The Nature of Alkali Metal Ion Interactions with Cyclic Polyfunctional Molecules. I. Vibrations of Alkali Ions Encaged by Crown Ethers in Solution

Andreas T. Tsatsas,[1] Robert W. Stearns, and William M. Risen, Jr.*

Contribution from the Department of Chemistry, Brown University, Providence, Rhode Island 02912. *Received October 30, 1971*

Abstract: Frequencies of the quantized motion of cations encaged in cyclic polyether (crown) systems have been determined from solvent- and anion-independent bands in the far ir spectra of dissolved crown–alkali-metal-salt complexes in pyridine and DMSO. The analysis of the forces with which the cations are encaged shows that the Na^+–crown and K^+–crown forces are nearly equal for dibenzo-18-crown-6, and that cation selectivity in these cases does not derive from differences in ion–crown encagement forces. The forces between cations and solvent molecules (DMSO, pyridine) are evaluated from cation-motion frequencies which are shown to be independent of the nature of the counterion in several salt solutions. The combined results from solvated and crown-encaged cations are shown to establish the basis for evaluation of molecular scale forces involving antibiotic–cation complex species postulated to be responsible for ion-selective transport properties.

In work recently reported from this laboratory[2–5] and others,[6–16] it has been demonstrated that vibrational bands due to quantized motion of simple ions in solution, first reported by Edgell, *et al.*,[6] for the motion of alkali metal cations relative to their counterions and solvent molecules in tetrahydrofuran solution can be observed in the far infrared spectra of related noncrystalline, condensed-phase systems. These bands provide an unique method for probing the forces of interaction between ions and their neighboring environment in both solutions[7] and such related systems as ionic organic copolymers,[3,4] ionic glasses,[5,8] and ion-enclosure compounds. Thus, with vibrational analysis of these spectral features the force fields for ion–surroundings motion can be obtained and compared with theoretically calculated potential fields and energies of interaction to elucidate the ion–surroundings forces.

In general, variations in the cation's motion frequencies in solution are expected to occur with variations of (a) the size, shape, and charge (charge distribution) of its counterion, or (b) the nature of the solvent. These frequencies should differ, in turn, from those of cations vibrating in an encaging environment such as that provided by cyclic polyether compounds. Such compounds occur as "crown ethers" and as antibiotics, such as enniatin B, nonactin, or valinomycin. Since they are known to selectively enhance both ion binding in solution[17] and ion transport across membranes,[18] the nature of ion–cyclic polyether interactions is of obvious interest.

The present study was undertaken to investigate the effects on the cation motion frequencies in solution caused by ion encagement and to obtain the ion–cage interaction force information the frequencies reflect. It was, therefore, of particular interest in the design of this investigation that the cyclic polyether–metal ion complexes be good models for ion–antibiotic (selective ion transport) systems.

From reported studies of alkali metal salts in solution, it is clear that the cation-motion frequencies can be either anion dependent or independent of the anion, and they are solvent dependent. Because knowledge of these dependencies is necessary to obtain ion–solvent forces and to interpret the spectra of ion-encagement complexes, we have also studied the variations in cation-motion frequencies of salts in solution as a function of both anion and solvent.

The macrocyclic polyether informally named dibenzo-18-crown-6 by Pedersen[19] was chosen as the ion-encaging compound. This compound is refered to simply as the crown ether hereinafter, unless otherwise noted. Pedersen isolated crystalline 1:1 complexes of this compound with MSCN ($M^+ = Na^+, K^+, Rb^+$) and postulated that the alkali metal ion is centrally located within the polyether ring with the anion above or below the plane of the ring. The planar configuration of the six oxygen atoms and the postulated cation and anion positions have been established by crystal structure determinations, as shown in Figure 1a.[20] This crown ether is one of several known to enhance the solubility of inorganic salts in organic solvents[19] and to increase the

---

[1] Abstracted in part from the Ph.D. thesis of A. T. Tsatsas, Brown University, 1971.

[2] A. T. Tsatsas and W. M. Risen, Jr., *J. Amer. Chem. Soc.*, **92**, 1789 (1970).

[3] A. T. Tsatsas and W. M. Risen, Jr., *Chem. Phys. Lett.*, **7**, 354 (1970).

[4] A. T. Tsatsas, J. W. Reed, and W. M. Risen, Jr., *J. Chem. Phys.*, **55**, 3260 (1971).

[5] G. J. Exarhos and W. M. Risen, Jr., *Chem. Phys. Lett.*, **10**, 484 (1971).

[6] W. F. Edgell, A. T. Watts, J. Lyford IV, and W. M. Risen, Jr., *J. Amer. Chem. Soc.*, **88**, 1815 (1966).

[7] W. F. Edgell, J. Lyford, R. Wright, and W. M. Risen, Jr., *ibid.*, **92**, 2240 (1970).

[8] C. A. Angell, J. Wong, and W. F. Edgell, *J. Chem. Phys.*, **51**, 4519 (1969).

[9] (a) B. W. Maxey and A. I. Popov, *J. Amer. Chem. Soc.*, **89**, 2230 (1967); (b) *ibid.*, **90**, 4470 (1968); (c) *ibid.*, **91**, 20 (1969).

[10] J. L. Wuepper and A. I. Popov, *ibid.*, **91**, 4352 (1969).

[11] M. K. Wong, W. J. McKinney, and A. I. Popov, *J. Phys. Chem.*, **75**, 56 (1971).

