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^{13}C CP-MAS NMR of Hofmann-type Clathrates

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The ^{13}C CP-MAS NMR spectra of two Hofmann-type clathrates, diamagnetic $Cd(NH_3)_2Ni(CN)_4 \cdot 2C_6H_6$ and paramagnetic $Ni(NH_3)_2$-$Ni(CN)_4 \cdot 2C_6H_6$, were analyzed. The guest benzene gives a singlet spectral line in the diamagnetic host and a doublet in the paramagnetic one. The doublet is due to the paramagnetic anisotropy at the crystallographically-independent two carbon atoms in the crystal structure.

A number of wide-line ^1H NMR investigations hvae been carried out for Hofmann's clathrates[1-3)] and for the series of Hofmann-type $M(NH_3)_2M'(CN)_4 \cdot 2G$ clathrates.[4-8)] The motional behavior of the guest and the host moieties, such as benzene and ammonia, was interpreted in the diamagnetic host (M = Cd);[5-7)] the effects of the paramagnetism on the spectra were analyzed in the Hofmann-type series of M = Mn, Fe, Co, Ni, and Cu[8)] in comparison with the spectrum observed for the diamagnetic host clathrate. In this communication we report on the high-resolution ^{13}C solid-state cross-polarization magic angle spinning (CP-MAS) NMR of the diamagnetic $Cd(NH_3)_2Ni(CN)_4 \cdot 2C_6H_6$ and the paramagnetic $Ni(NH_3)_2Ni(CN)_4 \cdot 2C_6H_6$.

Sample specimens of catena-[diamminecadmium(II) tetra-μ-cyanonickelate(II)]-benzene(1/2) (abbreviated to Cd-Ni-Bz) and catena-[diamminenickel(II) tetra-μ-cyanonickelate(II)]-benzene(1/2) (Ni-Ni-Bz) were prepared as fine crystals grown at the interface between the aqueous solution containing the host moieties at pH 10 and the organic phase of benzene diluted with toluene.[9)] The products were identified by chemical analyses, powder X-ray diffractions, and infrared spectra.

The ^{13}C CP-MAS NMR spectra were recorded on a JEOL GX-270[10)] and a Bruker AH-250[11)] spectrometers. The measuaring conditions on the JEOL were: operating field strength at 6.43 T (67.80 MHz for ^{13}C) with a 28 kHz sweep width, recycle delay time of 7.000 s, proton decoupling field at 1 mT. About 200 mg sample specimens were spun at 3 kHz in Delrin rotors; the probe temperature was around 300 K under ambient conditions. On the Bruker the field strength of 5.87 T was applied; other conditions were similar to those applied on the JEOL. The spectra recorded on the two different spectrometers were essentially the same with regards to the chemical shifts and the relative intensities. All the CP-MAS chemical shifts were referred to a methyl carbon signal of acetone (29.50 ppm from TMS = tetramethylsilane) used as an external reference. The errors in chemical shifts were estimated to be ±1 ppm; more positive shift represents deshielding. The typical spectra are shown in Fig. 1 for the diamagnetic Cd-Ni-Bz (a) and for the paramagnetic Ni-Ni-Bz (b), respectively. The sepctral data are summarized in Table 1.

The sharp and strong peak at 129.9 ppm of the diamagnetic Cd-Ni-Bz is assigned to the benzene carbons; for neat benzene the band has been observed at 128.5 ppm.[12] A weak signal of 127.2 ppm at the high-field side is assigned to the cyanide carbons. Since the peak intensity increased remarkably by applying pulse intervals longer than that for the benzene carbons, the cyanide carbons have the relaxation time longer than that of the benzene carbons. The 129.9 ppm shift of the benzene carbons supports that the electronic surrounding of the guest benzene molecule is almost unchanged from that in the neat state. The observed singlet is consistent with the rotational or reorientaional motion of the benzene molecule about its sixfold axis as has been concluded from the results of wide-line ^{1}H NMR,[7] although there are two crystallographically-independent benzene carbons, C(2) on the twofold axis and C(3) at the general position (4.679(4) and 4.902(6) Å from the cadmium(II), respectively) in the crystal structure of the P4/m space group.[13,14] The 1.4 ppm low-field shift from the neat state of benzene is due to the effect of magnetic surroundings by the host skeletons rich in π-electrons of the cyanide groups.

The band at 127.2 ppm assigned to the cyanide carbons shows the ca. 11 ppm high-filed shift from that observed at 138.0 ppm for the tetracyanonickelate(II) anion in aqueous solution.[12] As the cyanide group forms a Ni-C-N-Cd linkage in the host structure, the distribution of π-electron densities should change from that in the dissolved complex anion; the high-filed shift suggests the electron densities are lowered around the carbon atom.

The paramagnetic Ni-Ni-Bz gave the spectrum more broadened and biased than that of the diamagnetic Cd-Ni-Bz. The two strong peaks around 120-150 ppm range are assigned to benzene carbons as a doublet. The intensity ratio of ca. 2:1 for the band at 145.4 ppm to that at 121.0 ppm allows us to assign the former to C(3) at the general position and the latter to C(2) on the twofold axis; the distance from the paramagnetic nickel(II) is 4.54 Å for the former and 4.80 Å for the latter.[15] A peak at ca. 68 ppm can be assigned tentatively to the cyanide carbons, although it is difficult to ascertain the assignment owing to the

