A Deuteron Magnetic Resonance Study of the Motion of Ligands in $[Co(ND_3)_5(D_2O)](ClO_4)_3$

Takeshi Ito

Department of Chemistry, Faculty of Engineering, Yokohama National University, Minami-ku, Yakohama

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The deuteron magnetic resonance of single crystals of aquopentamminecobalt(III) perchlorate was measured at various temperatures. The observed quadrupole coupling shows that $[Co(ND_3)_5(D_2O)]^{3+}$ ions execute a rapid isotropic reorientation at high temperatures (above 320°K), while only a C_3 axis reorientation of the ligand ND_3 groups is present at low temperatures (below 290°K). No anisotropic uniaxial reorientation was observed about the C_4 axis parallel to the Co–(D_2O) direction. At temperatures between 310°K and 320°K, the spectrum of a fast exchange limit was observed, together with the spectrum of a slow exchange limit. This anomaly may be explained by the classical rotation of the D_2O ligand.

When clusters of atomic groups rotate in crystals, there are several possibilities with regard to the symmetry of the crystal and the cluster. If both the symmetry of the crystal and that of the cluster are cubic, the reorientational motion of such a cluster may be isotropic because there is no preferential axis of reorientation. On the other hand, in the case of the crystal whose symmetry is lower than cubic, the possibility of some anisotropy in such a motion exists because of the effect of the crystal field even if the cluster has cubic symmetry. In fact, reorientational motion about a single C_3 or C_4 axis is observed in a suitable temperature range for a few compounds.[1-3] In the case of a cluster symmetry lower than cubic, such as *trans*-MA_4X_2 and MA_5X-type complex ions, the M–X bond is the preferential axis for reorientational motions because the motions about all the C_3 axes or C_4 axes except the M–X bond cause an exchange of the A ligand for a different ligand, X, and the motion is usually anisotropic. By proton magnetic resonance studies of cobalt ammine complexes, motional narrowing has been observed in several pentammine and tetrammine complexes at temperatures lower than room temperature, but the second moment of these complexes at room temperature are twice or more as large as those of hexammine complexes.[4-6] This presumably suggests that only the anisotropic uniaxial motion about a C_4 axis parallel to the Co-X bond direction is excited.

In the present work, the deuteron magnetic resonance of single crystals of aquopentamminecobalt(III) perchlorate is studied as one of the singular cases mentioned above. About this crystal it has been reported that the symmetry of the crystal is cubic, while that of the $[Co(NH_3)_5(H_2O)]^{3+}$ ion is lower than cubic, and that the cluster ions are statistically oriented in three possible orientations in the crystal.[7,8] Therefore, it is very interesting to know whether the motion of this tetragonal cluster ion is anisotropic or not in the cubic crystal field.

Experimental

The sample was prepared by the standard method.[9] Deuteration was performed by the repeated isotope exchange of $[Co(NH_3)_5(H_2O)](ClO_4)_3$ with D_2O. The single crystals were obtained by the slow cooling of a saturated solution of $[Co(ND_3)_5(D_2O)](ClO_4)_3$ in D_2O. The crystals exhibit {111} faces. The typical sample used was about $10\times10\times10$ mm^3. The measurements were carried out at 10 MHz using a Robinson-type oscillator detector with field sweep and field modulation (230 cps). The field calibration was performed by means of a D_2O signal at various frequencies, as measured by means of an electronic counter. Temperature control was accomplished by using an electric heater wound outside the probe.

Results and Discussion

The observed spectrum at room temperature consists of three pairs of lines (hereafter, these will be denoted

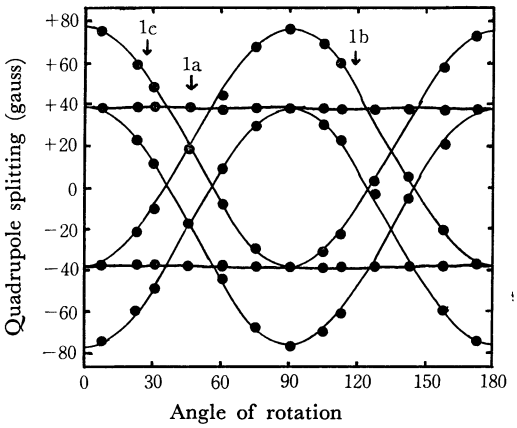

Fig. 1. Rotation pattern of deuteron magnetic resonance of $[Co(ND_3)_5(D_2O)](ClO_4)_3$ at room temperature, for the rotation about one of the crystal axes. θ is the angle between the applied external magnetic field H_0 and the crystal axis.

