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The Molecular Structure and Motion of Ammonia in $Cd(NH_3)_2Ni(CN)_4.2C_6D_6$*

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The structure and motion of the ammonia molecule in the host lattice of benzene-d_6 chathrate compound, $Cd(NH_3)_2Ni(CN)_4 . 2C_6D_6$, was studied by proton magnetic resonance spectroscopy. The proton spectra of the single crystal oriented in the magnetic field at an angular interval were analyzed by Andrew's classical-theory of the three-spin system magnetically isolated in solid. The predominance of the intramolecular dipole-dipole interaction of protons was supported experimentally by a comparison of the spectra of $Cd(NH_3)_2Ni(CN)_4 . 2C_6H_6$, $Cd(ND_3)_2Ni(CN)_4 . 2C_6H_6$, and $Cd(NH_3)_2Ni(CN)_4 . 2C_6D_6$. The proton-proton distance in the triangular plane of the ammonia molecule, the plane which was orientated perpendicularly to the c-axis of the crystal, was determined to be 1.78 ± 0.01 Å from the peak splitting. The tunneling of the ammonia molecule about its C_{3v} axis in this clathrate was confirmed in the 80-420°K temperature range from the constancy of the line width as a function of temperature. The structural application of these results to other diammine complexes was attempted.

Introduction

The crystal structure of a Hofmann-type clathrate, $Cd(NH_3)_2Ni(CN)_4 . 2C_6H_6$, has been explained on the basis of the results of X-ray diffractometry, as is shown in Figure 1.[1,2,3] In this tetragonal structure the nickel ions in the square-planar configuration and the cadmium ions in the octahedral configuration are combined alternatively with cyanide bridges, and forming as a whole a two-dimensional infinite network, which is parallel to the {001} plane of the crystal. Two ammonia molecules coordinating to a cadmium ion in a *trans* configuration stick out to the both sides of the plane. The paramagnetism of nickel(II) ion should be quenched in the square planar configuration as the tetracyanoniccolate anion,[1,4,5] Benzene molecules are trapped between these networks in such a manner that the ring plane is vertical to the network plane. Thus, the ring plane is parallel to the c-axis of the crystal.

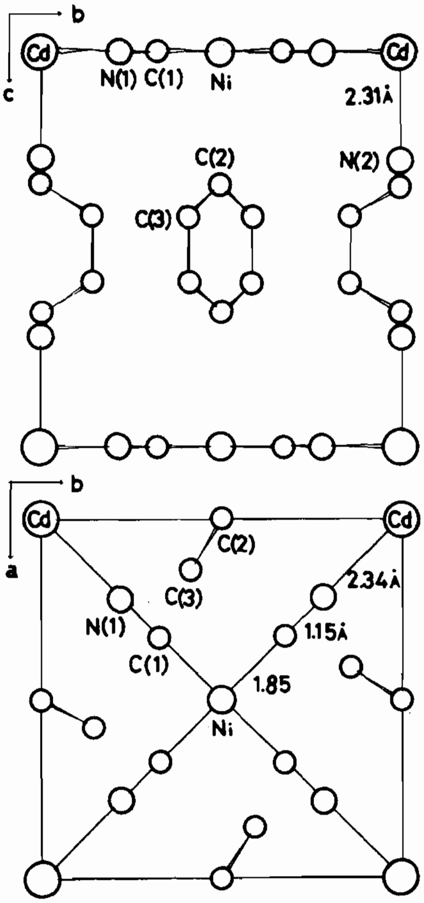

Figure 1. Crystal structure of $Cd(NH_3)_2Ni(CN)_4 . 2C_6H_6$; tetragonal system with a space group $P_{4/m}$, a=b=7.57 Å, c=8.31 Å, and Z=1.

However, no explicit interpretation of the structure and the motion of the ammonia molecule coordinated to the metal ion, M^{2+}, in the octahedral configuration has yet been given. In this paper, by means of wide line proton resonance, the proton-proton distance, the orientation, and/or the motion of the proton triangular plane of an ammonia molecule

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(*) The Metal Cyanide Aromatics. IX. Read in a preliminary form at the 21st Annual Meeting of the Chemical Society of Japan, Suita, April, 1968.

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in a single crystal of diamagnetic Hofmann-type clathrate, $Cd(NH_3)_2Ni(CN)_4 . 2C_6D_6$, will be discussed. As the proton has a magnetic moment considerably larger than the other nuclei,[6] the influence of the other nuclei on the shape of the proton signal is negligible in this specimen. Therefore, the magnetic dipole-dipole interaction among the resonant nuclei is limited to within the magnetically isolated ammonia molecule itself; *i.e.*, intramolecular interaction is dominant.

