

Preparation, and Thermal and Electronic Properties of Double Complex Salts and Cyanide-bridged Complexes Containing Cationic Copper(II) Complexes and Hexacyanoferrate(II) Ion

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Reaction of copper(II) ion with hexacyanoferrate(II) ion, $[\text{Fe}(\text{CN})_6]^{4-}$, in an aqueous solution containing such an amine as en (1,2-ethanediamine), tn (1,3-propanediamine), dien (bis(2-aminoethyl)amine), or dpt (bis(3-aminopropyl)amine), gave two types of complexes: Double complex salts, $[\text{Cu}(\text{en or tn})_2][\text{Fe}(\text{CN})_6] \cdot n\text{H}_2\text{O}$ ($n=5-8$), and cyanide-bridged complexes, $[(\text{Cu}(\text{dien or dpt}))_2(\text{NC})_2\text{Fe}(\text{CN})_4] \cdot 4\text{H}_2\text{O}$. The infrared spectra of the complexes in the ν_{CN} region revealed that the complexes, $[(\text{Cu}(\text{dien or dpt}))_2(\text{NC})_2\text{Fe}(\text{CN})_4] \cdot 4\text{H}_2\text{O}$, contain cyanide bridges, while in $[\text{Cu}(\text{en or tn})_2][\text{Fe}(\text{CN})_6] \cdot n\text{H}_2\text{O}$, no cyanide bridge is present. The thermal reactions of the complexes in the solid state were investigated by means of derivatography under dynamic conditions (D conditions). It was found that dehydration from $[\text{Cu}(\text{en})_2][\text{Fe}(\text{CN})_6] \cdot n\text{H}_2\text{O}$ resulted in formation of cyanide bridge in the apical position of square planer $[\text{Cu}(\text{en})_2]^{2+}$. For $[(\text{Cu}(\text{dien or dpt}))_2(\text{NC})_2\text{Fe}(\text{CN})_4] \cdot 4\text{H}_2\text{O}$, dehydration resulted in the formation of additional cyanide bridges. All the complexes showed metal to metal (iron(II) to copper(II)) charge-transfer transitions (MMCT) in the near ultraviolet or visible region. The complexes, $[\text{Cu}(\text{en or tn})_2][\text{Fe}(\text{CN})_6] \cdot n\text{H}_2\text{O}$, exhibited the outer sphere iron(II) to copper(II) charge-transfer bands (OSMMCT) in the near ultra-violet region. $[(\text{Cu}(\text{dien or dpt}))_2(\text{NC})_2\text{Fe}(\text{CN})_4] \cdot 4\text{H}_2\text{O}$ and the dehydrated complexes prepared by thermal reaction showed the inner-sphere iron(II) to copper(II) charge transfer bands (ISMMCT) in the visible region. A good correlation was observed between the energies of the MMCT and the d-d band maxima of copper(II) ions.

Reaction of various metal ions with $[\text{Fe}(\text{CN})_6]^{4-}$ forms a series of Prussian Blue type complexes which have cyanide-bridged structure and are polymeric in nature.¹⁻⁴ It is also known that $[\text{Fe}(\text{CN})_6]^{4-}$ forms cation-anion ion pair with various cationic complexes in solution and they tend to form so called double complex salts or cyanide-bridged complexes which consist of discrete structural units.⁵⁻⁷ These complexes are of particular interest in studying the electron-transfer phenomena in the solid state. Unfortunately, no well characterized complex has been known except for those containing cationic Ru^{III} complexes as counter part or counter ion.⁵⁻⁷ Further studies are needed for advanced elucidation of the solid state electron transfer of metal complexes. In this study, we prepared new double complex salts and cyanide-bridged complexes containing cationic copper(II) complexes and hexacyanoferrate(II) anion, $[\text{Cu}(\text{en or tn})_2][\text{Fe}(\text{CN})_6] \cdot n\text{H}_2\text{O}$ ($n=5-8$) and $[(\text{Cu}(\text{dien or dpt}))_2(\text{NC})_2\text{Fe}(\text{CN})_4] \cdot 4\text{H}_2\text{O}$, where en represents 1,2-ethanediamine, tn 1,3-propanediamine, dien bis(2-aminoethyl)amine, and dpt bis(3-aminopropyl)amine. Their structures and electronic properties were investigated by means of infrared and electronic spectroscopies.

