# Alkali-metal Complexes with Neutral Molecular Receptors containing Nitrogen Donor Atoms: a Crystallographic and Multinuclear Magnetic Resonance Study†

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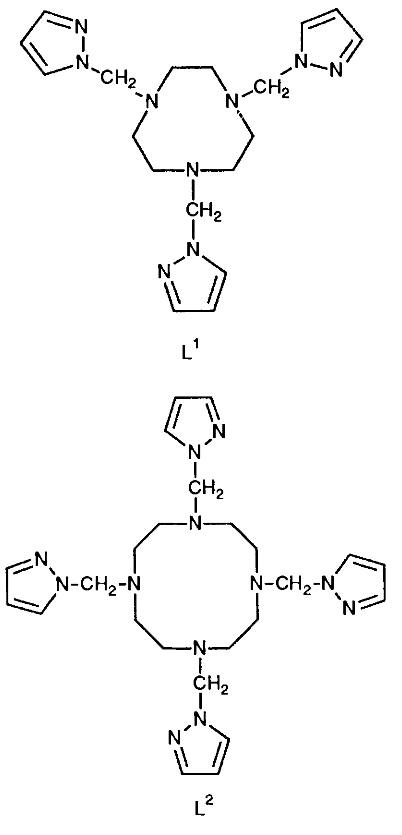
The pyrazole-functionalized macrocyclic ligands 1,4,7-tris(pyrazol-1-ylmethyl)-1,4,7-triazacyclononane $L^1$ and 1,4,7,10-tetrakis(pyrazol-1-ylmethyl)-1,4,7,10-tetraazacyclododecane $L^2$ form stable complexes of formula $[ML]BPh_4$ (M = Li or Na, L = $L^1$ or $L^2$) with alkali-metal cations. The crystal and molecular structure of $[LiL^1]BPh_4$ has been determined by X-ray diffraction: space group $P\bar{1}$, $a = 11.985(5)$, $b = 18.596(6)$, $c = 20.932(4)$ Å, $\alpha = 110.96(3)$, $\beta = 91.38(3)$ and $\gamma = 108.63(3)°$. The metal ion is in a six-co-ordinated environment formed by the nitrogen atoms of the macrocyclic frame and by the unsubstituted nitrogen atoms of the pendant pyrazole groups. This structure is compared with that previously reported for $[NaL^2]BPh_4$ which contains eight-co-ordinated sodium. The $^1H$, $^{13}C$, $^7Li$ and $^{23}Na$ NMR spectral data for the compounds in solution are presented.

Cyclic and acyclic ethers have been known for a long time as good receptors for alkali metals and the numerous studies on their complexes have allowed an appreciation of the relationships between molecular architecture and chemical function.[1] The continuing search for new synthetic molecular receptors capable of host–guest relationships with organic and inorganic ions has recently shown that also calixarenes, owing to their rigid structures and their ability to preorganize donor atoms around the periphery of a central cavity, form a valuable class of molecular receptors.[2] Notwithstanding the large interest in the above host molecules that invariably contain oxygen donors, it has recently become apparent that polydentate molecules containing amine[3] or amine and imine[4] nitrogen atoms form stable compounds with low-atomic-number alkali metals, particularly lithium. Such molecules present the nitrogen donors either on a macrocyclic ring which provides a hole of the proper size to accommodate the cation[4] or on a macrobicyclic framework forming a cavity into which the metal fits.[3] It appears accordingly that the most important factors which determine the complexing ability of these ligands are the rigidity of the receptor skeleton and the arrangement of the donors about the co-ordination sphere of the metal ions.

Described herein are lithium and sodium complexes with the potentially hexa- and octa-dentate ligands 1,4,7-tris(pyrazol-1-ylmethyl)-1,4,7-triazacyclononane $L^1$, and 1,4,7,10-tetrakis(pyrazol-1-ylmethyl)-1,4,7,10-tetraazacyclododecane $L^2$, which provide flexible frameworks, with three or, respectively, four nitrogen atoms on their pendant arms and the remaining N donors in macrocyclic rings whose bonding cavity is too small to accommodate cations. A preliminary account of the crystal structure of the sodium derivative $[NaL^2]BPh_4$ has already appeared.[5]



Scheme 1

## Experimental

All reactions and manipulations were carried out in the air. Solvents were freshly distilled from the appropriate drying agents immediately before use. Electronic spectra were recorded in the range 300–1000 nm with a Perkin-Elmer Lambda 9 spectrophotometer; concentrations of the solutions were about $10^{-4}$ mol dm$^{-3}$. The $^1H$ NMR spectra of the $[ML^1]BPh_4$ (M = Li or Na) compounds and all of the $^{13}C$, $^7Li$ and $^{23}Na$ NMR spectra were obtained on a Bruker CXP instrument operating at 90.02, 22.67, 34.98 and 23.80 MHz, respectively. The $^1H$ NMR spectra of the compounds $[ML^2]BPh_4$ (M = Li or Na) were collected on a Bruker MSL instrument operating at 200.13 MHz. The $^1H$ and $^{13}C$ chemical shifts are reported in ppm downfield with respect to the internal standard $SiMe_4$, the $^7Li$ chemical shifts downfield with respect to LiCl (0.30 mol

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

dm$^{-3}$) in $D_2O$ as external standard, and the $^{23}$Na chemical shifts relative to NaCl (0.25 mol dm$^{-3}$) in $D_2O$ as external standard (0.0 ppm).[6] The NMR spectroscopic data are summarized in Tables 3–5. Elemental analyses (Li and Na) were performed by Mikroanalytisches Labor Pascher, Remagen, FRG. The ligand $L^2$ was synthesised as described previously;[7] $L^1$ was obtained through the same procedure from 1,4,7-triazacyclononane[8] and 1-(hydroxymethyl)pyrazole[9] in 1:3 stoichiometric ratio.

*Synthesis of the Compounds.*—$[LiL^1]BPh_4$. The salt $LiBPh_4$ (0.33 g, 1 mmol) dissolved in absolute ethanol (20 cm$^3$) was added to an acetone solution (30 cm$^3$) of $L^1$ (0.37 g, 1 mmol). White crystals of $[LiL^1]BPh_4$ were obtained by slow concentration of the resulting solution under reduced pressure at room temperature. The product was collected by suction filtration, washed with small amounts of ethanol followed by diethyl ether, and finally dried in a vacuum oven. Recrystallization from acetone and ethanol gave the pure product. Yield 90%. Crystals used for X-ray work, containing $Me_2CO$ solvate molecules (see below), were obtained by slow evaporation in a desiccator of a dilute solution of the complex in an acetone–ethanol mixture. The complex is soluble in $Me_2CO$, $CH_2Cl_2$ and $CHCl_3$ (Found: C, 72.45; H, 6.90; Li, 0.95; N, 18.05. $C_{42}H_{47}BLiN_9$ requires C, 72.50; H, 6.80; Li, 1.00; N, 18.10%).

