less electronegative substituents (P < I < Cl) to the metal or reduction in metal d-orbital energies (Ir < Rh), results in longer O–O bonds, lower O–O bond orders, and stronger M–O_2 binding.

An identical bonding scheme can be applied to structures containing the less electronegative S_2 molecule. Sulfur–iridium $p\pi(S_2) \rightarrow d\,(Ir)\ \sigma$ bonding is complemented by $d\pi(Ir) \rightarrow p\pi^*(S_2)$ back-donation. Using the 1.889-Å S–S length[12] in disulfur (bond order 2) and the S_2^{2-} distance of 2.12 Å in Na_2S_2[39] (bond order 1) as rough guides, the sulfur–sulfur distance of 2.066 (6) Å in $[Ir(S_2)(dppe)_2]^+$ corresponds to somewhat more than a single bond. On the other hand, the 1.625 (23)-Å O_2 bond in $[Ir(O_2)(dppe)_2]^+$ is 0.13 Å longer than the peroxo linkage in Na_2O_2,[40] suggesting an O–O bond order significantly less than one. As might have been predicted from simple electronegativity considerations, $\pi^*(O_2)$ is a better electron acceptor than $\pi^*(S_2)$.

Unlike oxygen, sulfur has lower lying d-type orbitals that have been invoked in the explanation of certain artifacts of sulfur chemistry.[11] If these orbitals do accept $d\pi(Ir) \rightarrow d\pi(S_2)$ electron density, Ir–S and S–S bonds might display more multiple-bond character. But the lower effective nuclear charge on the $[Ir(S_2)(dppe)_2]^+$ sulfur atoms, resulting from the lack of more electronegative substituents plus iridium-to-sulfur electron flow, implies little $d\pi(Ir) \rightarrow d\pi(S)$ interaction.

The short, 1.73-Å disulfur linkage in $[NbCl(Cp)_2(S_2)]$ reflects the drastic difference in Nb(III)–S_2 and Ir(I)–S_2 bonding. The electron-poor, d^2 niobium(III) ion evidently stabilizes S_2 *via* $p\pi^*(S_2) \rightarrow d\pi(Nb)$ *forward* π donation of the same type postulated in most earlier metal halide or chalconide complexes. Since this represents a reversal in π-electron flow, opposing secondary effects might also be expected.

Ginsberg and Lindsell[14] have indicated that S_2 is not displaced when O_2 is bubbled through an $[Ir(S_2)(dppe)_2]Cl$ solution for 12 hr. We therefore conclude that the Ir–S_2 bond lengths and angles cited herein correspond to those belonging to an irreversible disulfur carrier. To provide the background for a more quantitative analysis, it is clearly necessary to obtain additional structural data on closely related disulfur and diselenium complexes.

Acknowledgments. We are indebted to Dr. A. P. Ginsberg for supplying crystals as well as pertinent chemical information in advance of publication. Support of this work by the National Institutes of Health is gratefully acknowledged.

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[40] R. L. Tallman, J. L. Margrave, and S. W. Bailey, *J. Amer. Chem. Soc.*, 79, 2979 (1957).

Oxygen-17 Nuclear Magnetic Resonance Studies of Aqueous Nickel Ion

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Abstract: In aqueous solutions of nickelous ion, the bulk water nmr line widths of oxygen-17 have been measured from about 0 to 150° at 2.00 and 8.134 MHz. The chemical shift of bulk water oxygen was similarly measured at 8.143 MHz. The ^{17}O nmr spectrum of water in the first coordination sphere of Ni^{2+} ion has been reexamined under more favorable experimental conditions. The results of these studies are consistent with six equivalent waters composing the first coordination sphere of Ni^{2+} over the temperature range covered. The enthalpy and entropy of activation for water exchange has been calculated to be 13.9 kcal/mol and 10 eu, respectively, with a scalar coupling constant (A/h) to the ^{17}O of $2.4 \times 10^{+7}$ Hz. In agreement with the results of Fiat, a small residual chemical shift of ^{17}O of bulk water was observed at low temperature. It is concluded that the shift must be attributed to second coordination sphere interactions. The experimental frequency dependence of the relaxation of ^{17}O caused by scalar coupling has been used to calculate a correlation time for the electronic relaxation of Ni^{2+} of 1.1×10^{-12} sec at 160°. In the low-frequency limit at 2.00 MHz, the electronic relaxation times, T_{1e} and T_{2e}, are found to be 5.8×10^{-12} sec at 160°, with an activation energy of 1.2 kcal/mol. Another independent measure of the electronic relaxation correlation time has been obtained by extending the work of Morgan and Nolle on protons to 220 MHz. The apparent lack of a dispersion region in the frequency dependence of the dipolar coupling to the protons has been shown to be due to a competing frequency dependence of the electronic relaxation. An electronic correlation time of 1.0×10^{-12} is consistent with these data as well.

