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Crown Ether Complexed Ion Pairs: Solution and Solid-State Structures of the (2*S*,6*S*)-2,6-Dimethyl-1,4,7,10,13,16-hexaoxacyclooctadecane Complex of Potassium Nitrate

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The structure of the (2*S*,6*S*)-2,6-dimethyl-1,4,7,10,13,16-hexaoxacyclooctadecane complex with the potassium nitrate ion pair ($C_{14}H_{28}KNO_9$) has been studied in chloroform solution and in the solid state by FTIR spectroscopy. The solid-state structure has also been determined by X-ray diffraction. The monoclinic crystals conform to space group $P2_1$ with a = 12.486 (5) Å, b = 8.515 (3) Å, c = 18.587 (9) Å, β = 91.97 (4)°, and Z = 4. The close correspondence of the solution and solid-state infrared spectra indicates that the structure is similar in both phases. The solution spectrum suggests that the ion pairs are externally complexed by the crown ether. which has a conformation with approximate D_{3d} symmetry (ignoring the methyl substituents), similar to that observed for K^+ complexes of unsubstituted 18-crown-6, and that the nitrate is coordinated to the K^+ in a bidentate manner.

Introduction

Crown ethers generally form two-dimensional complexes, leaving open coordination sites on the metal cation with which the anion and solvent can interact. In fact, numerous studies[1] have shown that while crown ethers weaken the anion–cation interaction, ion pairing is still extensive in solvents of low permittivity and polarity and in some cases even persists to a smaller degree in more permittive and polar solvents.[2] In addition, X-ray diffraction studies of solid complexes have revealed specific anion–cation interactions in many instances.[3] Even the "noncoordinating" perchlorate anion has been shown to act as a bidentate ligand in the $NaClO_4$ complex of benzo-15-crown-5.[4] The association of the anion with the complexed cation has been demonstrated to significantly influence both anion reactivity[5] and the crown–cation interaction, causing changes in complex stability[6] and structure.[7]

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 give either crown-separated or externally complexed contact ion pairs.[8] More specific information about the coordination geometry of the anion has been obtained from resonance Raman measurements of the permanganate anion,[9] from measurements of electric dipole moments of the tosylate anion,[10] from the ^{1}H NMR spectrum of the fluorenyl anion,[8] and from the infrared spectrum of the enolate anion.[11] 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 that 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 investigation of ion pairing in crown ether complexes,[12] we have studied the structure of the (2*S*,6*S*)-2,6-dimethyl-1,4,7,10,13,16-hexaoxacyclooctadecane (**1**) complex with potassium nitrate ion pairs in chloroform solution and in the solid state, using FTIR spectroscopy. The solid-state structure has also been determined by X-ray diffraction. We have previously demonstrated that the induced circular dichroism of the $n \rightarrow \pi^*$ transition of NO_3^- can be used to probe the nature and extent of ion pairing in solutions of crown ether complexes of alkali-metal and alkaline-earth-metal nitrates.[12,13] Some questions about the structure of these ion pairs remain however, including the mode of nitrate coordination and the conformation of the crown ether.

Experimental Section

Preparation. The preparation of optically pure (2*S*,6*S*)-2,6-dimethyl-18-crown-6 has been reported,[14] using previously established techniques.[15] The 1:1 KNO_3 complex of **1** was prepared by stirring an excess of anhydrous KNO_3 with a solution of the crown ether in chloroform under dry N_2 overnight. The solution was then filtered and the complex isolated as needlelike crystals by slow evaporation under dry N_2. Elemental analysis of a single crystal was consistent with 1:1 complex formation. Anal. Calcd for $C_{14}H_{28}KNO_9$: C, 42.73; H, 7.17; N, 3.56. Found: C, 42.66; H, 7.09; N, 3.53. The molecular weight of the complex in chloroform was determined by vapor-phase osmometry to be 391 (theoretical 393), indicating that the complex forms a discrete ion pair in solution.

