

the extent of delocalized  $\pi$  bonding. Numerous experimental techniques have illustrated the importance of delocalized bonding in the  $\alpha$ -diimines and even more pertinently in their metal complexes.<sup>56</sup> Delocalized bonding can be considered minimal in aliphatic amine ligands such as ethylenediamine. The fact that the planarity of the OMPA chelate ring found in  $\text{Cu}(\text{OMPA})_3(\text{ClO}_4)_2$  is also found in  $\text{Co}(\text{OMPA})_3(\text{ClO}_4)_2$  and  $\text{Mg}(\text{OMPA})_3(\text{ClO}_4)_2$  indicates a lack of significant  $d\pi$ - $p\pi$  bonding in this trigonal copper complex. Further, the lengths of the bonds found in the chelate ring do not support a significant  $\pi$ -bonding contribution in these complexes.<sup>17</sup> It would appear that  $\pi$ -bonding effects are

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the most likely source of the appearance of low-energy ligand field bands in the near-infrared spectrum, although the exact nature of these transitions remains in question.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,  
CALIFORNIA STATE COLLEGE, LOS ANGELES, CALIFORNIA 90032

## A Direct Proton Magnetic Resonance Cation Hydration Study of Lanthanum, Zinc, Cerium, Iron, and Nickel Perchlorates and Erbium Nitrate in Aqueous Solution

By ANTHONY FRATIELLO,\* VICKI KUBO, SHIRLEY PEAK, BERNARD SANCHEZ, AND RONALD E. SCHUSTER

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A cation hydration study of diamagnetic  $\text{La}(\text{ClO}_4)_3$  and  $\text{Zn}(\text{ClO}_4)_2$  and paramagnetic  $\text{Ce}(\text{ClO}_4)_3$ ,  $\text{Er}(\text{NO}_3)_3$ ,  $\text{Fe}(\text{ClO}_4)_2$ , and  $\text{Ni}(\text{ClO}_4)_2$  in aqueous solution has been carried out by a direct proton magnetic resonance (pmr) method. The technique is based on the ability to slow ligand and proton exchange thereby permitting the observation of separate resonance signals for bound and bulk water molecules. Temperatures required for study varied from  $-30^\circ$  for  $\text{Ni}^{2+}$  to  $-120^\circ$  for  $\text{Zn}^{2+}$  and they were made possible by dilution of the aqueous solutions with acetone and, when necessary, Freon 12. Area integrations led to hydration numbers of 6 for all cations except  $\text{Er}^{3+}$  which was involved in extensive complex formation and could not be studied in great detail. Spectral evidence for inner-shell complex formation also was obtained in the  $\text{Ce}^{3+}$  solutions leading to the possibility of a greater maximum hydration number than 6 for this species.

### Introduction

During recent years, direct oxygen-17<sup>1-7</sup> and proton magnetic resonance (pmr)<sup>8-15</sup> methods have been applied to cation hydration studies in aqueous solution and aqueous solvent mixtures. The success of these experiments lies in the ability to slow ligand and proton exchange thereby permitting the direct observation of a resonance signal for water molecules in the cation solvation shell. When this is possible, area evaluations lead to accurate measurements of cation hydration numbers,<sup>1-15</sup> competitive solvation,<sup>8</sup> and

complex formation.<sup>12-15</sup> Species studied by oxygen-17 and proton magnetic resonance spectroscopy include  $\text{Al}^{3+}$ ,  $\text{Be}^{2+}$ ,  $\text{Ga}^{3+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Pt}^{2+}$ , and  $\text{Pt}^{4+}$ ,<sup>1-9,11</sup> while pmr studies alone have been made for  $\text{Mg}^{2+}$ ,  $\text{In}^{3+}$ ,  $\text{Sc}^{3+}$ ,  $\text{Y}^{3+}$ ,  $\text{Th}^{4+}$ ,  $\text{UO}_2^{2+}$ ,  $\text{Sn}^{4+}$ , and  $\text{Zn}^{2+}$ ,<sup>10,12-15</sup> the last in a preliminary manner.

Several of the ions to be described here have been studied by a variety of methods including Raman<sup>16-19</sup> and electronic absorption<sup>20-24</sup> spectroscopy of aqueous solutions, and analytical, conductometric, and spectroscopic measurements of crystalline complexes.<sup>25-33</sup>

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TABLE I  
WATER-ACETONE-FREON 12 SOLUTIONS OF  $\text{La}(\text{ClO}_4)_3$ ,  $\text{Zn}(\text{ClO}_4)_2$ ,  $\text{Ce}(\text{ClO}_4)_3$ ,  $\text{Er}(\text{NO}_3)_3$ ,  $\text{Fe}(\text{ClO}_4)_2$ ,  
AND  $\text{Ni}(\text{ClO}_4)_2$  AT 100 MHz