The first hydration sphere of nickelous ion in aqueous solution has been studied in the past by ^{17}O nmr.[1-4] The results of these studies have led to some perplexing contradictions which have cast doubt on the previous chemical knowledge of the Ni^{2+} ion or on the adequacy of the general exchange theory governing nmr line widths. From proton nuclear magnetic resonance measurements near −30° in concentrated aqueous salt so-

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[1] T. J. Swift and R. E. Connick, *J. Chem. Phys.*, 37, 307 (1962); 41, 2553 (1964).

[2] R. E. Connick and D. Fiat, *ibid.*, 44, 4103 (1966).

[3] D. Fiat in "Magnetic and Electric Resonance and Relaxation," North Holland Publishing Co., Amsterdam, 1967.

[4] A. G. Desai, H. W. Dodgen, and J. P. Hunt, *J. Amer. Chem. Soc.*, 92, 798 (1970).

lutions, Swift and Weinberger[5] found a coordination number of six for nickel ion. Fiat[3] has interpreted the oxygen-17 data at temperatures above 0° as evidence for four "slowly" exchanging waters and two more rapidly exchanging waters. While the two sets of data are not necessarily in conflict because of the temperature differences, such an implied inequivalence of the six first coordination sphere waters is unexpected on the basis of other chemical properties.

A recalculation of the relaxation processes for oxygen-17 in solutions of nickelous ion, which made use of estimates of the electronic relaxation time[2,6] of Ni^{2+}, has revealed that there is an appreciable contribution from the scalar coupling relaxation process in addition to the $\Delta\omega$ process at temperatures above 70°. More importantly, the earlier data at 2 MHz[1] were found to be inconsistent with theory, if the electronic relaxation time estimates are correct.

Also, Morgan and Nolle[6] were unable to find the frequency dependence expected from theory of the longitudinal and transverse relaxation times of protons of water in solutions of nickelous ion. They could find no frequency dependence whatsoever up to 60 MHz.

The purpose of the present work is to clear up these apparent contradictions.

Theory

A discussion of the transverse relaxation of the bulk waters due to exchange with dilute paramagnetic metal ions has been given by Swift and Connick.[1] They found that the contribution to the bulk water relaxation time, T_{2p}, arising from the presence of dilute paramagnetic metal ions could be described by

$$\frac{1}{T_{2p}} = \frac{P_m}{\tau_m}\frac{\dfrac{1}{T_{2m}^2} + \dfrac{1}{T_{2m}\tau_m} + \Delta\omega_m^2}{\left[\left(\dfrac{1}{T_{2m}} + \dfrac{1}{\tau_m}\right)^2 + \Delta\omega_m^2\right]} \qquad (1)$$

where τ_m is the lifetime of the water molecules in the first coordination sphere of the paramagnetic metal ion, $1/T_{2m}$ is the rate of the relaxation of the ^{17}O of the bound waters, $\Delta\omega_m$ is the difference in resonance frequency of the bound waters and the observed resonance, and P_m is a mole ratio of the waters in the bound sites to those elsewhere. P_m is given by

$$P_m = \frac{x_m}{x_{H_2O}} = \frac{n[Ni^{2+}]}{55.5 - n[Ni^{2+}]} \qquad (2)$$

where x is the mole fraction of oxygen nuclei of water in the indicated environment, n is the coordination number of the paramagnetic ion, and brackets indicate the concentration of the enclosed species in moles per 1000 g of water. No simplification of eq 1 is adequate in describing the entire temperature range covered for Ni^{2+}.

The bulk water chemical shift has been shown by Swift and Connick[1] to obey

$$\Delta\omega_{H_2O} = \frac{-P_m\Delta\omega_m}{\tau_m^2\left[\left(\dfrac{1}{T_{2m}} + \dfrac{1}{\tau_m}\right)^2 + \Delta\omega_m^2\right]} \qquad (3)$$

The notation is identical with that of eq 1. The chemical shift of the bound waters relative to pure water, $\Delta\omega_{H_2O-m}$, is expected to be given by the Bloembergen equation[7]

$$\Delta\omega_{H_2O-m} = \omega S(S+1)\frac{g_{eff}\beta}{\gamma_I}\frac{A}{3kT} \qquad (4)$$

where ω is the precessional frequency of the nuclei in question, $g_{eff}\beta$ and γ_I are the gyromagnetic ratios of the unpaired electrons and the nucleus, A is the scalar coupling constant in ergs, and S is the electron spin quantum number.

