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Characterization of Prussian Blue Analogs of the Type $M_3[Fe(CN)_5CO]_2 \cdot xH_2O$

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A series of compounds of the type $M_3[Fe(CN)_5CO]_2 \cdot xH_2O$ (M=Mn, Co, Ni, Cu, and Zn) have been studied by means of the X-ray diffraction powder patterns, magnetic measurements, infrared, electronic, and Mössbauer spectra. Three compounds $M_3[Fe(CN)_5CO]_2 \cdot xH_2O$ (M=Mn, Co, and Ni) crystallize in the face-centered cubic system. Copper compound $Cu_3[Fe(CN)_5CO]_2 \cdot 18.5H_2O$ belongs to the tetragonal system, zinc compound $Zn_3[Fe(CN)_5CO]_2 \cdot 13.5H_2O$ being amorphous. The structure of these compounds is described as a three-dimensional framework of two octahedral coordination units FeC_6 in the low spin state and $MN_{10/3}O_{8/3}$ in the high spin state. The back donation in the $Fe(CN)_5CO^{3-}$ moiety is enhanced by the bridge formation through CN^- and CO ligands, *i.e.* upon the formation of $M_3[Fe(CN)_5CO]_2 \cdot xH_2O$ from the corresponding sodium salt.

A number of Prussian blue analogs have been synthesized by the reaction of hexacyanometalate ions $Me(CN)_6^{n-}$ with the first row transition metal ions. Substituted pentacyanoferrate ions such as $Fe(CN)_5X^{n-}$ (X=NO, CO, NH_3, and H_2O) are also known to react with the first row transition metal ions to yield insoluble polynuclear complexes similar to Prussian blue analogs.[1] Most of these transition metal salts of substituted pentacyanoferrates having a general formula $M[Fe(CN)_5X] \cdot xH_2O$ (M=Mn, Fe, Co, Ni, Cu, and Zn) are shown to crystallize in the face-centered cubic system characteristic of Prussian blue analogs.[2]

In spite of considerable interest in $M[Fe(CN)_5X] \cdot xH_2O$, there have been relatively few systematic studies on the transition metal salts of carbonylpentacyanoferrate(II) ions of the type $M_3[Fe(CN)_5]_2 \cdot xH_2O$. Brown and Brown[3] have investigated transition metal salts of the $Fe(CN)_5CO^{3-}$ ion such as $Co_3[Fe(CN)_5CO]_2 \cdot xH_2O$ to demonstrate the bridge structure of carbonyl ligands. On the basis of Keggin's structure model,[4] Ludi *et al.*[5] have proposed a modified crystal structure model for $Mn_3[Co(CN)_6]_2 \cdot xH_2O$, in which the cubic unit cell contains one and a third formula units. In view of the similarity in composition between $Mn_3[Co(CN)_6]_2 \cdot xH_2O$ and $M_3[Fe(CN)_5CO]_2 \cdot xH_2O$, it is of interest to find whether the crystal structure of transition metal salts of carbonylpentacyanoferrate(II) ions can be understood according to this modified structure model by Ludi *et al.* or not.

In the previous paper we showed that a three-dimensional framework is formed by the bridging of cyanide ligands upon the formation of $Fe[Fe(CN)_5X]$ (X=CO, NH_3, and H_2O) from $Na_3[Fe(CN)_5CO] \cdot H_2O$.[6] Furthermore, we discussed the influence of the bridge formation on the electronic structure of the $Fe(CN)_5X^{3-}$ moiety and the dependence of the electronic structure of the central iron(II) ion on the ligand X. The present work was attempted to characterize Prussian blue analogs of the type $M_3[Fe(CN)_5CO]_2 \cdot xH_2O$ (M=Mn, Co, Ni, Cu, and Zn). This type of compounds provides a good model to study a change in the electronic structure of the $Fe(CN)_5CO^{3-}$ moiety with the systematic change in the counter cation M^{2+} from manganese(II) to zinc(II) ion.

