a comparison of the latter value with the experimentally observed $\Delta V^{\ddagger}$ values in Table IV, one can conclude that the transition state for the electron-transfer process is approximately halfway along the reaction coordinate on a volume basis. This means that both the Co(III) and Fe(II) centers have approached a half-reduced/half-oxidized geometry in the transition state.

In summarizing we conclude that the $\Delta V^{\ddagger}$ data for the electron-transfer step within the ion pair can be explained on the basis of volume changes on the individual ions, of which the largest effect originates from the iron center. No evidence for any significant mechanistic difference between the investigated systems can be observed on the basis of these data.

Acknowledgment. We gratefully acknowledge financial support from the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the Max-Buchner-Forschungsstiftung.

Registry No. $Co(NH_3)_5H_2O^{3+}$, 14403-82-8; $Co(NH_3)_5py^{3+}$, 31011-67-3; $Co(NH_3)_5Me_2SO^{3+}$, 44915-85-7; $Fe(CN)_6^{4-}$, 13408-63-4.

Contribution from the Department of Chemistry,
Michigan State University, East Lansing, Michigan 48824

Competitive NMR Study of the Complexation of Several Cations with 18-Crown-6, 1,10-Diaza-18-crown-6, and Cryptand-2,2,2 in Nonaqueous Solutions

Roger D. Boss and Alexander I. Popov*

Received October 7, 1985

Previously reported competitive NMR studies of formation constants of macrocyclic complexes have been extended to several new systems. The technique was found to be applicable to solutions containing two cations and a common ligand where the analysis of the NMR data makes it possible to determine simultaneously both formation constants. It also was used in systems where the exchange of the probe cation between the free and the complexed sites is slow and two resonances of the probe nucleus are observed. It is possible, therefore, to use the competitive technique to study the stabilities of metal complexes of diaza polyoxa macrobicyclic ligands (cryptands) where slow exchange at room temperature is often observed. Formation constants for several 18C6 and DA18C6 complexes are reported in acetonitrile, acetone, and propylene carbonate solutions. These results are discussed with respect to the size and charge of the cation, the solvating ability of the solvent, and the nature of the ligand binding groups.

Introduction

In a previous publication[1] we described a competitive NMR technique for the determination of stability constants of metal ion complexes with macrocyclic ligands. This method is essentially independent of the solvent (solubilities permitting), it can be used for the determination of stability constants that are higher than 10^5 (upper limit for the direct NMR technique), and it allows NMR studies of complexes of cations with unsuitable NMR properties such as low receptivity, high quadrupole moments, etc.

In this paper we describe the application of this technique to several new solvents, to systems with very high stability constants, and to systems where the cation exchange between the free and complexed site is slow at the temperature of measurement so that two cationic resonances are observed.

Experimental Part

Cesium, rubidium, and potassium tetraphenylborates were prepared and purified by following the procedure of Mei et al.[2] Barium tetraphenylborate was prepared by the procedure described by Khol'kin et al.[3] followed by drying at 40 °C for 2 days under vacuum in the dark. Thallium(I) perchlorate (K&K) and acetone (Baker) were purified by the procedure described by Lee et al.[4] Sodium tetraphenylborate (Aldrich), barium perchlorate (Alfa), and lithium perchlorate (Alfa) were dried for several days under vacuum at 45 and 70 °C, respectively. Acetonitrile (Baker) was purified as described previously.[1] Propylene carbonate (Aldrich) was refluxed under reduced pressure over calcium hydride at 90–100 °C and then fractionally distilled under the same pressure. The middle fraction (~60%) was retained.

The ligand 18-crown-6 (18C6) (Aldrich) was purified and dried as previously described.[1] The ligands Kryptofix-2,2 (1,10-diaza-18-crown-6, DA18C6) and Kryptofix-2,2,2 (C222) were obtained from MCB and used as obtained except for being dried under vacuum at room temperature for 2 days.

