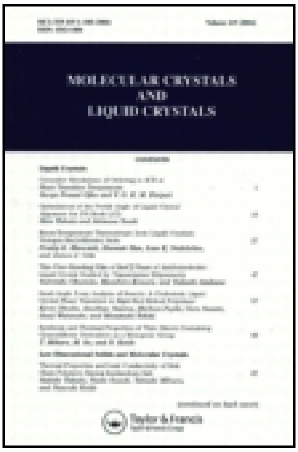

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Magnetic Local Structures of Prussian-Blue Analogs: Hyperfine Coupling of the Cyanide Ions and the Coordination Water Molecules as Studied by Solid-State 13 C and D NMR

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Magnetic Local Structures of Prussian-Blue Analogs: Hyperfine Coupling of the Cyanide Ions and the Coordination Water Molecules as Studied by Solid-State ^{13}C and D NMR

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Hyperfine coupling constant (HFCC) of a CN ligand must be sensitive to its coordination bond and local magnetic structures of Prussian-blue analogs. The HFCC of carbon atom of ^{13}CN ligand was determined to be -23, -39 and -21 MHz for $M=Li^+$(x=0.2, y=1.40), Na^+(x=0.5, y=1.26) and Mg^{2+}(x=0.2, y=1.32) of $M_xCo_y[Fe(^{13}CN)_6]\cdot zH_2O$ in the high-spin state, respectively, from ^{13}C-NMR spectrum. A larger magnitude of the HFCC of the $M=Na^+$ complex suggests a unique local structure to exhibit a thermally induced spin phase transition around 240K. In the low-spin phase of the $M=Na^+$ complex, a ^{13}C-NMR signal showing a positive HFCC of $Fe^{II}(S=0)$-CN-$Co^{II}(S=3/2)$ species was observed together with an intense signal of $Fe^{II}(S=0)$-CN-$Co^{III}(S=0)$. Three kinds of crystal water molecules were distinguished by the magic angle spinning D-NMR for the deuterated $M=Na^+$ complex in the high-spin phase. Two of them interact with magnetic ions and are mobile even below the spin phase transition temperature.

Keywords: Co-Fe polycyanide; magnetic local structures; hyperfine coupling constant; crystal water; D MAS NMR; ^{13}C-NMR

INTRODUCTION

Cobalt-iron polycyanide $M_xCo_y[Fe(CN)_6]\cdot zH_2O$ as a Prussian-blue analog changes its spin states between $Fe^{III}(S=1/2)$-CN-$Co^{II}(S=3/2)$ (the high spin state; HS) and $Fe^{II}(S=0)$-CN-$Co^{III}(S=0)$ (the low spin state; LS), accompanied with electron transfer. Its spin transition can be controlled by a concentration of doped alkali cation M[1,2] and by photo irradiation at low temperature[2,3]. The doping of alkali cation is considered to control the Co ligand field by the substitution of water molecules of $[Co(H_2O)_n(CN)_{6-n}]$ with CN ligand of $[Fe(CN)_6]$ for maintaining a charge balance[4]. For a sufficient amount of nitrogen atoms around the Co^{II} ion, the Co^{II} ion can become low spin and its reducing power is increased to stabilize the Fe^{II}-CN-Co^{III} state. The size and the concentration of doped cation may affect the averaged fcc lattice constant and coordination bond length of Fe-CN-Co. This changes the strength of the Co ligand field.

To elucidate an effect of the doped cation on the local coordination bonds of Fe-CN-Co, we determined the hyperfine coupling constant (HFCC) of the carbon atom of CN ligand from the solid-state ^{13}C-NMR spectrum for a series of Co-Fe polycyanides $M_xCo_y[Fe(CN)_6]\cdot zH_2O$, where $M=Li^+(x=0.2, y=1.40)$, $Na^+(x=0.5, y=1.26)$, and $Mg^{2+}(x=0.2, y=1.32)$ and ^{13}C was enriched up to 99%. The complex with $M=Na^+$ exhibited thermally induced spin phase transition, whereas the complexes with $M=Li^+$ and Mg^{2+} showed no transition.

