

## Ligand Exchange and Conformational Site Exchange Processes in the 2:1 Complex of 1,4,7,10-Tetraoxacyclododecane with Sodium Thiocyanate

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The stoichiometry of the 12-crown-4 complex with NaSCN in solution is shown by titration, using  $^{13}\text{C}$  chemical shift, to be 2:1. The decomplexation barrier as determined by  $^{13}\text{C}$  DNMR in the presence of excess ligand is  $\Delta G^\ddagger \sim 11$  kcal/mol, much higher than any of the two barriers to conformational exchange within the complexed ligand in the [3333] conformation, determined by  $^{13}\text{C}$  and  $^1\text{H}$  DNMR as  $\Delta G^\ddagger \sim 7$  and  $\sim 8$  kcal/mol (1 kcal=4.184 kJ). This surprising conformational mobility within the complexed ligand may be understood on the basis of a multi-step process involving alternately conformational changes and changes of coordination number.

We have previously described the preparation of a series of crystalline cation complexes of 1,4,7,10-tetraoxacyclododecane (12-crown-4), some of which showed by analysis a 1:1, others a 2:1 stoichiometry.<sup>1</sup> The IR spectra were particularly simple and nearly identical for the solid 1:1 complex of

lithium salts<sup>1</sup> and 2:1 complexes of sodium salts (Fig. 1). From the presence of just two sharp bands in the 800–1000  $\text{cm}^{-1}$  region assigned to  $\text{CH}_2$  rocking, it was concluded that all four monomer units of each ring had the same conformation  $ag^+g^+$  so as to give a quadrangular [3333] conformation with all ether oxygens in side positions pointing in the same direction (Fig. 2). Dynamic  $^1\text{H}$  and  $^{13}\text{C}$  NMR studies<sup>1</sup> on solutions of the 1:1 complex of 12-crown-4 with LiSCN revealed a slow-exchange spectrum, as expected for the  $C_4$  symmetry of the proposed conformation, and two conformational exchange processes, also as expected.

Subsequently, X-ray studies by Frank<sup>2</sup> on the 2:1 complex of 12-crown-4 with NaSCN confirmed the proposed sandwich structure and the rather high coordination number of eight for the sodium cation and revealed an overall  $D_4$  (square-antiprismatic) symmetry (Fig. 3). The same features were estab-

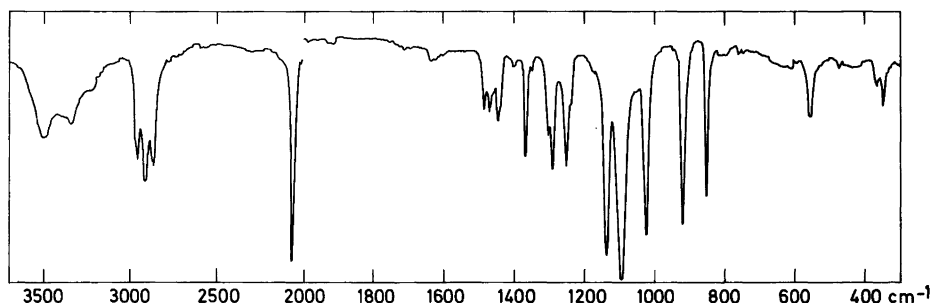


Fig. 1. IR-spectrum of the 2:1 complex of 1,4,7,10-tetraoxacyclododecane with NaSCN pressed in KBr.

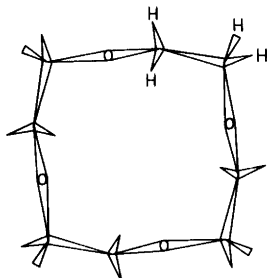


Fig. 2. The "square" [3333] conformation of 1,4,7,10-tetraoxacyclododecane.

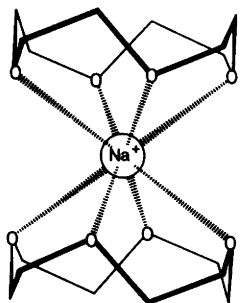


Fig. 3. The sandwich structure of the 2:1 complex of 1,4,7,10-tetraoxacyclododecane with sodium salts.<sup>2-4</sup>

lished independently by van Remoortere and co-workers on 2:1 complexes with NaCl<sup>3</sup> and NaOH.<sup>4\*</sup> Varying coordination numbers and geometries had been found earlier for the sodium cation in its 1:1 complexes with larger crown ethers: pentagonal pyramidal hexa-coordination for benzo-15-crown-5/NaI,<sup>7</sup> pentagonal bipyramidal hepta-coordination for 18-crown-6/NaSCN<sup>8</sup> and hexagonal bipyramidal octa-coordination for dibenzo-18-crown-6/NaBr.<sup>9</sup> In all these cases the coordination is completed by water molecules or the counter-ion.

