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^{39}K and ^{13}C Nuclear Magnetic Resonance Studies of Potassium Cryptates in Nonaqueous Solutions

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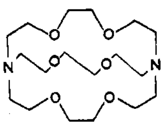
Potassium complexes with cryptands C222, C221, and C211 were studied in several nonaqueous solvents by potassium-39 and carbon-13 NMR. In the case of the first two complexes the exchange between the two potassium sites was slow, and separate ^{39}K signals for the free and complexed ion were observed in solutions containing an excess of K^+ ion. Separate ^{13}C signals were also observed for the C222·K^+ system with an excess of the ligand. The limiting chemical shifts for the above complex were independent of the solvent, indicating that the cation was located in the interior of the cavity (*inclusive* complex). The cavities of the other two ligands appear to be too small to accommodate K^+ ion, and therefore, the complexes must have an *exclusive* configuration. In the case of the C211·K^+ complex the exchange was fast, and only one ^{39}K signal was observed. In this case, it was possible to calculate the formation constant of the complex from the variation of the ^{39}K chemical shift with the ligand/K^+ mole ratio. The values obtained showed strong dependences on the donor abilties of the solvents and varied between log $K_f > 4$ in acetone and no measurable complexation in dimethyl sulfoxide.

Introduction

In several previous publications we[1] and others[2,3] have shown that the nuclear magnetic resonance of the lithium-7, sodium-23, and cesium-133 nuclei offers a very convenient and sensitive probe for studying complexes of these ions in solutions. It was of interest to us to expand these studies to potassium complexes with macrocyclic ligands such as crown ethers and cryptands. In this paper we wish to report studies of the complexation of K^+ ion by cryptands C222 (I), C221 (II), and C211 (III) in several nonaqueous solvents. Since we wished to follow the complexation reaction by monitoring the change in the chemical environment of the ligands as well as of the cation, the carbon-13 NMR of the cryptands was also investigated.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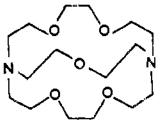
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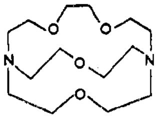
III

Previous studies of potassium-39 resonance in solutions have been rather sparse.[4] The ^{39}K chemical shifts of several potassium salts in aqueous solutions were studied as a function of concentration by Deverell and Richards[5] and by Bloor and Kidd,[6] who found that the direction and the magnitude of the ^{39}K chemical shift were strongly dependent on the concentration of the salt and on the nature of the counterion. The kinetics of complexation of K^+ by crown ether, dibenzo-18-crown-6, was studied by potassium-39 NMR by Shporer and Luz,[7] and the variation in the potassium-39 chemical shifts as a function of concentration and counterion in nonaqueous solvents was reported by us in a preliminary paper.[8]

Experimental Section

Chemicals. Potassium hexafluorophosphate (Pfaltz and Bauer) was purified by recrystallization from aqueous solutions and then dried under vacuum at ~110 °C for 72 h.

Table I. Chemical Shifts of the Potassium-39 Signal with Cryptands C222 and C221 in Various Solvents[a,b]

solvent	δ (free ion)	δ (C222·K^+)	δ (C221·K^+)
nitromethane	−22.3	2.5	
methanol	−11.3	2.5	14.4
acetone	−12.1	3.0	12.6
dimethylformamide	−5.3	2.0	14.3
acetonitrile	−1.8	2.4	13.5
pyridine	0.2		15.0

[a] Ligand/K^+ mole ratio of 0.5. [b] Due to broad lines and low sensitivity, the chemical shifts are accurate to ±0.5 ppm.

Solvents used in this investigation were dried with an appropriate dehydrating agent[9] and fractionally distilled. Whenever possible, the water contents of the purified solvents were checked with Karl Fischer titration and were always found to be below 100 ppm. The solutions of the ligand and of KPF_6 were prepared and mixed in a drybox under a nitrogen atmosphere.

Cryptand C222 (EM Laboratories) was recrystallized from hexane and dried under vacuum at ~40 °C for 48 h. Cryptands C221 and C211, which are oily liquids at room temperature, were dried under vacuum before use.

