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Coloured aza-cages for lithium encapsulation

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The two azacages 1-2,4-dinitrobenzene-7,13-dimethyl-1,4,7,10,13-pentaazabicyclo[5.5.5]eptadecane (1) and 1-2,4-dinitroben-zene-1-2,4-dinitrobenzene-8,14-dimethyl-1,5,8,11,14-pentaazabicyclo [7.5.5]nonadecane (2) have been synthesized by two different synthetic routes. The basicity behavior in mixed water/DMSO solution has been studied by potentiometry (25 °C, I = 0.10 mol dm^{-3}): logK_1 = 12.76(8), logK_2 = 3.84(5) for (1). The low solubility of (2) prevents the accurate basicity constants determination. Crystals of (2) are monoclinic, space group $P2_1/a$, with a = 11.944(3), b = 13.587(6), c = 15.034(4) Å, β = 90.36(2)° and Z = 4; final R = 0.059 (wR^2 = 0.1632) for 1211 unique observed reflections with I > 2σ(I). Both cages are able to encapsulate Li^+ ion, the ^{7}Li NMR spectra (CD_3OD) of $[Li(1)]^+$ and $[Li(2)]^+$ show sharp signals at 3.52 and 2.50 ppm respectively and indicative of high deshielded cation.

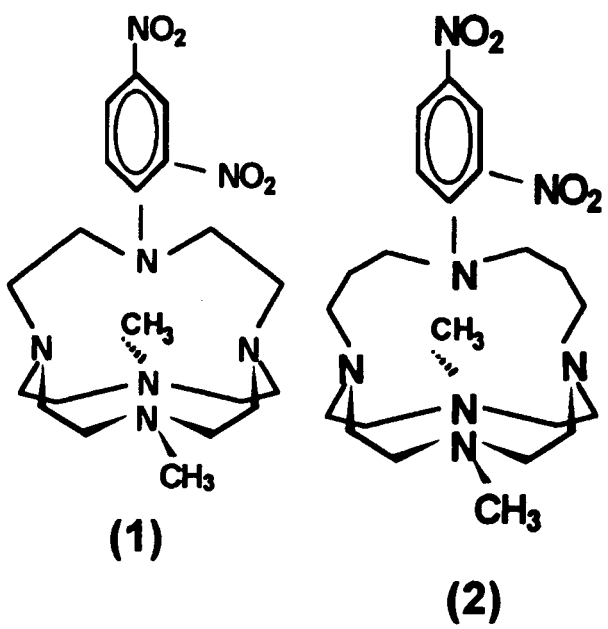
INTRODUCTION

The main aim of the present work is to investigate the possibility of employing aza-cages as selective lithium chromoionophores,[1–4] having much studied a family of aza-cages able to encapsulate lithium ion in aqueous solution with total discrimination toward sodium ion.[5–10] This is quite an unusual property, obtained by shaping a small rigid cavity in these molecules, which allow the exclusive insertion of the small lithium ion, being all the other alkaline metal ions simply too big to be inserted into the cavity. We want modify these molecules attaching to their periphery a chromophor sensible to the presence of the Li^+ into the cavity. The overall molecular framework has not to be altered because the complexing characteristics must be preserved. Mainly for synthetic reasons we have started with nitrobenzene group derivatives. The two compounds 1-2,4-dinitrobenzene-7,13-dimethyl-1,4,7,10,13-pentaazabicyclo [5.5.5] eptadecane (1) and 1-2,4-dinitrobenzene-8,14-dimethyl-1,5,8,11,14-pentaazabicyclo[7.5.5]nonadecane (2) have been synthesized (see scheme 1).

EXPERIMENTAL SECTION

General Methods

The ^{1}H, ^{13}C and ^{7}Li, NMR spectra were recorded at 200, 50, and 77.78 MHz respectively. Dioxane was used as standard in ^{13}C NMR (δ = 67.4 ppm). In ^{1}H spectra in D_2O peak positions are reported relative to HOD at 4.75 ppm. LiCl aqueous solution (10^{-3} mol dm^{-3}) was used as standard in ^{7}Li NMR.