The purpose of the present investigation was to study by NMR spectroscopy the stoichiometry of the 12-crown-4/NaSCN complex in solution, the relative stabilities of complexes present and bar-

\* The [3333] conformation is also adopted in the 1:1 complex with CaCl<sub>2</sub>,<sup>5</sup> four water molecules completing the octa-coordination. An entirely different conformation is present in the 1:1 complex with CuCl<sub>2</sub>,<sup>6</sup> it is obviously a result of the strong tendency for Cu(II) to acquire octahedral hexa-coordination, the remaining two ligands being Cl<sup>-</sup>.

riers to ligand exchange (decomplexation). A further aim was to study the conformational site exchange processes within the complexed ring, since in the previous study<sup>1</sup> of the 12-crown-4/LiSCN complex, very broad <sup>13</sup>C lines were obtained at slow exchange. Finally, it was of interest to study the influence of the identity of the cation and of the stoichiometry of the complex on the height of the conformational barriers.

## STOICHIOMETRY IN SOLUTION

In contrast with the situation for many other crown ether complexes with alkali cations<sup>10</sup> the chemical shift of the single <sup>13</sup>C NMR line of 12-crown-4 complexed with sodium salts (66.8 ppm) is markedly different from that of 12-crown-4 alone (71.5 ppm). It was, therefore, possible to perform a simple titration by adding increasing amounts of solid sodium thiocyanate to a solution of 12-crown-4 in methanol. The resulting curve (Fig. 4) shows a single sharp bend when 0.5 mol has been added and no further change. There is thus no indication of any other species in solution than the 2:1 sandwich complex as found for the crystal. Furthermore, the sharpness of the bend and the straightness of each branch of the curve suggest that the complexation constant for the second step is very large, even though the methanol solvent might be expected to compete strongly, and that the constant for the first step is much smaller. Unfortunately, neither of these values can be determined quantitatively from the shape of the titration curve through iterative least-squares approximations.

## LIGAND EXCHANGE

When a solution in CHCl<sub>2</sub>F containing more than two equivalents of 12-crown-4 per equivalent of

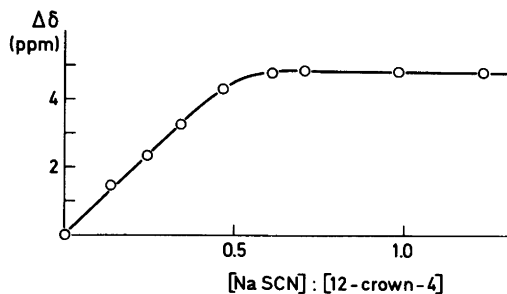


Fig. 4. Titration of 1,4,7,10-tetraoxacyclododecane in methanol with solid NaSCN.

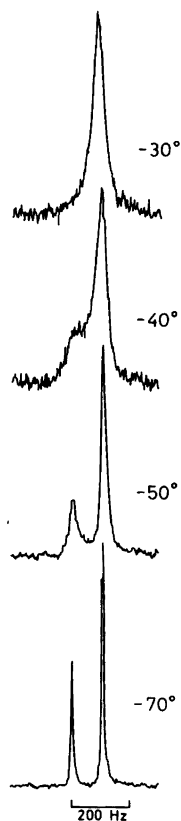


Fig. 5. 25 MHz  $^{13}\text{C}$  NMR spectra down to  $-70^\circ\text{C}$  of a 3:1 mixture of 1,4,7,10-tetraoxacyclododecane and NaSCN in  $\text{CHCl}_2\text{F}$  solution.

