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The Metal Ammine Cyanide Aromatics Clathrates. XVI. Wide-Line NMR Studies of the Three-Spin Systems of Ligand Ammonia in Paramagnetic Hofmann-type Clathrates

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Wide-line NMR studies of ammonia molecules in Hofmann-type clathrates with the general formula jo $M(NH_3)_2M'(CN)_4 \cdot 2C_6D_6$ are reported. In the Hofmann-type clathrates, two ammonia molecules coordinate to the paramagnetic metal ions in *trans* positions and have only a slight interaction with each other. In powder samples, the proton NMR spectra of ammonia give fine structures with three components, which are caused by dipolar interaction between protons of the rotating triangular three-spin system. The signals shift to the higher-field side under the influence of the paramagnetic moments of the metal ions. The temperature dependence of the shifts and line shapes, where M is iron(II), cobalt(II), nickel(II), and copper(II), will be reported on. No rigid ammonia was found, even at the temperature of liquid nitrogen.

Previously, in this laboratory, the Hofmann-type clathrates with general formula of $M(NH_3)_2M'(CN)_4 \cdot 2G$ have been prepared.[1-4] Their structure, determined on the basis of the single-crystal X-ray diffraction data, are illustrated in Fig. 1.[5-8] The clathrates consist of an inorganic host lattice formed infinite net planes, $[M(NH_3)_2M'(CN)_4]_\infty$, and aromatic guest molecules, G, such as benzene or aniline, trapped

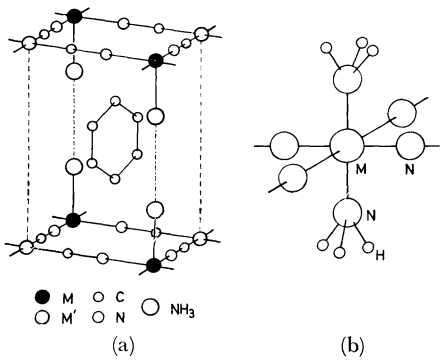

Fig. 1. Structure of Hofmann-type clathrates, $M(NH_3)_2M'(CN)_4 \cdot 2C_6H_6$.
(a) A cavity for one benzene molecule.
(b) Coordination of ammonia molecule to a divalent metal ion.

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in the lattice. Here, M means the divalent transition metal ions, Mn, Fe, Co, Ni, Cu, Zn, and Cd, which occupy the octahedral site, $M(NH_3)_2(NC)_4$, and M′ is divalent Ni, Pd, or Pt, in the square-palnar site, $M'(CN)_4$. To the metal ion, M, four bridging cyanide ions coordinate with nitrogen atoms in the square-planar configuration and two ammonia molecules in *trans* positions (Fig. 1b).

As has been reported in previous papers, the clathrates whose octahedral sites are occupied by Zn or Cd are diamagnetic, and those containing paramagnetic divalent transition metals are high-spin complexes. The temperature dependence of the paramagnetic susceptibility obeys Curie's law throughout the range from 76 to 300 K.[4]

Beside the structure determination, wide-line NMR studies were undertaken, and the motion of the guest molecules was successfully studied.[9] Two ammonia ligands attached to an octahedral metal ion appear to be magnetically well shielded from each other, and the NMR signals split into fine structures which could not be observed in other, ordinary metal ammine complexes.[10]

A diamagnetic clathrate, $Cd(NH_3)_2Ni(CN)_4\cdot 2C_6D_6$, has already been studied by Miyamoto.[11] He used single crystals containing deuterated benzene and analyzed the ammonia spectra by the use of the three-spin-system model of Andrew and Bersohn;[12] he thus obtained the proton-proton distance from the line splitting in the fine structures, and also from the second-moment data. No rigid ammonia was found at the temperature of liquid nitrogen.

In paramagnetic substances, a wide-line NMR is influenced by electron spins and so is the source of much information about structures. The subjects of the present report are paramagnetic Hofmann-type clathrates containing divalent transition metals, Mn, Fe, Co, Ni, and Cu, in the high-spin state.

Apart from their interest in the connection with the phenomena of clathration, these compounds were used to study the general problem of the magnetic behavior of ammonia molecules coordinated to paramagnetic cations. The situations are favorable; the NMR spectra show fine structures, the metals take a series of electron configurations from d^5 to d^9, and moreover, all the complexes are isostructural.

