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Crystal Structure and Photo-Reaction of a New Coordination Polymer: $[Ni(en)_2]_4[Fe(CN)_5NO]_2[Fe(CN)_6]\cdot 6H_2O$

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A new photo-responsive coordination polymer of $[Ni(en)_2]_4[Fe(CN)_5NO]_2[Fe(CN)_6]\cdot 6H_2O$ was synthesized. In this compound, Ni–CN–Fe forms one-dimensional standing-wave-like chains, onto which photo-functional groups of pentacyanonitrosylferrate(II) are appended. Photo-irradiation with blue light at less than 200 K transformed the pentacyanonitrosylferrate(II) from the ground state to a metastable state, which could be reverted to the original state by irradiation with red light.

The alkali salts of pentacyanonitrosylferrate(II) are well known for their photo-reactivity.[1–5] Photo-irradiation with 350–580 nm light can induce a metal-to-ligand charge transfer (MLCT) from Fe to NO (Fig. 1), which brings about a metastable state with an extremely long lifetime below 200 K.[2] This metastable state can be reverted to the ground state by irradiation with light of 600–1200 nm wavelength or by a thermal treatment above 200 K. Although the photo-reactivity of the mononuclear compounds of pentacyanonitrosylferrate(II) has been studied extensively, little attention has been paid to the photo-reactions of pentacyanonitrosylferrate(II) in coordination polymers. In fact, the coordination polymers are very important from the viewpoint of applications because they are very stable with respect to solvents, while the alkali salts of pentacyanonitrosylferrate(II) are soluble in water and susceptible to moisture. In addition, by imbedding pentacyanonitrosylferrate(II) into the coordination network, the functional group may interact with the neighboring atoms in the network and the electronic changes on the pentacyanonitrosylferrate(II) may vary the whole electronic structure of the coordination polymer. Recently, we investigated the photo-reaction behavior of a coordination polymer of nickel pentacyanonitrosylferrate(II) ($NiFe(CN)_5NO\cdot 5.3H_2O$).[6] It was found that the photo-reactions of the pentacyanonitrosylferrate(II) in this coordination polymer were similar to those of the mononuclear compounds. The difference between the mononuclear compound and the coordination polymer was that the electronic change on the pentacyanonitrosylferrate(II) in the coordination polymer had a great influence on the magnetic interaction between neighboring metallic nuclei. The photo-induced MLCT in pentacyanonitrosylferrate(II) enhances the magnetic interaction among the neighboring nickel nuclei and as a result changes the magnetic properties of the compound. A molecular solid such as this is especially important from the viewpoint of molecular devices, because it is one possible method by which we can collect, transform and transfer information at the molecular level. In this paper we report on a new coordination polymer in which pentacyanonitrosylferrate(II) is coordinated to a one-dimensional metal-cyanide chain. Its crystal structure, magnetic properties and photoreaction behavior will be reported.

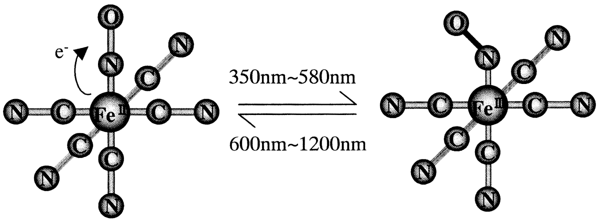

Fig. 1. Photo-reactivity of $Fe(CN)_5NO^{2-}$ in sodium salt.

Experimental

Materials: $[Ni(en)_3]Cl_2$ was prepared following the method described in the literature and re-crystallized from boiled water.[7] The $Na_2[Fe(CN)_5NO]$ (Wako Chemicals) was of reagent grade, and was used as-purchased.

