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BONDING NATURE
OF COORDINATION POLYMERS, $\text{KM}[\text{Co}(\text{CN})_6]$

BY

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BONDING NATURE OF COORDINATION POLYMERS, $\text{KM}[\text{Co}(\text{CN})_6]$

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ABSTRACT

All the coordination polymers of the type $\text{KM}[\text{Co}(\text{CN})_6]$, where M is Mn, Fe, Co, Ni, Cu or Zn, have the same face-centered cubic unit cell as that of Prussian blue analogs. The lattice constants increase with the decrease of the crystal field stabilization energy of $\text{M}(\text{II})$ ion in the octahedral weak field. Both $\text{C}\equiv\text{N}$ and $\text{Co}-\text{C}$ stretching vibrations are shifted to the higher frequency side as compared with those of simple cyanide complex $\text{K}_3[\text{Co}(\text{CN})_6]$. This phenomenon is explained in terms of the linkage structure of cyanide ligand. Magnetic susceptibility data and electronic spectra indicate that the $\text{M}(\text{II})$ coordinated by the nitrogen ends of cyanide ligands is high spin state and in the octahedral weak field while the carbon-coordinated $\text{Co}(\text{III})$ is low spin state and in the octahedral strong field.

INTRODUCTION

A variety of hexacyanometalate ions react with first row transition metal ions to form such coordination polymers that cyanide ligands play a role of bridged group. Prussian blue, a well-noted blue dye, is counted among these compounds. Since KEGGIN and MILES (1936) reported that it has a face-centered cubic unit cell (Fig. 1), many subsequent investigators have studied a number of isomorphous compounds with it (SHRIVER 1966; BEASLEY 1968). In spite of many reports on compounds of the type $\text{M}_3[\text{Co}(\text{CN})_6]_2$ (VACIAGO and MUGNOLI, 1958; MAER, BEASLEY, et al. 1968; LUDI, GÜDEL, et al. 1970), there have been few examples concerning $\text{KM}[\text{Co}(\text{CN})_6]$ obtained by the reaction of hexacyanocobaltate(III) ion with divalent transition metal ion $\text{M}(\text{II})$. Moreover, except for several reports (SHRIVER, SHRIVER, et al. 1965; BROWN and SHRIVER, 1969), most of them deal with the results of a

single method, e.g., infrared spectra or electronic spectra.

It is the purpose of the present work to describe collectively the bonding nature of $\text{KM}[\text{Co}(\text{CN})_6]$ on the basis of the results of X-ray powder pattern, magnetic susceptibility, infrared and electronic spectra.

EXPERIMENTAL

Preparation of Compounds. Potassium hexacyanocobaltate(III) $\text{K}_3[\text{Co}(\text{CN})_6]$ was prepared by the published method (BIGELOW 1946) and recrystallized three times from water. The chlorides and sulfates of the divalent first row transition metals used were reagent grade. The compounds of the type $\text{KM}[\text{Co}(\text{CN})_6]$ were synthesized by the following method: A 0.02 M solution of $\text{K}_3[\text{Co}(\text{CN})_6]$ was added stoichiometrically to a 0.02 M solution of the divalent transition metal salts. The precipitates obtained were decanted several times, filtered or centrifuged, washed with distilled water until the reactions of chloride or sulfate ions turn out negative in the filtrate, and dried to constant weight in an oven at 140°C . When the precipitate was colloidal and hardly sank, organic solvents such as ethyl or methyl alcohols were added to the solution in order to prevent it from forming a gelatinous precipitate. Since certain compounds obtained were extremely sensitive to the atmospheric moisture, they were handled in a nitrogen-filled glove bag and exposure to air was minimized in the whole operations. The identity and purity of the dry compounds were checked by the analysis of metal contents. The results were as follows: Found: Co, 19.1; Mn, 17.6%. Calcd for $\text{KMn}[\text{Co}(\text{CN})_6]$: Co, 19.07; Mn, 17.77%. Found: Co, 19.0; Fe, 18.7%. Calcd for $\text{KFe}[\text{Co}(\text{CN})_6]$: Co, 19.01; Fe, 18.02%. Found: Co, 36.0%. Calcd for $\text{KCo}[\text{Co}(\text{CN})_6]$: Co, 37.65%. Found: Co, 17.5; Ni, 19.0%. Calcd for $\text{KNi}[\text{Co}(\text{CN})_6]$: Co, 18.84; Ni, 18.77%. Found: Co, 17.8; Cu, 18.9%. Calcd for $\text{KCu}[\text{Co}(\text{CN})_6]$: Co, 18.56; Cu, 20.01%. Found: Co, 19.0; Zn, 21.1%. Calcd for $\text{KZn}[\text{Co}(\text{CN})_6]$: Co, 18.46; Zn, 20.47%.