Experimental

Sodium carbonylpentacyanoferrate(II) was prepared by the literature method and purified by recrystallization.[7] A series of compounds of the type $M_3[Fe(CN)_5CO]_2 \cdot xH_2O$ (M=Mn, Co, Ni, Cu, and Zn) were precipitated by the addition of an excess of 0.05 mol dm^{-3} MCl_2 to 0.05 mol dm^{-3} $Na_3[Fe(CN)_5CO]$. The precipitate obtained was allowed to stand for 24 h for aging, collected on a glass filter by suction, washed with distilled water, alcohol, and finally ether, then dried over calcium chloride. The compounds prepared were analyzed chelatometrically: Found: Fe, 12.4; Mn, 18.0%. Calcd for $Mn_3[Fe(CN)_5CO]_2 \cdot 17.5H_2O$: Fe, 12.30; Mn, 18.15%. Found: Fe, 12.9; Co, 19.9%. Calcd for $Co_3[Fe(CN)_5CO]_2 \cdot 15.0H_2O$: Fe, 12.77; Co, 20.21%. Found: Fe, 11.9; Ni, 17.5%. Calcd for $Ni_3[Fe(CN)_5CO]_2 \cdot 18.0H_2O$: Fe, 12.30; Ni, 18.97%. Found: Fe, 12.0; Cu, 20.1%. Calcd for $Cu_3[Fe(CN)_5CO]_2 \cdot 18.5H_2O$: Fe, 11.73; Cu, 20.03%. Found: Fe, 13.0; Zn, 22.1%. Calcd for $Zn_3[Fe(CN)_5CO]_2 \cdot 13.5H_2O$: Fe, 12.88; Zn, 22.61%. X-Ray diffraction powder patterns were taken with a Rigaku-Denki X-ray diffractometer at room temperature. The lattice constants were determined using Fe $K\alpha$ radiation (λ=1.937 Å) and sodium chloride as a standard. Infrared spectra were recorded on a Hitachi Perkin-Elmer Model 225 grating infrared spectrophotometer in the range 200 to 4000 cm^{-1} by the Nujol mull and CsI disk methods. The calibration of wave numbers was made using polystyrene film and water vapor absorption. Diffuse reflection spectra were measured with the Hitachi Perkin-Elmer Model 139 spectrophotometer equipped with the standard integrating attachment using alumina as a standard. Magnetic susceptibilities were measured at room temperature by the Gouy method using $Hg[Co(SCN)_4]$ as a calibrant.[8] Diamagnetic corrections were carried out with Pascal's constants.[9] Mössbauer spectra were measured with a constant-acceleration transducer of the Canberra type. A ^{57}Co source in Pd foil with an original intensity of about 10 mCi which was supplied by Radiochemical Centre, Amersham was used at room temperature. The absorbers with a thickness of about 5 mg of natural iron per cm^2 were kept at 77 or 300 K. The Doppler velocity was calibrated with natural iron foil kept at room temperature.

Results and Discussion

Crystal Structure. A series of compounds of the type $M_3[Fe(CN)_5CO]_2 \cdot xH_2O$ (M=Mn, Co, and Ni) showed the X-ray diffraction powder patterns very similar to those for Prussian blue analogs belonging to the face-centered cubic system. This indicates that compounds other than copper and zinc compounds are isomorphous with Prussian blue analogs: space group O_h^5–F_{m3m}. According to the modified structure model proposed for $Mn_3[Co(CN)_6]_2 \cdot xH_2O$ by Ludi, *et al.*,[5] the unit cell contains 1 1/3 formula units of $M_3[Fe(CN)_5CO]_2 \cdot xH_2O$. As Fig. 1 shows, 4M coordinated by 3 1/3 nitrogen atoms of cyanide ligands, 2 oxygen atoms of water molecules and 2/3 oxygen atom of carbonyl ligands are distributed at the 4a (0,0,0) positions, while 2 2/3 Fe coordinated by five carbon atoms of cyanide ligands and a carbon atom of the carbonyl ligand occupy the 4b(1/2,1/2,1/2) positions in the face-centered cubic unit cell. The 24e (*x*,0,0) positions are occupied by 16C, 13 1/3 N, and 10 1/3 O atoms. Eight water molecules coordinate to M to fill the empty nitrogen positions. Additional water molecules are distributed around 8c(1/4,1/4,1/4) positions and have a zeolitic nature. These water molecules could be readily removed on heating and are responsible for the different degree of hydration.

