Oxygen-17 Magnetic Resonance Studies of Ion Solvation. The Hydration of Aluminum(III) and Gallium(III) Ions

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Abstract: The hydration of aluminum(III) and gallium(III) ions has been studied by oxygen-17 nuclear magnetic resonance. The oxygen-17 signal of the noncoordinated water molecules was shifted to a lower field than that of coordinated molecules by the addition of cobaltous perchlorate. The magnetic field was modulated at a frequency of 2000 cps and the first side band of the absorption mode recorded. Nuclear magnetic resonance relaxation times and the rate of water molecule exchange have been calculated from the data by a least-squares fit of 13 parameters to theoretical equations. The lifetimes of the water molecules in the hydration sphere at 25° were found to be: 7.5 sec for Al(III) (by extrapolation from the high-temperature data) and 5.5×10^{-4} sec for Ga(III) ions. The enthalpies of activation are 27 and 6.3 kcal/mole and the entropies of activation 28 and −22 eu for Al(III) and Ga(III) ions, respectively. The transverse relaxation time of oxygen-17 bound to Al(III) ions at 25° was found to be 3.2×10^{-4} sec and ascribed to the time-dependent perturbation of the interaction between the quadrupole moment of the oxygen-17 nuclei and the intramolecular electric field gradients existing in the water molecule, due to the tumbling of the complex. The intermolecular contribution arising from the charge of the ion is negligible relative to that of intramolecular mechanism. The kinetic parameters are discussed in terms of the ionic charge, radius, and structure of the complex. Correlations with the charge, ionic size, and ligand field stabilization energies of other ions are shown to be consistent with the obtained data.

The kinetic and thermodynamic parameters and structural characteristics for the exchange of water molecules between the hydration sphere of metal ions and the noncoordinated water molecules have been studied by various physicochemical methods. This topic has been extensively reviewed.[2-7] By the flow adaptation of the isotopic dilution method, estimates for the rate of exchange of water molecules have been obtained.[8] For Al^{3+} it has been found that $t_{1/2} > 0.02$ sec at 25° and that the coordination number is 6.[8]

Nuclear magnetic resonance provides ready means by which the kinetics of water exchange and that of other ligands with the water molecules can be studied. Only in few cases was it possible to observe the nmr spectra of the hydration sphere.[9-15] Under conditions of slow exchange, it was possible to observe the solvation spheres of the diamagnetic ions Be^{2+}, Al^{3+}, and Ga^{3+} by adding cobaltous ions to the aqueous solution and shifting the oxygen-17 nmr signal of the noncoordinated water molecules to a lower field than that of the coordinated ones.[12]

By this method the coordination numbers of these ions, the chemical shift, and the relaxation times of the oxygen-17 nuclei of the bound water molecules have been determined.[13-15] These results have shown that, owing to the small chemical shift between the coordinated and noncoordinated water molecules, relative to the line width of the coordinated water molecules at low rates of exchange, there is a superposition of a wide signal of the nuclei in the hydration sphere on a narrower signal of the nuclei of the unbound water molecules. The area of the latter is much larger, and therefore it is difficult to observe the signal of the solvation sphere and to obtain by this method the chemical shift, the relaxation times, and the kinetic and thermodynamic parameters for the exchange reaction. In the present study of the hydration of Al^{3+} and Ga^{3+} ions, some of these parameters have been determined by the addition of cobaltous ions to aqueous solutions of these ions.

The rates of exchange of the water molecules between the hydration sphere and the bulk were studied by analyzing the shape of the oxygen-17 absorption signal of the solvation sphere of the water. In the temperature range studied, exchange narrowing exists between the water molecules bound to the cobaltous ions and the unbound water molecules, and the coalesced signal is shifted to a lower field. The exchange of the water molecules is between three different magnetic environments: the bulk, the molecules coordinated to the diamagnetic ions, and the molecules coordinated to the paramagnetic ions. To a very good approximation it may be assumed that the water in the hydration sphere of the Al^{3+} and Ga^{3+} ions exchanges only with the nonbound water. This approximation is particularly good for low concentrations of the paramagnetic ions.

Method of Calculation. McConnell suggested the following equations for the nuclear magnetic resonance line shape in the presence of chemical exchange between

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(1) (a) Weizmann Institute of Science; (b) University of California.

(2) (a) H. Taube, *Progr. Stereochem.*, 3, 95 (1962); (b) O. Ya. Samoilov, "Structure of Aqueous Electrolytes Solutions and the Hydration of Ions," Consultants Bureau Enterprises, Inc., New York, N.Y., 1965.

(3) J. L. Kavanau, "Water and Solute-Water Interactions," Holden-Day, Inc., San Francisco, Calif., 1964.

(4) J. P. Hunt, "Metal Ions in Aqueous Solutions," W. A. Benjamin, Inc., New York, N.Y., 1963.

(5) D. R. Rasselnsky, *Chem. Rev.*, **65**, 467 (1965).

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

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

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(11) D. Fiat, Z. Luz, and B. L. Silver, *J. Chem. Phys.*, in press.

(12) J. A. Jackson, J. F. Lemons, and H. Taube, *ibid.*, **32**, 553 (1960).

(13) R. E. Connick, and D. Fiat, *J. Chem. Phys.*, **39**, 1349 (1963).

(14) D. Fiat and R. E. Connick, *J. Am. Chem. Soc.*, **88**, 4754 (1966).

(15) T. J. Swift, O. G. Fritz, Jr., and T. A. Stephenson, *J. Chem. Phys.*, **46**, 406 (1967).

two different magnetic environments, A and B[16]

$$\frac{dG_A}{dt} + \alpha_A G_A = -\gamma H_1 M_{0A} + \frac{G_B}{\tau_B} - \frac{G_A}{\tau_A} \qquad (1)$$

$$\frac{dG_B}{dt} + \alpha_B G_B = -\gamma H_1 M_{0B} + \frac{G_A}{\tau_A} - \frac{G_B}{\tau_B} \qquad (2)$$

$$G = v + iu \qquad (3)$$

where v and u are, respectively, the absorption and dispersion modes in the Bloch phenomenological equations.

$$\alpha = \frac{1}{T_2} + i(\omega_0 - \omega) = \frac{1}{T_2} + i\Delta\omega$$

T_2 is the transverse relaxation time, M_0 is the magnetization in the z direction (the direction of the applied static field) at thermal equilibrium with the lattice, and τ_j is the lifetime of the nuclei in the environment j.

