CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
WASHINGTON STATE UNIVERSITY, PULLMAN, WASHINGTON 99163

Kinetics of Water Exchange in Aquoammine and Malonatocobalt(II) Complexes[1]

BY PATRICK E. HOGGARD, HAROLD W. DODGEN, AND JOHN P. HUNT*

Received May 25, 1970

Kinetic data for water exchange in $Co(H_2O)_6^{2+}$, $Co(NH_3)(H_2O)_5^{2+}$, $Co(NH_3)_2(H_2O)_4^{2+}$, and $Co(malonate)(H_2O)_4$ are reported. The k_1 (per water molecule) values at 25° are 2.24 (±0.05) × 10^6, 1.55 (±0.2) × 10^7, 6.5 (±1) × 10^7, and 2.2 × 10^7 sec^{-1}, respectively. The corresponding ΔH^* and ΔS^* values (kcal/mol and cal/mol deg) are 10.3 ± 0.2, 5.1 ± 0.6; 12.6 ± 0.6, 17 ± 3; 9.4 ± 1.5, 7 ± 5; 12.9 ± 0.8, 18 ± 4. Scalar coupling constants (A/h) for ^{17}O based on $\mu_{eff} = 5.02$ are, in the same order, 1.20 (±0.02) × 10^7, 1.20 (±0.1) × 10^7, 1.16 (±0.1) × 10^7, and 1.15 (±0.1) × 10^7 Hz. The rate of exchange for $Co(mal)_2(H_2O)^{2-}$ is greater than 10^8 M sec^{-1} at 25°. Discussion of the labilizing effects of ligands is given. The increased rates are not accounted for simply by a decrease in ΔH^*. Comparison of cobalt and nickel data suggests that different mechanisms are involved for the two metals.

Introduction

Water-exchange kinetic data in aquo and substituted aquo ions are of interest in part because of their use in consideration of the mechanisms of net substitution reactions. The effects of various ligand substitutions on the kinetic behavior of remaining water molecules are of interest in themselves in attempting to assess the factors responsible for them. In addition, structure information can sometimes be obtained regarding the nature of the aquo ions. Comparisons between different metals (*e.g.*, Co and Ni) are also of some theoretical and practical interest. We have reported considerable results on Ni(II)[2] obtained by ^{17}O nmr line broadening and shift measurements. In this report we present data on some cobalt systems which have received much less attention.

Experimental Section

The nmr spectrometer used employed a Knight–Watkins–Pound marginal oscillator and a phase-sensitive detector.[3] Square-wave modulation was used to produce two absorption curves, 180° out of phase. For some measurements the oscillator frequency was locked to a primary reference provided by a General Radio 1164-A frequency synthesizer, using an error circuit tuned to a 100-kHz secondary reference, also provided by the frequency synthesizer. At 14 MHz this resulted in an accuracy of ±10 Hz with a stability of ±1 Hz over the period of several measurements. Signal enhancement was obtained using a Fabri-Tek 1052-LSH signal averager. A magnetic field continuously variable up to 24.6 kG was provided by a Varian V-3800 15-in. electromagnet, with a field inhomogeneity of *ca.* 0.05 G and regulated to within 1 ppm. The ^{17}O resonance was ordinarily observed at 14.2 MHz, with some measurements at lower frequencies. Sample temperatures were controlled to ±0.1° using a silicone fluid (Dow Corning 200) circulation system.

The ^{17}O water was provided by YEDA R and D Co. Ltd., Rehovoth, Israel, and was enriched to 7 atom % ^{17}O (with 56% ^{18}O and normalized H content). It was multiply distilled *in vacuo* for reuse. Other reagents were AR grade.

Solutions of $Co(NO_3)_2 \cdot 6H_2O$ and NH_3 (1.6 M, in 2 M NH_4NO_3) were prepared and standardized. Cobalt analysis was by electrodeposition.[4] Experimental solutions were prepared by adding these standard solutions by volume together with a measured amount of NH_4NO_3 to enriched $H_2{}^{17}O$. Cobalt salt concentrations were below 0.6 M and NH_3 concentrations below 0.08 M. All ammine solutions contained 2 M NH_4NO_3. For cobalt(II)–malonate systems solutions were prepared by adding standard Co(II) solutions by volume and sodium malonate and malonic acid by weight to a measured volume of enriched water.

