$R(E_a)$. The nondirectional effects could arise from different orientations as ion pairs or from the association of additional anions with an ion pair oriented as described by Mason. The charge on $[Co(en)_3]^{3+}$ is neutralized in an ion pair formed with PO_4^{3-}, but not with anions of lower charge.

The singly charged anions show no evidence of preferred orientation of anions about the complex cation (Figures 1 and 2) as all the bands show some increase in R. Random orientation of the anions might be expected to increase R because of polarization effects and/or slight lowering of the symmetry.

The effects of electrolytes must be due to several factors. Mason's model for the interaction between $[Co(en)_3]^{3+}$ and PO_4^{3-} can account for the major effect in this case which is the most favorable one for such preferred orientation. In other cases, the other factors become increasingly important until the effect of such preferred orientation disappears for the singly charged anions.

Contribution from the Whitmore Laboratory,
Pennsylvania State University, University Park, Pennsylvania

Proton Magnetic Resonance Studies of the Solvation of Cations in N,N-Dimethylformamide Solutions of Cobalt(II) and Nickel(II) Perchlorates and the Direct Determination of the Solvation Number of Cobalt(II)[1]

By NICHOLAS A. MATWIYOFF

Received December 6, 1965

At temperatures below -38° the proton nmr signals of N,N-dimethylformamide (DMF) in the first coordination sphere of Co(II) in DMF solutions can be distinguished. From the relative intensities of these signals, a primary solvation number of six was calculated for Co(II). The relative widths of these signals below -55° require that DMF should be coordinated to Co(II) *via* the oxygen atom and that the Co–O–C angle be bent. Above -55° the widths of the signals are dominated by the rate of exchange of DMF between the primary solvation sphere and the bulk solvent. Throughout a wide temperature range, the width of the *bulk* solvent formyl proton signal of DMF solutions of $Co(ClO_4)_2$ and $Ni(ClO_4)_2$ is dependent on the rate of exchange of DMF between the bulk solvent and the species $M(DMF)_6^{2+}$. From the line width data the exchange parameters k_1 (sec^{-1} at 25°), ΔH^* (kcal), and ΔS^* (eu) were calculated for $Ni(DMF)_6^{2+}$ and $Co(DMF)_6^{2+}$, respectively: 3.8×10^3, $+15.0 \pm 0.5$, 8 ± 2; and 3.9×10^5, $+13.6 \pm 0.5$, 12.6 ± 2. For the Co(II) system, the exchange parameters obtained from the bulk solvent line broadening are in excellent agreement with those calculated from the widths of the proton signals of $Co(DMF)_6^{2+}$. Both the Co(II) and Ni(II) systems exhibit large proton contact chemical shifts from which the scalar coupling constants were calculated. Some comparisons are made between these data and those obtained for other Co(II) and Ni(II) systems.

Introduction

Recently nuclear magnetic resonance (nmr) spectroscopy has been applied to the study of a number of rapid substitution reactions involving metal ions in solution.[2-6] Of particular interest is that, under the proper conditions, nmr signals of the solvent molecules in the first coordination sphere of a metal ion can be detected. Thus, Jackson, Lemons, and Taube[7] have shown that it is possible to distinguish separate ^{17}O nmr signals arising from water in the first coordination sphere of selected diamagnetic cations and from that in the bulk solvent. Connick and Fiat,[8] using water enriched in ^{17}O, obtained the primary solvation numbers of Al(III) and Be(II) (six and four, respectively) by comparing the integrated intensities of the two ^{17}O signals. By lowering the temperature of methanol–water solutions of $Mg(ClO_4)_2$, Swinehart and Taube[9] were able to increase the mean lifetime of the solvent molecules in the first coordination sphere of Mg(II) sufficiently to allow the direct observation of the proton (OH) nmr signals of aquo–methanol complexes. Luz and Meiboom[10] have shown that, even with the paramagnetic ions Co(II) and Ni(II) in methanol–water solutions at low temperatures, the proton nmr signals of methanol and water in the first coordination sphere can be detected, and the rate of exchange of solvent molecules between the bulk solvent and the coordination sphere can be calculated from the widths of the signals. The exchange rates obtained in this manner were used to elucidate the relaxation mechanisms which contribute to the line widths of the nmr signals of the *bulk* solvent protons over a wide range of temperatures.[11]

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[1] This research was supported by the Pennsylvania State University through a National Science Foundation institutional grant.

[2] T. J. Swift and R. E. Connick, *J. Chem. Phys.*, **37**, 307 (1962).

[3] H. G. Hertz, *Z. Elektrochem.*, **64**, 53 (1960).

[4] R. G. Pearson, J. Palmer, M. M. Anderson, and A. L. Allred, *ibid.*, **64**, 110 (1960).

[5] R. G. Pearson and R. D. Lanier, *J. Am. Chem. Soc.*, **86**, 765 (1964).

[6] H. H. Glaeser, H. W. Dodgen, and J. P. Hunt, *Inorg. Chem.*, **4**, 1061 (1965), and references therein.

[7] J. A. Jackson, J. F. Lemons, and H. Taube, *J. Chem. Phys.*, **33**, 533 (1960).

[8] R. E. Connick and D. N. Fiat, *ibid.*, **39**, 1349 (1963).

[9] J. H. Swinehart and H. Taube, *ibid.*, **37**, 1579 (1962).

[10] Z. Luz and S. Meiboom, *ibid.*, **40**, 1058, 1066 (1964).

[11] Z. Luz and S. Meiboom, *ibid.*, **40**, 2686 (1964).

N,N-Dimethylformamide (DMF) has solvent properties similar to those of water and methanol and shows promise as a nonaqueous medium for ionic reactions: it readily forms octahedral complexes with transition metal ions, $M(DMF)_6^{2+}$, for which[12] the Dq values and β parameters are not significantly different from those for water[13] and methanol[14] complexes; it has a wide liquid range (+153 to −67°) and has a relatively large dielectric constant,[15] 36.7 at 25°. In this paper we report an nmr study of the proton line widths in DMF solutions of Ni(II) and Co(II) in the temperature range −75 to 110°. From the data it has been possible not only to calculate the rate of exchange of DMF between the first coordination spheres of these ions and the bulk of the solution but also to observe directly, at low temperatures, the nmr signals of the protons in DMF coordinated to Co(II). From the relative intensities of these signals, a primary solvation number of six is obtained for Co(II) in these solutions. From the widths of the signals it can be concluded that DMF coordinates to cobalt through the oxygen atom and that the angle, Co–O–C, is less than 180°.