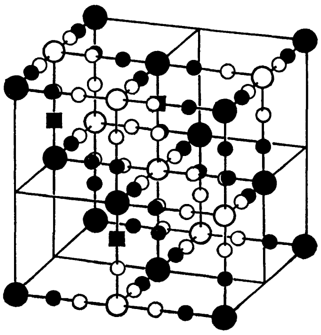

Fig. 1. The structure of $M_3[Fe(CN)_5CO]_2 \cdot xH_2O$.
The number of Fe, C, N, and O does not correspond exactly to the modified structure model and water molecules are not shown for brevity. Symbols: ●, 4M at 4a; ○, 2⅔Fe at 4b; ○, 16C at 24e; •, 13⅓N at 24e; ■, 2⅔O at 24e.

The crystal structure can be described as a three-dimensional framework of the two octahedral coordination units FeC_6 and $MN_{10/3}O_{8/3}$, where the formula of the latter complex represents an average composition. However, the space group is not O_h^5–F_{m3m} in a strict sense because the symmetry group of the $Fe(CN)_5CO^{3-}$ moiety is not O_h but C_{4v}. In fact, the diffraction powder pattern of the cobalt compound was very diffuse, suggesting that the site symmetry of cobalt ions is lowered due to the C_{4v} symmetry of the $Fe(CN)_5CO^{3-}$ moiety. The preparation of $Fe_3[Fe(CN)_5CO]_2 \cdot xH_2O$ was unsuccessful even in the rigorously purified nitrogen atmosphere since this compound is readily oxidized to give iron(III) carbonylpentacyanoferrate(II) $Fe[Fe(CN)_3CO] \cdot xH_2O$ which is described elsewhere in detail.[6] As reported on $Cu[Fe(CN)_5NO]$,[2] copper compound $Cu_3[Fe(CN)_5CO]_2 \cdot 18.5H_2O$ does not crystallize in the face-centered cubic system but in the tetragonal system. The zinc compound fails to give crystalline precipitate in the present preparative way, *i.e.* it is amorphous. Table 1 lists the lattice constants calculated from the X-ray diffraction powder patterns. The lattice constants obtained fall within the range typical of those commonly found for Prussian blue analogs. Moreover, the lattice constants decrease with the increase of the crystal field stabilization energy of M^{2+} ion in the octahedral weak field, which is quite similar to

TABLE 1. LATTICE CONSTANTS AND MAGNETIC MOMENTS

Compound[a)]	Lattice constant Å	Magnetic moment μ_{eff}/BM[b)]
$Mn_3[Fe(CN)_5CO]_2$	10.38±0.01	5.65
$Co_3[Fe(CN)_5CO]_2$	10.21±0.03	4.77
$Ni_3[Fe(CN)_5CO]_2$	10.13±0.01	2.93
$Cu_3[Fe(CN)_5CO]_2$	a=10.15±0.02 c=10.03±0.02	1.72
$Zn_3[Fe(CN)_5CO]_2$	Amorphous	Diamagnetic

a) Water molecules are not shown for clarity. b) 1 BM $=9.273 \times 10^{-24}$ A m².

TABLE 2. INFRARED ABSORPTION FREQUENCIES OF $M_3[Fe(CN)_5CO]_2 \cdot xH_2O$ AND $Na_3[Fe(CN)_5CO] \cdot H_2O$

Compound	Absorption frequencies/cm^{-1}					
	ν_{CN}	ν_{CO}	δ_{Fe-CO}	δ_{Fe-CN}	$\nu_{Fe-C(CO)}$	$\nu_{Fe-C(CN)}$
$Mn_3[Fe(CN)_5CO]_2 \cdot 17.5H_2O$	2113 s	2020 s	625 s	585 s	543 wb	479 m 462 s
$Co_3[Fe(CN)_5CO]_2 \cdot 15.0H_2O$	2122 s	2028 s	624 s	586 s	537 m	500 s 470 sh
$Ni_3[Fe(CN)_5CO]_2 \cdot 18.0H_2O$	2132 s 2095 sh	2017 s	627 s	586 s	546 w	485 sh 466 m
$Cu_3[Fe(CN)_5CO]_2 \cdot 18 \cdot 5H_2O$	2138 s 2097 w	2026 s	626 s	586 s	537 m	492 s 471 m
$Zn_3[Fe(CN)_5CO]_2 \cdot 13.5H_2O$	2132 s	2037 s	626 s	588 s	535 sh	493 s 468 m
$Na_3[Fe(CN)_5CO] \cdot H_2O$	2118 sh 2109 sh 2102 sh 2095 s 2087 s	2033 s 1999 s 1981 s	627 vs 621 s	589 s	537 sh 517 mb	432 sh 427 s

vs=Very strong; s=strong; m=medium; w=weak; sh=shoulder; wb=weak and broad; mb=medium and broad.