X-ray Diffraction. The X-ray diffraction patterns of the powdered samples were measured with a Rigaku-Denki X-ray diffractometer. The lattice constants were determined using the manganese-filtered Fe K_α -radiation: $1.936 \text{ \AA}$, and NaCl as an internal standard.

Magnetic Measurement. The magnetic susceptibilities were determined at room temperature by the Gouy method in a heterogenous magnetic field with a field strength of about 10 k Gauss. The Gouy tubes were calibrated with $\text{Hg}[\text{Co}(\text{NCS})_4]$ (16.44×10^{-6} at 20.0°C) as a standard (FIGGIS and NYHOLM, 1958). The diamagnetic corrections were calculated using the Pascal constants (LEWIS and WILKINS, 1960).

Infrared Spectrum. The infrared spectra were obtained from mull in Nujol and KBr disk with a Hitachi EPI infrared spectrophotometer, which was equipped with sodium chloride or potassium bromide prisms. The wavenumbers were calibrated using a polystyrene film and frequencies were believed accurate to 3.0 and 4.5 cm^{-1} in the NaCl and KBr prism regions respectively. The frequency data in the present work had been taken from those in the KBr disk method because the difference in both methods could not be appreciable.

Electronic Spectrum. The reflection spectra for the powdered samples were measured using the Hitachi Perkin-Elmer UV-VIS spectrophotometer with the standard integrating sphere attachment and alumina as a reference. The mull transmittance technique was employed for the liquid paraffin suspension of mull samples (COTTON, GOODGAME, et al. 1961).

RESULTS AND DISCUSSION

Lattice Parameters and Magnetic Susceptibilities. The space group of the compounds of the type $\text{KM}[\text{Co}(\text{CN})_6]$ is $\text{O}_h^5\text{-F}_{m3m}$, where 4 Co atoms are placed at the 4a positions, 4 M atoms at the 4b positions, 4 K atoms being statistically distributed at the 32f positions. The absolute position of heavy atoms, such as Co and M, has been determined in terms of the X-ray diffraction analysis, while the position of relatively light atoms like N and C has not been obtained as yet because of their low atomic scattering factors and the poor crystallinity of the compounds. Here we assume that the atomic distances Co-C (1.89 Å) and C-N (1.15 Å) of $\text{K}_3[\text{Co}(\text{CN})_6]$ obtained from the neutron diffraction analysis by CURRY and RUNCIMAN (1952) are kept also in $\text{KM}[\text{Co}(\text{CN})_6]$. This assumption makes it possible for us to calculate the atomic distance M-N in $\text{KM}[\text{Co}(\text{CN})_6]$ by the use of the lattice constants. These calculated atomic distances are summarized in

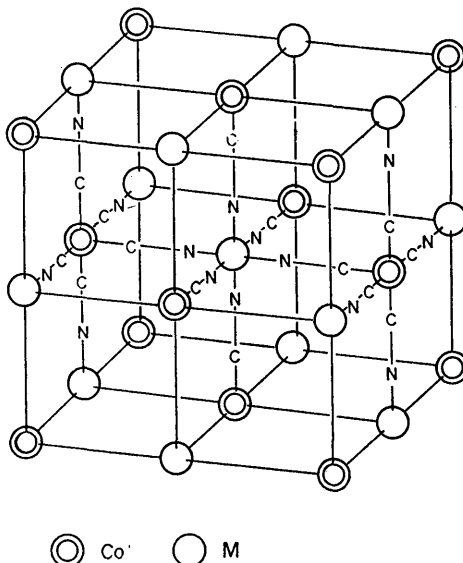


Fig. 1. The unit cell of $\text{KM}[\text{Co}(\text{CN})_6]$. Potassium ions and most of the $\text{C}\equiv\text{N}$ groups are not shown for brevity.