[12] W. J. McKinney and A. I. Popov, *ibid.*, **74**, 535 (1970).

[13] J. L. Wuepper and A. I. Popov, *J. Amer. Chem. Soc.*, **92**, 1493 (1970).

[14] J. C. Evans and G. Y.-S. Lo, *J. Phys. Chem.*, **69**, 3223 (1965).

[15] M. J. French and J. L. Wood, *J. Chem. Phys.*, **49**, 2358 (1958).

[16] E. G. Hohn, J. A. Olander, and M. C. Day, *J. Phys. Chem.*, **73**, 3880 (1969).

[17] H. K. Frensdorff, *J. Amer. Chem. Soc.*, **93**, 600 (1971), and references therein.

[18] D. C. Tosteson, *Fed. Proc.*, **27**, 1269 (1968).

[19] C. J. Pedersen, *J. Amer. Chem. Soc.*, **89**, 7017 (1967); **92**, 386, 391 (1970).

[20] D. Bright and M. R. Truter, *Nature (London)*, **225**, 176 (1970); *J. Chem. Soc. B*, 1544 (1970).

Table I. Frequencies (cm^{-1}) of Ion Motion in Solution

	THF	DMSO	Py	THF	DMSO	Py
		Na^+			K^+	
SCN^-	202 ± 4	205 ± 4^a	183 ± 4^c		150 ± 3^f	139 ± 3
BPh_4^-	197 ± 4^e	203 ± 4^b	180 ± 4^d		152 ± 4	135 ± 3^g
PF_6^-	192 ± 4	198 ± 4	180 ± 4		147 ± 4	134 ± 3
		Na^+–Crown			K^+–Crown	
SCN^-		215 ± 4	217 ± 4		169 ± 3	170 ± 3
BPh_4^-		213 ± 4	212 ± 4		167 ± 3	169 ± 4
PF_6^-		210 ± 5	214 ± 4		170 ± 5	167 ± 3

[a] 200 ± 3 (ref 9a). [b] 198 ± 3 (ref 9a), 203 (ref 7). [c] 180 ± 3 (ref 17). [d] 179 ± 3 (ref 12), 175 (ref 15). [e] 198 (ref 7), 175 (ref 15). [f] 153 ± 3 (ref 9a). [g] 133 (ref 15).

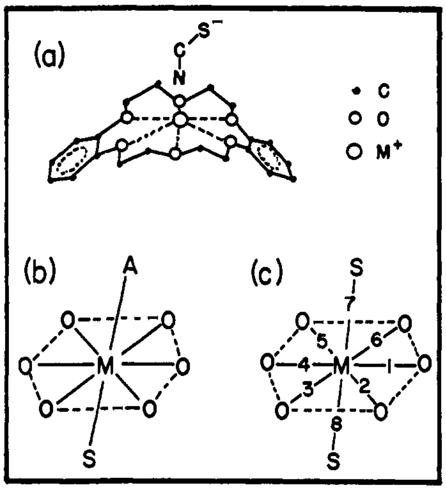

Figure 1. The structure of the RbSCN-dibenzo-18-crown-6 complex and two vibrational models (see text) for the dissolved M^+–crown aggregate.

permeability of biological membranes to alkali metals in a manner similar to that of the naturally occurring antibiotics mentioned above. In these functions, dibenzo-18-crown-6 demonstrates alkali metal selectivity.

In our studies of ion–multipole interactions in solution, such as those that dominate in solutions of simple $M^+AB_x^-$ salts in polar nonaqueous solvents, the crown complexes also play an important role because the geometry of atoms which interact with the cation is known. This geometrical information removes a significant variable from ion–multipole calculations of the potential functions, U, whose second derivative along the vibrational normal coordinates, $(\partial^2 U/\partial Q^2)|_0$, is most directly comparable to our spectral results.

The salts and solvents in which ion-motion bands were studied here were chosen to provide significant variations in their properties, while satisfying the rather demanding experimental strictures of solubility and far infrared transmittance. Thus, tetrahydrofuran (THF), dimethyl sulfoxide (DMSO), and pyridine constitute a series in which dipole moment and dielectric constants, as well as the atom providing the principal cation solvation ability, are varied. In the M^+SCN^-, $M^+PF_6^-$, and $M^+B(C_6H_5)_4^-$ salts, variations in shape and charge distribution are found, while the experimentally useful property of different anion masses is maintained. These salts have the additional advantage of forming crown ether-encagement compounds, which makes their solution study useful in interpreting ion–crown complex spectra. Ion-motion frequencies for several of these systems have been reported, as noted below and in Table I.

Experimental Section

The dibenzo-18-crown-6 (crown ether) used was kindly furnished by Dr. M. L. Nadler of the Du Pont Co. Its purity was confirmed by its infrared spectrum[21] and physical properties. The alkali metal salts of SCN^-, PF_6^-, and $B(C_6H_5)_4^-$ were reagent-grade commercial preparations, except for $LiB(C_6H_5)_4$ and $KB(C_6H_5)_4$ which were prepared from purified $NaB(C_6H_5)_4$ (*i.e.*, $NaBPh_4$) according to Szwarc, *et al.*[22] Solvents used (THF, DMSO, and pyridine) were reagent grade chemicals dried over molecular sieves and vacuum deaerated and distilled. Reagent grade absolute methanol was used in preparative work without further purification.

