Acta Chemica Scandinavica A 36 (1982) 219–225

Dynamic NMR Studies of Lithium Cation Complexes of 1,5,9,13-Tetraoxacyclohexadecanes

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The complexation of lithium ions with sixteen-membered cyclic oligoethers has been investigated by ^{1}H, ^{13}C and ^{7}Li nuclear magnetic resonance spectroscopy. For 1,5,9,13-tetraoxacyclohexadecane acting as ligand, a decomplexation barrier of $\simeq 54$ kJ mol^{-1} was determined and its 3,3,7,7,11,11,15,15-octamethyl derivative gave a decomplexation barrier of $\simeq 71$ kJ mol^{-1}. These barriers were obtained using ^{1}H and ^{13}C probes. A barrier of 79 kJ mol^{-1} has been measured for the decomplexation reaction of the latter using a ^{7}Li probe. Reasons for this difference are discussed. Conformational barriers in the ligands have been determined and variation in chemical shifts of free and complexed cyclic ethers are discussed on the basis of conformational shift effects.

Some years ago we communicated[1] on the ability of the 16-membered cyclic tetramers of oxetan (trimethylene oxide) (A) and 3,3-dimethyloxetan (B) to complex lithium salts. Several lithium complexes with crown ethers,[2-4] cyclic decapeptides[5] and cryptands[6] have been characterized. High selectivity towards lithium cation has been reported for 14-crown-4,[2,4] [2.1.1] cryptand[6] and 1,10-dioxa-4,7-diaza-11-phosphocycloundecane.[7] Simon and his co-workers[8] have synthesized acyclic ionophores capable of selectively binding lithium, notably the *N,N'*-diheptyl-*N,N'*,5,5-tetramethyl-3,7-dioxanonane diamide shows the highest selectivity. Quite recently Cram and co-workers[9] reported on some remarkably strong complexands for lithium; the spherands have for good reasons been characterized as scavengers.

Lithium complexing agents have been shown to alter the reactivity and stereochemistry in reduction reaction with $LiAlH_4$ and $LiBH_4$[10] and cause change in product composition in reaction with R_2CuLi.[11] The [2.1.1] cryptand has been shown to influence polymerization of styrene initiated by lithium.[12]

NMR techniques are very well-suited for the study of complexing interactions. Information about structural features of complexes and ligands can be obtained and kinetic and thermodynamic parameters can be gained from such measurements. In addition, direct information about stoichiometry of complexes is obtainable from NMR methods. Popov and coworkers have used the ^{7}Li NMR technique to study the complexation of lithium ion by cryptands [2.1.1], [2.2.1] and [2.2.2][13] and the kinetics of the [2.1.1] · Li^+ decomplexation reaction in various solvents.[14] Just recently Smetana and Popov reported their ^{7}Li NMR study of lithium complexes of 12-crown-4, 15-crown-5 and 18-crown-6 in various solvents.[15] Jagur-Grodzinski and co-workers[16] have studied the tetradentate amido ethers designed by Simon and his co-workers[8] by ^{1}H and ^{7}Li NMR methods in various solvents.

Results of ^{1}H, ^{13}C and ^{7}Li NMR investigations of ligands A and B and their complexes with lithium salts in various solvents are discussed in the present paper.

EXPERIMENTAL

Synthesis of oxetan.[17] 208 g of 1,3-propanediol (Fluka AG) dissolved in 111 ml sulfuric acid (98 %) was slowly added to 442 g of a 54.5 % boiling NaOH solution kept in a flask fitted with a mechanical stirrer and a reflux condenser. The cyclic ether was co-distilled with water. Two layers were formed and the organic phase was collected. The water phase was salted out and extracted with dichloromethane. The ether phase and the dichloromethane solution

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were dried over solid KOH and CaH_2 before distillation. The yield of cyclic ether was 35 ml of oxetan (16.5 %), b.p. 48 °C.

