

Multinuclear Macromolecular Metal Complexes III.[†] Preparation and Properties of Poly(vinylamine)copper(II) Complex Coordinately Bonded with Hexacyanoferrate(II)

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ABSTRACT: A new multinuclear macromolecular metal complex, poly(vinylamine)copper(II) complex coordinately bonded with hexacyanoferrate(II), has been prepared by mixing aqueous solutions of poly(vinylamine)copper(II) and potassium hexacyanoferrate(II) in order to investigate the effects of macromoleculization of a mixed metal complex. The interactions between metals in different complex moieties of poly(vinylamine)copper(II) and hexacyanoferrate(II) were studied spectroscopically. A mixed metal polymer complex which has Fe(II), Cu(II), and vinylamine of the poly(vinylamine) repeating unit in the ratio of 1 : 1 : 20 has been prepared. In the IR spectrum of the mixed metal polymer complex, intermetallic CN stretching vibration band has been obtained. A broad visible absorption peak at 480 nm which did not appear in the spectra of its parent complexes has been shown. Cu(II) signal of its ESR spectrum in aqueous glassy solution appeared between the signals of poly(vinylamine)copper(II) and $\text{Cu}_2[\text{Fe}(\text{CN})_6]$ and was assigned to an inorganic cluster with cyanide bridged metals. These spectral data suggest that this mixed metal polymer complex has a cyanide bridged structure and interactions between metals of different complex moieties through the cyanide bridges.

KEY WORDS Poly(vinylamine) / Ferricyanide / μ Bridged Bond / Mixed Valence Complex /

Polynuclear metal complexes having different metal with mixed valence states show interesting behavior in the fields of catalysis, magnetism, electricity, and photoelectrochemistry.² There are some applications of these complexes to such fields. However, there are a few investigations on polymeric systems.^{3,4} Therefore, we studied the preparation and chemical functions of multinuclear macromolecular metal complexes having mixed valence states or different metals. It is well-known that

the cyanoferrate ion may coordinate through nitrogen atoms when the cyanide ion acts as a bridging ligand.⁵ The physical properties of such a type of coordinate ion have been investigated for hexacyanoferrate(II) or (III) with various metal ions, in particular, magnetic exchange interactions between the two-metal ions, as well as their roles in heteronuclear intervalence charge transfer.⁶⁻⁸ We studied the preparation of Prussian blue as well as its Cu(II) and Co(II) analogs ionically

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bonded to poly(vinylamine hydrochloride). In that system, the mixed metal complexes were introduced into a polymer by poly-ionic bonding between inorganic polyanion of Prussian blue as well as its analogs and organic polycation of poly(vinylamine hydrochloride).¹ On the other hand, the poly(vinylamine)copper(II) complex as a polymer complex and hexacyanoferrate(II) as a low molecular weight complex can be expected to make a mixed metal polymer complex, whose complex moiety is introduced onto poly(vinylamine) by coordination bonding.

The present paper is concerned with the preparation and characterization of a mixed metal polymer complex between hexacyanoferrate(II) and the poly(vinylamine)copper(II) complex (PVAm-Cu(II)).

EXPERIMENTAL

Materials

$K_4[Fe(CN)_6]$ was reagent grade, and purified by recrystallization from water. The polymer complex, PVAm-Cu(II), was prepared according to a previously reported procedure.⁹ The copper content was 5 mol% against the repeating units of PVAm.

Preparation of PVAm-Cu(II)-[Fe(II)(CN)₆]

The mixed metal polymer complex was obtained by mixing aqueous solutions of the PVAm-Cu(II) and $K_4[Fe(CN)_6]$ in a 1:1 molar ratio for metals. 2 ml of 5 mM $[Fe(CN)_6]^{4-}$ were added to 2 ml of 5 mM PVAm-Cu(II) complex. 1 ml of aqueous 0.5 M KCl was added to make up a solution of 5 ml. The ionic strength of the system was maintained at 0.1 M (KCl), and the pH of the mixed solutions was adjusted with HCl or KOH solution. The mixed metal polymer complex was isolated after dialysis of the solution by distilled water for 24 hours.

Measurements

The metal content was determined by

HITACHI 170-70 Zeeman-effect atomic absorption spectrophotometer. Electronic spectra of solutions were measured with a JASCO UVIDEK-505 UV/VIS digital spectrophotometer using 1 cm quartz cells. ESR spectra were measured with a Varian E-line EPR spectrometer and 100-KHz field modulation using the X-band (9.196 GHz at 320 K) and microwave power of 100 mW. *g*-Values were calculated using solid 2,2-diphenyl-1-picrylhydrazyl (dpph) as a reference. Infrared spectra were recorded on a JASCO IR-A302 spectrophotometer in the range 330 to 5040 cm^{-1} for film samples.

