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A Hydrogen-1 and Nitrogen-14 Magnetic Resonance Study of the Exchange of Acetonitrile on Cobalt(II)

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A ^1H and ^{14}N magnetic resonance study of acetonitrile exchange between the first coordination sphere of cobalt(II) and bulk solvent is reported. Relaxation of both nuclei occurs *via* a "Δw"[1] mechanism and in the case of ^1H a significant relaxation contribution also arises from dipolar interactions. The value of $k_1(25°)$ from the rate law $r = 6k_1[Co(CH_3CN)_6{}^{2+}]$ is $(3.2 \pm 0.3) \times 10^5$ sec^{-1}, $\Delta H^{\ddagger} = 11.4 \pm 0.5$ kcal mol^{-1}, $\Delta S^{\ddagger} = 5.0 \pm 2.0$ eu, and $A/h = 8.56 \times 10^6$ Hz from ^{14}N data. The values obtained from ^1H data are $k_1(25°) = (3.5 \pm 0.5) \times 10^5$ sec^{-1}, $\Delta H^{\ddagger} = 11.4 \pm 0.5$ kcal mol^{-1}, and $\Delta S^{\ddagger} = 5.2 \pm 2.2$ eu.

Cobalt(II) ion in acetonitrile solution induces relaxation of the ^1H and ^{14}N nuclei of the bulk solvent, and the relative importance of the factors determining the effectiveness of the relaxation differs for the two nuclei as shown by ^1H and ^{14}N magnetic resonance studies. The determination of the contribution made by such factors to the observed nuclear relaxation is important in the derivation of the kinetic parameters for acetonitrile exchange between the first coordination sphere of cobalt(II) and bulk solvent, from relaxation data. It is anticipated from the data treatment developed by Swift and Connick[1] that such parameters should be independent of the solvent nucleus observed, as is shown to be the case for the cobalt(II)–acetonitrile system in this study.

Experimental Section

Materials.—Redistilled acetonitrile and toluene were dried and stored over Linde 4A Molecular Sieves. Hexakis(acetonitrile)-cobalt(II) perchlorate was prepared by a method similar to that of Matwiyoff and Hooker.[2] Infrared spectra of concentrated Nujol mulls of the complex exhibited no water peak in the 3500-cm^{-1} region.

Reference solutions of pure acetonitrile and zinc(II) perchlorate in acetonitrile and the acetonitrile solutions of hexakis(acetonitrile)cobalt(II) perchlorate were prepared by weight and transferred to nmr tubes under dry nitrogen. The solutions in the nmr tubes were degassed, by freezing and evacuating, prior to sealing under vacuum. For ^1H measurements, solutions containing 2% toluene as internal reference were sealed in standard pmr tubes. For ^{14}N measurements 10-mm o.d. Pyrex nmr tubes, with a 3-mm o.d. thermocouple well centrally sited, were used.

Nmr Measurements.—All pmr measurements were made in triplicate at least, on Varian A-60 and DP-60 spectrometers equipped with calibrated variable-temperature probes. Line width measurements were reproducible to within ±1%, and shift measurements, made from toluene, were reproducible to ±1 Hz. Nitrogen-14 measurements were made at 3.07 MHz on previously described[3] modified Varian equipment. Absorption mode signals were obtained by both side-band[4] and first-derivative methods, which gave identical results after correction of the first-derivative line widths for modulation broadening,[5] which never exceeded 5% of the total line width at half signal amplitude. The first-derivative method gave greater signal intensity and consequently line widths >2.5 G were usually determined by this method. Line width and chemical shift measurements[3] were made in triplicate at least and were reproducible to within 0.1 and 0.2 G, respectively. The temperature of samples in the variable-temperature probe was measured with a copper–constantan thermocouple. All ^1H and ^{14}N measurements were made at radiofrequency levels well below saturation. No significant broadening or shift of the ^1H and ^{14}N bulk resonances was observed in a 0.654 *m* $Zn(ClO_4)_2$ acetonitrile solution over the experimental temperature range.

