

## MULTINUCLEAR NMR STUDIES OF ALKALI IONS IN NONAQUEOUS SOLVENTS

Alexander I. Popov

Department of Chemistry, Michigan State University, East Lansing, Michigan  
48824, USA

**Abstract** - Nuclear magnetic resonance of alkali elements is a very sensitive probe of the immediate chemical environment of an alkali ion in solutions and can be used to study ion-ion, ion-solvent and ion-ligand interactions. In particular, this technique has been used to determine contact ion pair formation constants, to compare solvating abilities of different solvents and to study the thermodynamics of complexation reactions of alkali ions with macrocyclic polyethers (crowns) and diazapolyoxamacrobicyclic ligands (cryptands) in nonaqueous solvents.

### INTRODUCTION

During the past decade there has been a very rapid expansion of the use of multinuclear NMR for the studies of thermodynamics and kinetics of reactions in solutions. To a very large extent this expansion is the result of progress in NMR instrumentation and, particularly to the introduction of Fourier transform NMR spectroscopy.

Among the many nuclei susceptible to NMR measurements probably the most popular group of elements, aside from the proton and carbon-13, have been the alkalis. All alkali elements have at least one natural isotope with  $I > 1/2$  (Table 1) and, therefore, a quadrupole

TABLE 1. Nuclear Properties of Alkali Elements (Natural Isotopes)

Nucleus	NMR frequency (MHz) at 14.09 kgauss	Natural Abundance (%)	Spin	Sensitivity relative to $^1\text{H}$ at constant field
$^6\text{Li}$	8.827	7.43	1	$8.51 \times 10^{-3}$
$^7\text{Li}$	23.315	92.57	3/2	0.294
$^{23}\text{Na}$	15.868	100	3/2	$9.27 \times 10^{-2}$
$^{39}\text{K}$	2.800	93.08	3/2	$5.08 \times 10^{-4}$
$^{40}\text{K}$	3.480	$1.19 \times 10^{-2}$	4	$5.21 \times 10^{-3}$
$^{41}\text{K}$	1.539	6.91	3/2	$8.39 \times 10^{-6}$
$^{85}\text{Rb}$	5.792	72.8	5/2	$1.05 \times 10^{-2}$
$^{87}\text{Rb}$	19.630	27.2	3/2	0.177
$^{133}\text{Cs}$	7.864	100	7/2	$4.74 \times 10^{-2}$

moment; nevertheless with the exception of rubidium, the resonance lines are quite narrow and, in the case of  $^7\text{Li}$  and  $^{133}\text{Cs}$  the natural linewidths are less than 1 Hz. Thus in most cases chemical shifts can be measured quite precisely. The sensitivities of measurements vary with the nucleus but, in general, they are adequate to detect the resonance signals down to 0.01 M solutions especially when the Fourier transform technique is combined with a high field superconducting solenoid. Figure 1 shows  $^{39}\text{K}$  signal for a 0.005 M solution of KPF<sub>6</sub> in acetonitrile obtained at a field of 42.3 kG.

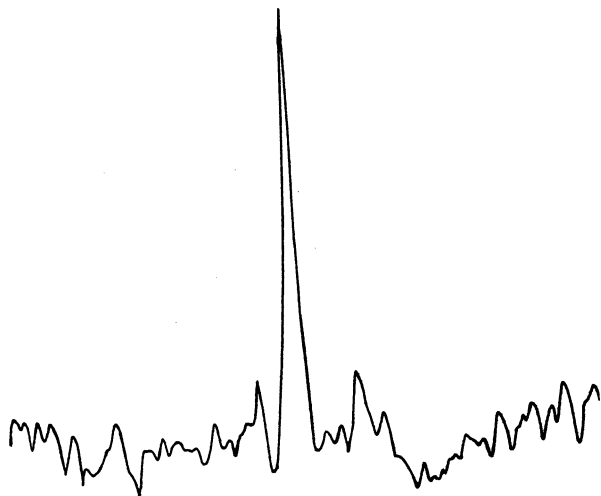


Figure 1. Potassium-39 NMR resonance of 0.005 M solution of  $KPF_6$  in acetonitrile. Field strength of 42.3 kG, 2000 scans.