Experimental Section

The solutions were prepared by weight using anhydrous DMF and the solid complexes, $Co(DMF)_6(ClO_4)_2$ and $Ni(DMF)_6(ClO_4)_2$. All transfers were accomplished in an anhydrous nitrogen atmosphere. Eastman White Label DMF was distilled twice from BaO under a pressure of approximately 30 mm, and the middle fraction retained was stored over Linde 3A Molecular Sieves. The metal ion amide complexes were prepared by the method of Drago, *et al.*[12] *Anal.* Calcd for $Ni(DMF)_6(ClO_4)_2$: C, 31.05; H, 6.08; N, 12.07. Found: C, 31.00; H, 6.04; N, 11.87. *Anal.* Calcd for $Co(DMF)_6(ClO_4)_2$: C, 31.03; H, 6.04; N, 12.05. Found: C, 30.98; H, 5.99; N, 11.91.

Proton nmr spectra were obtained at 60 Mc using a Varian A-60 spectrometer equipped with a variable-temperature probe and a Varian variable-temperature control system, V-6057. Spectra were obtained at 40 Mc using the Varian HR-40 spectrometer equipped with the variable-temperature probe, V-4331A, and the variable-temperature unit, V-4257. For studies above room temperature a regulated flow of compressed nitrogen gas was passed directly over the heating elements in the variable-temperature systems, but, for studies below room temperature, the gas was first passed through a copper coil immersed in a large dewar flask of liquid nitrogen. In each case the temperature was monitored by measuring the peak separations of methanol and ethylene glycol[16] and could be held to within ±1° of a given temperature. The temperature dependence reported for these peak separations was checked using a calibrated thermocouple sealed in anhydrous samples contained in 5-mm nmr tubes and was found to be accurate within ±1°.

The magnetic fields scanned with both spectrometers were calibrated using an audiooscillator monitored by a frequency counter. Line positions were reproducible to within ±1 cps and line widths to within ±0.2 cps. Chemical shifts were measured separately with respect to both cyclopentane and toluene as internal standards, but the choice of the standard did not affect the shift in any case. The complete spectrum of all of the solutions could be recorded using the HR-40 spectrometer, but the formyl proton signal of the DMF in the first coordination sphere of Co(II) is outside the range of the A-60 spectrometer.

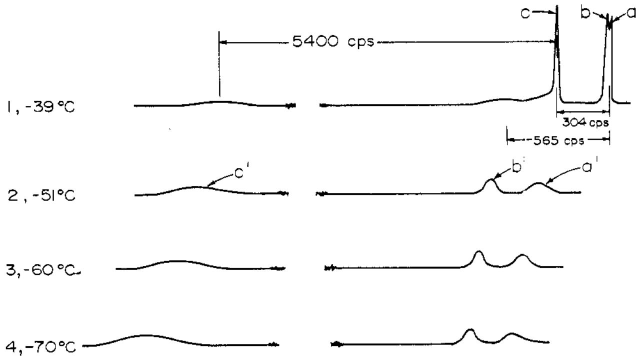

Figure 1.—Composite proton nmr spectra of a DMF solution of $Co(ClO_4)_2$, P_{Co} = 0.0779, as a function of temperature at 60 Mc. The magnetic field increases from left to right.

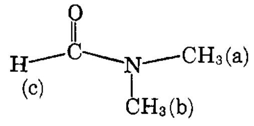

Figure 2.—DMF protons corresponding to the assignments in Figure 1.

The *apparent* magnetic field homogeneity obtained with both spectrometers, operated under slow passage conditions and at radiofrequency powers well below the saturation level, was found to be markedly dependent on the temperature. The ranges of line widths of the formyl proton in anhydrous oxygen-free DMF obtained using the A-60 spectrometer, after adjusting the field for optimum resolution, are: 1.4–1.8 cps at −65 to −20°; 1 cps at −20 to +50°; 3 cps at 50 to 90°; and 5 cps above 90°. The corresponding values obtained using the HR-40 are 2, 1–2, 2–3, and 4–5 cps, respectively. Thus, it is apparent that, at the higher temperatures, "machine broadening" of narrow signals can be important. (See section 3 of Results and Discussion.)

Results and Discussion

1. Solvation Number of Co(II).—In Figure 1 are reproduced composite proton nmr spectra of DMF solutions of $Co(ClO_4)_2$ obtained at low temperatures. The bulk DMF peaks, a b, and c, are given for trace 1 only, and peaks a and b were recorded at a reduced radiofrequency power level. The assignment of these peaks to the protons labeled in Figure 2 can be made on the basis of the arguments advanced by Hatton and Richards.[17] Peak c′, which can be assigned to the formyl proton of the DMF coordinated to Co(II), was recorded at 40 Mc, but its chemical shift was adjusted to 60 Mc to simplify Figure 1. The areas of peaks a′ and b′, which can be assigned to the methyl protons *cis* and *trans*, respectively, to the oxygen atom in coordinated DMF (see section 2), are each 3 times that of peak c′. Peak c′ was recorded using a larger radiofrequency power level than was used for the other peaks. No other peaks could be detected in spectra which were recorded at 60 and 40 Mc using a variety of radiofrequency power levels, sweep widths, and sweep rates.[18]

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[12] R. S. Drago, M. D. Joesten, and L. LaRoche, *Inorg. Chem.*, **2**, 124 (1963).

[13] C. E. Schaeffer and C. K. Jørgensen, *J. Inorg. Nucl. Chem.*, **8**, 143 (1958).

[14] V. Imhof and R. S. Drago, *Inorg. Chem.*, **4**, 427 (1965).

[15] C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill Book Co., Inc., New York, N. Y., 1955.

[16] Publication No. 87-100-110, Varian Associates, Palo Alto, Calif., pp 29, 32.

[17] J. V. Hatton and R. E. Richards, *Mol. Phys.*, **3**, 253 (1960).

[18] In DMF solutions of $Co(ClO_4)_2$ containing small amounts of water, it is possible to distinguish signals arising from both DMF complexes and aquo–DMF complexes.