Results and Data Treatment

^{14}N Relaxation and Shift Data.—The relaxation of the nuclei of acetonitrile solvent, induced by cobalt(II), may be expressed by

$$T_{2p} = (1/T_2 - 1/T_{2A})^{-1} \qquad (1)$$

where T_2 and T_{2A} are the observed transverse relaxation times of bulk acetonitrile in solutions containing cobalt(II), and of acetonitrile alone, respectively. The ^{14}N T_{2p} data are given in Table I.

When induced relaxation of solvent nuclei occurs in the first coordination sphere of cobalt(II) T_{2p} may be related to the rate of solvent exchange on cobalt(II) in dilute solution by the expression[1]

$$T_{2p} = \frac{\tau_M}{P_M}\left[\frac{(T_{2M}^{-1} + \tau_M^{-1})^2 + \Delta w_M{}^2}{T_{2M}^{-2} + (T_{2M}\tau_M)^{-1} + \Delta w_M{}^2}\right] \qquad (2)$$

where τ_M is the mean lifetime of a solvent molecule in the first coordination sphere, P_M is the mole fraction of solvent coordinated, T_{2M} is the transverse relaxation time of the solvent nucleus of interest in the first coordination sphere, and Δw_M is the difference in resonant frequency of this nucleus in coordinated solvent and the bulk solvent.

The ^{14}N data are consistent with a "Δw" nuclear relaxation mechanism such that eq 2 reduces to

$$T_{2p} = \tau_M P_M{}^{-1} + (P_M \tau_M \Delta w_M{}^2)^{-1} \qquad (3)$$

which describes the variation of T_{2p} over the experimental temperature range. In Figure 1 the computed best fit of eq 3 to the ^{14}N data is shown as a solid curve and the two terms of the expression are shown as broken lines. The species $Co(CH_3CN)_6{}^{2+}$ is assumed to be the kinetically predominant species in solution[2] such that

$$\tau_M = k_1{}^{-1} = 6[Co(CH_3CN)_6{}^{2+}]r^{-1} = (kT/h)\exp(-\Delta H^{\ddagger}/RT)\exp(\Delta S^{\ddagger}/R) \qquad (4)$$

where r and k_1 are the rate and rate constant, respectively, for the exchange of acetonitrile on cobalt(II) ion, and k is the Boltzmann constant. The kinetic

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

(2) N. A. Matwiyoff and S. V. Hooker, *Inorg. Chem.*, **6**, 1127 (1967).

(3) R. J. West and S. F. Lincoln, *Aust. J. Chem.*, **24**, 1169 (1971). Equation 2 in this reference should read $T_{2p} = 2(\gamma\Delta)^{-1}$, and in Table I $T_{2p}' = T_{2p}P_M$.

(4) J. V. Acrivos, *J. Chem. Phys.*, **36**, 1097 (1962).

(5) H. J. Wahlquist, *ibid.*, **35**, 1708 (1961).

TABLE I

^{14}N RELAXATION DATA[a]

Temp, °C	$10^6 P_M T_{2p}$	Temp, °C	$10^6 P_M T_{2p}$	Temp, °C	$10^6 P_M T_{2p}$
Soln 1		Soln 2 (Contd)		Soln 4	
50.0	13.6	15.0	7.99	74.5	59.6
43.0	9.14	14.0	7.74	70.0	38.9
36.5	5.96	8.0	12.3	65.0	29.8
26.0	5.08	6.5	13.8	60.0	22.0
21.5	5.44			56.0	14.7
14.0	8.43	Soln 3		52.0	12.7
7.0	13.7	75.0	55.6	50.0	12.9
		69.5	34.8	47.0	8.90
Soln 2		65.0	27.0	43.0	10.0
52.0	11.8	60.0	21.6	42.0	7.06
50.0	15.3	56.0	16.3	38.0	5.16
44.5	9.09	46.5	9.20	37.0	5.74
42.5	8.87	38.0	5.76	33.0	4.65
36.0	6.46	0.5	19.3	31.5	4.97
36.0	6.29	−1.0	19.8	29.0	4.74
29.0	5.43	−5.0	29.5	23.0	5.18
27.0	5.18	−10.0	44.6	17.0	6.39
23.0	5.77	−15.0	68.7	10.0	9.68
22.0	6.23	−16.0	69.5	6.0	12.7
				0.5	19.8
				−1.0	24.4

[a] The Co(II) concentrations were 0.04811, 0.06158, 0.2249, and 0.1096 *m* in solutions 1, 2, 3, and 4, respectively.

