ORIGINAL ARTICLE

Nuclear magnetic resonance study of the stoichiometry and stability of lithium ion complexes with two small size crown ethers in binary nitromethane–acetonitrile mixtures

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Abstract Lithium-7 NMR spectrometry was used to study the complexation reaction between lithium ions and different small size crown ethers12-crown-4 (12C4), benzo-12-crown-4 (B12C4) in a number of binary nitromethane (NM)–acetonitrile (AN) mixtures. The exchange between the free and complexed lithium ion was fast on the NMR time scale and a single population average resonance was observed. Both 1:1 and 2:1 (sandwich) complexes were observed between lithium ion and 12C4 and B12C4 in pure nitromethane solution. Stepwise formation constants of the 1:1 and 2:1 (ligand/metal) complexes were evaluated from computer fitting of the NMR-mole ratio data to equations which relate the observed metal ion chemical shifts to formation constants. There is an inverse linear relationship between the logarithms of the stability constants and the mole fraction of acetonitrile in the solvent mixtures. The stability order of the 1:1 and 2:1 complexes was found to be $12C4.Li^+ > B12C4.Li^+$. The optimized structures of the free ligands and their 1:1 and 2:1 complexes with Li^+ ion were predicted by ab initio theoretical calculations using the Gausian 98 software, and the results are discussed.

Keywords Macrocyclic complexes · Crown ethers · Lithium ion · Lithium-7 NMR · Complexation constants · Nitromethane acetonitrile mixtures

Introduction

Since the first synthesis of macrocyclic polyether(crown) compounds that are capable of forming selective complexes with the alkali ions, extensive research has been carried out on the stability and selectivity of the resulting complexes [1–5]. Due to their pronounced selectivity and extraction efficiency, crown ether derivatives have been extensively used as suitable neutral ion carriers for selective transport through liquid membranes and for constructing polymeric membrane sensors for different metal ions [6–9]. Information about the selectivity and stability of metal ion complexes with macrocyclic ligands are of critical importance development of new methods for their removal, concentration, purification and determination from their mixtures. It is known several factors influence the formation of crown ether complexes of metal ions in solution [1–3]. The most emphasized factor is the cavity size-cation diameter ratio, although its importance has been questioned in the case of large crown ether complexes [4–6]. Other important factors are the number and the nature of hetero-atoms participating in cation binding, the nature of substituting groups on the macrocycle, the conformations of the free and complexed crown ethers and, especially, the nature of solvent. Among these parameters, the ability of solvent molecules to solvate the cations and, thus, to compete with the crown binding sites for the coordination positions around a cation is of fundamental importance. Equally important, but often given much less attention, is the considerable interaction of some solvents with certain macrocyclic ligands [7]. Thus, there is an increasing interest in the study of complexation in binary mixed solvent systems and their interpretation in terms of solute preferential salvation by one of the mixed solvent components [8–11].

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Among different methods employed for the complexation of metal ion–macrocycle complexes in solution [12, 13], nuclear magnetic resonance is well known as a powerful technique for studying thermodynamics [4, 12, 14–17] and exchange kinetics of a number of metal ion–macrocycle complexes in different nonaqueous and mixed solvents [11, 16, 18–22].

In this paper we used lithium-7 NMR to determine the stoichiometry and stability of Li$^+$ ion complexes with 12-crown-4 (12C4) and benzo-12-crown-4 (B12C4) in binary nitromethane (NM)–acetonitrile (AN) mixtures at 21.0 ± 0.1 °C.

Experimental

Reagent grade 12C4 (Merck) and B12C4 (Fluka) were used without any further purification except for vacuum drying over P_2O_5. Lithium perchlorate (Merck) was purified and dried by a previously reported method [20]. Spectroscopic grade nitromethane (NM, Merck) and acetonitrile (AN, Merck) were used as received.