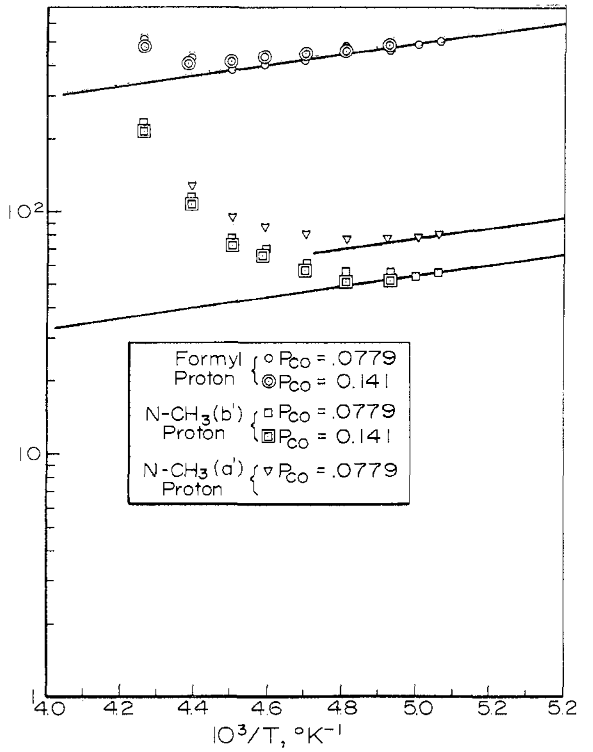

Figure 3.—Temperature dependence of $(\pi T_{2p})^{-1}$ for the formyl and methyl protons in the complex $Co(DMF)_6^{2+}$.

The solvation or coordination number, n, of cobalt in the complex, $Co(DMF)_n^{2+}$, can be obtained readily using the ratios of the area of peak c to those of a′, b′, and c′: $A_c/A_{a'}$, $A_c/A_{b'}$, and $A_c/A_{c'}$, respectively. The areas were obtained both by planimetry of the recorded signals and by manual integration. The solvation numbers calculated with data obtained from the spectra of eight solutions in which the mole ratio, Co^{II}/DMF, was varied from 0.006 to 0.025 are: 5.8 ± 0.3 from the ratio $A_c/A_{c'}$; 6.0 ± 0.1 from $A_c/A_{b'}$; and 6.0 ± 0.1 from $A_c/A_{a'}$. No significant deviation of these values was observed either as a function of temperature (in the range −45 to −70°) or of composition. It is surprising that, in the most concentrated solution studied here, the primary solvation sphere is well defined even though there are, on the average, only 5.5 moles of DMF available to solvate each "mole" of $Co(DMF)_6(ClO_4)_2$. Similar results have been obtained by Swinehart and Taube[9] and Connick and Fiat.[8]

Unfortunately, it was not possible to detect any nmr signals other than those of the bulk solvent in DMF solutions of $Ni(ClO_4)_2$ under a variety of conditions.

2. Relaxation of the Protons in $[Co(DMF)_6]^{2+}$.—In Figure 3 are plotted the widths of the lines c′, b′, and a′, as a function of temperature for a representative set of solutions. Solution of the Bloch equations, with the inclusion of chemical exchange between two nonequivalent sites[4,19,20] (here the bulk solvent and the primary coordination sphere), results in eq 1, which relates the transverse relaxation rate observed, $1/T_{2p}$, to the mean lifetime, τ_m, and the transverse relaxation time, T_{2m}, of the proton in the coordination sphere.

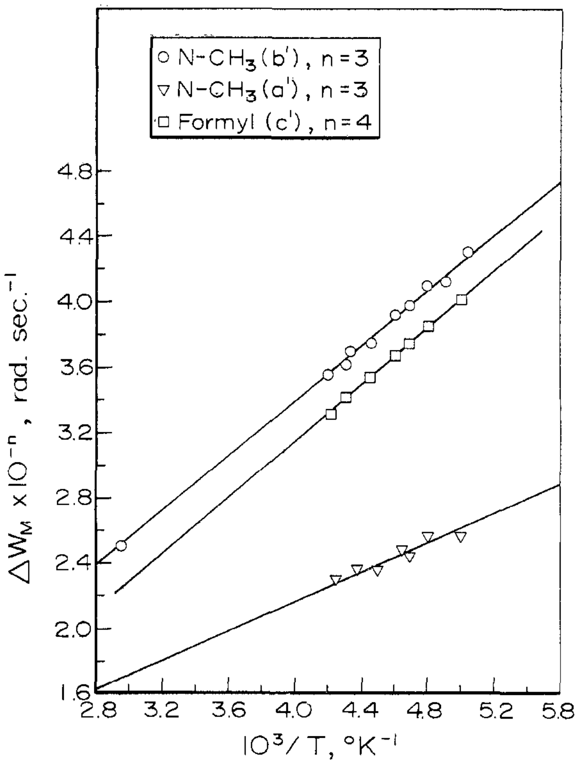

Figure 4.—Temperature dependence of $\Delta\omega_m$ for the protons of the $Co(DMF)_6^{2+}$ complex in DMF solutions at 60 Mc.

$$\frac{1}{T_{2p}} = \frac{1}{T_{2m}} + \frac{1}{\tau_m} \tag{1}$$

The transverse relaxation rate observed is related to the full width of the nmr line at half the maximum height $\Delta\nu$ by

$$\frac{1}{T_{2p}} = \pi\Delta\nu \tag{2}$$

Equation 1 is valid under the conditions of slow exchange, *i.e.*, $\tau_m\Delta\omega_m \gg 1$, where $\Delta\omega_m$ is the chemical shift between the proton in the bulk solvent and that in the coordination sphere. A summary of the $\Delta\omega_m$ values observed is contained in Figure 4. Since the values of τ_m in this temperature range are of the order 10^{-2} to 10^{-3} sec (see section 3), the conditions of slow exchange obtain for the data in Figure 3.

Each set of data in Figure 3 can be fitted to two straight lines: (a) One line fits the data at the higher temperatures and, because of its large negative slope, is associated with line broadening due to the exchange of DMF between the two sites ($1/T_{2p} = 1/\tau_m$). Values of τ_m and the activation energy for exchange calculated using this line are in excellent agreement with the corresponding values calculated by the methods of section 3. (b) The other line, which fits the data at the lower temperatures where the chemical exchange contribution to the line width is negligible, can be associated with the temperature dependence of the re-

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[19] L. H. Piette and W. A. Anderson, *J. Chem. Phys.*, **30**, 899 (1959).
[20] H. M. McConnell, *ibid.*, **28**, 430 (1958).

laxation rate, $1/T_{2m}$, of the proton in the first coordination sphere of cobalt(II).