the phenomena observed for other Prussian blue analogs.[10)]

IR Spectra and Bridge Structure of Cyanide and Carbonyl Ligands. The infrared absorption frequencies observed for $M_3[Fe(CN)_5CO]_2 \cdot xH_2O$ are listed in Table 2 along with those for $Na_3[Fe(CN)_5CO] \cdot H_2O$. In the CN stretching region, very intense absorption bands typical of cyanide complexes were observed in the range 2095 to 2138 cm^{-1}. Since the $Fe(CN)_5CO^{3-}$ moiety belongs to point group C_{4v}, two different species of CN stretching modes $2A_1+E$ are expected to appear in $M_3[Fe(CN)_5CO]_2 \cdot xH_2O$. However, the CN stretching mode was observed as a single intense band with the exception of $M_3[Fe(CN)_5CO]_2 \cdot xH_2O$ (M=Ni and Cu). Taking into account the high site symmetry of the $Fe(CN)_5CO^{3-}$ moiety, the environment of the iron(II) ion is approximated to O_h symmetry even though one of six cyanide ligands is substituted for a carbonyl ligand. On the other hand, four shoulders other than the main strong absorption band were observed for $Na_3[Fe(CN)_5CO] \cdot H_2O$. This splitting of the CN stretching bands must be due to the lowering in the site symmetry of the $Fe(CN)_5CO^{3-}$ moiety. The CN stretching bands of $M_3[Fe(CN)_5CO]_2 \cdot xH_2O$ are observed at higher frequencies than the main strong band (2095 cm^{-1}) of the corresponding sodium carbonylpentacyanoferrate(II). This shift of the CN stretching mode to higher frequencies is considered to be characteristic of the bridge formation of cyanide ligands.[11)] Moreover, it is noteworthy that the increasing order in the CN stretching frequencies is very similar to that of the electronegativity of M^{2+} ion or the crystal field stabilization energy in the octahedral weak field.

A strong absorption band assigned to the CO stretching mode appeared at the lower frequencies side of the CN stretching bands. The CO stretching vibration of $M_3[Fe(CN)_5CO]_2 \cdot xH_2O$ was observed as a single broad band whereas the CO stretching modes of $Na_3[Fe(CN)_5CO] \cdot H_2O$ appeared at 1981, 1999, and 2033 cm^{-1} as three strong absorption bands. Of these three bands the absorption bands at 1981 and 1999 cm^{-1} must be caused by hydrogen bonding between the oxygen end of carbonyl ligand and water of crystallization. This is in marked contrast to the fact that the CO stretching band is scarcely affected although the Fe–CO–M bridge is formed in going from $Na_3[Fe(CN)_5CO] \cdot H_2O$ to $M_3[Fe(CN)_5CO]_2 \cdot xH_2O$.

The symmetric and antisymmetric OH stretching modes of water were observed in the range 3340 to 3440 cm^{-1}, while the bending mode appeared in the range 1590 to 1610 cm^{-1}. This observation agrees with that of Prussian blue analogs by Ludi *et al.*;[5)] there are two different types of water molecules such as lattice and coordinated water. However, the rocking and wagging vibrations of the coordinated water molecules could not be found probably due to their weakness and/or broadening.

The δ_{Fe-CO} bending and $\nu_{Fe-C(CO)}$ stretching modes appeared in the range 624 to 627 and 535 to 546 cm^{-1}, respectively. It is worth noting that the frequencies of both δ_{Fe-CO} and $\nu_{Fe-C(CO)}$ modes are almost independent of the bridge formation. This is probably because the effect of the bridge formation is compensated by the hydrogen bonding through the oxygen end of the carbonyl ligand. A similar phenomenon was also observed for transition metal salts of substituted pentacyanonitrosylferrates(II).[2)] On the other hand, both of the $\nu_{Fe-C(CN)}$ stretching and δ_{Fe-CN} bending modes are simplified in going from $Na_3[Fe(CN)_5CO] \cdot H_2O$ to $M_3[Fe(CN)_5CO]_2 \cdot xH_2O$ because the site symmetry of the $Fe(CN)_5CO^{3-}$ moiety is higher in the latter than the former. The $\nu_{Fe-C(CN)}$ stretching bands observed in the range 462 to 500 cm^{-1} are shifted to higher frequencies upon the formation of $M_3[Fe(CN)_5CO]_2 \cdot xH_2O$ while the δ_{Fe-CN} bending band observed in the range 585 to 588 cm^{-1} is scarcely affected. A shoulder located at the lower frequency side of the $\nu_{Fe-C(CN)}$ stretching band is strong evidence for the bridge structure of cyanide ligand.[12)] Indeed, the MN stretching modes were confirmed in nickel and copper compounds. However, no absorption band could be observed in other compounds because the absorption band is very weak in intensity or lies out of the present experimental region.