Scheme 1

*To whom correspondence should be addressed.

Materials

Unless specified otherwise, reagent-grade reactants and solvents were used as received from chemical suppliers. Benzene was distilled over P_4O_{10}. Anhydrous DMF was obtained by distillation over CaH_2 of commercial DMF under reduced pressure and kept over molecular sieves. The synthetic pathway followed for compounds (**1**) and (**2**) is reported in Figure 1.

1-2,4-dinitrobenzene-7,13-dimethyl-1,4,7,10,13-penta-azabicyclo[5.5.5]eptadecane-trihydrochloride monohydrate. (**1**)·3·$HClH_2O$ 1.3 g (5 mmol) of cage 4, 10-dimethyl-1,4,7,10,15-pentaazabyciclo[5.5.5]-epta-decane, obtained following the procedure reported in ref. 7, 1.1 g (11 mmol) of K_2CO_3, and 0.9 g (5 mmol) of 1-fluoro-2,4-dinitrobenzene were introduced into an Er lenmeyer flask containing 50 cm^3 of dry $CHCl_3$. The

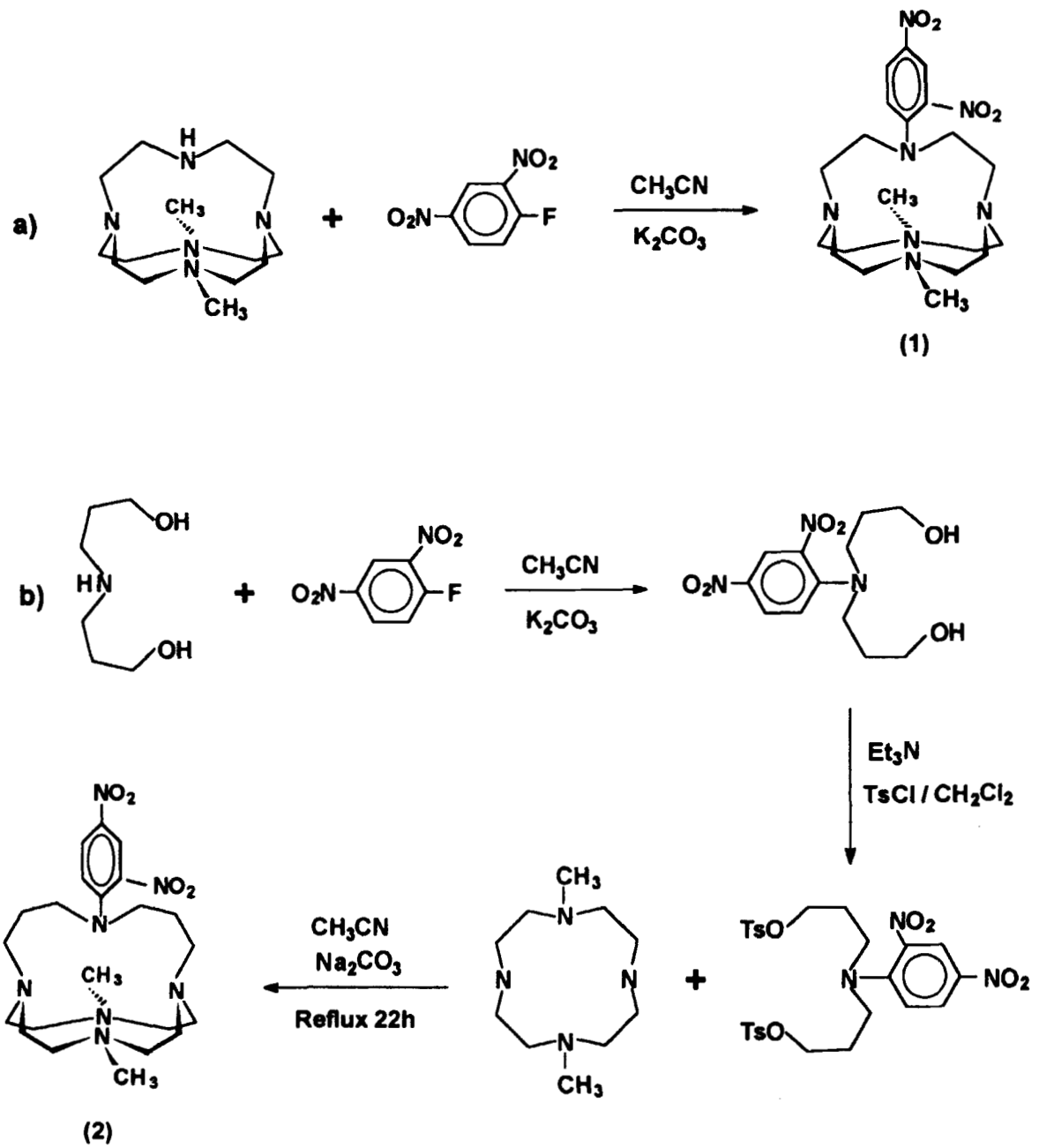


Figure 1 Synthetic routes followed for: a) compound (**1**); b) compound (**2**).

reaction mixture was magnetically stirred and kept at room temperature for 48 h. The reaction mixture was then evaporated to dryness on a rotary evaporator. The residue was treated with a small amount of water (10 cm^3) and the resulting solution was extracted with $CHCl_3$ (5 × 15 cm^3), the combined extracts were dried over Na_2SO_4. The $CHCl_3$ was removed under reduced pressure and the red oil residue (1.7 g) was transformed in the hydrochloride salt by dissolving in 10 cm^3 of EtOH and subsequently treated with 2 cm^3 of concentrate HCl. The resulting reaction mixture was evaporated to dryness on a rotary evaporator and the residue treated with 10 cm^3 of EtOH and evaporated. The last procedure was repeated three times in order to remove water. The residue was then