On addition of cyclohexane, colorless crystals separated, which were filtered off, washed with cyclohexane, and dried in vacuo. Anal. Calcd for C₁₄H₃₁N₅O₄Li: C, 44.74; H, 8.83; N, 18.63. Found: C, 44.8; H, 8.9; N, 18.5.

Crystals of [LiL][ClO₄] suitable for X-ray analysis were obtained by slow evaporation of a cyclohexane/CHCl₃ solution of [LiL][ClO₄].

Materials. All potentiometric and calorimetric measurements were carried out at constant ionic strength *I* = 0.15 mol dm⁻³. The ionic medium was prepared with NaCl (Merck Suprapur). Standardized CO₂-free solutions of NaOH, used in the potentiometric measurements, were prepared according to standard procedures.¹¹

Protonation and Complex Formation Constants. The potentiometric titrations were carried out with a fully automatic apparatus as described in ref 12. Three titration curves (143 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 13. Ten aqueous solutions of the ionic medium (NaCl), containing different amounts of the complex [LiL][ClO₄] (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 SUPERQUAD¹⁴ was used to process the potentiometric data and calculate the basicity and stability constants.

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Table I. Crystallographic Data for [LiL][ClO₄] and [CuL]Br₂·3H₂O

	[LiL][ClO ₄]	[CuL]Br ₂ ·3H ₂ O
mol formula	C ₁₄ H ₃₁ ClLiN ₅ O ₄	C ₁₄ H ₃₁ Br ₂ CuN ₅ O ₃
mol wt	375.81	546.83
space group	<i>P</i> 2 ₁ / <i>n</i>	<i>Cmc</i> 2 ₁
<i>a</i> , Å	15.046 (11)	11.629 (1)
<i>b</i> , Å	8.893 (4)	13.031 (1)
<i>c</i> , Å	15.305 (8)	14.702 (1)
β , deg	113.58 (4)	
<i>V</i> , Å ³	1877 (32)	2227.9 (3)
<i>Z</i>	4	4
<i>F</i> (000)	807.81	1116
μ , cm ⁻¹	1.79	45.57
<i>D</i> _c , g cm ⁻³	1.33	1.63
radiation	graphite-monochromated Mo K α (λ = 0.7107 Å)	
<i>T</i> , °C	25	25
<i>w</i>	1/ $\sigma^2(F_o)$	1/ $\sigma^2(F_o)$
GOF	3.461	3.655
<i>R</i> ^a	0.065	0.068
<i>R</i> _w ^b	0.049	0.061

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

Table II. Positional Parameters ($\times 10^4$) for C₁₄H₃₁ClLiN₅O₄ with Their Esds in Parentheses

atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Li	2650 (7)	7738 (11)	5166 (7)
Cl	4693 (2)	1931 (3)	7347 (1)
O1	4957 (4)	652 (7)	6966 (4)
O2	4471 (5)	1428 (7)	8085 (4)
O3	5471 (5)	2915 (7)	7635 (5)
O4	3883 (4)	2566 (7)	6649 (4)
N1	1574 (4)	8969 (6)	5263 (4)
N2	2738 (4)	9233 (6)	4157 (3)
N3	3774 (4)	6523 (6)	5114 (4)
N4	1764 (4)	5880 (6)	4754 (4)
N5	3405 (4)	8042 (8)	6577 (4)
C1	870 (4)	6758 (7)	4238 (4)
C2	733 (4)	7909 (8)	4895 (4)
C3	1506 (5)	10259 (7)	4639 (5)
C4	2442 (5)	10545 (7)	4557 (5)
C5	3801 (5)	9067 (8)	4496 (5)
C6	4085 (5)	7402 (7)	4474 (5)
C7	3322 (5)	5070 (7)	4723 (4)
C8	2222 (4)	5257 (7)	4149 (4)
C9	1558 (4)	4677 (7)	5314 (4)
C10	2289 (4)	9259 (7)	3116 (4)
C11	1901 (5)	9357 (8)	6270 (5)
C12	2625 (5)	8186 (8)	6891 (4)
C13	3965 (5)	6635 (8)	6792 (4)
C14	4476 (4)	6478 (8)	6114 (4)

Spectroscopy. A 300-MHz Varian VXR-300 instrument was used to record the ¹³C spectra at an operating frequency of 75.43 MHz and the ⁷Li spectra at 116.59 MHz. The UV-vis spectra were recorded on a Perkin-Elmer Lambda 9 spectrophotometer.

