is strongly reminiscent of the spectrum of the powdered sample in Figure 2. More particularly, observation of the C, D, and E lines supports an analysis in terms of a tetrameric structure at least. The best fit of the experimental spectrum is obtained with the following set of parameters: $g_{\perp} = 2.415$, $g_{\parallel} = 1.980$, $A_{1\perp} = 480$ MHz, $A_{1\parallel} = 557$ MHz, $A_{2\perp} = 980$ MHz, and $A_{2\parallel} = 731$ MHz (Figure 6). It may be emphasized that this type of spectrum is characteristic of most of the blue complexes obtained from lactams or pyrimidines, which, therefore, may retain an oligomeric structure in solution. A somewhat different type of spectrum characterizes the blue complexes prepared from ligands involving a C(O)–NH_2 group. A typical spectrum is represented in Figure 6. These spectra display a too limited number of broad and ill-resolved hyperfine lines to probe simulation models. The poor quality of the spectra may be tentatively attributed to a broadening of the lines due to unresolved hyperfine interactions with ^1H nuclei of the ligand.

Finally, the less ambiguous data regarding the structure of amorphous blue complexes are likely afforded by ESR spectroscopy. This emphasized the need for a suitable analysis of the related spectra. It is of interest to note that, in many cases, this can be achieved by using a relatively simple model, which may be directly compared with the structure of Lippard's blue.[3,7,18]

Registry No. $[Pt(NH_3)_2(H_2O)_2]^{2+}$, 20115-64-4; bis($\mu$-1-methylhydantoinato-*N*,*O*)bis(*cis*-diammineplatinum(II)) dinitrate, 83710-06-9; *cis*-dichlorodiammineplatinum(II), 15663-27-1.

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A Competitive NMR Technique for Measurements of Metal Ion–Macrocyclic Polyether Complexation Constants in Solutions

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An NMR technique has been developed for the determination of formation constants of metal ion complexes that uses competition of two metal cations for a given ligand. The technique is applicable in a wide variety of media, but it is particularly useful for reactions in aprotic solvents. This technique allows measurement of complexes of metal ions whose nuclear properties make precise NMR measurements very difficult, if not impossible. It also allows measurements of formation constants that are too large to be measured by the conventional NMR technique involving a single cation. The feasibility of this technique is first illustrated by measurements of formation constants determined previously by other techniques. Results are also given for a series of 18-crown-6 complexes with a variety of cations, including a paramagnetic cation, Ni^{2+}, in dimethylformamide solutions with formation constant values varying from $\log K_f < 1.23$ to $\log K_f = 4.21$. The precision of the determination is limited by the precision of the known formation constant used in the competitive reaction and by the precision of the chemical shift measurements.

Introduction

Practically every physicochemical technique known to chemists has been used, at one time or another, for the measurements of equilibrium constants in solutions. The vast majority of such measurements have been carried out in aqueous solutions, where electrochemical techniques are particularly effective. On the other hand, in nonaqueous solutions, and particularly in aprotic solvents, electrochemical techniques are often not effective due to difficulties of finding reversible electrodes in these media. In such cases spectroscopic techniques must be used; however, lack of sensitivity often precludes measurements of large equilibrium constants (e.g., $>10^5$).

This problem is particularly troublesome in the NMR studies of complexation reactions of macrocyclic ligands (crown ethers and cryptates) with a variety of cations in aprotic media. In many cases formation constants can be determined from the variation of the chemical shift of the studied cation with the ligand:cation mole ratio.[1,2] The accuracy of the method depends on the chemical shift range of the nucleus and on the accuracy with which the resonances can be measured (difficult with broad lines); under the best conditions, the upper limit of K_f is only somewhat larger than 10^4. Of course, the difficulties are exacerbated when the cationic nuclei have low receptivities or when they are paramagnetic.

Cox, Schneider, and their co-workers[3–6] have developed a competitive potentiometric technique for the determination of large formation constants of macrocyclic complexes. They use a silver/silver ion electrode, which behaves reversibly in a number of aprotic solvents, to probe the competition between the Ag^+ cation and the studied cation for a given ligand. When the K_f of the silver complex is known, that of the other complex can be obtained. This method works particularly well for systems where the Ag^+ ion forms fairly stable complexes ($K > 10^4$), as in the case of the cryptates. The usefulness of the technique, of course, is limited to solvents where the Ag/Ag^+ electrode behaves reversibly and where other cations, which may be present, and the counterions, do not influence the electrode potential.

