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Bonding Nature of Coordination Polymers, $M_3[Ir(CN)_6]_2.xH_2O$[1]

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The bonding nature of coordination polymers of the type $M_3[Ir(CN)_5]_2\,xH_2O$ has been studied, where M is Mn, Fe, Co, Ni, Cu or Zn. The X-ray powder diffraction indicates that these compounds have a face-centered cubic unit cell characteristic of Prussian blue analogs. The lattice constats decrease with the increase of the crystal field stabilization energy of M^{II} in the octahedral weak field. In the infrared spectra both $C\equiv N$ and Ir-C stretching bands are shifted to the higher frequency side compared with those of potassium hexacyanoiridate(III). This shift is attributable to the linkage structure $Ir\text{-}C\equiv N\text{-}M$ of cyanide ligand. The absorption bands in the visible region are assigned as the d-d transition of M^{II} while those in the ultraviolet region are attributed to the ligand field transition of Ir^{III}. Electronic spectra and magnetic data lead to the conclusion that M^{II}, coordinated by the nitrogen ends of cyanide ligands and water molecules, is high spin state and carbon-coordinated Ir^{III} is low spin state.

Introduction

There has been considerable interest in "coordination polymers" containing cyanide ligands as bridged group. Among these compounds are counted the coordination polymers of the type $M_3^I[M^{II}(CN)_6]_2\cdot xH_2O$, where M^I is Mn, Fe, Co, Ni, Cu or Zn and M^{II} is Co, Rh or Ir. The bonding nature of these series of compounds is to resemble each other since the central metal ion M^{II} has an identical electronic configuration nd^6 ($n = 3\sim5$). However, most of the investigations have been concerned with $M_3[Co(CN)_6]_2\cdot xH_2O$, though a few have been made on $M_3[Rh(CN)_6]_2\cdot xH_2O$ and $M_3[Ir(CN)_6]_2\cdot xH_2O$. As for $M_3[Co(CN)_6]_2\cdot xH_2O$ it was shown that it has a face-centered cubic unit cell typical of Prussian blue analogs.[2] Furthermore, Ludi *et al.*[3] have recently proposed new structural model for $Mn_3[Co(CN)_6]_2\cdot xH_2O$ and its related compounds based on the structural model which was reported on Prussian blue about 36 years ago by Keggin and Miles.[4] Besides these structural works there have been many studies by electronic and infrared spectra.[5] In spite of these extensive studies on $M_3[Co(CN)_6]_2\cdot xH_2O$ hardly any reports on $M_3[Rh(CN)_6]_2\cdot xH_2O$ and $M_3[Ir(CN)_6]_2\cdot xH_2O$ have been made except for the X-ray diffraction studies by Ferrari *et al.*[6]

It is the purpose of the present work to describe the bonding nature of $M_3[Ir(CN)_6]_2\cdot xH_2O$ on the basis of X-ray powder patterns, magnetic susceptibilities, infrared and electronic spectra.

Experimental Section

Potassium hexacyanoiridate(III) $K_3[IrCl_6]$ was prepared by the following method: Potassium hexachloroiridate(III) $K_3[IrCl_6]$ synthesized according to the literature[7] was fused with potassium cyanide for an hour at 200°C. The crude product obtained was dissolved in water and the solution was filtered in order to separate the iridium metal produced during the fusion by the reduction. Then the filtrate was concentrated to obtain crystals. A series of compounds $M_3[Ir(CN)_6]_2\cdot xH_2O$ were precipitated by adding in excess a 0.02M solution of sulfate or chloride of the divalent first row transition metal to a 0.02M solution of $K_3[Ir(CN)_6]$. The precipitates obtained were filtered, washed with distilled water till chloride or sulfate ions could not be detected in the filtrate, finally washed with alcohol, and dried to constant weight over silica gel. The preparation of iron compound was carried out in an atmosphere of hydrogen in order to prevent partial oxidation of ferrous ion and exposure to air was minimized in the whole operations. The metal contents of the compounds were chacked by the usual method[8] and the water content determined by the thermogravimetric analysis. The results were as follows: Found: Mn, 14.4; Ir, 34.1; H_2O, 19.2%. Calcd for $Mn_3[Ir(CN)_6]_2\cdot 12H_2O$: Mn, 15.29; Ir, 35.67; H_2O, 20.06%. Found: Fe, 13.8; Ir, 29.3; H_2O, 28.9%. Calcd for $Fe_3[Ir(CN)_6]_2\cdot 20H_2O$: Fe, 13.68; Ir, 31.40; H_2O, 29.42%. Found: Co, 15.3; Ir 32.4; H_2O; 22.1%. Calcd for $Co_3[Ir(CN)_6]_2\cdot 15H_2O$: Co, 15.46; Ir, 33.61; H_2O; 23.63%.