Chemical shifts of alkali nuclei are very sensitive to the immediate environment of an alkali ion in solution, thus the alkali metal NMR is a very sensitive technique for the detection of ion-ion, ion-solvent and ion-ligand interactions.

The magnitude of the paramagnetic screening constant  $\sigma_p$ , for an alkali nucleus, is proportional to  $\langle r^{-3} \rangle_p \Delta E^{-1}$  where  $\langle r^{-3} \rangle_p$  is the expectation value for the outermost p-electron of the element and  $\Delta E$  is the average excitation energy (1). Since  $\langle r^{-3} \rangle_p$  and  $\Delta E^{-1}$  both increase with increasing atomic number (2), the magnitude and, therefore, the range of  $\sigma_p$  steadily increases in going from  $Li^+$  to  $Cs^+$ . Thus the usual range of the chemical shifts varies from  $\sim 10$  ppm for  $Li^+$  to several hundred ppm for  $Cs^+$ .

The popularity of alkali metal NMR is undoubtedly related to the biological importance of lithium, sodium and potassium ions and to attempts to elucidate their behavior in living systems. In addition, the advent of new complexing agents, such as antibiotic ionophores, macrocyclic polyethers (crowns) and diazapolyxamacrobicyclic ligands (cryptands) which can form stable complexes with alkalis, has opened a new chapter in the coordination chemistry of these elements.

#### CONCENTRATION DEPENDENCE OF CHEMICAL SHIFTS

The concentration and counterion dependences of alkali chemical shifts for alkali salts in aqueous solutions were explored in detail by Richards and co-workers (3). As can be seen from Figure 2, the magnitude of the chemical shift strongly depends on the counterion and on the salt concentration. The concentration dependence of the chemical shifts was ascribed primarily to the Debye-Huckel type of cation-anion interactions. Similar measurements in nonaqueous solutions seem to indicate that the cationic chemical shifts result from the formation of contact ion pairs (4), primarily influenced by the nearest neighbors. Thus, for example, in glacial acetic acid solutions,  $^7Li$  chemical shifts are only very slightly dependent on the salt concentration (5) although the low dielectric constant of the solvent (6.2 at 25°C) predicts a considerable amount of ionic association and experimental results show that even for strong electrolytes the ion pair dissociation constants are of the order of  $\sim 10^{-6}$  (6). The above NMR results, together with the observation that the frequency of the far infrared band of  $Li^+$  vibration in an acetic acid solvent cage is anion independent (7), strongly argue that the ion pairs in glacial acetic acid must be solvent-separated.

Concentration-dependent chemical shifts can be used to calculate contact ion pair formation constants. In all such cases the exchange is fast on the NMR time scale and only one, population-average, signal is obtained

$$\delta_{obs} = \delta_f X_f + \delta_{ip} X_{ip} \quad (1)$$

where  $\delta_f$  and  $\delta_{ip}$  are the chemical shifts of the free ion and the ion in the ion pair respectively, and  $X_f$  and  $X_{ip}$  are the respective populations of the two species. It can be easily shown that

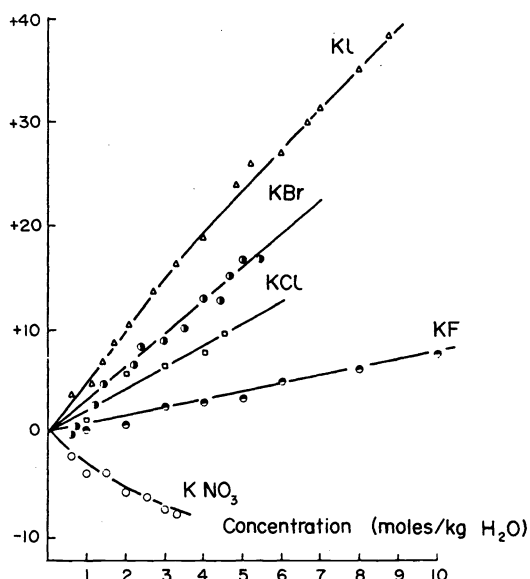


Figure 2. Potassium-39 chemical shifts in aqueous solutions (3b).

