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A Direct Proton Magnetic Resonance Cation Hydration and Complex Formation Study of Lanthanide Salt Solutions in Water-Acetone Mixtures[1]

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A cation hydration study of diamagnetic Lu^{3+}, paramagnetic Er^{3+} and Yb^{3+}, and, in a preliminary manner, paramagnetic Pr^{3+}, Nd^{3+}, Tb^{3+}, Dy^{3+}, Ho^{3+}, and Tm^{3+} has been carried out by a low-temperature, direct pmr technique. At temperatures ranging from −60° (Dy^{3+} and Tm^{3+}) to −120° (Pr^{3+}), proton and ligand exchange are slow enough to permit the observation of separate signals for bulk and coordinated water molecules. In several cases, when signal broadening prevented the observation of a coordinated water peak by absorption nmr methods, a wide-line technique was used. Detailed experiments gave minimum hydration numbers of 6 for Lu^{3+} and 6 or 7 for Er^{3+} and Yb^{3+}. Extensive complex formation with nitrate ion at all concentrations was indicated for these three ions, and Er^{3+} and Yb^{3+} may complex perchlorate ion in some cases. Preliminary coordination numbers are presented for the remaining ions studied.

Introduction

The applicability of direct ^{17}O[3-5] and ^{1}H[6-10] nmr techniques to cation hydration studies has been demonstrated for a variety of diamagnetic and paramagnetic electrolyte solutions.[11] With these methods, a coordinated water peak can be observed if the lifetime of a water molecule or its protons in the cation solvation shell and bulk medium is comparable to the reciprocal of the separation of the signals arising from these environments. The ^{17}O nmr measurements have been possible for several diamagnetic [Al^{3+}, Be^{2+}, Ga^{3+}, Mg^{2+}, $(CH_3)_3Pt^+$, $(NH_3)_2Pt^{2+}$ [3-5,11]] and paramagnetic [Fe^{2+}, Co^{2+}, Ni^{2+} [5,11]] systems, while the greater sensitivity of the ^{1}H nmr technique has extended the range of the diamagnetic cations which can be studied [Al^{3+}, Ga^{3+}, In^{3+}, Be^{2+}, Mg^{2+}, Sc^{3+}, Y^{3+}, Zn^{2+}, Sn^{4+}, UO$_2$$^{2+}$, ZrO^{2+}, Th^{4+}, La^{3+} [6-11]]. Matwiyoff and Darley[9] successfully applied the direct ^{1}H pmr method to a hydration study of paramagnetic Co^{2+}, thereby demonstrating the feasibility of investigating other paramagnetic systems of comparable exchange rates, magnetic moments, and signal-broadening properties. For example, similar measurements have been made for Fe^{2+}, Ni^{2+}, Ce^{3+}, and Er^{3+}, the last in a preliminary manner.[10]

The trivalent lanthanide cations have attracted much attention because of their strong complexing tendencies and the structural features of the species they form and more recently for the use of their complexes as "chemical shift reagents" to simplify complicated pmr spectra of organic molecules.[12,13]

Although many coordination number studies of the trivalent lanthanides in solid complexes have been made,[14-22] direct cation hydration number measurements in solution were reported only recently.[10] This paper represents an extension of the pmr method to more rare earth cations. Detailed results will be presented for Er^{3+}, Yb^{3+}, and diamagnetic Lu^{3+}, and preliminary spectral data will be given for Pr^{3+}, Nd^{3+}, Tb^{3+}, Dy^{3+}, Ho^{3+}, and Tm^{3+}.

Experimental Methods

The acetone-d_6 (Van Ness Associates, 99.7%), dichlorodifluoromethane (Freon 12), dimethyl sulfoxide (DMSO), and lanthanide salts (Research Inorganic) were the highest commercial quality available, and with the exception of drying the solvents over CaSO$_4$, all were used without further purification. Deionized water was used in all solutions. The samples were prepared by adding an appropriate amount of acetone-d_6 and Freon 12 (*in vacuo*) when necessary to a weighed amount of aqueous salt stock solution. The stock solution was analyzed by passage through a Dowex 50W-X8 cation-exchange resin and titration of the resultant acid solution.

All nmr measurements were made on a Varian HA-100 spectrometer equipped with a variable-temperature accessory for measurements from −150 to +200°. To accommodate the large chemical shifts produced by the paramagnetic rare earth cations these spectra were recorded in the field sweep mode with 17-kHz side-band modulation. The usual absorption mode nmr method involves cooling the sample in the spectrometer probe until ligand and proton exchange are slow enough on the nmr time scale to permit the observation of separate bulk and coordinated water peaks. The spectral resolution is maximized and the water signals are integrated electronically. In some cases, at temperatures low enough to reduce the exchange rate, the increased solution viscosity broadened the coordinated water peak beyond detection. However, the presence of the coordinated water peak was confirmed by derivative-mode spectra recorded using a Princeton Applied Research Corp. lock-in amplifier (Model 122) and a Hewlett-Packard audio oscillator (Model 200 CD).