Salt	Mole ratios		Temp, °C	$\Delta\nu_{\text{C-B}}$ , Hz (coor bulk)	$\Delta\nu^{1/2}$ , Hz		Cation hydration no.
	Salt:H <sub>2</sub> O	H <sub>2</sub> O:acetone:F-12 <sup>a</sup>			(coor)	bulk)	
$\text{La}(\text{ClO}_4)_3$	1.00:11.8	1.0:14.0:5.0	-110	158			6.0
$\text{La}(\text{ClO}_4)_3$	1.00:11.8	1.0:18.0:6.5	-105	162			6.1
$\text{La}(\text{ClO}_4)_3$	1.00:12.6	1.0:15.0:6.5 <sup>b</sup>	-105	90			6.0
$\text{La}(\text{ClO}_4)_3$	1.00:13.1	1.0:4.0:1.5	-110	153			6.1
$\text{La}(\text{ClO}_4)_3$	1.00:16.0	1.0:9.0:3.5	-110	145			6.2
$\text{La}(\text{ClO}_4)_3$	1.00:16.4	1.0:20.0:6.0	-110	175			6.4
$\text{Zn}(\text{ClO}_4)_2$	1.00:10.0	1.0:14.0:4.5	-120	140			6.4
$\text{Zn}(\text{ClO}_4)_2$	1.00:12.5	1.0:18.0:6.0	-120	140			5.9
$\text{Ce}(\text{ClO}_4)_3$	1.00:6.50	1.0:15.0:5.0 <sup>c</sup>	-115	1,200 2,100 3,000	Broad ~570 Broad	135	4.5
$\text{Ce}(\text{ClO}_4)_3$	1.00:6.50	1.0:20.0:4.0	-115	1,350 2,300 3,300	Broad ~520 Broad	150	4.5
$\text{Ce}(\text{ClO}_4)_3$	1.00:10.5	1.0:15.0:7.5	-115	1,450 2,450 3,500	Broad	125	5.5
$\text{Ce}(\text{ClO}_4)_3$	1.00:13.2	1.0:15.0:5.0	-115	1,250 2,200 3,300	Broad	75	5.5
$\text{Er}(\text{NO}_3)_3$	1.00:8.0	1.0:20.0:0 <sup>c</sup>	-75	-4,300	2100	300	~1.0
$\text{Fe}(\text{ClO}_4)_2$	1.00:13.0	1.0:1.0:0 <sup>c</sup>	-50	17,800	3500	1300	5.8
$\text{Fe}(\text{ClO}_4)_2$	1.00:14.0	1.0:1.0:0	-40	15,300			
			-50	16,800			
			-60	17,800	3000	800	5.6
			-70	19,000			
			-80	20,800			
$\text{Ni}(\text{ClO}_4)_2$	1.00:6.0	1.0:2.0:0 <sup>c</sup>	-30	2,600	4200	500	4.4
$\text{Ni}(\text{ClO}_4)_2$	1.00:12.8	1.0:2.0:0	-30	2,500	4000	220	5.4

<sup>a</sup> F-12 is dichlorodifluoromethane. <sup>b</sup> Sample was acidified to a 1:4 mole ratio of  $\text{HClO}_4$  to  $\text{La}^{3+}$ . <sup>c</sup> All paramagnetic salt solutions contained acetone- $d_6$  instead of acetone to avoid signal overlap.

Generally, coordination numbers of 6 have been reported for  $\text{Fe}^{2+}$  and  $\text{Zn}^{2+}$ ,<sup>17-19,21,22,25</sup> but some ambiguity exists concerning the values for  $\text{Ce}^{3+}$ ,  $\text{Er}^{3+}$ ,  $\text{La}^{3+}$ , and  $\text{Ni}^{2+}$ .<sup>23-34</sup> Coordination numbers as high as 12 have been postulated for the rare earth ions in crystal complexes,<sup>23-33</sup> and hydration numbers of 4 and 6 have been reported for  $\text{Ni}^{2+}$ .<sup>4,34</sup> With suitable experimental refinements, the pmr method was extended to these ionic systems to demonstrate its utility in determining hydration numbers for all types of cations and to remove some of the ambiguities mentioned above.

### Experimental Methods

All salts, acetone, acetone- $d_6$  (99.5%), and dichlorodifluoromethane (Freon 12) were reagent grade and, with the exception of the acetones which were dried over  $\text{CaSO}_4$  before use, they were used as received. The samples were prepared by the addition of acetone or acetone- $d_6$  to an aqueous stock solution, the concentration of which had been determined by passage through a Dowex 50W-X8 cation-exchange column and titration of the resultant solution. The  $\text{La}(\text{ClO}_4)_3$  and  $\text{Zn}(\text{ClO}_4)_2$  stock solution concentrations also were calibrated by mixing with a known amount of acetone and comparing the signal integrations. The temperatures required for the  $\text{Er}^{3+}$ ,  $\text{Fe}^{2+}$ , and  $\text{Ni}^{2+}$  measurements were attainable with water-acetone mixtures. However, the addition of Freon 12 to aqueous acetone-salt solutions was required to achieve temperatures below  $-100^\circ$  for the  $\text{Ce}^{3+}$ ,  $\text{La}^{3+}$ , and  $\text{Zn}^{2+}$  investigations. Although this increased the complexity of these systems, the absence of hydrogen atoms in Freon 12 and the inert nature of this compound prevented spectral complications. As will be discussed later, the further decrease in dielectric constant produced by the presence of this component may enhance complex formation in the paramagnetic solutions. After the Freon 12 was added *in vacuo*, the samples were sealed

and stored in a Dry Ice-acetone mixture until their spectra could be recorded, usually within a few hours or less.

