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# Complexes of Copper(II) Dipeptides with Hexacyanoferrate(III)

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*Four complexes of hexacyanoferrate(III) with copper(II) dipeptides such as Cu(II)-glycylglycine, Cu(II)-glycyl-L-tyrosine and Cu(II)-glycyl-L-tryptophan (1:1), have been prepared and characterized by electronic, infrared and EPR spectroscopy. They show d–d transitions between 600–700 nm, and their $\mu_{eff}$ values (2.17 to 2.65 BM) are less than the $\mu_{eff}$ value of 2.83 B.M. for two unpaired electrons. They have two types of CN stretching vibrations due to bridging and terminal CN groups. The EPR data of these complexes suggest that their ground state is $d_{x^2-y^2}$. They seem to be polymeric with one of the cyanides of ferricyanide being more strongly bonded at axial position than the other at equatorial position of Cu(II).*

## Introduction

Galactose oxidase, a copper enzyme, catalyzes the oxidation of galactose by molecular oxygen. In the presence of ferricyanide, the rate of the above reaction becomes much faster and this increase in rate is possibly due to interaction of ferricyanide with the enzyme. This interaction of ferricyanide with the enzyme is also responsible for the loss of EPR signal [1–3]. There are two mechanisms suggested for the loss of EPR signal. First, the ferricyanide being a mild oxidizing agent at biological pH, it might oxidize the copper(II) to copper(III) of the enzyme having diamagnetic $d^8$ configuration. Second, the Fe(III) in ferricyanide might be strongly antiferromagnetically coupled to Cu(II) in the enzyme through cyanide bridging. The cyanide ions are known to bridge in an end-to-end fashion between transition metal ions in polymeric and dimeric complexes [4–6]. A cyanide bridging between Cu(II) and Fe(III) has also been proposed for cyanide complex of oxidized cytochrome $a_3$ [7]. So cyanide bridged heteronuclear complexes containing Cu(II) and Fe(III) can serve as models for cyanide complex of fully oxidized cytochrome $a_3$ and these studies will also help us to understand the magnetic exchange interactions between Cu(II) and Fe(III), in this enzyme.

A previous communication from this laboratory on magnetic and EPR studies of interaction of ferricyanide with copper(II)-glycylglycine indicated that ferricyanide forms a complex with copper(II)-glycylglycine by cyanide bridging [8]. Here we report the synthesis and spectral studies of isolated complexes of ferricyanide with copper(II)-glycylglycine, -glycyl-L-tyrosine and -glycyl-L-tryptophan.

## Experimental

### *Materials*

Glycylglycine (Gly·Gly), glycyl-L-tyrosine (Gly·Tyr) and glycyl-L-tryptophan (Gly·Trp) were purchased from Sigma, U.S.A. Potassium ferricyanide was bought from Polypharm, India. Other commercially available reagent grade chemicals were used without further purification.

### *Preparation of Complexes*

$Cu(Gly\cdot Gly)\cdot 3H_2O$ (Ia), $Cu(Gly\cdot Tyr)\cdot 4H_2O$ (IIa) and $Cu(Gly\cdot Trp)\cdot 3H_2O$ (IIIa) were prepared according to the methods described in the literature [9–11].

#### *$K_3[Cu(Gly\cdot Gly)\cdot Fe(CN)_6]\cdot 6H_2O$ (Ib)*

To a solution of 0.248 g of Ia in 20 ml of water, a solution of 0.329 g of $K_3[Fe(CN)_6]$ in 10 ml of water was added. The pH of the mixture was adjusted to 8 and it was stirred for two hours and then kept at room temperature for two days. The reddish brown complex obtained was filtered, washed with water, methanol and then diethyl ether. The complex was finally dried in air. *Anal.* Found: C, 19.2; H, 2.9; N, 17.5; Cu, 10.2%. Calcd. for $K_3[C_{10}H_6N_8O_3CuFe]\cdot 6H_2O$: C, 19.02; H, 2.85; N, 17.76; Cu, 10.07%.