Growth of a Single Crystal: This compound was obtained by mixing $[Ni(en)_3]Cl_2$ and $Na_2[Fe(CN)_5NO]$ in aqueous solution. The reaction rate and the speed of growth of the crystal of $[Ni(en)_2]_4[Fe(CN)_5NO]_2[Fe(CN)_6]\cdot 6H_2O$ were well controlled by the rate-limited dissociation reactions of $[Ni(en)_3]^{2+}$ and $[Fe(CN)_5NO]^{2-}$ in solution. After several days, an orange needle-like crystal structure appeared. Experiments found that the composition and the crystalline structure of the resultant solid were independent of the mixing ratio of the $[Ni(en)_3]^{2+}$ and $[Fe(CN)_5NO]^{2-}$. Anal. Calcd. for $Ni_4Fe_3C_{32}N_{34}H_{76}O_8$: Ni, 16.0; Fe, 11.4; C, 26.2; N, 32.5; H, 5.2%. Found: Ni, 16.1; Fe, 11.5; C, 26.3; N, 32.9; H, 5.3%.

Physical Measurement: IR and UV-visible spectrum measurements were performed at both room temperature and at 14 K. A closed-cycle helium cryostat (Iwatani Plantech Corp.) was used to control the temperature. The IR spectra were obtained using a Bio-RAD spectrophotometer (FTS-40A), and the UV-visible spectra were recorded with a UV-3100PC spectrophotometer (Shimadzu). The sample for IR measurement was ground up with KBr and pressed into a disk. The sample for UV-visible measurement was held between quartz plates. Magnetic susceptibilities were measured with a super-conducting quantum interference device (SQUID) magnetometer (QUANTUM DESIGN). Mössbauer spectra were measured using a Wissel MVT-1000-type spectrometer with a $^{57}Co/Rh$ source in transmission mode. An Hg–Xe lamp was used as a light source and sharp cut-off filters were used to obtain blue light with a wavelength of between 290–480 nm and a red light with a wavelength of 620–750 nm. The light was guided by an optical fiber to irradiate the samples in the cryostat and the SQUID.

Solution and Refinement of the X-ray Structures: X-ray diffraction measurements were performed on a Mac Science MXC18 using graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ nm) at room temperature. The crystallographic data are summarized in Table 1. The data were collected at room temperature using the ω-2θ scan mode to a maximum 2θ value of 55° at a scan speed of 10.0°/min (in omega). The weak reflections ($I < 3\sigma(I)$) were rescanned (up to a maximum of four scans), and the counts were accumulated to ensure good counting statistics. Stationary background counts were recorded on each side of the reflection. The cell parameters were determined by 21 reflections over a 2θ range of $28.96° \leq 2\theta \leq 34.50°$. The octant measured was +h, ±k, +l.

The details of the structure were solved using direct methods and refined using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final positional parameters of the atoms along with their estimated standard deviations are listed in Table 2. All diagrams and calculations were performed using Crystan (MacScience, Japan).

Table 1. Crystal Data for $[Ni(en)_2]_4[Fe(CN)_5NO]_2[Fe(CN)_6]\cdot 6H_2O$

Formula	$Ni_4Fe_3C_{32}N_{34}H_{76}O_8$
Formula weight	1467.578
Crystal system	Monoclinic
Space group	$P21/_n$
a	14.754(3)
b	29.096(6)
c	7.414(2)
β	102.85(2)
V	3101(1)
Z	2
D_c	1.554
μ(Mo-$K\alpha$)	20.254
No of reflcns	4240
$R^{a)}$	0.049
$R_w^{b), c)}$	0.067

a) $R = \Sigma\,|F_0 - |F_c||/\Sigma|F_0|$.
b) $Rw = [(\Sigma w(|F_0 - |F_c||)^2/\Sigma F_0^2)]^{1/2}$.
c) $w = 1/\sigma^2(F_0)$.