By using 2,2-dimethyl-1,3-propanediol (Fluka AG) as the starting material, 3,3-dimethyloxetan was synthesized after the same procedure in about the same yield, b.p. 78 – 82 °C.

Synthesis of the tetramers (Ligands A and B). These were synthesized after a modified procedure originally described by Rose.[18] The monomeric cyclic ether (15 ml) dissolved in benzene (200 ml) (Merck *p.a.*) was slowly added to a solution of boron-trifluoride ethyl etherate (2 ml) (Fluka AG) in benzene (300 ml) (Merck *p.a.*); the solution was kept in a flask equipped with a mechanical stirrer. The whole reaction was run under an inert atmosphere. The reaction mixture was kept at room temperature for 24 h. The mixture was then treated with powdered anhydrous $KHCO_3$ (2.5 g) for 24 h in order to neutralize the Lewis acid. The solvent was evaporated off on a rotavapour. A semi-solid material was obtained after removal of solvent. The tetramers were isolated by sublimation under vacuum at 50 – 60 °C. The yield was 0.7 g (6.4 %) for the octamethyl tetramer, m.p. 157 °C. The melting point for the parent tetramer was 70 °C and the yield was 10 %.

Preparation of LiSCN. Li_2SO_4 (Merck *p.a.*) and $Ba(SCN)_2$ (Merck *p.a.*) were separately dissolved in water in a 1:1 mol ratio. The solutions were mixed together and most of the water was evaporated before filtering off the $BaSO_4$. The rest of the water was removed on a rotavapour. Benzene was added by azeotropic distillation. The LiSCN was then dried in vacuum with P_2O_5 for 72 h.

$LiClO_4$, $LiBF_4$ and $LiPF_6$ (ALFA Chemicals) were used without further purification.

Deuterated solvents (Merck) were taken from sealed ampoules and used without further purification. 1,2-Dichloroethane (Merck) was freshly distilled before use. The samples were prepared in a glove box under a dry nitrogen atmosphere.

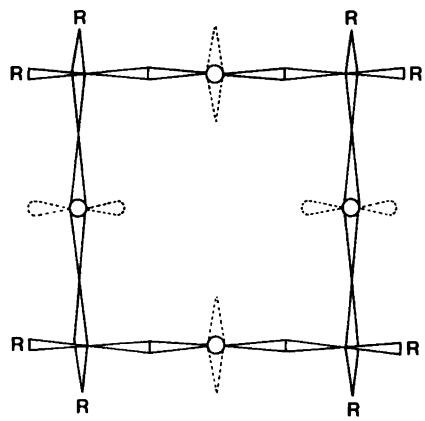
NMR Spectroscopy. The ^1H NMR spectra were recorded at 98 MHz on a Varian HA-100 spectrometer operating in the continuous sweep mode, and at 99.54 MHz on a Jeol FX-100 spectrometer operating in the Fourier transform mode equipped with a ^1H and ^{13}C dual probe. 5 mm o.d. sample tubes were used. The HA-100 spectrometer had a proton internal lock, and the deuterium signal in solvents served as internal lock for the FX-100 instrument. Me_4Si was used as an internal reference. The variable temperature units on the two spectrometers were calibrated with ethylene glycol and methanol. All temperatures were measured with a copper-constantan thermocouple situated in the probe a few centimeters below the sample.

The ^{13}C spectra were obtained with 5 mm o.d. tubes on the Jeol FX-100 spectrometer operating at 25 MHz and are Fourier transforms of accumulated free induction decays under the following conditions: 45° pulse angle, 8 K data points, 5000 Hz spectrum width and an exponential broadening function corresponding to 1 Hz broadening. The chemical shifts were referenced to internal Me_4Si.