All instrumentation, solution preparation, data treatment, and calculations for rapidly exchanging systems were carried out as previously described.[1] For those systems that were exchanging sufficiently slowly so that two separate resonance bands for the free and complexed species were observed at room temperature, a different procedure had to be used. When separate bands were present, a solution was prepared that had both salts and the ligand at equal concentrations (mole ratios 1:1:1). The observed resonance bands were manually fitted to Lorentzian profiles. The parameters obtained from this fit (intensity, position, and width) were then corrected for the effect due to the delay between the end of the excitation pulse and the beginning of acquisition and for the effect due to the exponential multiplication (which is done to increase signal-to-noise). The equations for a resonance band thus collected and processed, as opposed to the true Lorentzian profile desired, is given by Strasser and others.[5] The Lorentzian bands defined by corrected parameters are then directly integrated. The properly corrected band areas were then used to calculate the concentrations of the free and complexed species. These concentrations are then used to calculate all other concentrations. Once all concentrations are known, it is a trivial process to calculate the unknown formation constant.

Results and Discussion

A. Determination of High Stability Constants of Crown Complexes. In the previous publication we reported the determination of the formation constant of Ba^{2+} macrocyclic complexes is not possible (at this time at least) by the direct measurements of the ^{135}Ba or ^{137}Ba resonances because of low receptivities and high quadrupole moments of these nuclei.[6] We therefore used the competitive technique (with the Na^+ ion as the competing ion and as the observed nucleus), to obtain the formation constant of log $K_f = 4.21 \pm 0.19$ for the $Ba^{2+}\cdot$18C6 complex in dimethylformamide solution.

The stability of the above complex should be considerably higher in acetone, acetonitrile, or propylene carbonate solution since the latter solvents have much lower solvating ability than DMF[7] and would compete less with the ligand for the cationic coordination sites. As previously mentioned, however, one of the limitations of the competitive NMR technique[1] results from occasionally limited solubilities of salts and/or complexes in the solvents of interest.

---

(1) Boss, R. D.; Popov, A. I. *Inorg. Chem.* **1985**, *24*, 3660.

(2) Mei, E.; Popov, A. I.; Dye, J. L. *J. Phys. Chem.* **1977**, *81*, 1677.

(3) Khol'kin, A. I.; Kotzitiskii, V. P.; Gindin, L. M.; Ovechkina, L. G. *Izv. Sib. Otd. Akad. Nauk Sssr, Ser. Khim. Nauk* **1976**, 66.

(4) Lee, Y. C.; Allison, J.; Popov, A. I. *Polyhedron* **1985**, *4*, 441.

(5) (a) Strasser, B. O.; Hallenga, K.; Popov, A. I. *J. Am. Chem. Soc.* **1985**, *107*, 789. (b) Strasser, B. O. Ph.D. Thesis, Michigan State University, East Lansing, MI 48824, **1984**. (c) Szczgyiel, P. M.S. Thesis, Michigan State University, East Lansing, MI 48824, **1984**.

(6) Harris, R. K.; Mann, B. E. *NMR and the Periodic Table*; Academic: New York, **1978**; p 7.

(7) Gutmann, V.; Wychera, E. *Inorg. Nucl. Chem. Lett.* **1966**, *2*, 257.

(8) Lin, J. D.; Popov, A. I. *J. Am. Chem. Soc.* **1981**, *103*, 3773.

Table I. Stability Constants (log K_f) of 18-Crown-6 Complexes in Acetonitrile, Acetone, and Propylene Carbonate Solutions[a]

	log K_f						
solvent	Li^+	Na^+	K^+	Rb^+	Cs^+	Tl^+	Ba^{2+}
acetonitrile	2.34 ± 0.04[b]	4.21 ± 0.10 3.8 ± 0.2[c]	5.46 ± 0.10		4.83 ± 0.18 >4[d]	5.81 ± 0.14 >5[e]	8.88 ± 0.41
propylene carbonate	2.69 ± 0.11[b]	5.16 ± 0.13 >4[c]	6.14 ± 0.14	5.22 ± 0.16	4.45 ± 0.06 4.14 ± 0.2[d]		>9
acetone	1.50 ± 0.02[d]	4.57 ± 0.06 >4[c]	6.00 ± 0.18	5.18 ± 0.04	4.62 ± 0.5 >5[d]	6.18 ± 0.09 >5[e]	8.54 ± 0.32

[a] The uncertainties for stepwise procedures include those in the value of the probe complex or complexes. [b] Reference 14. [c] Reference 8. [d] Reference 2. [e] Reference 15.