$$\delta_{\text{obs}} = \frac{-1 \pm (1 + 4K_{\pm}^2 C_t^M)^{1/2}}{2K_{\pm}^2 C_t^M} (\delta_f - \delta_{\text{ip}}) + \delta_{\text{ip}} \quad (2)$$

where  $K$  is the ion pair formation constant,  $C_t^M$  is the concentration of the salt and  $\gamma_{\pm}$  is the mean activity coefficient. The values of  $K$  and  $\delta_{\text{ip}}$  can be obtained from a nonlinear least-squares iteration program (8).

#### INFLUENCE OF SOLVENTS

Solvent dependence of alkali chemical shifts is shown in Table 2. Kidd and Bloor argue convincingly that in the case of the  $^{23}\text{Na}$  resonance the chemical shifts are determined by the

TABLE 2. Chemical Shifts for Alkali Ions in Nonaqueous Solvents; ppm, Negative Shifts are Paramagnetic Vav Reference

Solvent	$\text{Li}^+(\text{a})$	$\text{Na}^+(\text{b,c})$	$\text{K}^+(\text{b,d})$	$\text{Cs}^+(\text{b,c})$
Nitromethane	0.4	15.0	21.1	59.8
Acetonitrile	2.8	8.1	0.4	-32.0
Propylene Carbonate	0.6	—	11.5	35.2
Acetone	-1.3	9.6	10.5	26.8
Formamide	—	3.8	—	27.9
Methanol	0.5	3.4	10.1	45.2
Dimethylformamide	-0.5	4.8	2.8	0.5
Dimethyl Sulfoxide	1.1	-0.4	-7.8	-68.0
Pyridine	-2.5	-1.6	-0.8	-29.4

(a) vs 4.0 M aq.  $\text{LiClO}_4$ , ref. 5; (b) vs aq. soln. at infinite solution; (c) ref. 11; (d) ref. 12; (e) ref. 8.

paramagnetic screening constant (9) and this argument certainly must be valid for the  $^{39}\text{K}$  and  $^{133}\text{Cs}$  resonances. Since the solvent-induced paramagnetic shift is determined by the overlap of the outer  $p$  orbital of an alkali ion with the outer orbitals of the solvent molecule, one can expect to find some correlation between the magnitudes of the paramagnetic shifts of the

alkali ions and the electron-donating ability of the solvent molecules. Unfortunately, at this time, we do not have a quantitative theory of the donor (or solvating) abilities of solvents. There are, however, several empirical scales of the donor abilities of solvents mostly based on spectroscopic or thermodynamic experimentally determinable quantities. One of these, the Gutmann donicity scale (10) based on the enthalpy of complexation of the given solvent with antimony(V) chloride seems to correlate quite well with the  $^{23}\text{Na}$  chemical shifts in these solvents (11) (Figure 3). The relationship is somewhat less admirable for  $^{133}\text{Cs}$  (Figure 4) and for  $^{39}\text{K}$  (12) and fails completely in the case of  $^7\text{Li}$  (5). It should be remembered, however, that in the latter case the diamagnetic and the paramagnetic screening con-