Table 1. Lattice parameters and magnetic moments.

Compound	Lattice constant (Å)	M-N distance (Å)	μ_{eff} (B.M.)
KMn[Co(CN) ₆]	10.43±0.01	2.18	6.14
KFe [Co(CN) ₆]	10.26±0.01	2.09	5.97
KCo [Co(CN) ₆]	10.23±0.01	2.08	5.42
KNi [Co(CN) ₆]	10.22±0.04	2.07	3.38
KCu [Co(CN) ₆]	10.12±0.02	2.02	1.99
KZn [Co(CN) ₆]	10.28±0.01	2.10	diamag.

Table 1. It is very instructive to compare these calculated atomic distances with those obtained in analogous compounds, for example, Ni-N distance; 2.11 Å in Ni(CN)₂NH₃ $\frac{1}{4}$ H₂O (RAYNER and POWELL, 1958), and M-N distance; 2.08–2.21 Å in M₃[Co(CN)₆]₂·12 H₂O (LUDI and GÜDEL, 1968). From this comparison it is proved that our assumption is reasonable and further the distance M-N in KM[Co(CN)₆] is short enough to expect a coordination bonding between them.

The lattice constants of KM[Co(CN)₆] change with the variation of M(II) from Mn(II) to Zn(II). Therein exists a regularity in the order, that is, the lattice constants decrease with the increase of the crystal field stabilization energy of the

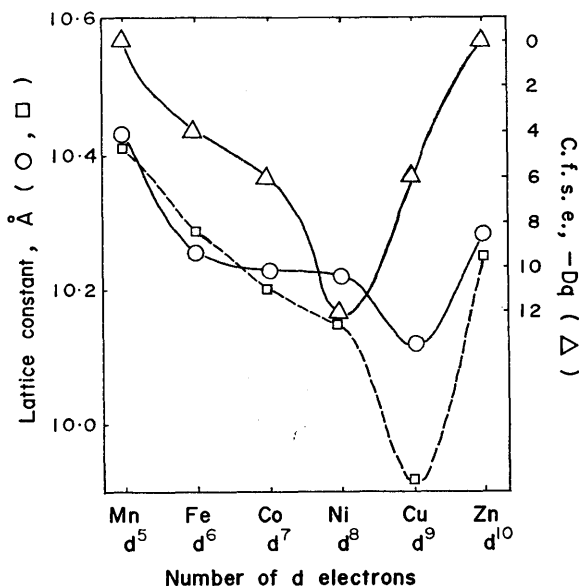


Fig. 2. Lattice constants as compared with crystal field stabilization energies. □: taken from Ref. (FERRARI et al., 1959).

$\text{M}(\text{II})$ ion in the octahedral weak field. This tendency is illustrated in Fig. 2., where the lattice constants of $\text{M}_3[\text{Co}(\text{CN})_6]_2 \cdot 12 \text{H}_2\text{O}$ reported by FERRARI et al. (1959) are also plotted for comparison. An abnormally small lattice constant of $\text{KCu}[\text{Co}(\text{CN})_6]$ may result from the stabilization of $\text{Cu}(\text{II})$ ion in the nitrogen hole* on account of the dynamic Jahn Teller effect (SCHLÄFER and GLIEMANN, 1969). This is supported by the fact that no influence of the descent in symmetry has been observed on the crystallographic separations at room temperature in spite of the splitting of the d-d band which occurred in the visible region.