Results

In Table I, a detailed summary of the pmr data obtained with aqueous solutions of Lu^{3+}, Er^{3+}, and Yb^{3+} salts is pre-

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Table I. Water Proton Magnetic Resonance Chemical Shift, Line Width, and Cation Hydration Number Data for Water-Dimethyl Sulfoxide (DMSO)-Acetone-d_6 (A-d_6) Solutions of Lanthanide Salts

	Mole ratios					$\Delta\nu_{1/2}$,[b] Hz		Cation coord no.	
Salt	Salt:H_2O	Salt:DMSO	H_2O:A-d_6	Temp, °C	$\Delta\nu_{C-B}$,[a] Hz	Coord	Bulk	DMSO	H_2O
$Lu(ClO_4)_3$	1:10^{d}	1:1.1	1:20^{c}	−100	165			1.1	4.8
	1:10^{d}	1:1.6	1:20		186			1.6	4.5
	1:10		1:20		220				5.9
	1:15		1:8		150				6.1
	1:15		1:20		225				6.0
	1:15		1:20		260				5.8
	1:18^{e}		1:20^{c}		90				6.1
	1:20		1:20		210				5.9
	1:15^{f}		1:20		100				4.5
$Lu(NO_3)_3$	1:6		1:20	−95	330				2.1
	1:6^{e}		1:25		230				2.2
	1:8^{f}		1:65		215				2.2
	1:10		1:20		335				2.3
	1:10^{e}		1:20		160				2.1
	1:10		1:45		380				2.2
	1:13		1:20		340				2.4
	1:13^{e}		1:20		225				2.2
	1:8	1:4	1:20		Ppts				
$Er(ClO_4)_3$	1:6		1:15	−95 to −100	−10,700^{g}	8,700	1,600		5.7
	1:6		1:25						6.2
	1:7		1:15						6.1
	1:8^{h}		1:15						4.2
	1:10^{h}		1:25						4.5
	1:16^{h}		1:15						5.8
	1:16^{h}		1:20						5.9
	1:20^{h}		1:15						6.4
	1:25^{h}		1:15						6.3
	1:16^{h}	1:2.0	1:15					2.0	
	1:16^{h}	1:4.4	1:15					3.9	
	1:16^{h}	1:4.0	1:20					4.0	
	1:16^{h}	1:6	1:20					4.0	
	1:16^{h}	1:7	1:20					3.7	
	1:16^{h}	1:8	1:20					4.0	
	1:16^{h}	1:8	1:15					4.0	
	1:16^{h}	1:8	1:25					4.1	
	1:16^{i}	1:8	1:25					4.0	
	1:22^{j}	1:8	1:15					4.1	
	1:8^{k}		1:17^{c}						3.2
	1:9^{l}		1:16^{c}						2.8
$Er(NO_3)_3$	1:9		1:15	−75	−4,200	2,800	400		1–2
$Yb(ClO_4)_3$	1:6		1:15	−95 to −100	−7,200	1,500	300		4.0
					−12,950	1,500			
	1:15		1:15		−5,600	1,900	200		4.2
					−12,200	2,500			
	1:22^{h}		1:15						3.6
	1:18^{m}		1:20						~0
	1:6	1:1.2	1:15		−5,700	1,700	300	1.2	
					−11,000^{n}	900			
	1:20^{e}	1:1.1	1:15		−6,600			1.1	
					−11,000^{n}				
	1:10^{e}	1:1.9	1:20		−6,400^{n}			1.9	
	1:20^{e}	1:2.0	1:15					2.0	
	1:20^{e}	1:3.1	1:15					3.1	
	1:20^{e}	1:4.3	1:15					3.9	
	1:17^{i}	1:5.0	1:10					3.9	
	1:27^{i}	1:6.3	1:10					4.1	
	1:27^{i}	1:7.0	1:10					4.1	
	1:33^{o}	1:8.4	1:4					3.7	
	1:48^{h}	1:9.2	1:6					4.3	
$Yb(NO_3)_3$	1:5		1:15	−60	−7,600	1,700	200		2.0
	1:6^{f}		1:20		−8,100	1,800	200		1.8
	1:13^{f}		1:15		−8,600	1,100	100		1.6
$Pr(ClO_4)_3$	1:7		1:20^{c}	−110	+5,200	700	500		(6)
					+3,000	1,500			
$Nd(ClO_4)_3$	1:8		1:20^{c}	−120	+1,200	1,700	400		(6)
$Tb(NO_3)_3$	1:4		1:20	−70	+21,700^{g}	10,500	700		(2)
$Dy(NO_3)_3$	1:7		1:15	−60	+14,000^{g}	12,000	4,000		(3)
$Ho(ClO_4)_3$	1:7		1:20	−90	+16,000^{g}	11,000	2,600		(3)
$Tm(NO_3)_3$	1:4		1:20	−60	−19,000^{g}	3,200	900		(2)

