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Multinuclear NMR Study of 2,2′-Bipyridine Complexes with Alkali Cations in Nonaqueous Solvents

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Nuclear magnetic resonance of lithium-7, sodium-23, potassium-39, cesium-133 and carbon-13 nuclei was used to study the interactions of the alkali metal ions with 2,2′-bipyridine (BP) in several nonaqueous solvents. The stabilities of the complexes were found to be in the order $Li^+ > Na^+ > K^+$*. Complex formation was not detected for the* Cs^+*–BP system. The stabilities of the complexes are very dependent on the medium and vary inversely with the solvating abilities of the solvents. A* $Li^+\cdot(BP)_2$ *complex was identified in nitromethane solutions, but the stoichiometries of other complexes could not be established from the NMR measurements.*

Introduction

While some fifteen years ago the coordination chemistry of the alkali cations was very largely unknown and was thought to be non-existent, the discovery of the macrocyclic ligands – crown ethers – by Pedersen in 1967 [1] and of macrobicyclic ligands – cryptands – by Lehn and co-workers two years later [2], opened a new chapter in coordination chemistry of metal ions and during the past decade numerous papers appeared describing syntheses of new macrocyclic ligands and their complexing properties. Much less popular are the studies of the alkali complexes with the more conventional ligands, although as shown by an excellent recent review article by Poonia and Bajaj [3], some attempts to study such complexes have been made even in the pre-macrocycle days. In most cases, however, such work was directed towards the isolation of new solid adducts of the alkali salts with a variety of chelating and non-chelating ligands [3]. For example, the first solid alkali complex of 2,2′-bipyridine seems to be $(K\cdot BP)^+Ph_4B^-$, recently isolated by Grillone and Nocilla [4]. However, few attempts have been made to study the existence and the stability of such adducts in solutions, and particularly in nonaqueous solutions.

In general, interactions of 'conventional' ligands with the alkali ions are quite weak and often they are beyond the sensitivities of most physicochemical techniques. Therefore, in order to detect the formation of such complexes it is necessary to use very sensitive probes and to optimize the experimental conditions. Thus, for example, it is preferable to observe alkali ion–ligand interactions in nonaqueous solvents whose solvating abilities are inferior to that of water.

In recent years we [5] and others [6] have used NMR resonances of the alkali nuclei to detect changes in the immediate chemical environment of the alkali ions in solutions, and in particular, to study the thermodynamics of complexation reactions involving macrocyclic ligands. The sensitivity of this technique makes it particularly useful for studies of very weak interactions. Recently we wished to extend our studies of alkali complexes to other ligands besides the macrocycles. This paper reports our preliminary studies on the use of multinuclear NMR to detect weak alkali complexes in solutions. We selected 2,2′-bipyridine as the ligand since, according to Poonia [7], it reacts at best exceedingly weakly with the alkali salts (as compared, for example, with 1,10-phenanthroline) and thus provides a good test for the sensitivity of our technique.

Experimental

Materials

Lithium perchlorate (Fisher) was dried at 190 °C for several days, sodium tetraphenylborate (Baker) was dried under vacuum at 60 °C for 72 h, potassium hexafluoroarsenate (Alfa-Ventron) was recrystallized from water and vacuum dried at 100 °C for 24 h; cesium thiocyanate (Rocky Mt. Res.) was recrystallized from absolute ethanol and dried under vacuum; 2,2-bipyridine (G. F. Smith) was dried under vacuum for 24 h at room temperature.

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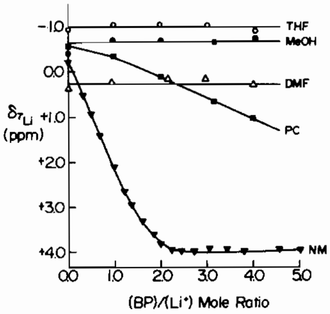

Fig. 1. Lithium-7 chemical shift as a function of the (BP)/(Li^+) mol ratio; $LiClO_4$ (0.05 *M*) in nitromethane and $LiBPh_4$ (0.05 *M*) in other solvents.

Methods used for the purification of solvent have been described in a previous publication [8].

