J. Am. Chem. Soc. **1986**, *108*, 3621–3629

Circular Dichroism Studies of Crown Complexed Ion Pairs: A Comparison of the Alkali and Alkaline Earth Nitrate Complexes of Chiral Crown Ethers

R. Brian Dyer,[†] David H. Metcalf,[†] Robert G. Ghirardelli,[†] Richard A. Palmer,*[†] and Elizabeth M. Holt*[‡]

Contribution from the Department of Chemistry, Duke University, Durham North Carolina 27706, and the Department of Chemistry, Oklahoma State University, Stillwater, Oklahoma 74078.

Received October 29, 1985

Abstract: A series of four chiral 18-crown-6 macrocycles, (2*S*,6*S*)-2,6-dimethyl-1,4,7,10,13,16-hexaoxacyclooctadecane and its (2*R*,3*R*)-2,3-dimethyl isomer and (2*S*,6*S*,11*S*,15*S*)-2,6,11,15-tetramethyl-1,4,7,10,13,16-hexaoxacyclooctadecane and its (2*R*,3*R*,11*R*,12*R*)-2,3,11,12-tetramethyl isomer, have been synthesized. Complexes of these crowns with alkali and alkaline earth nitrate ion pairs have been characterized in chloroform solution, with particular emphasis on the induced circular dichroism (CD) observed in the nitrate $n \rightarrow \pi^*$ transition. The nitrate CD spectra observed for the alkali complexes are distinctly different from those of the corresponding alkaline earth complexes. The sign and intensity patterns in the CD have been interpreted in terms of the coupled oscillator theory for host–guest complexes. Structures based on the CD data for these ion pairs in solution have been proposed and compared to crystal structure data.

Crown ethers were demonstrated by Pedersen[1] to have the important ability to solubilize inorganic salts in aprotic, nonpolar solvents by complexing the metal cation. Pedersen also discovered that the reactivity of the hydroxide anion was greatly enhanced under these conditions,[1] which he attributed to the lack of solvation of the anion. Subsequently, other investigators observed such enhancement for a variety of anions and postulated that it was due to the formation of "naked" anions,[2] which are both unsolvated and unassociated with the complexed cation. However, numerous studies[3] have since shown that while crown ethers weaken the anion–cation interaction, ion pairing is extensive in aprotic, nonpolar solvents and in some cases even persists to a smaller degree in protic solvents.[3c] The association of the anion with the complexed cation has been demonstrated to significantly influence both anion reactivity[4] and the crown–cation interaction, causing changes in complex stability[5] and structure.[6]

Investigations of the specific nature of anion association with the complexed counterion in solution have generally focused on the relative tightness of the ion pairs, spurred by Smid's discovery that crown complexes of fluorenyl salts gave either crown separated or externally complexed contact ion pairs.[7] More specific information about the coordination geometry of the anion has been obtained from resonance Raman measurements of the permanganate anion,[8] from measurements of electric dipole moments of the tosylate anion,[9] from the ^{1}H NMR spectrum of the fluorenyl anion, and from the infrared spectrum of the enolate anion.[10] Apart from these few examples, however, structural studies of crown ether complexes in solution have tended to focus on the crown conformation. The paucity of studies which address the specific coordination geometry of the anion and the limited applicability of these techniques to other systems illustrate the difficulty in obtaining such information.

As part of a continuing effort[11] to use chiroptical techniques to probe both the persistence of ion pairing in crown ether complexes and the solution structure of these ion pairs, we wish to report the use of circular dichroism (CD) to investigate the complexation of alkali nitrate and alkaline earth nitrate ion pairs by a series of four novel, chiral 18-crown-6 macrocycles, (2*S*,6*S*)-2,6-dimethyl-1,4,7,10,13,16-hexaoxacyclooctadecane (**1**)[12] and its (2*R*,3*R*)-2,3-dimethyl isomer (**2**) and (2*S*,6*S*,11*S*,15*S*)-2,6,11,15-tetramethyl-1,4,7,10,13,16-hexaoxacyclooctadecane (**3**) and its (2*R*,3*R*,11*R*,12*R*)-2,3,11,12-tetramethyl isomer (**4**).

While crown ether complexes of alkali and alkaline earth cations of similar size might be expected to have very different solution structures, few such comparative studies have been done. The only direct comparison appears to be Smid's investigations of crown complexed alkali and alkaline earth fluorenyl ion pairs, which does suggest that there are distinct structural differences between these two types of ion pairs.[7] These differences must be due in part to the greater charge density of the alkaline earths. In addition, the ion pair structure of the alkaline earths can be influenced by steric factors which result from the presence of two anions. These can sandwich the complex, effectively shielding the cation from the solvent, either holding the cation in the center of the crown cavity or forming an asymmetric, mixed tight ion pair and crown separated ion pair. In this paper, the induced circular dichroism of the nitrate ion has been used to investigate analogous differences in the structures of crown complexed alkali nitrate and alkaline earth nitrate ion pairs.

Experimental Section

Synthesis of Chiral Crowns. (2*S*,6*S*)-4-Oxaheptane-2,6-diol (5). In a modification of our previously published procedure,[13] potassium *tert*-butoxide was used as the base and 1,2-dimethoxyethane (DME) as the solvent. Thus, 36 g (0.23 mol) of (*S*)-2-[(tetrahydro-2-pyranyl)oxy]-1-propanol in 100 mL of sodium dried DME was added to a solution of 25.8 g (0.23 mol) of *t*-BuOK in 200 mL of DME. After refluxing for 1 h, 71 g (0.23 mol) of (*S*)-1-(*p*-toluenesulfonoxy)-2-[(tetrahydro-2-pyranyl)oxy]propane in 200 mL of dry DME was added with stirring and brought to reflux temperature. After 16 h, the mixture was worked up to yield 64 g of crude THP ether. The crude ether was treated with a large excess of methanol and made acidic as above and then worked up

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[†] Duke University.

[‡] Oklahoma State University.

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in the same manner. Fractional distillation yielded 27 g (90%) of **5**: bp 65–70 °C (0.20 Torr); $[\alpha]_{546}$ +32.7° (neat); ^{1}H NMR ($CDCl_3$) δ 1.13 (6 H, d), 2.40 (2 H, s), 3.40 (4 H, m), 4.00 (2 H, m); ^{13}C NMR ($CDCl_3$) δ 18.5, 65.7, 76.4.

(2*S*,6*S*)-2,6-Dimethyl-1,4,7,11,13,16-hexaoxacyclooctadecane (1). Following the method of Greene[14] for the preparation of 18-crown-6, 8.5 g (76 mmol) of *t*-BuOK in 200 mL of dry DME was added under nitrogen to 10 g (76 mmol) of diol **5** in 200 mL of dry DME. After 0.5 h, 39.2 g (78 mmol) of 1,11-bis(*p*-toluenesulfonoxy)-3,6,9-trioxaundecane in 200 mL of dry DME was added at twice the rate of a second solution of 8.5 g (76 mmol) of *t*-BuOK in 200 mL of dry DME. The mixture was refluxed for 16 h, and then the solvent was stripped and the remaining solids were dissolved in water and extracted three times with ether. The ether layers were combined and dried over anhydrous $MgSO_4$, and then the solvent was removed. Fractional distillation gave 11.0 g (50%) of product **1** as a pale yellow oil (pure by GC, NMR). Further purification was necessary for the CD studies and was accomplished by forming the KNO_3 complex. The pale yellow oil was stirred with excess KNO_3 in $CHCl_3$ for 12 h. The solution was then filtered and the $CHCl_3$ mostly removed. Addition of DME caused the KNO_3 complex to be formed as white needles. After the solution was cooled for 12 h, the needles were collected by filtration and washed with cold DME to yield 10 g of complex. The complex was dissolved in H_2O which was then extracted three times with $CHCl_3$. The $CHCl_3$ layers were combined and dried over molecular sieves. The $CHCl_3$ was removed and the remaining oil was distilled to yield 5 g of colorless crown **1**: bp 116–120 °C (0.2 Torr); IR (neat film, KRS-5 plates) 2972 (s), 2934 (s), 2874 (s), 1455 (w), 1373 (w), 1348 (w), 1296 (w), 1250 (w), 1130 (s), 987 (w), 941 (w), 918 (w), 841 (w) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.13 (6 H, d), 3.45–3.75 (22 H, m with sharp singlet at 3.60); ^{13}C NMR ($CDCl_3$) δ 16.9, 68.5, 70.8, 71.0, 74.8, 75.3; VPO MW = 285. Anal. Calcd for $C_{14}H_{28}O_6$: C, 57.51; H, 9.65. Found: C, 57.25; H, 9.64.

