35° in the sample holder of a Varian T-60 nmr spectrometer, and 2-methyl-2-chloro-3-butyne was injected through the septum. The tube was shaken and rapidly placed in the spectrometer probe. The reaction was followed for one second-order half-life and the second-order rate constant based on the best straight line through 10–15 points. The time required to sweep through the two peaks caused a systematic time error of 8 sec which was significant for the first few points. The average of five runs gave $k_2 = 5.15 \times 10^{-2}\ M^{-1}\ \mathrm{sec}^{-1}$ with a standard deviation of $0.8 \times 10^{-2}\ M^{-1}\ \mathrm{sec}^{-1}$.

Method B.—The disappearance of 1 was followed spectrophotometrically. At least a 15-fold excess of α-chloroacetylene was used and pseudo-first-order rate constants were determined from the slope of a plot of ln $(D_\infty - D_t)$ against time, where D_t is the absorbance at time t and D_∞ the absorbance after at least 10 half-lives. Absorption was measured at the peaks at both 440 and 387 nm. Ten milligrams of 1 was weighed into a small bottle fitted with a septum. The bottle was thoroughly flushed

with nitrogen and 1.5 ml of a solution of the α-chloroacetylene (*ca*. 0.2 M) in degassed benzene was injected. The bottle was shaken thoroughly and placed in a water bath held to within 0.1° of the stated temperature. Aliquots (100-μl) were taken at intervals and diluted to 1.6 ml with degassed benzene. The spectrum was taken in a 1.0-cm cell. Reactions were followed for 1–2 half-lives, and pseudo-first-order rate constants were based on the least-squares line through 5–10 points. Second-order rate constants (Table I) calculated from these values were satisfactorily independent of acetylene concentration.

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Nuclear Magnetic Resonance Line-Broadening Study of Cobalt(II) and Nickel(II) in Dimethyl Sulfoxide and Trimethyl Phosphate

BY N. S. ANGERMAN AND R. B. JORDAN

The effects of cobalt(II) and nickel(II) on the proton nmr of dimethyl sulfoxide (DMSO) and trimethyl phosphate (TMPA) have been studied. Chemical exchange controlled line broadening was found only for nickel(II) in DMSO, in which case the exchange rate is $4.2 \times 10^3\ \mathrm{sec}^{-1}$ at 25° with $\Delta H^{\pm} = 12.1\ (\pm 0.3)$ kcal mol^{-1} and $\Delta S^{\pm} = 1.3\ (\pm 0.5)$ eu. In all other cases the chemical exchange was too fast to measure and only dipolar line broadening was observed. Chemical shifts were measured in all cases. The hyperfine coupling constants (A/h) for Ni^{2+} in DMSO and TMPA are 7.50×10^4 and 7.16×10^3 Hz, and for Co^{2+} in DMSO, the constant is 2.08×10^4 Hz. The chemical shift for the Co^{2+}–TMPA system changes from positive to negative as the temperature decreases. This observation, combined with a spectrophotometric study, indicates an octahedral–tetrahedral equilibrium of the type Co(TMPA)$_4^{2+}$ + 2TMPA $\rightleftharpoons$ Co(TMPA)$_6^{2+}$. The position of this equilibrium does not permit the extinction coefficient or hyperfine coupling constant of the tetrahedral species to be determined with any certainty. However if an extinction coefficient of 500 is assumed for Co(TMPA)$_4^{2+}$, then a self-consistent fit of the temperature dependence of the absorbance, chemical shift, and line broadening can be obtained. The fit is far from unique however and a range of extinction coefficients from about 400 to 1200 would also fit the data. It has been found that the activation enthalpy for solvent exchange in a number of systems may be predicted by assuming that the activation enthalpy is made up of a general solvation term, which is constant for a given solvent and charge on the metal ion, and a crystal field contribution.

Introduction

The method of studying solvent-exchange rates by nmr line broadening has become widely used since the original work of Swift and Connick[1] on the water exchange rate of various transition metal ions. It is hoped that studies with several metal ions in a number of solvents will lead to an understanding of the factors controlling the exchange rate of solvent molecules from the inner coordination sphere of the metal ion. A number of studies of nmr line broadening by nickel(II), cobalt(II),[2–7] and vanadyl ion[8,9] have recently appeared

in the literature. The present study attempts to fill in some of the gaps so that comparisons can be made between these metal ions in a more extended range of solvents.

The results in dimethyl sulfoxide (DMSO) are an extension of previous results of Thomas and Reynolds.[7] Only the nickel(II) in DMSO system shows chemical-exchange control of the nmr line broadening and only upper or lower limits can be established for the exchange rates of cobalt(II) in DMSO and for both cobalt(II) and nickel(II) in trimethyl phosphate (TMPA). Interpretation of the chemical shift and visible spectral data for cobalt(II) in TMPA indicates the presence of an equilibrium mixture of tetrahedral and octahedral species.

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(2) Z. Luz and S. Meiboom, *ibid.*, **40**, 1058, 2686 (1964).
(3) H. Glaeser, H. W. Dodgen, and J. P. Hunt, *Inorg. Chem.*, **4**, 206 (1965).
(4) N. A. Matwiyoff, *ibid.*, **5**, 788 (1966).
(5) N. A. Matwiyoff and S. V. Hooker, *ibid.*, **6**, 1127 (1967).
(6) D. K. Ravage, T. R. Stengle, and C. H. Langford, *ibid.*, **6**, 1252 (1967).
(7) S. Thomas and W. J. Reynolds, *J. Chem. Phys.*, **46**, 4164 (1967).

