in Table I. Acid-catalyzed proton transfer from a cationic primary hydration sphere to bulk definitely does occur, and the occurrence is not restricted to paramagnetic transition metal ions, but is quite likely a phenomenon to be expected for hydrated ions in general.

The subject of acid-catalyzed proton transfer from hydrated cations in aqueous mixed solvents is one for which significantly more data are needed before valid comparisons can be made with the mechanistic conclusions reached in studies of pure aqueous solutions and such studies are currently in progress.

Acknowledgment. We wish to express our sincere appreciation to Professor N. A. Matwiyoff of The Pennsylvania State University for making his data available to us and for many discussions. In addition we wish to acknowledge the financial support of the National Science Foundation and of the Public Health Service in the form of research grants to T. J. S.

Direct Determination of the Solvation Number of the Magnesium(II) Ion in Water, Aqueous Acetone, and Methanolic Acetone Solutions

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Abstract: At temperatures below −60° the proton magnetic resonance (pmr) signals of the solvent molecules within the primary coordination sphere of the Mg^{2+} ion in aqueous acetone, methanolic acetone, and concentrated aqueous solutions can be distinguished from those of the bulk solvent. From a comparison of the areas of the pmr lines of the solvent in the free and coordinated sites, the composition of the primary solvation sphere of the Mg^{2+} ion in these solvents was found to be $Mg(CH_3OH)_6{}^{2+}$ in methanolic acetone and $Mg(OH_2)_6{}^{2+}$ in aqueous acetone and water. The relative coalescence temperatures of the coordinated and free solvent pmr signals indicate that the order of increasing lability of the complex ions is $Mg(CH_3OH)_6{}^{2+} < Mg(OH_2)_6{}^{2+}$ in aqueous acetone $< Mg(OH_2)_6{}^{2+}$ in water.

A study of the Mg^{2+} ion–water complexes using direct techniques is of importance not only with respect to the difficult task of elucidating the solution chemistry of the coordination compounds of the representative elements, but also because the complexes are implicated in a number of enzyme-catalyzed reactions.[1-3] Direct techniques such as isotope dilution (ID), which provides a kinetic distinction between the solvent molecules within and those outside the first coordination sphere of the metal ion, and proton magnetic resonance (pmr) spectroscopy, which provides a magnetic distinction, have been applied successfully to the characterization of several labile complexes of the Mg^{2+} ion at low temperatures: $Mg(CH_3OH)_{6-n}(OH_2)_n{}^{2+}$ in aqueous methanol (ID and pmr);[4,5] $Mg(CH_3OH)_6{}^{2+}$ in methanol (pmr);[6] and $Mg(NH_3)_5{}^{2+}$ in liquid ammonia (pmr).[7]

Although the rate of exchange of the water molecules from the first coordination sphere of Mg^{2+} has been evaluated using sonic relaxation and temperature-jump techniques,[8-10] the lability of the complex $Mg(OH_2)_n{}^{2+}$ precludes the direct determination of the coordination number, n, in dilute aqueous solutions. However, we have been able to distinguish the pmr signals of the $Mg(OH_2)_6{}^{2+}$ ion from those of the bulk solvent at low temperatures (<−70°) in concentrated aqueous solutions of $Mg(NO_3)_2$ and $Mg(ClO_4)_2$. In addition, we have been able to show that the $Mg(OH_2)_6{}^{2+}$ ion exists in aqueous acetone solutions over a much wider range of temperatures and molar ratios, $[Mg(ClO_4)_2]:[H_2O]$. The use of acetone as a diluent is advantageous because it not only decreases the rate of exchange between H_2O and $Mg(OH_2)_6{}^{2+}$ but it also magnifies the chemical shift difference between the two species. Since acetone is a weak donor molecule[11] to which the Mg^{2+} ion can coordinate, we also include in this report the results of a series of control experiments in which the complex, $Mg(CH_3OH)_6{}^{2+}$, was characterized in anhydrous methanolic acetone solutions of $Mg(ClO_4)_2$.