The distribution of species in these solutions was calculated from the known amounts of added reagents. The measured pH provided initial estimates for all species concentrations. These were then refined using a computer program based on Secant 1620[5] to solve the simultaneous nonlinear equations involved. The cobalt–ammonia complex formation constants used were those of Bjerrum.[6] The enthalpy of formation of the monoammine complex was determined calorimetrically by Yatsimirskii and Milyukov[7] as −3.20 kcal/mol and this value was used for the enthalpies of formation of higher complexes as well. Variation in enthalpies are in general small for metal–ammine complexes (those for the cadmium–ammonia complexes are each given as −3.5 kcal/mol, for example[7]). Acid dissociation constants (NH_4^+) and enthalpies used were those of Spike.[7] All of these constants were determined in 2 M NH_4NO_3 media. The equilibrium constant and enthalpy for the dissociation of water used were those given by Ackermann.[8] The equilibrium data for malonate complexes are less certain than for the ammines. A value for log K_1 at 30° and $\mu = 0.25$ of 2.65 was used based on a study of Monk.[9] The enthalpy of formation for the mono complex was estimated from data of McAuley and Nancollas[10] to be 2 kcal/mol. Powell and Johnson[11] gave a value for log K_2 (30°) of 1.5. We found empirically that our data were better fit using 1.7. No direct measurements on the monohydrogenmalonatocobalt(II) complex were found but a value of log K (30°) of 0.55 seems reasonable.[12] The enthalpies of formation for the dimalonato and monohydrogenmalonato complexes were arbitrarily taken to be zero. Malonic acid dissociation constants were those of Cannan and Kibrick[13] with enthalpies given by Hamer[14] and Gelles and Nancollas.[15] Ionic strength corrections to $\mu = ca.$ 0.25 were made using the relationships of Manning and Monk.[16] In the final fitting of the malonate data the equilibrium cobalt complex parameters were varied slightly to give a best fit (see later) and the numbers given above are the final ones used. Solution compositions were calculated as a function of temperature as the equilibria are

---

[1] This work was supported in part by the U. S. Atomic Energy Commission and is Report No. RLO-2040-20.

[2] A. G. Desai, N. W. Dodgen, and J. P. Hunt, *J. Amer. Chem. Soc.*, **92**, 798 (1970).

[3] R. Murray, H. W. Dodgen, and J. P. Hunt, *Inorg. Chem.*, **3**, 1576 (1964).

[4] D. H. Brophy, *Ind. Eng. Chem., Anal. Ed.*, **3**, 363 (1931).

[5] Written by J. T. Godfrey, Advanced Technology Laboratories, General Electric Co.

[6] J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Sons, Copenhagen, 1941.

[7] L. G. Sillén and A. E. Martell, Ed., "Stability Constants of Metal Ion Complexes," Chemical Society, London, 1964.

[8] T. Ackermann, *Z. Elektrochem.*, **62**, 411 (1958).

[9] C. B. Monk, *J. Chem. Soc.*, 2456 (1965).

[10] A. McAuley and G. H. Nancollas, *ibid.*, 989 (1963).

[11] J. E. Powell and D. K. Johnson, *J. Chromatogr.*, **44**, 212 (1969).

[12] J. L. Schubert, E. L. Lind, W. M. Westfall, R. Pleger, and N. C. Li, *J. Amer. Chem. Soc.*, **80**, 4799 (1958).

[13] R. K. Hannan and A. Kibrick, *ibid.*, **57**, 2314 (1935).

[14] W. J. Hamer, J. O. Burton, and S. F. Acree, *J. Res. Nat. Bur. Stand.*, **34**, 369 (1940).

[15] E. Gelles and G. H. Nancollas, *J. Chem. Soc.*, 4847 (1956).

[16] P. G. Manning and C. B. Monk, *Trans. Faraday Soc.*, **57**, 1996 (1961).

shifted considerably over the temperature range covered in these experiments. Compositions of each solution at 25° are listed in Table I.

TABLE I
SOLUTION COMPOSITIONS AT 25°

(A) Ammine Data

Soln	Total [Co(II)], *M*	Total [NH_3], *M*	pH	% Co-$(H_2O)_6^{2+}$	% Co-(NH_3)-$(H_2O)_5^{2+}$	% Co-$(NH_3)_2$-$(H_2O)_4^{2+}$	% Co-$(NH_3)_3$-$(H_2O)_3^{2+}$
I	0.0455	0.0284	6.90	55.9	35.9	7.7	0.4
II	0.0555	0.0331	6.80	56.7	35.5	7.3	0.4
III	0.0447	0.0546	7.28	30.0	44.8	22.0	2.9
IV	0.0440	0.0799	7.50	15.6	40.3	35.2	8.0
V	0.0464	...	4.18	99.9	...	...	...
VI	0.0384	...	4.3	99.9	...	...	...
VII	0.154	...	4	99.9	...	...	...