#### *$K_3[Cu(Gly\cdot Tyr)\cdot Fe(CN)_6]$ (IIb)*

To a solution of 0.372 g of IIa in 25 ml of water, a solution of 0.329 g of $K_3[Fe(CN)_6]$ in 10 ml of

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TABLE I. Electronic Spectral Maxima, $\nu$(CN) Vibrations and $\mu_{eff}$ of Copper(II) Dipeptides and Their Ferricyanide Derivatives.

| Complex | Reflectance spectral $\lambda_{max}$ in nm | Absorption[a] spectral $\lambda_{max}$ ($\epsilon_{max}$) in nm | $\nu$(CN) $cm^{-1}$ | $\mu_{eff}$[c] |
|---|---|---|---|---|
| Ia | 678 | 640(85) | – | 1.92 |
| Ib | 500 | – | 2160(sh)[b] | |
| | | | 2105(s) | 2.67 |
| | | | 2080(s) | |
| IIa | 630 | 637(75) | – | 1.90 |
| IIb | 500 | – | 2160(sh) | 2.31 |
| | | | 2095(s,br) | |
| IIc | 496 | 486(1033) | 2170(sh) | |
| | | | 2120(s) | 2.17 |
| | | | 2090(s) | |
| IIIa | 590 | 630(92) | – | 1.83 |
| IIIb | 500 | 490(1274) | 2150(sh) | |
| | | | 2090(s) | 2.23 |
| | | | 2050(s) | |
| $K_3[Fe(CN)_6]$ | 414 | 422(1130) | 2118(s) | 2.34 |

[a]Solvent was water. [b]Sh = shoulder, s = strong, br = broad. [c]Temperature was between 295 and 300 K.

water was added. The pH of the solution was adjusted to 8 and it was stirred for two hours and then kept in a desiccator for slow evaporation. A reddish brown complex was obtained after four days. This complex was filtered, washed with water, methanol and finally by diethyl ether. It was dried in air. *Anal.* Found: C, 33.0; H, 1.83; N, 17.4; Cu, 9.2%. Calcd. for $K_3[C_{17}H_{12}N_8O_4CuFe]$: C, 32.44; H, 1.91; N, 17.81; Cu, 10.09%.

*$K_3[Cu(Gly\cdot Tyr)\cdot Fe(CN)_6]\cdot H_2O$ (IIc)*

The deep red filtrate obtained after filtration of IIb (see above) was concentrated to about half of its volume by slow evaporation at room temperature. Acetone was then added to it drop by drop until the red turbidity was obtained. The solution was then kept in a freezer for two days when the complex settled down. This complex was filtered, washed with a mixture of cold water and acetone (1:2 v/v) followed by acetone and then dried in a vacuum desiccator over anhydrous calcium chloride. *Anal.* Found: C, 31.2; H, 2.2; N, 17.8; Cu, 9.9%. Calcd. for $K_3[C_{17}H_{12}N_8O_4CuFe]\cdot H_2O$: C, 31.54; H, 2.16; N, 17.32; Cu, 9.82%.

*$K_3[Cu(Gly\cdot Trp)\cdot Fe(CN)_6]\cdot H_2O$ (IIIb)*

0.329 g of $K_3[Fe(CN)_6]$ in 10 ml of water and 0.377 g of IIIa in 30 ml of water were mixed and the resulting solution was concentrated to 10 ml by evaporating it in a desiccator. Acetone was then added drop by drop until the red turbidity was obtained. The mixture was cooled in a freezer for two days when a reddish brown complex was obtained. This was filtered, washed with a mixture of cold water and acetone (1:2 v/v), followed by acetone and dried in a vacuum desiccator over anhydrous calcium chloride. *Anal.* Found: C, 34.6; H, 2.1; N, 18.5; Cu, 9.8%. Calcd. for $K_3[C_{19}H_{13}N_9O_3CuFe]\cdot H_2O$: C, 34.04; H, 2.24; N, 18.81; Cu, 9.48%.

*Physical Measurements*

The electronic absorption and reflectance spectra of the complexes were recorded on a Varian Superscan-3 spectrophotometer. The infrared spectra in the Nujol mull were obtained using a Perkin-Elmer Model-577 Infrared spectrophotometer in the range of 4000 to 400 $cm^{-1}$. The instrument was calibrated using polystyrene film. The magnetic susceptibility of the complexes at room temperature was determined by the Gouy method [12]. The electron paramagnetic resonance (EPR) spectra of the complexes, both at room temperature and at liquid nitrogen temperature (77 K) were recorded on an X-band E-112 ESR spectrometer using TCNE (g = 2.00277) as g marker. A mixture of ethylene glycol and water in the ratio of 1:1 (v/v) was used as solvent for recording solution and frozen solution EPR spectra of the complexes. X-ray powder diffraction patterns were obtained from powdered complexes using a Philips X-ray Diffractometer (Model: PW-1140) employing CuK$\alpha$ ($\lambda$ = 1.5418 Å) radiation. The d values for the strongest, second strongest and third strongest peaks were calculated using the equation, $\lambda = 2d\sin\theta$. The intensity of the strongest peak $I_1$ was taken as 100, and the second strongest peak $I_2$ and the third strongest peak $I_3$ were taken as percentage of maximum intensity $I_1$ [13].