Results and Discussion

Crystal Structure and Physical Properties: Figure 2 shows the ORTEP drawing of one half unit of $[Ni(en)_2]_4[Fe(CN)_5NO]_2[Fe(CN)_6]\cdot 6H_2O$. One unit cell of the compound contains two $[Fe(CN)_6]^{4-}$ anions, four $[Fe(CN)_5NO]^{2-}$ anions, and eight *cis*-$[Ni(en)_2]^{2+}$ cations (Fig. 3a). The Fe(1) of $[Fe(CN)_6]^{4-}$ occupies an inversion center of the unit cell. Nitrogen N(9) coordinates to an adjacent nickel Ni(1) of *cis*-$[Ni(en)_2]^{2+}$, which is coordinated by an equatorial nitrogen N(12) on the $[Fe(CN)_5NO]^{2-}$. C(12)N(12) is the only ligand of $[Fe(CN)_5NO]^{2-}$ that coordinates to nickel. Nitrogen atoms of N(10) and N(11) in $[Fe(CN)_6]^{4-}$ each coordinate to their neighboring Ni(2) atom to form a chain along the *c*-axis. As shown in Figure 3b, the chain along the c-axis formed by Fe(1) and Ni(2) is likened to a standing-wave, in which Fe(1) is the node and two Ni(2) cations form the loop. $[Ni(en)_2][Fe(CN)_5NO]$ hangs on to the node of this chain. The bond lengths between Fe and C are in the range from 1.908 Å to 1.964 Å. The bond length of Fe(2)–C(14) in the axis of the $[Fe(CN)_5NO]^{2-}$ takes a value of 1.964(16) Å, which is very slightly longer than the other bonds. In the $[Fe(CN)_5NO]^{2-}$, the bond length of Fe(2)–N(17) is 1.656(13)Å and the angle of the Fe(2)–N(17)–O(1) bond is 179.3(14)°, which agrees with the data found for the $Na_2[Fe(CN)_5NO]$ in the ground state.[5] The angles for the Ni–N–C groups are not linear, and they are 152.8(11)° for Ni(1)–N(9)–C(9), 149.7(11)° for Ni(2)–N(10)–C(10) and 169.6(12)° for Ni(1)–N(12)–C(12) respectively.

Magnetic measurements showed that this material was paramagnetic over a temperature range from room temperature to 2 K (Fig. 4). The paramagnetism of the compound should be ascribed to the diamagnetism of Fe^{II} in $[Fe(CN)_6]^{4-}$, which prohibits the spin exchange interaction between the nearest metal centers in the one dimensional chain. The value of μ_{eff} at 300 K can be calculated by the equation:

$$\mu_{eff} = 2.828\,(\chi T)^{1/2} \tag{1}$$

as 5.92 μ_B, which is a little bit larger than the spin-only value of 5.66 μ_B at the high-temperature limit for the system with four Ni^{II} ions:

$$\mu_{eff} = g_{Ni}(4S_{Ni}(S_{Ni} + 1))^{1/2} \tag{2}$$

where the local Zeeman factor, g_{Ni}, is assumed to be 2 and the

Table 2. Fractional Atomic Coordinates & U(iso)