The chemical shift, line width, and area measurements were made with a Varian HA-100 MHz spectrometer, equipped with a variable-temperature probe for studies from  $-150^\circ$  to  $+200^\circ$ . The  $\text{Ni}^{2+}$  spectra were integrated manually because of signal overlap. The spectrometer was operated in the scan mode for recording the paramagnetic solution spectra. The pmr method otherwise was essentially the same for the diamagnetic and paramagnetic solutions.<sup>8</sup> The sample was cooled in the spectrometer probe until the water pmr peak broadened and separated into signals corresponding to the free and coordinated environments. The chemical shifts, areas, and line widths were measured at the temperature of maximum spectral sharpness.

### Results

A summary of the nmr data and cation hydration numbers is presented in Table I, and representative spectra for these systems are shown in Figures 1-6. The precision of the hydration number measurements was 5-10% in the aqueous solutions of  $\text{Fe}^{2+}$ ,  $\text{La}^{3+}$ , and  $\text{Zn}^{2+}$ , but signal broadness and overlap lowered the precision to 10-15% in the  $\text{Ce}^{3+}$ ,  $\text{Er}^{3+}$ , and  $\text{Ni}^{2+}$  cases. Chemical shift measurements were made with a precision of 0.05-0.1 and 1-2 ppm for the diamagnetic and paramagnetic solutions, respectively, and over a wide temperature range for a  $\text{Fe}^{2+}$  solution.

Line width measurements were made in the paramagnetic solution spectra only to permit a rough correlation with the magnetic properties of the cations. However, the broadness mentioned above severely limited the precision of these measurements in all but the  $\text{Fe}^{2+}$  case.

### Discussion

As demonstrated in several previous studies,<sup>8-15</sup> the

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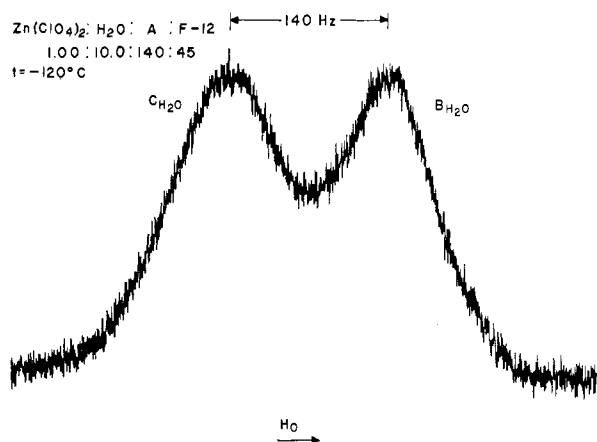


Figure 1.—The water pmr spectrum of a  $\text{Zn}(\text{ClO}_4)_2$  solution in a water-acetone-Freon 12 mixture, recorded on a Varian HA-100 spectrometer. The signals arising from bulk water ( $\text{B}_{\text{H}_2\text{O}}$ ) and water molecules bound in the  $\text{Zn}^{2+}$  solvation shell ( $\text{C}_{\text{H}_2\text{O}}$ ) are labeled. The mole ratios of all species also are shown.

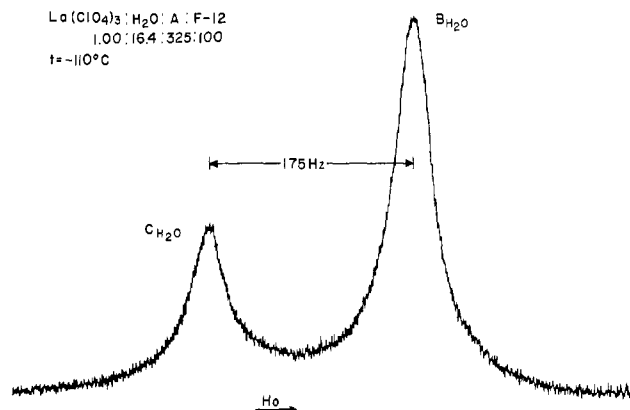


Figure 2.—The water pmr spectrum of a  $\text{La}(\text{ClO}_4)_3$  solution in a water-acetone-Freon 12 mixture, recorded on a Varian HA-100 spectrometer. The signals arising from bulk water ( $\text{B}_{\text{H}_2\text{O}}$ ) and water molecules bound in the  $\text{La}^{3+}$  solvation shell ( $\text{C}_{\text{H}_2\text{O}}$ ) are labeled. The mole ratios of all species also are shown.

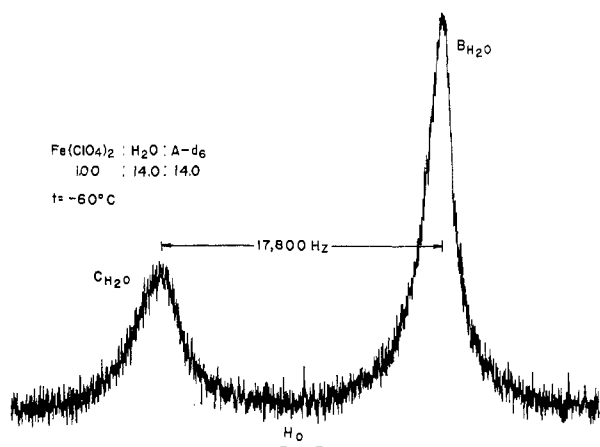


Figure 3.—The water pmr spectrum of a  $\text{Fe}(\text{ClO}_4)_2$  solution in a water-acetone- $d_6$  mixture, recorded on a Varian HA-100 spectrometer. The signals arising from bulk water ( $\text{B}_{\text{H}_2\text{O}}$ ) and water molecules bound in the  $\text{Fe}^{2+}$  solvation shell ( $\text{C}_{\text{H}_2\text{O}}$ ) are labeled. The mole ratios of all species also are shown. The acetone- $d_6$  proton impurity peak is superimposed on the bulk water.