These equations describe a first-order dependence of the rate of change of the magnetization, G, on the rate of exchange of the nuclei between the different environments. It is also assumed that M_z is constant in time and equal to M_0.

The solution to these equations, assuming steady-state conditions, is

$$G = K\frac{BC + AD + i(AC - BD)}{C^2 + D^2} \qquad (4)$$

where

$$K = -\gamma H_1 M_0$$

$$A = \tau_A\tau_B(P_A\Delta\omega_B + P_B\Delta\omega_A)$$

$$B = \tau_A\tau_B + \tau_A\tau_B\left(\frac{P_A}{T_{2B}} + \frac{P_B}{T_{2A}}\right)$$

$$C = \left(1 + \frac{\tau_A}{T_{2A}}\right)\left(1 + \frac{\tau_B}{T_{2B}}\right) = \tau_A\tau_B\Delta\omega_A\Delta\omega_B - 1$$

$$D = \left(1 + \frac{\tau_A}{T_{2A}}\right)\tau_B\Delta\omega_B + \left(1 + \frac{\tau_B}{T_{2B}}\right)\tau_A\Delta\omega_A$$

P_j is the ratio of the number of nuclei in the j environment to their number in all environments.

Most of the experiments carried out in the present study were done by the side-band method.[17,18] The solution of the Bloch phenomenological equations assuming steady-state conditions with regard to the rate of change of H_0, but not with regard to the magnetic field modulation, is[18]

$$m = v' + iu' = \gamma H_1 M_0 T_2 \sum_{k,n=-\infty}^{+\infty} \frac{J_k(\beta)J_n(\beta)[1 - i(\Delta\omega + k\omega_m)T_2] \exp[i(k - n)\omega_m t]}{1 + (\Delta\omega + k\omega_m)^2 T_2{}^2 + \gamma^2 H_1{}^2 T_1 T_2 J_k{}^2(\beta)} \qquad (5)$$

where $\beta = \gamma H_m/\omega_m$, H_m is the modulating field, $\omega_m/2\pi$ is the modulating frequency, and $J_k(\beta)$ is a Bessel function of the first kind.

In the lock-in detector m is mixed with a reference signal $s(t) = \cos(\omega_m t - \Phi)$ in such a way that the integral over a cycle gives the dc output; thus only terms with $(n - k) = \pm 1$ will contribute to the dc signal.

The detected signal is given by

$$S_D = \int_0^{2\pi/\omega_m} m(t)s(t)\,dt$$

Carrying out the integration for the center band and the positive and negative side bands, one obtains eq 6, where Φ is the audio-phase detector angle defined above and Ψ

$$\frac{\omega_m}{\pi}S_D = 2J_0 \sin\Phi\,[\sin\Psi\, G_{real}(\omega) - \cos\Psi\, G_{imag}(\omega)] + [(J_0 + J_2)\cos\Phi\cos\Psi - (J_0 - J_2)\sin\Phi\sin\Psi] \times G_{real}(\omega + \omega_m) + [(J_0 + J_2)\cos\Phi\sin\Psi + (J_0 - J_2) \times \sin\Phi\cos\Psi]G_{imag}(\omega + \omega_m) - [(J_0 + J_2)\cos\Phi\cos\Psi + (J_0 - J_2)\sin\Phi\sin\Psi]G_{real}(\omega - \omega_m) - [(J_0 + J_2) \times \cos\Phi\sin\Psi - (J_0 - J_2)\sin\Phi\cos\Psi]G_{imag}(\omega - \omega_m) \qquad (6)$$

is the radiofrequency phase angle between the v and u modes.

Curve Fitting. The curve-fitting procedure starts with a parametric family of curves, represented as

$$F(t_1, \bar{x}_1, \ldots, \bar{x}_n)$$

and its form, in our case, is suggested by the theory of eq 4 and 6. An attempt is made to determine a set of values for $\bar{x}_1, \ldots, \bar{x}_n$ such that $F(t_1, \bar{x}_1, \ldots, \bar{x}_n)$ is a best approximation to the data, Y_1, in some sense. Throughout the present study, the "best values" for the parameters mean best in the "least-squares sense," that is, the best $x_1, \ldots, x_n$ are those for which $[Y_t - \mathbf{F}(t_i, x_1, \ldots, x_n)]^2$ is minimal.

The curve fitting was accomplished by means of an IBM 7094 program called LSQVMT.[19] The method used for the function minimization is by Davidson.[20]

Nmr Curve Fitting. The first attempt at curve fitting used as the functional form

$$G_{real} = K_1\frac{AD + BC}{C^2 + D^2} + K \qquad (4a)$$

where ω is the independent variable, and K_1, C, τ_B, T_{2A}, T_{2B}, ω_{0A}, ω_{0B}, and P_A are the parameters. The datum used was the positive first harmonic of the nmr spectrum.

Now the majority of the data had both the positive and negative first harmonics so that the fitting was attempted using

$$G_{real} = K_1\left(\frac{A_1D_1 + B_1C_1}{C_1{}^2 + D_1{}^2}\right) + K_2\left(\frac{A_2D_2 + B_2C_2}{C_2{}^2 + D_2{}^2}\right) + K \qquad (4b)$$

where A_1, B_1, C_1, D_1 and A_2, B_2, D_2 differ from A, B, C, D only in that

$$\Delta\omega_{A1} = \omega_{0A1} - \omega \qquad \Delta\omega_{B1} = \omega_{0B1} - \omega$$

$$\Delta\omega_{A2} = \omega_{0A2} - \omega \qquad \Delta\omega_{B2} = \omega_{0B2} - \omega$$

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(16) H. M. McConnell, *J. Chem. Phys.*, **28**, 430 (1958).

(17) J. V. Acrivos, *ibid.*, **36**, 1097 (1962).

(18) W. A. Anderson, "NMR and EPR Spectroscopy," Pergamon Press, New York, N. Y., 1960, p 180.

(19) Lawrence Radiation Laboratory Computer Program ZO EO LSQV.

(20) A detailed description of this method appears in "Variable Metric Method for Minimization" by W. C. Davidson, appearing as an Argonne National Laboratory Report, No. ANL-5990 Rev. The program LSQVMT contains minor modifications by Eric R. Beals.

