NMR and Infrared Studies of the Complexation Reaction of 18-Crown-6 with Some Organic Solvents

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Abstract: Carbon-13 NMR and infrared spectrometric techniques were used to study the complexation of a macrocyclic ligand, 18-crown-6 (18C6), with acetonitrile and with nitromethane in acetone, chloroform, benzene, and carbon tetrachloride solutions. The studies were complicated by the self-association of acetonitrile as well as by weak interactions of the crown ether with acetone and chloroform. Both 1:1 and 1:2 complexes were observed for the 18C6–CH$_3$CN and 18C6–CH$_3$NO$_2$ systems in benzene solution, but only 1:1 complex was observed for the first system in acetone solutions. The formation constants of the acetonitrile and the nitromethane complexes with 18C6 were determined. The strength of the 18C6-solvent interaction varies in the order: nitromethane > acetonitrile > chloroform > acetone >> benzene, carbon tetrachloride. The results indicate that ligand–solvent interactions have a very important effect on the stabilities of the ligand–metal ion complexes.

It is well recognized that cation–solvent interactions strongly influence thermodynamics and kinetics of complexation reactions involving these cations and various organic or inorganic ligands. In contrast, the importance of ligand–solvent interactions has been largely ignored, although more than a decade ago Hinz and Margerum[1] have shown that the difference in the solvation of a linear and a cyclic polyaza ligand can account for the ~10^6-fold increase in the stability constant of the Ni^{2+} complex with the cyclic ligand.

It seems reasonable to assume that cyclic polyethers (crown ethers) and diazapolyoxa macrobicyclic ligands (cryptands) also interact with organic solvent molecules and that these interactions can have an important effect on the formation of the alkali complexes with these ligands. Numerous solid adducts of organic molecules and crown ethers have been isolated.[2] Among these we note particularly 18-crown-6 (18C6) adducts with acetonitrile,[3] formamide,[4] and nitromethane[5] since these latter are widely used organic solvents. The crystal structures of the 18C6·(CH$_3$CN)$_2$,[6] 18C6·(CH$_3$NO$_2$)$_2$,[5] and 18C6·(HCONH$_2$)$_2$[7] complexes have been determined.

Quantitative data on the ligand–solvent interactions are quite sparse. Association constants of 18C6 with nitromethane, acetonitrile, and malononitrile in deuteriobenzene solutions were measured by proton NMR by de Boer et al.[5] Similarly, stabilities of 18C6 complexes with acetonitrile (in CCl$_4$)[8] and with dimethyl sulfate, dimethyl carbonate, and dimethyl oxalate (in C$_6$D$_6$)[9] were determined by ^{1}H NMR. The K_f values are given in Table I.

Solvent–macrocyclic ligand interactions can modify the complexing abilities of the ligands by altering their conformation and/or by varying the thermodynamics of ligand desolvation. The importance of the first factor was illustrated by our recent studies[10] of the influence of solvent properties on the conformation of cryptand C221. The importance of ligand solvation is also evident from the studies by Abraham et al.[11] who showed that the enthalpies of transfer of cryptand C222 and of crown ether 18C6 from water to methanol are 13.9 and 13.6 kcal mol^{-1}, respectively.

Table I. Association Constants of the Complexes of 18-Crown-6 with Various Guest Molecules

guest	background solvent	temp, K	$K_{1:1}$, L mol^{-1}	$K_{1:2}$, L mol^{-1}
malononitrile[a]	C$_6$D$_6$	300	150 ± 15	11 ± 2.8
acetonitrile[a]	C$_6$D$_6$	300	0.48 ± 0.05	
nitromethane[a]	C$_6$D$_6$	300	1.2 ± 0.12	2.5 ± 0.6
acetonitrile[b]	CCl$_4$	298	2.1 ± 0.1	
dimethyl sulfate[c]	C$_6$D$_6$	301	0.6	
dimethyl carbonate[c]	C$_6$D$_6$	298	0.8	
dimethyl oxalate[c]	CCl$_4$/C$_6$D$_6$ (1/4 v/v)	301	0.6	

[a] Reference 6. [b] Reference 8. [c] Reference 9.

These very large enthalpies of transfer amply demonstrate the strength of ligand–solvent interactions.

It is interesting to note that in the vast majority of cases, where the enthalpy and the entropy of the macrocyclic complex formation were determined in nonaqueous solvents, the complexes were found to be enthalpy stabilized but entropy destabilized.[12-15] This effect is quite contrary to that observed in chelation reactions (at least in aqueous solutions). It has been established quite early that the high stability of EDTA complexes is primarily entropic in origin.[16] The desolvation of the cations during the complex formation increases the total entropy of the system due to the increase in the translational entropy. In the case of the macrocyclic complexes this effect seems to be offset by the decrease in the conformation entropy of the ligand upon complex formation. It should also be noted that the resulting macrocyclic complex may also be (to some extent, at least) solvated.

It seems that the understanding of the mechanism of macrocyclic complex formation and of the "macrocyclic effect"[1] cannot be complete without some quantitative knowledge of solvent–ligand interactions. The study reported below is an attempt in this direction.

Experimental Section

Reagents. The ligand 18-crown-6 (Aldrich) was purified by the usual technique of converting it to the crystalline acetonitrile complex, filtering the solution, and driving off acetonitrile under vacuum.[3]

Carbon tetrachloride (Mallinckrodt) and chloroform (Fisher) were refluxed over phosphorus pentoxide for 3 days and then fractionally

(1) Hinz, F. P.; Margerum, D. W. *J. Am. Chem. Soc.* **1974**, *96*, 4993; *Inorg. Chem.* **1974**, *13*, 2941.
(2) Vogtle, F.; Sieger, H.; Muller, W. M. *Top. Curr. Chem.* **1981**, *98*, 107.
(3) Gokel, G. W.; Cram, D. J.; Liotta, C. L.; Harris, H. P.; Cook, F. L. *J. Org. Chem.* **1974**, *39*, 2445.
(4) Vogtle, F.; Muller, W. M.; Weber, E. *Chem. Ber.* **1980**, *113*, 1130.
(5) de Boer, J. A. A.; Reinhoudt, D. N.; Harkema, S.; van Hummel, G. J.; de Jong, F. *J. Am. Chem. Soc.* **1982**, *104*, 4073.
(6) R. L. Garrell, personal communication.
(7) Watson, W. H.; Galloy, J.; Grossie, D. A. *J. Org. Chem.* **1984**, *49*, 347.
(8) Gold, H. S.; Rice, M. R. *Talanta* **1982**, *29*, 637.
(9) Van Zon, A.; Onwezen, Y.; Tomassen, H. P. M. *Recl. Trav. Chim. Pays-Bas.* **1983**, *102*, 290.
(10) Schmidt, E.; Tremillon, J.-M.; Kintzinger, J.-P.; Popov, A. I. *J. Am Chem. Soc.* **1983**, *105*, 7563.
(11) Abraham, M. H.; Danil de Namor, A. F.; Lee, W. H. *J. Chem. Soc., Chem. Commun.* **1977**, 893. Abraham, M. H.; Ling, H. C. *Tetrahedron Lett.* **1982**, *23*, 469.