It seemed to us that the competition method of Cox and Schneider could be applied to the NMR measurements where it would be largely indepedent of the solvent and where, depending on circumstances, various cations with suitable NMR properties could be used as probes for nuclei with less satisfactory properties, such as high quadrupole moment, high Steinheimer antishielding factor, low natural abundance, and/or paramagnetism. Such a technique could significantly expand the use of NMR spectroscopy for studies of reactions in solutions.

Some years ago Zink and co-workers[7] reported the use of thallium-205 NMR measurements for the determination of *relative* formation constants of the Tl^+ ion and of another cation M^+. This technique is useful for the determination of the selectivity order but it is limited to the systems where the ligand:metal cation ratio is such that the ligand is totally in the complexed form, which may not be true for some systems. It is also not applicable to cases where complexes with stoichiometries other than 1:1 are also formed.

More recently, Reid and Rabenstein[8,9] have used the proton NMR of mercaptoacetic acid, as a function of pH, to monitor

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(3) Cox, B. G.; Schneider, H. *J. Am. Chem. Soc.* **1977**, *99*, 2809.

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the competition of mercaptoacetic acid with various thiol-containing compounds for CH_3Hg^{II}. This technique requires preparation of solutions of mercaptoacetic acid, thiol, and CH_3Hg^{II} in the proportions 1:1:1. They have also used the proton NMR of glutathione to monitor the competition of glutathione and hemoglobin for CH_3Hg^{II}. Their method for this is analogous to that of Zink, except that it is the CH_3Hg^{II} which must be completely complexed.

Experimental Part

Cesium thiocyanate (Pfaltz and Bauer) was recrysallized twice from methanol and then dried at 45 °C under vacuum for 2 days. Potassium thiocyanate (Fisher) and sodium tetraphenylborate (Aldrich) were used as obtained, except for drying for 2 days under vacuum at 45 °C. Cesium tetraphenylborate was prepared and dried as described by Mei et al.[10] Cesium chloride (Alfa), potassium chloride (Fisher), sodium nitrate (Baker), cesium nitrate (Alfa), barium nitrate (Allied Chemical), and strontium nitrate (Baker) were used as obtained except for drying at 120 °C for 2 days. Calcium nitrate (Fisher) and nickel(II) nitrate (Allied Chemical) were used as received except for drying at room temperature at pressures of 10^{-5} torr for 3–5 days. Magnesium nitrate (Baker) and lanthanium(III) nitrate (Alfa) were also dried at 10^{-5} torr for 3 days at room temperature and for 1 day at 50–60 °C. All salts were stored in a drybox under dry nitrogen atmosphere.

Acetonitrile (Baker), AN, was refluxed over CaH_2 for 7 days, followed by fractional distillation with the middle 60% fraction retained. Methanol (MCB), MeOH, was refluxed over Mg and I_2 for 2 days and then fractionally distilled with the middle 60% fraction retained. *N*,*N*-Dimethylformamide (Mallinckrodt), DMF, was refluxed for 3 days over CaH_2 and then fractionally distilled with the middle 60% fraction retained. In each case, the solvents were checked for water content by gas chromatography and were found to contain less than 70 ppm of water. The solvents were stored over freshly activated Linde 3-Å molecular sieves for at least 2 days prior to use.

The ligand 18-crown-6 (18C6) was obtained from the Aldrich Chemical Co. and purified as described earlier;[11] the purified ligand was vacuum dried for 2 days at room temperature. Dibenzo-27-crown-9 (DB27C9) was obtained from the Parish Chemical Co., recrystallized twice from *n*-heptane, and dried for at least 2 days under vacuum.

All NMR measurements were made on a Bruker WH-180 multinuclear NMR spectrometer. At the field strength of the WH-180 cesium-133 resonates at 23.62 MHz and sodium-23 resonates at 47.61 MHz. All samples were measured in 10-mm-o.d. NMR tubes (Wilmad) with a 4-mm-o.d. coaxial insert (Wilmad) containing lock solvent and a chemical shift reference (0.5 M CsBr in D_2O or 0.1 M NaCl in D_2O). All measurements are corrected for bulk diamagnetic susceptibility, by the equation of Martin, et al.:[12]

$$\delta_{cor} = \delta_{obsd} + \frac{4\pi}{3}(\chi_{ref} - \chi_{soln}) \qquad (1)$$

All chemical shifts are given vs. infinitely dilute aqueous solutions of Cs^+ and of Na^+ ions for the ^{133}Cs and ^{23}Na measurements respectively. Measurements were made at the probe temperature of approximately 22 °C.