[a] Spectra were recorded at 100 MHz and only the water shift values are given. [b] Only the water line width values are given. [c] Freon 12, dichlorodifluoromethane, was present in a 1:3 mole ratio (Freon 12:A-d_6). [d] Solution acidified to a 0.1:1 mole ratio of $HClO_4$ to salt. [e] Solutions acidified to a 1:1 mole ratio of $HClO_4$ salt. [f] Solution acidified to a 1:1 mole ratio of HNO_3 to salt. [g] Observed in derivative spectrum. [h] Solutions acidified to a 2:1 mole ratio of $HClO_4$ to salt. [i] Solutions acidified to a 3:1 mole ratio of $HClO_4$ to salt. [j] Solutions acidified to a 5:1 mole ratio of $HClO_4$ to salt. [k] Solution acidified to a 1.5:1 mole ratio of HNO_3 to salt. [l] Solution acidified to a 2.5:1 mole ratio of HNO_3 to salt. [m] The solution contained a 1:1 mole ratio of $Al(ClO_4)_3$ to $Yb(ClO_4)_3$. [n] A coordinated water pmr peak also was observed but an area integration was not possible. [o] Solution acidified to a 6:1 mole ratio of $HClO_4$ to salt.

sented, along with preliminary results for several other rare earth salts. Representative pmr spectra for all these cation solutions are shown in Figures 1-5. In all but a few cases, the measurements were possible at temperatures within the range of acetone mixtures, −100° as a lower limit. When lower temperatures were required, Freon 12 was added to reduce the freezing point of the solution. The separation in hertz between the coordinated and bulk water signals, designated by $\Delta\nu_{C-B}$, is positive for a shift of the coordinated water peak to lower field (higher frequency) and negative for a displacement to higher field. A few line width measurements were made in the paramagnetic salt solutions to permit a rough correlation with the magnetic properties of the cations. However, the precision of these measurements was severely limited by signal broadening and in some cases by signal overlap.

The Lu^{3+} solution spectra are typical of diamagnetic systems; that is, the bulk and coordinated water signals are well-separated (~200 Hz) and relatively narrow (~30-40 Hz). These factors permit area integrations and coordination number measurements with a precision of about 5%. Although chemical shifts were determined with a 1% precision in these Lu^{3+} systems, the resonance positions of the coordinated and, in particular, the bulk water peaks depend on acid and solvent concentrations and temperature. Thus, the $\Delta\nu_{C-B}$ values can be considered only in a qualitative manner.

The precision of the shift (~1-2 ppm) and coordination number (~10%) measurements was lower in the paramagnetic solution spectra because of the much greater signal line widths. In fact, as seen in Table I, at the low temperatures needed to slow exchange in the Er^{3+}, Tb^{3+}, Dy^{3+}, Ho^{3+}, and Tm^{3+} solutions, the coordinated water peak was too broad to be observed by the usual absorption methods. In these systems, the spectral behavior of the water signal as the sample was cooled gave a clear indication that the slow-exchange condition had been achieved. An area comparison of the total water signal at high temperatures to the bulk water peak at low temperatures provided the detailed hydration data for the $Er(ClO_4)_3$ solutions of Table I and the appropriate values listed for the other ions mentioned above. This technique will be discussed more extensively later. Due to a lower water exchange rate in $Er(NO_3)_3$ solutions, measurements were possible at higher temperatures (−75°). Consequently, separate bulk and coordinated water peaks were observed. However, the low intensity and the broadness of the coordinated water peak permitted only an estimate of the cation hydration number.

The $Yb(ClO_4)_3$ solution spectral data reflect the fact that two bound water peaks, displayed upfield from the bulk, are observed in these systems. The $Yb(NO_3)_3$ solutions exhibited one coordinated water peak and lower hydration numbers. Note again a typical feature of these lanthanide salt solutions; that is, ligand or proton exchange, whichever dominates, is slower in nitrate solutions. For example, measurements were possible at −60° with the $Yb(NO_3)_3$ solutions, but only at temperatures in the range of −100° for $Yb(ClO_4)_3$ solutions.