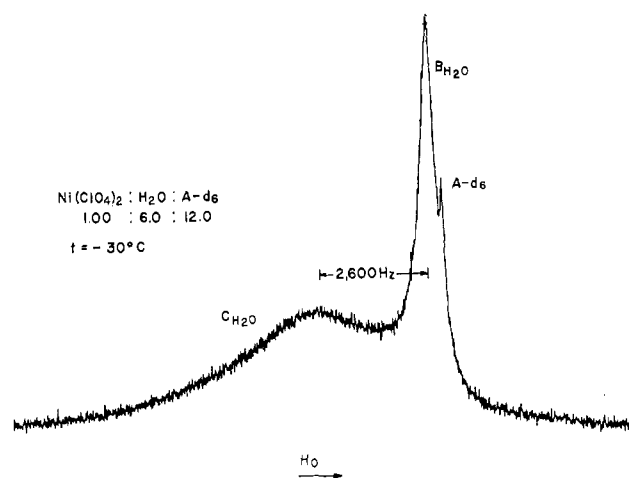


Figure 4.—The water pmr spectrum of a  $\text{Ni}(\text{ClO}_4)_2$  solution in a water-acetone- $d_6$  mixture, recorded on a Varian HA-100 spectrometer. The signals arising from acetone- $d_6$  proton impurities ( $\text{A}-d_6$ ), bulk water ( $\text{B}_{\text{H}_2\text{O}}$ ), and water molecules bound in the  $\text{Ni}^{2+}$  solvation shell ( $\text{C}_{\text{H}_2\text{O}}$ ) are labeled. The mole ratios of all species also are shown.

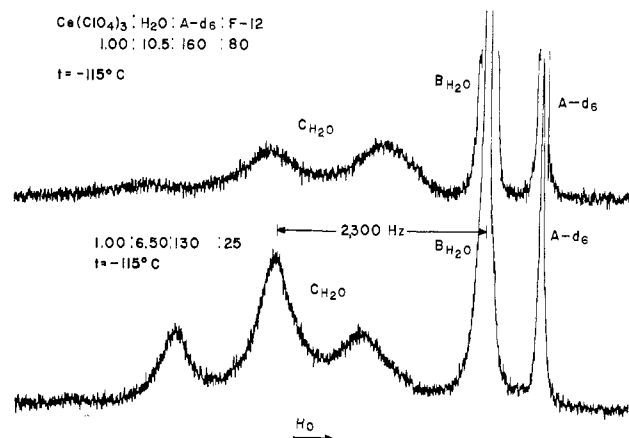


Figure 5.—The water pmr spectra of two  $\text{Ce}(\text{ClO}_4)_3$  solutions in water-acetone-Freon 12 mixtures, recorded on a Varian HA-100 spectrometer. The signals arising from acetone- $d_6$  proton impurities ( $\text{A}-d_6$ ), bulk water ( $\text{B}_{\text{H}_2\text{O}}$ ), and water molecules bound in the  $\text{Ce}^{3+}$  solvation shell ( $\text{C}_{\text{H}_2\text{O}}$ ) are labeled. The mole ratios of all species also are shown.

direct observation of a pmr signal for water coordinated to a cation is possible when ligand and proton exchange have been slowed sufficiently to satisfy the relationship  $\tau \approx (2\pi\Delta\nu)^{-1}$ .<sup>35</sup> Here  $\tau$  is the lifetime of the proton in the cation solvation shell and  $\Delta\nu$  is the separation in Hz of the signals arising from the free and coordinated water molecules. From Table I it can be seen that the water signal separations vary from about 150 Hz for the diamagnetic  $\text{La}^{3+}$  and  $\text{Zn}^{2+}$  solutions to  $10^3$ – $10^4$  Hz in the paramagnetic systems. Therefore  $\tau$  varies from  $\sim 10^{-3}$  sec for the  $\text{La}^{3+}$  and  $\text{Zn}^{2+}$  solvation shell water protons to  $\sim 10^{-4}$ – $10^{-5}$  sec for the paramagnetic solutions. Using the criterion that systems undergoing more rapid exchange require lower temperatures before separate water pmr signals will be observable, exchange rates for the system of Table I decrease in the order  $\text{Zn}^{2+} > \text{Ce}^{3+}$ ,  $\text{La}^{3+} > \text{Er}^{3+} > \text{Fe}^{2+} > (\text{Co}^{2+}) > \text{Ni}^{2+}$ . The  $\text{Co}^{2+}$  measurement described elsewhere was possible at temperatures below  $-38^\circ$ .<sup>11</sup> This trend agrees