treated with 7 cm^3 of EtOH and to the solution obtained 1 cm^3 of diethyl ether was added. The reaction mixture was kept at 4°C for 1 h, then the yellow precipitate was filtrate, washed with diethyl ether and dried under vacuum at 100°C for 2 h. Yielded 1.8 g (79%) (**1**)3HClH_2O, mp 206–207°C. Anal. Calcd for $C_{20}H_{38}N_7O_5Cl_3$: C, 42.67; H, 6.80; N, 17.42. Found: C, 42.7; H, 7.0; N, 17.2. ^{13}C NMR (D_2O) δ 150.0, 142.2, 141.7, 129.3, 123.4, 50.08, 48.37, 44.0.

2,4-dinitrobenzene-dipropanolamine. 5.0 g (37 mmol) of dipropanolamine, prepared according to the synthetic procedure described in ref. 11, 5.5 g of K_2CO_3 (39 mmol), and 6.9 g (37 mmol) of 2,4-dinitrobenzene were suspended in 80 cm^3 of CH_3CN. The reaction mixture was stirred at room temperature for 44 h, then filtered and vacuum evaporated to yield the crude product as a waxy yellow solid which was recrystallized from hot benzene (yield 7.1 g, 64%). Anal. Calcd for $C_{12}H_{17}N_3O_6$: C, 48.16; H, 5.72; N, 14.04. Found: C, 48.0; H, 5.8; N, 13.9.

O,O'-Bis(p-tolylsulfonyl)-2,4-dinitrobenzene-dipropanolamine. 7.0 g (23 mmol) of 2,4-dinitrobenzene-dipropanolamine and 10.6 cm^3 (105 mmol) of triethylamine were dissolved in 100 cm^3 of CH_2Cl_2. The solution was cooled at −5°C and over a period of 1 h 150 cm^3 of CH_2Cl_2 containing 13.0 g of p-tolylsulfonylchloride (70 mmol) were added. After the addition, the reaction mixture was kept at 0°C for 12 h, under stirring, then extracted three time with 75 cm^3 of H_2O each. The organic layer was dried on Na_2SO_4, filtered and concentrated under vacuum. An orange oil was obtained which was washed with EtOH (yield 11.9 g, 84%). Anal. Calcd for $C_{26}H_{29}N_3O_{10}S_2$: C, 51.39; H, 4.81; N, 9.22. Found: C, 50.7; H, 5.0; N, 9.0.