Atom	x/a	y/b	z/c	U(iso)	Atom	x/a	y/b	z/c	U(iso)
Ni(1)	0.37712(11)	0.34056(5)	0.38945(22)	0.0276(7)	O(1)	1.0741(12)	0.3734(6)	0.8433(19)	0.09(1)
Ni(2)	0.71813(10)	0.45202(6)	0.10705(19)	0.0265(7)	O(2)	0.2044(8)	0.4420(5)	0.1808(16)	0.056(6)
Fe(1)	0.50000(11)	0.50000(6)	0.50000(21)	0.0177(9)	O(3)	0.4514(10)	0.4114(5)	0.9358(18)	0.076(8)
Fe(2)	1.04115(12)	0.33697(7)	0.48673(26)	0.0322(8)	O(4)	0.7771(17)	0.2646(8)	0.1254(31)	0.16(2)
N(1)	0.5128(8)	0.3444(5)	0.3380(18)	0.041(6)	H(1)	0.533(12)	0.345(6)	0.251(24)	0.10(5)
N(2)	0.4534(10)	0.3205(5)	0.6533(18)	0.047(7)	H(2)	0.510(12)	0.365(6)	0.340(23)	0.13(5)
N(3)	0.3555(10)	0.2714(5)	0.2991(21)	0.047(7)	H(3)	0.63(3)	0.35(1)	0.52(5)	0.06(5)
N(4)	0.3116(9)	0.3534(4)	0.1099(16)	0.042(6)	H(4)	0.60(2)	0.30(1)	0.46(4)	0.06(6)
N(5)	0.7153(9)	0.3804(5)	0.0583(18)	0.048(7)	H(5)	0.589(12)	0.303(6)	0.745(24)	0.12(5)
N(6)	0.8263(10)	0.4490(6)	−0.0423(19)	0.049(7)	H(6)	0.570(14)	0.346(6)	0.693(26)	0.16(6)
N(7)	0.7375(9)	0.5225(4)	0.1616(17)	0.044(6)	H(7)	0.434(16)	0.316(8)	0.762(32)	0.06(5)
N(8)	0.8121(9)	0.4473(4)	0.3673(15)	0.037(6)	H(8)	0.43(2)	0.29(1)	0.57(4)	0.06(5)
N(9)	0.3880(8)	0.4107(4)	0.4600(16)	0.036(5)	H(9)	0.356(12)	0.246(6)	0.372(23)	0.11(5)
N(10)	0.6111(8)	0.4516(4)	0.2532(15)	0.035(6)	H(10)	0.409(13)	0.260(6)	0.268(23)	0.09(5)
N(11)	0.6274(8)	0.4645(4)	0.8580(14)	0.037(6)	H(11)	0.223(18)	0.274(9)	0.159(34)	0.06(5)
N(12)	1.2467(8)	0.3378(4)	0.4604(18)	0.040(6)	H(12)	0.28(2)	0.24(1)	0.07(4)	0.05(5)
N(13)	1.0174(9)	0.4296(5)	0.2784(20)	0.050(7)	H(13)	0.358(13)	0.298(6)	−0.023(24)	0.12(5)
N(14)	1.0003(12)	0.2963(7)	0.0897(23)	0.07(1)	H(14)	0.258(13)	0.313(6)	−0.090(24)	0.10(5)
N(15)	1.0559(12)	0.2349(6)	0.6018(26)	0.08(1)	H(15)	0.321(13)	0.378(6)	0.035(25)	0.05(5)
N(16)	0.8293(9)	0.3361(5)	0.4447(21)	0.052(7)	H(16)	0.25(2)	0.36(1)	0.15(4)	0.06(5)
N(17)	1.0612(8)	0.3586(4)	0.6985(17)	0.044(6)	H(17)	0.702(15)	0.354(7)	0.133(28)	0.06(5)
C(1)	0.5781(16)	0.3296(16)	0.4985(34)	0.13(2)	H(18)	0.66(2)	0.39(1)	−0.02(4)	0.06(5)
C(2)	0.5498(16)	0.3229(16)	0.6547(34)	0.10(2)	H(19)	0.761(13)	0.340(6)	−0.111(25)	0.08(5)
C(3)	0.2832(14)	0.2707(6)	0.1291(27)	0.07(1)	H(20)	0.842(13)	0.358(6)	0.036(23)	0.11(5)
C(4)	0.300(2)	0.310(1)	0.009(2)	0.07(1)	H(21)	0.863(18)	0.400(9)	−0.198(36)	0.05(5)
C(5)	0.7887(18)	0.3688(9)	−0.0435(36)	0.08(1)	H(22)	0.754(4)	0.412(2)	−0.254(8)	0.05(5)
C(6)	0.8099(15)	0.4073(9)	−0.1486(25)	0.08(1)	H(23)	0.818(12)	0.474(6)	−0.098(23)	0.12(5)
C(7)	0.8112(18)	0.5292(8)	0.3293(30)	0.07(1)	H(24)	0.882(12)	0.445(6)	0.041(24)	0.05(5)
C(8)	0.8148(13)	0.4904(6)	0.4629(22)	0.062(9)	H(25)	0.736(11)	0.548(6)	0.074(23)	0.05(5)
C(9)	0.4267(8)	0.4454(4)	0.4796(16)	0.025(5)	H(26)	0.678(14)	0.521(7)	0.193(26)	0.06(5)
C(10)	0.5710(7)	0.4697(4)	0.3478(15)	0.025(5)	H(27)	0.813(12)	0.555(6)	0.383(23)	0.07(5)
C(11)	0.5813(8)	0.4775(4)	0.7221(15)	0.024(5)	H(28)	0.881(13)	0.525(6)	0.291(24)	0.11(5)
C(12)	1.1703(10)	0.3373(5)	0.4708(18)	0.035(6)	H(29)	0.870(16)	0.493(8)	0.560(32)	0.05(5)
C(13)	1.0267(9)	0.3995(5)	0.3584(20)	0.037(6)	H(30)	0.76(2)	0.49(1)	0.52(4)	0.06(5)
C(14)	1.0159(11)	0.3108(5)	0.2364(21)	0.044(7)	H(31)	0.814(12)	0.425(6)	0.423(24)	0.07(5)
C(15)	1.0500(10)	0.2727(6)	0.5621(22)	0.048(8)	H(32)	0.860(13)	0.442(6)	0.351(23)	0.11(5)
C(16)	0.9074(10)	0.3351(5)	0.4593(21)	0.039(7)					

