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Light-Induced Mixed-Valence State of $Fe^{II}[Fe(CN)_5NO]\cdot xH_2O$

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A long-living metastable state is produced in $Fe^{II}[Fe(CN)_5NO]\cdot xH_2O$ by an irradiation of 488 nm light at 200 K. A strong near-infrared band of about 10000 cm^{-1} and a $\nu(CN)$ band at 2070 cm^{-1} that newly appear in the metastable state point to development of the mixed-valence state analogous to Prussian blue. An iron-to-nitrosyl charge transfer in pentacyanonitrosylferrate(2−), $[Fe(CN)_5NO]^{2-}$, explains the formation of the mixed-valence state, because the charge transfer causes a pair of iron(II) and iron(III) atoms bridged by CN^- that has the same local structure as Prussian blue. In addition to the formation of the metastable state, the prolonged irradiation causes an irreversible change of $Fe^{II}[Fe(CN)_5NO]\cdot xH_2O$ and leads to the formation of a photoproduct. The photoproduct also has infrared spectra characteristic of the mixed-valence state. Mössbauer spectra of the photoproduct show that a low-spin iron ion in pentacyanonitrosylferrate(2−) is divalent and a high-spin iron outside of pentacyanonitrosylferrate(2−) is trivalent. Therefore, the charge-transfer between the two non-equivalent iron ions is thought to follow the intra-molecular charge transfer in pentacyanonitrosylferrate(2−).

The light-induced metastable states in sodium pentacyanonitrosylferrate (sodium nitroprusside, $Na_2[Fe(CN)_5NO]\cdot 2H_2O$, abbreviated as SNP, hereafter) and several nitrosyl complexes of ruthenium and osmium have become a subject attracting the interest of many researchers.[1—10] Upon irradiation of blue light at low temperature (< 100 K, typically), a long-living electronically excited molecule is produced in the crystal.[1] Because the blue light causes transitions in both directions between the ground state and the metastable state (long-living excited state), the crystal reaches a photo-stationary state under the continuing irradiation. The metastable state decays to the ground state reversibly by the temperature rise or the radiation of red region.[2] Temperatures at which the decay becomes notable vary depending on compounds in the range from 182 K (SNP) to 267 K (*trans*-$[Ru(H_2O)(en)_2NO]Cl_3$, en: ethylenediammine).[8,9] Because of a reversible color change in the population and depopulation of the metastable state, a potential use of the nitrosyl complexes for the information storage has been suggested.[2—4] Another interesting optical property has been found in the metastable state of the SNP single crystal; that is, polarization of the light traveling along the crystallographic *c*-axis is modified in a narrow wavelength range.[7,8]

Woike et al. studied some transition metal salts of pentacyanonitrosylferrate(2−), i.e. Mn, Co, Ni, Cu, Zn, Ag, Hg salts of pentacyanonitrosylferrate(2−), by means of the DSC measurements.[3] They observed exothermic peaks due to the relaxation of the metastable states at temperatures similar to that of SNP. We examined the light-induced changes of infrared spectra of $M^{II}[Fe(CN)_5NO]\cdot xH_2O$ (M = Fe,Co,Ni,Zn) and found that spectral changes are considerably different for the case of M = Fe from those for the others, in spite of their common crystal structure. Moreover, we noticed that the pale brown color of the powder of $Fe^{II}[Fe(CN)_5NO]\cdot xH_2O$ (abbreviated as FeNP, hereafter) gradually changes to bluish green when the sample is kept in the light at ambient temperature. These observations motivated us to start the present study. In this paper, we investigated light-induced changes of FeNP by means of infrared and Mössbauer spectroscopy.

Experimental

Pale brown powder of FeNP was precipitated by mixing aqueous solutions of sodium nitroprusside and iron(II) sulfate. Two types of crystal structures were obtained depending on the mixing conditions; one precipitated when the aqueous solutions of 40 °C were quickly mixed, and the other precipitated when those of 70 °C were stirred and mixed gradually. An X-ray diffraction pattern of the former was able to be indexed based on the face-centered cubic lattice and was similar to that of Prussian blue ($Fe_4[Fe(CN)_6]_3\cdot xH_2O$), whereas the latter was of the monoclinic form reported by Reguera et al.[11] We used the cubic form for the measurements below.

The water content in FeNP depends on its drying conditions. In the present case the *x* value of $Fe^{II}[Fe(CN)_5NO]\cdot xH_2O$ was typically determined to be 3.9 for an air-dried sample by thermogravimetric analysis.

Single crystals were grown by the gel method as follows: An agar gel including iron(II) sulfate was prepared; an aqueous solution

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of sodium nitroprusside was poured onto the gel and the mixture was kept in the dark for three days; the gel was dissolved in warm water and insoluble fine crystals were separated.

The crystals obtained are cubes having sides of ca. 150 μm length. Unexpectedly, their crystal structure is face-centered cubic and identical to that of quickly precipitated powder, judging from powder X-ray diffractometry. Polarizing microscopic observations show that the single crystal of FeNP is optically isotropic and exhibits brownish red color under the transmitting illumination. The color of FeNP is similar to that of SNP, even though it is considerably thicker.

