taking account of the different numbers of oxalate groups in the various species. This intensity enhancement in the complexes is not easily explained by simple models. It must involve severe interactions between adjacent bonds. The enhancement for the complexes can come about through coupling either with C–C or with M–O. A normal coordinate analysis of oxalate complexes[15] shows that coupling with C–C is considerable. In fact, the intensity of the *ca.* 900-cm^{-1} band (usually assigned as approximately C–C stretching) is lower in the complexes than in free oxalate. Coordination of the oxalate might enhance this coupling through changing the geometry of the oxalate from D_{2d} when free in solution[16] to something more nearly planar in the complex. Consistent with this is the result for dimethyl oxalate which shows an enhancement of the intensity in the two polarized bands and which has been assigned a structure intermediate between staggered and eclipsed.[17] In any case, the intensity coupling between oxalate modes and the metal–oxalate modes is apparently small and there is a significant difference between metal–oxygen bonding in oxalate complexes and in acetylacetonate complexes.[9]

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Proton Magnetic Resonance Studies of the Acetonitrile Complexes of Cobalt(II) and Nickel(II) in Acetonitrile Solutions

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Received October 25, 1966

The transverse relaxation rates and the chemical shifts of the bulk solvent protons in acetonitrile solutions of the complexes $Co(CH_3CN)_6^{2+}$ and $Ni(CH_3CN)_6^{2+}$ have been measured at 100 and 60 Mc. From the temperature dependence of the relaxation rates, the parameters k_1 (sec^{-1} at 25°), $\Delta H^{\ddagger}$ (kcal), and $\Delta S^{\ddagger}$ (eu) were calculated for the rate of exchange of acetonitrile between the bulk solvent and the Co(II) and Ni(II) complexes, respectively: 1.4×10^5, 8.1, -7.5; and 3.9×10^3, 10.9, -8.8. The coupling constants, A/h (cps), calculated from the chemical shifts are -2.28×10^4 for the Co(II) complex and -2.63×10^5 for that of Ni(II). It was found that only a single metal ion–solvent complex need be invoked to account for the data obtained over the complete range of temperatures, -45 to $+79°$. At temperatures below $-35°$, the proton nmr signal of acetonitrile in the first coordination sphere of Co(II) was distinguished From the relative intensity of this signal the primary solvation number, 5.7 ± 0.3, was calculated. The chemical shifts and transverse relaxation rates of the protons in the primary coordination sphere of Co(II) are consistent with those calculated from the data obtained for the bulk solvent protons.

Introduction

In conjunction with a general study of the kinetic and structural aspects of metal ion solvation in nonaqueous solvents, we have extended our proton nmr measurements of the rates of solvent exchange between the primary coordination spheres of metal ions and the free solvent to the solutions of $Co(ClO_4)_2$ and $Ni(ClO_4)_2$ in acetonitrile. The application of this nmr technique to the study of the kinetics and stoichiometry of solvation in a variety of systems has been discussed elsewhere.[2]

One important question concerning the nature of the metal ion–solvent interaction which has arisen is that even if metal ion–solvent complexes can be kinetically distinguished, does a *single* complex exist over the accessible range of temperature and solution compositions in a given system or does an equilibrium exist among kinetically distinguishable complexes of different coordination numbers and geometries?[3] Although the range of systems investigated by the nmr technique is limited, it is interesting, and somewhat surprising, that to account for the nmr relaxation data in a variety of systems, it is only necessary to invoke a single metal ion–solvent complex. These systems include, for example: $M(CH_3OH)_6^{2+}$ in CH_3OH,[4] $M(DMF)_6^{2+}$ in DMF,[2] $Al(DMSO)_6^{3+}$ in DMSO,[5] $Al(DMF)_6^{3+}$ in DMF,[6] $Mg(H_2O)_6^{2+}$ in aqueous acetone,[7] $Mg(CH_3OH)_6^{2+}$ in CH_3OH,[7] $Al(H_2O)_6^{3+}$ and $Be(H_2O)_4^{2+}$ in water,[8] and $Ni(NH_3)_6^{2+}$ in liquid ammonia[9,10] (where M is Co^{2+} and Ni^{2+}, DMSO is dimethyl sulfoxide, and DMF is N,N-dimethylformamide). The data obtained from more inert systems

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amenable to convenient study by the isotope dilution technique, $\mathrm{Cr(OH_{26})^{3+}}$[11] and $\mathrm{Rh(OH_2)_6^{3+}}$[12] in water, can also be interpreted in terms of a single, kinetically well-defined metal ion–solvent complex.

In a few cases, the nmr data apparently require the presence of more than one cation–solvent complex. Swift and Connick[13] proposed an octahedral–tetrahedral transformation, $\mathrm{Co(OH_2)_6^{2+} \rightarrow Co(OH_2)_4^{2+}}$, to account for the relaxation of the ^{17}O nucleus in the aqueous solution of $\mathrm{Co^{2+}}$ at elevated temperatures. This coordination number change was confirmed by Swift in a study of the relaxation times of aqueous solutions of Co(II) using the temperature-jump technique.[14] In the latter study, a coordination number change for the zinc ion–water complex was also detected. The nonintegral solvation numbers calculated for the alkaline earth and zinc family ions from the change these ions induce in the proton line widths of aqueous solutions of $\mathrm{Mn(NO_3)_2}$ indicate that the ions may exist in aqueous solution as mixtures of at least two distinct hydrated forms.[15]