(12) Shamsipur, M.; Rounaghi, G.; Popov, A. I. *J. Solution Chem.* **1980**, *9*, 701. Lin, J. D.; Popov, A. I. *J. Am. Chem. Soc.* **1981**, *103*, 3773.
(13) Cox, B. G.; Garcia-Rosas, J.; Schneider, H. *J. Am. Chem. Soc.* **1981**, *103*, 1384.
(14) Cox, B. G.; Schneider, H.; Stroka, J. *J. Am. Chem. Soc.* **1978**, *100*, 4746.
(15) Lamb, J. D.; Izatt, R. M.; Christensen, J. J.; Eatough, D. J. In "Coordination Chemistry of Macrocyclic Compounds"; Melson, G. A., Ed.; Plenum Press: New York, 1979; Chapter I.
(16) Wright, D. L.; Holloway, J. H.; Reilley, C. N. *Anal. Chem.* **1965**, *37*, 884.

distilled. Acetonitrile (Baker) was refluxed over calcium hydride for 1 week and then fractionally distilled. Acetone (Mallinckrodt) was purified in the same way, but with Drierite as the drying agent. Nitromethane (Aldrich, Gold Label) was refluxed over calcium hydride under reduced pressure for 2 days and then fractionally distilled under reduced pressure. Benzene (Fisher) was purified by several extractions with concentrated sulfuric acid to remove thiophene. It was then washed with water to remove sulfuric acid, refluxed over calcium hydride for 3 days, and then fractionally distilled. The water content of all solvents, except nitromethane, was determined by gas chromatography utilizing the standard addition method. In all cases the water content was below 50 ppm. The water content of nitromethane had to be checked by proton NMR since nitromethane decomposes in the GC. Since the water peak was not detected in the proton NMR spectrum, the water content of nitromethane was judged to be below 100 ppm.

The deuterated solvents acetone-d_6 (Stohler Isotope Chemicals, SIC), chloroform-d (Cambridge Isotope Laboratories), and acetonitrile-d_3 (Aldrich Gold Label) were used as received.

Carbon-13 Measurements. Carbon-13 measurements were made on a Bruker WM-250 spectrometer operating at a field of 58.7 kG and a frequency of 62.9 MHz. The sample solutions were placed in a 10-mm o.d. NMR tube. The lock solvent was placed in a 5-mm o.d. NMR tube which was then coaxially inserted into the sample tube. For the acetonitrile–benzene, acetonitrile–chloroform, and nitromethane–benzene studies, acetone-d_6 was used as the lock, and the methyl carbon peak of acetone-d_6 was used as the external reference. Chloroform-d was used as both the lock and external reference for the acetonitrile–acetone studies. A sealed coaxial insert containing Me$_4$Si in acetone-d_6 was used for the lock and external reference for the acetonitrile–carbon tetrachloride studies. In all cases, the chemical shifts were corrected for the differences in bulk magnetic susceptibilities between the sample and the reference.

Proton NMR Measurements. Proton NMR measurements were carried out on a Bruker WM-250 spectrometer operating at a field strength of 58.7 kG and 250.00 MHz. Sample configuration was the same as for the carbon-13 measurements. A sealed coaxial insert of Me$_4$Si in acetone-d_6 was used as the lock and the external reference. Again, all proton chemical shifts were corrected for the difference in bulk magnetic susceptibilities between the sample and the reference.

Infrared Measurements. Infrared spectra of acetonitrile and 18-crown-6 in carbon tetrachloride, chloroform, and benzene solutions were obtained on a Digilab 15 FT-IR spectrometer. Standard demountable cells (Barnes Engineering Co.) were used with Irtran-II disks. The path length was maintained at 0.5 mm. Since the Irtran-II windows absorb below 800 cm^{-1}, the spectra obtained covered the 4000–800-cm^{-1} spectral region. In all spectra, interfering solvent bands were substracted out.

The deconvolution of overlapping bands was carried out by assuming that the line shape of the bands can be described by a Lorentzian–Gaussian product:[17]

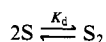$$I = I_0\{\exp[-(\nu - \nu_0)^2/2\sigma^2]\}\{1 + (\nu - \nu_0)^2/\sigma^2\}^{-1} \qquad (1)$$

where I is an intensity (in absorbance units) at frequency ν; ν_0 is the position of the line center with maximum intensity, I_0; and σ is the variance ($\sigma = 1.46\Delta\nu_{1/2}$ where $\Delta\nu_{1/2}$ is the band halfwidth). After deconvolution the areas under the bands were evaluated by using Simpson's rule.

Evaluation of Equilibria Constants. In the solutions under investigation, multiple equilibria occur. Therefore, the observed carbon-13 chemical shift, δ_{obsd}, is a population weighted average of the chemical shifts of the individual species, δ_i, occurring in solution:

$$\delta_{obsd} = \sum_i \delta_i X_i \qquad (2)$$

where X_i is the fraction of the ith species. These fractions depend upon the values of the equilibria constants and on analytical concentrations. An expression for the observed chemical shift can, therefore, be derived so as to include the equilibria constants. Then the equilibria constants are adjusted using a weighted, nonlinear least-squares program KINFIT[18] until the difference between the experimental and calculated chemical shifts is minimized.

The acetonitrile–benzene and nitromethane–benzene systems can be used as examples to describe the derivation of the expressions for the δ_{obsd}. It was found that for both species the dimerization was the dominant reaction; i.e.,

$$2S \xrightleftharpoons{K_d} S_2$$

(17) Davis, A. R.; Irish, D. E.; Roden, R. B.; Weerheim, A. J. *Appl. Spectrosc.* **1972**, *26*, 384.

(18) Dye, J. L.; Nicely, V. A. *J. Chem. Educ.* **1971**, *48*, 443.