^7Li NMR spectra at 38.66 MHz were measured on the Jeol FX-100 spectrometer equipped with a variable frequency probe using 10 mm o.d. sample tubes. CD_3NO_2 was used as a solvent. A 4.0 M solution of $LiClO_4$ in H_2O in a 1 mm o.d. melting point capillary inserted coaxially in the tube was used as an external standard. The observed chemical shifts were not corrected for the bulk diamagnetic susceptibility of the solvents. The temperature measurements were done in the same fashion as for the ^1H and ^{13}C dual probe. The spectra are Fourier transforms of free induction decays, and the following conditions were used: 10000 to 50000 transients, 4 K data points, 2000 Hz and 45° pulse angle.

RESULTS AND DISCUSSION

^1H and ^{13}C NMR studies. The ^1H and ^{13}C chemical shifts for ligand A (1,5,9,13-tetraoxacyclohexadecane) (Fig. 1A) are given in Table 1. The ^1H and ^{13}C chemical shifts of the 1:1 complex between ligand A and LiSCN are also included in Table 1. The ^1H chemical shift of ligand A changes



A: – R = – H

B: – R = – CH_3

Fig. 1. The [4444] conformation of ligands A and B.

Table 1. ^{1}H and ^{13}C chemical shifts in ppm from TMS for ligands A and B in uncomplexed state and complexed with lithium cation in $CDCl_3$ as a solvent.

Probe	Ligand				Lithium complex			
	$-CH_2-$	$-CH_2O-$	$-CH_3$	$-C-$	$-CH_2-$	$-CH_2O-$	$-CH_3$	$-C-$
Ligand A								
^{1}H	1.81[a]	3.55[b]	–	–	1.91[a]	3.64[b]	–	–
^{13}C	30.2	66.1	–	–	28.9	72.1	–	–
Ligand B								
^{1}H	–	3.07	0.83	–	–	3.33	0.87	–
^{13}C	–	75.6	22.6	36.3	–	82.1	22.4	36.3

[a] Center of a quintet. [b] Center of a triplet.

very little on complexing. The ^{13}C chemical shifts of the CH_2O carbon, however, are very much dependent on whether LiSCN is present or not.

We have investigated the ^{1}H and ^{13}C NMR spectra of both the free ligand A and its 1:1 $LiBF_4$ complex at variable temperature. The ligand A has a temperature-independent ^{13}C spectrum, and although the ^{1}H spectrum is temperature-dependent, no slow-exchange spectrum is reached down to $-140\,°C$ at 100 MHz. The 1:1 $LiBF_4$ complex also shows no ^{13}C temperature variable spectrum, but here a slow-exchange ^{1}H spectrum is obtained at $-130\,°C$. The spin-system, however, is too complicated for analysis at the magnetic field used.

When the ^{13}C NMR spectrum of the solution of a 1:1 mixture of ligand A and its 1:1 complex with LiSCN in $CDCl_3$ (*i.e.*, the stoichiometry is two parts in ligand A and one part in LiSCN) is recorded at ambient temperature, we observe single resonances for the various chemically different carbons, and the chemical shifts are mean averages of those in the free ligand and in the complexed form, respectively. By lowering the temperature, a dynamic NMR pehnomenon is observed, and the limiting low-temperature spectrum shows resonances equivalent to those observed in the uncomplexed and the complexed ligand, respectively, in 1:1 ratios. The interpretation of the variable temperature ^{13}C spectrum is that we observe a decomplexation process most simply described as eqn. (1), whose corresponding free energy of activa-

$$\mathrm{Li^+C\ Ligand\ A + Ligand\ A^* \rightleftharpoons Li^+C\ Ligand\ A^* + Ligand\ A} \quad (1)$$

tion is about 54 kJ mol^{-1} ($\Delta G^{\neq}$). The kinetic and thermodynamic parameters for the process described in eqn. (1) are given in Table 2.

The stoichiometry of the complex is solvent dependent and also varies with the anion present. The lithium salts LiBr, LiCl, LiI, $LiPF_6$, $LiBF_4$ all form 1:1 complexes in solvents tried: $CDCl_3$, CD_3NO_2 and CD_3CN. Also LiSCN gives 1:1 complexes in $CDCl_3$, but in $CHCl_2F$ (Freon 21) two equivalents of lithium salt are bound to ligand A. The ^{13}C chemical shifts in the 2:1 complex and in

Table 2. Kinetic and thermodynamic parameters for the decomplexation reaction of ligand A complexed with LiSCN in $CDCl_3$ as a solvent.