TABLE II. X-ray Powder Diffraction Data for Ia, Ib, IIa, IIc and $K_3[Fe(CN)_6]$.

| Complex | $d_1$ (Å) | $I_1/I_{max} \times 100$ | $d_2$ (Å) | $I_2/I_{max} \times 100$ | $d_3$ (Å) | $I_3/I_{max} \times 100$ |
|---|---|---|---|---|---|---|
| $K_3[Fe(CN)_6]$ | 4.114 | 100 | 2.940 | 58 | 2.998 | 45 |
| Ia | 3.750 | 100 | 7.970 | 97 | 8.506 | 85 |
| Ib | 5.250 | 100 | 3.590 | 68 | 3.530 | 68 |
| IIa | 6.710 | 100 | 3.750 | 88 | 8.040 | 67 |
| IIb | 3.526 | 100 | 3.520 | 87 | 3.466 | 71 |
| IIc | 3.530 | 100 | 3.590 | 95 | 5.010 | 94 |
| IIIa | 6.862 | 100 | 3.917 | 52 | 7.436 | 50 |
| IIIb | 3.59 | 100 | 4.98 | 85 | 2.40 | 43 |

## Results and Discussion

Four complexes of ferricyanide with Cu(II) dipeptides such as Ib, IIb, IIc and IIIb were prepared and characterised by infrared, visible and EPR spectroscopy. The infrared spectra of these complexes show a broad peak between 1590 to 1610 $cm^{-1}$, which can be assigned to carbonyl stretching with ionisation of peptide N–H hydrogen [14]. The cyanide frequencies of these complexes fall in the range of 2030 to 2170 $cm^{-1}$, and are given in Table I. The infrared spectrum of ferricyanide shows a sharp intense peak at 2118 $cm^{-1}$, which is assigned to terminal $\nu(C\equiv N)$ vibration. This cyanide stretching vibration was further split in the complexes due to lowering of symmetry of ferricyanide from regular octahedron. The $\nu(C\equiv N)$ vibration of bridged cyanide is usually observed at greater frequency than the terminal cyanide [14, 15]. Therefore, the shoulder appearing between 2150 to 2170 $cm^{-1}$ in all these complexes is due to $\nu(C\equiv N)$ vibration of the bridged cyanide, and the lower frequency bands between 2085 and 2105 $cm^{-1}$ are assigned to terminal $\nu(C\equiv N)$ vibration.

The X-ray powder patterns ($d_1$, $d_2$ and $d_3$ spacings and intensities) of $K_3[Fe(CN)_6]$, Ia, Ib, IIa, IIb, IIc, IIIa and IIIb were measured and they are given in Table II. The X-ray powder patterns of these complexes indicate that Ib, IIb, IIc and IIIb are a single compound and not components of a mixture [13].

The reflectance spectra of Ib, IIb, IIc and IIIb in solid state show a characteristic broad band around 500 nm, and they are given in Table I. The reflectance spectrum of $K_3[Fe(CN)_6]$ shows a band at 415 nm, which is identified as $T_{2g} \leftarrow L(CN^-)_g$ symmetry forbidden ligand to metal transition. This is achieved by vibronic (vibrational electronic) coupling [16]. The broad band around 500 nm in Ib, IIb, IIc and IIIb seems to be of the same origin as that of the 415 nm band of $K_3[Fe(CN)_6]$, because the intensity of the former band is much higher than the intensity of normal d–d transition. The Ib and IIb are water insoluble (larger polymeric species) and therefore, their absorption spectra in solution could not be determined. However, IIc and IIIb are water soluble and they show the broad bands at 486 and 490 nm respectively (see Table I). The extinction coefficients of these bands are comparable to the extinction coefficient of the 422 nm band of $K_3[Fe(CN)_6]$ in solution. Therefore, the characteritic band around 490 nm in these complexes also in solution arises due to ligand to metal ($T_{2g} \leftarrow L(CN^-)_g$) charge transfer transition.