Uehara *et al.* demonstrated that the thermal reaction of the double complex salts such as $[(\text{Cr or Co})(\text{OH}_2)(\text{NH}_3)_5][(\text{Cr or Co})(\text{CN})_6]$ in the solid state afforded various types of the cyanide-bridged complexes.^{8,9} The thermal cyanide-bridging reactions are highly dependent on the nature of the metal ions contained in the cationic and anionic moieties. It is well known that the stereochemistry of the copper(II) complexes is flexible with respect to the coordination number and geometry.¹⁰ Therefore, the solid state thermal reaction of the present double complex salts and cyanide-bridged complexes containing copper(II) ions is also expected to form various types of cyanide-

bridged complexes. The thermal cyanide-bridging reaction of the present complexes is also one of the subjects of this study.

Experimental

Preparation of Complexes. $[\text{Cu}(\text{en})_2][\text{Fe}(\text{CN})_6] \cdot n\text{H}_2\text{O}$ (**1a**) ($n=5-8$). To a solution of 1 mmol of $\text{K}_4[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$ in 20 cm³ of water was added a solution containing 2 mmol of $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 5 mmol of en in 20 cm³ of water. To the resulting mixture was added 10 cm³ of methanol with stirring. The solution was allowed to stand overnight to give violet crystals, which were collected by filtration, washed with cold water, and air-dried. The complex salt contained 5–8 mol of water depending on the experimental conditions. Found: C, 24.95; H, 6.33; N, 29.45%. Calcd for the penta hydrate $\text{C}_{14}\text{H}_{42}\text{N}_{14}\text{O}_5\text{Cu}_2\text{Fe}$ (MW 669.57): C, 25.11; H, 6.32; N, 29.29%.

$[\text{Cu}(\text{tn})_2][\text{Fe}(\text{CN})_6] \cdot 5\text{H}_2\text{O}$ (**2a**). The complex was prepared in a similar way to that of **1a**. Dark blue crystals were collected by filtration, washed with cold water, and air-dried. Found: C, 29.98; H, 6.92; N, 27.13%. Calcd for $\text{C}_{18}\text{H}_{50}\text{N}_{14}\text{O}_5\text{Cu}_2\text{Fe}$ (MW 725.67): C, 29.79; H, 6.94; N, 27.03%.

$[(\text{Cu}(\text{dien}))_2(\text{NC})_2\text{Fe}(\text{CN})_4] \cdot 4\text{H}_2\text{O}$ (**3a**). To a solution of 1 mmol of $\text{K}_4[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$ in 20 cm³ of water was added a solution containing 2 mmol of $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 2.5 mmol of dien in 20 cm³ of water. After a few minutes dark green crystals began to appear. The crystals deposited were collected by filtration, washed with cold water, and air-dried. Found: C, 27.08; H, 5.57; N, 27.30%. Calcd for $\text{C}_{14}\text{H}_{34}\text{N}_{12}\text{O}_4\text{Cu}_2\text{Fe}$ (MW 617.48): C, 27.23; H, 5.50; N, 27.23%.

$[(\text{Cu}(\text{dpt}))_2(\text{NC})_2\text{Fe}(\text{CN})_4] \cdot 4\text{H}_2\text{O}$ (**4a**). The complex was prepared in a similar way to that of **3a**. Dark green crystals deposited from an aqueous solution turned blue upon drying in air. Found: C, 32.05; H, 6.02; N, 25.13%. Calcd for $\text{C}_{18}\text{H}_{42}\text{N}_{12}\text{O}_4\text{Cu}_2\text{Fe}$ (MW 673.59): C, 32.09; H, 6.29; N, 24.69%.

Dehydrated Complexes. The dehydrated complexes, **1b**, **3b**, and **4b**, were obtained by heating **1a**, **3a**, and **4a**, respectively, for a given period of time at constant temperature with thermobalance (*vide infra*). Since the dehydrated

complexes were hygroscopic more or less, the measurements were carried out as soon as possible after preparations.

