lower field than those of the corresponding Co(III) complexes, which agrees with earlier work.[19]

The AB proton coupling constants (15.6–18.4 cps) for all of the complexes are similar to those obtained in other metal–EDTA complexes.[10–14,19] The decrease in the coupling constant of the unbound acetate CH_2 group from approximately 18 to 17 cps during the ionization of the carboxylic acids appears to be characteristic. The additional small coupling (~1 cps) observed for the B protons in the acetate chelate rings of the tetradentate complexes may arise from coupling with the rhodium nucleus ($I = {}^1/_2$).

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Ammonia Exchange of Nickel–Ammine Complex in Aqueous Ammonia Measured by Proton Magnetic Resonance[1,2]

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The exchange rate of $Ni(NH_3)_6^{2+}$ in aqueous ammonia is determined by proton magnetic resonance. The relaxation time T_2 is obtained from the line width of the water resonance, and T_1 is measured by the saturation recovery method. At −17°, the exchange is fairly slow and the $Ni(NH_3)_6^{2+}$ resonance occurs at high field about 9500 Hz from the solvent resonance, with a full width of about 2600 Hz. The hyperfine coupling constant is negative and large: $A/h = -1.70 \times 10^6$ Hz. The exchange rate (sec^{-1}) of the NH_3 molecules is $\log (1/\tau) = 13.53 - (2610/T)$. If NaOH is added to the solution, complexes such as $Ni(NH_3)_5OH^+$ are formed, and the NH_3 is more labile: $\log (1/\tau) = 13.79 - (2610/T)$ in 0.103 *M* NaOH and $13.97 - (2610/T)$ in 0.326 *M* NaOH. The exchange rates are the same as the rates obtained by ^{14}N nmr, demonstrating that individual protons exchange at a much slower rate.

Introduction

Water-exchange rates in aqueous solutions of transition metal ions have been determined by ^{17}O nuclear magnetic resonance.[3] Hunt, *et al.*,[4,5] determined the ammonia-exchange rate of a solution containing $Ni(NH_3)_6^{2+}$ in aqueous ammonia by ^{14}N resonance. In the present investigation, the proton-exchange rate of this complex is determined by proton nmr. By comparison of the ^{14}N and ^1H results, the importance of the exchange of individual protons follows. The exchange rate in anhydrous ammonia has also been measured by ^{14}N resonance.[5] Swift and Lo[6] obtained a different result by proton resonance, but this work has been criticized by Rice and Wayland,[7] who confirm Hunt's[5] results.

Basic Equations

The protons of ammonia and water in the bulk of the solution exchange rapidly, and only a single peak is observed. Several processes[8] contribute to the relaxation rate, $1/T_1$, of these protons

$$\frac{1}{T_1} = \frac{1}{T_{1A}} + \frac{P}{T_{1M} + \tau} + \frac{P}{T_{1C}} \qquad (1)$$

The contribution $1/T_{1A}$ represents the relaxation rate in the absence of paramagnetic ions. T_{1M} is the relaxation time of the ammonia protons in the first coordination sphere of the Ni, and τ is their lifetime. P is the mole fraction of these protons. Thus, in the present case

$$P = 18[Ni(NH_3)_6^{2+}]/\{3[NH_3] + 2[H_2O]\} \qquad (2)$$

The third term of eq 1 represents the dipole relaxation of NH_3 and H_2O protons surrounding a complex nickel ion. The protons in the second and higher coordination shells relax by interaction with the magnetic dipole of the unpaired, "magnetic" electrons of the nickel complex.

For slow exchange, $|\tau\Delta\omega| \gg 1$, and the spectrum consists of two resonances, separated by a chemical shift $\gamma\Delta H = \gamma(H_M - H_A) = -\Delta\omega = -(\omega_M - \omega_A)$. The weak resonance γH_M at high field is due to $Ni(NH_3)_6^{2+}$.

The chemical shifts are measured with respect to an internal standard R. The resonance separation $\gamma\Delta H$ can be obtained by measuring the chemical shift $\delta\omega$ relative to R as a function of the nickel concentration

$$\delta\omega - \delta\omega_A = P(\delta\omega_M - \delta\omega_A) = P\Delta\omega \qquad (3)$$

The electron–proton coupling constant, A/h, follows from the resonance separation by [3,9]

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[1] Presented in part at the 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966; Abstract No. H99.

[2] The effect of hydroxide ions was presented at the 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967; Abstract No. L75.

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

[4] J. P. Hunt H. W. Dodgen, and F. Klanberg, *Inorg. Chem.*, **2**, 478 (1963).