Therefore, the observed chemical shift, δ_{obsd}, of acetonitrile or of nitromethane can be written in terms of the chemical shifts of the monomer, δ_S, and the dimer, δ_{S_2}:

$$\delta_{obsd} = \delta_S\left(\frac{[S]}{C_S}\right) + 2\delta_{S_2}\left(\frac{[S_2]}{C_S}\right) \qquad (3)$$

where C_S is the total concentration of S, [S] is the concentration of monomeric S, and [S$_2$] is the concentration of dimeric S. Given the following relationships,

$$C_S = [S] + 2[S_2] = [S] + 2K_d[S]^2 \qquad (4)$$

$$\frac{[S]}{C_S} + \frac{2[S_2]}{C_S} = 1.0 \qquad (5)$$

the following expression for δ_{obsd} can be derived:

$$\delta_{obsd} = \frac{1 + 4C_SK_d - \sqrt{1 + 8C_SK_d}}{4C_SK_d}(\delta_{S_2} - \delta_S) + \delta_S \qquad (6)$$

In the above expression, δ_{obsd} and C_S are experimental variables and δ_S is the chemical shift at infinite dilution. The unknown parameters are δ_{S_2} and K_d which are determined by using the KINFIT program to analyze the chemical shift data for MeCN–benzene and MeNO$_2$–benzene systems.

When 18-crown-6 is added to a solution of either acetonitrile or nitromethane in benzene, three simultaneous equilibria are occurring: dimerization and formation of 1:1 and 1:2 complexes, between 18-crown-6 and either acetonitrile or nitromethane:

$$2S \xrightleftharpoons{K_d} S_2$$

$$S + L \xrightleftharpoons{K_1} SL$$

$$SL + S \xrightleftharpoons{K_2} SLS$$
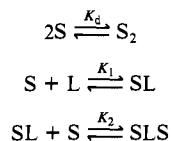
where L refers to 18-crown-6. The observed chemical shift for either acetonitrile or nitromethane can be written in terms of δ_S, δ_{S_2}, δ_{SL}, and δ_{SLS}, where δ_{SL} and δ_{SLS} refer to the chemical shifts of the 1:1 and 1:2 complexes, respectively:

$$\delta_{obsd} = \frac{1}{C_S}\{\delta_S[S] + 2\delta_{S_2}[S_2] + \delta_{1:1}[SL] + 2\delta_{1:2}[SLS]\} \qquad (7)$$

$$\delta_{obsd} = \frac{1}{C_S}\{\delta_S[S] + 2\delta_{S_2}K_d[S]^2 + \delta_{1:1}K_1[S][L] + 2\delta_{1:2}K_1K_2[S]^2[L]\} \qquad (8)$$

In the above expression, δ_{obsd}, C_S, and C_L are the experimental variables. The known parameters in the S–benzene study are δ_S, δ_{S_2}, and K_d. The unknown variables are, therefore, K_1, K_2, δ_{SL}, and δ_{SLS}.

Results and Discussion

All previous solution studies of the complexation of crown ethers by neutral molecules were carried out in an "inert" background solvent. However, solvents are never completely "inert". Dipole–dipole interactions, dipole-induced dipole interactions, as well as London, or dispersion, forces can occur in solution and may lead to self-association of the neutral molecules, complexation between the neutral molecule and background solvent, and/or complexation between the background solvent and the crown ether. The extent of such interactions depends upon the background solvent used. Obviously, these side reactions do affect the complexation between the crown ether and the solvent molecule.

A. NMR Studies of Solvent Mixtures. In these studies, the carbon-13 chemical shifts of either acetonitrile, or nitromethane, were measured as a function of mole fraction, X, of the above species in the background solvent; the results are shown in Figures 1–3. The chemical shift of acetonitrile is very solvent dependent; furthermore, the chemical shift behavior of the methyl and nitrile carbons of acetonitrile, as well as that of the background solvent carbon(s), must be explained by the same set of equilibria.

Concentration dependence of the ^{13}C resonance of the methyl group of acetonitrile in carbon tetrachloride solutions parallels that of the carbon atom of CCl$_4$, and may indicate an interaction between the two species. The behavior of the nitrile carbon is quite different and suggests self-association of acetonitrile. The chemical shift data were analyzed using the KINFIT program and multiple data sets. Various models were used to analyze the data:

Table II. Equilibria Constants for Solvent–Solvent Interactions

solvent system	equilibria	equilibrium constants L mol^{-1}	^{13}C chemical shifts, ppm
AN–CCl$_4$	$2S \xrightleftharpoons{K_d} S_2$	$K_d = 0.56 \pm 0.27$	$\delta_S^{CH_3} = 2.75 \pm 0.07$
	$S + C \xrightleftharpoons{K_{d/d}} SC$	$K_{d/d} = 0.28 \pm 0.07$	$\delta_{SC}^{CH_3} = 2.63$
	$SC + \xrightleftharpoons{K'_d} S_2C$	$K'_d = 0.56 \pm 0.22$	$\delta_{S_2}^{CH_3} = 1.3 \pm 0.1$
	$S_2 + C \xrightleftharpoons{K''_d} S_2C$	$K''_d = 0.28 \pm 0.06$	$\delta_{S_2C}^{CH_3} = 2.2 \pm 0.1$
			$\delta_{SC}^{CN} = \delta_S^{CN} = 115.23$
			$\delta_{S_2}^{CN} = \delta_{S_2C}^{CN} = 119.2 \pm 0.3$
			$\delta_C^{CCl_4} = 97.14$
			$\delta_{SC}^{CCl_4} = 97.24 \pm 0.06$
			$\delta_{S_2C}^{CCl_4} = 95.79 \pm 0.06$
AN–C$_6$H$_6$	$2S \xrightleftharpoons{K_d} S_2$	$K_d = 0.0224 \pm 0.0007$	$\delta_S^{CH_3} = -29.54$
			$\delta_{S_2}^{CH_3} = -24.1 \pm 0.1$
			$\delta_S^{CN} = 86.20$
			$\delta_{S_2}^{CN} = 94.1 \pm 0.3$
NM–C$_6$H$_6$	$2S \xrightleftharpoons{K_d} S_2$	$K_d = 0.0205 \pm 0.0008$	$\delta_S^{CH} = 31.49$
			$\delta_{S_2}^{CH_3} = 37.7 \pm 0.2$
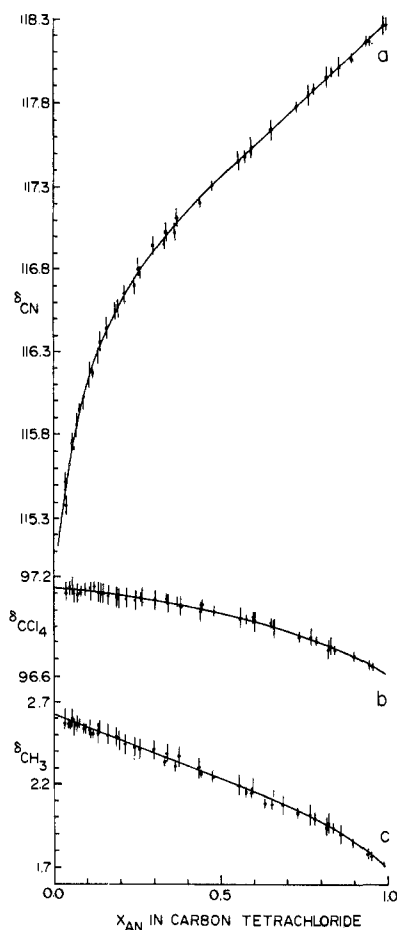
Figure 1. Plots of the carbon-13 chemical shifts of the methyl (c) and nitrile (a) carbons of AN and the carbon of carbon tetrachloride (b) as a function of mole fraction of AN.