(B) Malonate Data

Soln	Total [Co(II)], *M*	Total[a] [malonate], *M*	pH	% Co-$(H_2O)_6^{2+}$	% Co-(mal)-$(H_2O)_4$	% Co-$(mal)_2$-$(H_2O)_2^{2-}$	% Co-(Hmal)-$(H_2O)_5^{+}$
VIII	0.0414	0.145	4.0	19.6	58.1	15.9	6.4
IX	0.0803	0.141	3.6	44.4	38.9	3.9	12.8

[a] Sodium malonate plus malonic acid.

For all solutions there was no apparent oxidation to Co(III). Solutions were made up with several times the ammonia concentration of the most concentrated solution used here, and these showed no spectral changes upon prolonged heating and standing for several months, indicating that oxidation can be ignored. In addition, up to pH 8 there should be less than 1% interference from the hydrolysis[17] of $Co(H_2O)_6^{2+}$.

The reference solution or blank used for these studies was in each case identical with the solution used, except for the substitution of Zn^{2+} ions for Co^{2+}. In general each point represents the average of eight spectra (sixteen absorption curves) for the Co(II) solutions and at least four spectra for the reference solutions, with half of all spectra run in the reverse direction in order to average out small field drifting effects.

Treatment of Data and Results

A detailed description of the methods used in treating the data has been presented.[18-20] The observations consist of measured line broadenings and paramagnetic shifts of the bulk water ^{17}O nmr line in the presence of various aquoamminecobalt(II) species. Line broadenings are treated in terms of the quantity $T_{2p}'' = 2m(Co)/\gamma\Delta$, where $m(Co)$ is the total molality of all Co(II) species, γ is the magnetogyric ratio for ^{17}O (3628 G^{-1} sec^{-1}), and Δ is $(W_{obsd} - W_0)$. W_{obsd} represents the full line width in gauss for the Co(II) solutions, measured at half-maximum absorption, and W_0 the same quantity for the blank solution. Paramagnetic shifts are treated in terms of the shift function $Q = TS \cdot m(H_2O)/m(Co)$, where T is the absolute temperature, $m(H_2O)$ and $m(Co)$ refer to the molalities of free water and total cobalt ion, and S is the fractional paramagnetic shift, $(\Delta\omega/\omega_0)$ relative to the $H_2{}^{17}O$ blank. $\Delta\omega = \omega_{obsd} - \omega_0$ is the observed shift of the bulk water signal in the presence of Co(II) ions, ω_0 being the resonant frequency (in radians per second) for ^{17}O in the blank solution (which, however, shows no measurable shift relative to pure water). $\Delta\omega_M = \omega_M - \omega_0$ refers to the shift, relative to the reference solution, of the resonance frequency of the oxygen bound to the Co(II).

Solutions V–VII were used to obtain data for the hexaaquocobalt(II) species. Observed values for T_{2p}'' and Q are plotted in Figure 1. The widths of the blank varied from *ca.* 0.15 to 0.35 G over the temperature range used.

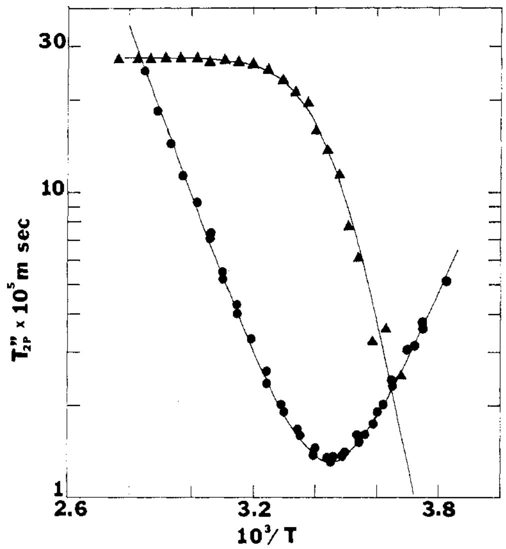

Figure 1.—Semilogarithmic plots of T_{2p}'' and Q *vs.* $10^3/T$ for $Co(H_2O)_6^{2+}$. Solid lines are calculated from final parameters: ○, T_{2p}'' data; ▲, shift data.