The temperature dependence of the exchange lifetime is expected to follow the familiar expression for the rate of chemical reaction

$$\tau_m = \frac{h}{kT}\exp\left[\frac{\Delta H^{\ddagger}}{RT} - \frac{\Delta S^{\ddagger}}{R}\right] \qquad (5)$$

where $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are the enthalpy and entropy of activation for water exchange.

The relaxation of ^{17}O caused by the Ni^{2+} ion has been shown to be due to scalar coupling[1,2] which has the following functional form[8]

$$\frac{1}{T_{2m}} = \frac{S(S+1)}{3}\left(\frac{A}{\hbar}\right)^2\tau_e \qquad (6)$$

$$\tau_e = \left[T_{1e} + \frac{T_{2e}}{1 + \omega_S^2T_{2e}^2}\right] \qquad (7)$$

where T_{1e} and T_{2e} are the longitudinal and transverse relaxation times of the electrons and ω_S is the precessional frequency of the electrons. The coupling mechanism between the Ni^{2+} ion and the water protons can easily be shown to be dominated by a dipole–dipole interaction. The scalar coupling constant is known to be 1.1×10^5 cps.[9] Using the electronic relaxation times in Table III in eq 6 for a 0.1 M solution yields a value $T_2[Ni^{2+}] = 5.75$ sec M. Comparison of this value with the data in Figure 5 shows the scalar contribution to the total line width to be negligibly small. The dipolar coupling contribution to transverse relaxation for the present conditions is[2,10,11]

$$\frac{1}{T_2} = \gamma_I^2\gamma_S^2\hbar^2S(S+1)\frac{1}{15d^6}\left\{7T_{1e} + \frac{13T_{2e}}{1 + \omega_S^2T_{2e}^2}\right\} \qquad (8)$$

where γ_I and γ_S are the gyromagnetic ratios of the nucleus and the electrons, d is the distance of separation of the two dipoles, ω_S is the precessional frequency of the electrons, and T_{1e} and T_{2e} are the transverse and longitudinal relaxation times of the paramagnetic electrons on Ni^{2+}.

Experimental Section

Dilute nickelous perchlorate solutions in 10% $H_2{}^{17}O$ were prepared in the following manner. A stock solution of $Ni(ClO_4)_2 \cdot 6H_2O$ was prepared from reagent grade crystals in natural-abundance distilled water. The solution was analyzed to be 1.249 M[12] in Ni^{2+} with no detectable amounts of other paramagnetic impurities. Solutions of *ca.* 1-ml volume and desired concentration were then prepared by analytic dilution of the stock solution. Perchloric acid

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

(6) L. O. Morgan and A. W. Nolle, *J. Chem. Phys.*, **31**, 365 (1959).

(7) N. Bloembergen, *ibid.*, **27**, 595 (1957).

(8) A. Abragam, "The Principles of Nuclear Magnetism," Oxford University Press, London, 1961, p 311.

(9) B. B. Wayland and W. L. Rice, *Inorg. Chem.*, **5**, 54 (1966).

(10) I. Solomon, *Phys. Rev.*, **99**, 559 (1955).

(11) A. Abragam, ref 8, p 334.

(12) M expresses moles per liter of solution at room temperature.

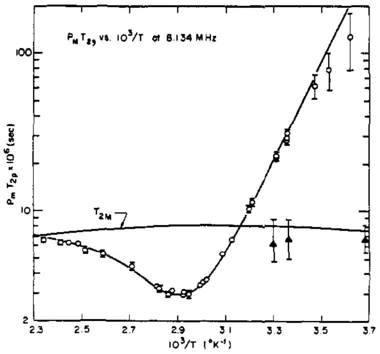

Figure 1. P_mT_{2p} *vs.* reciprocal of absolute temperature at 8.134 MHz for the ^{17}O nmr of aqueous solutions of $Ni(ClO_4)_2$: (○) bulk water data with line resulting from curve fitting, (△) bound water line-width data with curve labeled "T_{2m}" resulting from calculations as explained in the text.