Figure 2. Plots of the carbon-13 chemical shifts of the methyl (c) and nitrile (b) carbons of AN and the carbons of benzene (a) as a function of mole fraction of AN.

(1) dimerization of acetonitrile only; (2) dimerization of acetonitrile and formation of a 1:1 MeCN–CCl$_4$ complex; and (3) dimerization of acetonitrile, formation of a 1:1 MeCN–CCl$_4$ complex, and formation of a 2:1 MeCN–CCl$_4$ complex. The third method gave the best agreement with the observed ^{13}C chemical shift behavior for the carbons of acetonitrile and of carbon tetrachloride. In this model, the nitrile carbon chemical shifts of the S$_2$ and S$_2$C species are assumed to be equal as are the chemical shifts of the S and SC species. This is not an unreasonable assumption since the nitrile carbon is separated by three bonds from the site of interaction between the methyl group and carbon tetrachloride. The chemical shifts of the methyl carbon of acetonitrile and the carbon of CCl$_4$ were considered to be different

for each of the species occurring in solution. Equilibrium constants obtained from the computer analysis are tabulated in Table II. Based on the above results it is possible to suggest probable structures for the S$_2$, SC, and S$_2$C species (Figure 4).

The uncertainties for these equilibrium constants are fairly large since *nine* unknown parameters were determined simultaneously. However, these results indicate that the self-association of acetonitrile is the dominant reaction. These results are in agreement with vapor pressure data for the MeCN–CCl$_4$ system which forms a low-boiling azeotrope.[19] The formation of low-boiling azeotropes results when the cohesive forces between unlike components are

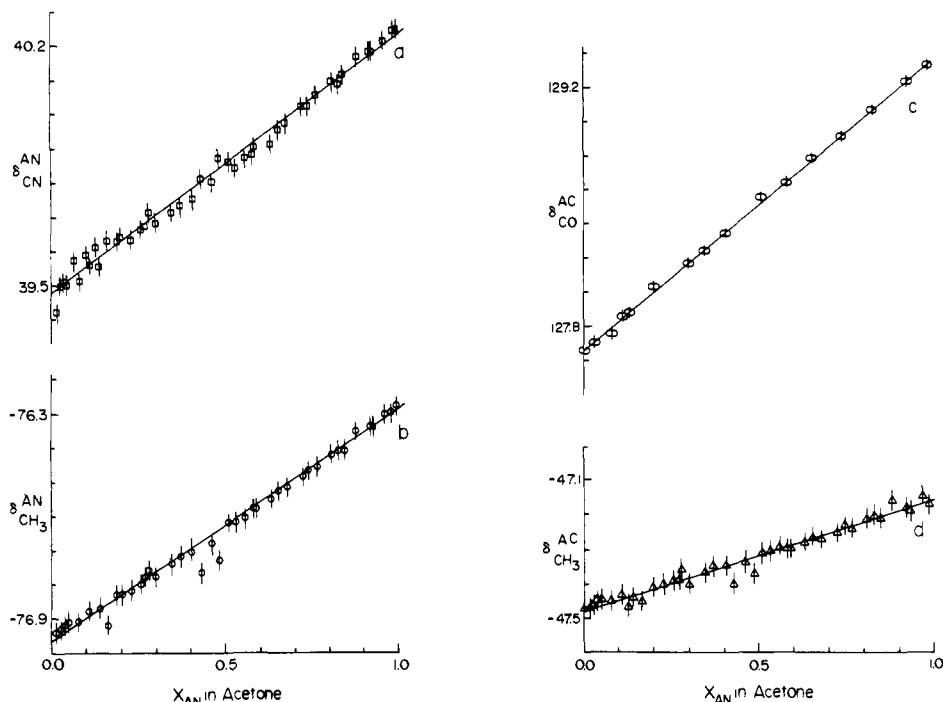(19) Brown, I.; Smith, F. *Aust. J. Chem.* **1954**, *7*, 269.

Figure 3. Plots of the carbon-13 chemical shifts of the methyl (b) and nitrile (a) carbons of AN and the methyl (d) and carbonyl (c) carbons of AC as a function of mole fraction of AN.
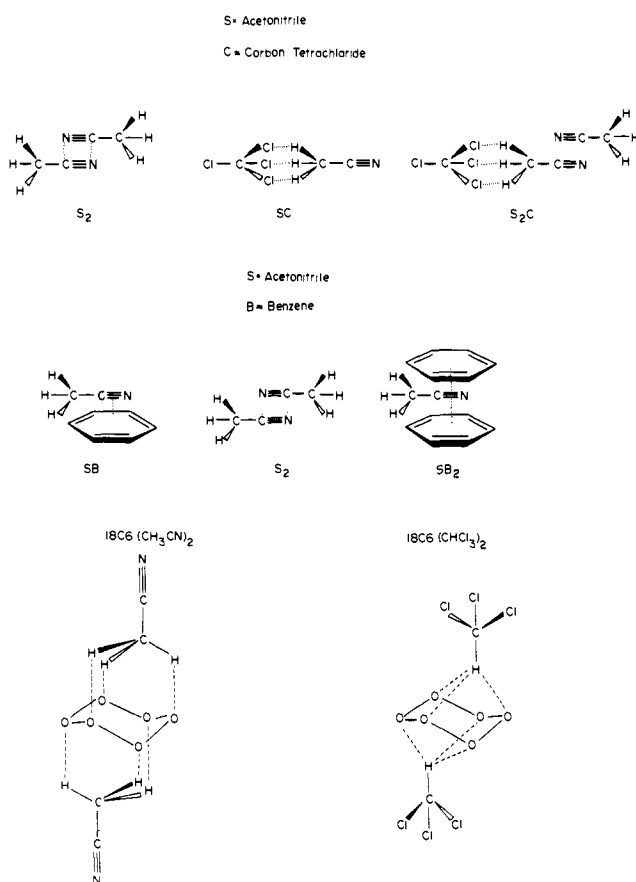