[5] H. H. Glaeser, G. A. Lo, H. W. Dodgen, and J. P. Hunt, *ibid.*, **4**, 206 (1965).

[6] T. J. Swift and H. H. Lo, *J. Am. Chem. Soc.*, **88**, 2994 (1966).

[7] W. L. Rice and B. B. Wayland, *Inorg. Chem.*, **7**, 1040 (1968).

[8] N. Bloembergen and L. O. Morgan, *J. Chem. Phys.*, **34**, 842 (1961).

[9] N. Bloembergen, *ibid.*, **27**, 595 (1957).

$$\frac{\Delta H}{H} = -\frac{\Delta\omega}{\omega} = \frac{A}{3kT}\frac{\gamma_S}{\gamma_I}S(S+1) \tag{4a}$$

$$= -\frac{A}{\hbar}\frac{g|\beta|S(S+1)}{3kT\gamma_I} \tag{4b}$$

where $\beta = e\hbar/2mc$ is the Bohr magneton in Gaussian units and $\gamma_S = -g|\beta|/\hbar$ is the gyromagnetic ratio of the electron.

The relaxation processes which contribute to $1/T_1$ contribute to $1/T_2$ to the same extent. Thus, an equation analogous to eq 1 applies to T_2 in the limit of slow exchange and in the limit of fast exchange. At intermediate rates, the exchange causes additional broadening,[3] and

$$\frac{1}{T_{2p}} = \frac{1}{T_2} - \frac{1}{T_{2A}} = \frac{P}{T_{2C}} + \frac{P}{\tau}\,\frac{(1/T_{2M}{}^2) + (1/T_{2M}\tau) + \Delta\omega^2}{[(1/T_{2M}) + (1/\tau)]^2 + \Delta\omega^2} \tag{5}$$

In many cases an approximate form of the third term is sufficiently accurate. For slow exchange, $|\tau\Delta\omega| \gg 1$, and when $|\Delta\omega| \gg 1/T_{2M}$, eq 5 simplifies to

$$\frac{1}{T_{2p}} = \frac{P}{T_{2C}} + \frac{P}{\tau} \tag{6}$$

For rapid exchange, $|\tau\Delta\omega| \ll 1$, and when $1/\tau \gg 1/T_{2M}$, eq 5 simplifies to

$$\frac{1}{T_{2p}} = \frac{P}{T_{2C}} + \frac{P}{T_{2M}} + P\tau\Delta\omega^2 \tag{7}$$

The last terms in eq 6 and 7 represent the exchange broadening.

Experimental Section

Solutions containing varying amounts of $Ni(NO_3)_2$, NH_3, NaOH, and NH_4NO_3 were prepared volumetrically from standard solutions of these compounds. The nickel content was determined by direct titration[10] with disodium dihydrogen ethylenediaminetetraacetate (EDTA) using ammonium purpurate (murexide) as an indicator or, alternatively, by addition of a slight excess of a standard solution of NaCN and back-titration of the excess with a standard solution of $AgNO_3$ in the presence of iodide. Both methods gave the same result within 1%. The mole fraction P of the complexed protons follows from the nickel concentration by eq 2, taking into account the density of the ammonia solutions. The ammonia content was determined by titration with standard acid.

The light absorption spectra of the solutions were determined between 350 and 650 nm (mμ) at room temperature as a function of the NaOH concentration, using a Spectronic 505 spectrophotometer.

A Varian A-60 high-resolution nmr spectrometer was used to measure the relaxation times from close to the freezing point to close to the boiling point of the solutions. Only a single resonance was observed at all temperatures, and the full line width at half-maximum, $1/\pi T_2$, was determined for the nickel solutions as well as for the aqueous ammonia solvent. The inhomogeneous broadening was usually less than 1.0 Hz, as determined from the line width of water or acetone.

The chemical shift $\delta\nu = -(\gamma/2\pi)\delta H$ of the nickel solutions as well as of the solvent was measured using sodium 3-(trimethylsilyl)-1-propanesulfonate as an internal standard.

The spin-lattice relaxation times T_1 were determined by the saturation recovery method[11,12] for the nickel solutions as well as the aqueous ammonia. The relative standard deviation of T_1 is about 12%.

Results and Discussion

The relaxation rates, corrected for the relaxation of the Ni-free solvent, are presented in Figure 1. The spin-lattice relaxation time T_{1A} of the solvent is found to be independent of the ammonia concentration (4.9 and 10.6 *M*), as might be expected. The following T_{1A} values in seconds are obtained for air-saturated water and aqueous ammonia: 3.0 (37°), 1.7 (8°), 1.3 (−5°), 1.0 (−11°), and 0.4 (−33°).