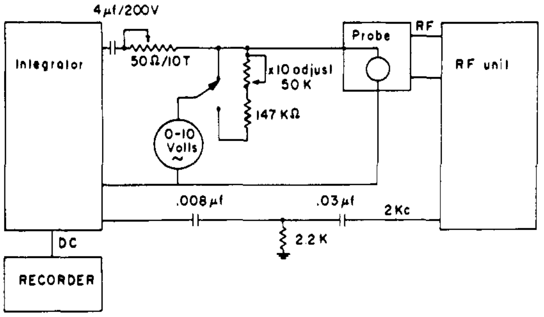

Figure 1. Wiring circuit for the use of high-frequency modulation to the detection of oxygen-17 signals.

where $\omega_{0A1} - \omega_{0A2} = 4175$ cps and $\omega_{0B1} - \omega_{0B2} = 4175$ cps. Equations 4a and 4b involve the assumption that the center band is absent and that the first harmonic resembles the absorption mode, as was indeed the case to a very good approximation. Further improvement was achieved by an attempt to fit the data to eq 6.

Experimental Section

The ^{17}O resonance signals were recorded with a Varian Associates Model V-4200 wide-line spectrometer at 5.772 MHz for Al^{3+} and 8.133 MHz for Ga^{3+}. Both the derivative method and the side-band detection technique were employed.[13,17,18] The side-band method eliminated the possibility of broadening through high modulation amplitudes.

As the width of the lines exceeded the highest modulation frequency, 400 Hz, of the Varian sweep unit, the Varian integrator was used for modulating the magnetic field at a frequency of 2088 Hz (Figure 1).

The solutions of aluminum(III) and gallium(III) salts were prepared from analytical grade materials in water enriched to 10% ^{17}O, acidified with perchloric acid. The concentrations of the salts were determined analytically.

Temperature studies were carried out by flowing heated or cooled nitrogen in the annular space between the sample cell and a dewar. The temperature was measured with a copper-constantan thermocouple to an accuracy of 0.1° and kept constant within ~0.2°. Transverse relaxation times and rates of exchanges were determined from line width. Upper limits for the longitudinal relaxation times were obtained by the radiofrequency saturation method. For Al^{3+} measurements were done in the temperature interval 21.5–105° and for Ga^{3+} at 10–56°.

Results

A. Aluminum(III) Ions. The kinetic parameters for the water-exchange reaction between the sphere of hydration and the unbound water molecules were obtained from the temperature dependence of the absorption nuclear magnetic resonance spectra of the first side band. The kinetic parameters and the relaxation times of the bound molecules could be calculated from the temperature dependence of the bound-water signal. Because of the slow rate of exchange from about room temperature up to about 80°, well-resolved spectra for the bound and unbound water molecules were obtained. From about 80° the exchange between the two sites broadened the lines, and the rate of exchange was calculated from this broadening (Figure 2). Extrapolation of the high-temperature branch to low-temperatures yielded values for the lifetime of the water molecules in the sphere of hydration, whereas extrapolation of the low-temperature branch yielded values for the transverse relaxation time of the ^{17}O nuclei in the hydration sphere. A plot of τ_B, the lifetime of the ^{17}O of the water molecule in the hydration sphere, *vs.* the reciprocal of the absolute temperature yielded a straight line (Figure 3). The enthalpy and entropy of activation for the exchange reaction of the water molecules between the aquo complex and the bulk have been calculated from the variation of τ_B with temperature and the following equation[21]

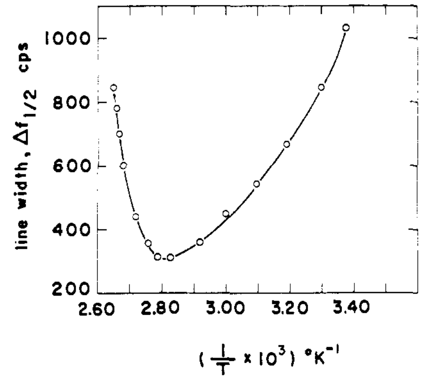

Figure 2. Temperature dependence of the oxygen-17 line width, $\Delta f_{1/2}$, of water molecules coordinated to Al^{3+} ions at 5.772 MHz, 1.55 *M* $AlCl_3$, 0.25 *M* $Co(ClO_4)_2$, 0.5 *M* $HClO_4$ (solution A).

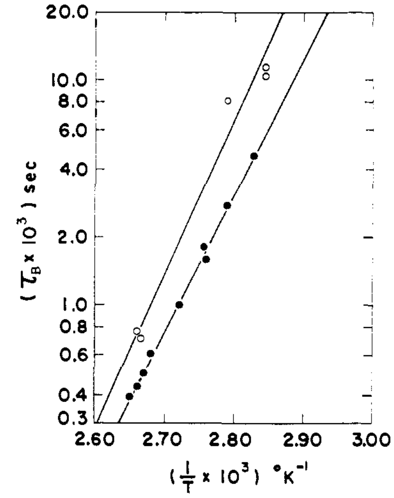

Figure 3. Temperature dependence of the lifetime of water molecules, τ_B, coordinated to Al^{3+} ions: ●, lifetimes calculated from the broadening of the lines at high temperatures; ○, lifetimes obtained by the method of least-squares fit to theoretical line shapes (solution A).

$$\tau_B = \left(\frac{kT}{h}\right)^{-1} \exp\left(\frac{\Delta H^\ddagger}{RT} - \frac{\Delta S^\ddagger}{R}\right) \qquad (7)$$

where k is the Boltzmann constant, h is Planck's constant, T is the absolute temperature, and $\Delta H^\ddagger$ and $\Delta S^\ddagger$ are the enthalpy and entropy of activation, respectively, for the exchange reaction. The results for the kinetic parameters and the relaxation times are summarized in the first column of Table I, where T_{2B} and T_{1B} are the transverse and longitudinal relaxation times, respectively, of the ^{17}O nuclei in the sphere of hydration.

The values thus obtained are to some extent uncertain due to the extrapolation of the high- and low-temperature branches and ascribing the difference between the widths measured at high temperatures and the values obtained by extrapolation of the low-temperature

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(21) H. Eyring, *Chem. Rev.*, 17, 65 (1935).

