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Bonding Nature of Coordination Polymers, $M^{II}[Fe(CN)_5NO]\cdot 2H_2O$

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Coordination polymers of the type $M^{II}[Fe(CN)_5NO]\cdot 2H_2O$ (M^{II} = Mn, Fe, Co, Ni, Cu or Zn), except for $Mn[Fe(CN)_5NO]\cdot 2H_2O$, have a typical structure of Prussian blue analogs. The lattice constants decrease with the increase of the crystal field stabilization energy of M^{II} in the octahedral weak field. In the infrared spectra C≡N stretching bands are shifted to the higher frequency side compared with those of the parent compound $Na_2[Fe(CN)_5NO]\cdot 2H_2O$, whereas Fe-N and N=O stretching bands and Fe-NO bending band are observed at about the same position. This phenomenon could be explained in terms of the linkage structure $Fe\text{-}C\equiv N\text{-}M^{II}$. Magnetic susceptibility data and electronic spectra indicate that $M^{II}[Fe(CN)_5NO]\cdot 2H_2O$ consists of the high spin M^{II} coordinated by the nitrogen ends of cyanide ligands and the low spin Fe^{II} coordinated by the carbon ends of cyanide ligands and the nitrogen end of nitrosyl ligand.

Introduction

There has been considerable interest in Prussian blue and a variety of related compounds which are called "coordination polymers". Most of them contain cyanide ligands as a bridged group.[1] Among these compounds are a series of coordination polymers of the type $M^{II}[Fe(CN)_5NO]\cdot 2H_2O$ which are obtained by the reaction of pentacyanonitrosylferrate(II) ion with the first row transition metal ion M^{II}, where M^{II} is Mn, Fe, Co, Ni, Cu or Zn. There had been no reports on the property of $M^{II}[Fe(CN)_5NO]\cdot 2H_2O$ in the literature until that Cambi and Clerici[2] reported on that of anhydrous $M^{II}[Fe(CN)_5NO]$, though many investigations had been accumulated both on the hexacyanometalates of the first row transition metals and on alkali pentacyanonitrosylferrates(II). About 12 years ago the property of $M^{II}[Fe(CN)_5NO]\cdot 2.5H_2O$ (M^{II} = Fe, Co or Ni) was studied by Salvadeo[3] and it was shown that these three compounds belong to Prussian blue analogs. The chemical composition of $M^{II}[Fe(CN)_5NO]\cdot 2H_2O$ ($Cu[Fe(CN)_5NO]$, in the case of M^{II} = Cu) was confirmed by the potentiometric and thermometric titration.[4] The effect of pressure on the bonding in anhydrous $M^{II}[Fe(CN)_5NO]$ (M^{II} = Fe, Cu and Zn) was studied using Mössbauer resonance.[5] Furthermore, while this work was in progress there appeared two papers, one of which reported the Mössbauer and infrared spectra of $M^{II}[Fe(CN)_5NO]\cdot \chi H_2O$[6] and the other of which dealt with the infrared spectra of $Co_3[Fe(CN)_5CO]_2\cdot 5.7H_2O$.[7] In spite of these recent extensive studies there have been relatively few systematic ones on the electronic spctra of $M^{II}[Fe(CN)_5NO]\cdot 2H_2O$.

It is the purpose of the present work to describe collectively the structure and bonding nature of $M^{II}[Fe(CN)_5NO]\cdot 2H_2O$ on the basis of X-ray powder pattern, magnetic susceptibility, infrared and electronic spectra.