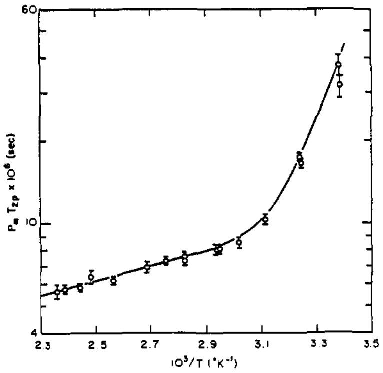

Figure 2. P_mT_{2p} *vs.* reciprocal of absolute temperature at 2.000 MHz for the bulk ^{17}O nmr of aqueous solutions of $Ni(ClO_4)_2$, with the solid curve the result of curve fitting as discussed in the text.

was added in all cases to a concentration of 0.10 *M*. The water was then distilled off *in vacuo* and water enriched to 10% $H_2{}^{17}O$ distilled into the sample. Weight differences indicated the amount of natural-abundance water removed and enriched water added. The concentration of the final sample could be easily calculated. The sample for the bound water studies was prepared in *ca.* 20% $H_2{}^{17}O$-enriched water normalized in deuterium obtained from the Weizmann Institute. To avoid isotopic dilution, reagent grade anhydrous silver perchlorate and anhydrous nickelous chloride were mixed in the appropriate molar amounts in the 20% enriched water. The silver chloride precipitate was separated from the solution by decantation. The solution was analyzed to be 3.70 *M* in Ni^{2+}.

The bulk water ^{17}O resonance signals were recorded with a Varian Associates Model V-4200 wide-line spectrometer operated at 8.134 and 2.000 MHz. Temperature was controlled by flowing heated or cooled dry nitrogen past the sample. The probe was protected from damaging temperatures by a dewared insert into which the sample was placed. The temperature was measured to ±0.1° with a copper–constantan thermocouple immediately outside the sample tube and regulated to ±0.5°.

Chemical shifts were measured by successive scans of the sample and a standard pure water sample replaced between scans. The large magnetic field was varied by passing a ramp dc current through the modulation coils of the probe. Linear extrapolations between the position of resonance of the standard as a function of time allowed for a correction of the errors due to drift in the large magnetic field.

Bound water measurements were recorded on the same instrument at a fixed frequency of 8.134 MHz. Signal averaging was accomplished using a Varian Associates Model 1024 time averaging computer. The internal ramp of the computer was fed directly to the sweep input of the power supply with the super stabilizer removed from the system. Derivative-mode detection was employed, with care being taken to avoid modulational broadening. A measurement of absolute field as a function of magnet current was made, using a spinning coil gaussmeter, or the determination of the chemical shifts.

Results and Discussion

Bulk Water Measurements. The bulk water relaxation data are given as a function of the reciprocal of the absolute temperature at 8.134 MHz in Figure 1 and 2.00 MHz in Figure 2. The data are tabulated in Tables I and II. The solid curve through the data points in Figure 1 is a theoretical calculation using eq 1 and the parameters given in Table III, which were determined from a computer fit to all of the data using a convergent nonlinear least-squares curve fitting technique. In these calculations, and those which follow, the results are dependent upon the *g* value for the electron. This value has never been measured for Ni^{2+} in aqueous solution. Esr work on hydrated salts of Ni^{2+} indicates an isotropic *g* value of 2.25, which is relatively independent of the anions involved.[13] The assumption will be made that this value is the same for solutions.

The $\tau_e{}^0$ and *V* in Table III are defined by

$$\tau_e = \tau_e{}^0 \exp(V/RT) \qquad (9)$$

where τ_e is the effective electronic relaxation time for Ni^{2+} as defined in eq 7 and *V* is the activation energy for the electronic relaxation. *V* was not a parameter in the computer program. The fit to the 8.134-MHz data is insensitive to the value of *V* from 0 to 2 kcal. The value of 0.6 kcal was chosen for reasons to be discussed below. Since the 2.000-MHz data are relatively insensitive to A/h, $\Delta H^{\pm}$, and $\Delta S^{\pm}$ over the temperature range covered, the 8.134-MHz parameters were used in the calculation of the theoretical curve in Figure 2.

Table I. Bulk Water Relaxation Data at 8.13 MHz

$10^3/T$, °K^{-1}	T_{2H_2O}, msec	T_{2p}, msec	$P_m \times 10^3$
3.357	6.60	13.4	2.357
3.309	7.20	9.62	2.357
3.196	8.85	4.53	2.357
3.085	11.4	2.28	2.357
3.008	13.2	1.52	2.357
2.946	14.5	1.27	2.357
2.878	16.1	1.40	2.357
2.704	20.5	1.93	2.357
2.587	23.6	2.28	2.357
2.514	26.3	2.37	2.357
2.444	29.6	2.63	2.357
3.357	6.60	12.27	2.357
3.305	7.25	9.29	2.357
2.997	13.3	1.43	2.357
2.921	15.1	1.24	2.357
2.860	16.5	1.22	2.357
2.820	17.4	1.37	2.357
2.486	27.6	2.63	2.357
2.412	31.0	2.60	2.357
2.342	34.9	2.75	2.357
3.358	6.36	8.21	3.395
3.212	8.60	3.17	3.395
3.121	10.5	1.95	3.395
3.010	13.1	1.08	3.395
2.814	17.7	1.00	3.395
2.925	15.1	0.917	3.395
3.621	3.3	37.58	3.395
3.531	4.4	23.25	3.395
3.469	5.25	18.47	3.395