(4*S*,8*S*)-4,8-Dimethyl-3,6,9-trioxaundecane-1,11-diol (6). The general procedure of Ammann et al.[15] was used to prepare diethyl (4*S*,8*S*)-4,8-dimethyl-3,6,9-trioxaundecane-1,11-dioate from the starting diol **5**. Thus, to 15 g (0.11 mol) of **5** in 300 mL of dry CH_2Cl_2, 41 g (0.26 mol, 30% excess) of ethyl diazoacetate (71% in CH_2Cl_2) was added under nitrogen. Some boiling stones were added to promote smooth evolution of nitrogen produced, then 2 mL of boron trifluoride diethyl etherate catalyst was added slowly, with stirring, over a period of 2 h, until evolution of nitrogen ceased. The solution was neutralized by addition of $NaHCO_3$ and filtered, and the solvent was stripped to yield 24 g of crude diester. The diester was reduced with $LiAlH_4$ in the usual manner. Fractional distillation yielded 14 g (60%) of **6** as a pale yellow oil: bp 98–110 °C (0.1 Torr); ^{1}H NMR δ 1.13 (6 H, d), 2.90 (2 H, br s), 3.40–3.80 (14 H, m); ^{13}C NMR ($CDCl_3$) δ 16.1, 61.3, 70.2, 74.0, 74.7. The dimesylate **7** was prepared from this diol with methanesulfonyl chloride, in the usual manner.

(2*S*,6*S*,11*S*,15*S*)-2,6,11,15-Tetramethyl-1,4,7,10,13,16-hexaoxacyclooctadecane (3). Following the general procedure described above for the cyclization reaction, 3.25 g (29 mmol) of *t*-BuOK in 200 mL of dry DME was added under nitrogen to 3.8 g (28 mmol) of diol **5** in 200 mL of dry DME. After 0.5 h, 15 g (28 mmol) of dimesylate **7** in 200 mL of dry DME was added at twice the rate of a second solution of 3.25 g (29 mmol) of *t*-BuOK in 200 mL of dry DME. The mixture was refluxed for 12 h and then worked up as described for **1**. Fractional distillation yielded 3.9 g (44%) of **3** as a pale yellow oil. Attempted complexation with KNO_3 by the method used with **1** failed; however, the $NaNO_3$ complex was made by using the same procedure. Isolation of the crown yielded 1.4 g of colorless oil **3**: bp 95–100 °C (0.05 Torr); IR (neat film, KRS-5 plates) 2970 (s), 2934 (s), 2868 (s), 1456 (w), 1373 (m), 1340 (w), 1292 (w), 1257 (w), 1132 (s), 1117 (s), 987 (w), 955 (w), 883 (w), 818 (w) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.10 (12 H, d), 3.40–3.80 (20 H, m with sharp s at 3.70); ^{13}C NMR δ 16.75, 68.78, 74.85, 75.51; VPO MW = 328. Anal. Calcd for $C_{16}H_{32}O_6$: C, 59.90; H, 10.07; Found: C, 59.79; H, 9.92.

(2*R*,3*R*)-(−)-2,3-Butanediol (8). This diol was prepared according to the procedure of Ledingham et al.[16] by fermentation of glucose by *Bacillus polymyxa* (21830, American Type Culture Collection, Rockville, MD).[17] After completion of fermentation (about 1 week), the broth was extracted with diethyl ether, the solvent and water were stripped off, and the resulting dark oil was fractionally distilled to give **8** as a colorless oil, which solidifies upon storing over molecular sieves at 10 °C (lit. mp 19 °C). A typical yield per liter of fermentation broth is 15 g of diol: bp 50 °C (0.05 Torr); $[\alpha]_{546}$ −15.2° (neat; lit. $[\alpha]_{546}$ −15°); ^{1}H NMR δ 1.18 (6 H, d), 2.42 (2 H, br s), 3.50 (2 H, d of q).

(4*R*,5*R*)-4,5-Dimethyl-3,6-dioxaoctane-1,8-diol (9). Diethyl (4*R*,5*R*)-4,5-dimethyl-3,6-dioxaoctane-1,8-dioate was prepared from the starting diol **8** with use of the ethyl diazoacetate procedure described above. Thus, 25 g (0.26 mol) of **8** in 500 mL of dry CH_2Cl_2 was reacted with 80 g of an 87% ethyl diazoacetate in CH_2Cl_2 solution (0.61 mol) and 3 mL of boron trifluoride–diethyl etherate catalyst. The reaction was worked up as before, and the diester was fractionally distilled (bp 85–100 °C (0.025 Torr)). The diester was then reduced with $LiAlH_4$ in the usual manner. The product diol was fractionally distilled, yielding 25 g (58%) of **9**: bp 75–82 °C (0.05 torr); ^{1}H NMR δ 1.18 (6 H, d), 2.90 (2 H, br s), 3.40–3.80 (10 H, m); 98% pure by GC analysis.

(2*R*,3*R*)-2,3-Dimethyl-1,4,7,10,13,16-hexaoxacyclooctadecane (2). Following the general procedure described above for the cyclization reaction, 5.7 g (32 mmol) of the diol **9** in 400 mL of dry DME was stirred with 1 equiv of *t*-BuOK for 0.5 h under nitrogen. A solution of 15.6 g (34 mmol) of 1,8-bis(*p*-toluenesulfonoxy)-3,6-dioxaoctane in 200 mL of dry DME was then added at twice the rate of a solution of the second equivalent of *t*-BuOK in dry DME. The mixture was refluxed for 24 h and then worked up and distilled as described above, yielding 3.9 g (40%) of a pale yellow oil (98% pure by GC analysis). Further purification was accomplished by forming the KNO_3 complex, in the same manner as for the 2,6-dimethyl isomer **1**. The crown **3** was recovered from this complex as a colorless oil: bp 112–120 °C (0.04 Torr); IR (neat film, KRS-5 plates) 2970 (s), 2935 (s), 2870 (s), 1456 (w), 1373 (w), 1348 (w), 1296 (w), 1248 (w), 1117 (s), 991 (w), 945 (w), 849 (w) cm^{-1}; ^{1}H NMR δ 1.16 (6 H, d), 3.40–3.75 (22 H, m with strong s at 3.65); ^{13}C NMR δ 15.5, 69.0, 70.7, 70.9, 71.1, 78.9; VPO MW = 287. Anal. Calcd for $C_{14}H_{28}O_6$: C, 57.51; H, 9.65. Found: C, 57.37; H, 9.63.

(2*R*,3*R*,11*R*,12*R*)-2,3,11,12-Tetramethyl-1,4,7,11,13,16-hexaoxacyclooctadecane (4). The synthesis of this crown was accomplished by a one-pot, four-piece cyclization, similar to the method used for the preparation of its tetraphenyl analogue.[18] A solution of 7.6 g (84 mmol) of diol **8** and 37 g (89 mmol) of 1,5-bis(*p*-toluenesulfonoxy)-3-oxapentane in 500 mL of dioxane was stirred over 10 g of powdered NaOH. The mixture was refluxed for 3 days, and then the NaOTs and excess NaOH were removed by filtration and the dioxane was stripped to leave a brown oil which was fractionally distilled to yield 6 g (44%) of yellow 2,3,11,12-tetramethyl-18-crown-6 (**4**) (95% pure by GC analysis). Further purification was accomplished by stirring the crown with excess $Ca(NO_3)_2$ in $CHCl_3$ for 2 days to form the $Ca(NO_3)_2$ complex. The solution was then filtered and allowed to evaporate slowly, forming truncated octahedral crystals of the complex. The crown **4** was recovered as described above, as a colorless oil: bp 120–125 °C (0.05 Torr); IR (neat film, KRS-5 plates) 2974 (s), 2930 (s), 2866 (s) 1456 (m), 1373 (w), 1350 (w), 1290 (w), 1244 (w), 1136 (s), 1111 (s), 1005 (w), 943 (w), 853 (w) cm^{-1}; ^{1}H NMR δ 1.18 (12 H, d), 3.35–3.80 (20 H, m with strong s at 3.70); ^{13}C NMR δ 15.9, 69.4, 71.1, 79.5; VPO MW = 330. Anal. Calcd for $C_{16}H_{32}O_6$: C, 59.90; H, 10.07. Found: C, 59.90; H, 10.13.

Circular Dichroism Measurements. CD spectra were recorded on a JASCO Model ORD-CD-5 with SS-20 modification. The instrument was calibrated in the region of the nitrate absorption by using an aqueous solution of the (tris(hydroxymethyl)amino)methane salt of *d*-camphorsulfonic acid, according to the method of Pearson et al.[19] Fisher spectrograde chloroform with a UV cutoff of at least 4.0 μm^{-1} was used to prepare the CD solutions. The 0.75% ethanol stabilizer was removed by passing the solvent through a short column of neutral alumina just before use. It was then dried by distillation from CaH_2 and stored over freshly activated molecular sieves. Solutions of metal nitrate crown complexes were prepared by stirring the anhydrous metal nitrate with a slight excess of crown in chloroform under dry nitrogen overnight.