X-ray Structure Analysis. Crystals of [LiL][ClO₄] and [CuL]Br₂·3H₂O were mounted on a Enraf-Nonius CAD4 automatic diffractometer and used for data collection. A summary of the crystallographic data is reported in Table I. Unit cell dimensions were determined from angular settings of 25 carefully centered reflections. The intensities of three standard reflections were monitored periodically for stability control during data collection. Intensities were corrected for Lorentz and polarization effects. Data sets for both structures were empirically corrected for absorption effects once the structures had been solved.¹⁵ All calculations were performed on a IBM Personal System/2 Model 80 computer with the SHELX-76 set of programs¹⁶ that uses the analytical approximation for the atomic scattering factors and anomalous dispersion corrections for all the atoms from ref 17. 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

Table III. Positional Parameters ($\times 10^4$) for [C₁₄H₃₁N₅]CuBr₂·3H₂O with Their Esds in Parentheses

atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Br	7236 (3)	-5354 (2)	0
Cu	5000	-1725 (4)	2688 (5)
N1	5000	-221 (29)	2579 (33)
N2	6618 (17)	-1712 (19)	2748 (21)
N3	5000	-2758 (32)	1647 (29)
N4	5000	-2437 (27)	3920 (24)
C1	6074 (23)	-38 (24)	2143 (17)
C2	6983 (20)	-617 (20)	2596 (22)
C3	7058 (33)	-2406 (28)	1977 (21)
C4	6054 (25)	-3208 (24)	1773 (20)
C5	5000	-2312 (32)	538 (28)
C6	7011 (30)	-2267 (25)	3586 (21)
C7	6084 (25)	-1982 (23)	4297 (20)
C8	5000	520 (41)	3461 (37)
O1	5000	-4749 (32)	3771 (26)
O2	5000	-3632 (35)	6085 (32)
O3	5000	-3221 (35)	7846 (38)

Table IV. Selected Bond Distances (Å) and Angles (deg) for C₁₄H₃₁ClLiN₅O₄ with Their Esds in Parentheses

Distances			
Li-N1	2.008 (13)	Li-N4	2.056 (11)
Li-N2	2.083 (12)	Li-N5	2.015 (11)
Li-N3	2.036 (13)		
Angles			
N4-Li-N5	117.1 (5)	N2-Li-N3	90.5 (5)
N3-Li-N5	89.5 (5)	N1-Li-N5	88.5 (5)
N3-Li-N4	90.5 (5)	N1-Li-N4	91.1 (5)
N2-Li-N5	122.2 (5)	N1-Li-N3	177.9 (6)
N2-Li-N4	120.7 (5)	N1-Li-N2	90.0 (5)

Table V. Selected Bond Distances (Å) and Angles (deg) for [C₁₄H₃₁N₅]CuBr₂·3H₂O with Their Esds in Parentheses

Distances			
Cu-N1	1.97 (4)	Cu-N3	2.04 (4)
Cu-N2	1.88 (2)	Cu-N4	2.04 (4)
Angles			
N3-Cu-N4	112 (1)	N1-Cu-N3	127 (1)
N2-Cu-N4	87.8 (9)	N1-Cu-N2	89.7 (7)
N2-Cu-N3	92.4 (8)	N2-Cu-N2'	175 (1)
N1-Cu-N4	122 (1)		

were produced by the program ORTEP.¹⁸

[LiL][ClO₄]. The structure was solved by using direct methods and successive Fourier syntheses. Anisotropic thermal parameters were used for all the non-hydrogen atoms. The hydrogen atoms linked to the carbon atoms were introduced in calculated positions. A ΔF map, calculated in the final stage of the refinement, showed unambiguously the presence of a hydrogen atom linked to the N(5) atom. Thermal parameters of 0.05 Å² were assigned to all hydrogen atoms.

