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Complexation of Cesium Ion with Ferric Halides in Aqueous Solution. Evidence from Cesium-133 Nuclear Magnetic Resonance

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Received April 18, 1972

Nuclear magnetic relaxation rates and shifts of $^7Li^+$ and $^{133}Cs^+$ in aqueous solutions containing Fe^{3+} and various counteranions are reported. In general the results for $^7Li^+$ can be understood in terms of dipolar interaction with the Fe^{3+} unpaired electrons alone. However, for $^{133}Cs^+$ in the presence of the counteranion of Cl^- and F^- the relaxation rates are faster than expected from the dipolar mechanism, T_2 is considerably shorter than T_1, and large paramagnetic shifts are observed. These results are interpreted in terms of ion pair formation between Cs^+ and ferric halide complexes. The degree of ion pairing and some properties of these ion pairs are estimated from the nmr results.

Introduction

Nmr measurements have been used extensively to study interactions between paramagnetic ions and solvent molecules or counteranions in their first coordination sphere.[1,2] Relatively little work has, however, been done on the interaction between paramagnetic cations and other cations in the solution.[3,4] In the present work such interactions, studied by magnetic resonance of Li^+ and Cs^+ in aqueous solutions containing Fe^{3+}, are reported.

The nuclear relaxation of alkali metal ions in solutions involves predominantly the modulation of the quadrupolar interaction and can adequately be interpreted in terms of the general theory of relaxation. In general the resonances of sodium and rubidium are considerably broader than those of lithium and cesium due to the greater quadrupole interaction of the former.[5-7] In the presence of paramagnetic cations there is an additional contribution to the relaxation rate due to hyperfine interaction with the paramagnetic ion. In most cases this contribution comes solely from the direct dipolar interactions with the unpaired electron. However, a particularly large effect on the relaxation rate observed in certain cases cannot be explained in terms of dipolar interaction alone, and scalar interaction must therefore be invoked. This is found for Cs^+ in solutions containing Fe^{3+} and Cl^- or F^-. Such an effect implies specific ion pairing between the alkali metal ion (Cs^+) and the ferric halogeno complex, and in this paper we are mainly concerned with its study. Similar bridge complexes are believed to occur in certain oxidation reduction reactions involving halide ions.[8]

Experimental Section

Materials and Solutions.—All salts used were of analytical grade and were used without further purificaton. Solutions of $LiNO_3$, LiCl, NaF, $CsNO_3$, and CsF were made up gravimetrically. These salts were dried at 100° under vacuum before use. Solutions of $Fe(NO_3)_3$ were prepared from the hydrated salt and the concentration was determined by titration. Solutions of various F^- concentrations at constant Cs^+ were obtained by judiciously mixing CsF, $CsNO_3$, and NaF.

Viscosity measurements were performed using the "Ubbelohde" viscometer.

Nmr measurements of ^7Li and ^{133}Cs were made mainly at 14,000 G, although some measurements were also made at lower fields. Nmr shifts were measured using a Varian DP-60 spectrometer by comparing the position of the desired signal with that of a standard solution in the following way: low frequency (300–500 Hz) modulation was applied and one of the side bands, together with the main resonance in one solution, was recorded. Then without stopping the field sweep, the solutions were changed in time to record the other side band. This procedure was repeated several times sweeping the field in both directions. Nuclear relaxation times, T_1 and T_2, were measured with a Bruker 322 S pulse spectrometer. All measurements were done at 23 ± 2°.

Results and Discussion

Dipolar Interaction between Alkali Metal Ions and Fe^{3+}.—Nuclear relaxation measurements of ^7Li and ^{133}Cs were performed in aqueous solutions of lithium and cesium salts in the presence of Fe^{3+} and various anions. In Figure 1 the results for the longitudinal relaxation rate normalized to unit viscosity for some of the salts are plotted *vs.* the concentration of Fe^{3+}. A few measurements of the transverse relaxation rates were also performed and the results were found to be similar to those for T_1, with the T_1/T_2 ratio ranging between 1.10 and 1.30. These results are consistent with expectation if dipolar interaction between the diamagnetic cations and Fe^{3+} is the dominant interaction mechanism affecting the nuclear relaxation rates. Under these conditions the relaxation rates are given by[9]

$$\frac{1}{T_1} = \alpha^2\left[\frac{1}{12}\overset{(0)}{J}(\omega_S) + \frac{3}{2}\overset{(1)}{J}(\omega_I) + \frac{3}{4}\overset{(2)}{J}(\omega_S)\right] \qquad (1)$$

$$\frac{1}{T_2} = \alpha^2\left[\frac{1}{6}\overset{(0)}{J}(0) + \frac{1}{24}\overset{(0)}{J}(\omega_S) + \frac{3}{4}\overset{(1)}{J}(\omega_I) + \frac{3}{2}\overset{(1)}{J}(\omega_S) + \frac{3}{8}\overset{(2)}{J}(\omega_S)\right] \qquad (2)$$

where $\alpha^2 = \gamma_I^2\gamma_S^2\hbar^2S(S + 1)$ and the J's are spectral densities defined in ref 9 and 10. For the present sys-