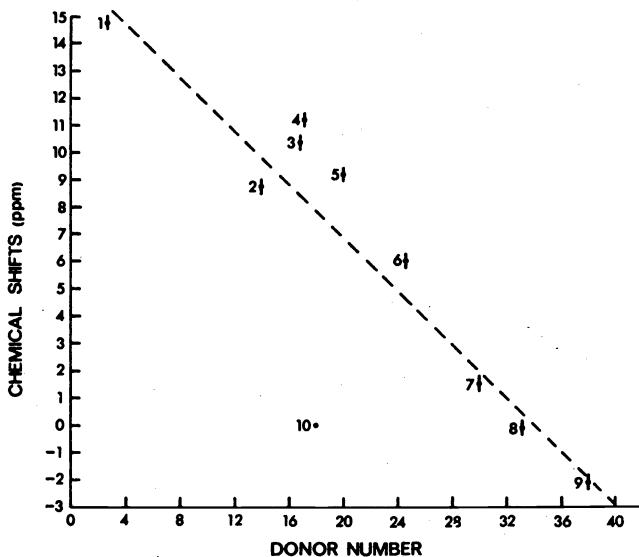


Figure 3. Sodium-23 chemical shifts vs Gutmann donor numbers. Reference - aq.  $\text{Na}^+$  at infinite dilution. 1. nitromethane, 2. acetonitrile, 3. acetone, 4. ethyl acetate, 5. THF, 6. DMF, 7. DMSO, 8. pyridine, 9. hexamethylphosphoramide, 10. water (11b).

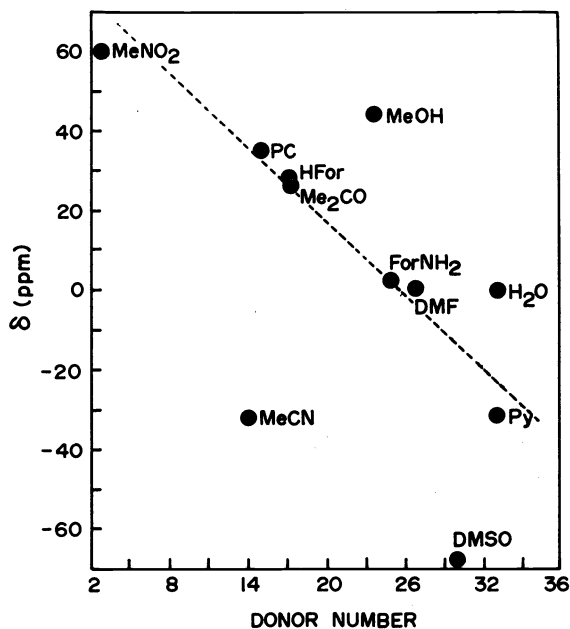


Figure 4. Cesium-133 chemical shifts vs Gutmann donor number. References - aq.  $\text{Cs}^+$  at infinite dilution (8).

stants are of the same order of magnitude and, therefore, ring currents and neighbor anisotropy effects influence the magnitude and the direction of the chemical shifts (13).

### COMPLEXATION REACTIONS

Since the alkali metal chemical shifts are excellent probes of the immediate environment of the corresponding metal ion in solution, it is natural that this technique has been used extensively for the studies of alkali metal complexes (4). Such studies are becoming quite numerous and only a few examples of some work in the author's laboratory are given below to illustrate the technique as applied to complexes of macrocyclic polyethers and cryptands (Figure 5).

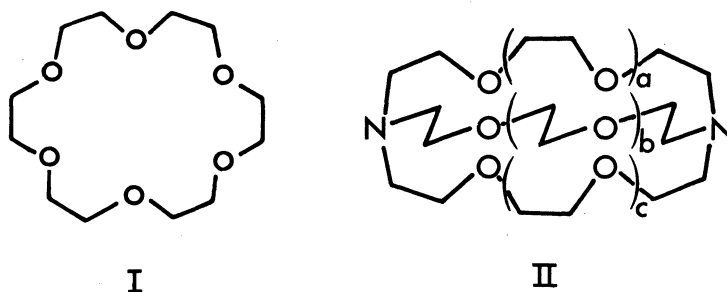


Figure 5. I - 18-crown-6; II - cryptands.  $a=b=0, c=1$ , C211;  $a=0, b=c=1$ , C221;  $a=b=c=1$ , C222.