(8) N. S. Angerman and R. B. Jordan, *ibid.*, **48**, 3983 (1968).
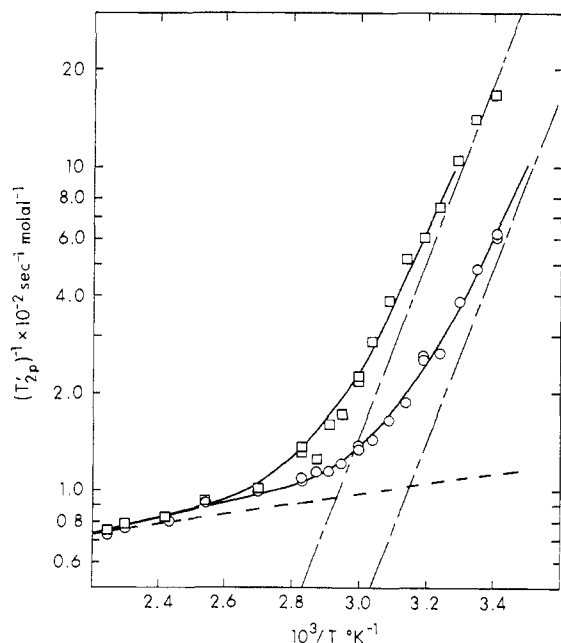(9) N. S. Angerman and R. B. Jordan, *Inorg. Chem.*, **8**, 69 (1969).

Figure 1.—Temperature dependence of $(T_{2p}')^{-1}$ for solutions of nickel(II) in dimethyl sulfoxide, at 60 MHz (O) and 100 MHz (□).

Experimental Section

Preparation of Complexes.—Hydrated nickelous and cobaltous perchlorates were prepared in the usual way from the respective carbonates and perchloric acid.

The complexes of $Ni(ClO_4)_2$ and $Co(ClO_4)_2$ with dimethyl sulfoxide (DMSO) and trimethyl phosphate (TMPA) were prepared by mixing the appropriate hydrated perchlorate salt (10 g) and solvent (50 ml) and Linde 3A Molecular Sieves. The solution was stirred for 24 hr, and then the molecular sieves were removed by filtration. This process was repeated three times, all operations being carried out under vacuum. The solvent volume was then reduced, by vacuum distillation, to an amount suitable to bring about crystallization of the metal ion complex. The absence of water was established from the lack of an infrared band at about 3500 cm^{-1} when the crystals were run in a Nujol mull between sodium chloride disks on a Perkin-Elmer Model 337 infrared spectrometer. Carbon and hydrogen analyses further serve to characterize the compounds. *Anal.* Calcd for $Ni(DMSO)_6(ClO_4)_2$: C, 19.84; H, 4.99. Found: C, 19.40; H, 4.79. Calcd for $Ni(TMPA)_6(ClO_4)_2$: C, 19.69; H, 4.96. Found: C, 19.63; H, 4.78. Calcd for $Co(DMSO)_6$-$(ClO_4)_2$: C, 19.84; H, 4.99. Found: C, 20.09; H, 5.18. Calcd for $Co(TMPA)_6(ClO_4)_2$: C, 19.68; H, 4.96. Found: C, 19.45; H, 5.07. The complexes were stored under vacuum and subsequent handling was done in a suitable vacuum apparatus or under a dry nitrogen atmosphere.

The solvents, dimethyl sulfoxide (Fisher Scientific Co.) and trimethyl phosphate (Aldrich Chemical Co.), were purified by double vacuum distillation from Linde 3A Molecular Sieves, retaining the middle fraction of each distillation. Six samples at different complex concentrations, in the range 0.01–0.1 m, were prepared for each of the systems studied by weighing the appropriate amounts of complex and solvent in a container under vacuum.

The absorption spectra of the complexes were recorded on a Cary Model 14 spectrophotometer. The results agree well with previously published spectra[10-12] except that for $Co(ClO_4)_2$ in TMPA where bands were observed at 535 mμ (ϵ 179), 580 mμ (ϵ 191), and 630 mμ (ϵ 184), and a broad band was centered at

1550 mμ (ϵ 36). The extinction coefficients are quoted for a spectrum at 24.1°. Gutmann and Bohunovsky[10] reported bands at 505 and 545 mμ while Jørgensen[13] observed bands at 464 and 515 mμ. The spectra reported in both cases are rather typical of octahedral cobalt(II), whereas the spectrum observed in the present study has more the features of tetrahedral cobalt(II) and is similar but not identical with that reported recently by Frankel,[14] who observed bands at 632 mμ (ϵ 235), 600 mμ (ϵ 205), 583 mμ (ϵ 205), and 552 mμ (ϵ 150). It has been found in this study that 1 drop of water in 5 ml of Co(II) TMPA solution produces a solution with a spectrum identical with that reported by Jørgensen. It is concluded that traces of water result in formation of mixed aquo–TMPA cobalt(II) octahedral complexes.

The nmr spectra were obtained using Varian A-56/60 and HA-100 spectrometers with standard variable-temperature probes and temperature controllers as described previously.[8,9] Line widths and chemical shifts were reproducible to ±2 Hz on both machines. Toluene and cyclohexane were used as internal reference for shift measurements. The same shift was found with both references. Six solutions at different metal ion concentrations were prepared for each system studied. Concentrations were generally chosen so that the line broadening was 5–20 Hz. The line broadening shows a direct dependence on the metal ion concentration in all of the systems studied.

Results and Discussion

1. Solvent Proton Relaxation in Dimethyl Sulfoxide Solutions of $Ni(ClO_4)_2$.—This system shows features typical of those observed previously for nickel(II) in water,[1] methanol,[2] dimethylformamide,[4] and acetonitrile.[4] The theory developed by Swift and Connick[1] and recounted in ref 2 and 4 serves to explain the results.

The nmr relaxation time T_{2p}' was determined from the nmr line broadening using the expression.

$$(T_{2p}')^{-1} = \frac{(T_{2p})^{-1}}{P_m} = \frac{\pi(\Delta\nu_{obsd} - \Delta\nu_{sol})}{P_m} \qquad (1)$$

where $\Delta\nu_{obsd}$ is the full line width at half-height of the bulk solvent resonance in an m molal solution, $\Delta\nu_{sol}$ is the line width in the pure solvent, and P_m is the solvation number times m divided by the free solvent concentration.