The solid MSCN-crown complexes ($M = Na^+, K^+$) were prepared by Pedersen's method 3.[19] The $MBPh_4$-crown and MPF_6-crown complexes were prepared similarly, although greater quantities of absolute methanol were required to initially dissolve the alkali metal salt and the crown ether. The solubilities of the $MBPh_4$-crowns and the MPF_6-crowns are lower than those of the MSCN-crowns. The salt-crown complexes were crystallized and freed of residual methanol and crown ether *in vacuo*. With the exceptions of anion vibrations, the KBr pellet spectra in the 4000–600-cm^{-1} region of all salt–crown complexes agreed with the reported[19] spectrum of the KSCN-dibenzo-18-crown-6 complex and showed the characteristic variations from that of free crown ether. The RbSCN- and CsSCN-crown complexes were isolated, but their solubilities in DMSO and pyridine are too low for the study of their ion motion in solution. In agreement with previous results,[19] the LiX-dibenzo-18-crown-6 complexes were not isolable.

Far infrared spectra in the 33–800-cm^{-1} region were measured with a Beckman IR-11 spectrophotometer. A special type of sealed liquid cell with heat-polished high density polyethylene was used,[23] with typical path lengths of 0.40 mm for pyridine solutions and 0.10 mm for DMSO solutions. Each spectral measurement was repeated several times with a reproducibility of 1% T, resolution of 2 cm^{-1}, and calibrated[24] accuracy of better than 1 cm^{-1}.

The band maximum uncertainties reported here reflect the breadth of the bands and the consequent uncertainty inherent in careful peak maximum identification. They do not reflect experimental spectral accuracy, which is high (*ca.* 1 cm^{-1}). This is seen in Figures 2 and 3, in which the ion-motion bands for salt solutions are compared to analogous salt–crown complex results.

Spectral Results

Salts in Solution. In the far infrared spectrum (100–650 cm^{-1}) of each of the crown-complex forming M^+X^- salts ($M^+ = Na^+, K^+$; $X^- = PF_6^-, SCN^-, BPh_4^-$) dissolved in THF, DMSO, or pyridine, there is one band whose frequency is strongly cation dependent.

---

(21) For details of the vibrational analyses and model construction see ref 1, parts 2, 3, and Appendix B.

(22) D. N. Bhattacharyya, C. L. Lee, and M. Szwarc, *J. Phys. Chem.*, 69, 608 (1965).

(23) A. T. Tsatsas and W. M. Risen, Jr., *Appl. Spectrosc.*, 24, 383 (1970).

(24) Calibration in the 600–33-cm^{-1} region was performed with the results of L. R. Blaine, *J. Res. Nat. Bur. Stand., Sect. C*, 67, 207 (1963); L. R. Blaine, E. K. Plyler, and W. S. Benedict, *J. Res. Nat. Bur. Stand., Sect. A*, 66, 223 (1962).

Table II. Band Positions (cm^{-1}) for M$^+$X$^-$ Salts in THF, DMSO, and Py[a]

Salt	Solvent								
NaSCN	THF		202		478 m	485 m			
	DMSO		205		465 w				
	Py		183		473 m				
KSCN	THF								
	DMSO	150			465 m				
	Py	139			472 m				
NaBPh$_4$	THF		197		469 m			613 m	624 w
	DMSO		203	254 w	470 m				
	Py		180	257 w	470 m			613 w	625 w
KBPh$_4$	THF								
	DMSO	152		256 w	470 m			613 s	626 m
	Py	135			470 m				624 w
NaPF$_6$	THF		192				559 s		
	DMSO		198				559 s		
	Py		180				559 s		
KPF$_6$	THF						559 m		
	DMSO	147					559 s		
	Py	134					559 s		

[a] w = weak, vw = very weak, m = medium, s = strong.

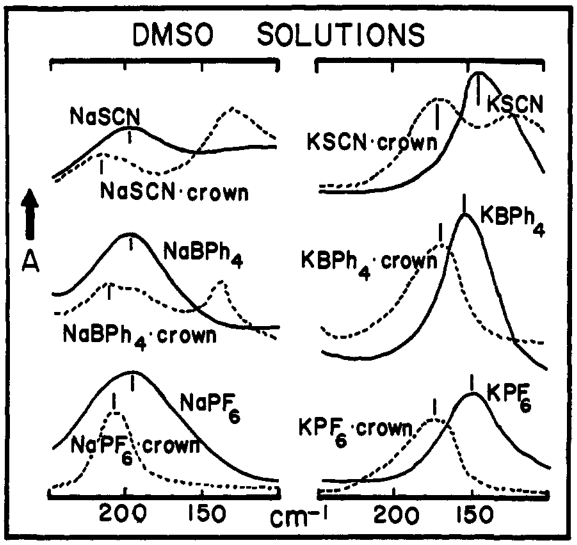

Figure 2. Far infrared spectra of DMSO solutions of M$^+$X$^-$ salts (M$^+$ = Na$^+$, K$^+$; X$^-$ = SCN$^-$, BPh$_4^-$, PF$_6^-$) and of analogous M$^+$X$^-$-dibenzo-18-crown-6 systems.