We chose to study the acetonitrile solutions of $\mathrm{Ni(ClO_4)_2}$ and $\mathrm{Co(ClO_4)_2}$ partially because of the interest in acetonitrile as a versatile solvent.[16] Also it appeared that the metal ions in these systems might exist in more than one solvated form and allow a convenient study of the kinetics and thermodynamics of solvation number changes in solution. Wickenden and Krause[17] have reported that the following transformations of the solid complexes readily take place: $\mathrm{Ni(CH_3CN)_6(ClO_4)_2 \rightarrow Ni(CH_3CN)_4(ClO_4)_2 \rightarrow Ni(CH_3CN)_2(ClO_4)_2}$. Despite the facility with which coordinated acetonitrile can be removed from the first coordination sphere of $\mathrm{Ni^{2+}}$ in the solid complexes, the nmr data we report here are consistent with the existence of a sole complex, $\mathrm{M(CH_3CN)_6^{2+}}$, over a wide range of solution compositions and temperatures.

Experimental Section

Materials.—Fisher reagent grade acetonitrile was distilled from $\mathrm{P_2O_5}$ three times and the middle fraction retained, which was stored over Linde 3A Molecular Sieves, was shown to be free of volatile contaminants by vapor phase chromatographic analysis (concentration limit for the detection of water, 10^{-4} *M*). Fisher reagent grade $\mathrm{Ni(H_2O)_6(ClO_4)_2}$ and $\mathrm{Co(H_2O)_6(ClO_4)_2}$ were recrystallized from water and dried at room temperature *in vacuo*.

Preparation of the $\mathrm{M(CH_3CN)_6(ClO_4)_2}$ Complexes.—To 0.01 mole of the hexahydrate, $\mathrm{M(ClO_4)_2 \cdot 6H_2O}$ (M represents $\mathrm{Co^{2+}}$ or $\mathrm{Ni^{2+}}$), was added 0.12 mole of dimethoxypropane (Dow Chemical Co.). After the mixture had been agitated for 1 hr, 0.24 mole of acetonitrile was added and the complex was precipitated from the resulting solution by the addition of a large excess of dry diethyl ether. The solid obtained was treated for 1 hr with a slurry of $\mathrm{P_2O_5}$ in acetonitrile, following which the resulting mixture was filtered and the complex was precipitated from the filtrate by the addition of diethyl ether. The resulting solid was recrystallized from acetonitrile alone, and the product was "dried" for 1 hr *in vacuo* at 25°.

Anal. Calcd for $\mathrm{Co(CH_3CN)_6(ClO_4)_2}$: Co, 11.7; $\mathrm{ClO_4}$, 39.5. Found:[18] Co, 12 0; $\mathrm{ClO_4}$, 39.3. Calcd for $\mathrm{Ni(CH_3CN)_6(ClO_4)_2}$: Ni, 11.7, $\mathrm{ClO_4}$, 39.5. Found:[18] Ni, 11.6; $\mathrm{ClO_4}$, 39.4.

The water content of the complexes was found to be less than 0.05 mole of $\mathrm{H_2O}$ per mole of $\mathrm{Co^{2+}}$ and 0.1 mole of $\mathrm{H_2O}$ per mole of $\mathrm{Ni^{2+}}$, by titration with the Karl Fischer reagent. Since the proton nmr spectra of concentrated solutions of the complexes in acetonitrile exhibited no water peaks at a variety of temperatures and since only a single methyl peak arising from $\mathrm{CH_3CN}$ in the first coordination sphere of cobalt could be detected in the $\mathrm{Co(ClO_4)_2}$ solutions, it is assumed that, if water is present in the more dilute solutions used for the measurements reported here, it has a negligible effect on the data.[22]

Solutions of the complexes for the nmr measurements were prepared by weight using vessels which had been baked at 120° and then flushed with dry nitrogen. All transfers were completed under an anhydrous nitrogen atmosphere and the nmr tubes were sealed after the solutions had been prepared.

Measurements.—Proton nmr spectra were obtained at 60 Mc using a Varian A-60 spectrometer and at 100 Mc using a Varian HA-100 spectrometer operated in the HR mode. Each spectrometer was equipped with a variable-temperature probe and the Varian variable-temperature control system, V-6057. The systems were calibrated and the measurements obtained in the manner described previously.[2] The chemical shifts were measured relative to the internal standard toluene (2% by volume) and were reproducible to within ±1 cps. The line widths were reproducible to within the larger of the two values, ±0.2 cps or ±1%.

Results and Discussion

(1) **Solvation Number of Co(II).**—Several 100-Mc proton nmr spectra obtained at low temperatures using an acetonitrile solution of $\mathrm{Co(ClO_4)_2}$ are reproduced in Figure 1. The low-field signal was recorded at a lower recorder input level than the high-field one. The high-field signal of low intensity is assigned to the protons in the primary coordination sphere of Co(II) and the other to the protons of the "free" solvent. No additional signals, other than those attributable to ^{13}C–H interactions, could be detected in the spectra over a 10,000-cps sweep range, employing a variety of radiofrequency power levels, sweep rates, and amplifier gain settings (see footnote 22).