1) R. E. Rechards, *Trans. Faraday Soc.*, **57**, 210 (1961).
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3) T. Ito and T. Chiba, This Bulletin, **42**, 108 (1969).
4) S. Hayashi, *Kogyo Kagaku Zasshi*, **68**, 1449 (1965).
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6) G. R. Murray, Jr. and J. S. Waugh, *J. Chem. Phys.*, **29**, 207 (1958).
7) Y. Okaya, N. Stemple, S. Hoshino, and R. Pepinsky, *Bull. Amer. Phys. Soc.*, **3**, 59 (1958).
8) H. Hartmann and H. Sillescu, *Theoret. Chim. Acta*, **2**, 371 (1964).
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as lines 1a, 1b, and 1c). The rotation pattern of this spectrum is shown in Fig. 1. In most of the metal ammine complexes, the $ND_3(NH_3)$ ligand makes a rapid C_3-axis reorientation even at 77°K. In this case, the averaged electric field gradient at deuterons in ND_3 is in the direction of the Co-N bond. Therefore, assuming the axially symmetric field gradient about the Co-N bonds, we obtain the deuteron quadrupole coupling constant of $e^2qQ/h=67.1$ kHz. This value seems reasonable when compared with the deuteron quadrupole coupling constant, which is about 180 kHz for the rigid ND_4^+[10,11] and which is estimated to be about 60 kHz by averaging the C_3-axis reorientation of ND_3. The spectrum at 77°K is almost identical except that the splittings are about two percent greater than those at room temperature. This may be due to the difference between the amplitudes of torsional vibrations at 77°K and those at room temperature. No D_2O signal was observed over the temperature range from 77°K to room temperature. The intensity of the D_2O signal should be one- and two-fifteenth as large as that of the ND_3 signal for stationary and rapid 180°-flipping D_2O respectively. Possibly, the failure to detect the D_2O signal is due to the lack of sensitivity in the apparatus.

The features of the absorption lines at temperatures higher than room temperature are more interesting. The intensity of the absorption lines, 1a, 1b, and 1c, gradually decreases with an increase in the temperature. A new absorption line (line 2) at the Larmor frequency appeared at high temperatures, as is shown in Fig. 2. The line broadening and reappearing must be due to the reorientation of the $[Co(ND_3)_5(D_2O)]^{3+}$ ion. Since the quadrupole splitting of the high-temperature line is almost zero, it is evident that this reorientational motion is not uniaxial but isotropic. However, as can clearly be seen in Fig. 2, both the low-temperature lines (1a, 1b) and the high-temperature line (2) are simultaneously observed at some temperatures. Such an anomalous phenomenon of the coexistence of spectra of a slow exchange limit and of a fast exchange limit can be explained by only the theory of simple motional averaging. In tracing the motional broadening of deuteron resonance lines, there is commonly a range of temperature where the spectrum is completely washed out and unobservable between the two limitting ranges. Therefore, the 1 and 2 lines must be due to the different origins. To explain these facts, we should examine the following three possibilities:

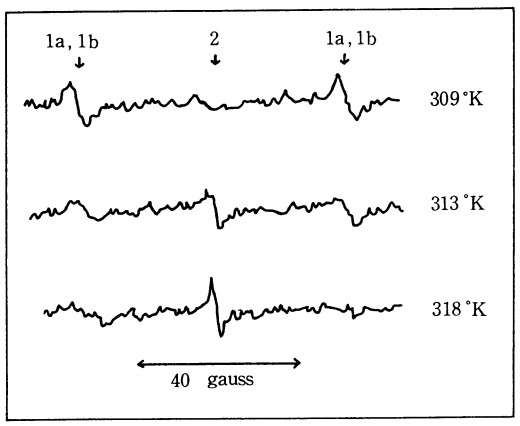

Fig. 2. Line broadening at 309°K, 313°K and 318°K. The magnetic field is applied parallel to the crystal axis.

(A) Although there is only one equivalent site in this crystal, the crystal fields acting on the individual complex cations may be slighly different from each other because the complex cations are randomly oriented in the crystal.[7,8] As a result, the rates of the reorientation of complex cations may not all be the same. Therefore, the 1 and 2 lines may be signals from the cations with a slower rate of reorientation and with a faster rate of reorientation respectively.

(B) In this crystal, the order-disorder phase transition was reported at 314°K.[7] If the rate of reorientation is slow in the ordered phase and fast in the disordered phase, the 1 and 2 lines may originate from the complex cations in the ordered phase and the disordered phase respectively, because both phases usually coexist near the transition temperature.