Electronic Structure and Chemical Environment of M^{2+} Ion. The nature of counter cation, M^{2+} ion, is supposed to affect the electronic structure of the $Fe(CN)_5CO^{3-}$ moiety upon formation of $M_3[Fe(CN)_5CO]_2 \cdot xH_2O$ from $Na_3[Fe(CN)_5CO] \cdot H_2O$. Therefore, it is very important to understand in what ligand field the counter cation is situated or what symmetry the environment of the counter cation has. Magnetic measurements as well as electronic spectra will be a sophisticated mean for this purpose. The effective magnetic moment, μ_{eff}, per M^{2+} ion of $M_3[Fe(CN)_5CO]_2 \cdot xH_2O$ was calculated from the magnetic susceptibilities at room temperature and listed in Table 1. The effective Bohr magnetons calculated agreed with the expectation that Prussian blue analogs of the type $M_3[Fe(CN)_5CO]_2 \cdot xH_2O$ consist of $Fe(CN)_5CO^{3-}$ moieties in the low spin state and M^{2+} ions in the high spin state. As shown in Fig. 2, the absorption bands of electronic spectra in the visible region are very similar in position to those of hexaaqua complexes of M^{2+} ion. This is in good agreement with the magnetochemical conclusion that M^{2+} ion is in the high spin state. Accordingly, the absorption bands are assignable on the basis of the term diagram for M^{2+} ion in the octahedral weak field.[13)] Two very weak shoulders occurred in $Mn_3[Fe(CN)_5CO]_2 \cdot 17.5H_2O$ at approximately 17.6 and 23.0×10^3 cm^{-1} which may be assigned to the spin-forbidden transitions, $^6A_{1g} \rightarrow ^4T_{1g}$ and $^4T_{2g}$ respectively. The absorption band at 16.8×10^3 cm^{-1} for $Co_3[Fe(CN)_5CO]_2 \cdot 15.0H_2O$ is very intense and low in energy as compared with that expected for the corresponding transition $^4T_{1g}(F) \rightarrow ^4T_{1g}(P)$ in the octahedral weak field, indicating that the environment of Co^{2+} ions is distorted from O_h symmetry. An absorption maximum and a shoulder which appear in $Ni_3[Fe(CN)_5CO]_2 \cdot 18.0H_2O$ at 16.0 and 25.6×10^3 cm^{-1} are assigned to the spin-allowed transitions $^3A_{2g}(F) \rightarrow ^3T_{1g}(F)$ and $^3T_{1g}(P)$ respectively. The energies of these two transitions are comparable to those of the corresponding hexaaqua complexes. The absorption band of $Cu_3[Fe(CN)_5$-

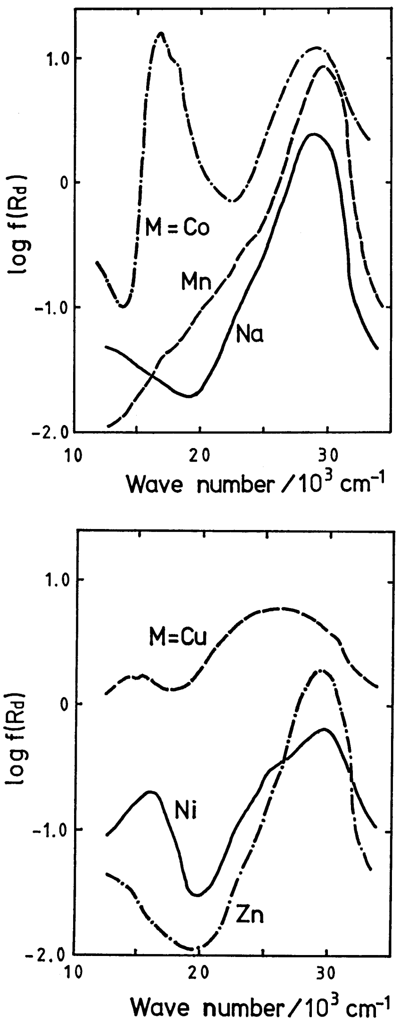

Fig. 2. Electronic spectra of $M_3[Fe(CN)_5CO]_2 \cdot xH_2O$ and $Na_3[Fe(CN)_5CO] \cdot H_2O$.