The relaxation rate, $1/T_{2m}$, is dominated by the interaction of the proton with the unpaired electrons of Co(II). Solomon[21] and Bloembergen[22] have developed equations for the longitudinal and transverse relaxation rates, $1/T_{1m}$ and $1/T_{2m}$, of nuclei bonded to paramagnetic ions and, under the conditions which obtain in these experiments, their equations reduce to

$$\frac{1}{T_{1m}} = \frac{1}{T_{2m}} = \frac{4}{3}\frac{\mu_{eff}^2\gamma_I^2\beta^2}{r^6}\tau_c + \frac{2}{3}\frac{S(S+1)A^2}{\hbar^2}\tau_s \tag{3}$$

where γ_I is the proton magnetogyric ratio, β is the Bohr magneton, μ_{eff} is the effective magnetic moment, S is the electron spin of Co(II), $A/\hbar$ is the electron spin–nuclear spin coupling constant, r is the distance between the proton and the paramagnetic ion, τ_c is the correlation time for the nuclear spin–electron spin interaction, and τ_s is the electron spin relaxation time.[23] In eq 3, the first term is due to the dipole–dipole interaction between the electrons and the proton, and the second term is due to the hyperfine interaction arising from a nonzero electron spin density at the proton. The hyperfine interaction is also responsible for the large chemical shifts, "contact" shifts, observed here and in other paramagnetic systems.[24,25] The coupling constant for the hyperfine interaction, $A/\hbar$, can be obtained from the data in Figure 4 with the aid of the Bloembergen equation[26]

$$\frac{\Delta\omega_m}{\omega} = -A\frac{\mu_{eff}\sqrt{S(S+1)}\beta}{3kT\gamma_I} \tag{4}$$

where ω is the frequency at which the chemical shift, $\Delta\omega_m$, is observed (60 Mc), k is the Boltzmann constant, and T is the absolute temperature. The values of $A/\hbar$ obtained for the protons c′, b′, and a′ are 2.44×10^6, 1.58×10^5, 2.56×10^5 radians sec^{-1}, respectively. The effective magnetic moment, μ_{eff} for Co(II) in DMF solutions, used in eq 4 is 5.1 BM at 25° and was obtained by the method of Evans.[27]

In general, the correlation time for the dipolar interaction will be determined by the more rapid of the two processes: electron spin relaxation and the tumbling of the complex. Swift and Connick[2] have estimated that τ_s is $<5 \times 10^{-12}$ sec for the $Co(OH_2)_6^{2+}$ complex at 25°, and Luz and Meiboom[10] have obtained a value of 5×10^{-13} sec for the $Co(CH_3OH)_6^{2+}$ complex at −60°. The τ_s value for the latter should not be significantly different from that for $Co(DMF)_6^{2+}$. In the discussion which follows we have assumed τ_s is 5×10^{-13} sec, but the qualitative conclusions are not changed by assuming a value as large as 5×10^{-12}. A small τ_s is consistent with the observation that the Co(II)–DMF systems do not exhibit an electron spin resonance signal even at liquid nitrogen temperatures. In view of the small τ_s, the contribution of the tumbling of the complex ion to the dipolar term can be neglected. Consequently the correlation time for the dipolar interaction is τ_s. Because the dipolar term dominates the broadening at low temperatures (see below), support for this conclusion is obtained by considering the Arrhenius activation energies, E_a [$1/T_{2m}$ = constant $\times$ $e^{-E_a/RT}$], for the line broadening in the low-temperature regions of Figure 3. For all three protons, E_a is -1 ± 0.1 kcal. This result is significantly less than the activation energy expected for tumbling (or diffusion), 3–5 kcal.[15,28]

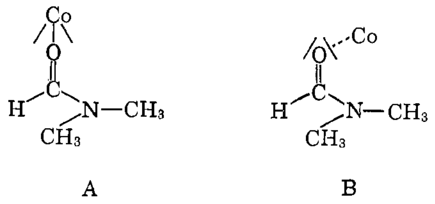

Figure 5.—Linear (A) and angular (B) coordination modes for the $Co(DMF)_6^{2+}$ complex. In B, the C–O–C angle is 120° based on sp² hybridization of the oxygen atom in its σ bonds.

If the appropriate values of $A/\hbar$ and τ_s are substituted in eq 3, it can be shown that the hyperfine contribution to the broadening of the protons in the first coordination sphere of Co(II) is negligible. Since the dipolar term, which has an r^{-6} dependence, dominates the broadening, rough limits can be placed on the orientation of DMF in the coordination sphere. First, since the formyl proton (c′) is much broader than that of either of the methyl protons, coordination of DMF to Co(II) must occur preferentially *via* the oxygen atom.[29]

In all reasonable structures based on nitrogen coordination, a methyl group is closer to the Co(II) ion than the formyl proton. The same conclusion has been reached by other workers who have studied the coordination of amides to other Lewis acids by nmr[30,31] and infrared[32] spectroscopy. Second, the proton labeled a′ in Figures 2–4 should be the $N-CH_3$ proton *cis* to the oxygen atom since, in all conformations based on Co–O–C coordination, it is closer than the *trans* NCH_3 groups to the Co(II) ion.

Finally, as shown in Figure 5, two modes of coordination of DMF *via* the oxygen atom to Co(II) are possible—linear (Figure 5A) and angular (Figure5 B).

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[21] I. Solomon, *Phys. Rev.*, **99**, 559 (1955).

[22] N. Bloembergen, *J. Chem. Phys.*, **27**, 572 (1957).

[23] R. A. Bernheim, T. H. Brown, H. S. Gutowsky, and D. E. Woessner, *ibid.*, **30**, 950 (1959).

[24] D. R. Eaton, A. D. Josey, W. D. Phillips, and R. E. Benson, *ibid.*, **37**, 347 (1962).

[25] B. B. Wayland and R. S. Drago, *J. Am. Chem. Soc.*, **87**, 2372 (1965), and references therein.

[26] N. Bloembergen, *J. Chem. Phys.*, **27**, 595 (1957).