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Found: Ni, 14.1; Ir, 30.7; H_2O, 26.1%. Calcd for $Ni_3[Ir(CN)_6]_2 \cdot 18H_2O$: Ni, 14.71; Ir, 32.12; H_2O, 27.09%. Found: Cu, 17.7; Ir, 33.8; H_2O, 16.6%. Calcd for $Cu_3[Ir(CN)_6]_2 \cdot 10H_2O$: Cu, 17.86; Ir, 36.01; H_2O, 16.88%. Found: Zn, 17.5; Ir, 34.9; H_2O, 20.2%. Calcd for $Zn_3[Ir(CN)_6]_2 \cdot 12H_2O$: Zn, 17.68; Ir, 34.67; H_2O, 19.49%.

The X-ray diffraction powder patterns were obtained with a Rigaku-Denki X-ray diffractometer using Cu Kα-radiation: 1.542Å, at room temperature. Densities of the polycrystalline samples were measured pycnometrically in redistilled toluene at 25.0°C with great caution against the change of water content. The samples under toluene were pumped in a vacuum desiccator to remove adsorbed air.[9] The chemical composition of the samples was checked again after the density measurements. The infrared spectra were recorded in the range 350 to 4000 cm^{-1} by the KBr disk method with a Hitachi EPI-2 infrared spectrophotometer. The wavenumbers 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[10] was calculated from the reflectance data and plotted against wavenumbers. The mull transmittance spectra were obtained using mull suspension in liquid paraffin.[11] The magnetic susceptibilities were measured by the Gouy method with $Hg[Co(NCS)_4]$ (16.44×10^{-6} cgs units at 20.0°C)[12] as a standard at room temperature. The diamagnetic correction were calculated with the Pascal constants.[13]

Results and Discussion

Structure and Magnetic Moment. The X-ray diffraction powder patterns have indicated that the compounds of the type $M_3[Ir(CN)_6]_2 \cdot xH_2O$ are isomorphous with $M_3[Co(CN)_6]_2 \cdot xH_2O$. Thus the crystals of these compounds belong to space group O_h^5—F_{m3m} and have the face-centered cubic unit cell which is common to Prussian blue analogs. Ferrari et al.[6] explained the structure of $M_3[Ir(CN)_6]_2 \cdot 12H_2O$ in terms of the original structural model first proposed for Prussian blue by Keggin and Miles,[4] in which the unit cell contains two formula units. However, density measurements have revealed that the new structural model recently proposed for the compound of the type $M_3[Co(CN)_6]_2 \cdot xH_2O$ by Ludi *et al.*[3] is also applicable to the series $M_3[Ir(CN)_6]_2 \cdot xH_2O$. In this structural model the unit cell contains 1 1/3 formula units (Figure 1): 4M at 4a (0,0,0), 2 2/3 Ir statistically distributed at 4b (1/2,1/2,1/2) 16C and 16N at 24e (x 0, 0), 8 water molecules belonging to the coordination octahedron of M situated close to the empty nitrogen positions, and additional water molecules distributed around 8c (1/4,1/4,1/4). The lattice constants of $M_3[Ir(CN)_6]_2 \cdot xH_2O$ vary with every change of M, therein exists a regularity that they decrease with the increase of the crystal field stabilization energy of M^{II} in the octahedral weak field (Figure 2). This suggests that the ion M^{II} is in the weak crystal field and participates in coordination bonding. The lattice constant of $Cu_3[Ir(CN)_6]_2 \cdot 10H_2O$ is unusually small as compared with those of the other compounds of this series. This peculiarity of copper compound is also observed in $M_3[Co(CN)_6]_2 \cdot xH_2O$ and $M_3[Rh(CN)_6]_2 \cdot xH_2O$[13] which are isomorphous with $M_3[Ir(CN)_6]_2 \cdot xH_2O$. Based on the above structural model, statistically four nitrogen ends of cyanide ligands and two oxygen atoms of water molecules coordinate to the copper ion to form to a first approximation an octahedral weak field. Although the nitrogen end of cyanide ligand is located near

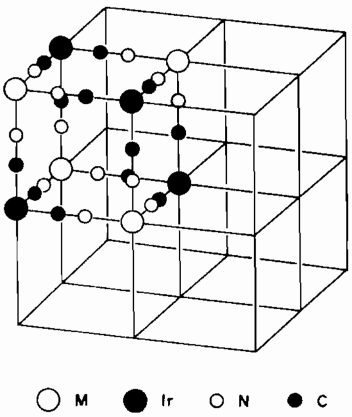

Figure 1. The unit cell of $M_3[Ir(CN)_6]_2 \cdot xH_2O$.

