Electrohydrodynamic Mass Spectrometric Studies of Some Polyether–Cation Complexes

Victor F. Man, J. Dale Lin, and Kelsey D. Cook*

Contribution from the Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37996. *Received December 17, 1984*

Abstract: The relative stability constants (K_s) of complexes of 18-crown-6 (18C6) with various cations in glycerol have been assessed with electrohydrodynamic mass spectrometry (EHMS). The results clearly corroborate the importance of steric campatability between the cation and the cavity of the crown. The mass spectral data uniquely reflect the effects of solvation and ion pairing in the formation of these complexes through the resolution of differently solvated and ion-paired species. The high sensitivity of EHMS enables the measurement of K_s for weakly bound complexes ($Li^+ \cdot 18C6$ and $(CH_3)_4N^+ \cdot 18C6$) which have not been detected by other methods.

The selectivity shown by certain cyclic polyethers (crowns) toward cations (including alkali metals) constitutes one of the interesting features which distinguish them from most noncyclic ligands. This selectivity promotes the use of crowns in a variety of applications.[1-4]

Crown selectivity results from variation of complex formation constants (K_f) with cation size and charge. The most successful approaches to determining K_f's cation–crown complexes have involved the use of calorimetric titrations.[5-10] Systematic studies of the thermodynamics of reactions of mono- and divalent cations with various crown ether analogues have been reported.[11-13] Such studies provide macroscopic thermometric information about the overall interactions but are not indicative of the underlying microscopic competing processes such as the solvation and ion pairing of the various species in solution.

Because of the variation in complex mass resulting from solvation or ion pairing, mass spectrometry (MS) is a promising approach to obtaining more detailed information about these microscopic interactions. Conventional MS (electron impact and chemical ionization) has been used as a probe of the structures and fragmentation patterns of crown ethers.[14-16] There has also been some effort to apply desorption MS techniques, principally field desorption (FD) and fast atom bombardment (FAB), for studies of cation–crown complexes.[17-22] Desorption ionization is attractive because of its compatability with thermally labile nonvolatile samples. In FD,[23] the preformed ions are not desorbed directly from solution but rather from a coated emitter following solvent evaporation. Thus, FD results may not simply or directly reflect solution equilibrium chemistry. In fact, it has been observed[17,18] that exchange between the central cation of crown complexes and added or even adventitious free cations is extensive under FD conditions. When the complex is especially labile (such as the ammonium or silver complexes), contamination from preceding samples (despite the use of a new emitter for each sample) as well as exchange with Co^{2+} from the surface of the cobalt dendrite has also been observed.[17,18] Even clearer evidence[17] that FD ion intensities do not reflect solution stabilities comes from the high intensities for Li^+, Na^+, and Cs^+ complexes compared to the K^+ complex, contrary to trends in the solution K_f's. FD spectra evidently reflect gas-phase complex formation rather than solution equilibria.[17,18]

FAB ion sources[24] operate with the analyte dispersed in glycerol or other viscous, nonvolatile media. Bombardment with fast atoms (several kilovolts) promotes desorption of ionized species directly from the liquid matrix. Thus, FAB spectra may be expected to reflect solution behavior better than FD. In studies of crown complexation with MA or MA_2 salts, the FAB process yielded intense molecular ions of the type $[\text{crown} \cdot M^{n+} \cdot A_{n-1}^-]^+$, where M^{n+} and A^- denote the metal substrate and its counteranion. There was a marked absence of solvent (glycerol) attached to such complexes and little or no evidence of multiply charged ions.[21,22] While quantitative K_f information may be obtainable,[21,22] appreciable fragmentation persists in FAB spectra, complicating quantitative interpretation. More importantly, sample bombardment by energetic particles may have thermal effects that upset the local solution equilibria being sampled. Though likely to be significant, the magnitude of these effects cannot be assessed from literature values because no FAB mass spectrometrically determined K_f's have been reported.

Particle bombardment is avoided in electrohydrodynamic mass spectrometry (EHMS),[25-30] where the preformed ions are extracted