1-2,4-dinitrobenzene-8,14-dimethyl-1,5,8,11,14-pentaazabicyclo[7.5.5]nonadecane (2). 2.0 g (10 mmol) of the macrocycle 1,7-dimethyl-1,4,7,10-tetraazacyclododecane, obtained following the procedure reported in ref. 11, 1.6 g (16 mmol) of Na_2CO_3, and 6.0 g (10 mmol) of O,O'-Bis(p-tolylsulfonyl)-2,4-dinitrobenzenedipropanolamine were introduced into an Erlenmeyer flask containing 50 cm^3 of dry CH_3CN. The reaction mixture was kept at room temperature for 28 h and then 3 h refluxing. The reaction mixture was then evaporated to dryness on a rotary evaporator and 15 cm^3 of water were added. The resulting solution was extracted with $CHCl_3$ (5 × 20 cm^3), the combined extracts were dried over Na_2SO_4 and filtered. The $CHCl_3$ was removed under reduced pressure and the red oil residue was dissolved in 15 cm^3 of EtOH and treated with 2 cm^3 of concentrated perchloric acid. The diperchlorate salt obtained as small yellow crystals was washed three time with 10 cm^3 of EtOH and recrystallized from water, washed with diethylether and dried under vacuum. Yield 5.2 g (68%) (**2**)·2$HClO_4$, mp 198–200 °C. Anal. Calcd for $C_{22}H_{39}Cl_2N_7O_{12}$: C, 39.64; H, 5.90; N, 14.71. Found: C, 40.2; H, 6.0; N, 14.6. Standard workup of the diperchlorate salt gave the free amine (**2**) as a red solid which was recrystallised from hot *n*-hexane. Anal. Calcd for $C_{22}H_{37}N_7O_4$: C, 56.75; H, 8.01; N, 21.06. Found: C, 56.9; H, 8.1; N, 21.0.

CAUTION: Perchlorate salts of organic ligands are potentially explosive; these compounds must be handled with great caution!

X-ray structure analysis. Single crystal analysis (**2**) was carried out with an Enraf-Nonius CAD4 X-ray diffractometer; a list of the crystallographic data is reported in Table 1. A prismatic yellow crystal of approximate dimensions 0.3 × 0.4 × 0.3 mm of (**2**) was mounted on the diffractometer and used for data collection at room temperature with graphite-monochromatized Mo-Kα radiation. Cell parameters were determined by least-squares refinement of diffractometer setting angles for 25 carefully centered reflections. The crystals of compound (**2**) belong to the monoclinic crystal family, space group $P2_1/a$, with a = 11.944(3), b = 13.587(6), c = 15.034(4) Å, β = 90.36(2)°, V = 2440(1) $Å^3$ and Z = 4. Two standard reflections were monitored during data collection and no loss of intensity observed. Intensities data were corrected for Lorentz and polarization effects. An absorption correction was applied, by using the Walker and Stuart method,[12] to the solved structure. The structure was solved by direct methods using the SIR92 package,[13] and refined by the full-matrix least-squares technique with all the non-hydrogen atoms anisotropic and the hydrogen atoms in calculated positions with overall, fixed thermal parameter U = 0.074 $Å^2$. The function minimized was $\Sigma w(|Fo|^2 - |Fc|^2)^2$, with the weighting scheme calculated in agreement to the resolution program (weighting factor 0.0972). The final agree

Table 1 Crystal data and structure refinement for (**2**)