Table I. Crystal Data for [K(2*S*,6*S*)-2,6-Me_2-18-crown-6]NO_3

formula	$C_{14}H_{28}KNO_9$	$F(000)$	844
mw	393.47	μ(Mo Kα), cm^{-1}	3.06
a, Å	12.486 (5)	λ(Mo Kα), Å	0.71069
b, Å	8.515 (3)	D_{calcd}, g cm^{-1}	1.323
c, Å	18.587 (9)	Z	4
α, deg	90.0	no. of obsd reflcns	2324
β, deg	91.97 (4)	R, %	6.2
γ, deg	90.0	R_w, %	6.2
V, Å^3	1976.0 (14)	space group	$P2_1$

Crystal Structure. Collection and Reduction of X-ray Data. The crystallographic data are summarized in Table I. A roughly equidimensional (0.2 mm) chunk from a colorless rod-shaped crystal of the KNO_3 complex of **1** was sealed in a capillary 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 (4625 points) were collected at room temperature with a graphite monochromator, a variable scan

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(1) For example, see: (a) Eastman, M. P.; Ramirez, D. A.; Jaeger, C. D.; Watts, M. T. *J. Phys. Chem.* **1977**, *81*, 1928. (b) Miller, J. M.; Clark, J. H. *J. Chem. Soc., Chem. Commun.* **1982**, 1318. (c) Bozic, L. T.; Bozic, B. *Croat. Chem. Acta* **1984**, *57*, 119.

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Table II. Non-Hydrogen Positional Parameters for $[K(2S,6S)\text{-}2,6\text{-}Me_2\text{-}18\text{-crown-}6]NO_3$

atom	x ($\sigma(x)$)	y ($\sigma(y)$)	z ($\sigma(z)$)
K1	−0.3028 (2)	−0.3546 (3)	0.9112 (1)
K2	−0.7935 (2)	0.3646	0.5825 (1)
N1	−0.6252 (9)	0.1429 (15)	0.6690 (8)
O111	−0.6904 (9)	0.2146 (20)	0.7036 (5)
O112	−0.6226 (9)	0.1695 (17)	0.6064 (6)
O113	−0.5653 (9)	0.0459 (13)	0.6963 (6)
N2	−0.8856 (8)	0.3331 (13)	0.1652 (5)
O211	−0.8660 (10)	0.2010 (15)	0.1796 (7)
O212	−0.8459 (7)	0.3833 (14)	0.1099 (5)
O213	−0.9435 (7)	0.4175 (12)	0.1995 (5)
O1	−0.7153 (6)	0.6644 (10)	0.5459 (4)
C2	−0.6254 (9)	0.6508 (19)	0.5006 (7)
C3	−0.6672 (10)	0.5666 (19)	0.4352 (7)
O4	−0.7046 (6)	0.4159 (11)	0.4506 (4)
C5	−0.7246 (8)	0.3209 (16)	0.3892 (6)
C6	−0.7599 (8)	0.1627 (16)	0.4089 (6)
O7	−0.8580 (6)	0.1747 (10)	0.4456 (4)
C8	−0.8985 (11)	0.0283 (15)	0.4708 (6)
C9	−0.9870 (10)	0.0553 (15)	0.5215 (7)
O10	−0.9449 (5)	0.1248 (10)	0.5841 (4)
C11	−1.0164 (8)	0.1218 (16)	0.6431 (6)
C12	−0.9706 (9)	0.2123 (16)	0.7023 (6)
O13	−0.9610 (7)	0.3668 (11)	0.6838 (5)
C14	−0.9302 (10)	0.4675 (21)	0.7408 (6)
C15	−0.9104 (10)	0.6285 (18)	0.7154 (6)
O16	−0.8203 (6)	0.6287 (11)	0.6732 (4)
C17	−0.7971 (11)	0.7777 (14)	0.6464 (7)
C18	−0.6991 (11)	0.7664 (16)	0.6030 (7)
C19	−0.5332 (9)	0.5620 (22)	0.5409 (8)
C20	−0.7668 (12)	0.0531 (2)	0.3434 (8)
O101	−0.3626 (5)	0.3855 (9)	0.8220 (4)
C102	−0.3053 (9)	0.2424 (14)	0.8303 (5)
C103	−0.1968 (9)	0.2796 (16)	0.8612 (6)
O104	−0.2031 (5)	0.3445 (11)	0.9315 (4)
C105	−0.1021 (9)	0.3857 (16)	0.9624 (7)
C106	−0.1132 (8)	0.4404 (15)	1.0378 (6)
O107	−0.1794 (6)	0.5742 (10)	1.0334 (4)
C108	−0.1852 (10)	0.6614 (21)	1.0955 (6)
C109	−0.2154 (10)	0.8285 (16)	1.0755 (7)
O110	−0.3185 (6)	0.8267 (10)	1.0400 (4)
C111	−0.3482 (12)	0.9818 (15)	1.0197 (7)
C112	−0.4541 (11)	0.9780 (16)	0.9820 (7)
O113	−0.4481 (6)	0.8978 (10)	0.9169 (4)
C114	−0.5435 (10)	0.8900 (17)	0.8772 (4)
C115	−0.5381 (10)	0.7825 (18)	0.8156 (8)
O116	−0.5087 (6)	0.6326 (11)	0.8388 (4)
C117	−0.5205 (9)	0.5166 (19)	0.7856 (6)
C118	−0.4752 (9)	0.3664 (17)	0.8094 (6)
C119	−0.2930 (10)	0.1509 (23)	0.7618 (6)
C120	−0.1511 (10)	0.3136 (17)	1.0849 (7)