Measurements. The thermal reactions of the complexes were traced under dynamic conditions (D conditions) by using MOM Type-OD-102 Derivatograph. The measurements were carried out under a constant flow of nitrogen gas at heating rate of $2^{\circ}\text{C min}^{-1}$. The electronic spectra in solution and nujol mull were measured with a Jasco UVIDEK 505 UV/VIS recording digital spectrophotometer and those in powder on a Hitachi EPU-2A spectrophotometer. Infrared spectra were obtained by a KBr-disk method with a Jasco A-3 infrared spectrophotometer.

The electronic spectra of **1a**, **2a**, and **4a** in aqueous solution were measured by the addition of 0.1 mol equivalent (against Cu^{II} concentration) of the corresponding amine to suppress the formation of reddish brown colloidal suspension, which is probably $\text{Cu}_2[\text{Fe}(\text{CN})_6] \cdot n\text{H}_2\text{O}$. The electronic spectrum of **3a** in an aqueous solution could not be obtained because of its low solubility.

Results and Discussion

Derivatography. The derivatograms of the en complex, **1a**, revealed that the complex contains 5–8 mol of water depending on the preparative conditions. The representative derivatogram of the pentahydrate complex is given in Fig. 1. The TG curve of the complex shows weight loss at $60\text{--}100^{\circ}\text{C}$ and then a clear plateau is obtained. This weight loss corresponds to evolution of water molecules. The dpt complex, **4a**, also shows a similar behavior to that of **1a**: Four moles of water are evolved at $30\text{--}100^{\circ}\text{C}$ and then a clear plateau appears. The appearance of the clear plateaus in the TG curves indicates that the dehydrated complexes of **1a** and **4a** are easily obtained by thermal reaction. For the dien complex, **3a**, the evolution of 4 mol of water is seen up to *ca.* 130°C , immediately followed by a slow successive weight loss. Therefore, it seems difficult to obtain the dehydrated complex in pure state under dynamic conditions. Preliminary experiments, however, show-

ed that the isothermal heating of the complex at 120°C for 5 h gave considerably pure anhydrous complex, which was used for infrared and electronic spectral measurements. The complicated TG curve of the tn complex, **2a**, suggests that it is difficult to obtain the dehydrated complex. All the complexes decomposed in complicated manners after dehydration. Although the decomposition products could not be characterized, the compounds obtained by heating at 200°C for 0.5 h still showed the strong ν_{CN} bands at $2080\text{--}2040\text{ cm}^{-1}$, which are indicative of the presence of $[\text{Fe}(\text{CN})_6]^{4-}$ moiety.¹¹ This implies that the decompositions occur in the Cu^{II} moieties, but not in $[\text{Fe}(\text{CN})_6]^{4-}$ moiety.

It should be noted that the decompositions of

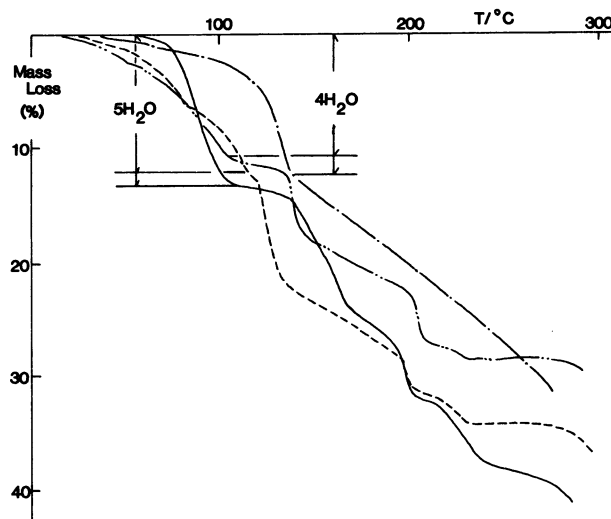


Fig. 1. Derivatograms of $[\text{Cu}(\text{en})_2]_2[\text{Fe}(\text{CN})_6] \cdot 5\text{H}_2\text{O}$ (**1a**) (—), $[\text{Cu}(\text{tn})_2]_2[\text{Fe}(\text{CN})_6] \cdot 5\text{H}_2\text{O}$ (**2a**) (---), $[(\text{Cu}(\text{dien}))_2(\text{NC})_2\text{Fe}(\text{CN})_4] \cdot 4\text{H}_2\text{O}$ (**3a**) (-.-), and $[(\text{Cu}(\text{dpt}))_2(\text{NC})_2\text{Fe}(\text{CN})_4] \cdot 4\text{H}_2\text{O}$ (**4a**) (-.-.-).