Method. A series of solutions were prepared containing a constant amount of the salts of the two cations (0.01 M each) and varying amounts of the ligand. Chemical shifts of the probe cation were determined, and the data were analyzed with the use of the nonlinear-least-squares program KINFIT.[13] In all studies reported in this paper the exchange of the probe cation between the free and the complexed sites was fast and only one population-averaged signal was observed.

When the two cations, M^+ and N^+, both form only 1:1 complexes with ligand L, we have the two simultaneous equilibria

$$M^+ + L \overset{K_M}{\rightleftharpoons} ML^+ \qquad (2)$$

$$N^+ + L \overset{K_N}{\rightleftharpoons} NL^+ \qquad (3)$$

A polynomial equation in the free ligand concentration [L] was derived from the mass balance and the equilibrium constant expression:

$$K_MK_N[L]^3 - [K_MK_N(C_L - C_M - C_N) - K_M - K_N][L]^2 - [K_M(C_L - C_M) + K_N(C_L - C_N) - 1][L] - C_L = 0 \qquad (4)$$

where C_L, C_M, and C_N are the analytical concentrations of the ligand, the metal ion M^+, and metal ion N^+, respectively. The observed chemical shift, δ_{obsd}, of the metal ion M^+ is given by the expression

$$\delta_{obsd} = \frac{\delta_0 + \delta_1[L]K_M}{1 + K_M[L]} \qquad (5)$$

where δ_1 is the chemical shift of the complexed metal ion M^+ and δ_0 is the chemical shift of the free M^+.

If the metal ion N^+ forms both 1:1 and 1:2 complexes, according to the equilibria

$$N^+ + L \overset{K_{N_1}}{\rightleftharpoons} NL^+ \qquad (6)$$

$$NL^+ + L \overset{K_{N_2}}{\rightleftharpoons} NL_2^+ \qquad (7)$$

the expression for the free-ligand concentration becomes

$$K_MK_{N_1}K_{N_2}[L]^4 - [K_MK_{N_1}K_{N_2}(C_L - C_M - 2C_N) - K_MK_{N_1} - K_{N_1}K_{N_2}] \times [L]^3 - [K_MK_{N_1}(C_L - C_M - C_N) + K_{N_1}K_{N_2}(C_L - 2C_N) - K_M - K_{N_1}][L]^2 - [K_{N_1}(C_L - C_N) + K_M(C_L - C_M) - 1][L] - C_L = 0 \qquad (8)$$

The observed chemical shift for the metal ion M^+ would still be given by eq 5, but if the metal ion N^+ is the probe nucleus, the observed chemical shift is given by

$$\delta_{obsd} = \frac{\delta_0 + \delta_1K_{N_1}[L] + \delta_2K_{N_1}K_{N_2}[L]^2}{1 + K_{N_1}[L] + K_{N_1}K_{N_2}[L]^2} \qquad (9)$$

where δ_2 is the chemical shift of the NL_2^+ complex and the other symbols are as previously defined.

During the fitting process, the polynominal for the free-ligand concentration (either eq 4 or eq 8) is solved and the chemical shift calculated (eq 5 or 9) for each trial set of unknown parameters for each solution. Adjustment then is made of the unkown parameters (the unknown formation constant—either K_M or K_{N_1}—and the chemical shifts) until the sum of the squares of the differences between the calculated and experimentally determined chemical shifts is minimized.

It should be noted that the values for the experimentally determined formation constants are reported with two uncertainties. The first uncertainty, inside the parentheses, is the uncertainty for the calculated value when the known formation constant is used as constant (i.e., as a value without uncertainty). The results are then combined with the known uncertainty of the formation constant of the known complex to give the overall uncertainty in the value of the measured K_f.

Results and Discussion

Model calculations for the behavior of a competitive two-cation system indicates the sensitivity of the technique. When a metal ion, M^+, whose formation constant, K_{M^+}, is assumed to be 10^3 M^{-1}, is in the presence of another metal ion, N^+, whose formation constant, K_{N^+}, is allowed to vary from 0 to 10^6 M^{-1}, the set of calculated chemical shift vs. mole ratio of ligand plots is obtained, which are shown in Figure 1. An inspection of these curves indicates that they do contain the information needed to calculate the value for the formation constant of the "N" complex, within a wide range of values of K_{N^+} (at least 6 orders of magnitude), and that a change in the value of the "N" formation constant results in the maximum change in the chemical shift behavior for those values of the formation constant which are more nearly equal to the value of the known formation constant. Consequently, the precision of the calculated value for the unknown formation constants is affected by the "match" of the values of the known and unknown formation constants, with the least precise values for the unknown being those which are the least equal to the value of the known constant. Further, it should be obvious that it is impossible to calculate a value for an unknown formation constant with the overall precision better than the precision of the known formation constant.

