

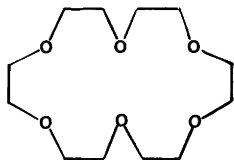
Determination of a Conformational Process in a Cesium Tetrafluoroborate Complex of 1,4,7,10,13,16-Hexaoxacyclooctadecane by Dynamic Nuclear Magnetic Resonance Spectroscopy

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The ¹H and the natural-abundance ¹³C NMR spectra of a cesium tetrafluoroborate complex of 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6) have been measured over a temperature range of –40 to –140 °C. One conformational process is found and the free-energy barrier is 29.26 ± 1.25 kJ mol⁻¹. At low temperatures a 2:1 complex between the hexaether and the cesium ion is found to be the most stable one.

We here report a dynamic nuclear magnetic resonance (DNMR) study of a complex between cesium tetrafluoroborate and 1,4,7,10,13,16-hexaoxacyclooctadecane ("18-crown-6") (*1*). To our knowledge



this is the first determination of a conformational process in the 18-crown-6 polyether to date.

Dunitz *et al.*¹ have determined the X-ray structure of a 1:1 complex between cesium thiocyanate and *1* where the conformation of *1* has D_{3d} symmetry, with torsion angles about C–C bonds close to 65° and those about the C–O bonds close to 180°. The cesium cation is displaced by 1.44 Å from the mean plane made up of the six oxygens, because Cs(I) with an ionic radius of 1.65 Å² is too large to fit into the central cavity (radius of 1.40 Å) of *1* (Fig. 1).

Provided that the complex retains its structure in solution, it lends itself to DNMR studies. Due to the displacement of the cation out from the mean plane of the ring, the two carbons in the O–C–C–O units no longer have the same environment and are therefore different even though the ring has a highly symmetrical conformation (D_{3d}).

A cesium tetrafluoroborate complex of *1* was isolated from a reaction mixture resulting from treatment of ethylene oxide with BF₃ and with CsBF₄ present in order for the cesium cation to

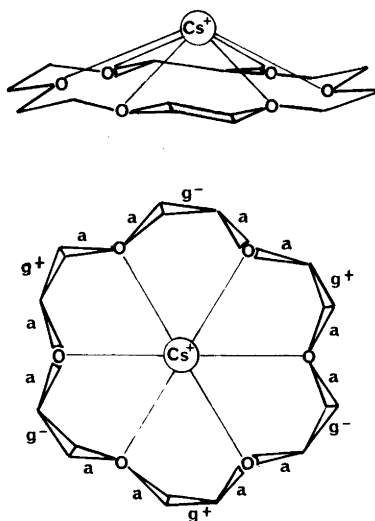


Fig. 1. The crystal conformation ¹ of the 18-crown-6 in the (18-crown-6)·CsNCS complex.

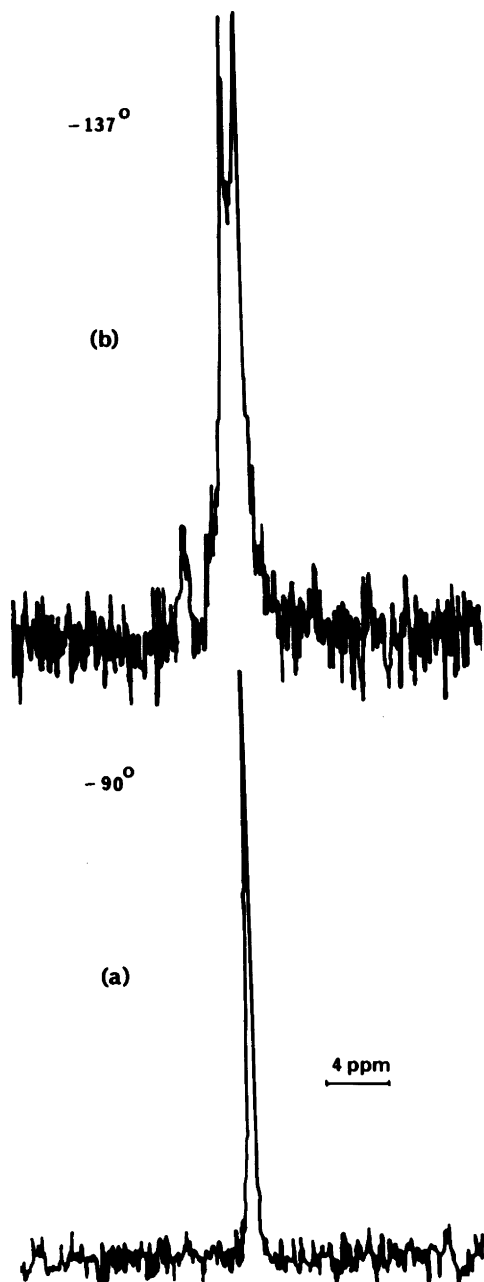


Fig. 2. Proton-decoupled 25.05 MHz ^{13}C NMR spectra of $(18\text{-crown-}6)_2 \cdot \text{CsBF}_4$ (a) above and (b) below coalescence temperature.

act as a "templating" ion.³ Recrystallization from methanol gave white needles. Analysis showed it to be a 1:1 complex.