An attempt was made to displace water molecules and anions from the solvation shells of Lu^{3+}, Er^{3+}, and Yb^{3+} by the addition of DMSO. In all cases, only a coordinated DMSO pmr peak was observed at low concentrations of this base. When the mole ratio of DMSO to cation (Er^{3+} or Yb^{3+}) exceeded 4:1, a bulk DMSO peak appeared. In agreement with the water signal displacements, the coordinated DMSO peak appeared at lower field than the bulk in the diamagnetic Lu^{3+} solution spectra and upfield by about 1000 Hz in the Er^{3+} and Yb^{3+} cases. As indicated in Table I (footnote *n*), a coordinated water peak of low intensity was observed in the 1:1 and 2:1 mole ratio DMSO-$Yb(ClO_4)_3$ solutions.

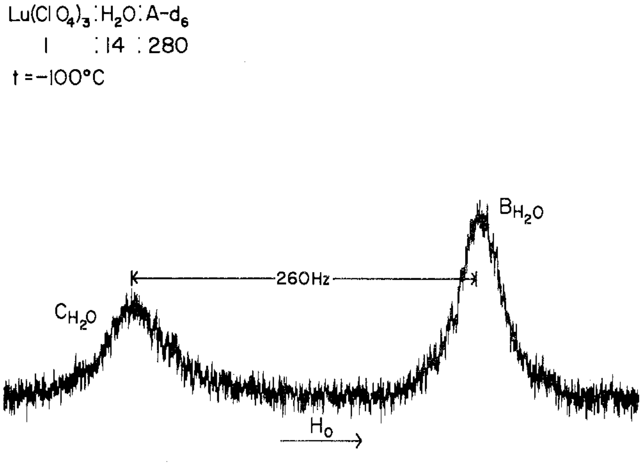

Figure 1. The water pmr spectrum of a $Lu(ClO_4)_3$ solution in a water–acetone-d_6 mixture, recorded on a Varian HA-100 spectrometer. The signals arising from bulk water (B_{H_2O}) and water molecules coordinated to Lu^{3+} (C_{H_2O}) are labeled. The mole ratios of all species also are given.

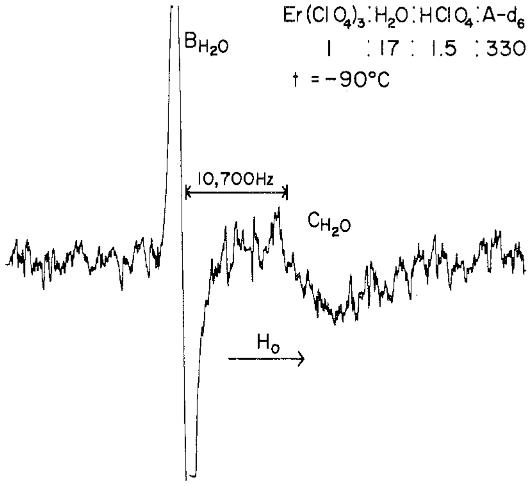

Figure 2. The pmr derivative spectrum of an $Er(ClO_4)_3$ solution in a water–acetone-d_6 mixture, recorded on a Varian HA-100 spectrometer. The signals arising from bulk water (B_{H_2O}) and water molecules coordinated to Er^{3+} (C_{H_2O}) are labeled. The acetone-d_6 proton impurity peak is superimposed on the bulk water signal. The mole ratios of all species also are given.

Spectral data for six additional lanthanide cations are listed in Table I to permit a comparison of these initial results and experimental conditions to the Er^{3+} and Yb^{3+} cases. The hydration numbers are enclosed in parentheses as an indication that they are only tentative values based on one solution concentration. The Pr^{3+} and Nd^{3+} hydration numbers were measured by direct area integrations of the separate bulk and coordinated water peaks, while the remaining ions were studied by the method used with Er^{3+} solutions.