The ^{15}NO analogue of FeNP was prepared from iron(II) sulfate and $Na_2[Fe(CN)_5{}^{15}NO]\cdot 2H_2O$ (^{15}N atom % in NO = 96) that was synthesized following a method in the literature.[12]

Spectroscopic measurements were carried out at various temperatures in the near-, mid-, and far-infrared region. FeNP powder was dispersed in a KBr pellet for the near- and mid-infrared region, and was dispersed in a polyethylene sheet for the far-infrared region. The sample was attached to the cold finger of a liquid nitrogen cryostat (Oxford Instruments, DN1754) equipped with CaF_2 windows. For measurements in the far-infrared region, two additional polyethylene windows were fitted on the cryostat. A sample was rotated by 45° with respect to the normal orientation so that both the far-infrared beam and the visible laser beam could pass through the sample. Spectrometers utilized were JASCO FT/IR-5300 for the mid-infrared region and Perkin–Elmer System 2000 for the near- and far-infrared region.

A 488.0 nm line from an Ar ion laser was utilized to produce the metastable state at several temperatures from 77 to 300 K.

As shown later, radiation causes an irreversible change of FeNP to some extent and produces a photoproduct.[13] To obtain enough of the photoproduct for use in powder X-ray diffraction and spectroscopic measurements, the procedures given below were followed: (1) Fine powder of FeNP was dispersed in a small amount of ethanol; this mixture was spread over a glass plate and dried. (2) The sample on a glass plate was exposed to white light from a desk lamp for 4 d. (3) The powder was scraped off and ground on an agate mill. (4) Steps from (1) to (3) were repeated six times. The powder, which is initially colored pale brown, darkens and results in a bluish green colored powder.

Mössbauer spectra were taken by using a Wissel constant-acceleration transducer coupled with an ORTEC 5500 multichannel analyzer. A ^{57}Co source in rhodium was purchased from The Radiochemical Center, Amersham, England. The spectra were obtained at 293 K and fitted to Lorentzian curves using an iterative least-squares computer program. The isomer shifts were referred to the symmetry center of the sextet of natural iron foil kept at 293 K.

Results and Discussion

1. Light-Induced Changes of Infrared Spectra. Metastable State. Near- and mid-infrared spectra before and after the 488 nm irradiation at 200 K are shown in Fig. 1. Before irradiation, vibrational bands of the crystal water (3655, 3420, and 1616 cm^{-1}), ν(CN) (2187 cm^{-1}), and ν(NO) (1972 cm^{-1}) are observed; by irradiation at 200 K, the following bands emerge: An intense and broad band at around 10000 cm^{-1} (called **A**-band, hereafter), a broad shoulder of ν(OH) (**B**-band), a multiplet at around 2070 cm^{-1} (**C**-band), and a band at 1794 cm^{-1} (**D**-band). In the far-infrared region, new bands appear at 500 and 250 cm^{-1}, as shown in Fig. 2. The spectrum of irradiated FeNP does not change if it is kept in the dark at 200 K. When temperature is raised to 300 K, the new bands lose intensities and the spectrum returns nearly to the original form. Thus, the state produced by irradiation is metastable. However, in

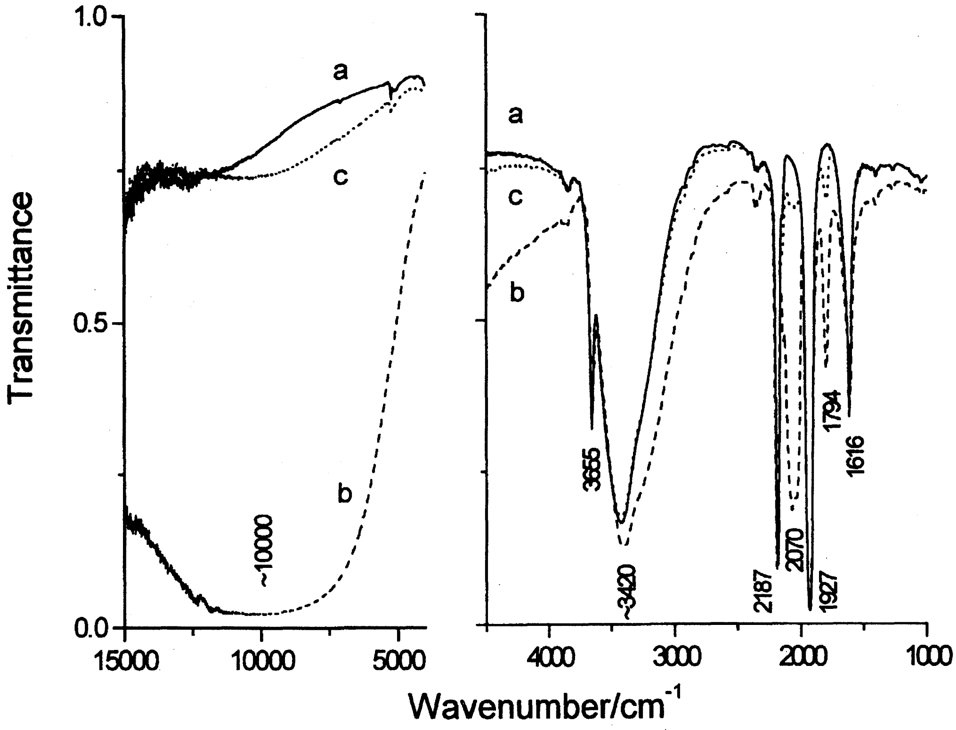

Fig. 1. Mid- and near-infrared spectra of $Fe[Fe(CN)_5NO]\cdot xH_2O$. a: before irradiation, b: immediately after 488 nm irradiation for 30 min, c: after being kept in the dark at 300 K for an hour.