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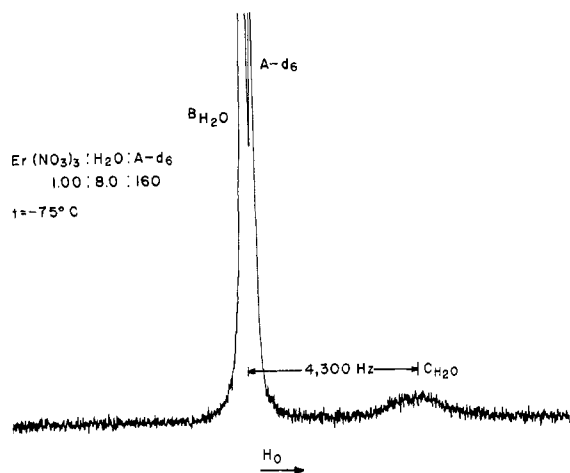


Figure 6.—The water pmr spectrum of an  $\text{Er}(\text{NO}_3)_3$  solution in a water-acetone- $d_6$  mixture, recorded on a Varian HA-100 spectrometer. The signals arising from acetone- $d_6$  proton impurities (A- $d_6$ ), bulk water ( $\text{B}_{\text{H}_2\text{O}}$ ), and water molecules bound in the  $\text{Er}^{3+}$  solvation shell ( $\text{C}_{\text{H}_2\text{O}}$ ) are labeled. The mole ratios of all species also are shown.

well with estimates of the room-temperature ligand exchange rates observed for pure aqueous solutions of these ions by relaxation techniques.<sup>36-39</sup> The minor exception is the  $\text{Zn}^{2+}$  cation for which ligand exchange is slower than the  $\text{Ce}^{3+}$  and  $\text{La}^{3+}$  solutions. This correlation does not necessarily indicate that exchange of whole water molecules is the dominant process at the temperatures of study here. In fact, a proton-exchange process is implied by the low temperatures required for the  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ , and  $\text{Fe}^{2+}$  studies, in view of the ligand-exchange rates of  $\sim 10^4$ ,  $10^5$ , and  $10^6 \text{ sec}^{-1}$  for these systems, respectively, at  $+25^\circ$ . If ligand exchange were the dominant process to be overcome, separate water signals would be anticipated at higher temperatures. Similar estimates cannot be made for the  $\text{Er}^{3+}$  ion for which ligand exchange has not been measured and the  $\text{Ce}^{3+}$ ,  $\text{La}^{3+}$ , and  $\text{Zn}^{2+}$  solutions in which ligand exchange proceeds with a room-temperature rate of  $\sim 10^8 \text{ sec}^{-1}$ .<sup>36-39</sup> Since the present study is concerned primarily with the hydration properties of these ions, the exact nature of the exchange process need not be known at this point.

To achieve the low temperatures required for the study of the  $\text{La}^{3+}$ ,  $\text{Zn}^{2+}$ , and  $\text{Ce}^{3+}$  solutions, a new solvent combination was devised. The water-acetone combination allows studies to  $-100^\circ$ , a sufficient limit for all previous diamagnetic cations,<sup>8-10,12-15</sup>  $\text{Co}^{2+}$ ,<sup>11</sup> and even the  $\text{Er}^{3+}$ ,  $\text{Fe}^{2+}$ , and  $\text{Ni}^{2+}$  measurements reported here. However, ions involved in more rapid exchange processes must be cooled below this temperature. For example, a hydration number of 6 was measured for  $\text{Zn}^{2+}$  at  $-120^\circ$  in a water-acetone-acetaldehyde mixture.<sup>13</sup> Although both organic components are inert and do not compete with water for sites in the cation solvation shell, the hydration of acetaldehyde can lead to the appearance of extraneous signals. Freon 12 also is a suitable diluent for these water-acetone solutions because in addition to being noncompetitive with water for cation solvation, it has

no hydrogen atoms, it produces a similar resultant solution freezing point and viscosity, and it is nonreactive. The inert nature of the Freon 12 in our systems was anticipated from its general properties and verified by the  $\text{Zn}^{2+}$  result of Table I. The hydration number of 6 agrees with that obtained in the water-acetone-acetaldehyde system. The negligible solvating tendency of acetone has been demonstrated conclusively in several previous studies.<sup>8-10,12-15</sup> Further, in the  $\text{La}^{3+}$  and  $\text{Zn}^{2+}$  solutions where acetone rather than acetone- $d_6$  was used, only one resonance peak was observed for this component even at the low temperatures of study.

Since solvent competition can be ruled out, the hydration number of 6 observed for  $\text{Zn}^{2+}$  represents the total number of solvent molecules in this cation solvation shell. Hexahydrated zinc has been characterized by several techniques including room-temperature Raman spectroscopy<sup>17</sup> and crystal complex formation.<sup>25</sup> It is unlikely that extensive hydrolysis or complex formation is occurring in these  $\text{ClO}_4^-$  solutions. The addition of acid to check for hydrolysis was prevented by the resultant signal broadening and overlap. However, this process is not extensive in pure aqueous solution.<sup>40</sup> Raman measurements also have detected no complex formation in aqueous  $\text{Zn}(\text{ClO}_4)_2$  solutions even in nearly saturated solutions.<sup>17</sup> Admittedly the much lower temperature and dielectric constant of the present study would tend to enhance complex formation. On the basis of the room-temperature values for acetone ( $\epsilon$  20) and Freon 12 ( $\epsilon$  2) and the known temperature dependence of this parameter for pure acetone,<sup>41</sup> a rough estimate of the dielectric constant for these solutions would be about 30-40. In contrast, the much lower concentrations used here,  $\sim 0.5 \text{ m}$ , would tend to minimize contact ion pairing and make the analogy to the Raman studies a valid one.