For a solution having a known concentration of cobalt, the solvation number n of cobalt in the complex, $\mathrm{Co(CH_3CN)_n^{2+}}$, is readily calculated from the ratio of the areas of the high- and low-field signals. The areas were obtained by manual integration, but since the amplitudes of the signals differ appreciably for the solutions of interest, it was not possible to record them at the same recorder input level and obtain an accurate area for both. Instead, for each determination, a calibration curve of signal area *vs.* recorder input level was constructed. From these linear correlation plots

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(22) A study in progress in this laboratory indicates that in acetonitrile solutions containing more than 1 mole of water per mole of $\mathrm{Co(ClO_4)_2}$, it is possible to distinguish proton nmr signals arising from "free" water and the complexes: $\mathrm{Co(CH_3CN)_6^{2+}}$, $\mathrm{Co(H_2O)(CH_3CN)_5^{2+}}$, and $\mathrm{Co(H_2O)_2(CH_3CN)_4^{2+}}$. Although the aquoacetonitrile complexes are more labile than $\mathrm{Co(CH_3CN)_6^{2+}}$, the presence of free water in the solution exerts a negligible effect on the rate of solvent exchange of $\mathrm{Co(CH_3CN)_6^{2+}}$.

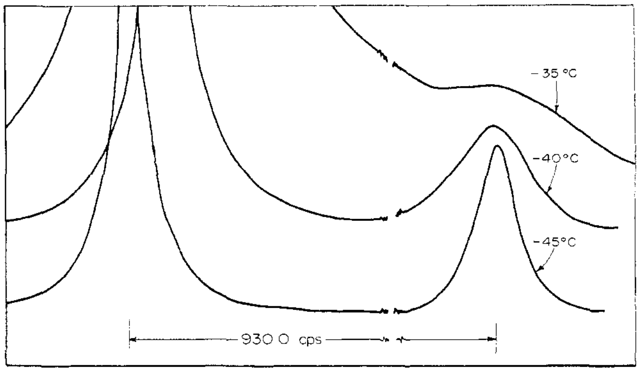

Figure 1.—Proton nmr spectra of an acetonitrile solution of $Co(ClO_4)_2$, P_{Co} = 0.0752, as a function of temperature at 100 Mc. The magnetic field increases from left to right.

the ratio of the areas was obtained at a common input level. The average primary solvation number calculated from data obtained using four different solutions in which the mole ratio, Co(II)/acetonitrile, was varied from 0.0032 to 0.0247 is 5.7 ± 0.3 at each of the temperatures: −45, −40, and −35°. No consistent trend of the calculated solvation number was discernible with either the temperature or the solution composition. The rather wide error limits can be attributed in large part to the errors in the indirect method for evaluating the ratios of areas.

These data then are consistent with a primary solvation number of six for Co(II) in acetonitrile solutions at low temperatures. The proton relaxation data to be discussed below indicate that this primary solvation number is maintained at the higher temperatures and that the six solvent molecules are kinetically equivalent, as expected if the symmetry about Co(II) is the regular octahedral one deduced from the visible spectra of Co^{2+} in acetonitrile solutions.[23] The existence of an equilibrium between the predominant species, $Co(CH_3CN)_6^{2+}$, and complexes of higher and/or lower solvation numbers (*e.g.*, $Co(CH_3CN)_5^{2+}$ or $Co(CH_3CN)_5ClO_4^{+}$) cannot be excluded but these complexes, if present, must exert a negligible effect on the nmr data, within the limits of our errors.

For example, in Table I are collected the chemical shifts and line widths obtained at 100 Mc for the proton nmr signals of the complex $Co(CH_3CN)_6^{2+}$. The chemical shifts of the acetonitrile molecules in the primary coordination sphere of Co(II), when corrected to 60 Mc, conform to the plot of *bulk* solvent chemical shift *vs.* temperature that applies to this system for the higher temperatures at which the exchange of acetonitrile between the free solvent and the coordination sphere is rapid (see Figure 3 and the discussion relating to it). In this rapid chemical exchange limit only a single acetonitrile resonance, shifted from the position of the free solvent resonance by a "contact" interaction[24,25] with Co(II), is distinguishable. In the calculation of this contact shift, it is assumed that six kinetically equivalent groups are coordinated to Co(II).

TABLE I

TEMPERATURE DEPENDENCE OF THE PROTON CHEMICAL SHIFTS AND LINE WIDTHS OF THE COMPLEX, $Co(CH_3CN)_6^{2+}$

$10^3/T$, °K^{-1}	P_{Co}[a]	δ[b] (100 Mc)	δ[c] (60 Mc)	$\Delta\nu_0$[d]
4.39	0.01918	941.	565.	108.
4.39	0.0752	930.	558.	107.
4.39	0.1482	930:	558.	107.
4.34	0.01918	884.	530.	131.
4.34	0.0752	892.	535.	129.
4.29	0.01918	870.	522.	138.
4.29	0.0752	860.	515.	139.
4.20	0.01918	. . .	. . .	185.
4.20	0.0752	790.	475.	187.

[a] Composition of the solution in terms of the ratio, moles of coordinated acetonitrile: total number of moles of acetonitrile. [b] Chemical shift observed at 100 Mc for the protons in $Co(CH_3CN)_6^{2+}$ with respect to those of free acetonitrile in the same solution, cps. [c] δ (100 Mc) adjusted to 60 Mc. [d] Line width, cps, of the protons in $Co(CH_3CN)_6^{2+}$ observed at 100 Mc.