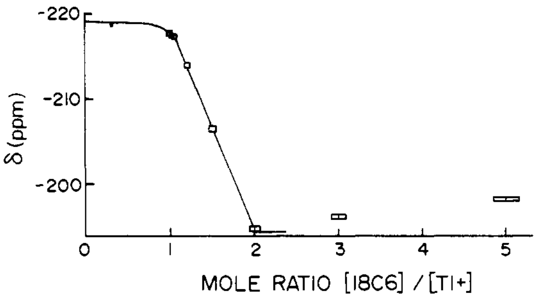

Figure 1. Experimental and calculated thallium-205 chemical shifts as a function of the 18C6:Tl^+ mole ratio for solutions containing $TlClO_4$, $Ba(ClO_4)_2$, and 18C6 in acetone. The points at mole ratios greater than 2 were not included in the fit.

In acetone solutions the $Cs^+ \cdot 18C6$ complex (log K_f = 4.62) should be a good probe for measuring the stability of the $Ba^{2+} \cdot 18C6$ complex; however neither the tetraphenylborate nor the perchlorate could be used due to the insolubility of the $Ba^{2+}18C6 \cdot 2BPh_4^-$ complex and of $CsClO_4$, respectively. Cesium halides were not used because of their tendency to form ion pairs.

A multistep method, which avoids solubility difficulties, was therefore used. With the $Cs^+ \cdot 18C6$ complex as the known, the formation constant of the $Na^+ \cdot 18C6$ complex was found to be log $K_f^{Na^+}$ = 4.57 ± 0.05 by sodium-23 NMR. Sodium-23 NMR was then used on the $NaClO_4$–$TlClO_4$–18C6 system in acetone to determine the formation constant of the $Tl^+ \cdot 18C6$ complex, which gave log $K_f^{Tl^+}$ = 6.19 (± 0.03) ± 0.09. It should be noted that the first uncertainty is given for the calculated value determined without the uncertainty in the known formation constant; the second value is the combined uncertainty of the two determinations. Thallium-205 NMR measurements were then used on the $TlClO_4$–$Ba(ClO_4)_2$–18C6 system which finally gave log $K_f^{Ba^+}$ = 8.54 (±0.22) ± 0.32. The thallium-205 chemical shifts that are plotted in Figure 1 exhibit behavior indicative of the formation of a very weak $Tl^+ \cdot 2(18C6)$ complex. Analysis of the sodium-23 NMR data for the $NaClO_4$–$TlClO_4$–18C6 and $TlClO_4$–$Ba(ClO_4)_2$–18C6 systems indicates that the formation constant for this 1:2 complex is less than 5 M^{-1}, and, therefore, negligible when compared to the 1:1 formation constants of the Tl^+ and Ba^{2+} complexes with 18C6. Although the experimental uncertainity for the formation constant of the $Ba^{2+} \cdot 18C6$ complex is fairly large, it results from the combined uncertainties of four separate determinations.

B. Simultaneous Study of Two Complexes. As an extension of the competitive NMR techniques we tried to determine simultaneously the formation constants of two complexes in systems containing two cations and one ligand. Model calculations show the feasibility of this technique on condition that the formation constants of the cations, whose NMR were observed, would be determinable by the direct NMR method (i.e., are less than 10^5). For such cases the calculated curves (Figure 2) reveal information concerning both formation constants, with the information about the observation formation constant being present near the mole ratio of 2, while near a mole ratio of 1 we have information about the ratio of the formation constants. Thus it should be possible to extract the value of both formation constants from one experiment.

