carbon solvents. Both predictions were realized without exception. When y is 2, 3, or 4, the general formula simplifies to $[Cl_{x-1}GaR_{3-x}B_2]^+,Cl^-$, $[Cl_{x-2}GaR_{3-x}B_3]^{2+},2Cl^-$, and $[Cl_{x-3}GaR_{3-x}B_4]^{3+},3Cl^-$, respectively. All such adducts would be expected to precipitate from toluene, which was observed in all cases. Moreover, it is assumed that the strongest base, NH_3, is able to dissociate all Ga–Cl bonds initially present in the acid when the reaction temperature is –45 °C. This would give values of y equal to 1, 2, 3, and 4 when x equals 0, 1, 2, and 3, respectively. These are the observed results (Table I).

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Nitrogen-14 Magnetic Resonance Studies of the Effect of Pressure on the Exchange of Acetonitrile Solvent on Nickel(II) and Cobalt(II)

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The following volumes of activation have been obtained by nitrogen-14 FT NMR at 0–160 MPa for processes occurring in acetonitrile: for diffusion by rotation perpendicular to the C_{3v} molecular axis, +6.3; for solvent exchange with $Ni(CH_3CN)_6^{2+}$, +7.3; and for solvent exchange with $Co(CH_3CN)_6^{2+}$, +6.7 $cm^3 \, mol^{-1}$. The mechanistic significance of these results is discussed.

Introduction

Recent articles by Meyer, Newman, and Merbach[2,3] describing the effects of pressure on the rates of exchange of acetonitrile solvent with hexakis(acetonitrile)nickel(II) and -cobalt(II), as measured by proton NMR, prompted us to report our parallel studies of these processes using nitrogen-14 NMR. The advantages of the latter technique in this context have been demonstrated by Lincoln and West;[4-6] in essence, the ^{14}N nucleus, being nearest to the paramagnetic center in the complexes, experiences a much larger chemical shift than do the protons in coordinated CH_3CN, so giving an extended temperature range in which the Swift–Connick equation[7,8] (see below) approximates closely to the Eyring (or Arrhenius) equation governing the temperature dependence of the inner-sphere solvent-exchange process. In any event, the importance of determining NMR kinetic parameters by at least two independent methods is only too well illustrated by the history of sharp disagreement over enthalpies and entropies of activation for acetonitrile exchange at Co(II) and Ni(II).[2,3]

Modern commercial Fourier transform NMR machines offer further advantages over the continuous-wave apparatus used in the pioneering work of Lincoln and West;[4,5] the higher magnetic fields routinely available give greater chemical shifts, lower concentrations of the complex ions can be used (so reducing the risk of ion pairing or anion complexing), and cumulative pulsing permits the use of relatively small samples. Nevertheless, the NMR sensitivity of ^{14}N remains poor, relative to ^1H, and we chose to trade off field homogeneity in the sample and the range of accessible pressures (200 MPa

maximum, 160 MPa in practice) against improved sensitivity by using a longer rf coil and greater sample diameter (and hence slightly reduced pressure vessel wall thickness) than in the static high-pressure probe design of Vanni, Earl, and Merbach[9] upon which our device is based.

Experimental Section

Materials. Baker Analyzed acetonitrile was fractionally distilled twice from 3A or 4A molecular sieves before use. The water content of the distillate was undetectable by Karl Fischer titration ($<1 \times 10^{-4}$ M; in this article, M means mol dm^{-3} at 291 K and 0.1 MPa). Subsequent handling of the solvent, preparation of solutions, and the final stages of preparation of the complexes were always done in a glovebag under dry nitrogen.