Empirical formula	$C_{22}H_{37}N_7O_4$
Formula weight	463.59
Temperature	298 K
Wavelength	0.71069 Å
Crystal system	monoclinic
Space group	$P2_1/a$
Unit cell dimensions	a = 11.944(3) Å
	b = 13.587(6) Å
	c = 15.034(4) Å
	β = 90.36(2) deg.
Volume	2440(1) Å^3
Z	4
Density (calculated)	1.262 Mg/m^3
Absorption coefficient	0.089 mm^{-1}
F(000)	1000
Crystal size	0.3 × 0.4 × 0.3 mm
Theta range for data collection	2.64 to 24.97 deg.
Index ranges	$-14 \le h \le 14$, $0 \le k \le 16$, $0 \le l \le 13$
Scan rate	variable
Scan mode	θ − 2θ
Scan width, deg min^{-1}	0.6 + 0.35 tgθ
Reflections collected	4130
Unique obs. reflections [I > 2sigma(I)]	1211
Refined parameters	301
Transmission factors	0.96 − 0.97
w	$1/[\sigma^2(F_o^2) + (0.0972\ P)^2]^{1/2}$
P	$F_o^2/3 + 2\ F_c^2/3$
Largest diff. peak and hole	0.189 and −0.169 e.Å^{-3}
R [I > 2σ(I)][a]	0.0594
wR^2 (all data)[b]	0.1632

[a] $R = \Sigma \| F_o| - | F_c \| / \Sigma | F_o |$
[b] $wR^2 = [\Sigma\ w(F_o^2 - F_c^2)^2/\Sigma\ wF_o^4]^{1/2}$

Table 2 Atomic coordinates (×10^4) of (**2**), with estimated standard deviations in parentheses

	x/a	y/b	z/c
N(1)	8744(4)	189(3)	6728(3)
C(1)	9666(4)	489(4)	6278(4)
C(2)	10758(5)	105(4)	6384(4)
N(2)	11022(4)	−794(5)	6895(4)
O(1)	10513(4)	−1548(4)	6695(3)
O(2)	11755(4)	−757(5)	7456(4)
C(3)	11689(5)	509(5)	5981(4)
C(4)	11546(5)	1286(5)	5423(4)
N(3)	12541(6)	1731(6)	5021(4)
O(3)	12389(4)	2506(4)	4609(3)
O(4)	13444(4)	1360(4)	5137(4)
C(5)	10497(5)	1646(5)	5232(4)
C(6)	9592(5)	1253(4)	5628(4)
C(7)	7677(4)	736(4)	6605(4)
C(8)	7715(4)	1749(4)	7040(4)
C(9)	6543(5)	2098(4)	7302(4)
N(4)	6160(3)	1552(3)	8082(3)
C(10)	4949(4)	1433(4)	8102(4)
C(11)	4493(4)	737(5)	7398(4)
N(5)	5066(3)	−211(4)	7362(3)
C(12)	4764(5)	−737(5)	6544(4)
C(13)	4856(5)	−806(4)	8146(4)
C(14)	5732(5)	−1583(4)	8303(4)
N(6)	6787(3)	−1178(3)	8650(3)
C(15)	7756(5)	−1756(4)	8346(4)
C(16)	8153(5)	−1394(4)	7454(4)
C(17)	8729(5)	−399(4)	7551(4)
C(18)	6759(5)	−1009(4)	9599(4)
C(19)	7664(5)	−334(4)	9958(4)
N(7)	7733(4)	612(3)	9499(3)
C(20)	8770(5)	1112(5)	9761(4)
C(21)	6745(5)	1240(4)	9655(4)
C(22)	6584(5)	1992(4)	8918(4)

ment factors were R = 0.059 and wR^2 = 0.1632 for 1211 unique observed reflections with $I > 2\sigma(I)$ and 301 parameters. In Table 2 the final atomic coordinates with estimated standard deviations have been reported.

All calculations, carried out on a DEX 486-DX computer, were performed with the SHELXL-93 set of programs.[14] The molecular plot was produced by means of the ORTEP program.[15]

Potentiometric measurements. Me_4NNO_3 (Fluka) was used as an ionic medium. The potentiometric apparatus and its mode of operate have already been reported.[16] The E° was calculated by using the Gran method.[17] The value found for the ionic product of water was pK_w = 15.59. The program SUPERQUAD[18] was used to treat the data and calculate the protonation constants.