The temperature dependence of the line broadening may be described by a combination of limiting conditions 10(b) and 10(d) of Swift and Connick.[1] If τ_m^{-2}, $(T_{2m}\tau_m)^{-1} \gg (T_{2m})^{-2}$, then

$$(T_{2p}')^{-1} = T_{2m}^{-1} + \tau_m\Delta\omega_m^2 \qquad (2)$$

The curves in Figure 1 were initially resolved by eye into two straight-line portions—one representing the T_{2m}^{-1} and the other $\tau_m\Delta\omega_m^2$, the two terms in eq 2.

In order to calculate the exchange lifetime, τ_m, it is necessary to determine $\Delta\omega_m$. Swift and Connick developed the equation relating the observed chemical shift of the solvent protons due to the paramagnetic ion, $\Delta\omega$, and $\Delta\omega_m$. For the limiting conditions governing eq 2, the chemical shift is given by

$$\Delta\omega = \frac{P_m\Delta\omega_m}{1 + \tau_m^2\Delta\omega_m^2} \qquad (3)$$

(10) V. Gutmann and O. Bohunovsky, *Monatsh. Chem.*, **99**, 740 (1968).
(11) V. Gutmann and H. Brady, *ibid.*, **99**, 763 (1968).
(12) H. L. Schläfer and H. P. Opitz, *Z. Elektrochem.*, **65**, 372 (1961).
(13) C. K. Jørgensen, *Acta Chem. Scand.*, **8**, 1495 (1954).
(14) L. S. Frankel, *J. Chem. Phys.*, **50**, 943 (1969).

The results of the shift measurements at 60 and 100 MHz are shown in Figure 2. At high temperature τ_m is short and $\tau_m{}^2\Delta\omega_m{}^2 \ll 1$; then $\Delta\omega$ shows the expected Curie-law temperature dependence since

$$\Delta\omega = P_m \Delta\omega_m \qquad (4)$$

and[15]

$$\frac{\Delta\omega_m}{\omega} = \left(\frac{A}{\hbar}\right)\frac{g\beta(S)(S+1)}{3kT\gamma_I} \qquad (5)$$

An upfield shift gives a negative coupling constant, A/h. As indicated by combination of eq 4 and 5, the coupling constant may be calculated from the slope of the linear high-temperature region in Figure 2, or by direct calculation using eq 5 and assuming $\Delta\omega_m = 0$ when $(T°K)^{-1} = 0$. The latter method gives a somewhat better idea of the error in A/h and tests the assumption about the limiting value of $\Delta\omega_m$. The shift data for Ni^{2+} in dimethyl sulfoxide give an average value of 7.5×10^4 Hz for A/h taking a coordination number of 6 for nickel(II) in dimethyl sulfoxide.

The $(T_{2m})^{-1}$ relaxation may be described by the equation

$$(T_{2m})^{-1} = \frac{4}{3}\left\{\frac{\gamma_I{}^2\beta^2 g^2(S)(S+1)}{r_i{}^6}\right\}\tau_c +$$

$$\frac{16}{9}\left\{\frac{\gamma_I{}^2\beta^2 g^2 S(S+1)\rho[m]N}{r_o{}^3 \times 10^3}\right\}\tau_c +$$

$$\frac{2}{3}(A/\hbar)^2(S)(S+1)\tau_s \qquad (6)$$

where r_i and r_o are the inner- and outer-sphere interaction distances, ρ is the density, N is Avogadro's number, and $[m]$ is the metal ion molality. Previous studies on Ni^{2+} indicate that τ_c and τ_s are equal to the electron spin relaxation time. The first and second terms in eq 6 give the contribution of the inner-[16] and outer-sphere[2] dipole–dipole relaxation mechanism and the third term is due to the electron–nuclear hyperfine interaction.[16] The $(T_{2m})^{-1}$ relaxation as given by eq 6 may be represented in general as a constant times $\exp(E_a/RT)$, where E_a is the apparent activation energy for the correlation time τ. Thus $(T_{2m})^{-1} = C \exp(E_a/RT)$, where C depends on the relaxation mechanism.

A computer program was used to fit the line-broadening data to the complete equation developed by Swift and Connick. In the fitting procedure each $(T_{2p}')^{-1}$ value was multiplied by a weighting factor equal to the reciprocal of its value. The $(T_{2m})^{-1}$ was treated as a constant times an exponential as described in the previous paragraph. All of the parameters except the hyperfine coupling constant were adjusted. The computer uses initial guesses in an iterative method to calculate least-squares, best-fit values for $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for τ_m, E_a, and the constant C in the $(T_{2m})^{-1}$ term. At 100 MHz the values obtained are 12.09 (± 0.25) kcal
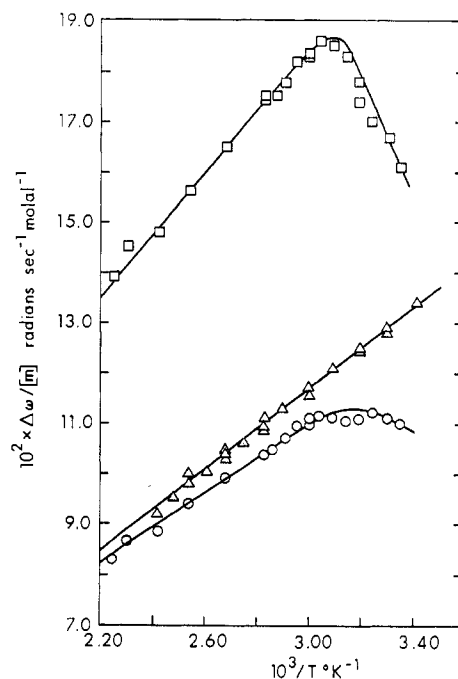

Figure 2.—Temperature dependence of the chemical shift ($\Delta\omega$) for solutions of nickel(II) in dimethyl sulfoxide at 60 Mz (O) and 100 MHz (□) and of cobalt(II) in dimethyl sulfoxide at 60 MHz (△).

mol^{-1}, -1.15 (± 0.50) eu, 0.337 (± 0.500) kcal mol^{-1}, and 100.8 $\pm$ 5.0 sec^{-1}. The best fit of the 60-MHz data gave 12.20 (± 0.31) kcal mol^{-1}, -1.50 (± 0.45) eu, 0.652 (± 0.200) kcal mol^{-1}, and 102.0 $\pm$ 3.5 sec^{-1}. The values from each set of data agree within the 95% confidence limit errors on the least-squares fit.

