

Nuclear Magnetic Resonance Studies of Some Sodium Ion Complexes with Crown Ethers and [2]Cryptands in Various Solvents

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Abstract: Sodium-23 and carbon-13 NMR were used to study sodium ion complexes with crown ethers 15C5, B15C5, and 18C6 as well as cryptands C211, C221, C222, and C222B in water and in a number of nonaqueous solvents. The stabilities of the complexes varied in the order $\text{Na}^+ \cdot 18\text{C}6 > \text{Na}^+ \cdot 15\text{C}5 > \text{Na}^+ \cdot \text{B}15\text{C}5$. In most cases the cationic exchange between the free and complexed sites was rapid. However, in the $\text{NaBPh}_4 \cdot 18\text{C}6$ -THF and $\text{NaBPh}_4 \cdot 18\text{C}6$ -dioxolane systems the exchange was slow enough to observe two ^{23}Na resonances in solutions containing an excess of the sodium salt. Two signals merged when NaBPh_4 was replaced by NaClO_4 or NaI . In all solvents studied the four cryptands formed stable complexes with the sodium ion. The limiting chemical shifts showed some solvent dependence in the 30 to -70°C temperature range. The chemical shift of the complexed sodium ion moved downfield in the order $\text{Na}^+ \cdot \text{C}222 < \text{Na}^+ \cdot \text{C}222\text{B} < \text{Na}^+ \cdot \text{C}221 < \text{Na}^+ \cdot \text{C}211$.

During the past several years we and others have shown^{1,2} that multinuclear NMR is a very powerful (although not ideal) technique for the studies of alkali complexes with macrocyclic ligands, particularly in nonaqueous solutions. In this paper we report the use of sodium-23 NMR (as well as some ^{13}C measurements) for a study of the sodium ion complex with three crown ethers, 18-crown-6 (18C6), 15-crown-5 (15C5), and monobenzo-15-crown-5 (B15C5), as well as with cryptands C211, C221, C222, and monobenzo-C222 (Figure 1) in water and in several nonaqueous solvents (Table I), which have been selected so as to cover a broad range of dielectric constants and donor abilities.

Experimental Section

A. Reagents. Sodium salts used in this study were of reagent grade quality and were not further purified before use except for drying. Sodium tetraphenylborate (J. T. Baker) was dried under vacuum at 50°C for 3 days. Sodium perchlorate, iodide (Matheson Coleman and Bell), and chloride (J. T. Baker) were dried at 110°C for 3 days. Tetra-butylammonium iodide (TBAI, Aldrich) was recrystallized first from water and then from a 9:1 ethylacetate:95% ethanol mixture. The purified product was dried under vacuum at 50°C for 3 days.

Macrocyclic polyether 18-crown-6 (Aldrich) was twice recrystallized from acetonitrile and dried under vacuum at $\leq 40^\circ\text{C}$ for 3 h and then at room temperature. The purified product melted at $37\text{--}38^\circ\text{C}$ (lit. $39\text{--}40^\circ\text{C}$). Macrocycle 15-crown-5 (Aldrich) is a liquid; it was purified by a vacuum distillation and dried under vacuum over Drierite at room temperature. Dibenzo-18C6 (Parish) was recrystallized twice from benzene and dried under vacuum over Drierite at room temperature, mp $165\text{--}166^\circ\text{C}$ (lit.³ mp 164°C). Monobenzo-15C5 was synthesized following Pedersen's method³ by M. Shamsipur in this laboratory. It was recrystallized twice from *n*-heptane and dried under vacuum over Drierite at room temperature, mp $79\text{--}80^\circ\text{C}$ (lit.³ mp $79\text{--}79.5^\circ\text{C}$).

Cryptands C222, C221, C211, and C222B (Figure 1) were obtained from the EM Laboratories. The first compound is a solid at room temperature. It was recrystallized twice from hexane and dried under vacuum at room temperatures over Drierite, mp 69°C (lit.⁴ mp $65\text{--}69^\circ\text{C}$). Other cryptands are viscous liquids and, except for drying, were used as received.

Acetonitrile (MeCN), dimethyl sulfoxide (Me_2SO), nitromethane (MeNO_2), propylene carbonate (PC), pyridine (Py), and acetone (Me_2CO) were purified by previously outlined procedures.⁵ Tetrahydrofuran (THF) was refluxed over metallic potassium and benzophenone for 24 h and then fractionally distilled; 1,3-dioxolane (DiOx) was refluxed over calcium hydride and then fractionally distilled. The same procedure was followed for dimethylformamide (DMF) except that the solvent was refluxed under reduced pressure.

(1) Popov, A. I. *Pure Appl. Chem.* **1979**, *51*, 101 and references listed therein.

(2) Laszlo, P. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 254.

(3) Pedersen, C. J. *J. Am. Chem. Soc.* **1967**, *89*, 2495, 7017.

(4) Dietrich, B.; Lehn, J.-M.; Sauvage, J.-P.; Blanzat, J. *Tetrahedron* **1970**, *92*, 4989.