The only data previously available were those of Umemoto and Danyluk[13] for $Ni(NH_3)_2Ni(CN)_4\cdot 2C_6H_6$ and $2C_6D_6$; our interpretations are different from theirs.

Experimental

Materials. The clathrates investigated were prepared by the methods described in the previous papers.[2,4] When M was Mn, Fe, or Co, the preparations and measurements were carried out in a nitrogen atmosphere to protect the metal ions from oxidation. The powder samples of about one gram for each species were sealed in a glass tube 10 mm in diameter, avoiding the oxidation of the sample and the escape of benzene from the clathrates.

Apparatus. The NMR spectra were recorded with a JEOL-JNM-W30 spectrometer (30 MHz) of the Anderson-bridge type. The spectra of the clathrates were recorded as derivative curves at temperatures from 100 to 296 K, the measurements being made with a copper-constantan thermocouple. The samples were cooled with a cold nitrogen stream from a liquid nitrogen bottle. To ascertain the values of the shifts of the signals from the Larmor frequency, isopentane (mp 113 K) in a capillary on the wall of the sample tube was used as the reference compound.

Results and Discussion

The Wide-line NMR Spectra of $M(NH_3)_2Ni(CN)_4\cdot 2C_6H_6$. The superimposed spectra of the protons of benzene and ammonia molecules in Hofmann-type clathrates at room temperature are shown in Fig. 2.

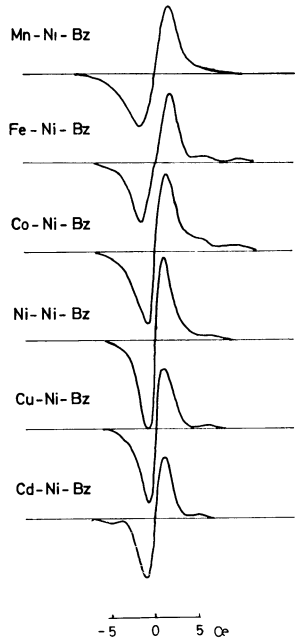

Fig. 2. Wide-line NMR spectra of ammonia protons and benzene protons in Hofmann-type clathrates, $M(NH_3)_2Ni(CN)_4\cdot 2C_6H_6$ at 296 K.

The signal of diamagnetic clathrate is symmetric with respect to the Larmor frequency, whereas the signals of the paramagnetic ones are asymmetric; the degree of asymmetry grows with the paramagnetic moments of the compounds. Apparently, the asymmetry is mainly due to the large shift of the ammonia protons. The signals of benzene protons do not vary for different clathrates at room temperature.

The Spectra of $M(NH_3)_2Ni(CN)_4\cdot 2C_6D_6$. As is shown in Fig. 3, ammonia in the Hofmann-type clathrates which contain deuterated benzene gives NMR spectra at 296 K with fine structures, typical of a trianglar three-spin system, except in the case of the manganese compound.

In Figs. 4—7, the signals of ammonia in four complexes in the derivative form at various temperatures are

9) T. Miyamoto, T. Iwamoto, and Y. Sasaki, *J. Mol. Spectrosc.*, **35**, 244 (1970).
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shown. All the spectra show a higher-field shift at lower temperatures, though they have delicate variations in shape. If they are compared as integral forms, the distances between the three peaks are constant. The shift increases to the higher-field side, and the tails of the signals are more elongated to the lower-field side, so that the accurate computation of the second moments was not possible, in practice. As will be shown later, the long tailing in the spectra demonstrates that the shift depends upon the angle of the *c*-axis of the crystallines in the magnetic field.

Analyses of Ammonia Spectra. The above features of the spectra were explained theoretically and provide knowledge of the molecular structure.