For the Co(II) species studied the inequalities $\tau_M^{-1} \gg T_{2M}^{-1}$ and $|\Delta\omega_M| \gg T_{2M}^{-1}$ are valid. In this case the Swift–Connick equations describing the line broadening and paramagnetic shift reduce to[18,19]

$$T_{2p}'' = \frac{m(H_2O)}{n}\,\frac{\tau_M + 1/\tau_M\Delta\omega_M^2}{1 + 1/T_{2M}\tau_M\Delta\omega_M^2} \qquad (1)$$

$$Q = \frac{nT\Delta\omega_M}{\omega_0(1 + \tau_M^2\Delta\omega_M^2)} \qquad (2)$$

In particular, when $\Delta\omega_M^2 \gg T_{2M}^{-1}\tau_M^{-1}$ the expression for T_{2p}'' becomes

$$T_{2p}'' = \frac{m(H_2O)}{n}(\tau_M + 1/\tau_M\Delta\omega_M^2) \qquad (3)$$

In these equations τ_M is the mean lifetime of a water molecule in the bound state, n is the number of coordinated water molecules, and T_{2M} is the transverse relaxation time of a bound water molecule. These quantities were considered to have the following temperature dependences: $\tau_M = (h/kT)\exp(\Delta H^*/RT - \Delta S^*/R)$; $\Delta\omega_M/\omega_0 = \alpha/T$ (Curie's law); $T_{2M} = B\exp(A/RT)$, this being an empirical equation to account for the observed, but slight, temperature dependence of T_{2M}.

Equations 2 and 3 were used to fit the line-broadening and shift data for the $Co(H_2O)_6^{2+}$ ion. These equations require three parameters. Empirical parameters were chosen which it was felt would exhibit the least interdependence in the fitting process. It is seen that τ_M and $1/\tau_M\Delta\omega_M^2$ produce two approximate straight lines of nearly opposite slope on a semilogarithmic plot such as Figure 1. If D_1 is the value of $T_{2p}'' \times 10^5$ at the intersection of the two lines and D_2 the value of $10^3/T$ at the intersection, then with the addition of the activation enthalpy for τ_M, ΔH^*, the equations for the line

---

[17] J. A. Bolzan and A. J. Arvia, *Electrochim. Acta*, **7**, 589 (1962).

[18] T. J. Swift and R. E. Connick, *J. Chem. Phys.*, **37**, 307 (1962); **41**, 2553 (1964).

[19] H. H. Glaeser, H. W. Dodgen, and J. P. Hunt, *Inorg. Chem.*, **4**, 1061 (1965).

[20] A. G. Desai, H. W. Dodgen, and J. P. Hunt, *J. Amer. Chem. Soc.*, **91**, 5001 (1969).

TABLE II

KINETIC PARAMETERS FOR EXCHANGE OF H_2O WITH $Co(H_2O)_6^{2+}$

	This work	Ref 22	Ref 24	Ref 18
Medium	2 M NH_4NO_3, pH 4.2	0.35 M $HClO_4$	0.2 M $HClO_4$	0.1 M $HClO_4$
k_1(298°K), sec^{-1}	2.24 ($\pm$0.05) $\times 10^6$	2.15 $\times 10^6$ [a]	2.35 ($\pm$0.2) $\times 10^6$ [a]	1.35 $\times 10^6$
ΔH^*, kcal/mol	10.3 $\pm$ 0.2	10.4	11.9 $\pm$ 0.7	8.0
ΔS^*,[c] eu	5.1 $\pm$ 0.6	5.3	10.6[a]	−4.1
A/h,[b] Hz	1.20 ($\pm$0.02) $\times 10^7$	1.31 $\times 10^7$ [a]	1.35 $\times 10^7$	1.14 $\times 10^7$ [a]

[a] Calculated from data presented. [b] Calculated using $\mu_{eff} = 5.02$. [c] From k_1.

broadening and shift can be synthesized to include the temperature dependences described above.