[27] D. F. Evans, *J. Chem. Soc.*, 2003 (1959).

[28] P. F. Cox and L. O. Morgan, *J. Am. Chem. Soc.*, **81**, 6409 (1959).

[29] It might seem that the nonequivalence observed for the NCH_3 protons in the coordination sphere is sufficient proof since oxygen, but not nitrogen, coordination would preserve (if not enhance) the resonance structure which leads to restricted rotation about the C–N bond. However, a study of scaled molecular models shows that structures based on nitrogen coordination are highly hindered and can lead to nonequivalence of the $N-CH_3$ groups due to steric restriction of rotation.

[30] R. S. Drago and D. A. Bafus, *J. Phys. Chem.*, **65**, 1066 (1961).

[31] S. J. Kuhn and J. S. McIntyre, *Can. J. Chem.*, **43**, 995 (1965), and references therein.

[32] C. S. Schmulbach and R. S. Drago, *J. Am. Chem. Soc.*, **82**, 4484 (1960).

These modes of coordination are analogous to those proposed for the coordination to metal ions of water, in particular, and oxygen donors, in general:[33] (a) trigonal coordination in which the metal ion is symmetrically aligned between the lone electron pairs of the water molecule, that is, aligned with the permanent dipole of water; or (b) tetrahedral coordination in which the metal ion bonds to one of the lone pairs of the water molecule. Although it has not been possible to distinguish between these coordination modes for the water molecule, X-ray studies[34-37] indicate that tetrahedral or angular coordination is preferred for the metal ion–oxygen atom bonds in oxy anion complexes. The line-broadening data summarized in Figure 3 strongly suggest that angular coordination of DMF to Co(II) also occurs.

The average distances between the various protons and the Co(II) ion for the two coordination modes are summarized in Table I and were calculated using models constructed with the aid of data listed by Pauling[38] for the bond angles and distances in representative amides: the angles O═C—N, H—C—N, (OC)—N—(CH$_3$), and CH$_3$—N–CH$_3$, are taken to be 123.6, 103.9, 123, and 120°, respectively; and the distances O–C, (OC)–H, (OC)–N, N–(CH$_3$), (NCH$_2$)–H, and Co$^{\text{II}}$(octahedral)–O[39] are taken to be 1.24, 1.07, 1.34, 1.47, 1.09, and 1.38 A, respectively. The average distance between the NCH$_3$ protons and Co(II) was calculated by assuming that there is free rotation about the CH$_3$–N bond and that all conformations are equally populated. The line widths observed at $-70°$ are also listed in Table I.

Table I

The Average Proton–Cobalt Distances, R_{av}, and Proton Line Widths Calculated for Linear and Angular Coordination Modes of Co(DMF)$_6^{2+}$

Coordination mode	Proton	R_{av}, A	$\Delta\nu$,[a] cps	$\Delta\nu$,[b] cps
Linear	*cis*-NCH$_3$ (to the C–O bond)	3.98	88	77
	trans-NCH$_3$	5.19	17	54
	Formyl	3.45	204	490
Angular (angle Co–O–C 120°)	*cis*-NCH$_3$	4.70	32	77
	trans-NCH$_3$	5.03	21	54
	Formyl	2.70	891	490

[a] Line width calculated using eq 3. [b] Line width observed.

With the aid of eq 3, it is found that the values of R_{av} in Table I require the line widths listed in column 4 and the following ratios of line widths in the dipolar region, formyl:*cis*-NCH$_3$:*trans*-NCH$_3$: linear coordination, 1:0.43:0.083; and angular coordination, 1:0.036:0.024. The ratios observed at $-70°$ are 1:0.15:0.11. Thus, acceptable agreement of the experimental data is not obtained with either of the limiting coordination modes. However, the pattern of the line widths and the line width ratios strongly suggest that the Co–O–C angle is bent. Although excellent agreement between the experimental data and those calculated for a model with a Co–O–C angle of 140° can be obtained, the calculation is merely suggestive because of the many assumptions inherent in the application of eq 3.

3. Relaxation of the Bulk Solvent Protons in DMF Solutions of Co(ClO$_4$)$_2$.—The temperature dependence of the line broadening of the bulk solvent formyl protons can be conveniently analyzed using the equations developed by Swift and Connick.[2] For the exchange of DMF between the bulk solvent and the complex, Co(DMF)$_6^{2+}$, the applicable equations are

$$\frac{1}{T_{2\text{p}}} = (\tau_{\text{f}})^{-1}\left[\frac{(1/T_{2\text{m}})^2 + (1/T_{2\text{m}}\tau_{\text{m}}) + \Delta\omega_{\text{m}}^2}{(1/T_{2\text{m}} + 1/\tau_{\text{m}})^2 + \Delta\omega_{\text{m}}^2}\right] \tag{5}$$

$$\Delta\omega_{\text{f}} = \frac{P_{\text{m}}\Delta\omega_{\text{m}}}{(\tau_{\text{m}}/T_{2\text{m}} + 1)^2 + (\tau_{\text{m}}\Delta\omega_{\text{m}})^2} \tag{6}$$

where τ_{f} is the mean lifetime of DMF in the bulk solvent, $\Delta\omega_{\text{f}}$ is the chemical shift of the bulk solvent protons in the presence of Co(II) with respect to the pure solvent, P_{m} is the fraction of the total number of solvent molecules bonded in the complex Co(DMF)$_6^{2+}$, and the remaining symbols have been defined in context with eq 1–4.[40]

As shown by Swift and Connick, eq 5 can be simplified by considering the following limiting conditions.

(1) Relaxation occurs rapidly by means of a large change in the precessional frequency of the protons in the DMF undergoing exchange and $1/T_{2\text{p}}$ is controlled by the rate of chemical exchange.

$$\frac{1}{T_{2\text{p}}} = \frac{P_{\text{m}}}{\tau_{\text{m}}} = \frac{1}{\tau_{\text{f}}} \tag{7a}$$

if $\Delta\omega_{\text{m}}^2 \gg (1/T_{2\text{m}})^2, (1/\tau_{\text{m}})^2$.