Figure 6 illustrates the plots of cesium-133 chemical shifts as a function of 18-crown-6/ $\text{Cs}^+$  mole ratio in different solvents (14), and clearly shows the importance of the solvent

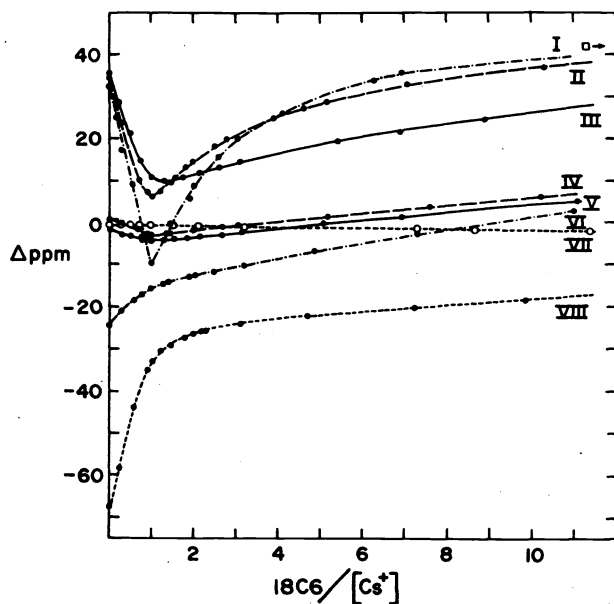


Figure 6. Plot of cesium-133 chemical shift vs 18-crown-6/ $\text{Cs}^+$  mole ratio in different solvents. Concentration of cesium salts is 0.001 M in all cases: (I)  $\text{CsBPh}_4$  in PY, (II)  $\text{CsBPh}_4$  in  $\text{Me}_2\text{CO}$ , (III)  $\text{CsBPh}_4$  in PC, (IV)  $\text{CsBPh}_4$  in DMF, (V)  $\text{CsI}$  in DMF, (VI)  $\text{CsBPh}_4$  in MeCN, (VII)  $\text{CsI}$  in  $\text{H}_2\text{O}$ , (VIII)  $\text{CsBPh}_4$  in  $\text{Me}_2\text{SO}$ .

properties in complexation reactions. In particular, it is interesting to note that in the case of propylene carbonate, acetone, and especially pyridine solutions the  $^{133}\text{Cs}$  chemical shift moves downfield as the 18C6/ $\text{Cs}^+$  mole ratio increases from 0 to 1. Beyond this point, however, further addition of the ligand reverses the chemical shift of the nucleus. This behavior is indicative of a two-step complexation reaction, first the formation of a stable 1:1 complex followed by the addition of a second molecule of the crown ether to give a 2:1 sandwich compound. A detailed analysis of the results in pyridine solutions at different temperatures gave results shown in Table 3. Only minimum values of  $K_1$  could be obtained by our technique.

TABLE 3. Thermodynamic Parameters for the Formation of the 1:1 and 2:1 18C6/Cs<sup>+</sup> Complexes in Pyridine Solutions (ref. 14b)

Temperature (°K)	K <sub>1</sub> (min) (M <sup>-1</sup> )	K <sub>2</sub> (M <sup>-1</sup> )
297	10 <sup>5</sup>	79 ± 2
285	10 <sup>6</sup>	121 ± 5
272	10 <sup>6</sup>	218 ± 14
255	10 <sup>6</sup>	432 ± 58
244	10 <sup>6</sup>	623 ± 35
235	5 × 10 <sup>6</sup>	1173 ± 160

$$\Delta G_2^0(298) = -2.58 \pm 0.02 \text{ kcal mole}^{-1}; \Delta H_2^0 = -5.8 \pm 0.2 \text{ kcal mole}^{-1};$$

$$\Delta S_2^0 = -10.7 \pm 0.6 \text{ e.u.}$$

It is seen that the stability of the 2:1 complex drastically increases as the temperature is lowered and that the complex is enthalpy stabilized but entropy destabilized.

