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Hyperfine coupling and local structures of octacyanomolibudenum magnetic complexes and related compounds as studied by solid state ¹³C and ²H NMR

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Abstract

Three-dimensional polymeric complex of $Cu_2[Mo(CN)_8] \cdot 8H_2O(1)$ is known to undergo a transition from paramagnetic to ferromagnetic state by irradiation with blue light. To elucidate the local structure of this polymeric complex, which is important for switching to ferromagnet, we studied hyperfine coupling of ¹³C-enriched cyanide ions of **1** and of closely related structure known polycyanide complexes of $Fe_2^{II}[Mo^{IV}({}^{13}CN)_8] \cdot 8H_2O(2)$, $Mn_2^{II}[Mo^{IV}({}^{13}CN)_8] \cdot 8H_2O(3)$, $[Cu^{II}(bpy)_2]_2[Mo^{IV}({}^{13}CN)_8] \cdot 5H_2O \cdot CH_3OH(4)$, UV-irradiated $K_4[Mo^{IV}({}^{13}CN)_8] \cdot 2D_2O(5)$, $Cs_3[Mo^{V}({}^{13}CN)_8] \cdot 2H_2O(6)$, $[Cu_2^{II}(tren)_2^{13}CN](BF_4)_3(7)$, and $[Ni_2^{II}(tetren)_2^{13}CN](ClO_4)_3(8)$ by solid-state ¹³C NMR spectrum. We found two distinct ¹³C NMR signals for the cyanide ions in a paramagnetic phase of **1**, i.e. high frequency and low frequency peak. Each of high- and low-frequency peak shows a positive (+19 MHz) and negative (-2 MHz) hyperfine coupling constant (hfcc), respectively. Then we assume that there are two distinct coordination structures for Cu(II) ions of **1**. The peak with positive hfcc was also observed for **2** and **3**, in which the cyanide ions of $[Mo^{IV}(CN)_8]^4$ coordinate to Fe(II) and Mn(II), respectively, in a square planar (SQP) structure. The negative hfcc of -0.79 MHz, which resembles the low frequency peak of **1**, was observed for the ¹³C atom of one of the CN ions of **4**, which coordinates to the Cu(II) ion an equatorial plane of trigonal bipyramidal (TBP) structure. Based on these NMR results, it is suggested that there are two distinct Cu(II) coordination environments in **1**, namely SQP and the structure that is largely distorted from SQP. The distortion may be important for ferromagnetic switching by photoinduced electron transfer from Mo(IV) to Cu(II) ion in a collective manner in the solid state.

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1. Introduction

Photoinduced ferromagnetic switching is one of the fascinating subjects in the field of molecular magnetism. The octacyanometalate ions of a form $[M^{IV}(CN)_8]^{4-}$ have been employed as building blocks of the photosensitive magnetic materials [1-3].¹ The solution photo-

chemistry of octacyanomolibudate ion has been studied for many years. The irradiation with light of a solution containing $[Mo^{IV}(CN)_8]^{4-}$ in its charge-transfer bands results in a photo-oxidation of $Mo^{IV}(S=0)$ to $Mo^V(S=1/2)$ with the ejection of a solvated electron [4–6]. A similar photo-reaction was observed for a simple compound of K₄[Mo^{IV}(CN)₈] · 2H₂O in the solid state [7], in which a reduction of crystal water molecule accompanied with photo-oxidation of the Mo^{IV}(S=0) to Mo^V(S=1/2) was assumed. Several irreversible photo-oxidation reactions in the solid state have been reported for extended multinuclear complexes [1,7].

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¹ M: MO and W.