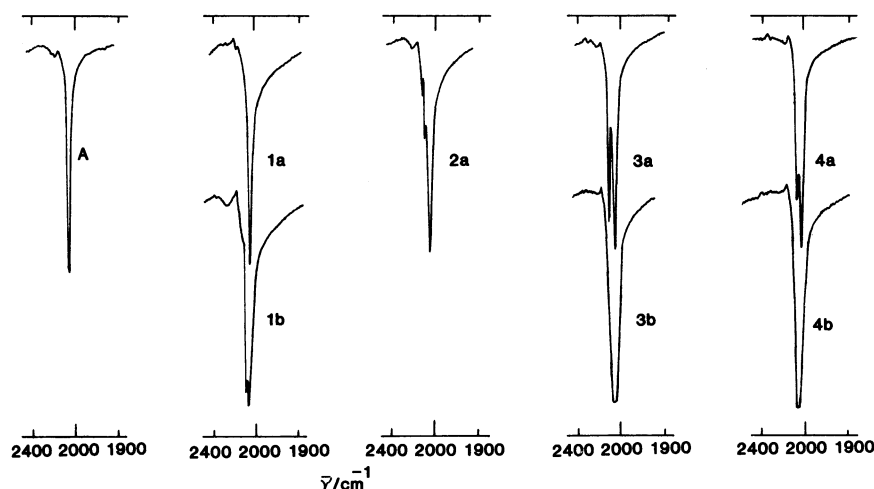


Fig. 2. Infrared spectra of $\text{K}_4[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$ (**A**), $[\text{Cu}(\text{en})_2]_2[\text{Fe}(\text{CN})_6] \cdot 5\text{H}_2\text{O}$ (**1a**), dehydrated complex (**1b**) of **1a**, $[\text{Cu}(\text{tn})_2]_2[\text{Fe}(\text{CN})_6] \cdot 5\text{H}_2\text{O}$ (**2a**), $[(\text{Cu}(\text{dien}))_2(\text{NC})_2\text{Fe}(\text{CN})_4] \cdot 4\text{H}_2\text{O}$ (**3a**), dehydrated complex (**3b**) of **3a**, $[(\text{Cu}(\text{dpt}))_2(\text{NC})_2\text{Fe}(\text{CN})_4] \cdot 4\text{H}_2\text{O}$ (**4a**), and dehydrated complex (**4b**) of **4a**.

$[\text{Cu}(\text{en})_2]^{2+}$ and $[\text{Cu}(\text{tn})_2]^{2+}$ moieties began to take place at *ca.* 140 °C and 120 °C, respectively. $[\text{Cu}(\text{en})_2]\text{SO}_4$ and $[\text{Cu}(\text{tn})_2]\text{SO}_4$ have been shown to be stable up to 250 °C and 200 °C, respectively.¹² It is well known that the thermal stabilities of complexes are highly dependent on the counter ion.¹² Low stabilities of the present complexes may be attributable to an effect of the counter ion, $[\text{Fe}(\text{CN})_6]^{4-}$, *i.e.*, it is likely that coordination ability of nitrogen atom of NC-Fe to copper(II) ion is strong enough to weaken the Cu-en and Cu-tn bonds (*vide infra*). This is in line with the fact that the complexes easily decomposed in an aqueous solution to form reddish brown colloidal suspension, which is probably $\text{Cu}_2[\text{Fe}(\text{CN})_6] \cdot n\text{H}_2\text{O}$.