Hexakis(acetonitrile)cobalt(II) and -nickel(II) perchlorates were made by the method of Matwiyoff and Hooker.[10] The water content of the solids was less than 0.05 mol/mol of metal ion M^{2+}, but the M^{2+} contents of the vacuum-dried solids, as measured by EDTA titration, were somewhat higher than calculated for $M(CH_3CN)_6$-$(ClO_4)_2$, apparently because of loss of some coordinated acetonitrile.[11] Accordingly, the concentrations of $M(CH_3CN)_6^{2+}$ present in solutions made up for the NMR experiments were determined by analysis of each solution by EDTA titration immediately after use. These solutions were made up either from the solid salt directly or by dissolving $Ni(ClO_4)_2 \cdot nH_2O$ in acetonitrile and removing the water by Soxhlet extraction with a 4A molecular sieve in the thimble;[12] in the latter case, the water content of the final solution (Karl Fischer) was less than 0.01 mol/mol of M^{2+}, and the electronic spectra and NMR line-broadening results were identical with those obtained from solutions made from the solid acetonitrile complexes. The visible spectrum of $Ni(CH_3CN)_6^{2+}$ in solution showed absorbance maxima at [wavelength λ in nm (molar absorbance ϵ in $M^{-1} \, cm^{-1}$)] 715 (1.34), 577 (5.89), and 362 (7.82); the Beer–Lambert law was precisely obeyed up to 0.13 M at least. For $Co(CH_3CN)_6^{2+}$, the single visible-region band had a maximum at 476 nm (ϵ 16.4 $M^{-1} \, cm^{-1}$) and a shoulder at 520 nm. These spectra agree satisfactorily with those in the literature.[11,13]

NMR Measurements. A Bruker WH-90 (90 MHz ^1H, 6.479 MHz ^{14}N) spectrometer with multinuclear-accessory and quadrature de-

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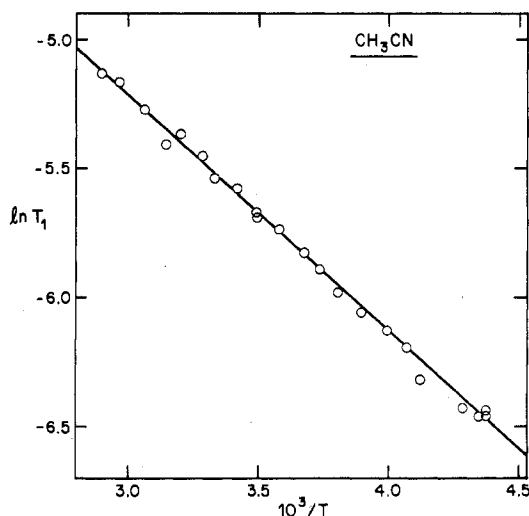(13) Hathaway, B. J.; Holah, D. G. *J. Chem. Soc.* **1964**, 2400.

Figure 1. Temperature dependence of the ^{14}N longitudinal relaxation time T_1 of pure acetonitrile.

tection was used in the ^2H lock mode. Samples for studies at atmospheric pressure, variable temperature, were sealed under dry nitrogen in a 10-mm NMR tube with a coaxial capillary containing the lock compound (CD_3OCD_3 at low temperatures, D_2O at higher) and thermostated with flowing nitrogen while spinning by using the Bruker temperature-control accessory. The sample temperature was measured before and after each experiment by using a copper-constantan thermocouple referred to ice water; the accuracy of the couple was checked against calibrated thermometers periodically.

NMR spectra at elevated pressures were obtained by using a static probehead which is generally similar to that described by Vanni, Earl, and Merbach[9] but which has some significant differences. The sample was contained in a glass tube (4-mm o.d., 2.4-mm i.d.) closed with a Teflon piston and double-wound externally with 52 turns of AWG-32 copper wire, tuned to 6.479 MHz. A copper–constantan thermocouple junction or, alternatively, a temperature-sensing diode was placed directly beneath the sample tube, and the leads from this and from the rf coil passed through a Vespel polyimide Bridgman seal in the lower jam nut of the titanium (IMI-680) pressure vessel. A Teflon spacer kept the sample tube accurately centered in the pressure vessel, which was thermostated with a circulating liquid (water, methanol, etc.) in a jacket of either brass or Lucite. The whole unit was fitted into a modified Bruker probehead casing, with plastic sides to minimize heat conduction, which contained the matching circuit and external lock capsule (D_2O). The response of the diode was calibrated over the 0–160 MPa pressure range employed, as was that of the thermocouple, as this was slightly more pressure dependent than expected from the literature.[14] Pressure was transmitted from a 200-MPa hand pump with hydraulic oil and monitored with a digital transducer-activated gauge (Autoclave Engineers, Inc., Model DPS-0601) which was accurate to ±1% according to a dead weight standard.