Instrumentation. Potassium-39 NMR measurements were carried out in the Fourier transform mode on a Bruker-180 spectrometer at 8.403 MHz and a field strength of 42.3 kG. Nonspinning 20-mm tubes were used. A saturated potassium nitrite solution in D_2O was used as the external standard. The chemical shifts are referred to an aqueous potassium salt solution at infinite dilution, and they are corrected for the differences in the bulk diamagnetic succeptibility between the nonaqueous solvent and the deuterium oxide reference by using the relationship of Live and Chan.[10] Since the contribution of the salt to the bulk diamagnetic succeptibility of the solution is small[11] and since our solutions were dilute (<0.1 M), no correction for the salt was applied.

Carbon-13 NMR measurements were made on a Varian CFT-20 spectrometer at a field strength of 18.7 kG and a resonance frequency of 20 MHz. The shifts were measured vs. Me_4Si.

Results and Discussion

Mixtures of potassium hexafluorophosphate (0.02 M) and C222 (0.01 M) were prepared in five different solvents, nitromethane, methanol, acetone, dimethylformamide, and acetonitrile, and the ^{39}K chemical shift of these solutions was determined. Two distinct ^{39}K signals were observed in the first

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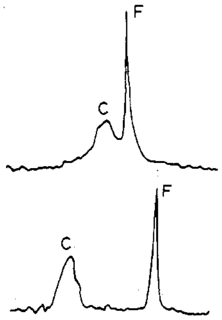

Figure 1. Potassium-39 resonance of a 0.02 M KPF_6 and 0.01 M C222 solution: upper curve, acetone; lower curve, nitromethane.

three solvents, corresponding to the free and the complexed K^+ ions (Figure 1). In the other two solvents the signals more or less overlapped, but the individual resonances still could be distinguished, so that at room temperature in all five solvents the exchange is slow by the NMR time scale. In acetone and nitromethane solutions, the signal for the free solvated cation is much narrower than the signal of the cation inside the macrocyclic cavity. The resonance frequencies are given in Table I.

It is immediately obvious that while the resonance frequency of the free solvated cation is strongly dependent on the solvent, there is very little solvent dependence of the resonance of the complexed ion. Previously we observed similar results with the $C211{\cdot}Li^+$ system,[12] i.e., in the case where the size of the cation matched that of the cryptand cavity.

The sizes of the C222 and C221 cavities have been estimated to be 2.8 and 2.2 Å, respectively,[13] while the size of the K^+ ion seems to be somewhere between 2.66 (Pauling) and 2.98 Å (Morris).[14] In either case there is a good consonance between the ionic size and the cavity size of C222. Potassium ion, therefore, should form an inclusive complex[15] with C222, and it should be effectively insulated from the solvent.

It should be noted that in the case of the exclusive complex, of course, we have no information on the *extent* of cation penetration inside the ligand cavity when the complex is in the solution. From our measurements we can only say that when the cationic chemical shift becomes independent of the solvent, the cation is very effectively insulated from the medium, and, therefore, it must be located inside the ligand cavity. Thus our definition of an *exclusive* complex is, of necessity, an operational one.

A somewhat different situation is observed with cryptand C221. Here again in acetonitrile, dimethylformamide, and methanol solutions the exchange is slow at room temperature, and two signals are obtained when the solutions contain an excess of the salt (Figure 2). In aqueous solution, however, the exchange is fast, and only one broad signal is obtained.

The chemical shifts of K^+ ion complexed by C221 are much more paramagnetic than those of the $C222{\cdot}K^+$ complex, indicating a larger overlap of the orbitals of the donor atoms of the ligand with the outer p orbital of the cation. It is also evident that in this case the chemical shifts are much more solvent dependent.

A recent crystal structure determination of the $C221{\cdot}Na^+$ and $C221{\cdot}K^+$ complexes[16] has shown that in the latter case the cation is too large to fit inside the ligand cavity, and an *exclusive* type of cryptate is formed. An inclusive complex is formed with the smaller sodium ion.