If it is assumed that T_{2m} is controlled by the hyperfine interaction, then τ_s is calculated to be 1.8×10^{-10} sec, using a coupling constant A/h of 7.5×10^4 Hz in the third term of eq 6. This value of τ_s seems much longer than that expected from previous studies. Alternatively the inner- and outer-sphere dipolar relaxation may control T_{2m}. If r_i and r_o are taken as 4.5₀ and 6.7₅ Å, then a correlation time of 9.45×10^{-12} sec is calculated to be consistent with the observed $(T_{2m})^{-1}$ at 25°. The inner- and outer-sphere contributions are 266 and 38 sec^{-1}, the sum agreeing exactly with the value of 304 sec^{-1} determined by extrapolation from high temperature. This correlation time is consistent with previous values for the electron spin relaxation time of nickel(II) in methanol, dimethylformamide, and acetonitrile.

There is very poor agreement between the activation parameters reported here and those given by Thomas and Reynolds[7] ($\Delta H^{\ddagger}$, 8 kcal mol^{-1}; $\Delta S^{\ddagger}$, -16 eu) and by Blackstaffe and Dwek[17] ($\Delta H^{\ddagger}$, 8.7 kcal mol^{-1}; $\Delta S^{\ddagger}$, -11 eu). However our results agree quite well with those obtained by Matwiyoff in a separate study. Preliminary results from the latter study, reported as a footnote in ref 7, have been refined to give $\Delta H^{\ddagger} = 11.7 \pm 0.8$ kcal mol^{-1} and $\Delta S^{\ddagger} = -1 \pm 1$ eu.[18]

(15) N. Bloembergen, *J. Chem. Phys.*, **27**, 595 (1957).

(16) (a) I. Solomon, *Phys. Rev.*, **99**, 559 (1966); (b) N. Bloembergen, *J. Chem. Phys.*, **27**, 572 (1957).

(17) S. Blackstaffe and R. A. Dwek, *Mol. Phys.*, **15**, 279 (1968).

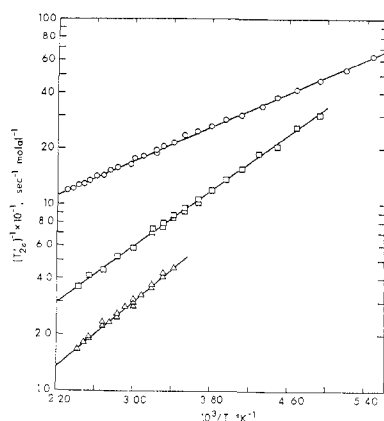(18) N. A. Matwiyoff, private communication.

Figure 3.—Temperature dependence of $(T_{2p}')^{-1}$ for solutions of cobalt(II) in dimethyl sulfoxide ($\triangle$) and trimethyl phosphate ($\square$) and nickel(II) in trimethyl phosphate ($\bigcirc$).

There is reasonable agreement for the values of $(P_m T_{2p})^{-1}$ at different temperatures. For example Thomas and Reynolds gave 1.27×10^3 and 7.34×10^2 sec^{-1} for $P_m(T_{2p})^{-1}$ at 23 and 34°. These values may be compared to values of 1.18×10^3 and 6.80×10^2 interpolated from Figure 1 at 23 and 34°.

The hyperfine coupling constant of $7.5_7 \times 10^4$ Hz is not in good agreement with the value of 9.3×10^4 Hz calculated[19] from the shift at 40° measured by Thomas and Reynolds[7] nor with the value of 8.7×10^4 Hz obtained by Blackstaffe and Dwek.[17] A similar discrepancy is found in the cobalt(II) system discussed later, but the source of the difficulty is not known. Because the complete temperature dependence of the shift has been measured and found to agree with the line-broadening results, it is felt that the value found in this study at least has more experimental basis.

2. Solvent Proton Relaxation in Dimethyl Sulfoxide Solutions of Co(ClO₄)₂.—The usual plot of log $(T_{2p}')^{-1}$ vs. the reciprocal of the absolute temperature is shown in Figure 3. The small temperature dependence (E_a, 1.9_6 kcal mol^{-1}) and increasing $(T_{2p}')^{-1}$ with decreasing temperature is typical of a T_{2m}-controlled relaxation. Thus the results should be explained by one or a combination of the terms in eq 6. It was found that hyperfine interaction relaxation does not contribute significantly and that the observed T_{2p}^{-1} may be calculated from the inner-sphere and outer-sphere dipolar contributions (first and second terms of eq 6), using $r_i = 4.5_0$ Å and $r_o = 6.7_5$ Å and a correlation time of 4.4×10^{-13} sec. This latter value agrees reasonably well with previous estimates of the electron spin relaxation time of cobalt(II) from similar work in other systems.[2,4] A lower limit of about 8.5×10^5 sec^{-1} may be placed on the exchange rate of one solvent molecule from the coordination sphere of cobalt(II).

The chemical shift data in Figure 2 were used in eq 4 and 5 to calculate[20] the hyperfine coupling constant of $2.0_8 \times 10^4$ Hz. As noted previously this value does not agree with the value 5.9×10^5 Hz calculated from

(19) Calculated from the shift data in ref 7 and the magnetic moment of 3.36 BM obtained by F. A. Cotton and R. Francis, *J. Am. Chem. Soc.*, **82**, 2986 (1960).