(5) Smetana, A. J.; Popov, A. I. *J. Solution Chem.* **1980**, *9*, 183.

Table I. Solvents Used in the Study

solvent	dielectric constants	donor values ^a
pyridine	12.4	33.1
water	78.5	33.0
dimethyl sulfoxide	46.7	29.8
<i>N,N</i> -dimethylformamide	36.7	26.6
tetrahydrofuran	7.6	20.0
1,3-dioxolane	—	—
acetone	20.7	17.0
propylene carbonate	65.0	15.1
acetonitrile	37.5	14.1
nitromethane	35.9	2.7

^a Reference 22.

The water content of all solvents, except acetone, was measured with a Karl Fischer automatic titrator (Photovolt Aquatest II) and was always found to be less than 100 ppm. The water content of acetone was also less than 100 ppm as measured by gas chromatography. Deuterated $\text{Me}_2\text{SO}-d_6$ (Stohler Isotope Chemicals) was used as received.

Nuclear magnetic resonance measurements were usually carried out on 0.050 M solutions of sodium tetraphenylborate. If the salt was insufficiently soluble in a given solvent to yield a solution of the above concentration, either sodium iodide or sodium perchlorate solutions were used.

B. Instrumentation. Most of the sodium-23 NMR measurements were obtained with a Varian DA-60 spectrometer operating at a field of 14.09 kG and a frequency of 15.871 MHz in the pulsed Fourier transform mode. The spectrometer is equipped with a wide-band probe capable of multinuclear operation⁶ and with a homebuilt lock which used the DA-60 console to lock the magnetic field on an external proton resonance. Some sodium-23 NMR data were obtained with a Bruker HFX-90 spectrometer operating at a field of 21.14 kG and a frequency of 23.81 MHz in the pulsed Fourier transform mode. A 3.0 M aqueous sodium chloride solution was used as an external reference and the reported sodium-23 chemical shifts are referred to this solution. The reported data were also corrected for the differences in bulk diamagnetic susceptibilities between the sample and reference solution.⁷ The paramagnetic (downfield) shift from the reference is designated as positive.

Carbon-13 NMR measurements were performed on a Varian CFT-20 spectrometer operating at a field of 18.68 kG and a frequency of 20.0 MHz in the pulsed Fourier transform mode. The sample solution was placed in an 8 mm o.d. NMR tube which was coaxially centered in the 10 mm o.d. NMR tube containing a mixture of the reference and lock solvents (50% v/v acetone: D_2O). The methyl carbon resonance of acetone was used as the external reference. All carbon-13 chemical shifts were corrected for the differences in bulk diamagnetic susceptibilities of solvents and referred to the internal Me_4Si resonance in acetone. The

(6) Traficante, D. D.; Simms, J. A.; Muleay, M. J. *Magn. Reson.* **1974**, *15*, 484.

(7) Live, D. H.; Chan, S. I. *Anal. Chem.* **1970**, *42*, 791.

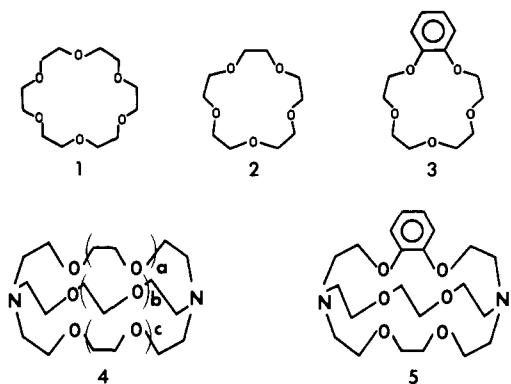


Figure 1. Macrocyclic ligands used in this investigation: (1) 18C6; (2) 15C5; (3) B15C5; (4) $a = b = c = 1$, C222, $a = b = 1$, $c = 0$, C221, $a = 1$, $b = c = 0$, C211; (5) C222B.

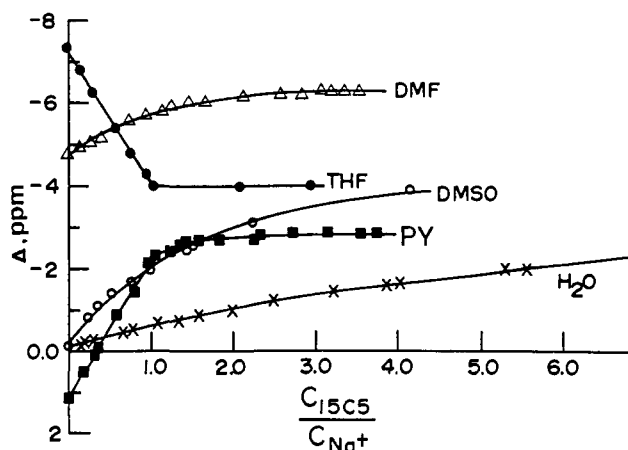


Figure 2. The variation of the ^{23}Na chemical shift as a function of $15\text{C}5/\text{Na}^+$ mole ratio in water, pyridine, dimethyl sulfoxide, tetrahydrofuran, and dimethylformamide solutions.

paramagnetic (downfield) shifts are designated as positive.