$[\text{Cu}(\text{en or tn})_2][\text{Fe}(\text{CN})_6] \cdot n\text{H}_2\text{O}$. The infrared spectrum of $[\text{Cu}(\text{en})_2]_2[\text{Fe}(\text{CN})_6] \cdot 5\text{H}_2\text{O}$ is given in Fig. 2. The complex shows a strong ν_{CN} band at 2040 cm^{-1} , which is essentially identical to that of $\text{K}_4[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$. This clearly indicates that no significant interaction is present between $[\text{Cu}(\text{en})_2]^{2+}$ and $[\text{Fe}(\text{CN})_6]^{4-}$ moieties, and the complex can be formulated as double complex salt, $[\text{Cu}(\text{en})_2]_2[\text{Fe}(\text{CN})_6] \cdot 5\text{H}_2\text{O}$. The electronic spectrum of the complex in the solid state exhibits a band at 18300 cm^{-1} and a shoulder at *ca.* 25000 cm^{-1} (Fig. 3). The former band is assigned to the d-d transitions of $[\text{Cu}(\text{en})_2]^{2+}$ moiety. A shoulder at *ca.* 25000 cm^{-1} is not observed in the electronic spectra of the individual complexes, $[\text{Cu}(\text{en})_2]^{2+}$ and $[\text{Fe}(\text{CN})_6]^{4-}$. Therefore, this shoulder can be assigned to the outer sphere metal to metal (iron(II) to copper(II)) charge transfer transition (OSMMCT). The electronic spectrum in water (*ca.* 5×10^{-3} M. (1 M = 1 mol dm^{-3})) exhibits two bands at 17800 cm^{-1} and 31200 cm^{-1} with a very small shoulder at *ca.* 24000 cm^{-1} (Fig. 3). The two bands are due to the d-d transitions of $[\text{Cu}(\text{en})_2]^{2+}$

and $[\text{Fe}(\text{CN})_6]^{4-}$, respectively. The very small shoulder at *ca.* 24000 cm^{-1} is assigned to OSMMCT. Such low intensity of the shoulder is ascribed to the low ion pair formation under the experimental conditions and to the low oscillator strength expected for the OSMMCT.¹³

As was mentioned before, 5 mol of water of **1a** is evolved at 60–100 °C in the solid state. During the dehydration process, the original violet complex turned blue. The dehydrated complex, **1b**, shows two ν_{CN} bands at 2065 cm^{-1} and 2040 cm^{-1} (main band) (Fig. 2). It is well known that if the M-CN group forms a M-CN-M' type bridge, ν_{CN} shifts in a higher wave number region.¹⁴ Thus in the dehydrated complex, Fe-CN-Cu type bridge is formed, *i.e.*, nitrogen atom of NC-Fe coordinates to the apical position of square planer $[\text{Cu}(\text{en})_2]^{2+}$. At the present stage, however, it is not clear whether the cyanide bridges are formed in both of $[\text{Cu}(\text{en})_2]^{2+}$ ions. A coordination to the apical position of square planer copper(II) complex has been known to be weak and termed as "semi-coordination".¹⁵ A splitting of ν_{CN} band of the dehydrated complex, **1b**, (*ca.* 25 cm^{-1}) is much smaller than that of the dien complex, **3a**, (*ca.* 60 cm^{-1}). This smaller splitting of ν_{CN} band of **1b** may be interpreted in terms of a weaker coordination of nitrogen atom of NC-Fe to copper(II) ion (*vide infra*).

The dehydrated complex, **1b**, shows two bands at 17700 cm^{-1} and 23800 cm^{-1} in the solid state (Fig. 3). The former band is assigned to the d-d transitions of $[\text{Cu}(\text{en})_2]^{2+}$ and the latter is ascribed to inner sphere MMCT (ISMMCT). The red shift of the d-d band maximum of Cu^{II} moiety in the dehydrated complex also supports a coordination of nitrogen atom of NC-Fe to the apical position of $[\text{Cu}(\text{en})_2]^{2+}$. Hathaway *et al.* studied the electronic spectra of various $[\text{Cu}(\text{en})_2]\text{X}_2$ type complexes ($\text{X} = \text{Cl}^-, \text{Br}^-, \text{NO}_3^-, \text{etc.}$).¹⁶