Experimental Section

The compounds of the type$M^{II}[Fe(CN)_5NO]\cdot 2H_2O$ were synthesized by the following method: A 0.05*M* solution of the divalent transition metal salt (chloride or sulfate) was added in slightly excess to a 0.05*M* solution of commercially available $Na_2[Fe(CN)_5NO]\cdot 2H_2O$. The pH of the solution was adjusted in order to prevent metal ion M^{II} from forming hydroxide. The precipitates obtained were left overnight for aging, collected by filtration or centrifugation, washed with distilled water till chloride or sulfate ions could not be detected in the filtrate, finally washed with 95% ethanol, and dried over calcium chloride to constant weight. The products were analyzed by the usual method and the results were as follows: Found: Fe, 18.3; Mn, 18.0; H_2O, 10.6%. Calcd for $Mn[Fe(CN)_5NO]\cdot 2H_2O$: Fe, 18.14; Mn, 17.89; H_2O, 11.74%. Found: Fe, 35.8; H_2O, 13.1%. Calcd for $Fe[Fe(CN)_5NO]\cdot 2H_2O$: 36.29; H_2O, 11.70%. Found: Fe, 17.4; Co, 19.7; H_2O; 16.9%. Calcd for $Co[Fe(CN)_5NO]\cdot 2H_2O$: Fe, 17.96; Co, 18.96; H_2O, 16.90%. Found: Fe, 17.4; Ni, 17.5; H_2O, 17.1%. Calcd for $Ni[Fe(CN)_5NO]\cdot 2H_2O$: Fe, 17.89; Ni, 18.09; H_2O, 11.50%. Found: Fe, 17.6; Cu, 20.2%. Calcd for $Cu[Fe(CN)_5NO]$: Fe, 17.71; Cu, 20.14%. Found: Fe, 16.5; Zn, 19.9; H_2O, 14.6%. Calcd for $Zn[Fe(CN)_5NO]\cdot 2H_2O$: Fe, 17.60; Zn, 20.60; H_2O, 11.36%.

The X-ray powder diffraction patterns were record-

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ed with a Rigaku-Denki X-ray diffractometer. The lattice constants were determined using Fe $K\alpha$ radiation 1.937 Å, and sodium chloride as an internal standard. The infrared spectra were measured in the range 350 to 4000 cm^{-1} by the KBr disk method using the Hitachi EPI-2 infrared spectrophotometer equipped with the KBr and NaCl prisms. The wavenumbers recorded here were calibrated with a polystyrene film and believed accurate to 3.5 cm^{-1} in the NaCl region and 4.0 cm^{-1} in the KBr region respectively. The diffuse reflection spectra were measured with the Hitachi Perkin-Elmer 139 UV-VIS spectrophotometer equipped with the standard integrating sphere attachment using alumina as a standard. The Kubelka-Munk function[8] was calculated from the reflectance data and plotted against wavenumbers. The mull transmittance spectra were obtained by the method described in the literatures using mull suspension in liquid paraffin.[9] The magnetic susceptibilities were measured by the Gouy method with $Hg[Co(NCS)_4]$ (16.44×10^{-6} cgs units at 20.0°C)[10] as a standard at room temperature. The diamagnetic corrections were calculated with the Pascal constants.[11]

Results and Discussion

Structure. The X-ray diffraction powder patterns have indicated that the compounds of the type $M^{II}[Fe(CN)_5NO]\cdot2H_2O$, except for M^{II} = Mn and Cu, have the face-centered cubic unit cell characteristic of Prussian blue analogs.[3,12] However, the crystals are not isomorphous with Prussian blue analogs in an exact sense, since $M^{II}[Fe(CN)_5NO]\cdot2H_2O$ contains the nitroprusside ion $Fe(CN)_5NO^{2-}$ which has C_{4v} symmetry, whereas Prussian blue analogs contain the ion $M(CN)_6{}^{n-}$ which has O_h symmetry. In the three-dimensional framework of $M^{II}[Fe(CN)_5NO]\cdot2H_2O$ the principal axis C_4 of the nitroprusside ion, which coincides with Fe-N-O axis, does not orientate in any specified direction. The ligand NO^+ occupies statistically one-sixth of the 24e positions in space group $F_{m3\bar{m}}-O_h$ at random fashion. The residual five-sixths of the 24e positions are occupied by the cyanide ligands which coordinate to iron atom through the carbon end. Water molecules are reversively removed on heating without changing the framework. The thermogravimetric analysis revealed that the compounds $M^{II}[Fe(CN)_5NO]\cdot2H_2O$ loss their water molecules around 100°C, regardless of the kind of metal ion M^{II}. Accordingly, the water molecules do not coordinate to the metal ions in the crystal but merely serve to fill the empty space of the lattice. This is supported also by the fact that any M^{II}-O stretching vibrations cannot be observed in the far infrared region.