All nuclear magnetic resonance measurements were carried out on a BRUKER 300 MHz FT-NMR spectrometer with a field strength of 70.49 kg. At this field, lithium-7 resonates at 116.64 MHz. A 4.0 M aqueous LiCl solution was used as external reference and the reported ^{7}Li chemical shifts referred to this solution. Paramagnetic (down field) shift from the reference is designated as being positive. The concentration of all LiClO$_4$ solutions used was 5.0×10^{-3} M. All measurements were carried out at a probe temperature of 21.0 ± 0.1 °C.

Results and discussion

Lithium-7 chemical shifts were measured as a function of [crown]/[Li$^+$] ion mol ratios in various binary AN–NM mixtures at 21.0 ± 0.1 °C. In all cases studied, only one population-averaged resonance for the Li$^+$ ion was observed irrespective of the crown/metal ion mol ratio (Fig. 1), indicating that the mean lifetime for the exchange of the metal ion between the two sites (i.e., free ion in the bulk solution and the complex) is smaller than $\sqrt{2}/\pi\Delta\nu$, where $\Delta\nu$ is the difference between the characteristic resonance frequency of the two sites in hertz.

All the resulting ^{7}Li chemical shift versus [crown]/[Li$^+$] plots are shown in Figs. 2 and 3. As can be seen, in general, the behavior of the chemical shift as a function of the [crown]/[Li$^+$] mol ratio can be approximately divided into three groups, as follows:

B12C4 and 12C4 in pure NM (Figs. 2 and 3) the ^{7}Li chemical shift (downfield or upfield) varies almost linearly

with the [crown]/[Li$^+$] mole ratio from 0 to 1, but further addition of the ligands results in an observable inflection point in the resulting curve. The ^{7}Li will then tend to level off at mole ratio >2. This behavior is indicative of successive formation of 1:1 and 2:1 (crown:Li$^+$) species in solution. The formation of such sandwich complexes have already been reported in the literature [1, 2, 23].

B12C4 and 12C4 in all NM–AN mixtures and in pure AN (Figs. 2 and 3), an increase in the crown ether concentration gradually shifts the ^{7}Li resonance downfield and the chemical shifts does not seem to reach a limiting value even at mol ratios of about 4. Such a chemical shift-mole ratio behavior emphasizes the formation of weaker 1:1 complexes in solution.

Formation constants of the resulting complexes were evaluated from the variation of the observed chemical shift with the [crown]/[Li$^+$] mol ratio. Assuming that only a 1:1 crown-Li$^+$ complex is formed in solution, and that the fast exchange conditions prevail, it has been shown previously that the observed chemical shift of the ^{7}Li nucleus is given by [24]:

$$\delta_{obs} = \{[(K_1C_{Li} - K_1C_{Crown} - 1) + (K_1^2C_{Crown}^2 \\ + K_12C_{Li}^2 - 2K_1^2C_{Crown}C_{Li} \\ + 2K_1C_{Crown} + 2K_1C_{Li} + 1)^{1/2}](\delta_{Li} - \delta_{LiCrown})/ \\ 2K_1C_{Li}\} + \delta_{LiCrown} \tag{1}$$

where K_1 is the formation constant, C_{Crown} and C_{Li} are the analytical concentrations of the crown ether and lithium ion, respectively, and δ_{Li} and $\delta_{LiCrown}$ are the respective chemical shifts of the free and complexed lithium ion.

When both 1:1 and 2:1 (crown:lithium) complexation occur in solution, the free crown concentration, [Crown], can be obtained from Eq. 2:[17]

$$K_1K_2[Crown]^3 + \{K_1[1 + K_2(2C_{Li} - C_{Crown})]\} \\ [Crown]^2 + [1 + K1(C_{Li} - C_{Crown})] \\ [Crown] - C_{Crown} = 0 \tag{2}$$

and the observed chemical shift of ^{7}Li is given by:

$$\delta_{obs} = \left\{\delta_{Li} + \delta_{LiCrown}[Crown] + K_1K_2[Crown]^2\delta_{Li(Crown)2}\right\}/ \\ \{1 + K_1[Crown] + \\ K_1K_2[Crown]^2\} \tag{3}$$