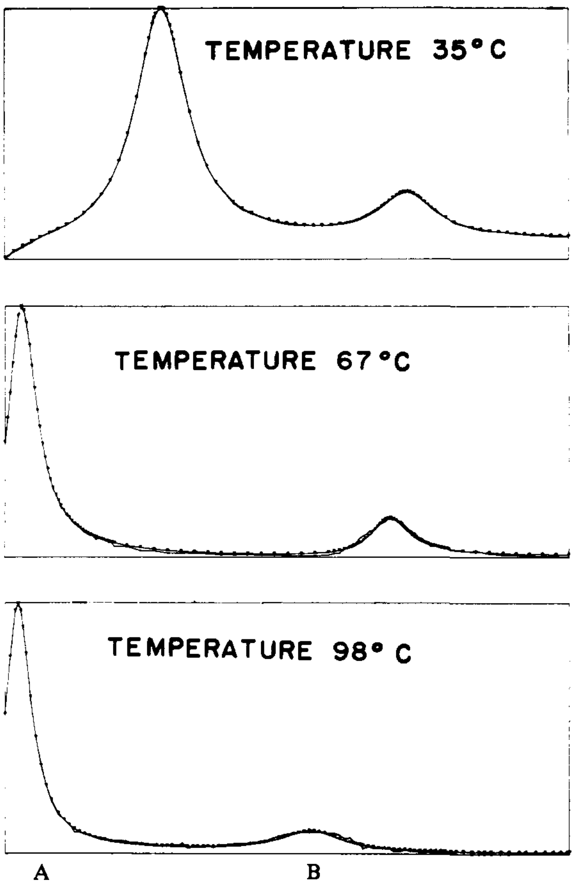

Figure 4. Examples of least-squares fit of the first side band to eq 4: (A) bulk water; (B) water of hydration (solution A).

data to exchange broadening. By a least-squares fit of the theoretical equations (eq 4 and 6, Figures 4 and 5, respectively) to the experimental curves at each temperature, the value for the rate of exchange (Figure 3) and the transverse relaxation times of the ^{17}O in the hydration sphere (Figure 6) were calculated. The calculated parameters are summarized in the second column of Table I.

Table I. Parameters for the Exchange of ^{17}O between the Hydration Sphere of Al^{3+} Ions and the Unbound Water Molecules

	Direct measurement of line widths	Method of least squares
$(T_{2B})_{25°}$, sec	3.2×10^{-4}	3.5×10^{-4}
$(T_{1B})_{25°}$, sec	$\leq 9 \times 10^{-3}$	
$\tau_{B,25°}$, sec	7.5	4.5
$\Delta H^{\ddagger}$, kcal/mole	27	30.5
$\Delta S^{\ddagger}$, eu	28	40

The temperature dependence of the oxygen-17 chemical shift between the coordinated and noncoordinated water molecules is governed, mainly, by two independent factors: at low temperatures, by the dependence of the chemical shift of the noncoordinated water molecules on temperature due to the exchange with the water molecules coordinated to Co^{2+} ions, and at high temperatures, by the exchange with the water molecules coordinated to the Al^{3+} ions (Figure 7).

B. Gallium(III) Ion. The rate of exchange of water coordinated to Ga^{3+} ion at room temperature exceeds that of Al^{3+} by four orders of magnitude, and, as there are natural limits to the temperature range adequate for aqueous solutions, it did not seem likely that low enough temperatures could be reached to allow well-resolved lines of the ^{17}O bound and unbound water molecules. It was found necessary to calculate the parameters for the exchange of the water molecules by the method of least-squares fit (Figure 8). A plot of τ_B values *vs.* reciprocal of temperatures is given in Figure 9. The values obtained for the parameters for the exchange of ^{17}O between the hydration sphere of Ga^{3+} ions and the unbound water molecules are $\tau_{B,25°} = 5.5 \times 10^{-4}$ sec, $\Delta H^{\ddagger} = 6.3$ kcal/mole, and $\Delta S^{\ddagger} = -22$ eu. Because of the rapid exchange, it was impossible to obtain accurate values of T_1 and T_2 for the water coordinated to Ga^{3+}.

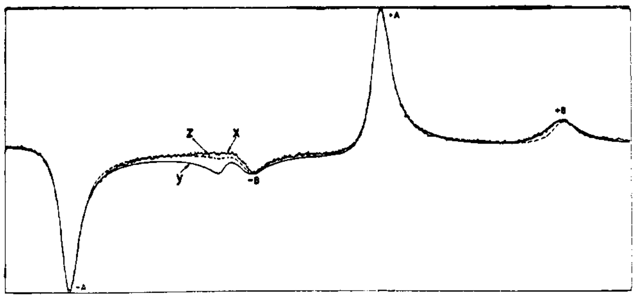

Figure 5. Example of least-squares fit of recorded spectra at 57° to eq 6 (solution A): (A) bulk water; (B) water of hydration; (X) recorded spectra; (Y) fit to recorded spectra excluding data between half-height of the bulk water peaks. All parameters free. Best fit obtained for $\tau_B = 6.7 \times 10^{-2}$ sec; $T_{2A} = 1.1 \times 10^{-3}$ sec; $T_{2B} = 5.6 \times 10^{-4}$ sec; $P_A = 0.76$; $\omega_{0B} - \omega_{0A} = 15.0 \times 10^3$ radians; $\psi = -0.12$ radian; $\Phi = 0.29$ radian; Z—fit to all the recorded spectra. Best fit obtained for $\tau_B = 7.8 \times 10^{-2}$ sec; $T_{2A} = 1.1 \times 10^{-3}$ sec; $T_{2B} = 7.7 \times 10^{-4}$ sec; $P_A = 0.82$; $\omega_{0B} - \omega_{0A} = 15.3 \times 10^3$ radians; $\psi = -0.04$ radian; $\Phi = 0.28$ radian.

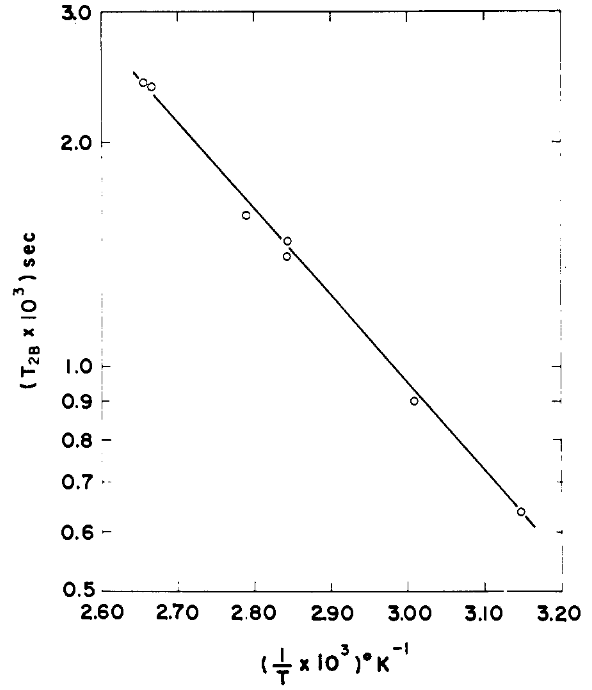

Figure 6. Temperature dependence of the oxygen-17 transverse relaxation times, T_2, at 5.772 MHz of water molecules coordinated to Al^{3+} ions (solution A).