The energies of the d-d band maxima of the complexes have been shown to be highly dependent on the degree of interaction between X and $[\text{Cu}(\text{en})_2]^{2+}$ in the apical position. The energy of the band maximum of the hydrated complex, **1a**, is comparable to that of $[\text{Cu}(\text{en})_2](\text{NO}_3)_2$, where NO_3^- ions weakly coordinate to the square planer $[\text{Cu}(\text{en})_2]^{2+}$ in the apical position. Thus it is probable that in the hydrated complex, semi-coordination of water molecules to $[\text{Cu}(\text{en})_2]^{2+}$ in the apical position is present. During the dehydration process, water molecules coordinated are removed and subsequently nitrogen atom of NC-Fe comes into the apical position of $[\text{Cu}(\text{en})_2]^{2+}$. The observed red shift of the d-d band maximum of $[\text{Cu}(\text{en})_2]^{2+}$ moiety upon semi-coordination of nitrogen atom of NC-Fe implies that the ligand field strength of nitrogen atom of NC-Fe is stronger than that of H_2O . A color change from violet to blue was also observed in the solid **1a** on standing it for several days at room temperature without weight loss. This fact suggests that the coordination ability of nitrogen atom of NC-Fe is stronger than that of H_2O .

The tn complex, **2a**, shows a strong ν_{CN} band at 2040 cm^{-1} with two small bands at 2150 and 2080 cm^{-1} (Fig. 2). The small bands may be ascribed not to cyano-

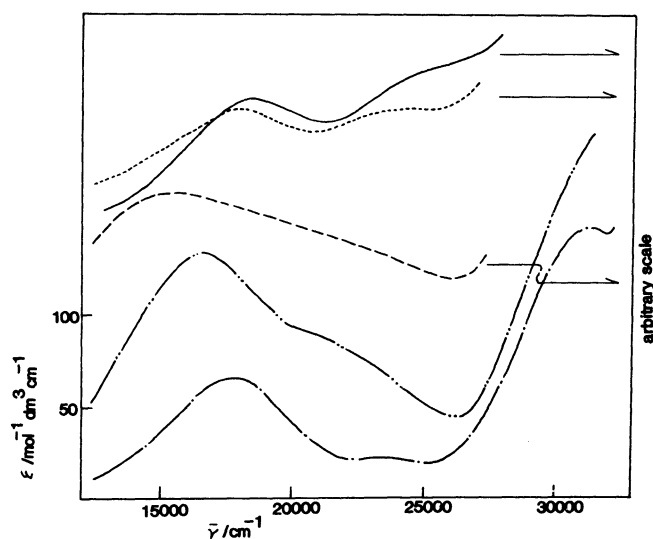


Fig. 3. Nujol mull spectra of $[\text{Cu}(\text{en})_2]_2[\text{Fe}(\text{CN})_6] \cdot 5\text{H}_2\text{O}$ (**1a**) (—), dehydrated complex (**1b**) of **1a** (·····), and $[\text{Cu}(\text{tn})_2]_2[\text{Fe}(\text{CN})_6] \cdot 5\text{H}_2\text{O}$ (**2a**) (----), and absorption spectra of $[\text{Cu}(\text{en})_2]_2[\text{Fe}(\text{CN})_6] \cdot 5\text{H}_2\text{O}$ (**1a**) (—·—) and $[\text{Cu}(\text{tn})_2]_2[\text{Fe}(\text{CN})_6] \cdot 5\text{H}_2\text{O}$ (**2a**) (—·—) in water.

nide bridge, but to lower symmetry of $[\text{Fe}(\text{CN})_6]^{4-}$ moiety in the crystals. Therefore, we believe that no significant interaction between $[\text{Cu}(\text{tn})_2]^{2+}$ and $[\text{Fe}(\text{CN})_6]^{4-}$ moieties is present and the complex can be formulated as double complex salt, $[\text{Cu}(\text{tn})_2][\text{Fe}(\text{CN})_6] \cdot 5\text{H}_2\text{O}$. The electronic spectrum of the complex in the solid state exhibits a very broad band in the visible region, which may be due to an overlapping of the d-d band of $[\text{Cu}(\text{tn})_2]^{2+}$ and OSMCT (Fig. 3). The position of the OSMCT is not clear in this complex. On the other hand, the electronic spectrum in an aqueous solution shows the d-d band of $[\text{Cu}(\text{tn})_2]^{2+}$ at 16700 cm^{-1} and a shoulder at *ca.* 22000 cm^{-1} , which is assigned to the OSMCT.