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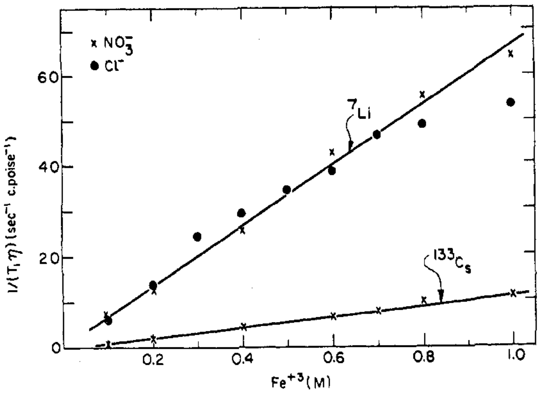

Figure 1.—$1/T_1$, normalized to unit viscosity, of Cs and Li in aqueous solutions of $CsNO_3$, $LiNO_3$, and LiCl as a function of the molar concentration of the corresponding ferric salt.

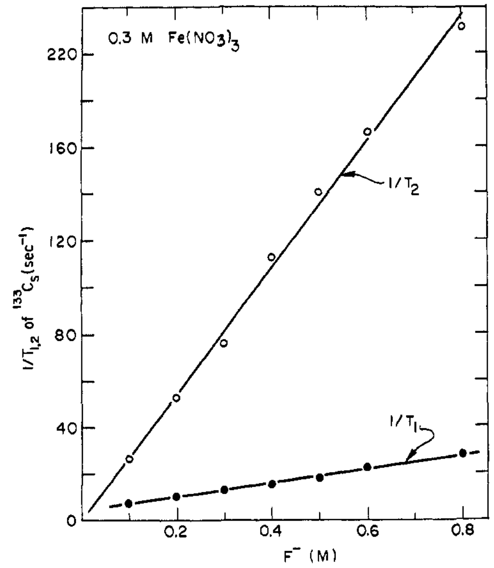

Figure 2.—$1/T_1$ and $1/T_2$ of ^{133}Cs in aqueous solutions containing 0.3 *M* $Fe(NO_3)_3$ and 0.5 *M* Cs^+ as a function of F^- concentration.

tems it is safe to assume that the correlation times for the dipolar interaction are determined by the Brownian diffusional motion, therefore $(\omega_I\tau)^2 \ll 1$ and $(\omega_S\tau)^2 \gg 1$ from which eq 1 and 2 reduce to

$$\frac{1}{T_{1A}} = \frac{8\pi^2\alpha^2N\eta}{25kT} + \frac{1}{T_1^0} \qquad (3)$$

$$\frac{1}{T_{2A}} = \frac{28\pi^2\alpha^2N\eta}{75kT} + \frac{1}{T_2^0} \qquad (4)$$

where the "natural" relaxation rates $1/T_1^0$ and $1/T_2^0$ have been added. In eq 3 and 4, η is the viscosity of the solution and N is the number of the paramagnetic ions per cubic centimeter. It is thus expected that a plot of $1/T_1\eta$ *vs.* the concentration of paramagnetic ions would be linear with a slope proportional to γ_I^2. Excluding the results at higher concentrations of LiCl this is very nearly so; the observed ratio of the slopes for the ^7Li and ^{133}Cs curves in Figure 1 is 6.1 which must be compared with $\gamma_{Li}^2/\gamma_{Cs}^2 = 8.78$. Also the expected ratio $T_1/T_2 = 1.10$–1.30 is consistent with the expected ratio 1.17 from eq 3 and 4.

In contrast with the examples described above we found cases for which this model could not explain the experimental results. They are described in the next paragraph.