As a test, a cesium-133 NMR study was carried out for a series of solutions containing $CsPh_4B$, $NaPh_4B$, and DA18C6 in acetonitrile solution. The observed ^{133}Cs chemical shifts were fitted to a model containing 1:1 complexes of both metal ions, with both formation constants unknown. The original data and the curve calculated from the result of such a fit are shown in Figure 3. The determined values of the formation constants (log $K_{Cs^+ \cdot DA18C6}$ = 2.254 ± 0.009 and log $K_{Na^+ \cdot DA18C6}$ = 4.49 ± 0.02) are in quite good agreement with the literature value of 2.26 ± 0.02 obtained for the cesium complex by ^{133}Cs NMR and the values of 2.48 ± 0.04 and 4.30 ± 0.06 obtained for the Cs^+ and Na^+ complexes, respectively, by conductance measurements (see Table II).

A sodium-23 NMR chemical shift study was carried out for a series of solutions containing $NaPh_4B$, KPh_4B, and 18C6 in AN. The observed sodium-23 chemical shifts were fitted to a model containing 1:1 complexes of both cations, with the $Na^+ \cdot 18C6$ formation constant of Lin[8] (log K = 3.8 ± 0.2) as known and that of the $K^+ \cdot 18C6$ complex as unknown. The original data are shown in Figure 4, along with the calculated curve. The negative deviation of the calculated curve from the data near a mole ratio of 2 is a clear indication that the value of the formation constant of the $Na^+ \cdot 18C6$ complex we used is too small. The experimental data were refitted, but with both formation constants unknown. The curve calculated from this fit is also given in Figure 4. The improvement of the fit is obvious. The formation constant of the

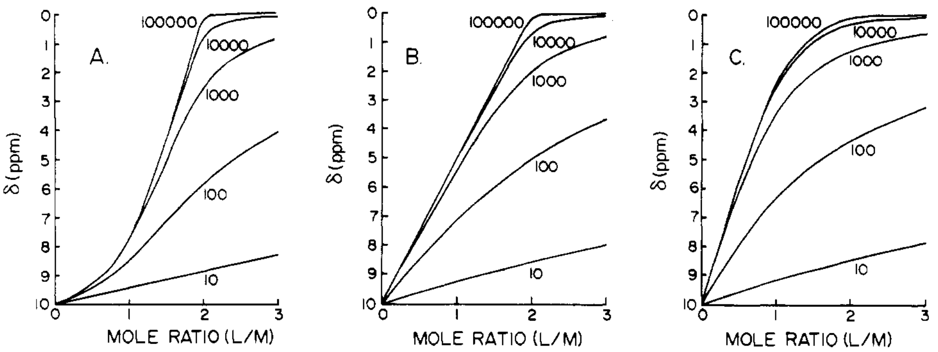

Figure 2. Calculated chemical shifts vs. mole ratio of ligand to one of the metal ions, as a function of the formation constant for the metal ion that is monitored by NMR, for solutions of two metal ions, both at 0.01 M, that form 1:1 complexes. The ratio of the monitored formation constant to that of the nonobserved formation constant is as follows: A, 0.10; B, 1.0; C, 10.0.

Table II. Stability Constants (log K_f) of Diaza-18-crown-6 and C222 Complexes in Acetonitrile, Acetone, and Propylene Carbonate Solutions[a]

solvent	log K_f						
	Li^+	Na^+	K^+	Rb^+	Cs^+	Tl^+	Ba^{2+}
acetonitrile (DA18C6)	4.39 ± 0.41[b]	4.49 ± 0.02	4.35 ± 0.04		2.254 ± 0.009	>7	>7
		4.30 ± 0.06[c]	4.32 ± 0.06[c]		2.48 ± 0.04[c]	>5[b]	
					2.26 ± 0.02[b]	6.8[f]	
acetonitrile (C222)		9.8 ± 0.3					
		9.63 ± 0.1[d]				11.4 ± 0.2	>15
		10.2[e]				11.9[e]	
propylene carbonate (DA18C6)	3.67 ± 0.25[b]	4.62 ± 0.03	4.31 ± 0.04	3.08 ± 0.03	1.945 ± 0.009		>7
					1.95 ± 0.02[b]		
acetone (DA18C6)	2.13 ± 0.08[b]	3.71 ± 0.06	3.86 ± 0.03	2.98 ± 0.06	2.07 ± 0.03	>5.5	>7
					1.89 ± 0.01[b]	>5[b]	

[a] The uncertainties for stepwise procedures include those in the value of the probe complex or complexes. [b] Reference 16. [c] Reference 17. [d] Reference 9. [e] Reference 18. [f] Reference 19.

