X-Ray Crystal and Molecular Structure of the Complex between Dibenzo-14-crown-4 and LiSCN

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The crystal structure of the title compound shows that in the complex the Li^+ cation is penta-co-ordinated to the 4 ethereal oxygens and to the N of the SCN^- anion, in a nearly square pyramidal geometry, where Li is 0.79 Å out of the plane of the oxygens; the average Li–O distance is 2.04 Å and Li–N is 1.96 Å.

Crown ethers are known to form stable and sometimes selective complexes with alkali and alkaline earth metal cations.[1–6] The type of interactions and the selectivity of the complexation have been shown to be directly dependent on the ratio between the diameter of the cation and the size of the crown ether's 'cavity'.[4,6]

Relatively little is known about the nature of interaction of the Li^+ ion with these cyclic polyethers. A number of recent studies indicate that Li^+ is complexed by the 12—19 membered crown ethers both in solution[7–9] and in the crystalline state.[10–14] Dibenzo-14-crown-4 (DB-14-C-4)† is a particularly promising stable and selective ionophore for Li^+. Solvent polymeric membranes[15] containing DB-14-C-4 display significant preference for alkali metal cations over alkaline earth metal cations, and they show especially high selectivity towards lithium.[16] In addition, it was observed that incorporation of large lipophilic anions into this type of membrane leads to an increase in the selectivity for lithium ion.

In order to provide a structural basis for these results, and for the development of improved selectivity for lithium ion, we analysed crystallographically the complexes of DB-14-C-4 with a series of lithium salts. We now report the crystal and molecular structure of the LiSCN complex of DB-14-C-4.

Crystal data: $LiC_{18}H_{20}O_4SCN$, $M = 365.38$, space group *Pnam*, $\lambda(\text{Cu-}K_\alpha) = 1.54178$ Å, $a = 9.453(1)$, $b = 13.259(1)$, $c = 15.274(1)$ Å, $U = 1914.5(3)$ Å^3, $D_c = 1.27$ g cm^{-3}, $Z = 4$, $\mu(\text{Cu-}K_\alpha) = 15.87$ cm^{-1}.

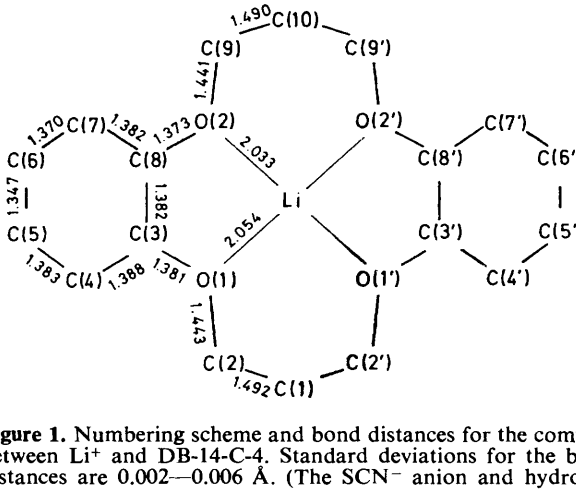

Figure 1. Numbering scheme and bond distances for the complex between Li^+ and DB-14-C-4. Standard deviations for the bond distances are 0.002—0.006 Å. (The SCN^- anion and hydrogen atoms are omitted for clarity.)

Single crystals were grown by slow evaporation from 2,2,2-trifluoroethanol solution. The integrated intensities of 1499 independent reflections ($3 \leqslant 2\theta \leqslant 130$ °) were measured on a Syntex $P2_1$ automated four circle diffractometer. Corrections were made for background, radiation damage, and Lorentz and polarization effects. Absorption was corrected for in the usual way.[17] 1470 Reflections (98% of the total) [with $F \geqslant 2.5\,\sigma(F)$] were included in further calculations. The structure was solved by direct methods[18] and refined by a block-diagonal least-squares procedure.[19] All hydrogen atoms were located in difference electron density maps and refined isotropically while all non-hydrogen atoms were refined using anisotropic thermal parameters. Refinement converged to R 0.050 and R_w 0.056.‡ The molecular scheme, showing the atom numbering system and bond lengths, is shown in Figure 1,§ and a stereoview of the final structure of the complex is shown in Figure 2. The complex has a mirror plane of symmetry containing C-1, C-10, Li^+, and SCN^- and this relates the two halves of the molecule. The Li atom is co-ordinated by 4 oxygens of the crown ether and by the nitrogen of the SCN anion in the observed 1 : 1 stoicheiometry. This five-co-ordinated geometry is almost a perfect square pyramid. The asymmetric unit (O-1, O-2, and C-1 to C-10, inclusive) of the crown ether itself shows an average deviation of only 0.04 Å from planarity. The angle between this plane and that of the mirror-related plane is 121° (Figure 2). The four ethereal oxygens are coplanar, and the Li^+ cation is 0.79 Å out of this plane. The diagonal distance across the ring between opposite oxygens is 3.77 Å, resulting in an adjusted diameter¶ of the cavity of 0.97 Å which is, in fact, too small to accommodate the Li^+ cation (effective diameter is 1.18—1.52 Å)** within the plane

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† 7,8,16,17-Tetrahydro-6*H*,15*H*-dibenzo[*b*,*i*][1,4,8,11]tetraoxacyclotetradecin.