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Ferromagnetic ordering with blue light irradiation at low temperature was found for Cu₂[Mo(CN)₈] · 8H₂O [2,3]. The critical temperature was 35 K and this photoinduced phase was transformed to the original form with increasing temperature up to 200 K. Reversible change of the magnetism with blue and red light irradiation was found at low temperature [3]. In this change of the magnetism, a reduction of Cu(II) to Cu(I) occurs by electron transfer from Mo(IV) ion with blue light irradiation. The coordination structure of this reducible Cu(II) ion before irradiation must be crucial for the photoinduced ferromagnetism. However, detailed structure of this compound is not known. Therefore, we tried to elucidate the local structure of $Cu_2[Mo(^{13}CN)_8] \cdot 8H_2O$ (1) by a measurement of hyperfine coupling constant (hfcc) of ¹³C atoms of ¹³C enriched cyanide ions. The hfcc of a CN ligand must be sensitive to its coordination bond and local magnetic structures of a variety of polycyanide complexes [8,9]. We studied the plus and minus sign and the magnitude of hfcc of ¹³C enriched cyanide ions of 1 and of closely related structure-known polycyanide complexes of $Fe_{2}^{II}[Mo^{IV}({}^{13}CN)_{8}] \cdot 8H_{2}O(2), Mn_{2}^{II}[Mo^{IV}]$ $[^{13}CN)_{8}] \cdot 8H_{2}O(3), [Cu^{II}(bpy)_{2}]_{2}[Mo^{IV}(^{13}CN)_{8}] \cdot 5H_{2}O \cdot$ CH₃OH (4), UV-irradiated K₄[Mo^{IV}(¹³CN)₈] · 2D₂O (5), Cs₃[Mo^V(¹³CN)₈] · 2H₂O (6), [Cu₂^{II}(tren)₂¹³CN] (BF₄)₃ (7), and [Ni₂^{II}(tetren)₂¹³CN](ClO₄)₃ (8) by temperature dependence of solid-state ¹³C NMR spectrum.

Broad-line ¹³C NMR spectrum of higher spin system has been reported for Mn_{12} -acetate cluster [10–12]. Methyl groups of acetate ions were enriched with ¹³C isotope. Although the methyl carbon atoms are apart from the magnetic Mn ions, the spectrum width is larger than 4000 ppm for powder sample at 250 K and no magic angle spinning spectrum was reported. In our case, the carbon atoms of cyanide ions closely locate to magnetic metal ions.

2. Experimental

2.1. Sample preparations

2.1.1. $K_4[Mo^{IV}({}^{13}CN)_8] \cdot 2H_2O(5)$

Warning! Although we have experienced no difficulties, this procedure may produce HCN gas. 99% ¹³C enriched specimen was synthesized by a similar method reported for normal compound [13]. 1.0 g of MoO₃ and 4.6 g of 99% ¹³C enriched K¹³CN were milled in a mortar. 7.5 ml of H₂O was slowly added to the milled mixture in drop-wise at 0 °C and then 1.1 g of 85% aqueous (NH₂)₂ was added. Under ambient temperature, 4.5 ml conc. HCl was added very slowly to the above solution in 1 h. Resulting solution was heated up to 86 °C for 1 h and was cooled down to room temperature. Pouring the solution into 85 ml of CH₃OH results in immediate precipitation of brown yellow powder. 12.5 ml aqueous solution of the filtered powder was heated to boil with activated carbon. The solution was filtered and poured into 85 ml of CH₃OH results in immediate precipitation of yellow powder. The treatment with activated carbon and recrystallization were repeated three times. The last treatment with D₂O instead of H₂O gave a deuterated analogue of K₄[Mo^{IV}(¹³CN)₈] · 2D₂O. *Anal.* Calc. for **5**: C, 20.6; H, 0.79; N, 22.2. Found: C, 19.25; H, 0.96; N, 22.95%.

2.1.2. $Cu_2^{II}[Mo^{IV}({}^{13}CN)_8] \cdot 8H_2O(1)$

Slow addition of 0.2 M aqueous solution of CuCl₂ to 0.2 M aqueous solution of $K_4[Mo^{IV}({}^{13}CN)_8]$ gave redpurple powder [2]. Filtrated powder was dried in a desiccator. *Anal.* Calc. for 1: C, 16.70; H, 2.80; N, 19.48. Found: C, 16.95; H, 2.58; N, 19.97%. The same procedure with heavy water solution and deuterated analogue of **5** gave Cu₂[Mo(${}^{13}CN)_8$] · 8D₂O.

2.1.3. $Fe_2^{II}[Mo^{IV}({}^{I3}CN)_8] \cdot 8H_2O$ (2)

Compound **2** was synthesized after the reference [14] with 99% ¹³C enriched **5** instead of normal compound. *Anal.* Calc. for **2**: C, 17.44; H, 2.77; N, 20.35. Found: C, 15.88; H, 2.86; N, 18.80%. Powder X-ray diffraction pattern agreed well with the structure determined for a single crystal [15]. The compound **2** may be oxidized in the air. A fresh yellow powder sample became blue in a few days in the air. Evacuation of the virgin yellow powder led to color change to green-yellow. Electronic sate may be changed due to a loss of crystal water. Therefore, for the NMR measurement, a fresh yellow sample was sealed into a glass ample with N₂ gas for preventing a loss of crystal water and an effect of oxygen.

