Lithium Salt Complexes of 1,5,9,13-Tetraoxacyclohexadecanes

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Summary 1,5,9,13-Tetraoxacyclohexadecane and its 3,3,-7,7,1,1,15,15,-octamethyl derivative form stable complexes with two moles of lithium salts, some of which co-crystallize with uncomplexed tetraethers to give a 1 : 1 stoicheiometry.

In earlier studies of macrocyclic oligoethers we,[1] and other workers in this field,[2] have noted strong complexing ability for cations only when the oxygen atoms are separated by two carbon atoms, notably in the case of the cyclic oligomers of ethylene oxide. A mixed system, a 14-membered cyclic tetraether containing two trimethylene oxide units, has been reported[2] to give a 1 : 1 complex with LiSCN.

We now report that the 16-membered cyclic tetramers[3] of oxetan (trimethylene oxide) (I) and 3,3-dimethyloxetan (II), which uncomplexed have been shown to adopt the "square" diamond lattice conformation (Figure, a) both in solution[4] and in the crystal,[4,5] form complexes with lithium salts. No tendency for complex formation with sodium and potassium salts has been observed. The stoicheiometry of the crystalline complexes, prepared by adding an excess of lithium salt to a chloroform solution of the cyclic tetraether and evaporating the filtered solution, may be 1 : 1 (LiBr, LiI) or 2 : 1 (LiSCN).

In the case of the LiSCN complex of the octamethyl derivative (II) the exchange rate in chloroform is slow, since the n.m.r. spectrum at room temperature shows separate lines for protons belonging to the complexed ether and those belonging to added excess of uncomplexed ether. For the other complexes of both ethers the exchange is faster, since only averaged chemical shifts are observed under the same conditions for mixtures of crystallized complexes and uncomplexed ether.

A low-temperature n.m.r.-spectroscopic study has been limited to complexes of the octamethyl derivative because of the easy interpretation of these spectra. The 2 : 1 LiSCN complex of (II) showed, on cooling, a splitting of the methylene line into an AB-quartet and of the methyl line into a doublet; coalescence temperature −67°. The 1 : 1 LiBr complex of (II) showed a different low-temperature spectrum (coalescence temperature −100°) with a splitting of the methylene line into a singlet in the middle of an AB quartet (intensity ratio 1 : 1) and of the methyl line into a singlet in the middle of a doublet (also intensity 1 : 1). When more LiBr is added, both single lines begin to disappear, and when the ratio of total LiBr to cyclic ether is 2 : 1, the spectrum is the same as that of the LiSCN complex.

We conclude that the Li^+ cation is complexed in the same manner in both cases and that the cyclic tetraether adopts the same conformation. The observation of a 1 : 1 stoicheiometry for the lithium halide cases can therefore only be explained by co-crystallization of complex with uncomplexed ring, in analogy with the reported *X*-ray structure for a rubidium–sodium isothiocyanate complex of a more familiar type of cyclic oligoether.[6]

As to the nature of the conformation of the complexing ring, it must be entirely different from that of the salt-free ring of (II) (Figure, a), which requires a singlet and not a doublet for the methyl groups; its low-temperature spectrum is, however, not reached at −130°. A conformation of the type shown in the Figure, b, has a symmetry which would satisfy the observed spectrum of the complex. It may be difficult to co-ordinate two Li^+ cations symmetrically above and below this conformation, but a distorted ring might have internal mobility so as to produce such averaged symmetry.

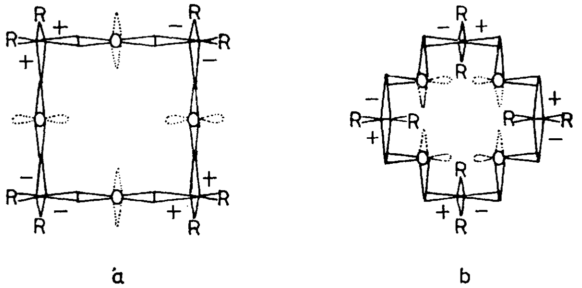

FIGURE. *The established conformation of* 1,5,9,13-*tetraoxacyclohexadecane when alone* (a) *and the suggested conformation in complexes with lithium salts* (b). R *may be hydrogen* (I) *or methyl* (II). + *and* − *signs refer to the sign of the dihedral angle in* gauche *bonds; the other bonds are* anti.

The i.r. spectra of complexed and free cyclic ether are significantly different in the region 600—1500 cm^{-1} and thus support a conformational change on complexing.

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