Vapor-Phase Osmometry and Conductance of Complexes. Solutions of the crown complexes in chloroform were prepared as above. Molecular weight determinations in chloroform were made at 35 °C on a Mechrolab Model 321 Vapor Pressure Osmometer equipped with a nonaqueous probe. The instrument was calibrated in the range 0.01–0.1 M with reagent grade benzil as a standard. Measured molecular weights of complexes in chloroform are as follows (actual MW given in parentheses): $[(\mathbf{1})Na^+]NO_3^-$, 385 (377); $[(\mathbf{1})K^+]NO_3^-$, 391 (393); $[(\mathbf{1})Rb^+]NO_3^-$, 436 (439); $[(\mathbf{1})Mg^{2+}](NO_3^-)_2$, 451 (440); $[(\mathbf{1})Sr^{2+}](NO_3^-)_2$, 509 (504); $[(\mathbf{1})Ba^{2+}](NO_3^-)_2$, 562 (553). Conductance measurements were obtained at 25 ± 0.05 °C with use of a Beckman Model RC-18A

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Table I. Crystal Data for $[(\mathbf{1})M^{2+}](NO_3^-)_2$ (M = Ca (I), Sr (II), and Ba (III)) and for $[(\mathbf{4})Ca^{2+}](NO_3^-)_2$ (IV)

	I	II	III	IV
formula	$C_{14}H_{28}CaN_2O_{12}$	$C_{14}H_{28}SrN_2O_{12}$	$C_{14}H_{28}BaN_2O_{12}$	$C_{16}H_{32}CaN_2O_{12}$
MW	456.5	504.0	553.7	484.5
a (Å)	12.080 (4)	8.296 (5)	8.380 (5)	9.430 (5)
b (Å)	11.656 (4)	8.338 (3)	8.430 (4)	9.430
c (Å)	7.693 (4)	8.313 (5)	8.410 (4)	26.077 (11)
α (deg)	90.0	105.33 (4)	80.20 (4)	90.0
β (deg)	105.32 (3)	105.52 (4)	106.56 (4)	90.0
γ (deg)	90.0	80.63 (4)	106.49 (4)	90.0
V (Å^3)	1044.6 (7)	531.8 (4)	543.4 (5)	2319.2 (20)
$F(000)$	484	260	278	1032
μ(Mo Kα) (cm^{-1})	3.91	29.05	20.28	3.20
μ(Mo Kα) (Å)	0.71069	0.71069	0.71069	0.71069
D_{calcd} (g cm^{-3})	1.451	1.573	1.69	1.387
Z	2	1	1	4
obsd. refl.	1340	2132	4072	1644
R (%)	24.8	8.9	7.5	6.8
space group	$P2_1$	P_1	P_1	$P4_12_12$

conductance bridge operating at 1 kHz and a Jones type conductivity cell. The cell constant (0.05041) was determined by numerous calibrations with aqueous KCl. Molar conductivities (Λ_m/ohm^{-1} cm^2 mol^{-1}) of complexes in chloroform are as follows: $[(\mathbf{4})Li^+]NO_3^-$, 0.1004; $[(\mathbf{4})K^+]NO_3^-$, 0.1142; $[(\mathbf{4})Sr^{2+}](NO_3^-)_2$, 0.0358; $[(\mathbf{4})Ba^{2+}](NO_3^-)_2$, 0.0562; $[(\mathbf{3})Li^+]NO_3^-$, 0.1301.

Determination of Crystal Structures. Crystal Preparation. Crystals of $[(\mathbf{1})M^{2+}](NO_3^-)_2$, M = Ca (I), Sr (II), and Ba (III) were grown from $CHCl_3$:DME (90:10) solutions by slow evaporation under dry argon. Analyses of single crystals were consistent with 1:1 complex formation: Anal. Calcd for $C_{14}H_{28}CaN_2O_{12}$: C, 36.84; H, 6.18; N, 6.14. Found: C, 36.78; H, 6.17; N, 6.12. Anal. Calcd for $C_{14}H_{28}SrN_2O_{12}$: C, 33.36; H, 5.60; N, 5.56. Found: C, 33.24; H, 5.35; N, 5.42. Anal. Calcd for $C_{14}H_{28}BaN_2O_{12}$: C, 30.37; H, 5.10; N, 5.06. Found: C, 30.47; H, 5.03; N, 4.96. Slow evaporation of a chloroform solution of the 1:1 complex of $[(\mathbf{4})Ca^{2+}](NO_3^-)_2$ (IV) yielded truncated octahedral crystals. Anal. Calcd for $C_{16}H_{32}CaN_2O_{12}$: C, 39.66; H, 6.66; N, 5.78. Found: C, 39.59; H, 6.58; N, 5.72.

Collection and Reduction of X-ray Data. The crystallographic data are summarized in Table I. Single crystals of each complex were sealed in capillaries and mounted on a Syntex P3 automated diffractometer. Unit cell dimensions were determined by least-squares refinement of the best angular positions for 15 independent reflections ($2\theta > 15°$) during normal alignment procedures, using molybdenum radiation (λ = 0.71069 Å). Data were collected at room temperature by using a variable scan rate, a θ–2θ scan mode and a scan width of 1.2° below Kα_1 and 1.2° above Kα_2 to a maximum 2θ value of 60°. Backgrounds were measured at each side of the scan for a combined time equal to the total scan time. The intensities of three standard reflections were remeasured after every 97 reflections and varied by less than 8%, so that corrections for decomposition were deemed unnecessary. Data were corrected for Lorentz, polarization, and background effects. After removal of redundant and space group forbidden data, 1340 (I), 2132 (II), 4072 (III), and 1644 (IV) reflections were considered observed [$I > 3.0\sigma(I)$].

Solution and Refinement of Structures. The structures were solved by conventional heavy-atom techniques. The metal atoms in each case were located by Patterson syntheses. Successive least-squares and difference Fourier cycles allowed location of the remainder of the non-hydrogen atoms. Refinement of scale factor and positional and anisotropic thermal parameters for all non-hydrogen atoms was carried out to convergence.[20] Hydrogen positional parameters were not determined. The atomic scattering factors were taken from Cromer and Mann,[21] and anomalous dispersion corrections were made in each case. The final cycle of refinement [function minimized $\sum(|F_o| - |F_c|)^2$] led to a final agreement factor R = 24.8 (I), 8.9 (II), 7.5 (III), and 6.8% (IV) [$R = (\sum||F_o| - |F_c||/\sum|F_o|)100$]. The final positional parameters of the refined atoms appear in Tables II–V, and the calculated bond angles and distances, thermal parameters, and observed and calculated structure factor amplitudes are included as supplementary material.

Results

Synthesis of Chiral Crowns. The series of chiral 18-crown-6 macrocycles **1–4** was synthesized according to Schemes I and II.

Table II. Positional Parameters for $[(\mathbf{1})Ca^{2+}](NO_3^-)_2$

atom	x ($\sigma(x)$)	y ($\sigma(y)$)	z ($\sigma(z)$)
Ca1	0.2617 (9)	0.3092	0.6108 (14)
N1	0.042 (4)	0.314 (5)	0.351 (5)
O101	−0.053 (4)	0.336 (6)	0.242 (7)
O102	0.084 (4)	0.214 (4)	0.415 (6)
O103	0.098 (3)	0.395 (4)	0.389 (5)
N2	0.509 (6)	0.280 (6)	0.817 (9)
O201	0.620 (4)	0.328 (6)	0.892 (7)
O202	0.433 (4)	0.305 (5)	0.862 (5)
O203	0.502 (4)	0.264 (5)	0.659 (7)
O1	0.306 (4)	0.274 (6)	0.310 (7)
N2	0.339 (3)	0.365 (4)	0.276 (5)
O3	0.342 (5)	0.476 (5)	0.501 (7)
O4	0.320 (6)	0.553 (8)	0.549 (11)
O5	0.252 (4)	0.473 (5)	0.816 (6)
O6	0.292 (6)	0.519 (8)	0.770 (9)
O7	0.095 (3)	0.352 (4)	0.767 (4)
O8	0.098 (11)	0.260 (15)	0.776 (16)
O9	0.215 (4)	0.144 (5)	0.801 (6)
O10	0.297 (10)	0.068 (10)	0.563 (16)
O11	0.286 (7)	0.098 (8)	0.505 (11)
O12	0.359 (3)	0.156 (3)	0.472 (4)

Table III. Positional Parameters for $[(\mathbf{1})Sr^{2+}](NO_3^-)_2$

atom	x ($\sigma(x)$)	y ($\sigma(y)$)	z ($\sigma(z)$)
Sr1	0.0402	0.6723	0.2749
N1	0.276 (3)	0.921 (4)	0.574 (4)
O101	0.379 (3)	0.992 (4)	0.691 (3)
O102	0.267 (4)	0.905 (4)	0.419 (4)
O103	0.182 (4)	0.826 (5)	0.590 (4)
N2	−0.189 (3)	0.454 (4)	−0.014 (3)
O201	−0.263 (4)	0.348 (4)	−0.125 (4)
O202	−0.179 (4)	0.451 (5)	0.134 (4)
O203	−0.103 (4)	0.542 (4)	−0.047 (4)
O1	0.229 (2)	0.695 (2)	0.055 (2)
O4	−0.044 (2)	0.923 (2)	0.088 (2)
O7	−0.190 (5)	0.933 (5)	0.279 (3)
O10	−0.200 (2)	0.762 (2)	0.466 (2)
O13	0.031 (2)	0.489 (2)	0.494 (2)
O16a	0.335 (4)	0.486 (2)	0.282 (5)
O16b	0.234 (4)	0.389 (4)	0.278 (5)
C2	0.217 (2)	0.849 (3)	0.018 (2)
C3	0.037 (3)	0.904 (3)	−0.053 (3)
C5	−0.224 (4)	0.966 (5)	0.037 (5)
C6	−0.213 (7)	1.036 (5)	0.175 (8)
C8	−0.277 (4)	0.966 (9)	0.345 (14)
C9	−0.229 (4)	0.982 (5)	0.541 (4)
C11	−0.185 (2)	0.682 (3)	0.599 (3)
C12	−0.142 (4)	0.494 (5)	0.524 (5)
C14	0.010 (2)	0.320 (3)	0.456 (3)
C15a	0.374 (7)	0.384 (5)	0.560 (5)
C15b	0.280 (7)	0.330 (6)	0.436 (7)
C17a	0.424 (4)	0.450 (3)	0.133 (4)
C17b	0.333 (6)	0.430 (5)	0.042 (6)
C18	0.394 (3)	0.616 (3)	0.096 (3)