Typically, the free-induction decay spectrum was accumulated over 1000 (standard-probehead) or 4000 (pressurizable-probe) pulses and Fourier-transformed with 0–5 left shifts, as necessary, to eliminate any pulse break through and so give a symmetrical Lorentzian peak after phasing. It was demonstrated that neither additional left shifting nor application of an artificial line-broadening factor (subsequently corrected for) had any effect on the measured line width $\nu_{1/2}$ at half-maximum amplitude. Values of $\nu_{1/2}$ were obtained manually from the plotted spectra, although the spectrometer's computer was also used on occasion to calculate $\nu_{1/2}$ directly (with the same results). Field-inhomogeneity corrections (typically 11 Hz) were established for the pressure probe and applied to the measured $\nu_{1/2}$.

Attempts to obtain ^{14}N NMR spectra of acetonitrile using an internally pressurized Vespel sample tube which was similar to that also described by Vanni et al.[9] but which had a wider bore (2-mm i.d., 8-mm o.d.) failed because of lack of sensitivity when used in a standard Bruker probehead, and in any event the tubes invariably split at ~80 MPa.
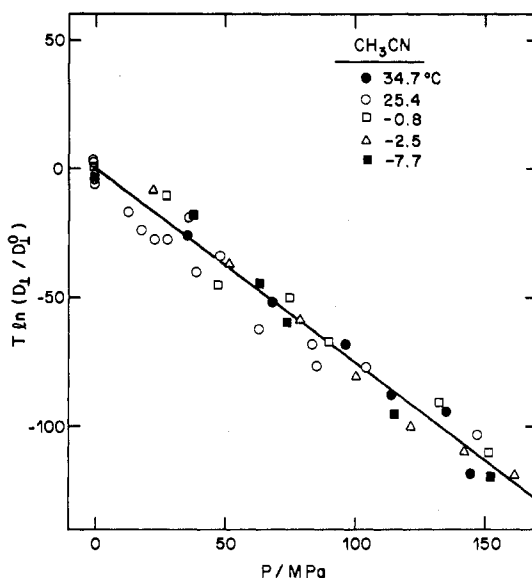
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Figure 2. Pressure dependence of the diffusion coefficient $D_\perp$ for reorientation of CH_3CN by rotation perpendicular to the C_{3v} axis.

Results

In the following, error limits are standard deviations except where otherwise stated.

Acetonitrile Alone. The transverse relaxation time ($=1/\pi\nu_{1/2}$) of ^{14}N in acetonitrile was found to equal the longtitudinal relaxation time T_1[15-17] and for convenience is hereinafter referred to as T_1. Its dependence on temperature T at 0.1 MPa is shown in Figure 1, in which the representative straight line (correlation coefficient $r = 0.9983$) is given by eq 1.

$$\ln T_1 = (-2.476 \pm 0.043) - (914 \pm 12)/T \qquad (1)$$

Hence, $T_1 = (3.92 \pm 0.17) \times 10^{-3}$ s at 298.15 K, and the activation energy $E_\perp$ for reorientation of CH_3CN by rotation about an axis perpendicular to the C_{3v} axis (diffusion coefficient $D_\perp$ (s^{-1}) = $3.45 \times 10^{13} T_1 = D_\perp^\circ \exp(-E_\perp/RT)$)[15-17] is 7.60 ± 0.10 kJ mol^{-1}, in excellent agreement with two previous reports,[16,17] although our T_1 values are longer (especially at the higher temperatures) than those reported by West and Lincoln.[18]

The variation of T_1 with pressure P is given by eq 2 where

$$(\partial \ln T_1/\partial P)_T = (\partial \ln D_\perp/\partial P)_T = -\Delta V_\perp^*/RT \qquad (2)$$

$\Delta V_\perp^*$ is the volume of activation for diffusion by rotation perpendicular to the molecular C_{3v} axis. Figure 2 shows that $\Delta V_\perp^*$ is independent of both T and P, within the experimental uncertainty, over the ranges studied. Accordingly, the data were reduced to a single straight-line relationship between $T \cdot \ln (T_1/T_1^\circ)$ and P with $r = 0.9891$, giving $\Delta V_\perp^* = +6.3 \pm 0.1$ cm^3 mol^{-1}. Bull and Jonas[15] reported $+8.5 \pm 1.4$ cm^3 mol^{-1} for this parameter; the agreement is satisfactory, since the overall uncertainty in our value may be estimated to be ±10%.

