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Cesium-133 NMR Studies of Crown Ether–Cs^+ Complexes in High Dielectric Amide Solvents

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Cesium-133 chemical shift and spin–lattice relaxation time measurements have been used to determine formation constants of the cesium ion complexes with 11 crown ethers, 15C5, 18C6, 21C7, DA18C6, DB18C6, DC18C6, DB21C7, DB24C8, DB27C9, DC21C7, and DC24C8, in formamide, *N*-methylformamide, dimethylformamide, and dimethylacetamide solutions. In the cases of 15C5, 18C6, DC21C7, and DC24C8, both LCs^+ and L_2Cs^+ complexes (L = crown ether) were observed; in all other systems only 1:1 complexes were formed. The formation of L_2Cs^+ complexes with DC21C7 and DC24C8 is surprising since both ligand cavities are larger than the cesium cation; previously, it was expected that only 1:1 complexes would form under such circumstances. In addition to the match between the cation diameter and ligand cavity, such factors as solvation of the complexation partners and the structure of the solvent itself affect the stability of the macrocycle–cation complexes. The selected amide solvents have similar donicities and dipole moments; in general, consistent with expectations for ion–dipole interactions, the calculated stability constants were larger in the lower dielectric constant media.

Introduction

Since the discovery of crown ethers by Pedersen in 1967,[1] several thousands of macrocyclic ligands have been synthesized, and their complexes with a variety of metal ions and with neutral molecules have been studied by a number of different physicochemical techniques. Perhaps the most fundamental thermodynamic property of a complex is its stability (in a given medium and at a given temperature), as expressed by its formation constant. In order to understand the formation of a macrocyclic complex, it is important to elucidate various factors that affect the complexation reaction equilibria.

Earlier work[2,3] indicated that one of the most important conditions influencing the stability of a macrocyclic complex is the relationship between the size of the macrocyclic cavity of the ligand and the size of the complexed ion; the better the ion adapts into the cavity, the more stable is the complex. It soon became apparent, however, that this generalization is valid only for rigid macrocyclic ligands.[4] Many other factors have been found to be important in ionic complexation reactions, in particular the solvating ability of the solvents vis-à-vis *both* the cation and the ligand, the dielectric constant of the solvent, the nature of the counter ion, etc.

In one of his classical papers Pedersen[5] has pointed out that if the size of the cation is larger than that of the macrocyclic cavity, sandwich complexes of the type $L{\cdot}M^+{\cdot}L$ (L = ligand) are formed. A number of such complexes, for example that of the cesium ion with 18C6, were isolated in the crystalline state.[5] It was soon shown[6] that such complexes also exist in solutions and that the complexation reaction occurs in two steps:

$$L + M^+ \rightleftarrows LM^+ \qquad LM^+ + L \rightleftarrows LM^+L$$

In 1985 Izatt et al. published a comprehensive compilation of some 3000 formation constants of macrocyclic complexes.[7] A careful study of these data shows that for many complexes the values of the formation constant reported by different investigators (who used a variety of physicochemical techniques) may differ by as much as 2 orders of magnitude. In many cases, reasons for such discrepancies are not obvious, and it is difficult to say a priori which value is more nearly correct.

Moreover, examination of this compilation reveals that the existence of the stepwise complexation reaction has been largely ignored in many systems where it is likely to exist and that complexation constants have been calculated on the basis of only a 1:1 complex. For example, although the stepwise complexation has been recognized for the cesium cation–18C6 system, this is not the case for many cesium complexes with *substituted* 18C6 moieties (e.g. dibenzo-18C6 or dicyclohexano-18C6). Yet the cavities of the latter ligands are no larger than that of 18C6.

In an attempt to clarify this apparent discrepancy we have studied cesium complexes with a number of crown ethers: 15C5; 18C6, dibenzo-18C6, dicyclohexano-18C6, and diaza-18C6 (Cryptofix 2.2); 21C7 and its dibenzo- and dicyclohexano- derivatives; dibenzo-24C8 and dicyclohexano-24C8; and dicyclohexano 27C9. Cavity sizes of these ligands are smaller than, equal to, or larger than the size of the cesium ion.[5] Measurements were carried out in high dielectric solvents, formamide and *N*-methylformamide, in order to minimize side effects from ion–ion interactions. For comparison, these studies were extended to similar amide solvents with lower dielectric constants, dimethylformamide and dimethylacetamide. Cesium-133 NMR measurements were used to determine the stability constants of the complexes, according to procedures previously developed in our laboratories.[8]

Experimental Section

Chemicals. Formamide (FA), *N*-methylformamide (NMF), *N,N*-dimethylformamide (DMF), and *N,N*-dimethylacetamide (DMA) (all Aldrich) were purified and dried by conventional methods[9,10] and stored in a drybox under dry nitrogen over freshly activated Linde 3-Å molecular sieves. The water content of solvents was determined by using a Varian Aerograph Model 920 gas chromatograph and was found to be always below 70 ppm. Deuterated water (KOR Isotopes) and benzene-d_6 (Aldrich) were used as received.