RESULTS AND DISCUSSION

Crystal Structure. The structure of the compound consists of discrete molecules of the unprotonated aza-macrocyclic cage (**2**). An ORTEP drawing of (**2**) with atom labeling is reported in Figure 2. In Tables 2 and 3 the atomic coordinates, bonding distances and angles have been reported respectively. The overall square-pyramidal molecular shape adopted by (**2**) is similar to that found for others aza-cages,[5–9,16] the small rigid cavity is present. A non-crystallographic C_2 axis, approximately passing through N(1) and the center of the least-squares plane formed by the four nitrogen atoms N(4), N(5), N(6) and N(7), is present. The last four basal nitrogen atoms are all in *endo* conformation respect to the ethylenic chains. The lone pair localized on N(1) points toward outside the macrocyclic cavity, this situation is imposed by the presence of the bulky 2,4-dinitrobenzene group attached to N(1) and is quite different from that found in the solid state of similar cage in which a much less bulky methyl group is attached to the apical nitrogen.[6] In the last case the lone pair is pointing toward the inside of the cavity and a proton is bound to it in the monoprotonated species. The presence of the bulky 2,4-dinitrobenzene group induces steric tension as indicated by the angles C(1)-N(1)-C(7) (119.0(5)°) and C(1)-N(1)-C(17) (126.5(5)°) which are quite different from those expected for an sp^3-hybridization. Steric interactions between the oxygen O(1) and the hydrocarbon chain connecting N(1) to N(6) causes the nitro group to rotate out of the plane of the aromatic ring. This nitro group is almost perpendicular to

the plane of the aromatic ring, this orientation reduces the electronic delocalization.

Basicity behavior. The low solubilities of (**1**) and (**2**) in water prevent their basicity constants determination in aqueous solution. For this reason a mixed solvent water/DMSO (50:50 by volume) has been employed to determine the basicity constants. The refined values for (**1**) are $\log K_1 = 12.76(8)$ and $\log K_2 = 3.84(5)$, while in the case of (**2**) in spite of the mixed solvent the solubility is too low to allow the determination of the basicity constants. Comparing the values found for (**1**) they are much lower than the values, $\log K_1 = 13.49(8)$ and $\log K_2 = 8.31(9)$, found for the related, unsubstituted cage 4,10-dimethyl-1,4,7,10,15-pentaazabicyclo[5.5.5]epta decane.[19] In this compound it has been proved that the first protonation involves the secondary amino group in apical position.[7] In (**1**) the apical nitrogen atom is tertiary and bound to a bulky, electrondrawing, dinitrobenzene group which reduce the nitrogen basicity. Furthermore, it is reasonable to expect for (**1**) a strained molecular structure similar to (**2**) (see **figure 2**), in which the presence of a bulky substituent on the apical nitrogen forces the nitrogen lone pair to point toward the outside the cavity and prevents the formation of any hydrogen bond network which could stabilize the monoprotonated species.

Lithium Complexes. Both cages are able to encapsulate selectively Li^+. The ^7Li NMR spectrum of the complex $[Li(1)]^+$, shows a sharp signal at 3.52 ppm, typical of the deshielded cation, not influenced by the solvent used: CD_3OD or $CDCl_3$, indicating that solvent molecules have not access to the coordination sphere of lithium. The ^{13}C NMR spectrum indicates a C_s symmetry, time-averaged on the NMR time scale. All these experimental evidences are consistent with a tight encapsulation of the Li^+ ion into the cage cavity. In the case of (**2**), having a slightly larger cavity than (**1**), the ^7Li NMR spectrum of the complex $[Li(2)]^+$ shows a signal at 2.50 ppm