Nickel(II) Perchlorate in Acetonitrile. Following Swift and Connick[7] and Merbach et al.[2,3] we define a ^{14}N transverse relaxation time T_{2p} due to interaction of CH_3CN solvent with a paramagnetic solute ion M (here, Ni^{2+}) in terms of the observed relaxation time T_2 ($=(\pi\nu_{1/2})^{-1}$), the mole fraction p_m of solvent coordinated to the ion, and the relaxation time of the solvent above (T_1, taken from eq 1 and 2).

$$T_{2p}^{-1} = p_m^{-1}(T_2^{-1} - T_1^{-1})(1 - p_m) \qquad (3)$$

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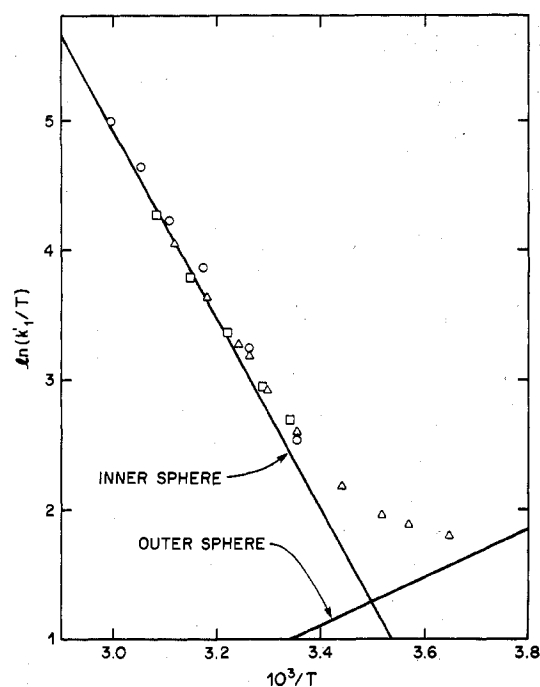(18) West, R. J.; Lincoln, S. F. *Aust. J. Chem.* **1971**, *24*, 1169.

Figure 3. Temperature dependence of k_1' $(=T_{2p}^{-1})$ for $Ni(CH_3CN)_6^{2+}$ in acetonitrile.

Then, if T_{2m} is the relaxation time of ^{14}N in CH_3CN coordinated to M in the absence of chemical exchange, $\Delta\omega_m$ is the chemical shift of ^{14}N in the complex relative to free CH_3CN, τ_m is the time constant for chemical exchange of CH_3CN between $M(CH_3CN)_m$ and bulk solvent, and T_{2os} is the contribution to T_2 from outer-sphere interactions between $M(CH_3CN)_m$ and CH_3CN, we have[2,6,7] eq 4.

$$\frac{1}{T_{2p}} = \frac{1}{\tau_m}\left[\frac{T_{2m}^{-2} + (T_{2m}\tau_m)^{-1} + \Delta\omega_m^2}{(T_{2m}^{-1} + \tau_m^{-1})^2 + \Delta\omega_m^2}\right] + \frac{1}{T_{2os}} \quad (4)$$

As has been demonstrated[4] for ^{14}N resonance in $Ni(CH_3CN)_m^{2+}$–CH_3CN, T_{2m}^{-2}, $\tau_m^{-2} \ll \Delta\omega_m^2$ for the temperature range of our experiments (Figure 3), so that

$$T_{2p}^{-1} = \tau_{2m}^{-1} + T_{2os}^{-1} \quad (5)$$

or, in terms of rate coefficients k

$$k_1' = k_1 + k_{os} \quad (6)$$

where, accepting that m in $Ni(CH_3CN)_m^{2+}$ is 6^4

$$k_1 = (\text{rate of } CH_3CN \text{ exchange})/6[Ni^{2+}] = $$
$$(\kappa T/h)\ \exp(\Delta S^*/R - \Delta H^*/RT) \quad (7)$$

and k_{os} may be assumed to follow the equation

$$k_{os} = A\ \exp(E_{os}/RT) \quad (8)$$

A computer least–squares fit of the data of Figure 3 gave $\Delta H^* = 60.8 \pm 1.1$ kJ mol⁻¹, $\Delta S^* = 25.8 \pm 2.8$ J K⁻¹ mol⁻¹, $k_1(298\ K) = 3.1 \times 10^3$ s⁻¹, $A = 4.2 \pm 1.1$ s⁻¹, and $E_{os} = 13 \pm 4$ kJ mol⁻¹. These data compare quite satisfactorily with the more reliable estimates of previous workers using various assumptions and nuclei (see compilation by Merbach et al.[3]), especially with regard to the k_1 values thereby represented. This and the demonstration in the Eyring plot (Figure 3) that outer-sphere contributions to k_1' are truly negligible at 35 and 57 °C confirm that, in the pressure experiments to be described, we are observing the effect of P upon k_1 exclusively.