The hydration number of 6 measured for  $\text{La}^{3+}$  is somewhat surprising in view of the ability of this cation to accommodate 6-12 solvent ligands in solid complexes.<sup>25-32</sup> The same considerations of concentration, hydrolysis, dielectric constant, and probably complex formation discussed above for  $\text{Zn}^{2+}$  also apply here. It was possible to study one solution containing a 1:4 mole ratio of  $\text{H}^+$  to  $\text{La}^{3+}$  and no significant increase in hydration number was observed. Calorimetric studies also indicate that hydrolysis is only slight in pure aqueous solution.<sup>42</sup> Similarly, studies which indicate that the extent of polymerization<sup>42</sup> and inner-shell complex formation<sup>16</sup> are minimal in pure aqueous solution may imply that these processes are not appreciable here. If this is the case and  $\text{La}^{3+}$  does exhibit a hydration number greater than 6, the additional water molecules or their hydrogen atoms could be involved in an exchange process which is still rapid at  $-115^\circ$ . Further cooling to  $-125^\circ$  produced no detectable increase in the hydration number. Additional tests for this occurrence and the processes mentioned above must await the application of other techniques and further refinements of this pmr method. At this point the direct pmr results of Table I indicate an inner-shell hydration number of at least 6 for  $\text{La}^{3+}$ . A maximum value of 6

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(40) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, Table 1.9.

(41) "Handbook of Chemistry and Physics," 49th ed, The Chemical Rubber Co., Cleveland, Ohio, 1968, p E59.

(42) G. Biedermann and L. Ciavatta, *Acta Chem. Scand.*, **15**, 1347 (1961).

for  $\text{La}^{3+}$  is consistent with electrostatic factors, although  $\text{La}^{3+}$  (1.15 Å) is somewhat larger than  $\text{Zn}^{2+}$  (0.74 Å)<sup>43</sup> or other ions studied previously in these laboratories.

The application of this pmr method to aqueous solutions of paramagnetic ions was carried out successfully by Matwiyoff and Darley in their study of  $\text{Co}^{2+}$ .<sup>11</sup> At temperatures below  $-38^\circ$ , a solvation shell signal was observed, displaced about 10,000 Hz downfield from the bulk water peak. Signal areas and chemical shift measurements as a function of temperature led to a hydration number of 6 for this ion, and a value of  $-3.7 \times 10^5$  Hz for the electron-bound water proton hyperfine coupling constant. Our initial attempts to extend this method to pure aqueous solutions of other paramagnetic systems were prevented by sample crystallization before exchange could be slowed ( $\text{Fe}^{2+}$ ,  $\text{Er}^{3+}$ ,  $\text{Ce}^{3+}$ ) or signal broadening ( $\text{Ni}^{2+}$ ). As seen from Table I and Figures 3-6, the addition of acetone- $d_6$  as a diluent, plus Freon 12 in the case of  $\text{Ce}^{3+}$ , minimized these problems and allowed the direct observation of bound water signals in all cases. The  $\text{Fe}^{2+}$  solution spectra, typified by Figure 3, were similar to those exhibited by  $\text{Co}^{2+}$  solutions.<sup>11</sup> The bound and free water signals have line widths of  $\sim 3000$  and  $\sim 1000$  Hz, respectively, and the chemical shift separation is about 20,000 Hz in these  $\text{Fe}^{2+}$  solutions. The large separation permitted an unambiguous signal area integration and a hydration number determination of about 6. The number is slightly lower than 6, a feature which may reflect some hydrolysis, complex formation, or most likely the precision of the measurements. Hydrolysis<sup>40</sup> and complex formation<sup>20</sup> apparently are not extensive in aqueous  $\text{Fe}(\text{ClO}_4)_2$  solution. At any rate this hydration number of 6 for  $\text{Fe}^{2+}$  agrees with the results of solution uv<sup>21,22</sup> and solid complex investigations,<sup>25</sup> and it must represent the maximum value for this ion in solution.