Discussion

The ability to detect separate resonance signals for water molecules in a cation solvation shell and in bulk medium is determined by the rate of ligand or proton exchange which prevails in the particular system. This observation usually can be made in a diamagnetic salt solution if the temperature is reduced until τ, the lifetime of the magnetically active nucleus in an environment, is greater than $(\Delta\nu)^{-1}$, the recip-

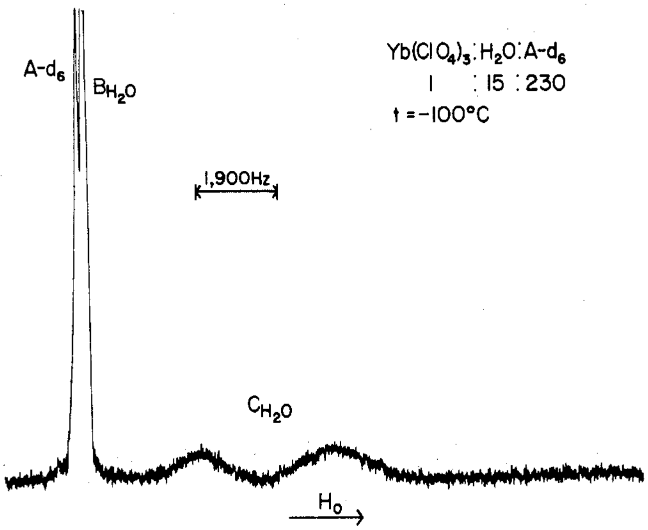

Figure 3. The pmr spectrum of an $Yb(ClO_4)_3$ solution in a water–acetone-d_6 mixture, recorded on a Varian HA-100 spectrometer. The signals arising from acetone-d_6 proton impurities (A-d_6), bulk water (B_{H_2O}), and water molecules coordinated to Yb^{3+} (C_{H_2O}) are labeled. The mole ratios of all species also are given.

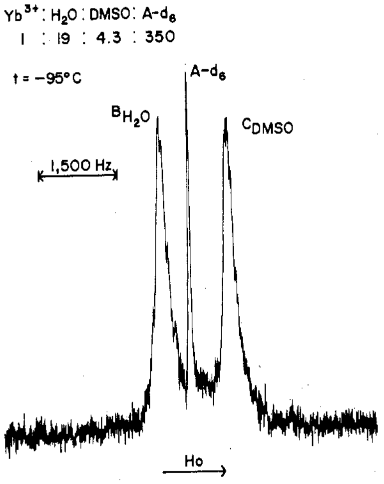

Figure 4. The pmr spectrum of an $Yb(ClO_4)_3$ solution in a water–dimethyl sulfoxide (DMSO)–acetone-d_6 mixture, recorded on a Varian HA-100 spectrometer. The signals arising from acetone-d_6 proton impurities (A-d_6), bulk water (B_{H_2O}), and DMSO molecules coordinated to Yb^{3+} (C_{DMSO}) are labeled. Bulk DMSO and coordinated water signals were not observed. The mole ratios of all species also are given.

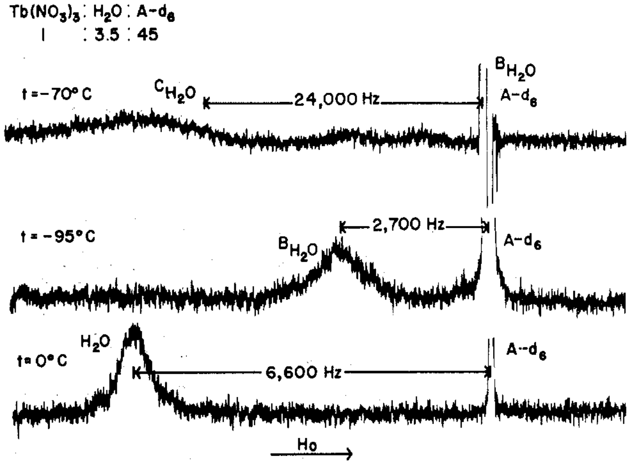

Figure 5. Absorption (0 and −95°) and derivative (−70°) pmr spectra of a $Tb(NO_3)_3$ solution in a water–acetone-d_6 mixture, recorded on a Varian HA-100 spectrometer. The signals arising from acetone-d_6 proton impurities (A-d_6), averaged water (H_2O), bulk water (B_{H_2O}), and water molecules coordinated to Tb^{3+} (C_{H_2O}) are labeled. The mole ratios of all species also are given.

rocal of the signal separation.[23] For example, at −100°, this slow-exchange condition is achieved in lutetium salt solutions, and even though the increased viscosity shortens the water proton transverse relaxation times (T_2), the signals are not excessively broadened. From the signal separation of the bulk and coordinated water molecules seen in Figure 1 and the $\Delta\nu_{C-B}$ values listed in Table I, τ can be estimated at 0.005-0.01 sec.