Table III. Selected Bond Angles (deg) and Distances (Å) for $[K(2S,6S)\text{-}2,6\text{-}Me_2\text{-}18\text{-crown-}6]NO_3$

K1–O211	2.786 (13)	K2–O4	2.760 (8)
K1–O212	2.798 (11)	K2–O7	3.098 (8)
K1–O101	2.850 (8)	K2–O10	2.784 (8)
K1–O104	2.868 (9)	K2–O13	2.862 (8)
K1–O107	2.766 (8)	K2–O16	2.837 (9)
K1–O110	2.868 (8)	N1–O111	1.22 (2)
K1–O113	2.816 (8)	N1–O112	1.19 (2)
K1–O116	2.862 (7)	N1–O113	1.21 (2)
K2–O111	2.855 (12)	N2–O211	1.18 (2)
K2–O112	2.728 (12)	N2–O212	1.24 (1)
K2–O1	2.824 (8)	N2–O213	1.21 (1)
O111–K2–O112	42.3 (3)	O211–N2–O213	125 (1)
O211–K1–O212	43.2 (3)	O212–N2–O213	119 (1)
O111–N1–O112	118 (1)	N1–O112–K2	103.2 (9)
O111–N1–O113	122 (1)	N1–O111–K2	95.7 (8)
O112–N1–O113	120 (1)	N2–O211–K1	100.4 (9)
O211–N2–O212	116 (1)	N2–O212–K1	98.1 (8)

Table IV. Macrocycle Dihedral Angles (deg) for $[K(2S,6S)\text{-}2,6\text{-}Me_2\text{-}18\text{-crown-}6]NO_3$

O1–C2–C3–O4	−61.9 (14)
C2–C3–O4–C5	−167.9 (9)
C3–O4–C5–C6	178.0 (9)
O4–C5–C6–O7	61.7 (11)
C5–C6–O7–C8	−177.2 (9)
C6–O7–C8–C9	167.8 (9)
O7–C8–C9–O10	−67.5 (12)
C8–C9–O10–C11	−165.8 (10)
C9–O10–C11–C12	−173.3 (10)
O10–C11–C12–O13	63.7 (12)
C11–C12–O13–C14	172.1 (10)
C12–O13–C14–C15	173.9 (10)
O13–C14–C15–O16	−67.2 (12)
C14–C15–O16–C17	179.3 (9)
C15–O16–C17–C18	179.2 (10)
O16–C17–C18–O1	60.5 (13)
C17–C18–O1–C2	178.4 (10)
C18–O1–C2–C3	−167.7 (11)
O101–C102–C103–O104	64.1 (12)
C102–C103–O104–C105	−178.4 (10)
C103–O104–C105–C106	−175.4 (10)
O104–C105–C106–O107	−61.4 (12)
C105–C106–O107–C108	−168.7 (10)
C106–O107–C108–C109	155.4 (9)
O107–C108–C109–O110	61.9 (12)
C108–C109–O110–C111	−179.2 (10)
C109–O110–C111–C112	179.1 (10)
O110–C111–C112–O113	−66.0 (13)
C111–C112–O113–C114	−179.2 (10)
C112–O113–C114–C115	−170.2 (11)
O113–C114–C115–O116	57.2 (14)
C114–C115–O116–C117	169.0 (10)
C115–O116–C117–C118	172.2 (10)
O116–C117–C118–O101	−63.4 (12)
C117–C118–O101–C102	−167.1 (9)
C118–O101–C102–C103	−165.7 (8)