Similar results have been obtained recently in the study of dibenzo-30-crown-10 complexation of Cs<sup>+</sup> ions in nonaqueous solutions. The data given in Table 4 clearly show that in all cases studied the complexation reaction is enthalpy stabilized but entropy destabilized (15).

TABLE 4. Thermodynamic Values for the Complexation of the Cs<sup>+</sup> Ion by DB30C10 in Various Solvents.

Solvent	log K (30°C)	$\Delta G^0$ (30°C) (kcal mole <sup>-1</sup> )	$\Delta H^0$ (kcal mole <sup>-1</sup> )	$\Delta S^0$ (e.u.)
Acetonitrile	3.39	-4.71	- 5.13	- 1.53
Pyridine	4.41	-6.13	- 7.94	- 5.93
Nitromethane	4.30	-6.97	- 7.95	- 6.66
Methanol	4.18	-5.81	-12.72	-22.82
Acetone	3.91	-5.50	-13.48	-26.19

The extent of destabilization strongly depends on the nature of the solvent. Similar behavior has been observed for some alkali cryptates and will be discussed later.

Cryptands or diazapolyoxamacrobicyclic ligands, have three dimensional cavities which can accommodate alkali (and other) ions of proper dimensions (16). The cryptands C211, C221 and C222 have cavity dimensions corresponding to the Li<sup>+</sup>, Na<sup>+</sup> and K<sup>+</sup> ions respectively. The stabilities of the resulting complexes depend on several factors the most important of which seems to be the relationship between the ligand cavity size and the ionic radii of the cations. Some of the results obtained by Lehn *et al.* by potentiometric titrations in aqueous solutions are given in Table 5.

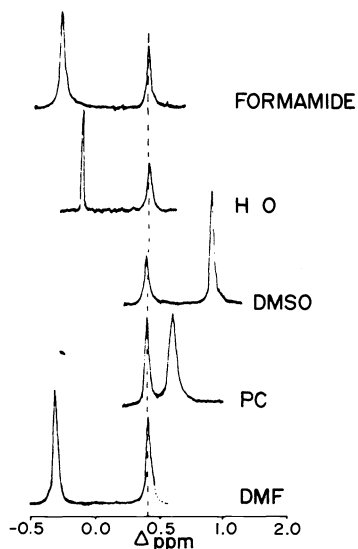
Lithium-7 nuclear magnetic resonance studies on lithium complexes with C222, C221 and C211 (18) showed that the first two ligands form weak 1:1 complexes with Li<sup>+</sup> ion in solvents of low donicity, such as nitromethane. Only one, population averaged, <sup>7</sup>Li signal was observed indicating fast Li<sup>+</sup> exchange between the two sites.

On the other hand, with cryptand C211, whose cavity snugly accommodates Li<sup>+</sup> ion, two <sup>7</sup>Li signals were observed even in solvents of high donicity, as long as the mole ratio of ligand/Li<sup>+</sup> was less than unity. It is interesting to note that while the frequency of the alkali nucleus of the free ion is strongly dependent on the solvents, the resonance of the ion inside the cryptand cavity is completely independent of the solvent (Figure 7).

It is readily seen that in the latter case the ligand completely insulates the cation from the solvent. Likewise the data shown in Figure 7 support the previously made assumption that the alkali chemical shifts are determined by the nearest neighbors.

TABLE 5. Stability Constants of Alkali Cryptates in Aqueous Solutions (17)

Ligand	log K			
	Li <sup>+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Cs <sup>+</sup>
C211	5.3	2.8	<2	<2
C221	2.5	5.4	3.9	<2
C222	<2	3.9	5.4	<2
C322	<2	1.6	2.2	2.2

Figure 7. Lithium-7 NMR spectra of Li<sup>+</sup>·C211 cryptate in various solvents. Conc. of C211 = 0.25 M, conc. Li<sup>+</sup> = 0.50 M (18).