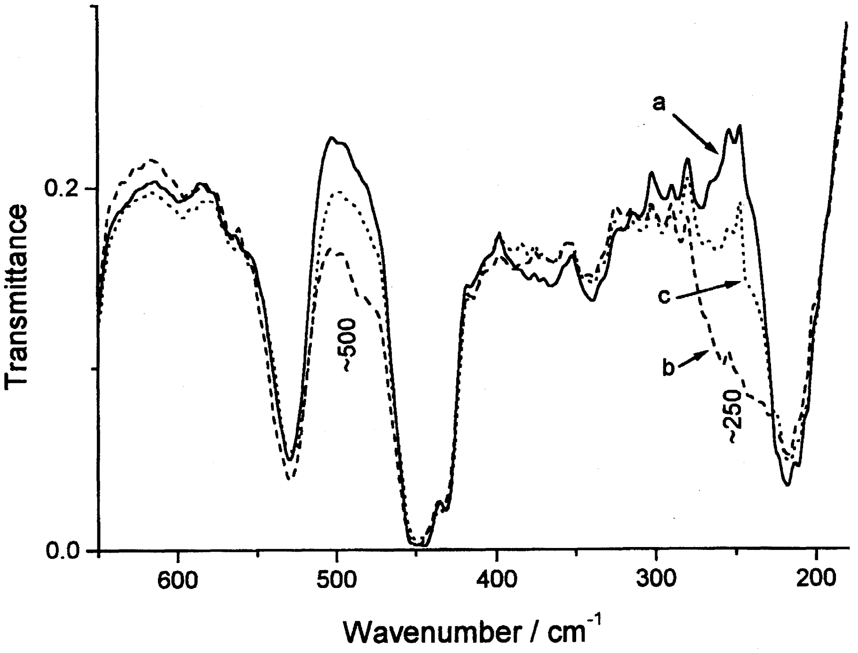

Fig. 2. Far-infrared spectra of Fe[Fe(CN)$_5$NO]$\cdot x$H$_2$O. a: before irradiation, b: immediately after 488 nm irradiation for 30 min, c: after being kept in the dark at 300 K for an hour.

contrast to SNP, the reversibility is not complete; namely, **A**—**D**-bands and bands at 500 and 250 cm^{-1} are observed weakly even at 300 K. These bands do not disappear a day later. Therefore, a small portion of the sample is considered to change irreversibly. The nature of the photoproduct caused by the prolonged irradiation will be discussed later.

The evolution of the metastable state bands under the irradiation at 200 K is shown in Fig. 3. The absorption above 4000 cm^{-1} is due to a tail of **A**-band. Intensities of the bands of the metastable state, **A**—**D**, increase with irradiation time, although a saturating tendency is revealed. The origin of **A**-band and **C**-band is discussed later in connection with spectra of the photoproduct and Prussian blue. **B**-band at 3090 cm^{-1} could be ascribed to ν(OH) of the hydrogen-bonded water. The frequency of ν(OH) is known to decrease as the hydrogen-bonding becomes stronger. Two absorption maxima of ν(OH), 3655 and 3420 cm^{-1} (see Fig. 1), in the ground state are assigned to weakly and moderately hydrogen-bonded OH groups, respectively. The remarkably lower frequency of the **B**-band suggests that a part of the crystal water participates in a strong hydrogen bonding in the metastable state.

Next, **D**-band is unambiguously assigned to ν(NO) of the metastable state, taking into account spectra of a ^{15}NO complex shown in Fig. 4. ν(OH) of FeNP before irradiation (1927 cm^{-1}) and **D**-band of irradiated FeNP (1794 cm^{-1}) shift to 1908 and 1769 cm^{-1}, respectively. Frequency ratios of the ^{15}N species to the normal species are 0.990 and 0.986 for the 1927 and the 1794 cm^{-1} bands, respectively. These values are comparable to the calculated value for a free NO molecule of 0.982. In the case of SNP, two metastable states, MS1 and MS2, are known to exist.[3)] In MS1 and MS2, the ν(NO) frequencies are observed at 1836 and 1655 cm^{-1}, respectively, whereas it is observed at 1949 cm^{-1} in the ground state.[5,8)] The down shift of ν(NO) observed in the metastable state of FeNP is close to that of MS1 of SNP. Thus, nitrosyl in the metastable state of FeNP is thought to be analogous to that in MS1 of SNP. A negative peak at 1927 cm^{-1} in Fig. 3 corresponds to the weakening of ν(NO) due to the depletion of the ground state.