2.1.4. $Mn_2^{II}[Mo^{IV}({}^{13}CN)_8] \cdot 8H_2O(3)$

Compound **3** was synthesized after the reference [15] with 99% ¹³C enriched **5** instead of normal compound. *Anal.* Calc. for **3**: C, 17.22; H, 2.86; N, 20.09. Found: C, 16.66; H, 2.55; N, 20.05%.

2.1.5. $[Cu^{II}(bpy)_2]_2[Mo^{IV}({}^{13}CN)_8] \cdot 5H_2O \cdot CH_3OH$ (4)

Polycrystalline sample of **4** was obtained after the method of reference [1] with 99% ¹³C enriched **5** instead of normal compound. *Anal.* Calc. for **4**: C, 49.98; H, 3.91; N, 19.62. Found: C, 47.31; H, 4.08; N, 18.53%. Powder X-ray diffraction pattern agreed well with the structure determined for a single crystal [1].

2.1.6. $Cs_3[Mo^V({}^{13}CN)_8] \cdot 2H_2O(6)$

Polycrystalline sample of **6** was obtained after the method of reference [16] with 99% ¹³C enriched **5** instead of normal compound. *Anal.* Calc. for **6**: C, 13.00; H, 0.55; N, 15.17. Found: C, 12.96; H, 0.72; N, 15.18%. Powder X-ray diffraction pattern agreed well with the structure determined for a single crystal [17].

2.1.7. $[Cu_2^{II}(tren)_2^{13}CN](BF_4)_3(7)$ and $[Ni_2^{II}(tetren)_2^{13}CN](ClO_4)_3(8)$

Blue crystals of 7 and purple crystals of 8 were obtained after the methods of reference [18] by slow evaporation of the solvent. Colorless crystals also appeared and were taken off. *Anal.* Calc. for 7: C, 22.12; H, 5.14; N, 17.86. Found: C, 21.85; H, 5.06; N, 17.64%. *Anal.* Calc. for 8: C, 24.35; H, 5.73; N, 18.38. Found: C, 24.65; H, 5.46; N, 18.73%. Powder X-ray diffraction patterns of 6 and 7 agreed well with the respective structure reported for each single crystal [18].

2.2. Solid-state NMR

The ¹³C NMR spectrum was measured by an echo pulse sequence for static powder crystalline sample at an external magnetic field of 7.05 T with a Bruker DSX300 spectrometer. Various irradiation frequencies were used to cover the wide spectrum. The envelope of all the echo signals displays a whole spectral line shape. When a line shape is almost symmetric, we assume that the isotropic shift is the center of the spectrum. The shift was measured from external second reference of the powder crystalline sample of K¹³CN (169.6 ppm from TMS). Assuming a small zero-field splitting, the observed isotropic shift δ_{iso} consists of the Fermi contact term, the dipole interaction term (pseudo contact) and the temperature independent diamagnetic term (chemical shift) as follows [19,20]:

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

$$\delta_{\text{Fermi}} + \delta_{\text{Pseudo}} = \frac{\mu_{\text{B}}}{3k_{\text{B}}T} \frac{A_{\text{C}}}{\gamma_{\text{C}}/2\pi} S(S+1).$$
(2)

Electron spin induced on the ¹³C nucleus by electron spin of a magnetic metal ion causes a Fermi contact shift of the NMR resonance line, while anisotropy of the *g*tensor of magnetic metal ions gives a pseudo-contact shift. The coefficient $A_{\rm C}$ in Eq. (2) is defined as the hfcc of the ¹³C nucleus in Hz unit, which includes principal values of anisotropic *g* tensor.

Magic angle spinning ¹³C and ²H NMR (MAS NMR) spectra were measured by a similar method described in reference [21] at a resonance frequency of 75.4 and 46.1 MHz, respectively, and at a magic angle spinning speed of ca. 9 kHz with a Bruker DSX300 spectrometer. The MAS technique gives a high resolution spectrum with an isotropic shift in some cases. The thermometer of the MAS NMR probe and an effect of spinning speed on temperature increase were carefully calibrated [21,22]. Uncertainty of the temperature measurement was within ± 2 K. The ²H NMR shift was measured from the external second reference of CD₃OD (CD₃: 3.35 ppm).