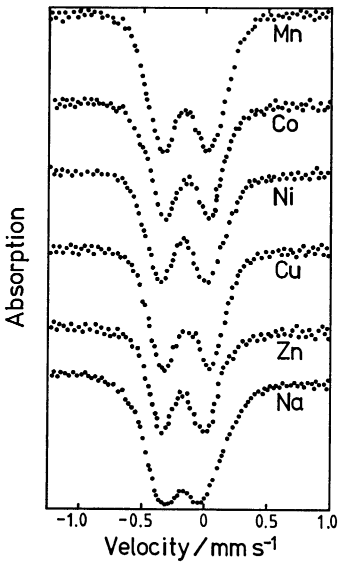

Fig. 3. Mössbauer spectra of $M_3[Fe(CN)_5CO]_2 \cdot xH_2O$ and $Na_3[Fe(CN)_5CO] \cdot H_2O$ at room temperature.

TABLE 3. MÖSSBAUER PARAMETERS OF $M_3[Fe(CN)_5CO]_2 \cdot xH_2O$

Compound[a]	Isomer shift[b] mm s^{-1}		Quadrupole splitting[b] mm s^{-1}	
	78 K	300 K	78 K	300 K
$Mn_3[Fe(CN)_5CO]_2$	−0.085	−0.147	0.338	0.353
$Co_3[Fe(CN)_5CO]_2$	−0.085	−0.154	0.311	0.357
$Ni_3[Fe(CN)_5CO]_2$	−0.087	−0.153	0.362	0.378
$Cu_3[Fe(CN)_5CO]_2$	−0.093	−0.149	0.381	0.371
$Zn_3[Fe(CN)_5CO]_2$	−0.081	−0.148	0.368	0.344
$Na_3[Fe(CN)_5CO]$	−0.058	−0.138	0.287	0.247

a) Water molecules are not given for brevity. b) With uncertainty of 0.008 mm/s.

$CO]_2 \cdot 18.5H_2O$ assignable to the transition $^2E_{2g} \rightarrow {}^2T_{2g}$ is split into two bands (14.1 and 15.2×10^3 cm^{-1}) due to the lowering of the environment of Cu^{2+} ion from O_h symmetry. This splitting of the d-d transition is responsible for the heterogeneous environment around Cu^{2+} ion rather than the Jahn-Teller effect because the Cu^{2+} ion is surrounded by 10/3 N and 8/3 O statistically. A very broad intense band observed at about 26.0×10^3 cm^{-1} is associated with the so-called intervalence electron transfer band. This type of intense absorption band was also observed for $Fe[Fe(CN)_5CO] \cdot xH_2O$.[14]

Influence of Bridge Formation on the Electronic Structure of $Fe(CN)_5CO^{3-}$ Moiety. The bridge formation of the cyanide and carbonyl ligands is expected to influence the electronic structure of the $Fe(CN)_5CO^{3-}$ moiety. The bonding character between iron(II) and carbon atoms would change upon the systematic change in the counter cation. The Mössbauer and electronic spectra afford useful information about these problems. The Mössbauer spectra of $M_3[Fe(CN)_5CO]_2 \cdot xH_2O$ are shown in Fig. 3 where that of $Na_3[Fe(CN)_5CO] \cdot H_2O$ is also presented for comparison. All the compounds of the type $M_3[Fe(CN)_5CO]_2 \cdot xH_2O$ exhibited a relatively small quadrupole splitting doublet which is comparable to that of sodium carbonylpentacyanoferrate(II). The Mössbauer parameters obtained at 77 and 300 K are summarized in Table 3.