Figure 4. Structures proposed for the AN dimer, S_2; $CCl_4 \cdot CH_3CN$, SC; $CCl_4 \cdot (CH_3CN)_2$, S_2C; $C_6H_6 \cdot CH_3CN$, SB; $(C_6H_6)_2 \cdot CH_3CN$, SB_2; $18C6 \cdot (CH_3CN)_2$; and $18C6 \cdot (CHCl_3)_2$.
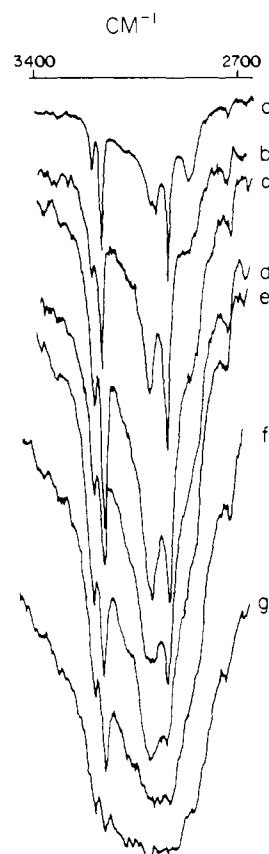

Figure 5. Infrared spectra of the C–H stretch of AN for solutions of AN in carbon tetrachloride. Concentrations are (a) $\chi_{AN} = 0.0808$, (b) $\chi_{AN} = 0.2081$, (c) $\chi_{AN} = 0.4196$, (d) $\chi_{AN} = 0.5062$, (e) $\chi_{AN} = 0.6677$, (f) $\chi_{AN} = 0.7644$, and (g) $\chi_{AN} = 1.0000$.

smaller than those within the pure liquids.[20] Therefore, in the MeCN–carbon tetrachloride system, the MeCN–MeCN inter-

actions are stronger than the MeCN–CCl_4 interactions.

Infrared spectra were obtained for solutions of acetonitrile in CCl_4. Figures 5 and 6 show ν_1, the C–H stretch between 2960 and 2940 cm^{-1} and ν_2, the C–N stretch between 2270 and 2250 cm^{-1}, as a function of the mole fraction of the solute. Both of

(20) Moore, W. J. "Physical Chemistry", 4th ed.; Prentice-Hall: Englewood Cliffs, N.J., 1972; p 254.
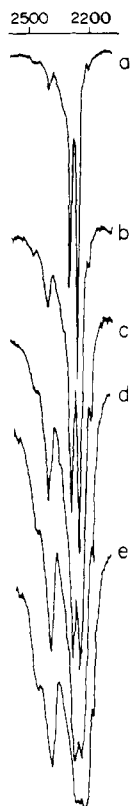
2500 2200

Figure 6. Infrared spectra of the CN stretch of AN for solutions of AN in carbon tetrachloride. Concentrations are (a) χ_{AN} = 0.0808, (b) χ_{AN} = 0.2081, (c) χ_{AN} = 0.5062, (d) χ_{AN} = 0.7644, and (e) χ_{AN} = 1.0000.

these vibrations have A_{1g} symmetry. The changes observed for ν_1 and ν_2 as a function of acetonitrile concentration, therefore, must be due to different species arising from the MeCN–MeCN and MeCN–CCl$_4$ interactions occurring in solution. Figure 7 shows an expanded spectrum of the ν_2 vibration of 0.42 M deuterated acetonitrile, MeCN-d_3. This spectrum was deconvoluted and the results are tabulated in Table III in the supplementary material. Raman studies[21] of solutions of acetonitrile in CCl$_4$ have shown that deconvolutions of ν_2 bands are difficult because of interference by hot bands of the type $\nu_2 + \nu_8 - \nu_8$. These hot bands occur at the low-frequency side of the ν_2 band. The ν_1 band is not complicated by hot bands. Raman studies of this band at low concentrations of acetonitrile in carbon tetrachloride indicate a clustering of acetonitrile molecules and some MeCN–CCl$_4$ interaction.

In benzene solutions, the chemical shifts for the methyl and nitrile carbons of acetonitrile exhibit the same curvature. Furthermore, the nitrile carbon does not show as much curvature in benzene as it did in CCl$_4$. Generally, the stronger the interaction, the more curvature is observed in the chemical shift–concentration plots. Therefore, the self-association of acetonitrile appears to be weaker in benzene than in CCl$_4$. Since the curvature of the δ vs. concentration plot for the methyl carbon of acetonitrile is the same as that observed for the nitrile group, it can be concluded that the self-association of acetonitrile and its interaction with benzene occur through the nitrile group. Proposed structures for the MeCN·(C$_6$H$_6$) and MeCN·(C$_6$H$_6$)$_2$ species are shown in Figure 4.

Because the benzene carbon-13 chemical shift variation with concentration has a constant slope, it is not possible to separate the MeCN–MeCN and MeCN–benzene interactions as it is for the CCl$_4$ system. A proton NMR study was done to see if it would be feasible to separate these interactions. Although the proton chemical shifts of both the benzene and methyl group of MeCN
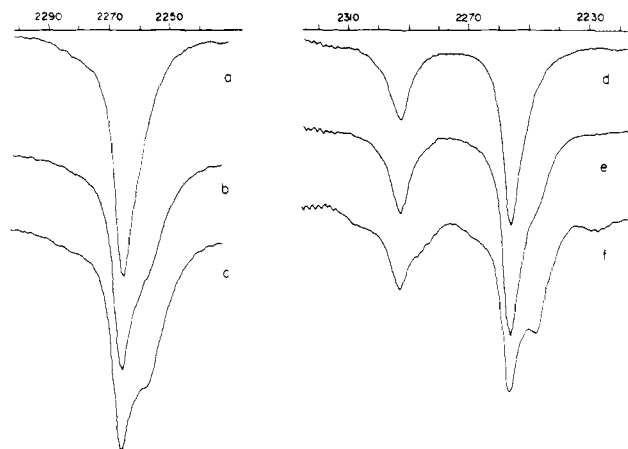
(21) Yarwood, J.; Arndt, R. In "Molecular Association: Including Molecular Complexes"; Foster, R., Ed.; Academic Press: London, 1979; Vol. 2, Chapter 4.