(C) In contrast with (A) and (B), the 1 and 2 lines may be due to the same type of complex cations, not different types. In this case, the 1 and 2 lines may be considered to originate from ND_3 and D_2O respectively.

Of course, the propriety of these interpretations should be examined by taking the experimental results of the proton second moment, the spin-lattice relaxation time in the laboratory frame (T_1), and that in the rotating frame ($T_{1\rho}$) into consideration. For this compound, the second moment decreases smoothly as the temperature increases in the range from 290°K to 340°K. The spin-lattice relaxation times, T_1 and $T_{1\rho}$, have no discontinuity over the temperature range studied. $T_{1\rho}$ has a sharp minimum at 333°K.[12]

In the case of Model (A), either a very broad linewidth transition of a proton resonance or a shallow minimum in a spin-lattice-relaxation-time-*versus*-temperature curve should appear, because various correlation times of reorientation can be expected. However, the experimental results are contradictory. Therefore, this model may be inadequate. In the case of Model (B), the correlation time of reorientation should exhibit a discontinuity at the temperature of phase transition. In fact, the broadening of the 1 lines and the narrowing of the 2 line occur more quickly at temperatures near the transition point. Therefore, it is certain that the phase transition is accompanied by a discontinuity in the correlation time of reorientation. However, if the signals due to the stationary and rotating ions are observed in the ordered and disordered phase respectively, the difference between the correlation times in the two phases must be considerably large. As a result, the spin-lattice relaxation time should have a clear discontinuity at the transition temperature. However, the experimental results do not exhibit such a discontinuity.

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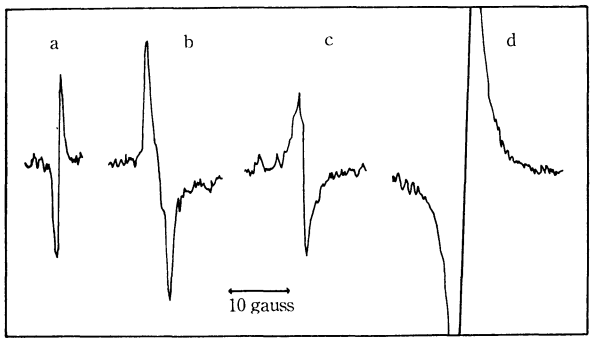

Fig. 3. Deuteron magnetic resonance spectra of $[Co(ND_3)_5(D_2O)](ClO_4)_3$ at 365°K. (a): $\theta=0°$, with small modulation; (b): $\theta=0°$, with large modulation; (c): $\theta=45°$, with small modulation; (d): $\theta=45°$, with large modulation. θ is the angle between the external magnetic field H_0 and the crystal axis.

Moreover, in order to test the possibility of Model(B), the following experiment was made at a temperature sufficiently above the transition point (365°K), as is shown in Fig. 3. If the external magnetic field, H_0, is applied parallel to the crystal axis (θ=0°), a sharp line is observed when the modulation width is small (Fig. 3a), and the peak intensity of this line scarcely changes with an increase in the modulation width (Fig. 3b). On the other hand, if H_0 is applied parallel to the bisector of the crystal axes (θ=45°), a somewhat broad line is observed when the modulation width is small (Fig. 3c). The peak intensity of this line is markedly increased with an increase in the modulation width (Fig. 3d). This suggests that the absorption line consists of a sharp and a broad component at this temperature, and that the latter component is too broad to be observed when H_0 is applied parallel to the crystal axis. Since only one phase should exist at this temperature, Model (B) may be inadequate to explain these experimental results, in which case only Model (C) is possible.

The line widths due to the motion, $\Delta\nu_M$, at the limit of slow and rapid exchange rates have been derived from the general formula as follows:[13,14]

$$\text{slow exchange limit: } \Delta\nu_M = \frac{1}{4\pi\tau_c} \text{ (inside lines 1a, 1b)} \quad (1)$$

$$\text{and} \qquad \Delta\nu_M = \frac{1}{2\pi\tau_c} \text{ (outside line 1c)} \quad (2)$$

$$\text{rapid exchange limit: } \Delta\nu_M = \frac{4}{9}(\nu_1^2 + \nu_2^2 + \nu_3^2)\,\tau_c, \quad (3)$$