$T = exp\,[2\pi^2 U]$; $U = U_{\text{iso}}$ or U_{eqv}; $U_{\text{eqv}} = \frac{1}{3}\sum_{i=1}^{3}\sum_{j=1}^{3} U_{ij}\alpha_i\alpha_j \mathrm{a}_i \mathrm{a}_j$

spin number of the nickel is $S_{\text{Ni}} = 1$.

The IR spectrum shows four peaks for ν(CN) at 14 K. These vibrations are located at 2060, 2115, 2136 and 2192 cm^{-1}. As the coordination structure of CN in this compound is very complex, it is difficult to assign the four vibrations to definite bonds. The vibration of NO in $[\text{Fe(CN)}_5\text{NO}]^{2-}$ appears at 1909 cm^{-1} (Fig. 5). This vibration is almost 45 cm^{-1} lower than that in the reactant $\text{Na}_2[\text{Fe(CN)}_5\text{NO}]$.[6] It is well known that ν(NO) is sensitive to the counter-ion and the solvent molecule in the crystal.[8–16] The vibration value varies from 1965 to 1940 cm^{-1} in the different alkaline and alkaline-earth hydrated salts of $[\text{Fe(CN)}_5\text{NO}]^{2-}$. Dehydration of these compounds shifts the vibration to lower wavenumbers by about 20–40 cm^{-1}. The lowest vibration of NO reported is 1908 cm^{-1}, which was found in a tetrabutylammonium salt after dehydration.[17, 18] The ν(NO) of $[\text{Ni(en)}_2]_4[\text{Fe(CN)}_5\text{NO}]_2[\text{Fe(CN)}_6]\cdot 6\text{H}_2\text{O}$ reported in this paper is the lowest documented value observed in undehydrated compounds.

The UV-visible absorption spectrum is shown in Fig. 6. The absorption band around 400 nm can be assigned to the transitions of $^1\text{A}_1 \rightarrow {}^1\text{E}_1$, $^1\text{A}_1 \rightarrow {}^1\text{A}_1$, and $^1\text{A}_1 \rightarrow {}^1\text{A}_2$ for pentacyanonitrosylferrate(II), in which the MLCT $^1\text{A}_1 \rightarrow {}^1\text{E}_1$ appears in the range from 441 to 481 nm.[19, 20] Therefore, it is reasonable to expect that irradiation with light in the range of 441–481 nm could induce an MLCT from Fe to NO in pentacyanonitrosylferrate(II), which can produce a metastable state with a long lifetime.[20]

Photo-Induced Changes: Changes in the electronic state of $[\text{Fe(CN)}_5\text{NO}]^{2-}$ in the coordination polymer after irradiation with blue light with a wavelength of 290–480 nm were observed in the IR and UV-visible spectra taken at 14 K. The changes in the UV-visible spectra were found in the range of 300–400 nm (Fig. 6). This change can be ascribed to the appearance of $[\text{Fe(CN)}_5\text{NO}]^{2-}$ in the metastable state, whose electronic structure is different from that in the ground state.[4, 6, 21] The appearance of the metastable state is also supported by the change in the IR spectra. A decrease in the intensity of the absorption at 1909 cm^{-1} and a new peak at 1792 cm^{-1} were observed after irradiation (Fig. 5). Both of these two vibrations can be assigned to the ν(NO) of $[\text{Fe(CN)}_5\text{NO}]^{2-}$. The vibration at 1909 cm^{-1} is the ν(NO) in the ground state while that at 1792 cm^{-1} is the ν(NO) in the metastable state.[6] The low