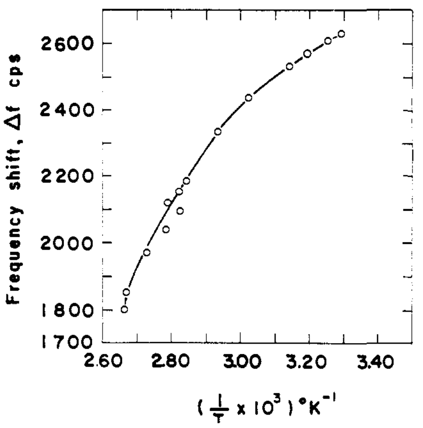

Figure 7. Temperature dependence of the oxygen-17 chemical shift, Δf, between the coordinated and noncoordinated water molecules (solution A).

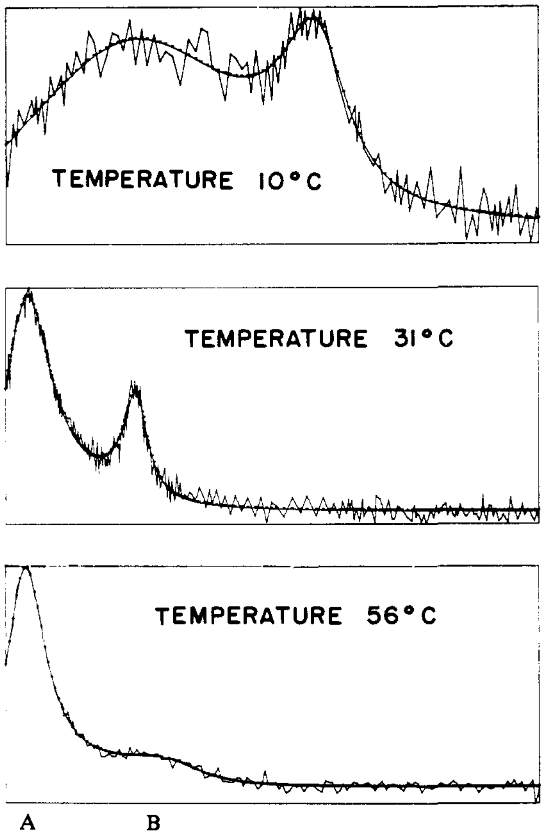

Figure 8. Examples of least-squares fit of the first side band to eq 4; (A) bulk water; (B) water of hydration; 1.7 *M* $Ga(ClO_4)_3$, 0.2 *M* $Co(ClO_4)_2$, 0.6 *M* $HClO_4$ (solution B).

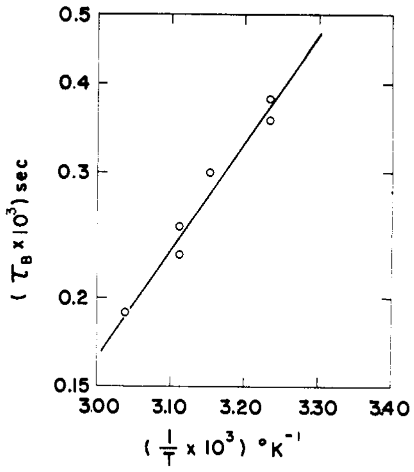

Figure 9. Temperature dependence of the lifetime of water molecules, τ_B, coordinated to Ga^{3+} ions, obtained by the method of least-square fit to theoretical line shapes (solution B).

Discussion

The Kinetic and Thermodynamic Parameters for the Exchange Reaction between the Water Molecules Coordinated to the Metal Ion and the Solvent. The thermodynamic and kinetic parameters for the exchange reaction of the water molecules between the aquo complex and the noncoordinated water molecules should be discussed in terms of the structure of the activated complex involved in the exchange. The energy barrier for the exchange reaction is a function of the charge and size of the metal ion and the energy of electronic rearrangement required to form the activated complex. Because of the closed shell structure of the Al^{3+} and Ga^{3+} ions, the interactions between these metal ions and the ligands are primarily of electrostatic nature.

Table II gives heats of hydration and bond energies of some trivalent ions calculated for an octahedral structure of the aquo complex. The values are seen to be about the same although the kinetic and thermodynamic parameters differ considerably (Table III).

Table II. The Heat of Hydration and Bond Energies of Al^{3+}, Ga^{3+}, Cr^{3+}, and Fe^{3+}

Ion	Born heat of hydration, kcal/mole	Heat of hydration of the aqueous ion, kcal/mole	Bond energies, kcal/mole
Al^{3+}	−513[a]	−1122[b]	112[a]
Ga^{3+}	−452[a]	−1124[b]	122[a]
Cr^{3+}	−450[a]	−1105[b]	119[a]
Fe^{3+}	−437[b]	−1072[b]	116[b]

[a] Calculated. [b] F. Basolo and R. A. Pearson, "Mechanism of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1960, Chapter 2.

Table III. Kinetic Parameters for the Exchange Reaction of Water Molecules between the Aquo Complex and the Solvent

Ion	r,[a] Å	$\Delta H^{\ddagger}$, kcal/mole	$\Delta S^{\ddagger}$, eu	$\tau_{B,25^\circ}$, sec
Al^{3+}	0.51	27[b]	28[b]	6.0[b]
Ga^{3+}	0.62	6.3[b]	−22[b]	5.5×10^{-4} [b]
Ti^{3+}	0.76	6.1[c]	−15[c]	1.0×10^{-5} [c]
Cr^{3+}	0.63	27.6[d]	10[e]	50–60 hr[d]
Fe^{3+}	0.64			5×10^{-5} [f]
Co^{3+}	0.63			28 hr[g]
Be^{2+}	0.35			3×10^{-4} [h]
Mg^{2+}	0.66			$\backsim 10^{-5}$ [i]
Mn^{2+}	0.80	8.1[j]	2.9[j]	3.2×10^{-8} [j]

[a] R. C. Weast, Ed., "Handbook of Chemistry and Physics," 47th ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1966, p F-124. [b] From Table I. [c] A. M. Chmelnick and D. Fiat, to be published. [d] J. P. Hunt and R. A. Plane, *J. Am. Chem. Soc.*, **76**, 5960 (1954). [e] Calculated from data in ref *d*. [f] R. E. Connick, "Advances in Chemistry of Coordination Compounds," S. Kirschner, Ed., The Macmillan Co., New York, N. Y., 1961, p 15. [g] A. C. Rutenberg and H. Taube, *J. Chem. Phys.*, **20**, 825 (1952). [h] Reference 14. [i] Reference 6. [j] Reference 7.