Experimental Section

1. Materials. The hexahydrate of $Mg(ClO_4)_2$[12] was prepared by dissolving MgO (Fisher Certified Reagent) in an excess of 30%

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(1) E. L. Smith, *Advan. Enzymol.*, **12**, 191 (1951).

(2) B. G. Malmstrom and A. Rosenberg, *ibid.*, **21**, 131 (1959).

(3) M. Eigen and G. G. Hammes, *ibid.*, **25**, 1 (1963).

(4) J. H. Swinehart, T. E. Rogers, and H. Taube, *J. Chem. Phys.*, **38**, 398 (1963).

(5) J. H. Swinehart and H. Taube, *ibid.*, **37**, 1579 (1962).

(6) S. Nakamura and S. Meiboom, *J. Am. Chem. Soc.*, **89**, 1765 (1967).

(7) T. J. Swift and H. H. Lo, *ibid.*, **89**, 3988 (1967).

(8) M. Eigen and K. Tamm, *Z. Elektrochem.*, **66**, 107 (1962).

(9) H. Diebler, M. Eigen, and G. G. Hammes, *Z. Naturforsch.*, **15b**, 554 (1960).

(10) M. Eigen and G. G. Hammes, *J. Am. Chem. Soc.*, **82**, 5951 (1960).

(11) R. S. Drago and K. F. Purcell in "Non-Aqueous Solvent Systems," T. C. Waddington, Ed., Academic Press Inc., New York, N. Y., 1965.

(12) The preparation of the magnesium salt was necessary because

$HClO_4$ (Baker Reagent) and boiling the solution gently until crystals began to form. After the solutions had been allowed to cool, crystals of $Mg(ClO_4)_2 \cdot 6H_2O$ (contaminated by $HClO_4$) were collected by filtration. The salt was then recrystallized several times from triply distilled water and "dried" to constant weight in a vacuum desiccator. A solution of 1 equiv of $Mg(ClO_4)_2 \cdot 6H_2O$ prepared in this manner displaced 1.013 equiv of H^+ ion from a cation-exchange resin and contained 1.011 ± 0.001 equiv of the Mg^{2+} ion as determined by titration with a standard solution of EDTA (ethylenediaminetetraacetic acid) using Eriochrome Black T as the indicator.[13] The salt $LiClO_4 \cdot H_2O$ was prepared in a similar manner. Magnesium nitrate hexahydrate (Baker Reagent) was used without additional purification. For several experiments, $Mg(ClO_4)_2 \cdot 2H_2O$ was used and was prepared by heating the hexahydrate over P_2O_5 *in vacuo* at 80° for approximately 24 hr. One equivalent of $Mg(ClO_4)_2 \cdot 2H_2O$ contained 1.100 equiv of the Mg^{2+} ion (EDTA titration) and 1.90 equiv of water (Karl Fischer titration).

Acetone (Fisher Reagent) was purified using the method of Shipsey and Werner.[14] Methanol (Fisher Reagent) was refluxed over and distilled from magnesium powder; the middle fraction retained was stored over Linde 3A Molecular Sieves.

2. Preparation of $Mg(CH_3OH)_6(ClO_4)_2$. The complex, which has not been described before, was prepared from $Mg(ClO_4)_2 \cdot 2H_2O$ and methanol using the general method outlined by Drago, *et al.*[15] It was recrystallized several times from 10% methanolic methylene chloride.

Anal. Calcd for $Mg(CH_3OH)_6(ClO_4)_2$: Mg, 5.75; CH_3OH, 46.3. Found: Mg, 5.9; CH_3OH, 46.0.

The Mg^{2+} ion content was determined by titration with EDTA[13] and the methanol content using a pmr method.[16]

3. Preparation of Solutions. All solutions were prepared by weight and delivered directly into 5-mm nmr tubes which were then sealed immediately. All hygroscopic materials were transferred in a glove bag under a dry nitrogen atmosphere, A random selection of the samples was analyzed for Mg^{2+} ion content using an EDTA titration. In each case, the content was the same as that calculated from the weight composition.