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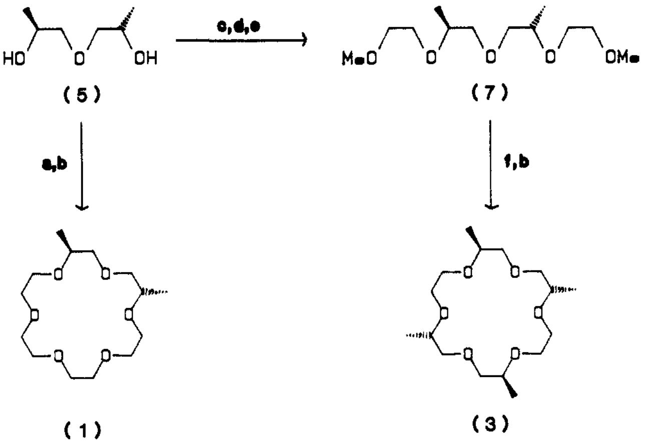
(20) Stewart, J. M., Ed. "The XRAY System-Version of 1980, Tech. Rep. TR-446," Computer Science Center, University of Maryland, College Park, MD.

(21) Cromer, D. T.; Mann, J. B. *Acta Crystallogr.* **1968**, *A24*, 321.

Table IV. Positional Parameters for $[(\mathbf{1})Ba^{2+}](NO_3^-)_2$

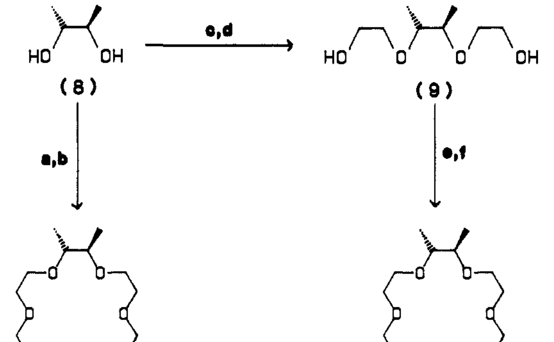
atom	x ($\sigma(x)$)	y ($\sigma(y)$)	z ($\sigma(z)$)
Ba1	0.0382	0.0098	0.9773
N1	−0.267 (3)	−0.231 (3)	0.733 (2)
O101	−0.370 (2)	−0.332 (3)	0.649 (3)
O102	−0.286 (3)	−0.149 (6)	0.826 (5)
O103	−0.146 (3)	−0.241 (4)	0.746 (5)
N2	0.373 (4)	0.256 (4)	1.224 (5)
O201	0.494 (2)	0.341 (3)	1.320 (3)
O202	0.389 (3)	0.168 (5)	1.136 (6)
O203	0.189 (2)	0.239 (4)	1.219 (3)
O1	−0.147 (1)	0.262 (1)	0.889 (1)
O4	−0.146 (1)	−0.074 (2)	1.226 (2)
O7	0.047 (1)	−0.182 (1)	1.279 (1)
O10	0.260 (1)	−0.175 (1)	0.965 (2)
O13	0.262 (2)	0.001 (2)	0.786 (1)
O16	0.048 (2)	0.311 (2)	0.777 (2)

Scheme I



(a) $TsO(CH_2CH_2O)_4Ts$. (b) 2 *t*-BuOK. (c) $N_2CHCO_2C_2H_5$, BF_3. (d) $LiAlH_4$. (e) MsCl. (f) (2*S*,6*S*)-4-Oxaheptane-2,6-diol (**5**).

Scheme II



(a) $(TsOCH_2CH_2)_2O$. (b) 2 NaOH. (c) $N_2CHCO_2C_2H_5$, BF_3Et_2O. (d) $LiAlH_4$. (e) $TsO(CH_2CH_2O)_3Ts$. (f) 2 *t*-BuOK.

Table V. Positional Parameters for $[(\mathbf{4})Ca^{2+}](NO_3^-)_2$

atom	x ($\sigma(x)$)	y ($\sigma(y)$)	z ($\sigma(z)$)
Ca1	0.4880 (1)	−0.4880	−0.2500
N1	0.7129 (7)	−0.7129	−0.2500
O10	0.7184 (6)	0.3896 (6)	−0.2198 (2)
O11	0.8049 (6)	−0.8049	0.2500
N2	0.2628 (6)	−0.2628	−0.2500
O20	0.3041 (6)	0.6790 (6)	−0.2904 (2)
O21	0.1720 (6)	−0.1720	−0.2500
O1	0.4141 (5)	0.3770 (5)	−0.1682 (1)
C2	0.3216 (8)	0.2571 (9)	−0.1718 (3)
C3	0.2033 (11)	0.2972 (10	−0.2084 (3)
O4	0.2732 (5)	0.3459 (5)	−0.2541 (2)
C5	0.1994 (10)	0.3238 (13)	−0.2990 (4)
C6	0.2825 (10)	0.3321 (10)	−0.3432 (3)
O7	0.3884 (5)	0.4289 (6)	−0.3431 (2)
C8	0.4789 (10)	0.4430 (11)	−0.3837 (3)
C9	0.5787 (10)	0.5482 (10)	−0.3806 (3)
C10	0.1054 (10)	0.3990 (14)	−0.1898 (4)
C11	0.4035 (12)	0.1248 (9)	−0.1871 (4)
H2	0.2568	0.2880	−0.1318
H3	0.1541	0.2056	−0.2143
H51	0.1205	0.2329	−0.2911
H52	0.1162	0.4868	−0.3106
H61	0.2430	0.3010	−0.3813
H62	0.3911	0.2332	−0.3367
H81	0.4335	0.4053	−0.4161
H82	0.4768	0.3646	−0.3489
H91	0.6239	0.5800	−0.4116
H92	0.6912	0.4797	−0.3876
H101	0.1673	0.4699	−0.1686
H102	0.0541	0.4543	−0.2049
H103	0.0694	0.4206	−0.1548
H111	0.3720	0.1577	−0.2277
H112	0.4830	0.1575	−0.1674
H113	0.3415	0.0329	−0.1853

The 18-crown-6 ring was selected because of the wide range in complexing ability of the achiral parent compound. Chirality is conferred on these crowns by the presence of methyl substituents, which places chiral centers directly on the ring. The 2,6-dimethyl and 2,6,11,15-tetramethyl crowns (**1** and **3**) were synthesized from the chiral precursor (*S*)-(+)-ethyl lactate. The synthesis of the basic chiral unit of these crowns, (2*S*,6*S*)-4-oxaheptane-2,6-diol **5**, and its use in the preparation of chiral macrocyclic polyethers have been previously reported.[11,13] The 2,3-dimethyl and 2,3,11,12-tetramethyl crowns (**2** and **4**) were synthesized from the chiral precursor (2*R*,3*R*)-(−)-2,3-butanediol obtained from fermentation of glucose by *Bacillus polymyxa*.[16] The basic synthetic procedures for the construction of the macrocyclic rings are Williamson reactions and are in general adaptations of the original procedures used by Pedersen.[1] Since no bond to asymmetric carbon is broken in these procedures, the original configurations of the chiral precursors, (*S*) and (*R*), respectively, should be preserved. This presumption has been verified by X-ray diffraction.[22,23] These substituted macrocyclic rings have been designed such that at least one twofold axis of symmetry is retained, which assures that they are formally homeotopic, reducing the number of species which must be considered in solution. Completely saturated macrocycles were used since our investigation of ion pairing required that they be transparent in the near-UV spectral region. The variation in number and position of methyl substituents on the macrocyclic ring has allowed evaluation of the influence of these substituents on the crown–cation association and on the interaction of the complexed cation with the nitrate anion.