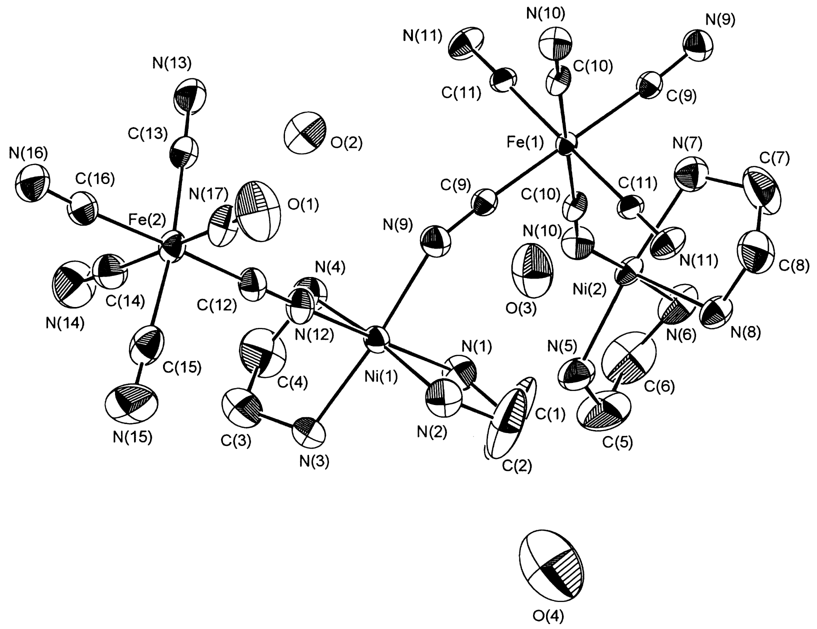

Fig. 2. ORTEP drawing of the asymmetric unit showing the 30% probability ellipsoids and the atomic labeling scheme.

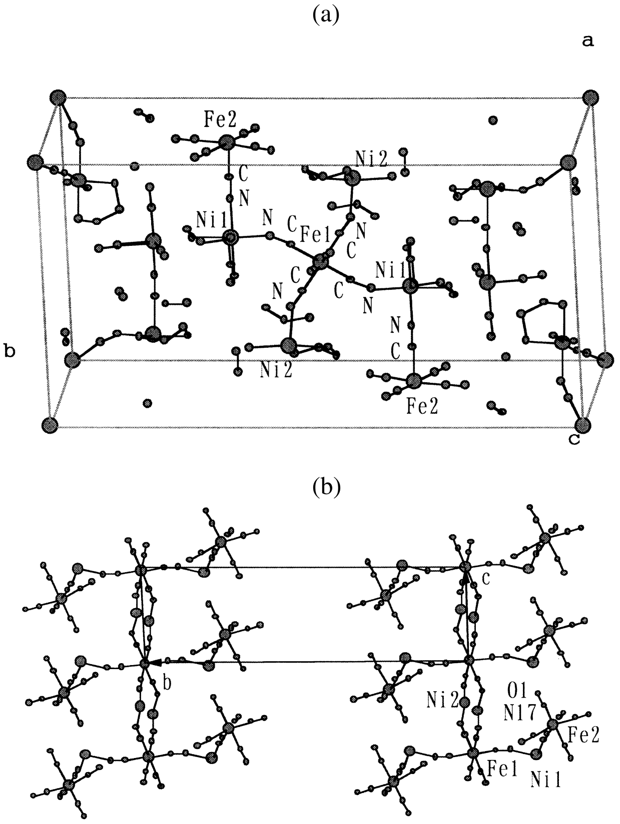

Fig. 3. (a) Unit cell of $[Ni(en)_2]_4[Fe(CN)_5NO]_2[Fe(CN)_6]\cdot 6H_2O$ (water molecules omitted). (b) A view of the crystal packing depicting the chain structure along the *c*-axis (omitted ethylenediammine molecules and water molecules).

wavenumber-side shift of ν(NO) is the result of the photo-induced MLCT, which transfers electrons into the anti-bond of the NO. The NO bond was weakened, and as a result the vibration was shifted to lower wavenumber. These spectral changes indicate that $[Fe(CN)_5NO]^{2-}$ keeps its photo-reactivity after being appended to the coordination polymer. The ratio of the metastable $[Fe(CN)_5NO]^{2-}$ moieties after irradiation was estimated to be 6% based on the change in the IR spectra. All of the changes induced by blue light irradiation can be recovered by red light irradiation.