The methanolic and aqueous acetone solutions slowly develop (in 2 to 3 days) a yellow color which is probably due to mesityl oxide and phorone which are formed by the acid-catalyzed condensation and dehydration of acetone.[17,18] The color development is accompanied by the appearance and growth of a number of C–H pmr lines to the low- and high-field sides of the acetone resonance. Within 5 or 6 hr after the preparation of the methanolic acetone solutions, signals characteristic of diacetone alcohol and the hemiketal of acetone[19,20] could be distinguished in the pmr spectra. The solvation numbers of the Mg^{2+} ion calculated from the spectra of these aged solutions are 5–15% less than those obtained from fresh solutions and continue to decrease slowly as a function of time. For this reason the samples were stored at liquid nitrogen temperatures and the pmr spectra of the aqueous and methanolic acetone solutions were recorded within 12 and 3 hr after preparation, respectively. For a given solution, the pmr spectra recorded at different times within the latter limits, and the solvation numbers calculated therefrom, are identical. In those spectra no signals other than those of acetone and H_2O (or CH_3OH) could be distinguished.

4. Measurements. Proton nmr spectra were recorded using the Varian A-60A spectrometer equipped with a V-6040 temperature-control unit. The systems were calibrated and the measurements made in the manner described previously.[21] Infrared and Raman spectra were obtained with Perkin-Elmer Model 21 and Cary Model 81 spectrometers, respectively. The areas of the nmr signals were obtained by planimetry and manual integration.

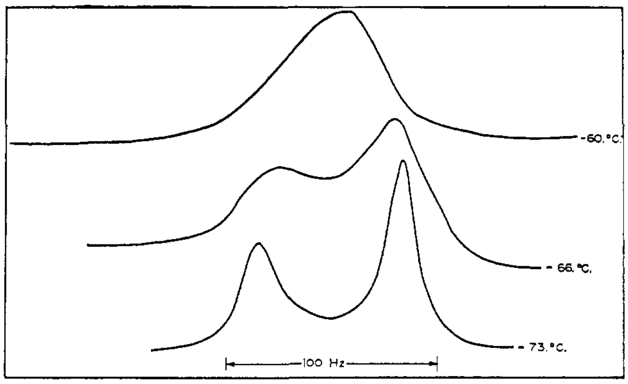

Figure 1. The temperature dependence of the 60-MHz pmr spectrum of a solution of $Mg(ClO_4)_2$ in aqueous acetone. The solution composition (in moles) is $Mg(ClO_4)_2$, 0.384; H_2O, 4.782; and acetone, 13.98. Only the water region of the spectrum is depicted. The magnetic field increases from left to right.

Results

In Figure 1 are reproduced the pmr spectra of a representative aqueous acetone solution of $Mg(ClO_4)_2$ as a function of temperature. Only the O–H region of the spectrum is depicted; the acetone C–H resonance is located approximately 150 Hz upfield from the high-field O–H signal. The low-field O–H signal is assigned to the water molecules in the first coordination sphere of the Mg^{2+} ion and the high-field one to water at all sites outside the first coordination sphere. The assignments are based upon the following considerations: (a) at a constant molar ratio, $[Mg(ClO_4)_2]$:[acetone], the area of the low-field OH signal relative to that of acetone remains constant, but the relative area of the high-field one increases as the concentration of water is increased (see Figure 2); and (b) the O–H resonance of aqueous acetone solutions of $LiClO_4$ at the temperatures listed in Figure 1 consists of a single peak.

The solvation numbers of the Mg^{2+} ion, calculated by using the known compositions of a set of representative solutions and the relative areas of the free and coordinated water pmr signals, are listed in Table I. Table II contains a summary of the temperature dependence of the chemical shifts and line widths of these signals. No coordinated acetone signal could be distinguished in the pmr spectra of any solution within the range of compositions represented in Table I. For the solutions having a molar ratio, $2 \geq [H_2O]:[Mg(ClO_4)_2] < 6$, a coordinated acetone resonance could be distinguished 6 Hz downfield from that of free acetone at temperatures less than −60°. The average solvation number calculated from the areas of the coordinated acetone and water signals of the latter solutions is 6 ± 0.3.