$[NaL^1]BPh_4$. The same procedure was used to obtain the sodium derivative (yield 87%) (Found: C, 70.75; H, 6.75; N, 17.60; Na, 3.15. $C_{42}H_{47}BN_9Na$ requires C, 70.90; H, 6.65; N, 17.70; Na, 3.25%).

The $L^2$ derivatives were also obtained as above: $[LiL^2]BPh_4$ (yield 90%) (Found: C, 70.15; H, 7.00; Li, 0.65; N, 20.65. $C_{48}H_{56}BLiN_{12}$ requires C, 70.40; H, 6.90; Li, 0.85; N, 20.55%); $[NaL^2]BPh_4$ (yield 85%) (Found: C, 69.00; H, 6.85; N, 20.10; Na, 2.70. $C_{48}H_{56}BN_{12}Na$ requires C, 69.05; H, 6.75; N, 20.15; Na, 2.75%).

*Extraction Experiments.*—Solutions of alkali-metal and ammonium picrates were prepared in water by treating picric acid with the appropriate metal hydroxide or ammonia in slight excess (5.0%) with respect to the stoichiometric ratio. The extraction experiments were carried out at room temperature using aqueous solutions (10 cm$^3$) of alkali-metal or ammonium picrates (about $10^{-4}$ mol dm$^{-3}$) and solutions in $CH_2Cl_2$ (10 cm$^3$) of either $L^1$ or $L^2$, whose concentration was 20% higher than that of the metal or ammonium cations. In a typical experiment the $CH_2Cl_2$ solution of the receptor and the aqueous solution of the picrate were mixed and immediately after the electronic spectra of both phases were registered. Thereafter the two layers were stirred with a magnetic rod and the absorbance of each phase was measured spectrophotometrically at intervals of 5 or 10 min for a period of 1 h and finally after 1 d. The percentage of the picrate ion was computed by comparing the molar absorption coefficient at 354 nm for the water solutions of the metal or ammonium picrates[10] with that of the water solutions of the extraction experiments. The percentage in the organic phase was computed by difference.

*Crystal Structure Determination of* $[LiL^1]BPh_4{\cdot}0.5Me_2CO$.—*Crystal data.* $C_{43.5}H_{50}BLiN_9O_{0.5}$, $M = 724.69$, triclinic, space group $P\bar{1}$, $a = 11.985(5)$, $b = 18.596(6)$, $c = 20.932(4)$ Å, $\alpha = 110.96(3)$, $\beta = 91.38(3)$, $\gamma = 108.63(3)°$, $U = 4078(2)$ Å$^3$, $Z = 4$, $D_c = 1.180$ g cm$^{-3}$, $F(000) = 1544$, $\mu$(Cu-K$\alpha$) = 5.27 cm$^{-1}$.

*Data collection.* A prismatic crystal (0.30 × 0.50 × 1.00 mm) was mounted on an Enraf-Nonius CAD4 diffractometer [$\lambda$(Cu-K$\alpha$) = 1.5418 Å, graphite monochromator]. Unit-cell parameters were determined from least-squares refinement of 24 reflections having $44 < 2\theta < 54°$. The intensities of $\pm h, \pm k, +l$ reflections in the $2\theta$ range 6–110° were measured in the $\omega$–$2\theta$ scan mode with a scan width $(1.10 + 0.14 \tan\theta)°$ and variable (4–16° min$^{-1}$) scan speed. Three standard reflections measured every 6000 s showed a steady, 10% overall, decay, which was corrected for. Out of 10 237 reflections measured 7968 having $I > 3\sigma(I)$ were used in subsequent calculations. Intensity data were corrected for Lorentz and polarization effects. A correction for absorption effects by an empirical procedure,[11] performed at isotropic convergence when the structure was solved, yielded no significant differences in parameter values with respect to those obtained from refinements in which the uncorrected data were used. In view of this and of the small $\mu$ value no correction for absorption was applied to the data used in the final refinement. Additional computer programs used in the crystallographic calculations are listed in refs. 12–14. Scattering factors for the neutral atoms and $Li^+$ were taken from ref. 15.

*Structure solution and refinement.* The structure was solved by direct methods.[12] A set of Fourier maps yielded the positions of all non-hydrogen atoms. The least-squares refinement was performed in two blocks, the function $\Sigma w(|F_o| - |F_c|)^2$ being minimized, where $w = [\sigma^2(F_o) + 0.0015F_o^{\,2}]^{-1}$. In the final cycles, anisotropic thermal parameters were assigned to all atoms heavier than Li in the cations or anions. Hydrogen atoms were introduced in calculated positions with C–H 1.00 Å and $U_H$ values 20% larger than the $U_{eq}$ of the corresponding carbon atoms. The model chosen for the solvate acetone molecule, which was affected by disorder, consisted of two regular triangles of C atoms, with a common central C atom and complementary population parameters. The size of each triangle was refined and its atoms were assigned an overall isotropic thermal parameter, whereas the central C atom was refined anisotropically. The final cycle (987 parameters, largest shift/error ratio < 0.05:1) gave $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.075$ and $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^{\,2}]^{\frac{1}{2}} = 0.086$. Extreme values of residual electron density in the final $\Delta F$ Fourier map were 0.66 and −0.30 e Å$^{-3}$, all peaks > 0.3 e Å$^{-3}$ being in the region occupied by the solvent.

Atomic coordinates are listed in Table 1 and selected bond lengths and angles in Table 2.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

## Results and Discussion

The reaction of the potentially hexa- and octa-dentate ligands $L^1$ and $L^2$, with $LiBPh_4$ and $NaBPh_4$ in acetone–absolute ethanol mixture gives complexes of general formula $[ML]BPh_4$ (M = Li or Na, L = $L^1$ or $L^2$) which have been isolated in the solid state. The structure in the solid state of the complex $[LiL^1]BPh_4{\cdot}0.5Me_2CO$ has been established by X-ray diffraction methods. The behaviour in solution of the complexes has been investigated by means of $^1$H, $^{13}$C, $^7$Li and $^{23}$Na NMR spectroscopy. Extraction experiments on aqueous solutions of some alkali-metal and ammonium picrates have been carried out using $CH_2Cl_2$ solutions of either $L^1$ or $L^2$.