(2) Relaxation of the protons in the first coordination sphere occurs rapidly and $1/T_{2\text{p}}$ is controlled by the rate of chemical exchange.

$$\frac{1}{T_{2\text{p}}} = \frac{P_{\text{m}}}{\tau_{\text{m}}} \tag{7b}$$

if $(1/T_{2\text{m}})^2 \gg \Delta\omega_{\text{m}}^2, (1/\tau_{\text{m}})^2$.

(3) Chemical exchange is rapid and $1/T_{2\text{p}}$ is controlled by the rate of relaxation through the change in the precessional frequency.

$$\frac{1}{T_{2\text{p}}} = P_{\text{m}}\tau_{\text{m}}\Delta\omega_{\text{m}}^2 \tag{7c}$$

if $(1/\tau_{\text{m}})^2 \gg \Delta\omega_{\text{m}}^2 \gg (1/T_{2\text{m}}\tau_{\text{m}})$.

(4) Chemical exchange is rapid but $1/T_{2\text{p}}$ is controlled by the rate of proton relaxation in the coordination sphere.

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(33) See, for example, C. K. Jørgensen, "Inorganic Complexes," Academic Press Inc., New York, N. Y., 1963, p 21 ff.

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(40) Actually, $(T_{2\text{p}})^{-1}$ should be corrected for the "outer sphere" exchange and dipolar contributions to the observed line widths. At the concentrations of Co(ClO$_4$)$_2$ discussed here these effects are negligible. All values of $(T_{2\text{p}})^{-1}$ were corrected however, by subtracting the $(T_{2\text{p}})^{-1}$ values obtained for the pure solvent.

$$\frac{1}{T_{2\text{P}}} = \frac{P_{\text{m}}}{T_{2\text{m}}} \tag{7d}$$

if $(1/T_{2\text{m}}\tau_{\text{m}}) \gg (1/T_{2\text{m}})^2$, $\Delta\omega_{\text{m}}^2$.

The variation of τ_{m} with temperature is given by

$$\frac{1}{\tau_{\text{m}}} = k_1 = (kT/h)e^{(\Delta S^*/R)-(\Delta H^*/RT)} \tag{8}$$

where k_1 is a first-order rate constant, and ΔS^* and ΔH^* are the entropy and enthalpy of activation for the exchange. The activation energies for chemical exchange processes not only are generally much larger than those for dipolar relaxation processes (see section 2)[2,5,10] but also lead to much larger changes in τ_{m} as a function of temperature than those commonly observed for $\Delta\omega_{\text{m}}$. Consequently, in the appropriate systems, the temperature dependence of $(T_{2\text{p}})^{-1}$ often includes regions throughout which the data can be analyzed solely in terms of one of the limiting equations (7a–7d).

In Figure 6, the temperature dependence of $(T_{2\text{p}})^{-1}$ for the formyl proton of the bulk solvent DMF is summarized. The plot was constructed using data obtained at 60 and 40 Mc with six independent solutions in which the concentration of $\text{Co(ClO}_4)_2$ was systematically varied between the limits $2 \times 10^{-3} \leq P_{\text{m}} \leq 2 \times 10^{-2}$. The variation of $(T_{2\text{p}})^{-1}$ suggests that four distinct processes contribute to the relaxation.

The two linear regions of steep slope in the temperature range, $3.3 \leq 10^3T^{-1} \leq 4.3$, certainly should correspond to processes dependent on τ_{m}. Using the temperature dependencies of $1/T_{2\text{m}}$ and $\Delta\omega_{\text{m}}$ established in section 2, together with the τ_{m} values obtained from Figure 3, it can be seen that the lower temperature data fulfill the conditions in (7a) above, and the higher temperature data fulfill the conditions in (7c). As required by eq 7a, the values of $(T_{2\text{p}})^{-1}$ at the lower temperatures are not affected by changing the frequency from 60 to 40 Mc. Correspondingly, at the higher temperatures as required by eq 7c, the $(T_{2\text{p}})^{-1}$ values obtained at 60 Mc are very nearly nine-fourths the values obtained at 40 Mc. In addition, the conditions leading to (7c) require that the chemical shift, $\Delta\omega_{\text{f}}$, should have reached its maximum value at a given temperature in the high-temperature region and be given by the simple relationship

$$\Delta\omega_{\text{f}} = P_{\text{m}}\Delta\omega_{\text{m}} \tag{9}$$

That this condition is also met can be seen by comparing the $\Delta\omega_{\text{m}}$ values for the formyl proton plotted in Figures 4 and 7. The $\Delta\omega_{\text{m}}$ values contained in the latter were calculated from eq 9 using data obtained with six solutions having P_{m} values the same as those for Figure 6. In Figure 6, the lines drawn through the experimental points in the interval $3.3 \leq 10^3T^{-1} \leq 4.3$ were constructed by fitting the points to eq 7a and 7c. The chemical exchange parameters resulting from this curve-fitting process are listed in Table II together with those obtained by fitting the data in Figure 3 to eq 1. A discussion of these parameters is deferred to section 5.

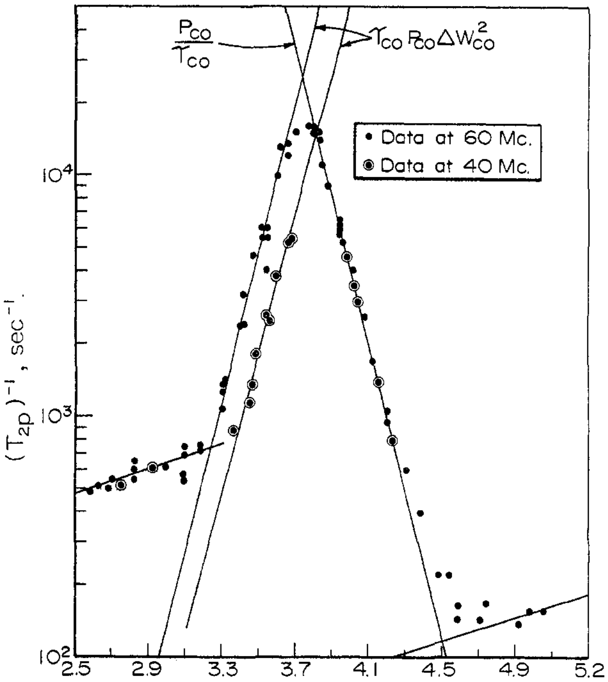

Figure 6.—Temperature dependence of $(T_{2\text{p}})^{-1}$ for the formyl proton in DMF solutions of $\text{Co(ClO}_4)_2$. All data normalized to $P_{\text{m}} = 1$.