As a test of the method, the K_f values of Frensdorff[14] for the 18C6 complexes of cesium and potassium ions in methanol were used, with the formation constant for the potassium complex being treated as an unknown. When the experimentally obtained cesium-133 chemical shifts for a series of solutions containing CsCl, KCl, and 18C6 in methanol are fitted to the model described

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(10) Mei, E.; Popov, A. I.; Dye, J. L. *J. Phys. Chem.* **1977**, *81*, 1677. Mei, E. Ph.D. Thesis, MSU, East Lansing, MI, 1977.

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Table I. Comparison of Formation Constant Values Obtained by the Competition Method with Their Literature Values (Probe Nucleus ^{133}Cs)

system	probe complex	known log K_f	studied complex	calcd log K_f	lit. value
$Cs^+/K^+/Cl^-/18C6/MeOH$	$Cs^+\cdot 18C6$	4.62 ± 0.04[a]	$K^+\cdot 18C6$	6.18 (±0.04) ± 0.08	6.10 ± 0.04[a]
$Cs^+/Na^+/Ph_4B^-/18C6/DMF$	$Na^+\cdot 18C6$	2.10 ± 0.07[b]	$Cs^+\cdot 18C6$	4.03 (±0.08) ± 0.20	3.95 ± 0.14[c]
	$Cs^+\cdot(18C6)_2$	$K = 2.44 \pm 0.05$ M^{-1}[c]			
$Cs^+/Na^+/Ph_4B^-/18C6/AN$	$Na\cdot 18C6$	4.21 ± 0.10[b]	$Cs^+\cdot 18C6$	4.83 (±0.07) ± 0.18	>4[c]
	$Cs^+\cdot(18C6)_2$	$K = 3.7 \pm 0.6$ M^{-1}[c]			
$Cs^+/K^+/SCN^-/DB27C9/AN$	$Cs^+\cdot DB27C9$	4.06 ± 0.04[d]	$K^+\cdot DB27C9$	4.10 (±0.02) ± 0.08	3.9 ± 0.8[g]
	$Cs^+\cdot SCN^-$	$K_{ip} = 41 \pm 14$[e]			
	$K^+\cdot SCN^-$	$K_{ip} = 0.59 \pm 0.42$[f]			

[a] Reference 14. [b] This work. [c] Reference 10. [d] Reference 16. [e] Reference 17. [f] Reference 18. [g] Reference 15.

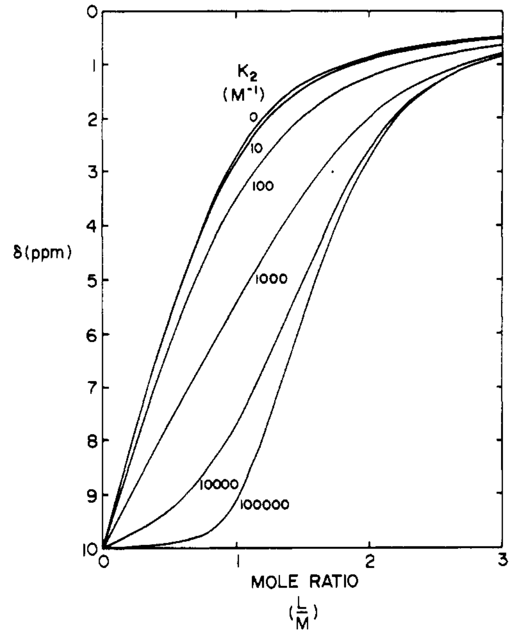

Figure 1. Calculated chemical shifts vs. mole ratio of ligand to one of the metal ions, as a function of the formation constant for the metal ion that is not monitored by NMR, for solutions of two metal ions, both at 0.01 M, that form 1:1 complexes, when the formation constant for the observed metal ion is 10^3 M^{-1}.