NaSCN is cooled, the single  $^{13}\text{C}$  line starts to broaden at  $-20^\circ\text{C}$  and then splits on further cooling into two sharp lines at  $-60^\circ\text{C}$ , coalescence temperature  $-40^\circ\text{C}$ . The spectra shown in Fig. 5 were obtained using a 3:1 ratio of 12-crown-4 to salt whereby the lines are directly identified by their relative intensities 1:2 in the slow-exchange spectrum. Note however that the peak height ratio at  $-50^\circ\text{C}$  is close to 1:4, the reason being that the weaker line is twice as broad as the stronger line due to the inverse dependency of the line width on the site lifetime in this exchange region. The calculated activation free energy  $\Delta G^\ddagger = 11.0 \pm 0.3$  kcal/mol exceeds by far any conformational barrier within any of the two conformations adopted by the uncomplexed ring, and also the barrier to their interconversion,<sup>11</sup> and must therefore be considered as an overall decomplexation barrier, that is, some

step in a process most simply described as  $(12\text{-crown-4})_2 \cdot \text{Na}^+ \rightleftharpoons 12\text{-crown-4} \cdot \text{Na}^+ + 12\text{-crown-4}$ . One might expect large solvation changes on going from a 2:1 sandwich complex to a 1:1 complex, but further measurements by dynamic  $^{13}\text{C}$  NMR spectroscopy in both  $\text{CDCl}_3$  and methanol, using a 4:1 ratio of 12-crown-4 to salt, yielded essentially the same activation free energies of  $11.0 \pm 0.5$  and  $10.6 \pm 0.5$  kcal/mol. This suggests that the leaving ring may only become partially detached before it is replaced partially in the coordination sphere about sodium by the entering ring, and that such loosening goes parallel with conformational changes within both (see next section).

It may seem surprising that the decomplexation barrier is so much higher than any of the conformational barriers, since reported decomplexation barriers have sometimes<sup>12</sup> been interpreted in terms of some rate-determining conformational step. The  $\Delta G^\ddagger$  value of  $\sim 11$  kcal/mol observed for the present 2:1 complex is strikingly close to reported values for decomplexation barriers of related 1:1 crown ether complexes, such as the sodium complex of dibenzo-18-crown-6<sup>12</sup> ( $E_a = 11.7 - 13.3$  kcal/mol), the potassium complexes of dibenzo-18-crown-6<sup>13</sup> ( $E_a = 12.6$  kcal/mol) and of a macrobicyclic nonaether<sup>14</sup> ( $\Delta G^\ddagger = 12.1 - 12.3$  kcal/mol), and the cesium complexes of 18-crown-6<sup>15,16</sup> ( $\Delta G^\ddagger = 12.0$  kcal/mol) and of dicyclohexano-18-crown-6<sup>16</sup> ( $\Delta G^\ddagger = 11.9$  kcal/mol). Also, 2,2,2-cryptates of alkali salts show decomplexation barriers of similar magnitude<sup>17</sup> ( $\Delta G^\ddagger = 14.2 - 15.8$  kcal/mol).

#### CONFORMATIONAL PROCESSES IN THE COMPLEX

On further cooling of solutions in  $\text{CHCl}_2\text{F} - \text{CHClF}_2$  (1:1) containing the same mixture of free and sodium-complexed 12-crown-4 below  $-90^\circ\text{C}$ , further changes occur in the  $^{13}\text{C}$  NMR spectrum at 25 MHz (Fig. 6). The single line of the complexed ring undergoes a further broadening and is split at  $-130^\circ\text{C}$  into two lines of equal intensity ( $T_c = -115^\circ\text{C}$ ,  $\Delta G^\ddagger \sim 7$  kcal/mol), whereas the single line of the free ring stays sharp.

This shows that a process corresponding to the lower-energy process in the [3333] conformation of the free ring (which averages the two types of carbon and is the only one observable by  $^{13}\text{C}$  DNMR) has a higher activation free energy in the sodium-complex than in the lithium complex<sup>1</sup> (5.6 kcal/mol) or in the free ring<sup>1</sup> (5.5 kcal/mol). The