Let y_1 be the right-hand asymptote, $m(H_2O)\tau_M/n$, with units of $T_{2p}'' \times 10^5$, y_2 the left-hand asymptote, $m(H_2O)/n\tau_M\Delta\omega_M^2$, with the same units, and x the ordinate, with units of $10^3/T$; then

$$y_1 = 10^{\log(xD_1/D_2)+(\Delta H^*/4.58)(x-D_2)}$$

$$y_2 = 10^{3\log(D_2/x)+\log(D_1)+(\Delta H^*/4.58)(D_2-x)}$$

The line broadening and paramagnetic shift can be expressed in terms of these asymptotic lines as

$$T_{2p}'' \times 10^5 = y_1 + y_2 \qquad (4)$$

$$Q = \frac{Tm(H_2O) \times 10^5}{\omega_0(1 + y_1/y_2)(y_1y_2)^{1/2}} \qquad (5)$$

The parameters D_1, D_2, and ΔH^* were varied around initial estimates, obtained from standard curve-fitting procedures,[19] to obtain the best visual fit to the data. The calculated curves using the best values of these parameters are displayed in Figure 1 as solid lines. The excellent agreement with the experimental data gives us some confidence in the derived kinetic parameters and in the appropriateness of the equations used to fit the data.

The first-order rate constant ($k_1 = 1/\tau_M$) is derived from y_1 directly. The scalar coupling constant, A/h, can be calculated from the limiting shift, Q_0, obtained at high temperatures. The coupling constant is related to the shift of the bound water molecules by

$$S = \Delta\omega_M/\omega_0 = \frac{2\pi\mu_{eff}\beta(A/h)}{3kT\gamma_n}[S(S+1)]^{1/2} \qquad (6)$$

where μ_{eff} is the effective magnetic moment in Bohr magnetons, γ_n is the nuclear magnetogyric ratio, S is the resultant electron spin, k the Boltzmann constant, and β is the Bohr magneton in cgs units. From eq 2 the high-temperature limiting value of Q, Q_0, is seen to be $Q_0 = nT\Delta\omega_M/\omega_0$. Substituting for $\Delta\omega_M$ in equation 6

$$A/h = \frac{3k\gamma_n}{2\pi\beta\mu_{eff}[S(S+1)]^{1/2}}\left(\frac{Q_0}{n}\right) \qquad (7)$$

For high-spin cobalt(II) complexes this can be evaluated numerically as

$$A/h = \frac{1.331 \times 10^7}{\mu_{eff}}\left(\frac{Q_0}{n}\right) \qquad (8)$$

For $Co(H_2O)_6^{2+}$ in aqueous solution, $\mu_{eff} = 5.02$ BM.[21] There are apparently no data for the hexaamminecobalt(II) ion in solution, and, lacking any estimates for the mixed complexes, μ_{eff} has been taken as 5.02 BM in all cases.

The kinetic parameters derived for $Co(H_2O)_6^{2+}$ in the above fashion are listed in Table II together with previous results. It will be noted that the values derived in this work are substantially the same as those of Chmelnick and Fiat,[22] determined in a 0.35 M $HClO_4$ medium.

Solutions I–IV contained, in addition to $Co(H_2O)_6^{2+}$ ion, varying amounts of $Co(NH_3)(H_2O)_5^{2+}$ and $Co(NH_3)_2(H_2O)_4^{2+}$, with a small amount of $Co(NH_3)_3(H_2O)_3^{2+}$ species. In order to obtain the contributions to the line broadening and the shift from individual species, it was assumed that these properties are additive;[20] that is

$$\frac{1}{T_{2p}}(\text{obsd}) = \sum_{i=0}^{3} \frac{x_i}{T_{2p}''(i)}$$

$$Q(\text{obsd}) = \sum_{i=0}^{3} x_iQ(i)$$

where x_i is the mole fraction of Co(II) represented by the ith complex, and $T_{2p}''(i)$ and $Q(i)$ are the relaxation time and shift functions of the ith complex (i is the number of bound NH_3 molecules). Neglecting the very small contribution of the triammine species to the line broadening, a resolution of the line-broadening curves for the monoammine and diammine species was made using the data from solutions I and III and the known line-broadening curve for the hexaaquo species. The simultaneous linear equations at each temperature were solved using the previously calculated species distributions to generate values for $T_{2p}''(i)$ for the monoammine and diammine species over an appropriate temperature range.[20] The resolved curves exhibited a large amount of scatter, primarily because the minima for these curves lie at temperatures below 0°; and for all practical purposes only the anti-Arrhenius (negative slope) portion of the curves contributes to the observed line broadening for temperatures under consideration. Because of this, the monoammine and diammine species contribute significantly to the line broadening only over a small temperature range near the minima of their line-broadening curves. The shift curves were resolved in the same manner, with a relatively greater degree of accuracy.