Results and Discussion

A. Crown Ethers. The variation of the sodium-23 resonance frequency was measured in different solvents as a function of the ligand/ $[\text{Na}^+]$ mole ratio and the results are shown in Figures 2–5. With one exception (discussed below) only one population-averaged signal was observed, indicating a fast exchange of the metal ion between the two cationic sites.

In general the behavior of the chemical shift as a function of the ligand/cation mole ratio can be approximately divided into three groups:

1. An increase in the ligand concentration *gradually* shifts the ^{23}Na resonance upfield and the chemical shift does not seem to reach a limiting value even at fairly high values of the mole ratio. A typical example is the behavior of the $\text{Na}^+\cdot 15\text{C}5$ systems in water and in DMF (Figure 2) and it is indicative of the formation of a weak complex. It is only observed in strongly solvating solvents such as water, Me_2SO and DMF.

2. The chemical shift (paramagnetic or diamagnetic) varies linearly with the mole ratio until the mole ratio of 1:1 is reached; further addition of the ligand does not change the resonance frequency. Such behavior is observed for the $\text{Na}^+\cdot 18\text{C}6$ system in THF and Me_2CO solutions (Figure 4) and it indicates the formation of a stable 1:1 complex. It usually occurs in solvents of medium and low donicity.

3. In some cases the chemical shift varies linearly with the mole ratio between mole ratios of 0 and 1, but a further addition of the ligand causes a reversal in the direction of the chemical shift. Such behavior is clearly seen for the $\text{Na}^+\cdot 15\text{C}5$ and $\text{Na}^+\cdot \text{B}15\text{C}5$ systems in nitromethane solutions (Figures 3 and 4). It clearly implies a two-step reaction, the formation of a stable $\text{Na}\cdot\text{L}$ complex followed by the addition of a second ligand molecule to give a

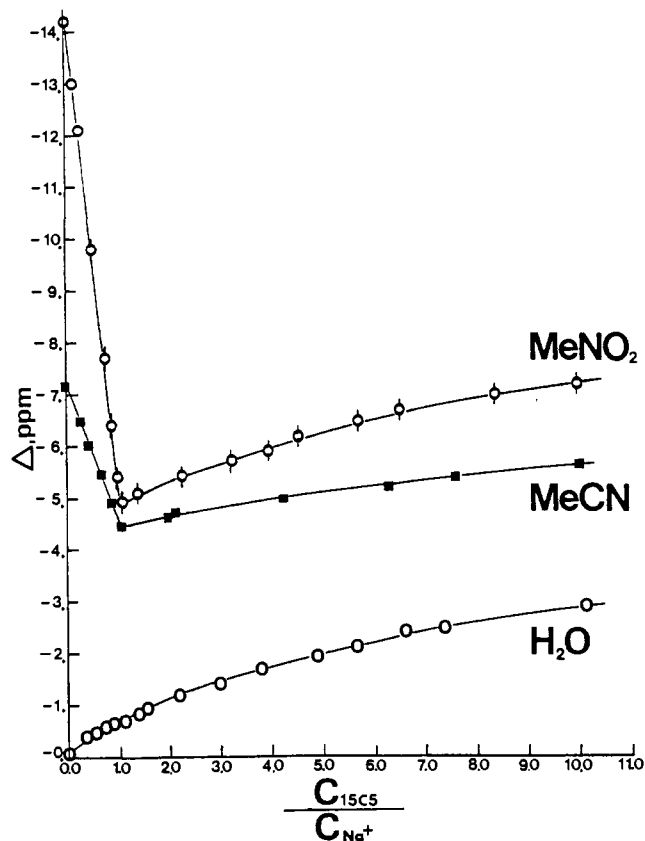


Figure 3. The variation of the ^{23}Na chemical shift as a function of $15\text{C}5/\text{Na}^+$ mole ratio in water, acetonitrile, and nitromethane solutions.