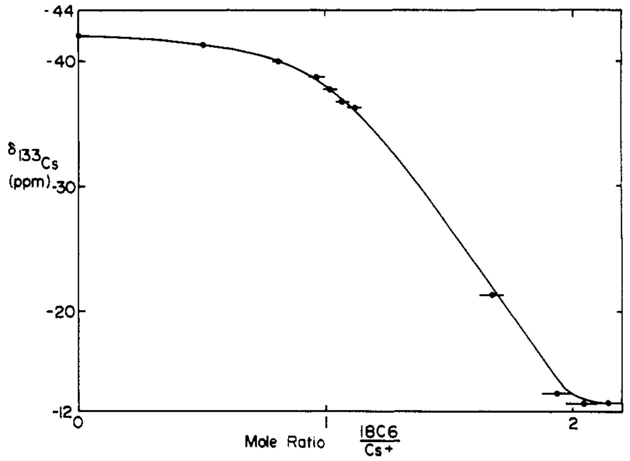

Figure 2. Experimental and calculated cesium-133 chemical shifts as a function of 18C6:Cs^+ mole ratio for solutions containing CsCl, KCl, and 18C6 in MeOH.

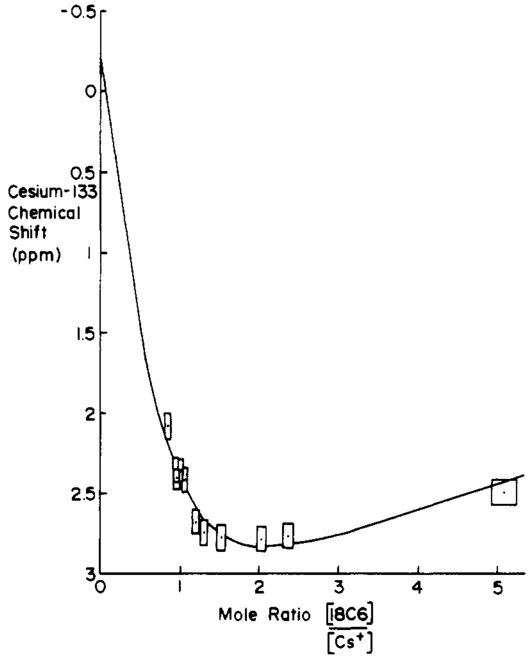

Figure 3. Experimental and calculated cesium-133 chemical shifts as a function of 18C6:Cs^+ mole ratio for solutions containing $CsPh_4B$, $NaPh_4B$, and 18C6 in DMF. The minimum of the curve is a clear indication of formation of the $Cs^+\cdot(18C6)_2$ complex.

by eq 4 and 5, with the value of the cesium complex formation constant of Frensdorff (log $K_{Cs^+\cdot 18C6} = 4.62 \pm 0.04$) being used as a constant, the calculated value for the potassium complex formation constant becomes log $K_{K^+\cdot 18C6} = 6.18$ (±0.04) ± 0.08, which is in excellent agreement with that of Fresndorff (log $K_{K^+\cdot 18C6} = 6.10 \pm 0.04$); the results are given in Table I. The experimentally obtained cesium-133 chemical shifts are plotted in Figure 2 as a function of $(18C6):(Cs^+)_{total}$ mole ratio along with the curve calculated from the theoretical equations, by using the results of the computer fit.

As a second test of the method, the value for the formation constant of the 1:1 complex of cesium ion with 18C6 in dimethylformamide was treated as an unknown with the 1:2 complex formation constant of Mei et al.[10] ($K_{1:2} = 2.44 \pm 0.05$ M^{-1}) being used as known. Before the data could be obtained, it was necessary to determine the value for a "known" complex. A conventional NMR study of 18C6 complexation of $NaNO_3$ in DMF was carried out by sodium-23 NMR. The value determined for the formation constant of the $Na^+\cdot 18C6$ complex ($K_{Na^+\cdot 18C6} = 125 \pm 20$ M^{-1}) was then used as known in a cesium-133 competitive NMR study of solutions of $CsPh_4B$, $NaPh_4B$, and 18C6 in DMF.

The experimentally obtained cesium chemical shifts were then fitted to the model described by eq 8 and 9. The result of this fit gave $K_{Cs^+} = [10.8\ (\pm 2.1) \pm 5] \times 10^3$ M^{-1}, which is in agreement with that of Mei of $K_{Cs^+} = (9 \pm 3) \times 10^3$ M^{-1}.[10] The experimental points and the calculated curve are shown in Figure 3. It should be noted that the reversal of the direction of the chemical shifts clearly indicates the formation of a 1:2 complex.

In order to show that the competitive NMR method is capable of determining values for formation constants where the conventional NMR method results in giving only the lower limits of the formation constant, the K_f of the sodium–18C6 complex in acetonitrile was determined directly to be log $K = 4.21$ ● 0.10, and this value was used as a probe to determine the formation constant of the 1:1 complex of cesium with 18C6 in this solvent. Its value has been reported[10] to be > 10^4 M^{-1}, with the 1:2 formation constant being 3.7 ± 0.6 M^{-1}.