RESULTS AND DISCUSSION

Formation of PVAm-Cu(II)-[Fe(II)(CN)₆]

The addition of hexacyanoferrate(II) solution to PVAm-Cu(II) solution gave the mixed metal polymer complex, PVAm-Cu(II)-[Fe(II)(CN)₆]. This complex is soluble in water, whereas the cluster formed from $[Fe(CN)_6]^{4-}$ and Cu^{2+} is insoluble completely in any solvent. The aqueous solution of PVAm-Cu(II)-[Fe(II)(CN)₆] has a blue-purple color.

The infrared spectrum of the mixed metal polymer complex in the film state shows a splitting of the CN stretching vibration mode as apparent from curve (a) in Figure 1. Two well-resolved bands appear at 2028 and 2106 cm^{-1} respectively; one of them (at lower energy side) is assigned to the terminal CN stretching mode with respect to the parent $K_4[Fe(CN)_6]$ ($\nu_{CN} = 2026 \text{ cm}^{-1}$), and the other (at higher energy side) to the intermetallic CN stretching mode. This shift to higher frequency of the CN stretching band by bridging is due to the strong back donation of metal to the cyanide π orbital thus enhancing the carbon-nitrogen bond strength.¹⁰ This observation is supported by IR data of (b) in Figure 1 on the cyanide bridged multiheteronuclear complex of $Cu_2[Fe(CN)_6]$. The appearance of the intermetallic CN band indicates that some CN

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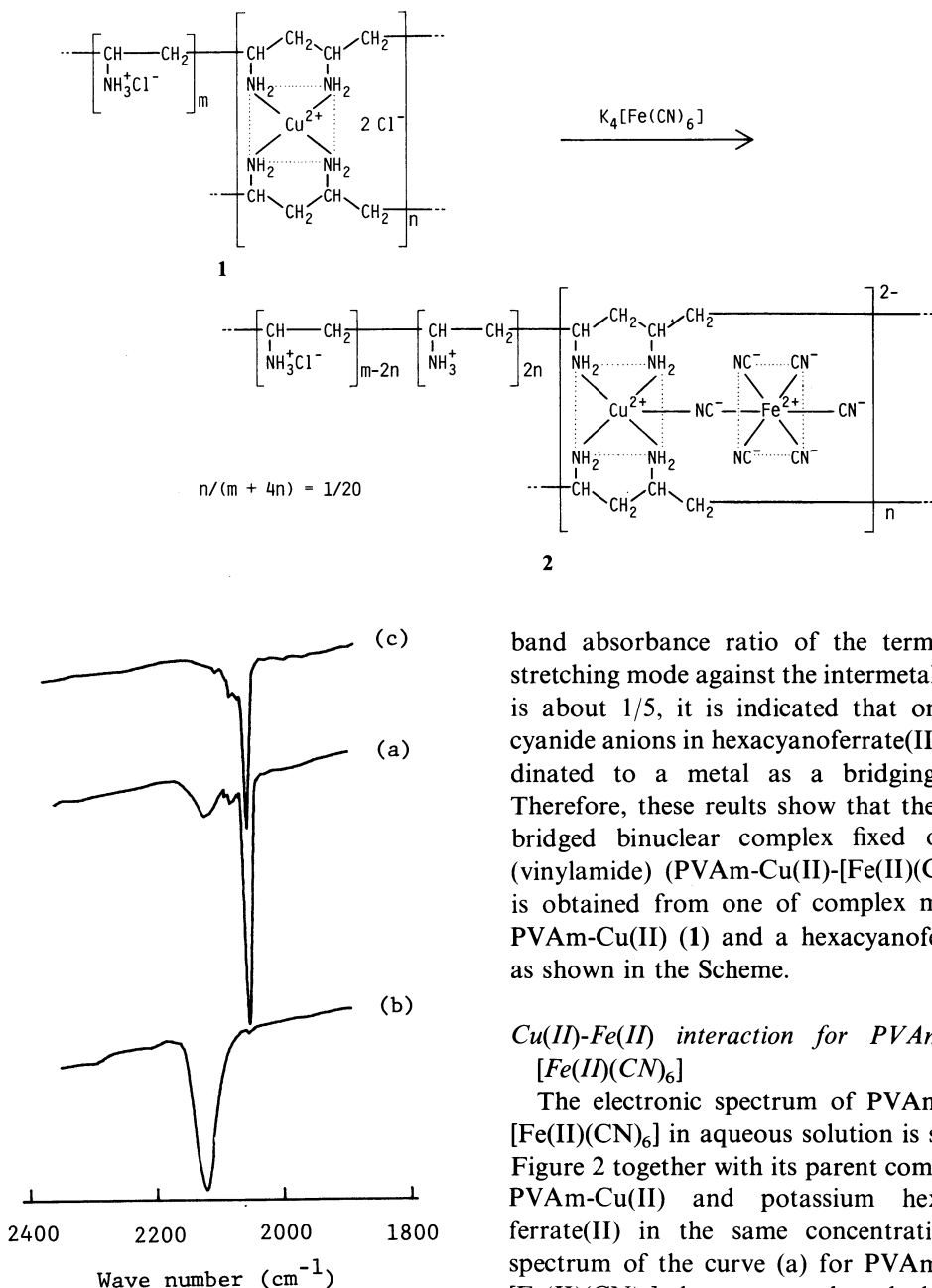