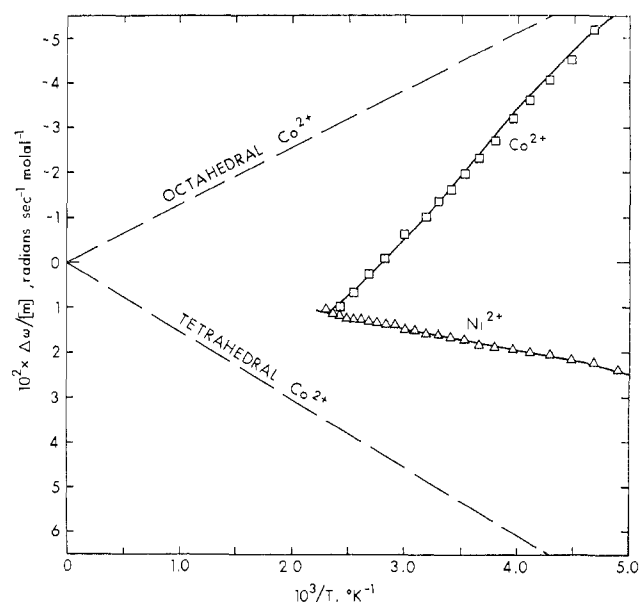(20) Using μ_{eff} of 5.01 BM from ref 19.

Figure 4.—Temperature dependence of the chemical shift for solutions of cobalt(II) and nickel(II) in trimethyl phosphate. The solid line for cobalt(II) is calculated from the limiting shifts for the octahedral and tetrahedral species (dashed lines) using the equilibrium concentrations noted in Table I.

the data in ref 7. The source of this disagreement is unknown.

3. Solvent Proton Relaxation in Trimethyl Phosphate Solutions of Ni(ClO₄)₂.—The temperature dependence of the line broadening in this system (Figure 3) is also typical of T_{2m}-controlled relaxation. The apparent activation energy (E_a) is 1.0_4 kcal mol^{-1}. The quantitative interpretation of the data indicates that the inner- and outer-sphere dipolar interactions only are contributing to T_{2m}, as found for nickel(II) in dimethyl sulfoxide. Inner- and outer-sphere interaction distances of 4.9_0 and and 7.5_5 Å[9] and a correlation time of 3.17×10^{-12} sec were found quantitatively to predict the observed line broadening.

The variation of the chemical shift with temperature in this system is shown in Figure 4. If the spin-only magnetic moment is assumed for nickel(II) in trimethyl phosphate, then the hyperfine coupling constant is found to be $7.1_6 \times 10^3$ Hz.

4. Solvent Proton Relaxation in TMPA Solutions of Co(ClO₄)₂.—The temperature dependence of $(T_{2p}')^{-1}$ shown in Figure 3 is typical of that expected if $(T_{2p}')^{-1} = P_m(T_{2m})^{-1}$. The mechanism for the T_{2m} relaxation is discussed below.

The unusual feature of this system is the temperature dependence of the chemical shift (Figure 4). Values of the shift at representative temperatures are given in Table I. The shift actually changes sign at about 80°, whereas according to eq 5 it can be either positive or negative, depending on the sign of the coupling constant, but cannot change sign. Introduction of a pseudocontact shift[21] cannot resolve the anomaly because the pseudocontact shift also varies as $1/T$.

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

TABLE I

CALCULATED AND OBSERVED NMR RESULTS FOR THE
COBALT(II)–TRIMETHYL PHOSPHATE SYSTEM

Temp, °C	Species concn, *m* [A]	[B]	[S]	Shift,[a] Hz $(\Delta\nu_s)_{obsd}$	$(\Delta\nu_s)_{calcd}$	Broadening,[a] $\Delta\nu_{obsd} - \Delta\nu_{sol}$, Hz Obsd	Calcd
140	0.354	0.141	4.88	7.95	3.33	5.7	5.7
120	0.345	0.150	4.86	5.55	2.24	6.5	6.4
100	0.334	0.161	4.83	2.38	0.82	7.0	7.1
80	0.322	0.173	4.81	0.40	−1.03	8.3	8.1
60	0.308	0.187	4.79	−4.75	−3.43	9.2	9.4
40	0.292	0.203	4.75	−7.70	−6.58	11.5	11.2
30	0.282	0.213	4.73	−10.6	−8.50	12.1	12.2
20	0.273	0.222	4.72	−12.8	−10.8	13.6	13.5
10	0.262	0.233	4.69	−15.4	−13.4	14.8	14.8
0	0.250	0.245	4.67	−18.4	−16.4	16.4	16.8
−10	0.238	0.257	4.65	−21.4	−19.5	18.9	18.9
−20	0.225	0.270	4.62	−25.4	−23.4	23.2	21.8
−30	0.210	0.285	4.59	−28.6	−27.9	24.6	24.8
−40	0.195	0.300	4.56	−32.3	−33.1	29.4	29.2
−50	0.178	0.317	4.53	−35.7	−39.6	33.0	34.0
−60	0.162	0.333	4.49	−44.5	−45.8	41.3	40.3
−70	0.146	0.349	4.47				

[a] The concentration of Co(ClO$_4$)$_2$ in trimethyl phosphate is 0.495 *m*.