The temperature dependence of the chemical shift separation between bound and bulk water is shown in Table I and Figure 7 for one of the  $\text{Fe}(\text{ClO}_4)_2$  solutions. The  $\Delta\nu_{\text{C-B}}$  values exhibit a linear reciprocal temperature behavior as predicted by the Bloembergen equation<sup>44</sup>

$$\frac{\Delta\nu_{\text{C-B}}}{\nu_0} = \frac{A}{h} \frac{2\pi g\beta S(S+1)}{3\gamma kT} \quad (1)$$

where  $\nu_0$  is the resonance frequency,  $A/h$  is the electron-water proton hyperfine coupling constant,  $g$  is  $\sim 2.0$  for  $\text{Fe}^{2+}$ ,<sup>45</sup>  $\beta$  is the Bohr magneton,  $S$  is the electron spin for  $\text{Fe}^{2+}$ , and  $\gamma$  is the proton magnetogyric ratio. From the slope of the plot in Figure 7, a coupling constant of  $-9.7 \times 10^5$  Hz was obtained for this system, a value which is about 3 times that of the  $\text{Co}^{2+}$  case.<sup>11</sup>

As seen in Figure 4, the broadness of the bound water signal and the resultant overlap with the bulk water peak presented a hindrance to accurate area evaluation in the  $\text{Ni}(\text{ClO}_4)_2$  solution spectra. The signal areas were integrated manually in these cases, with a precision of 10-15%, to yield the values shown in Table I. The data show that if the water to  $\text{Ni}^{2+}$  mole ratio is reduced sufficiently, inner-shell complex formation is induced

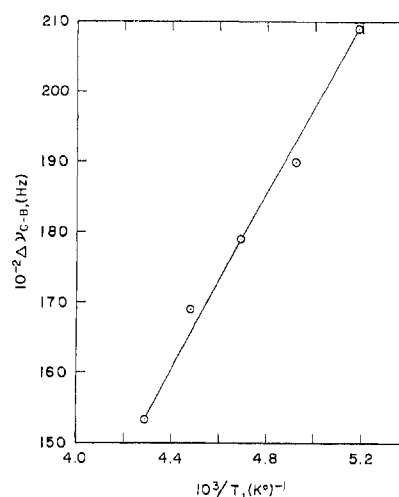


Figure 7.—A plot of  $\Delta\nu_{\text{C-B}}$  vs. reciprocal temperature for the bound and bulk water pmr signals of a  $\text{Fe}(\text{ClO}_4)_2$  solution in a water-acetone- $d_6$  mixture.

and the hydration number decreases from a value of 5.5 to 4.4. The contact ion-pairing process does not appear to be as extensive in the system of higher water content and, in fact, the low hydration number (5.5) may be due solely to signal overlap errors in the 13:1 solution. The hydration number of approximately 6 shown in Table I agrees with a reliable estimate obtained by an indirect pmr method.<sup>34</sup> Although separate oxygen-17 nmr signals were observed for aqueous  $\text{Ni}^{2+}$  solutions, it was not possible to determine the hydration number accurately.<sup>4</sup>

Attempts to narrow the line width of the bound water signal by increasing the acetone- $d_6$  concentration and by the addition of Freon 12 have been unsuccessful thus far. This probably is due to the large effective magnetic moment of  $\text{Ni}^{2+}$ <sup>46</sup> and the inherent broadening which it produces. However, additional experiments with different anions and other solvent compositions are planned.

The data for the  $\text{Ce}^{3+}$  and  $\text{Er}^{3+}$  systems are significant in that they demonstrate the applicability of this pmr technique to paramagnetic ions of the rare earth series. Also,  $\text{Ce}^{3+}$  is a good example of the compromise which must be effected between the signal broadening which can be qualitatively estimated from the magnetic moment of the ion and the increased solution viscosity at low temperatures. The effective magnetic moments of a variety of paramagnetic ions, estimated from pmr relaxation measurements, reflect values almost an order of magnitude greater for  $\text{Fe}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Er}^{3+}$ , as compared to  $\text{Ce}^{3+}$ .<sup>46</sup> Thus, the reduced signal broadening produced by this ion makes it possible to study its solutions at temperatures low enough to slow exchange, in spite of the greater viscosities encountered.

The pmr spectra for two  $\text{Ce}(\text{ClO}_4)_3$  solutions are shown in Figure 5 and they show a three-line pattern for the bound water signals. It is not clear whether the three signals arise from nonequivalent water molecules in the same solvation complex or different  $\text{Ce}^{3+}$  complexes in solution. However, when these samples are cooled, the two bound water peaks at lower field appear first, and the bound water signal furthest upfield ap-

(46) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, N. Y., 1959, Chapter 9.

(43) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 514.

(44) N. Bloembergen, *J. Chem. Phys.*, **27**, 595 (1957).

(45) E. König in H. Landholt and R. Börnstein, "Magnetic Properties of Coordination and Organo-Metallic Transition Metal Compounds," Springer-Verlag, New York, N. Y., 1966, Table 4.

pears at lower temperatures. Thus, the bound water molecules, whatever their environment, exchange at different rates. Although the relative areas of the bound water signals could not be accurately determined, they are all intense in the 6:1 water-Ce<sup>3+</sup> solution, and in total they correspond to an average hydration number of ~4.5 for this ion. At higher water mole ratios, the bound water signal at lowest field decreases in intensity and the cation hydration number increases to almost 6. At higher water concentrations and when the solutions were acidified, the three-signal pattern for bound water was still present but broadening prevented accurate integrations. The value shown in Table I for the acidified solution may be somewhat in error but it does rule out the presence of extensive hydrolysis. The hydration number result in the 6:1 water-Ce<sup>3+</sup> solution must reflect inner-shell complex formation and the multiple bound water pattern which also is present at higher water concentrations may indicate that this complexing process is still prevailing. At this point, one can only state that the Ce<sup>3+</sup> hydration number is at least 6 by direct measurement and possibly greater if complex formation with ClO<sub>4</sub><sup>-</sup> is occurring. Measurements with other anions are underway to resolve this matter.