rate, a 0–20 scan mode, and a scan width of 1.2° below $K\alpha_1$ and 1.2° above $K\alpha_2$ 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 measured in octants $\pm h,+k,+l$ and were corrected for Lorentz, polarization, and background effects. μ was calculated to be 3.06 cm^{-1}, and since the crystal was approximately equidimensional and the absorption coefficient low, transmission coefficients were not determined. Likewise, no absorption or extinction corrections were made. After removal of redundant and space-group-forbidden data, 2324 reflections were considered observed [$I > 3.0\sigma(I)$]. Although the acentric space group deduced ($P2_1$) has the same systematic absences as the centric group $P2_1/m$, the certain presence of the chiral crown ether in the structure makes the choice of space group unambiguous. For the same reason tests for chirality were superfluous.

Solution and Refinement of Structure. The structure was solved by direct methods using MULTAN80.[16] Refinement of scale factor, positional, and anisotropic thermal parameters for all non-hydrogen atoms was carried out to convergence.[17] Hydrogen positional parameters for methylene carbons were calculated assuming normal geometry and a C–H distance of 0.97 Å. Methyl hydrogens were not located. Hydrogen positional parameters were included in the final cycles of refinement. The hydrogen atoms were assigned isotropic thermal parameters of $U = 0.03$. All parameters associated with hydrogen atoms were held invariant. The final cycle of refinement [function minimized $\sum(F_o - F_c)^2$] led to a final agreement factor of $R = 6.2\%$ [$R = (\sum(F_o - F_c)/\sum F_o) \times 100$]. Anomalous dispersion corrections were made for K. Scattering factors were taken from Cromer and Mann.[18] A weighting scheme was applied in the final cycles of refinement to deemphasize the high- and low-in-

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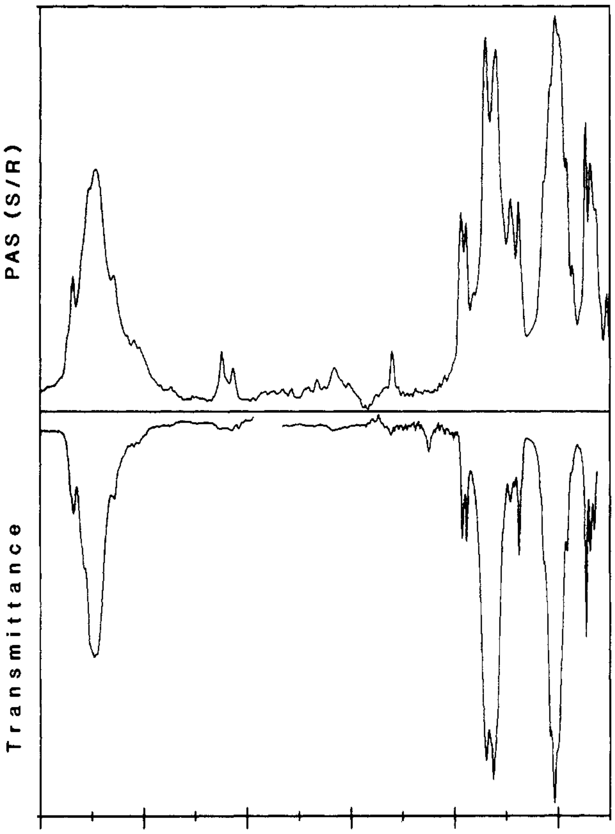

Figure 1. Transmission FTIR spectrum of $[(2,6\text{-Me}_2\text{-18-crown-6})K]^+$-$NO_3^-$ in $CDCl_3$ (bottom) and photoacoustic FTIR spectrum of the solid complex (top).

tensity data. The validity of this weighting scheme is supported by the observation that the average weighted ΔF values differ by less than a factor of 3 for 20 equally populated groups of F_o of similar intensities. The final positional parameters of the refined atoms appear in Table II, selected bond distances and angles are given in Table III, and the dihedral angles of one of the two crystallographically distinct macrocycles are listed in Table IV. Complete tables are included as supplemental material.