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(13) K. H. Hellwege and A. M. Hellwege, Ed., "Magnetic Properties of Transition Metal Compounds," Springer-Verlag, New York, N. Y., 1966.

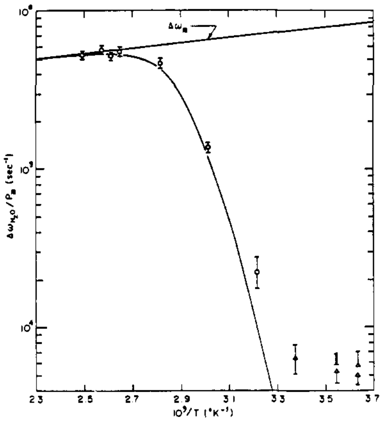

Figure 3. $\Delta\omega_{H_2O}/P_m$ *vs.* reciprocal of absolute temperature at 8.134 MHz for the ^{17}O chemical shift of the bulk water in aqueous solutions of $Ni(ClO_4)_2$. Curved line is the result of a calculation using eq 3 and the parameters in Table III: (○) 0.0314 *M* nickelous perchlorate, 0.10 *M* perchloric acid; (△) 0.392 *M* nickelous perchlorate, 0.10 *M* perchloric acid in a spherical container.

Only the τ_e^0 and *V* had to be changed in order to fit the 2.00-MHz data. These values are given in Table I.

The values for $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and A/h vary significantly from those given earlier.[1,2] The variations appear to be due to the previous neglect of the $1/T_{2m}$ term and to less accurate, noncomputer fits to the data.

Table II. Bulk Water Relaxation Data at 2.00 MHz

$10^3/T$, °K^{-1}	T_{2H_2O}, msec	T_{2p}, msec	$P_m \times 10^3$
2.363	31.0	1.66	3.395
2.389	30.1	1.71	3.395
2.441	28.3	1.70	3.395
2.480	27.1	1.89	3.395
2.564	24.5	1.84	3.395
2.687	21.0	2.03	3.395
2.754	19.0	2.16	3.395
2.822	17.5	3.08	2.357
2.825	17.5	2.22	3.395
2.941	14.7	3.43	2.357
2.949	14.6	2.39	3.395
3.021	12.8	2.51	3.395
3.107	10.8	3.04	3.395
3.111	10.7	4.38	2.357
3.241	8.08	5.14	3.395
3.244	8.05	6.85	2.357
3.367	6.28	10.33	3.395
3.382	6.26	15.91	2.357
3.383	6.25	9.41	3.395

Table III. Parameters Determined by Fitting Relaxation Data

	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	A/h, Hz	τ_e^0, sec	V, kcal
8.134 MHz	13.9	10	2.4×10^7	3.8×10^{-12}	0.6
2.000 MHz				2.36×10^{-12}	1.2

In Figures 1 and 2, the deviations from the straight lines observed at low temperatures may not be real. The vertical error lines correspond to one standard deviation, but the water blank is quite large. For example, at the lowest point in Figure 1, the value of $1/T_{2p}$ was only one-tenth of the observed line width. Calculations show that the deviations could not be from dipole–dipole, scalar, or quadrupole coupling effects in the second coordination sphere.

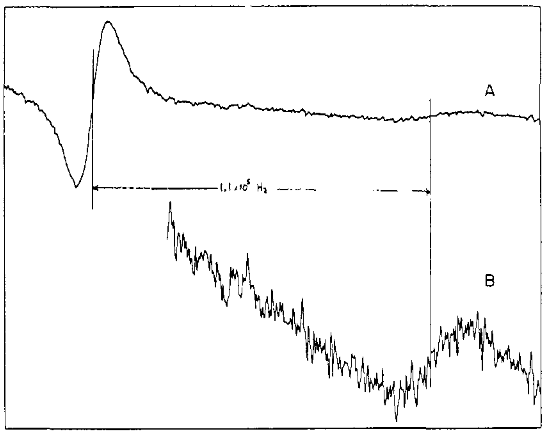

Figure 4. ^{17}O nmr spectra of a 3.7 *M* aqueous solution of nickelous perchlorate and 0.10 *M* perchloric acid at 25°: (A) the bulk waters on the left 1.11×10^5 Hz upfield from the bound waters on the right. A is the average of 100 scans, B is an amplification of A.