Synthesis of Crown Complexes. The alkali and alkaline earth nitrate complexes of each crown were synthesized by stirring the anhydrous metal nitrates with a solution of the crown in chloroform under N_2. The metal nitrates, which are themselves insoluble in chloroform, are in most cases gradually solubilized in the presence of 1 equiv of crown ether to form 1:1 complexes. However, the K^+, Rb^+, Sr^{2+}, and Ba^{2+} complexes of the tetramethyl crowns could not be formed by this method, even after being stirred for several days. These complexes had to be preformed in methanol, which was then removed in vacuo. The resulting complexes dissolved readily in chloroform. Apparently it is the increased lipophilicity provided by the methyl substituents which enables these crowns to solubilize the metal nitrates in chloroform, something the unsubstituted 18-crown-6 is unable to accomplish. Elemental analyses of complexes isolated from these chloroform solutions are consistent with 1:1 complex formation. In addition, vapor-phase osmometry and conductance measure-

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(22) Holt, E. M.; Malpass, G. D. Jr.; Ghirardelli, R. G.; Palmer, R. A.; Rubin, B. *Acta Crystallogr.* **1984**, *C40*, 394; **1984**, *C40*, 396.

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Table VI. Circular Dichroism Data for the n → π* Nitrate Transition of the Dimethyl-18-crown-6 Metal Nitrate Complexes

	2,6-dimethyl-18-crown-6			2,3-dimethyl-18-crown-6		
cation	E (μm^{-1})	$[\theta]^a$	$10^5 g^b$	E (μm^{-1})	$[\theta]^a$	$10^5 g^b$
Li^+	3.31	+8	+21	3.39	−2	−5
Na^+	3.28	+3	+7	3.33	*c*	*c*
K^+	3.28	−2	−5	3.28	+9	+22
Rb^+	3.29	−1	−3	3.28	+4	+10
Mg^{2+}	3.31	+20	+52	3.33	−11	−28
Ca^{2+}	3.40	+23	+58	3.40	−42	−106
Sr^{2+}	3.39	+30	+75	3.39	−53	−133
Ba^{2+}	3.33	+14	+36	3.38	−17	−43

[a] Molecular ellipticity, deg·cm²·dmol⁻¹. [b] Anisotropy factor (see text). [c] Too weak to be detected.

Table VII. Circular Dichroism Data for the n → π* Nitrate Transition of the Tetramethyl-18-crown-6 Metal Nitrate Complexes

	2,6,11,15-tetramethyl-18-crown-6			2,3,11,12-tetramethyl-18-crown-6		
cation	E (μm^{-1})	$[\theta]^a$	$10^5 g^b$	E (μm^{-1})	$[\theta]^a$	$10^5 g^b$
Li^+	3.29	+9	+23	3.36	−7	−18
Na^+	3.29	+7	+18	3.31	−1	−3
K^+	3.33	−4	−10	3.28	+16	+40
Rb^+	3.33	−2	−5	3.28	+14	+35
Mg^{2+}	3.39	+48	+121	3.40	−9	−24
Ca^{2+}	3.39	+79	+199	3.39	−62	−160
Sr^{2+}	3.34	+90	+227	3.28	−36	−91
Ba^{2+}	3.33	+39	+98	3.28	−28	−71

[a] Molecular ellipticity, deg·cm²·dmol⁻¹. [b] Anisotropy factor (see text).

ments indicate that the nitrate ions are essentially completely ion paired in chloroform. The vapor-phase osmometry measurements also preclude the possibility that these ion pairs exist as aggregates in solution since the effective molecular weight in each case is that of a discrete 1:1 crown complexed ion pair.

Circular Dichroism of Complexes. An induced circular dichroism in the lowest energy (n → π*) transition of the nitrate ion is observed for the metal nitrate complexes of these chiral crowns in chloroform. The CD spectra for the alkali nitrate complexes of 2,6-dimethyl-18-crown-6 (**1**) in chloroform are shown in Figure 1. The molecular ellipticity and energy maxima for the nitrate n → π* transition of the alkali and alkaline earth nitrate complexes of all four crowns are summarized in Tables VI and VII. The molecular ellipticities for the alkaline earth complexes are calculated per mole of nitrate, to permit direct comparison with those observed for the alkali complexes. The calculated anisotropy factors are also summarized in the tables. The anisotropy factor, *g*, is a unitless measure of the CD intensity which is characteristic of the type of transition involved and is defined as

$$g = \frac{\Delta\epsilon}{\epsilon} = \frac{(\epsilon_l - \epsilon_r)}{1/2(\epsilon_l + \epsilon_r)} = \frac{4R}{D} \tag{1}$$

where R and D are the rotational and dipole strengths of the transition, respectively. The g values observed for these complexes are small, typical of electric and magnetic dipole forbidden transitions.[24]

Description of Crystal Structures. The crystal structures of the calcium, strontium, and barium nitrate complexes of 2,6-dimethyl-18-crown-6 are disordered. The alkaline earth cation and nitrate positions refine well for all three compounds. However, a different degree of disorder exists in the crown ether ring in each case, being greatest in the Ca^{2+} complex and least in that of Ba^{2+}. In the Ca^{2+} complex, the crown displays a "necklace" of 12 half-occupancy oxygen atoms, indicating disorder of the entire crown ether ring about the N–Ca–N axis. The best model for this disorder (producing the best agreement factor) involved four partial occupancy crown ether rings with a resulting half-occupancy coincidence at the oxygen positions. The Sr^{2+} structure displays disorder in the C15–O16–C17 portion of the ring, these atoms being better described by two half-occupancy positions. While more reasonable behavior is seen for the other atoms of the ring, the C6–O7–C8 group suffers a lesser but similar disorder.

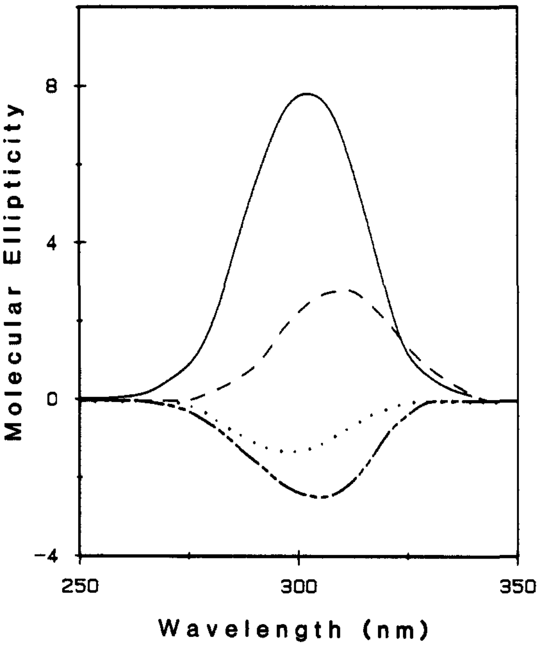

Figure 1. CD spectra for the alkali metal nitrate complexes of 2,6-dimethyl-18-crown-6 (**1**) in $CHCl_3$: (—) Li^+, (---) Na^+, (···) Rb^+, and (- - -) K^+.

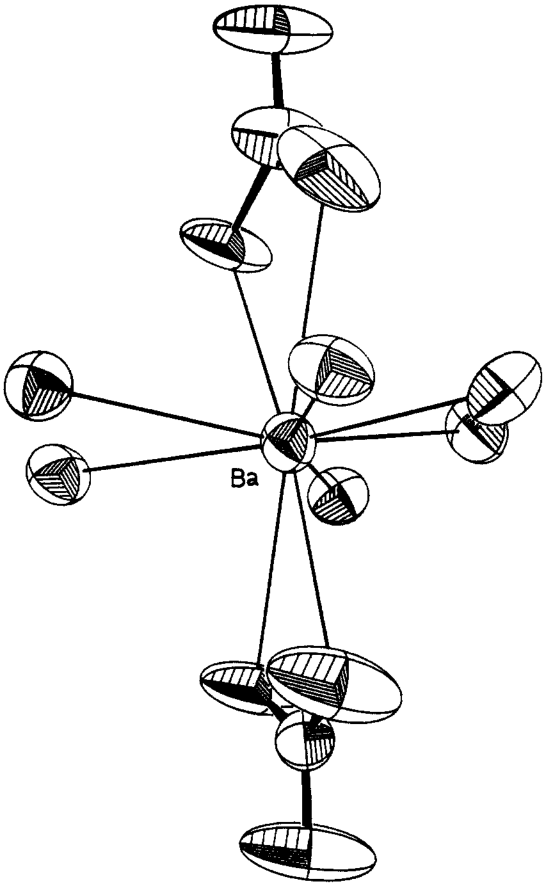

Figure 2. Ortep plot of the structure of the $Ba(NO_3)_2$ complex of 2,6-dimethyl-18-crown-6 (**1**), with 50% probability ellipsoids. The missing methylene bridges and methyl substituents of the crown are disordered.

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[24] Charney, E. "The Molecular Basis of Optical Activity: Optical Rotatory Dispersion and Circular Dichroism"; John Wiley and Sons: New York, 1979; p 94.