As Fig. 2 shows, the intense absorption bands commonly observed for the electronic spectra of $M_3[Fe(CN)_5CO]_2 \cdot xH_2O$ in the range 29.2 to 29.8×10^3 cm^{-1} are assigned to the lowest spin-allowed transition of the $Fe(CN)_5CO^{3-}$ moiety. This assignment is supported by the fact that a relatively strong band is also observed for $Zn_3[Fe(CN)_5CO]_2 \cdot 13.5H_2O$ and $Na_3[Fe(CN)_5CO] \cdot H_2O$ in the near ultraviolet region in which no d-d transition other than that of the $Fe(CN)_5CO^{3-}$ moiety is expected. Since carbonyl and cyanide ligands are located near each other in the spectrochemical series, the iron(II) ion is considered to be situated to a first approximation in the environment of O_h symmetry. Consequently, the intense band in the near ultraviolet region is assigned to the spin-allowed transition $^1A_{1g} \rightarrow {}^1T_{2g}$. This point of view is consistent with the following facts. The solution spectrum of $Na_3[Fe(CN)_5CO]$ resembles closely that of $K_4[Fe(CN)_6]$.[15] The quadrupole splittings of both

$M_3[Fe(CN)_5CO]_2 \cdot xH_2O$ and $Na_3[Fe(CN)_5CO] \cdot H_2O$ are not only small, but also their isomer shifts are comparable to that of potassium hexacyanoferrate(II).[16] The carbonyl and cyanide ligands are located near each other in the partial isomer shift and partial quadrupole splitting proposed by Bancroft *et al.*[17]

The temperature-variation in the quadrupole splittings may be associated with the thermal vibration of the crystal lattice. Evidently the quadrupole splittings increase upon formation of $M_3[Fe(CN)_5CO]_2 \cdot xH_2O$ from $Na_3[Fe(CN)_5CO] \cdot H_2O$. This indicates that the charge distribution around the iron nucleus in $M_3[Fe(CN)_5CO]_2 \cdot xH_2O$ is more aspherical than that in $Na_3[Fe(CN)_5CO] \cdot H_2O$ because the quadrupole splitting is due to non-zero electric field gradients at the nucleus which are caused by the aspherical charge distribution of ligand and/or crystal lattice. Unfortunately, such systematic tendency as found for the variation in the lattice constants is not always observed for the increasing order of the quadrupole splittings. Therefore, only a single factor of electronegativity of M(II) ions, size of M(II) ions, d_π-orbitals of M(II) ions to form the back donation, etc. does not play a principal role in the electric field gradient at the iron nucleus, but some combination of these factors must contribute to the quadrupole splittings of $M_3[Fe(CN)_5CO]_2 \cdot xH_2O$.

The isomer shifts of $M_3[Fe(CN)_5CO]_2 \cdot xH_2O$ fall within the range characteristic of low-spin iron(II) complexes.[18] The isomer shifts at 300 K are generally smaller than those at 77 K. This temperature shift in the isomer shifts is ascribed to the second-order Doppler effect. The isomer shifts decrease in going from $Na_3[Fe(CN)_5CO] \cdot H_2O$ to $M_3[Fe(CN)_5CO]_2 \cdot xH_2O$. As is well known, the isomer shift of iron compounds is a measure of the total s-electron density at the iron nucleus and the former decreases with the increase in the latter. Thus the decrease of the isomer shifts accompanied by the formation of $M_3[Fe(CN)_5CO]_2 \cdot xH_2O$ is responsible for the increase of the total s-electron density at the iron nucleus, which is caused by the decreased shielding effect of 3d-electrons. This delocalization of iron 3d-electrons is due to the increased back donation, in other words, due to the increased tendency of the cyanide and carbonyl ligands to withdraw electrons from the central iron atom. On the other hand, the spin-allowed transition $^1A_{1g} \rightarrow {}^1T_{1g}$ in $M_3[Fe(CN)_5CO]_2 \cdot xH_2O$ is slightly shifted to higher frequencies compared to the corresponding transition in $Na_3[Fe(CN)_5CO] \cdot H_2O$. As pointed out in Prussian blue analogs of the type $M[Fe(CN)_5NO] \cdot xH_2O$,[2] this blue shift is also correlated with an increase in the back donation. In conclusion, the coordination of M(II) ions to the nitrogen and oxygen ends of carbonyl ligands leads to the increased back donation from the filled iron d_π-orbitals to the empty ligand antibonding π^*-orbitals.

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