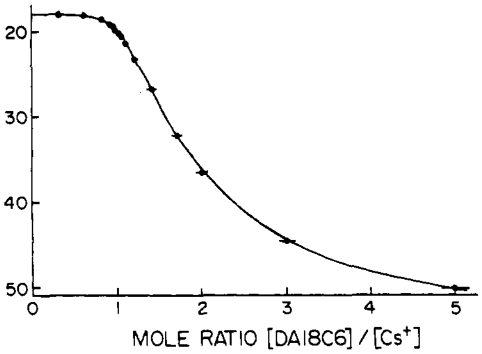

Figure 3. Experimental and calculated cesium-133 chemical shifts as a function of the DA18C6:Cs^+ mole ratio for solutions containing $CsPh_4B$, $NaPh_4B$, and DA18C6 in acetonitrile.

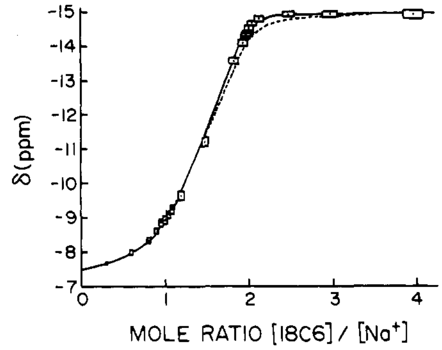

Figure 4. Experimental and calculated sodium-23 chemical shifts as a function of the 18C6:Na^+ mole ratio for solutions containing $NaPh_4B$, KPh_4B, and 18C6 in acetonitrile. The curve calculated from the current results (—) and that obtained by using the value of Lin[8] as a constant (--) are both plotted for comparison.

Na^+·18C6 complex from this fit (log $K = 4.21 \pm 0.10$) is much more accurate and precise (primarily due to the use of a higher field instrument with consequent reduction in the chemical shift uncertainity).

C. Slow-Exchanging Systems. Repeated attempts to measure the formation constants of cryptates by the competitive method were unsuccessful since in these systems the exchange kinetics at room temperature are not sufficiently fast to allow the use of the equation that defines the observed chemical shift as a simple weighted average of the free and complexed species. However, in the case of a slow exchange the NMR spectrum shows separate bands for the free and complexed cation. It should be possible to integrate these bands to provide direct measurements of the relative concentrations of the free and complexed species. Because slow exchange for metal ions is generally associated with stable complexes (log $K_f > 5$) it is only rarely possible to use direct integration of slow-exchange bands to measure the formation constant for the complex (due to the difficulty in the observation and subsequent integration of the resonance band of the free metal ion, whose concentration at a 1:1 mole ratio is very low). However, the competitive method, when applied to two cations that form stable complexes, essentially measures the ratio of the formation constants. Consequently, the amount of the metal that is free (at a mole ratio of 1:1:1) is greatly increased. Thus, the use of direct integration to determine a modest ratio could result in the determination of quite large formation constants. Therefore, an attempt to use a slow-exchange spectrum in a competitive study was made.

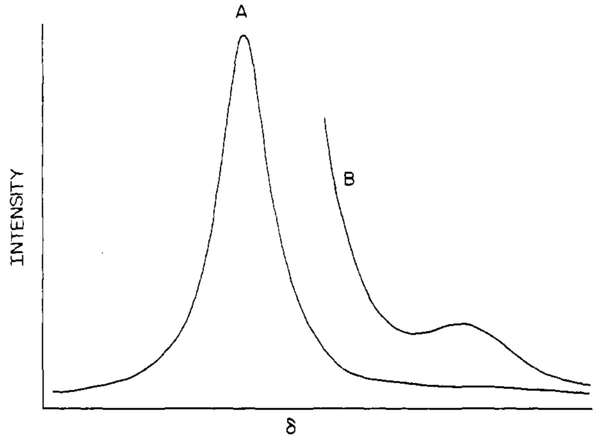

Figure 5. Plot of the sodium-23 NMR spectrum for a 1:1:1 solution of $NaClO_4$, $TlClO_4$, and C222 in acetonitrile. Curve B is drawn at 5× the vertical scale.