The crystal structure of $Mn[Fe(CN)_5NO]\cdot2H_2O$ is so complicated that its space group has not been determined as yet. This exceptional structure seems to arise from the following two reasons. One is that the ionic radius of M^{II} is unusually large compared with those of other metal ions of this series and hence the packing in the crystal lattice is unfavourable to the cubic one. This point of view is consistent with the result that the corresponding cadmium compound $Cd[Fe(CN)_5NO]\cdot2H_2O$ does not have a cubic lattice because the ionic radius of Cd^{II} is larger than those of the divalent first row transition metal ion.[13] The other is that the crystal field stabilization energy of Mn^{II} ion is zero in the weak crystal field because of its half filled $3d^5$ electronic configuration (where the crystal field stabilization energy is abbreviated as c. f. s. e.). The c. f. s. e., in fact, plays an important role in the crystal formation of Prussian blue analogs. A good evidence for this is furnished by the fact that the lattice constant of $M^{II}[Fe(CN)_5NO]\cdot2H_2O$ listed in Table I decreases in the order Zn > Fe > Co > Ni as the c. f. s. c. of M^{II} in the octahedral weak field increases in the order Zn(0Dq) < Fe(4Dq) < Co(6Dq) < Ni(12Dq). This phenomenon has been observed in other Prussian blue analogs, for example, in a series of compounds of the type $KM^{II}[Co(CN)_6]$, where M^{II} is Mn, Fe, Co, Ni, Cu or Zn.[14] The crystal lattice of $Cu[Fe(CN)_5NO]$ is distorted from the face-centered cubic lattice to form a tetragonal lattice (a = 10.35 Å, c = 9.80 Å). Density measurements have substansiated this point of view, that is, the density 1.78 g/cm^3 calculated for formula units per cell was in good agreement with the experimental value 1.75 g/cm^3.

Table I. Lattice constants and atomic distances.

Compound	Lattice constant (Å)	Atomic distance (Å) M-N	Atomic distance (Å) M-O
$Fe[Fe(CN)_5NO]\cdot2H_2O$	10.35±0.01	2.12	2.42
$Co[Fe(CN)_5NO]\cdot2H_2O$	10.28±0.01	2.08	2.38
$Ni[Fe(CN)_5NO]\cdot2H_2O$	10.22±0.02	2.05	2.35
$Cu[Fe(CN)_5NO]\cdot2H_2O$	a=b=10.35	2.12	2.42
	c=9.80	1.84	2.12
$Zn[Fe(CN)_5NO]\cdot2H_2O$	10.36±0.03	2.12	2.42

The X-ray powder diffraction study was insufficient to obtain the correct atomic distances of $M^{II}[Fe(CN)_5NO]\cdot2H_2O$ containing such lighter atoms as hydrogen, carbon, nitrogen and oxygen. Accordingly, it was assumed that the atomic distances: Fe—C, 1.90 Å; Fe—N, 1.63 Å; C—N, 1.16 Å; N—O, 1.13 Å, which were obtained from the X-ray diffraction analysis of the single crystal $Na_2[Fe(CN)_5NO]\cdot2H_2O$ by Manoharan and Hamilton,[15] hold also in the compounds of the type $M^{II}[Fe(CN)_5NO]\cdot2H_2O$. This assumption makes it possible for us to estimate the atomic distances M—N and M—O in $M^{II}[Fe(CN)_5NO]\cdot2H_2O$ from the lattice constants. The calculated values are listed in Table I. From this estima-

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tion it has appeared that relatively strong coordination bonding exists between M^{II}—N while the atomic distance M^{II}—O is not so short as to expect strong interaction between them.

