

## Interaction of Hexacyanoferrate(III) with some Copper(II) Complexes

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### Abstract

The interaction between hexacyanoferrate(III) and some copper complexes of different geometry was studied. In solution, and in the presence of coordination unsaturation of copper, 1:1 and 2:1 Cu:Fe adducts formed and were characterized by the absence of any copper electron paramagnetic resonance (EPR) signal. The magnetic susceptibility of the 1:1 adducts is essentially equal to the sum of those due to the parent compounds. Solid state studies confirm the solution data. In the light of the present results the absence of the EPR signal of  $[\text{Fe}(\text{CN})_6]^{3-}$ -treated galactose oxidase is discussed.

### Introduction

By interaction of hexacyanoferrate(III) with the copper enzyme galactose oxidase (GaO), the copper(II) electron paramagnetic resonance (EPR) signal disappears. This was attributed either to the formation of a formally Cu(III) ( $d^8$ , diamagnetic) enzyme or to the antiferromagnetic coupling of the Fe(III) of hexacyanoferrate with the Cu(II) of GaO [1]. Studies on low molecular weight complexes have confirmed that a direct interaction of hexacyanoferrate(III) with Cu(II) is possible, due to the bridging capability of  $\text{CN}^-$  between different metal ions [2–4].

The interaction between both bis(N-R-ethylenediamine)copper(II) complexes [3] and copper(II)-glycylglycine [4a] with hexacyanoferrate(III) in solution causes the disappearance of the EPR signal of copper, without line broadening. For the former complexes, the reason is related to the mechanism of coupling at the level of the electronic relaxation rate, while for the latter the disappearance

of the signal is attributed to the formation of antiferromagnetically coupled compounds. In agreement, the magnetic susceptibility data are the sum of those of the constituent complexes for solid Cu(II) bis(N-R-ethylenediamine)- $[\text{Fe}(\text{CN})_6]^{3-}$  adducts, and much less than the value expected for two unpaired electrons in the case of Cu(II)-dipeptides- $[\text{Fe}(\text{CN})_6]^{3-}$  adducts, in the solid, and for Cu(II)-glycylglycine also in solution.

The present paper reports the results obtained on the interaction of  $[\text{Fe}(\text{CN})_6]^{3-}$  with some Cu(II) complexes of different geometry. This interaction occurs in the copper equatorial position, a case that should be similar to that of the Cu(II)-dipeptides in solution, in the copper axial position, the situation described for the Cu(II) bis(N-R-ethylenediamine) complexes, and in a coordination site of an intermediate distorted geometry.

### Experimental

#### Materials

All chemicals were reagent grade and were used without further purification.

#### Preparation of the Complexes

$[\text{Cu}(\text{dien})]^{2+}$  (dien = bis-2-aminoethylamine) aqueous solutions were prepared either from  $[\text{Cu}(\text{dien})]\text{Cl}_2 \cdot \text{H}_2\text{O}$  or  $[\text{Cu}(\text{dien})](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ . The preparation of the former compound according to the literature [5] sometimes gives a gummy product and thus was substituted by the following: to 3.41 g  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  dissolved in the minimum volume of methanol, a solution of 2.2 ml dien in 11 ml methanol was added dropwise. The gummy product which was obtained changed to a blue-greenish powder-like precipitate by heating and subsequent cooling. After separation by suction, the compound

was dissolved in the minimum amount of water to which some methanol was added, followed by ethyl ether up to the formation of some turbidity. Dark blue elongated crystals of  $[\text{Cu}(\text{dien})]\text{Cl}_2 \cdot \text{H}_2\text{O}$  separated on standing.  $[\text{Cu}(\text{dien})](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$  was prepared as described in ref. [5].

$[\text{Cu}(\text{dienMe}_5)](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$  ( $\text{dienMe}_5 = \text{bis}(2\text{-dimethylaminoethyl})\text{methylamine}$ ,  $\text{CH}_3\text{N}[\text{CH}_2\text{CH}_2\text{-N}(\text{CH}_3)_2]_2$ ) was prepared by addition of 3.0 mmol copper perchlorate in ethanol to 3.8 mmol  $\text{dienMe}_5$  dissolved in few ml ethanol. After heating, the solvent was evaporated by suction and the residue was dissolved in propanol, to which some drierite was added. After two days the solution was filtered and petroleum ether added. Dark blue crystals separated. (Found C 22.26; H 5.45; N 8.52%.  $\text{C}_9\text{H}_{27}\text{N}_3\text{O}_{10}\text{-CuCl}_2$  requires C 22.92; H 5.73; N 8.91%).

To obtain a higher yield and a product free from  $[\text{Fe}(\text{CN})_6]^{4-}$  the preparation previously reported [2] of  $[\text{Cu}(\text{dien})]_3[\text{Fe}(\text{CN})_6]_2 \cdot 6\text{H}_2\text{O}$  has been modified: to 0.676 g  $\text{K}_2\text{S}_2\text{O}_8$  and 1.64 g  $\text{K}_3[\text{Fe}(\text{CN})_6]$  dissolved in 60 ml  $\text{H}_2\text{O}$ , a solution of 0.622 g  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  and 0.35 ml dien in 40 ml  $\text{H}_2\text{O}$  was added. After a short period at  $+4^\circ\text{C}$  the green solution allows dark green crystals to separate. The crystals were collected by filtration, washed with water, and air dried.