2290 2270 2250   2310 2270 2230

Figure 7. Infrared spectra of the CN stretch of AN and AN-d_3 for solutions of AN and 18C6 in carbon tetrachloride. Concentrations are (a) 0.4243 M AN-d_3, [18C6]/[AN-d_3] = 0.00; (b) 0.4254 M AN-d_3, [18C6]/[AN-d_3] = 0.1161; (c) 0.4232 M AN-d_3, [18C6]/[AN-d_3] = 0.2012; (d) 0.4677 M AN, [18C6]/[AN] = 0.00; (e) 0.4555 M AN, [18C6]/[AN] = 0.0748; and (f) 0.4190 M AN, [18C6]/[AN] = 0.2980.

showed a concentration dependence, no curvature was observed. Therefore, these interaction cannot be analyzed by proton NMR.

The analysis of the carbon-13 chemical shifts for the MeCN–benzene system shows that the self-association of acetonitrile is the dominant reaction. The chemical shift data for the methyl and nitrile carbons were computer analyzed using a dimerization model. The results are shown in Table II. It should be emphasized that the K_d value obtained is a conditional constant since it is not possible to separate the MeCN–MeCN interaction from the MeCN–benzene interaction.

These results are in agreement with vapor pressure studies on these systems. The MeCN–benzene system forms a low-boiling azeotrope;[22] therefore, the self-association of MeCN should be the dominant reaction. Furthermore, the boiling point of the MeCN–carbon tetrachloride system[19] deviates more greatly from the boiling points of its pure components than does the boiling point of the MeCN–benzene azeotrope. These results suggest that the MeCN–C$_6$H$_6$ interactions are stronger than the MeCN–CCl$_4$ interactions. It should be noted that in a study of the MeCN–benzene system, Goates and his co-workers[23] were able to isolate, at 249 K, a solid compound with the composition (C$_6$H$_6$)$_2$·CH$_3$CN.

Unlike the MeCN–CCl$_4$ and MeCN–benzene systems, the MeCN–acetone system does not form an azeotrope.[24] Therefore, it is probable that the intermolecular forces between MeCN–MeCN, MeCN–Me$_2$CO, and Me$_2$CO–Me$_2$CO are approximately the same. As Figure 3 shows, no curvature is observed in the chemical shift plots as a function of concentration for either the methyl and nitrile carbons of acetonitrile or for the methyl and carbonyl carbons of acetone. Therefore, no particular interaction is dominant.

Analogous to the MeCN–benzene system, the MeNO$_2$–benzene system forms a low-boiling azeotrope.[22] The curvatures in the observed chemical shift–concentration plots for the above two systems are very similar. Therefore, the chemical shift data for the MeNO$_2$–benzene system were computer analyzed using a dimerization model. The results of this analysis are tabulated in Table II.

B. NMR Studies of 18-Crown-6 and Background Solvent. Carbon-13 NMR concentration studies were carried out for 18-crown-6, in CCl$_4$, benzene, and acetone solutions as a function of the ligand concentration. The purpose of these studies was to see whether the background solvent complexed the crown. In both

(22) "Handbook of Chemistry and Physics", 57th ed.; Weast, R. C., Ed.; Chemical Rubber Publishing Co.: Cleveland, OH, 1976; pp 1–36.
(23) Goates, J. R.; Ott, J. B.; Budge, A. H. *J. Phys. Chem.* **1961**, *65*, 2162.
(24) Gmehling, J.; Onken, U.; Arlt, W. "Vapor-Liquid Equilibrium Data Collection: Aldehydes and Ketones, Ethers"; Deckema: Frankfurt, 1979; p 143.

Table IV. Association Constants of the Complexes of 18-Crown-6 with Acetonitrile and Nitromethane at 298 K

guest	background solvent	$K_{1:1}$, L mol^{-1}	$K_{1:2}$, L mol^{-1}	^{13}C chemical shifts, ppm
acetonitrile[a]	C_6H_6	1.0 ± 0.2	0.26 ± 0.04	$\delta_{1:1}{}^{CH_3} = -28.5 \pm 0.1$ $\delta_{1:2}{}^{CH_3} = -25.2 \pm 0.7$
acetonitrile[b,c]	AC	0.57 ± 0.07		$\delta_{1:1}{}^{CN} = 41.2 \pm 0.2$
acetonitrile[a]	CHCl$_3$	<0.4		
nitromethane[a]	C_6H_6	1.3 ± 0.2	1.4 ± 0.3	$\delta_{1:1}{}^{CH_3} = 34.6 \pm 0.3$ $\delta_{1:2}{}^{CH_3} = 37 \pm 1$

[a] External lock and reference in acetone-d_6. All chemical shifts are relative to the methyl carbon of acetone-d_6. [b] External lock and reference in chloroform-d_6. All chemical shifts are relative to the carbon of chloroform-d. [c] The carbon-13 chemical shift of uncomplexed acetonitrile, δ_S, was calculated using the relationship: $\delta_S = \delta_\infty + (\delta - \delta_\infty)(0.97)([AN])$, where δ_∞ is the chemical shift of AN in AC at infinite dilution and δ is the chemical shift of pure AN.
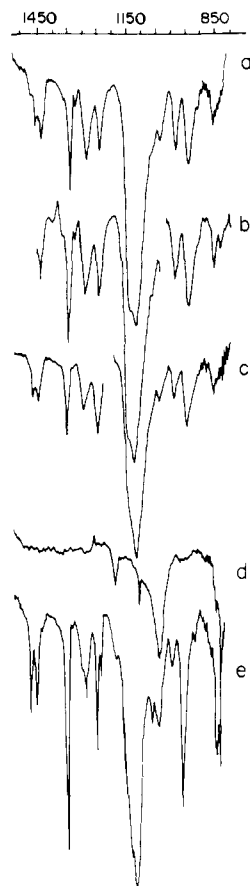

Figure 8. Infrared spectra of 18C6 from 1500 to 800 cm^{-1} where (a) 0.0749 M 18C6 in carbon tetrachloride, (b) 0.07 M 18C6 in benzene, (c) 0.0443 M 18C6 in chloroform, (d) 0.8649 M AN-d_3 in carbon tetrachloride, and (e) 0.0711 M 18C6 and 0.9262 M AN-d_3 in carbon tetrachloride.

