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# ION PAIRING IN METAL NITRATE COMPLEXES OF OPTICALLY ACTIVE CROWN ETHERS DETECTED BY CIRCULAR DICHROISM

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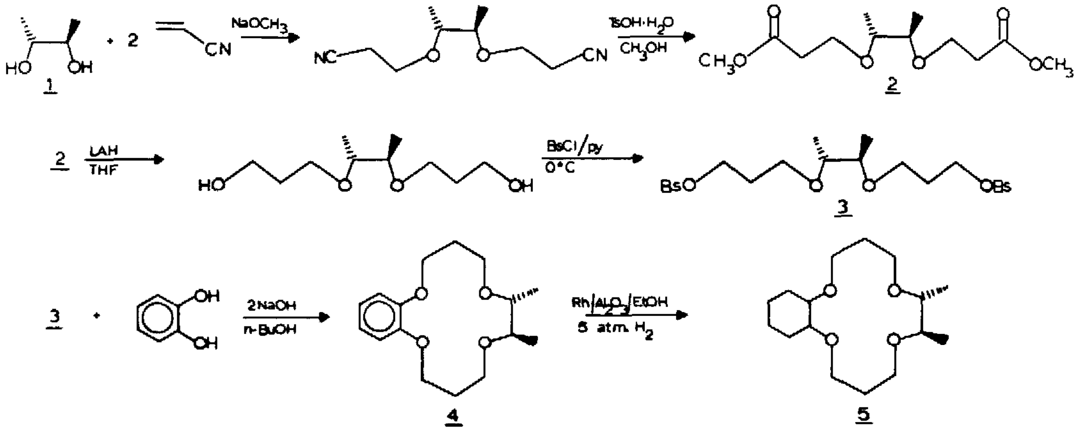
Summary: The detection by circular dichroism of ion pair formation in the lithium nitrate complexes of two new optically active crown ethers is described.

One of the most important properties of crown ethers[1] is their ability to solubilize certain inorganic salts in nonpolar media. Anions of salts so dissolved are unusually reactive, and numerous synthetic systems which capitalize on this reactivity have been devised.[2] Prominent examples include the "purple benzene" reagent, a mild and efficient oxidant, consisting of $KMnO_4$ solubilized in benzene by addition of dicyclohexano-18-crown-6[3], and the "naked anion" complexes of 18-crown-6 with KF and KOAc, which provide extraordinarily nucleophilic $F^-$ and $OAc^-$ ions.[4] In the latter systems, conductance measurements have shown that the $F^-$ and $OAc^-$ anions exist primarily as free ions in acetonitrile solution. However, $^{55}Mn$ NMR indicates that the 18-crown-6·$KMnO_4$ complex exists in benzene solution as an ion pair.[3]

Numerous techniques have been utilized to study crown ether complexes of ion pairs, including ESR,[5] measurement of electric dipole moments,[6] and absorption spectroscopy.[7] A recent review by Kolthoff[8] and a two volume monograph edited by Szwarc[9] discuss crown ether complexes of ion pairs in detail. Here we wish to report the use of circular dichroism measurements to study ion pair formation in the lithium nitrate complexes of two

Scheme I



new optically active crown ethers, namely, (9R,10R)-9,10-dimethyl-5,6,9,10,12,13,-hexahydro[b]benzo-1,4,8,11-tetraoxacyclotetradecin (4) and (7R,8R)-7,8-dimethyl-2,6,9,13-tetraoxabicyclo[12.4.0]octadecane (5).

Polyether 4 was prepared (Scheme I) by a procedure similar to that used to prepare the achiral parent compound, benzo-14-crown-4.[10] (Optically pure (2R,3R)-2,3-butanediol (1) is available from Tridom Chemical Inc., Hauppaauge, N.Y.) Elemental analysis, $^{1}H$ and $^{13}C$ NMR spectra, and mass spectra (parent ion at m/e = 280) are consistent with the assigned structure. In addition, molecular weight determination by vapor phase osmometry gives the correct molecular weight to within 6 per cent. The cyclohexano derivative 5 was prepared by hydrogenation of 4, and GC analysis revealed only one product, probably the cis isomer.[11] *The lithium nitrate complex of 4 can be prepared by slow evaporation of* acetonitrile-toluene mixtures containing equimolar quantities of 4 and $LiNO_3$ under a stream of dry nitrogen at room temperature and pressure; elemental analysis is consistent with an anhydrous 1:1 complex (m.p. 178-181°C).