Series of experiments with $Ni(ClO_4)_2$ solutions in acetonitrile in the pressurizable probe showed that $\ln k_1$ was a linear function of P, that the extrapolated k_1 at zero pressure (k_1^o)
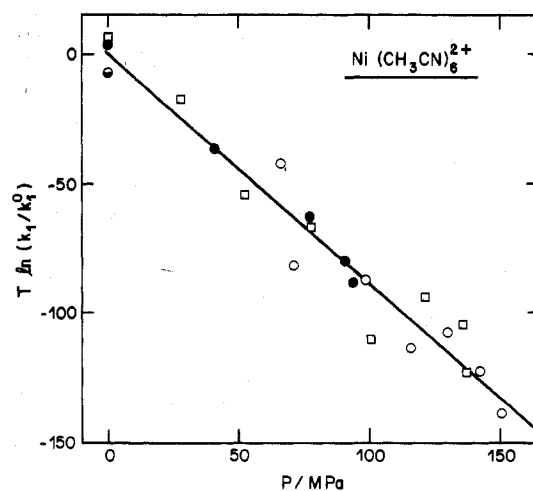

Figure 4. Pressure dependence of rate coefficient k_1 for exchange of CH_3CN solvent with $Ni(CH_3CN)_6^{2+}$: filled circles, $c_m = 0.0396$ M, $p_m = 0.01256$, $T = 56.6$ °C; open circles, $c_m = 0.0396$ M, $T = 34.7$ °C; open squares, $c_m = 0.1550$ M, $p_m = 0.0491$, $T = 34.7$ °C.

agreed with the values obtained with the standard probehead, and that the volume of activation was independent of the concentration c_m of nickel salt and of both pressure and temperature, within the respective experimental uncertainties. The data are therefore all presented together in Figure 4, in which the representative straight line $(r = 0.9767)$ gives $\Delta V^* = +7.3 \pm 0.3$ cm³ mol⁻¹.

Cobalt(II) Perchlorate in Acetonitrile. Experiments using the standard probehead confirmed West and Lincoln's observations,[5] qualitatively at least; i.e., the full Swift–Connick equation (4) must be used for temperatures above about 0 °C, but k_1 is the only significant contribution to T_{2p}^{-1} in the temperature range 0 to –10 °C and possibly lower. Our line width measurements on cobalt(II) perchlorate solutions agreed fairly well with those of West and Lincoln,[5] but our values of the pure solvent relaxation time T_1 were larger, leading to smaller values of T_{2p} (eq 3) and hence greater rate coefficients k_1. Thus, at –0.8 and –7.7 °C (the temperatures of our variable-pressure experiments), we found $10^4(k_1/s^{-1}) = 10.3$ and 7.2, respectively; the values calculated from the activation parameters of West and Lincoln[5] are 5.0 and 2.8. The discrepancy is not serious in the context of the pressure studies, however, since we are concerned with the *relative*, rather than the absolute, values of k_1 as a function of pressure. A detailed reinvestigation of the temperature dependence of k_1 for the cobalt(II) system was therefore not completed at this time.

Experiments with the pressurizable probe showed that for the $Co(CH_3CN)_6^{2+}$–CH_3CN exchange, just as for the nickel(II) analogue, ΔV^* was independent of P, T, and c_m, within the experimental uncertainty. Figure 5 displays the collected results; the representative straight line $(r = 0.9629)$ gives $\Delta V^* = +6.7 \pm 0.4$ cm³.