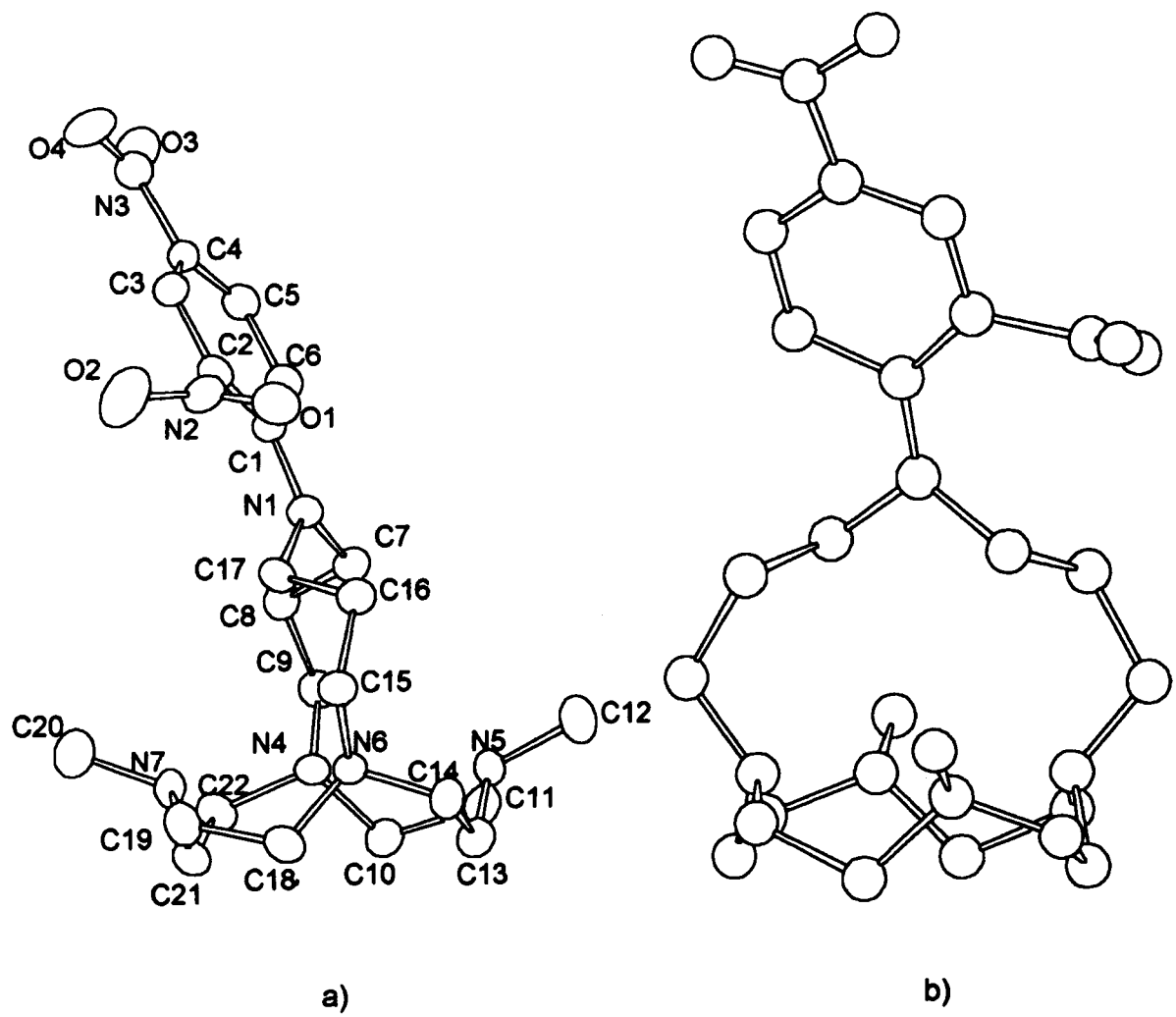


Figure 2 ORTEP drawing of **2**; a) sideview; b) front view. The thermal ellipsoids are at 30% probability level.

Table 3 Bond distances/Å and angles/° of (**2**), with estimated standard deviation in parentheses