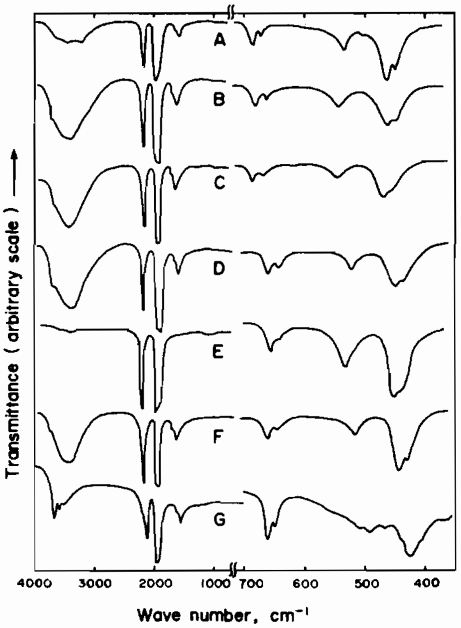

Figure 1. Infrared spectra of $M^{II}[Fe(CN)_5NO] \cdot 2H_2O$. A, $Mn[Fe(CN)_5NO] \cdot 2H_2O$; B, $Fe[Fe(CN)_5NO] \cdot 2H_2O$; C, $Co[Fe(CN)_5NO] \cdot 2H_2O$; D, $Ni[Fe(CN)_5NO] \cdot 2H_2O$; E, $Cu[Fe(CN)_5NO]$; F, $Zn[Fe(CN)_5NO] \cdot 2H_2O$; G, $Na_2[Fe(CN)_5NO] \cdot 2H_2O$.

Infrared Spectra. The infrared spectra of $M^{II}[Fe(CN)_5NO] \cdot 2H_2O$ are reproduced in Figure 1, where the spectral pattern of $Na_2[Fe(CN)_5NO] \cdot 2H_2O$ is also shown for comparison. Three fundamental modes of the free water molecules were observed at ~3400 cm^{-1} (symmetric), ~1620 cm^{-1} (bending) and ~3670 cm^{-1} (antisymmetric), respectively. However, the wagging, rocking, twisting and metal-oxygen stretching modes characteristic of coordinated water, which Nakagawa and Shimanouchi[16] have studied in detail in terms of the normal coordinate analysis, have not been observed in the far infrared region. This indicates that the water molecules in $M^{II}[(CN)_5NO] \cdot 2H_2O$ do not coordinate to the metal ion but are included as water of hydration. This point of view is compatible with the results of the thermogravimetric analysis.

In the C≡N stretching region several C≡N stretching bands are expected for $M^{II}[(CN)_5NO] \cdot 2H_2O$ containing the ion unit $Fe(CN)_5NO^{2-}$ which has approximately C_{4v} symmetry. However, the C≡N stretching vibration was, in reality, observed as a single broad band in the range 2161 to 2180 cm^{-1}. On the other hand, sodium pentacyanonitrosylferrate(II) exhibits four bands at 2173, 2162, 2157, and 2143 cm^{-1}, which Khanna *et al.*[17] have assigned to ν_1 CN(axial); ν_2 CN(radial) (A_1), ν_{10} CN(radial) (B_1) and ν_{16} CN(radial) (E), respectively. Bearing in mind that ν_{10} CN(radial) (B_1) of $Na_2[Fe(CN)_5NO] \cdot 2H_2O$ becomes infrared active owing to the site symmetry of the symmetry of the crystal, the broad C≡N stretching band of $M^{II}[Fe(CN)_5NO] \cdot 2H_2O$ is assigned to the modes of the A_1 and E species because the crystal of $M^{II}[Fe(CN)_5NO] \cdot 2H_2O$ belongs approximately to the space group O_h^5—F_{m3m}. The C≡N stretching bands of $M^{II}[Fe(CN)_5NO] \cdot 2H_2O$ are shifted to the higher frequency side by 6~25 cm^{-1} as compared with the frequency, 2155 cm^{-1}, which is weighted according to the degeneracy of ν_1, ν_2 and ν_{16} vibrations of $Na_2[Fe(CN)_5NO] \cdot 2H_2O$. Though the magnitude of the shift is not so large as that of other Prussian blue analogs, this shift is evidence for the existence of the linkage structure Fe-C≡N-M^{II}.[18]