*Crystal Structure of* $[LiL^1]BPh_4{\cdot}0.5Me_2CO$.—The structure of the compound $[LiL^1]BPh_4{\cdot}0.5Me_2CO$ consists of $[LiL^1]^+$ cations, $BPh_4^-$ anions, and acetone solvate molecules affected by disorder. The crystallographic asymmetric unit contains the ions corresponding to two $[LiL^1]BPh_4$ formula units and one solvent molecule. The $Li^+$ ion in each of the two independent $[LiL^1]^+$ complex cations is surrounded by a set of six N atoms (Figs. 1 and 2), three of which belong to the macrocycle, the other three being provided by the dangling pyrazole groups. The co-ordination geometry and the dimensions of the co-ordination polyhedra in the two $[LiL^1]^+$ cations are closely similar (Table 2) so that mean values of geometrical parameters will be generally quoted in the following. The co-ordination geometry is intermediate between trigonal prismatic and octahedral. The basal faces of the prism, respectively defined by the macrocycle and the pyrazole nitrogens, are rotated by *ca.* 40° with respect to each other about the pseudo-three-fold axis

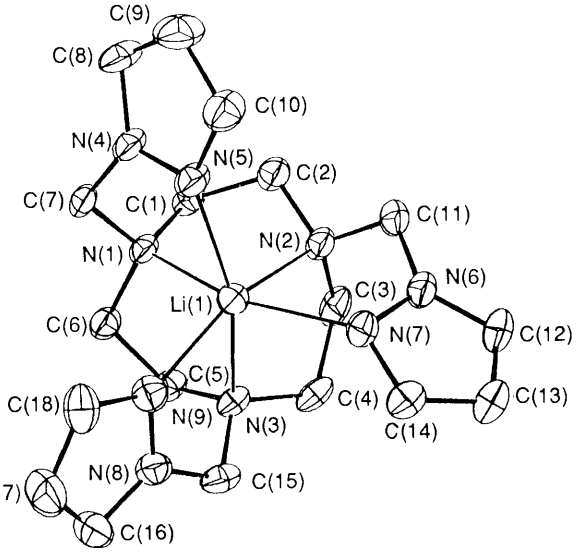

**Fig. 1** View of one of the two independent $[LiL^1]^+$ cations in the structure of $[LiL^1]BPh_4{\cdot}0.5Me_2CO$, along the pseudo-three-fold axis. An analogous labelling criterion has been adopted for the other cation, which has a closely similar structure to that shown.

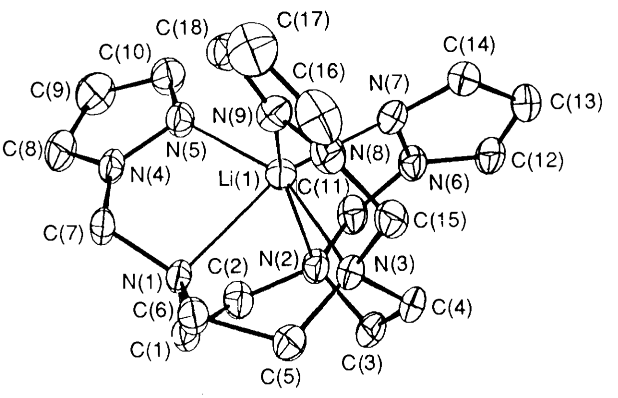

**Fig. 2** View of the $[LiL^1]^+$ cation along a direction perpendicular to the pseudo-three-fold axis

of the complex cation passing through the $Li^+$ ion position (Fig. 1). The planes of the basal faces are substantially parallel, their normals forming angles $< 2°$ with each other (Fig. 2). The metal ions deviate by 1.56(2) Å from the plane of the macrocycle nitrogens and by 0.89(1) Å from that of the pyrazole N atoms, so that the distance between these planes in proximity of the $Li^+$ position is 2.45(2) Å. Additional parameters relevant to an estimate of the dimensions of the cages surrounding the metal ions are the non-bonded N···N distances between the macrocycle nitrogens (2.85–2.88 Å) and between the pyrazole nitrogens (3.28–3.50 Å). The distances to the metal formed by the pyrazole nitrogens [2.15(5) Å, mean] are shorter than those formed by the aminic ones [2.27(2) Å] in agreement with what is generally observed.[5,7,16a] The present Li–N distances are in the range of those found for other lithium derivatives formed by macrocyclic ligands, although close comparisons are difficult due to the spread of values reported and to the preponderant effects of constraints imposed by individual ligands.[3,4]

The structure of the compound $[NaL^2]BPh_4$ has recently been reported as a part of a preliminary communication.[5] A view of the $[NaL^2]^+$ cation is shown here for convenience (Fig. 3). A two-fold axis passes through the $Na^+$ ion which is octa-co-ordinated in a prismatic arrangement of N atoms; with the basal faces rotated by *ca.* 31.4° about the two-fold axis with respect to each other. The Na–N distances are, in the mean, 2.702(4) Å and 2.582(5) Å for the macrocycle and the pyrazole nitrogens, respectively, showing consistent increases of *ca.* 0.43 Å with respect to the corresponding mean distances in the

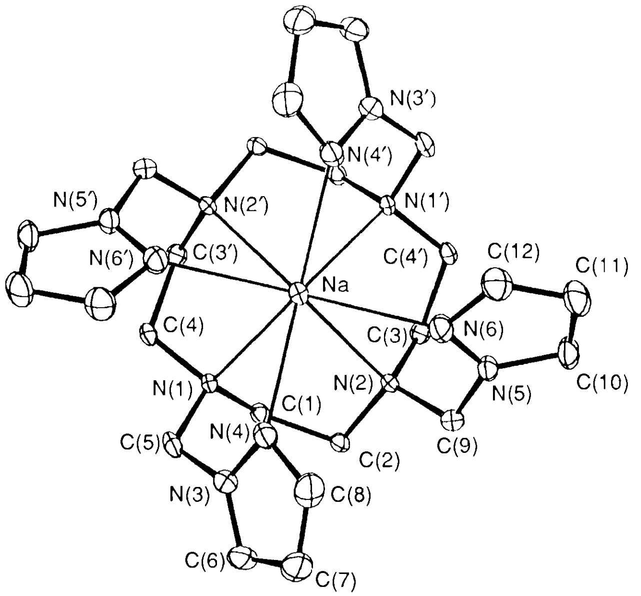

**Fig. 3** Structure of the $[NaL^2]^+$ cation. Primed atoms are related to the corresponding unprimed ones by a two-fold axis passing through the sodium atom position.

$[LiL^1]^+$ cation. Such increases are well in line with those expected in view of the ionic radii of the two metals involved, when the change in co-ordination number is taken into account.[17] The N atoms forming the two sets of four basal donors in the $[NaL^2]BPh_4$ structure do not deviate significantly from the respective planes. The metal ion lies 1.627(3) Å from the plane of the macrocycle N atoms and 1.029(3) Å from that of the pyrazole donors. The separation between such planes, which are parallel by symmetry, is 2.66(1) Å. The N···N non-bonded distances measure 3.05(1) (macrocycle) and 3.35(1) Å (pyrazole N atoms), both values being averages over two symmetry-independent distances. Remarkably, the latter value is in the range of those found for the lithium $L^1$ derivative. This suggests that N···N distances in the range 3.3–3.5 Å are dictated by non-bonded interactions between the pyrazole groups of the dangling arms without additional constraints imposed by the flexible ligands.