More recently Desai, Dodgen, and Hunt[4] have gathered data at 14.1 MHz from 0 to 88°. In exchange-controlled regions their 14.1-MHz data are in complete agreement with our 8.13-MHz data. However, their $\Delta H^{\ddagger}$ calculated from the 14.1-MHz data is only 12.3 kcal/mol. The agreement of the two sets of experimental points lends credence to the observation that the exchange-controlled region could be best fit by a curved line with increasing slope at higher temperatures. The value of $\Delta H^{\ddagger}$ appears to change from about 11 kcal/mol near 0° to nearly 14 kcal/mol at 60°. This result could be formally described by an apparent $\Delta C_p^{\ddagger}$ equal to about 40 cal/deg. The $\Delta H^{\ddagger}$ reported for the 8.13-MHz data is an average value giving the best fit to our data from 0 to *ca.* 130°. No attempt was made to computer fit the data with a variable $\Delta H^{\ddagger}$ because of the smallness of the curvature.

The chemical shift of the bulk water can provide a check on the accuracy of the parameters in Table III. Figure 3 gives the experimental data as a function of the reciprocal of the absolute temperature. The solid line is the result of a calculation based on eq 3 and the parameters in Table III. The agreement is seen to be excellent in the high-temperature region, which is most sensitive to the parameters. The lower temperature shifts deviate systematically from the predicted contribution from the first coordination sphere. This effect has been observed previously[3] and was then attributed to two of the six bound water molecules which were hypothesized to exchange much faster than the other four. As will be shown below, direct observation of the chemical shift of the bound water resonance is inconsistent with this interpretation.

Bound Water Measurements. A representative spectrum of the bound water resonance is shown in Figure 4. The temperature was controlled through the use of a dewared insert between the sample and the probe. The use of water enriched to 20% $H_2{}^{17}O$ and employment of signal averaging gave a significant improvement in resolution over the previous work.[2]

The bound water chemical shift data are summarized in Table IV for several temperatures. The chemical shift has the expected $1/T$ dependence. The bound

Table IV. Bound Water Chemical Shift Measurements

	1.5°	8.0°	24.6°	33°
$\Delta\omega_{H_2O-m}$, Hz	1.23×10^5	1.18×10^5	1.11×10^5	1.08×10^5

water line width can be shown in the limit of large chemical shift to be

$$1/T_2 = 1/T_{2m} + 1/\tau_m \qquad (10)$$

and should increase with increasing temperature because of the temperature dependence of $1/\tau_m$. This is verified experimentally. The experimental value for $1/T_{2m}$ is obtained by subtracting $1/\tau_m$, known from bulk water measurements, from the measured bound water line width. These results are shown plotted as triangles in Figure 1 and are seen to agree within experimental uncertainties with the calculated line labeled T_{2m}. The method of calculation of this line will be explained later.

Even with the improved experimental conditions, an accurate coordination number from relative signal intensities could not be obtained. A more accurate method is available by combining the bulk and bound water chemical shift data.

In the limit of rapid exchange, eq 3 reduces to

$$\Delta\omega_{H_2O} = -P_m\Delta\omega_m = -x_m\Delta\omega_{H_2O-m} \qquad (11)$$

where x_m is the mole fraction of oxygen nuclei of the water in the first coordination sphere of the nickel ions and $\Delta\omega_{H_2O-m}$ is the difference in resonance frequency of the oxygen of pure water and the oxygens of waters coordinated to nickel ion. (This equation is actually exact for rapid exchange regardless of the metal ion concentration.) Substituting for x_m from eq 2 and rearranging

$$n = (55.5)\Delta\omega_{H_2O}/[Ni^{2+}]\Delta\omega_{H_2O-m} \qquad (12)$$

The line $\Delta\omega_m$ is shown in Figure 3 and is approached above about 127°. The bound water chemical shift can be calculated at this temperature using eq 4 and the value at low temperature. The value when inserted in eq 12 yields

$$n = 6.0 \pm 0.20$$

which agrees excellently with the measurement of Swift and Weinberger[5] from proton nmr at lower temperature. Thus it is concluded that, contrary to earlier evidence, the oxygen-17 nmr data are consistent with a sixfold coordination of nickel ion with all six waters equivalent.