The effective Bohr magneton, μ_{eff} , per formula unit $\text{KM}[\text{Co}(\text{CN})_6]$ was calculated using the average magnetic susceptibilities obtained from several measurements. The results are listed in Table 1. The calculated values for $\text{KCo}[\text{Co}(\text{CN})_6]$, $\text{KNi}[\text{Co}(\text{CN})_6]$ and $\text{KCu}[\text{Co}(\text{CN})_6]$ are slightly higher as compared with those reported by RICHARDSON et al. (1940) and CsÁSZÁR et al. (1966). Further the values for the other compounds are also somewhat larger than those expected for the usual high spin $\text{M}(\text{II})$ ion in the octahedral weak field. However, this difference is not so large as to lead to other conclusion. The magnetic susceptibility data and the dependence of the lattice constants on the crystal field stabilization energy in the octahedral weak field lead to the following conclusion: The $\text{M}(\text{II})$ ion in the nitrogen hole (4b position) is in the octahedral weak field and high spin state. On the other hand, the $\text{Co}(\text{III})$ ion in the carbon hole (4a position) is in the octahedral strong field and low spin state.

Infrared Spectra. The infrared spectra of $\text{KM}[\text{Co}(\text{CN})_6]$ have exhibited a characteristic $\text{C}\equiv\text{N}$ stretching band and a variety of combination bands in the NaCl region. As shown in Table 2., the $\text{C}\equiv\text{N}$ stretching frequencies are shifted to the higher frequency side by 30–40 cm^{-1} as compared with that of the potassium hexacyanocobaltate(III) $\text{K}_3[\text{Co}(\text{CN})_6]$. The following two reasons are considered for the shifting of the $\text{C}\equiv\text{N}$ stretching frequencies. One, pointed out by Dows et al. (1961), is that bridged cyanide groups give a higher absorption frequency against terminal cyanide groups because the presence of a second metal atom $\text{M}(\text{II})$ constrains the motion of cyanide groups. The other is an inductive effect that the $\text{M}(\text{II})$, coordinated by the nitrogen end of cyanide groups, withdraws electric charge accumulated on the central metal ion $\text{Co}(\text{III})$ through the cyanide groups and consequently the $\text{C}\equiv\text{N}$ stretching frequency increases.

In Table 2. are listed several combination bands observed for $\text{KM}[\text{Co}(\text{CN})_6]$ in appreciable intensities. In order to assign these combination bands it is very convenient to make use of the results of the normal coordinate analysis carried out with $\text{K}_3[\text{Co}(\text{CN})_6]$ by NAKAGAWA et al. (1962) and JONES (1962; 1964). According to them there are two types of combination bands in $\text{K}_3[\text{Co}(\text{CN})_6]$. One comes from the combination of the $\text{C}\equiv\text{N}$ stretching vibration with $\text{Co}-\text{C}$ stretching or $\text{Co}-\text{CN}$ bending vibrations. For example, the combinations, $\nu_2 + \nu_6$, $\nu_3 + \nu_8$, $\nu_3 + \nu_7$, etc.** , belong to this type. The other originates from the combination of two

* Metal ions $\text{Co}(\text{III})$ and $\text{M}(\text{II})$ are placed in two types of sites: carbon "hole", in which the $\text{Co}(\text{III})$ is octahedrally coordinated by the carbon end of cyanide, nitrogen hole in which the $\text{M}(\text{II})$ is octahedrally coordinated by the nitrogen end of cyanide.

** The number of the frequencies and character of vibrations is the same as that given in Ref. (JONES 1962).

Co-C stretching vibrations, Co-C stretching and Co-CN bending vibrations, or two Co-CN bending vibrations such as $\nu_2 + \nu_6$, $\nu_3 + \nu_8$, $\nu_3 + \nu_7$, etc. This type of combination band was observed in the range 870 to 970 cm^{-1} . The assignment of the combination band in $\text{KM}[\text{Co}(\text{CN})_6]$ is simplified because the ν_8 vibration (Co-CN bending) should be weakened on account of the linkage structure, $\text{Co-C}\equiv\text{N-M}(\text{II})$. Therefore, the following assignment is possible: For the first type the combination bands observed in the range 2630 to 2854 cm^{-1} may be assigned to $\nu_2(\text{CN}) + \nu_6(\text{CoC})$ vibrations, and those observed around 2920 cm^{-1} are attributable to $\nu_3(\text{CN}) + \nu_7(\text{CoC})$ or $\nu_1(\text{CN}) + \nu_7(\text{CoC})$. For the second type the combination bands assigned to $\nu_4(\text{CoC}) + \nu_7(\text{CoC})$ have been observed in the range 915 to 935 cm^{-1} for each compound. The assignments of individual absorption frequencies are given in Table 2.