Figure 1. Infrared spectra of PVAm-Cu(II)-[Fe(CN)₆]⁴⁻ (a), Cu₂[Fe(CN)₆] (b), and K₄[Fe(CN)₆] (c) for film (a) and KBr discs (b), (c).

anions in hexacyanoferrate(II) are bound to metals by the nitrogen side as a bridging ligand. As shown (a) in Figure 1, since the

band absorbance ratio of the terminal CN stretching mode against the intermetallic mode is about 1/5, it is indicated that one of six cyanide anions in hexacyanoferrate(II) is coordinated to a metal as a bridging ligand. Therefore, these results show that the cyanide bridged binuclear complex fixed on poly(vinylamide) (PVAm-Cu(II)-[Fe(II)(CN)₆] (2) is obtained from one of complex moiety of PVAm-Cu(II) (1) and a hexacyanoferrate(II) as shown in the Scheme.

Cu(II)-Fe(II) interaction for PVAm-Cu(II)-[Fe(II)(CN)₆]

The electronic spectrum of PVAm-Cu(II)-[Fe(II)(CN)₆] in aqueous solution is shown in Figure 2 together with its parent complexes of PVAm-Cu(II) and potassium hexacyanoferrate(II) in the same concentration. The spectrum of the curve (a) for PVAm-Cu(II)-[Fe(II)(CN)₆] shows a new broad absorption band at 480 nm which is not assigned to either the parent complexes of PVAm-Cu(II) (b) or hexacyanoferrate(II) (c), and shows a sensible bathochromic shift of the copper(II) d-d band for PVAm-Cu(II) comolex moiety from that band at 590 nm for parent com-

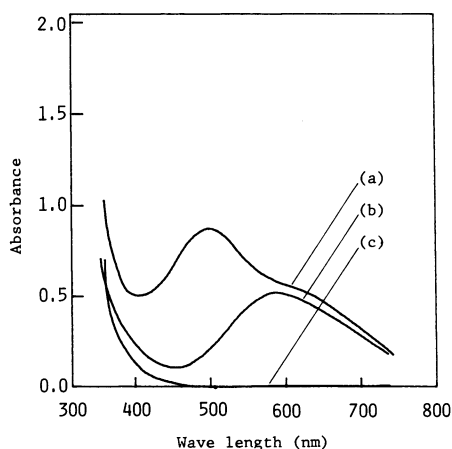


Figure 2. Electronic spectra of the mixed system of PVAm-Cu(II) and $K_4[Fe(CN)_6]$ solution ($[Cu]=[Fe]=2 \times 10^{-3} \text{ mol l}^{-1}$) (a), as well as the parent complex solutions of PVAm-Cu(II) ($[Cu]=2 \times 10^{-3} \text{ mol l}^{-1}$) (b), and $K_4[Fe(CN)_6]$ ($[Fe]=2 \times 10^{-3} \text{ mol l}^{-1}$) (c) at $\mu=0.1$ (KCl), pH=4.8.

plex of PVAm-Cu(II). But this band shift is observed in the lower Fe/Cu molar ratios, since the position of the copper(II) band is apparently influenced by the new band in the higher Fe/Cu molar ratios. These band shifts indicate that the d-d transition energy of copper(II) complexes decreases, in other words, the copper(II)-amine bond in the complex becomes slightly weak by additionally forming the new copper(II)-cyanide bond at the axial position of the planar copper(II)-amine complex on the polymer.¹¹