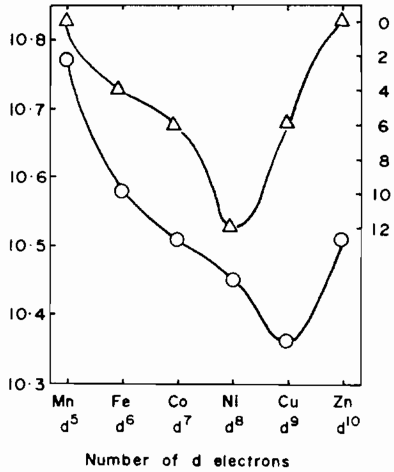

Figure 2. Lattice constants as compared with crystal field stabilization energies (c.f.s.e.).

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Table I. Lattice constants, densities and magnetic moments of $M_3[Ir(CN)_6]_2 . xH_2O$

Compound	Lattice constant (Å)	Density ρ_{calc} (g/cm³)	Density ρ_{exp} (g/cm³)	Magnetic moment μ_{eff} (B.M.)
$Mn_3[Ir(CN)_6]_2 . 12H_2O$	10.74±0.03	2.07	1.93	5.82
$Fe_3[Ir(CN)_6]_2 . 20H_2O$	10.58±0.04	2.22	2.29	5.65
$Co_3[Ir(CN)_6]_2 . 15H_2O$	10.51±0.04	2.12	2.18	4.94
$Ni_3[Ir(CN)_6]_2 . 18H_2O$	10.45±0.05	2.25	2.32	3.24
$Cu_3[Ir(CN)_6]_2 . 10H_2O$	10.36±0.04	2.15	2.13	1.92
$Zn_3[Ir(CN)_6]_2 . 12H_2O$	10.51±0.03	2.10	2.11	diamagnetic

water in the spectrochemical series,[14] the symmetry of environment of the copper ion is not octahedral in an exact sense. Therefore, some distortion of the octahedral symmetry, which cannot be observed crystallographically at room temperature, probably contributes to the exceptionally small lattice constant in $Cu_3[Ir(CN)_6]_2 \cdot 10H_2O$. This point of view is consistent with the fact that the d-d band ($^2E_g \rightarrow ^2T_{2g}$) around 13.6 kK is split into two peaks.

The effective Bohr magneton per M of the formula unit $M_3[Ir(CN)_6]_2 \cdot xH_2O$ was calculated from the magnetic susceptibility data and the results are summarized in Table I. The values obtained are in good agreement with the assumption that M^{II} is present as a high spin complex in $M_3[Ir(CN)_6]_2 \cdot xH_2O$ and Ir^{III} as a low spin one, respectively. The magnetic moments and the dependence of the lattice constants on the crystal field stabilization energy of the octahedral weak field lead to the following conclusion: The ion M^{II} coordinated by the nitrogen end of cyanide ligands and the oxygen atoms of water molecules is situated in the octahedral weak field and high spin state and, on the contrary, the ion Ir^{III} coordinated by the carbon ends of cyanide ligands is placed in the octahedral strong field and low spin state.

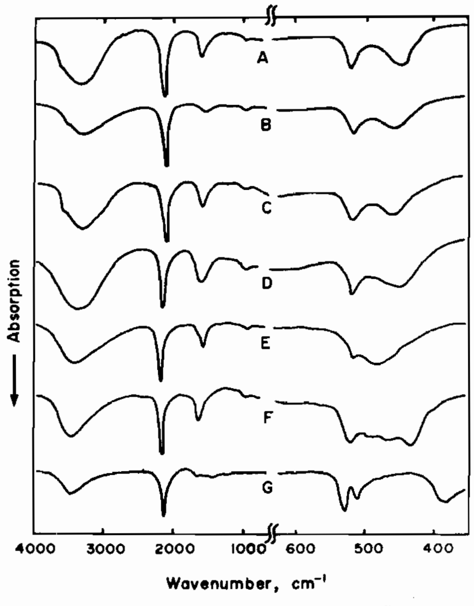

Figure 3. Infrared spectra of $M_3[Ir(CN)_6]_2 \cdot xH_2O$. A, $Mn_3[Ir(CN)_6]_2$; B, $Fe_3[Ir(CN)_6]_2$; C, $Co_3[Ir(CN)_6]_2$; D, $Ni_3[Ir(CN)_6]_2$; E, $Cu_3[Ir(CN)_6]_2$; F, $Zn_3[Ir(CN)_6]_2$; G, $K_3[Ir(CN)_6]$.