Table 2. Infrared spectra of $\text{KM}[\text{Co}(\text{CN})_6]$ (cm^{-1})

Compound	C $\equiv$ N str. ν_8	Co-C str. ν_7	Combination band		
			$\nu_3 + \nu_7$ or $\nu_1 + \nu_7$	$\nu_2 + \nu_6$	$\nu_4 + \nu_7$
$\text{KMn}[\text{Co}(\text{CN})_6]$	2155 ^{vs}	440 ^s	2925 ^{vw}	2630 ^{vw}	917 ^w
$\text{KFe}[\text{Co}(\text{CN})_6]$	2165 ^{vs}	464 ^s	2925 ^{vw}	2850 ^{vw}	929 ^w
$\text{KCo}[\text{Co}(\text{CN})_6]$	2168 ^{vs} , 2125 ^{sh}	450 ^s	2924 ^{vw}	2854 ^{vw}	928 ^w
$\text{KNi}[\text{Co}(\text{CN})_6]$	2164 ^{vs} , 2124 ^{sh}	482 ^s	2915 ^{vw}	2844 ^{vw}	935 ^w
$\text{KCu}[\text{Co}(\text{CN})_6]$	2169 ^{vs} , 2134 ^{sh}	460 ^s			930 ^{vw}
$\text{KZn}[\text{Co}(\text{CN})_6]$	2164 ^{vs}	447 ^s		2654 ^{vw}	920 ^w

Abbreviation: str, stretching; vs, very strong; s, strong; w, weak; vw, very weak; sh, shoulder.

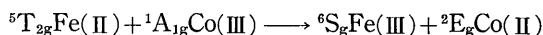
On the other hand, a few absorption bands occurred in the far infrared region, where are usually expected a variety of metal-ligand stretching and bending vibrations. However, as mentioned above, the bending vibration ν_8 should be weakened in $\text{KM}[\text{Co}(\text{CN})_6]$. Consequently the broad bands observed around 450 cm^{-1} can be assigned to Co-C stretching vibration. It is noticed again that the frequency of these absorption bands is shifted to higher frequency side compared with that of $\text{K}_3[\text{Co}(\text{CN})_6]$ obtained at 416 cm^{-1} by JONES (1963). This indicates that the Co-C bond becomes stronger on the formation of the coordination polymers $\text{KM}[\text{Co}(\text{CN})_6]$ from $\text{K}_3[\text{Co}(\text{CN})_6]$. In this case the strengthening of the Co-C bond would be caused by the increase of σ -bonding character rather than π -bonding one because the contribution of the so-called back bonding from the d_π orbitals of $\text{Co}(\text{III})$ to the ligand antibonding π^* orbitals tends to decrease the C $\equiv$ N stretching frequency.

Electronic Spectra. The diffuse reflection and mull transmittance spectra of $\text{KM}[\text{Co}(\text{CN})_6]$ were measured in the visible and ultraviolet regions. The typical