3. Results and discussion

3.1. Hyperfine coupling constants of cyanide ions and local coordination structures of 1

Fig. 1 illustrates a typical ¹³C NMR spectrum of cyanide ions of 1. We found two distinct signals corresponding to two different electronic states of the cyanide ions. Largely shifted values from the diamagnetic shift of K¹³CN (origin of abscissa) indicates an effect of electronic spins of Cu^{II} ions in this compound 1, in which Mo^{IV} ions are diamagnetic. Since each peak exhibited a small anisotropy and was almost symmetric, the isotropic shift described in Eqs. (1) and (2) was determined as the maximum point of the peak. Temperature dependence of the isotropic shift is plotted as a function of inverse temperature in Fig. 2 for both high and low frequency peaks. This figure indicates a good linear relation between the isotropic shift and inverse temperature as suggested in Eqs. (1) and (2). The hfcc of each peak was determined from the slope of this figure to be +19 and -2.0 MHz for high and low frequency peak, respectively. The plus and minus sign of the hfcc indicates that there are two different coordination structures for the cyanide ions. Nitrogen atoms of the cyanide ions are coordinated to Cu^{II} ions. Intensity ratio of the two signals suggests almost 3:1 population of different coordination structures.

To estimate the coordination structures of cyanide ions around magnetic metal ions, we determined the hfcc of cyanide ions for two other compounds 2 and 3, which have a similar unit formula to 1. The crystal structure of 2 is known, and 2 and 3 are believed to be isomorphous [1]. The coordination structure of 2 is illustrated in Fig. 3, where Fe^{II} ion has square-planner N-coordination of four cyanide ions and axial coordination of two water molecules. Typical ¹³C NMR spectrum is shown in Fig. 4(a) and (c) for 2 and 3, respectively. Only a single peak was observed both for



Fig. 1. Typical ¹³C NMR spectrum of 99% ¹³C enriched cyanide ions of $Cu_2^{II}[Mo^{IV}({}^{13}CN)_8] \cdot 8H_2O$ (1) at 294 K. The spectrum was measured with a spin echo technique. The envelope of many echo signals is illustrated. Magic angle spinning (MAS) at 10 kHz indicated no resolution enhancement for the higher frequency peak, whereas MAS technique was effective for the low frequency signal.



Fig. 2. Temperature dependence of isotropic ^{13}C NMR shift of $\text{Cu}_2{}^{II}[\text{Mo}^{IV}({}^{13}\text{CN})_8] \cdot 8\text{H}_2\text{O}~(1) \blacksquare$, low frequency peak and \Box , high frequency peak; \blacktriangle , Fe $_2{}^{II}[\text{Mo}^{IV}({}^{13}\text{CN})_8] \cdot 8\text{H}_2\text{O}~(2)$; \blacktriangledown , $\text{Mn}_2{}^{II}[\text{Mo}^{IV}({}^{13}\text{CN})_8] \cdot 8\text{H}_2\text{O}~(2)$; \blacksquare , $\text{Mn}_2{}^{II}[\text{Mo}^{IV}({}^{13}\text{CN})_8] \cdot 8\text{H}_2\text{O}~(3)$. The origin of the abscissa is the diamagnetic shift of polycrystalline sample of K^{13}\text{CN}. The hyperfine coupling constants determined from the slopes of this figure with Eqs. (1) and (2) are +19 MHz (high frequency peak) and -2.0 MHz (low frequency peak) for 1, +4.9 MHz for 2, and +2.3 MHz for 3.

2 and 3. A small signal near 0 ppm is impurity due to slight decomposition.² The spectrum is almost symmetric and the isotropic shift was determined as the center of the signal. Temperature dependence of the ¹³C NMR shifts is plotted in Fig. 2 for 2 and 3 together with 1. Positive slope for 2 and 3, which have square planar N-coordination structure around the magnetic metal center, resembles the slope of high frequency peak of 1. Thus we assigned the high frequency peak of ¹³C NMR spectrum of 1 to the cyanide ions that have square planar like N-coordination to Cu^{II} ion in 1. The derived values of higc are summarized in Table 1.