*Behaviour of the Complexes in Solution.*—The $^1H$, $^{13}C$, $^7Li$ and $^{23}Na$ NMR data in *ca.* $10^{-3}$ mol $dm^{-3}$ $CD_2Cl_2$ solutions are reported in Tables 3–5. The $L^1$ complexes exhibit a single sharp resonance (Table 4) both for $^7Li$ and $^{23}Na$. In particular, $[LiL^1]BPh_4$ presents a $^7Li$ resonance shifted downfield with respect to that of an equimolar solution of $LiBPh_4$ in $CD_2Cl_2$. On the other hand, the $^{23}Na$ shift of $[NaL^1]BPh_4$ in $CD_2Cl_2$ solution cannot be compared with that of NaCl in $D_2O$ solution because the resonances are very sensitive to the nature of both the solvent and the anion. The sharp $^7Li$ ($\nu_{\frac{1}{2}}$ 1 Hz) and $^{23}Na$ ($\nu_{\frac{1}{2}}$ 48 Hz) signals are suggestive of no exchange or, at most, of a slow exchange of the cations on the NMR time-scale and of a symmetric electric field gradient around the metal ions.[18] The $^7Li$ spectra have been measured as a function of the ligand:lithium mole ratio as well as of the concentration. Those with mole ratio $< 1$ exhibit several sharp $^7Li$ signals (Table 4): besides those attributable to the complexed $Li^+$ cation in $[LiL^1]^+$ and to uncomplexed $Li^+$ in $Li^+BPh_4^-$ ion pairs, there are additional resonances with intermediate shifts with respect to those of the former species. The relative intensities and, to a lesser extent, the shifts of such resonances are concentration dependent. Such features are indicative of the coexistence of $[LiL^1]^+$ complex cations, uncomplexed $Li^+BPh_4^-$ ion pairs, and of the same ion pairs interacting with the $L^1$ ligand. Similar behaviour has previously been observed for solutions of lithium salts and macrocyclic ligands in solvents with low relative permittivity.[19] The $^7Li$ NMR spectrum of a solution containing