To explain the temperature variation of the shift it is necessary to assume that there are at least two cobalt-(II) species in equilibrium in solution and that their relative concentrations change with temperature. Furthermore, to explain the change in sign of the observed shift, the hyperfine coupling constant must have a different sign for the two species. In view of the known tendency of cobalt(II) to form tetrahedral complexes with bulky, weakly bonding ligands, it seems most probable that the two species are octahedral Co(TMPA)$_6^{2+}$ and tetrahedral Co(TMPA)$_4^{2+}$, the tetrahedral species being favored at high temperature. A spectrophotometric study, discussed below, also supports this assignment of the species. The possibility of octahedral mixed aquo–TMPA complexes causing the results is not consistent with the spectrophotometric study, nor is it expected that such species would have coupling constants with opposite signs judging from previous work on mixed aquo–methanol[2] and aquo–chloro complexes.[22]

These considerations all indicate the presence of a tetrahedral species, and a quantitative description of the shift data was undertaken. The equilibrium involved may be written as

$$A + 2S \rightleftharpoons B \qquad (7)$$

where [A] represents the molality of tetrahedral Co(TMPA)$_4^{2+}$, [B] the molality of octahedral Co(TMPA)$_6^{2+}$, and [S] the molality of free solvent molecules. An equilibrium constant is then defined for the above reaction by

$$K = \frac{[B]}{[A][S]^2} = \exp\left(-\frac{\Delta H}{RT} + \frac{\Delta S}{R}\right) \qquad (8)$$

The observed chemical shift ($\Delta\omega_{obsd}$) is the sum of the contributions from the tetrahedral species ($\Delta\omega_A$) and octahedral species ($\Delta\omega_B$)

$$\Delta\omega_{obsd} = P_{mA}\Delta\omega_A + P_{mB}\Delta\omega_B \qquad (9)$$

$$\Delta\omega_{obsd} = \frac{4[A]}{[S_0] - (4[A] + 6[B])}\left(\frac{C_A}{T}\right) + \frac{6[B]}{[S_0] - (4[A] + 6[B])}\left(\frac{C_B}{T}\right) \qquad (10)$$

where [S$_0$] is the solvent molality in the pure solvent. These equations are derived in an obvious way from eq 4 and 5. The constants C_A and C_B depend on the hyperfine coupling constant and other physical constants as seen by comparison to eq 5.

It was hoped that a more meaningful fit of the shift data might be obtained if ΔH and ΔS were determined independently from a spectrophotometric study.

The spectrum of cobalt(II) in trimethyl phosphate was recorded at temperatures between 24.1 and 82.5°. The results of this study are given in Table II. It

TABLE II

SPECTROPHOTOMETRIC RESULTS FOR THE
COBALT(II)–TRIMETHYL PHOSPHATE SYSTEM

Temp, °C	10^2K, m^{-2}	Species concn,[a] *m* 10^3[A]	10^3[B]	Absorbance[a] Obsd 630 mμ	580 mμ	535 mμ	Calcd[b] 535 mμ
24.1	3.53	2.13	3.83	1.32	1.36	1.28	1.27
34.0	3.24	2.25	3.71	1.37	1.44	1.33	1.33
49.0	2.87	2.42	3.54	1.46	1.55	1.40	1.40
60.8	2.62	2.55	3.41	1.52	1.64	1.42	1.43
74.0	2.40	2.68	3.28	1.61	1.76	1.48	1.48
82.5	2.27	2.76	3.20	1.69	1.85	1.51	1.50

[a] Total cobalt(II) concentration is 5.96×10^{-3} *m*. [b] ϵ_A is assumed to be 500 M^{-1} cm^{-1}.

should be noted that the central peak at 580 mμ shows a greater relative increase with temperature than the 630-mμ peak which in turn increases more than the 535-mμ peak. This effect has been noted previously for tetrahedral cobalt(II) by Katzin[23] and is attributed to the increasing width and overlap of the peaks at higher temperature causing the intensity of the center peak to increase fastest. The procedure of Katzin has been followed in that the least affected peak, that at 535 mμ, has been used to calculate the temperature dependence of the equilibrium constant for tetrahedral–octahedral interconversion. It was assumed that the absorbance of the octahedral species can be neglected at 535 mμ; this assumption is consistent with numerous previous spectral studies on cobalt(II).

The temperature dependence of the absorbance at 535 mμ, (Ab)$_{535}$, is then given by

$$\frac{(Ab)_{535}}{\rho} = \frac{\epsilon_A M}{[S]_0^2 \exp[(-\Delta H/RT) + (\Delta S/R)] + 1} \qquad (11)$$

where ρ is the solvent density,[24] ϵ_A is the molar extinction coefficient of the tetrahedral species, and M is the molal cobalt(II) concentration.

The variation of (Ab)$_{535}$ with temperature may be fit to eq 11 by the least-squares computer program using ϵ_A, ΔH, and ΔS as adjustable parameters. It was found that the best fit of the data to eq 11 gave a value of 1.26×10^3 for ϵ_A. This value seems unreasonably high when compared to the extinction coefficients of other similar tetrahedral cobalt(II) species;[25,26] a

(22) A. H. Zeltman, N. A. Matwiyoff, and L. O. Morgan, *J. Phys. Chem.*, **72**, 121 (1968).

(23) L. I. Katzin, *J. Chem. Phys.*, **35**, 467 (1961).

(24) The temperature dependence of the density was calculated from the empirical equation $\rho = 1.800 - (2.00 \times 10^{-3}T)$, where T is the absolute temperature.

(25) D. W. Herlocker and R. S. Drago, *Inorg. Chem.*, **7**, 1479 (1968).

(26) M. Baaz, V. Gutmann, G. Hampel, and J. R. Masaguer, *Monatsh. Chem.*, **93**, 1416 (1962).

value of about 500 would seem more normal. It was found however that the fit of the absorbance data was rather insensitive to the magnitude of ϵ_A and a value as low as 350 gave reasonable agreement with the observed absorbancies.

Since it was apparent that a unique fit could not be obtained from the available data, a value of 500 for ϵ_A was assumed arbitrarily. The fit based on this choice of ϵ_A is useful only in that it shows that the spectrophotometric and chemical shift measurements are quantitatively consistent with the proposed equilibrium (eq 7). The calculated values in Table I and II were obtained using $\Delta H = 1.5_8$ kcal mol^{-1}, $\Delta S = 11.9_6$ eu, and coupling constants (calculated from C_A and C_B, assuming $\mu = 4.9$ BM) $(A/h)_A = 4.8_5 \times 10^4$ Hz and $(A/h)_B = -6.20 \times 10^4$ Hz. The negative sign of the octahedral coupling constant is consistent with the positive sign obtained for the P–CH$_3$ protons in the Co(II)–O=P(CH$_3$)(OCH$_3$)$_2$ system,[14] if the hyperfine coupling is due to a spin polarization mechanism. The protons are one atom further removed in O=P(OCH$_3$)$_3$ than in O=P(CH$_3$)(OCH$_3$)$_2$ from the cobalt(II).