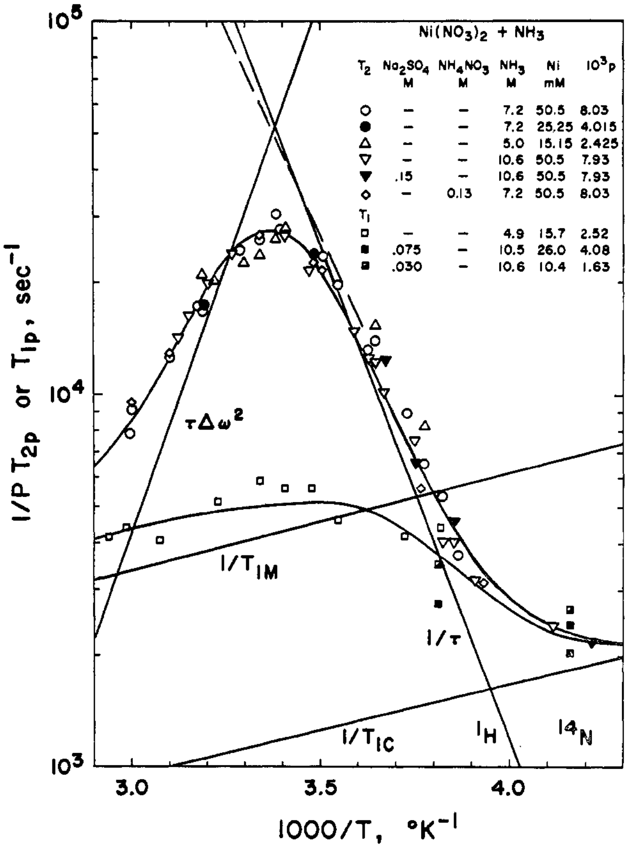

Figure 1.—Relaxation rate of various solutions containing nickel nitrate in aqueous ammonia. The squares are spin-lattice relaxation rates $1/PT_{1p}$. The exchange rate of the complexed NH_3 is $1/\tau$. For comparison, the exchange rate measured by ^{14}N magnetic resonance is sketched in as a broken line.

The solvent peaks were appreciably broadened[13] at low temperatures; for example, 10.7 *M* ammonia had a width $1/\pi T_{2A}$ of 4.8 Hz at −14°.

The compositions of the various nickel solutions are given in Figure 1. The results fall on the same bell-shaped curve, demonstrating that the exchange rate is independent of the NH_3 concentration, in agreement with Hunt's observation.[4]

The curves were calculated from the straight lines using eq 1–7 and represent a best fit to the data.

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[10] G. Schwarzenbach, "Complexometric Titration," Interscience Publishers, New York, N. Y., 1957, p 80.

[11] A. L. Van Geet and D. N. Hume, *Anal. Chem.*, **37**, 983 (1965).

[12] A. L. Van Geet, *ibid.*, **40**, 304 (1968).

[13] A. L. Van Geet and R. Marsch, Abstracts, 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, No. M160.

Knowing the value of T_{1p} makes it possible to calculate exchange rates in the high-temperature region as well. At very low temperatures, the T_{1p} and T_{2p} curves come together, and the data suggest strongly that this occurs also at high temperatures. Thus, it is virtually certain that $T_{1M} = T_{2M}$ and $T_{1C} = T_{2C}$. The contact shift $\Delta\omega$ is proportional to $1000/T$, and this temperature dependence should be taken into account when the exchange rate is calculated from the $\tau\Delta\omega^2$ line.

For comparison, the ^{14}N-exchange rates determined by Hunt[4] are also shown in Figure 1; these results are the same within experimental error. It is quite possible that the $1/T_{1C}$ line is really located much lower than the line shown. It so, our results will virtually coincide with those of Hunt. The agreement demonstrates that entire NH_3 molecules exchange; exchange of individual protons must be small by comparison. At best, the data are consistent with a contribution by proton exchange several times smaller than NH_3 exchange at temperatures above 25°.

One might expect that an exchange contribution by protons will be affected by the pH of the solution. Lowering the pH from 12.0 to 11.0 by addition of NH_4NO_3 does not affect the exchange rate, as shown in Figure 1.

At high temperature, the spin-lattice relaxation of the protons in the bulk of the solution occurs primarily in the first coordination sphere of the nickel ion, with $T_{1M} = T_{2M} = 0.3$ msec at 60°. The contribution of the second and higher coordination spheres to the relaxation, $1/T_{1C}$, is several times smaller. At low temperature, the exchange becomes slow, and the first coordination sphere can no longer contribute to the relaxation.