**Table 1** Atomic coordinates for $[LiL^1]BPh_4 \cdot 0.5Me_2CO$[a]

| Atom | *x* | *y* | *z* | Atom | *x* | *y* | *z* |
|---|---|---|---|---|---|---|---|
| Li(1) | 0.2067(5) | 0.2371(3) | 0.7808(3) | C(42) | 0.6458(3) | 0.6404(2) | 0.8614(2) |
| Li(2) | 0.0430(5) | 0.8342(3) | 0.7063(3) | C(43) | 0.7426(4) | 0.6196(3) | 0.8742(2) |
| N(1) | 0.1343(2) | 0.3412(2) | 0.8061(2) | C(44) | 0.8465(3) | 0.6797(3) | 0.9147(2) |
| N(2) | 0.2975(3) | 0.3175(2) | 0.8913(2) | C(45) | 0.8531(3) | 0.7598(3) | 0.9409(2) |
| N(3) | 0.3575(2) | 0.3347(2) | 0.7639(2) | C(46) | 0.7542(3) | 0.7800(2) | 0.9276(2) |
| N(4) | −0.0290(2) | 0.2314(2) | 0.8105(2) | C(51) | 0.5633(3) | 0.8419(2) | 0.8945(2) |
| N(5) | 0.0339(3) | 0.1809(2) | 0.8008(2) | C(52) | 0.5673(3) | 0.8786(2) | 0.8465(2) |
| N(6) | 0.3681(3) | 0.2069(2) | 0.8680(2) | C(53) | 0.6002(3) | 0.9635(2) | 0.8655(2) |
| N(7) | 0.3173(3) | 0.1703(2) | 0.8012(2) | C(54) | 0.6300(3) | 1.0148(2) | 0.9337(2) |
| N(8) | 0.2730(3) | 0.2368(2) | 0.6500(2) | C(55) | 0.6249(4) | 0.9813(3) | 0.9827(2) |
| N(9) | 0.1799(3) | 0.1953(2) | 0.6727(2) | C(56) | 0.5930(3) | 0.8971(2) | 0.9631(2) |
| N(10) | 0.2139(3) | 0.8886(2) | 0.7819(2) | C(61) | 0.4671(3) | 0.6897(2) | 0.7933(2) |
| N(11) | 0.1557(2) | 0.7641(2) | 0.6447(2) | C(62) | 0.5324(3) | 0.6979(2) | 0.7403(2) |
| N(12) | 0.0243(3) | 0.7355(2) | 0.7519(1) | C(63) | 0.4836(4) | 0.6574(3) | 0.6701(2) |
| N(13) | 0.1012(3) | 0.9664(2) | 0.8438(2) | C(64) | 0.3649(4) | 0.6036(3) | 0.6505(2) |
| N(14) | 0.0003(3) | 0.9207(2) | 0.7960(2) | C(65) | 0.3009(3) | 0.5915(2) | 0.7008(2) |
| N(15) | 0.1575(3) | 0.8546(2) | 0.5893(2) | C(66) | 0.3498(3) | 0.6337(2) | 0.7705(2) |
| N(16) | 0.1007(3) | 0.8949(2) | 0.6365(2) | C(71) | 0.4262(3) | 0.7141(2) | 0.9221(2) |
| N(17) | −0.1595(3) | 0.6865(2) | 0.6791(2) | C(72) | 0.3402(3) | 0.7515(2) | 0.9393(2) |
| N(18) | −0.1289(3) | 0.7492(2) | 0.6571(2) | C(73) | 0.2468(4) | 0.7241(3) | 0.9728(2) |
| C(1) | 0.1661(3) | 0.3928(2) | 0.8797(2) | C(74) | 0.2369(4) | 0.6588(3) | 0.9918(2) |
| C(2) | 0.2087(4) | 0.3530(3) | 0.9224(2) | C(75) | 0.3189(4) | 0.6212(2) | 0.9766(2) |
| C(3) | 0.4105(3) | 0.3799(3) | 0.8912(2) | C(76) | 0.4124(3) | 0.6487(2) | 0.9423(2) |
| C(4) | 0.4531(3) | 0.3584(3) | 0.8206(2) | C(81) | 0.8730(3) | 0.3641(2) | 0.6112(2) |
| C(5) | 0.3196(3) | 0.4030(2) | 0.7654(2) | C(82) | 0.9465(3) | 0.3174(3) | 0.6028(2) |
| C(6) | 0.1846(3) | 0.3819(2) | 0.7598(2) | C(83) | 1.0517(5) | 0.3354(4) | 0.5783(2) |
| C(7) | 0.0062(3) | 0.2965(2) | 0.7835(2) | C(84) | 1.0901(4) | 0.4019(4) | 0.5605(3) |
| C(8) | −0.1210(4) | 0.2115(3) | 0.8446(3) | C(85) | 1.0218(5) | 0.4495(3) | 0.5649(2) |
| C(9) | −0.1183(4) | 0.1455(3) | 0.8564(3) | C(86) | 0.9128(4) | 0.4295(3) | 0.5906(2) |
| C(10) | −0.0206(4) | 0.1289(3) | 0.8292(3) | C(91) | 0.8098(3) | 0.3956(2) | 0.7355(2) |
| C(11) | 0.3132(4) | 0.2579(3) | 0.9173(2) | C(92) | 0.9166(3) | 0.4614(2) | 0.7637(2) |
| C(12) | 0.4701(3) | 0.1941(3) | 0.8786(3) | C(93) | 0.9579(4) | 0.4999(3) | 0.8337(2) |
| C(13) | 0.4873(4) | 0.1472(3) | 0.8157(3) | C(94) | 0.8931(4) | 0.4745(3) | 0.8794(2) |
| C(14) | 0.3920(3) | 0.1334(2) | 0.7690(2) | C(95) | 0.7858(4) | 0.4099(3) | 0.8547(2) |
| C(15) | 0.3825(4) | 0.2892(3) | 0.6971(2) | C(96) | 0.7476(3) | 0.3723(3) | 0.7845(2) |
| C(16) | 0.2508(5) | 0.2151(4) | 0.5808(3) | C(101) | 0.6669(3) | 0.3906(2) | 0.6315(2) |
| C(17) | 0.1395(6) | 0.1592(4) | 0.5581(3) | C(102) | 0.6227(3) | 0.4440(2) | 0.6796(2) |
| C(18) | 0.0985(4) | 0.1487(3) | 0.6150(3) | C(103) | 0.5386(3) | 0.4744(2) | 0.6603(2) |
| C(19) | 0.3057(3) | 0.8885(2) | 0.7364(2) | C(104) | 0.4984(3) | 0.4512(2) | 0.5921(2) |
| C(20) | 0.2804(3) | 0.8019(2) | 0.6804(2) | C(105) | 0.5422(4) | 0.4008(3) | 0.5425(2) |
| C(21) | 0.0961(3) | 0.6799(2) | 0.6400(2) | C(106) | 0.6263(3) | 0.3719(3) | 0.5629(2) |
| C(22) | 0.0768(3) | 0.6756(2) | 0.7094(2) | C(111) | 0.6842(3) | 0.2503(2) | 0.6318(2) |
| C(23) | 0.0855(3) | 0.7826(2) | 0.8223(2) | C(112) | 0.5811(4) | 0.2041(3) | 0.5853(2) |
| C(24) | 0.2124(4) | 0.8410(3) | 0.8253(2) | C(113) | 0.5222(5) | 0.1213(3) | 0.5690(3) |
| C(25) | 0.2160(3) | 0.9707(2) | 0.8206(2) | C(114) | 0.5641(5) | 0.0808(3) | 0.6003(3) |
| C(26) | 0.0756(5) | 0.0000(3) | 0.9071(2) | C(115) | 0.6647(6) | 0.1225(3) | 0.6474(4) |
| C(27) | −0.0442(5) | 0.9758(3) | 0.9020(2) | C(116) | 0.7227(4) | 0.2052(3) | 0.6616(3) |
| C(28) | −0.0879(4) | 0.9259(3) | 0.8320(2) | B(1) | 0.5261(3) | 0.7427(2) | 0.8750(2) |
| C(29) | 0.1442(4) | 0.7709(2) | 0.5787(2) | B(2) | 0.7579(3) | 0.3494(3) | 0.6516(2) |
| C(30) | 0.2159(4) | 0.9007(3) | 0.5552(3) | C(121) | 0.3263(5) | 0.0950(4) | 0.3584(3) |
| C(31) | 0.1963(4) | 0.9735(3) | 0.5811(3) | C(122)[b] | 0.1832(5) | 0.0524(5) | 0.3433(5) |
| C(32) | 0.1254(4) | 0.9668(3) | 0.6307(2) | C(123)[b] | 0.4059(6) | 0.0515(5) | 0.3083(4) |
| C(33) | −0.1041(3) | 0.7004(2) | 0.7473(2) | C(124)[b] | 0.3902(7) | 0.1732(5) | 0.4294(4) |
| C(34) | −0.2357(3) | 0.6170(3) | 0.6316(2) | C(125)[c] | 0.2430(11) | 0.0692(9) | 0.4031(6) |
| C(35) | −0.2595(3) | 0.6348(3) | 0.5772(2) | C(126)[c] | 0.4330(10) | 0.1696(8) | 0.3887(6) |
| C(36) | −0.1917(3) | 0.7165(3) | 0.5942(2) | C(127)[c] | 0.2981(12) | 0.0497(9) | 0.2829(3) |
| C(41) | 0.6467(3) | 0.7212(2) | 0.8884(2) | | | | |

[a] In this and the following crystallographic Table estimated standard deviations in the least significant digit(s) are given in parentheses. Atoms Li(1)–C(36) belong to the two cations in the asymmetric unit, C(41)–B(2) to the anions, and C(121)–C(127) to the two images of the disordered acetone molecule. [b] Atomic position affected by disorder, site with population parameter (p.p.) 0.606(2). [c] p.p. = 0.394(2).

a 1:1 ligand:metal ratio exhibits a concentration-independent, single and sharp resonance at the same frequency as that occurring for a solution of authentic $[LiL^1]BPh_4$. This peak does not change upon further ligand additions (spectra recorded up to a 2:1 ligand:lithium mole ratio). The unique $^7Li$ resonance indicates that the complexed cation in $CD_2Cl_2$ solution is fully shielded from the influence of the medium and of the anion as expected for a six-co-ordinate $[LiL^1]^+$ species in solution as it is in the solid state (Fig. 1).