[CuL]Br₂·3H₂O. The structure was solved by the heavy-atom technique, with the use of a Patterson map and successive Fourier syntheses. The correct space group (*Cmc*2₁) was assigned during structure solution and subsequent refinement. It was impossible to determine the absolute configuration because the two configurations did not show, in the refinement, behavior significantly different. The copper and the bromide were refined anisotropically, while the carbon and nitrogen atoms, as well as the three oxygen atoms of the water molecules, were introduced with isotropic temperature factors, because of the rather small number of observed reflections (observed reflections numbered 524, refined parameters numbered 67). The hydrogen atoms were introduced in calculated positions with an overall temperature factor *U* = 0.05 Å².

Results and Discussion

In the following discussion the chemical properties of the title compound (L) are compared with those of the related cage 12,17-dimethyl-1,5,9,12,17-pentazaabicyclo[7.5.5]nonadecane^{4,5} (hereafter abbreviated as L1), in which two propylenic chains are bound to the secondary nitrogen atom instead of ethylenic chains. As expected, small changes in the molecular framework of such

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highly preorganized molecules generate remarkable change in the chemical properties. In the cage L there are potentially five protonation sites, but at most the tetrahydrobromide (L·4HBr) salt is isolated from concentrated HBr. In aqueous solution L behaves as a triprotic base, being a relatively strong base in the first protonation step ($\log K_1 = 12.48$), a moderate base in the second protonation step ($\log K_2 = 9.05$), and a very weak base in the third protonation step ($\log K_3 < 1$). This basicity behavior is quite different from that found for the related cage L1, which behaves as a "Proton Sponge" in the first step of protonation.^{4,5} Moreover, in spite of its high basicity in aqueous solution, the cage L1 does not form the tetrahydrobromide salt even in concentrated HBr, the tribromide L1·3HBr being the most protonated, isolated salt. The exceptional basicity of L1 in the first protonation step has been ascribed to the presence of an array of six hydrogen bonds, involving the apical $>NH_2^+$ group and the four tertiary nitrogen atoms in a unique conformational environment.^{4,5,9} This hydrogen—bond framework, which makes the monoprotonated species [HL1]⁺ particularly stable from the thermodynamic point of view, is not achievable in the case of L, where the presence of shorter ethylenic chains in the bridging unit produces slight conformational changes with respect to L1. The basicity of L, in the first protonation step, is significantly higher than that of the monocyclic macrocycle 1,7-dimethyl-1,4,7,10-tetraazacyclododecane (I) ($\log K_1 = 10.76$, from ref 10), indicating that the bicyclic topology plays, also in L, an important role in determining its proton—binding characteristics. In the second protonation step of L there is a remarkable lowering of basicity ($\log K_2 = 9.05$), with respect to the first protonation step, which is probably due to the electrostatic repulsion between positive charges closely located within the small molecular framework. Unfortunately no safe conclusion about the location of the proton(s) in the various protonated species can be drawn by the NMR techniques (¹H, ¹³C) in this case.

Metal Complexes. Small cations can be encapsulated into the cavities of these rather rigid macrobicyclic cages with a high degree of selectivity.^{4,6,8} The cage L has been especially synthesized for lithium encapsulation. Indeed, Li⁺ is encapsulated also by L1,⁴ but due to the high affinity for proton of L1, there is a strong competition between the metal ion and the proton. The methyl derivative of L1, the cage 5,12,17-trimethyl-1,5,9,12,17-pentaa-zabicyclo[7.5.5]nonadecane (L2), whose basicity has been reduced by introducing a H₃C—N< group in the apical position, encapsulates Li⁺ very well in aqueous solution and forms a very stable complex ($\log K = 3.2$, from ref 4). With L, both the basicity of the cage and the cavity size have been reduced with respect to L1 and the resulting binding capability of L toward Li⁺ is increased. Actually the value of the equilibrium constant for reaction 1 is 63 000 ($\log K = 4.8 \pm 0.1$), which, to our knowledge, is the



highest value for a lithium complex involving azamacrocycles in aqueous solution. In addition, the lithium encapsulation is not influenced by the presence of the Na⁺ ion, even in high concentration, showing that L is able to fully discriminate between lithium and sodium ions.