The relaxation is caused by dipole–dipole interaction with the unpaired electrons, and $1/T_{1M}$ is proportional to the correlation time τ_c of the interaction. The activation energy of 1.2 kcal at high temperature is smaller than the activation energy of the viscosity. A larger value would be expected if τ_c corresponds to the rotation of the complex.[14] The small value can be explained if one assumes that the relaxation time of the electron[7] is short enough to contribute to τ_c also.

Contact Shift.—The chemical shift relative to the solvent is presented in Figure 2. At low temperature, the resonance is due to the NH_3 and H_2O in the bulk of the solution, and the shift is close to zero. At high temperature the exchange is fast, and the resonance is the average of the $Ni(NH_3)_6{}^{2+}$ and the $NH_3 + H_2O$ in the bulk of the solution. This resonance is shifted upfield, indicating that the $Ni(NH_3)_6{}^{2+}$ resonance occurs at high field at a distance $\Delta\omega = -45{,}000$ radians/sec. This result is in excellent agreement with the value obtained from Figure 1. At the maximum of the $1/T_{2p}$ curve, $|\tau\Delta\omega| = 1$, and $|\Delta\omega| = 52{,}000$ radians/sec. Of course, this value of $\Delta\omega$ belongs to a higher value of $1000/T$.

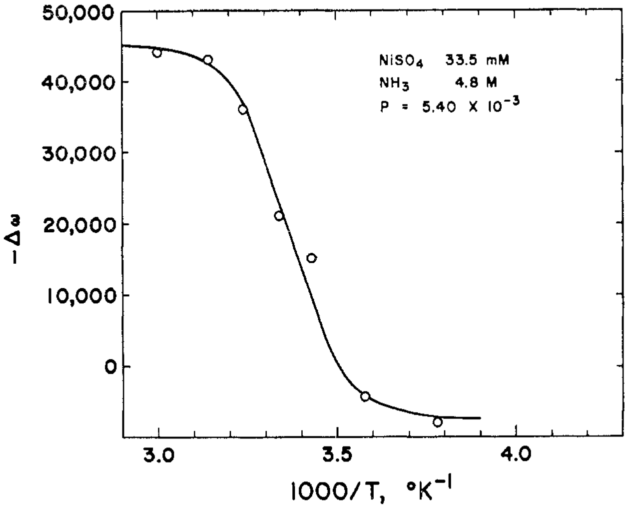

Figure 2.—Chemical shift relative to the solvent. $\Delta\omega = -\gamma\Delta H = 2\pi(\delta\nu - \delta\nu_A)/P$, where $\delta\nu$ is the observed chemical shift of the nickel solution relative to the internal standard, and $\delta\nu_A$ is the same for the nickel-free solvent.

The separate $Ni(NH_3)_6{}^{2+}$ resonance which occurs at low temperature is quite weak and very broad. At −17°, its full width is $(1/\pi T_{2M}) + (1/\pi\tau) = 2600$ Hz. No doubt, this is the reason why an attempt to find this peak failed. The instrument used for this was a Varian HA100 high-resolution spectrometer, as a wide-line system was not available.

The hyperfine proton–electron coupling constant follows from $\Delta\omega$ by eq 4b. With $S = 1$ and $g = 2.3$, the result is $A/h = -1.70 \times 10^6$ sec^{-1}.

Wayland and Rice[15] measured the contact shift of nickel perchlorate in liquid ammonia, and their result is in good agreement with our value. Swift and Lo[6] find $A/h = 3 \times 10^6$ sec^{-1}, but this result has been criticized by Rice and Wayland.[7]

The upfield shift is surprising because downfield shifts occur in the aquo complexes of all first-row transition elements.[16] The molecular orbitals containing the unpaired electrons have appreciable hydrogen 1s character. Thus, net unpaired electron spin density is placed directly at the hydrogen nucleus, and a positive coupling constant occurs in the aquo complexes.[16]

In the ammonia complex of nickel, most of the unpaired spin density is confined to the "lone-pair" orbitals of the nitrogen. These orbitals have small or negligible 1s character, and the unpaired spin cannot reach the hydrogen nuclei directly.[17] The unpaired electrons polarize the hydrogen 1s electron pair, causing a small unpairing. In this way, negative spin density is induced at the hydrogen nucleus, and a negative coupling constant A/h occurs. A similar situation occurs in an aromatic ring, where the sign of the spin density

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(14) R. A. Bernheim, T. H. Brown, H. S. Gutowski, and D. E. Woessner, *J. Chem. Phys.*, **30**, 950 (1959).