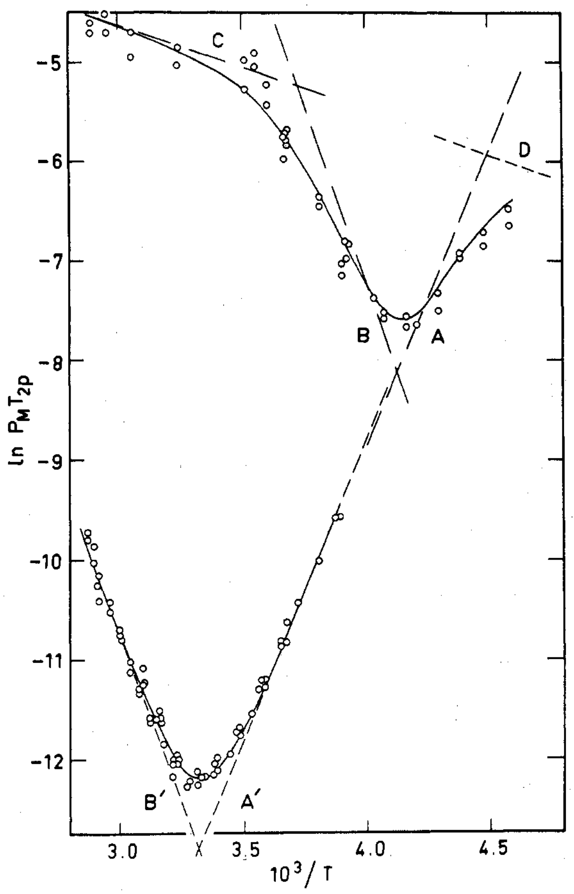

Figure 1.—Variation of ln P_MT_{2p} with T^{-1}. The upper set of data points are from ^{1}H measurements and the solid curve represents a best fit and contains the components (A) τ_M, (B) $(\tau_M\Delta w_M{}^2)^{-1}$, (C) T_{2M}, and (D) T_{2O} which are shown as broken lines. The lower set of data points are from ^{14}N measurements and the solid curve represents a best fit and contains the components (A′) τ_M and (B′) $(\tau_M\Delta w_M{}^2)^{-1}$ which are shown as broken lines.

parameters derived from the ^{14}N data are $k_1(25°) = (3.2 \pm 0.3) \times 10^5\ \mathrm{sec}^{-1}$, $\Delta H^{\ddagger} = 11.4 \pm 0.5$ kcal mol^{-1}, and $\Delta S^{\ddagger} = 5.0 \pm 2.0$ eu.

The ^{14}N bulk solvent chemical shift, S, values are listed in Table II and ln $TSP_M{}^{-1}$ is plotted against 1/T in Figure 2 in which a limiting TS value is approached at the high-temperature extreme. A ^{14}N scalar coupling constant, A/h, value of 8.56×10^6 Hz was calculated using the expression[6]

TABLE II

^{14}N SHIFT DATA[a]

Temp, °C	S, ppm	Temp, °C	S, ppm	Temp, °C	S, ppm
70.0	1040	49.0	1030	34.0	830
70.0	1060	49.0	1040	34.0	810
70.0	1040	49.0	1100	34.0	830
62.5	1070	49.0	1040	30.5	670
62.5	1040	39.0	980	30.5	660
62.5	1050	39.0	970	30.5	660
55.0	1040	39.0	990	27.0	580
55.0	1060	38.0	970	27.0	570
55.0	1040	38.0	980	27.0	510
		38.0	930		

[a] Concentration of Co(II) was 0.2249 *m*.