The growth rate of **A**—**D**-bands depends on temperature even if the power of radiation is constant. It increases at lower temperatures in the region below ca. 250 K. This fact indicates that the metastable state formation requires not only radiation but also thermal activation, which is in contrast to the case of SNP.

Quite differently from SNP, the metastable state of FeNP is formed even at room temperature. This is due to the slow decay rate of the metastable state in comparison with that of SNP. In fact, the temperature at which the thermal decay becomes evident is about 250 K, which is notably higher than 180 K of SNP.[3,8)] Figure 5 shows changes of the mid-infrared spectrum caused by the irradiation at 300 K and following temporal changes. Although the irradiation at 300 K causes **C**- and **D**-bands, the situation is different from the irradiation at 200 K in the following two points: The reversibility is much poorer, indicating the photoproduct forms with higher efficiency; **C**- and **D**-bands lose intensity gradually after the irradiation, showing the decay of the metastable state. The former point suggests that both the radiation and thermal activation are necessary for the formation of the photoproduct. Concerning the latter point, the time dependence of the **D**-band intensity is not be represented by a single exponential decay function. This is in contrast to the case of SNP and suggests a complicated decay process of the metastable state.

Photoproduct. As mentioned above, the reversibility of the metastable state formation is not complete, but a little

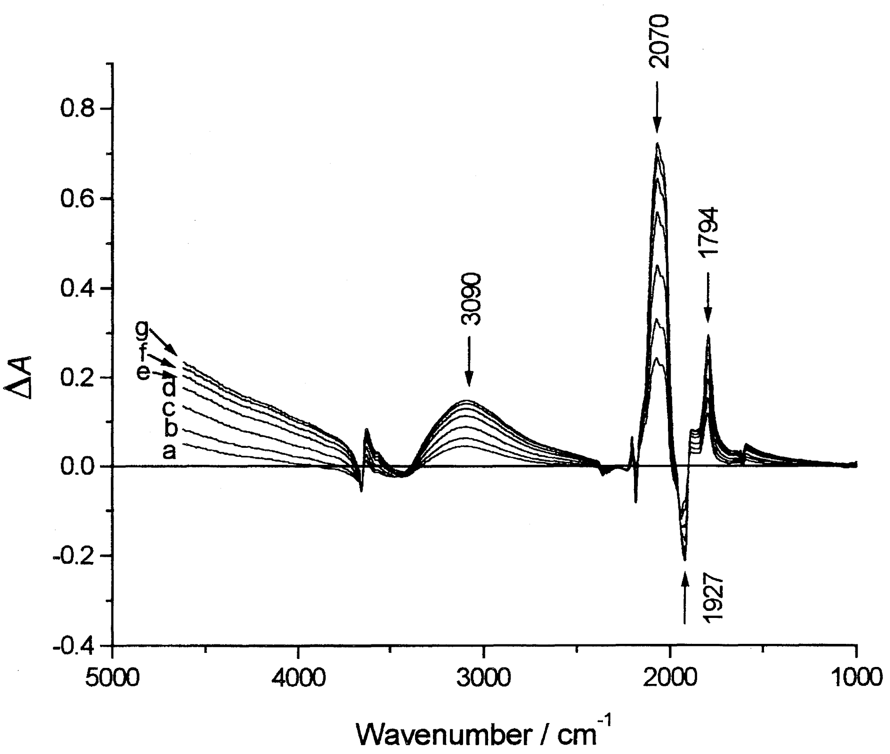

Fig. 3. Difference spectra as a function of time of 488 nm irradiation at 200 K. a: 0.25, b: 0.5, c: 1.0, d: 2.0, e: 3.0, f: 4.0, g: 5.0 h. The reference is the spectrum before irradiation.