Since Pake successfuly determined the structure of the water molecule in gypsum by NMR,[7] various wide-line NMR studies of the molecular structures of solid compounds have been treated so far.[8] Murray studied the molecular motion of amminecobalt complexes in terms of the temperature dependence of the line width.[9] As for the effect of paramagnetic ions on the protons of ammonia, Kim investigated the shift and distortion of the proton spectra in several paramagnetic complexes of transition metal ions.[10] In order to obtain the precise data, it is necessary to prepare a large single crystal of a high quality from the experimental point of view. The splendid results of single crystal experiment will help the structural investigation of other diamminecomplexes even in powder samples.

Experimental Section

a. Apparatus. The NMR spectra were recorded with a JEOL-30W spectrometer of the Anderson-bridge type. The magnetic field strength was calibrated by means of the proton resonance in an aqueous solution of copper sulfate.[11] The modulation amplitude was chosen as low as possible,[12] and its contribution to the second moment was corrected by Andrew's method.[13] The RF power was set at an intensity low enough to avoid saturation ($<$ *ca.* 40 m oe.).[14] Throughout a measurement run, the proton resonance site observed was reproducible within ±0.05 oe. The single crystal sample was fixed with a cover glass into glass tube 10 mm in inner diameter, while the powdered samples were packed in sealed tubes of the same size.

b. Samples. Single Crystal of $Cd(NH_3)_2Ni(CN)_4 . 2C_6D_6$. This sample was prepared by the following method. Equimolar amounts (0.05 mole) of cadmium chloride and potassium tetracyanoniccolate were dissolved into 100 ml of an aqueous solution buffered at pH 10-11 with an ammonia ammonium chloride mixture. Onto the surface of the aqueous phase, 0.05 mole of deuterobenzene-d_6 (purity 99.6% up) was then slowly placed. These two phases were kept in contact for 45 days at room temperature (20-25°C). A crude mica-like canary yellow crystal which thereupon grew on the interface was picked out and washed with ethanol and ether. After having then been left for several days in a dissiccator in the presence of benzene-d_6 vapor, it was cut down to a single crystal about $15 \times 10 \times 0.5$ mm^3 in size. The flat plane of 15×10 mm^2 corresponds to the $\{001\}$ plane, as may be expected from the crystal structure in Figure 1.

Polycrystalline Powders of Deutero- and Nondeutero- Clathrates and Other Diamminecomplexes. These powders were prepared by methods previously reported[1,15] and usual ways.[16,17,18]

Results

a. The Spectra of the Deuterated and Nondeuterated Polycrystalline Powders. Figure 2 shows the proton spectra of the benzene-deuterated (a), the ammonia-deuterated (b) and the non deuterated (c) clathrates at 296 °K. The superposition of the (a) spectrum and (b) spectrum bears a striking resemblance to the (c) spectrum. Benzene molecules « caged » in the inorganic host lattice have the narrow line-width and reorient their hexadaxis.[19]

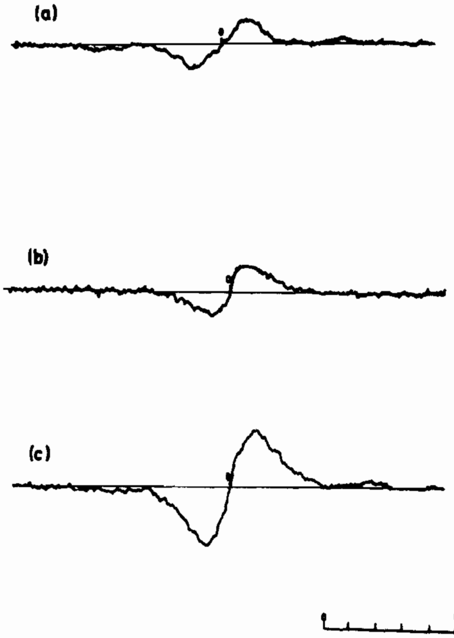

Figure 2. Proton spectra of powdered samples at 296°K. (a) $Cd(NH_3)_2Ni(CN)_4 . 2C_6D_6$; (b) $Cd(ND_3)_2Ni(CN)_4 . 2C_6H_6$; (c) $Cd(NH_3)_2Ni(CN)_4 . 2C_6H_6$.

b. $Cd(NH_3)_2Ni(CN)_4 . 2C_6D_6$ *Single Crystal.* Figure 3 shows some representive spectra of the single crystal as derivative curves and as their integrated forms.