The N=O stretching bands of $M^{II}[Fe(CN)_5NO] \cdot 2H_2O$ were observed at about the same frequency as that of $Na_2[Fe(CN)_5NO] \cdot 2H_2O$ (1947 cm^{-1}). Furthermore, the Fe-N stretching and Fe-NO bending bands, which were observed at 650 and 662 cm^{-1} respectively, were quite similar in shape and position with those of $Na_2[Fe(CN)_5NO] \cdot 2H_2O$. The Fe-N and N-O stretching and Fe-NO bending vibrations are almost independent of the formation of the coordination polymer $M^{II}[Fe(CN)_5NO] \cdot 2H_2O$. It follows that changes in Fe-N and N-O bond orders accompanied by the formation of the linkage structure are not so large as observed on bridge adduct $Na_2[Fe(CNBF_3)_5NO]$ by Shriver and Posner.[19] On the contrary, the Fe-C stretching and Fe-CN bending vibrations are strongly influenced by the formation of the coordination polymers. The spectra in the range from 400 to 550 cm^{-1}, where a variety of Fe-C stretching and Fe-CN bending vibrations are expected, are much simpler than that of $Na_2[Fe(CN)_5NO] \cdot 2H_2O$. This simplicity of the spectra is ascribed to the linkage structure Fe-C≡N-M^{II}. In general, the Fe-CN bending vibrations of hexacyanometalate complexes are observed at higher frequency than the Fe-C stretching one.[20] Accordingly, two strong absorption bands between 430-450 cm^{-1}, one of which is shoulder, are assigned to the Fe-C stretching and a higher weak band around 550 cm^{-1} is assigned to the Fe-CN bending vibration. These assignments are rather tentative because we cannot definitely distinguish the Fe-C stretching mode from the Fe-CN bending one.

Electronic spectra. The diffuse reflection and mull transmittance spectra are illustrated in Figure 2. A variety of absorption bands assigned to the *d-d* transition of M^{II} are observed in the visible region. These *d-d* bands are so similar in position to those of the corresponding aquo complex of M^{II} that they are expected to be assigned in terms of the weak-ligand field theory. This is supported by the magnetic moment data (Table III), that is, the effective Bohr magneton calculated per M^{II} of $M^{II}[Fe(CN)_5NO] \cdot 2H_2O$ is in good agreement with the assumption that M^{II} coordinated by the nitrogen ends of cyanide lig-

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Table II. Infrared spectra of $M^{II}[Fe(CN)_5NO] \cdot 2H_2O$ (cm^{-1}).

Compound	CN str.	NO str.	Fe-NO bend.	Fe-N str.	Fe-CN bend.	Fe-C str.
$Mn[Fe(CN)_5NO] \cdot 2H_2O$	2161	1948	659	645	509	537, 426
$Fe[Fe(CN)_5NO] \cdot 2H_2O$	2167	1945	658	640	520	441, 429
$Co[Fe(CN)_5NO] \cdot 2H_2O$	2180	1947	660	642	517	443, 430
$Ni[Fe(CN)_5NO] \cdot 2H_2O$	2179	1950	658	641	521	445, 434
$Cu[Fe(CN)_5NO]$	2180	1957	658	636	533	447, 437
$Zn[Fe(CN)_5NO] \cdot 2H_2O$	2169	1958	659	642	515	440, 429

Table III. Magnetic moments and electronic spectra of M^{II}-$[Fe(CN)_5NO] \cdot 2H_2O$.

Compound	μ_{eff} (B.M.)	Band position	(kK) Assignment
$Mn[Fe(CN)_5NO] \cdot 2H_2O$	6.00	20.5	$^1A_1 \rightarrow {}^1E$
		24.4	$\rightarrow {}^1A_1$
		29.0	$\rightarrow {}^1A_2$
		34.9	$\rightarrow {}^1E$
		40.5	$\rightarrow {}^1E$
$Fe[Fe(CN)_5NO] \cdot 2H_2O$	5.03	11.0	$^5T_{2g} \rightarrow {}^5E_g$
		22.7	$^1A_1 \rightarrow {}^1E$
		27.8	$\rightarrow {}^1A_1$
		29.8	$\rightarrow {}^1A_2$
		34.6	$\rightarrow {}^1E$
		40.1	$\rightarrow {}^1E$
$Co[Fe(CN)_5NO] \cdot 2H_2O$	4.47	16.0	$^4T_{1g} \rightarrow {}^4A_{2g}$
		20.2	$\rightarrow {}^4T_{1g}(P)$
		21.0	$^1A_1 \rightarrow {}^1E$
		25.0	$\rightarrow {}^1A_1$
		29.7	$\rightarrow {}^1A_2$
		34.6	$\rightarrow {}^1E$
		40.2	$\rightarrow {}^1E$
$Ni[Fe(CN)_5NO] \cdot 2H_2O$	2.67	14.3	$^3A_{2g} \rightarrow {}^3T_{1g}(F)$
		17.5	$\rightarrow {}^1E_g$
		27.2	$\rightarrow {}^3T_{1g}(P)$
		20.4	$^1A_1 \rightarrow {}^1E$
		25.1	$\rightarrow {}^1A_1$
		29.5	$\rightarrow {}^1A_2$
		34.7	$\rightarrow {}^1E$
		40.0	$\rightarrow {}^1E$
$Cu[Fe(CN)_5NO]$	1.88	15.3	$^2E_g \rightarrow {}^2T_{2g}$
		16.5	
		23.1	$^1A_1 \rightarrow {}^1E$
		25.6	$\rightarrow {}^1A_1$
		30.0	$\rightarrow {}^1A_2$
		34.6	$\rightarrow {}^1E$
		40.0	$\rightarrow {}^1E$
$Zn[Fe(CN)_5NO] \cdot 2H_2O$	diamagnetic	21.0	$^1A_1 \rightarrow {}^1E$
		25.2	$\rightarrow {}^1A_1$
		29.5	$\rightarrow {}^1A_2$
		34.5	$\rightarrow {}^1E$
		40.0	$\rightarrow {}^1E$