Infrared Spectra. The infrared spectra of $M_3[Ir(CN)_6]_2 \cdot xH_2O$ are reproduced in Figure 3, where the spectral pattern of $K_3[Ir(CN)_6]$ is shown for comparison. Three fundamental modes of water molecules were observed at ~3400 cm^{-1} (symmetric), ~3635 cm^{-1}(antisymmetric) and ~1610 cm^{-1}(bending). The rocking, wagging and metal-oxygen stretching bands characteristic of coordinated water are expected to be present in the far infrared region. However, such absorption bands could not be identified definitely in this region because they are usually very weak and broad as pointed out in the aquo complexes of M.[15] The strong C≡N stretching bands typical of hexacyanometalate ions have been observed in the range 2168 to 2185 cm^{-1}. These bands are shifted to the higher frequency side by 38~55 cm^{-1} compared with that of the parent complex $K_3[Ir(CN)_6]$ (2130 cm^{-1}). Furthermore, the magnitude of the shift is about the same as that reported on Prussian blue analogs. Therefore, it is concluded that the cyanide ligands of $M_3[Ir(CN)_6]_2 \cdot xH_2O$ coordinate to the metal ions through both carbon and nitrogen ends to form a linkage structure Ir-C≡N-M^{II}. Observation of the C≡N stretching vibration as a single sharp band means that all the cyanide ligands of $M_3[Ir(CN)_6]_2 \cdot xH_2O$ are involved in bridge bonding. It is noticeable that the C≡N stretching frequency increases with the lattice constant. This is consistent with the concept that bridged cyanide group give a higher absorption frequency against terminal cyanide groups because the presence of a second metal atom M constrains the motion of cyanide groups.[16]

A weak absorption band observed in the range 981 to 989 cm^{-1} has been assigned to the combination, $\nu_2(E_g)+\nu_7(F_{1u})$,* of $Ir(CN)_6^{3-}$ on the basis of the results of the normal coordinate analysis carried out with $K_3[Ir(CN)_6]$ by Jones.[17] In the far infrared region a strong absorption band assignable to the Ir-CN bending vibration ν_7 was observed around 530 cm^{-1}. This bending vibration should be shifted to the higher frequency side compared with that of $K_3[Ir(CN)_6]$ on account of the linkage structure Ir-C≡N-M. However, only a little shift was, in reality, observed as compared with 525 cm^{-1} of $K_3[Ir(CN)_6]$, an average of 531 and 518 cm^{-1}, which are split into

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(*) The number of frequencies is the same as that of Ref. 17.

Table II. Observed absorption infrared frequencies for $M_3[Ir(CN)_6]_2 \cdot xH_2O$ (in cm^{-1})

Compound	H₂O ν_{anti}	ν_{sym}	ν_{bend}	Ir(CN)$_6^{3-}$ ν_6	ν_7	ν_8	$\nu_2+\nu_7$
$Mn_3[Ir(CN)_6]_2$	3640	3390	1611	2177	530	456	983
$Fe_3[Ir(CN)_6]_2$	3635	3377	1608	2190	530	476	981
$Co_3[Ir(CN)_6]_2$	3630	3380	1611	2183	531	471	989
$Ni_3[Ir(CN)_6]_2$	3640	3400	1612	2183	532	478	986
$Cu_3[Ir(CN)_6]_2$		3435	1606	2185	530	485	984
$Zn_3[Ir(CN)_6]_2$		3395	1608	2168	531	430	988

two peaks due to the site symmetry of the crystal. A relatively broad band which appears in the range 430 to 485 cm^{-1} is attributable to the Ir-C stretching vibration ν_8. This Ir-C stretching band is also shifted to the higher frequency side compared with that of $K_3[Ir(CN)_6]$ (390 cm^{-1}). The magnitude of the shift varies with the nature of M, but it is noteworthy that the increasing order of Ir-C frequency is the same as that of the C≡N stretching vibration except for the iron compound. This indicates that upon the formation of linkage structure Ir-C≡N-M the Ir-C stretching frequency is strongly affected by kinematic coupling.