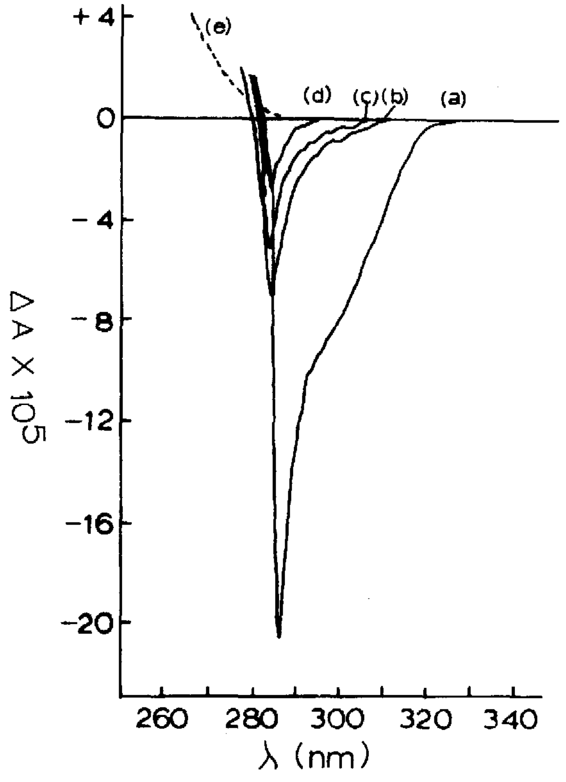


Figure 1. Nitrate CD intensity in 4·$LiNO_3$ complex as a function of solvent composition: (a) 100% $CHCl_3$; (b) 90% $CHCl_3$/10% TFE; (c) 80% $CHCl_3$/20% TFE; (d) 62% $CHCl_3$/38% TFE; (e) 100% TFE

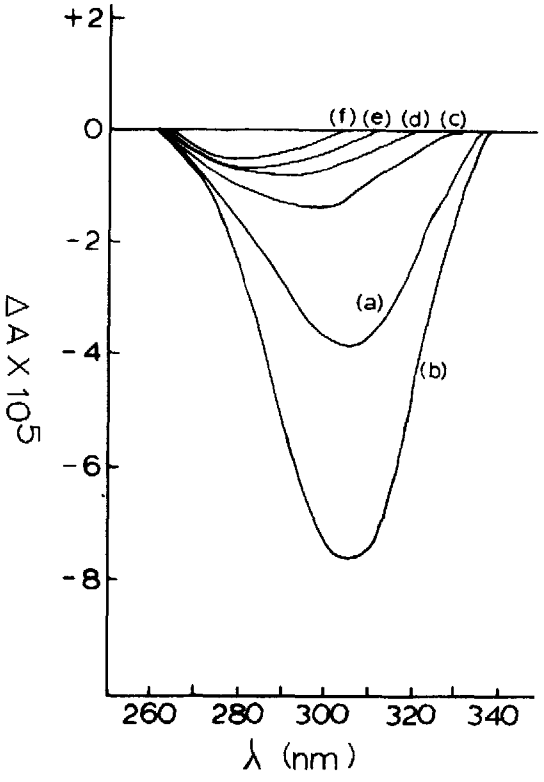


Figure 2. Nitrate CD intensity in 5·$LiNO_3$ complex as a function of solvent composition and concentration:
(a) 100% $CHCl_3$, << 0.02M;
(b) 100% $CHCl_3$, < 0.02M;
(c) 90% $CHCl_3$/10% TFE, 0.01M;
(d) 80% $CHCl_3$/20% TFE, 0.01M;
(e) 62% $CHCl_3$/38% TFE, 0.01M;
(f) 50% $CHCl_3$/50% TFE, 0.01M