It should also be possible to confirm the equivalence of the species present at the low and high temperatures by demonstrating that the rate constants for chemical change calculated from the line widths of $Co(CH_3CN)_6^{2+}$ at the lower temperatures and of the bulk solvent at the higher ones are the same. Under the conditions of slow chemical exchange (of CH_3CN between $Co(CH_3CN)_6^{2+}$ and the free solvent) which apply to the data in Table I, the widths of the proton nmr lines of $Co(CH_3CN)_6^{2+}$ are given by the equation[26,27]

$$\pi\Delta\nu = \frac{1}{T_{2P}} = \frac{1}{T_{2M}} + \frac{1}{\tau_M} \tag{1}$$

in which $\Delta\nu$ is the full width of the line at one-half the maximum amplitude, $1/T_{2P}$ is the observed transverse relaxation rate, $1/T_{2M}$ is the transverse relaxation rate of the proton in $Co(CH_3CN)_6^{2+}$, and τ_M is the mean lifetime of the complex, $Co(CH_3CN)_6^{2+}$. Although the large apparent Arhenius activation energy, +7.9 kcal, associated with the temperature dependence of the line widths, $\Delta\nu_0$, contained in Table I is characteristic of a process dependent upon τ_M, it is not possible to directly evaluate τ_M since T_{2M} itself is not known. Since the solvent freezes below −45°, data could not be obtained at temperatures low enough that a process dependent upon T_{2M} alone controls the proton relaxation.

(2) **Relaxation of the Bulk Solvent Protons in Acetonitrile Solutions of $Co(ClO_4)_2$ and $Ni(ClO_4)_2$.**—The temperature dependence of the line broadening of the bulk solvent protons can be conveniently analyzed using the equations developed by Swift and Connick.[13] For the exchange of CH_3CN between the free solvent and the complex, $M(CH_3CN)_6^{2+}$, the applicable equations are

$$\pi\Delta\nu = \frac{1}{T_{2P}} = (\tau_f)^{-1}\frac{(1/T_{2M})^2 + (1/T_{2M}\tau_M) + \Delta\omega_M{}^2}{(1/T_{2M} + 1/\tau_M)^2 + \Delta\omega_M{}^2} \tag{2}$$

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$$\Delta\omega = \frac{P_M \Delta\omega_M}{(\tau_M/T_{2M} + 1)^2(\tau_M \Delta\omega_M)^2} \tag{3}$$

where τ_f is the mean lifetime of CH_3CN in the free solvent, $\Delta\omega$ is the contact chemical shift of the bulk solvent protons, P_M is the fraction of the total number of solvent molecules bonded in the complex $M(CH_3CN)_6^{2+}$, $\Delta\omega_M$ is the chemical shift of the protons in $M(CH_3CN)_6^{2+}$ with respect to those in the free solvent, and the remaining terms have been defined in context with eq 1.[28] Two limiting conditions applied to eq 2 and 3 are of interest with respect to the data we have obtained: (1) Relaxation occurs rapidly by means of a large change in the precessional frequency of the protons in CH_3CN undergoing exchange and $1/T_{2P}$ is controlled by the rate of chemical exchange.

$$\frac{1}{T_{2P}} = \frac{P_M}{\tau_M} = \frac{1}{\tau_f} \tag{4}$$

if $\Delta\omega_M^2 >> (1/T_{2M})^2, (1/\tau_M)^2$. (2) Chemical exchange is rapid and $1/T_{2P}$ is controlled by the rate of relaxation through the change in the precessional frequency of the protons.

$$\frac{1}{T_{2P}} = P_M \tau_M \Delta\omega_M^2 \tag{5}$$

$$\Delta\omega = P_M \Delta\omega_M \tag{6}$$

if $(1/\tau_M)^2 >> \Delta\omega_M^2 >> 1/T_{2M}\tau_M$. The variation of τ_M with temperature is given by

$$\frac{1}{\tau_M} = k_1 = \frac{kT}{h} e^{(\Delta S^{\ddagger}/R) - (\Delta H^{\ddagger}/RT)} \tag{7}$$

In Figure 2, the temperature dependence of $(P_{Co} \cdot T_{2P})^{-1}$ for the protons of acetonitrile solutions of $Co(ClO_4)_2$ is summarized. The plot was constructed using data obtained at 100 and 60 Mc with eight independent solutions in which the concentration of Co^{2+} was systematically varied between the limits, $6.76 \times 10^{-3} \leqslant P_{Co} \leqslant 7.52 \times 10^{-2}$. The variation of $(P_{Co} \cdot T_{2P})^{-1}$ suggests that two distinct processes contribute to the relaxation. Because the low-temperature data, $4.15 < 10^3/T < 4.5$, are independent of the frequency and exhibit a large positive Arrhenius activation energy, +8.7 kcal, the relaxation rate should be chemical exchange controlled and conform to eq 4 and 7. The high-temperature data ($10^3/T < 4.1$) which exhibit a large *negative* activation energy, −9.2 kcal, fulfill the conditions for which the relaxation rate is limited by the change of the precessional frequency of the protons and conforms to eq 5. For a given temperature, the ratio of the relaxation rates obtained at 60 and 100 Mc, 0.32 ± 0.04, is in acceptable agreement with that required by eq 5: $(60/100)^2$ or 0.36. In addition the conditions leading to eq 5 also require that the chemical shifts, $\Delta\omega$, conform to eq 6 and exhibit a temperature dependence given by the Bloembergen equation[29]

$$\frac{\Delta\omega_M}{\omega} = -\frac{A\mu_{eff}\sqrt{S(S+1)}\beta}{3kT\gamma_I} \tag{8}$$

where ω is the frequency (60 Mc) at which the "contact" chemical shift ($\Delta\omega_M$) is observed, A/h is the coupling constant for the contact interaction, S is the electron spin of Co(II), μ_{eff} is the effective magnetic moment, 5.2 BM,[23] of Co(II) in $Co(CH_3CN)_6^{2+}$, γ_I is the proton magnetogyric ratio, and β is the Bohr magneton. It is evident from an inspection of Figure 3, in which both the bulk solvent ($\Delta\omega/P_M 2\pi$) and coordinated solvent ($\Delta\omega_M/2\pi$) chemical shifts are plotted as a function of the temperature, that these requirements are satisfied. The bulk solvent shifts were obtained using four independent solutions in which the composition was varied between the limits, $7.5 \times 10^{-3} \leqslant P_{Co} \leqslant 8.0 \times 10^{-2}$. As discussed previously, P_{Co} is calculated assuming a primary coordination number of six for Co(II).