Infrared Measurements. All infrared measurements were made on an IBM 9195 FTIR spectrometer. The photoacoustic FTIR spectrum of the solid complex (Figure 1) was obtained by using an IBM Instruments P/N A6120890 standard sample-gas-microphone PAS cell, in which the the sample is placed in a stainless-steel cup and is not in contact with the infrared cell window.[19] Several single crystals of the complex were finely ground and placed in the sample cup, and the cell was then flushed with dry He for 5 min. to remove atmospheric H_2O and CO_2. A mirror velocity of 0.059 cm/s (vel = 0) was used, which corresponds to an optical velocity of 0.235 cm/s. This yields an effective photoacoustic modulation frequency ranging from 141 Hz at 600 cm^{-1} to 940 Hz at 4000 cm^{-1}. A total of 512 sample scans were acquired at a resolution of 8 cm^{-1}. The spectrum was normalized to a Norit A carbon black reference spectrum collected under the same conditions and plotted as a sample/reference (S/R) ratio (Figure 1).

The transmission FTIR spectrum of the complex in $CDCl_3$ solution (0.01 M) was obtained by using a ZnSe cavity cell with a 0.5-mm path length.[19] The inertness of this cell was tested by leaving a solution of the complex in the cell overnight, after which no changes in the spectrum or etching of the cell were observed. The liquid-N_2-cooled MCT detector was used, and 128 sample scans were acquired at 2-cm^{-1} resolution. The spectrum of $CDCl_3$ was obtained in the same manner and subtracted from the spectrum of the complex. The resulting transmission spectrum is plotted in Figure 1. The intense solvent absorptions below 800 cm^{-1} obscure any sample bands in this region.

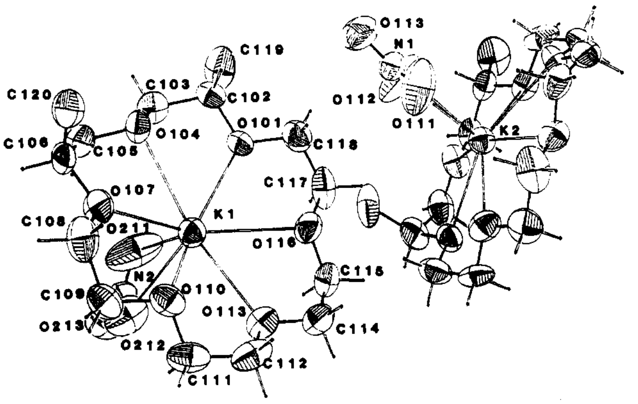

Figure 2. Thermal ellipsoid plot of the structure of $[(2,6\text{-Me}_2\text{-18-crown-6})K]^+NO_3^-$ showing the two crystallographically distinct molecules.

Results and Discussion

Crystal Structure. The structure of the KNO_3 complex of **1** is illustrated in Figure 2. The structure contains two crystallographically distinct complexes. However, in both cases, the crown has the relatively flat, diamond lattice conformation with approximate D_{3d} symmetry (ignoring the methyl substituents). The average dihedral angles about C–C bonds in the two rings are (±)63.8 (3.0) and (±)62.3 (3.0)°, and those about C–O bonds, 173.4 (5.1) and 171.6 (7.2)° (Table IV), compared to the ±60 and 180° angles expected for the ideal $(ag \pm a)_6$ pattern for D_{3d} symmetry with equal bond distances and exactly tetrahedral bond angles.[20] The average bond distances and angles in the two rings are C–C = 1.48 (2) Å, C–O = 1.40 (1) Å, C–O–C = 113.9 (10)°, and O–C–C = 109.8 (10)° (see supplementary material) compared to 1.46–1.52 Å, 1.39–1.45 Å, 112.6°, and 109.5°, respectively, observed for solid-state complexes of 18-crown-6.[21] The oxygen atoms of the two rings are approximately coplanar (standard deviation 0.12 Å for O1, O4, O7, O10, O13, O16 and standard deviation 0.24 Å for O101, O104, O107, O110, O113, O116), with the K^+ displaced from the mean plane by 0.66 and 0.64 Å, respectively. This conformation is very similar to that of the unsubstituted 18-crown-6 in the KNCS complex.[22] In fact, in the 10 structures of $(18\text{-crown-6})K^+$ of which we are aware,[7,22-29] there is only one in which the crown does not have this conformation. However, in that case, the K^+ does not occupy the ring cavity at all but is displaced by 1.6 Å toward the strongly coordinating phthalocyanine anion.[7]