Cesium iodide and cesium perchlorate (both Alfa) were used as obtained, except for drying at 120 °C for 2 days. Cesium tetraphenylborate was prepared by the metathetical reaction as described by Mei[11] and then dried for 2 days under vacuum at 70 °C. Crown ethers were purified as follows: 15-crown-5 (15C5, Aldrich) was fractionally distilled under reduced pressure and dried under vacuum for 3 days; 18-crown-6 (18C6, Aldrich) was purified by converting it to the crystalline acetonitrile complex,[12] filtering the solution, and driving off acetonitrile under vacuum at room temperature for 2 days; dibenzo-18-crown-6 (DB18C6, Parish) was recrystallized twice from benzene and dried under vacuum for 3 days; dicyclohexano-18-crown-6 (DC18C6, Parish) was obtained as a mixture of isomers A (cis-syn-cis) and B (cis-anti-cis) and dried under vacuum for 3 days; diaza-18-crown-6 (DA18C6, MCB), 21-crown-7 (21C7, Parish), dicyclohexano-21-crown-7 (DC21C7, Parish), and dicyclohexano-24-crown-8 (DC24C8, Parish) were used as received

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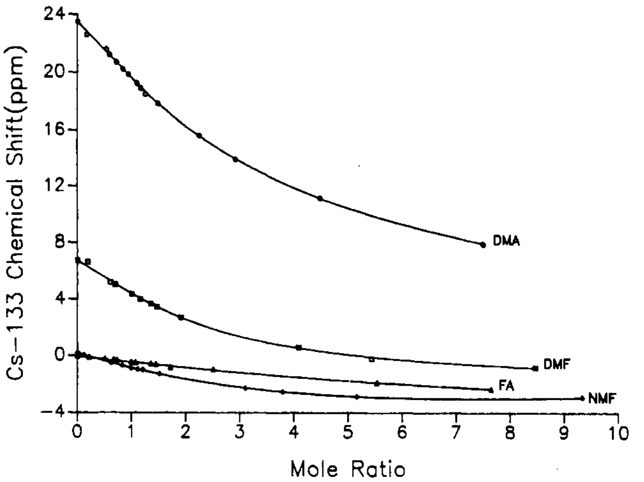

Figure 1. Cesium-133 chemical shifts vs 15C5:Cs$^+$ mole ratio in amide solutions. The solutions were 0.05 M in cesium iodide.

except for drying under vacuum for 2 days at room temperature; dibenzo-21-crown-7 (DB21C7, Parish), dibenzo-24-crown-8 (DB24C8, Parish), and dibenzo-27-crown-9 (DB27C9, Parish) were recrystallized twice from *n*-heptane and then dried under vacuum for 2 days at room temperature. The dicyclohexano derivatives were obtained as mixtures of cis isomers. All solutions were prepared and stored in a glovebox under dry nitrogen atmosphere.

NMR Measurements. Chemical Shift Measurement. Cesium-133 measurements were carried out on a Bruker WH-180 multinuclear NMR spectrometer with a field strength of 43.2 kG; at this field cesium-133 resonates at 23.62 MHz. All solutions were measured in 10-mm-o.d. tubes (Wilmad) with a 4-mm-o.d. insert (Wilmad) coaxially placed inside the larger tube. The insert contained a chemical shift reference and the lock (0.5 M CsBr in D_2O). The chemical shifts are given versus infinitely dilute aqueous solutions of cesium ions. Paramagnetic chemical shifts were taken to be positive. Since the salt concentrations were always low, the magnetic susceptibility of the solution was taken to be equal to the diamagnetic susceptibility of the solvent, as suggested by Templeman and Van Geet.[13] All chemical shift measurements were corrected for the difference in bulk diamagnetic susceptibility between the sample and the reference.[14]

T_1 Measurement. Cesium-133 relaxation times were measured by the inversion–recovery pulse sequence 180°–τ–90°, with 14–16 different values of τ.[15] Experimental data were fitted to the conventional three-parameter equation[14] by using the KINFIT nonlinear least squares program.[16]