It has been reported that the spectrum of the adduct of Cu^{2+} and hexacyanoferrate(II), namely, copper ferrocyanide having a characteristic red-brown color in the solid state shows a broad band at 474 nm which is assigned to intermetal charge transfer from carbon coordinated Fe(II) to nitrogen coordinated Cu(II), by analogy with the 704 nm band of Prussian blue which has the homonuclear intervalence charge transfer from Fe(II) to Fe(III) in the solid state.¹² In this case, the 480 nm band observed in the solid state of PVAm-Cu(II)- $[Fe(II)(CN)_6]$ seems assignable to the intermetallic charge trans-

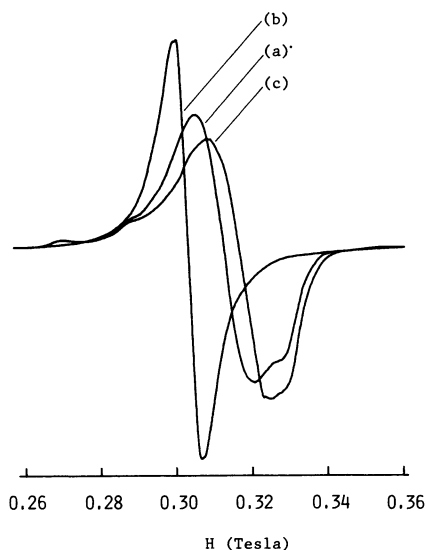


Figure 3. ESR spectra of PVAm-Cu(II)- $[Fe(CN)_6]^{4-}$ (a), $Cu_2[Fe(CN)_6]$ (b), and PVAm-Cu(II) (c) in aqueous glassy solutions at 230 K with 9.197 GHz microwave at $[Cu]=1.5 \times 10^{-3} \text{ mol l}^{-1}$, pH=4.8, $\mu=0.1$ (KCl).

fer from carbon coordinated Fe(II) to nitrogen coordinated Cu(II), namely, the heteronuclear intervalence charge transfer.

The ESR signal and its parameter of PVAm-Cu(II)- $[Fe(II)(CN)_6]$ are showed in Figure 3 together with data of PVAm-Cu(II) and $Cu_2[Fe(CN)_6]$ which is multiheteronuclear cluster having cyanide bridges between metals. The ESR signal of (c) in Figure 3 for the parent copper(II) complex in glassy solution at 230 K has typical of tetragonal hyperfine line. Two g -values at $g_{\parallel}=2.202$ and $g_{\perp}=2.070$ are obtained as well as hyperfine coupling constant ($A_{\parallel}=1720 \times 10^{-4} \text{ cm}^{-1}$). As is expected, the signal of the parent $[Fe(CN)_6]^{4-}$ complex is not observed, since this Fe(II) complex having the filled t_{2g} level (d^6) shows diamagnetism. The ESR signal for $Cu_2[Fe(CN)_6]$ shown by curve (b) in Figure 3 has a g -value of $g=2.164$ and narrow signal line width of $69 \times 10^{-4} \text{ T}$. In the equimolar mixed solution of PVAm-Cu(II) and hexacyanoferrate(II), ESR signal showed as curve (a) in Figure 3 was obtained for the glassy solution at 230 K with the pa-

rameters of $g_{\parallel}=2.209$, $g_{\perp}=2.098$, and $A_{\parallel}=1790 \times 10 \text{ cm}^{-1}$. Cu(II) complex signal in the curve (a) shifts between the signals of PVAm-Cu(II) (c) and $\text{Cu}_2[\text{Fe}(\text{CN})_6]$ (b), and shows narrowing of the signal line width from $164 \times 10^{-4} \text{ T}$ to $156 \times 10^{-4} \text{ T}$. The curve (a) in Figure 3 has no signal at $g=2.164$ where the $\text{Cu}_2[\text{Fe}(\text{CN})_6]$ cluster shows a signal. This indicates that the $\text{Cu}_2[\text{Fe}(\text{CN})_6]$ cluster is not contaminated in the equimolar mixed solution of PVAm-Cu(II) and hexacyanoferrate(II). These results indicate that the copper(II) ion of mixed metal polymer complex is in a mixed state of PVAm-Cu(II) whose copper(II) ion is coordinated by four amino groups and $\text{Cu}_2[\text{Fe}(\text{CN})_6]$ whose copper(II) ion is coordinated by cyanide ions at its nitrogen side, and suggest that the Cu(II) signal incurs some effect of heteronuclear intervalence charge transfer with regard to the rate of electron transfer.

The present data indicate that hexacyanoferrate(II) coordinately binds by cyanide ion with planar copper(II) complex at axial position giving rise to bridged binuclear complex which shows the heteronuclear in-

tervalence charge transfer interaction between iron(II) and copper(II).

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