CCl$_4$ and benzene, the chemical shift of 18C6 is independent of concentration. However, in acetone the crown chemical shift shifts upfield with increasing crown concentration.

Figure 8 shows infrared spectra of 18C6 in CCl$_4$, benzene, chloroform, and a solution of MeCN-d_3 in CCl$_4$. The spectra indicate that the conformation of 18C6 is strongly solvent dependent. The infrared spectra of 18C6 in CCl$_4$ and benzene match the spectrum of liquid 18C6 at 50 °C obtained by Dale and Kristiansen,[25] whereas the spectrum of 18C6 and MeCN-d_3 in CCl$_4$ matches that of the crystalline KBr·18C6 complex.[25] The spectrum of 18C6 in chloroform lies approximately between the two.

At 50 °C, liquid 18C6 exists as a mixture of conformers.[25] Very likely, the same should be true of 18C6 solutions in CCl$_4$ and in benzene. In the crystalline KBr·18C6 complex, the crown has approximate D_{3d} symmetry. It can, therefore, be assumed that in CCl$_4$ solutions, MeCN-d_3 complexes 18C6 and that the conformation of the crown in that complex is close to the D_{3d} sym-

metry. The infrared spectra show, therefore, that while neither CCl$_4$ or benzene complexes 18C6, there is a weak interaction between 18C6 and chloroform.

A ^{13}C study of acetone in acetone–benzene–18C6 systems showed that the chemical shifts of the carbonyl and methyl carbons of acetone change upon the addition of 18C6; it can be therefore concluded that acetone weakly complexes 18C6.

C. Complexation of 18C6 with Acetonitrile and Nitromethane. The complexation of 18C6 with acetonitrile was studied in carbon tetrachloride, chloroform, benzene, and acetone solutions. Although the MeCN–CCl$_4$ system was the best characterized, the limited solubility of the MeCN·18C6 complex in CCl$_4$ made a mole ratio study difficult. However, greater solubilities were found in benzene, chloroform, and acetone solutions.

An infrared study of the MeCN–18C6–CCl$_4$ system was carried out. Figure 7 shows the infrared spectra of ν_2 vibrations of MeCN and MeCN-d_3, both free and complexed by 18C6. For MeCN-d_3, the intensity of ν_1, the CD stretch at 2118 cm^{-1}, increases upon complexation with 18C6. No new bands appear near ν_1. However, a new band does grow out of ν_2, the CN stretch which occurs at 2265 cm^{-1} for MeCN-d_3 and 2255 cm^{-1} for acetonitrile (the band at 2295 is the $\nu_3 + \nu_4$ combination band in Fermi resonance with the ν_2 band[26]). For both MeCN-d_3 and MeCN, the new band appears at lower frequencies. These observations agree well with those obtained by McLachlan[27] in his Raman studies of the single crystals of 18C6·2CH$_3$NO$_2$, 18C6·2CH$_3$CN, 18C6·2CD$_3$CN, and 18C6·Ac$_2$O. They also agree with the Raman studies done by Gold and Rice.[8]

The complexation of 18C6 and MeCN in chloroform was studied by both carbon-13 NMR spectroscopy and infrared spectroscopy. Between [18C6]/[MeCN] mole ratios of 0.0 to 3.5, the carbon-13 chemical shifts of the methyl and nitrile groups of MeCN exhibit a linear concentration dependence. Therefore, it can be concluded that in chloroform the complexation of 18C6 with acetonitrile is very weak, since chloroform also complexes 18C6. It may partially also result from interactions between MeCN and chloroform, similar to those observed between MeCN and CCl$_4$. The infrared spectra obtained for solutions of 18C6 and MeCN-d_3 in chloroform further point out the weakness of complexation between 18C6 and MeCN-d_3. In these spectra, the ν_2 band due to the complexation appears as a shoulder. These spectra as well as those for the MeCN-d_3 and 18C6 in CCl$_4$ were deconvoluted using KINFIT. The results of these deconvolutions are shown in Table III in the supplementary material.

Carbon-13 chemical shifts of acetonitrile carbons were measured in the presence of 18C6 as a function of [18C6]/[MeCN] mole ratio at a fixed concentration of MeCN in benzene and in acetone. The chemical shift plots for the methyl carbon of MeCN in benzene showed two breaks indicative of the formation of two complexes. The model used to analyze the chemical shift data was described previously. The results of this analysis are tabulated in Table IV. Infrared studies of MeCN and 18C6 solutions in benzene showed the same changes as observed for the same solutions in CCl$_4$.

For MeCN and 18C6 in acetone solutions, only one break is apparent in the chemical shift plot. Therefore, only one MeCN–

(25) Dale, J.; Kristiansen, P. O. *Acta Chem. Scand.* **1972**, *26*, 1471.

(26) Duncan, J. L.; McKean, D. C.; Tullini, F.; Nivellini, G. D.; Pena, J. P. *J. Mol. Spectrosc.* **1978**, *69*, 123.
(27) McLachlan, R. D. *Spectrochim. Acta, Part A* **1974**, *30*, 2153.
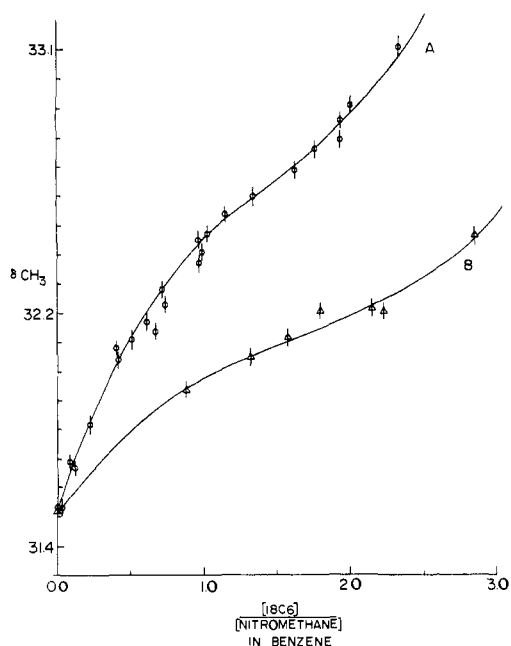
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Figure 9. Plots of the carbon-13 chemical shifts of the methyl carbon of nitromethane as a function of [18C6]/[NM] mole ratio: (A) solutions prepared using 25 μL of NM and diluting to 2 mL with benzene; (B) 25 μL of NM diluted to 5 mL.