A solution of $LiClO_4$, $NaClO_4$, and cryptand C222 (at a mole ratio of 1:1:1) was prepared in acetonitrile. The sodium-23 NMR spectrum was observed to show a slow-exchange spectrum, and the band areas of the two resonances were determined. From the areas of the corrected bands and the value reported by Cox et al.[9] for the Li^+·C222 formation constant (log $K_{Li^+\cdot C222} = 6.9 \pm 0.1$), the value for the Na^+·C222 formation constant was calculated to be log $K_{Na^+\cdot C222} = 9.8 \pm 0.3$, which is in a good agreement with that of Cox et al.[9] (log $K_{Na^+\cdot C222} = 9.63 \pm 0.1$).

A similar study using sodium-23 NMR to observe an 1:1:1 solution containing $NaClO_4$, $TlClO_4$, and C222 in acetonitrile gave the value of the formation constant for the Tl^+·C222 complex as log $K_{Tl^+\cdot C222} = 11.4 \pm 0.2$. The spectrum is shown in Figure 5. A study using sodium-23 to study a 1:1:1 solution of $NaClO_4$, $Ba(ClO_4)_2$, and C222 in the same solvent resulted in the observation of only the free band, thus indicating that the Ba^{2+}·C222 complex is exceedingly stable. Similar results were obtained for a thallium-205 study of an 1:1:1 $TlClO_4$–$Ba(ClO_4)_2$–C222 solution in AN. From a previous study it is known that the width of the resonance for the Tl^+·C222 complex is less than twice that of the free Tl^+ in AN;[10] hence it is possible to use the observed signal-to-noise for the "free" resonance to determine that log $K_{Ba^{2+}\cdot C222} \geq 15.0$.

---

(9) Cox, B. G.; Garcia-Rosas, J.; Schneider, H. *J. Am. Chem. Soc.* **1981**, *103*, 1384.

(10) Rounaghi, G. Ph.D. Thesis, Michigan State University, East Lansing, MI 48824, 1980.

These results for C222 complexes, using direct integration of slow-exchange resonance bands, show that it is possible to use the competitive NMR method for cryptands (or any other slow-exchange system), so long as the known and unknown formation constants differ by a factor of 10^3–10^4.

D. Comparison of the Complexation of 18C6 and DA18C6. The results given above, as well as those of a series of conventional, direct competitive, and stepwise competitive NMR studies of the complexation of Na^+, K^+, Rb^+, Cs^+, Tl^+, and Ba^{2+} in AN, AC, and PC (as well as some available literature values) with 18C6 and DA18C6 are given in Tables I and II, respectively. From the values given in Tables I and II the effect on the strength of the complex formation of several factors can be deduced. First, for the complexation of 18C6 in a given solvent the complexation, as a function of the cation, follows the expected trend based on the fit of the cation into the cavity of the ligand (with Ba^{2+} forming a particularly stable complex due to the ion–dipole interactions increasing over those of the similar size 1+ cations, K^+ and Tl^+). The trend for DA18C6 is similar to that for 18C6, but it follows what would be expected for a ligand with a cavity size which is slightly smaller than that of 18C6. The formation constant for the Tl^+ ion is slightly larger due to the increased interaction of the relatively "soft" Tl^+ and the nitrogen of the DA18C6, which is softer than the analogous oxygens of 18C6.

Comparisons between solvents for a given cation and ligand should reflect the solvating ability of the solvent, with the largest formation constant associated with the weakest solvent. Gutmann donor numbers, although simplistic, have been used to characterize the solvating ability of the solvent toward cations. For the solvents at hand (Gutmann donor numbers = 14.1 (AN), 15.1 (PC), and 17.0 (AC)) we would then expect that the largest formation constant should be in AN and the smallest in AC and the value in PC should be intermediate. The values for the formation constants of the DA18C6 complexes generally follow the expected pattern, but the values for the 18C6 complexes do not seem to follow this pattern.