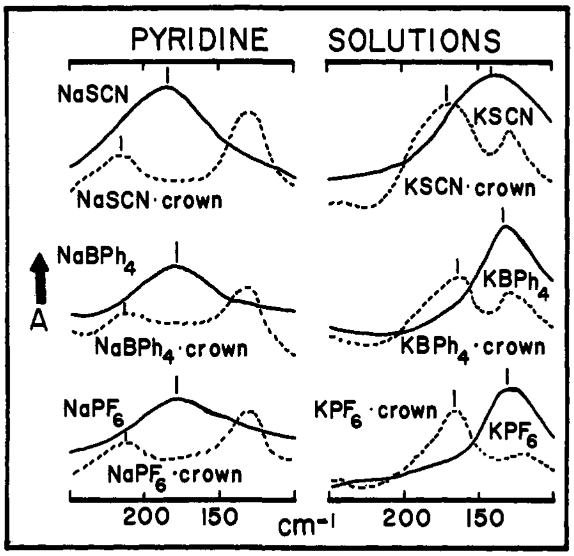

Figure 3. Far infrared spectra of pyridine solutions of M$^+$X$^-$ salts (M$^+$ = Na$^+$, K$^+$; X$^-$ = SCN$^-$, BPh$_4^-$, PF$_6^-$) and of analogous M$^+$X$^-$-dibenzo-18-crown-6 systems.

All other bands in the spectra, which are reported in Table II are due to predominantly anion or solvent vibrations.

The strongly cation-dependent bands, due to vibrations in the ranges 180–205 and 135–150 cm^{-1} for the Na$^+$ and K$^+$ salt solutions, respectively, are the most important features of the spectra. As shown in Figure 4, the frequency variation is approximately accounted for by the cation-mass variation, assuming initially that the vibrational reduced mass is approximately that of the cation. Thus, we assign these bands to quantized cation vibrational motion in solution. This assignment is supported by previous work.[7,9–11]

The frequencies of cation motion in solutions are solvent dependent, with those for DMSO solutions occurring 15–20 cm^{-1} higher than analogous ones for pyridine solutions. In these solvents our results show no significant anion dependence. However, in agreement with previous work we find specific anion dependence of the Na$^+$ motion bands in THF. Such anion dependence in THF, which has been more clearly demonstrated by Edgell, *et al.*,[7] indicates significant anion participation in the near-neighbor environment of the cation, because the shifts in a given solvent result from the effect of the anion on the force field and reduced

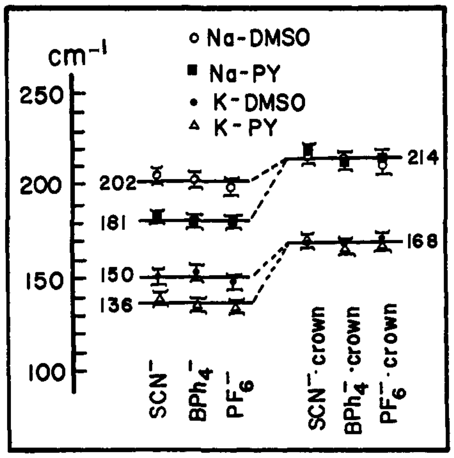

Figure 4. Comparison of ion motion band frequencies for salts and M$^+$–crown systems in DMSO and pyridine solutions.

Table III. Band Positions (cm^{-1}) for M^+X^-–Crown Complexes in DMSO and Py

Complex	Solvent																
NaSCN–	DMSO					215	(243)				467 m	515 vw	530 vw		602 w	615 w	
crown	Py	137 s				217	224 vw		278 m	339 w	462 m^{d} 471 m	516 w	531 vw				
KSCN–	DMSO		169						275 vw		467 w		528 vw		602 w	617 vw	
crown	Py		170							340 vw	470 w	508 vw	531 vw				
$NaBPh_4$–	DMSO					213		254 w			470 m	515 w	530 w		603 w	614 m	626 w
crown	Py	135 s				212		257 w	281 w	339 w	470 m	517 w	531 w			615 w	626 w
$KBPh_4$–	DMSO		167	188 vvw	212 vvw			258 w[a]			470 m	512 vw	530 vw		601 w	613 s	625 w
crown	Py		165					256 w	272 vw	340 vw	471 m	513 vw	531 vw			616 w	627 w
$NaPF_6$–	DMSO					210					467 w			559 s	602 w		
crown	Py	136 vw				214			277 w	340 w	459 w^{d} 471 w	516 vw	532 vw	599 s			
KPF_6–	DMSO		170								468 w			599 s	602 w		
crown	Py		167	188 vvw	212 vvw				272 m	340 m	461 w^{d} 470 w	510 w	530 w	599 s			

[a] Complex envelope in this region extending to higher frequencies; s = strong, m = medium, w = weak, vw = very weak, and d = doublet.

mass of the vibration. This result is consistent[7,16] with ion pairing of the salts in THF. On the other hand, no participation of the anion in the primary solvation shell of the cation is indicated for pyridine and DMSO solutions. This is consistent with the reports of Popov and coworkers, who found ion-motion frequency dependence on only the cation and solvent for a number of simple salts in these and related solvents.[9–13]

The other bands reported in Table II are due to predominantly solvent or anion internal modes. For example, the M^+SCN^- salt solution spectra contain a band in the 465–480-cm^{-1} region, which is ν_2 of SCN^-, a vibration of π symmetry that is characteristic of the bending motion of SCN^-. This band may be split into two components in either the solid state or such concentrated solutions as that of NaSCN in THF. Similarly, the PF_6^- salts have a strong absorbance at *ca.* 559 cm^{-1}, which is ν_4 of T_{1u} symmetry, a predominantly F–P–F bending mode. The BPh_4^- salts have in-plane and out-of-plane phenyl deformations and Ph–B–Ph deformation modes occurring as the 625-, 615-, 470-, and 225-cm^{-1} bands.