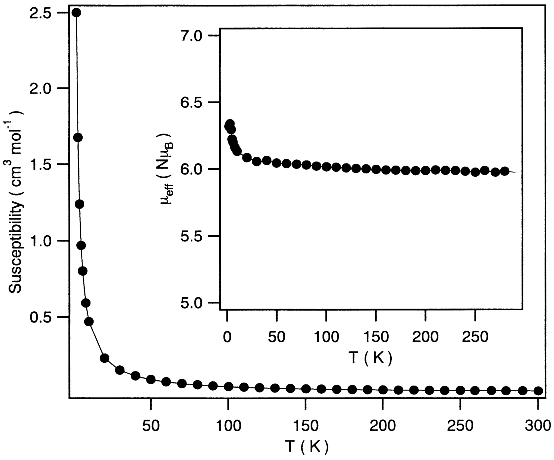

Fig. 4. Temperature dependent magnetization shows that the compound of $[Ni(en)_2]_4[Fe(CN)_5NO]_2[Fe(CN)_6]\cdot 6H_2O$ is paramagnetic from room temperature to 2 K. The inset shows the effective magnetic moment.

^{57}Fe Mössbauer spectra also support this assignment. Spectra were measured at 13 K and fitted with symmetric Lorentzian doublets by a least-squares fitting program. Figure 7a shows the Mössbauer spectrum before illumination. The spectrum consists of a single absorption peak (Isomer Shift: IS = 0.10 mm/s), indicating the presence of Fe^{II} (low spin), derived from $[Fe(CN)_6]^{4-}$, and a doublet absorption peak (IS = 0.37

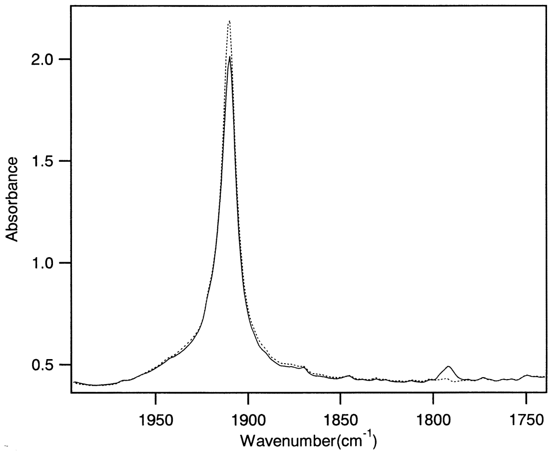

Fig. 5. IR spectra before and after irradiation at 14 K. The dotted line is the spectrum before irradiation and the solid line is that after irradiation.

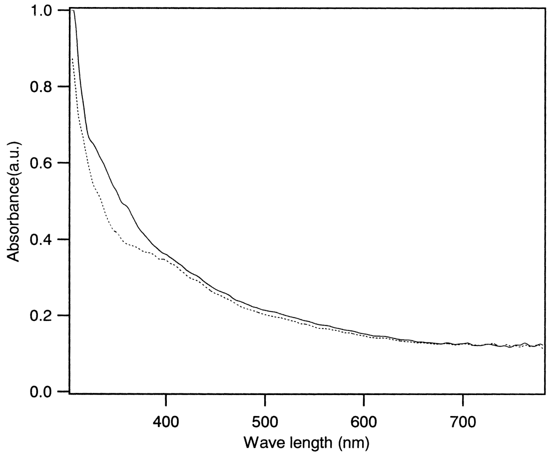

Fig. 6. UV-visible spectra before and after irradiation at 14 K. The dotted line is the spectrum before irradiation and the solid line is that after irradiation.

mm/s, Quadrupole Splitting: QS = 1.85 mm/s), indicating Fe^{II} (low spin) derived from $[Fe(CN)_5NO]^{2-}$. The large QS indicates the axially symmetric charge asymmetry of the 3d electrons in $[Fe(CN)_5NO]^{2-}$. After illumination, a doublet absorption peak with larger QS (IS = 0.35 mm/s, QS = 2.69 mm/s) appeared in the Mössbauer spectrum (Fig. 7b). The new doublet peak indicates the appearance of a metastable state $[Fe^{*}(CN)_5NO]^{2-}$, which is produced by the photo-induced MLCT reaction. The value of $QS^{*}/QS = 2.69/1.85 = 1.45$ that is found in this compound is consistent with the reported ratio of QS^{*} ($[Fe^{*}(CN)_5NO]^{2-}$)/QS ($[Fe(CN)_5NO]^{2-}$ found in mononuclear compounds,[22,23] indicating that the photo-induced metastable state of the $[Fe(CN)_5NO]^{2-}$ in the coordination polymer is comparable with its electrical states in the mononuclear compounds.