where K_1 and K_2 are the stepwise formation for 1:1 and 2:1 complexes, respectively, and δ_{Li}, $\delta_{LiCrown}$ and $\delta_{Li(Crown)2}$ are the respective chemical shifts for the lithium ion, and its 1:1 and 2:1 crown complexes. For evaluation of the formation constants from the chemical shift-mole ratio data, a non-linear least-squares curve fitting program KINFIT [25] was used. Adjustable parameters are the
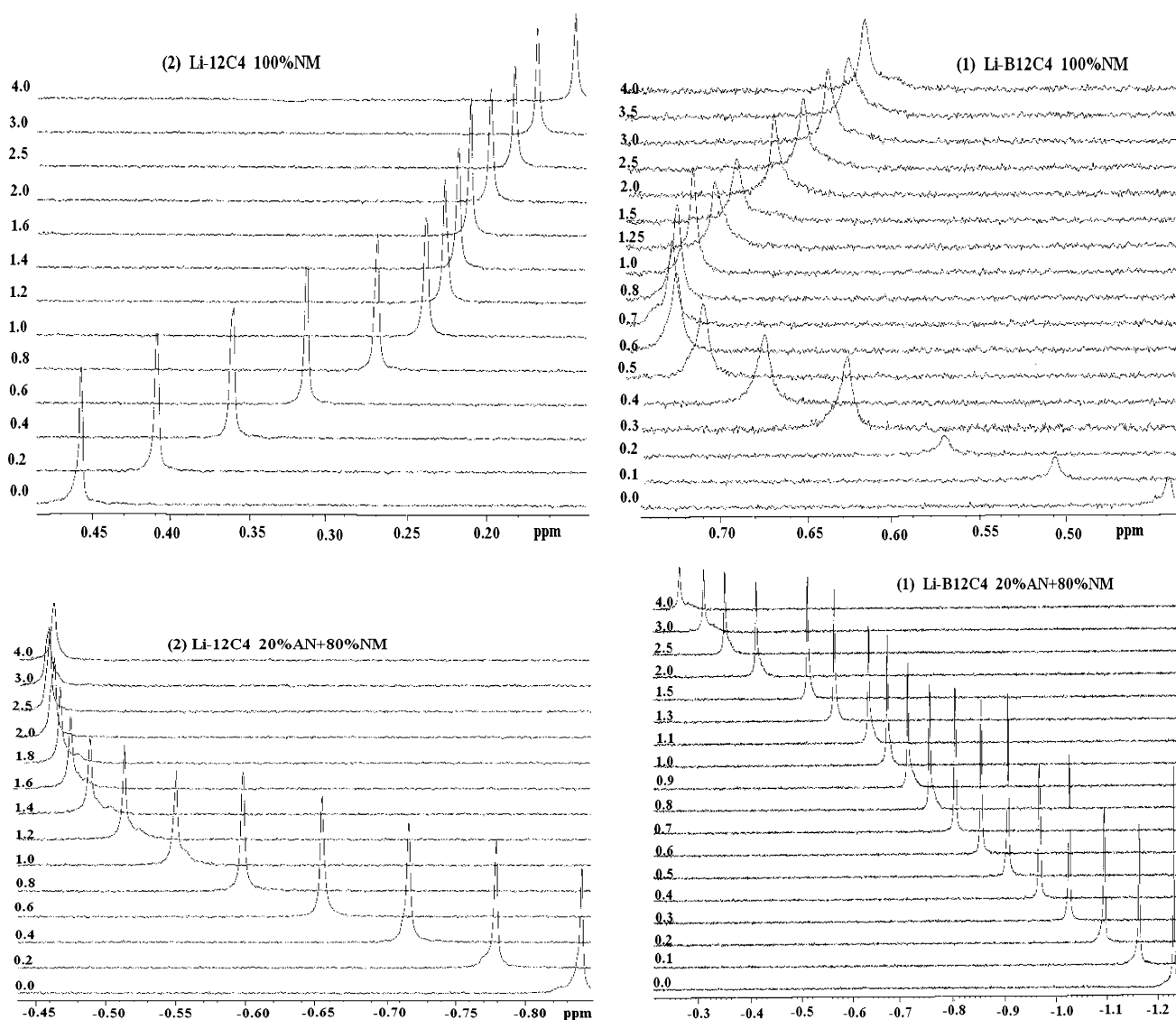
Fig. 1 ^{7}Li NMR spectra of (1) B12C4, (2) 12C4 at various [Crown]/[Li$^+$] mol ratios (MR) in pure NM and 20% AN + 80% NM

