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Complexes of Copper(II) Dipeptides with Hexacyanoferrate(III). Magnetic and Spectroscopic Properties

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Abstract

The interaction between hexacyanoferrate(III) and two copper(II) dipeptide complexes, such as Cu(II)-glycylhistidine and Cu(II)-glycylphenylalanine, has been investigated by electronic and EPR spectroscopy and by magnetic susceptibility measurements. In both cases the magnetic susceptibility values sum to those corresponding to the parent complexes. However, the electronic relaxation time of the copper(II) ion in the mixed complexes is modified so much that the copper(II) EPR signal disappears suggesting the existence of a specific metal–metal interaction probably through a cyanide bridge. This hypothesis is also supported by the appearance of an hypsochromic shift of the Cu(II) electronic band after addition of hexacyanoferrate(III).

Introduction

Galactose oxidase is a copper containing enzyme which catalyzes the oxidation of galactose by molecular oxygen. Addition of hexacyanoferrate(III) increases the rate of the above interaction and is also responsible for the loss of the Cu(II) EPR signal [1]. Two mechanisms are suggested for the loss of the EPR signal. Firstly, oxidation by ferricyanide of Cu(II) to a Cu(III) $3d^8$ diamagnetic electronic configuration; secondly, an antiferromagnetic coupling between the two S = ½ spin states of the two metals that could bridge through the cyanide atoms.

Cyanide bridged heteronuclear complexes containing Cu(II) and Fe(III) can help to understand the interaction between the two metals in the enzyme. A previous report on the interaction of ferricyanide with the Cu(II)-glycylglycine complex suggested the occurrence of an antiferromagnetic coupling between the two metals [2]. On the other hand, the same interaction studied in several low molecular weight complexes, where the ferricyanide interacts in the apical or equatorial position of the copper atom, showed that the magnetic moments of the two metals were unaffected whilst a perturbation was observed at the level of the copper relaxation rate [3, 4]. Here we report the interaction between hexacyanoferrate(III) and two dipeptide–Cu(II) complexes previously characterized [5].

Experimental

Glycylhistidine (GlyHis) and Glycylphenylalanine (GlyPhe) were purchased from Serva, Germany. Potassium ferricyanide and $Cu(NO_3)_2 2H_2O$ were Merck products. The complexes were obtained by mixing the copper salt and the dipeptide in water in a 1:1 ratio and bringing the pH to 7.0 by addition of concentrated NaOH. The electronic absorption spectra were recorded on a Varian Cary 17 spectrophotometer. The EPR spectra were recorded on a X band Bruker ER-200D instrument. Volume magnetic susceptibility measurements were performed with a superconducting magnetometer [6], that allows an overall accuracy of 0.03% of the volume susceptibility of water used as diamagnetic reference.

Results and Discussion

Cu(II) is known to be able to interact with peptides to give stable complexes. In particular it has been shown that Cu(II) complexes with dipeptides such as GlyHis and GlyPhe give rise at pH 7 to a square planar configuration with one of the four copper ligands being a water molecule [5]. The room temperature EPR spectrum of the Cu(II)-GlyPhe compound is shown in Fig. 1. Because of

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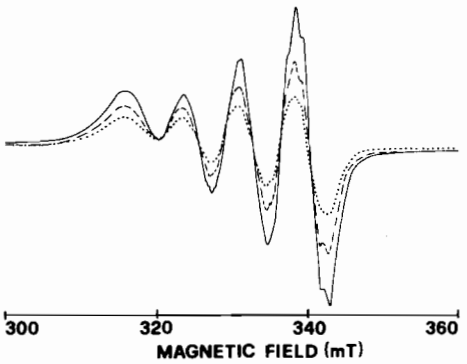

Fig. 1 X band room temperature EPR spectrum of 5.0 mM Cu(II)-GlyPhe (——) and after addition of 2 mM (------) and 3 mM (·····) $K_3[Fe(CN)_6]$.

TABLE I. Optical Absorption Energies of the d–d Band of Copper.