(1) Pederson, C. J. *J. Am. Chem. Soc.* **1968**, *89*, 7017.
(2) Izatt, R. M.; Eatough, D. J.; Christensen, J. J. *Struct. Bonding (Berlin)* **1973**, *16*, 161.
(3) Lehr, J. M. *Struct. Bonding (Berlin)* **1973**, *16*, 1.
(4) Ovchinnikov, Y. A.; Ivanov, V. T.; Shkrob, A. M. "Membrane-Active Complexes"; Elsevier: New York, 1974.
(5) Christensen, J. J.; Izatt, R. M.; Hansen, L. D. *Rev. Sci. Instrum.* **1965**, *36*, 779.
(6) Hansen, L. D.; Izatt, R. M.; Eatough, D. J.; Jensen, T. E.; Christensen, J. J. *Proc. Symp. Anal. Calorim.*, 3rd, **1974**, 7–16.
(7) Hansen, L. D.; Izatt, R. M.; Christensen, J. J. In "New Developments in Titrimetry"; J. Jordan, Ed.; Marcel Dekker: New York, 1974.
(8) Hansen, L. D.; Jensen, T. E.; Mayne, S.; Eatough, D. J.; Izatt, R. M.; Christensen, J. J. *J. Chem. Thermodyn.* **1975**, *7*, 919.
(9) Christensen, J. J.; Eatough, D. J.; Ruckman, J.; Izatt, R. M. *Thermochim. Acta* **1972**, *3*, 203.
(10) Eatough, D. J.; Christensen, J. J.; Izatt, R. M. *Thermochim. Acta* **1972**, *3*, 219.
(11) Izatt, R. M.; Terry, R. E.; Haymore, B. L.; Hansen, L. D.; Dalley, N. K.; Avondet, A. G.; Christensen, J. J. *J. Am. Chem. Soc.* **1976**, *98*, 7620.
(12) Izatt, R. M.; Terry, R. E.; Nelson, D. P.; Chan, Y.; Eatough, D. J.; Bradshaw, J. S.; Hansen, L. D.; Christensen, J. J. *J. Am. Chem. Soc.* **1976**, *98*, 7626.
(13) Lamb, J. D.; Izatt, R. M.; Swain, C. S.; Christensen, J. J. *J. Am. Chem. Soc.* **1980**, *102*, 475.
(14) Constantin, E.; Kotzyba-Hilbert, F.; Lehn, J. M.; Saigo, K.; Selva, A.; Traldi, P. *Org. Mass Spectrom.* **1982**, *17*, 651.
(15) Lee, Y. C.; Popov, A. I.; Allison, J. *Int. J. Mass. Spectrom. Ion Phys.* **1983**, *51*, 267.
(16) Bose, A. K.; Prakash, O.; Hu, G. Y.; Edasery, J. *J. Org. Chem.* **1983**, *48*, 1780.
(17) Neil, B. H. H.; Youngless, T. L.; Bursey, M. M. *Inorg. Nucl. Chem. Lett.* **1980**, *16*, 141.
(18) Neil, B. H. H.; Fraley, D. F.; Bursey, M. M. *Inorg. Nucl. Chem. Lett.* **1981**, *17*, 121.
(19) Games, D. E.; Kane-Maguire, L. A. P.; Parsons, D. G.; Truter, M. R. *Inorg. Chim. Acta* **1981**, *49*, 213.
(20) Parsons, D. G.; Truter, M. G.; Brookes, P. W.; Hall, K. *Inorg. Chem. Acta* **1982**, *59*, 15.
(21) Johnstone, R. A. W.; Lewis, J. A. S. *Int. J. Mass Spectrom. Ion Phys.* **1983**, *46*, 451.
(22) Johnstone, R. A. W.; Lewis, J. A. S. *Tetrahedron* **1983**, *39*, 1597.
(23) For a recent review of FD see: Rollgen, F. W. *Springer Ser. Chem. Phys.* **1983**, *25*, 2.
(24) For a recent review of FAB see: Rinehart, K. L. *Science (Washington, D.C.* **1982**, *218*, 254.
(25) Evans, C. A., Jr.; Hendricks, C. D. *Rev. Sci. Instrum.* **1972**, *43*, 1527.
(26) Colby, B. N.; Evans, C. A., Jr. *Anal. Chem.* **1973**, *45*, 1884.
(27) Simons, D. S.; Colby, B. N.; Evans, C. A., Jr. *Int. J. Mass Spectrom. Ion Phys.* **1974**, *15*, 291.

0002-7863/85/1507-4635$01.50/0 © 1985 American Chemical Society

directly from solution by the action of an applied electrostatic field, imparting little or no excess internal energy to the sampled ions.[31] EH spectra are therefore often simpler than corresponding FAB and FD spectra and are more likely to reflect true solution equilibria. However, quantitative interpretation of EH spectra can be complicated by the difficulty of obtaining reproducible emission for some solutions and by the variability of ion sampling and detection efficiencies (sensitivities).[32] Emission stability appears to depend mainly on matrix parameters, with solution conductivity and vapor pressure being the most important.[27,28,30] Glycerol solutions generally give stable emission because of the low vapor pressure, high viscosity, and good solvent properties of this matrix. However, a wide variation has been noted in EHMS sensitivities for various analyte ions in glycerol.[32] Factors thought to be important include charge density and ion pairing, which may vary significantly with the charge and size of the central cation for samples such as crown complexes. Thus, the successful quantitation of EH spectra of crown complexes could be expected to require accurate correlation of spectral intensities with solution concentrations by correcting for variations in sensitivity.

We report here a systematic and quantitative EHMS study of the complexation of 18-crown-6 (18C6) in glycerol with a series of alkali and alkali-earth cations and with silver, ammonium, and tetramethylammonium cations. Although solubility limitations required some exceptions, most samples employed nitrate counterions in order to minimize possible effects arising from variation of ion pairing with different anions. The ionic radii of the cations studied span a fairly broad range relative to the cavity size of the 18C6 ring (1.34–1.43 Å, based on X-ray crystallographic data[33]) and therefore a wide range of expected K_f's. Use of a suitable internal standard is invoked to allow the determination of relative sensitivities for the various crown complexes. Since relative ion intensities (analyte/internal standard) are used to obtain these sensitivities, effects of variations in absolute intensities which arise from random variations in ion emission are reduced. The sensitivities thus obtained are then used to determine the relative complex stability constants from spectra of solutions involving competitive complexations.

Experimental Section

Macrocyclic polyether 18-crown-6 (Sigma, ~99% purity) was used as received. Reagent-grade $LiNO_3$ (J. T. Baker), $NaNO_3$, KNO_3, NH_4NO_3, $Na(CH_3COO)$, $SrCl_2·6H_2O$, $CaCl_2·2H_2O$, $Ba(CH_3COO)_2$ (Mallinckrodt), $CsNO_3$, $Sr(CH_3COO)_2$ (A. D. Mackay), RbCl (Alfa), NaBr (Allied Chemical), $(CH_3)_4NBr$, $(C_3H_7)_4NBr$ (Eastman), $AgNO_3$ (MC/B), and glycerol (Fisher) were also used without further purification. $RbNO_3$ was prepared by adding excess concentrated nitric acid (MC/B) to RbCl and then heating to dryness. Solutions of 18C6 with binary mixtures of monovalent cation nitrates were generally prepared by dissolving 3.0 mol % of each salt and 0.50 mol % of 18C6 in glycerol (100 mol %). This provided good conductance and stable emission.[27] However, neither $CsNO_3$ nor $(CH_3)_4NBr$ ($(CH_3)_4NNO_3$ was unavailable) was soluble at this level. Thus, a solution mixture of $CsNO_3$ and $NaNO_3$ was prepared by dissolving 1.6 mol % of each salt and 0.27 mol % of 18C6 in glycerol (maintaining the salt/crown ratio utilized in the other experiments). Similarly, a mixture of $(CH_3)_4NBr$ and NaBr was prepared by dissolving 2.0 mol % of each salt and 0.35 mol % of 18C6 in glycerol. Nitrate salts of alkali earths are generally of low solubility. Use of an acetate counterion generally allowed preparation of binary mixtures with 3.0 mol % each of an alkali and alkali-earth salt (plus 0.5 mol % 18C6). However, not even the acetate salt of calcium was sufficiently soluble. Thus, a mixture of calcium and strontium chlorides was used to reach the desired 3.0 mol %.