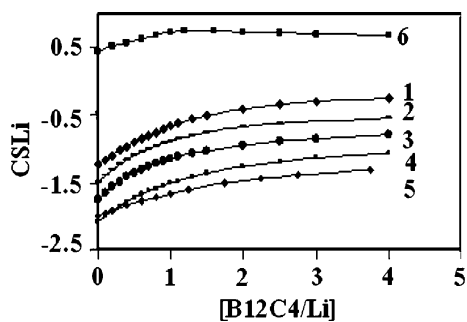**Fig. 2** ^{7}Li chemical shift as a function of [Crown]/[Li$^+$] mol ratio in various acetonitrile–nitromethane mixtures: B12C4; (1) 20% AN, (2) 40% AN, (3) 60% AN, (4) 80% AN, (5) 100% AN, (6) 100% NM

Fig. 3 ^{7}Li chemical shift as a function of [Crown]/[Li$^+$] mol ratio in various acetonitrile–nitromethane mixtures: 12C4; (1) 20% AN, (2) 40% AN, (3) 60% AN, (4) 80% AN, (5) 100% AN, (6) 100% NM
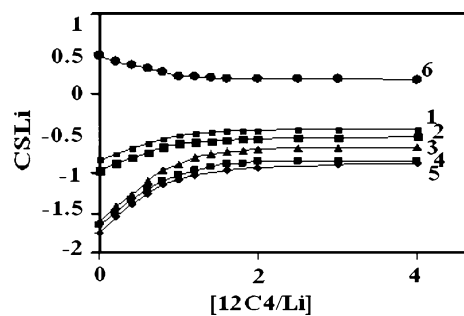
stepwise formation constants and the corresponding chemical shifts (i.e., K_1 and $\delta_{LiCrown}$ for Eq. 1, and K_1, K_2, $\delta_{LiCrown}$ and $\delta_{Li(Crown)2}$ for Eqs. 2 and 3).

The formation constants of the complexes were obtained by computer fitting of the chemical shifts-mole ratio data to the appropriate equations which relate the observed

chemical shift to the formation constants, as described above. The results are summarized in Table 1. Our assumption of 1:1 and 2:1 stoichiometries for the resulting complexes proved to be reasonable in the light of fair agreement between the observed and calculated chemical shifts. It should be noted that the method generally becomes unreliable for very stable complexes (i.e., $K_1 > 10^5$). It is seen that there is a satisfactory agreement between the formation constants obtained for the Li^+-crown complexes in pure acetonitrile with those previously reported in the literature.

As is obvious, the method used for the calculation of formation constants does not take into account possible ion association in $LiClO_4$ solutions. The literature indicates that in acetonitrile the ionic association of the salt is quite small [26]. It is reasonable to expect that similar condition will prevail in nitromethane, which has about the same dielectric constant as actonitrile. Thus, at the low lithium perchlorate concentration used, it seems unlikely that complex formation has significant competition by ion pair formation [15].

The data given in Table 1 clearly indicate that, in a given AN–NM mixtures, the stability of 1:1 Li^+ complexes decreases in the order 12C4 > B12C4. Obviously, the consonance between the ionic size of Li^+ ion and the size of the macrocyclic ring is an important factor in determining the stabilities of the Li^+-crown ether complexes. According to Pedersen and Frensdorff [1] the cavity sizes of 12C4 and 15C5 are 1.2–1.5 Å and 1.7–2.2 Å, respectively. They should be nearly the same for the corresponding benzo-substituted crown ethers. Lithium ion with an ionic diameter of 1.72 Å [27] seems to have the best fitting condition for the cavities of 15-crowns; thus they form the most stable complexes in the series. On the other

hand, 12C4 and B12C4 have both smaller cavities and lower number of donating oxygen atoms in their structure and, consequently, their lithium ion complexes are much weaker than those with 15-crowns.