$[(\text{Cu}(\text{dien or dpt}))_2(\text{NC})_2\text{Fe}(\text{CN})_4] \cdot 4\text{H}_2\text{O}$. The dien complex, **3a**, shows a splitting of ν_{CN} band at 2110 and 2050 cm^{-1} (main band), indicating the presence of cyanide bridge (Fig. 2). A possible structure of this complex is a discrete trinuclear $\text{Cu}-\text{NC}-\text{Fe}-\text{CN}-\text{Cu}$ structure. The splitting of the ν_{CN} (60 cm^{-1}) is much larger than that of the dehydrated en complex, **1b**. Such a large difference in ν_{CN} splitting between **1b** and **3a** seems to be attributable to a strength of copper(II)-nitrogen bonding ($\text{Cu}-\text{NC}-\text{Fe}$), *i.e.*, the stronger the $\text{Cu}-\text{NC}$ bonding, the larger the ν_{CN} splitting. In the case of the en complex, **1b**, nitrogen atom of $\text{NC}-\text{Fe}$ binds to $d_{x^2-y^2}$ orbital of square planar $[\text{Cu}(\text{en})_2]^{2+}$ (out of plane bonding), whereas it is possible that in the dien complex, **3a**, nitrogen atom of $\text{NC}-\text{Fe}$ binds to $d_{x^2-y^2}$ orbital (in plane bonding); the inplane bonding is much stronger than the out of plane bonding.

The complex shows the d-d band maximum of Cu^{II} moiety at 15900 cm^{-1} and the ISMMCT at 22000 cm^{-1} in the solid state (Fig. 4). In general, tridentate ligands such as dien and dpt tend to adopt a meridional form in copper(II) complexes.¹⁷⁾ Although a square planar structure having N_4 (dien and $\text{NC}-\text{Fe}$) donor set might

be a plausible one, the energy of the d-d band maximum of the complex seems to be low for square planar copper(II) complexes with N_4 (dien and $\text{NC}-\text{Fe}$) donor set, and this probably suggests that water molecules coordinate to copper(II) ion to form octahedral or five-coordinate structure. The dehydration from the complex caused a color change from green to blue. For the dehydrated complex, **3b**, the splitting of ν_{CN} disappears and the ν_{CN} band becomes broad (Fig. 2). In the dehydrated complex, two more coordination sites are available for the coordination of $\text{NC}-\text{Fe}$; therefore, it is likely that in the dehydrated complex, additional one or two cyanide bridges are formed and the strength of $\text{Cu}-\text{N}(\text{NC}-\text{Fe})$ bondings are not identical, resulting in an observed broadening of ν_{CN} band because of overlapping of various ν_{CN} bands. The complex may be polymeric. The d-d band of Cu^{II} moiety of the dehydrated complex becomes a shoulder and ISMMCT shifts to red (Fig. 4).

The dpt complex, **4a**, exhibits a splitting of ν_{CN} band (2090 and 2050 cm^{-1} (main band)) (Fig. 2). The splitting (*ca.* 40 cm^{-1}) is, however, smaller than that of the dien complex (*ca.* 60 cm^{-1}). This implies that the coordination of $\text{NC}-\text{Fe}$ to Cu^{II} ion is weaker than that in the dien complex **3a**, *i.e.*, cyanide bridge seems to occur in the apical position. The dpt complex is soluble in water, whereas the dien complex is insoluble at all. This remarkable difference in solubility may reflect a change in structure. This would be reconciled with the result derived from the above infrared spectra.

The bands at 15300 and 19400 cm^{-1} are ascribed to the d-d transitions of Cu^{II} moiety and the ISMMCT, respectively (Fig. 4). The fact that the dpt complex shows the d-d band in lower energy side than the dien complex is attributable to weaker ligand field strength of dpt than that of dien. In the dehydrated complex, **4b**, the splitting of ν_{CN} also disappears