Calculational Methods. The formation constants of 1:1 complexes were calculated from the variation of the ^{133}Cs chemical shift with the ligand:Cs$^+$ mole ratio. It has been shown previously[8] that the observed chemical shift is given by

$$\delta_{obs} = \{[(K_1C_M - K_1C_L - 1) + (K_1^2C_L^2 + K_1^2C_M^2 - 2K_1^2C_LC_M + 2K_1C_L + 2K_1C_M + 1)^{1/2}](\delta_M - \delta_{ML})/2K_1C_M\} + \delta_{ML} \quad (1)$$

where K_1 is the concentration formation constant for the 1:1 complex, C_L and C_M are the stoichiometric concentrations of the ligand and the cesium ion, respectively, and δ_M and δ_{ML} are the chemical shifts characteristic of the free and complexed cesium ion, respectively. Since cesium-133 chemical shifts of the free cesium ion depend on the concentration of the salt and on the counter ion, δ_M values were adjusted accordingly.[10,17]

When both 1:1 and 2:1 complexes are formed, the expression for the free ligand concentration is

$$C_{FL} = \frac{-(1 + K_1C_{FM}) + [(1 + K_1C_{FM})^2 + 8K_1K_2C_{FM}C_L]^{1/2}}{4K_1K_2C_{FM}} \quad (2)$$

and the observed chemical shift is given by

$$\delta_{obs} = \frac{\delta_M + K_1C_{FL}\delta_{ML} + K_1K_2C_{FL}^2\delta_{ML2}}{1 + K_1C_{FL} + K_1K_2C_{FL}^2} \quad (3)$$

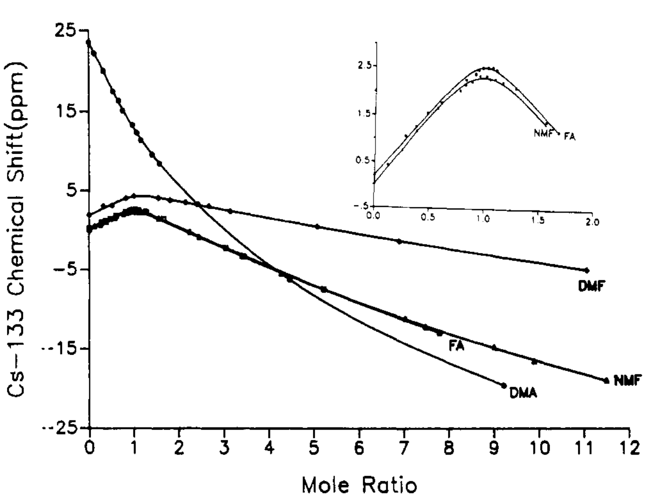

Figure 2. Cesium-133 chemical shifts vs 18C6:Cs$^+$ mole ratio in amide solutions. The solutions were 0.05 M in cesium iodide except DMF solutions, which were 0.01 M in CsI. Inset: Expanded view of titration curves in FA and NMF in the O-2 18C6:Cs$^+$ mole ratio region.

Table I. Solvent Properties and Logarithms of the Formation Constants of Cs$^+$ Ion Complexes with Nine Crown Ethers in Selected Amide Solvents at 25 °C

	solvent			
	FA	NMF	DMF	DMA
donor number	24[a]	25[b]	26.6[a]	27.8[a]
dielectric constant[c]	110.0	182.4	36.71	37.8
dipole moment[c]	3.37	3.86	3.86	3.72

	log *K*			
ligand	FA	NMF	DMF	DMA
15C5	1.14 ± 0.01	1.03 ± 0.07	0.91 ± 0.04	0.61 ± 0.03
18C6 (1:1)	3.3 ± 0.1	2.9 ± 0.1	>4[d]	2.7 ± 0.3
18C6 (2:1)	−0.4 ± 0.1	0.04 ± 0.02	0.37 ± 0.01	0.40 ± 0.02
21C7	2.81 ± 0.08	2.5 ± 0.2	3.61 ± 0.06	3.19 ± 0.06
DA18C6	0.2 ± 0.1	0.07 ± 0.04	0.61 ± 0.07[e]	0.4 ± 0.1
DC18C6	*f*	1.7 ± 0.1	3.5 ± 0.1[g]	3.26 ± 0.07
DB18C6	$K \approx 0$	$K \approx 0$	1.48 ± 0.04[g]	1.2 ± 0.2
DB21C7	*f*	2.36 ± 0.04	2.84 ± 0.1[h]	2.76 ± 0.07
DB24C8	*f*	2.24 ± 0.09	2.10 ± 0.04[h]	2.08 ± 0.03
DB27C9	*f*	2.6 ± 0.1	2.20 ± 0.01[h]	2.14 ± 0.08

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where K_2 is the equilibrium constant of the second step, δ_{ML2} is the chemical shift of the 2:1 complexed metal ion, C_{FL} and C_{FM} are the concentrations of free ligands and free metal ions, respectively, and the other symbols are as previously defined. During the fitting process, the polynominal for the free-ligand concentration (eq 2) is solved and the chemical shift is calculated (eq 3) for each trial set of unknown parameters. Then adjustments of unknown parameters are made until the sum of the squares of the differences between the calculated and experimentally determined chemical shifts is minimized.