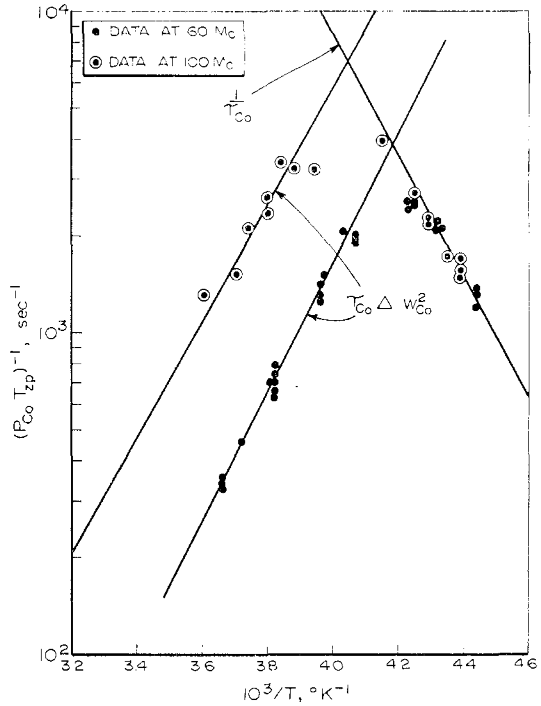

Figure 2.—Temperature dependence of $(P_{Co}T_{2P})^{-1}$ for the methyl proton in acetonitrile solutions of $Co(ClO_4)_2$.

The temperature variation of $(P_{Ni}T_{2P})^{-1}$ summarized in Figure 4 can be analyzed in a similar fashion. The measurements were obtained using four solutions in which the concentration of Ni^{2+} was varied between the limits, $2.68 \times 10^{-3} \leqslant P_{Ni} \leqslant 7.29 \times 10^{-2}$. The high-temperature data, $10^3/T < 3.1$, can be fitted to a straight line whose slope corresponds to the large negative Arrhenius activation energy, −12.4 kcal. At the higher temperatures then the relaxation rates should conform to eq 5 and 7. Correspondingly, the relaxation rates in the temperature range $3.3 \leqslant 10^3/T \leqslant 3.64$

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[28] $(T_{2P})^{-1}$ should be corrected for the "outer-sphere" exchange and dipolar contributions to the observed line widths. At the concentrations of $M(ClO_4)_2$ discussed here these effects are negligible. All values of $(T_{2P})^{-1}$ were corrected, however, by subtracting the $(T_{2P})^{-1}$ values obtained for the pure solvent (2.0 ± 0.3π radians sec^{-1}) over the complete range of temperatures studied.

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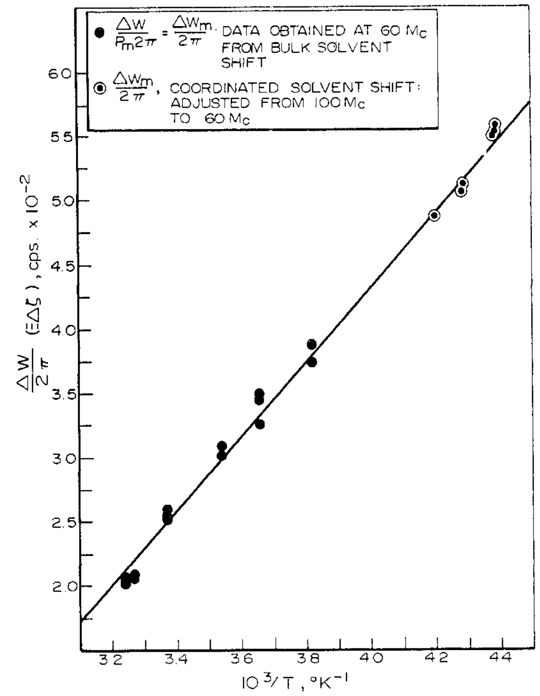

Figure 3.—Temperature dependence of the bulk solvent and coordinated solvent chemical shifts in acetonitrile solutions of $Co(ClO_4)_2$.