The temperature dependence of $(T_{2p}')^{-1}$ in this system (Figure 3) is typical of a T_{2m}-controlled relaxation process. The observed $(T_{2p}')^{-1}$ is consistent with inner- plus outer-sphere dipolar broadening caused by both the tetrahedral (A) and octahedral (B) species. Using A and B concentrations calculated from the equilibrium constant determined previously, the best fit of the broadening data gave correlation times (at 25°) and apparent activation energies of 2.2×10^{-12} sec and 1.54 kcal mol^{-1} for A and $4.5_5 \times 10^{-12}$ sec and 0.37 kcal mol^{-1} for B. Again these parameters are only quoted to show that reasonable values fit the data. The correlation times seem to be normal values for the electron spin relaxation time on cobalt(II).

Conclusions

The general results of this nmr study are summarized in Table III. The ligand-exchange rate has only been

TABLE III
Solvent-Exchange Rates and Proton-Coupling Constants

Compound	Solvent	k_{ex} (25°), sec^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu	A/h, Hz
Ni(ClO$_4$)$_2$	DMSO	5.2×10^3	12.1	-1.3	$7.5_7 \times 10^4$
Ni(ClO$_4$)$_2$	TMPA	$>1.8 \times 10^2$	...	...	$7.1_6 \times 10^3$
Co(ClO$_4$)$_2$	DMSO	$>1.5 \times 10^4$	...	...	$2.0_8 \times 10^4$
Co(ClO$_4$)$_2$	TMPA	$>6.3 \times 10^3$	...	...	$-6.2_0 \times 10^{4}$ [a] $4.8_5 \times 10^{3}$ [b]

[a] Octahedral. [b] Tetrahedral.

measured for the dimethyl sulfoxide–nickel(II) system; in all other cases the exchange rate was too fast to control the proton relaxation times. The inability to observe chemical exchange controlled line broadening for cobalt(II) in DMSO does not imply that the exchange is unusually fast in this system but rather is simply a result of the rather high melting point (18.5°) of DMSO. Generally exchange rates at 25° for nickel(II) systems are about 10^2 times slower than for

cobalt(II) and this relationship may apply for DMSO as well; therefore, it would be necessary to go significantly below 18.5° before exchange could be observed for cobalt(II) in DMSO.

The kinetic parameters from this and previous studies are summarized in Table IV along with the

TABLE IV
Solvent-Exchange Rate Parameters and Dq Values for Nickel(II) and Cobalt(II) Systems[a]

Solvent	Nickel(II)			Cobalt(II)			
	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu	Dq, cm^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu	Dq, cm^{-1}	$(\Delta H^{\ddagger})_{Co}^{calcd}$, kcal mol^{-1}
H$_2$O	11.0	0.6	870	8.0	-4.1	861	8.0
CH$_3$OH	15.8	8.0	837	13.8	7.2	875	13.4
DMF	15.0	8.0	812	13.6	12.6	880	13.0
CH$_3$CN	10.9	-8.8	1104	8.1	-7.5	1100	7.2
DMSO	12.1	-1.3	773	...	...	...	...
NH$_3$	11.0	2.0	1095	11.2	10.2	1080	7.3

[a] References to the original work may be found in the recent review by T. R. Stengle and C. H. Langford, *Coord. Chem. Rev.*, 2, 349 (1967).

relevant crystal field splitting parameter Dq. Basolo and Pearson[27] have proposed that the relative exchange rates may be explained by the differences in loss of crystal field stabilization on going from the octahedral complex into the transition state for the exchange reaction. This theory predicts qualitatively that the $\Delta H^{\ddagger}$ for exchange should parallel the Dq value and quantitatively that in the case of Ni^{2+} (d^8) there should be a destabilization of $1.8Dq$ on formation of the most stable transition state, the "octahedral wedge." It is apparent from the results for nickel(II) in Table IV that even the qualitative predictions of this theory are not followed. For instance, the Dq values for CH$_3$OH, DMF, and DMSO are all lower than that of water, yet $\Delta H^{\ddagger}$ for water exchange is lower than for the other three solvents.

More recently Spees, Perumareddi, and Adamson[28] have proposed a significant variation of the previous crystal field theory, in which they assumed that spin pairing of the electrons occurs whenever possible on formation of the transition state. This theory was applied with reasonable success to the aquation reactions of chromium(III) and cobalt(III). However our attempts to apply the theory to the exchange reactions of nickel and cobalt have been a notable failure. The predicted activation energies are at least a factor of 2 and, with apparently reasonable assumptions, as much as a factor of 4 too large. The nickel(II)–methanol system may be used as an example. Spees, *et al.*, predict for a high-spin d^8 system that the crystal field contribution to the activation energy for the most favorable intermediate is $(-2.84Dq + 12B + 3C)$; B and C are the Racah parameters. Interpretation of the visible spectrum of Ni(CH$_3$OH)$_6$$^{2+}$ following the

(27) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, John Wiley & Sons, Inc., New York, N. Y., 1967, p 145.

(28) S. T. Spees, J. R. Perumareddi, and A. W. Adamson, *J. Am. Chem. Soc.*, 90, 6626 (1968).

method outlined by Lever[29] gives $Dq = 837$ cm^{-1} and $B = 949$ cm^{-1}. The activation energy is then $(9020 + 3C)$ cm^{-1} or $(25.8 + 3C)$ kcal mol^{-1}. This is already 10 kcal mol^{-1} greater than the observed value, and if the usual assumption that $C = 4B$ is used, then the activation energy is 58 kcal mol^{-1}.