Results and Discussion

A. 15C5, 18C6, and 21C7. Complexation reactions between the cesium cation and the unsubstituted crown ethers 15C5, 18C6, and 21C7 were studied in the selected amide solvents by cesium-133 NMR. The chemical shifts as a function of the ligand:cation mole ratio are shown in Figures 1–3. Stability constants were determined as described in the Experimental Section;

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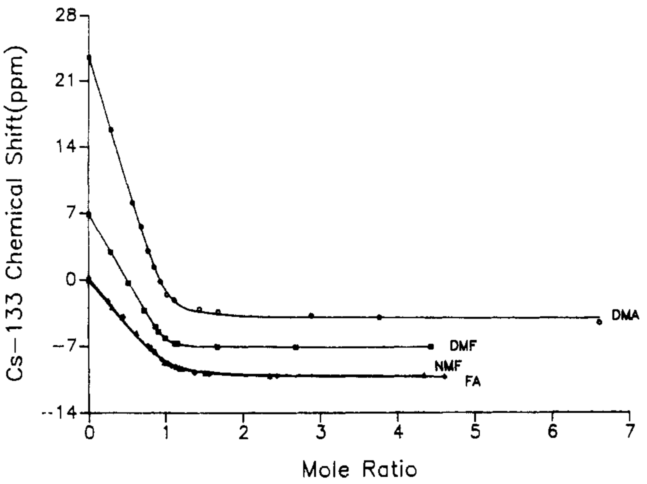

Figure 3. Cesium-133 chemical shifts vs 21C7:Cs^+ mole ratio in amide solutions (0.05 M CsI).

Table II. Limiting Chemical Shifts (ppm) of Cs^+ Complexes with 15C5, 18C6, and 21C7

	solvent			
ligand	FA	NMF	DMF	DMA
15C5	-7.0 ± 0.6	-3.9 ± 0.2	-3.5 ± 0.1	-3.5 ± 0.9
18C6 (1:1)	3.0 ± 0.1	3.1 ± 0.1	3.29 ± 0.07	11.7 ± 0.5
18C6 (2:1)	-43 ± 29	-46 ± 38	-47.5 ± 0.4	-52 ± 1
21C7	-10.3 ± 0.1	-10.4 ± 0.3	-7.14 ± 0.04	-4.1 ± 0.1

the results are listed in Table I, and limiting chemical shifts, determined by the computer fit, are given in Table II.

Analysis of the titration curves for 15C5 complexes indicates that both LCs^+ and L_2Cs^+ complexes are formed in all four solvents. However, as seen in Table I, 1:1 complexes are already rather unstable, and the equilibrium constants for the second complexation step are too small to be determined by our technique. (When methanol, a solvent with a lower dielectric constant and weaker solvating power, is used and where stable 15C5–Cs^+ complexes are formed, the 2:1 complexation constant is an order of magnitude smaller than that of the 1:1 complex.[18])

In the 18C6–Cs^+ system, as expected, analysis of the titration curves indicates the presence of 1:1 and 2:1 complexes. In FA and NMF solutions, when the 1:1 mole ratio is reached (Figure 2, inset), the titration curve changes direction from downfield to upfield. This behavior unambiguously indicates a stepwise complexation reaction.[19] The titration curve in DMF (where a lower Cs^+ concentration was employed) provides a similar but a somewhat less striking example. In DMA solutions, the change in curvature is monotonic, but the computer fitting of the data gives much better results when the model includes both complexes. The difference between log K_1 and log K_2 of about 3 in each solvent (Table I) is consistent with previously reported results[3,20] in methanol. From Table II, it is seen that the values of the chemical shifts for the 2:1 complex are closely grouped; this indicates that the cation is effectively insulated from the solvent, as would be expected for a 2:1 sandwich complex.