The ¹³C NMR spectrum of [LiL][ClO₄] in CHCl₃ solution exhibits eight sharp signals at room temperature (see Figure 3), with the two methyl carbons not equivalent. The spectrum is consistent with a time-averaged C₂ symmetry with the metal ion in the symmetry plane containing the two methyl carbons and the NH group. The ⁷Li spectrum of an aqueous solution containing a mixture of [LiL][ClO₄] and LiCl exhibits two sharp peaks (see Figure 2), one for the complexed lithium (+2.85 ppm) and one for the free lithium, indicating a slow exchange between the two species on the NMR time scale. Furthermore, the chemical shift of the complexed Li is essentially independent of the solvent, in agreement with a tight encapsulation of the metal ion and the absence of coordinated solvent molecules.¹⁹ Both the value of the equilibrium constant and that of the ⁷Li chemical shift indicate

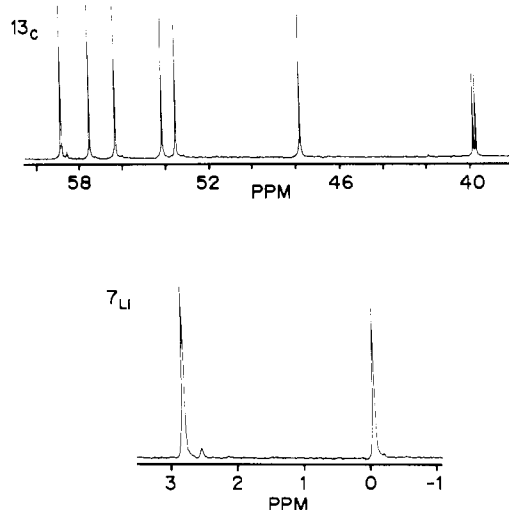


Figure 2. ¹³C (top) and ⁷Li (bottom) NMR spectra of [LiL]⁺ complex in aqueous solution.

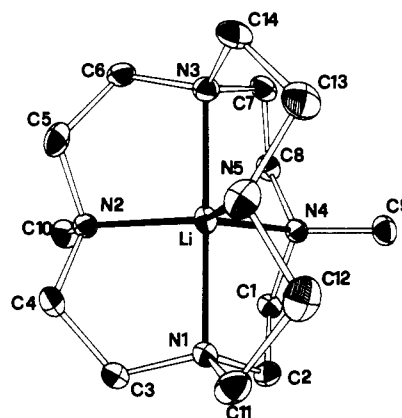


Figure 3. ORTEP drawing of the [LiL]⁺ cation in [LiL][ClO₄], showing the numbering scheme adopted.

a greater ability of L to bind lithium when compared with those of the other lithium cage complexes. To confirm this statement, the X-ray analysis of [LiL][ClO₄] has been carried out. The lithium ion is wholly encapsulated by the ligand and lies at the center of a fairly regular trigonal-bipyramidal arrangement of the five nitrogen atoms (see Figure 3). Indeed, the bond angles N—Li—N are 117.07, 120.73, and 122.19°, whereas the bond angles N_{apex}—Li—N range from 88.48 to 91.08°. The Li—N mean distance of 2.04 Å (range 2.008–2.083 Å) is the shortest found with lithium cryptates, namely 2.29 Å (2.14–2.45 Å) with [LiL2][ClO₄]⁸ and 2.288 Å with [Li(211)]²⁰ (211 = 4,7,13,18-tetraoxa-1,10-diazabicyclo[8.5.5]icosane). When compared with the sum of the nitrogen van der Waals radius (1.50 Å) and Li⁺ radius (≈0.80 Å), i.e. 2.30 Å, these distances indicate fairly strong Li—N interactions for the [LiL][ClO₄] complex, in agreement with its high thermodynamic stability.