Glycerol solutions for the determination of relative sensitivities were prepared with a salt/crown ratio of 11:1. For best emission, the salt concentration was 5.5 mol % when possible. The exceptions due to low solubilities were $CsNO_3$ (1.7 mol %), $(CH_3)_4NBr$ (2.0 mol %), $Ba(CH_3COO)_2$ (4.0 mol %), $Sr(CH_3COO)_2$ (4.0 mol %), $CaCl_2·2H_2O$ (4.0 mol %), and $SrCl_2·6H_2O$ (4.0 mol %). One additional exception (due to sampling difficulty; see below) was $LiNO_3$ (4.4 mol %). These experiments required use of an internal standard. The criteria for a suitable standard were that it not interact with the crown and that it be soluble in glycerol. Ideally, other solution interactions should also be small, so that the sensitivity for the standard would be high and its spectrum would contain a single peak (or at most a small number of peaks due to solvated ions). Tetrapropylammonium bromide (TPABr) was found to fulfill these basic requirements. Its limited solubility (only about 0.13 mol % in glycerol) was adequately offset by the high sensitivity for the TPA ion in EHMS. This ion was detected with good intensity, and no solvation (indicating a low degree of solvent interaction) when the standard was present at about 0.1 mol %. (It is interesting to note that pyridinium and tetraethylammonium cations were found to be unsuitable as internal standards because ions attributable to their crown complexes were detected. Such complexes have not been reported previously, and their detection illustrates the extreme sensitivity of EHMS in the study of these complexes.)

All salt solutions were degassed overnight under vacuum ($\lesssim 1 \times 10^{-2}$ torr) with mild heating (~65 °C) before the addition of 18C6. Afterwards, 18C6 was added, followed by a few additional hours of degassing without heating before EHMS analysis. This procedure appears to have minimized vaporization losses of the volatile uncomplexed crown.

Mass spectral experiments were performed with a double-focusing mass spectrometer (AEI MS902) equipped with an EH ion source described elsewhere.[27,30] Source emitter potential was about +8.2 kV, extractor potential was roughly −1.5 kV, and the collector was fixed at ground potential. Exact emitter potential and spectrometer electrostatic analyzer (ESA) potential were empirically matched; thus, only ions that had not undergone any metastable evaporative loss of solvating glycerol molecules prior to the ESA were detected.[29] Spectrometer resolution of about 600 was employed. Typical ion emission current was 10^{-6} A. The gain of the electron multiplier was roughly 10^5–10^6. Sample consumption was on the order of a few microliters per hour. Most data presented are averages of about 10 spectra. The intensity of each sampled species was measured from the peak height of the most abundant ion in each isotope cluster. Ion abundances were than corrected by calculation to include contributions from all isotopes. Some of the metals employed had several major naturally occurring isotopes, in which case this correction was significant. Calculational correction proved more precise and reliable than attempting to measure the abundance of each of several ions in an isotope cluster.

Viscosity measurements were made by a falling-ball method[34] by using a 2.4-mm sapphire ball dropped through 12 mL of solution contained in a 9.9 mm i.d. graduated cylinder. These experiments were performed at ambient temperature (~20 °C) without regulation. No effort was made to calibrate the viscometer, since only relative viscosities were of interest. Degassing the solutions had very little effect on their viscosities.

Table I. Ions Detected in EH Mass Spectra of a Glycerol Solution Containing 5.56 mol % NH_4NO_3, 0.50 mol % 18C6, and 0.093 mol % $(C_3H_7)_4NBr$[a]

ions	rel intens (including isotopes), % for deg of solvn				
	$n = 0$	$n = 1$	$n = 2$	$n = 3$	$n = 4$
$NH_4^+·G_n$			9.2	1.1	0.1
NH_4^+·18C6	100.0	0.3			
$(C_3H_7)_4N^+$	46.8				

[a] G = glycerol. Ions attributable to matrix and trace impurities (e.g., $Na^+·G_n$) are not included. Of these, only $H^+·G_2$ (2.2%) exceeded 1% relative intensity.

Results and Discussion

The EHMS results shown in Table I serve to illustrate the types and intensities of ions observed in crown solutions with singly charged cations (e.g., NH_4^+). An oscillographic trace of a single scan is also included (Figure 1) to demonstrate the typical mass spectral quality obtained. For the mass range involved, the peaks are well resolved and assignments can be confirmed by isotopic abundances. The most prominent ions are $(C_3H_7)_4N^+$ (when present as the internal standard) and 18C6·M^+. In spectra of the alkali earths (e.g., Ba^{2+}, Table II), ion-paired complexes

(28) Stimpson, B. P.; Evans, C. A., Jr. *J. Electrost.* **1978**, *5*, 411.
(29) Stimpson, B. P.; Simons, D. S.; Evans, C. A., Jr. *J. Phys. Chem.* **1978**, *82*, 660.
(30) Stimpson, B. P.; Evans, C. A., Jr. *Biomed. Mass Spectrom.* **1978**, *5*, 52.
(31) Cook, K. D.; Chan, K. W. S. *Int. J. Mass Spectrom. Ion Proc.* **1983**, *54*, 135.
(32) Chan, K. W. S.; Cook, K. D. *Anal. Chem.* **1983**, *55*, 1306.
(33) Truter, M. R. *Struct. Bonding (Berlin)* **1973**, *16*, 71.
(34) Daniels, F.; Williams, J. W.; Bender, P.; Alberty, R. A.; Cornwell, C. D.; Harriman, J. E. "Experimental Physical Chemistry", 7th Ed.; McGraw-Hill: New York, 1970; pp 161–162.