Measurements

Lithium-7, sodium-13 and cesium-133 NMR measurements were carried out in the Fourier transform mode on a highly modified Varian DA-60 spectrometer equipped with a variable frequency probe [9] and operating at 14.09 kgauss and at 23.32, 15.87 and 7.871 MHz respectively for the three nuclei. Non-spinning 10 mm tubes were used. The chemical shifts are referred to 4.0 *M* $LiClO_4$ in H_2O, 3.0 *M* NaCl in H_2O and infinite dilution chemical shift of Cs^+ ion in water respectively and they were corrected for the difference in the bulk diamagnetic susceptibilities between the non-aqueous solvent and water by using the relationship of Live and Chan [10].

Potassium-39 spectra were obtained on a WH-180 Bruker spectrometer operating at a field strength of 42.28 kgauss and a frequency of 8.403 MHz. Non-spinning 15 mm sample tubes were coaxially mounted with 20 mm tubes containing D_2O as the lock. A saturated potassium nitrite solution in D_2O was used as the external standard. The observed chemical shifts were corrected as described above.

Carbon-13 NMR spectra were obtained on a Varian CFT-20 spectrometer at a field strength of 18.79 kgauss and a resonance frequency of 20 MHz. The shifts were measured with respect to the ^{13}C signal of the TMS.

Results

Lithium-7, sodium-23, potassium-39 and cesium-133 chemical shifts (δ) and the line widths at half-height ($\Delta\nu_{1/2}$) were determined as a function of the ligand/metal ion mol ratio (MR). In all cases only one, population-averaged, resonance signal was observed.

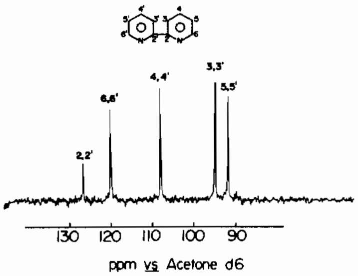

Fig. 2. Carbon-13 NMR spectrum of a 0.20 *M* solution of 2,2'-bipyridine in nitromethane.

Li^+ Complex

The variations of the ^7Li chemical shift as a function of the MR are shown in Fig. 1. It is seen that in tetrahydrofuran, dimethyl formamide and methanol solutions, the ^7Li resonance frequency is independent of the ligand concentration, *i.e.* the environment of the Li^+ ion is not affected by the addition of the ligand. The above solvents have a relatively strong solvating ability *vis-a-vis* metal cations (as expressed by the Gutmann donor numbers [11] of 20.0, 26.6 and 27.5 [12] respectively) and can compete successfully with the ligand for a position in the primary solvation shell of the lithium ion. In propylene carbonate, solvent of intermediate donor character (D.N. = 15.1), the downfield shift of the ^7Li resonance with increasing MR, (~1.5 ppm) shows some Li^+–BP interaction, but the complex is rather weak since there is no indication of the chemical shift leveling off at higher ligand/Li^+ mol ratios. By contrast, in the poorly solvating nitromethane (D.N. = 2.7) the mol ratio plot (Fig. 1) suggests the presence of a quite stable 2:1 (BP:Li) complex.

In order to obtain further evidence for this stoichiometry, we measured the ^{13}C NMR chemical shifts of the BP carbons at various *metal/BP* mol ratios since carbon-13 resonance is known to be sensitive to the conformational changes of the ligands [13, 14] upon complexation. The carbon-13 NMR spectrum of 2,2'-bipyridine is shown in Fig. 2. The addition of $LiClO_4$ to BP in nitromethane solutions results in a downfield shift of the carbon-13 resonances (Fig. 3) and the chemical shifts tend to level off at a mol ratio of about 0.5. Thus the ^{13}C measurements support the formation of a stable $Li(BP)_2^+$ complex in nitromethane solutions.

Lithium complexes with 2,2'-BP were studied by Fenton and Newman [15] and by Vogtle *et al.* [16]. The first authors observed a change in the infrared spectrum of the ligand upon addition of lithium hexafluoroacetylacetonate and inferred the formation of a lithium ion–bipyridine complex of unknown stoichiometry. The second group reported the isolation of a crystalline complex $LiSCN \cdot BP \cdot \frac{1}{2}H_2O$.