Cation–Crown Ether Complexes in Solution. The far infrared spectra of the Na^+ and K^+ salt–crown ether complexes with dibenzo-18-crown-6 have been measured in DMSO and pyridine. The Rb^+ and Cs^+ analogs are not sufficiently soluble in these solvents, and none of the cation–crown complexes are sufficiently soluble in THF to permit their far infrared spectra to be measured.

One cation-dependent band is observed in the spectrum of each MX–crown species in solution. This band is in addition to those shown to be due to solvent, anion, or crown internal vibrations by the data of Table III. However, it is clear from the comparisons shown in Figure 4 that the frequencies of cation motion in the crown encagement species are significantly higher than those for the simple salt solutions in the same solvents. From Figure 4 it is also seen that the vibration of crown-encaged Na^+ is at 213 ± 4 cm^{-1} (maxima), is independent of both solvent and anion, to within the limits set here, and is at a higher frequency than those for the simple salts in the same solvents. Similarily, the vibrational motion of crown-encaged K^+ occurs at 167 ± 3 cm^{-1} (maxima), which is higher than the 136–150-cm^{-1} range for the cation vibration in salts in the same solvents. Again, this frequency is independent of solvent and anion.

The observations that the ion-motion frequency is significantly different when the cation is encaged than when no crown ether is present, that it is independent of solvent and anion variations, and that it shifts as a strong function of the cation mass lead to the following band assignment. The bands at 213 ± 4 cm^{-1} for Na^+–crown complexes and 167 ± 3 cm^{-1} for K^+–crown complexes correspond to an infrared active vibration of the encaged M^+ ion in the plane of the M^+–crown ring defined by M^+ and the six ethereal oxygens. The vibrational analysis presented below is based, in part, on this assignment of the ion-motion bands summarized in Table I.

Analysis of Cation Motion Vibrational Modes

Method. For the vibrational frequency of ion motion in an ion-containing aggregate, there corresponds a normal mode of that aggregate, which may be the only mode of its irreducible representation or it may be one of several modes belonging to its irreducible representation of the aggregate's point group.[21] If it is the only such mode, the normal coordinate is given by the normalized symmetry coordinate, and the *symmetrized* force constant can be computed directly, for example, as F_{ii} when the secular equation $|\mathbf{F} - \mathbf{G}^{-1}\lambda| = 0$ is employed.[25] If it is the only one of several such modes to have its eigenvalue in a given region it is given approximately by that symmetry coordinate, and F_{ii} may be computed within the energy factoring approximation discussed by Wilson, *et al.*[26] Within these constaints, the relation $F_{ii} = 4\pi^2c^2\omega_i^2/G_{ii}$ is valid and F_{ii} is obtained. In treating the salt solutions and the M^+–crown complexes, vibrational models are postulated on the basis of the spectral assignments, and from them the values of G_{ii} and F_{ii} and the forms of F_{ii} are obtained.

Salts in Solution. Two considerations largely shape the construction of vibrational models for the salts (MPF_6, MSCN, and $MBPh_4$) in DMSO and pyridine solution. The first is the fact that there is no anion dependence of the vibrational frequency although there is both cation and solvent dependence. The second is that both experimental and steric considerations indicate that about four or six polar solvent molecules are involved in primary shell (nearest-neighbor) solvation of Na^+ in nonaqueous solvents. On the basis of such considerations, the cation vibrational models in DMSO and pyridine are postulated to be M^+S_x, involving the cation and effectively 6, 4, or 2 solvent molecules, as follows.

With four solvent molecules situated most symmetrically about the cation, the aggregate has T_d symmetry, in which the only infrared-active stretching mode is of T_2 type. Since there are no other stretching modes of T_2 type for MS_4^+ in T_d, this mode can mix only with either high frequency internal solvent modes or very low frequency aggregate skeletal bending modes with this model. Thus the symmetry coordinates for this mode, of which one is $[S_a(T_2) = {}^1/_2(r_1 - r_2 + r_3 - r_4)]$, closely approximate the normal coordinates and are so used to compute G_{ii} and F_{ii}. The values of $F_{ii}(T_2)$ equal the function $(k_r - k_{rr})$, where k_r is the M^+–S (S = solvent) force constant and k_{rr} is the associated interaction force constant.

Table IV. Cation–Solvent Force Constants

	ω_i, cm^{-1}	$m(\text{DMSO})^a = 78$ $m(\text{Py}) = 79$ $F_{ii}{}^{b,c}$	$m(\text{DMSO})^a = 48$ $m(\text{Py}) = 38$ $F_{ii}{}^{b,c}$	$m(\text{DMSO})^a = 16$ $m(\text{Py}) = 14$ $F_{ii}{}^{b,c}$
Na^+DMSO_4	202	0.34	0.30	0.20
Na^+Py_4	181	0.27	0.23	0.15
K^+DMSO_4	150	0.28	0.24	0.14
K^+Py_4	136	0.23	0.18	0.10
$Na^+DMSO_{2\text{ or }6}$	202	0.24	0.22	0.16
$Na^+Py_{2\text{ or }6}$	181	0.19	0.17	0.12
$K^+DMSO_{2\text{ or }6}$	150	0.21	0.18	0.12
$K^+Py_{2\text{ or }6}$	136	0.17	0.14	0.09

[a] Mass units are amu. [b] F_{ii} units are 10^5 dyn cm^{-1}. [c] F_{ii} for MS_4^+ based on T_d and for $MS^+_{2\text{ or }6}$ based on $D_{\infty h}$, as discussed in text.