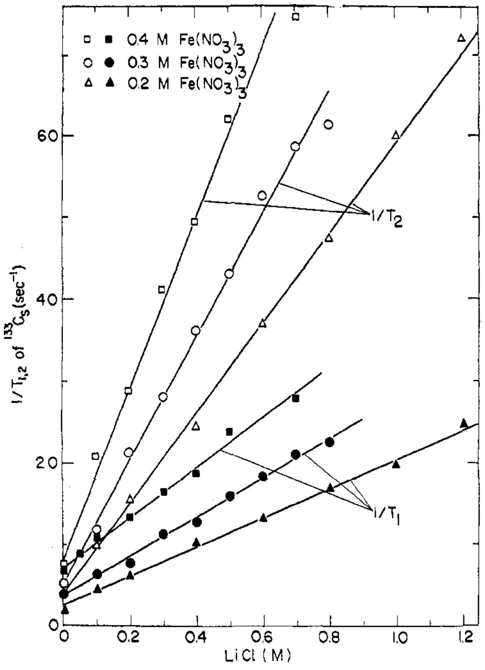

Figure 3.—$1/T_1$ and $1/T_2$ of ^{133}Cs as a function of LiCl concentration in aqueous solutions containing 0.5 *M* $CsNO_3$ and various concentrations of $Fe(NO_3)_3$.

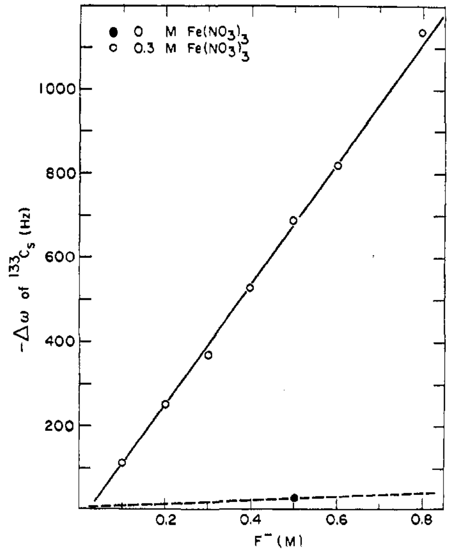

Figure 4.—Chemical shift of ^{133}Cs (open circles) in aqueous solution containing 0.3 *M* $Fe(NO_3)_3$ and 0.5 *M* Cs^+ as a function of F^- concentration. The full circle is the shift measured at the absence of Fe^{3+}.

Scalar Interaction between Cs^+ and Fe^{3+} in the Presence of F^- and Cl^-.—The effect of Fe^{3+} on the nuclear relaxation rates of Cs^+ in the presence of Cl^- and F^- is particularly large; also T_1 differs considerably from T_2. The Cs^+ relaxation rates in solutions containing various concentrations of Fe^{3+} ions as functions of $[F^-]$ and $[Cl^-]$, respectively, at 8 MHz are plotted in Figures 2 and 3. Figures 4 and 5 show significant effect observed on the ^{133}Cs shift. (Similar measurements performed by Lutz[3c] on ^7Li indicated a very small shift.) Some measurements of T_1 and T_2 made at different radiofrequencies (5–8 MHz) showed

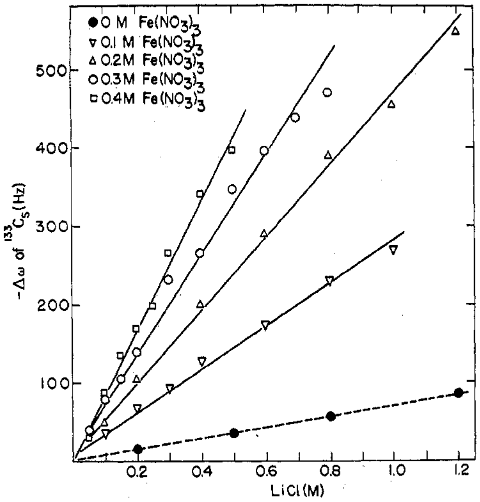

Figure 5.—Chemical shift of ^{133}Cs in aqueous solutions containing 0.5 *M* $CsNO_3$ and various concentrations of $Fe(NO_3)_3$ as function of LiCl concentration.

no dependence, within our experimental accuracy, of the relaxation times on frequency for F^-, and only a small effect on T_1 for the Cl^- solution was found. These results cannot be explained by direct dipole-dipole interaction with Fe^{3+} alone and indicate quite clearly that intimate labile complexes between Cs^+ and Fe^{3+} involving F^- or Cl^- and characterized by specific magnetic parameters are formed. They may be imagined as bridged ion pairs of the type Fe–X–Cs (where X is either F^- or Cl^-). Fast exchange between the free and the complexed forms averages out magnetic parameters of Cs^+ in the two environments and only the weighted average values are observed.

In the range of concentration studied, the effect on the relaxation rates and shift is very nearly linear with $[X^-]$. In general a more complicated dependence on $[X^-]$ would be expected, except if FeX^{2+} is the dominant species. From the known complexation constants of Fe^{3+} [11,12] with F^- and Cl^-, it follows that in the concentration range under consideration both FeX^{2+} and FeX_2^+ are significantly abundant. Therefore, the linear dependence of the results in Figures 2–5 is surprising and might result from an accidental cancellation of the parameters of the FeX_2^+ species. However, the initial slopes can be used to discuss the magnetic parameters of the monosubstituted Fe^{3+} ion pair complexes and this is done below.