Crown ether 21C7 has a cavity with dimensions close to that of the cesium ion [21C7, 3.4–4.3 Å, depending on molecular model type;[5] Cs^+, 3.38 Å (Pauling scale)]. As expected, therefore, only the 1:1 complex was observed. In all studied solvents, the variation of the chemical shift with the L:Cs^+ mole ratio was monotonic and the data could not be fitted to a stepwise complexation reaction. The selectivity of 21C7 for the Cs^+ ion has been previously noted.[20,21]

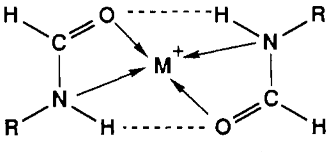

Figure 4. Proposed chelate structure of the M^+ $(HCONHR)_2$ complex. M^+ = alkali-metal ions. R = H, CH_3.

It is interesting to note that the chemical shift of uncomplexed cesium ion is essentially the same in formamide and *N*-methylformamide solutions. Therefore, the electronic environment of the cesium ion in these two hydrogen-bonding solvents is very nearly the same, but is quite different from that in dimethylformamide and dimethylacetamide (see, for example, Figure 1). Moreover, the addition of a given amount of a crown ether produces very similar chemical shifts, and in the case of 18C6 and 21C7 in FA and NMF, the titration curves very nearly overlap (Figures 2 and 3).

In 1983, Bukowska reported[22] that Raman and infrared studies of lithium and sodium perchlorate solutions in NMF indicate that stable 2:1 *solvent–cation* complexes are formed. The proposed schematic structure is given in Figure 4. Assuming the structure to be correct, one would expect that the electronic environment of the cation must be nearly the same whether the solvent is FA or NMF, and therefore the ^{133}Cs chemical shift must also be nearly the same. It also follows that upon addition of either crown ether very similar changes in the environment of the cation must occur, leading to the overlap of titration curves.

Since the cavity of the crown ether 21C7 matches particularly well the size of the cesium ion, a stable 1:1 cesium complex should be formed in all of our solvents. The results confirm this expectation. Somewhat surprisingly, except in DMA solutions, the stability constants were found to be slightly smaller than those for the 1:1 complex with 18C6 (Table I). Gokel et al.[4] have reported that, in methanol solution of the simple crown ethers, 18C6 most strongly binds Na^+, K^+, NH_4^+, and Ca^{2+} ions. Of course it is not really proper to compare equilibrium constants for one-step and two-step complexation reactions. Moreover, the differences in the two sets of formation constants are quite small (Table I) and are close to the calculated experimental errors. Nonetheless, our results demonstrate again that the hole-size criterion for complex stability is not dominant for Cs^+ complexes with unsubstituted crown ethers.

B. DA18C6, DB18C6, and DC18C6. Unlike 18C6, all substituted 18-crown-6 polyethers studied here show only 1:1 LCs^+ complexes in our amide solvents. The calculated values of log *K* are generally rather low.

Replacement of two oxygen atoms in the 18C6 ring by two NH groups to form DA18C6 lowers the stability of the cesium complex. Similar results have been observed by Frensdorff for potassium complexes in methanol solutions.[6] An amine nitrogen is a softer base than the ether oxygen, and its interaction with a hard acid, Cs^+, is weak. The results are shown in Table I.

Dibenzo-18-crown-6 is more rigid than the unsubstituted crown ether, and thus the stability of cation complexes decreases. The cavity size of DB18C6 is somewhat smaller than that of 18C6; if the size relationship were the governing factor, both 1:1 and 2:1 cesium complexes should be formed. However, as seen in Table I, no measurable complexation occurs in FA and NMF solutions, and the 1:1 formation constants calculated in the other two solvents are small. If 2:1 complexes exist in these solvents, the values of K_2 are likely to be too small[7] to be measurable by our methods. It should be noted that Frensdorff did observe[6] potentiometrically 1:1 and 2:1 complexes in the DB18C6–Cs^+ system in methanol, with log K_1 = 3.55 and log K_2 = 2.92.

The case of DC18C6 (mixture of cis isomers), which is more flexible than DB18C6, seems to be somewhat more complicated. A weak 1:1 complex is formed in NMF solutions. Measurements could not be carried out in FA due to the insolubility of the ligand

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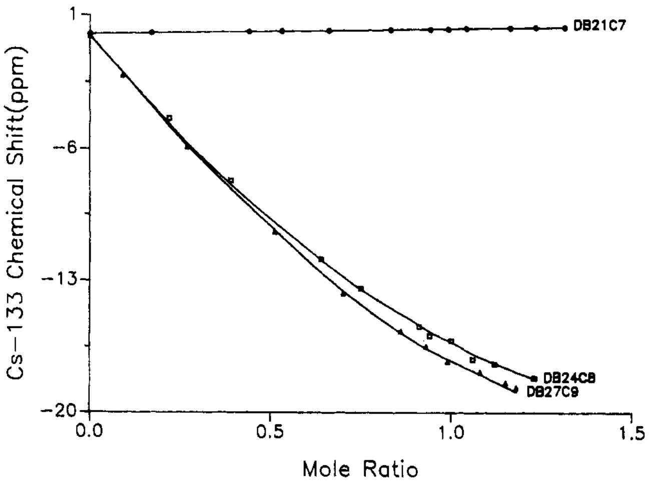

Figure 5. Cesium-133 chemical shifts vs ligand:Cs^+ mole ratio in NMF solutions. Ligands = DB21C7, DB24C8, and DB27C9 (0.05 M CsI).