spectra are shown in Fig. 3, where occur various types of absorption maxima assigned to the d-d and charge-transfer bands. As described in the preceding sections, $\text{KM}[\text{Co}(\text{CN})_6]$ is composed of high spin $\text{M}(\text{II})$ in the nitrogen hole and low spin $\text{Co}(\text{III})$ in the carbon hole. Hence, it is convenient to classify its electronic spectrum into the following three types: The first type appears ordinarily in the visible region and originates from the $\text{M}(\text{II})$ ion in the nitrogen hole, the second is located mainly in the ultraviolet region and comes from the $\text{Co}(\text{III})$ ion in the carbon hole, and the third results from the charge-transfer between $\text{M}(\text{II})$ and $\text{Co}(\text{III})$. As for the first type the electronic spectra of $\text{KCo}[\text{Co}(\text{CN})_6]$, $\text{KNi}[\text{Co}(\text{CN})_6]$ and $\text{KCu}[\text{Co}(\text{CN})_6]$ have been reported in the range 9,000 to 30,000 cm^{-1} by Császár et al. (1966). Moreover, on the basis of the mull transmittance spectra of $\text{KNi}[\text{Co}(\text{CN})_6]$, SHRIVER et al. (1965) have shown that the nitrogen end of cyanide is situated near below NH_3 on the spectrochemical series and its Δ value ranges between 9,500 and 10,100 cm^{-1} . Therefore, the spectra classified into the first type, except for that of $\text{KCu}[\text{Co}(\text{CN})_6]$, will not be discussed here in detail. The d-d band of the $\text{Cu}(\text{II})$ in $\text{KCu}[\text{Co}(\text{CN})_6]$ has a strong resemblance to that of the aquo complex in both shape and position. The symmetry of the nitrogen-coordinated $\text{Cu}(\text{II})$ ion must be distorted from the complete octahedral one. As pointed out in the preceding section, this distortion has not been found crystallographically but the observed d-d band is splitted into two peaks (Fig. 3.). This gives a strong evidence for the dynamic Jahn Teller effect.

For the second type, two spin-allowed d-d bands assignable to the transitions $^1\text{A}_{1g} \rightarrow ^1\text{T}_{1g}$ and $^1\text{T}_{2g}$ were observed for each compound of the type $\text{KM}[\text{Co}(\text{CN})_6]$ in the ultraviolet region. On the basis of the MO calculation, GRAY et al. (1963) have assigned two bands of $\text{K}_3[\text{Co}(\text{CN})_6]$ observed at 32,050 and 38,460 cm^{-1} to the transitions $^1\text{A}_{1g} \rightarrow ^1\text{T}_{1g}$ and $^1\text{A}_{1g} \rightarrow ^1\text{T}_{2g}$, respectively. Both of the spin-allowed transitions of $\text{KM}[\text{Co}(\text{CN})_6]$ are shifted to higher frequency side compared with those of $\text{K}_3[\text{Co}(\text{CN})_6]$ (This is here referred to as blue shift). The blue shift of the spin-allowed bands is compatible with the explanation of the preceding section that the Co-C bond is strengthened by the presence of the $\text{M}(\text{II})$ at the nitrogen end of cyanide ligand and the increase of the σ -bonding character contributes to the strengthening of the Co-C bond. This indicates that the blue shift of the spin-allowed bands is caused by an elevation of the energy level of the antibonding $e_g^*(\sigma)$ orbitals rather than a lowering in that of the bonding $t_{2g}(\pi)$ orbitals. In addition a spin-forbidden weak band assignable to the transition $^1\text{A}_{1g} \rightarrow ^3\text{T}_{1g}$ of the $\text{Co}(\text{III})$ ion in the carbon hole was observed in the range 26,000—30,000 cm^{-1} . This band makes it possible to calculate the Δ value in the carbon hole. The calculated Δ value for $\text{KM}[\text{Co}(\text{CN})_6]$ ranges from 36,800 to 39,300 cm^{-1} ($\text{B}=256\text{--}363\text{ cm}^{-1}$ and $\text{C}=2,300\text{--}4,300\text{ cm}^{-1}$), which is larger than $\Delta=34,800\text{ cm}^{-1}$ obtained for $\text{K}_3[\text{Co}(\text{CN})_6]$ (GRAY and BEACH, 1963) and 35,900 cm^{-1} estimated for $\text{KM}[\text{Co}(\text{CN})_6]$ using the strong field model (BRATERMAN 1966). The increase of the Δ value is a general trend accompanied by the formation of coordination polymers containing bridged cyanide groups from the simple hexacyanometalate ions.