Attempts to dissolve the complex at -78°C in a mixture of CHCl_2F and CHCl_3 (in a ratio of 2:1) always resulted in a finely divided precipitate. The precipitate was shown to consist of CsBF_4 without organic material present. A solubility study in CDCl_3 gave the following results: At room temperature the complex dissolved, but by lowering the temperature below -30°C , precipitation occurred. By adding an equivalent amount of *l* to the cold solution the precipitate slowly dissolved. From these observations it seems reasonable to conclude that the 1:1 stoichiometry of the isolated crystalline complex is retained in solution at ambient temperature, but at lower temperature a 2:1 complex between 18-crown-6 and CsBF_4 is formed and the stability of the $\text{Cs}(+) \supset (18\text{C}6)_2$ increases with decreasing temperature.⁴ These findings are in agreement with observations by Popov *et al.*⁵ in a ^{13}C NMR study of the complexation of cesium tetraphenylborate (CsBPh_4) by *l* in pyridine.

As shown in Fig. 2, the ^{13}C NMR spectrum at 25.05 MHz is distinctly temperature dependent and shows a single resonance which splits into two separate lines of equal intensity. The free energy of activation (ΔG^\ddagger)⁶ as calculated from the absolute rate theory,⁷ is 7.0 ± 0.3 kcal/mol at -130°C .

The ^1H NMR spectrum at 99.6 MHz of the same sample also shows a dynamic NMR effect (Fig. 3). Although it is impossible to decide whether one or more processes are operating in the ^1H DNMR spectrum, there is no change below -135°C . This is in agreement with the ^{13}C DNMR spectrum because the process which is responsible for exchange of carbons in the $\text{O}-\text{C}-\text{C}-\text{O}$ units should also be observable in the ^1H spectrum. The temperature range in which changes in the ^1H spectrum occur is rather wide (-90 to -130°C) and suggests a second process of higher energy, but the featureless structure of the signals prohibits a closer determination. At very low temperature the ^1H spectrum should consist of an $\text{AA}'\text{BB}'$ pattern, but due to dipolar broadening this pattern is not observable.

The process observed by ^{13}C DNMR can be easily interpreted on the basis of a complex in which $\text{Cs}(+)$ is sandwiched between two 18-crown-6 rings in the D_{3d} conformation as depicted in Fig. 4; each $\text{O}-\text{C}-\text{C}-\text{O}$ unit undergoes the conformational exchange $\text{ag}^+\text{a} \leftrightarrow \text{ag}^-\text{a}$ ⁸ so that the average

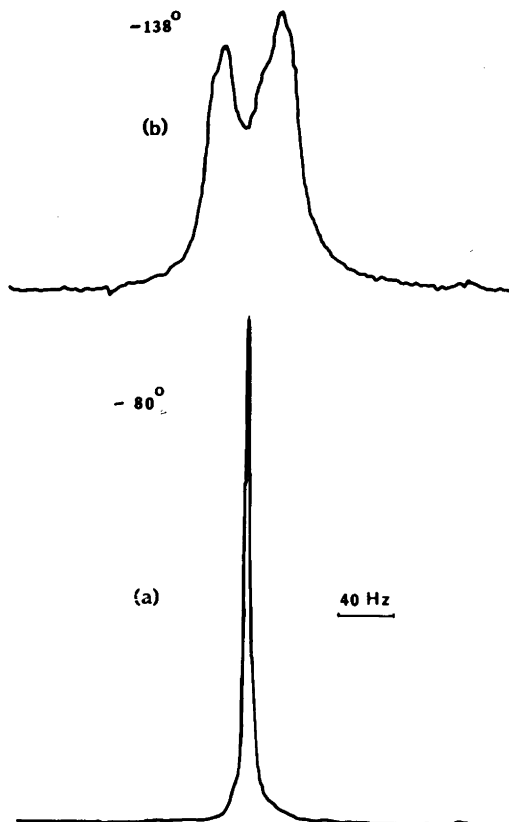


Fig. 3. 99.6 MHz ^1H NMR spectra of (18-crown-6)· CsBF_4 under (a) fast exchange and (b) slow exchange.

distance from both carbon atoms to cesium becomes equal. It might be argued that an alternative conformation of C_6 symmetry, analogous to the C_5 conformation adopted by 15-crown-5 in its sandwich complex with BaBr_2 ⁹ and the C_4 conformation adopted by 12-crown-4 in its sandwich

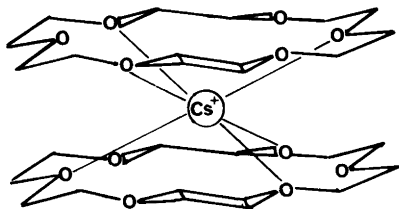


Fig. 4. A possible 2:1 complex between 18-crown-6 and Cs^+ .