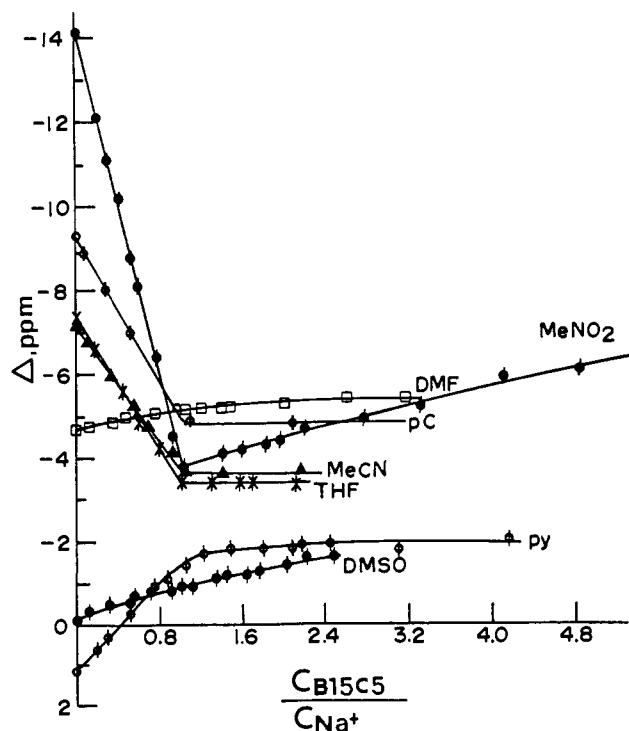


Figure 4. The variation of the ^{23}Na chemical shift as a function of $\text{B}15\text{C}5/\text{Na}^+$ mole ratio in seven nonaqueous solvents.

sandwich $\text{Na}\cdot\text{L}_2$ complex. It usually occurs in cases where the ring size is smaller than the cationic diameter and in solvents with low solvating ability. It has been previously observed for the $\text{Cs}^+\cdot 18\text{C}6$ system in several solvents⁸ as well as for $\text{Li}^+\cdot 12\text{C}4$

Table II. Formation Constants and Limiting ^{23}Na and ^{13}C Chemical Shifts of Na-Crown Complexes in Various Solvents

solvent	18C6		15C5		B15C5	
	$\log K_f$	δ_{lim}	$\log K_f$	δ_{lim}	$\log K_f$	δ_{lim}
H ₂ O	0.82 ± 0.05	-10.2 ± 0.3	0.44 ± 0.05	-5.1 ± 0.3		
THF	>4	-17.0 ± 0.3	>4	-4.4 ± 0.2	>4	-3.8 ± 0.3
Me ₂ CO	>4	-16.4 ± 0.3				^c
PC	>4	-16.1 ± 0.3	^c	-5.9 ± 0.3	^c	-5.2 ± 0.6
MeNO ₂	>4	-16.7 ± 0.3	$\log K_1 > 4; K_2 = 1.6 \pm 0.2$	-11.1 ± 0.6^b	$\log K_1 > 4; K_2 = 0.8 \pm 0.3$	^c
MeCN	3.8 ± 0.2	-15.3 ± 0.3	>4 ^d	^c	>4	-4.1 ± 0.2
Py	>3 ^d	70.0 ± 0.1^e	2.68 ± 0.08	-3.2 ± 0.2	2.6 ± 0.1	-2.4 ± 0.3
Me ₂ SO	1.41 ± 0.07^d	70.4 ± 0.1^e	1.31 ± 0.06	-5.3 ± 0.3	1.1 ± 0.2	-3.2 ± 0.6
DMF	2.31 ± 0.05^d	70.4 ± 0.1^e	1.97 ± 0.05	-6.8 ± 0.2	1.6 ± 0.1	-6.0 ± 0.3

^a While a 2:1 complex is formed, the K_2 is too small to be determined by our technique. ^b Limiting chemical shift of the 2:1 complex. ^c Could not be determined accurately. ^d Obtained with ^{13}C NMR. ^e ^{13}C chemical shifts.

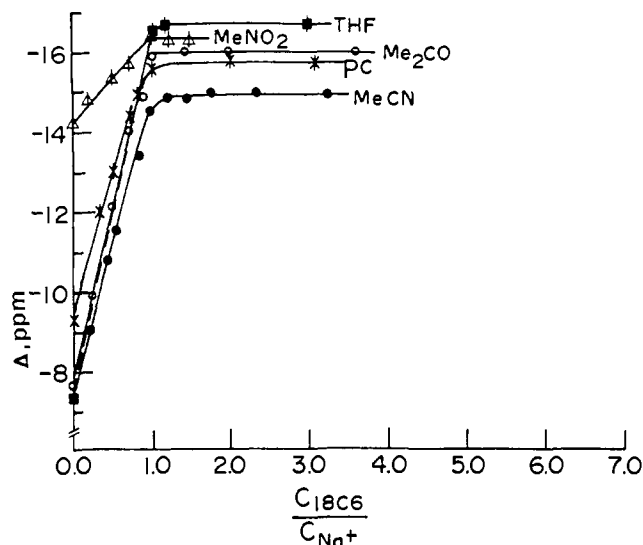


Figure 5. The variation of the ^{23}Na chemical shift as a function of 18C6/ Na^+ mole ratio in five nonaqueous solvents.

system in nitromethane and propylene carbonate solutions.⁵

The successive formation of the 1:1 and 2:1 complex is also indicated by the variation of the half-height line width with the ligand/cation mole ratio (Figure 6). The line width increases rapidly to the mole ratio of one and then decreases as more and more ligand is added to the Na^+ ion solution. This variation strongly indicates that, as expected, the electrical field gradient around the Na^+ ion is much more symmetrical in the 2:1 "sandwich" complex than in the 1:1 complex.