Electronic Spectra. The reflection and mull transmittance spectra of $M_3[Ir(CN)_6]_2 \cdot xH_2O$ are shown in Figure 4. The reflection spectra observed in the visible region are so similar to those of the corresponding aquo complexes of M^{II} that the d-d bands in this region are expected to be assigned in terms of the weak-field theory. According to the modified structural model described in the preceding section, M^{II} is

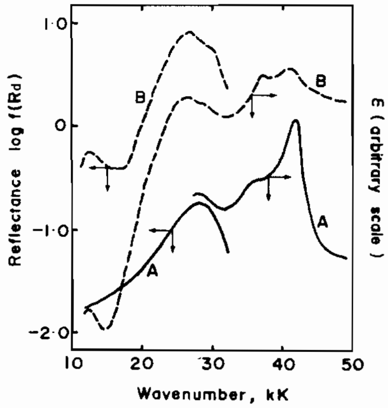

Figure 4, n. 1. Reflection and mull transmittance spectra of $M_3[Ir(CN)_6]_2 \cdot xH_2O$. A, $Mn_3[Ir(CN)_6]_2$; B, $Fe_3[Ir(CN)_6]_2$; C, $Co_3[Ir(CN)_6]_2$; D, $Ni_3[Ir(CN)_6]_2$; E, $Cu_3[Ir(CN)_6]_2$; F, $Zn_3[Ir(CN)_6]_2$.

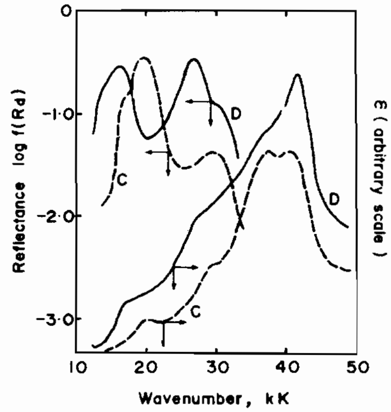

Figure 4, n. 2.

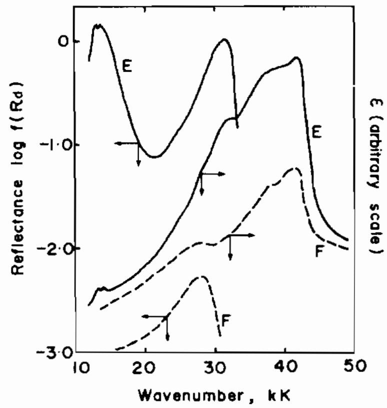

Figure 4, n. 3.

Table III. Electronic spectra of $M_3[Ir(CN)_6]_2 \cdot xH_2O$.

Compound	Band position (kK)	Assignment
$Mn_3[Ir(CN)_6]_2$	27.5	$^1A_{1g}\rightarrow{}^3T_{1g}$
	36.0	$\rightarrow{}^1T_{1g}$
	41.8	$\rightarrow{}^1T_{2g}$
$Fe_3[Ir(CN)_6]_2$	13.0	$^5T_{2g}\rightarrow{}^5E_g$
	27.0	charge-transfer
	30.0	$^1A_{1g}\rightarrow{}^3T_{1g}$
	37.2	$\rightarrow{}^1T_{1g}$
	41.2	$\rightarrow{}^1T_{2g}$
$Co_3[Ir(CN)_6]_2$	16.8	$^4T_{1g}\rightarrow{}^4A_{2g}$(?)
	19.8	$\rightarrow{}^4T_{1g}$(P)
	29.8	$^1A_{1g}\rightarrow{}^3T_{1g}$
	37.0	$\rightarrow{}^1T_{1g}$
	40.8	$\rightarrow{}^1T_{2g}$
$Ni_3[Ir(CN)_6]_2$	14.2	$^3A_{2g}\rightarrow{}^1E_g$(?)
	16.4	$\rightarrow{}^3T_{1g}$(F)
	27.0	$\rightarrow{}^3T_{1g}$(P)
	30.0	$^1A_{1g}\rightarrow{}^3T_{1g}$
	37.0	$\rightarrow{}^1T_{1g}$
	41.6	$\rightarrow{}^1T_{2g}$
$Cu_3[Ir(CN)_6]_2$	13.4	$^2E_g\rightarrow{}^2T_{2g}$
	13.8	
	31.4	$^1A_{1g}\rightarrow{}^3T_{1g}$
	38.2	$\rightarrow{}^1T_{1g}$
	41.6	$\rightarrow{}^1T_{2g}$
$Zn_3[Ir(CN)_6]_2$	27.8	$^1A_{1g}\rightarrow{}^3T_{1g}$
	37.0	$\rightarrow{}^1T_{1g}$
	41.6	$\rightarrow{}^1T_{2g}$