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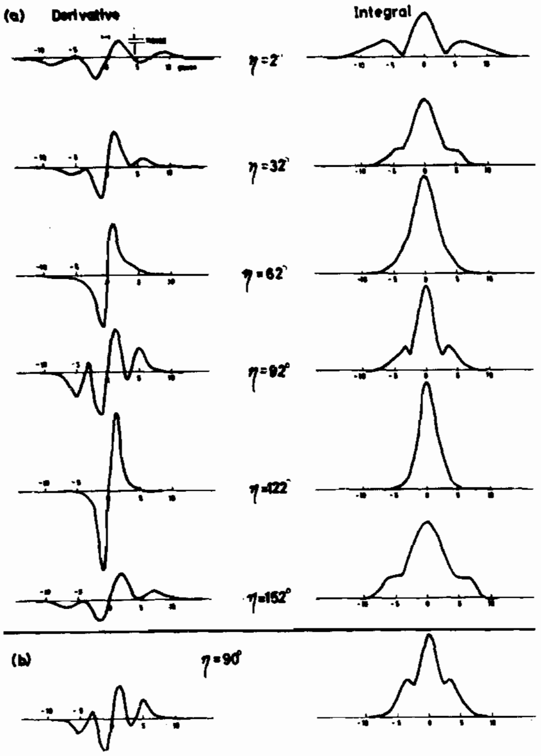

Figure 3. Proton spectra of the single crystal $Cd(NH_3)_2Ni(CN)_4 \cdot 2C_6D_6$. Rotated (a) about the [hk0]axis and (b) about the c-axis. ($\gamma = \eta$)

The derivative curves were recorded at 296 °K on the rotation of the single crystal about the [hk0] axis at an angular interval of *ca.* 10 degrees in a magnetic field to which the }hk0{ planes were kept parallel. Each of the spectra consists of a central main peak and a pair of side peaks; the satellite peaks are both at the same distance from the central peak. The intensity ratio of the main to the side peaks was *ca.* 2.8 – 3.3. The line splitting between the central and the side peaks is clearly dependent on the rotation angle, γ, which refers to the angle between the applied field, H_o, and the [hk0] axis of the crystal. The dependence of the line splitting is plotted against the rotation angle in Figure 4 along with a calculated curve derived from the following theory.

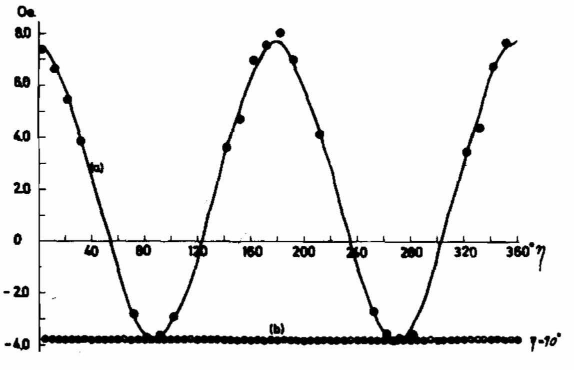

Figure 4. The angular dependency of line splitting. Solid circles: rotated about the [hk0] axis. Open circles: rotated about the c-axis. Solid line: theoretical curve with $\alpha = 3.74$ oe.

c. *The Analysis of Spectra. Line Splitting Method for Determination of p-p Distances.* Andrew and Bersohn[20] calculated the line shape for a triangular configuration of identical nuclei. When the ammonia molecule is rotating about its normal axis to the proton triangular plane, absorption lines are given as follows:

$$H_o = H^*$$

$$H_o = H^* \pm \alpha(3\cos^2\eta - 1) \qquad (1)$$

where $H^* = h\nu/2\mu$ is the resonant field for a magnetic nucleus with a magnetic moment μ; ν is the applied radiofrequency; η refers to the angle between the externally-applied field and the rotation axis of the ammonia molecule in C_{3v} symmetry; and $\alpha = (3/2)\mu r^{-3}$ is the interaction field parameter as a function of r, the proton-proton distance in the triangular plane. The line splitting is, thus, given as $\alpha(3\cos^2\eta - 1)$ as a function of the η angle. The energy diagram of the system is shown in Figure 5.