N(1)-C(1)	1.359(7)	N(4)-C(10)	1.456(7)
N(1)-C(7)	1.486(7)	N(4)-C(22)	1.478(7)
N(1)-C(17)	1.473(7)	C(10)-C(11)	1.528(8)
C(1)-C(2)	1.413(8)	C(11)-N(5)	1.459(8)
C(1)-C(6)	1.428(8)	N(5)-C(12)	1.465(8)
C(2)-N(2)	1.476(9)	N(5)-C(13)	1.452(8)
C(2)-C(3)	1.383(8)	C(13)-C(14)	1.505(8)
N(2)-O(1)	1.228(8)	C(14)-N(6)	1.469(7)
N(2)-O(2)	1.213(8)	N(6)-C(15)	1.474(7)
C(3)-C(4)	1.400(9)	N(6)-C(18)	1.445(8)
C(4)-N(3)	1.467(9)	C(15)-C(16)	1.508(8)
C(4)-C(5)	1.373(9)	C(16)-C(17)	1.524(8)
N(3)-O(3)	1.235(9)	C(18)-C(19)	1.515(8)
N(3)-O(4)	1.203(9)	C(19)-N(7)	1.461(7)
C(5)-C(6)	1.348(8)	N(7)-C(20)	1.464(7)
C(7)-C(8)	1.524(8)	N(7)-C(21)	1.476(7)
C(8)-C(9)	1.532(8)	C(21)-C(22)	1.518(8)
C(9)-N(4)	1.464(6)		
	Angles/°		
C(1)-N(1)-C(17)	126.5(5)	C(1)-N(1)-C(7)	119.0(5)
C(17)-N(1)-C(7)	111.1(4)	N(1)-C(1)-C(2)	125.6(5)
N(1)-C(1)-C(6)	120.8(5)	C(2)-C(1)-C(6)	113.6(5)
C(3)-C(2)-C(1)	123.2(6)	C(3)-C(2)-N(2)	112.7(5)
C(1)-C(2)-N(2)	124.0(5)	O(2)-N(2)-O(1)	124.0(7)
O(2)-N(2)-C(2)	118.6(6)	O(1)-N(2)-C(2)	117.3(5)
C(4)-C(3)-C(2)	118.7(6)	C(3)-C(4)-C(5)	121.1(6)
C(3)-C(4)-N(3)	118.4(6)	C(5)-C(4)-N(3)	120.5(7)
O(4)-N(3)-O(3)	124.0(7)	O(4)-N(3)-C(4)	119.7(7)
O(3)-N(3)-C(4)	116.2(7)	C(6)-C(5)-C(4)	120.0(6)
C(6)-C(5)-C(4)	120.0(6)	C(5)-C(6)-C(1)	122.9(6)
N(1)-C(7)-C(8)	112.0(4)	C(7)-C(8)-C(9)	111.4(5)
N(4)-C(9)-C(8)	109.9(5)	C(10)-N(4)-C(9)	112.9(4)
C(10)-N(4)-C(22)	111.3(4)	C(9)-N(4)-C(22)	111.7(4)
N(4)-C(10)-C(11)	113.8(5)	N(5)-C(11)-C(10)	113.6(4)
C(13)-N(5)-C(11)	112.6(5)	C(13)-N(5)-C(12)	111.5(5)
C(11)-N(5)-C(12)	109.9(5)	N(5)-C(13)-C(14)	113.2(5)
N(6)-C(14)-C(13)	112.7(5)	C(18)-N(6)-C(14)	112.6(4)
C(18)-N(6)-C(15)	114.5(4)	C(14)-N(6)-C(15)	111.3(4)
N(6)-C(15)-C(16)	110.7(5)	C(15)-C(16)-C(17)	110.4(5)
N(1)-C(17)-C(16)	114.1(5)	N(6)-C(18)-C(19)	115.3(5)
N(7)-C(19)-C(18)	114.0(5)	C(20)-N(7)-C(19)	109.4(4)
C(20)-N(7)-C(21)	111.4(4)	C(19)-N(7)-C(21)	112.7(5)
N(7)-C(21)-C(22)	111.8(5)	N(4)-C(22)-C(21)	112.9(5)

insensible to the solvent used. The ^{13}C NMR spectrum of $[Li(2)]^+$ is fluxional and cannot be resolved. The Li^+ complexation is not influenced by the presence of Na^+, even at high concentration, confirming the total selectivity of these ligands toward Li^+. Both cages are colored as expected for nitro derivatives: λ_{max} = 347 nm and 391 nm in methanol for (**1**) and (**2**) respectively. Unfortunately on lithium complexation the colors of the ligands do not change. What really changes is the absorption intensity: ϵ = 12700 and 7000 for (**1**) and $[Li(1)]^+$ respectively.

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