Low frequency peak of 1 indicates that a part of cyanide ions of 1 exhibits negative hfcc and their N-coordination structures are different from the square planar structure. The negative hfcc was observed for 4, which has an N-coordination to Cu(II) ion in an equatorial plane of trigonal bipyramidal structure as shown in Fig. 5. A typical ¹³C NMR spectrum of 4 is illustrated in Fig. 6. Three different isotropic peaks, i.e. α , β , γ , were identified. Two of eight cyanide ions of 4 are directly coordinated to magnetic Cu(II) ions and their ¹³C



Fig. 3. Structure of coordination network of $Fe_2^{II}[Mo^{IV}({}^{13}CN)_8] \cdot 8H_2O$ (2) after reference [12].

NMR signals should exhibit broader width and largest magnitude of hfcc, while other six cyanide ions are free of coordination. The peak γ , which shows largest width, was assigned to the cyanide ions coordinated to Cu(II) ions. Fig. 7 shows their shifts plotted as a function of inverse temperature and the peak γ exhibits the largest magnitude of hfcc. The sign of the hfcc of the peak γ is negative, which is similar to the low frequency peak of 1. It is considered that the N-coordination geometry of the cyanide ion with a negative hfcc of 1 is largely deformed from the square planar. It is not clear at present whether two distinct Cu(II) ions exist in 1, one of which is a square planar type and the other is largely deformed from the square planar, or all the Cu(II) ions are deformed form the square planar, in which three of the four N-coordination bonds are similar to the square planar and the rest one is deformed from the square planar type. Any how, such native deformation of N-coordination bond from the square planar structure in 1 is probably relevant to stabilize the reduced Cu(I) ion, which is produced by blue light irradiation.

We also investigated the motional behavior of crystal water molecules of deuterated analogue of **1**. Solid-state ²H NMR spectrum is narrow, which indicates rapid and almost isotropic rotation of the crystal water molecule (D₂O) at 295 K. A similar behavior was observed for Prussian-blue analogue [23,24]. Magic angle spinning ²H NMR spectrum showed an intense peak at 6.5 ppm at 295 K. This shift value is almost typical for diamagnetic

² The compound **2** decomposed in the air. A fresh yellow powder sample became dark blue in a few days in the air. The blue sample exhibited a completely different ¹³C NMR signal from virgin yellow sample as shown in Fig. 4(b). The signal of blue sample locates near 0 and 3000 ppm, one of which near 0 ppm is the almost the same shift observed as a small peak in Fig. 4(a). Evacuation of the virgin yellow powder led to color change to yellow-green. Electronic sate of **2** may be slightly hanged due to a loss of crystal water. Therefore, for the NMR measurement of **2**, a fresh yellow sample was sealed into a glass ample with N₂ gas for preventing a loss of crystal water and an effect of oxygen.



Fig. 4. Typical ¹³C NMR spectrum of 99% ¹³C enriched cyanide ions of: (a) $Fe_2^{II}[Mo^{IV}({}^{13}CN)_8] \cdot 8H_2O$ (2), (b) a specimen of 2 stored in the air and (c) $Mn_2^{II}[Mo^{IV}({}^{13}CN)_8] \cdot 8H_2O$ (3). Each spectrum is constructed with many echo signals measured with different excitation frequencies. The origin of the abscissa is the diamagnetic shift of polycrystalline sample of K¹³CN.

compounds and suggests no strong interaction between the crystal water molecules and the magnetic Cu(II) ion in contrast to the crystal structure of Fe(II) compound **2**, in which crystal water molecules directly coordinate to the Fe(II) ion. A small peak of MAS ²H NMR was also observed at 28 ppm. However, the intensity was only 3%

Table 1 Hyperfine coupling constant of ¹³C nucleus of compounds **1**, **2**, **3**, and **4**

Compound	1	2	3	4
Spin S of magnetic metal ion	Cu(II)	Fe(II)	Mn(II)	Cu(II)
	1/2	2	5/2	1/2
Hfcc	+19 MHz (not known)	+4.9 MHz (SQP)	+2.3 MHz (SQP)	
				+0.44 MHz
				-0.24 MHz
	-2 MHz			-0.79 MHz
	(not known)			(EP-TBP)
\mathbf{W}				

Compounds are $Cu_2^{II}[Mo^{IV}({}^{13}CN)_8] \cdot 8H_2O$ (1), $Fe_2^{II}[Mo^{IV}({}^{13}CN)_8] \cdot 8H_2O$ (2), $Mn_2^{II}[Mo^{IV}({}^{13}CN)_8] \cdot 8H_2O$ (3), and $[Cu^{II}(bpy)_2]_2[Mo^{IV}({}^{13}CN)_8] \cdot 5H_2O \cdot CH_3OH$ (4). SQ represents the square planer structure and EP-TBP means equatorial plane of trigonal bipyramidal.