(15) B. B. Wayland and W. L. Rice, *Inorg. Chem.*, **6**, 2270 (1967). It should be noted that the right-hand side of the equation for A/h is incorrect and should be multiplied by $h/2\pi$. The numerical results are not affected however.

(16) B. B. Wayland and W. L. Rice, *ibid.*, **5**, 54 (1966). It should be noted that the right-hand side of eq 2 is incorrect and should be multiplied by $1/h\gamma_e$. The numerical results are not affected however.

(17) B. B. Wayland and W. L. Rice, *J. Chem. Phys.*, **45**, 3151 (1966). See preceding comment.

alternates along the ring.[18,19] Heteronitrogen atoms transmit unpaired spin density five times better than heterooxygen atoms in aromatic rings.

Effect of Hydroxide Ions.—To obtain more information about the mechanism of the exchange, sodium hydroxide was added to the solutions. It was thought that OH^- ions might abstract protons from the $Ni(NH_3)_6^{2+}$ complex, leading to an increase in the exchange rate.

Indeed, a rate increase is observed (Table I). A rather high concentration of NaOH is necessary to obtain a noticeable result. When the data are plotted as in Figure 1, the same bell-shaped curves result except for a displacement to low temperature. The best fit is obtained when the slope of the $1/\tau$ line is the same as is Figure 1.

TABLE I

EFFECT OF NaOH ON THE RELAXATION RATE OF 50.5 mM $Ni(NO_3)_2$ IN 7.2 M NH_3

[NaOH] = 0.103 M		[NaOH] = 0.326 M	
$1000/T$, °K^{-1}	$10^{-3}/PT_{2p}$, sec^{-1}	$1000/T$, °K^{-1}	$10^{-3}/PT_{2p}$ sec^{-1}
3.00	7.7		
3.10	9.5		
3.12	11.0		
3.16	12.1		
3.27	17.1	3.27	13.8
3.29	18.2		
3.40	26.5	3.41	20.7
3.47	28.2	3.47	26.5
3.54	27.0	3.54	27.3
3.63	20.7	3.65	26.2
3.73	13.7	3.71	18.6
3.78	10.3		
3.83	8.3	3.84	9.2
3.91	5.6	3.94	5.8

The exchange rates are

$$\log (1/\tau) = 13.53 - (2610/T) \quad \text{(no NaOH)} \tag{8}$$

$$\log (1/\tau) = 13.79 - (2610/T) \quad (0.103\ M\ \text{NaOH}) \tag{9}$$

$$\log (1/\tau) = 13.97 - (2610/T) \quad (0.326\ M\ \text{NaOH}) \tag{10}$$

The rate increase is probably not caused by the abstraction of protons. The following interpretations were considered.

(1) Complexes such as $Ni(NH_3)_5OH^+$ are formed. The NH_3 molecules of this complex are more labile than in $Ni(NH_3)_6^{2+}$. Indeed a precipitate occurs at temperatures above 45° in the solution containing 0.33 M NaOH. However, the solutions have the same light absorption spectra at room temperature, regardless of the NaOH concentration. This is still consistent with an OH^--substituted complex, since the absorption spectra probably are not affected much by the substitution.

(2) The OH^- forms ion pairs with $Ni(NH_3)_6^{2+}$, and these might have a different rate of ammonia exchange. If so, one would expect that SO_4^{2-} would have a more drastic effect than OH^-. This is not the case, as seen in Figure 1.

(3) Two competing exchange reactions occur. The rate-determining steps are the substitution of NH_3 by, respectively, H_2O and OH^-. The activation energy is 11.9 kcal for both reactions. This explains the data, but it is surprising that both reactions have the same activation energy.

(4) The OH^- abstracts individual protons from the complex. Hunt[20] has made some preliminary studies of the effect of 0.1 M NaOH on the ^{14}N nmr resonance and finds a large increase in line width. This shows that OH^- catalyzes the exchange of NH_3 molecules.

The first interpretation fits the data well and is probably the correct one. It is difficult to compare rates determined by nmr with those determined by other methods.[21] Therefore, it is gratifying that ^1H and ^{14}N nmr give the same result. This substantiates further the reliability of the nmr method.

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[19] D. R. Eaton, W. D. Phillips, and D. J. Caldwell, *ibid.*, **85**, 397 (1963).

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[21] H. S. Gutowsky, J. Jones, and T. H. Siddall, III, *J. Am. Chem. Soc.*, **89**, 4300 (1967).