Complex	ΔE (cm^{-1})	ϵ (cm^{-1} M^{-1})
Cu(II)-GlyPhe	15,873 ± 50	40
+ $K_3[Fe(CN)_6]$	16,129 ± 50	45
Cu(II)-GlyHis	16,666 ± 50	25
+ $K_3[Fe(CN)_6]$	17,240 ± 50	25

rapid rotation in solution the anisotropy of the g and A tensors is averaged so that the spectrum has a single g value of 2.12 with four hyperfine lines separated by 7.1 mT. In frozen solution two g values are observed ($g_\parallel$ = 2.23, $g_\perp$ = 2.06) with $A_\parallel$ = 17.2 mT. The lines are sharp, the half width being about 4.0 mT, consistent with an orbitally non degenerate ground state. On the other hand hexacyanoferrate(III) has a degenerate $^2T_1$ ground state and gives rise to a very broad EPR line which becomes detectable only at liquid hydrogen temperature [7]. Addition of the hexacyanoferrate(III) to the Cu(II)-dipeptide complex leads to a decrease in the intensity of the Cu(II) signal at both room (Fig. 1) and liquid nitrogen temperature. The Cu(II) EPR signal decreases without any line broadening and has almost completely disappeared when the Fe(III)/Cu(II) ratio equals 1. From the intensity of the EPR signal an apparent affinity constant between Cu(II)-GlyPhe and $[Fe(CN)_6]^{3-}$ of *ca.* 5 × 10^2 M^{-1} has been estimated. The electronic spectrum of the hexacyanoferrate Cu(II)-GlyPhe adduct shows essentially the same absorption of the ferricyanide ion but also shows a sensible hypsochromic shift of the copper(II) d–d band with respect to that of the parent copper(II) complex (Table I). The same behaviour is observed for the electronic and EPR spectra of the Cu(II)-GlyHis compound. The experimental magnetic susceptibility values are reported in Table II. The measurements were performed as volume susceptibility using water as diamagnetic reference, and from the experimental data the magnetic moment of the compounds can be obtained by the following formula:

TABLE II. Magnetic Susceptibility Measurements in Solution at 300 K.

Complex	μ (BM)	Cu (mM)	Fe (mM)	$\Sigma_i\mu_i^2 c_i$ $(BM)^2$(mM)
Cu(II)-GlyHis	2.0 ± 0.1			
Cu(II)-GlyPhe	1.9 ± 0.1			
$K_3[Fe(CN)_6]$	2.4 ± 0.1			
Cu(II)-GlyHis + $K_3[Fe(CN)_6]$		4.8	4.3	40.0 ± 3.0
Cu(II)-GlyPhe + $K_3[Fe(CN)_6]$		4.9	4.3	37.0 ± 3.0

$$[\chi_{cc} - \chi_{cc}^{H_2O}]\,8T = \Sigma_i\mu_i^2 C_i$$

where χ_{cc} is the measured volume susceptibility of the sample, $\chi_{cc}^{H_2O}$ is that of water, and c_i and μ_i are the concentration and the magnetic moment of the paramagnetic species present in the sample. The theoretical value of $\Sigma_i\mu_i^2 c_i$ calculated for a coupled and uncoupled system are 2 and 40 $(BM)^2$ mM respectively, which when compared with the experimental values reported in Table II indicate that these systems are uncoupled. On the other hand the disappearance of the Cu(II) EPR signal suggests that some sort of interaction occurs on addition of hexacyanoferrate(III). Moreover the hypsochromic shift of the d–d absorption band of copper(II) atom in the electronic spectra of the mixed complexes indicates that the extraligand binds into the equatorial plane probably displacing the water molecule. Nevertheless, in both complexes such interaction does not affect the value of the magnetic moment of the two metals, indicating an undetectable antiferromagnetic coupling. Such behaviour agrees with the results reported for other low molecular weight copper complexes [3, 4], but is in contrast with the results reported for the Cu(II)-GlyGly compound [2]. However, in the latter case the magnetic measurements were carried out with a less sensitive instrument.

In our opinion hexacyanoferrate(III) interacts with the copper(II) metal ion perturbing its electronic relaxation rate such that it produces the disappearance of the Cu(II) EPR signal, but does not appear able to give rise to a detectable antiferromagnetic coupling. Such a mechanism could also operate for the galactose oxidase enzyme.

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