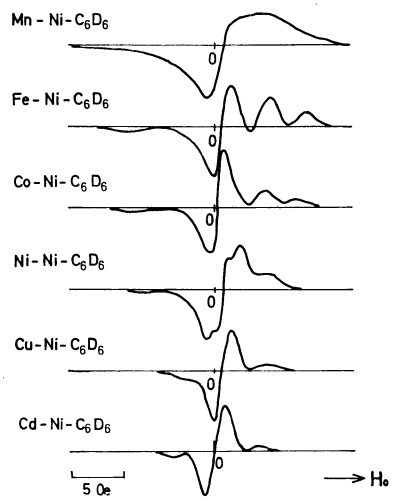


Fig. 3. Wide-line NMR spectra of ammonia protons in Hofmann-type clathrates, $M(NH_3)_2Ni(CN)_4\cdot 2C_6D_6$ at 296 K.

In order to consider the system,[10,11] we take the effective spin Hamiltonian of the system as:

$$H_{\text{eff}} = H^\circ + H_1' + H_2' + H_3'$$

$$H^\circ = -\sum_{j=1}^{3}\gamma_N\hbar I_{zj}H_0$$

$$H_1' = \sum_{i>j}\frac{\gamma_N{}^2\hbar^2(3\cos^2\theta_{ij}-1)}{2r_{ij}}(\mathbf{I}_i\cdot\mathbf{I}_j-3I_{zj}I_{zi})$$

$$H_2' = -\sum_{j=1}^{3}\frac{\gamma_N\hbar(3\cos^2\theta_j-1)}{r_j^3}(\gamma_e\hbar\langle S_z\rangle)I_{zj}$$

$$H_3' = \sum_{j=1}^{3}a_j\langle S_z\rangle I_{zj}$$

$$a_j = \frac{8\pi}{3}\gamma_N\gamma_e\hbar^2\delta_j$$

$$\delta_j \equiv \langle\Psi_1|\sum_k\delta(r_{kj})S_{kz}|\Psi_1\rangle/S_z \qquad (1)$$

where the four terms, H°, H_1', H_2', and H_3', are the Zeeman term, the dipolar interaction between three protons, the dipolar interaction between paramagnetic moment and protons, and the Fermi-type contact interaction respectively. In Eq. (1), r_{ij} is the distance between the i and j nuclei, r_j is the distance between the metal ion and the j nucleus, θ_j is the angle between the applied field, $\boldsymbol{H}_0$, and $\boldsymbol{r}_j$, a_j is the coefficient of the contact interaction, Ψ_1 is a wave function of the electrons, and $\boldsymbol{r}_{kj}$ is the vector between the electron and j nucleus. The other symbols have their usual meanings.

In the present compounds, the paramagnetism obeys Curie's law, so we assumed the time-average value of the z component of the electron spin, $\langle S_z\rangle$, to be:

$$\langle S_z\rangle = \frac{\gamma_N\hbar S(S+1)}{3kT}H_0 \qquad (2)$$

When the applied magnetic field is large enough, *i.e.*, $H^\circ \gg H'$, H' is treated as a first-order perturbation.

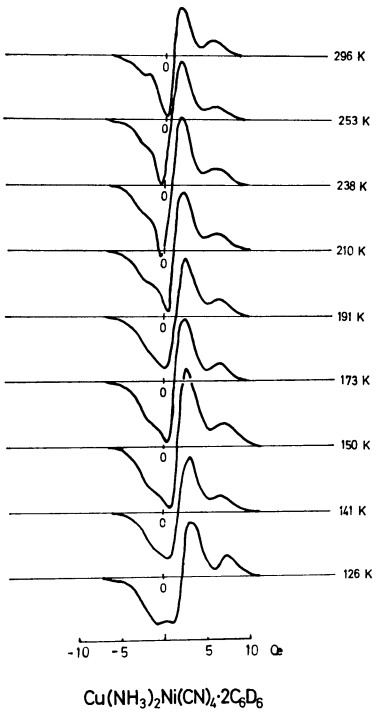


Fig. 4. Wide-line NMR spectra of ammonia of $Cu(NH_3)_2Ni(CN)_4\cdot 2C_6D_6$ at various temperatures.