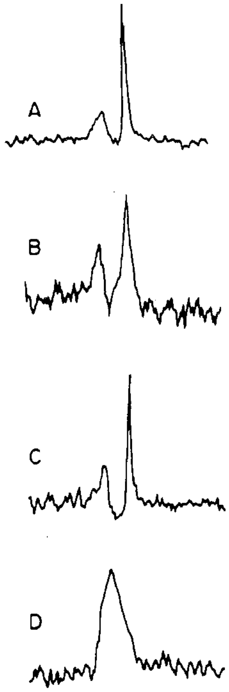

Figure 2. Potassium-39 resonance of a 0.02 M KPF_6 and 0.01 M C221: A, acetonitrile; B, dimethylformamide; C, methanol; D, water.

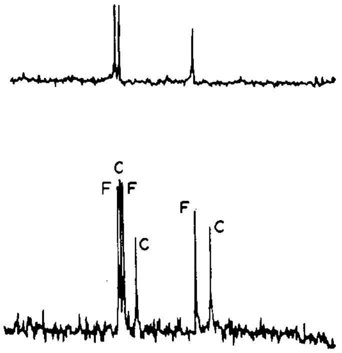

Figure 3. Carbon-13 NMR of C222 and $C222{\cdot}K^+$: upper spectrum, free ligand; lower spectrum, 0.05 M C222 + 0.025 M K^+. Acetone solutions.

Cesium-133 NMR studies of the $C222{\cdot}Cs^+$ system in several nonaqueous solvents showed a temperature-dependent equilibrium between the exclusive and inclusive forms of the cesium cryptate.[17] It seems reasonable to assume that an exclusive $C221{\cdot}K^+$ complex can also exist in solutions. The possibility of a temperature-dependent exclusive $\rightleftharpoons$ inclusive equilibrium cannot be discounted, but further work is needed to elucidate this point.

In all nonaqueous solvents used in this work, only one ^{39}K signal was observed when a stoichiometric amount of the ligands was added to the potassium ion. These results indicate that both $C222{\cdot}K^+$ and $C221{\cdot}K^+$ complexes are quite stable in our solvents and that the NMR technique we used previously for the determination of complexity constants from the variation of the cationic chemical shift with ligand/cation mole ratio[18] cannot be used in this case since this technique is only useful if the formation constants of 1:1 complexes are less than

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Table II. Carbon-13 Chemical Shifts (δ) for Cryptand C222 and Its Potassium Complex

	K^+/C222 mole ratio											
	0			0.5			1.0			2.0		
solvent	NCH_2	OCH_2	OCH_2	NCH_2	OCH_2	OCH_2	NCH_2	OCH_2	OCH_2	NCH_2	OCH_2	OCH_2
acetone	58.28	71.75	72.54	58.37	71.76	72.55						
				55.61	69.32	72.04[a]	55.61	69.31	72.14[a]	55.61	69.21	72.07[a]
dimethylformamide	58.03	72.51	72.29	58.09	71.57	72.36						
				55.61	69.22	71.92[a]	55.54	69.21	71.97[a]			
dimethyl sulfoxide	58.09	71.68	72.37	58.00	71.59	72.24						
				55.53	69.31	72.08[a]	55.54	69.31	72.07[a]			

[a] Complex.

10^5. Indeed, the formation constants of the C222·K^+ complex in dimethylformamide, dimethyl sulfoxide, propylene carbonate, and acetonitrile solutions have been recently measured potentiometrically by Gutknecht et al.,[19] and log K_f values varied between 6.9 and 11.1.

As seen in Figures 1 and 2, the line width corresponding to the complexed K^+ ion is much larger than that for the free ion. For example, in methanol solutions the line width of the free ion (0.02 M) is 24 Hz and those for C222·K^+ and C221·K^+ are both ~60 Hz. The line broadening on complexation is probably due to the interaction of the ^{39}K quadrupole with the unsymmetrical electrical field gradient inside the ligand cavity.

Since the carbon-13 spectrum of cryptands is rather simple and the chemical shifts are reasonably sensitive to complexation, carbon-13 NMR is a useful adjunct to the ^{39}K studies of the alkali-ion resonances. Lehn et al. have used this technique to study the formation of some [3]cryptates.[20-22]

As shown in Figure 3, the ^{13}C spectrum of C222 consists of three lines corresponding to the three different carbon atoms of the ligand.[23] The addition of a less than stoichiometric amount of potassium hexafluorophosphate to a C222 solution in acetone, dimethylformamide, and dimethyl sulfoxide results in two signals for each carbon atom, corresponding to the free and the complexed ligand, respectively. Again we have a slow intermolecular exchange between the two ligand sites. As seen from the data given in Table II, the three carbons are affected differently by complexation. The largest chemical shift is observed for the N–CH_2 carbon. Upon the addition of the stoichiometric amount of K^+ ion, the signals corresponding to the free ligand disappear. Further increase in K^+ concentration does not affect the chemical shift, once again indicating the formation of a stable complex.