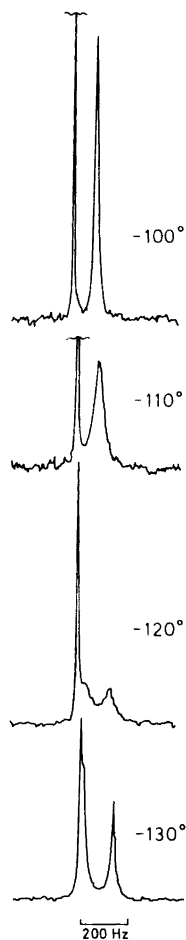


Fig. 6. 25 MHz  $^{13}\text{C}$  NMR spectra down to  $-130^\circ\text{C}$  of a 3:1 mixture of 1,4,7,10-tetraoxacyclododecane and NaSCN in a 1:1 mixture of  $\text{CHCl}_2\text{F}$  and  $\text{CHClF}_2$ .

activation energy is, however, still much lower than the decomplexation barrier and it can be concluded that the mechanism (interpreted as a sequence of four *syn*-eclipsing steps<sup>1,11</sup>) does not require that the ring be first decomplexed and then taken back again. It is not clear why the barrier is higher than in the lithium complex. Possibly, the ether oxygens have less freedom to pass each other in the *syn*-eclipsing because of the crowding of eight oxygens around sodium, while lithium, having only four oxygens and the anion, may be more free to readjust its coordination geometry during the process.

To be able to determine the activation energy for the higher-energy process averaging geminal hydrogens in the sodium complexed [3333] conformation, it became necessary to perform  $^1\text{H}$  DNMR spectroscopy and at much higher field, equivalent to a frequency of 251 MHz. Also the low-energy process could then be reexamined by  $^{13}\text{C}$  DNMR at the correspondingly higher frequency of 63.1 MHz, and the spectra (Fig. 7) of the 2:1 complex alone confirmed that the single line at 65.1 ppm above  $-100^\circ\text{C}$  splits into just two lines of equal intensity in the slow exchange spectrum. These are separated by 320 Hz and the barrier was determined more accurately ( $T_c = -112^\circ\text{C}$ ,  $\Delta G^\ddagger = 7.1 \pm 0.2$  kcal/mol).

The  $^1\text{H}$  DNMR spectra are shown in Fig. 8. The expected two processes are not, however, seen distinctly separated. The slow exchange spectrum below  $-120^\circ\text{C}$  shows three bands of intensity

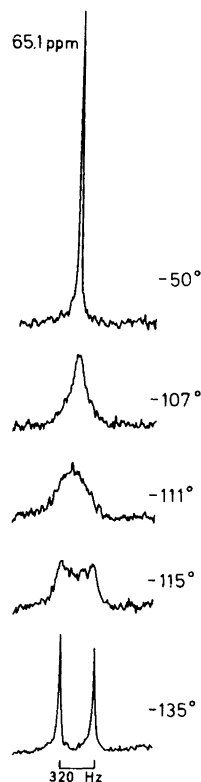


Fig. 7. 63.1 MHz  $^{13}\text{C}$  NMR spectra down to  $-135^\circ\text{C}$  of a 2:1 mixture of 1,4,7,10-tetraoxacyclododecane and NaSCN (= sandwich complex) in a 1:1 mixture of  $\text{CHCl}_2\text{F}$  and  $\text{CHClF}_2$ .

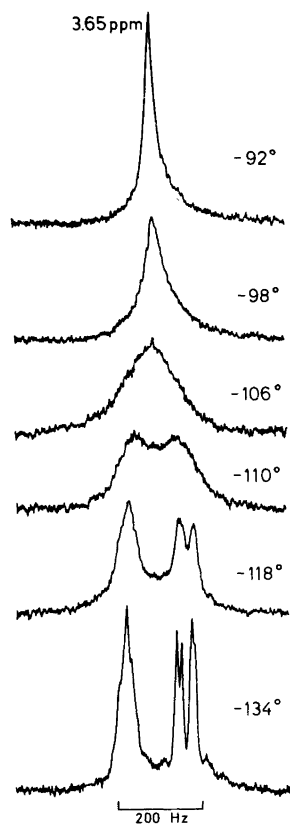


Fig. 8. 251 MHz  $^1\text{H}$  NMR spectra down to  $-134^\circ\text{C}$  of a 2:1 mixture of 1,4,7,10-tetraoxacyclododecane and NaSCN in a 1:1 mixture of  $\text{CHCl}_2\text{F}$  and  $\text{CHClF}_2$ .