Table VIII. Selected Bond Angles (deg) and Distances (Å) for $[(1)M^{2+}](NO_3^-)_2$ (M = Ca (I), Sr (II), and Ba (III))

	I	II	III
M–O102	2.53 (4)	2.73 (3)	2.71 (3)
M–O103	2.47 (4)	2.64 (3)	2.91 (3)
M–O202	2.43 (4)	2.62 (4)	2.89 (2)
M–O203	2.87 (5)	2.63 (3)	2.82 (3)
N1–O101	1.26 (6)	1.20 (4)	1.19 (3)
N1–O102	1.30 (8)	1.24 (5)	1.20 (6)
N1–O103	1.16 (7)	1.25 (6)	1.01 (4)
N2–O201	1.43 (8)	1.21 (4)	1.23 (4)
N2–O202	1.10 (9)	1.22 (4)	1.20 (7)
N2–O203	1.20 (9)	1.22 (2)	1.49 (4)
N1–M–N2	167.3 (18)	177.0 (7)	176.9 (13)
M–crown oxygen atoms	2.68 (7) av	2.70 (2)	2.80 (3)
st. dev. N, O101, O102, O103: plane 1	0.009	0.038	0.046
st. dev. N2, O201, O202, O203: plane 2	0.166	0.037	0.049
angle plane 1/plane 2	84.5	9.22	6.75

Table IX. Dihedral Angles (deg) for $[(4)Ca^{2+}](NO_3^-)_2$

C8′–C9′–O1–C2	170.1
C9′–O1–C2–C3	131.0
O1–C2–C3–O4	53.0
C2–C3–O4–C5	150.1
C3–O4–C5–C6	-162.1
O4–C5–C6–O7	-35.7
C5–C6–O7–C8	177.9
C6–O7–C8–C9	177.3
O7–C8–C9–O1′	28.4

The Ba^{2+} complex shows six ordered oxygen positions but disorder of the bridging ethylene groups. It is clear, however, that in each of the three structures, the metal atom is surrounded by a nearly planar ring of crown ether oxygen atoms. The nitrate ions are ordered in all three structures and are coordinated to the metal ion in a bidentate manner, on opposite sides of the mean ring plane. The positions of the ordered atoms in the Ba^{2+} complex are illustrated in Figure 2. Bidentate coordination is typical of nitrate bonding and has been previously observed in many crown complexes, including those of $LiNO_3$,[22] $Co(NO_3)_2$,[25] and $Eu(NO_3)_3$.[26] The average M–O(nitrate) distance (Table VIII) increases with increasing metal radius and is approximately the sum of the ionic radius of the metal plus the van der Waals radius of oxygen, which means that the ions are essentially in contact with one another.

In contrast to these disordered structures, the structure of the crystalline $Ca(NO_3)_2$ complex of 2,3,11,12-tetramethyl-18-crown-6 is ordered (Figure 3). Like the corresponding $Ca(NO_3)_2$ complex of **1**, the calcium is ten coordinate, bound to the six crown oxygens as well as two trans, bidentate nitrates. The calcium is situated exactly in the mean plane of the crown and, along with the nitrogen and nonbonded oxygen of each nitrate anion, lies on a twofold axis which relates one half of the crown ether ring to the other half. The conformation of the crown can be specified by the dihedral angles (Table IX) about C–C bonds, which are all close to 65° (synclinal, sc), and those about C–O bonds, which are all close to 180° (antiperiplanar, ap). The conformation is therefore very similar to the nonangular diamond lattice conformation with approximate D_{3d} symmetry (i.e., having exclusively O–CH_2–CH_2–O units with ap,sc$^\pm$,ap dihedral angles of alternating sign) most often adopted by the parent 18-crown-6 in its complexes.[27] The methyl substituents are all in axial positions, such that two methyl groups on opposite sides of the ring protrude above each face of the crown, forming "channels" in which the nitrates are located. The plane of each nitrate group forms a 90° angle with the mean plane of the crown ether oxygen atoms and the two nitrate planes form an angle of 36.3° with respect to each other.

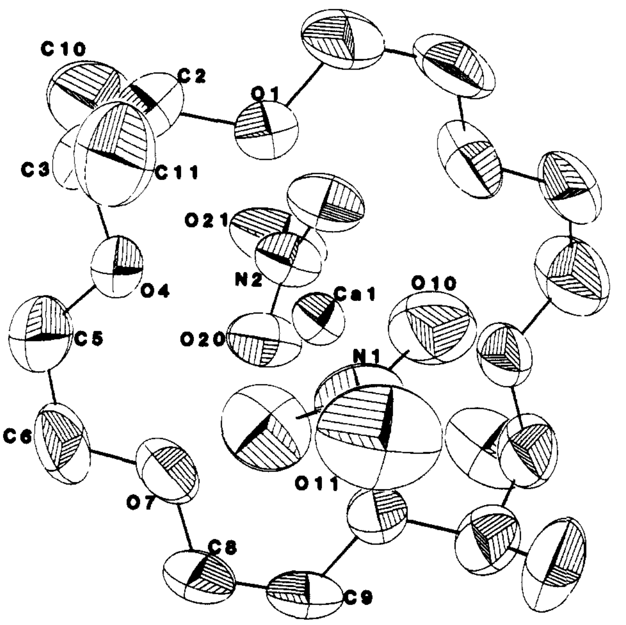

Figure 3. Ortep plot of the structure of the $Ca(NO_3)_2$ complex of 2,3,11,12-tetramethyl-18-crown-6 (**4**), with 50% probability ellipsoids.

Discussion

Electronic Structure of NO_3^-. An understanding of the nature of the weak nitrate transition at 3.33 μm^{-1} is an essential prerequisite to an analysis of the induced CD in the nitrate ion pairs. This transition has been reliably assigned as $A_1' \rightarrow A_1''$ $[n(a_2') \rightarrow \pi^*(a_2'')]$.[28,29] The transition is forbidden in D_{3h} by electric and magnetic dipole and electric quadrupole mechanisms. It gains intensity through vibronic coupling with one of the two ϵ normal vibrational modes, which allows it to borrow intensity from the strong, in-plane polarized, electric dipole transition at 5.26 μm^{-1}. It is important to note that, unlike $n \rightarrow \pi^*$ transitions commonly observed for carbonyl chromophores, there is no net rotation of electric charge and consequently no magnetic dipole moment associated with this transition. The energies of the $n \rightarrow \pi^*$ transition of the crown complexed ion pairs are summarized in Tables VI and VII. It has been shown that the energy of this transition is dependent on solvent polarity.[30] We observe a similar dependence of the energy of the nitrate transition on the charge density and thus the polarizing power of the complexed cation. In general, for cations of greater charge density, the transition occurs at higher energy. However, the Mg^{2+} complexes show unexpectedly low energies for this transition as a consequence of their structure (vide infra).

Nitrate CD and the Coupled Oscillator Model. The appearance of circular dichroism in the $n \rightarrow \pi^*$ absorption band of nitrate is significant in two ways. First, for a planar chromophore such as nitrate to obtain the colinear components of the electric and magnetic transition moments necessary to exhibit optical activity, it must be perturbed by an asymmetric environment. This indicates that the nitrate is ion paired with the complexed metal ion, allowing the electronic system of the chiral crown host to participate in the transition. Circular dichroism is thereby induced in the inherently achiral nitrate ion. We have previously reported this effect for the metal nitrate complexes of 2,3-benzo-(9*R*,10*R*)-9,10-dimethyl-14-crown-4 in chloroform.[11b] The only other reported incidence of optical activity in the nitrate $n \rightarrow \pi^*$ transition is that observed in the solid state for the enantiomorphous crystals of tris(ethylenediamine)M(II) nitrates (M = Mn, Co, Ni, Cu, Zn, and Ru).[29,31] The general phenomenon of induced

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(31) Yang, M. C.-L.; Palmer, R. A. *J. Am. Chem. Soc.* **1975**, *97*, 5390.

CD in host–guest systems, however, is more common. Most pertinent to this discussion is the observation of induced CD for the inclusion complexes of achiral aromatic chromophores with cyclodextrins. It has been demonstrated that the appearance of induced CD is characteristic of the formation of these inclusion complexes with well-defined structure. The orientation of substituted benzene molecules in the cyclodextrin cavity has been successfully predicted on the basis of the sign of the induced circular dichroism.[32] Likewise, the CD data presented here should be indicative of the ion pair *structure*, in addition to the detection of metal nitrate ion pair *formation*.

To illustrate the sensitivity of the CD to ion pair structure, several important differences between the CD spectra of the alkali and alkaline earth complexes in Tables VI and VII should be noted. First, the intensity of the CD observed for the alkaline earth complexes is, in general, an order of magnitude greater than that of the alkali complexes. This difference in intensity is not due to a difference in the degree of association of the nitrate anion(s) since the conductance of these solutions indicates that the nitrates are completely ion paired with the complexed cations in all cases. This intensity difference can therefore be attributed to a difference in the structure of the group IA and IIA (group 1 and 2)[46] complexes.