18C6 complex is formed. The carbon-13 chemical shift data were computer analyzed after correction for the chemical shift of the uncomplexed acetonitrile. The results of this analysis are shown in Table IV. Because acetone forms a weak complex with 18C6, K_1 in acetone is much smaller than K_1 in benzene.

It is interesting to note that the nitrile group of acetonitrile is affected the most by complexation with 18C6. This is the case for the Raman studies done on the solid complexes[8,27] as well as the solution studies reported in this paper. It does not mean however, that the nitrile group interacts with 18C6. For example, a crystal structure of the 18C6·2CH$_3$CN complex, shows that the methyl protons of acetonitrile are hydrogen-bonded to the ether oxygens of 18C6.[6] Furthermore, as discussed previously, the symmetry of 18C6 in chloroform solution approaches D_{3d}. However, in a CCl$_4$ solution of MeCN-d_3 the crown has D_{3d} symmetry. The D_{3d} symmetry of 18C6 in chloroform results because there is only one hydrogen bonding to three ether oxygens (Figure 4). If the methyl group of MeCN-d_3 complexes the crown, then three hydrogens are bonding to three ether oxygens resulting in a rigid conformer with D_{3d} symmetry as shown in Figure 4.

The complexation of 18C6 and nitromethane was also studied in benzene solution: the results, obtained at 25 °C, are shown in Figure 9. The chemical shift plots of the methyl carbon show two breaks indicating the formation of two complexes. The results of the analysis of the data are tabulated in Table IV.

As seen in Table IV, nitromethane forms more stable complexes with 18C6 than does acetonitrile, and that in the former case K_1 $\approx K_2$.[28] Instances of cooperative effect in macrocyclic complexation reactions are well documented by Rebek.[29] In these reactions macrocyclic ligands usually undergo conformational changes;[30] it seems reasonable, therefore, to assume that in the case of nitromethane the formation of the 1:1 complex predisposes the ligand to accept the second solvent molecule. This effect is not observed with acetonitrile, probably because in this case the

methyl group is less electropositive than that of nitromethane[31,32] and a less rigid complex is formed with 18C6.

D. Effect of Ligand Solvation on the Thermodynamics of Metal Cation Complexation. the equilibrium constant for metal cation-crown complexation is given by the following expression:

$$M^+ + L \overset{K}{\rightleftharpoons} ML^+ \qquad K = [ML^+]/[M^+][L] \qquad (9)$$
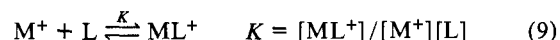
where M^+ refers to the metal cation, L to the crown, and ML^+ to the complex. Since we have an ion–molecule reaction, the effect of activity coefficients can be ignored in dilute solutions. Experimentally, however, in solvents which also complex the crown, a conditional equilibrium constant, K', is measured. This conditional equilibrium constant can be defined by the following expression:

$$M^+ + L' \overset{K'}{\rightleftharpoons} ML^+ \qquad K' = [ML^+]/[M^+][L'] \qquad (10)$$
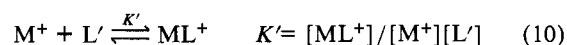
where [L'] refers to the concentration of crown uncomplexed by M^+. This concentration [L'] includes the concentration of crown in all its solvated forms as shown:

$$[L'] = [L] + [SL] + [SLS]$$

where [L] is the concentration of crown not complexed by the solvent and [SL] and [SLS] are the concentrations of the 1:1 and 1:2 crown:solvent complexes, respectively. The thermodynamic and conditional equilibrium constants are related to one another by the following expression:

$$K' = \alpha_L K$$

where

$$\alpha_L = \frac{1}{1 + K_1[S] + K_1K_2[S]^2}$$

In the expression for α_L, [S] is the concentration of monomeric solvent and K_1 and K_2 are the formation constants for the 1:1 and 1:2 crown–solvent complexes, respectively.

Using the above equation and the values for K_1 and K_2 obtained for 18–crown–6 and either MeCN or MeNO$_2$ in benzene, α_L was calculated to see the effect of ligand–solvent interactions on the stabilities of the ligand–metal ion complexes. In these calculations the assumption was made that the analytical concentration of solvent, C_S, is primarily due to the monomeric and dimeric forms of the solvent. For a solution of 18-crown-6 and metal cation in either MeCN or MeNO$_2$, this is a valid assumption since the analytical concentration of solvent is much greater than the analytical concentrations of either the ligand or metal ion. Using this assumption, α_L for MeNO$_2$ and 18-crown-6 was determined to be 3.39 × 10^{-3}, whereas α_L for MeCN and 18-crown-6 was 1.89 × 10^{-2}. Therefore, in MeNO$_2$, K_{18C6} = 294.65K'_{18C6}, and in MeCN, K_{18C6} = 52.85K'_{18C6} where K_{18C6} is the thermodynamic formation constant for the complexation of a metal ion and 18-crown-6 and K'_{18C6} is the conditional formation constant. These results clearly show how great an effect ligand–solvent interactions can have on the complexation of metal cations.

Registry No. Acetonitrile, 75-05-8.

Supplementary Material Available: Table of results of deconvolution of the CN band of AN-d_3 (2 pages). Ordering information is given on any current masthead page.

(28) de Boer et al. (ref 5) reported $K_2 > K_1$ for this system.
(29) Rebek, J., Jr. *Acc. Chem. Res.* **1984**, *17*, 258.
(30) See, for example: Chock, P. B.; Eggers, F.; Eigen, M.; Winkler, R. *Biophys. Chem.* **1977**, *6*, 239, and the infrared measurements reported in this paper. It should also be noted that, especially in nonaqueous solvents, macrocyclic complexation reactions have negative entropies of complexation largely due to conformational changes (ref 12–14).

(31) Huheey, J. E. "Inorganic Chemistry", 2nd ed.; Harper and Row: New York, 1978; p 171.
(32) Reutov, O. A.; Beletskaya, I. P. "CH-Acids"; Pergamon Press: Oxford, 1978; p 43.