These complexes show a very broad absorption band in the region of 600 to 700 nm. The position of the maxima of these complexes cannot be ascertained. The intensity of absorption in this region is comparable to d–d transition in Cu(II) dipeptides. Therefore, it is suggested that these broad bands arise due to Cu(II) d–d transitions. In order to verify the shift of d–d transition band in complexes of Cu(II) dipeptides with ferricyanide compared with their corresponding Cu(II) dipeptides, a dilute solution ($10^{-3}$ *M*) of ferricyanide was added to a freshly prepared solution of Ia ($10^{-3}$ *M*) in water. The band at 640 nm due to d–d transition in Ia was blue shifted to 615 nm with intensity enhancement. The blue shift in this complex indicates that the ferricyanide binds strongly to Ia in the equatorial plane by replacing the coordinated water molecule in Ia [17]. This conclusion is certainly true in solution, but not in solid state.

In our previous communication [8], the interaction of ferricyanide with Ia in solution was reported. It has been suggested that the disappearance of EPR signal of Cu(II) of Ia at liquid nitrogen is due to antiferromagnetic coupling between Cu(II) of Ia and Fe(III) of $K_e[Fe(CN)_6]$ through a cyanide bridge. The improved magnetic susceptibility data of the above system were obtained and the corrected molar susceptibility values of Ia, $K_3[Fe(CN)_6]$, and Ia + $K_3[Fe(CN)_6]$ (molar ratio of 1:1) are 1580 $\times$ $10^{-6}$ (1.95 B.M.), 1901 $\times$ $10^{-6}$ (2.15 B.M.) and 2262 $\times$ $10^{-6}$ (2.33 B.M.) respectively.

TABLE III. EPR Spectral Data of Polycrystalline Cu(II) Dipeptides and Their Complexes with Ferricyanide.

| Complex | Temperature | $g_z$ | $g_y$ | $g_z$ |
|---|---|---|---|---|
| Ia | R.T.[a] | 2.215 | 2.087 | 2.061 |
| | 77 K | 2.215 | 2.088 | 2.060 |
| Ib | R.T. | 2.317 | 2.099 | 2.063 |
| | 77 K | 2.314 | 2.101 | 2.062 |
| IIa | R.T. | Isotropic g value = 2.107, peak to peak width = 155 gauss | | |
| | 77 K | Isotropic g value = 2.105, peak to peak width = 123 gauss | | |
| | 77 K | (2.243)[b] | (2.068)[b] | (2.003)[b] |
| IIb | R.T. | 2.309 | 2.154[c] | 2.065 |
| | 77 K | 2.313 | 2.140[c] | 2.062 |
| IIc | R.T. | Isotropic g value = 2.149, peak to peak width = 93 gauss | | |
| | 77 K | Isotropic g value = 2.149, peak to peak width = 93 gauss | | |
| | 77 K | (Isotropic g value = 2.152, peak to peak width = 105 gauss)[b] | | |
| IIIa | R.T. | 2.183 | 2.082 | 2.059 |
| | 77 K | 2.183 | 2.084 | 2.061 |
| | 77 K | (2.228)[b] | (2.053)[b] | (2.001)[b] |
| IIIb | R.T. | Isotropic g value = 2.149, peak to peak width = 80 gauss | | |
| | 77 K | Isotropic g value = 2.145, peak to peak width = 90 gauss | | |
| | 77 K | (Isotropic g value = 2.149, peak to peak width = 108 gauss)[b] | | |

[a]R.T. = 27 °C. [b]The g values in brackets are obtained from frozen solution spectra of the complexes. [c]There is an additional signal at the low field side of $g_y$ which may be due to some small impurity of IIa.

The effective magnetic moments ($\mu_{eff}$) of Ia, Ib, IIa, IIb, IIc, IIIa, IIIb and $K_3[Fe(CN)_6]$ in solid state were calculated from their magnetic susceptibility data at room temperature, and they are given in Table I. The $\mu_{eff}$ values of Cu(II) complexes such as Ia, IIa and IIIa fall in the range of 1.83 to 1.92 B.M. indicating that these complexes are magnetically dilute [18]. The potassium ferricyanide also shows $\mu_{eff}$ value with an unpaired electron in Fe(III) [12]. The $\mu_{eff}$ values of Ib, IIb, IIc and IIIb are much less than the expected $\mu_{eff}$ value for two unpaired electrons *i.e.* $\mu_{eff}$ = 2.83 B.M. This lowering of $\mu_{eff}$ values in the solid state at room temperature can be explained in terms of antiferromagnetic coupling between Cu(II) and Fe(III) through a cyanide bridge as suggested above [8].