The formation constants of the 1:1 complex were obtained from the variation of the observed chemical shift with the ligand/ Na^+ mole ratio. The procedure has been described in previous publications.⁹ It should be noted that the method generally becomes unreliable for very stable complexes ($K_f > 10^5$).

In the cases where both 1:1 and 2:1 complexes are formed, the linear portion of the curve between mole ratios of 0 and 1 denotes a very stable 1:1 complex whose formation constant usually cannot be determined by our technique. An upper limit of K_{f2} , i.e., the equilibrium constant for the second step of the complexation reaction, was calculated on the assumption that due to the stability of the first complex, solutions with ligand/ Na^+ mole ratios greater than one contain negligible amounts of uncomplexed Na^+ ion, i.e., that the observed chemical shift is due to a rapid exchange of the sodium ion between only two sites, $\text{Na}^+\cdot\text{L}$ and $\text{Na}^+\cdot\text{L}_2$. The results of these calculations are shown in Table II.

Complexation of the Na^+ ion by 18C6 in Py, DMF, and Me₂SO solutions broadened the ^{23}Na resonance to the point where precise measurements of the chemical shifts were impossible with our

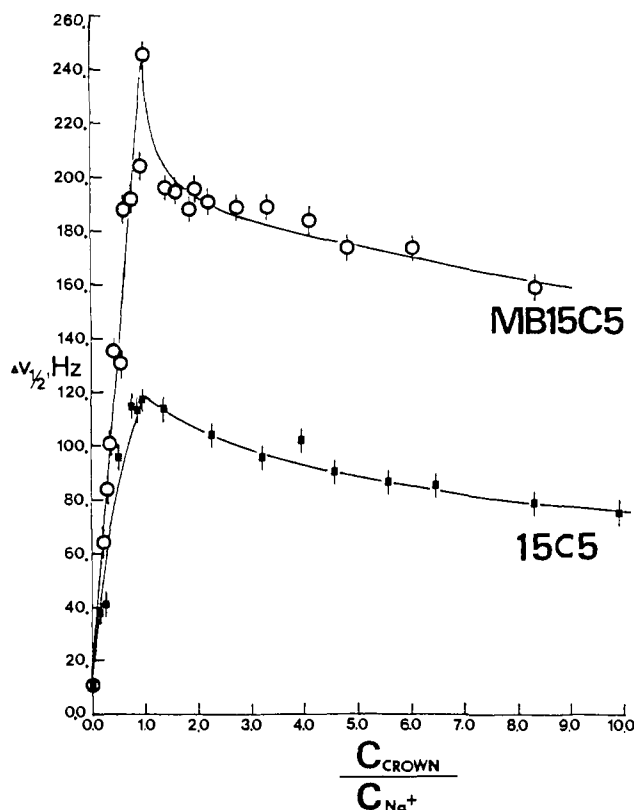


Figure 6. The variation of the ^{23}Na resonance line width at half-height with the crown/ Na^+ mole ratio in nitromethane solutions. The solutions were 0.05 M in NaBPh_4 .

instrumentation. Therefore, carbon-13 NMR was used to study the complexation reaction in these three solvents. Here again the formation constants and the limiting chemical shifts were measured by a previously described technique⁹ and the results are included in Table II. A comparison of this technique with that of ^{23}Na NMR showed a satisfactory agreement as long as $K_f < \sim 200$. Thus for the Na·15C5 complex in DMF solution, ^{13}C measurements gave $\log K_f$ value of 1.88 ± 0.04 while the ^{23}Na NMR value was 1.97 ± 0.05 . Since the complexation reaction produces only small shifts of the ^{13}C resonance of the ligand carbon atoms, this technique, in general, is less accurate for stable complexes than the measurements of the alkali nuclei resonances. It has been pointed out recently by Wilson¹⁰ that carbon-13 NMR measurements are useful for the study of weak molecular complexes if the formation constant values do not exceed 100. In general, our results agree with this assessment.

Since 15C5 and B15C5 crown ethers form 1:1 and 2:1 complexes with Na^+ ion in nitromethane solution, the possibility of the formation of both complexes in other solvents could not be

(9) Roach, E. T.; Handy, P. R.; Popov, A. I. *Inorg. Nucl. Chem. Lett.* 1973, 9, 359.

(10) Wilson, N. K. *J. Phys. Chem.* 1979, 83, 2649.

ruled out, although the ^{23}Na NMR measurements do not seem to indicate a two-step complexation reaction. However, it is seen from Table II that in cases where the existence of both complexes was evident, the formation constant for the first complex is about four orders of magnitude larger than the second. On this basis it seems reasonable to suppose that the formation of an appreciable amount of the 2:1 complex in pyridine, Me_2SO , and DMF solutions would be unlikely. Such a possibility cannot be ruled out however for the tetrahydrofuran and propylene carbonate solutions.

It should be noted that in our calculations of the complex stability constants we ignore possible cation-anion interactions, i.e., the formation of contact or solvent-separated ion pairs. Electrical conductance studies showed that sodium tetraphenylborate is essentially completely dissociated in acetonitrile¹¹ and in dimethyl sulfoxide¹² solutions. On this basis it is reasonable to assume that in solvents with comparable or higher dielectric constants, such as water, propylene carbonate, nitromethane, and dimethylformamide, the formation of ion pairs in 0.05 M solution of NaBPh_4 should be negligible.