As regards the third type, in $\text{KFe}[\text{Co}(\text{CN})_6]$ an intense absorption band attributable to the charge-transfer



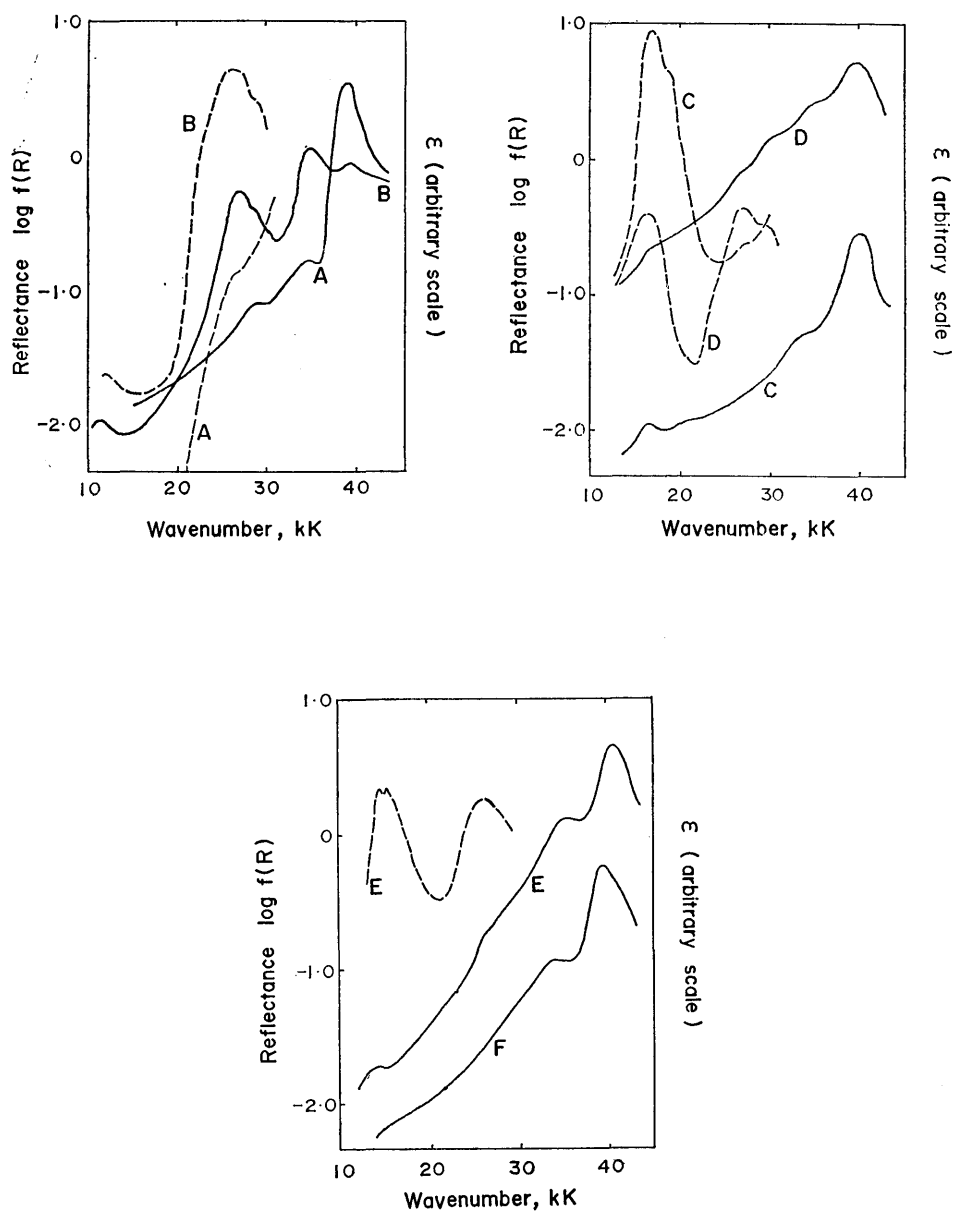
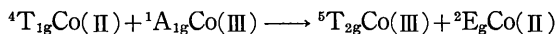


Fig. 3. Reflection spectra (---) and mull transmittance spectra (—) of KM[Co(CN)₆]. A, KMn[Co(CN)₆]; B, KFe[Co(CN)₆]; C, KCo[Co(CN)₆]; D, KNi[Co(CN)₆]; E, KCu[Co(CN)₆]; F, KZn[Co(CN)₆].