ands and the oxygen end of nitrosyl ligand is in the high spin state and Fe^{II} of nitroprusside ion is in the low spin state. On the basis of these facts the d-d bands of M^{II} in $M^{II}[Fe(CN)_5NO] \cdot 2H_2O$ were assigned and the results are summarized in Table III. The ligand field splitting parameter 10Dq calculated from the position of the d-d bands ranges 7.9 to 15.9 kK. These values are comparable with 10Dq = 9.5-10.1 kK reported on $KNi[Co(CN)_6]$ by Shirver *et al.*[21] As for anhydrous $Cu[Fe(CN)_5NO]$ the absorption band assigend to the transition $^2E_g \rightarrow {}^2T_{2g}$ in the octahedral field is split into two peaks. As pointed out in the preceding section of the structure, this is

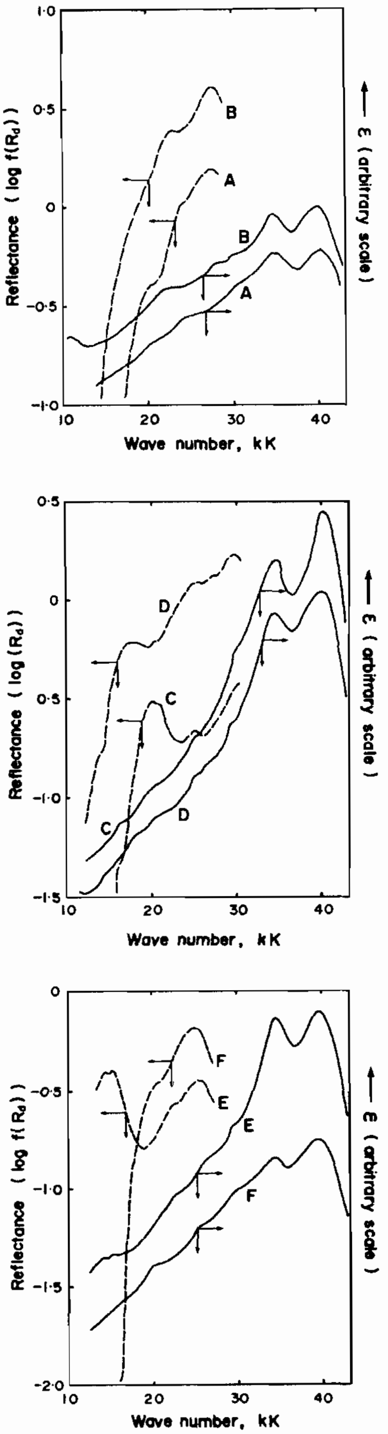

Figure 2. Electronic spectra of $M^{II}[Fe(CN)_5NO] \cdot 2H_2O$. A, $Mn[Fe(CN)_5NO] \cdot 2H_2O$; B, $Fe[Fe(CN)_5NO] \cdot 2H_2O$; C, $Co[Fe(CN)_5NO] \cdot 2H_2O$; D, $Ni[Fe(CN)_5NO] \cdot 2H_2O$; E, $Cu[Fe(CN)_5NO]$; F, $Zn[Fe(CN)_5NO] \cdot 2H_2O$.