The NO_3^- groups are planar (N2, O211, O212, O213, standard deviation 0.006 Å; N1, O111, O112, O113, standard deviation 0.003 Å) and tilted with respect to the mean plane of oxygen atoms by 86.52° (plane of N2, O211, O212, O213 to O101–O116 oxygen plane; 75.59° for N1, O111, O112, O113 plane to O1–O16 plane.)

The chirality of **1** was assumed to be *S*,*S* on the basis of the synthetic procedure for the preparation of the chiral synthon of this crown, (2*S*,6*S*)-4-oxaheptane-2,6-diol,[15] and the fact that no bonds to the asymmetric carbons of this diol were broken in the cyclization procedure. The structure was therefore refined in the *S*,*S* configuration.

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Table V. Infrared Frequencies (cm^{-1}) and Assignments for $[(\mathbf{1})K]^+NO_3^-$ in $CDCl_3$ Solution, Assuming D_{3d} Symmetry of the Crown Ring

$[(\mathbf{1})K]^+NO_3^-$	$[(18\text{-crown-}6)K]^+SCN^-$ [a]	assignment	poly(ethylene glycol) [b]
1474 s	1472 m	CH_2 scissor (A_{2u}, E_u)	1470 m (A_2, E_1)
1454 m	1452 w	CH_2 scissor (E_u)	1453 w (E_1)
1428 w	1433 m	CH_2 wag (E_u)	1415 m (E_1)
1377 w	1377 w	CH_2 wag (E_u)	1364 m (E_1)
1348 m	1347 s	CH wag (A_{2u})	1345 s (E_1)
1281 s	1285 s	CH_2 twist (E_u)	1283 m (E_1)
1250 s	1246 s	CH_2 twist (A_{2u})	1244 m (E_1)
	1233 m	CH_2 twist (E_u)	1236 w (E_1)
1150 w	1148 sh	CH_2 rock (E_u)	1149 s (E_1)
			1119 s (E_1)
1107 vs, b	1106 vs, b	COC asym str (E_u)	1102 vs (A_2)
1091 sh	1087 sh	COC sym str, CC str	
1064 m	1058 w	CH_2 rock	1062 m (E_1)
987 w	1017 sh		
972 m	961 vs	CH_2 rock, twist	963 s (A_2)
833 m	838 s	CH_2 rock (E_u)	844 s (E_2)

[a] Data from ref 36. [b] Data from ref 35; assignments based on C_3 symmetry.

This crown is one of a series of chiral crowns that we have synthesized with methyl groups attached directly to the ring.[13] The strategy in placing the chiral centers directly on the ring is to chirally perturb the ring such that chiroptical techniques can be used to probe the structure of complexes of these crowns. The methyl substitutents might be expected to twist the crown slightly due to steric interactions. This has been observed in the CsNCS complex of *rac*-6,8,15,17-tetramethyldibenzo-18-crown-6, which has a significantly different conformation than the CsNCS complex of the unsubstituted dibenzo-18-crown-6. The substituted crown has C–O dihedral angles that differ by as much as 34° from those of the unsubstituted crown.[30] In this conformation, the tetramethyl crown lacks short contacts involving methyl groups, which may account for these differences. However, in the KNO_3 complex of **1**, the methyl groups do not appear to significantly distort the crown from the relatively flat D_{3d} conformation observed in the K^+ complexes of unsubstituted 18-crown-6. This may be due to the fact that in this conformation there are no short contacts involving the methyl groups, which are well separated from each other. Despite the relatively small perturbation caused by the methyl substituents, the optical activity of complexes of **1** is moderately intense and very sensitive to the crown conformation. Thus, placing methyl substituents on the ring offers a way of probing the structure of crown complexes without significantly changing the structure relative to the unsubstituted crown.