The EPR spectra of the polycrystalline complexes were obtained both at room temperature (300 K) and liquid nitrogen temperature (77 K) and the EPR parameters [19] are given in Table III. The ferricyanide has a $^2T_1$ ground state and therefore has a large spin orbit coupling constant, which is responsible for nonobservation of its EPR signal at liquid nitrogen temperature [20]. The complex Ia has a distorted square pyramidal structure [21], and it shows an EPR spectrum corresponding to axial symmetry with slightly rhombic distortion as shown by its three g values (see Table III). The ground state of Ia involves $d_{x^2-y^2}$ because R = $g_y - g_x/g_z - g_x$ which is less than 1 in Ia [18]. The

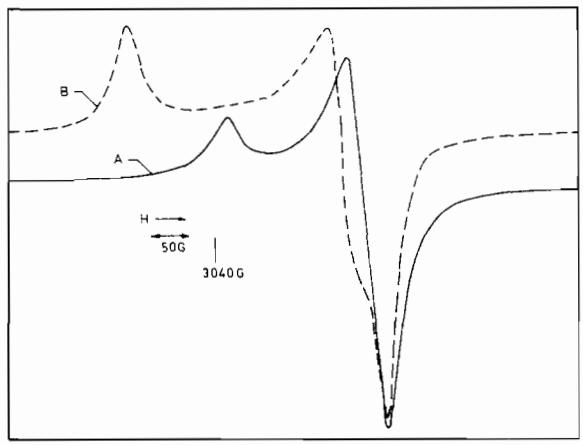


Fig. 1. Powder EPR spectra of $Cu(Gly\cdot Gly)\cdot 3H_2O$ (A) and $K_3[Cu(Gly\cdot Gly)\cdot Fe(CN)_6]\cdot 6H_2O$ (B) at 300 K.

complex Ib shows a spectrum similar to Ia with considerable increase in rhombicity and $g_z$ values as compared to that of Ia. The ground state of Ib also involves $d_{x^2-y^2}$, because R < 1. The powder spectra of both Ia and Ib at 300 K are given in Fig. 1 (A and B). The Ia has two coordinated water molecules, one is in the equatorial plane and the other is in the axial position [21]. In the 1:1 complex of Ia with ferricyanide (Ib), the cyanides of ferricyanide can coordinate to Cu(II) through nitro-

gens by replacing both the water molecules of Ia. This gives rise to a polymeric structure [6]. The increase in $g_z$ value of Ib can be explained if one assumes strong binding of CN at axial position of Cu(II) as compared to binding of another CN at equatorial position. This must increase the metal–ligand bond length in equatorial plane and it thus increases the $g_z$ value of Ib as compared to Ia [22]. It seems that a 1:1 mixture of Ia and ferricyanide in solution has species [8] different from those of the isolated species of Ib. The EPR spectrum of Ib is broader than that of Ia (see Fig. 1), and this may be due to dipole–dipole coupling between the magnetic moments of Cu(II) and Fe(III) in Ib [23].

The IIa shows a broad asymmetric signal with g value, $g_o$, of 2.107 with the peak to peak width of 155 gauss in polycrystalline solid. Its frozen solution spectrum at 77 K gives three g values (see Table III) corresponding to rhombic distortion from which $g_o$ is obtained by the relationship, $g_o = (g_x + g_y + g_z)/3$ [24] as 2.105. This is very close to its powder spectra at 300 and 77 K. The IIb shows rhombic distortion at 300 and 77 K and its $g_z$ value is larger than the $g_z$ value of IIa in frozen solution at 77 K. The $g_o$ values of 2.176 (300 K) and 2.155 (77 K) of IIb are also larger than the 2.107 value of IIa. The IIc shows $g_o$ of 2.149 at 300 and 77 K, which is larger than the corresponding $g_o$ values of IIa. The 93 gauss peak to peak width of IIc is smaller than the 155 gauss peak to peak width of IIa. The IIIa shows rhombic distortion at 300 to 77 K and has $g_o$ values in the range of 2.108–2.109. This is again smaller than $g_o$ values in the range of 2.145 to 2.149 of IIIb. Thus, these data indicate that one of the CN of ferricyanide is more strongly bonded at axial position than another at equatorial position in IIb, IIc and IIIb and the narrow peak width may be due to exchange coupling [23].

Four complexes of Cu(II) dipeptides with ferricyanide have been isolated. In these 1:1 complexes, one of the cyanides of ferricyanide is more strongly bonded at axial position than another at equatorial position of Cu(II). They are not good models of complexes formed between galactose oxidase and ferricyanide whereas the complex formed between Cu(II) glycylglycine and ferricyanide in solution is a good model for enzyme and ferricyanide interaction.

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