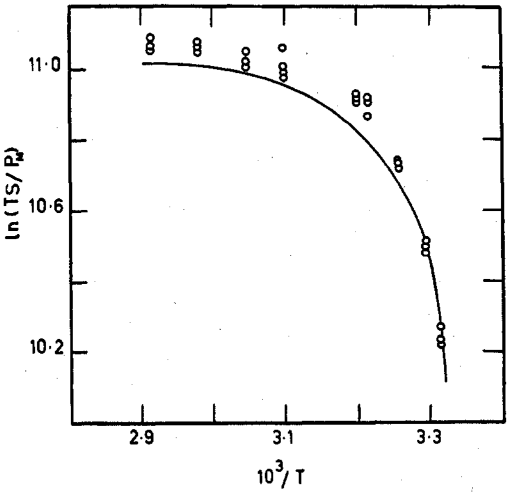

Figure 2.—Variation of ln $TSP_M{}^{-1}$ with T^{-1} derived from ^{14}N measurements. The data points are calculated directly from shift measurements, and the solid curve is the variation of ln $TSP_M{}^{-1}$ predicted from T_{2p} data.

$$\frac{\Delta w_M}{w} = \frac{-A[S(S+1)]^{1/2}}{h(3kT\gamma)}\mu_{\mathrm{eff}} \qquad (5)$$

where S is the electron spin for cobalt(II), γ is the ^{14}N magnetogyric ratio, and $\mu_{\mathrm{eff}} = 5.2$ BM.[7] A value of $A/h = 8.33 \times 10^6$ Hz was calculated from the T_{2p} data *via* eq 3. The dependence of $TSP_M{}^{-1}$ on temperature for a ^{14}N "Δw" relaxation mechanism is given by[3]

$$TSP_M{}^{-1} = -\Delta w_M T(1 + \tau_M{}^2\Delta w_M{}^2)^{-1} \qquad (6)$$

This function, calculated from A/h and τ_M values obtained from the T_{2p} data, is plotted as a solid curve in Figure 2. The near coincidence of this curve and the observed $TSP_M{}^{-1}$ values demonstrate the internal consistency of the ^{14}N S and T_{2p} data.

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

(7) B. J. Hathaway, D. G. Holah, and E. A. Underhill, *J. Chem. Soc.*, 2444 (1962). No temperature variation for μ_{eff} is reported in this reference.

TABLE III

^{1}H RELAXATION DATA[a]

Temp, °C	$10^6 P_M T_{2p}$	Temp, °C	$10^6 P_M T_{2p}$	Temp, °C	$10^6 P_M T_{2p}$
Soln 5		Soln 6 (Contd)		Soln 7 (Contd)	
11.5	6900	34.9	7800	8.5	7400
4.4	4390	−25.0	625	7.0	6320
−0.6	3210	−35.0	472	4.4	5350
−1.5	3010	−45.0	955	−0.6	2540
−1.6	3440	−50.0	1010	−1.6	3280
−11.0	1720	−55.0	1520	−11.0	1570
−17.0	785			−17.0	892
−18.0	1120	Soln 7		−18.0	938
−27.0	541	73.0	9900	−19.0	1090
−33.0	524	65.0	12900	−27.0	515
−40.0	660	54.0	8900	−40.0	740
		54.0	6900	−45.0	981
Soln 6		34.9	6600	−50.0	1220
73.0	8900	11.5	5100	−55.0	1290
65.0	8900				

[a] The Co(II) concentrations were 0.06158, 0.1597, and 0.3308 *m* in solutions 5, 6, and 7, respectively.

TABLE IV

^{1}H SHIFT DATA[a]

Temp, °C	S, ppm	Temp, °C	S, ppm	Temp, °C	S, ppm
73.0	0.216	14.0	0.458	−23.0	0.583
68.0	0.223	4.0	0.498	−26.0	0.277
65.0	0.233	−5.0	0.557	−28.0	0.233
58.0	0.280	−11.0	0.560	−28.0	0.200
54.0	0.283	−18.0	0.617	−29.0	0.327
47.0	0.292	−21.0	0.545	−33.0	0.300
37.0	0.355	−23.0	0.507	−34.0	0.150
27.0	0.415	−23.0	0.433	−36.0	0.383

[a] Concentration of Co(II) was 0.3309 *m*.