It has been noted above that the range of chemical shifts varies directly with the atomic number of the alkali nucleus. Thus NMR measurements are particularly fruitful in the case of cesium-133 nucleus. In addition, the narrowness of the resonance line permits very accurate determinations of the chemical shifts. Figure 8 shows cesium-133 chemical shift as a function of C222/Cs<sup>+</sup> mole ratio in six nonaqueous solvents (19). It is readily seen that in propylene carbonate, acetone, acetonitrile and pyridine solutions a stable 1:1 complex is formed. The four limiting resonance frequencies are not identical but the differences are small compared to the overall chemical shift for the free solvated ion. We can conclude, therefore, that the cesium ion is not completely enclosed in the cryptand cavity.

The remarkably large paramagnetic shift ( $\sim 280$  ppm in pyridine solution) shows a strong overlap of the electron pairs of the solvent molecules with the *p* orbital of the cesium ion, i.e., the cation must fit quite tightly into the somewhat stretched cavity of the ligand (20). The tightness of the fit however, does not necessarily indicate the formation of a very stable complex.

The two solvents with high donicity, DMF and DMSO solvate Cs<sup>+</sup> quite strongly and can compete with the C222 cryptand for the Cs<sup>+</sup> ion. Therefore, the chemical shifts change only very gradually and do not reach a limiting value. The formation constants of the Cs<sup>+</sup>·C222 complex in different solvents have been determined from the data shown in Figure 8 and are given below in Table 6. It is seen that with the exception of pyridine there is an expected reverse relationship between the donor strength of the solvents and the stability of the Cs<sup>+</sup>·C222 complex. Similar results have been previously observed with Cs<sup>+</sup>·18C6 (14) and Cs<sup>+</sup>·DB30C10 (Table 3) complexes. It seems reasonable to assume that pyridine being a "soft" base does not solvate Cs<sup>+</sup> ion, a "hard" acid, to the extent predicted by the donor number. Ahmad and Day (21) reach the same conclusion from their studies of sodium tetraethylaluminum in non-aqueous solvents by proton NMR.

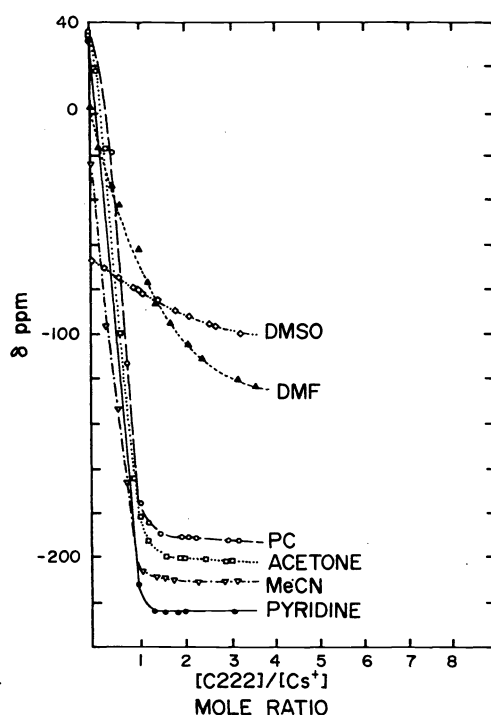


Figure 8. Cesium-133 chemical shifts vs C222/Cs<sup>+</sup> mole ratio in various solvents (19).

TABLE 6. Formation Constants of Cesium Complex With Cryptand C222 in Various Solvents

Solvent	Solvent Donor Number <sup>(a)</sup>	log K <sub>f</sub>
Pyridine	33.1	>5
Dimethyl Sulfoxide	29.8	1.95
Dimethylformamide	26.6	2.16
Acetone	17.0	4.03
Propylene Carbonate	15.1	3.97
Acetonitrile	14.1	4.57

(a) from ref. 10.

#### "BASEBALL" COMPLEX

The solvent dependence of the <sup>133</sup>Cs limiting chemical shift for the Cs<sup>+</sup>·C222 complex was studied as a function of temperature in DMF, PC, and acetone solutions (22). The results are shown in Figure 9.