The above conclusion requires that the low-temperature chemical shift discussed previously be attributed to waters outside the first coordination sphere. A similar effect of nearly equal magnitude has been observed[14] for Cr^{3+} which, because of the extremely slow first sphere exchange rate, can be due only to water outside the first coordination sphere.

The magnitudes and direction of the shifts can help to identify the type of orbitals of the metal ion involved in the interaction with second coordination sphere oxygens.[15] Donation of electron density by the oxygen into a half-filled orbital of the metal ion would leave unpaired electron density on the oxygen. Since the donated electron density must be spin paired with the paramagnetic electrons on the metal, the unpaired electron spin left on the oxygen will be parallel to those on the metal ion. The external magnetic field produces a net component of this spin aligned with the field, producing a downfield or paramagnetic shift. Experimentally Ni^{2+}, which has only completely and half-filled d orbitals, gives a downfield shift for the second sphere waters, which is consistent with the above picture. Similar reasoning (using Hund's rule) suggests that donation by oxygens into an empty orbital should produce an upfield shift. The downfield shift for Cr^{3+} indicates that donation by the second sphere waters into the half-filled t_{2g} orbitals is more effective than that into the empty e_g in producing unpaired electron density on the oxygens.

Since the attraction of second coordination sphere waters to the metal ion should be almost entirely electrostatic in nature, the position of the second sphere waters is most reasonably on the center of the faces of the octrahedron formed by the first sphere waters. This position allows the closest approach between the centers of charge. Assuming the bonding orbitals of the second sphere waters are symmetric about a line joining the oxygen and metal nuclei, bonding to the t_{2g} orbitals is symmetry allowed. However, bonding to the center of the faces is incompatible with the symmetry of the e_g orbital. The fact that significant donation to the e_g orbitals is observed in Ni^{2+} would lead one to the conclusion either that the waters involved are not at the center of the faces or that the assumption as to axial symmetry of the oxygen orbitals is faulty. Certainly both of these reasons could contribute to the observed result. The position of the second sphere waters remains unknown; however, the faces are certainly electrostatically most stable. But molecular vibrations about these positions are undoubtedly large and frequent, thereby allowing significant donation to e_g orbitals.

Electronic Relaxation Rates of Ni^{2+}. Information concerning electronic relaxation rates can be calculated from the values of $1/T_{2m}$ as a function of frequency. Comparison of Figures 1 and 2 shows that $1/T_{2m}$ is indeed a function of frequency. However, straightforward calculations show that the effect is not nearly as large as would be predicted by eq 6. An arbitrary temperature of 160° is chosen for the following calculations, since this lies well into the $1/T_{2m}$ region for relaxation at 2 MHz. The $1/T_{2m}$ from Figure 2 at this temperature inserted in eq 6 yields

$$\tau_e = 1.16 \times 10^{-11}\ \text{sec}$$

Equations 6 and 7 can be used to estimate $1/T_{2m}$ at 8.134 MHz, using the above value of τ_e assuming $T_{1e} = T_{2e}$ at 2.00 MHz. If T_{1e} and T_{2e} are assumed to be frequency independent up to 8.134 MHz, eq 6 and 7 give

$$1/T_{2m}(\text{predicted at 8 MHz}) = 1.24 \times 10^5\ \text{sec}^{-1}$$

Experimentally, $1/T_{2m}$ has been found to be $(1.40 \pm 0.05) \times 10^5\ \text{sec}^{-1}$. This difference lies well outside experimental error and can only be accounted for by a faulty assumption as to the frequency independence of T_{1e} and T_{2e}.

Regardless of the physical origin of the relaxation, the various theories for triplet electronic relaxation times

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[14] M. Alei, Jr., *Inorg. Chem.*, 3, 44 (1964).

[15] Z. Luz and R. G. Shulman, *J. Chem. Phys.*, 43, 3750 (1965).