not placed in the octahedral field in an exact sense. Nevertheless it is assumed that M^{II} is situated to a first approximation in the octahedral environment made up of the nitrogen ends of cyanide ligands and the oxygen atoms of water molecules since the former is located near the latter in the spectrochemical series. The d-d transitions of the visible region were assigned on the basis of this assumption and the individual assignments are summarized in Table III. The ligand field splitting parameter 10Dq has been calculated 12,000 to 14,000 cm^{-1} from the position of the d-d transitions. These values are slightly larger than $10Dq = 9{,}500 \sim 11{,}000$ cm^{-1} estimated for $KNi[Co(CN)_6]$ by Shriver *et al.*[14] The above assignments of the d-d transitions is based on the idea that M^{II} is situated in the octahedral weak field. This point of view is in good agreement with the results of the effective Bohr magneton calculated per M^{II} of $M_3[Ir(CN)_6]_2 \cdot xH_2O$ using the magnetic susceptibilities at room temperature (Table I).

The absorption bands of the ultraviolet region can be readly assigned on the basis of the fact that Ir^{III} is situated in the octahedral strong field. The relatively weak band commonly observed for $M_3[Ir(CN)_6]_2 \cdot xH_2O$ in the range 28.0 to 31.5 kK is assigned to the spin-forbidden transition ${}^1A_{1g} \rightarrow {}^3T_{1g}$. The strong absorption bands observed around 36.5 and 41.5 kK are assigned to the spin-allowed transitions ${}^1A_{1g} \rightarrow {}^1T_{1g}$ and ${}^1A_{1g} \rightarrow {}^1T_{2g}$, respectively. The 10Dq value produced by the carbon ends of cyanide ligands can be calculated from the energies of two spin-allowed and spin-forbidden transitions. According to the strong field theory for the d^6 electronic configuration, the transition energies are related to the parameters as follows:

$$E({}^1A_{1g} \rightarrow {}^3T_{1g}) = 10Dq - 3C$$

$$E({}^1A_{1g} \rightarrow {}^1T_{1g}) = 10Dq - C$$

$$E({}^1A_{1g} \rightarrow {}^1T_{2g}) = 10Dq + 16B - C$$

where the $B^2/10Dq$ factor is ignored in view of the large values of 10Dq and small values of B commonly observed. The parameter 10Dq which is calculated from the above Formula using the experimental data listed in Table III ranges from 40.0 to 41.0 kK ($B = 200 \sim 370$ cm^{-1} and $C = 3.6 \sim 4.0$ kK). This value is comparable with $10Dq = \sim 42.3$ kK which was estimated for the parent complex $K_3[Ir(CN)_6]$ by Alexander and Gray.[18]

The iron compound $Fe_3[Ir(CN)_6]_2 \cdot 20H_2O$ exhibits an intense absorption band at 25 kK. This band can be assigned to the charge-transfer band of the following type

$${}^5T_{2g}Fe^{II} + {}^1A_{1g}Ir^{III} \rightarrow {}^6S_gFe^{III} + {}^2E_gIr^{II}$$

which was first proposed for Prussian blue by Robin[19] and later extended to Prussian blue analogs by Braterman.[20] The iron compound alone gives particularly the above type of charge-transfer band in the lower wavenumber region. This may be attributable to the lower ionization potential from ferrous to ferric ion as compared with that of the other ions from M^{II} to M^{III}.

In summary, the coordination polymers of the type $M_3[Ir(CN)_6]_2 \cdot xH_2O$ have a face-centered cubic unit cell characteristic of the Prussian blue analogs. In these compounds the carbon ends of cyanide ligands coordinate strongly to Ir^{III} to form a strong ligand field, whereas the nitrogen ends do weakly to M^{II} together with water molecules to form a weak ligand field. Thereby the cyanide ligand plays a role of bridged groups in these coordination polymers.

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