Table III. Spin–Lattice Relaxation Times for Free and Complexed Cesium Ion in NMF Solutions

solution	T_1, s	solution	T_1, s
0.05 M CsI	1.27	0.01 M $CsBPh_4$	1.08
0.05 M CsI + 0.5 M DB21C7	2.73	0.01 M $CsBPh_4$ + 0.1 M DB21C7	2.68

in this solvent. On the other hand, the formation constants in DMF and DMA are fairly large; however, as was the case with 21C7, the stepwise complexation reaction is ruled out by the analysis of our data. The nature of solute–solvent interactions clearly has an effect on the DC18C6–Cs^+ equilibrium. Weak 1:1 complexes are formed in high dielectric constant solvents with moderate donor numbers (e.g. NMF); strong 1:1 complexes are formed when the dielectric constant is lower (e.g. DMF); in less polar solvents (e.g. methanol), both 1:1 and 2:1 complexes are observed: $\log K_1 = 4.25$; $\log K_2 = 2.84$.[18]

C. DB21C7, DB24C8, and DB27C9. With these large ligands, one would not expect the formation of sandwich complexes with the cesium ion, and indeed in NMF and DMA solutions only a fairly stable 1:1 complex is found. Measurements could not be carried out in FA since all three ligands are insoluble in this solvent. Previously obtained results in DMF solutions[23] are consistent with those obtained in this investigation and are given for comparison in Table I. The cesium ion should fit particularly well in the cavity of DB21C7, and the value of $\log K_1$ for this member of the dibenzo crown series is in fact the highest, not only in the solvents of Table I but also (via calorimetric titration) in methanol.[20]

Titration curves for the Cs^+ ion with DB21C7, DB24C8, and DB27C9 in NMF are shown in Figure 5. A curious behavior was observed in the case of DB21C7. The usual mole ratio plot gave a horizontal line, which should indicate the absence of any interaction between the cation and the ligand. Since this result, although perfectly reproducible, was completely unexpected, the spin–lattice relaxation time was calculated from measured NMR line shapes for the free cesium ion and the ion in the presence of a 10-fold excess of the ligand. The data, given in Table III, clearly indicate cation–ligand interaction. Mole ratio studies were then carried out with cesium perchlorate and tetraphenylborate instead of cesium iodide. In both cases, a normal titration curve was obtained (Figure 6); the average value of the logarithm of the formation constant calculated from those data is 2.36 ± 0.04.

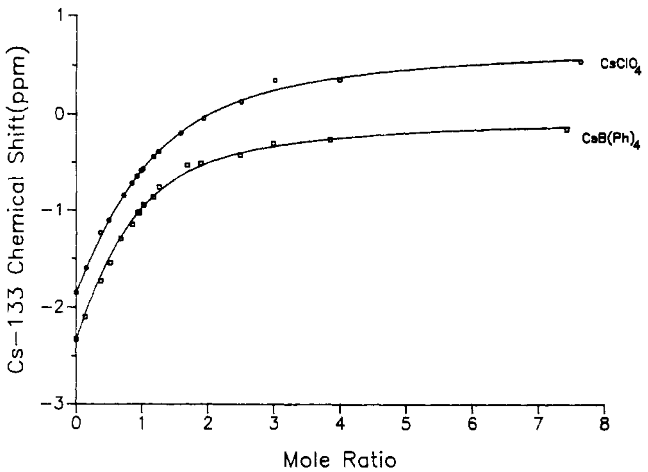

Figure 6. Cesium-133 chemical shifts vs. DB21C7:Cs^+ mole ratio in NMF solutions. The solution was 0.01 M in cesium perchlorate or 0.01 M in cesium tetraphenylborate.