Carbon-13 resonance was also studied in the C221·K^+ system in acetone solutions. In this case, solutions with an excess of the ligand showed only one population-average signal, indicating a fast intermolecular exchange.

Addition of cryptand C211 to a potassium hexafluorophosphate solution in dimethylformamide, acetone, pyridine, and acetonitrile led to a downfield shift of the ^{39}K resonance (Figure 4), indicating some cation–ligand interaction. No chemical shift was observed, however, in dimethyl sulfoxide. In contrast to the C222·K^+ and C221·K^+ complexes, only a single ^{39}K resonance was observed at all C211/K^+ mole ratios, indicating a fast intermolecular exchange. In this case it was possible to determine the formation constant of the complex and the limiting chemical shift from the variation of the cationic chemical shift with the ligand/cation mole ratio. This technique has been described previously.[18] The results are shown in Table III.

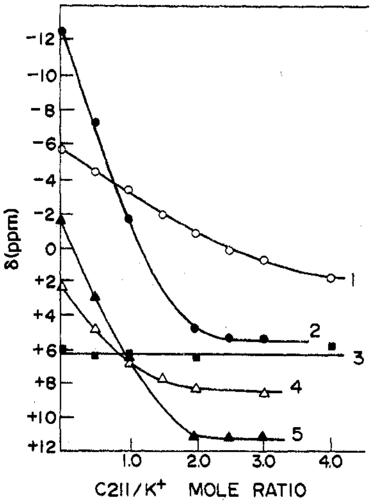

Figure 4. Potassium-39 chemical shifts as a function of C211/K^+ mole ratio in various solvents: 1, dimethylformamide; 2, acetone; 3, dimethyl sulfoxide; 4, pyridine; 5, acetonitrile.

Table III. Formation Constants and the Limiting Chemical Shifts of the C211·K^+ Complex

solvent	log K_f, M^{-1}	δ_{lim}
acetone	>4	5.44 ± 0.05
acetonitrile	2.8 ± 0.2	11.8 ± 0.4
pyridine	2.5 ± 0.1	9.1 ± 0.1
dimethylformamide	1.0 ± 0.1	13.0 ± 0.2
dimethyl sulfoxide	no complexation	

It is seen that C211 forms rather weak complexes with the K^+ ion and that the stability of the C211·K^+ cryptate strongly depends on the nature of the solvent. With the exception of pyridine, the stability seems to vary inversely with the solvating ability of the solvent as expressed by the Gutmann donor numbers.[24] It was pointed out previously[25] that a weak alkali cation–pyridine interaction may reflect the "soft base" character of the solvent. Although the cavity size of C211 is much smaller than the size of the potassium ion, it is interesting to note that the ligand still has enough complexing ability to form a weak complex with this cation. Lehn and Sauvage studied the C211·K^+ interaction potentiometrically in aqueous and in methanolic solutions and found a log K_f of >2.0 and 2.3, respectively.[26] These results seem to be in good agreement with our data. The data given in Figure 4 and Table III showed that the limiting ^{39}K chemical shift of the C211.K^+ complex is strongly influenced by the medium. Such influence,

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of course, would be expected for the exculsive complexes where the solvent has an ample opportunity to interact with the unshielded side of the cation.

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Registry No. C222·K$^+$, 32611-95-3; C221·K$^+$, 32611-87-3; C211·K$^+$, 32824-90-1; K$^+$, 24203-36-9.