Some ion pairing undoubtedly occurs in solvents with intermediate and low dielectric constants, such as acetone, pyridine, and especially tetrahydrofuran. In fact, in THF the ion pair formation constant for NaBPh_4 at ambient temperature was found to be 1.24×10^4 .¹³ No such data seem to be available for sodium tetraphenylborate in pyridine or acetone solutions but in the latter solvent the ion pair formation constant for sodium iodide was found to be equal to 79¹⁴ and, therefore, some ionic association in NaBPh_4 solutions should be likely. In the above three solvents, therefore, the formation constants reported in this paper indicate only the *relative* complexing abilities of the three ligands.

In general, in all of the solvents used in this study, the stabilities of the sodium complexes decrease in the order $18\text{C6} > 15\text{C5} > \text{B15C5}$. Similar results are reported by Izatt et al.,¹⁵ who find $\log K_f$ values for $\text{Na}^+ \cdot 15\text{C5}$ and $\text{Na}^+ \cdot 18\text{C6}$ complexes in water to be 0.70 and 0.80, respectively. The same values, within experimental error, were found potentiometrically by Hoiland et al.¹⁶ Both sets of values are in reasonable agreement with those found in this investigation (Table II).

The above order does not follow the trend expected on the basis of the consonance between the size of the "crown" and of the Na^+ ion if either Pauling's or Goldschmidt's ionic radii are compared. Thus the ring sizes of 15C5 and 18C6 are 1.7–2.2 and 2.6–3.2 Å, respectively¹⁷ (estimated from molecular models) while the Na^+ ion diameter is 1.90 Å (Pauling) or 1.96 Å (Goldschmidt).¹⁸ On this basis we would expect that, other factors being equal, 15C5 should form a more stable complex with the Na^+ ion than 18C6. It should be noted, however, that exact dimensions of the Na^+ ion are not known unambiguously; for example, Witte and Wolfel¹⁹ and Schoknecht²⁰ derived a value of 2.34–2.36 Å for the Na^+ ion diameter which would correspond nicely to the cavity size of 18C6.

It was also shown by Bush and Truter²¹ that large crowns can alter their conformation so as to enable all of the donor atoms to coordinate to the cation. Thus 18C6 with six donor atoms could form a more stable complex than 15C5 and still more than B15C5 since the addition of the benzene ring to 15C5 would reduce somewhat the cavity size as well as the basicity of the oxygen atoms.³

The data shown in Table II clearly illustrate the important

Table III. Limiting ^{23}Na NMR Chemical Shifts of $\text{Na}^+ \cdot \text{C211}$, $\text{Na}^+ \cdot \text{C221}$, $\text{Na}^+ \cdot \text{C222}$, and $\text{Na}^+ \cdot \text{C222B}$ Cryptates in Various Solvents at Ambient Temperature

solvent	salt ^a	$\delta_{\text{Na}^+ \cdot \text{C211}}$	$\delta_{\text{Na}^+ \cdot \text{C221}}$	$\delta_{\text{Na}^+ \cdot \text{C222}}$	$\delta_{\text{Na}^+ \cdot \text{C222B}}$
H_2O	NaI	12.3	-4.8		
	NaCl	12.7	-4.8		
PY	NaBPh_4	10.8 ^b	-5.0	-12.5 ^b	-9.9
	NaClO_4	10.8	-5.0		
	NaI	11.5	-5.2	-12.4	-9.8
	NaSCN		-5.1		-10.0
Me_2SO	NaBPh_4	9.8			-8.4
	NaI		-4.7		
DMF	NaBPh_4	10.1	-5.3	-11.5 ^b	-8.8
	NaClO_4	10.1			
	NaI	10.0	-5.2		
THF	NaBPh_4	10.7	-4.2	-12.1	
	NaClO_4	8.1			
	NaClO_4	8.1			
Me_2CO	NaBPh_4	10.5	-4.1		
	NaI ^c	10.8			
MeCN	NaBPh_4	11.2	-4.0	-11.2	-8.9
	NaClO_4	11.2	-4.1		
	NaI	11.4	-4.0		
MeNO_2	NaBPh_4	~11	-3.7	-10.9	-8.7
PC	NaBPh_4		-4.5	-11.4 ^b	
	NaBPh_4		-3.8	-11.8	-9.2
2-nitropropane	NaBPh_4		-3.8	-11.8	-9.2
95% MeOH ^d	NaCl	11.15	-4.5	-11.40	

^a The solutions were 0.05 M in sodium salt unless otherwise noted. ^b The solutions were 0.10 M in NaBPh_4 . ^c The solutions were 0.025 M in sodium salt. ^d Data taken from ref 22. Solutions were 0.25 M in NaCl in MeOH-D₂O 95/5 solution.

influence of the solvent properties on the complexation reactions. As expected, the magnitude of the dielectric constant does not seem to have a notable effect on the stabilities of the macrocyclic complexes. On the other hand, the donor (or solvating) ability of the solvent, as expressed by the Gutmann donicity scale,²² plays a very important role in the complexation reactions.