Fig. 5. Molecular and coordination structure of $[Cu^{II}(bpy)_2]_2-[Mo^{IV}({}^{13}CN)_8]\cdot 5\ H_2O\cdot CH_3OH$ (4) [1].

of the peak at 6.5 ppm and the small peak was tentatively assigned to an impurity.

3.2. Photoreaction of 5 in aqueous solution and in the crystalline phase, and ${}^{13}C$ NMR spectrum of $[Mo^V({}^{13}CN)_8]^{3-}$ ion

To obtain an information about hfcc of ¹³C atom given by photoinduced Mo(V) ion (S = 1/2) in the crystalline phase of K₄[Mo^{IV}(¹³CN)₈] · 2D₂O (**5**), we measured ¹³C NMR spectrum for ca. 50 mg of light irradiated powder specimen of **5**. By irradiation with a light (ca. 300–800 nm) of a Xe lamp at room temperature for a few days, we observed a very broad ¹³C NMR spectrum overlapped by a sharp central line of a diamagnetic species of **5** as shown in Fig. 8(a). Signal-to-noise ratio is



Fig. 6. A typical magic angle spinning ¹³C NMR spectrum of cyanide ions of 99% ¹³C enriched sample of $[Cu^{II}(bpy)_2]_2[Mo^{IV}(^{13}CN)_8] \cdot 5$ -H₂O · CH₃OH (**4**), which was measured at 300 K with a spinning speed of 9 kHz. The shift was measured from TMS and a second reference of K¹³CN (169.6 ppm from TMS) was used. α , β and γ indicate signals of isotropic shift. Peaks indicated by asterisks are spinning side bands, which were clearly distinguished from the isotropic shifts by using several different spinning speeds.



Fig. 7. Temperature dependence of the isotropic shift of ¹³C NMR lines indicated by α , β and γ in Fig. 6. Each temperature slope gave hfcc of +0.44 (α), -0.24 (β) and -0.79 MHz (γ), respectively.

bad because of conversion from Mo(IV) to Mo(V) is not enough. The amount of the conversion from Mo(IV) to Mo(V) was estimated to be ca. 1.4% from the MAS ²H NMR spectrum of OD⁻ ion produced by a reduction of D₂O molecule as shown in Fig. 9.³ Intensity of the sharp signal of diamagnetic **5** with long relaxation time was diminished by short repetition time for accumulation



Fig. 8. ¹³C NMR spectrum of cyanide ion of $[Mo^V({}^{13}CN)_8]^{3-}$ of (a) UV-irradiated $K_4[Mo^{IV}({}^{13}CN)_8] \cdot 2D_2O$ (5) and (b) $Cs_3[Mo^V({}^{13}C-N)_8] \cdot 2H_2O$ (6). The origin of the abscissa is the diamagnetic shift of polycrystalline sample of $K^{13}CN$. The signal near 0 ppm was assigned to decomposed fragment, which is diamagnetic.

of the signal. The signal of ¹³C NMR of $[Mo^{V}(^{13}CN)_8]^{3-}$ is very broad and a center of the broad signal is almost temperature independent in contradiction to a prediction by Eqs. (1) and (2). To clarify this behavior, we also studied ¹³C NMR spectrum of Cs₃[Mo^V(¹³CN)₈] · 2H₂O (**6**) in the crystalline phase. The spectrum is also very broad and almost temperature independent as illustrated in

³ It is noted that reduction of the crystal water molecule hydrogenbonded to the N atom of Mo(IV)-CN by an electron transfer from Mo(IV) ion with UV-irradiation was concluded in the crystalline phase. Such a reaction was proposed in solution and in the solid state [7].