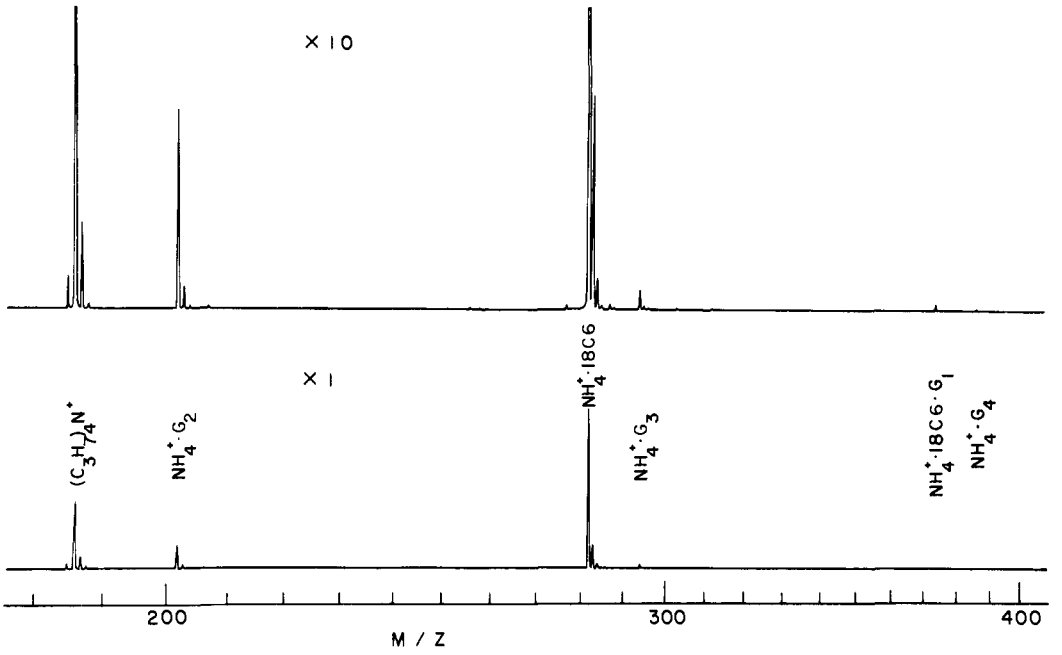

Figure 1. EH mass spectrum of a glycerol solution containing 5.56 mol % NH_4NO_3, 0.50 mol % 18C6, and 0.093 mol % $(C_3H_7)_4NBr$ (G = glycerol). Unlabeled peaks can be attributed to the glycerol matrix (e.g., $H^+ \cdot G_2$ at m/z 185) or to trace Na^+ or K^+ impurities (e.g., $Na^+ \cdot 18C6$ at m/z 287).

Table II. Ions Detected in EH Mass Spectra of a Glycerol Solution Containing 4.03 mol % $Ba(CH_3COO)_2$, 0.37 mol % 18Cl6, and 0.084 mol % $(C_3H_7)_4NBr$ (G = Glycerol)

	rel intens (including isotopes), %, for deg of solvn							
ions	$n = 0$	$n = 1$	$n = 2$	$n = 3$	$n = 4$	$n = 5$	$n = 6$	$n = 7$
$Ba^{2+} \cdot G_n$						<0.1	<0.1	<0.1
$(Ba \cdot CH_3COO)^+ \cdot G_n$				<0.1	0.1	<0.1	<0.1	
$Ba^{2+} \cdot 18C6 \cdot G_n$			0.3	0.1				
$(Ba \cdot CH_3COO)^+ \cdot 18C6 \cdot G_n$	3.2	20.1	0.2					
$(C_3H_7)_4N^+$	100.0							

$(18C6 \cdot M^{2+}A^- \cdot G_n$; A^- = counteranion; G = glycerol) are much more abundant than the corresponding unpaired species $(18C6 \cdot M^{2+} \cdot G_n)$. In both cases, the uncomplexed cations are also observed at low intensity, generally with extensive solvation and, in the case of the divalent cations, substantially ion-paired as well. Thus, the data not only reflect the intrinsic 1:1 complex stoichiometry of the cation–crown complex, as expressed in eq 1 and 2, but also contain information concerning solvation and ion pairing

$$M + L \overset{K_f}{\rightleftharpoons} M \cdot L \tag{1}$$

$$K_f = \frac{[M \cdot L]}{[M][L]} \tag{2}$$

equilibria. A more complete description of the overall system can be written as in eq 3.

$$\begin{array}{ccccccccc} \cdots & \overset{G}{\rightleftharpoons} & (MA) \cdot G_1 & \overset{G}{\rightleftharpoons} & (MA) & \overset{L}{\rightleftharpoons} & (MA) \cdot L & \overset{G}{\rightleftharpoons} & (MA) \cdot L \cdot G_1 \overset{G}{\rightleftharpoons} \cdots \\ & & \updownarrow A & & \updownarrow A & & & & \\ \cdots & \overset{G}{\rightleftharpoons} & M \cdot G_1 & \overset{G}{\rightleftharpoons} & M & \overset{L}{\rightleftharpoons} & M \cdot L & \overset{G}{\rightleftharpoons} & M \cdot L \cdot G_1 \overset{G}{\rightleftharpoons} \cdots \end{array} \tag{3}$$

Conventional methods for determination of K_f are unable to resolve the various solvated and ion-paired species involved in the complex equilibria of eq 3. Although these species are clearly resolved in the EH spectra, their relative mass spectral sensitivities are not, in general, known. While this impedes determination of equilibrium constants associated with the individual steps of eq 3, the relative stability of various metal cation–crown complexes should nevertheless be reflected in spectra of solutions in which there is competition for a small amount of crown between two metal ions present in excess (e.g., Table III). In such experiments, the total equilibrium concentration of the complex of each metal should determine the total intensity of ions arising from that metal–crown complex. Thus, comparison of these intensity *totals* should provide insight into relative complex stabilities (analogous to those obtained by conventional means) while spectral details reflect solvation and ion pairing effects.