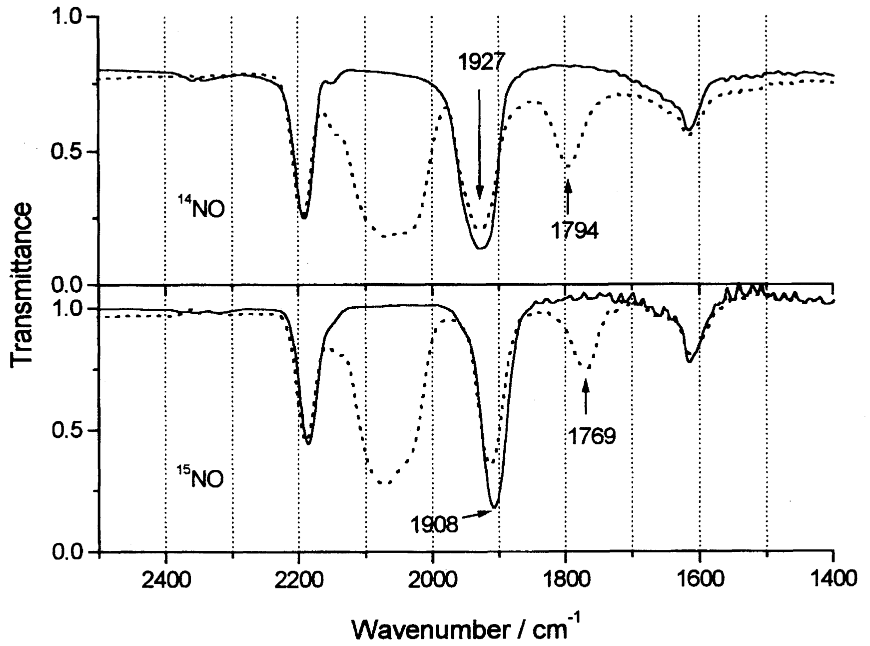

Fig. 4. Infrared spectra of $Fe[Fe(CN)_5{}^{14}NO]\cdot xH_2O$ (upper frame) and $Fe[Fe(CN)_5{}^{15}NO]\cdot xH_2O$ (lower frame) at 200 K. Solid lines are spectra before irradiation and dotted lines are spectra after three hours irradiation of 488 nm.

portion of the sample changes irreversibly. By irradiation with white light in ambient condition for a long time, we obtained a bluish green powder. Its powder X-ray diffraction is similar to those of original FeNP and Prussian blue, and it is indexed based on the face-centered cubic lattice. The lattice constant is 10.23 Å, which is shorter than 10.37 Å of original FeNP and longer than 10.16 Å of Prussian blue. The bluish green powder is crystallographically of a single phase, but it is a mixture of the original and the irreversibly changed molecular species, as will be shown by infrared and Mössbauer spectroscopy. In this section, we use the term "photoproduct" for the bluish green powder.[13)]

Near- and mid-infrared spectra of original FeNP, the metastable state, the photoproduct and Prussian-blue are shown in Fig. 6. The photoproduct, the metastable state, and Prussian blue have strong and broad near-infrared ab-

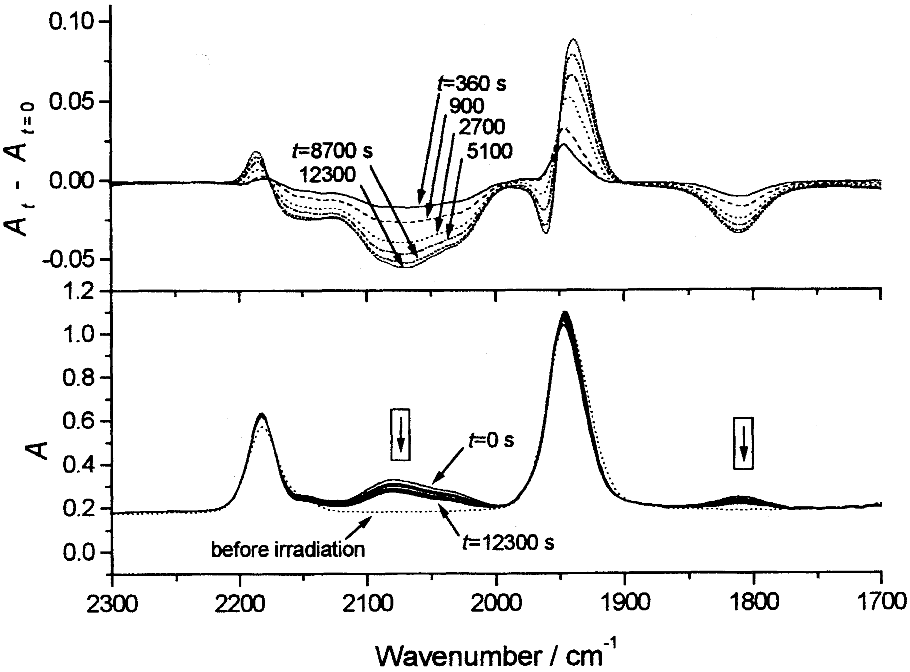

Fig. 5. Temporal change of the infrared spectra of $Fe[Fe(CN)_5NO]\cdot xH_2O$ irradiated at 300 K (lower frame). The time at which the irradiation was stopped corresponds to $t=0$. Difference spectra with a reference of a spectrum at $t=0$ are shown in the upper frame.