In the pmr spectra of concentrated aqueous solutions of $Mg(ClO_4)_2$ and $Mg(NO_3)_2$, the signals of water coordinated to the Mg^{2+} ion can also be distinguished, although over a more limited temperature range than for aqueous acetone solutions. At −70 and −80°,

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the commercially available reagent was found to be contaminated with either acidic or basic materials, depending upon the sample, and some samples contained a paramagnetic impurity. These contaminants, by broadening the pmr lines, interfere with the detection of the coordinated solvent signal.

(13) G. Schwarzenbach, "Complexometric Titrations," Interscience Publishers, Inc., New York, N. Y., 1957.

(14) K. Shipsey and E. A. Werner, *J. Chem. Soc.*, **103**, 1255 (1913).

(15) R. S. Drago, D. W. Meek, M. D. Joesten, and L. LaRoche, *Inorg. Chem.*, **2**, 124 (1963).

(16) N. A. Matwiyoff and W. G. Movius, *J. Am. Chem. Soc.*, **89**, 6077 (1967).

(17) S. Nagakura, A. Minegishi, and K. Stanfield, *ibid.*, **79**, 1033 (1957).

(18) O. H. Wheeler, *ibid.*, **79**, 4191 (1957).

(19) The Mg^{2+} ion appears to shift the equilibrium in favor of the hemiketal more effectively than does the H^+ ion.[20] A quantitative study of this reaction which appears to involve the coordination of the hemiketal to the Mg^{2+} ion is in progress.

(20) J. M. Jones and M. L. Bender, *J. Am. Chem. Soc.*, **82**, 6322 (1960).

(21) N. A. Matwiyoff, *Inorg. Chem.*, **5**, 788 (1966).

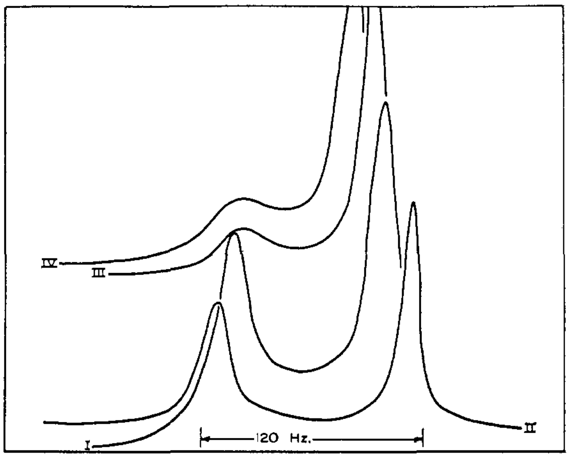

Figure 2. The composition dependence of the 60-MHz pmr spectra of aqueous acetone solutions of $Mg(ClO_4)_2$ at −80°. Solution compositions (in moles), $[Mg^{2+}]$:$[H_2O]$:[acetone], are (I) 0.499, 6.48, 11.83; (II) 0.257, 3.18, 12.10; (III) 0.293, 6.83, 12.35; and (IV) 0.452, 8.31, 11.28. The spectra were recorded at different spectrum amplitudes.

the pmr spectra of the former solutions consist of two broad, but distinct, signals, the low-field one assigned to water within and the high-field one to water outside the first coordination sphere of the Mg^{2+} ion. Above −65° only a single broad line is distinguished, and below −85°, because of the high viscosity of the solutions, the free and coordinated water signals broaden and overlap extensively. In Table III are summarized the coordination numbers calculated from the areas of the free and coordinated water signals at −70 and −80°.