Fig. 9. Magic angle spinning ²H NMR spectrum of UV-irradiated $K_4[Mo^{IV}(^{13}CN)_8] \cdot 2D_2O$ (5). (a) Full-width spectrum including spinning side bands and (b) isotropic shift. The full width spectrum (a) indicates 180° flip motion of D_2O molecule in the solid state around the molecular C_2 axis. A small signal at 7.9 ppm of (b) was assigned to OD^- ion produced by UV-irradiation, $Mo^{IV} + D_2O \rightarrow Mo^V + OD^- + 1/2D_2$ (1). The intensity of this signal is 1.4% of total intensity of D signals including all of the spinning side bands. A large signal at 5.4 ppm is crystal water molecule, which is independent of UV-irradiation. The signal of OD^- ion showed no spinning side band, which indicates rapid isotropic rotation of OD^- ion in the crystalline lattice of 5.

Fig. 8(b). For these compounds, relaxation time of electron spin may not be matched to the assumed condition to derive the Eqs. (1) and (2) for 13 C NMR in the solid state.

In contrast to the above result for the crystalline phase, well resolved ¹³C NMR signals were observed for light irradiated D₂O solution of a deuterated analogue of 5 as illustrated in Fig. 10. Color of the solution changed immediately from yellow to green by light irradiation under a similar condition to the polycrystalline phase. The observed shifts of ¹³C NMR signals for the irradiated solution are not so large, suggesting that the paramagnetic species of [Mo^V(¹³CN)₈]³⁻ was not detected. The hfcc of carbon nucleus of $[Mo^{V}(^{13}CN)_{8}]^{3-1}$ was estimated from quantum mechanical calculation based on UB3LYP/LanL2DZ for an anti-prism coordination structure of $[Mo^V({\rm ^{13}CN})_8]^{3-}$ in crystalline phase of 6. The values are -26.9 to -31.7 MHz. All the values are negative and the magnitude is similar to the value of [33] MHz determined by ESR for the $[Mo^{V}(CN)_{8}]^{3-}$ ion in an aqueous solution of $K_3[Mo^V(CN)_8]$ [25].



Fig. 10. ¹³C NMR spectrum of cyanide ion of D₂O solution of K_4 [Mo^{IV}(¹³CN)₈] · 2D₂O (a) before and (b) after UV-irradiation. The origin of the abscissa is the diamagnetic shift of polycrystalline sample of K^{13} CN. Since the reaction product was not identified, signal assignment was impossible for spectrum (b). Two spectra were measured with MAS NMR probe for solid.

3.3. A possible effect of polymeric sequential coordination structure on the linewidth of ^{13}C NMR spectrum of cyanide ion

To investigate further what is the origin of very broad and almost temperature independent ¹³C NMR spectrum observed for UV irradiated 5 and for 6, we tried to measure the ¹³C NMR spectrum for Cu(II) and Ni(II) dimmer compounds of 7 and 8 in their crystalline phase. We suspected that isolated electron spin or localized exchange interactions closed within a molecule would bring about a very broad ¹³C NMR spectrum. Our ¹³C NMR measurements for three-dimensional polymeric cyanide complexes such as Prussian-blue analogues [25] and for one-dimensional Ni(II) and Cu(II) chain complexes [26,27], which have extended exchange interactions, showed narrower and temperature dependent spectrum and we were able to apply Eqs. (1) and (2). An exception is hexacyanoferrate ion $[Fe^{III}(^{13}CN)_6]^{3-}$ in the solid state [23]. This compound showed relatively narrow and temperature dependent ¹³C NMR spectrum. The compounds 7 and 8 are dinuclear complex of Cu(II) and Ni(II), in



Fig. 11. ¹³C NMR spectrum of cyanide ion of (a) $[Cu_2^{II}(tren)_2^{13}CN](BF_4)_3$ (7) and (b) $[Ni_2^{II}(tetren)_2^{13}CN](ClO_4)_3$ (8). The origin of the abscissa is the diamagnetic shift of polycrystalline sample of K¹³CN.

which two identical magnetic metal ions are linked by a cyanide ion and relatively large antiferromagnetic interaction is closed within a molecule in the solid state [18]. Typical ¹³C NMR spectra for **7** and **8** are illustrated in Fig. 11. Very broad and almost temperature independent spectrum was found both for Cu(II) (**7**) and Ni(II) (**8**). A condition of relaxation time of electron spin may be not matched with an assumption for Eqs. (1) and (2). It requires a detailed investigation of spin-lattice relaxation of electron spin to clarify the mechanism of this behavior.

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