The circular dichroism (CD) of the $LiClO_4$ complex of 4 in methanol shows two positive bands at 222 and 274 nm which are assigned to the $^1L_A$ and $^1L_B$ transitions of the substituent aromatic chromophore. This spectrum contrasts with that of the $LiNO_3$ complex of 4 in $CHCl_3$ (Figure 1, curve (a)) which shows a negative band near 290 nm in the region of the $NO_3^-$ $n \rightarrow \pi^*$ transition. Since the $NO_3^-$ ion is inherently achiral, the appearance of an induced CD band in this region indicates that the $NO_3^-$ ion is associated, as part of an ion pair, with the chiral lithium ion-crown complex in $CHCl_3$. (The stronger, positive $^1L_B$ band of the aromatic chromophore ($[\theta]_{274} \approx 250$ deg·cm$^2$·dmole$^{-1}$) overlaps with the nitrate absorption region, making a determination of the $NO_3^-$ $n \rightarrow \pi^*$ CD band maximum difficult.) Similar induction of circular dichroism in ionic benzophenone derivatives by complexation with chiral crown ethers was recently reported by Kaneko, et al.[12] A solution of the complex in 50% $CHCl_3$/50% cyclohexane (v/v) shows no increase in $NO_3^-$ CD intensity, implying that in $CHCl_3$ ion pair formation is complete. From this observation it is possible to estimate a value of about 60 deg·cm$^2$·dmole$^{-1}$ for the $[\theta]_{290}$ value of the $4{\cdot}LiNO_3$ ion pair.

Addition of 2,2,2-trifluoroethanol (TFE) to the chloroform solution causes a reduction of the $NO_3^-$ CD band intensity, with the concentration of 4 and $LiNO_3$ held constant (Figure 1). Two explanations can be invoked for this behavior. One involves the dissociation of nitrate alone from the crown-cation-anion species:

$$\underline{4}{\cdot}Li^+,NO_3^- \rightleftharpoons \underline{4}{\cdot}Li^+ + NO_3^- \qquad (1)$$

The other involves complete dissociation of the salt (probably as an ion pair) from the crown:

$$\underline{4}{\cdot}Li^+,NO_3^- \rightleftharpoons \underline{4} + LiNO_3 \qquad (2)$$

In equilibria (1) and (2) we make no distinction between contact and solvent separated ion pairs. In either case, nitrate ions which are not associated with the chiral crown ether presumably would not contribute to the $NO_3^-$ CD intensity. We favor the former explanation (equilibrium (1)) for the following reasons: in 100% TFE, strong splitting of the $^1L_B$ aromatic band, which is a good indicator of complex formation in benzo-crown ethers,[1] indicates that the complex is not completely dissociated in this solvent. In fact, the formation constant K of the lithium ion complex of benzo-14-crown-4 (benz-14/4) in TFE can be determined spectrophotometrically by monitoring changes in the $^1L_B$ band of the substituent aromatic ring as a function of lithium ion concentration.[13] These occur up to about a 1.1:1.0 cation:crown mole ratio, beyond which the spectrum remains unchanged. Overlays of absorption spectra measured at various lithium ion concentrations show three well defined isosbestic points, strongly suggesting that only the free crown ether and its 1:1 lithium complex exist in solution. From these experiments log K for the equilibrium $Li^+ + \text{benz-14/4} \rightleftarrows Li^+\text{benz 14/4}$ in TFE was calculated to be 4.69 ± 0.06. Based on this K value, the percent lithium ion-crown complex dissociated in 100% TFE is estimated to be less than 5% at the concentrations used in the CD study. The large changes in the $NO_3^-$ CD which occur upon addition of TFE are therefore not due to a shift to the right in equation (2), but rather to a shift to the right in the ion-pair equilibrium (1).

The aliphatic cyclohexane analog 5 displays the same type of ion pairing activity in $CHCl_3$ as does 4, (Figure 2) but the absence of the aromatic ring allows determination of the shape and $[\theta]_{max}$ of the $NO_3^-$ CD band. In Figure 2, curve (a) shows the CD spectrum of a $2x10^{-2}M$ solution of 5 in which some $LiNO_3$ has dissolved; curve (b) was obtained after more $LiNO_3$ had been dissolved. In curves (c) through (f) the concentration of the complex is held constant and the solvent composition is varied, producing a reduction in $NO_3^-$ CD intensity, as before. Induced circular dichroism has also been observed in the nitrate ions of the $4{\cdot}Zn(NO_3)_2$ complex. It is not clear whether the $NO_3^-$ ions in this complex actually occupy a coordination site on the zinc(II) ion, or are ion-paired to the complex by outer-sphere association.

The detection of ion pair formation by circular dichroism represents a novel method of observing ion-pairing.[14] In addition, the orientation of the inherently achiral chromophoric anion with respect to the chiral cationic complex will determine the nature of the CD. Therefore, CD may provide an important method for studying the structures of ion pairs in solution, and we are currently extending the technique to other systems in order to explore this possibility.

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