It has been pointed out above that in THF solutions of NaBPh_4 and 18C6 two ^{23}Na resonances were observed when the sodium salt was present in excess. A 0.05 M solution of NaBPh_4 in this solvent showed one peak at -7.7 ppm; a solution, 0.03 M in 18C6 and 0.05 M in NaBPh_4 showed two resonances at -7.9 and -17.1 ppm. When the concentration of 18C6 was raised to 0.06 M, only the -17.1 ppm peak remained.

Substitution of NaBPh_4 by the same concentration of NaI or NaClO_4 under the same experimental conditions resulted in only one population-averaged resonance. Gradual addition of tetrabutylammonium iodide to a solution which was 0.05 M in NaBPh_4 and 0.025 M in 18C6 initially resulted in a collapse of the two bands into one broad band. As the concentration of the tetrabutylammonium iodide was further increased, the line width of the resonance decreased and the frequency of the resonance gradually moved toward the value obtained with the NaI-18C6 system.

Identical results were obtained with another cyclic ether, 1,3-dioxolane used as solvent, i.e., two ^{23}Na signals were observed with $\text{NaBPh}_4 \cdot 18\text{C6}$ solutions with an excess of salt, and only one when NaBPh_4 was replaced by NaClO_4 . Attempts were made to use other sodium salts and to replace 18C6 with dibenzo-18C6 but the salts and the ligand were found to be essentially insoluble in THF and dioxolane.

The fact that in the NaBPh_4 -18C6-THF system the cationic exchange is slow and that it is definitely anion dependent is certainly interesting and is undoubtedly related to cation-anion interactions. At the present time, however, the experimental data are too meager to permit a reasonable interpretation. This work is being continued.

B. Cryptands. Sodium-23 resonance of the sodium ion complexed by the four cryptands, shown in Figure 1, was also studied in various solvents. In most systems two signals, corresponding

(11) Kay, R. L.; Hales, B. J.; Cunningham, G. P. *J. Phys. Chem.* **1967**, *71*, 3925.

(12) Atlani, C.; Justice, J. C.; Quintin, M.; Dubois, J. E. *J. Chim. Phys. Phys.-Chim. Biol.* **1969**, *66*, 180.

(13) Comyn, J.; Dainton, F. S.; Ivin, K. J. *Electrochim. Acta* **1968**, *13*, 1851.

(14) Janz, G. J.; Tait, M. J. *Can. J. Chem.* **1967**, *45*, 1101.

(15) Izatt, R. M.; Terry, R. E.; Haymore, B. L.; Hansen, L. D.; Dalley, N. K.; Avondet, A. G.; Christensen, J. J. *J. Am. Chem. Soc.* **1976**, *98*, 7620.

(16) Hoiland, H.; Ringseth, J. A.; Brun, T. S. *J. Solution Chem.* **1979**, *8*, 779.

(17) Pedersen, C. J. *J. Am. Chem. Soc.* **1970**, *92*, 386.

(18) Morris, D. F. C. *Struc. Bonding (Berlin)* **1968**, *4*, 63.

(19) Witte, H.; Wolfel, E. *Z. Phys. Chem.* **1955**, *3*, 296.

(20) Schoknecht, G. *Z. Naturforsch., A* **1957**, *12A*, 983.

(21) Bush, M. A.; Truter, M. R. *J. Chem. Soc., Perkin Trans. 2* **1972**, 345.

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

to the resonances of the free and the complexed cation, were obtained for solutions containing an excess of sodium salt. Occasionally the two resonances seemed to blend into one very broad signal; for example, the addition of C221 to a DMF solution of sodium tetraphenylborate results in only very small displacement of the ^{23}Na resonance although the half-height line width of the resonance broadens considerably.

The chemical shifts of the complexed Na^+ ion are given in Table III. It is immediately obvious that the shifts are very much dependent on the nature of the ligand, i.e., the shift moves downfield as the size of the central cavity decreases, indicating an increasing overlap of the donor orbitals of the ligands' heteroatoms with the outer orbitals of the Na^+ ion. Our results agree very well with those obtained by Lehn and Kintzinger in $\text{MeOH-D}_2\text{O}$ mixture.²³ In nearly all cases the chemical shift became constant at the 1:1 ligand/ Na^+ mole ratio, indicating that the complexes are quite stable, i.e., $K_f > 10^4$. Only in the case of the $\text{Na}^+\text{-C211}$ system in water did the chemical shift continue to change somewhat beyond the 1:1 mol ratio.