Table I. Solvation Numbers, n, of the $Mg(OH_2)_n^{2+}$ Ion in Aqueous Acetone Solutions

Solution composition, (moles) [Mg(II)]	[H_2O]	[Acetone]	Temp, °C	Solvation no., n^a
0.107	1.522	12.10	−67.5	5.9 ± 0.2
			−71.5	6.0 ± 0.2
			−73.0	6.0 ± 0.1
			−79.0	6.0 ± 0.1
			−83.0	6.0 ± 0.1
0.257	3.18	12.10	−71.5	6.0 ± 0.3
			−74.0	5.9 ± 0.2
			−79.0	5.9 ± 0.1
			−83.0	6.0 ± 0.1
0.293	6.83	12.35	−71.5	5.8 ± 0.2
			−73.0	6.0 ± 0.2
			−79.0	5.9 ± 0.1
			−90.0	6.0 ± 0.1
0.384	4.782	13.98	−70.0	6.0 ± 0.3
			−85.0	6.0 ± 0.1
0.427	2.56	12.40	−71.5	6.0 ± 0.1[b]
			−85.0	6.0 ± 0.1[b]
0.499	6.48	11.83	−71.5	5.9 ± 0.2
			−90.0	5.9 ± 0.1
0.452	8.31	11.38	−71.5	5.8 ± 0.3
			−80.0	5.9 ± 0.1
0.512	13.02	11.91	−71.5	5.9 ± 0.2
			−78.0	6.0 ± 0.1

[a] Number cited is the average obtained from five spectra. [b] No free water signal was distinguished. The solvation number was obtained from the relative areas of the free acetone and coordinated water signals.

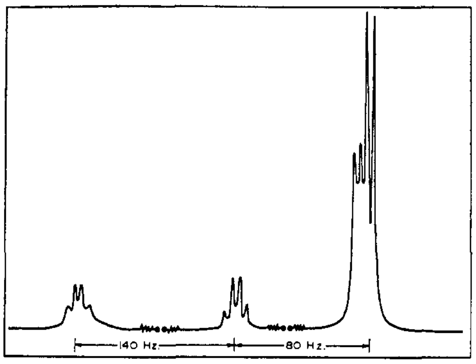

Figure 3. The pmr spectrum, in the methanol region, of a methanolic acetone solution of $Mg(ClO_4)_2$ at −60°. The solution composition (in moles) is $Mg(ClO_4)_2$, 0.55; CH_3OH, 6.72; and acetone, 11.65.

Table II. Temperature Dependence of the Chemical Shifts and Line Widths of the Free and Coordinated Water Signals of Aqueous Acetone Solutions of $Mg(ClO_4)_2$ at 60 MHz

Code[a]	$\Delta\nu_c$[b]	$\Delta\nu_f$[b]	$\Delta\omega_c$[c]	$\Delta\omega_f$[c]	Temp, °C
I	40	32	242	140	−67.5
II	40	34	239	158	
I	34	28	242	141	−69.5
II	36	30	242	158	
III	36	30	240	169	
I	29	22			−71.5
II	31	25			
III	31	27			
I	26	19	249	139	−73.0
II	28	21	244	158	
III	31	25	246	158	
I	22	15			−76.0
II	24	18			
III	28	22			
I	18	12	252	142	−79.0
II	21	14	251	158	
III	28	20	251	171	
I	19	13			−82.0
II	22	15			
III	30	21			

[a] Code refers to the solution composition in moles of Mg(II), H_2O, and acetone, respectively: (I) 0.107, 1.52, and 12.10; (II) 0.257, 3.18, and 12.10; and (III) 0.499, 6.48, and 11.83. [b] Width of the line at half the maximum height in Hz (± 0.5); $\Delta\nu_c$ refers to the coordinated water signal and $\Delta\nu_f$ to that of free water. [c] Chemical shift in Hz (±1) downfield with respect to the methyl resonance of the internal standard toluene.

The pmr spectrum reproduced in Figure 3 is representative of those obtained for methanolic acetone solutions of $Mg(CH_3OH)_6(ClO_4)_2$. Only the methanol region of the spectrum is depicted. Based upon considerations discussed previously, the low-field doublet in the spectrum is assigned to the C–H resonance of methanol within and the high-field doublet to methanol outside the first coordination sphere of Mg^{2+}. Analogous assignments are made for the low-field methanol O–H quartets. (The multiplets are due to the spin–spin coupling of the C–H and O–H protons.) Depending upon the composition of the solutions, the coalescence temperature for the O–H signals is −26 ± 5°, and that for the C–H protons is −50 ± 4°.