Table III. Ions Detected in EH Mass Spectra of a Glycerol Solution Containing 3.00 mol % $AgNO_3$, 3.37 mol % $NaNO_3$, and 0.51 mol % 18C6 (G = Glycerol)

	rel intens (including isotopes), % for deg of solvn				
ions	$n = 0$	$n = 1$	$n = 2$	$n = 3$	$n = 4$
$Na^+ \cdot G_n$			3.8	5.7	1.7
$Ag^+ \cdot G_n$			0.6	1.1	0.2
$Na^+ \cdot 18C6 \cdot G_n$	100.0	2.8			
$Ag^+ \cdot 18C6 \cdot G_n$	28.1				

Quantitation of K_f comparisons still requires knowledge of the relative overall sampling and detection efficiencies for each complex. Therefore, as a first step in evaluating the relative stability of metal–crown complexes, the EHMS sensitivity for each M·18C6 complex (relative to the internal standard, TPA) was determined. These sensitivities may be represented by a ratio, S, defined as

$$S(M \cdot 18C6) = \frac{\sum_{m,n} I_{M \cdot 18C6 \cdot A_m \cdot G_n} / \sum I_{\text{int std}}}{C_{M \cdot 18C6 \cdot A_m} / C_{\text{int std}}} \tag{4}$$

where $\sum_{m,n} I_{M \cdot 18C6 \cdot A_m G_n}$ and $\sum I_{\text{int std}}$ are the total intensities (estimated from mass spectral peak heights) of all detected ions (including ion-paired and solvated clusters and isotopes) incorporating the complex and internal standard, respectively (although in the latter case, only one ion, $(C_3H_7)_4N^+$, was observed). $C_{M \cdot 18C6}$ and $C_{\text{int std}}$ are the total concentrations of the complex and internal standard, respectively. In these single complexation experiments, the metal/crown ratio was maintained at 11:1 to ensure virtually

Table IV. Sensitivities for M^+·18C6 Relative to Tetrapropylammonium Cation (Internal Standard)

M^+	anion	$S(M^+\cdot 18C6)$
Li^+	NO_3^-	0.064
Na^+	NO_3^-	0.44
Na^+	CH_3COO^-	0.52
Ag^+	NO_3^-	0.66
K^+	NO_3^-	0.61
NH_4^+	NO_3^-	0.39
Rb^+	NO_3^-	0.52
Cs^+	NO_3^-	0.39
$(CH_3)_4N^+$	Br^-	0.42

Table V. Sensitivities for M^{2+}·18C6 Relative to Tetrapropylammonium Cation (Internal Standard)

M^{2+}	anion	$S(M^{2+}\cdot 18C6)$
Ca^{2+}	Cl^-	0.088
Sr^{2+}	Cl^-	0.031
Sr^{2+}	CH_3COO^-	0.067
Ba^{2+}	CH_3COO^-	0.055

Table VI. Average Solvation Numbers and Ionic Radius[36] for M^+, M^{2+}, and $(MA)^+$

cation	r, Å	n
Li^+	0.68	2.9
Na^+	0.97	2.8
Ag^+	1.26	2.7
K^+	1.33	2.4
NH_4^+	1.43	2.1
Rb^+	1.47	2.3
Cs^+	1.67	2.0
$(CH_3)_4N^+$		0.3
Ca^{2+}	0.99	5.5
$(CaCl)^+$		4.0
Sr^{2+}	1.12	5.5
$(SrCl)^+$		4.0
$(SrCH_3COO)^+$		4.4
Ba^{2+}	1.34	5.8
$(BaCH_3COO)^+$		4.2

complete complexation of the crown. Under these conditions, $C_{M\cdot 18C6}$ could be reasonably assumed to be approximately equal to the total concentration of added crown. The crown would be 99.9% complexed if the K_f was moderate ($K_f \sim 100$) and 91% complexed even for an extremely low K_f (~ 1).

The experimentally determined sensitivities for the M^+·18C6 and M^{2+}·18C6 complexes relative to the TPA internal standard are listed in Tables IV and V, respectively. In general, S values for M^{2+}·18C6 are about an order of magnitude smaller than those for M^+·18C6 (with the exception of the lithium complex, to be discussed separately below). This may be mainly attributed to stronger interactions between the 2+ ions and the solvent, which can impede sampling by increasing the potential barrier which must be overcome to remove the ion from solution. In addition, detection efficiencies for more heavily solvated ions may be reduced because there is a greater chance for in-flight desolvation subsequent to sampling.[32] An indication of the extent of interaction of a cation (M) with the solvent (G) is its average degree of solvation, $\bar{n}$, defined as

$$\bar{n} = \frac{\sum_n n I_{M\cdot G_n}}{\sum_n I_{M\cdot G_n}} \quad (5)$$

$\bar{n}$ values obtained in this study for the various M^+, M^{2+}, $(MA)^+$, and crown complex ions are listed in Tables VI and VII. For a simple free cation, $\bar{n}$ varies directly with ion charge density. Once bound by either an anion or a ligand, the bare cation has part of its positive charge shielded, and therefore interactions with the solvent are reduced, accounting for the smaller $\bar{n}$ observed for these bound cations. The large difference between S values for crown complexes of mono- and divalent metals is consistent with the solvation correlation. However, there appears to be no systematic trend in the small variations among S values within each group.