Arranging two solvent molecules about the cation most symmetrically results in a linear MS_2^+ aggregate with $D_{\infty h}$ symmetry. In $D_{\infty h}$ there is one infrared-active stretching mode, given by $S(\Sigma_u^+) = 2^{-1/2}(r_1 - r_2)$, where r_i is a displacement along the M^+–S distance, This mode in $D_{\infty h}$ has the same form as the only infrared-active stretch of the MS_6 model (O_h symmetry), which is of T_{1u} type. Thus one computes the same value for F_{ii}, which is $(k_r - k_{rr})$, under either $D_{\infty h}$ or O_h approximations when aggregate bending modes are neglected. Since Na^+ may exist as M^+S_6 in DMSO,[13] the value for $F_{ii}(O_h,T_{1u})$ is of interest, but it is reported as $F_{ii}(D_{\infty h},\Sigma_u^+)$, since in $D_{\infty h}$ the bends are symmetry excluded that are only neglected on the basis of energy factoring in O_h.

The values of F_{ii} in Table IV show that the net M^+–solvent force constant in each model, regardless of the effective solvent mass, is greater for each cation in DMSO than for the corresponding one in pyridine. Although it is not evident from the spectra alone, it is also clear that in each model the Na^+–solvent net force field is greater than the analogous K^+–solvent field.

In order to make more detailed comparisons of the M^+–solvent force constants with one another and with those for the cation–crown interactions, the results must be based on effective solvent mass and solvated cation composition assumptions. We employ the F_{ii} (Table IV) for which the effective solvent masses are $m(\text{DMSO}) = 48$ and $m(\text{Py}) = 38$, although the same trends are generally observed with other effective masses. These effective masses reflect the motion of S=O and C–N–C groups, respectively, in vibration with the cation and are in accord with the observed shifts of internal solvent modes in high frequency infrared spectra.[9c,12,27] Clearly effective solvent masses that are those of either the entire molecule or just the solvating atom are unrealistically high or low, respectively.

For the salts in pyridine, the M^+S_4 models are employed on steric grounds and on the basis of analogy with nmr results for Na^+ in THF,[16,28,29] 1-methyl-2-pyrrolidone (1M2Py),[13] and other solvents.[11] The model for the solvated cation in DMSO is also taken to be M^+S_4 in this discussion, but this is more difficult to assign. Wuepper and Popov[13] concluded from their nmr study of $NaAlBu_4$ plus DMSO in dioxane solutions that in that case a DMSO to Na^+ ratio of 6 corresponds to a solvate species. This was based on a plot of DMSO proton resonance shift *vs.* DMSO to $NaAlBu_4$ mole ratio. Although the data at high and low values of this ratio extrapolate to intersection at 6, there is a distinct break when the ratio is 4. The reported analysis of the data requires, as the authors point out, that significant assumptions must be made to take into account both DMSO–dioxane interactions and solvation of the $AlBu_4^-$ in addition to other smaller effects. On the basis of the break in the reported nmr data themselves, the common Na^+ solvation number of 4 in related polar solvents, and the fact that the solvation number of the related cation Li^+ is lower in DMSO than in 1M2Py,

---

(25) E. B. Wilson, J. C. Decius, and P. C. Cross, "Molecular Vibrations," McGraw-Hill, New York, N. Y., 1955.

(26) Reference 25, Sections 4–8 and Appendix IX.

(27) L. Corroin, B. J. Fox, and R. C. Lord, *J. Chem. Phys.*, **21**, 1170 (1953).

(28) E. Schaschel and M. C. Day, *J. Amer. Chem. Soc.*, **90**, 503 (1968).

(29) C. N. Hammonds and M. C. Day, *J. Phys. Chem.*, **73**, 1151 (1969).

we employ the MS_4^+ model for Na^+ and K^+ in DMSO as well as in pyridine. This permits direct comparison of the force field elements in these two cases. Although this is tentative, we note that all of the solid DMSO solvates formed by Maxey and Popov[30] have DMSO to M^+ ratios of less than or equal to 4, even with anions as large as tetraphenylborate.

The resulting F_{ii} for M^+–solvent distention are 0.30 (Na^+–DMSO), 0.24 (K^+–DMSO), 0.23 (Na^+–Py), and 0.18 mdyn Å^{-1} (K^+–Py). The implications of these variations are discussed later.

Alkali Ions Encaged in Crown Ether. Since there is no anion or solvent dependence of the frequencies of the ion motion bands of the M^+–crown ether aggregates in DMSO or pyridine, we have assigned the bands to the motion of the cation in the plane of the six oxygen atoms forming the polyether cage.

The crystal structure analyses[20] that have been reported for M^+–crown species (with dibenzo-18-crown-6, specifically) indicate near "normal" K–O and Rb–O distances and abnormally long Na–O distances, where the normal distance is $(r^{M^+}{}_{ionic} + r^{O}{}_{vdw})$. It is known that the ring size is essentially constant, and it is evident that the M^+ is symmetry required to be in the center of the ring (*i.e.*, on its local sixfold axis). The M–O distances result from these factors and are not determined primarily by M^+–O interaction energy minimization.