In Table IV are summarized the chemical shift and coupling constant parameters obtained from the spectra of a few representative solutions of $Mg(ClO_4)_2$ in methanolic acetone. The solvation number of the Mg^{2+} ion in these solutions was calculated using low-resolution pmr spectra in the O–H region. Under low-

Table III. Solvation Numbers, n, and Proton Chemical Shifts of the $Mg(OH_2)_n^{2+}$ Ion in Aqueous Solutions

Soln compn	Temp, °C	Solvation no., n	$\Delta\omega_c$[a]
4.00 m $Mg(ClO_4)_2$	−70.0	5.9 ± 0.3	43
	−80.0	6.0 ± 0.2	47
3.00 m $Mg(ClO_4)_2$	−70.0	6.0 ± 0.2	45
2.96 m $Mg(NO_3)_2$	−80.0	6.1 ± 0.3	48

[a] Chemical shift of the coordinated water signal, in Hz (±3), with respect to the free water signal.

Table IV. Proton Chemical Shift and Coupling Constant Parameters of $Mg(CH_3OH)_6^{2+}$ and Free Methanol in Methanolic Acetone Solutions at 60 MHz[a]

		$Mg(CH_3OH)_6^{2+}$			Free methanol		
Code[b]	Temp, °C	$\Delta\omega$(OH)	$\Delta\omega$(CH)	J	$\Delta\omega$(OH)	$\Delta\omega$(CH)	J
I	−72.0	297	91	5	170	82	5
II	−72.0	300	93	5	153	85	5
III	−72.0	298	91	5	175	80	5
I	−64.0	298	90	5	160	80	5
II	−64.0	299	92	5	147	81	5
III	−64.0	298	91	5	170	80	5
I	−58.0	296	89	5	154	79	5
II	−58.0	296	89	5	143	79	5
III	−58.0	295	87	5	165	79	5

[a] Chemical shifts $\Delta\omega$, in Hz (±2) downfield with respect to the CH_3 resonance of the internal standard toluene. J is the (OH)–(CH) spin–spin coupling constant, in Hz (±0.5). [b] Code refers to solution composition in moles of Mg(II), CH_3OH, and acetone, respectively: (I) 0.555, 6.72, 11.65; (II) 0 265, 2.40, and 11.90; and (III) 0.500, 7.90, and 11.65.

resolution conditions, two broadened Lorentzian lines with no multiplet character were obtained. The number calculated for solutions, having the range of compositions (in moles) $0.160 \leq [Mg^{2+}] \leq 0.376$: $0.960 \leq [CH_3OH] \leq 7.90$:11.65 = [acetone], is 6.0 ± 0.07, at temperatures in the range −25 to −80°. No coordinated acetone resonance could be distinguished in any of the spectra of solutions for which $[CH_3OH]$:$[Mg^{2+}] \geq 6$.

The ir and Raman spectra of the aqueous and acetone solutions of $Mg(ClO_4)_2$ and $Mg(NO_3)_2$ at 28° were recorded in an effort to detect the coordination of anions and/or acetone to the Mg^{2+} ion. However, in each case the spectra in the ClO_4^-, NO_3^-, and acetone regions were similar to those of analogous $LiClO_4$ and $LiNO_3$ solutions. Small differences (<20 cm^{-1}) in characteristic vibrational frequencies were noted in the spectra of the Li^+ and Mg^{2+} solutions, but no pronounced splitting of degenerate modes, which occurs when NO_3^- or ClO_4^- are coordinated to a metal ion,[22] could be distinguished. No coordinated acetone carbonyl vibration could be detected for those aqueous solutions having a molar ratio $[H_2O]$:$[Mg^{2+}] \geq 6$. For the solutions in which the ratio was <6, an additional carbonyl vibration, assigned to coordinated acetone, occurs approximately 20 cm^{-1} to the low-energy side of that for free acetone.