Meanwhile, our results obtained in pure NM, as a low solvating ability solvent, clearly indicated the formation of 2:1 sandwich complexes between 12C4 and B12C4 and Li^+ ion. It is interesting to note that, there are some literature reports on the formation of such 2:1 sandwich complexes between Li^+ ion and 12C4 [23].

Table 1 shows that among 12-crowns used, where the ring frame remains the same, the formation constants of the resulting Li^+ complexes decrease in the order 12C4 > B12C4. The presence of benzo group in B12C4 would cause a significant decrease in the stability of the resulting lithium complex, compared with Li^+-12C4. This behavior could be due to some combination of the electron withdrawing effect of the benzo groups which weaken the electron-donor ability of the ring oxygens and the reduced flexibility of the macrocycle preventing the molecule to wrap itself around the central cation. The net result is a much weaker cation–crown interaction of Li^+ ion and B15C5 and, especially, DB15C5.

The fundamental importance of solvent properties on the stabilities of the Li^+-crown ether complexes is very evident from the data given in Table 1. In general, complex stability decreases with increasing amounts of acetonitrile in the solvent mixture. It is well known that the solvating ability of the solvent, as expressed by the Gutmann donor number [28] plays a key role in different complexation reactions [3, 4, 6, 11–24]. Acetonitrile and nitromethane are solvent of similar dielectric constants (i.e., $\varepsilon_{AN} = 37.5$ and $\varepsilon_{NM} = 35.6$) but of quite different donor numbers (i.e., $DN_{AN} = 14.1$ and $DN_{NM} = 2.7$) [28]. Consequently, in the course of complexation of Li^+ ion with crown ethers, acetonitrile more strongly competes with crown ethers for the metal ion than does nitromethane. Thus, it is not surprising that addition of nitromethane to acetonitrile will increase the stability of Li^+-crown ether complexes considerably. Similar behavior has been frequently reported for different metal ion-ligand systems in various mixed solvents [11, 29–34]. Such monotonic behavior could be related to the preferential salvation of the cation by AN molecules.

To obtain more information about the conformational changes of the crown ethers used upon complexation with lithium ion, the molecular structures of the free ligands and their 1:1 and 2:1 complexex with Li^+ were optimized using the Gaussian 98 software package [35]. The input files were generated using the Hyperchem program [36]. The structures of the free ligands were optimized based on the 6.31 G* basic set at the restricted

Table 1 Formation constants of Li complexes with small crown ethers in various acetonitrile–nitromethane mixtures at 21 °C

Solvent composition		log K_f	
% AN	χ AN	12C4	B12C4
100	1.00	3.42 ± 0.05	2.21 ± 0.02
		3.40[a]	
80	0.86	3.45 ± 0.04	2.58 ± 0.04
60	0.69	3.48 ± 0.04	2.75 ± 0.06
40	0.50	3.53 ± 0.05	2.89 ± 0.06
20	0.27	3.58 ± 0.04	3.09 ± 0.05
0	0.00	3.65 ± 0.04	3.70 ± 0.06
		(log K_2 = 2.93 ± 0.02)	(log K_2 = 1.08 ± 0.02)