2:1:1 in agreement with the presence of four spin-coupled protons, two of which coincide. The detailed assignment of the bands to the four protons of the monomer unit (Fig. 2) is difficult. On heating, they should first coalesce pairwise to two bands (=AB quartet) representing the averaged chemical shifts for geminally different hydrogens, then coalesce further to the single line at  $\delta$  3.65. The lower estimated limit for the activation free energy ( $T_c = -115^\circ\text{C}$ ,  $\Delta G^\ddagger \sim 7$  kcal/mol) is in good agreement with the value obtained from the  $^{13}\text{C}$  DNMR spectra, and the higher limit ( $T_c = -105^\circ\text{C}$ ,  $\Delta G^\ddagger \sim 8$  kcal/mol) is only about 1 kcal/mol higher. Thus, the higher-energy process of the sodium-complexed ring has a barrier in the same range as found for the lithium complexed ring<sup>1</sup> ( $8.2 \pm 0.3$  kcal/mol) and the free ring<sup>1</sup> ( $6.8 \pm 0.3$

kcal/mol), and again much lower than the decomplexation barrier. Any mechanism proposed for geminal exchange that involves a decomplexation step must, therefore, be discarded. For the free ring a sequence of four steps, each involving a rotation of a  $\text{CH}_2\text{O}$  unit about adjoining bonds, and with the smaller ether oxygen passing through the ring, has been proposed<sup>11</sup> as the mechanism for geminal exchange. However, all four oxygens will then be turned outwards and the crown ether must loosen completely from the cation, whose coordination number becomes reduced to only four. It is difficult to see why solvent molecules should not now enter to maintain a fuller coordination and why the ring, before coming back with the side carrying the exposed ether oxygens, should not have become mixed with other free crown-ether molecules in the solution. Clearly, the crown-ether rings have a most surprising conformational mobility within this complex.

We propose tentatively that geminal site exchange occurs through a series of steps involving partial conformational change and change of coordination number. Thus, in a given ring a rotational step changes the conformation from [3333] to [39] (see preceding paper<sup>11</sup>) with one oxygen now pointing out so as to reduce the coordination number from 8 to 7. A second rotational step converts the conformation from [39] to [66] with two oxygens pointing out and the coordination number reduced to the still acceptable level of 6. The whole ring now rotates as such to bring the two outer oxygens in and the two inner oxygens out, with unchanged coordination for sodium. Reversing all steps re-establishes octacoordination with the inverted [3333] conformation. The crown ether has thus never left the coordination sphere and there has been no need for solvent molecules to enter.

It seems likely that ligand exchange, when taking place, does so most easily at the turning point of this sequence of events. Now and then a molecule (1 out of  $\sim 600$  at 233 K) during rotation as such may loosen completely and become replaced by one of the free crown-ether molecules from the solution. These are anyway present at this temperature largely in the same [66] conformation.

## EXPERIMENTAL

The titration experiment (Fig. 4) was performed by adding portions of solid NaSCN (about 8 mg = 0.1 mmol) to a solution of 12-crown-4 (about 175 mg = 1

mmol) in methanol (2 ml) directly in the NMR tube and measuring the  $^{13}\text{C}$  chemical shift after each addition. The instrument was a Jeol FX-60 operating at 14.1 kG with protons noise decoupled.

The  $^{13}\text{C}$  DNMR spectra of the sodium complex in the presence of excess of 12-crown-4 (Figs. 5 and 6) were obtained on a Jeol FX-100 instrument operating at 23.5 kG with protons noise decoupled. The  $^1\text{H}$  and  $^{13}\text{C}$  DNMR spectra of the 2:1 complex alone (Figs. 7 and 8) were obtained on a superconducting solenoid spectrometer constructed by Professor F. A. L. Anet (UCLA) and operating at 59 kG.  $^{13}\text{C}$  spectra are Fourier transforms of accumulated free-induction decays and were obtained in 10 mm tubes with the magnetic field locked on a  $^{19}\text{F}$  peak of the solvent ( $\text{CHCl}_2\text{F}-\text{CHClF}_2$ ) and with protons noise decoupled.  $^1\text{H}$  spectra were obtained in 5 mm sample tubes. Tetramethylsilane was used as an internal reference. All temperatures on both instruments were measured with a copper-constantan thermocouple situated in the probe a few centimeters below the sample. Free energies of activation were estimated from rate constants at the coalescence temperatures using the relation  $k = \pi\Delta\nu/\sqrt{2}$ .

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