Undoubtedly, the discriminating capability of L to bind certain metal ions instead of others is also based on the match between the size of the macrocyclic cavity and the metal ion radius. On these bases, we can expect that other metal ions of appropriate size and of no special stereochemical requirement will fit the cage cavity. This is certainly true for the Cu(II) ion, which indeed goes inside the cage cavity. A solid complex of stoichiometry CuL·Br₂·3H₂O has been isolated, and its electronic spectrum exhibits a band at 14 400 cm⁻¹ (ε 370 cm³ mol⁻¹) with shoulders at 13 000 and 17 900 cm⁻¹, both in solution and in the solid state. Such a spectrum is typical of five-coordinate trigonal-bipyramidal copper(II) complexes.²¹ The complex [CuL]Br₂ shows a great

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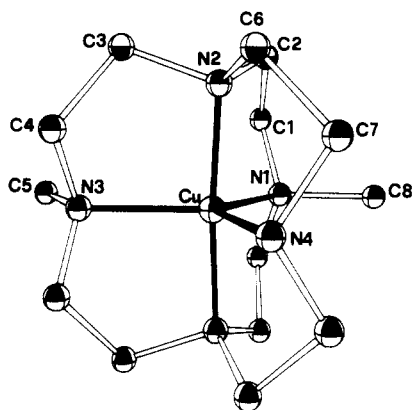


Figure 4. ORTEP drawing of the $[\text{CuL}]^{2+}$ cation in $[\text{CuL}]\text{Br}_2 \cdot 3\text{H}_2\text{O}$, showing the numbering scheme adopted.

inertness toward strong acid solutions, no change being observed over a period of months in both HCl and HClO_4 3 mol dm^{-3} aqueous solutions. Such a high kinetic inertness toward acidic decomposition, which has been also observed for $\text{Cu}(\text{II})$ complexes of the related cages,^{4,5,22} has been considered good experimental evidence for $\text{Cu}(\text{II})$ encapsulation.

To confirm the ability of L to encapsulate the $\text{Cu}(\text{II})$ ion, an X-ray crystal structure determination of $[\text{CuL}]\text{Br}_2 \cdot 3\text{H}_2\text{O}$ has been carried out, and the ORTEP drawing of the cation $[\text{CuL}]^{2+}$ is reported in Figure 4. The copper ion lies inside the cavity of the macrobicyclic ligand and is five-coordinated by the nitrogen donors of the ligand. The coordination geometry of Cu^{2+} is trigonal bi-

pyramidal with a symmetry plane through $\text{N}(1)$, $\text{N}(4)$, $\text{N}(3)$, and Cu , slightly more distorted than that of Li^+ in $[\text{LiL}]\text{ClO}_4$. Actually, the basal angles are 112 (1), 122 (1), and 127 (1) $^\circ$, whereas the angles among the apical and basal bonds range from 87.8 (9) to 92.4 (8) $^\circ$. However, the conformation adopted by the ligand is less strained in the copper complex than in the lithium analogue, as shown by the values of the bond angles within the chelate rings. Apparently, the shorter $\text{Cu}-\text{N}$ distances (average 1.98 Å; 1.88–2.04 Å) are more appropriate to the small cavity of this macrobicyclic ligand than the $\text{Li}-\text{N}$ ones (2.04 Å). In fact, the mean $\text{Cu}-\text{N}$ distance of 1.98 Å is a little shorter than that of 2.07 Å (2.03–2.11 Å) found with $[\text{CuL1}][\text{ClO}_4] \cdot \text{H}_2\text{O}$.⁴ In both lithium and copper complexes the $\text{M}-\text{N}$ apical distances are shorter than those in the equatorial plane. Finally, it can be noted that, with these trigonal-bipyramidal complexes $[\text{CuL}]^{2+}$ and $[\text{LiL}]^+$, the three substituents on the basal nitrogens, i.e. two methyl groups and a hydrogen atom, assume a "head-to-tail" orientation. A different arrangement holds with the square-pyramidal complexes $[\text{CuL1}][\text{ClO}_4] \cdot \text{H}_2\text{O}$ and $[\text{LiL2}][\text{BPh}_4]$ of the [7.5.5] cryptates.^{4,6,8} In such cases the two methyl substituents point toward the NH group.