Group	Probe	$\Delta\nu$ Hz	T_c K	k^a s^{-1}	$\Delta G_{T_c}^{\neq\,b}$ kJ mol^{-1}
$-CH_2-$	^{13}C	34	259	76	54.0
$-CH_2O-$	^{13}C	149	273	331	53.6

[a] Calculated according to Ref. 23. [b] Calculated according to Ref. 24.

Table 3. Kinetic and thermodynamic parameters for the decomplexation reaction or ligand B complexed with LiSCN in 1,2-dichloroethane as a solvent.

Group	Probe	$\Delta\nu$ Hz	T_c K	k s^{-1}	$\Delta G_{T_c}^{\neq}$ kJ mol^{-1}
$-CH_3$	^1H	4	315	9	71.5
$-CH_3$	^{13}C	6	323	13	72.4

the 1:1 complex between LiSCN and ligand A are the same. It is easy to determine the stoichiometry because of the large ^{13}C chemical shift difference of ligand A in uncomplexed and complexed form. This has been done either by titration above coalescence temperature, or by integration of the ^{13}C resonances obtained in a non-nuclear Overhauser experiment in the slow-exchange spectrum, as a function of the Li^+ concentration.

Ligand B (3,3,7,7,11,11,15,15-octamethyl-1,5,9,13-tetraoxacyclohexadecane) (Fig. 1B) was investigated in the same way as described for ligand A above. The chemical shifts for the various chemically different protons and carbons for the free ligand B and its 1:1 complex with LiSCN in $CDCl_3$ as a solvent at ambient temperature are given in Table 1. Here again, the same trend as seen for ligand A is observed for ligand B; small differences in ^1H chemical shifts, large differences in the ^{13}C chemical shift of CH_2O-carbons on complexing.

The decomplexation process observed by dissolving two equivalents of ligand B and one equivalent of LiSCN in 1,2-dichloroethane (with a few drops of C_6D_6 added, to serve as an internal deuterium lock) has a higher barrier ($\Delta G^{\neq} \simeq 71$ kJ mol^{-1}) than for the ligand A ($\Delta G^{\neq} \simeq 54$ kJ mol^{-1}); an effect that must be due to the methyl groups. The kinetic and thermodynamic parameters for the decomplexation reaction as given by eqn. (1) using ligand B instead of ligand A are given in Table 3.

The solution of a 1:1 ratio of LiSCN and ligand B in $CHCl_2F$ as a solvent was investigated at low temperature. Both the ^1H and the ^{13}C spectra are temperature-dependent. The low-temperature ^1H spectrum is shown in Fig. 2. The methylene protons split into an AB-quartet ($J_{AB}=8.8$ Hz) and the methyl protons into a doublet. In the ^{13}C spectrum, only the methyl carbons show a coalescence phenomenon. The activation free energy is 36.8(8) kJ mol^{-1} for the process observable both by ^1H and ^{13}C spectroscopy. The kinetic and thermodynamic parameters pertinent to this experiment are given in Table 4.

We did not observe a 2:1 complex between LiSCN and ligand B in $CHCl_2F$ as a solvent, as was the case with ligand A.

^7Li NMR studies. As shown in Table 5, we observe different ^7Li chemical shifts as a result of variation in environment around the ^7Li nucleus. We also observe a broadening by about 2 Hz of the ^7Li resonance for Li^+ in the complex with ligand B compared to the resonance of $LiClO_4$ in CD_3NO_2.