Either of the configurations shown in Figure 1b and 1c meets the requirements for a vibrational model, since there is neither solvent nor anion frequency dependence. However, to simplify the vibrational analysis by having the cation in the plane of the ring, and by keeping the point-group symmetry high, we take the configuration shown in Figure 1c to be the appropriate model. In that case there are two axial solvent molecules, and the aggregate model retains the D_{6h} symmetry of the metal ion and six oxygens.

For the MO_6S_2 aggregate of D_{6h} symmetry shown (Figure 1c), there are two infrared active stretching modes. The one assigned to the cation motion in the cage is the (E_{1u}) mode described by the symmetry coordinates $S_a(E_{1u}) = (12)^{-1/2}[2(r_1 - r_4) + (r_2 - r_3 - r_5 + r_6)]$ and $S_b(E_{1u}) = (^1/_2)[r_2 + r_3 - r_5 - r_6]$. The other is the A_{2u} mode described approximately by $S(A_{2u}) = (2)^{-1/2}[r_7 - r_8]$, which involves cation and solvent motion perpendicular to the cage plane.

In the vibrational analysis, formal calculation of G_{ii} is accomplished readily, and the frequency, ω_i, can be considered energy factored from such higher frequency motions as C–O stretching and C–C–O bending with reasonable assurance. However, it is necessary to assign effective masses to the ring "oxygens." Two reasonable reduced mass assignments were used, as noted in Table V which contains the calculated values of F_{ii}. The first is that "m_O" is simply 16 amu, and the second is that "m_O" is effectively that of M(C–O–C) and equal to 40 amu.

Regardless of which of these values is taken for "m_O," two results of interest are obtained. First the F_{ii} for the Na^+–crown case is nearly the same as that for the K^+–crown case. The form of F_{ii} is $(k + k'_{rr} - k''_{rr} - k'''_{rr})$, where k_r is the force constant for M^+–O distortion (internal coordinate r), and k'_{rr}, k''_{rr}, and k'''_{rr} are stretch–stretch interaction force constants. Clearly, then, the force of interaction between the encaged metal ion and the crown ether is the same for Na^+ and K^+.

Table V. Cation–Crown Ring Vibrational Forces

Aggregate	ω_i, cm^{-1}	m_O, amu	G_{ii}, amu^{-1}	F_{ii},[a] 10^5 dyn cm^{-1}
Na^+–crown	214 ± 4	16	0.1929	0.14
K^+–crown	168 ± 2	16	0.1394	0.12
Na^+–crown	214 ± 4	40	0.1554	0.17
K^+–crown	168 ± 2	40	0.1019	0.16

[a] $F_{ii} = (k_r + k'_{rr} + k''_{rr} - k'''_{rr})$.

Thus, the second result of interest is based on direct comparison of the values of F_{ii} from the M^+–crown cases with those from the M^+–solvent cases. This comparison is valid to the extent that each expresses the value of k_r, where r is a M^+–O (crown) or M^+–S (solvent) vibrational displacement, and that interaction constants between such displacements are negligible. That these interaction constants are negligible follows from the ion–multipole nature of the M^+–cage and M^+–solvent interactions and the fact that interaction force constants arise primarily from covalent bonding effects. The comparison shows that small amplitude displacement along an M^+–(solvent) coordinate (values for MS_4^+ given in text above) requires more force than it does along the analogous M^+–(crown oxygen atom) coordinate. Regardless of the choice of M^+S_x model, it is clear from such comparisons that the M^+–(crown oxygen atom) forces are significantly smaller than or at most the same magnitude as the M^+–S forces. The implications of these results are discussed below.

Discussion

The variation of the M^+–solvent force field elements with solvent, decreasing on going from DMSO to pyridine, *could* be explained qualitatively on the basis of the dipole moments of DMSO (3.9D) and pyridine (2.23D). If the ion–dipole attractive term dominates the complete potential energy function, it would be expected that the M^+–(DMSO) potential energy would be lower (more negative) than that for the M^+–(pyridine) interaction and that the force constants would reflect this by having F_{ii} for M^+–(DMSO) greater than that for M^+–(pyridine). Such an argument is often given, and is intuitively appealing, but it is too facile for the following reasons. The force constant function measures $(\partial^2 U/\partial Q)^2|_0$, the potential curvature, not the energetic stability, *per se*, of the aggregate. The curvature generally depends strongly on the interatomic repulsion potential, as well as the attractive potential, and these terms are not the same for different aggregates. Another reservation to the dipole moment and similar arguments is that the main contribution to the attractive potential is controlled by the electron distribution about the solvent's partial negative site rather than the solvent's overall dipole, and asserting that this contribution is equivalently expressed using the solvent dipole moments ignores the important detailed differences in electron distribution in the two solvent molecules.

The necessity for careful consideration of the ion–multipole potential function is also evident upon noting the variation of F_{ii} with cation. The force required for unit Na^+–solvent displacement is greater than that for

---

[30] B. W. Maxey and A. I. Popov, *J. Inorg. Nucl. Chem.*, **32**, 1029 (1970).

K^+–solvent displacement, despite the fact that K^+ is the more polarizable of these equally charged cations. Clearly, the repulsive portion of the potential, in helping define the M^+–solvent distances, serves to differentiate the two ion–solvent interactions.

For these reasons, we have initiated ion–multipole computations of U as a function of the assigned vibrational coordinate in order to evaluate both $U_{\min}$, the aggregate potential energy at the minimum energy configuration, and $(\partial^2 U/\partial Q^2)|_0$. The latter is to be compared with the values of F_{ii} found in this study. The results of this study will be reported later.