In the crystal, the nitrate ion is coordinated to the potassium ion in a bidentate manner, with an average K–O distance of 2.791 Å (Table III). This distance is approximately the sum of the ionic radius of K^+ (1.38 Å, estimated from crystal structure data for oxides of coordination number 6[31]) plus the van der Waals radius of oxygen (1.40 Å), which means that the ions form a contact pair. Bidentate coordination is typical of nitrate bonding and has been observed in numerous crown complexes,[12a,32] including the calcium, strontium, and barium nitrate complexes of **1**.[13]

Another interesting feature of this structure is the displacement of the potassium ion from the mean plane of the ring by 0.65 Å (average) toward the chelating nitrate. In complexes of 18-crown-6 with cations too large to fit in the cavity, a similar displacement of the cation has been observed (by 1.19 Å for Rb^+ and 1.44 Å for Cs^+).[33] However, the cavity of **1** is large enough to accommodate K^+, and thus the cause of this displacement is more likely to be the interaction with the anion. In fact, displacement of K^+ in complexes with 18-crown-6 has been observed in every structure that has a strongly coordinated anion. The extent of displacement seems to depend on the strength of interaction with the anion: hexamolybdate, 0.26 Å[24] (also having a water coordinated to the K^+, opposing the hexamolybdate anion); tosylate, 0.79 Å;[25] copper(II) dithiooxalate, 0.80 Å;[28] ethyl acetoacetate enolate, 0.90 Å;[22] molybdate, 0.92 Å;[23] phthalocyanine, 1.6 Å.[7] In contrast, in the KNCS complex of unsubstituted 18-crown-6, the K^+ sits exactly in the mean plane of the ligating oxygens (which is also a crystallographic inversion center).[22] The thiocyanates are disordered and weakly coordinated through either the N or S (3.19 Å from K^+). Likewise, in the three[26,27,29] $(18\text{-crown-}6)K^+$ structures with noncoordinated anions, the K^+ is situated exactly in the mean plane of the ring. These observations emphasize the fact that ion pairing can influence the crown–cation interaction and can even perturb the crown conformation.

Solution Structure. The sign and intensity of the induced CD in the nitrate $n \rightarrow \pi^*$ transition of this complex in chloroform suggest that the solution structure is very similar to that observed in the solid state.[13] Further evidence that the solid-state structure is maintained in solution is provided by the IR spectra. Comparison of the solid and solution IR spectra of the complex shows little difference between the two.

If we presume that the symmetry of the crown backbone can be approximated as D_{3d}, we would predict 30 IR-active vibrational frequencies ($10\ A_{2u} + 20\ E_u$) for the ring itself. Not all of these bands are observable in our experiment, since some occur at frequencies lower than 800 cm^{-1} (CO, CC internal rotations, CCO bend, COC bend) and are obscured by solvent bands. In the mid-IR region however, it is possible to assign most of these bands by analogy with the infrared spectrum of crystalline poly(ethylene glycol) (PEG). The D_{3d} conformation of the crown is similar to that of PEG, which has a helical structure, with monomer units having exclusively the anti,gauche,anti conformation. Consequently, there is a close correspondence of the frequencies of the crown bands with those of crystalline PEG, as first observed by Dale et al.[34] Furthermore, the vibrations of PEG have been completely assigned on the basis of a deuterium isotopic shift study of oriented PEG films and a normal-coordinate analysis of the spectra.[35] The spectrum of $[(18\text{-crown-}6)K]^+SCN^-$ has already been assigned by analogy to the PEG spectrum.[36] The frequencies (cm^{-1}) and assignments of the spectrum of $[(\mathbf{1})K]^+NO_3^-$ in $CDCl_3$ are summarized in Table V, together with those of $[(18\text{-crown-}6)K]^+SCN^-$ and PEG.

A significant perturbation from D_{3d} symmetry should remove the degeneracy of all E_u modes and thereby increase the number of IR bands observed. This has been seen, for example, in the

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Table VI. Energies (cm^{-1}) for the Components of ν_3 for Potassium Nitrate Contact Ion Pairs in Various Media

component	argon[a]	THF-d_8[a]	Me$_2$SO-d_6[a]	[(**1**)K$^+$]NO$_3^-$ in CDCl$_3$
ν_{3a}	1291	1330	1343	1346
ν_{3b}	1462	1383	1379	1382
$\Delta\nu_3$	171	53	36	36

[a] Data from ref 38.