Table 3. Electronic spectra of $\text{KM}[\text{Co}(\text{CN})_6]$

Compound	Band position (kK)	Assignment
$\text{KMn}[\text{Co}(\text{CN})_6]$	28.5	$^1\text{A}_{1g} \rightarrow ^3\text{T}_{1g}$
	34.5	$\rightarrow ^1\text{T}_{1g}$
	38.8	$\rightarrow ^1\text{T}_{2g}$
$\text{KFe} [\text{Co}(\text{CN})_6]$	11.2	$^5\text{T}_{2g} \rightarrow ^5\text{E}_g$
	26.5	charge transfer
	28.2	$^1\text{A}_{1g} \rightarrow ^3\text{T}_{1g}$
	34.8	$\rightarrow ^1\text{T}_{1g}$
	38.9	$\rightarrow ^1\text{T}_{2g}$
$\text{KCo} [\text{Co}(\text{CN})_6]$	17.0	charge transfer
	19.0	$^4\text{T}_{1g} \rightarrow ^4\text{T}_{1g}(\text{P})$
	27.0	$^1\text{A}_{1g} \rightarrow ^3\text{T}_{1g}$
	34.9	$\rightarrow ^1\text{T}_{1g}$
	40.0	$\rightarrow ^1\text{T}_{2g}$
$\text{KNi} [\text{Co}(\text{CN})_6]$	16.5	$^3\text{A}_{2g} \rightarrow ^3\text{T}_{1g}(\text{F})$
	27.0	$\rightarrow ^3\text{T}_{1g}(\text{P})$
	30.0	$^1\text{A}_{1g} \rightarrow ^3\text{T}_{1g}$
	34.5	$\rightarrow ^1\text{T}_{1g}$
	39.0	$\rightarrow ^1\text{T}_{2g}$
$\text{KCu} [\text{Co}(\text{CN})_6]$	14.9	$^2\text{E}_g \rightarrow ^2\text{T}_{2g}$
	15.5	
	26.5	$^1\text{A}_{1g} \rightarrow ^3\text{T}_{1g}$
	35.0	$\rightarrow ^1\text{T}_{1g}$
	40.8	$\rightarrow ^1\text{T}_{2g}$
$\text{KZn} [\text{Co}(\text{CN})_6]$	34.5	$^1\text{A}_{1g} \rightarrow ^1\text{T}_{1g}$
	39.0	$\rightarrow ^1\text{T}_{2g}$

was observed at $26,500\text{ cm}^{-1}$. In this region the spin-forbidden transition $^1\text{A}_{1g} \rightarrow ^3\text{T}_{1g}$ is to be expected, but in this case the absorption intensity observed is too high to be assigned to the spin-forbidden transition. Therefore, the above intense band was assigned to this type of charge-transfer transition, which was first proposed for Prussian blue by ROBIN (1962) and later extended to other Prussian blue analogs by BRATERMAN (1966). $\text{KCo}[\text{Co}(\text{CN})_6]$ showed also the same type of charge-transfer



at the lower frequency position $17,000\text{ cm}^{-1}$. SHRIVER et al. (SHRIVER and BROWN, 1969) associated the corresponding intense band of dry $\text{Co}_3[\text{Co}(\text{CN})_6]_2$ with the interstitial $\text{Co}(\text{II})$ ions (at 8c positions) capable of forming π -type complex. However, no such interstitial ions are present in $\text{KCo}[\text{Co}(\text{CN})_6]$ and consequently the

band observed at $17,000\text{ cm}^{-1}$ is assigned to the above type of charge-transfer transition.

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