A computer analysis of the cesium-133 chemical shifts for solutions containing $CsPh_4B$, $NaPh_4B$, and 18C6 in acetonitrile

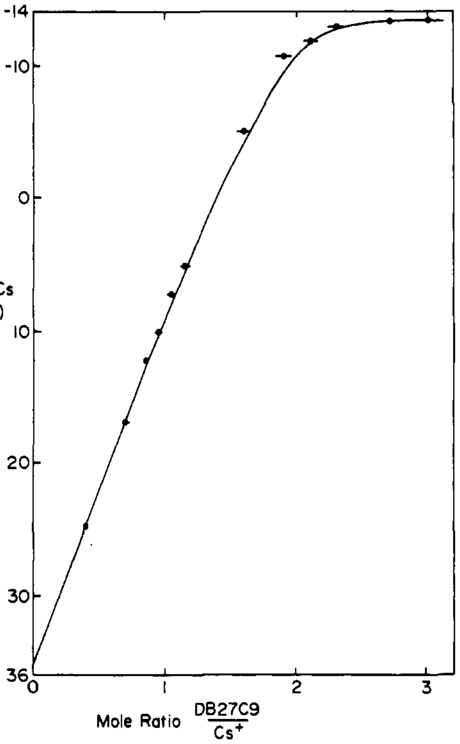

Figure 4. Experimental and calculated cesium-133 chemical shifts as a function of DB27C9:Cs^+ mole ratio for solutions containing CsSCN, KSCN, and DB27C9 in AN.

(using eq 8 and 9) gives the 1:1 formation constant for the $Cs^+\cdot18C6$ complex of log $K_{Cs^+1:1}$ = 4.83 (±0.07) ± 0.18, which is in good agreement with the previously reported value and demonstrates clearly that the competitive technique can indeed succeed where the conventional method falls short.

The receptivity of the ^{39}K nucleus is quite low (4.73 × 10^{-4} times that of ^1H), moreover, the resonance lines are quite broad. Consequently it is not a very suitable nucleus for quantitative NMR measurements. We applied the competitive technique to determine the formation constants of the $K^+\cdot DB27C9$ complex in acetonitrile solutions. Its value of log 3.9 ± 0.8 has been reported by Schmidt[15] on the basis of ^{39}K measurements. Poor nucleus properties of ^{39}K result in a large uncertainty.

The probe complex was $Cs^+\cdot DB27C9$, whose formation constant in this solvent was previously found to be log K = 4.06 ± 0.04[16] by ^{133}Cs NMR measurements. Since we used thiocyanate as the counterion, the situation was complicated by ion-pair formation with K_{ip}'s for Cs^+SCN^- and for K^+SCN- being 41.4 ± 14[17] and 0.59 ± 0.43,[18] respectively. In order not to obtain a "conditioned" constant, these values had to be incorporated into the calculations.

The Cs^+ chemical shifts were determined in the CsSCN/KSCN/DB27C9 system in acetonitrile, and the results are shown in Figure 4. Analysis of the data gave log K of 4.10 (±0.02) ± 0.08 for the $K^+\cdot DB27C9$ complex. This value is significantly more precise than the original value of Schmidt obtained by ^{39}K NMR. The advantage of using a probe nucleus with narrow lines and a wide chemical shift range is obvious.

Since the above results clearly illustrate the usefulness and the versatility of the competitive NMR method for the determinations of complexation constants, this technique was used for a study of alkaline-earth-metal cations, lead(II), and lanthanum(III) complexes with 18-crown-6 in dimethylformamide solutions by using sodium-23 NMR as the probe. For each of these cations, a series of solutions containing $NaNO_3$, $M(NO_3)_m$, and 18C6 in DMF were prepared and ^{23}Na chemical shifts measured at different ligand:Na^+ mole ratios used to determine the formation constant of the 18C6 complex with the cation M^{m+}. The results of these studies are given in Table II. It should be noted that the experimental and calculated curves shown in Figure 5 are very similar to the calculated curves of Figure 1. It should also be noted that in this case the known formation constant of the $Na^+\cdot18C6$ complex is 120, while the "known" formation constant in Figure 1 was assumed to be 1000. A cesium-133 competitive NMR study of a series of solutions containing $CsNO_3$, $Ni(NO_3)_2$, and 18C6 in DMF was performed in the hopes of showing that this method extends the applicability of NMR to paramagnetic cations. It is known that Ni^{2+} is paramagnetic in DMF,[19,20] but due to the low concentration of the Ni^{2+} in these solutions the magnetic susceptibilities measured for the solutions are insignificantly