spectrum of the simple 18-crown-6 complex of K$^+$, which has a D_{3d} ring conformation, as opposed to the spectrum of the uncomplexed crown, which has three different O–CH$_2$CH$_2$–O torsion angle sequences.[33] The (18-crown-6)K$^+$ complex has only two CH$_2$ rocking bands, whereas the free crown has five.[34] Likewise, in the dimethyl crown, the KNO$_3$ complex shows only the two CH$_2$ rocking bands in solution (Table V), but for the free crown the CH$_2$ rocking bands are significantly broadened and some of the other CH$_2$ bands are split. These observations are consistent with an approximate trigonal conformation for the ring skeleton in the KNO$_3$ complex of **1** in solution.

The infrared spectrum also indicates that the NO$_3^-$ is ion-paired to the complexed K$^+$, such that the symmetry of the NO$_3^-$ is lowered from D_{3h} to at most C_{2v}. This reduction in symmetry results in the splitting of the degenerate asymmetric stretching mode ν_3(E′) and the degenerate bending mode ν_4(E′) of nitrate. The degree of distortion of nitrate from D_{3h} symmetry has been demonstrated to be proportional to the splitting of ν_3(E′) in the infrared spectrum.[37] This splitting ($\Delta\nu_3$) is therefore an effective measure of the strength of cation–anion interaction. The values of $\Delta\nu_3$ for free ion pairs isolated in an argon matrix[38] and solvated ion pairs in THF-d_8 and Me$_2$SO-d_6 together with the value measured for [(**1**)K]$^+$NO$_3^-$ in CDCl$_3$ are listed in Table VI. The relatively small value of ν_3 observed for [(**1**)K]$^+$NO$_3^-$ indicates that the crown is very effective in softening the cation (as effective as the powerful cation-solvating solvent Me$_2$SO) and in reducing the strength of interaction of the complexed cation with the nitrate anion. However, the degree of splitting is still characteristic of a contact ion pair, with the crown being externally complexed to the K$^+$. The value of $\Delta\nu_3$ observed for the KNO$_3$ complex of **1** is smaller than those observed for the corresponding Na$^+$ ($\Delta\nu_3$ = 46 cm^{-1}) and Sr^{2+} ($\Delta\nu_3$ = 98 cm^{-1}) complexes, which indicates that the nitrate interaction is weaker in complexes with the cations of lower charge density. This observation is consistent with the nitrate $n \rightarrow \pi^*$ CD data,[13] which suggest that in solution the NO$_3^-$ is not as tightly bound and thus farther from the chiral centers of the crown ether in the KNO$_3$ complex of **1** than it is in the complexes with alkaline-earth-metal cations.

The energies of the two components of ν_3 are also very characteristic of the mode of bonding of the nitrate. Normal-coordinate calculations have been done for monodentate and bidentate coordination, to determine the changes in energy that would result from an increase in the polarization of the nitrate by the metal ion.[39] The calculations indicate that the splitting of ν_3 is such that the symmetric mode (A$_1$) is at higher energy than the asymmetric mode (B$_1$) for bidentate coordination and in the opposite sense for monodentate coordination. The energies and intensities of these components are therefore very sensitive to the mode of nitrate coordination. Since the energies and intensities of these components for the complex in solution are almost identical with those of the solid-state complex, we conclude that the nitrate is also coordinated through two oxygens in solution.

Conclusion

The KNO$_3$ complex of **1** exists as a contact ion pair, not only in the crystal, but also in chloroform. In fact, the infrared spectrum suggests that most of the structural features of the solid complex, including the crown conformation and the coordination mode of the nitrate, are maintained in solution. Although ion pairing in chloroform is hardly remarkable, the activation of anions in the presence of crown ethers is often cited as resulting from the disruption of ion pairs. The interaction of NO$_3^-$ with K$^+$ *is* surely weakened by the crown, although direct comparison of the strength of interaction with the free ion pairs was not possible due to the insolubility of KNO$_3$ in chloroform. Conversely, the crown–cation interaction is also influenced by the coordination of the anion, which causes the K$^+$ to be displaced from the mean plane of the crown ring, both in the solid state and in solution.

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Supplementary Material Available: Listings of calculated hydrogen positional and thermal parameters and bond angles and distances (6 pages). Ordering information is given on any current masthead page.

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