This is due to the neglect of the solvation of the ligand. Mosier-Boss and Popov[11] have shown that to correct for this complexation of 18C6 by AN the formation constants must be multiplied by 50 (or 1.7 must be added to log K). Mosier-Boss[12] has also shown that to perform the similar correction in AC less than 0.44 needs to be added to log K, while there are no current data for the solvation of 18C6 by PC. If the values in Table I are corrected for the solvation of the ligand, then the values in AN and AC follow precisely the expected behavior, with the behavior of PC being currently undecidable. It should be noted that these solvents do (or are expected to) solvate DA18C6, but in a manner that does not require any correction to the formation constant.

It has been shown by Frensdorff[20] that the replacement of two oxygen atoms of 18C6 by nitrogens lowered the formation constant of the potassium ion complex in methanol solution by 4 orders of magnitude (log K_f from 6.10 to 2.04) while that of the silver ion complex increased by 6 orders of magnitude (log K_f from 1.60 to 7.8). It seems that those results can be explained on the basis of the "soft–hard" acid–base concept of Pearson.[21] The hard acid K^+ interacts better with the hard base 18C6, while the softer Ag^+ prefers DA18C6.

Such an explanation does not fit our case. Comparisons of the data given in Tables I and II show that in all three solvents the potassium, rubidium, and cesium complexes with 18C6 are considerably more stable than those with DA18C6. The reverse, however, is observed with the lithium complexes, while those of sodium have, approximately, the same stability. Yet, on the "hard–soft" scale, the lithium ion has the greatest "hardness" of the alkalies and should prefer 18C6 to DA18C6. It should be noted however, that we have protons attached to the nitrogen atoms of DA18C6. These protons, when inside the cavity ("in–in" conformation) form an intramolecular hydrogen bond[15] that blocks the cavity to some extent, as shown by the space-filling model of DA18C6. This effect shows up particularly well in the comparison of the formation constant of the heavier alkali ions. For example, the ratio of the formation constants (K_f^{DA18C6}/K_f^{18C6}) in acetonitrile, propylene carbonate, and acetone is 0.83, 0.70, and 0.64 for potassium, ..., 0.54, and 0.58 for rubidium, and 0.47, 0.44, and 0.45 for cesium complexes. In this case steric considerations, therefore, seem to offer a better explanation than the "soft–hard" interaction.

Acknowledgment. The authors gratefully acknowledge the support of this work by the National Science Foundation, Grant No. CHE-8515474.

---

(11) Mosier-Boss, P. A.; Popov, A. I. *J. Am. Chem. Soc.* **1985**, *107*, 6168.
(12) Mosier-Boss, P. A. Ph.D. Thesis, Michigan State University, East Lansing, MI 48824, 1985.
(13) Dalley, N. K. In *Synthetic Multidentate Macrocyclic Compounds*; Izatt, R. M., Christensen, J. J., Eds.; Academic: New York, 1978.
(14) Smetana, A. J.; Popov, A. I. *J. Solution Chem.* **1980**, *9*, 183.
(15) Rounaghi, G.; Popov, A. I. *J. Inorg. Nucl. Chem.* **1981**, *43*, 911.
(16) Shamsipur, M.; Popov, A. I. *Inorg. Chim. Acta* **1980**, *43*, 243.
(17) Kulstad, S.; Malmsten, L. A. *J. Inorg. Nucl. Chem.* **1980**, *42*, 573.
(18) Kolthoff, I. M.; Chantooni, M. K. *Proc. Natl. Acad. Sci. U.S.A.* **1980**, *77*, 5040.
(19) Cox, B. G.; Firmen, P.; Horst, H.; Schneider, H. *Polyhedron* **1983**, *5*, 343.
(20) Frensdorff, H. K. *J. Am. Chem. Soc.* **1971**, *93*, 600.
(21) Pearson, R. G. *Hard and Soft Acids and Bases*; Dawden: Stroudsburg, PA, 1983.