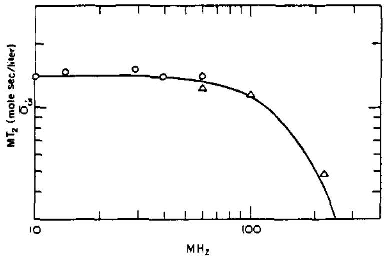

Figure 5. Product of molarity and proton T_2 *vs.* proton Larmor frequency for aqueous solutions of nickelous perchlorate 0.10 *M* in perchloric acid at 30°: (O) data from Morgan and Nolle (ref 6), (Δ) present work.

have identical correlation time and frequency dependencies.[16–18]

$$\frac{1}{T_{1e}} \propto \frac{8\tau_c}{1 + 4\omega_S{}^2\tau_c{}^2} + \frac{2\tau_c}{1 + \omega_S{}^2\tau_c{}^2} \tag{13}$$

$$\frac{1}{T_{2e}} \propto 3\tau_c + \frac{5\tau_c}{1 + \omega_S{}^2\tau_c{}^2} + \frac{2\tau_c}{1 + 4\omega_S{}^2\tau_c{}^2} \tag{14}$$

Ni^{2+} has a triplet ground state and can have only one longitudinal and one transverse relaxation time. The condition for the rigorous application of these formulas is

$$\tau_c \ll T_{1e}, T_{2e} \tag{15}$$

The assumption that $T_{1e} = T_{2e}$ at 2.00 MHz can be stated explicitly as

$$\omega_S{}^2\tau_c{}^2 \ll 1 \tag{16}$$

Under these conditions a simple manipulation of eq 13 and 14 yields

$$(T_{1e})(8\text{ MHz}) = (T_{1e})(2\text{ MHz}) \times 10 \times \left[\frac{8}{1 + 4\omega_S{}^2\tau_c{}^2} + \frac{2}{1 + \omega_S{}^2\tau_c{}^2}\right]^{-1} \tag{17}$$

$$(T_{2e})(8\text{ MHz}) = (T_{2e})(2\text{ MHz}) \times 10 \times \left[3 + \frac{5}{1 + \omega_S{}^2\tau_c{}^2} + \frac{2}{1 + 4\omega_S{}^2\tau_c{}^2}\right]^{-1} \tag{18}$$

The τ_c can now be adjusted so that the 8-MHz T_{1e} and T_{2e} when used in eq 6 and 7 give the experimental $1/T_{2m}$. This procedure yields

$$\tau_c = 1.1 \times 10^{-12} \text{ sec at } 160°$$

The adequacy of the assumption 16 can now be seen to be excellent

$$\omega_S{}^2\tau_c{}^2 = 3 \times 10^{-3}$$

The result raises the question of the validity of the calculation in that the correlation time for electronic relaxation is only a factor of 5 or so smaller than the relaxation time and therefore condition 15 is no longer strictly fulfilled. It seems reasonable, however, that the correlation time and frequency dependence of the relaxation time would be less sensitive to this restriction than would be the calculation of an absolute relaxation rate.

Another independent measure of this correlation time can be had by measuring the frequency dependence of the rate of relaxation of water protons in a Ni^{2+} solution. This has been done previously by Morgan and Nolle[6] for protons from 2 to 60 MHz. Their data are reproduced in Figure 5 along with the results of the present study at 60, 100, and 220 MHz.

The application of the electronic relaxation theories developed after the work of Morgan and Nolle can account for the lack of the expected dispersion region. The frequency dependence of T_{1e} and T_{2e} acts to cancel the dispersion region of the dipolar coupling up to 60 MHz. Above this frequency the T_{1e} frequency dependence dominates and causes the line width to increase very sharply. The solid line in Figure 5 is a plot of the expected dipolar frequency dependence using eq 8 and including the frequency dependence of T_{1e} and T_{2e} as predicted by eq 13 and 14. The correlation time which fits the data best is

$$\tau_c = 1.8 \times 10^{-12} \text{ sec at } 30°$$

Extrapolating back to 160° to compare with the previous result and using $V = 1.20$ kcal/mol gives

$$\tau_c = 1.0 \times 10^{-12} \text{ sec at } 160°$$

This remarkably good agreement is, of course, coincidental, considering the probable compounding of experimental errors along the way. The consistency of the two methods is gratifying under any circumstances.

All the quantities necessary to calculate the 8-MHz $1/T_{2m}$ as a function of temperature are now known. The results of these calculations involving eq 6, 7, 9, 17, and 18 are shown plotted in Figure 1 as the solid curve thus designated. The plot is obviously not linear. However, for the purpose of fitting the T_{2p} data in Figure 1, an effective slope in the high-temperature region of 0.6 kcal/mol was used as a quite adequate approximation. The correctness of the T_{2m} calculation is verified experimentally by measurement of the bound water resonance line width. The values at several temperatures have been plotted as triangles in Figure 1 and the agreement with the predicted values is good.[19]

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(19) NOTE ADDED IN PROOF. A. M. Chmelnick and D. Fiat (*J. Amer. Chem. Soc.*, **93**, 2875 (1971)) have recently reported several of the results given here.