Secondly, for a given crown, differences in the sign of the CD are only observed among the alkali nitrate complexes. For the group IA (group 1) complexes of **1** and **3**, for example, as the cation radius increases from Li^+ ($r = 0.68$ Å) to Rb^+ ($r = 1.47$ Å), the magnitude of the CD decreases and the sign changes from positive to negative between Na^+ and K^+. The dependence of the sign of the CD on the size of the cation can be correlated to the size relationship between the cation and the crown cavity. The cavity radius of the parent 18-crown-6 has been estimated[33] from crystal structure data of the K^+, Rb^+, and Cs^+ complexes to be 1.34–1.43 Å. Molecular mechanics calculations[34] indicate that for the lowest energy conformations, the cavity sizes of the substituted crowns do not differ significantly from that of 18-crown-6. Thus it is clear that cations which are smaller than the optimum cavity size of the crown (Li^+ and Na^+) give rise to a CD of opposite sign to that observed when the cation is a "good fit" or slightly larger (K^+ and Rb^+). The alkali complexes of crowns **2** and **4** show similar behavior, except that the signs of the CD are reversed, most likely due to the change in configuration of the chiral centers from (*S*) to (*R*). The CD of the alkaline earth complexes, however, is strikingly different. Although the cation size again varies from being too small (Mg^{2+} and Ca^{2+}) to being a good fit or larger (Sr^{2+} and Ba^{2+}), the sign of the CD is always the same for a given crown. Again, the sign of the CD for the crowns having (*R*) chiral centers is the inverse of those having (*S*) centers. It is clear from these CD data that there are important structural differences between the alkali and alkaline earth nitrate complexes.

In principle, the CD can be used to predict the geometry of the host–guest association, because the sign and intensity of the CD are dependent on the relative orientations of the chiral crown host and the achiral nitrate guest. Since the $n \rightarrow \pi^*$ transition gains intensity through a second-order electric dipole mechanism, the induced CD can be treated theoretically by using the model of coupled oscillators,[35] which has been widely used for interpreting the induced optical activity of inclusion complexes.[36] In this case, the electric dipole transition of the achiral nitrate guest becomes optically active through dipolar coupling with the transitions of the chiral crown host. The system formed by these coupled oscillators will possess electric and magnetic moments which are not orthogonal and thus will have a nonvanishing rotational strength, given by[37]

$$R_1 = \frac{-V_{12}\epsilon_1\epsilon_2}{hc(\epsilon_2^2 - \epsilon_1^2)} [\mathbf{r}_{21}\cdot\mu_2 \times \mu_1] \qquad (2)$$

where μ_2 and μ_1 are the transition moments of the crown host and nitrate guest respectively, $\mathbf{r}_{21}$ is the vector connecting their midpoints, and V_{12} is the interaction potential between the two.

The symmetry rule of Schellman,[37] a descriptive model based on this relationship, can be used to predict the sign of the CD, provided the system can be represented by two coupled oscillators and the relative orientations of these oscillators are known. A slightly modified application of the rule is made as follows. The phase of the two oscillators is chosen such that the interaction potential (given by the point dipole approximation) is negative, since a negative V_{12} is always associated with the transition of lower energy. The sign of the optical factor, $[\mathbf{r}_{21}\cdot\mu_2 \times \mu_1]$ will then determine the sign of the CD for this transition. It can be shown that if the oscillators are disposed to one another so as to determine a right-handed helix, the optical factor and thus the induced rotational strength will be positive.[37] Likewise, if they determine a left-handed helix, the induced rotational strength will be negative.

A second, more rigorous approach that can provide complementary information to the qualitative sign correlations of this descriptive model is the symmetry adapted coupled oscillator model of Schipper.[38] This model develops correlations of sign to the geometry of intercalation of the chromophoric guest in the chiral host. These sign correlations result from the symmetry of the system when the mode of intercalation is restricted to be along a major rotational symmetry axis of the host. While these symmetry requirements are not strictly met by the chiral crown hosts (which do not possess a true C_n ($n > 2$) axis), the pseudo-C_3 symmetry of the ring itself may give rise to sign correlations. The coordinated nitrate guest can be considered to be partially intercalated along this C_3 axis. According to this model, the sign of the rotational strength for a singly degenerate guest and a host system with $n > 2$ depends on the polarization of the guest transition relative to the host axes (x,y,z) such that

$$R_g(x) = R_g(y) = -2R_g(z) \qquad (3)$$

where $R_g(x)$ is the rotational strength induced in a guest transition which is polarized parallel to the x axis of the host. The sign of $R_g(x)$ is given by the sign of

$$H(0)[1 - 3(\Delta r/r)^2] \qquad (4)$$

where Δr and r are the distances from the guest origin to the host origin and to the individual host chromophores, respectively, and $H(0)$, the "host parameter", is purely a host function (in the limit $e_g \ll e_h$) whose sign depends on the orientation of the electric dipole transition moments of the host chromophores. The three factors which determine the sign of the nitrate CD are thus (i) the direction of polarization of the nitrate transition, which depends on the coordination mode of the nitrate, (ii) the distance of the nitrate from the crown, and (iii) the crown conformation, which will determine the sign of $H(0)$.

Our approach in these next sections is to propose reasonable structures for the crown complexed ion pairs and then to make general predictions about the CD using the models described above. The extent to which these predictions actually match the observed CD data reflects both the accuracy of the hypothesized structures and the appropriateness of the models.

Proposed Structures. Alkali Nitrate Complexes. The CD data for the monovalent complexes suggest that the ion pair structure depends on the size of the cation relative to that of the crown cavity. We propose that, with the larger alkali cations (K^+ and Rb^+), the crown has a nonangular diamond lattice conformation, such that the ring itself has approximate D_{3d} symmetry and that the cation is displaced from the mean plane of the ring, coordinated

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(32) See for example: (a) Harata, K.; Uedaira, H. *J. Chem. Soc. Jpn.* **1975**, *48*, 375. (b) Yamaguchi, H.; Ikeda, N.; Hirayama, F.; Uekama, K. *Chem. Phys. Lett.* **1978**, *55*, 75.

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to a bidentate nitrate. The noncoordinated oxygen and nitrogen of nitrate and the metal cation lie on the z axis which is perpendicular to the plane of the ring. This structure is a reasonable one primarily because it closely resembles the crystal structure of $[(1)K]^+NO_3^-$.[23] In this structure, the crown has the diamond lattice conformation with approximate D_{3d} symmetry and the nitrate is coordinated through two oxygens to the K^+, which is displaced from the plane of the ring 0.58 Å toward the chelating anion. Furthermore, the relatively strain free D_{3d} conformation is the one most commonly observed for complexes of 18-crown-6 and is invariably found with cations that fill the crown cavity.[27] Displacement of cations larger than the optimum cavity size from the mean plane of the ring has also been observed for the RbSCN[39] and CsSCN[40] complexes of 18-crown-6. In fact, even K^+, which is a "good fit" in the 18-crown-6 cavity, is displaced out of the mean plane of the ring in the five structures of K^+ complexes with 18-crown-6 which have strongly coordinated anions.[6,10,41]

Since the CD intensity for the Rb^+ complexes is always smaller than that of the K^+ ones, and this intensity is in part a function of the proximity of the chromophore to the perturbing host, it seems reasonable to propose that with Rb^+ the nitrate is farther from the chiral crown. If we assume that the M–N distance in solution is approximately the same as in the solid state, then we can estimate the magnitude of the difference in CD intensity using eq 2. (V_{12} is inversely proportional to r^3, yielding an inverse dependence of the rotational strength on r^2.) If we assume that the displacement from the plane of the ring is 1.2 Å for Rb^+ based on the $[(18\text{-crown-}6)Rb]^+SCN^-$ structure[39] and 0.58 Å for K^+ based on the $[(1)K]^+NO_3^-$ structure,[23] eq 2 predicts that the CD intensity will double when the cation radius is decreased from r = 1.48 Å (Rb^+) to r = 1.33 Å (K^+). This is exactly what is observed for all of the crowns except **4**. The anomalous behavior of this crown could be due to a larger displacement of the K^+ relative to Rb^+, suggesting that the cavity of this crown is effectively smaller than the others.

We can also predict the absolute sign of the CD using the descriptive model described above. The major difficulty in applying this model to the crown complexed ion pairs is that the crown host cannot be represented as a single chromophoric system. Contributions to the CD from pairwise interactions of the guest with individual host chromophores must therefore be considered. The individual host chromophores which should give the greatest contribution to the rotational strength are those closest in energy to the nitrate transition, in this case, the ether electric dipole transitions ($\sigma \rightarrow \sigma^*$, $n \rightarrow \sigma^*$). The six ether units can therefore be treated as the individual perturbing oscillators. Since these transitions occur in the mid-UV (above 4.0 μm^{-1}), well separated in energy from the nitrate transition, the direction of the effective transition moment of each ether unit can be approximated as along the direction of principal polarizability of the C–O bonds, which are directed toward the central cation. Pairwise interactions of the electric dipole moment of the nitrate, which oscillates in the plane of the nitrate (along the z axis in C_{2v} symmetry), and the six individual dipole moments of the ether units, which are directed toward the central cation, must therefore be considered.