It is seen that as the temperature is lowered the shifts become more paramagnetic and at ~ -100°C they tend to the same limiting value, i.e., at low temperatures the chemical shift is independent of the solvent.

These results suggest the presence of an inclusive complex at low temperatures and a temperature dependent equilibrium



The exclusive complex is illustrated schematically in Figure 10. The likely structure is the



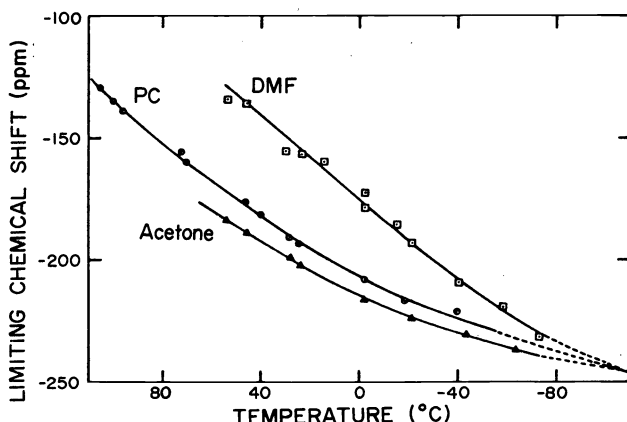


Figure 9. Limiting  $^{133}\text{Cs}$  chemical shifts at high C222/ $\text{Cs}^+$  mole ratios as a function of temperature in three nonaqueous solvents.

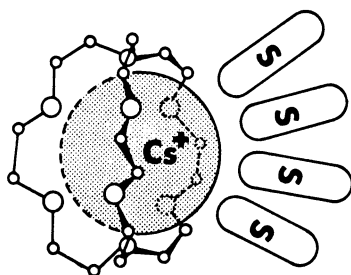


Figure 10. An "exclusive"  $\text{Cs}^+\cdot\text{C222}$  complex (19).

one in which the cation is partially enclosed in the hollow hemisphere of the ligand (like a baseball in a fielder's glove).

Analysis of the data obtained at different temperatures gave the thermodynamic parameters for the two-step complexation reaction (Table 7).

TABLE 7. Thermodynamic Parameters for the Formation of Exclusive and Inclusive  $\text{Cs}^+\cdot\text{C222}$  Complexes in Three Nonaqueous Solvents

Solvent	$\Delta H_1^0$ kcal mole $^{-1}$	$\Delta S_1^0$ e.u.	$\Delta H_2^0$ kcal mole $^{-1}$	$\Delta S_2^0$ e.u.
Acetone	-12.9	-26.8	-2.5	-5.6
Propylene carbonate	- 8.6	-13.7	-2.9	-7.0
DMF	- 5.7	-11.2	-2.6	-7.6

As expected,  $\Delta H_2^0$  and  $\Delta S_2^0$  are essentially independent of the solvent while  $\Delta H_1$  and  $\Delta S_1$  are solvent dependent. We would expect that the cation will be largely desolvated in the formation of the exclusive complex.

It is gratifying to note that very recently crystallographic analysis of cryptates  $\text{Na}^+\cdot\text{C221}$  and  $\text{K}^+\cdot\text{C221}$  (23) clearly showed that the latter complex is "exclusive" since the cation lies outside the cavity of the bicycle.

## CONCLUSIONS

It should be evident from the above discussion that multinuclear NMR offers a very powerful tool for the studies of reactions in solutions. With continuous improvement in NMR instrumentation the sensitivity of detection is constantly improving. It can be safely predicted that in the near future multinuclear NMR will become a routine tool for the studies of ionic solutions at low concentrations. In particular, the measurements of  $^{17}\text{O}$  and  $^{15}\text{N}$  resonances at natural isotopic abundances should greatly improve our knowledge of metal ion interaction

with organic and inorganic ligands.

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