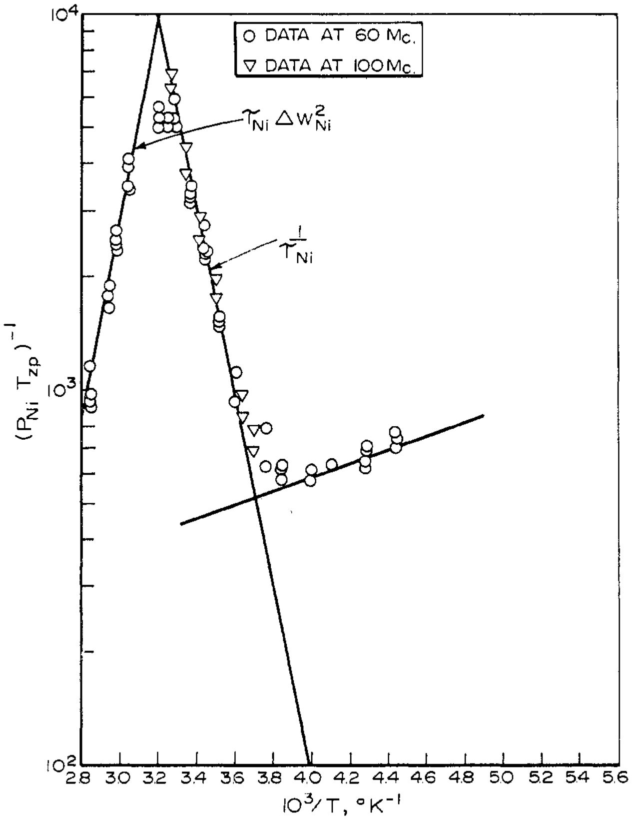

Figure 4.—Temperature dependence of $(P_{Ni}T_{2P})^{-1}$ for the methyl proton in acetonitrile solutions of $Ni(ClO_4)_2$.

exhibit a large positive activation energy (+11.5 kcal), are independent of the frequency, and should conform to eq 4 and 7.

Although the measurements at 100 Mc were not extended above 30° ($10^3/T$ = 3.3) for the $Ni(ClO_4)_2$ solutions, a confirmation of the mechanism for the relaxation of the bulk solvent protons at the high temperatures is obtained by comparing the chemical shifts, $\Delta\omega_M$, calculated using eq 4 and 7 and those ($\Delta\omega$) measured. Fitting the lower temperature data to eq 4 and the higher to eq 5 requires that, at the temperature $10^3/T = 2.9$, $\Delta\omega_M$ have the value 9.33×10^3 radians sec^{-1} at 60 Mc, and that the bulk solvent chemical shift ($\Delta\omega$) be given by eq 6 at temperatures $10^3/T \leq 2.9$. Applying eq 6 to the chemical shifts ($\Delta\omega$) measured at 60 Mc using solutions having the same compositions as those employed for the relaxation studies results in the values of $\Delta\omega_M = 9.4 \pm 0.2 \times 10^3$ radians sec^{-1} at $10^3/T = 2.9$ and $\Delta\omega_M = 9.0 \pm 0.2 \times 10^3$ radians sec^{-1} at $10^3/T = 2.8$. The volatility of the solvent precluded an extension of these measurements to higher temperatures.

There is an additional process which contributes to the relaxation of the bulk solvent protons in the solutions of $Ni(ClO_4)_2$. At temperatures $10^3/T \geqslant 4.0$, the relaxation rates can be fitted to a straight line which corresponds to the apparent activation energy, −0.9 kcal. In this temperature range, the relaxation is probably controlled by a dipole–dipole interaction between the paramagnetic ion and the acetonitrile molecules outside the first coordination sphere. The correlation time for the relaxation should be the electron spin relaxation time of Ni^{2+}. Consistent with this interpretation is the low activation energy for the process which has also been observed in the $Ni(ClO_4)_2$–DMF[2] and $Ni(ClO_4)_2$–CH_3OH[4] systems.

The chemical exchange parameters calculated from the lines fitted to the data in Figures 2 and 4 are listed in Table II, which also includes the coupling constants, A/h. The value of A/h for the cobalt complex at 25° was calculated from the line in Figure 3 using eq 8 and the measured value of μ_{eff}, 5.2 BM.[23] The coupling constant for the $Ni(CH_3CN)_6^{2+}$ complex was calculated using eq 8 and the value of $\Delta\omega_M$ obtained at the temperature $10^3/T = 2.9$, together with the measured value of μ_{eff}, 3.15 BM.[17]

(3) **General Discussion.**—As discussed above the data obtained for the $Co(ClO_4)_2$–acetonitrile solutions established that the primary solvation number of Co(II) in these solutions is six over a wide range of temperatures. The interpretation of the data for the $Ni(ClO_4)_2$ solutions is less straightforward. Although the temperature dependence of the relaxation rates and chemical shifts is consistent with the existence of a single Ni(II)–acetonitrile complex over the complete range of temperatures studied, the coordination number of Ni(II) in the complex cannot be determined from the nmr data alone. We have assumed that it is six because the analysis of the electronic absorption spectrum of Ni(II) in acetonitrile strongly suggests that there is a regular octahedral ligand field about the Ni(II) ion in these solutions.[17] However, this assumption may be open to some question in view of the rather surprising results obtained by Connick and Fiat[30]

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(30) R. E. Connick and D. N. Fiat, *J. Chem. Phys.*, **44**, 4103 (1966).

TABLE II

COUPLING CONSTANTS AND RATE PARAMETERS FOR SOLVENT EXCHANGE IN THE COMPLEXES, $M(CH_3CN)_6{}^{2+}$

	M	
	Co	Ni
k_1 (sec^{-1} at 25°)	1.4×10^5	3.9×10^3
$\Delta H^{\ddagger}$ (kcal) $\pm$ 0.5	8.1	10.9
$\Delta S^{\ddagger}$ (cal deg^{-1} $mole^{-1}$) $\pm$ 2	−7.5	−8.8
A/h (cps)	-2.28×10^4	-2.63×10^5

in their ^{17}O nmr study of aqueous solutions of $Ni(ClO_4)_2$.