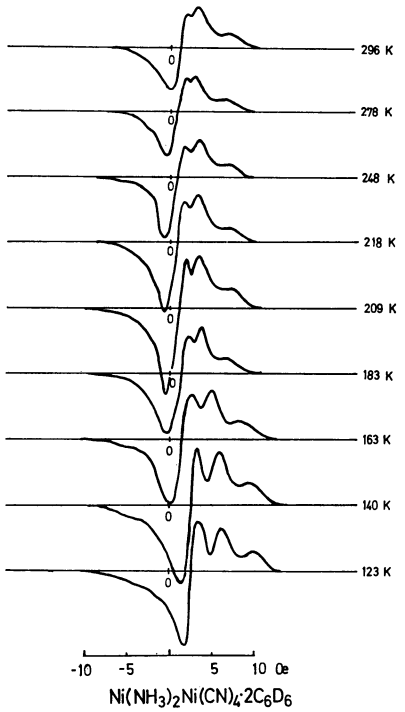
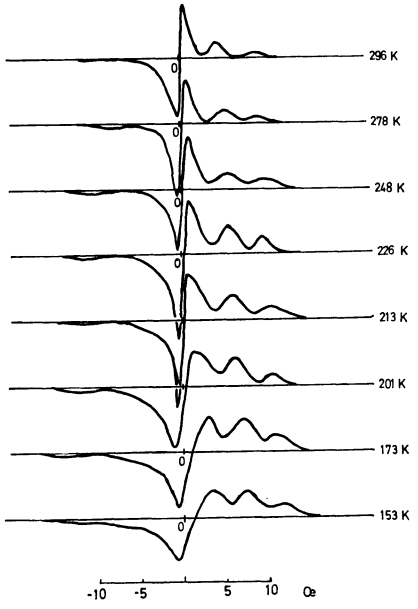


Fig. 5. Wide-line NMR spectra of ammonia of $Ni(NH_3)_2Ni(CN)_4\cdot 2C_6D_6$ at various temperatures.

Taking the spin eigenfunctions of the three-spin system ($\mathbf{I}_i=1/2$), and assuming that the ammonia molecules rotate about the three-fold axes, parallel to the c-axis of the crystals, we may obtain the diagonal matrix and then the energy diagram for this system shown in Fig. 9. The possible transitions are shown in Fig. 9; the selection rules are $\Delta M_I=\pm 1$, $\Delta\mathbf{J}=0$, and $\Delta\mathbf{I}=0$, where $\mathbf{J}=\mathbf{I}_1+\mathbf{I}_2$ and $\mathbf{I}=\mathbf{J}+\mathbf{I}_3$.

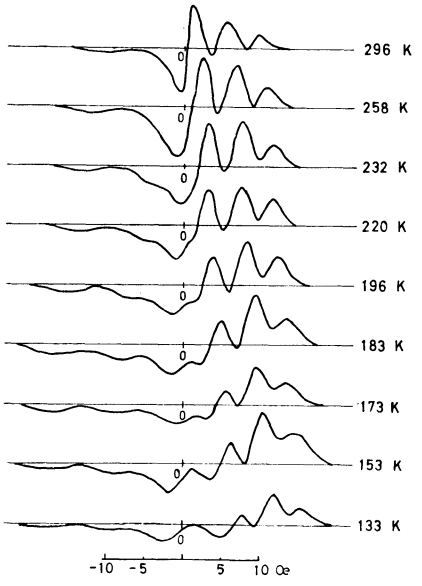
Since $\gamma_N\hbar\boldsymbol{H}^*=h\nu$, the absorptions occur at:

$$\begin{aligned}
&\mathbf{1} \quad \boldsymbol{H}_0=\boldsymbol{H}^*+\frac{1}{\gamma_N\hbar}(\mathrm{B}+4\mathrm{X}) \quad |-\tfrac{1}{2}>\rightarrow|-\tfrac{3}{2}>\\
&\mathbf{2,3} \quad \boldsymbol{H}_0=\boldsymbol{H}^*+\frac{1}{\gamma_N\hbar}\mathrm{B} \quad |\tfrac{1}{2}>\rightarrow|-\tfrac{1}{2}>\\
&\mathbf{4} \quad \boldsymbol{H}_0=\boldsymbol{H}^*+\frac{1}{\gamma_N\hbar}(\mathrm{B}-4\mathrm{X}) \quad |\tfrac{3}{2}>\rightarrow|\tfrac{1}{2}> \qquad (3)
\end{aligned}$$



$Co(NH_3)_2Ni(CN)_4{\cdot}2C_6D_6$

Fig. 6. Wide-line NMR spectra of ammonia of $Co(NH_3)_2$-$Ni(CN)_4\cdot 2C_6D_6$ at various temperatures.