Table VII. Average Solvation Numbers for M^+·18C6, M^{2+}·18C6, and $(MA)^+$·18C6

	$\bar{n}$		$\bar{n}$
Li^+·18C6	0.06	Ca^{2+}·18C6	2.4
Na^+·18C6	0.04	$(CaCl)^+$·18C6	1.0
Ag^+·18C6	0.01	Sr^{2+}·18C6	2.2
NH_4^+·18C6	0.00	$(SrCl)^+$·18C6	1.0
Rb^+·18C6	0.01	$(SrCH_3COO)^+$·18C6	0.9
Cs^+·18C6	0.00	Ba^{2+}·18C6	2.3
$(CH_3)_4N^+$·18C6	0.00	$(BaCH_3COO)^+$·18C6	0.9

Table VIII. Relative Viscosities Measured with a Falling-Ball Method[34]

samp comp	rel viscosities
pure glycerol	1.0
5.5 mol % $NaNO_3$	1.3
4.5 mol % $LiNO_3$	1.6
4.0 mol % $Ba(CH_3COO)_2$	3.8

The exceptionally small value of $S(Li^+\cdot 18C6)$ deserves comment. This value arises from the very low intensity of the Li^+·18C6 ion (and its solvated adducts) in the spectrum of the lithium/crown/internal standard solution. Three plausible causes are (1) a low abundance of the *complex* in solution due to incomplete complexation of the crown, (2) a low intrinsic sampling efficiency due to strong solvent interactions, and (3) a low abundance of the complex *ion* due to ion pairing (neutralization of the charge).

As mentioned previously, complexation should be extensive when the metal is in excess even if K_f is as small as 1. It will be shown below that K_f for the lithium complex is probably significantly greater than 1 and in any case greater than that for the tetramethylammonium complex, which does not have a correspondingly small value of S. Lithium complexation of the crown is therefore unlikely to have been incomplete.

Turning to the possible role of solvent interactions, two measures of these were considered: $\bar{n}$ and solution viscosity. As seen in Tables VI and VII, ions containing M^{2+} are generally more heavily solvated than corresponding M^+ ions, consistent with the low S values for the divalent complexes. However, $\bar{n}$ values for lithium and its complex are quite close to those for the corresponding sodium species, despite the large difference in S. Thus, the solvation of the lithium complex cannot directly account for its low sampling efficiency. Recent studies (to be reported in a subsequent publication) have suggested that solvent interactions can play an *indirect* role in determining detected ion currents by affecting analyte diffusion, independent of the direct solvation of analyte ions. Thus, the "secondary solvation shell" structure-making properties of lithium[35] may impede diffusion of complex ions to the emission surface by increasing solution viscosity, thereby decreasing sampling efficiencies without a corresponding increase in $\bar{n}$. However, viscosities measured by a falling-ball method[34] (Table VIII) show that while this effect may contribute to the low S value for the barium complex, it cannot account for the difference between sodium and lithium complex sampling efficiencies.

This leaves ion pairing as a possible explanation for the low intensity of lithium complex ions. The effect of ion pairing depends on the initial charge of the analyte. Reduction of charge from 2+ to 1+ can increase sampling efficiencies by reducing solvent interactions. However, ion pairing of a monovalent metal such as lithium (or more extensive ion pairing of a divalent metal) results in neutralization or charge reversal, which effectively precludes EH sampling and therefore reduces sensitivity.[32] Because the extent of ion pairing will certainly depend on the identity of the counterion present, these factors may account for the significant variation in measured S values for strontium complexes

(35) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 3rd ed.; Interscience Publishers: New York, 1972; Chapter 6.

Table IX. Ratio of Stability Constants ($K_s(M_1 \cdot 18C6)/K_s(M_2 \cdot 18C6)$) for $M^+ \cdot 18C6$ and $M^{2+} \cdot 18C6$[a]

M_1	M_2	$K_s(M_1 \cdot 18C6)/K_s(M_2 \cdot 18C6)$
Na^+	Li^+	7.7 ± 0.9
Na^+	Ag^+	5.5 ± 0.9
Na^+	K^+	0.062 ± 0.009
Na^+	NH_4^+	0.61 ± 0.02
Na^+	Rb^+	0.311 ± 0.006
Na^+	Cs^+	0.41 ± 0.02
Na^+	$(CH_3)_4N^+$	14.5 ± 2.0
Ca^{2+}	Sr^{2+}	~0[b]
Na^+	Sr^{2+}	0.120 ± 0.006
Na^+	Ba^{2+}	0.06 ± 0.01

[a] Uncertainties represent the standard deviation of the mean of values determined from at least four spectra. [b] No calcium complex ions were detected in the Ca^{2+}/Sr^{2+}/crown mixture.

prepared from acetate and chloride salts (Table V). The relatively small counterion dependence for S values of sodium complexes (Table IV) is consistent with the expectation that this ion should not be extensively ion-paired. The high charge density of the lithium ion would lead one to predict that its complexes may be extensively ion-paired. The low S value is consistent with this prediction, which is being tested in more detailed studies of counterion dependences currently under way.

The relative sensitivities of Tables IV and V provide the information necessary to estimate relative stabilities from ion intensities in spectra of solutions with competitive complexation equilibria. These solutions were prepared with approximately equimolar concentrations of two metal cations, each in excess of the small crown concentration. Resulting spectra (e.g., Table III) contained crown complexes of both cations. The relative complex concentrations can be estimated from these spectra by using eq 6.

$$\frac{C_{M_1 \cdot 18C6}}{C_{M_2 \cdot 18C6}} = \frac{\sum_{m,n} I_{M_1 \cdot 18C6 \cdot A_m \cdot G_n}/S(M_1 \cdot 18C6)}{\sum_{m,n} I_{M_2 \cdot 18C6 \cdot A_m \cdot G_n}/S(M_2 \cdot 18C6)} \quad (6)$$

As before, intensities of all ions containing the complex of a given cation are summed to represent its total intensity. If it is again assumed that all the crown is complexed (eq 7), then eq

$$C_{M_1 \cdot 18C6} + C_{M_2 \cdot 18C6} = [18C6]_0 \quad (7)$$

6 and 7 can be solved simultaneously to give the separate total concentrations of the two complexes.