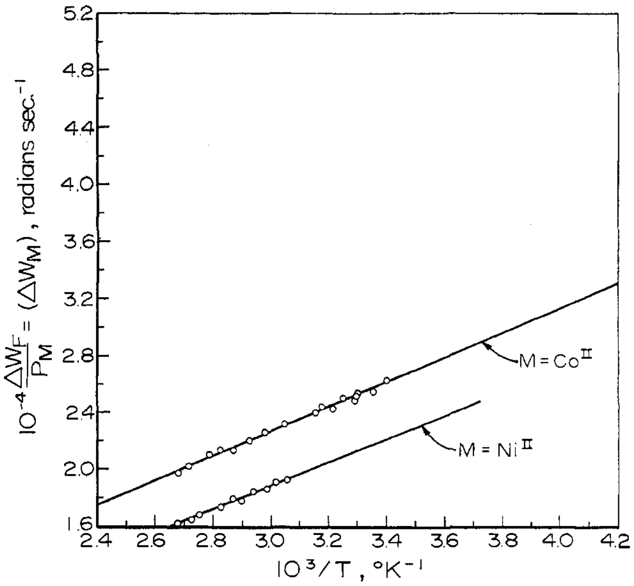

Figure 7.—Temperature dependence of $\Delta\omega_{\text{f}}/P_{\text{m}}$ for the formyl proton in DMF solutions of $\text{Co(ClO}_4)_2$ and $\text{Ni(ClO}_4)_2$ at 60 Mc.

At values of $10^3T^{-1} > 4.7$, chemical exchange is too slow to affect the observed line widths in Figure 6, and it is apparent that none of the limiting cases, eq 7a–7d, is applicable. In this range of temperature the relaxation is probably controlled by the dipole–dipole interaction between the paramagnetic ion and the DMF molecules *outside* the first coordination sphere. For the reasons discussed in section 2, the correlation time for the interaction is taken to be the electron spin relaxa-

TABLE II

PARAMETERS CALCULATED FROM FIGURES 3, 4, AND 6 FOR THE EXCHANGE OF DMF FROM THE FIRST COORDINATION SPHERE OF Co(II)

	Formyl proton		Methyl a′	Methyl b′
Parameter	Fig 6	Fig 3	(Fig 3)	(Fig 3)
k_1, sec^{-1} at 25°	4.0×10^5	3.8×10^5	3.9×10^5	3.9×10^5
$\Delta H^* \pm$ 0.5, kcal	13.6	13.7	13.4	13.4
$\Delta S^* \pm 2$, eu	12.6	12.5	12.9	12.9
A/h, cps	3.88×10^5	3.88×10^5	4.07×10^4	2.51×10^4

tion time of Co(II). This assumption is consistent with the small apparent Arrhenius activation energy, −1 kcal, calculated from the line fitted to the low-temperature data. A crude estimate of the importance of this dipolar contribution to the relaxation can be obtained by averaging the interaction over equally populated distances from d, the distance of closest approach of a formyl proton in the second solvation sphere, to an "infinite" distance using a form of eq 3

$$\frac{1}{T_{2p}} \cong \frac{4}{3} n \mu_{\text{eff}}^2 \gamma_I^2 \beta^2 \tau_s \int_d^\infty \frac{4\pi r^2 \text{d}r}{r^6} \cong \frac{16\pi n}{9} \frac{\mu_{\text{eff}}^2 \gamma_I^2 \beta^2 \tau_s}{d^3} \quad (10)$$

where n is the number of paramagnetic ions per unit volume of the solution. If d is calculated using eq 10 there is obtained a value, 7.0 A, which is not an unreasonable one for the coordination of DMF *via* an oxygen atom to a sterically hindered octahedral face of $Co(DMF)_6^{2+}$.[41]

Finally, the high-temperature data ($10^3T^{-1} > 3.0$) in Figure 6 appear to fulfill the conditions for the limiting case (7d). This possibility appears attractive in view of the low apparent activation energy −1 kcal, calculated using the line fitted to the data. In addition, if the low-temperature formyl proton line widths in Figure 3 are extrapolated to the temperatures $10^3T^{-1} > 3.0$, the values of T_{2m} obtained are in acceptable agreement with those obtained from the high-temperature line in Figure 6. However, there is still some uncertainty about the actual relaxation process because the line widths are relatively narrow in this temperature range and "machine broadening" of the signals of both the pure solvent and the solutions is undoubtedly important.

4. Relaxation of the Bulk Solvent Protons in DMF Solutions of $Ni(ClO_4)_2$.—The temperature dependence of $(T_{2p})^{-1}$ for the formyl proton in DMF solutions of $Ni(ClO_4)_2$ is plotted in Figure 8. The data were obtained at both 60 and 40 Mc using five solutions in which the concentration of $Ni(ClO_4)_2$ was systematically varied between the limits $5 \times 10^{-3} \leq P_m \leq 2 \times 10^{-2}$ (it was assumed that the primary solvation number of Ni(II) is six[12]). The variation of $(T_{2p})^{-1}$ with temperature in these solutions is similar to that observed for Co(II) and correspondingly is amenable to a similar analysis.

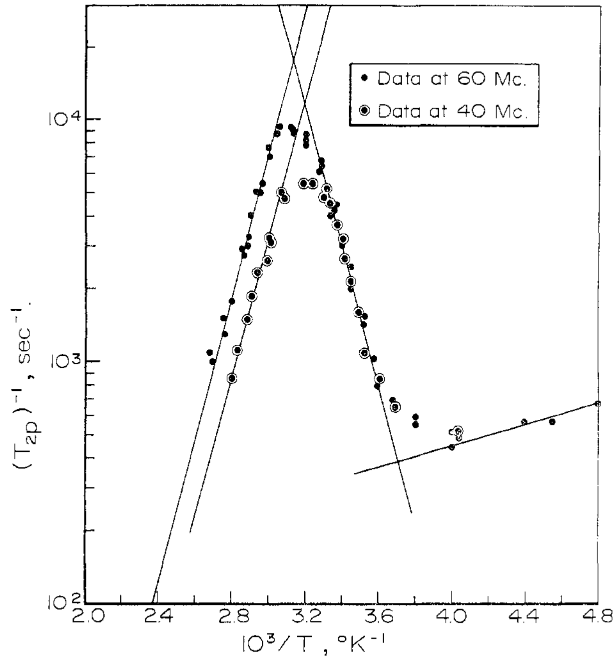

Figure 8.—Temperature dependence of $(T_{2p})^{-1}$ for the formyl proton in DMF solutions of $Ni(ClO_4)_2$ at 60 and 40 Mc. All data normalized to $P_m = 1$.