Discussion

The data in Table III demonstrate that the solvation number of the Mg^{2+} ion in concentrated aqueous nitrate and perchlorate solutions is 6 at low temperatures. This suggests to us that the ion $Mg(OH_2)_6^{2+}$ exists as a distinct kinetic entity in these solutions. An alternative interpretation of the data would require that the coordinated water be distributed among a variety of distinct hydrated species (*e.g.*, $Mg(OH_2)_5^{2+}$, $Mg(OH_2)_7^{2+}$, etc.) in a manner such that the average number of water molecules complexed to the Mg^{2+} ion be six and that the species of different coordination numbers exhibit nearly the same proton chemical shifts. The alternative interpretation, which should be considered in view of the report[23] of the indirect pmr determination of a hydration number of 4 for the Mg^{2+} ion in aqueous solutions at 30°, seems unlikely to us because (a) the solvation number obained for the Mg^{2+} ion in aqueous acetone solutions over a wide range of temperatures and molar ratios, $[H_2O]$:$[Mg^{2+}]$, is 6 (see Tables I and III); and (b) the solvation number of the Mg^{2+} ion, as a perchlorate salt in aqueous and aqueous acetone solutions, is unaffected by the presence of $LiClO_4$ (to the maximum concentration studied, 2 m) in the solutions initially having the compositions listed in Tables I and III.

In terms of the discussion above, it is of interest to consider the extent to which acetone influences the primary solvation of the Mg^{2+} ion. Certainly the pmr and vibrational spectra of aqueous and methanolic acetone solutions having molar ratios, $[H_2O]$ ($[CH_3OH]$): $[Mg^{2+}] \geq 6$, provide no evidence for the coordination of acetone to Mg^{2+}. It is more difficult to ascertain whether acetone, by influencing the "solvent structure," can induce a coordination number change indirectly when it is added to highly structured solutions of the Mg^{2+} ion. It has been suggested[23] that solvent effects may be of importance in inducing the Mg^{2+} ion to adopt solvation numbers of 4 and 6 in aqueous and methanol solutions, respectively. No such coordination number change occurs in the Mg^{2+}–methanol–acetone system. We have been able to show that $Mg(CH_3OH)_6^{2+}$, which has been characterized previously,[6,24] exists in acetone–methanol solutions over the complete range of solvent compositions. In any event, it is difficult to conceive of solvent effects which could induce Mg^{2+} to adopt a solvation number of 6 in concentrated aqueous solution at low temperatures and a solvation number of 4 in dilute aqueous solutions at higher temperatures. We conclude, therefore, that the formation of the complex ions, $Mg(OH_2)_6^{2+}$ and $Mg(CH_3OH)_6^{2+}$, is predominantly a function of the Mg^{2+}–solvent interaction *in the first coordination sphere*, and that the $Mg(OH_2)_6^{2+}$ ion should persist in dilute aqueous solutions.

From a comparison of the coalescence temperatures (relative to the chemical shift differences between the protons in the free and coordinated solvent sites[25]) the order of decreasing lability of the complex ions can be obtained: $Mg(OH_2)_6^{2+}$ in water > $Mg(OH_2)_6^{2+}$ in aqueous acetone > $Mg(CH_3OH)_6^{2+}$ in methanolic acetone. The following lower limits to the rate (k_1 at

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(22) K. Nakamoto, "Infra-Red Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963, pp 161–165.

(23) T. J. Swift and W. G. Sayre, *J. Chem. Phys.*, 44, 3567 (1966).

(24) In the study of Nakamura and Meiboom,[6] the CH pmr signal of $Mg(CH_3OH)_6^{2+}$ in methanol was detected as a relatively broad line only when $Cu(ClO_4)_2$ had been added to the solutions.

(25) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, pp 218–225.