The relatively high activation energy of the exchange reaction of $Al(H_2O)_6{}^{3+}$ is seen to be smaller than the bond energy, but it may well be that this is the energy required to change the coordination number from 6 to 5 with corresponding change in configuration. The net gain, due to decrease in repulsion between the ligands, the increase in attraction between them resulting from the smaller distance of approach, the increase in effective metal ion charge, and the increase in induced dipole moments in the ligands, could be of this order of magnitude. The large value of the entropy of activation also indicates that the coordination number of the activated complex is lower than that of the complex in its ground state. This would indicate an SN1 mechanism. The much lower enthalpy of activation for the Ga^{3+} and the negative value of the entropy of activation may indicate that in the transition state the coordination number is higher than in the octahedral ground state. This could occur as a result of the filled outer orbital (4d electrons) leading to a larger radius and smaller effective charge. The repulsion between the ligands would also be smaller because of the larger distances involved and the correspondingly smaller induced dipoles. It thus seems that the mechanism for exchange should be of an SN2 type.

Owing to the larger radius of the Ga^{3+} ion, the formation of a heptacoordinated Ga^{3+} ion involves a smaller decrease in entropy than the formation of a heptacoordinated Al^{3+} ion. The gain in entropy in the formamation of a pentacoordinated Al^{3+} ion from the octahedral one may be attributed primarily to the fact that one more particle is being formed. The large entropy effects may be related to the large negative entropies associated with the hydration of highly charged ions (restriction of degrees of freedom of solvent molecules in the vicinity of the ion) and the relatively more positive entropy of the molecules in the vicinity of the hydration sphere. The entropy of the molecules in the vicinity of the hydration sphere is considered to be more positive than that of the bulk, because of the disorder existing in between the ordered structure of the water in the hydration sphere and the relatively ordered structure of water in the bulk, resulting from hydrogen-bond interaction. Additional evidence to the plausibility of the assumption that the $Al(H_2O)_6{}^{3+}$ path of the exchange reaction is through an activated complex having less than six ligands can be found in the fact that solid $AlCl_3$ and $GaCl_3$ that are octahedrally coordinated are readily converted to tetracoordinated complexes in the form of M_2Cl_6. The expenditure of only 13.4 kcal/mole suffices to remove Al_2Cl_6 from the solid.

The positive value of the entropy of activation for exchange of water in the $Cr(H_2O)_6{}^{3+}$ ion (Table III) supports the hypothesis of an SN1 mechanism and consequently a pentacoordinated activated complex.

Table III reveals that the lifetimes of the water molecules coordinated to tervalent nontransition metal ions are longer the smaller the ionic radius, being the longest for Al^{3+} ion. It is also seen that, for tervalent metal ions and transition metal ions whose crystal field stabilization energy is relatively small (Ti^{3+} and Fe^{3+}), the lifetimes of the coordinated molecules increase with decrease in radius. For water molecules coordinated to the tervalent rare earth ions, lifetimes are relatively short[22] because of the larger ionic radii and the formation of eight- or nine-coordinated aquo complexes.

The lifetimes of the tervalent transition metal ions Cr^{3+} and Co^{3+} are very long. This is ascribed primarily to two contributions: large crystal field activation energies and the high ionic charge.

The lifetimes of water molecules coordinated to bivalent metal ions are in general shorter than those of water molecules coordinated to tervalent ions of equal radii because of the smaller electrostatic interaction energy; the lifetimes of water molecules coordinated to the Be^{2+} ion are the longest because of its small radius relative to all other ions. For bivalent transition metal ions a correlation between residence time and both ionic radius and crystal field activation energy may be made similar to that for trivalent ions.

Although, in general, it is possible to correlate the lifetimes of the coordinated water molecules with the ionic charge and radius and crystal field activation energies, it should be pointed out that as the structure of the complexes is not always of a regular octahedron,[7,9,10,13] only detailed studies of each complex can yield a correlation between the lifetimes of the coordinated water molecules and other parameters.

Mechanisms of Oxygen-17 Relaxation in Coordinated Water. The discussion here will be based on the study of the hydration of Al^{3+} ion. The dominating relaxation mechanism of oxygen-17 in pure water is known to be through the time-dependent perturbation of the interaction between the quadrupole moment of the oxygen-17 nuclei and the intramolecular electric field gradients existing in the water molecule.[23] It was shown that at a pH of about 7 a broadening of the oxygen-17 line occurs as a result of the indirect coupling between the oxygen-17 nuclei and the protons and as a result $1/T_2 > 1/T_1$, but that, under slightly basic (pH >9.5) or acidic (pH <5) conditions, the transverse and longitudinal relaxation times of oxygen-17 in water are equal and independent of the rate of proton exchange as the rate exceeds the limit that can affect the relaxation times.[24]

The relaxation of oxygen-17 nuclei in the aquo complex of diamagnetic ions under conditions of slow rate of exchange of the water molecules should also be governed by the quadrupole relaxation mechanism. The indirect coupling between the oxygen-17 nuclei and the proton is averaged out by the fast rate of protolysis, and therefore will have only a small contribution to the oxygen-17 relaxation times. The contribution to the relaxation time of the oxygen-17 of the water molecules bound to the metal ions through indirect coupling or pure dipolar interaction with the magnetic moments of the metal ions (in cases that they do possess magnetic moments) will also be negligible relative to the quadrupole relaxation. The quadrupole relaxation may occur through interactions with intra- and intermolecular field gradients. It will be shown that the intermolecular contribution arising from the charge of the ion is negligible relative to the intramolecular ones.

The correlation time for the tumbling of molecules in solution is calculated on the basis of Stokes' law for the diffusion constant D_S for rotation of a rigid sphere of

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(22) G. Geier, *Ber. Bunsenges. Physik. Chem.*, **69**, 617 (1965).