The $^1H$ NMR data for $[LiL^1]BPh_4$ in $CD_2Cl_2$ solution (Table 3) present features that are in line with a high co-ordination number of the cation in a highly symmetric environment. The hydrogen atoms of the ethylene chains of the macrocyclic ring yield a complicated multiplet, having an AA′BB′ pattern, that is split into two mirror-related groups of signals ($\delta_A$ 2.31–2.67, $\delta_B$ 1.54–1.90) and corresponds to two groups of magnetically non-equivalent protons, six of these being in equatorial positions and six in axial positions with respect to the plane of the co-ordinated 1,4,7-triazacyclononane ring.[20] The protons of the methylene arms yield a single

**Table 2** Selected bond distances (Å) and angles (°) for the compound $[LiL^1]BPh_4 \cdot 0.5Me_2CO$

| | | | |
|---|---|---|---|
| Li(1)–N(1) | 2.268(8) | Li(2)–N(10) | 2.259(6) |
| Li(1)–N(2) | 2.266(6) | Li(2)–N(11) | 2.280(7) |
| Li(1)–N(3) | 2.253(7) | Li(2)–N(12) | 2.310(8) |
| Li(1)–N(5) | 2.128(7) | Li(2)–N(14) | 2.189(7) |
| Li(1)–N(7) | 2.211(9) | Li(2)–N(16) | 2.148(8) |
| Li(1)–N(9) | 2.092(7) | Li(2)–N(18) | 2.110(6) |
| N(1)–Li(1)–N(2) | 78.0(2) | N(10)–Li(2)–N(11) | 78.3(2) |
| N(1)–Li(1)–N(3) | 78.6(2) | N(10)–Li(2)–N(12) | 77.6(3) |
| N(2)–Li(1)–N(3) | 79.1(2) | N(11)–Li(2)–N(12) | 77.7(3) |
| N(1)–Li(1)–N(5) | 78.9(3) | N(10)–Li(2)–N(14) | 78.3(2) |
| N(2)–Li(1)–N(7) | 77.5(2) | N(11)–Li(2)–N(16) | 77.5(2) |
| N(3)–Li(1)–N(9) | 78.9(2) | N(12)–Li(2)–N(18) | 78.5(2) |
| N(5)–Li(1)–N(7) | 105.9(3) | N(14)–Li(2)–N(16) | 107.6(3) |
| N(5)–Li(1)–N(9) | 102.1(2) | N(14)–Li(2)–N(18) | 101.0(3) |
| N(7)–Li(1)–N(9) | 102.9(3) | N(16)–Li(2)–N(18) | 103.8(3) |

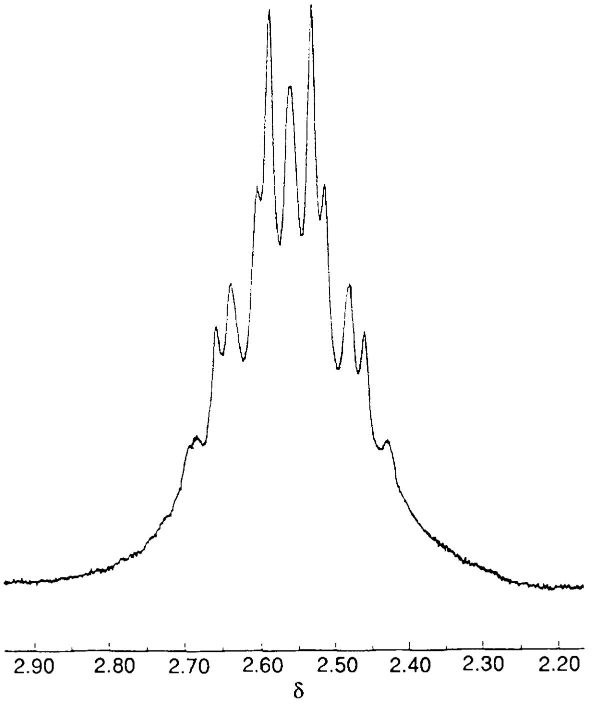

**Fig. 4** Proton NMR spectrum of the macrocyclic framework of $[NaL^2]BPh_4$ in $CD_2Cl_2$ (200 MHz)

resonance which is shifted to high field with respect to that of the free ligand (Table 3). The complexation reaction produces only small shifts of the $^{13}C$ NMR resonances of the ligand carbon atoms, as previously observed for alkali-metal complexes with crown ethers.[18]

The $^1H$ and $^{13}C$ NMR data for the $[NaL^1]BPh_4$ complex closely parallel those of the corresponding lithium derivative (Tables 3 and 5). Accordingly, six-co-ordination is also assigned to the $[NaL^1]^+$ cation in solution.

The NMR data for the $[LiL^1]BPh_4$ and $[NaL^1]BPh_4$ complexes in *ca.* $10^{-3}$ mol dm$^{-3}$ $(CD_3)_2CO$ solutions are reported in Table 4. The proton resonances of the alkane chains in the lithium derivative exhibit smaller shifts with respect to the free ligand in $(CD_3)_2CO$ than in $CD_2Cl_2$ solution. For the sodium complex in $(CD_3)_2CO$ the peaks occur approximately at the same frequency as for the free ligand, at variance with what is found for the $CD_2Cl_2$ solution. This suggests that sodium is less strongly co-ordinated than lithium by the $L^1$ ligand in acetone solution, both cations being less strongly co-ordinated in acetone than in dichloromethane solution, which is in accord with the greater donor ability of the former solvent. The easier access of co-ordinating solvent molecules to the $Na^+$ than the $Li^+$ cation may be due to the weaker ion–dipole interactions between the former ion and the ligand $L^1$ as well as to structurally based kinetic factors related to the cation:cage size ratios.

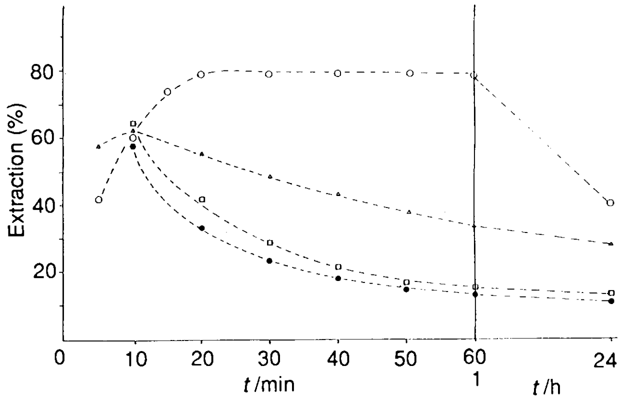

**Fig. 5** Extraction data for alkali-metal and ammonium picrates. Experimental conditions: aqueous phase (10 × $10^{-3}$ dm$^3$), *ca.* $10^{-4}$ mol dm$^{-3}$ picrate; organic phase ($CH_2Cl_2$, 10 × $10^{-3}$ dm$^3$), *ca.* 1.2 × $10^{-4}$ mol dm$^{-3}$ $L^2$; room temperature. Cations: $Li^+$ (○), $Na^+$ (□), $K^+$ (△), and $NH_4^+$ (●).