25°) and activation enthalpy (ΔH) for the solvent exchange reactions of the ions, $Mg(OH_2)_6^{2+}$ in aqueous acetone and $Mg(CH_3OH)_6^{2+}$ in methanolic acetone, were obtained from the temperature dependence of the coordinated solvent line widths: 1.3×10^5 sec^{-1} and 8.4 kcal; 2.5×10^4 sec^{-1} and 12 kcal, respectively. Accurate solvent exchange parameters for these systems are being obtained *via* a complete analysis of the line shapes.[26,27]

We have attempted to extend the techniques discussed here to the determination of the solvation numbers of a variety of cations in water, aqueous acetone, and methanol. No coordinated solvent pmr signal could be distinguished for the cations Li^+, Ca^{2+}, Zn^{2+}, Hg^{2+}, In^{3+}, Y^{3+}, and La^{3+}. However, the pmr signals of the complex ions $Be(OH_2)_4^{2+}$, $Ga(OH_2)_6^{3+}$, and $Co(OH_2)_6^{2+}$ can be distinguished readily in aqueous acetone and concentrated aqueous solutions at low temperature.[28,30] Details of these studies, including a complete line-shape analysis of the pmr signals, will be the subject of a future report.[30]

Acknowledgment. N. A. M. is grateful to the National Science Foundation for a postdoctoral fellowship, 1963–1964, during the tenure of which most of these studies were initiated.

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[26] Wawro and Swift[27] have completed such a study for the system Mg^{2+}–H_2O–acetone. The other systems are being analyzed in our laboratories.

[27] R. G. Wawro and T. J. Swift, private communication.

[28] While these studies were in progress Schuster and Fratiello[29] reported the detection of the pmr signal of $Al(OH_2)_6^{3+}$ in concentrated aqueous solutions of $AlCl_3$ at low temperatures.

[29] R. Schuster and A. Fratiello, *J. Chem. Phys.*, **47**, 1554 (1967).

[30] P. E. Darley and N. A. Matwiyoff, studies in progress.

Iron Carbonyl Complexes of Cyclooctatetraene Dimers

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Abstract: The prolonged irradiation of a mixture of $Fe(CO)_5$ with excess cyclooctatetraene yields two isomeric complexes $C_{16}H_{16}Fe(CO)_3$ (**1**, mp 118°; **2**, mp 172° dec). Both compounds react with excess of $Fe(CO)_5$ to produce a trinuclear iron carbonyl complex, $C_{16}H_{16}Fe_3(CO)_9$ (**3**, mp 170° dec) which was thermally degraded to two isomeric complexes $C_{16}H_{16}Fe_2(CO)_6$ (**4**, mp 191° dec; **5**, mp 191° dec). Complexes **1**, **3**, **4**, and **5** can also be prepared by the light-induced reaction of $Fe(CO)_5$ with the cyclooctatetraene dimer of mp 73°. With $Fe_2(CO)_9$ under mild conditions this olefin produces an additional complex (9) of composition $C_{16}H_{16}Fe(CO)_4$ which readily decarbonylates to produce **1**. Complex **1** in solution undergoes reversible valence isomerization similarly as the parent cyclooctatetraene dimer. Complex **2** does not fluctuate and was shown to be an $Fe(CO)_3$ complex of tetracyclo[$6.0^{1,8}.0^{9,16}.0^{10,15}.4$]hexadeca-2,4,6,11,13-pentaene. Complex **3** appears to be a bis(π-allyl)tricarbonyliron derivative of **2** in which two additional $Fe(CO)_3$ groups are attached to the cyclooctatriene moiety of this $C_{16}H_{16}$-$Fe(CO)_3$ system. Complex **4** is shown to be hexacarbonyl-π-pentacyclo[$4.4.0^{5,16}.0^{6,15}.0^{7,14}.0^{8,13}$] hexadeca-2,4,10,12-tetraenediiron, whereas **5** is probably a derivative of **1** in which an additional $Fe(CO)_3$ group is attached to the two free double bonds of the ligand. The oxidative degradation of all complexes with ferric chloride in acetonitrile was found to yield naphthalene.

The study of iron carbonyl complexes of cyclooctatetraene has produced numerous new compounds with unexpected structures and properties. Although almost ten years has elapsed since the discovery of the first complexes,[3–5] active research is continuing and has become especially intriguing in view of the structural nonrigidity of some of the complexes and related phenomena of structural and valence isomerization.[6–13]

Cyclooctatetraeneiron tricarbonyl is relatively unreactive toward typical dienophiles but is known to add tetracyanoethylene.[14,15] Recently, reaction of diphenylacetylene with $C_8H_8Fe(CO)_3$ has been reported[16] to

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