Discussion

Because the estimation of the pressure dependence of the chemical-exchange rates involves adjustment of the observed T_2 values for the pressure-dependent contribution of T_1 to the line width, in addition to a significant field inhomogeneity correction associated with the use of the pressurizable probehead, the uncertainty in ΔV^* is probably 1–2 cm³ mol⁻¹. Thus, our values are consistent with those of Merbach et al. (+9.6 and +9.9 cm³ mol⁻¹ for Ni^{2+} and Co^{2+}, respectively[2,3]) as these are subject to similar uncertainties. In the present study, the use of ^{14}N resonance, i.e., of the NMR of the ligand atom nearest the paramagnetic center and hence with the largest possible chemical shift, ensured that the assumptions T_{2m}^{-2}, $\tau_m^{-2} \ll \Delta\omega_m^2$ are fully justified, and one does not have
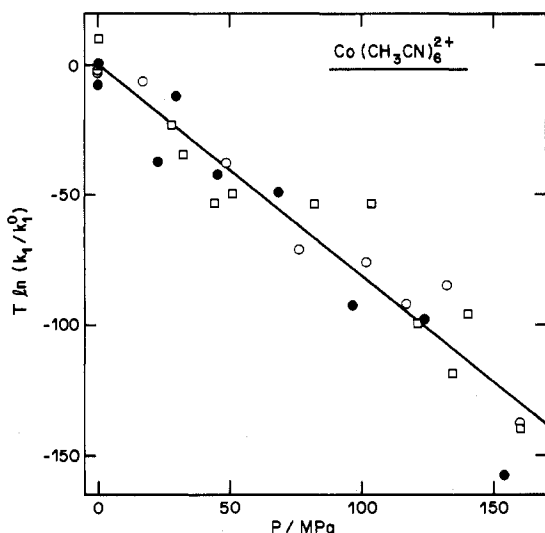
Figure 5. Pressure dependence of rate coefficient k_1 for exchange of CH_3CN solvent with $Co(CH_3CN)_6^{2+}$: filled circles, $c_m = 0.01636$ M, $p_m = 5.18 \times 10^{-3}$, $T = -7.7$ °C; open circles, $c_m = 0.0246$ M, $p_m = 7.80 \times 10^{-3}$, $T = -0.8$ °C; open squares, $c_m = 0.01320$ M, $p_m = 4.18 \times 10^{-3}$, $T = -0.8$ °C.

to resort to consideration of the behavior of the whole Swift–Connick equation as a function of pressure as must be done for ^1H resonance.[2,3] On the other hand, the low sensitivity of ^{14}N resonance contributes to experimental difficulties and hence reduces accuracy. A ΔV^* value of $+8 \pm 2$ cm^3 mol^{-1} for acetonitrile exchange on both Co^{2+} and Ni^{2+} would seem conservatively realistic.

The markedly positive and similar values of ΔV^* for acetonitrile exchange in $Ni(CH_3CN)_6^{2+}$ and $Co(CH_3CN)_6^{2+}$ indicate that they have a common dissociatively activated substitution mechanism. Certainly, this is in accordance with our understanding of substitution processes at nickel(II) centers in the solvent.[19] A further similarity brought into focus in this study is that between ΔV^* for the Co^{2+} and Ni^{2+} exchanges (+6.7 and +7.3 cm^3 mol^{-1}) and $\Delta V_\perp^*$ for the tumbling diffusion of acetonitrile (+6.3 cm^3 mol^{-1}). This suggests

that the M–N bond may be broken by a rotational rather than a translational motion of the ligand, i.e., by a twist rather than a massive displacement of the leaving group. This may account for the lack of obvious correlation between ΔV^* for most dissociatively activated solvent-exchange processes and the molar volume of the solvent.[2,3,20]

Although inner-sphere anionic complexing of $Ni(CH_3CN)_6^{2+}$ and $Co(CH_3CN)_6^{2+}$ can occur in acetonitrile with such weakly complexing ligands as nitrate[21,22] and in the solid state even with perchlorate,[11] the visible spectra of our solutions and the NMR results themselves were independent of the $M(ClO_4)_2$ concentration over the ranges used in our studies (up to 0.15 M for Ni^{2+}, 0.03 M for Co^{2+}). The possibility of inner-sphere complexing of M^{2+} by perchlorate in our solutions may therefore be discounted, but ClO_4^- may nevertheless become significantly involved in ion pairing with $M(CH_3CN)_6^{2+}$ at high concentrations in acetonitrile, which has a fairly low dielectric constant (36.0 at 0.1 MPa and 41.0 at 200 MPa, at 25 °C).[23] Ion pairing of solvent complexes by anions in aprotic solvents evidently results in a lowering of the solvent-exchange rate by about one-third or one-half;[24] this may explain why the $Co(CH_3CN)_6^{2+}$–acetonitrile exchange rates measured in this study were about twice as fast as those reported by West and Lincoln[5] and Merbach et al.,[2] who used $Co(ClO_4)_2$ concentrations 10 times higher then ours. We emphasize, however, that those differences are minor and do not significantly affect the salient features of their findings or ours.

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