(23) H. A. Christ and P. Diehl, "Magnetic and Electric Resonance and Relaxation," 12th Colloque Ampere, 1962, North Holland Publishing Co., Amsterdam, 1963, p 296.

(24) S. Meiboom, *J. Chem. Phys.*, **34**, 375 (1961).

radius a in a medium of viscosity η

$$D_S = \frac{kT}{8\pi a \eta} \tag{8}$$

The correlation time for the tumbling of a molecule of radius a is given by

$$\tau = \frac{4\pi\eta a^3}{3kT} \tag{9}$$

This equation applies to processes described by a random function of time, where the functions have the transformation properties of spherical harmonics of order two, and thus the equation is applicable to quadrupole relaxation through the tumbling of the molecules. The equation is subject to limitations due to the assumption made with regard to the shape of the molecules and use of the macroscopic value for the viscosity instead of the intrinsic (microscopic) one.

From volumetric considerations the radius of water molecules was calculated to be 1.78×10^{-8} cm. The ionic radius of oxygen is known to be 1.32×10^{-8} cm and that of the aluminum(III) ion is 0.51×10^{-8} cm. The distance between the Al^{3+} ion and the oxygen atoms of crystalline aluminum hydrate was found to be[25] 1.88×10^{-8} cm. This is in good agreement with the ionic radii given above for Al^{3+} and O^{2-} ions. Hence it is concluded that a value of 3.2×10^{-8} cm should be used for the radius of the $Al(H_2O)_6{}^{3+}$ complex ion. The radius of the water molecules could also be taken approximately as the radius of the O^{2-} ion, *i.e.*, 1.32×10^{-8} cm, which is different from that calculated from volumetric considerations.

The calculation of the correlation times requires the knowledge of the viscosity, and for water at 25° it is 0.01 P, whereas for the aluminum chloride solution used, having the composition of 1.5 *M* $AlCl_3$, 0.5 *M* $HClO_4$, and 0.25 *M* $Co(ClO_4)$, a value of 0.02 P will be used in the calculation.

The correlation time of the water molecules based on $a = 1.32 \times 10^{-8}$ cm is $\tau'_{H_2O} = 2.34 \times 10^{-12}$ sec; based on $a = 1.78 \times 10^{-8}$ cm, it is $\tau''_{H_2O} = 5.75 \times 10^{-12}$. The correlation time for the complex is $\tau_{complex} = 6.67 \times 10^{-11}$.

The calculated values show that conditions of the extreme narrowing, $\omega\tau << 1$, apply (ω = larmor frequency of the nucleus).

The quadrupole relaxation in liquids for the extreme narrowing case is given by

$$\frac{1}{T_1} = \frac{1}{T_2} = \frac{3}{40}\frac{2I+3}{I^2(2I-1)}\left(1+\frac{\xi^2}{3}\right)\left(\frac{eQ}{h}V_{ZZ}\right)^2 4\pi^2\tau \tag{10}$$

where $\bar{g}(2\omega_0) = \bar{g}(\omega_0) = \bar{g}(0) = 2\tau$. $\bar{g}(\omega)$ is the Fourier transform of the reduced correlation function $G(t)$

$$G(t) = \frac{F^{(m)}(t)F^{(m)*}(t+\tau)}{|F^{(m)}(t)|^2} \tag{11}$$

supposed to be the same for $F^{(m)}$. $F^{(m)}$'s are lattice functions that transform under rotation as spherical harmonics $Y_2{}^{(m)}$ of order two. ξ is the asymmetry parameter of the electric field gradient.

$$\xi = \frac{V_{XX} - V_{YY}}{V_{ZZ}} \tag{12}$$

$V_{\alpha\alpha}$ is the second derivative of the electrical potential with respect to axes fixed in the molecule. Q is the quadrupole moment of the nucleus.

$$eQ = \langle II|\sum_{i=1}^{A} e_i(3z_i^2 - r_i^2)|II\rangle \tag{13}$$

where the summation is carried over the A nucleons of the nucleus, e_i being the charge of nucleon i. For oxygen-17, $I = {}^5/_2$ and $Q = -4 \times 10^{-27}$ cm^2.

The quadrupole coupling constant defined by $(eQ/h)V_{ZZ}[1 + (\xi^2/3)]^{1/2}$ can be calculated from the ^{17}O line width of water under conditions of fast proton exchange, where the broadening due to the indirect coupling between the oxygen-17 and proton nuclei can be ignored. The line width at 25° for 0.5 *M* $HClO_4$ aqueous solution was found to be 53 cps, yielding the following values for the quadrupole constant: (a) substituting for τ the value of τ'_{H_2O} yields

$$\frac{eQ}{h}V_{ZZ}\left(1+\frac{\xi^2}{3}\right)^{1/2} = \frac{1}{T_2}\left(\frac{3}{40}\frac{2I+3}{I_2(2I-1)}\right)^{-1}\frac{1}{4\pi^2\tau} = 8.45 \times 10^6 \text{ Hz}$$

(b) substituting for τ the value of τ''_{H_2O} yields

$$\frac{eQ}{h}V_{ZZ}\left(1+\frac{\xi^2}{3}\right)^{1/2} = 5.4 \times 10^6 \text{ Hz}$$

The value obtained from the hyperfine structure in microwave spectroscopy is $(8.1 \pm 0.1) \times 10^6$ Hz[26] and is seen to be in much better agreement with (a) than with (b).

Assuming that the quadrupole coupling constant is not influenced by the bonding to the cation

$$\frac{(1/T_1)_{complex}}{(1/T_1)_{water}} = \frac{\tau_{complex}}{\tau_{water}}$$

case a gives

$$\frac{(1/T_1)_{complex}}{(1/T_1)_{water}} = 28.5$$

case b gives

$$\frac{(1/T_1)_{complex}}{(1/T_1)_{water}} = 11.6$$

whereas the experimental value is

$$(\Delta f_{1/2})_{complex,\ 25°} = 965 \text{ cps}$$

$$(\Delta f_{1/2})_{water,\ 25°} = 53 \text{ cps}$$

$$\frac{(1/T_1)_{complex}}{(1/T_1)_{water}} = 18.2$$

An estimate can be made of the quadrupole relaxation due to the gradient of the field of the triply charged aluminum ion. A reasonable assumption to be made is that, choosing the molecular Z axis to coincide with the radius vector pointing from the metal ion to a particular oxygen, $V_{XX} = V_{YY}$ and hence the asymmetry parameter $\xi = 0$

$$V_{ZZ} = 3e\frac{3z^2 - r^2}{r^5} = 3e\frac{2}{r^3} = 4.33 \times 10^{14}\frac{\text{esu}}{\text{cm}^2}$$

$$eQ/h = -1.82 \times 10^{-9}$$

$$(1/T_1) = 0.93 \text{ sec}^{-1}$$

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(25) R. W. G. Wycknoff, "Crystal Structure," Vol. III, Interscience Publishers, Inc., New York, N. Y., 1960, p 38.