Table II. Formation Constants of 18C6 Complexes with Metal Ions in DMF Solutions[a]

known complex	known log K_f	probe nucleus	unknown complex	calcd log K_f
$Na^+\cdot18C6$	2.10 ± 0.07[b]	^{23}Na	$Mg^{2+}\cdot18C6$	2.33 (±0.08) ± 0.15
			$Ca^{2+}\cdot18C6$	<1.30
			$Sr^{2+}\cdot18C6$	3.00 (±0.10) ± 0.19
			$Ba^{2+}\cdot18C6$	4.21 (±0.12) ± 0.19
			$Pb^{2+}\cdot18C6$	3.66 (±0.07) ± 0.12
			$La^{3+}\cdot18C6$	<1.23
$Cs^+\cdot18C6$	4.50 ± 0.05[b]	^{133}Cs	$Ni^{2+}\cdot18C6$	1.85 (±0.19) ± 0.26
$Cs^+\cdot(18C6)_2$	K = 2.44 ± 0.05 M^{-1}[c]			

[a] In all cases NO_3^- was the counterion. [b] This work. [c] Reference 10.

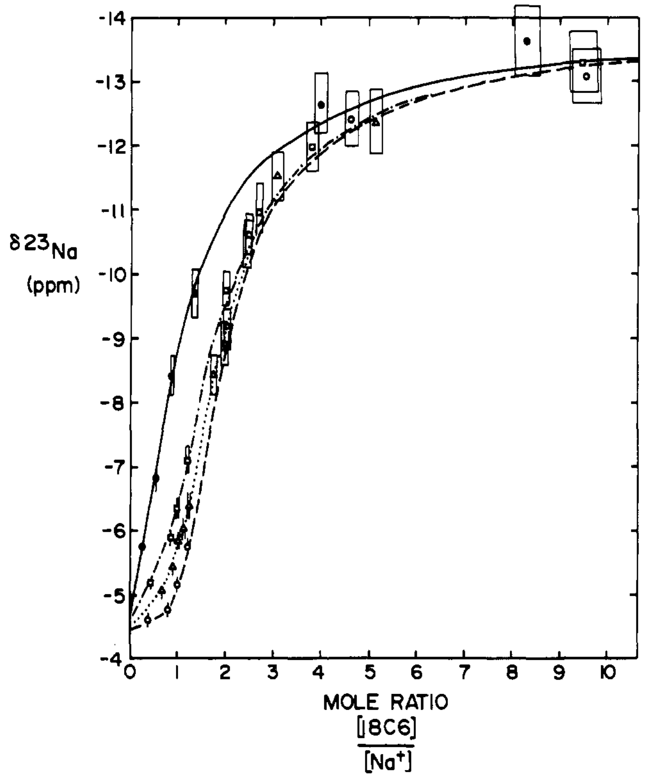

Figure 5. Experimental and calculated sodium-23 chemical shifts as a function of 18C6:Na^+ mole ratio for solutions containing $NaNO_3$ and 18C6 in DMF (●) and solutions containing $NaNO_3$, $M(NO_3)_m$, and 18C6 in DMF where M = Sr^{2+} (□), Pb^{2+} (△), and Ba^{2+} (○).

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different from that of pure DMF. Consequently, the measured chemical shifts were corrected for only the bulk diamagnetic susceptibility of DMF. The results of this study are also given in Table II.

The observed formation constants, together with those of Shih[17] for K^+ (log $K_{K^+\cdot 18C6}$ = 2.70 ± 0.04) Rounaghi[21] for Tl^+ (log $K_{Tl^+\cdot 18C6}$ = 3.35 ± 0.06), yield the selectivity series

$$La^{3+}, Ca^{2+} < Ni^{2+} < Na^+ < Mg^{2+} < K^+ < Sr^{2+} < Tl^+ < Pb^{2+} < Cs^+ < Ba^{2+}$$

Neglecting, for the moment, La^{3+}, Ca^{2+}, and Ni^{2+}, the trends indicate that, as the size of the cation increases, along a set of cations with the same charge, the formation constants increase, probably due to the decreasing solvation as the cation gets larger; as the charge increases for a given size of the cation, the formation constant increases, due to the increase of the ion–dipole interactions.