^{1}H Relaxation and Shift Data.—In contrast to the ^{14}N data, dipole–dipole interactions make significant contributions to the ^{1}H T_{2p} data listed in Table III. Four terms appear as components in the ^{1}H T_{2p} data over the experimental temperature range. Three terms T_{2M}, $(\tau_M \Delta w_M^2)^{-1}$, and τ_M arise from relaxation processes occurring in the first coordination sphere of $Co(CH_3CN)_6^{2+}$, and the fourth term, T_{2O}, is attributed to dipole–dipole induced relaxation of ^{1}H outside the first coordination sphere. The solid curve through the ^{1}H data in Figure 1 contains the four component terms shown individually as broken lines and represents best visual fit to the data. This curve corresponds to the kinetic parameters $k_1(25°) = (3.5 \pm 0.5) \times 10^5$ sec^{-1}, $\Delta H^{\ddagger} = 11.4 \pm 0.5$ kcal mol^{-1}, and $\Delta S^{\ddagger} = 5.2 \pm 2.2$ eu. In practice equally good visual data fits were obtained with $\Delta H^{\ddagger}$ values within the range 10.9–11.9 kcal mol^{-1}. The precise magnitude of the T_{2O} term is somewhat in doubt as extension of the experimental study to lower temperatures better to establish the contribution of this term to T_{2p} was precluded by the samples' freezing. In consequence of this the T_{2M} and T_{2O} terms were constrained to have identical activation energies, E_a, in the data fitting. The adoption of this equality was based on the assumption that the tumbling time, τ_t, and the electron spin relaxation time, τ_s, for $Co(CH_3CN)_6^{2+}$ are expected to be similar to τ_t ($\sim 2 \times 10^{-11}$ sec) and τ_s ($\sim 5 \times 10^{-13}$ sec) calculated for $Co(CH_3OH)_6^{2+}$ by Luz and Meiboom,[8] and consequently the correlation time, τ_c, and E_a for the dipolar interaction should be identical with those for τ_s. The E_a value for the T_{2M} and T_{2O} terms in Figure 1 is −1.7 kcal mol^{-1}. The Δw_M values used to calculate the $(\tau_M \Delta w_M^2)^{-1}$ contribution to $P_M T_{2p}$ were obtained directly from ^{1}H S data above 20° or from extrapolation of those data to lower temperatures.[9]

The ^{1}H shift data are listed in Table IV and are plotted as ln TSP_M^{-1} against $1/T$ in Figure 3 in which two major regions of shift temperature dependence are seen. At $1/T < 0.0034$, acetonitrile exchange is rapid such that complete environmental averaging of acetonitrile protons occurs and

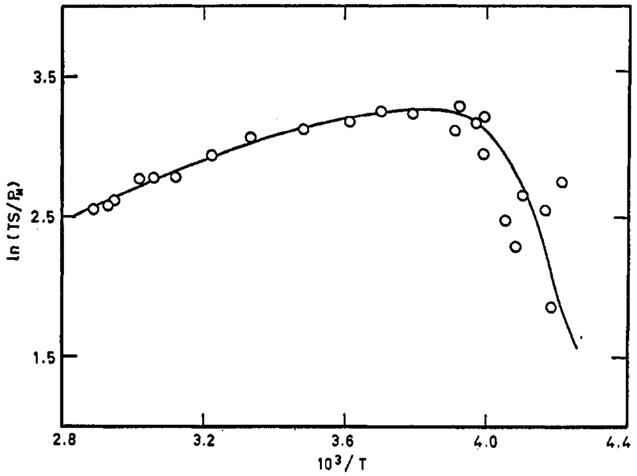

Figure 3.—Variation of ln TSP_M^{-1} with T^{-1} derived from ^{1}H measurements. The data points are calculated directly from shift measurements, and the solid curve is the variation of ln TSP_M^{-1} predicted from T_{2p} data.