The Gibbs free activation energy associated with the process (eqn. 2) may not represent the $\Delta G^{\neq}$

$$Li^+ \subset (\text{ligand A or B}) + {}^*Li^+ \rightleftharpoons {}^*Li^+ \subset (\text{ligand A or B}) + Li^+ \qquad (2)$$

associated with the forward reaction in eqn. (1). $\Delta G^{\neq}$ for the forward reaction in eqn. (2) might be dependent on the amount of free Li^+ in solution, and intermediate complexes of the type $Li^+ . {}^*Li^+ \subset$

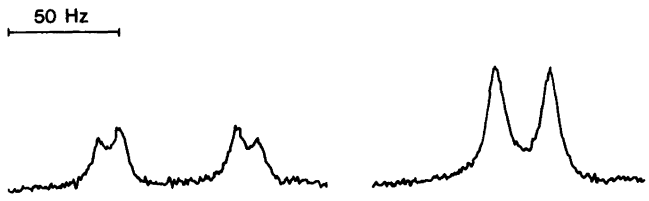


Fig. 2. The low-temperature ^1H spectrum at -110 °C of the solution of a 1:1 ratio of LiSCN and ligand B in $CHCl_2F$ as a solvent.

Table 4. Kinetic and thermodynamic parameters for conformational changes in ligand B in the 1:1 complex with LiSCN in $CHCl_2F$ as a solvent.

Group	Probe	$\Delta\nu$ Hz	T_c K	k s^{-1}	$\Delta G_{T_c}^{\neq}$ kJ mol^{-1}
$-CH_2O-$	^1H	61	183	137[a]	36.4
$-CH_3$	^{13}C	28	178	62	36.8
$-CH_3$	^1H	23	178	51	36.8

[a] A J-coupling constant of 8.8 Hz has been taken into consideration in calculation of k.

Table 5. ^7Li chemical shifts in ppm.

Compound	$^7Li^{a,b}$
4 M $LiClO_4$ in H_2O	0
$LiClO_4$ in CD_3NO_2[c]	−1.36
$LiClO_4$ complexed with ligand A	−1.66
$LiClO_4$ complexed with ligand B	−1.84

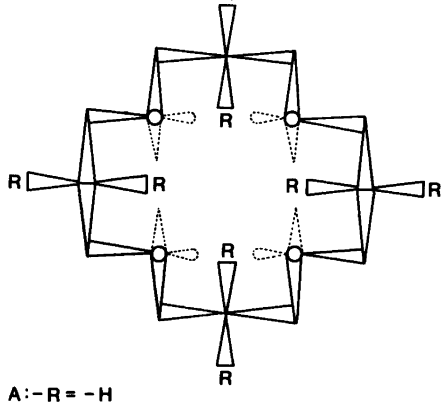
[a] No correction for bulk diamagnetic susceptibility has been made. [b] All ^7Li chemical shifts are reference to an external solution of 4 M $LiClO_4$ contained in a 1 mm melting point capillary and centered in a 10 mm NMR tube and upfield shifts are given as negative. [c] Concentration of 0.13 M $LiClO_4$.

(ligand A or B) might exist. At ambient temperature we observe separate resonances for Li^+ in complexed and uncomplexed state for ligand B. By choosing a composition of two equivalents of $LiClO_4$ and one equivalent of ligand B in CD_3NO_2 as a solvent, we observe a coalescence phenomenon at $\simeq 100\,°C$ with a corresponding activation free energy of 79 kJ mol^{-1} ($\Delta G^{\neq}$) which is about 8 kJ mol^{-1} above what we determined for the process according to eqn. (1). Unfortunately, the solubility of $LiClO_4$ in CD_3NO_2 below 0 °C is very limited, and therefore we were not able to do a similar experiment for ligand A because the coalescense temperature is below 0 °C.

From the experiments described above one can conclude: The decomplexation barriers excede by far any conformational barriers in the ligands and the $\Delta G^{\neq}$'s associated with the forward reaction in eqns. (1) and (2) are not necessarily the same.