The $^{23}Na$ and $^1H$ NMR spectra of $[NaL^2]BPh_4$ in $CD_2Cl_2$ solution exhibit comparable chemical shifts and overall patterns of the signals (Tables 3 and 4) to those of $[NaL^1]BPh_4$ in the same solvent. The $^{23}Na$ resonance of $[NaL^2]BPh_4$ in $CD_2Cl_2$ solution does not change either upon addition of the ligand or dilution. This behaviour suggests that the sodium cation is well isolated from the solvent, possibly with all eight donor atoms co-ordinated as in the solid state. As far as the $^1H$ NMR spectra are concerned, the hydrogens of the dangling groups yield sharp signals; the ethylene chains of the macrocycle on the other hand yield a complicated symmetrical pattern even at 200 MHz, Fig. 4. Analysed in terms of an AA′BB′ spin system as for the $L^1$ complexes, it is ascribed to two groups of magnetically unequivalent protons with respect to the plane of the co-ordinated 1,4,7,12-tetraazacyclododecane ring. The spread in chemical shifts ($\delta_A$ 2.61, $\delta_B$ 2.50) exhibited by the macrocycle protons upon co-ordination and the coupling constants within such an AA′BB′ spin system are smaller for $L^2$ than for $L^1$. This suggests that the magnetic inequivalence between the axial and equatorial ring protons decreases from the $L^1$ to the $L^2$ complex, either as a consequence of the change in ring size on going from $L^1$ to $L^2$, or of the arrangements attained by the ligands upon co-ordination, or both.

The $[LiL^2]BPh_4$ derivative yields two sharp resonances for complexed lithium. The $^1H$ NMR spectrum at 200 MHz (Table 3) shows for the hydrogens of the macrocycle an AA′BB′ pattern, having both chemical shifts and coupling constants comparable to those found for $[NaL^2]BPh_4$. On the other hand, for the hydrogens of both the methylene chains and the pyrazole groups, the spectrum exhibits sharp signals accompanied by weaker ones. These features are consistent with the presence of at least two species in solution which do not exchange, or exchange slowly on the NMR time-scale. Such species, yielding the same pattern for the hydrogens of the macrocycle and different signals for those of the dangling groups, probably differ in the number of pendant arms bound to the metal ion. The ability of the $L^2$ ligand to yield, through a significant conformational rearrangement, six-co-ordinate complexes in addition to the eight-co-ordinate $[NaL^2]^+$ has recently been pointed out.[7]

The metal picrate extraction technique[10] was employed to determine the transport ability and, possibly, the selectivity of the ligands $L^1$ and $L^2$ towards the alkali-metal and ammonium cations. The results of such experiments with $L^2$ are reported in Fig. 5. Comparable results were obtained for $L^1$. The ligands exhibit, at least for definite periods of time, remarkable ability to

**Table 3** Proton NMR spectroscopic data *

| Compound | Solvent | |
|---|---|---|
| $L^1$ | $CD_2Cl_2$ | Pyrazole 7.51 (d, 3 H, $H^3/H^5$, $^3J$ 1.8), 7.43 (d, 3 H, $H^3/H^5$, $^3J$ 2.0), 6.26 (t, 3 H, $H^4$, $^3J$ 1.8); $CH_2$ chain 4.96 (s, 6 H); $CH_2$ macrocycle 2.87 (s, 12 H) |
| $[LiL^1]BPh_4$ | $CD_2Cl_2$ | Pyrazole 7.52 (d, 3 H, $H^3/H^5$, $^3J$ 1.9), 7.38 (d, 3 H, $H^3/H^5$, $^3J$ 2.2), 6.32 (t, 3 H, $H^4$, $^3J$ 1.8); $CH_2$ chain 4.40 (s, 6 H); $CH_2$ macrocycle 2.49, 1.72 [AA′BB′, 12 H, $^2J(H^AH^{A'}) = {}^2J(H^BH^{B'})$ −6.2, $^3J(H^AH^B) = {}^3J(H^{A'}H^{B'})$13.5,$^3J(H^AH^{B'}) = {}^3J(H^{A'}H^B)$ 6.5] |
| | $(CD_3)_2CO$ | Pyrazole 7.92 (d, 3 H, $H^3/H^5$, $^3J$ 2.3), 7.79 (d, 3 H, $H^3/H^5$, $^3J$ 1.7), 6.54 (t. 3 H, $H^4$, $^3J$ 2.0); $CH_2$ chain 4.87 (s, 6 H); $CH_2$ macrocycle 2.88 (br, 6 H), 1.97 (br, 6 H) |
| $[NaL^1]BPh_4$ | $CD_2Cl_2$ | Pyrazole 7.62 (d, 3 H, $H^3/H^5$, $^3J$ 1.4), 7.37 (d, 3 H, $H^3/H^5$, $^3J$ 2.5), 6.29 (t, 3 H, $H^4$, $^3J$ 2.3); $CH_2$ chain 4.34 (s, 6 H); $CH_2$ macrocycle 2.43, 1.70 [AA′BB′, 12 H, $^2J(H^AH^{A'}) = {}^2J(H^BH^{B'})$ −6.8, $^3J(H^AH^B) = {}^3J(H^{A'}H^{B'})$15.5,$^3J(H^AH^{B'}) = {}^3J(H^{A'}H^B)$ 7.5] |
| | $(CD_3)_2CO$ | Pyrazole 7.87 (d, 3 H, $H^3/H^5$, $^3J$ 2.0), 7.70 (d, 3 H, $H^3/H^5$, $^3J$ 1.6), 6.44 (t, 3 H, $H^4$, $^3J$ 2.1); $CH_2$ chain 5.02 (s, 6 H); $CH_2$ macrocycle 2.08 (br, 12 H) |
| $L^2$ | $CD_2Cl_2$ | Pyrazole 7.70 (d, 4 H, $H^3/H^5$, $^3J$ 1.8), 7.48 (d, 4 H, $H^3/H^5$, $^3J$ 2.0), 6.25 (t, 4 H, $H^4$, $^3J$ 2.0); $CH_2$ chain 5.04 (s, 8 H); $CH_2$ macrocycle 2.83 (s, 16 H) |
| $[LiL^2]BPh_4$ | $CD_2Cl_2$ | Pyrazole 7.62 (d, 4 H, $H^3/H^5$, $^3J$ 1.9), 7.48 (d, 4 H, $H^3/H^5$, $^3J$ 1.9), 6.34 (t, 2 H, $H^4$, $^3J$ 1.9), 6.26 (t, 2 H, $H^4$, $^3J$ 1.9); $CH_2$ chain 4.27 (s, 4 H), 4.25 (s, 4 H); $CH_2$ macrocycle 2.61, 2.49 [AA′BB′, 16 H, $^2J(H^AH^{A'}) = {}^2J(H^BH^{B'})$ 4.3, $^3J(H^AH^B) = {}^3J(H^{A'}H^{B'})$ 4.7, $^3J(H^AH^{B'}) = {}^3J(H^{A'}H^B)$ −11.50] |
| | $(CD_3)_2CO$ | Pyrazole 7.78 (br, 4 H, $H^3/H^5$), 7.64 (br, 4 H, $H^3/H^5$), 6.33 (br, 4 H, $H^4$); $CH_2$ chain 4.65 (br, 8 H); $CH_2$ macrocycle 2.84 (br, 8 H), 1.97 (br, 8 H) |
| $[NaL^2]BPh_4$ | $CD_2Cl_2$ | Pyrazole 7.43 (d, 4 H, $H^3/H^5$, $^3J$ 2.0), 7.32 (d, 4 H, $H^3/H^5$, $^3J$ 2.0), 6.22 (t, 4 H, $H^4$, $^3J$ 2.0); $CH_2$ chain 4.21 (s, 8 H); $CH_2$ macrocycle 2.64, 2.47 [AA′BB′, 16 H, $^2J(H^AH^{A'}) = {}^2J(H^BH^{B'})$ 4.2, $^3J(H^AH^B) = {}^3J(H^{A'}H^{B'})$ 4.7, $^3J(H^AH^{B'}) = {}^3J(H^{A'}H^B)$ −12.3] |
| | $(CD_3)_2CO$ | Pyrazole 7.71 (d, 4 H, $H^3/H^5$, $^3J$ 2.2), 7.57 (d, 4 H, $H^3/H^5$, $^3J$ 1.6), 6.28 (t, 4 H, $H^4$, $^3J$ 2.0); $CH_2$ chain 4.66 (s, 8 H); $CH_2$ macrocycle 2.82 (br, 8 H), 2.71 (br, 8 H) |