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Spectra and Magnetism of Triclinic Crystals of Tetra-*n*-butylammonium Tribromo(quinoline)cobaltate and -nickelate

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The magnitudes and orientations of the principal paramagnetic susceptiblities of triclinic crystals incorporating the complex ions $M(quinoline)Br_3^-$ (M = Ni(II), Co(II)) have been measured throughout the temperature range 20–300 K. Unpolarized crystal transmission spectra have been recorded in the range 4000–26 000 cm^{-1} at 4 K, that for the cobalt complex confirming and augmenting previously published data. Quantitative agreement with all these data and also with the single-crystal ESR **g** tensor, reported by Bencini and Gatteschi for the cobalt complex, has been achieved with the angular-overlap model. Values for all AOM, interelectron repulsion, and spin–orbit coupling parameters have been defined. The quinoline ligand has been shown to act as a π acceptor in both complexes. The spin–orbit coupling coefficient appears anomalously small in the nickel complex.

Introduction

Current techniques for magnetochemistry and ligand field theory provide means to determine, in a semiquantitative manner, the separate extents of σ and π bonding between the metal and each ligand within a transition-metal complex.[1] In what may be regarded still as a developmental phase in the exploitation of the angular overlap model as applied to paramagnetic susceptibilities, ESR *g* values, and the d–d electronic spectra, our concern in any given study must be as much with establishing norms as with characterizing new bonding features and, at the same time, with testing the capacity of the method in ever more exacting circumstances.

The subject of the present study is the isomorphous pair of complex ions $M(Q)Br_3^-$, where M = Ni(II) and Co(II) and Q = quinoline. Of immediate chemical interest are the π-bonding roles of bromine and quinoline in these nominally tetrahedral species and a comparison of the π-bonding function of quinoline here with that of pyridine in other complexes which have been analyzed[2] in a similar way. A particular challenge, so far as both practical and theoretical techniques are concerned, centers on the triclinic nature of the lattice in which these complex ions crystallize[3] with tetra-*n*-butylammonium cations. We report here complete determinations of the triclinic crystal susceptibilities of each complex throughout the temperature range 20–300 K, using methods recently developed[4] for the measurement of the antiferromagnetism of several binuclear cobalt benzoates.[4,5] The present experiments describe the first successful measurements of triclinic paramagnets since the early work on $CuSO_4 \cdot 5H_2O$: a recent study[7] of the paramagnetism of a triclinic crystal did not experimentally establish both magnitudes and orientations of the principal susceptibilities as is done here. Set against the considerable difficulty in measuring triclinic susceptibilities are two advantages. Except where there are two or more paramagnetic centers in the crystallographic asymmetric unit, and this is not the case here, there is equality by identity between the crystal and molecular susceptibilities under circumstances of effective magnetic dilution. Further, the increased data set provided by the determination of the magnitudes and all orientations of the principal susceptibilities provides a more exacting property for the theoretical model to reproduce. The situation is particularly attractive in the present study in view of the relatively small number of parameters required to describe σ and π bonding from only two ligand types, one of which (bromine) is considered to π bond symmetrically about the metal–ligand axis and the other of which probably π bonds in one direction only (though this is to be verified).

We also report single-crystal, unpolarized, transmission spectra for both complexes down to liquid-helium temperatures, those for the cobalt complex confirming the detailed, polarized spectra reported elsewhere.[8] The magnitudes and orientations of the principal molecular *g* values of the cobalt complex have also been reported recently.[9] We have established parameter values which simultaneously reproduce all details of susceptibility, optical spectra, and, as appropriate, ESR properties in these two complexes, demonstrating a significant π-acceptor role for the quinoline ligands. The study also contributes to evidence of anomalous spin–orbit coupling in tetrahedral nickel(II) complexes.

Experimental Section

The complex salts $[(n\text{-}C_4H_9)_4N][M(C_9H_7N)Br_3]$ (M = Co, Ni) were prepared by the published method,[3] and satisfactory CNH analyses were obtained. Large crystals were prepared by slow evaporation of the reaction mixtures and also by recrystallization from butanol.

Susceptibilities. All susceptibility measurements were performed on crystals weighing 1–4 mg, by using our single-crystal Faraday balance[10] and procedures recently described.[4] As the present work is the first complete susceptibility study of a triclinic *paramagnet* for many years and the first based solely upon the Faraday method, we briefly review the procedure followed. The first stage follows that of Ghosh and Bagchi,[11] involving the measurement of the average

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