‡ Alternatively, refinement of the structure in the space group *Pna*2_1 yielded a value of 0.046 for R for 1470 observed reflections. Convergence was slow, and the structure was insignificantly different from that in the space group *Pnam*. The slightly lower value of R is probably due to the additional degrees of freedom in the space group of lower symmetry. Hence, we assign the structure to the more symmetric space group *Pnam*.

§ The atomic co-ordinates (including hydrogen atoms), for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication. The structure factor table (observed and calculated) and thermal parameters are available from the British Library as supplementary publication No. SUP 23550 (14 pp). For details see Notice to Authors No. 7, *J. Chem. Soc., Perkin or Dalton Trans.*, 1981, index issue.

¶ The distance between opposite oxygens across the cavity, subtracting the size of oxygen atoms. (See also ref. 4).

** The effective radius of the Li^+ ion was calculated to be 0.59 Å for tetra co-ordinated Li and 0.76 Å for hexaco-ordinated Li (R. D. Shannon, *Acta Crystallogr., Sect. A*, 1976, **32**, 751).

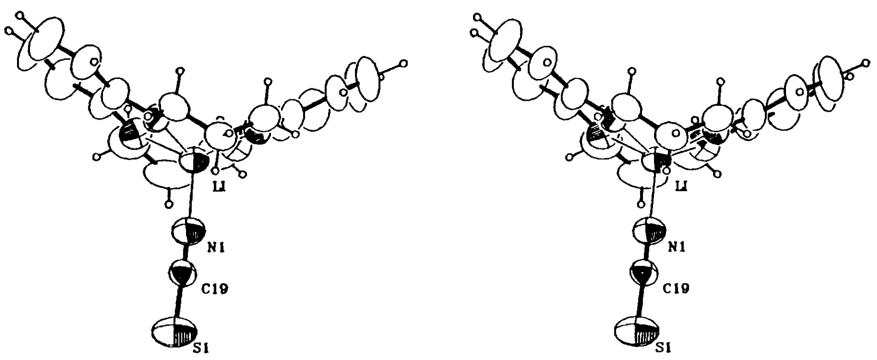

Figure 2. Stereoscopic drawing of the complex.

of the oxygens. The observed mean Li–O distance of 2.04 Å is intermediate between the short Li–O distance in tetrahedral complexes (mean value *ca.* 1.98 Å)[20] and the long Li–O distance in octahedral complexes (mean value *ca.* 2.16 Å)[10,20] and seems to be the usual lithium–ethereal oxygen bond length in penta-co-ordinated complexes with macrocyclic ligands.[12,14]

All bond lengths (Figure 1) and bond angles are within the expected range[21] except for the relatively short aliphatic C–C bond (mean value 1.49 Å), owing to a 'macrocyclic C–C shortening effect' which has been observed in a number of similar systems reported in the past.[4] The average C–C–O–C torsion angle is 178° (*trans*-conformation), and the average C–C–C–O torsion angle is 71° (close to the *gauche* conformation). These values are typical of ring systems[4] of comparable and larger size, and they indicate no significant ring strain due to complexation. There are no solvent molecules in the complex and abnormally short intermolecular interactions do not occur. Hence, the crystal packing probably has little effect on the structure of the complex.

The conformation, then, of the complex is probably the same in solution, especially in the apolar environment of polymeric synthetic membranes. As mentioned above, incorporation of DB-14-C-4 into such membranes creates for Li^+ cations[16] a selective transport system, which might be useful both for isolation of Li^+ from natural sources and for monitoring of Li^+ activities in biological systems.[22] A molecular model based on our crystal structure suggests that this high selectivity towards lithium, and the strong rejection of divalent cations such as those of magnesium, calcium, and barium[16] is due in part to the symmetric 'V' shaped conformation adopted by the crown ether in this complex (Figure 2). In this conformation the molecule is inflexible and the four oxygens are locked into a perfect arrangement for square pyramidal co-ordination to Li^+, which can thus also bond to the counter ion, SCN^-. Of course, there are also electrostatic and solvation effects. The 'cavity' is open only to one side. Hence, it is more difficult to bind doubly charged cations, because the neutralizing counter anions would be crowded on the 'other side' of the cation. Also, solvent interactions with doubly charged ions would favour dissociation, while the more easily desolvated Li^+ ion can associate with the ether and counter ion to give a neutral complex. These results might help us in designing a more selective ionophore for lithium, *e.g.* one with the same basic frame but with an intramolecular tail for the fifth co-ordination site, and in understanding how lithium might interact with biological ionophores.

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