In that study a separate ^{17}O nmr signal was observed for water in the primary coordination sphere of Ni(II). A comparison of the chemical shifts observed for the coordinated water signal and those calculated from the relaxation rates of the bulk solvent revealed that the primary solvation number of the Ni(II) ion in aqueous solutions may actually be *four* rather than six as inferred from the electronic absorption spectrum.[31-33] It is of some interest whether an accurate coordination number in the aqueous system can be evaluated from the integrated intensity of the coordinated water ^{17}O signal in solutions more highly enriched in ^{17}O. Unfortunately, we could not detect the proton nmr signal of acetonitrile coordinated to the Ni^{2+} using high-resolution spectrometers, but the studies are being continued using broad-line techniques.

The *negative* coupling constants, A/h, obtained for the contact interaction between the electron and nuclear spins in both the acetonitrile complexes require that the protons acquire negative spin density as a consequence of the contact interaction. If provisionally we assume that both complexes are octahedral and further that anisotropic contributions to the A/h values are negligible,[34] then the negative coupling constants observed for both complexes strongly suggest that the ligand protons acquire spin density principally *via* the σ-bonding orbitals of the metal ion. In the bond between the metal ion and acetonitrile, the nitrogen lone-pair orbital containing two paired electrons overlaps with the two metal ion σ or e_g orbitals. Since, in the e_g orbitals, each metal ion incorporates two unpaired electrons having a net spin polarization in the same direction as the applied field, any covalence in the metal ion–ligand interaction will favor the transfer to the ion of a lone-pair electron whose spin is opposed to the field. Consequently, the nitrogen lone-pair orbital will acquire a slight excess of electron spin having the same direction as the applied field, that is positive spin density.

Through spin correlation effects[37] this positive spin density at the nitrogen atom could induce negative spin density at the hydrogen atoms. An alternative and perhaps more reasonable process[38,39] for delocalizing the spin involves a σ–π configuration interaction in which the positive spin density in the nitrogen σ orbitals induces negative spin density in the filled π orbitals at the nitrile carbon atom. Delocalization of the negative spin density to the hydrogen atoms can then be accounted for *via* hyperconjugation.[38-40] The two other reasonable σ-bonding mechanisms which may be operative in some metal ion–ligand systems[25,37] apparently do not apply here for they require positive spin density at the hydrogen atoms: (1) a direct overlap of the hydrogen atom orbitals with those of the metal ion; or (2) the overlap of the metal ion e_g orbitals with a ligand orbital whose wave function incorporates at least a slight contribution from every atom in the ligand molecule.

The ratio of the value of the $Ni(CH_3CN)_6{}^{2+}$ coupling constant to that for $Co(CH_3CN)_6{}^{2+}$, 11.5, is rather large compared to the ratios, 1–3, obtained for other octahedral complexes in which delocalization occurs primarily *via* a σ-bonding interaction.[2,4,25] The comparison suggests that, in the $Co(CH_3CN)_6{}^{2+}$ complex, a delocalization process competes with that discussed above to place positive spin density at the hydrogen atoms. The t_{2g} orbitals of the Co^{2+} ion contain an unpaired electron whose moment is aligned with the applied field and have the proper symmetry to overlap the vacant π^* orbital of the nitrile groups. This t_{2g}–π^* overlap should transfer positive spin density to the nitrile carbon atom and, through hyperconjugation, should lead to positive spin density at the hydrogen atoms. The competing effects may account for the apparent reduction of A/h for the Co(II) complex with respect to that for the Ni(II) complex which having all electrons paired in the t_{2g} level cannot delocalize spin directly[41] into the ligand π orbitals. The overlap of the t_{2g} and π^* orbitals can also be invoked to account for the Dq value of acetonitrile, which appears anomalously large in the correlation between ligand donor strength and Dq value.[42]

The more rapid rate of the solvent substitution reaction of $Co(CH_3CN)_6{}^{2+}$ relative to that for the Ni(II)

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(31) O. Schmitz-Dumont, H. Gössling, and H. Brokopf, *Z. Anorg. Allgem. Chem.*, **300**, 157 (1959).

(32) O. G. Holmes and D. S. McClure, *J. Chem. Phys.*, **26**, 1686 (1957).

(33) A. D. Liehr and C. J. Ballhausen, *Ann. Phys.* (N.Y.), **2**, 134 (1959).

(34) The anisotropic or pseudo-contact contributions[35] to the chemical shifts and A/h values arise from anisotropy in the electronic g tensor. Since the electronic ground state of an octahedral Ni(II) complex is orbitally nondegenerate, the g value should be nearly isotropic and the psuedo-contact shift should be negligible. However, it has been found that octahedral crystalline compounds of Co(II) generally have positive values of $g_{\parallel} - g_{\perp}$.[36] In the complex $Co(CH_3CN)_6{}^{2+}$, this g value anisotropy should lead to a small positive pseudo-contact shift and a negative contribution to A/h. Inclusion of this contribution should not affect the qualitative arguments advanced above.

(35) H. M. McConnell and R. E. Robertson, *J. Chem. Phys.*, **29**, 1361 (1958), and references therein.

(36) G. E. Pake, "Paramagnetic Resonance," W. A. Benjamin, Inc., New York, N. Y., 1962.

(37) R. S. Milner and L. Pratt, *Discussions Faraday Soc.*, **34**, 88 (1962).

(38) J. P. Colpa and E. DeBoer, *Mol. Phys.*, **7**, 333 (1964).

(39) W. T. Dixon, *ibid.*, **9**, 201 (1965).

(40) D. B. Chestnut, *J. Chem. Phys.*, **29**, 431 (1958).