The total concentrations of the uncomplexed cations, C_{M_1} and C_{M_2}, then can be estimated by subtracting the complex concentrations from the initial concentrations of the corresponding cations, $[M_1]_0$ and $[M_2]_0$,

$$C_{M_1} = [M_1]_0 - C_{M_1 \cdot 18C6} \quad (8)$$

$$C_{M_2} = [M_2]_0 - C_{M_2 \cdot 18C6} \quad (9)$$

Finally, the relative stability constants of the two complexes can be compared as

$$\frac{K_s(M_1 \cdot 18C6)}{K_s(M_2 \cdot 18C6)} = \frac{C_{M_1 \cdot 18C6}}{C_{M_2 \cdot 18C6}} \cdot \frac{C_{M_2}}{C_{M_1}} \quad (10)$$

This ratio of stability constants, $K_s(M_1 \cdot 18C6)/K_s(M_2 \cdot 18C6)$, is subtly different from the ratio of intrinsic formation constants,

$$\frac{K_f(M_1 \cdot 18C6)}{K_f(M_2 \cdot 18C6)} = \frac{[M_1 \cdot 18C6]}{[M_2 \cdot 18C6]} \cdot \frac{[M_2]}{[M_1]} \quad (11)$$

in that the former also reflects the effects of solvation and ion pairing on the stability of the various species in solution. Although these effects are seldom specifically acknowledged, they are probably pertinent in most conventional determinations of "K_f".

The ratios of K_s's obtained in this study are listed in Table IX. Na^+ was chosen (arbitrarily) as the companion ion for most determinations of relative K_s's. However, to facilitate an overall comparison, the values were normalized to that for K^+ (the largest K_s) and plotted vs. the ionic radius[36] of the central cations in Figure 2. The results clearly demonstrate the importance of steric compatability between the cation and the cavity of the crown. It can be seen that K_s's for K^+ and Ba^{2+} are dramatically higher

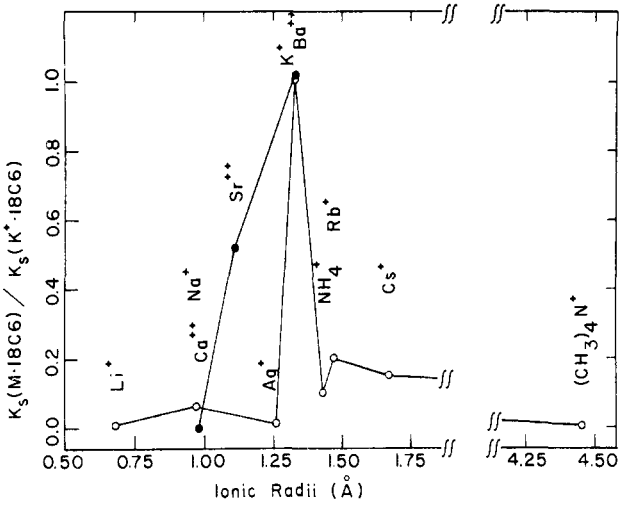

Figure 2. Relative stability constants (measured with EHMS in glycerol) for $M^+ \cdot 18C6$ (○) and $M^{2+} \cdot 18C6$ (●) vs. ionic radius of M.

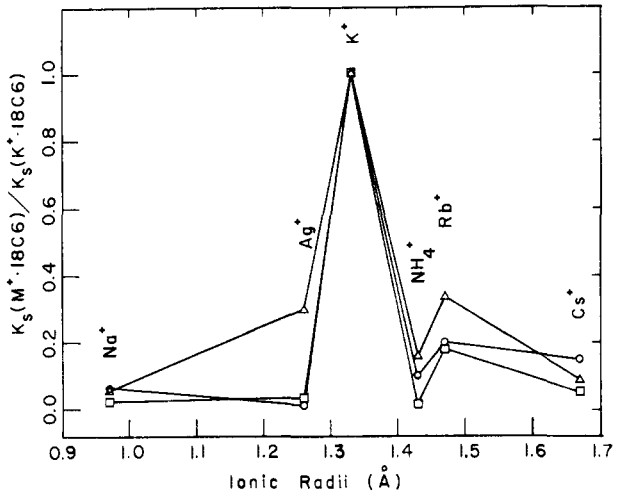

Figure 3. Comparison of the relative stability constants for $M^+ \cdot 18C6$ measured by using EHMS in glycerol (○) with those measured by using calorimetric titrations in water (△) and in methanol (□).

Table X. Comparison of K_s Results Obtained by EHMS (in Glycerol) with Those Obtained by Calorimetric Titrations (in Water and Methanol)

	calorimetric titration data[11,13]				EHMS
	water		methanol		glycerol
M	log K_s	R^a	log K_s	R^a	$K_s/K_s(K^+ \cdot 18C6)$
Li^+					0.0081
Na^+	0.8	0.059	4.36	0.020	0.062
Ag^+	1.50	0.30	4.58	0.033	0.011
K^+	2.02	1.00	6.06	1.00	1.00
NH_4^+	1.23	0.16	4.27	0.016	0.10
Rb^+	1.56	0.34	5.32	0.18	0.20
Cs^+	0.99	0.091	4.79	0.054	0.15
$(CH_3)_4N^+$					0.0043
Ca^{2+}	<0.5	0.03	3.86	0.0063	~0
Sr^{2+}	2.72	4.9	>5.5	0.28	0.52
Ba^{2+}	3.87	69.2	7.04	9.55	1.02

[a] $R = K_s/[K_s(K^+ \cdot 18C6)]$.

(36) "CRC Handbook of Chemistry and Physics", 54th ed., CRC Press: Boca Raton, FL, p F-194.

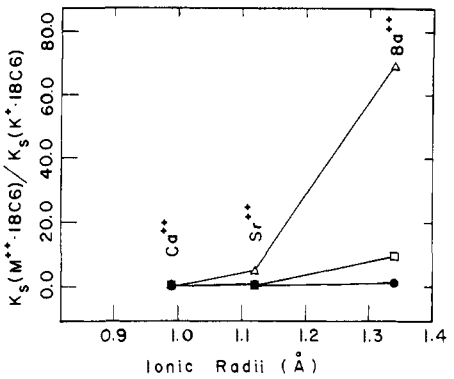

Figure 4. Comparison of the relative stability constants for $M^{2+}\cdot 18C6$ measured by using EHMS in glycerol (●) with those measured by using calorimetric titrations in water (△) and in methanol (□).

than the others, correlating with an extremely good match between the ionic radius of these ions and the cavity of 18C6 (1.34–1.43 Å).