Because of their low freezing points and viscosities and the absence of interfering pmr signals in their solutions, acetone-d_6 and, in a few cases, Freon 12 are used as diluents in hydration studies. The inert nature of these compounds, particularly acetone, has been demonstrated in so many cases[7,8,10] it can be assumed that they do not compete with water or DMSO molecules for sites in the cation solvation shell. Thus, the solvation numbers in Table I represent the total number of ligand molecules in the primary coordination shell of the cation at these temperatures of study. The hydration number of 6 measured for Lu^{3+} in perchlorate solution is the same as that found for La^{3+} in a similar study.[10] For both ions higher coordination numbers (6-9) have been reported in solid complexes,[14-22] but generally the value depends on the particular ligand used. If the Lu^{3+} coordination number is actually greater than 6, a variety of processes could account for the results in Table I. Hydrolysis, polymerization, and complex formation with ClO_4^- would lower the measured hydration number, and they cannot be ruled out in these solutions. However, the observation of only one coordinated water signal in all $Lu(ClO_4)_3$ solution spectra (Figure 1) indicates a magnetic equivalence of the six water molecules, and it minimizes the possible presence of anions in the cation solvation shell. The DMSO experiments, although limited by solubility, also imply negligible complex formation of Lu^{3+} with ClO_4^-. In diamagnetic salt solutions it has been shown that DMSO can displace anions, NO_3^- for example, from a cation solvation shell.[24,25] However, in $Lu(ClO_4)_3$ solutions, DMSO merely displaces coordinated water, and the total measured coordination number remains at 6. This negligible complexing tendency in ClO_4^- solutions is typical of diamagnetic salt systems even in media of low dielectric constant.[6-8,10,11,26] Since La^{3+} has a xenon inner-core electron configuration and Lu^{3+} has a xenon inner core plus a filled 4f level, each is diamagnetic and empirically little complex formation would be expected.

This is not the case in NO_3^- solution, where complexing frequently is detected by nmr methods even in diamagnetic salt solutions (Sc^{3+}, Y^{3+}, Th^{4+}, UO_2^{2+}, ZrO^{2+}).[27-29] When NO_3^- in the form of HNO_3 is added to a $Lu(ClO_4)_3$ solution in a 1:1 mole ratio (see Table I), the Lu^{3+} hydration number decreases to ~4.5. This reflects inner-shell complex forma-

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tion, probably by bidentate bonding with the displacement of two water molecules per anion. For the $Lu(NO_3)_3$ solutions, at several salt and solvent concentrations, the direct pmr area measurements gave a cation hydration number of slightly more than 2. Even when the ratio of NO_3^- to Lu^{3+} was increased to 4:1, a value of about 2 was still obtained. In view of the high NO_3^- concentration, the low dielectric constant, and low temperature, all factors which enhance complex formation, either Lu^{3+} is unable to bind more than two NO_3^- ions at the conditions of this study or significant monodentate bonding is occurring.

Thus, from the data of Table I, a minimum hydration number of 6 can be assigned to Lu^{3+} in these aqueous solutions. Although the processes mentioned above may not be extensive, a stronger possibility is the presence of additional coordinated water molecules which exchange more rapidly than the six observed here. This could be the case if the water molecules were farther from the central cation and less tightly bound. Attempts to detect additional signals were unsuccessful even at −130°, at which temperature the spectral pattern and the Lu^{3+} hydration number of 6 in ClO_4^- solution remained unchanged.

Since the coordinated–bulk water signal separations in the paramagnetic salt solution spectra are greater by a factor of 10^2–10^3 than those produced by diamagnetic salt systems, proportionately greater exchange rates can be tolerated when attempting to observe a coordinated water peak. However, the limiting factor in these systems is the effective magnetic moment of the paramagnetic cation and the decreased relaxation times of the bound water molecule protons. Thus, the decrease in exchange rate at lower temperatures is counteracted by an increase in solution viscosity, the coupling between the ion and coordinated water molecules, and signal broadening. Solutions of paramagnetic ions of low effective magnetic moment (<0.5 BM, based on water T_1 measurements[30]), for example, Ce^{3+}, Pr^{3+}, Nd^{3+}, and Yb^{3+} in the trivalent lanthanide series, can be studied at temperatures as low as −115° without excessive broadening. As seen in Figure 3 for the Yb^{3+} system, coordinated water peaks are readily observed and hydration numbers can be measured by direct integration. However, in solutions of paramagnetic cations of higher effective magnetic moment (>1.5 BM), for example, Tb^{3+}, Dy^{3+}, Er^{3+}, Ho^{3+}, and Tm^{3+},[30] signal broadening limits the temperature range of study. An excellent example of this situation is provided by Er^{3+} solutions. In $Er(NO_3)_3$ solutions, exchange is slow enough at −75° to permit the direct observation of a bound water signal. By contrast, temperatures as low as −100° must be reached with $Er(ClO_4)_3$ solutions before the more rapid exchange of these systems can be slowed. At this temperature, the coordinated water signal is too broad (~10,000 Hz) to be detected by the usual nmr absorption method.