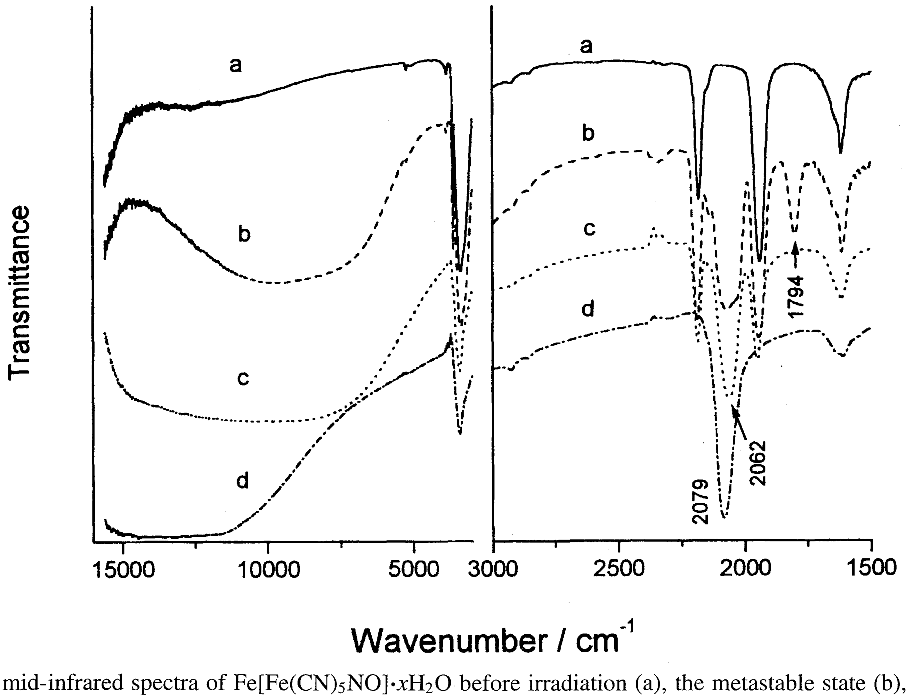

Fig. 6. Near- and mid-infrared spectra of $Fe[Fe(CN)_5NO]\cdot xH_2O$ before irradiation (a), the metastable state (b), the photoproduct (c), and Prussian blue (d). Measurements for the metastable state were done at 200 K, and the others were done at 300 K.

sorption bands. Judging from their positions, band widths, and intensities, **A**-bands of the metastable state and the analogous band of the photoproduct at ca. 10000 cm^{-1} are not vibrational bands, but should have the same origin as that of Prussian blue, though peak positions are somewhat lower than 14000 cm^{-1} in Prussian blue. Prussian blue is a well-known mixed-valence compound of the type ($-N\equiv C-Fe^{2+}-C\equiv N-Fe^{3+}-$) and exhibits a strong intervalence transition at around 14000 cm^{-1}.[14] The characteristic blue color of Prussian blue arises from this transition.

Another similarity between irradiated FeNP and Prussian blue is that they have a strong mid-infrared band at around 2070 cm^{-1}. A band at 2079 cm^{-1} of Prussian blue is assigned to ν(CN). Thus, **C**-band at 2070 cm^{-1} of the metastable state and a band at 2062 cm^{-1} of the photoproduct could be assigned to ν(CN) of the Prussian blue-like local structure. Under this assignment, there arises a question why the intensity of ν(CN) at 2187 cm^{-1} is not reduced upon irradiation (see Figs. 3 and 4). At present, we have no clear-cut explanation. Conversion from the normal CN group to the Prussian blue-like CN group might be too small to be detected, or the normal mode of the 2070 cm^{-1} band might be a different mode from that of 2187 cm^{-1} band, but an originally infrared inactive mode that becomes infrared active due to the reduction of the local symmetry. To make clear the problem, further studies including measurements of Raman spectra are necessary.

In the far-infrared region, as shown in Fig. 7, three bands of Prussian blue at 605, 502, and 241 cm^{-1} can be correlated to a band at 522 cm^{-1}, a doublet of 445 and 431 cm^{-1}, and a band at 213 cm^{-1} of FeNP, respectively. The higher frequencies in Prussian blue are consistent with the shorter lattice constant. Assuming that a broad band of about 516 cm^{-1} is an overlapping of the 522 cm^{-1} band and the 502 cm^{-1} band, the far-infrared spectrum of the photoproduct can be regarded as a superposition of those of original FeNP and Prussian blue. Thus, as well as in near- and mid-infrared spectra, the photoproduct is similar to Prussian blue in a far-infrared spectrum.

The 500 and 250 cm^{-1} bands of the metastable state may correspond to the 502 and 241 cm^{-1} bands of Prussian blue, respectively (see Fig. 2 and Fig. 7).

Differences between the metastable state and the photoproduct of FeNP are not clear. **D**-band of the metastable state is observed in the photoproduct, as shown in Figs. 1 and 5, but not observed in the photoproduct produced by 24 d irradiation, as shown in Fig. 6. This means that NO which causes **D**-band and is peculiar to the irradiated pentacyanonitrosylferrate(2−) ion disappears gradually. Further studies are needed to clarify what happens on the special nitrosyl ligand under the long-time exposure to light.