The methyl substituents destroy the center of symmetry of the diamond lattice conformation proposed for the crown in the K^+ and Rb^+ complexes, causing the ether dipoles to be chirally arranged about the z axis. This effect should be small and can viewed as a slight twist in the ring caused by the steric requirements of the methyl groups. The sense of this twist is such that the orientation of each individual ether dipole of the crown host with respect to the nitrate transition moment (along the z axis) determines a right-handed helix ($R > 0$) when the configuration of the chiral centers is (R) and a left-handed helix ($R < 0$) when the configuration is (S). This treatment correctly predicts that the sign of the CD observed for the K^+ and Rb^+ complexes of **1** and **3** will be negative while that observed for these complexes of **2** and **4** will be positive.

In contrast to the larger cations, we propose that Li^+ and Na^+ lie in the plane of the ring with the ether dipoles directed toward the central cation. In order to satisfy the bonding requirements of these smaller cations, two possible situations could occur. First, the crown ring could adopt the relatively strain free D_{3d} conformation, as it does with the larger cations. Since this conformation has a cavity diameter which is larger than Li^+ and Na^+, symmetric coordination would yield very long and hence weak metal–oxygen bonds. A second possibility would be for the crown ring to distort to yield a smaller cavity, a conformation which is undoubtedly more strained yet in which the metal ion can achieve better coordination to all six of the crown oxygens. The latter structure is more consistent with that found for the NaSCN complex of 18-crown-6, which is highly distorted, having one oxygen bent out of the mean plane by 1.95 Å, in an apical position.[42] In solution, ^{13}C NMR measurements show that Li^+ and Na^+ distort 18-crown-6 by conversion of units with ap,sc±,ap dihedral angles to sc±,sc±,ap units.[43]

We can predict which of these structures is most consistent with the CD data based on Schipper's model. If the crown has the former structure, then the host parameter $H(0)$ will be the same as for the larger cations and eq 4 predicts a change in sign will only occur if $\Delta r/r$ becomes less than $1/\sqrt{3}$. This is not the case, even for Li^+, which means that the difference in sign of the CD for the smaller cations must be due to a significant distortion of the regular diamond lattice crown conformation, which causes a change in sign of $H(0)$. Indeed, such a conformational change probably destroys the pseudo-C_3 symmetry of the crown and hence the applicability of this model. Our descriptive model also breaks down in this case, since the arrangement of the ether dipoles can no longer be viewed as a simple perturbation of the symmetric diamond lattice, and we cannot predict the absolute sign of the CD.

A third, but unlikely, possibility is that the mode of coordination of the nitrate could change from bidentate to monodentate, when coordination to the cation is more sterically hindered by the crown. However, monodentate coordination is rarely observed for nitrate in crystal structures, and direct evidence for bidentate coordination in solution has been obtained from the vibrational spectra of some of these complexes.[44]

Alkaline Earth Nitrate Complexes. For the group IIA (group 2) complexes in solution, we propose a solution structure in which the bidentate nitrates are coordinated to the complexed cation, one above and one below the plane of the ring. In this configuration, the metal ion is held in the center of the crown cavity and the nitrates are situated close to the macrocyclic ring. The ring itself is held in a relatively planar conformation, since the ether dipoles are directed toward the central cation and the coordinated nitrates hinder out-of-plane folding of the ring. Thus the crown conformation is not very sensitive to changing cation size. Bidentate nitrate coordination on opposite sides of the crown is observed in the crystal structures of all the alkaline earth complexes of crowns **1** and **4** (Figures 2 and 3). Crown **4** retains a relatively planar conformation in the $Ca(NO_3)_2$ complex, despite the fact that Ca^{2+} is significantly smaller than the crown cavity and might be expected to distort the conformation. Similarly, 18-crown-6 has the D_{3d} conformation in its complex with $Ca(SCN)_2$, with the thiocyanates coordinated on opposite sides of the ring.[45] In that structure, the ring is in several orientations related by rotation

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(46) In this paper the periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

in the mean plane, as in the structure of $[(\mathbf{1})\mathrm{Ca}]^{2+}(\mathrm{NO_3}^-)_2$. In each case this is probably due to the long, and hence relatively weak, metal–oxygen bonds. The CD data are consistent with the proposal that the average crown conformation sensed by the coordinated nitrates is relatively insensitive to the size of the cation, since the sign of the CD remains unchanged for the alkaline earth complexes of a given crown. If the average crown conformation does not change significantly, then the sign of $H(0)$ will remain constant. Since even for the smallest cation Mg^{2+}, $\Delta r/r > 1/\sqrt{3}$, eq 4 predicts the same sign for the CD of the complexes of all four metal ions.

Nitrate Configurational Contribution to the CD Intensity. The proposed alkaline earth complex structure is also consistent with the greater magnitude of the CD observed for these complexes as compared to the alkali complexes. The closer proximity of the nitrates to the chiral crown is one contributing factor, since the rotational strength is inversely proportional to the square of the distance between the two. Another factor is a unique result of the coordination of *two* opposed bidentate nitrates. This results because the nitrates form chelate rings which can impart an additional configurational chirality to these complexes, depending on the orientation of the rings relative to one another. If we define a twist angle α as the acute angle between the planes formed by each nitrate chelate ring, then for $0° < \alpha < 90°$ there will be a configurational contribution to the chirality of the complex and hence an additional contribution to the intensity of the CD. Obviously this contribution to the chirality cannot be present in the monovalent complexes.

We expect this contribution to vary among the four crowns, each of which has a different disposition of the methyl groups around the ring. This is because the orientation of the nitrates will primarily be influenced by the steric requirements of the methyl substituents, which protrude above the faces of the crown in the relatively flat diamond lattice conformation. This effect can be observed by comparing the CD intensity of the dimethyl crown complexes to that observed for the tetramethyl crown complexes. If we compare crowns **2** and **4**, for example, considering only the rotational strength induced by the interaction with the crown, we might expect the CD intensity for the alkaline earth complexes of **4** to be double that of the corresponding complexes of **2**, since **4** has twice the number of (*R*) chiral centers, symmetrically placed so as to give approximately twice the twist to the crown ring. We actually observe that the CD intensity for the alkaline earth complexes of **4** is always much less than twice that observed for the corresponding complexes of **2**, which we attribute to a difference in the nitrate–nitrate twist angle. The methyl substituents of **4** are located close together, on opposite ends of the ring, leaving a relatively open "channel" in each face of the crown (Figure 3). In fact, a projection of the structure of $[(\mathbf{4})\mathrm{Ca}^{2+}](\mathrm{NO_3}^-)_2$ from another perspective reveals that all four of the methyl substituents are virtually coplanar, such that the channels above and below the ring are parallel to each other. Steric interactions between the nitrates and the methyl groups would presumably cause the nitrates to be aligned along the channel of each face, in a nearly coplanar arrangement, such that the configurational contribution is minimized. On the other hand, the nitrates are not as constrained to coplanarity in complexes with **2** since there are only two methyl substituents, and thus the configurational contribution is likely to be greater.

In contrast, the nitrate configurational contribution for the complexes of **3** appears to be greater than for the complexes of **1** since the CD intensity is much more than doubled for the tetramethyl crown complexes. The angle between the "channels" formed by the widely spaced methyl groups of the tetramethyl crown **3** is about 60°, which should result in a sizable twist of the nitrates and consequently a large configurational contribution to the optical activity of the complexes. Again, the steric requirements of the dimethyl crown (**1**) are not as great, probably yielding a smaller twist angle between the nitrates. These angles were obtained from the crystal structures of the Ca^{2+}, Sr^{2+}, and Ba^{2+} complexes of **1** (Table VIII), and they are small as expected (except for Ca^{2+}, which is closer to 90°).

The nitrate configurational contribution to the CD intensity requires a somewhat rigid conformation of the crown, such that rotation of the nitrates is hindered. A small cation like Mg^{2+} allows considerable conformational mobility of the crown, whereas the conformation is made more rigid by Sr^{2+}, which fits well in the crown cavity. This is reflected in the decreasing disorder of the crown with increasing cation size in the crystal structures of the alkaline earth complexes of **1**. Consequently, the CD intensity is observed to depend on the fit of the cation, the maximum occurring for Sr^{2+}. The smaller intensity observed for the Ba^{2+} complexes may be due to the counter effect of increasing the cation radius, which not only moves the nitrates farther from the chiral centers but also allows the nitrates to rotate more freely.

Conclusion

Alkali and alkaline earth cations of similar size might be expected to have similar complex structures in the absence of ion pairing, based on the fit of the cation in the crown cavity. The differences which we have observed between the alkali and alkaline earth nitrate complexes demonstrate the profound effect that ion pairing can have on their structure. The presence of two coordinated anions in a divalent cation complex constrains the crown to adopt a relatively flat conformation, even for Mg^{2+}, whereas it is free to fold around the smaller alkali cations which have only one coordinated nitrate. The induced CD that results from the association of the nitrate is very sensitive to these differences and is thus a powerful probe of the ion pair structure.

Acknowledgment. This research was supported by the U.S. Army Research Office under Contract DAAG29-79-D-1001.

Supplementary Material Available: Tables of structure factors and calculated thermal parameters for the Sr^{2+} and Ba^{2+} complexes of **1** and for the Ca^{2+} complex of **4** (90 pages). Ordering information is given on any current masthead page.