$Fe(NH_3)_2Ni(CN)_4{\cdot}2C_6D_6$

Fig. 7. Wide-line NMR spectra of ammonia of $Fe(NH_3)_2$-$Ni(CN)_4\cdot 2C_6D_6$ at various temperatures.

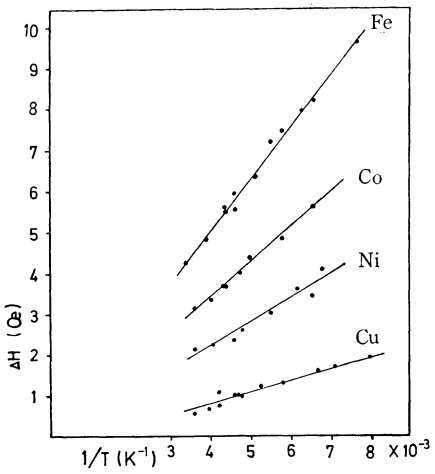


Fig. 8. Temperature dependency of paramagnetic shifts of Hofmann-type clathrates.

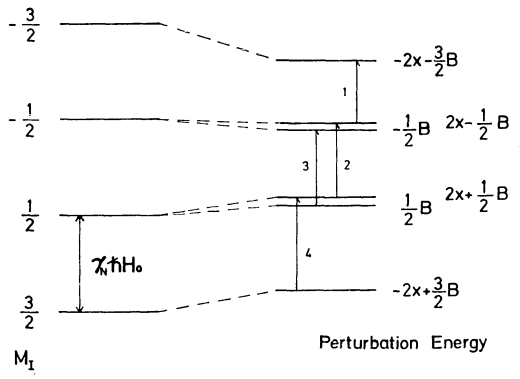


Fig. 9. Energy diagram for the three-spin system perturbed by a paramagnetic moment.

where

$$\mathrm{X}=\frac{3}{16}\gamma_N^2\hbar^2(1-3\cos^2\theta)r_{p\text{-}p}^{-3}$$

$$\mathrm{B}=\frac{1}{2}\gamma_N\hbar(3\cos^2\gamma-1)(1-3\cos^2\theta)r_{p\text{-}p}^{-3}$$

$$\times\ \gamma_e\hbar\langle S_z\rangle+a\langle S_z\rangle$$

and where θ and γ are angles between c-axis and the applied magnetic field and between c-axis and the vector $\boldsymbol{r}_j$ respectively.

The probabilities of the transitions are 1/4, 1/2, and 1/4 respectively. The theoretical spectra are illustrated in Fig. 10. In terms of the dipole-dipole interactions among protons, the signal consists of three components and the distance is $4\mathrm{X}/\gamma_N\hbar$, while the paramagnetic shift, $\mathrm{B}/\gamma_N\hbar$, equally contributes to each component and depends upon the reciprocal absolute temperature.

In powder samples, fine crystallites are distributed over the angle, θ, on which the positions of the signals for the segments depend. The theoretical line shape for polycrystalline samples is obtained in calculating $g(h)=P\cdot d(\cos\theta)/dh$, where P is a transition probability and where $h=\boldsymbol{H}_0-(\boldsymbol{H}^*+C)$; it is shown in Fig. 10; $g(h)=(-h/\alpha_i+1)^{-1/2}$; α_i and C are given in the caption of Fig. 10.

The Shift Caused by the Paramagnetic Moment. The observed spectra can be satisfactorily explained by