From the resolved shift curves it was apparent that Q_0/n (and thus, presumably, A/h) was in each case equal to the value for the hexaaquo species (4.54°K) within experimental error. A computer program was then used to synthesize the line-broadening and shift curves for solutions I–IV, using k_1 and ΔH^* for the monoammine and diammine species as dependent parameters and using the calculated species distributions over the entire temperature range. Equation 2 was used to synthesize shift curves for all species. Equation 3 was sufficient to synthesize the line-broadening curve

---

(21) H. Landolt and R. Börnstein, "Magnetic Properties of Coordination and Organo-Metallic Transition Metal Compounds," Vol. 2, Springer-Verlag, Berlin, 1966.

(22) A. M. Chmelnick and D. Fiat, *J. Chem. Phys.*, **47**, 3986 (1967).

for $Co(NH_3)(H_2O)_5^{2+}$, but eq 1 was needed for $Co(NH_3)_2(H_2O)_4^{2+}$. In addition, for solution IV, values for the triammine species were estimated ($k_1 = 2.5 \times 10^8$, $\Delta H^* = 11$, $T_{2M} = 3 \times 10^{-6}$ sec) and included in the fitting process. This accounts for a 5-10% contribution to the shift for solution IV and a slight contribution to the line broadening, calculated from eq 1. Parameters were varied around the initial estimates to obtain the best visual fit to the data. Errors were estimated by the degree to which a parameter might be varied, and a reasonable fit was still produced for all curves, by readjustment of all other parameters if necessary. As a final refinement Q_0/n was changed slightly for the diammine species to produce a somewhat better fit. Further variation of Q_0/n, for either the monoammine or the diammine species, in general produced a deterioration of the fitted line-broadening curves, particularly in the regions around the minima. The calculated curves and experimental points for the 14.2-MHz line-broadening data (solutions I, III, IV) are reproduced in Figure 2. Calculated curves and experimental points for the line-broadening data collected at 11.5 MHz are reproduced in Figure 3. Parameters for the magnetic shift data (collected at 14.2 MHz) are shown in Figure 4 together with the calculated curves. The agreement between calculated and experimental curves seems satisfactory considering the experimental precision.

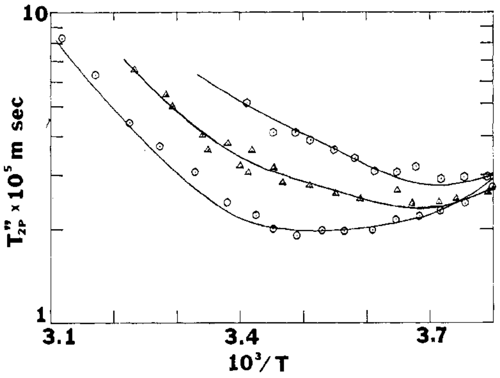

Figure 2.—Semilogarithmic plot of T_{2p}'' for solutions I, III, and IV (14.2 MHz): ○, solution I; Δ, solution III; ⬠, solution IV. Solid lines calculated from determined parameters.

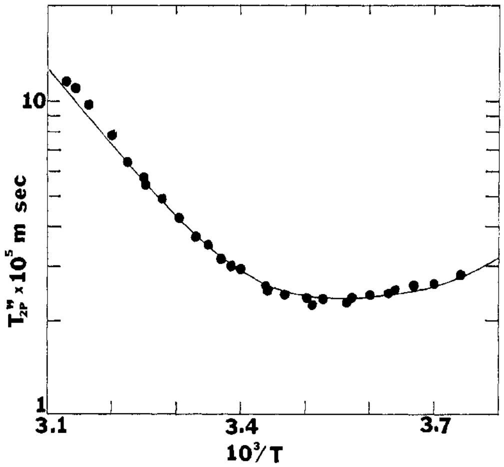

Figure 3.—Semilogarithmic plot of T_{2p}'' for solution II (11.5 MHz). Solid line calculated from determined parameters.

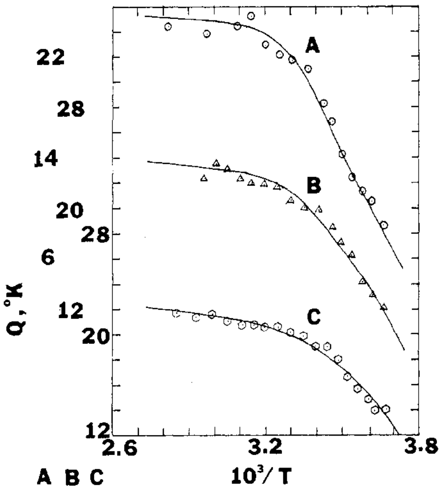

Figure 4.—Plot of paramagnetic shift function Q for solutions I, III, and IV (A, B, and C). Note displaced ordinates as indicated.