It is apparent that electron pairing costs much more energy than is gained back by increased crystal field stabilization in the transition state and, therefore, no electron pairing is likely to occur. This factor was not obvious in the cases considered by Spees, *et al.*, because the cobalt(III) complexes are completely spin paired in the reactant and in the case of chromium(III) the larger Dq values for the $+3$ ion were sufficient to cancel the energy change for interelectronic repulsion. In fact it seems questionable if the original proposal of spin pairing can be justified since $10Dq$ must be less than the pairing energy if the reactant is high spin and the d orbitals in the transition state are always separated by less than $10Dq$; therefore the electrons should remain unpaired.

More recently Breitschwerdt[30] has revised the calculations of Basolo and Pearson by using a more complete quantum mechanical treatment. The results show the same trends with differing d electronic configurations as those of Basolo and Pearson but the absolute values of the crystal field contributions to the activation energy $(\Delta H^{\ddagger}{}_{CF})$ are somewhat different. For a C$_{4v}$ square-pyramidal transition state the $\Delta H^{\ddagger}{}_{CF}$ for Fe^{2+}, Co^{2+}, Ni^{2+}, and Mn^{2+} are $2.87Dq$, $3.65Dq$, $4.80Dq$, and $2.80Dq$, respectively. Breitschwerdt has found that these values give good quantitative predictions of the $\Delta H^{\ddagger}$ for water exchange. However, this version of the crystal field theory also predicts that the activation energy for solvent exchange should parallel the spectroscopic Dq values and as already noted the opposite trend seems to be more generally observed.

The above discussion in this paper and similar arguments in previous work have emphasized the importance of crystal field effects without paying any heed to the possibility of reactant and transition-state solvation. The latter factor is well recognized but has proven very difficult to calculate because it is always necessary to take the difference between two relatively large solvation energies. It seems reasonable to assume that the total activation energy is made up of a crystal field contribution $(\Delta H^{\ddagger}{}_{CF})$ and a solvation contribution $(\Delta H^{\ddagger}{}_{sol})$ so that

$$\Delta H^{\ddagger} = \Delta H^{\ddagger}{}_{CF} + \Delta H^{\ddagger}{}_{sol} \qquad (12)$$

The $\Delta H^{\ddagger}{}_{sol}$ should be a constant for a given solvent for metal ions of the same charge exchanging by the same mechanism. If this assumption is correct, then only the differences in activation energies for the different metal ions can be predicted by crystal field theory. If the $\Delta H^{\ddagger}$ for solvent exchange on Ni^{2+} is taken as an arbitrary standard, then the $\Delta H^{\ddagger}$ for other metal ions may be calculated from the value for nickel(II) and the predicted differences in crystal field contributions. For example using the crystal field contributions given by Breitschwerdt

$$(\Delta H^{\ddagger})_{Co}{}^{calcd} = (\Delta H^{\ddagger})_{Ni}{}^{obsd} + (\Delta H^{\ddagger}{}_{CF})_{Co} - (\Delta H^{\ddagger}{}_{CF})_{Ni} \qquad (13)$$

$$= (\Delta H^{\ddagger})_{Ni}{}^{obsd} + 3.65(Dq)_{Co} - 4.80(Dq)_{Ni} \qquad (14)$$

The observed and calculated activation enthalpies for cobalt(II) are compared in Table IV. The agreement between calculated and observed values for $(\Delta H^{\ddagger})_{Co}$ is generally good except for the ammonia system. It was proposed by Glaeser, Dodgen, and Hunt[31] that ammonia exchange on cobalt(II) might involve an octahedral–tetrahedral equilibrium and the disagreement found here could be rationalized on this basis. Because the predicted $\Delta H^{\ddagger}$ is lower than the value found, it is also necessary to assume that the octahedral–tetrahedral mechanism in this system has a more favorable entropy by about 15 eu than the normal exchange mechanism.

As noted previously Breitschwerdt[30] has obtained good agreement between calculated and observed activation energies for water exchange of a number of divalent first-row transition metal ions. There are unfortunately very few data for this series of ions in nonaqueous solvents. The recently reported activation enthalpies of 7.4 and 8.5 kcal mol^{-1} for methanol[32] and ammonia[33] exchange on manganese(II) are not in good agreement with the predicted values of 11.0 and 5 kcal mol^{-1}. However, the calculated and observed activation enthalpies of 11.3 and 12.0 kcal mol^{-1},[34] respectively, for the iron(II)–methanol system are in reasonable agreement. The calculation in the latter two systems has assumed that the Dq for methanol is the same for nickel(II), manganese(II), and iron(II).

It is clear that more experimental values are needed in order to determine if the predictions made here are generally correct. Assuming the latter is true, it would be very useful to determine the values of $\Delta H^{\ddagger}{}_{sol}$ and hopefully correlate them with the physical properties of the solvent. Calculation of $\Delta H^{\ddagger}{}_{sol}$ requires an absolute knowledge of $\Delta H^{\ddagger}{}_{CF}$ whereas the activation energies calculated in this work depend only on the difference in crystal field contributions. In any case it appears that $\Delta H^{\ddagger}{}_{sol}$ decreases in the order CH$_3$OH $>$ DMF $>$ DMSO $>$ H$_2$O $>$ CH$_3$CN $>$ NH$_3$. This order, of course, assumes a similar exchange mechanism in all solvents.

(29) A. B. P. Lever, "Werner Centennial," Advances in Chemistry Series, No. 62, American Chemical Society, Washington, D. C., 1967, p 430.
(30) K. Breitschwerdt, *Ber. Bunsenges. Physik. Chem.*, **72**, 1046 (1968).
(31) H. H. Glaeser, H. W. Dodgen, and J. P. Hunt, *Inorg. Chem.*, **4**, 1061 (1965).
(32) H. Levanon and Z. Luz, *J. Chem. Phys.*, **49**, 2031 (1968).
(33) J. P. Hunt, private communication.
(34) F. W. Breivogel, Jr., private communication.