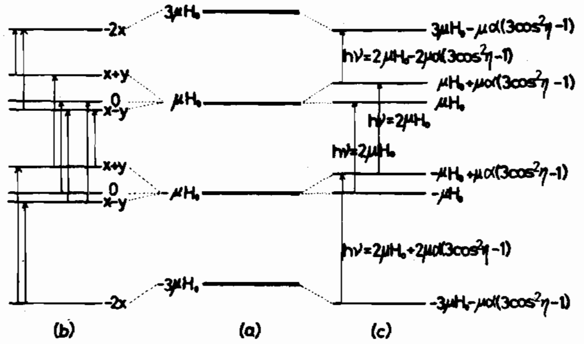

Figure 5. Energy diagram of three-spin system. (a) External field only . (b) External field and dipolar interaction in a rigid model. (c) External field and dipolar interaction in a rotation model. The notations X and Y have the same meaning as with Andrew.[20]

The agreement between the theoretical curve and the experimental plot is satisfactory with regard to the angular dependence. Both angles, the crystal-fixed angle, γ, and the molecular-fixed angle, η, coincided with each other in the single crystal of the clathrate. According to Eq. (1), a single « sharp » line should appear at $\eta = \cos^{-1}\frac{1}{\sqrt{3}}$ ($= 54°44'$). The spectrum recorded, however, had a fairly large line-width, which is probably also due to the effect of the modulation amplitude chosen as proper for the main peak of a certain η angle.[21] Moreover, the rotation of the specimen about the c-axis at an angular interval of *ca.* 5 degrees caused no change in the line splitting within limits of experimental error of ±0.020 oe., as had been predicted by Eq. (1) *viz.* $\eta = \pi/2$.

From the curve fitted to the experimental plot, the parameter, α, in Eq. (1) is given as 3.74 oe. from which the proton-proton distance (p-p), $r = (3\mu/2\alpha)^{1/3}$, can be calculated to be 1.78±0.01 Å.

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Second Moment Method. The second moment data are widely used to determine the p-p distance.[22] Gutowsky and Pake[23] derived the second moment equation for the rotar of magnetic nuclei from Van Vleck's equation.[24] When the vector r is perpendicular to the rotation axis of the ammonia, the second moment can be written as follows;

$$\langle \Delta H^2 \rangle_{rot} = \langle \Delta H^2 \rangle_{H-Hintra} + \langle \Delta H^2 \rangle_{H-Hinter} + \langle \Delta H^2 \rangle_{H-Nintra} + \langle \Delta H^2 \rangle_{outer} \qquad (2)$$

The ratio in magnitude of the three terms in Eq. (3), is derived as 200:4:1:0.003 in the present case. Latter three terms may be neglected because of the small contribution of the intermolecular second moment. From the values of the second moment obtained at the respective rotation angle, η, as Figure 6, the p-p distance, r, is calculated to be $r \geqslant 1.69$ Å.

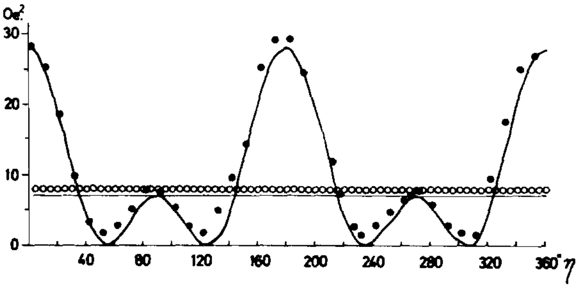

Figure 6. The angular dependency of the second moment. The solid line represents the second moment due to the intramolecular interaction given by $\Delta H^2 = (\alpha^2/2)(3\cos^2\eta - 1)$ with $\alpha = 3.74$ oe.

P-P Distance from Powder Samples. The spectrum of the powdered specimen, which is shown in Figure 2 (a), can be described in terms of the various orientations of the small crystalline granules. The line shape function, $F(H_o-H^*)$ may be represented by an average distribution of the angle function in Eq. (1). The experimental broad spectrum f(H) can be approximated simply with a Gaussian broadening function $G(H-H_o)$[25] as described by Pake,[7] in which β^2 is set at 1.47 oe.;[2]

$$f(H) = \int_{-\infty}^{+\infty} F(H-H^*) \,.\, G(H-H_o)dH_o$$

$$F(H_o-H^*) = \frac{3}{8}\,[1 \pm (H_o-H^*)/\alpha]^{-1/2}$$

$$\alpha < \pm(H_o-H^*) < 2\alpha \qquad (3)$$

$$G(H-H^*) = \frac{1}{\beta\sqrt{2}} \exp\left(-[H-H_o]^2/2\beta^2\right)$$

The agreement of the calculated line shape with the experimental spectrum is illustrated in Figure 7. This method can be applied for determination of p-p distance of other diamminecomplexes as will be discussed later.