This work has shown that when K^+ or Na^+ is taken into the crown ring, the force resisting unit displacement along the aggregate's infrared active mode is nearly the same in each case. And it has shown that, with the assumptions discussed above about interaction force constants, the M^+–crown-oxygen force constant is less than either of the M^+–solvent-atom constants.

These results are interesting to consider in light of thermodynamic studies on M^+–crown complexes. In several studies[17] it has been shown that in nonaqueous solvents the stability constants (overall equilibrium constants for the schematic reaction [$M^+(\text{solvent})_x$ + crown–($\text{solvent}_y \rightleftarrows M^+$–crown $(\text{solvent})_z)$]) are generally much greater than unity. Thus, this recent study by Frensdorff has shown that for several 18-6 type crowns (dibenzo-18-crown-6 and dicyclohexyl-18-crown-6) in methanol the K^+ aggregate stability constant (1×10^5 l./mol dibenzo-18-crown-6–K^+) is significantly higher than that for the Na^+ aggregate (2.4×10^4 l./mol dibenzo-18-crown-6–Na^+).

In showing how these sets of results are consonant and understanding the variation in stability constant on going from Na^+ to K^+, it is useful to consider Frensdorff's measurements of the stability constants in water and methanol for a number of cation (Li^+, Na^+, K^+, Cs^+, Ag^+)–crown complexes using several members of the crown polyether family.[17] He showed that the stability constant for a given cation–crown complex is lower in water than in methanol and attributed this to the difference between the M^+–water and M^+–methanol interactions. Smaller differences between the stabilities of Na^+–, K^+–, and Cs^+–crown complexes as a function of polyether ring size have been attributed to "competition" between M^+–crown attraction and M^+–solvent attraction. While these attributions are obviously true in general, it does not necessarily follow from them that among cations which fit into the ring of a given crown the differentiation in the same solvent is based on differences in M^+–crown forces.

In this regard, the calorimetric titrations of aqueous solutions of dicyclohexyl-18-crown-6 (either isomer) with acidic aqueous solutions of the salts of several cations, reported by Izatt, *et al.*,[31] are relevant. The heats of reaction at several temperatures were used to obtain values of K, $\Delta H°$, and $\Delta S°$ for the "reaction" [M^{n+} + crown = M^{n+}–crown]. Although their stability constant sequence was similar to that of Frensdorff, the measured $\Delta H°$'s are essentially zero in the Na^+, Li^+, and Mg^{2+} cases, and the sign of that for Ca^{2+} is different from that for Sr^{2+}. It is evident that the reaction is not well symbolized by ignoring solvation and that the differences in energetic stability of the M^{n+} crown aggregate may not control variations in either K or $\Delta H°$ among the ions in the above sequence.

Since, for the dibenzo-18-crown-6 case, the Na^+–crown and K^+–crown forces are essentially the same and the same in both DMSO and pyridine, we may interpret differences in K between these complexes in the same solvent as due to differences in stability of the solvated cations. Our results on the solvated cations show that the M^+–solvent forces are greater for Na^+ than for K^+. Thus, the thermodynamic differences between these two M^+–solvent—M^+–crown equilibria lie primarily in differences in the initial rather than the final state. We must note, however, that although the M^+–in-plane ring forces are nearly equivalent, the solvation in the dissolved M^+–crown aggregates may cause interesting stability constant variations such as those observed between 18-crown-6, cyclohexyl-18-crown-6, and dicyclohexyl-18-crown-6 complexes.

On the basis of our results and interpretation, we may predict that the stability constant with dibenzo-18-crown-6 will be higher for Na^+ in pyridine than for Na^+ in DMSO, and higher for K^+ in pyridine than for Na^+ in either pyridine or DMSO. Similarly, the stability constant for K^+ complex in DMSO should be nearly the same as, but slightly smaller than, that for Na^+ in pyridine.

The emphasis on the initial cation state in the ion selectivity, rather than on the complexed state, is particularity relevant to the selective ion transport properties of the antibiotics discussed in the introduction, because formation of alkali complexes with nonactin has been shown by Prestegard and Chan[32] to require complete stripping of the cation solvation shell. Thus, it is entirely possible, as suggested for nonactin,[32] that in macrocyclic polyfunctional ion enclosure systems it is ion solvation, rather than steric or electronic properties of the enclosing cavity, that dominates ion selectivity in solution. This leads to the conclusion that a wide range of encaging species will effectively encage cations and that design of molecules for antibiotic ion transport purposes will most profitably be pursued by concentrating on the substituents, external to the ion-cage region, and their interactions with the constituents of the membranes to be penetrated. This conclusion is being tested in this laboratory to determine the specific ion dependence of ion–antibiotic forces themselves. That work will be reported in a future publication.

Acknowledgment. We gratefully acknowledge support of the instrumental facilities by ARPA under Contract SD-86 with Brown University, the support of R. W. S. under the National Science Foundation, Undergraduate Research Program, and the support of the U. S. Army Research Office (Durham).

---

(31) R. M. Izatt, D. P. Nelson, J. H. Rytting, B. L. Haymore, and J. J. Christensen, *J. Amer. Chem. Soc.*, **93**, 1619 (1971).

(32) J. H. Prestegard and S. I. Chan, *ibid.*, **92**, 4440 (1970).