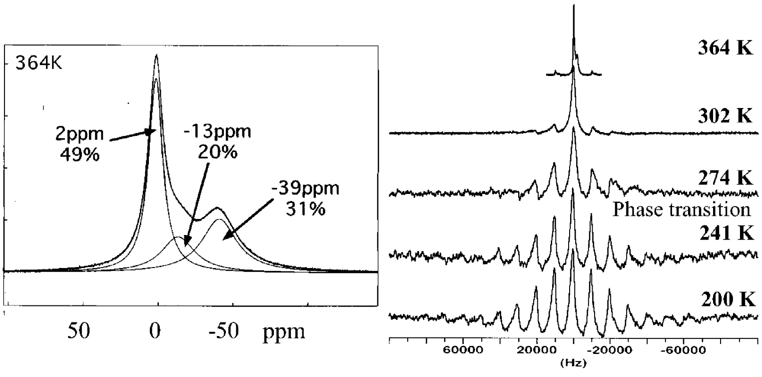
Local environment of the crystal water molecules was studied to clarify the character of their coordination to Co ion by magic angle spinning deuterium NMR for the deuterated compound with $M=Na^+$.

EXPERIMENT

Deuterated specimen of $M=Na^+$ complex was synthesized by adding a D_2O solution of 4M NaCl and 4mM anhydrous $CoCl_2$ to a D_2O solution of 4M NaCl and 4mM $K_3[Fe(CN)_6]$ to ensure complete deuteration of the crystal water. For ^{13}C-NMR measurement, ^{13}C-enriched (99%) $Na_{1.2}K_{1.8}[Fe(^{13}CN)_6]$ was prepared by using $K^{13}CN$ and then the complex of $M_xCo_y[Fe(^{13}CN)_6]\cdot zH_2O$, where $M=Li^+(x=0.2, y=1.40)$,

Na^+(x=0.5, y=1.26) or Mg^{2+}(x=0.2, y=1.32) was respectively synthesized by a similar method described above in H_2O solution. Powder X-ray diffraction pattern of all the synthesized specimens showed fcc structure with different lattice constants. The lattice constant is described later. Magic angle spinning deuterium NMR spectrum and ^{13}C-NMR spectrum were measured with a Bruker DSX 300 spectrometer. Direct current magnetic susceptibility was measured with a SQUID magnetometer (MPMS 5).

RESULTS AND DISCUSSION



(a) (b)

FIGURE 1 Magic angle spinning deuterium NMR of $Na_xCo_y[Fe(CN)_6]\cdot zD_2O$: isotropically shifted signal at 364 K (a), where three crystal waters were distinguished, and full range spectrum of ±100 kHz showing all spinning side bands (b).

Magic angle spinning (MAS) deuterium NMR spectrum of deuterated M=Na^+ complex was measured for a powder sample at a resonance frequency of 46.1 MHz and at a spinning speed of 10 kHz. The MAS technique gives an isotropic shift of deuterium[5]. The shift was measured from the external second reference of CD^*_3OD (3.35 ppm). Three different crystal waters were distinguished as shown in Figure 1 (a). Their isotropic shifts are +2 (49%), -13 (20%) and -39 ppm (31%).

The value in parentheses indicates each content. Almost a half of crystal waters shows a typical isotropic shift for diamagnetic one. Thus, the 50% of water molecules does not interact with magnetic ions but is occluded in interstitial lattice site as a zeolite water. Two different coordination waters with different negative hyperfine couplings were found. These water molecules weakly coordinate to Co ion. The result suggests that several different Co ions exist in the complex.

Envelop of the whole spinning side bands shown in Figure 1 (b) displays a line shape of D-NMR spectrum of the crystal waters. Typical bandwidth of the D-NMR spectrum of rigid water molecule in the solid state spreads over 4000 ppm (200 kHz). However, the spectral width of the complex at 364 K was very narrow as shown in Figure 1 (b). This indicates that a rapid motion of C_2-axis of all D_2O molecules occurs with large amplitude in the high temperature region. This motion became slow near 240 K. However, a 180°-flip motion of the D_2O molecules remained rapid down to 200 K.

Temperature dependence of the ^{13}C-NMR spectrum of M=Na^+ complex is shown in Figure 2 (a). The ^{13}C-NMR spectrum of static powder sample was measured by echo pulse sequence at an external magnetic field of 7.05 T and irradiation frequency was swept to cover the wide spectrum. The envelope of all echo signals is the spectral line shape. Line shape fitting by considering the anisotropy of the dipole interaction between ^{13}C nucleus and electron spins of Co and Fe ions and a broadening factor gave an isotropic shift. The isotropic shift is plotted as a function of inverse temperature in Figure 2 (b) together with those of the complexes of M=Li^+ and $Na_{1.2}K_{1.8}[Fe(^{13}CN)_6]$.