The formation constants ($\log K_f$) for $\text{Na}^+\text{-C211}$, $\text{Na}^+\text{-C221}$, $\text{Na}^+\text{-C222B}$, and $\text{Na}^+\text{-C222}$ complexes in water are 3.2, 5.4, 4.0, and 3.9, respectively.^{24,25} The values should be considerably higher in nonaqueous solutions. It is obvious that the magnitude of the ^{23}Na paramagnetic shift of the complexed cation is not directly related to the stability of the complexes.

Our measurements indicate (Table III) that with all four cryptates the chemical shift of the complexed sodium ion does depend on the medium, albeit to a small extent. It is evident, therefore, that the solvent has an access to the complexed cation.

The space-filling model of C221 clearly shows that due to the different lengths of the polyether strands, the ligand has an "open face" and that even when the cation is located in the center of

the cavity, it remains somewhat exposed to the solvent.

Similar small variations of the chemical shift are observed for the $\text{Na}^+\text{-C222}$ and $\text{Na}^+\text{-C222B}$ complexes. In these cases the cavity sizes are larger than that of the cation and there may be some penetration of solvent molecules into the cavity. In the case of C211, where the cavity size is considerably smaller than the cation, not only do the chemical shifts vary with the solvent, but in addition, in solvents with low dielectric constants (pyridine and tetrahydrofuran) the shifts clearly vary with the counterion. Therefore, the anions must be in some contact with the complexed cation and form a "tight" ion pair.

This behavior is different from cases where the cryptand forms an effective insulating layer around the metal ion in the center of the cavity. For example, we have shown previously that for the $\text{Li}^+\text{-C211}$ complex the ^7Li chemical shift of the complexed cation is completely independent of the solvent.²⁶ The same behavior was observed for the ^{133}Cs chemical shift for the $\text{Cs}^+\text{-C222}$ complex at low temperatures.²⁷⁻²⁹

Temperature dependence of the sodium-23 chemical shift for the $\text{Na}^+\text{-C211}$, $\text{Na}^+\text{-C221}$, and $\text{Na}^+\text{-C222}$ complexes was studied in a number of solvents. In the first case, the lines became so broad at low temperatures that accurate measurements of the chemical shifts were not possible. In the other two systems, while measurements could be carried out down to ca. -70°C , the ^{23}Na chemical shifts showed no tendency to converge at low temperatures.

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(26) Cahen, Y. M.; Dye, J. L.; Popov, A. I. *J. Phys. Chem.* **1975**, *79*, 1289.

(27) Mei, E.; Popov, A. I.; Dye, J. L. *J. Am. Chem. Soc.* **1977**, *99*, 6532.

(28) Mei, E.; Liu, L.; Dye, J. L.; Popov, A. I. *J. Solution Chem.* **1977**, *6*, 771.

(29) Kauffmann, E.; Dye, J. L.; Lehn, J.-M.; Popov, A. I. *J. Am. Chem. Soc.* **1980**, *102*, 2274.

(23) Kintzinger, J.-P.; Lehn, J.-M. *J. Am. Chem. Soc.* **1974**, *96*, 3313.

(24) Lehn, J.-M.; Sauvage, J.-P. *J. Am. Chem. Soc.* **1975**, *97*, 6700.

(25) Dietrich, B.; Lehn, J.-M.; Sauvage, J.-P. *J. Chem. Soc., Chem. Commun.* **1973**, 15.

Ab Initio Modeling of Substituent Effects in Hammett Correlations

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Abstract: Substituent effects have been modeled with the use of minimum basis set ab initio techniques. Substituted benzenes were perturbed with pure point charges to model nonbonded reaction centers. Two point charges were used to model a pure dipolar "substituent". Most substituents have essentially the same polarizability and, therefore, are independent of reaction center charge type. Phenyl, ethynyl, sulfonyl, and (in the para position) cyano groups are more polarizable while hydrogen and fluoro groups are less polarizable than "normal" substituents and must be treated with care. Nitro, cyano, and sulfonyl groups lack a mesomeric contribution to the destabilization of a positive reaction center. The boro group, on the other hand, has a mesomeric contribution. The stabilizing effect of a phenyl substituent is undoubtedly due to the polarizability of the benzene ring. Unipolar groups, such as the ammonium group, show apparent interaction with the benzene ring and appear as strong π donors even though mesomeric interactions are minimal. There is a slightly larger inductive effect at the para position than at the meta position. The effect is so small, however, that corrections of σ_1 values are not warranted. Comparisons with experimentally derived substituent constants show that Wepster's σ^{N} values are the best set of "normal" substituent constants while Yukawa's σ^{O} values still contain some through-bond resonance effects.

Organic chemists have always been intrigued with the effects that structural modifications have on chemical reactivity. Years of experimental observation have led to many empirical relationships. Although these relationships have been known for many years, the actual mechanism by which a substituent modifies chemical reactivity has yet to be adequately described. Topsom,¹

in his recent review on the nature and analysis of electronic effects, describes seven mechanisms by which a substituent can transmit its electronic effects to the reaction site. Thus far, these effects have not been completely separated and are usually grouped into

(1) R. D. Topsom, *Prog. Phys. Org. Chem.*, **12**, 1 (1976).