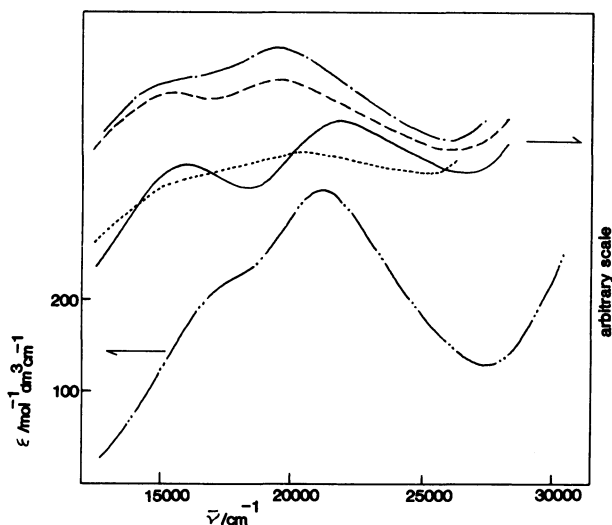


Fig. 4. Nujol mull spectra of $[(\text{Cu}(\text{dien}))_2(\text{NC})_2\text{Fe}(\text{CN})_4] \cdot 4\text{H}_2\text{O}$ (**3a**) (—), dehydrated complex (**3b**) of **3a** (.....), $[(\text{Cu}(\text{dpt}))_2(\text{NC})_2\text{Fe}(\text{CN})_4] \cdot 4\text{H}_2\text{O}$ (**4a**) (---), and dehydrated complex (**4b**) of **4a** (-.-), and absorption spectrum $[(\text{Cu}(\text{dpt}))_2(\text{NC})_2\text{Fe}(\text{CN})_4] \cdot 4\text{H}_2\text{O}$ (-.-.-) in water.

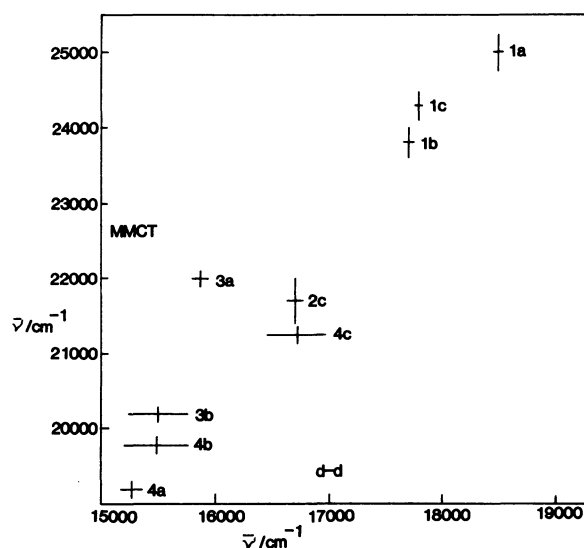


Fig. 5. Correlation between the energies of the d-d band maxima of Cu^{II} moieties and the energies of MMCT.

and the band becomes broad as well as that of the dien complex (Fig. 2). This broadening of ν_{CN} may be also due to the formation of additional cyanide bridges.

The electronic spectrum in an aqueous solution exhibits a strong band at 21300 cm^{-1} with a shoulder at *ca.* 17000 cm^{-1} (Fig. 4). The band at 21300 cm^{-1} is assigned to MMCT. This MMCT band is much more intense than those of the en and tn complexes. This is reasonably interpreted in terms of the presence of Cu-NC-Fe bridge in an aqueous solution as was found in the solid state.

Correlation between MMCT and d-d Transitions.

Figure 5 shows a correlation between the energies of MMCT and the d-d band maxima of Cu^{II} moieties. A good correlation is observed. The MMCT of the present complexes are assigned to one-electron jump from the t_{2g} orbital of the low spin iron(II) to the $e_g(dx^2-y^2)$ orbital of copper(II) ion in octahedral symmetry.²⁾ Therefore, the energies of the MMCT depend on the energy difference between the dx^2-y^2 orbital energy of Cu^{II} ion and t_{2g} orbital energy of Fe^{II} ion. Assuming that the t_{2g} orbital energies of Fe^{II} ions in the present complexes are almost constant, the energies of the MMCT are mainly dependent on the dx^2-y^2 orbital energies of Cu^{II} ions; the higher the energy of the d-d band maximum of Cu^{II} moiety, the higher the dx^2-y^2 orbital energy and the higher the energy of the MMCT.

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