$$TSP_M^{-1} = T\Delta w_M \qquad (7)$$

Linear extrapolation of TSP_M^{-1} to $1/T = 0$ yields a Δw_M value of −725 Hz in contrast to the *positive* Δw_M values observed within the experimental temperature range. At $1/T > 0.0039$, TSP_M^{-1} decreases rapidly as predicted[1] for decreasing acetonitrile exchange rates by

$$TSP_M^{-1} = -\Delta w_M \tau_M^{-2}[(1/T_{2M} + 1/\tau_M)^2 + \Delta w_M^2]^{-1} \qquad (8)$$

The solid curve in Figure 3 was calculated from eq 8 using T_{2M} and τ_M values derived from the $P_M T_{2p}$ data fit, and Δw_M values were calculated directly from the shift data at $1/T < 0.0034$ or extrapolated from them. The agreement between the TSP_M^{-1} data and the calculated curve is reasonable. An A/h value of -3.95×10^4 Hz was calculated[10] from the shift data at 25° using eq 5.

Discussion

The derivation of kinetic parameters from the ^{14}N T_{2p} data is considerably simplified by the predominance of the "Δw" relaxation mechanism in determining the temperature dependence of T_{2p} within the experimental

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(8) Z. Luz and S. Meiboom, *J. Chem. Phys.*, **40**, 1058, 1066 (1964).

(9) The shift data reported here are in excellent agreement with that in ref 2. In that study signals arising from bulk and coordinated acetonitrile were simultaneously observed at low temperature at 100 MHz and the observed shifts are coincident with a linear extrapolation of the high-temperature ln TSP_M^{-1} data in Figure 3 after allowance for the different operating frequencies. Similarly the T_{2p} data reported here are in good agreement with those reported over a narrower temperature range in ref 2.

(10) An A/h value of -2.28×10^4 Hz is reported in ref 2, but no temperature is quoted, and consequently it is not feasible to compare the two A/h values as the ^{1}H shift exhibits a non-Curie temperature dependence.

TABLE V

KINETIC PARAMETERS FOR THE EXCHANGE OF ACETONITRILE ON DIVALENT METAL IONS

M^{n+}	$k_1(25°)$, sec^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu
Mn^{2+} [a]	$(1.2 \pm 0.3) \times 10^7$	7.25 ± 0.25	-1.8 ± 0.8 [c]
Fe^{2+} [a]	$(5.5 \pm 0.8) \times 10^5$	9.7 ± 0.7	0.3 ± 2.2 [d]
Co^{2+} [a]	$(3.2 \pm 0.3) \times 10^5$	11.4 ± 0.5	5.0 ± 2.0 [g]
Co^{2+} [b]	$(3.5 \pm 0.5) \times 10^5$	11.4 ± 0.5	5.2 ± 2.2 [g]
Co^{2+}, [b]	1.4×10^5	8.1 ± 0.5	-7.5 ± 2 [e]
Ni^{2+} [a]	$(2.1 \pm 0.3) \times 10^3$	16.4 ± 0.5	12.0 ± 2.0 [d]
Ni^{2+} [b]	$(2.8 \pm 0.5) \times 10^3$	11.7 ± 0.1	-3.6 ± 1.0 [f]

[a] Nitrogen-14 data. [b] Hydrogen-1 data. [c] W. L. Purcell and R. S. Marianelli, *Inorg. Chem.*, **9**, 1724 (1970). [d] R. J. West and S. F. Lincoln, *Aust. J. Chem.*, **24**, 1169 (1971). [e] Reference 2. [f] D. K. Ravage, T. R. Stengle, and C. H. Langford, *Inorg. Chem.*, **6**, 1252 (1967). [g] This work.

temperature range. The contributions of the dipolar terms T_{2M} and T_{2O} to the ^1H T_{2p} data are significant, and consequently the ^{14}N data provide a cross-check on the validity of the ^1H T_{2p} data treatment. The kinetic parameters derived from the ^{14}N and ^1H T_{2p} data sets are compatible within the limitations of the data treatment, as is the case for ^1H and ^{14}N studies of ammonia exchange[11-13] on $Ni(NH_3)_6{}^{2+}$.