For these systems, a procedure similar to that employed in a Ni^{2+} study[31] was used to determine the Er^{3+} hydration numbers. The area ratio of the total water signal to that of the acetone-d_6 proton impurity was measured at 0°, a temperature high enough to ensure rapid exchange. Then at low temperatures (−95°) where the slow-exchange condition prevails, the bulk water to acetone-d_6 signal ratio was measured. From the difference in these area ratios, the amount of water coordinated, but not observed, was deduced.

The slow exchange limit was confirmed directly and unambiguously by wide-line derivative spectra, such as that for Er^{3+} in Figure 2, and also by the temperature dependence of the chemical shift and line width of the water pmr absorption signal. For example, at 0°, the exchange-averaged water signal in Er^{3+} solutions is upfield from the acetone-d_6 pmr signal by ~2000 Hz. As the temperature is lowered to −95°, the signal broadens and disappears into the base line, and a sharper signal of lower intensity reappears ~400 Hz upfield from the acetone-d_6 peak. This spectral behavior is typical of a system in which an exchange process is being slowed and separate resonance signals are appearing. This procedure is illustrated for a solution of $Tb(NO_3)_3$ in Figure 5, where a wide-line derivative spectrum confirms the presence of a coordinated water peak. Thus, in the absence of a wide-line nmr capability, this chemical shift behavior would justify the use of the area ratio technique to determine cation hydration numbers.

The data in Table I for Er^{3+} solutions indicate a cation coordination number of at least 6, a limited ability of DMSO to replace coordinated water molecules, and a tendency for this ion to form inner-shell complexes with NO_3^- and at certain concentrations, possibly even ClO_4^-. Although the Er^{3+} hydration number measurements were made by the water:acetone-d_6 area ratio method in ClO_4^- solutions, the first three entries for this cation in Table I offer a direct confirmation of six bound water molecules. In these solutions, the water to Er^{3+} mole ratio was very low, and as expected, when the sample was cooled to −95°, a bulk water signal either was not observed (6:1 systems) or was very small (7:1 system). It is not certain that the maximum hydration number is 6, since one must consider the possibility of complex formation with ClO_4^- and the presence of additional bound water molecules which are more labile. However, if present, Er^{3+}-ClO_4^- complexes are stable in these solutions only at high anion and low water content. A series of measurements were made in which the ClO_4^- to Er^{3+} mole ratio was maintained at 5:1, while the water to cation mole ratio increased from 8:1 to 25:1. Only at the lower water concentrations did complexes apparently form as indicated by the decrease in the Er^{3+} hydration number to about 4.5. At higher water:salt mole ratios (>15:1), the hydration number is about 6.

The water–DMSO series also confirms a low tendency for ClO_4^- to complex Er^{3+}. The DMSO solutions were stable, that is, no precipitate was evident, only in the presence of $HClO_4$. Up to a 4:1 mole ratio of DMSO to salt, solvation by this component is selective presumably at the expense of coordinated water. It was not possible to observe a bound water peak by wide-line nmr because of signal broadness and decreased intensity. A bulk DMSO signal appeared at higher concentrations, and the relative areas of the bulk and coordinated peaks gave a coordination number contribution of four molecules in all cases. This is not a competitive process with Er^{3+}-ClO_4^- complex formation, since four DMSO molecules are bound at ClO_4^- to cation mole ratios as high as 6:1 and 8:1 (see Table I). Rather, the competition must be between water and DMSO for Er^{3+} solvation sites. Solubility limitations precluded a more extensive concentration study to attempt a displacement of all six coordinated water molecules.

In NO_3^- systems, prepared by the addition of HNO_3 to $Er(ClO_4)_3$ solutions or by the use of $Er(NO_3)_3$ itself, strong inner-shell complexes form and the Er^{3+} hydration number decreases markedly from 6 to about 1 or 2. The coordinated water peak was detected in the $Er(NO_3)_3$ solutions but only

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[30] J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, N. Y., 1959, Chapter 9.

[31] T. J. Swift and G. P. Weinberger, *J. Amer. Chem. Soc.*, 90, 2023 (1968).

an approximate area measurement was possible. The low hydration number probably indicates that bidentate complex formation is occurring, since more than three water molecules are being displaced by the nitrate ions. However, one cannot discount the possibility of monodentate binding by NO_3^-, with the subsequent labilization of other bound water molecules.