Although a few ambiguities remain, the observations described above indicate that the mixed-valence state develops in both the metastable state and the photoproduct of FeNP. Now, we focus our attention on the reason why the irradiation brings about Prussian blue-like features in the spectra of FeNP. FeNP has the same crystal structure as Prussian blue and contains the three-dimensional (–N≡C–Fe$_{NP}$–C≡N–Fe^{2+}–) linkage in the ground state, where Fe$_{NP}$ is the iron in a pentacyanonitrosylferrate(2−) ion. As to the electronic configuration of the pentacyanonitrosylferrate(2−) ion, an approximate expression of [Fe^{2+}(CN)$_5$NO^{+}]$^{2-}$ is widely accepted on the basis of the molecular orbital calculation.[15,16] Therefore, in FeNP, the mixed-valence state is not realized in spite of the similar atomic arrangement to Prussian blue. This is supported by the brownish red color of the gel-grown single crystal of FeNP. Upon irradiation with white light, the pentacyanonitrosylferrate(2−) ion will be excited by 400—500 nm spectral component and will be transformed to the metastable state in the same way as in SNP. Concerning the nature of the metastable state of SNP, Woike et al. proposed a model in which the metal-to-ligand (NO) charge transfer (MLCT) takes place and a π^*(NO) orbital is occupied in the metastable state.[2,3] Since the population of π^*(NO) orbital leads to the decrease of the bond order of the nitrogen-oxygen bond, the remarkable down shift of ν(NO) takes place in the metastable state. Returning to the problem of FeNP, based on the MLCT model, the oxidation state of iron in pentacyanonitrosylferrate(2−) is considered to be changed to 3+ by the irradiation. This change of the oxidation state will produce the (–Fe$_{NP}$$^{3+}$–C≡N–Fe^{2+}–) or (–Fe$_{NP}$$^{2+}$–C≡N–Fe^{3+}–) linkages, in which the mixed-valence state is realized. The latter configuration occurs if the charge-transfer between the iron ions bridged by CN$^-$ might follow the intra-molecular charge-transfer and is in the same electronic configuration as that of Prussian blue. To determine the actual electronic configuration in the photoproduct, Mössbauer spectroscopy was applied. The results obtained are described in the next section.

The nature of the metastable state of pentacyanonitrosylferrate(2−) is a controversial subject, and some models other than the MLCT model have been proposed.[10,17—19] Recently, Carducci et al. showed that X-ray diffraction study of SNP points to the nitrosyl-linkage isomer for the metastable state.[10] However, it should be noted that the linkage isomer and the MLCT models are not contradictory to each other. It might be possible that the rotation or flipping of the NO ligand corresponds to the structural relaxation that follows the charge transfer.

2. Mössbauer Spectroscopy of the Photoproduct. The ^{57}Fe Mössbauer spectra of FeNP and the photoproduct, the bluish green powder obtained by 24 d irradiation, are shown in Fig. 8 and the obtained Mössbauer parameters are summarized in Table 1. A quadrupole doublet G$_1$ and three pairs of quadrupole doublets G$_2$—G$_4$ are observed for FeNP before the irradiation (see Fig. 8a). One is assigned to the quadrupole doublet coming form the [Fe(CN)$_5$NO]$^{2-}$ moiety and the others are attributed to the quadrupole doublets originating from the high-spin iron(II) ion.[11,20] In the pho-

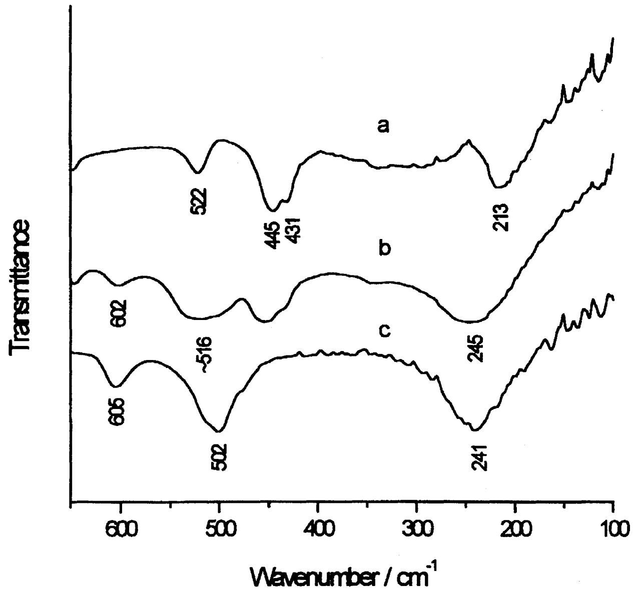

Fig. 7. Far-infrared spectra of Fe[Fe(CN)$_5$NO]·xH$_2$O before irradiation (a), the photoproduct (b), and Prussian blue (c) measured at 300 K.