Table 1. ^{13}C CP-MAS NMR spectral data

	Chemical shift (TMS=0)	
	C_6H_6	CN
$Cd(NH_3)_2Ni(CN)_4 \cdot 2C_6H_6$	129.9 ppm	127.2 ppm
$Ni(NH_3)_2Ni(CN)_4 \cdot 2C_6H_6$	145.4 121.0	68.1 (?)
neat C_6H_6	128.5	
$[Ni(CN)_4]^{2-}$ in aqueous solution[12]		138.0

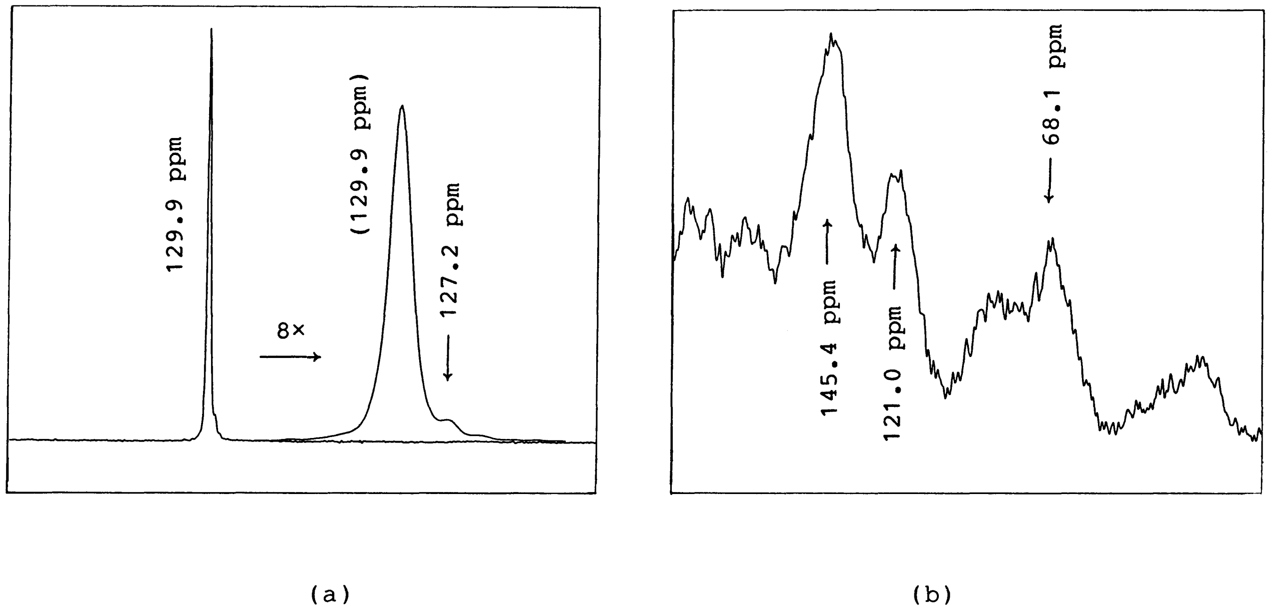
overlapping of some side bands of the strong doublet due to the benzene carbons. Since the paramagnetic nickel(II) is located next to the nitrogen atom of the cyanide group through the coordination bond with the Ni-N-C distance of 3.4 Å, the cyanide carbon should be influenced by the paramagnetism so much as to show the linewidth broader than that of the benzene carbons.

Chemical shifts in paramagnetic solids are generally dependent on the size of specimen to a considerable extent, because the effects of bulk magnetic susceptibility and magnetic anisotropy are much influenced by the size of specimen. However, the spectral lines, which were observed by two independent measurements on the two spectrometers different in sample size, coincided with each other with respect to the chemical shifts and the relative intensities; differences were observed for the number and shape of the side bands inevitable in the spectrum of magnetically anisotropic ^{13}C in paramagnetic specimens.

The 2:1 doublet assigned to the benzene carbons is composed of the stronger line with the larger low-field shift and the weaker line with the smaller high-field shift. The feature is interpreted in terms of pseudocontact shift by the paramagnetic nickel(II) in the host lattice. The pseudocontact shift $\Delta H/H$ in the axially symmetric field is given by the following equation:[16)]

$$\Delta H/H \propto [-\beta^2 S(S+1)/45kT](3g_{\parallel} + 4g_{\perp})(g_{\parallel} - g_{\perp})[(3\cos^2\theta_i - 1)/r_i^{\,3}]$$

where each notation is used with usual definition. Since the extent of the anisotropy is generally small in a paramagnetic nickel(II) complex with NiN_6 coordination environment so far observed in the EPR spectrum,[17)] the effect of the anisotropy on the pseudocontact shift has been neglected in the usual NMR spectrum. Although the NiN_6 octahedron in Ni-Ni-Bz is slightly compressed along the



(a) (b)

Fig. 1. ^{13}C CP-MAS NMR spectra of (a) Cd-Ni-Bz and (b) Ni-Ni-Bz. In (a) the spectrum (right) 8 times expanded along the abscissa is shown to depict the 127.2 ppm peak (shoulder) due to the cyanide carbons besides the main peak (left) on the original scale.

crystal c-axis with the 2.08 Å Ni-N(NH_3) and 2.15 Å Ni-N(CN) bond lengths, no precise data have been available for the anisotropy of the g-tensor. Assuming that the g-tensor is almost isotropic, the angular term appears to be responsible for the ca. 24 ppm splitting. The differences between the angular terms for C(2) and C(3) calculated at every 1 Å interval gave an almost constant value of 1.28×10^{28} m^{-3} within the range of 6 - 29 Å from the paramagnetic nickel(II) atom in the crystal structure. The doublet structure supports that the rotational or reorientational motion of the guest benzene molecule is not so fast enough to average the splitting of the components due to the paramagnetism.

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