complex with NaCl ¹⁰ and NaOH ¹¹ would also explain the DNMR spectrum. The process would then correspond to the conformational exchange $ag^+g^+ \leftrightarrow g^-g^-a$ within each $\text{O}-\text{C}-\text{C}-\text{O}$ unit.⁸ A C_6 conformation would have the advantage of directing all six oxygen atoms from each ring to the cesium cation, whereas the D_{3d} conformation brings only three oxygen atoms close to the cation (3.04–3.10 Å), the other three atoms being more distant (3.16–3.27 Å).¹ However, the ^{13}C chemical shift difference between the two types of carbons is rather small (~ 0.9 ppm), and this is in agreement with the conformational similarity of the carbons in the D_{3d} conformation. A much greater difference is expected between the “corner” carbon and the “side” carbon in a C_6 conformation due to an upfield γ -effect for the latter (~ 5 ppm is observed¹² for sodium complexes of 12-crown-4). We therefore believe that the cesium ion is coordinated to altogether six oxygen atoms (three from each ring) at a close distance and altogether six oxygen atoms at a somewhat longer distance, leaving the tetrafluoroborate anion apart. We further believe this to be true not only for the 2:1 sandwich complex in solution but probably also in infinite stacks in the crystalline 1:1 complex.

The mechanism for carbon site exchange in the highly symmetric conformation is most likely a simple eclipsing of the $\text{C}-\text{C}$ bonds in six separate steps, whereby also “close” and “distant” oxygen atoms are exchanged, as are “equatorial” and “axial” hydrogen atoms. No decomplexation would seem necessary to perform the flipping of ethylene groups hanging on a hexagonal array of oxygen atoms coordinated to cesium. The observed barrier of 7.0 kcal/mol is higher than the barrier of only 5.6 kcal/mol observed¹³ for the related exchange process of 12-crown-4 in its 1:1 complex with LiNCS and also interpreted as stepwise $\text{C}-\text{C}$ bond eclipsing without decomplexation. This difference may have to do with the quite different orientation of the oxygen lone pair electrons in the transition state.

To accomplish site exchange of geminal hydrogens requires that one of the two rings becomes detached, leaving a 1:1 complex, and is then taken back again from the other side, but requires no further process within the ring. If a higher limit of coalescence temperature in a possible second process as suggested in the ^1H DNMR spectrum is set at -95°C , the barrier height ΔG^\ddagger must be in the range 8 to 9 kcal/mol. This then can be considered

as a decomplexation barrier $\text{CsBF}_4 \cdot (18\text{-crown-6})_2 \rightleftharpoons \text{CsBF}_4 \cdot (18\text{-crown-6}) + (18\text{-crown-6})$, and is rather close to a ΔG^\ddagger barrier of 10.4 kcal/mol at the same temperature observed⁵ for the decomplexation process $\text{CsBPh}_4 \cdot (18\text{-crown-6}) \rightleftharpoons \text{CsBPh}_4 + (18\text{-crown-6})$ observed by ^{133}Cs NMR. A comparison with a corresponding process observed by ^1H DNMR for 12-crown-4 in its LiNCS complex is less relevant since in addition to decomplexation an extra conformational exchange within the ring is required to turn the oxygens over to the other side. The observed barrier¹³ ($\Delta G^\ddagger = 8.2$ kcal/mol) may then represent either the decomplexation step or the conformational change or be a composite barrier.

Several other crown ether complexes are currently being investigated by low temperature NMR spectroscopy.

EXPERIMENTAL

The complex was isolated from a reaction mixture as described earlier³ and recrystallized from methanol. Anal. $\text{C}_{12}\text{H}_{24}\text{O}_6 \cdot \text{CsBF}_4$: C, H. NMR spectra were obtained on a JEOL FX-100 instrument. The proton and ^{13}C FT-spectra were obtained with a standard 5-mm tube in a dual $^1\text{H}/^{13}\text{C}$ probe. All ^{13}C NMR spectra were obtained with proton noise decoupling. The solvent for all compounds was an approximately 2:1 mixture of CHClF_2 and CHCl_2F . Tetramethylsilane was used as an internal reference for both the ^1H and ^{13}C spectra. The averaged ^{13}C chemical shift for the hexaether is 69.9 ppm and the two low temperature resonances are split apart by 22 Hz at 25.05 MHz. The ^1H averaged chemical shift is δ 3.61. All temperatures were measured with a copper-constantan thermocouple situated in the probe a few centimeters below the sample. The free energy of activation was calculated from the rate constant by absolute rate theory⁷ with a transmission coefficient of 1. The rate constant was obtained at the coalescence temperature in the ^{13}C spectrum at -130°C by the expression $k = \tau \Delta\nu / \sqrt{2}$.⁶

Acknowledgements. We thank *Norges Teknisk-Naturvitenskapelige Forskningsråd* for financial support. The purchase of the JEOL FX-100 NMR instrument was partly supported through a grant from *Norges Almenvitenskapelige Forskningsråd*.

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Received July 30, 1979.