Thus, the high-temperature data characterized by a steep positive slope should correspond to the conditions for limiting case (7c), and, as required, the ratio of the $(T_{2p})^{-1}$ values obtained at 60 and 40 Mc is very nearly 9:4. Furthermore, the chemical shift of the bulk solvent formyl proton, $\Delta\omega_f$, is proportional to P_m as required by eq 9. The chemical shift data are summarized in Figure 7 and were obtained using five solutions having P_m values the same as those used for the data in Figure 8.

In the intermediate temperature region, $3.2 \leq 10^3T^{-1} \leq 3.6$, the conditions should correspond to those for the limiting case (7a). For the limiting case (7b) to apply would require a much larger value for the electron spin relaxation time, τ_s, of the Ni(II) ion than those obtained by Luz and Meiboom,[10] $\tau_s \leq 3 \times 10^{-12}$ sec for $Ni(CH_3OH)_6^{2+}$ at −60°, and by Swift and Connick,[2] $\tau_s \leq 1.3 \times 10^{-11}$ sec for $Ni(OH_2)_6^{2+}$ at 25°. The chemical exchange parameters calculated from the lines fitted to the data in the high (eq 7c) and intermediate (eq 7a) temperature range are listed in Table III. The magnetic moment, $\mu_{\text{eff}} = 3.1$ BM, of $Ni(DMF)_6^{2+}$ in DMF, required for the calculation of A/h, was obtained by the method of Evans.[26]

At very low temperatures, $10^3\ T^{-1} \geq 4.0$, chemical exchange is very slow and the line broadening should be controlled by the dipole–dipole interaction between the paramagnetic ion and the DMF molecules outside the

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(41) The line widths of the bulk solvent NCH_3 protons were not studied carefully over the complete range of temperatures because of the line-broadening effects due to the onset of rotation about the (O=C)—N bond at the higher temperatures and the overlap of the NCH_3 signals in the region of (7a). However it was observed that at temperatures $10^3T^{-1} > 4.5$ the widths of these signals are approximately one-fourth those of the formyl proton and exhibit the same temperature dependence. Qualitatively, this indicates that there is a preferred orientation of DMF even in the second solvation sphere.

TABLE III

PARAMETERS CALCULATED FROM FIGURES 7 AND 8 FOR THE EXCHANGE OF DMF FROM THE FIRST COORDINATION SPHERE OF Ni(II)

Parameter	Value
k_1, sec^{-1} at 25°	3.8×10^3
$\Delta H^* \pm 0.5$, kcal	15.0
$\Delta S^* \pm 2$, eu	8.0
A/h, cps	6.81×10^5

first coordination sphere. The correlation time for this interaction is taken to be the electron spin relaxation time of Ni(II), an assumption consistent with the low activation energy, −1 kcal, calculated from the line fitted to the low-temperature data. Using eq 10 and a τ_s value of 3×10^{-12} sec, a distance of closest approach d, 7.4 A, of the formyl proton in the second solvation sphere is calculated. This value is in reasonable agreement with that obtained for the $Co(ClO_4)_2$ solutions.

5. Discussion of the Chemical Exchange Parameters.—The parameters collected in Tables II and III are consistent with a mechanism generally accepted for the solvent substitution reactions of divalent metal ions,[42–44] for which the rate-determining step involves a transition state in which the breaking of the bond to the leaving group (DMF) is much more advanced than the formation of the bond to the entering group (DMF). In this context the absence of a large salt or anion effect is of particular interest—the exchange parameters at the various concentrations ($0.005 \leq P_{Co} \leq 0.14$ and $0.005 \leq P_{Ni} \leq 0.05$) are identical within experimental error. This of course does not preclude solvent exchange by anation, exclusive or concurrently, *via* an ion-pair intermediate, $[ClO_4Co(DMF)_6]^+$, for which the association constant may be large in this solvent. Eigen and co-workers,[45] for example, have found that the rates of anation of hydrated divalent metal ions are approximately independent of the anion. It is also of interest to note the apparent insensitivity of the exchange parameters to the macroscopic dielectric constant of the solvent. Over the temperature range −50 to +50° one might expect at least a twofold decrease of the dielectric constant of a polar species such as DMF.[15] Nevertheless, the parameters calculated from the high-temperature data (Figure 6) are the same as those from the low-temperature data (Figure 3). A similar but more dramatic effect has been observed by Baltisberger and King,[46] who showed that the rate constant for the replacement of water in $Cr(OH_2)_6^{3+}$ by methanol is nearly the same in the solvent water as in methanol.

That the rate of exchange of the Co(II) complex is more rapid than that of Ni(II) seems in accord with the crystal-field arguments advanced by Basolo and Pearson.[42] However, in view of the error limits in the data, it is uncertain whether the relative rates should be ascribed to an activation enthalpy effect (required by crystal-field arguments) or to an activation entropy effect. In any event, the crystal-field contribution to the net activation enthalpy is small, and whether such a contribution can prove *decisive* in governing the relative rates in even carefully selected systems is still open to question. Pertinent in this regard are the isotope dilution studies of Taube and co-workers,[47,48] who found that the activation enthalpies for the exchange of methanol with the hexasolvated ions Mg^{2+}, Co^{2+}, and Ni^{2+} are 12.5, 11.5, and 13.1 kcal mole^{-1}, respectively. There is no discernible contribution to these data from either crystal-field or "covalent" effects. The activation enthalpies for the exchange of ammonia with $Co(NH_3)_6^{2+}$ and $Ni(NH_3)_6^{2+}$, 11.2 and 11 kcal, respectively,[6] also exhibit an apparent independence of these effects. On the other hand, at least in qualitative accord with crystal-field predictions, the values of ΔH^* for the exchange of water with the hexaaquo ions Mn^{2+}, Co^{2+}, Ni^{2+}, and Fe^{2+} are 8.1, 8.0, 11.6, and 7.7 kcal, respectively.[2]

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