Conclusions. The marked difference in basicity behavior of L with respect to the related cage L1 is indicative of the key role played by the molecular preorganization in determining the proton-transfer properties. The high thermodynamic stability of $[\text{LiL}]^+$ complex in aqueous solution and the crystal structure indicate that L has the right cavity size to selectively encapsulate lithium. Further improvements on the lithium-binding capability could be achieved by inserting an appropriate substituent group on the secondary, apical nitrogen.

Supplementary Material Available: Tables of complete bond lengths and angles and positional and thermal parameters (6 pages); a listing of observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

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Gas-Phase Structures of Dimethylboron Azide and Dimethylboron Isocyanate. Electron Diffraction and ab Initio Study

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The gas-phase structures of $(\text{CH}_3)_2\text{BN}_3$ and $(\text{CH}_3)_2\text{BNCO}$ have been determined by electron diffraction. Both molecules have planar heavy-atom skeletons with bent BN_3 and BNCO moieties. Their geometries differ mainly in the BNY bond angle ($Y = \text{N}$ or CO), which is small ($\sim 120^\circ$) in the azide and large ($\sim 150^\circ$) in the isocyanate. The following skeletal distances (r_s) and bond angles (\angle_s) with 3σ estimated uncertainties have been derived. $(\text{CH}_3)_2\text{BN}_3$: $\text{BC} = 1.569$ (4) Å, $\text{BN}_\alpha = 1.436$ (6) Å, $\text{N}_\alpha\text{N}_\beta = 1.252$ (4) Å, $\text{N}_\beta\text{N}_\omega = 1.128$ (5) Å, $\text{CBC} = 122.8$ (5) $^\circ$, $\text{N}_\alpha\text{BC}_1 = 115.8$ (8) $^\circ$, $\text{N}_\alpha\text{BC}_2 = 122.1$ (8) $^\circ$, $\text{BN}_\alpha\text{N}_\beta = 118.9$ (8) $^\circ$, and $\text{N}_\alpha\text{N}_\beta\text{N}_\omega = 175.0$ (18) $^\circ$. $(\text{CH}_3)_2\text{BNCO}$: $\text{BC} = 1.563$ (4) Å, $\text{BN} = 1.425$ (5) Å, $\text{NC} = 1.206$ (6) Å, $\text{CO} = 1.167$ (5) Å, $\text{CBC} = 123.6$ (7) $^\circ$, $\text{NBC}_1 = 115.3$ (11) $^\circ$, $\text{NBC}_2 = 121.1$ (11) $^\circ$, and $\text{BNC} = 153.8$ (26) $^\circ$. (C_1 is the methyl carbon trans to Y .) Structure analyses with a large amplitude model for $(\text{CH}_3)_2\text{BNCO}$ and a double minimum potential for the BNCO in-plane bending motion suggest that the barrier at the linear configuration is ≥ 0.2 kcal/mol. HF calculations with 6-31G* basis sets reproduce the experimental structure of the azide satisfactorily. Relative to the ground state, a configuration with a linear BN_3 group and one with the azide group pointing out of the plane are respectively 15.0 and 12.1 kcal/mol less stable. For $(\text{CH}_3)_2\text{BNCO}$ the ab initio method predicts a linear BNCO structure, which is at variance with the experimental result.

Introduction

It was recognized long ago^{2–4} that structural and physical properties of boron–nitrogen compounds parallel those of the isoelectronic carbon–carbon species. In particular, the bond in amine–boranes $\text{X}_3\text{B}-\text{NY}_3$ can be compared to the single bond in alkanes, the bond in aminoboranes $\text{X}_2\text{B}=\text{NY}_2$ to the double bond

in alkenes, and the bond in iminoboranes $\text{XB}=\text{NY}$ to the triple bond in alkynes. Differences in chemical behavior and the higher reactivity of boron–nitrogen compounds have been attributed to the polarity and to the weakness of the BN bonds relative to the CC bonds. Haaland⁵ explains these differences in bonding properties by differentiating between covalent and dative bonds. Whereas all CC bonds (single, double, and triple) are covalent σ or π bonds, the single bond in amine–boranes is a dative σ bond and the π bond in aminoboranes and one π bond in iminoboranes are dative π bonds between the nitrogen lone pair and the empty

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