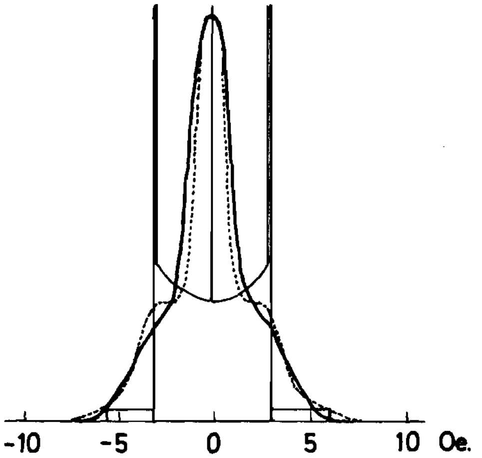

Figure 7. The experimental and theoretical line shape of the proton spectrum of polycrystalline $Cd(NH_3)_2Ni(CN)_4 \,.\, 2C_6D_6$. Solid line: obtained by the integration of the derivative spectrum (a) in Figure 2. Broken line: obtained from Eq. (3) with $\alpha = 3.74$ oe., $\beta^2 = 1.47$ oe.[2] The frame in the figure is the shape function $F(H_o-H^*)$.

Discussion

The Application of two Methods for the determination of p-p Distance. From the experimental point of view, generally the evaluation of a second moment should be undertaken very carefully because of the ambiguity of the tail parts of the spectrum. The discrepancy in the intensity ratio of the main peak to the side peaks between the experimental (2.8-3.3) and theoretical (2.0) values seems to indicate an unreliability in the result from the second moment method. On the other hand, a line splitting method can be clearly read out on a derivative spectrum. In the present case, the agreement of the experimental plot with the calculated curve is better in the line splitting method than in the second moment method. Hence, on the above-mentioned reasoning, it can be concluded that the line-splitting method is more reliable than the second moment method in determining the structural parameter in complex compounds.

The value from the second moment method may give the minimum value of the p-p distance, because only the intramolecular interaction is taken into account in the calculation. This value is consistent with that obtained from the line-splitting method, 1.78± 0.01 Å. The line-splitting method can be used for polycrystalline samples in favorable cases. For instance, splitting interval of both satellite peaks, 2α, was observed in other diammine complexes using a powdered specimen, though precision was low. In a powdered spectra, sometimes the line splitting magnitude cauld be overestimated because of the superposition of the main and the side components, and the p-p distance obtained from the line-splitting may give the maximum value of the true p-p distance. Hence, the combination of the splitting method, Eq. (3), with second moment will give the limits of p-p distance as shown in Table I.

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Table I. Line splittings, second moments, and p—p distances of other diamminecomplexes

	ΔH^2, oe.^{2}	α, oe.	r, Å
$Cd(NH_3)_2Ni(CN)_4 . 2C_6D_6$	—	3.74	1.78 ± 0.01
$K[Co(NH_3)_2(NO_2)_4]$	8.2	3.9_5	$1.7_6 - 1.6_7$
trans—$Pd(NH_3)_2Cl_2$	7.4	3.6_9	$1.7_9 - 1.7_0$
$Cd(NH_3)_2Cl_2$	12.9	3.68	1.79—1.55
$Hg(NH_3)_2Cl_2$	13.5	3.99	1.74—1.54
$Zn(NH_3)_2Cl_2$	9.8	3.6_4	$1.8_0 - 1.5_4$
NH_3 (gas)	—	—	1.62[27]
NH_4Cl	—	—	1.69 ± 0.01[29]

The Structure of the Clathrate. The p-p distance of the ammonia molecule coordinated to the cadmium ion was determined as 1.78 ± 0.01 Å, and the orientation of the equilateral triangle of protons was found to be perpendicular to the c-axis of the crystal for all the ammonia molemules in the $Cd(NH_3)_2Ni(CN)_4 . 2C_6D_6$ clathrate, that is, the c-axis of the crystal coincides with the C_{3v} axis of the ammonia molecule.