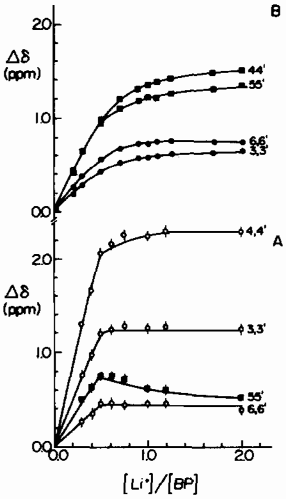

Fig. 3. Variation of the carbon-13 resonance of the BP carbons as a function of the metal ion/ligand mol ratio in nitromethane solutions, with (BP) = 0.20 M. Set A, $LiClO_4$; set B, $NaBPh_4$.

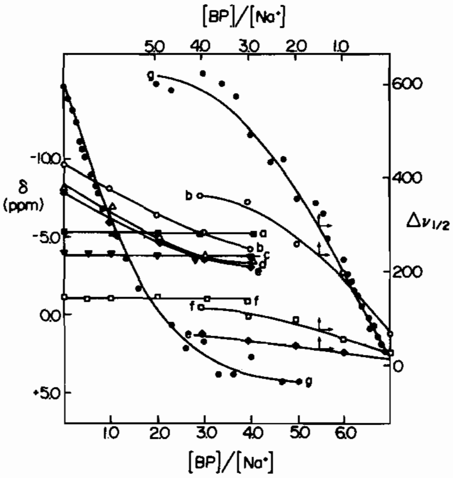

Fig. 4. Plots of sodium-23 chemical shifts (δ) and of the linewidth ($\Delta\nu_{1/2}$ in Hz) in various solvents: (a) DMF, (b) PC, (c) MeOH, (d) THF, (e) MeCN, (f) (DMSO), (g) $MeNO_2$; 0.15 M $NaBPh_4$ in nitromethane and 0.075 $NaBPh_4$ in other solvents.

They also referred to the use of ^{23}Na NMR for a qualitative differentiation of the stability of Na^+ ion complexes with *o*-phenanthroline, 2,2′,2″-terpyridine and 2,2′-bipyridine and concluded that the last ligand gives the least stable complex.

In our case, the small upfield shift of the resonance of carbons 5,5′ after the mol ratio of 0.5, may indicate the presence of an unstable 1:1 complex. However, the indications of the formation of a stable $Li(BP)_2^+$ complex are quite clear. It should be noted that nitromethane, despite its highly polar character, is a very poor solvating agent for metal cations and, therefore, it is very easily displaced by ligands with even a moderate donor strength.

It is interesting to note that the limiting ^{7}Li chemical shift in nitromethane of +4.0 ppm seems to be the largest downfield ^{7}Li chemical shift observed thus far from solutions of lithium salts and it is considerably further downfield than that observed for dilute lithium salt solutions in pyridine (+2.5 ppm [17]). On the other hand, the highest upfield shift seems to be that of fluorenyllithium diethyl ether complex in ether solvent of −6.2 ppm [18]. Although two different references were used for these measurements, 4.0 M $LiClO_4$ and 20% solution of LiCl (both aqueous), the difference between the two is smaller than the experimental error.

Our results seem to support the explanation proposed by Maciel *et al.* [19] for the very high and low shieldings of ^{7}Li in the acetonitrile and pyridine solutions respectively. The neighbor anisotropy effect is even stronger for the $Li(BP)_2^+$ complex than for Li^+ ion in pyridine solutions. In the $Li(BP)_2^+$ complex, Li^+ ion is coordinated to the nitrogen in the plane of the ring, while in the $Li^+Fl^-{\cdot}Et_2O$ complex it is located directly above the plane of the aromatic carbanion [18]. The resulting ^{7}Li shifts are 10 ppm apart, about twice as much as the total range of ^{7}Li shifts in dilute solutions of lithium salts in common solvents [17, 19].

Na^+ Complexes

The variation in the ^{23}Na resonance frequency and in the linewidth as a function of the ligand/[Na^+] mol ratio are shown in Fig. 4. It is seen, once again, that in strongly solvating solvents such as dimethylformamide, dimethylsulfoxide and methanol, the chemical shift remains independent of the mol ratio. In the tetrahydrofuran, acetonitrile and propylene carbonate solutions, the ^{23}Na resonance frequency shifts downfield as the concentration of BP is increased. At the same time the linewidths increase, especially in the PC solutions. It is evident that in these solvents there is a weak interaction between the ligand and the sodium ion, incidentally confirming the results of Vogtle *et al.* [16].