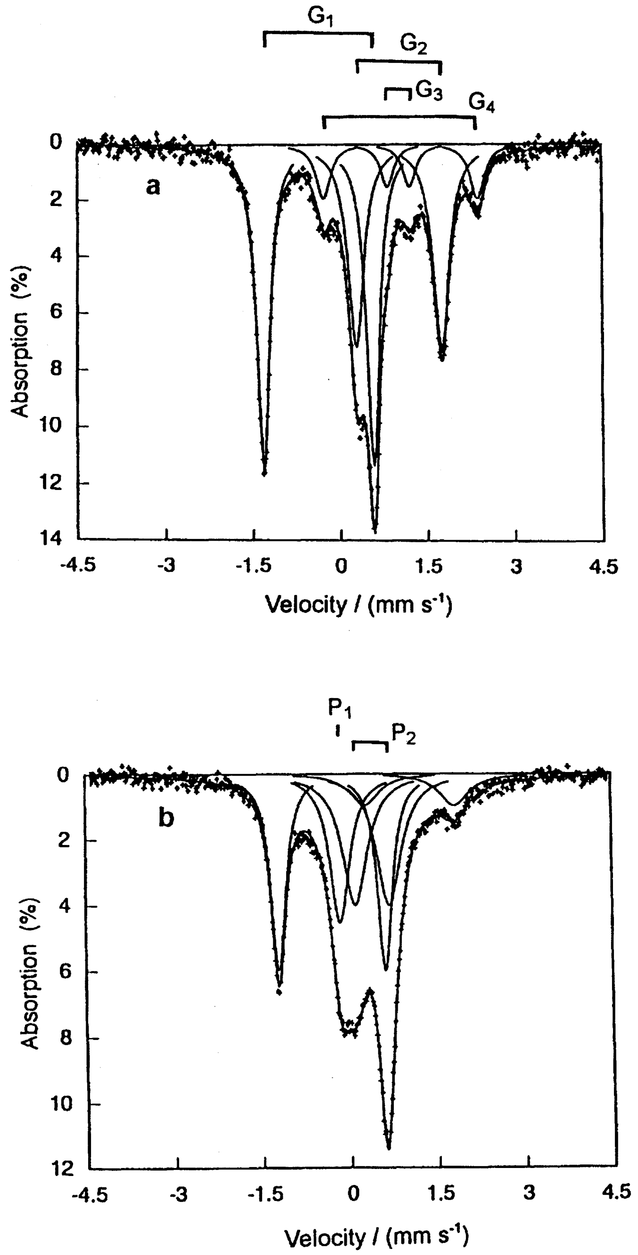

Fig. 8. Mössbauer spectra of $Fe[Fe(CN)_5NO]\cdot xH_2O$ before irradiation (a) and the photoproduct (b).

toproduct, an unresolved quadrupole P_1 and a quadrupole doublet P_2 newly appear besides the quadrupole doublets observed before the irradiation (see Fig. 8b). The new unresolved quadrupole doublet is assigned to the low-spin iron(II) ion, while the new quadrupole doublet is ascribed to the high-spin iron(III) ion. When calculated from the ratio of the absorption areas due to the low-spin iron, the conversion was about 36% in the photoproduct.

The Mössbauer parameters, i.e. isomer shift and quadrupole splitting of the new quadrupole doublet, are similar to those of the corresponding quadrupole doublet in Prussian blue.[21] The isomer shift of the new unresolved quadrupole doublet is also comparable to that of the $[Fe(CN)_6]^{4-}$ moiety in insoluble Prussian blue $Fe_4[Fe(CN)_6]_3\cdot xH_2O$.[22] Therefore, the linkage of $(-N{\equiv}C{-}Fe_{NP}{}^{2+}{-}C{\equiv}N{-}Fe^{3+}-)$ explains the Mössbauer spectrum of the photoproduct. As discussed in the previous section, it is supposed that the photo-excitation gives rise to the intra-molecular MLCT and the $(-N{\equiv}C{-}Fe_{NP}{}^{3+}{-}C{\equiv}N{-}Fe^{2+}-)$ mixed-valence network results by analogy with SNP. The Mössbauer data show that the charge-transfer between iron ions follows the intra-molecular MLCT.

Table 1. Mössbauer Parameters of $Fe[Fe(CN)_5NO]\cdot xH_2O$ before Irradiation and the Photoproduct at 293 K

Assignment		$\delta/(\mathrm{mm\,s^{-1}})$	$\Delta E_Q/(\mathrm{mm\,s^{-1}})$
Before irradiation			
$[Fe(CN)_5NO]^{2-}$ (low-spin)	G_1	−0.28	1.90
	G_2	1.11	1.49
Fe^{2+} (high-spin)	G_3	1.12	0.38
	G_4	1.15	2.65
Photoproduct			
$[Fe(CN)_5NO]^{3-}$ (low-spin)	P_1	−0.14	—
Fe^{3+} (high-spin)	P_2	0.42	0.59

Concluding Remarks

The mixed-valence state cannot be formed even though the crystal structure of FeNP is the same as that of Prussian blue, because the oxidation state of iron in $[Fe(CN)_5NO]^{2-}$ is Fe(II). This fact is evidenced by the brownish red color of the FeNP single crystal, which is similar to that of SNP, but quite different from that of Prussian blue. In the light-induced metastable state of the $[Fe(CN)_5NO]^{2-}$ ion, a charge transfer from iron to nitrosyl takes place and the mixed-valence state develops.

A prolonged irradiation causes the irreversible change of FeNP with aid of the thermal activation. Infrared spectra of the photoproduct prepared at ambient temperature are quite similar to those of Prussian blue in near-, mid-, and far-infrared region. Mössbauer spectra of the photoproduct indicate that the low-spin iron ion in pentacyanonitrosylferrate(2−) is divalent and that the high-spin iron ion outside of the pentacyanonitrosylferrate(2−) ion is trivalent. Thus, the linkage of $(-N{\equiv}C{-}Fe_{NP}{}^{2+}{-}C{\equiv}N{-}Fe^{3+}-)$ is qualified for the photoproduct.

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13) In this paper, we use the term "photoproduct" in two different meanings, namely, a *molecular species* that is changed irreversibly by light in a FeNP crystal, and a FeNP *crystal* which is densely populated by the irreversibly changed molecular species.

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