Neglecting the zero field splitting, the isotropic shift consists of the Fermi contact term, the pseudo contact (dipole) term and the temperature independent diamagnetic term as follows,

$$\delta_{\mathrm{iso}} = \delta_{\mathrm{Fermi}} + \delta_{\mathrm{Pseudo}} + \delta_{\mathrm{dia}} \tag{1}$$

$$\delta_{\mathrm{Fermi}} + \delta_{\mathrm{Pseudo}} = \frac{\mu_{\mathrm{B}}}{3k_{\mathrm{B}}T} \cdot \frac{A'_C}{\gamma_{\mathrm{C}}/2\pi} \quad . \tag{2}$$

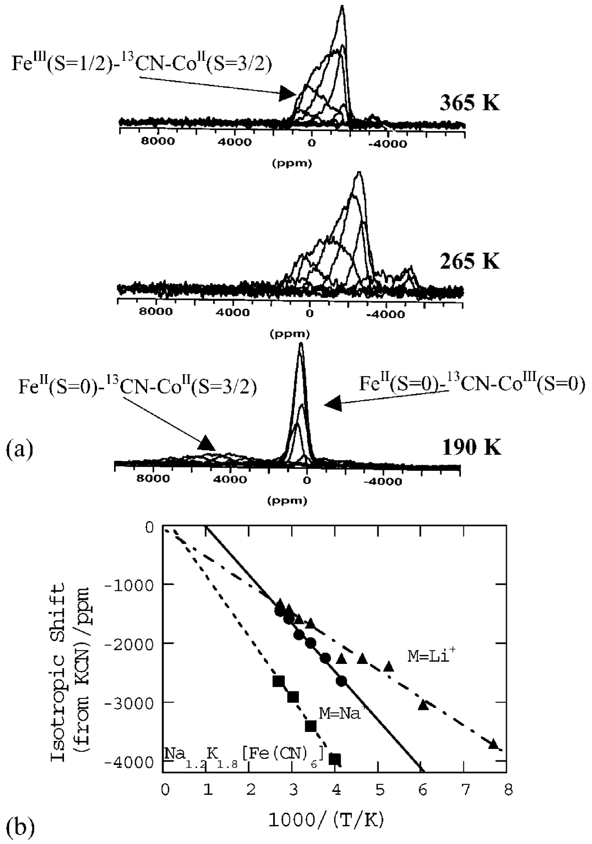


FIGURE 2 (a) ^{13}C-NMR spectrum of M=Na$^+$(x=0.5, y=1.26) complex above and below the spin phase transition near 240 K. (b) The temperature dependence of its isotropic shift (●) in the HS phase is compared with those of the M=Li$^+$(x=0.2, y=1.40) (▲) complex and the Na$_{1.2}$K$_{1.8}$[Fe(^{13}CN)$_6$] (■).

The coefficient A'_C is the HFCC of the ^{13}C nucleus in Hz including terms of anisotropic g tensors and spin quantum numbers of the two magnetic ions Fe and Co. The present definition of the HFCC is different from usual one[5,6]. The HFCC was determined to be -23, -39 and -21 MHz for M=Li$^+$, Na$^+$ and Mg^{2+}, respectively, from the slope of

δ_{iso} vs. $1/T$ along Eqs. 1 and 2 as shown in Figure 2 (b). The δ_{iso} of the M=Mg^{2+} complex is not shown in the figure for the sake of clarity. In the LS phase of the M=Na^{+} complex, lower field signal of Fe^{II}(S=0)-CN-Co^{II}(S=3/2) species exhibiting positive HFCC appeared as seen in Figure 2 (b). The result suggests that the negative HFCC from Fe^{III}(S=1/2) and the positive HFCC from Co^{II}(S=3/2) compete on the carbon atom of CN ligand in the HS phase. Indeed, the negative value of HFCC of the carbon atom of $Na_{1.2}K_{1.8}[Fe(^{13}CN)_6]$ is large (-50 MHz). The magnitude of HFCC of the M=Na^{+} complex in the HS phase is large in comparison with the complexes of M=Li^{+} and Mg^{2+}, although the lattice constant 10.26 Å of M=Na^{+} complex is larger than 10.22 (M=Li^{+}) and 10.23 Å (M=Mg^{2+}). The complex of M=Na^{+} exhibited thermally induced spin phase transition near 240 K, whereas complexes of M=Li^{+} and Mg^{2+} showed no transition and remained in the HS state down to low temperatures. The large absolute value of HFCC of the M=Na^{+} complex suggests a unique local structure to exhibit the thermally induced spin phase transition.

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