The kinetic parameters derived from the resolution are shown in Table III, along with the scalar coupling constants, T_{2M} and T_{1e} (the electronic longitudinal relaxation time, calculated[23] from $1/T_{2M} = {}^2/_3S(S+1)\cdot(A/\hbar)^2T_{1e}$), and the "activation energy" for T_{2M}. The errors shown are estimates based on the precision of the data and the fitting process.

Essentially the same procedures were used for the malonate data except that small variations in the equilibrium data were made to improve the fit and T_{2M} was not important. The fitting was most sensitive to the values used for the monomalonato species and less so for the others. Experimental points and the fitted curves are shown in Figures 5 and 6. Parameters of interest are given in Table III. The larger errors listed for the malonate species mainly reflect the larger uncertainties in the equilibria involved.

Discussion

The present data on $Co(H_2O)_6^{2+}$ are believed to be the most precise so far reported. Our results are very similar to those of Chmelnick and Fiat[22] and suggest that pH changes in the range 0–4 and ionic strength changes from 0.2 to 2 *M* have only a small effect. The early results of Swift[18] seem to be somewhat in error. The ΔH^* value of 11.9 obtained by Morgan, *et al.*,[24] seems to be somewhat high. The use of a higher magnetic field in our experiments should give a better determination of ΔH^* as no T_{2M} correction was necessary and a longer rate-controlled line-broadening region is found.

Both ammonia and malonate substitution produce a labilization of remaining water molecules. The ammine data are qualitatively similar to those for nickel.[2] The approximate additivity of the labilizing effects at 25° can be rationalized by a model in which electron donation by the ligand reduces the effective metal ion charge. Funahashi and Tanaka[25] suggested using Edward's[26] electron-donor parameters (*En*) to correlate

---

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

[24] A. H. Zeltmann, N. A. Matwiyoff, and L. O. Morgan, *J. Phys. Chem.*, **73**, 2689 (1969).

[25] S. Funahashi and M. Tanaka, *Inorg. Chem.*, **9**, 2092 (1970).

[26] J. O. Edwards, *J. Amer. Chem. Soc.*, **76**, 1540 (1954); **78**, 1819 (1956).

TABLE III
KINETIC AND NMR PARAMETERS FOR H_2O EXCHANGE

Species	$k_{total} = nk_1$, sec^{-1} (25°)	k_1(25°), sec^{-1}	ΔH^*, kcal/mol	ΔS^*, eu	A/h, Hz	T_{2M}, sec	T_{1e}, sec	E_a for T_{2M}, kcal/mol
$Co(H_2O)_6^{2+}$	1.34×10^7	$2.24 (\pm 0.05) \times 10^6$	10.3 ± 0.2	5.1 ± 0.6	$1.20 (\pm 0.02) \times 10^7$	...	...	...
$Co(NH_3)(H_2O)_5^{2+}$	7.8×10^7	$1.55 (\pm 0.02) \times 10^7$	12.6 ± 0.6	16.7 ± 2	$1.20 (\pm 0.1) \times 10^7$	...	...	...
$Co(NH_3)_2(H_2O)_4^{2+}$	2.6×10^7	$6.5 (\pm 1) \times 10^7$	9.4 ± 1.5	7 ± 5	$1.16 (\pm 0.1) \times 10^7$	1.5×10^{-4}	5×10^{-13}	2
$Co(Cl)(H_2O)_5^{+}$ [a]	8.5×10^7	1.7×10^7	13.8 ± 0.7	21 ± 3	1.35×10^7	4.4×10^{-5}	1.3×10^{-13}	...
$Co(mal)(H_2O)_4$	8.6×10^7	$2.2 (\pm 0.4) \times 10^7$	12.9 ± 0.8	18 ± 4	$1.15 (\pm 0.1) \times 10^7$	...	...	...
$Co(mal)_2(H_2O)_2^{2-}$	$>10^8$	...	...	...	...	...	...	...

[a] Reference 24.