The Er(NO<sub>3</sub>)<sub>3</sub> solution spectrum of Figure 6 and the extremely low hydration number listed in Table I are only preliminary in nature but they demonstrate the strong complexing tendency of the NO<sub>3</sub><sup>-</sup> anion. The bonding is probably bidentate to account for the hydration number but this conclusion must await the determination of the maximum value for Er<sup>3+</sup>. This

measurement may be possible with the ClO<sub>4</sub><sup>-</sup> or halide salts of this cation. Although the upfield displacement of the bound water signal from that of the bulk may indicate a positive sign for the hyperfine coupling constant, the low signal intensity and excessive line width prevented a detailed temperature study at this point.

In addition to expanded studies of the species described here to elucidate their complexing properties and to resolve any ambiguities concerning maximum hydration numbers, attempts to extend this pmr technique to other diamagnetic and paramagnetic ions presently are underway. Considerations of effective magnetic moments for a variety of paramagnetic species and solvent-exchange rates for examples of both types of ions indicate that the list of cations lying within the scope of this method is extensive.<sup>47</sup>

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(47) NOTE ADDED IN PROOF.—Recent measurements in our laboratories have indicated a maximum hydration number of 6-7 for Er<sup>3+</sup>. Bound water signals also have been observed in aqueous Lu<sup>3+</sup>, Pr<sup>3+</sup>, and Yb<sup>3+</sup> solutions. While this paper was in press a more refined oxygen-17 nmr hydration study of Fe<sup>2+</sup> and Ni<sup>2+</sup> was completed [A. M. Chmelnick and D. Fiat, *J. Amer. Chem. Soc.*, **93**, 2785 (1971)] confirming the results presented here.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,  
UNIVERSITY OF WESTERN ONTARIO, LONDON, CANADA

## Cationic Acetylenic Platinum(II) Compounds and Their Derivatives. II. Acetylene and Vinyl Ether Complexes

By M. H. CHISHOLM AND H. C. CLARK\*

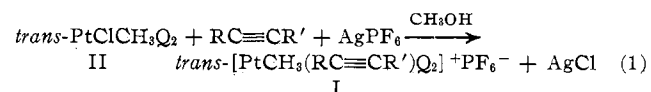
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Cationic acetylenic complexes of platinum(II), *trans*-[PtCH<sub>3</sub>(RC≡CR')Q<sub>2</sub>]<sup>+</sup>PF<sub>6</sub><sup>-</sup> (I), have been prepared by the reaction of *trans*-PtClCH<sub>3</sub>Q<sub>2</sub> (II), where Q = dimethylphenylphosphine or trimethylarsine, with alkyl- or aryl-disubstituted acetylenes and silver hexafluorophosphate in the presence of methanol as solvent. The nature of the platinum-acetylene bond is discussed in view of nmr and vibrational spectra of I. In several instances it was not possible to isolate I and reaction proceeded with the ultimate formation of [PtCH<sub>3</sub>Q<sub>2</sub>]<sup>+</sup>PF<sub>6</sub><sup>-</sup>. Reactions involving RC≡CR', where R and R' are CF<sub>3</sub>, COOCH<sub>3</sub>, CH<sub>2</sub>OH, and COOH, are also considered and evidence for vinyl ether formation is presented.

### Introduction

Our interest in both acetylenic<sup>1-3</sup> and cationic<sup>4-7</sup> complexes of platinum initiated a study of reaction 1 with the hope of isolating I. We recently described<sup>8,9</sup>

- (1) H. C. Clark and R. J. Puddephatt, *Chem. Commun.*, 92 (1970).
- (2) H. C. Clark and R. J. Puddephatt, *Inorg. Chem.*, **9**, 2670 (1970).
- (3) H. C. Clark, and R. J. Puddephatt, *ibid.*, **10**, 18 (1971).
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- (5) H. C. Clark and K. R. Dixon, *ibid.*, **91**, 596 (1969).
- (6) H. C. Clark, K. R. Dixon, and W. J. Jacobs, *ibid.*, **91**, 1346 (1969).
- (7) H. C. Clark and J. D. Ruddick, *Inorg. Chem.*, **9**, 1226 (1970).
- (8) M. H. Chisholm and H. C. Clark, *Chem. Commun.*, 763 (1970).
- (9) Part I: M. H. Chisholm and H. C. Clark, *Inorg. Chem.*, **10**, 1711 (1971).



reactions involving monoalkyl- and -aryl-substituted acetylenes, RC≡CH, in methanol and ethanol which led to the formation of methoxy- and ethoxycarbene complexes, respectively. The reaction is believed<sup>9a</sup> to

(9a) NOTE ADDED IN PROOF.—Since the submission of this paper, we have been able to isolate stable cationic vinyl ether complexes and hence must discard this mechanism. A general mechanism involving platinum-stabilized carbonium ions has been proposed, and this readily accounts for all the reactions of cationic acetylenic platinum complexes [M. H. Chisholm, H. C. Clark, and D. H. Hunter, *Chem. Commun.*, 809 (1971)].