(41) Overlap of the Ni^{2+} t_{2g} orbitals with the ligand π^* orbitals might produce *negative* spin density at the hydrogen atoms *indirectly via* t_{2g}–e_g configuration interactions which would stabilize configurations incorporating positive spin density in the t_{2g} level. Although such interactions alone can be invoked to account for the negative coupling constant of $Ni(CH_3CN)_6{}^{2+}$, they should be much less effective than the t_{2g}–π^* overlap mechanism for distributing *positive* spin density to the hydrogen atoms in the analogous Co(II) complex. Yet the coupling constant for the latter is *negative*. We conclude, therefore, that the σ delocalization process discussed above is the most important mechanism for delocalizing the spin density in both complexes.

(42) R. S. Drago and K. F. Purcell, "Coordinating Solvents," in "Non-Aqueous Solvent Systems," T. C. Waddington, Ed., Academic Press Inc., New York, N. Y., 1965, pp 217, 224.

complex arises largely from the difference in the activation enthalpies for the two reactions. This enhanced lability of octahedral Co(II) complexes with respect to those of Ni(II) has been noted for many other systems[2,4,10,13,43–45] and has been discussed in terms of crystal field theory.[45,46] The ambiguities in the crystal field interpretation have been considered elsewhere,[2,44] and a more critical evaluation of the factors affecting relative solvent substitution rates does not seem warranted until the appropriate data become available for a wider variety of cations, particularly those of the nontransition elements!

(43) M. Eigen, *Pure Appl. Chem.*, **6**, 97 (1963).

(44) J. S. Babiec Jr., C. H. Langford, and T. R. Stengle, *Inorg. Chem.*, **5**, 1362 (1966).

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

(46) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958.

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A Phosphorus-31 Nuclear Magnetic Resonance Study of Tertiary Phosphine Complexes of Platinum(II)[1]

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Received January 13, 1967

The phosphorus-31 nmr spectra of eleven *cis* and seven *trans* compounds of the type $(R_n(C_6H_5)_{3-n}P)_2PtCl_2$, where R = alkyl and *n* = 1, 2, or 3, show that the platinum-195 to phosphorus-31 coupling constant is always larger for the *cis* compound than for the corresponding *trans* compound and that the phosphorus chemical shift of the *cis* compound is upfield from that of the corresponding *trans* compound. The formation of the trisphosphine complex by addition of excess tertiary phosphine to the monomer has been demonstrated by conductivity and ^{31}P nmr measurements and confirmed by isolation of the compounds $[(CH_3(C_6H_5)_2P)_3PtCl]Cl$ and $[(C_3H_7(C_6H_5)_2P)_3PtCl]B(C_6H_5)_4$. The preparation of several new chlorine-bridged dimers is also reported.

Introduction

Pidcock, Richards, and Venanzi[2] reported in a brief note a few years ago that the ^{195}Pt–^{31}P coupling constant in *cis*-dichlorobis(tributylphosphine)platinum(II) is significantly larger than the coupling constant in the *trans* isomer. They also reported the coupling constants in various other phosphorus–platinum compounds, although no other *cis–trans* pairs were reported and chemical shifts were not cited.

The difference in coupling constants was ascribed to the increased π bonding between phosphorus and platinum in the *cis* case, in which the platinum can use d_{xz} and d_{yz} orbitals (in addition to in-plane π bonding by the d_{xy} orbital), as opposed to the *trans* case, in which platinum can use only the d_{xz} orbital (again, in addition to in-plane π bonding) with the x axis defined as the P–Pt–P direction. If this argument is correct, one would expect the phosphorus atoms in the *cis* compound to have a higher electron density than those in the *trans* isomer because of increased back donation by the electrons of the platinum d orbitals.

Results and Discussion

We have prepared pure *cis* isomers for eleven different tertiary phosphines and seven of the corresponding *trans* isomers as described in the Experimental Section. The phosphorus-31 nmr data are shown in Table I. For convenience, the coordination chemical shifts are listed in column 4. The coordination chemical shift is defined as the chemical shift (relative to any reference in general, but for this case relative to 85% H_3PO_4) of phosphorus in the complex compound minus the chemical shift (relative to the same reference) of phosphorus in the free ligand. This concept has been used before in several papers[3–6] on phosphorus coordination compounds.

The results in Table I substantiate the original observation[2] that the *cis*-tributylphosphine compound has a significantly larger coupling constant than the *trans* compound and show that this is true for all of the seven *cis–trans* pairs measured. In addition, the chemical shift of the *cis* isomer for a particular tertiary phosphine is always upfield from that of the *trans* isomer. This agrees with the simple shielding ideas outlined above, *i.e.*, a good σ donor on coordination produces a large downfield coordination chemical shift and increased metal to ligand π bonding produces an upfield coordination chemical shift. These ideas were discussed by Meriwether and Leto[3] in the first report on ^{31}P nmr of phosphorus coordination compounds. The results of ^{31}P studies of *trans*-$(R_3P)_3RhCl_3$ compounds[4] are opposite to those expected from the simple

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(1) Supported by the United States Air Force Office of Scientific Research under Grant No. AF-AFOSR-782-65.

(2) A. Pidcock, R. W. Richards, and L. M. Venanzi, *Proc. Chem. Soc.*, 184 (1962).

(3) L. S. Meriwether and J. R. Leto, *J. Am. Chem. Soc.*, **83**, 3192 (1961).

(4) S. O. Grim and R. A. Ference, *Inorg. Nucl. Chem. Letters*, **2**, 205 (1966).

(5) S. I. Shupack and B. Wagner, *Chem. Commun.*, 547 (1966).

(6) J. L. Burdett and L. L. Burger, *Can. J. Chem.*, **44**, 111 (1966).