(26) M. J. Stevenson and C. H. Townes, *Phys. Rev.*, **107**, 635 (1957).

Accurate calculation should also consider the antishielding factor, which for oxygen-17 is not known; nevertheless, from the above calculation it is obvious that the contribution to the oxygen-17 quadrupolar relaxation through interaction with intermolecular electric field gradients, originating from the electrical charge of the metal ion, can be ignored.

The Plausibility of Proton Resonance Studies. It is now possible to determine the conditions under which the rate of exchange of the protons between the aquo complex and the bulk may be measured by proton magnetic resonance. The rate constants for the hydrolysis of the aquo complex of the ion can be estimated from the equilibrium constant of hydrolysis and the number of collisions between the hydrogen ion and the complex.

$$[\mathrm{M(H_2O)_6}]^{3+} \underset{K_{-1}}{\overset{k_1}{\rightleftharpoons}} [\mathrm{M(H_2O)_5OH}]^{2+} + \mathrm{H^+}$$

Assuming that the rate of collisions is of the order of magnitude of 10^{10} sec^{-1} and the equilibrium constants of hydrolysis are[27] $K_A(\mathrm{Al}) = 1.12 \times 10^{-5}\ M$ and $K_A(\mathrm{Ga}) = 2.5 \times 10^{-3}\ M$, we obtain for the rate constant for hydrolysis $k(\mathrm{Al}) = 10^5$ sec^{-1} and $k(\mathrm{Ga}) = 2.5 \times 10^7$ sec^{-1}, exceeding the rate of exchange of the water molecules by few orders of magnitude.

The chemical shift of the protons in a molar solution of cobaltous perchlorate at 20° is 380 Hz at 60 MHz[28] and decreases with decrease of temperature due to approach of the conditions of slow exchange, and thus it is not possible to observe the hydration sphere of the aluminum ion by proton magnetic resonance, using $\mathrm{Co^{2+}}$ to shift the bulk water proton signal. It might be possible to observe it at very low temperatures using a paramagnetic ion whose coordinated water molecules exchange sufficiently fast at these low temperatures so that the rate of exchange of the water coordinated to the diamagnetic ion is lower than the chemical shift of the bulk water. Some of the rare earth metal ions might serve this purpose. The proton molal chemical shift of aqueous solutions of $\mathrm{Dy^{3+}}$ ions is -390 Hz; the rate of exchange and the enthalpy and entropy of activation are $k_{25°} = 6.3 \times 10^7$ sec^{-1}, $\Delta H^{\ddagger} = 12$ kcal/mole, and $\Delta S^{\ddagger} = 18$ eu, respectively.[29]

The rate of exchange will equal the chemical shift between the solvation shell and the bulk water at a temperature of ~ -22 and $\sim -69°$ for $\mathrm{Al^{3+}}$ and $\mathrm{Ga^{3+}}$, respectively. The rate of hydrolysis would be 4×10^{-4} sec assuming 12 kcal/mole for the free energy of activation for the hydrolysis reaction.

This calculation shows that it should be possible to observe the proton magnetic resonance signal of the hydrations phere of $\mathrm{Al^{3+}}$, but not of $\mathrm{Ga^{3+}}$ ions, and to study the rate of exchange of protons between the solvation sphere of $\mathrm{Al^{3+}}$ and the bulk at temperatures lower than $-22°$ in the presence of $\mathrm{Dy^{3+}}$.

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(27) F. A. Cotton and G. W. Wilkinson, "Advanced Inorganic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1966, p 437.

(28) Z. Luz and R. G. Shulman, *J. Chem. Phys.*, **43**, 3750 (1965).

(29) J. Reuben and D. Fiat, to be published.

The Formation of and Interrelation between Some μ-Peroxo Binuclear Cobalt Complexes. II[1a]

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Abstract: By means of isotopic labeling, the peroxo bridge in $[\mathrm{(NH_3)_5CoO_2Co(NH_3)_5}]^{4+}$ has been shown to originate from the gaseous oxygen used in the preparation. The bridging reaction adding an amido bridge to this ion has been investigated. At 35° in ammoniacal aqueous solution, especially in the presence of a small quantity of alkali hydroxide, transformation (*ca.* 30% in 90 min) to the dibridged complex ion, $[\mathrm{(NH_3)_4Co\text{-}\mu\text{-}NH_2\text{-}\mu\text{-}O_2\text{-}Co(NH_3)_4}]^{3+}$, occurs as proved by isolation of both the nitrate and the perchlorate as brown diamagnetic powders. Isomeric transformation of the dibridged ion in acidic solution, similar to that reported earlier for the analogous en complex, has been observed. Infrared absorption spectra of some dibridged dicobalt–ammine complexes have been studied. New or improved preparations for a number of dicobalt–peroxo–ammine complexes are included.

In the very early stages of the history of cobalt ammines, it was established that the initial oxygenation product of the cobalt(II) salt in aqueous ammonia is $[\mathrm{(NH_3)_5CoO_2Co(NH_3)_5}]\mathrm{X_4}$.[2,3] The structural constitution of the compound, however, remained unknown until the days of Werner. As is well-known,

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[1] (a) Based on work performed in part under the auspices of the U. S. Atomic Energy Commission; (b) Faculty of Science, Osaka City University, Osaka, Japan.

[2] (a) E. Fremy, *Ann. Chim. Phys.*, [3] **25**, 257 (1852); *cf. Chem. Zentr.*, **161**, 185 (1853). All the formulas given by Fremy in this literature can be transformed into the present system by doubling all the numbers of nitrogen and hydrogen atoms or else by halving all the numbers of oxygen, sulfur, and cobalt atoms. This is because the equivalence of atoms was not established correctly in his time. In spite of this, it seems remarkable that he at least gave the correct elemental constitution of the peroxo and other important cobalt ammines. (b) W. Gibbs, *Proc. Am. Acad. Arts Sci.*, **11**, 38 (1876).