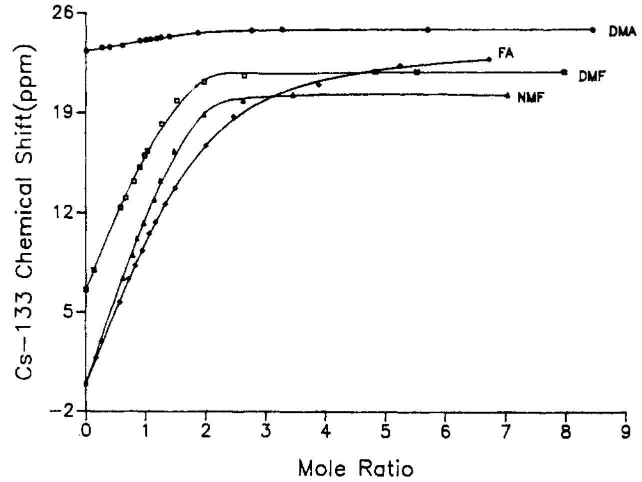

Figure 7. Cesium-133 chemical shifts vs. DC21C7:Cs^+ mole ratio in amide solutions (0.05 M CsI).

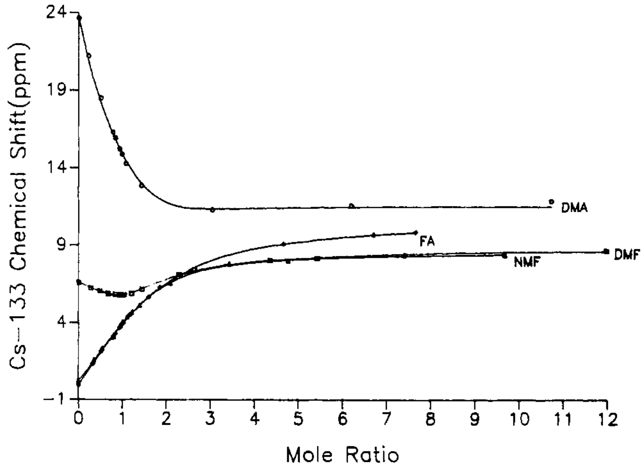

Figure 8. Cesium-133 chemical shifts vs. DC24C8:Cs^+ mole ratio in amide solutions. The solutions were 0.05 M in cesium iodide.

We have shown previously[10] that due to collisional interactions in solution, ^{133}Cs chemical shifts are concentration and anion dependent. With increasing concentration of the salt, the shift moves downfield for CsI and upfield for $CsClO_4$ and $CsBPh_4$. It seems, therefore, that the horizontal plot obtained with cesium iodide is due to an accidental coincidence between the ^{133}Cs chemical shift of 0.05 M CsI and the DB21C7–Cs^+ complex.

D. DC21C7 and DC24C8. Titration curves for Cs^+ with DC21C7 and DC24C8 in the chosen solvents are reproduced in Figures 7 and 8. In contrast to the dibenzo derivatives of large crowns, analysis of the data for DC21C7 and DC24C8 unambiguously reflects the formation of 1:1 and 2:1 complexes. In fact, the DC24C8–Cs^+ system in DMF solution shows a distinct minimum in the titration curve at 1:1 mole ratio (Figure 8). While in other systems curvatures change monotonically, the experi-

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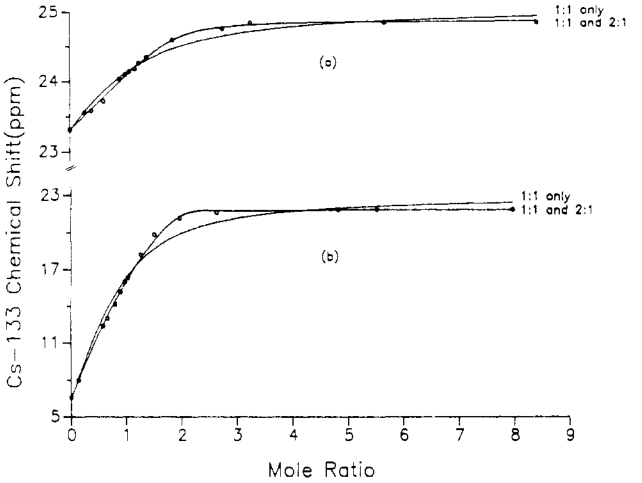

Figure 9. Computer fits of the calculated to the observed cesium-133 chemical shifts in (a) DMA and (b) DMF with added DC21C7. Calculations were based on the formation of only 1:1 complexes and on the formation of both 1:1 and 2:1 (DC21C7:Cs^+) complexes. Note the different ordinate scales for parts a and b.