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due to the distortion from the octahedral symmetry and Cu^{II} must be situated in a compressed octahedral environment as judged by the fact that the lattice constants a and b are larger than c. Such a compressed form is only rarely found, but an example is provided by the structure of a Hoffman-type clathrate.[22]

On the other hand, several absorption bands which are attributable to the transition within the nitroprusside ion, a constitutional unit of $M^{II}[Fe(CN)_5NO] \cdot 2H_2O$, were observed in the visible and ultraviolet regions. Each absorption band is successfully assigned on the basis of the results of the MO calculation carried out with $Na_2[Fe(CN)_5NO] \cdot 2H_2O$ by Manoharan and Gray.[23] The assignments of the individual absorption bands are listed in Table III together with the magnetic moments and the assignments of the *d-d* bands. Here it is noticeable that the transition $^1A_1 \rightarrow {}^1E$ ($2b_2 \rightarrow 7e$) observed in the range 20.8 to 22.7 kK and a part of the transition $^1A_1 \rightarrow {}^1A_1$ ($6e \rightarrow 7e$) observed between 24.4 and 27.5 kK are slightly shifted to the higher frequency side as compared with those observed in $Na_2[Fe(CN)_5NO] \cdot 2H_2O$ whereas all the other transitions in $M^{II}[Fe(CN)_5NO] \cdot 2H_2O$ are shifted to the lower frequency side. This phenomenon can be explained by making use of the energy level scheme reported on $Na_2[Fe(CN)_5NO] \cdot 2H_2O$.[23] As described in the preceding section, appreciable shift was not observed in the frequencies of the vibrations $\nu_{N\text{-}O}$, $\nu_{Fe\text{-}N}$ and $\nu_{Fe\text{-}NO}$. Therefore, there is not substantial change in the Fe-N and N-O bonds upon the formation of $M^{II}[Fe(CN)_5] \cdot 2H_2O$ from $Na_2[Fe(CN)_5NO] \cdot 2H_2O$. Hence it is reasonable to assume that the energy level of molecular orbital $7e(\pi^*NO)$, which is composed mainly of the d_π metal orbital and the ligand π-bonding or π-antibonding molecular orbitals, is the same in both $M^{II}[Fe(CN)_5NO] \cdot 2H_2O$ and $Na_2[Fe(CN)_5NO] \cdot 2H_2O$. Accordingly, the blue shift of the transition $^1A_1 \rightarrow {}^1E$ ($2b_2 \rightarrow 7e$) is ascribed to a lowering in the energy level of molecular orbital $2b_2(d_{xy})$. The lowering of the π-bonding molecular orbital contributes to an increase in the π-bonding nature between Fe-C. This tendency is also observed in the energy level of $6e(d_{xz}, d_{yz})$ for $Fe[Fe(CN)_5NO] \cdot 2H_2O$ and $Cu[Fe(CN)_5NO]$. Contrarily, the red shifts observed in the transitions $^1A_1 \rightarrow {}^1A_2(2b \rightarrow 3b_1)$, $^1A_1 \rightarrow {}^1E(6e \rightarrow 5a_1)$ and $^1A_1 \rightarrow {}^1E(6e \rightarrow 3b_1)$ result from a lowering in the energy levels of molecular orbitals $3b_1(d_{x2\text{-}y2})$ and $5a_1$ (d_{z^2}). This lowering in the energy level of the σ-antibonding molecular orbitals means a decrease of the σ-bonding nature between Fe-C. Of course, molecular orbital energy levels other than those described above should be considered in order to discuss the whole bonding strength between Fe-C. However, taking into account the shift of the Fe-C stretching vibrations to the higher frequency side upon the formation of $M^{II}[Fe(CN)_5NO] \cdot 2H_2O$, it is concluded that the increase in the π-bonding nature of the Fe-C bonding is greater than the decrease in the σ-bonding nature and consequently the strength of the bonding between Fe-C increases in tolal.

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