[a] Ref. [34]
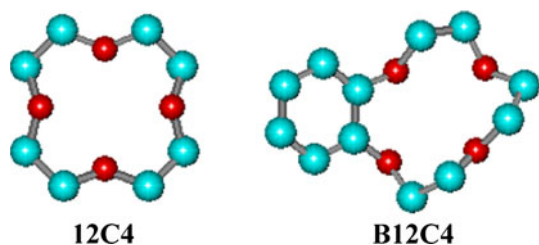
Fig. 4 Optimized structures of crown ethers
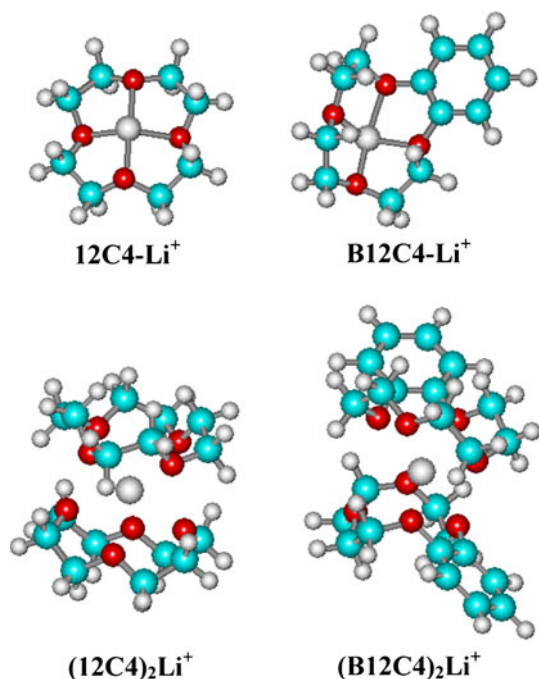
Fig. 5 Optimized structures of 1:1 and 2:1 complexes of crown ethers with Li^+ ion

Hartree–Fock (RHF) level of theory. The optimized structures of the crown ethers were then used to find out the structures of their 1:1 and 2:1 (sandwich) complexes with Li^+ ion.

The optimized structures of the crown ethers 12C4 and B12C4 and their 1:1 and 2:1 complexes are shown in Figs. 4 and 5, respectively. The computed energies for the fully optimized stable structures, the interatomic distances between Li^+ ion and the coordinated oxygen atoms of the rings together with their bond angles in gas phase are summarized in Table 2.

As is obvious from Fig. 4, the free ligands possess an open more or less flat two-dimensional conformation in which OCH_2CH_2O moieties adopt linear arrangements with all four O donors in exo orientation, in the case of two 12-crowns.

As it can be seen from Fig. 5, in the case of 1:1 complexation of smaller cavity crowns 12C4 and, especially, B12C4, the lithium ion has sited above the crowns' cavities and is coordinated to all four donating oxygen atoms of the rings. This conformation makes it possible for a second crown ether to get close to the central Li^+ ion from the other side to form a 2:1 sandwich. In the optimized structure of the 2:1 complex with Li^+, the lithium ion coordinates to all donor atoms of the two ligand molecules, in a symmetrical environment. For example, in the case of all three 15-crowns, due to consonance between the crown' cavity and lithium ionic size, the Li^+ ion is well-sited inside the crown cavity and is coordinated symmetrically to all five ether oxygens of the ring.

It is interesting to note that, in the case of 1:1 complexation, the calculated energies for the optimized structures of the resulting complexes (Table 2) decrease in the order $12C4.Li^+ > B12C4.Li^+$, which is exactly the same order observed in the corresponding formation constants obtained by ^7Li NMR measurements (Table 1). Meanwhile, the average Li–O bond distances and O–Li–O bond angles calculated for the 1:1 and 2:1 complexes (Table 2) are in satisfactory agreement with the previously reported corresponding values for coordination of lithium ion to neutral ligands [37–40].

Table 2 Selected geometrical parameters of 1:1 and 2:1 complexes of Li^+ Ion with different crown ethers obtained from HF/6-31G* calculations

System	E (atomic unit)	E (kcal mol^{-1})	Li–O bond length[a]	O–Li–O bond angle[a]
Li^+	−7.235537	–	–	–
12C4	−611.642281	–	–	–
12C4-Li^+	–	−96.9756	1.90	90
(12C4)$_2$Li$^+$	–	−125.1550	2.50	69
B12C4	−763.114994	–	–	–
B12C4-Li^+	–	−95.9765	2.0	83
(B12C4)$_2$Li$^+$	–	−134.053	2.50	70

[a] Average bon distance in angstroms and angles in degrees

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