Conformations. The crystal structure of ligand A has been determined by Groth[19] and the molecule has the "square" diamond lattice [4444] ring conformation with a D_{2d} symmetry. The IR-spectra in solid state and solution, respectively, of both ligand A and B show that these compounds are conformationally homogeneous. The *gem*-dimethyl groups in ligand B must necessarily occupy the corner positions, and therefore ligand B no doubt also occupies the same "square" ring conformation. In the conformation under discussion, two contributions to the ^{13}C NMR shifts should be of importance, namely the γ and the *vicinal-gauche* (V_g) effect.[20] The γ effect results in an upfield shift of about 5 ppm for the terminal carbons in a *gauche* butane fragment. The effect of heteroatoms in such a fragment is not clear, but for the sake of argument we do not differentiate between oxygen atom and methylene group in this respect. A third effect, V_t, occurs for the central carbons in an *anti* butane fragment, but its magnitude (0.8 ppm upfield) is very much smaller than that of either the γ or the V_g effect. For the carbon in the CH_2O groups in the [4444] conformation shown in Fig. 1 we count $\gamma + V_g + V_t$ chemical shift effects (the effect of the *gem*-dimethyl groups has been left out).

The ^1H and ^{13}C low-temperature spectra of 1:1 complex between ligand B and LiSCN are such that a conformation as shown in Fig. 3 would satisfy the observed spectra. We refer to this particular conformation as [16], which indicates a non-



A:- R = - H

B:- R = - CH_3

Fig. 3. The [16] ring conformation of ligands A and B.

corner conformation with a D_{2d} symmetry element. By comparing the changes in ^{13}C chemical shifts for both ligands A and B, in free and complexed state (Table 1), it is fair to conclude that both ligands have the same ring conformation when complexed. In addition, the particular changes in chemical shifts also support the [16] ring conformation for the ligands when complexed. In the [16] form the carbon in the CH_2O groups has lost the $\gamma + V_t$ chemical shift effects, which amounts to $\simeq 6$ ppm. That is exactly what we observe, downfield shifts for CH_2O carbons of 6.0 and 6.5 ppm for the complexed ligands A and B, respectively, compared to the free cyclic ethers.

Raymond *et al.*[21] have determined the crystal structure of the tetraaza analogue of ligand A, namely the 1,5,9,13-tetraazacyclohexadecane, which has a ring conformation identical with the one depicted in Fig. 3. By using structural data from their X-ray analysis, the cavity in our oxygen analogues ought to have a radius of about 0.7 Å. Here we have used an O---O edge distance of 2.9 Å and a van der Waals radius for oxygen of 1.40 Å. The lithium ion, whose radius is reported in the range of 0.60 – 0.78 Å, will fit very well into the cavity. A subsequent X-ray analysis of the LiSCN · ligand A complex confirms the proposed conformation[22] based on NMR results. The open [4444] form (Fig. 1), has a larger cavity, and the oxygen lone-pairs are directed in such a way that they do not give good interactions with a cation in the middle of the ring. The cavity of the open form can easily accomodate a sodium ion.

We have here an example of a situation where the guest (Li^+) organizes the host (ligand A and B) in order to get thermodynamically more stable complexes.

The variation in stoichiometry for the LiSCN complex of ligand A with the solvents used might be explained on the basis of the solvation of ion pairs. In chloroform the complex probably exists as a loose ion pair, while in $CHCl_2F$ we are dealing with a tighter ion pair, and we envision a structure as shown in Fig. 4 for the 2:1 complex between LiSCN and ligand A in $CHCl_2F$. The two Li^+ ions are displaced from the mean plane of the oxygens. As ahown in Fig. 3, a total of eight oxygen lone-pair electrons are pointing out from the mean plane of the oxygens, four on each side, and these lone-pair electrons give reasonable support for a 2:1 complex. For ligand B, however, such a complex is hard to envision, due to the steric hindrance of the methyl groups.

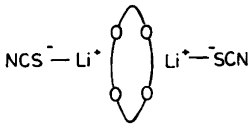


Fig. 4. Suggested structure for the tight ion pair 2:1 complex between LiSCN and ligand A in $CHCl_2F$.

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Received June 16, 1981.