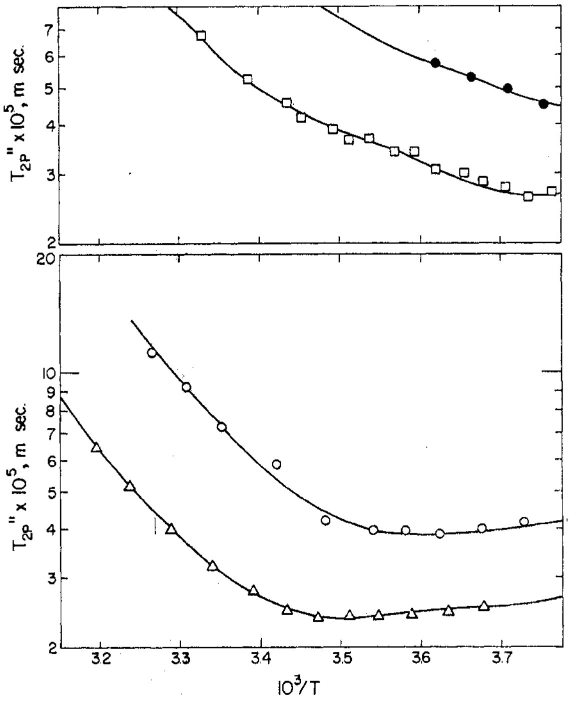

Figure 5.—Semilogarithmic plot of T_{2p}'' vs. $10^3/T$ for solutions VIII (upper graph) and IX: □, 14.2 MHz; ●, 8.5 MHz; △, 14.2 MHz; ○, 8.5 MHz. Solid lines are calculated.

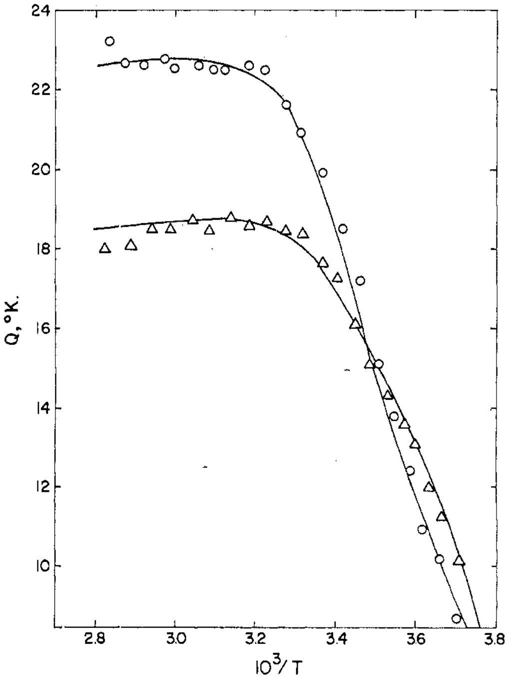

Figure 6.—Plot of Q vs. $10^3/T$ for solutions VIII and IX: △, solution VIII; ○, solution IX. Solid lines are calculated.

the data. Assuming that malonate behaves as two acetate groups, the observed labilization compared to ammonia is about what is expected (*En* for acetate is 0.95; for NH_3, 1.85). The effect of Cl^- is too large to be accounted for on this basis however as *En* for Cl^- is 1.24 while the rate for $Co(H_2O)_5Cl^+$ is a little larger at 25° than that for $Co(H_2O)_5NH_3^{2+}$.

The activation enthalpies do not show the regular decrease that might be expected from a simple electron donation model and in fact tend to be *higher* for the substituted ions. Clearly, entropy and solvation effects are important.

If one compares activation enthalpies for analogous cobalt and nickel species, one finds that they are similar (for hexaaquo and hexaammine ions) or *larger* for the cobalt species (monochloro, monoammine, diammine)[2] although the cobalt rates are *ca.* 100 times faster at 25°. This fact is at variance with the commonly held ideas based on crystal or ligand field calculations that cobalt will have a lower ΔH^*. One might conclude among other things that the calculations are wrong, that solvation cannot be assumed to be the same for the two metals, or that the cobalt exchanges go *via* a different mechanism as we have suggested earlier.[19] Possibly four-coordinate cobalt is involved.

Only a single water-exchange rate could be detected in the substituted species. The shift results, however, indicate that all the water molecules are exchanging. The observed rates may, therefore, be averages of closely similar values.

Acknowledgments.—We wish in addition to thank the Washington State University Research Committee for funds enabling purchase of the $^{17}OH_2$ and the National Science Foundation for funds providing for an electronics technician through an institutional grant to Washington State University.