Table IV. Logarithms of the Formation Constants and the Limiting Chemical Shifts (ppm) of Cs^+ Complexes with DC21C7 and DC24C8 at 25 °C

solvent	$\log K_1$	$\log K_2$	δ (1:1)	δ (2:1)
		Cs^+-DC21C7		
FA	2.4 ± 0.3	1.51 ± 0.03	11.5 ± 0.8	24.2 ± 0.2
NMF	>4	2.8 ± 0.3	13 ± 1	20.4 ± 0.3
DMF	>4	3.1 ± 0.5	18 ± 1	21.9 ± 0.1
DMA	>4	2.2 ± 0.2	24.08 ± 0.03	24.88 ± 0.03
		Cs^+-DC24C8		
FA	2.0 ± 0.2	1.23 ± 0.02	5.4 ± 0.5	10.8 ± 0.1
NMF	2.6 ± 0.5	1.67 ± 0.06	4.5 ± 0.5	8.63 ± 0.08
DMF	3.2 ± 0.2	1.37 ± 0.05	5.4 ± 0.1	8.86 ± 0.06
DMA	3.0 ± 0.4	1.9 ± 0.3	12.6 ± 0.6	11.4 ± 0.1

mental data clearly better fit the two-step reaction. This is illustrated in Figure 9 for the DC21C7–Cs^+ system in (a) DMA and (b) DMF.

As seen in Table IV, the limiting chemical shifts of the 2:1 complexes do not differ significantly among the solvents utilized, thus providing further indication of the sandwich structure of these species. Their numerical values differ, reflecting the different chemical environments of the Cs^+ in the two L_2Cs^+ complexes; however, the ~10 ppm difference is small relative to the broad span of cesium-133 chemical shifts. Formation constants of the complexes, also given in Table IV, show that both 1:1 and 2:1 complexes are reasonably stable.

These results are very much at variance with previous results from our and other laboratories.[7] With the sole exception of $(DB21C7)_2Cs^+$ reported by Frensdorff in methanol solutions,[6] sandwich complexes have not been observed in solutions when the size of the cation is equal to or smaller than that of the crown ether cavity. (The diameter of Cs^+ is 3.38 Å; cavity sizes of DC21C7 and DC24C8 are 3.4–4.3 and >4 Å respectively.[5])

Dicyclohexano crown ethers are much more flexible than their dibenzo analogs. The rather stable 1:1 complexes of Cs^+ with DC21C7 and DC24C8 likely form with rather open conformations of the macrocyclic ring. In both cases, molecular models clearly demonstrate that more puckered conformations (with smaller ring cavities) can be taken by the various cis isomers in which four proximal oxygen atoms point above the ring, with the remainder below. Such conformations would readily permit formation of sandwich complexes with Cs^+, the cation being coordinated with four oxygen atoms on each macrocycle and the rings skewed in relation to one another to form a snug cavity, which would maximize the ion–ligand interaction. Attempts to isolate single crystals of these 2:1 complexes unfortunately have proven unsuccessful.

Conclusions

The hitherto unsuspected formation of 2:1 sandwich complexes in cases where $r_{\text{cation}} < r_{\text{ligand}}$ necessitates review of literature values of many formation constants of crown ether–alkali-metal cation complexes that were determined under the assumption that the above condition precluded the second complexation step.

Our results confirm previous observations that while the consonance between the sizes of the ligand cavity and that of the cation has an important influence on the stability of a cation–ligand complex, it is only one of several important factors that determine the extent of the reaction. Certainly ligand–solvent interaction is also an important factor. Since the formation of crown ether complexes results from an ion–dipole interaction,[24] it is not surprising that the dielectric constant of the medium also affects the extent of the complexation reaction. In fact our results show that in solvents with high dielectric constant, formamide and *N*-methylformamide, the complexes are generally less stable than in the other two solvents. On the other hand, all four solvents have very similar dipole moments and similar donicities, and these factors should similarly affect complexation constants.

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Kinetics of Dissociation of Thorium(IV) Bound to PMA and PMVEMA

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The kinetics of dissociation of Th(IV) from its complexes with polymaleic acid (PMA) and poly(methyl vinyl ether)maleic acid (PMVEMA) were found to follow rate expressions that reflected seven separate terms ranging in lifetimes between 0.1 s and almost 1 h. The fraction of thorium dissociating by any one of the seven paths depended on the length of time during the first 2 days that the thorium had been bound to the polyelectrolyte prior to dissociation. After 48 h of binding, no further change was observed in the dissociation kinetics. These observations are interpreted in terms of the present models of metal–polyelectrolyte interaction.

Introduction

The binding of metal ions to polyelectrolytes has been described by a two-state model. In the "site-bound" state the cations are in direct contact with one or more charged groups of the polyelectrolyte. This binding is analogous to inner-sphere complexation in coordination chemistry. The second type of interaction has been called "atmospheric", "territorial", "condensed", and "delocalized" binding. In this state, the cations are associated generally with

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