The ^1H line-broadening study reported by Matwiyoff and Hooker[2] covered a narrower temperature range than that investigated in this work, and consequently the T_{2M} and T_{2O} contributions to T_{2p} were not observed in the earlier study. As a result the $\Delta H^{\ddagger}$ value derived by Matwiyoff and Hooker is too small, and k_1 and $\Delta S^{\ddagger}$ are proportionately at variance with the kinetic parameters derived from ^1H and ^{14}N data reported in this study (see Table V).

The *positive* ^{14}N A/h value is consistent with paramagnetic spin delocalization onto nitrogen by a σ-bonding interaction between cobalt(II) e_g orbitals and the orbital containing the nitrogen lone pair.[2] The *negative* ^1H A/h values observed over the experimental temperature range suggest a negative spin density at the hydrogen atoms, but the non-Curie temperature dependence of the ^1H shift data indicates that both Fermi contact and pseudocontact interactions may contribute to the ^1H shift. Kurland and McGarvey[14] have shown that for complexes with T_1 ground states a Zeeman mixing of excited states into the ground state may lead to a non-Curie temperature dependence. There appears to be no deviation from Curie behavior in the ^{14}N shift data, although it should be noted that the limiting shift region conforming to eq 7 is only just entered. This is consistent with the Fermi contact contribution associated with the coordinating ligand atom being significantly larger than the pseudocontact shift contribution to the observed shift.[14]

The kinetic parameters for the exchange of acetonitrile on divalent metal ions (Table V) exhibit a trend in which $k_1(25°)$ decreases from Mn^{2+} to Ni^{2+}, and the reverse trend for $\Delta H^{\ddagger}$. These trends are also observed for solvent exchange on these metal ions in ammonia, methanol, and water, which suggests a similarity in mechanism in these four solvents.[3] Recent crystal field calculations,[15] based on a square-pyramidal transition state for water exchange, which is consistent with the dissociative ligand substitution mechanism proposed[16,17] for these metal ions, predict the above trend in $\Delta H^{\ddagger}$.

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

[12] W. L. Rice and B. B. Wayland, *ibid.*, **6**, 2270 (1967).

[13] A. L. Van Geet, *ibid.*, **7**, 2027 (1968).

[14] R. J. Kurland and B. R. McGarvey, *J. Magn. Resonance*, **2**, 286 (1970).

[15] A. L. Companion, *J. Phys. Chem.*, **73**, 739 (1969).

[16] M. Eigen, *Pure Appl. Chem.*, **6**, 97 (1963).

[17] M. Eigen and R. J. Wilkins, *Advan. Chem. Ser.*, **No. 49**, 55 (1965)

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Inverse Hydrogen Isotope Effects in Some Metal Hydride Systems

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Several instances were found of metal hydrides in which replacement of hydrogen by deuterium or tritium resulted in a more stable compound. The experimental evidence consists in measurements of the dissociation pressures of pure isotopic species, and of the equilibrium distribution of hydrogen isotopes between gas and solid phases in systems of mixed isotopic content. Examples are VH_2, NbH_2, $(V,Nb)H_2$, and $LaNi_5H_6$. On the other hand, ternary hydrides formed by the intermetallics Mg_2Ni and TiFe exhibit an isotope effect which is in the opposite, and more usual, direction.

Introduction

An investigation of the reversible absorption of hydrogen by metals, mostly alloys, has been conducted at this laboratory over the past several years. It has resulted in the discovery, or improved characterization in terms of pressure–composition–temperature (P–C–T) relationships, of a number of new hydride phases.[1] Some attention has been given to properties other than P–C–T, as for instance magnetic properties;[2] and recently the effect of replacing normal hydrogen by deuterium was examined in vanadium di-

[1] (a) J. J. Reilly and R. H. Wiswall, Jr., *Inorg. Chem.*, **6**, 2220 (1967); (b) *ibid.*, **7**, 2254 (1968); (c) *ibid.*, **9**, 1678 (1970).

[2] S. Aronson, J. J. Reilly, and R. H. Wiswall, Jr., *J. Less-Common Metals*, **21**, 439 (1970).