where τ_c is the correlation time of this motion and where ν_i is the frequency difference at the site i from the center of gravity of the spectra (*i. e.*, $\nu_1+\nu_2+\nu_3=0$). As a result, the width of the motional averaged line is strongly dependent on the initial splitting. That is, the lines with a small splitting are averaged more effectively than the lines with a large splitting by motion. In the present case, if the motion of the D_2O ligand is a usual 180°-flip reorientation, the deuteron quadrupole splitting of D_2O is larger than that of the ND_3 under a rapid C_3-axis reorientation. However, if the motion of the D_2O ligand is a classical rotation about the Co–O bond axis and if its rate is sufficiently fast at this temperature, the averaged deuteron quadrupole splitting is very small because the bond angle of D_2O is close to the tetrahedral angle. Assuming that the bond angle of D_2O is 105°[15] and that the quadrupole coupling constant of stationary coordinated D_2O is 240 kHz,[14] we obtain the quadrupole coupling constant of D_2O averaged by such motion as 13.4 kHz. Therefore, the following explanation is possible: the 1 and 2 lines are the stationary signals of ND_3 and the motional averaged signal of the D_2O ligand respectively. Here we use the words "stationary" and "motional averaged" with respect to the motion of the whole complex cation. The stationary D_2O signal may not be observed because of its weakness, and the averaged ND_3 signal may be the broad component of the high-temperature spectrum. On the basis of this model, the correlation times of the motion of the complex ion are calculated from the line width due to the motion, $\Delta\nu_M$, which is itself estimated from the observed signal intensity by an apporoximate procedure.[16] The results thus obtained are shown in Fig. 4, together with those obtained from the proton second moment and the spin-lattice relaxation time in the rotating frame ($T_{1\rho}$). Although a considerable difference is observed between the correlation times derived from the deuteron resonance and those from the second moment or $T_{1\rho}$, the qualitative features of line broadening and reappearing may be explained by Model (C). This discrepancy may be due to the effect of the overmodulation. In the procedure of Chiba and Kakiuchi[16] the signal is as-

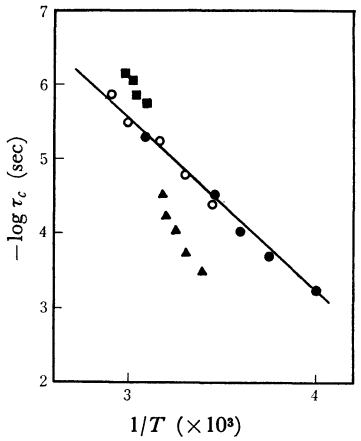

Fig. 4. Correlation times of the motion of aquopentammine-cobalt(III) ion calculated from the deuteron resonance, from the proton second moments and from the proton spin-lattice relaxation times in the rotating frame, $T_{1\rho}$. ○ from proton second moments; ● from proton $T_{1\rho}$; ▲ from deuteron resonance of ND_3; ■ from deuteron resonance of D_2O.

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15) G. Harzberg "Molecular Spectra and Molecular Structure II" D. Van Nostrand Company Inc. Princeton, New Jersey (1945), p. 489.
16) T. Chiba and Y. Kakiuchi, This Bulletin, **41**, 828 (1968).

sumed to be a first derivative; that is, the modulation width is assumed to be infinitely small. In the present experiment, however, a fairly large modulation was used, especially for the motional broadening lines, since the intensities of the lines are weak. As a result, the decrease in intensity due to the line broadening is smaller than that estimated by the procedure of Chiba and Kakiuchi.[16] Therefore, the correlation times derived from the motional narrowing lines of D_2O (■ in Fig. 4) may be smaller, and the motional broadening lines of ND_3 (▲ in Fig. 4) may be larger, than the respective true value. Using Eq. (3) and τ_c derived from the second moment and $T_{1\rho}$, we obtained the line width due to the motion as 3.93 kHz and 0.99 kHz in the cases of $\theta=0°$ and 45° respectively, for the signals of ND_3 at 365°K. These results do not contradict the experimental finding that the broad component of the absorption lines at 365°K is not observed in the case of $\theta=0°$, while it is observed in the case of $\theta=45°$, since the observable limit of line width due to the motion is estimated to be about 3 kHz.

For the crystal treated here, no anisotropy was found in the motion of the cluster, and the motion of the D_2O ligand may be similar to the reorientation of the ND_3 about a C_3 axis rather than the usual 180°-flip one. This suggests that the D_2O and ND_3 ligands are essentially undistinguishable in this crystal. This conclusion seems reasonable in view of the fact that the symmetry of the crystal is cubic in contrast with the lower symmetry of the cluster.

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