In nitromethane solutions we observe a very large downfield chemical shift of nearly 20 ppm between mol ratios of 0 and ~5 which indicates a rather drastic change produced in the environment of the Na^+ ion by the exchange of the solvent molecules in the first cationic solvation shell for the ligand molecule(s). This observation is not particularly surprising in view of the very low donor ability of the solvent and the very upfield resonance of the uncomplexed sodium ion. It is seen, however, that the limiting chemical shift is not reached even at a mol ratio of 5:1 indicating that the complex is unstable.

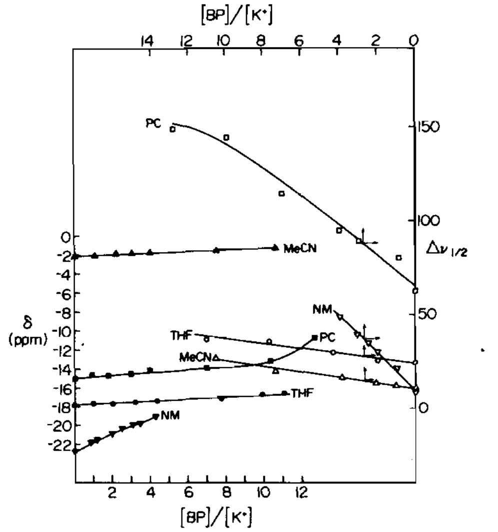

Fig. 5. Plot of potassium-39 chemical shifts (δ) and of the linewidth ($\Delta\nu_{1/2}$ in Hz) in various solvents. Salt used, 0.075 M $KAsF_6$.

It is interesting to note that in this solvent the line broadening upon complexation (12 to ~600 Hz) is comparable to that observed for the crown ether complexes [20–22] in which the planar structure of the crown ether complex drastically increases the asymmetry of the electric field at the sodium nucleus. Therefore, it seems likely that BP moleculed adopt a similar planar arrangement around the sodium ion, although we cannot unambiguously establish the stoichiometry of the complex in solution from our NMR measurements. Likewise, upon complexation carbon-13 NMR shows large downfield shifts for all carbons of the ligand but does not indicate the stoichiometry of the complex.

The limiting ^{23}Na chemical shift in nitromethane solution (5.0 ppm) suggests that BP molecules (i) effectively insulate the Na^+ ion from the surrounding solvent and (ii) provide more electronic density around Na^+ ion than the pyridine molecules ($\delta_{^{23}\mathrm{Na}}$ in pyridine ~ 1 ppm [5]). At least two BP molecules are necessary to eliminate the nitromethane molecules from the primary solvation layer of Na^+, so that the stoichiometry of the complex must be at least $Na^+ \cdot (BP)_2$.

Complexes with K^+ and Cs^+

The variation of ^{39}K chemical shift and in the linewidth are shown in Fig. 5. Only solvents with intermediate and weak solvating ability were investigated. Both the chemical shifts and the linewidths show much less change upon the addition of BP than was observed with Li^+ or Na^+, although the range of the chemical shift is considerably larger for ^{39}K than for ^{7}Li or ^{23}Na. It is obvious that the interaction is very weak even in nitromethane solutions. It should be noted that while Grillone and Nocilla succeeded in isolating the solid $(K \cdot BP)^+Ph_4B^-$ complex, in order to do so they had to have a 6–7 fold excess of the ligand [4].

In the case of the cesium salts, the ^{133}Cs resonance frequency was found to be independent of the BP/Cs^+ mol ratio in all solvents studied.

Conclusions

It is clearly seen from the above results that 2,2′-bipyridine does complex Li^+, Na^+ and K^+ ions in nonaqueous solvents and that the strength of the interaction varies in the order $Li^+ > Na^+ > K^+$ and it also varies inversely with the solvating ability of the solvents. No complex could be detected for Cs^+ ion and since ^{133}Cs NMR is particularly sensitive to environment [5], it can be concluded that in this case the extent of the interaction is very small or nonexistent.

Our measurements gave clear-cut indication for the formation of a 2:1 ligand:Li^+ complex in solutions but were much less definite for the heavier alkalies; however, it seems reasonable to expect that the same stoichiometry could be found in these cases, although the 2:1 complexes are probably quite stable.

Multinuclear NMR studies of alkali ion complexes with BP and with other ligands are being continued in our laboratories.

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