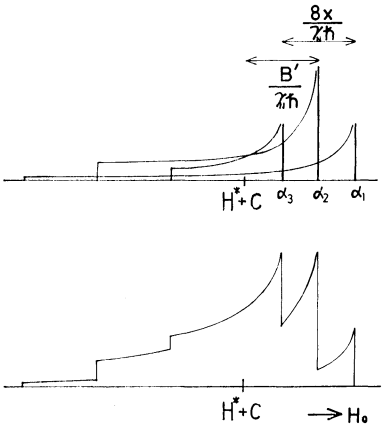


Fig. 10. Paramagnetic shifts and theoretical line shapes for components, where
$\alpha_1=1/2\gamma_e\hbar\langle S_z\rangle(3\cos^2\gamma-1)r_{p\text{-}e}^{-3}+3/4\ \gamma_N\hbar r_{p\text{-}p}^{-3}$
$\alpha_2=1/2\ \gamma_e\hbar\langle S_z\rangle(3\cos^2\gamma-1)r_{p\text{-}e}^{-3}$
$\alpha_3=1/2\ \gamma_e\hbar\langle S_z\rangle(3\cos^2\gamma-1)r_{p\text{-}e}^{-3}-3/4\ \gamma_N\hbar r_{p\text{-}p}^{-3}$
$C=a/\gamma_N\hbar\langle S_z\rangle$, $B'=B-a\langle S_z\rangle$
$r_{p\text{-}p}$ is the distance between adjacent protons, $r_{p\text{-}e}$ is the distance between metal ion and protons, and γ is the angle between $r_{p\text{-}e}$ and c-axis.

the above theoretical treatment of the shifts and line shapes. Both the isotropic and anisotropic paramagnetic interactions cause the signals to shift to the higher-field side; this makes the signal very asymmetric.

As the central peak in the three components does not always have the highest intensity in the powder samples shown in Fig. 10, we should read the value of the paramagnetic shift not at the highest peak, as has been done,[13] but at the central peak, *i.e.*, the second one from the higher-field side.

When the fine structure does not appear, as in the case of the previously-reported metal ammine complexes, the value of the shift cannot be read with certainty.

The linearity of the paramagnetic shift expressed by Eq. (2) is seemingly well demonstrated in Fig. 8. The paramagnetic shift thus measured contains the dipolar and the contact interaction, both of them proportional to $1/T$. The former is angular-dependent, but the latter is not. By the use of single-crystal samples, these two kinds of shifts could be measured separately.

The sole data[14] of the contact shift for metal ammine complexes have been obtained by the use of liquid ammonia solutions, in which the angular-dependent shift vanishes because of the thermal motion. The reported values for the hexammine complex ions, $[Mn(NH_3)_6]^{2+}$, $[Co(NH_3)_6]^{2+}$, $[Ni(NH_3)_6]^{2+}$, and $[Cu(NH_3)_6]^{2+}$, at 311 K are −0.68, 0.17, 0.50, and 0.34 Oe (recalculated for 30 MHz) respectively. In the present systems, the contact shifts may be of the same order and may be rather small compared to the total shift values.

The fine structure of the spectra indicates that the ammonia molecule in the compounds does not interact with the neighboring one at the *trans* position and the other nuclei; then, width become narrower than that of other ammine complexes. Furthermore, the fact that the values of the paramagnetic moments scarcely affect the dipolar broadening of the components, except for manganese clathrate, means that the electron spins on the metal ions next to the one to which ammonia coordinates do not interact with protons.

Structure and Motion of Ammonia. Using the above model, it is possible to obtain the proton-proton distance if the value of the line splitting X, in Eq. (3), is known with enough accuracy.

The spectra were transformed into the integral form and then analyzed to obtain the proton-proton distances by means of Eq. (3). The values of $r_{p\text{-}p}=1.7_0-1.7_9$ Å were obtained for all the clathrates, though the accuracy is not very high. The assumption of rigid ammonia would also explain the fine structure with three peaks, but numerical calculations lead to an abnormally long proton-proton distance.

The constancy of the X value on the change in the temperature suggests that ammonia molecules are not rigid even at the temperature of liquid nitrogen, and that the proton-proton interaction is not decoupled by the paramagnetism of the metal cation to which the ammonia molecules are coordinated.

The values of the shifts and the shape of the spectra of the ammonia protons were thus explained by the model of the triangular rotating three-spin system perturbed by the paramagnetism of the transition metal cation to which the ammonia ligands are coordinated.

Although the lattice is composed of infinite net planes with bridges of cyanide ions, the d-electrons of the metal ion appear to be around the divalent cations and are not delocalized.

The manganese clathrate is different from the other compounds; independent study of it necessary.

The author wishes to thank Professor Yukiyoshi Sasaki for encouraging him throughout this work.

14) B. B. Wayland and W. L. Rice, *Inorg. Chem.*, **6**, 2270 (1967).