Under conditions of fast exchange between the free and the ion paired complex the ^{133}Cs relaxation rates and shift are given by[9,13]

$$\frac{1}{T_1} = \frac{(1-P)}{T_{1A}} + P\left\{2d\left(3\tau_{1c} + \frac{7\tau_{2c}}{1+\omega_s^2\tau_{2c}^2}\right) + 2\beta\left(\frac{\tau_{2e}}{1+\omega_s^2\tau_{2e}^2}\right)\right\} \qquad (5)$$

$$\frac{1}{T_2} = \frac{(1-P)}{T_{2A}} + P\left\{d\left(7\tau_{1c} + \frac{13\tau_{2c}}{1+\omega_s^2\tau_{2c}^2}\right) + \beta\left(\tau_{1e} + \frac{\tau_{2e}}{1+\omega_s^2\tau_{2e}^2}\right)\right\} \qquad (6)$$

$$\Delta\omega = \frac{\omega P A \gamma_s S(S+1)}{3kT\gamma_I} \qquad (7)$$

where $d = S(S+1)\gamma_s^2\gamma_I^2\hbar^2/15r^6$, $\beta = S(S+1)A^2/3\hbar^2$, and P is the fraction of Cs^+ in the ion paired form. The parameters in the braces refer to ^{133}Cs in this form. In principle the results of Figures 2–5 should yield information on the magnetic parameters and complexation constants of the Cs^+–ferric complex. However, the number of unknown parameters involved is too large to allow a complete quantitative analysis and we are therefore forced to restrict ourselves to some qualitative conclusions.

The large difference between T_1 and T_2 in the fluoride and chloride solutions indicate clearly that a significant contribution to the T_2 relaxation comes from the secular part of the scalar interaction and also that the nonsecular part is small compared to it. Taking the difference of eq 6 and 7 and neglecting small uncancelled contributions from the dipolar terms we obtain

$$\frac{1}{T_2} - \frac{1}{T_1} = \frac{PA^2S(S+1)}{3\hbar^2}\tau_{1e} \qquad (8)$$

In this equation $\tau_{1e}^{-1} = T_{1e}^{-1} + \tau_h^{-1}$ where T_{1e} is the longitudinal electronic relaxation time of the FeX^{2+} complex and τ_h the mean lifetime of the ion pair. Now, the esr spectrum of the FeF^{2+} has a line width of 1000 G at X band and about 500 G at Q band[12] from which a value of $T_{1e} \simeq 4 \times 10^{-10}$ sec at 14,000 G is estimated.[13] Moreover T_{1e} is expected to decrease with decreasing magnetic field (*e.g.*, by a factor of 2.3 at 8000 G). Since $(1/T_2 - 1/T_1)$ is independent of the magnetic field it follows that τ_{1e} must be identified with τ_h.

From this result and consideration of diffusion controlled reactions τ_h^{-1} can be bracketed between the values (sec^{-1})

$$5 \times 10^9 < \tau_h^{-1} < 3 \times 10^{10} \qquad (9)$$

Using eq 8–10 the range of values for the isotropic hyperfine interaction constant, $A/\hbar$, in the Fe–X–Cs complex is calculated to be $(2\text{–}5) \times 10^6$ rads sec^{-1} and the fraction P in a solution containing 1 *M* fluoride and 0.3 *M* Fe^{3+} is 0.2–0.1, respectively. Using these conclusions and the results for T_1 a value of 4–4.9 Å for the Fe–X–Cs distance is estimated. This value may be compared with 5.0 Å, calculated from the ionic radii of Fe^{3+}, F^-, and Cs^+ in a linear configuration.

For $FeCl^{2+}$ there is less information on the electronic relaxation times, but it appears that they are shorter than for FeF^{2+}.[12] The lack of a significant field dependence of $1/T_1$ suggests, however, that here too τ_{1e} can be identified with τ_h. Proceeding as for the case of the fluoride complex and assuming values for τ_h^{-1} between 10^{10} and 3×10^{10} sec^{-1}, the following results are obtained: P for 1 *M* chloride solution and 0.4 *M* Fe^{3+} is 0.2–0.1, $A/\hbar = (1\text{–}3) \times 10^6$ rads sec^{-1}, and r = 3.8–4.8 Å. This is much lower than the value of 5.9 Å obtained from the ionic radii.

Acknowledgments.—We are grateful to Miss Pnina Weissman for carrying out part of the viscosity and nmr measurements.

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