A good test of the reliability of the relative K_s's of Table IX would be a comparison with literature values. Suitable data have been reported for calorimetric titration studies in aqueous and methanol solutions[11,13] and are listed in Table X, along with corresponding data from this study. A comparison of the trend of K_s ($M^+\cdot 18C6$) vs. M^+ ionic radius in the three different solvents (Figure 3) shows reasonable qualitative and even semiquantitative agreement. This suggests that for complexes of singly charged cations, there are only minor solvent effects on the relative magnitude of K_s. This is consistent with the observation of little interaction between the solvent and $M^+\cdot 18C6$ complexes ($\bar{n} \sim 0$) or uncomplexed M^+ ($\bar{n} \lesssim 3$) (see above).

By contrast, agreement is not as close for a similar comparison for M^{2+} (Figure 4). For example, K_s ($Ba^{2+}\cdot 18C6$) varies in the ratio of 1.0:9.6:69.2 in glycerol, methanol, and water, respectively. These substantial solvent effects are consistent with the observation of more extensive interaction between the solvent and ions containing doubly charged metals ($M^{2+}\cdot 18C6$ ($\bar{n} \sim 2$), $(MA)^+\cdot 18C6$ ($\bar{n} \sim 1$), M^{2+} ($\bar{n} \sim 6$), and (MA^+) ($\bar{n} \sim 4$)). The small K_s values for $M^{2+}\cdot 18C6$ in glycerol suggest that free M^{2+} cations are strongly solvated by this solvent, disfavoring complexation by the crown.

Conclusion

In summary, this work has clearly demonstrated the high sensitivity of EHMS and its ability to resolve individual species in the study of complexation chemistry. For example, we have been able to obtain K_s's for weakly bound complexes ($Li^+\cdot 18C6$ and $(CH_3)_4N^+\cdot 18C6$) which have not been detected by less sensitive methods such as calorimetric titration. The EHMS spectra gave detailed information about the individual species existing in solution, providing better insight into the complex solution chemistry, including solvation and ion pairing.

Acknowledgment. This work was supported by the National Science Foundation (Grant DMR-84-06825 jointly funded by the U.S. Army Research Office).

Registry No. Glycerol, 56-81-5.

Rotation of Methyl Groups in Hexamethylbenzene

V. Melissas, K. Faegri, Jr., and J. Almlöf*

Contribution from the Department of Chemistry, University of Oslo, Oslo Norway. *Received December 17, 1984*

Abstract: The structure of hexamethylbenzene has been studied by Hartree–Fock calculations. The equilibrium geometry possesses D_{3d} symmetry, with a barrier of 1.0 kcal/mol toward a geared rotation of the methyl groups. The results support neutron diffraction data but disagree with electron diffraction experiments and molecular mechanics calculations.

Hexamethylbenzene (HMB) is a prototype molecule for studying coupled, internal rotation, and its structural and dynamical properties have attracted considerable interest. It exhibits at least two crystal-phase transitions, the origin of which has sometimes been attributed to the different degree of correlation between the rotations of the methyl groups.[1-3]

The molecular structure of HMB has previously been determined by X-ray,[4] neutron,[5] and electron diffraction.[6] Molecular mechanics calculations have also been reported.[7,8]

The low-temperature crystal phase, i.e., the one for which the methyl groups were most accurately determined, exhibits approximate D_{3d} conformation (Figure 1b). The benzene ring is accurately planar, but the methyl carbons are bent 0.04–0.10 Å out of the ring plane, alternantly above and below.

The ED structure,[6] on the other hand, is of S_6 symmetry, with a methyl group orientation quite different from that of ref 5. The out-of-plane distortion of the methyl carbons is 0.26 Å, much larger than in the solid.

MM calculations also arrive at a large out-of-plane distortion for the methyl groups.[8] In addition, the benzene ring shows a strong and unexpected distortion, the dihedral angle being 9.6°.

Table I. Structural Parameters Obtained for HMB, Compared with Previous Experimental and Theoretical Results[a]

	present work	molecular mechanics, ref 8	electron diffraction, ref 6	neutron diffraction, ref 5	X-ray diffraction, ref 4
HCH	106.9	111	107.4	112.4	
ΔZ_1	0.011	0.034	0	0	0.004°
ΔZ_2	0.047	0.18	0.26	0.07[c]	0.02[c]
ϕ[b]	90°	90°	114.4°	90°	102°
R_{C-C}	1.413[e]	1.406	1.427	1.413[c]	1.410[c]
R_{C-C}	1.506[b]	1.517	1.531	1.506[c]	1.518[c]
ΔE[d]	1.0	2.6		0.46	

[a] ΔZ_1 and ΔZ_2 denote displacements of the ring and methyl carbons out of the least-squares plane. Distances are in Å, angles in degrees, and energies in kcal/mol. [b] Torsion angle; $\phi = 90°$ corresponds to a D_{3d} conformation (Figure 1a). [c] Average value. [d] ΔE is the barrier to coupled, conrotatory torsion of the methyl groups. [e] Assumed value.

The present calculations were undertaken in order to resolve some of these discrepancies. In particular, the low symmetry of

* Address correspondence to this author at his present address: Department of Chemistry, University of Minnesota, 207 Pleasant St., Minneapolis, MN 55455.

(1) Saëki, S.; Chihara, H. *Sci. Pap. Osaka Univ.* **1949**, *1*, 1.
(2) Rush, J. J.; Taylor, T. I. *J. Chem. Phys.* **1966**, *44*, 2749.
(3) Saheki, M.; Yamada, H.; Yoshioka, H.; Nakatsu, K. *Acta Crystallogr., Sect. B* **1976**, *B32*, 662.

0002-7863/85/1507-4640$01.50/0 © 1985 American Chemical Society