The photo-response of the present compound is different from the observation for nickel pentacyanonitrosylferrate. Although the ratio of metastable $[Fe(CN)_5NO]^{2-}$ moieties is larger than that in nickel pentacyanonitrosylferrate(II) (ratio of the metastable state is 1.7%), the magnetic properties of this compound do not change after irradiation. The reason for this dissimilarity should be ascribed to the difference between the positions of the pentacyanonitrosylferrate(II) in the two compounds. For pentacyanonitrosylferrate(II), photo-induced MLCT transfers an electron from Fe to NO, and induces spins in both the Fe and NO. As the magnetic interaction between the spins is anti-ferromagnetic, the magnetic properties of pentacyanonitrosylferrate(II) itself do not change after irradiation. However, if the pentacyanonitrosylferrate(II) acts as a linkage between the metal atoms, the electronic change to the iron in the pentacyanonitrosylferrate(II) can enhance the magnetic interactions between the neighboring coordinated metals and as a result change the magnetism. This is the case for nickel pentacyanonitrosylferrate(II), in which every pentacyanonitrosylferrate(II) is coordinated by five nickel atoms. The magnetic interaction between the nickel atoms is enhanced after irradiation, which changes the magnetism of the compound. For the compound reported in this paper, $[Fe(CN)_5NO]^{2-}$ is appended to a coordination polymer through one nickel atom (Fig. 3). It fails to act as a linkage between metal atoms to change the magnetic interaction.

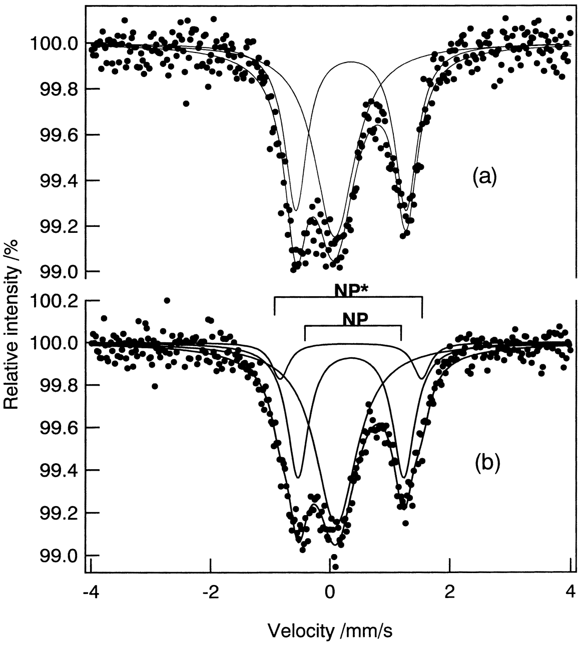

Fig. 7. ^{57}Fe Mössbauer spectra of $[Ni(en)_2]_4[Fe(CN)_5NO]_2[Fe(CN)_6]\cdot 6H_2O$ at 13 K (a) before and (b) after illumination.

Conclusion

We succeeded in the synthesis of a new coordination polymer that exhibits photo-reactivity by appending $[Ni(en)_2][Fe(CN)_5NO]$ to the magnetic main-chain formed by $[Ni(en)_2]^{2+}$ and $[Fe(CN)_6]^{4-}$. Just like its alkali salt, the electronic state of $[Fe(CN)_5NO]^{2-}$ in the side chain can be transferred from the ground state to the metastable state by irradiation with blue light and can be recovered by irradiation with red light. Experimental analysis also showed that only when pentacyanonitrosylferrate(II) acted as a linkage among spin sources could the magnetism of the compound be switched by its electronic change.

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