This is the first successful use of NMR to elucidate the structure of an ammonia molecule in a solid compound, and thereby a experimental evidence is given to Andrew's theory. A merit of this NMR method is that the method makes is possible to determine directly the p-p distance, the molecular motion and the orientation of the equilateral triangle by means of a strict solution of a spin Hamiltonian. The value of the p-p distance obtained presently supplies additional information as to the structure of the clathrate previously determined by X-ray diffractometry, by which alone it is difficult to determine the molecular motion and the precise position of the hydrogen atom.[26] The p-p distance, 1.78 ± 0.01 Å, is longer by 0.16 Å than that in gaseous ammonia and in ammonium chloride (1.69 ± 0.01 Å).[29] Although there is no correction for the vibrational motion as made in the case of hydrated water[30] or ammonium ion,[29] the effect may be negligibly small. The repulsion among the protons of an ammonia molecule may be increased by the coordination of the ammonia to a metal ion. Moreover, the π-electron system of the surrounding benzene molecules is likely to attract the protons of ammonia toward the benzene molecules by means of a weak hydrogen bond. The observed lengthening of the p-p distance may be caused by at least one of these factors, and thus enhancing of the ionicity of the N-H bond and enlarging of the H-H-H angle should occur, as a ethlenediammine molecule shows the increase of ionicity when it coordinates to platinum(II) ion.[31]

To compare the structure of ammonia in the clathrate with that in other diamminecomplexes, the measurement of p-p distance in various diamminecomplexes, have been carried out by NMR method. Results were given in Table I. The second moment in Table I represents well the degree of isolation of the ammonia molecule in solid, bing consistent with the result of X-ray diffractometry.[32] It is remarkable that the second moment of clathrate is scarecely influenced by the intermolecular contribution,[2] comparing with that of other diamminecomplexes. The experimentally-obtained second moment and apparently «additive» relationship of the line shapes in Figure 2 support the estimation that the ammonia molecule is isolated in the crystal structure of the Hofmann-type clathrate, the structure in which the intramolecular dipole-dipole interaction within an ammonia molecule should be predominant.[19]

Motion of Ammonia. The phenomena of motional narrowing is often explained well by assuming the motion of nuclear groups in a solid, as has been discussed for the methyl group by Gutowsky and his coworkers,[33-36] by Das[37] and Allen.[38] As for the ammonia molecule of the present clathrate, no change in the line-width throughout the temperature range from 80 °K to 420 °K has been observed in the spectra of the powdered specimen. The rotation of the ammonia may not be only possible mechanism to explain the line shape shown in Figure 7. Even a rigid three spin system could also have three peaks broadened by intermolecular interaction in powder samples. This ambiguity can, however, be removed by the calculation of p-p distance. By assuming a rigid system, Eq. 5 gives an abonormally lon p-p distance, 2.28 A. Furthermore, the angular dependency of the line splitting of the spectra of the single crystal can be interpreted only in terms of the rotation model, because a rigid system of three protons of an ammonia molecule may be expected to give an absorption spectrum with a fine structure and a maximum of seven components. So undoubtedly the ammonia molecule coordinating to a heavier cadmium ion in the host lattice of the clathrate rotates about its threefold axis within the 80-420°K temperature range.

According to Das, motion can be classified into two kinds, the classical rotation and the tunneling. In the present case, it may be preferable to suppose the tunneling mechanism in view of the constancy of the line-width with the temperature, although the line transition has not been observed to confirm the assignment.[38] Umemoto and Danyluk[39] reported the rigidness of an ammonia molecule at 100°K in a paramagnetic Hofmann-benzene clathrate, $Ni(NH_3)_2$-$Ni(CN)_4 . 2C_6D_6$, which is a homologous to the present diamagnetic sample, $Cd(NH_3)_2Ni(CN)_4 . 2C_6D_6$. Their discussion, however, is limited to the second moment concerned with the motion. Since the ammonia molecule in their compound coordinates directly to a paramagnetic nickel(II) ion, the effect of paramagnetism should been considered. Recently, the motion of ammonia molecules in various paramagnetic Hof-

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mann-type clathrates has been analyzed within the temperature range from 80°K to 300°K in terms of the line shape; these results also support the tunneling motion of the ammonia molecule coordinating to the paramagnetic metal ions.[40]

Thus, from the observation in this paper, it can be concluded that the three-spin system of the ammonia molecule coordinating to the cadmium ion in $Cd(NH_3)_2Ni(CN)_4 . 2C_6D_6$ has the p-p distance larger than gaseous ammonia and that the ligand ammonia molecule rotates around the bond axis between the cadmium and the ammonia even at liq N_2 temperature, just as in the case of other diamminecomplexes in Table I and of several hexamminecobalt(III) complexes, $[Co(NH_3)_6]X_3$, reported by Murray.[9]

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