* Chemical shifts referred to $SiMe_4$ ($J$ in Hz); s = singlet, d = doublet, t = triplet and br = broad; chemical shifts and coupling constants of the macrocyclic hydrogens which yield an AA′BB′ system successfully simulate the appearance of the $^1H$ NMR spectrum.

**Table 4** Sodium-23 and $^7Li$ NMR spectroscopic data *

| Compound | Solvent | Chemical shifts ($\nu_{\frac{1}{2}}$/Hz) |
|---|---|---|
| $[NaL^1]BPh_4$ | $CD_2Cl_2$ | 12.51(48) |
| $[NaL^2]BPh_4$ | $CD_2Cl_2$ | 9.69(98) |
| $LiBPh_4$ | $CD_2Cl_2$ | −2.85(2) |
| | $(CD_3)_2CO$ | 4.48(2) |
| $[LiL^1]BPh_4$ | $CD_2Cl_2$ | 1.67(1) |
| | $(CD_3)_2CO$ | 5.00(2) |
| $[LiL^2]BPh_4$ | $CD_2Cl_2$ | 0.41(2), 0.29(2) |
| | $(CD_3)_2CO$ | 4.90(2), 4.64(2) |

| | | Equivalents of $L^1$ | Chemical shifts ($\nu_{\frac{1}{2}}$/Hz) |
|---|---|---|---|
| $LiBPh_4$ | $CD_2Cl_2$ | 0.5 | 1.67(4), 0.71(6), −0.77(5), −2.85(6) |
| | | 1.0 | 1.67(1) |
| | | 1.5 | 1.67(1) |
| | | 2.0 | 1.67(1) |
| | | $L^2$ | |
| | $CD_2Cl_2$ | 0.5 | 0.41(2), −1.41(8) |
| | | 1.0 | 0.41(2) |
| | | 1.5 | 0.41(2) |
| | | 2.0 | 0.41(2) |

* Spectra were recorded on *ca.* $10^{-3}$ mol $dm^{-3}$ solutions: $^7Li$ chemical shifts are reported relative to 0.30 mol $dm^{-3}$ $LiCl-D_2O$, $^{23}Na$ relative to 0.25 mol $dm^{-3}$ $NaCl-D_2O$.

**Table 5** Carbon-13 NMR spectroscopic data *

| Compound | $C^5/C^3$ | $C^4$ | $CH_2$ bridge | $CH_2$ macrocycle |
|---|---|---|---|---|
| $L^1$ | 139.14, 129.22 | 105.42 | 72.43 | 52.77 |
| $[LiL^1]BPh_4$ | 141.27, 130.11 | 107.03 | 75.09 | 51.54 |
| $[NaL^1]BPh_4$ | 142.14, 131.44 | 106.70 | 74.53 | 50.54 |
| $L^2$ | 139.20, 130.01 | 105.54 | 70.19 | 49.97 |
| $[LiL^2]BPh_4$ | 140.90, 131.07 | 106.85 | 67.93 | 48.43 |
| $[NaL^2]BPh_4$ | 141.38, 131.18 | 106.33 | 69.53 | 48.46 |

* Recorded in $CD_2Cl_2$ with reference to $SiMe_4$. The tetraphenylborate signals having the expected shifts are omitted.

transport the $Li^+$, $Na^+$, $K^+$ and $NH_4{}^+$ cations into the organic phase. However, as appears from Fig. 5, such ability decreases with time, probably due to the interplay of time-dependent competing factors. This rather surprising result had never been reported previously for other receptors and alkali metals.[2] As the transport level decreases more slowly for $Li^+$ than for the other cations (Fig. 5, $t > 60$ min) a selectivity for $Li^+$ results. A possible rationalization of these results is based on the different solubility of the complexes in water *vs.* $CH_2Cl_2$ and on the complexation competition between water and the receptors. Complexation of the alkali-metal and ammonium cations by the receptor occurs rapidly in the organic phase where the concentration of the receptor is much higher than in water. Once formed, the picrate complexes are extracted into the aqueous phase where they are more soluble than in $CH_2Cl_2$. Analogous extraction experiments carried out using $NaBPh_4$ or $LiBPh_4$ in the place of the alkali-metal picrates have shown that both alkali-metal tetraphenylborates are completely and irreversibly extracted into the organic phase of the receptors. The $[ML]BPh_4$ (M = Li or Na, L = $L^1$ or $L^2$) derivatives are insoluble in water, whereas they are easily soluble in $CH_2Cl_2$.

The potentially hexa- and octa-dentate ligands $L^1$ and $L^2$, which present half of their donor atoms on pendant arms and the remaining half on a macrocyclic ring whose bonding cavity is too small to accommodate cations, yield stable metal complexes with lighter alkali metals. Upon co-ordination, about half of the co-ordination sphere is occupied by the macrocycle nitrogens, which attain a planar arrangement not only in the $L^1$ case but also when the tetra-aza $L^2$ ring is employed, the rest of the co-ordination sphere being occupied by the dangling groups. In this way the ligands provide rather close environments for the metal cations. The $L^1$ cavity is of the proper size for both the lithium and sodium ions, whereas the larger cavity provided by $L^2$ appears to suit better the sodium ion than the smaller lithium ion. Accordingly, complexation of $Li^+$ by $L^2$ may yield species with dangling groups unco-ordinated.

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