The spectra of the $Yb(ClO_4)_3$ and $Yb(NO_3)_3$ solutions and the data in Table I for these systems reveal (a) 4 coordinated water molecules in the presence of ClO_4^- and 1.5-2 water molecules in NO_3^- solutions at these temperatures of study, (b) selective solvation by DMSO to a limit of 4 molecules, at the expense of coordinated water, and (c) complex formation by NO_3^- and possibly ClO_4^- at all concentrations studied. The two coordinated water signals arising from $Yb(ClO_4)_3$ solutions (see Figure 3) and the low hydration numbers measured in these systems may indicate the simultaneous presence of ClO_4^- and water in the cation solvation shell. In the first two entries of Table I for the series, the ClO_4^- to Yb^{3+} mole ratio was 3:1. This sets a minimum of 7 for the Yb^{3+} coordination number if complexing by anion is complete and the bonding is monodentate, the type usually exhibited by this anion in solid complexes.[21,22] An even greater decrease in hydration number can be induced but the process depends on the water concentration. When $HClO_4$ solution was added to increase the ClO_4^- to Yb^{3+} mole ratio to 5:1, the hydration number decreased only slightly. However, the hydration number decreased essentially to zero when $Al(ClO_4)_3$ was added to increase the anion:Yb^{3+} mole ratio to 6:1. It may appear that the water concentration is high in this $Al(ClO_4)_3$ solution but this is not the case. Previous experiments have shown conclusively that Al^{3+} does not complex ClO_4^- to any noticeable extent, and this ion binds six water molecules.[7,26] Thus, in effect, six ClO_4^- anions and only twelve water molecules are available for interaction with Yb^{3+}. Under these conditions, displacement of the bound water molecules from the Yb^{3+} solvation shell is almost complete. In the pmr spectrum of this solution, signals are observed for $Al(H_2O)_6{}^{3+}$ and bulk water, in addition to extremely weak signals for water coordinated to Yb^{3+}.

As in the Er^{3+} studies, DMSO selectively solvates Yb^{3+} to a maximum of 4 molecules. This is true even at high mole ratios of anion to salt (9:1) and water to salt (50:1). An interesting feature of these spectra was the preferred replacement of specific coordinated water molecules by DMSO, reflecting a steric accommodation in the solvation complex. The spectra indicate that the bound water molecules giving rise to the signal further upfield (~11,000 Hz) from the bulk water peak are replaced preferentially. The area of this signal decreased more rapidly with DMSO addition than that of the other coordinated water peak.

The hydration number values of 1.5-2 measured in the $Yb(NO_3)_3$ solutions are the result of the extensive complex formation which prevails. Again, these results would be consistent with a Yb^{3+} coordination number of at least 6 or 7, if complexing by NO_3^- were not complete. The slight decrease in hydration number as the NO_3^- concentration is increased may indicate that this is the case.

Depending on the nature of the system, a range of coordination states, usually higher than six, is observed for these ions with all types of anions and bases.[14-22,32] In the solutions of this study, where the ligands need not be as tightly packed as in a solid, lower principal shell coordination numbers are possible. In solutions of the lanthanide shift reagents, a coordination number of 8, recently verified for Eu^{3+} by a direct nmr measurement, is likely.[13,33] In these systems, six coordination sites are occupied by the anion chelate, and the substrate being studied bonds at the two other sites. As mentioned previously, the presence of more bound water molecules of greater lability and not observable on the nmr time scale is a possibility in the solutions of this study.

Finally, some preliminary spectral data are presented in Table I for other members of the lanthanide series. The detection of coordinated water peaks in the Pr^{3+} and Nd^{3+} spectra at −110° is made possible by the low effective magnetic moments of these ions and the subsequent lack of excessive signal broadening. Direct hydration number measurements are possible in these cases, whereas the area ratio method used for Er^{3+} solutions is being applied in the Tb^{3+}, Dy^{3+}, Ho^{3+}, and Tm^{3+} solutions. Due to the low magnetic moments of the nonchelated Eu^{3+} and Sm^{3+} ions, their chemical shift and signal broadening properties in ClO_4^- and NO_3^- solutions are typical of diamagnetic ions. It appears that temperatures below −100° will be needed to achieve the slow-exchange condition in these solutions.

Registry No. Er^{3+}, 18472-30-5; Yb^{3+}, 18923-27-8; Lu^{3+}, 22541-24-8; Pr^{3+}, 22541-14-6; Nd^{3+}, 22541-15-7; Tb^{3+}, 22541-20-4; Dy^{3+}, 22541-21-5; Ho^{3+}, 22541-22-6; Tm^{3+}, 22541-23-7.

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