The formation constant for the La^{3+} complex seems to be quite low, most likely due to strong ion pairing with the nitrate ion, which does not preclude the formation of a $La^{3+}\cdot$18C6 complex but can reduce the relative amount of complex formed so much that it becomes impossible to measure accurately the formation constant without the knowledge of the extent of ion pairing. The low value for the formation constant for Ni^{2+} is explainable in terms of the geometry Ni^{2+} prefers for its complexes, which is octahedral. Because 18C6 is poorly suited to this geometry, the formation constant is fairly small.

At this time we have no explanation for the low formation constant for Ca^{2+}. It is still interesting to note that this type of behavior for Ca^{2+} has been seen before in water[22] and in 70:30 methanol/water mixtures.[23]

Conclusions

The competitive NMR method described above can be used to extend the applicability of the NMR technique to cations whose formation constants cannot be measured directly by this technique. Furthermore, this new competitive method allows the determination of formation constants that are greater than 10^5, and in principle, it should be possible to measure *very* large formation constants by the repeated application of the competitive technique with each succeeding formation constant becoming larger than the former one. In addition, this method can be used to determine the formation constants for some paramagnetic cation complexes.

Of course any technique has limitations, and this competitive technique is no exception. The need to be able to dissolve two cations with a common anion in a given solvent places restrictions on the systems that may be investigated. In order to determine the sought formation constants, there must be a known value within approximately 4 or 5 orders of magnitude and one of the cations must be suitable to the NMR technique. Because the uncertainty of the determined formation constant will be greater (on a percentage basis) than the uncertainty of the previously known formation constant, repeated application of the competition method will result in uncertainties that, eventually, would become excessively large. Finally, the probe nucleus must be in a fast exchange on the NMR time scale. At this time it appears doubtful that this technique can be applied generally to cryptates where, very often, the exchange is slow at room temperature. Further studies of the advantages and the limitations of this technique are being continued in our laboratory.

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Cooperative Excited-State Behavior in Platinum(II) Magnus-Type Double-Salt Materials. Active and Inactive Photosensitizers for H_2 Production in Aqueous Suspension

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Diffuse-reflectance and emission behavior are used to characterize the lowest excited state of the following $[Pt^{II}]^{2+}[Pt^{II}]^{2-}$ double salts and in some cases their hydrates: $[Pt(NH_3)_4][PtCl_4]$ (MGS), $[Pt(bpy)_2][PtCl_4]$ (PB(Cl); bpy = 2,2′-bipyridine), $[Pt(bpy)(MHB)][PtCl_4]$ (PHB(Cl); MHB = 4-methyl-4′-heptyl-2,2′-bipyridine), $[Pt(bpy)_2][Pt(CN)_4]$ (PBC), and $[Pt(bpy)(MHB)][Pt(CN)_4]$ (PHBC). All of the salts containing the $PtCl_4^{2-}$ anion have lowest excited states of the ligand field type. In green MGS, where metal-metal interaction is significant, no emission occurs, but in yellow PB(Cl)$\cdot 2.5H_2O$ and PHB(Cl), where interaction is weak, emission characteristic of $PtCl_4^{2-}$ is observed. In orange PBC$\cdot 2H_2O$ and PHBC$\cdot 2.5H_2O$ and their red anhydrates, the lowest excited state is assigned as a delocalized $^3Pt(5d_{z^2}–6p_z)$ state. Both salts exhibit strong emission (in PBC powder at room temperature, the emission quantum yield is 0.002 ± 0.001 and the lifetime is 16.8 ± 2.5 ns), which overlaps well with an intense visible absorption band. PBC and PHBC powders are active as photosensitizers for the reduction of water in EDTA solutions. In the presence of Pt(0) catalyst, H_2 production is sustained at a constant rate to >1 turnover with respect to photosensitizer, with no evidence for photosensitizer degradation. In the absence of Pt(0), PBC produces H_2 at a constant rate that is less than 1% of the rate in the presence of Pt(0), but again, without degradation. MGS, PB(Cl), and PHB(Cl) are photoinert and completely inactive as photosensitizers in this reaction. These results are interpreted in terms of the cooperative excited-state structure of these materials.

Introduction

The photosensitized reduction of water has been a subject of intensive research in the last several years,[1] due largely to the worldwide interest in solar energy conversion. Since the discovery of electron-transfer quenching of excited $Ru(bpy)_3^{2+}$ (bpy = 2,2′-bipyridine) in aqueous solution 12 years ago,[2] there has been

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