$[\text{Cu}(\text{dien})]_2[\text{Fe}(\text{CN})_6] \cdot 6\text{H}_2\text{O}$  was prepared as previously described [6].  $\text{K}_3[\text{Cu}(\text{dienMe}_5)(\text{OH})]_3[\text{Fe}(\text{CN})_6]_2 \cdot 6\text{H}_2\text{O}$  was obtained by addition of 0.5 mmol  $[\text{Cu}(\text{dienMe}_5)](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$  dissolved in the minimum amount of water, to 0.02 mol  $\text{K}_3[\text{Fe}(\text{CN})_6]$  dissolved in 50 ml  $\text{H}_2\text{O}$ . Further operations were analogous to those reported above for the corresponding dien compound. Green regular rhombic shaped platelets were obtained. (Found C 33.17; H 5.52; N 20.96%.  $\text{C}_{39}\text{H}_{84}\text{N}_9\text{O}_9\text{Cu}_3\text{Fe}_2\text{K}_3$  requires C 33.19; H 5.96; N 20.85%).

obtained by mixing a solution of 0.05 g  $[\text{Cu}(\text{dienMe}_5)](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$  in 10 ml  $\text{H}_2\text{O}$  with one containing 0.07 g  $\text{K}_3[\text{Co}(\text{CN})_6]$  in 8 ml  $\text{H}_2\text{O}$ . The resultant solution was stirred and left for 1 h. The light blue crystals formed were separated, washed with water, and dried. (Found C 34.74; H 5.80%; N 20.10.  $\text{C}_{24}\text{H}_{50}\text{N}_{12}\text{ClO}_6\text{CoCu}_2$  requires C 34.95; H 6.07; N 20.39%;  $\nu_3$  and  $\nu_2(\text{ClO}_4^-)$  at 1115 and 630  $\text{cm}^{-1}$  respectively).

$[\text{Cu}(\text{trans-diene})](\text{ClO}_4)_2$  ( $\text{trans-diene} = 5,7,7,12,14,14\text{-hexamethyl-1,4,8,11-tetra-azacyclotetradeca 4,11-diene}$ ) was obtained by reacting aqueous solutions of copper perchlorate with a methanolic solution of the free base, according to the procedure described for the *cis* compound [7]. The product was recrystallized from water.

#### Physical Measurements

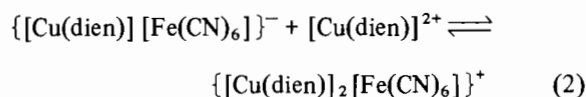
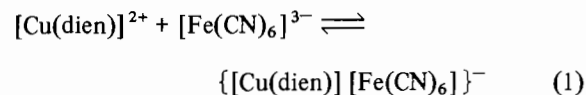
The electronic absorption and reflectance spectra were recorded on a Beckman DK1A spectrophotometer.

For the polarized light single crystal spectra in the wavelength range 400–800 nm, a Shimadzu MPS-50L spectrophotometer equipped with a microscope was used. The infrared (IR) spectra were measured with a Perkin-Elmer 577 spectrometer. Room temperature EPR spectra of aqueous solutions were obtained in silica capillary tubes with a Varian E-9 instrument. Conductivity measurements were performed at  $18^\circ\text{C}$  with an 'Analytical control' mod. 101 A instrument. The volume magnetic susceptibility measurements of solutions were obtained on a superconducting magnetometer [8], by determining the change in the magnetic flux when the sample examined was moved in and out of a single pick-up coil. The sample holder was a quartz tube 4.2 mm inside diameter, filled with 0.5 ml solution. Air was removed from the sample and replaced by nitrogen. The volume susceptibility of water, which can be determined with an accuracy of 0.03%, was used as a reference. The temperature in the sample compartment was regulated within  $0.3^\circ\text{C}$  and was stable during the measurements. Magnetic susceptibility measurements on solid samples were performed by the Gouy method at 4000 and 8000 G in the temperature range 100–300 K.

#### Results

Titration with hexacyanoferrate(III) of a solution of  $[\text{Cu}(\text{dien})]^{2+}$  progressively shift the main copper d–d transition from 16,400 to 17,100  $\text{cm}^{-1}$ , increase the intensity of the maximum from 70 to 113  $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ , and increase the absorbance at 24,000  $\text{cm}^{-1}$ , where the hexacyanoferrate(III) absorbs (Fig. 1A). A Job plot (Fig. 2), obtained either with the optical density change at 18,200 and 19,200  $\text{cm}^{-1}$  or with the corresponding conductivity variation, indicates the formation of both  $\text{Cu}(\text{II})\text{-Fe}(\text{III})$  and  $2\text{Cu}(\text{II})\text{-Fe}(\text{III})$  species.

In Fig. 3A the optical density change on hexacyanoferrate(III) addition at 18,200  $\text{cm}^{-1}$ , where the difference between the absorbance of hexacyanoferrate(III)-treated and untreated  $[\text{Cu}(\text{dien})]^{2+}$  is larger, is reported. The corresponding amplitude variation of the copper EPR spectrum is shown in Fig. 3B. A decrease of the signal without change in shape or line width is observed. By considering the equilibria:



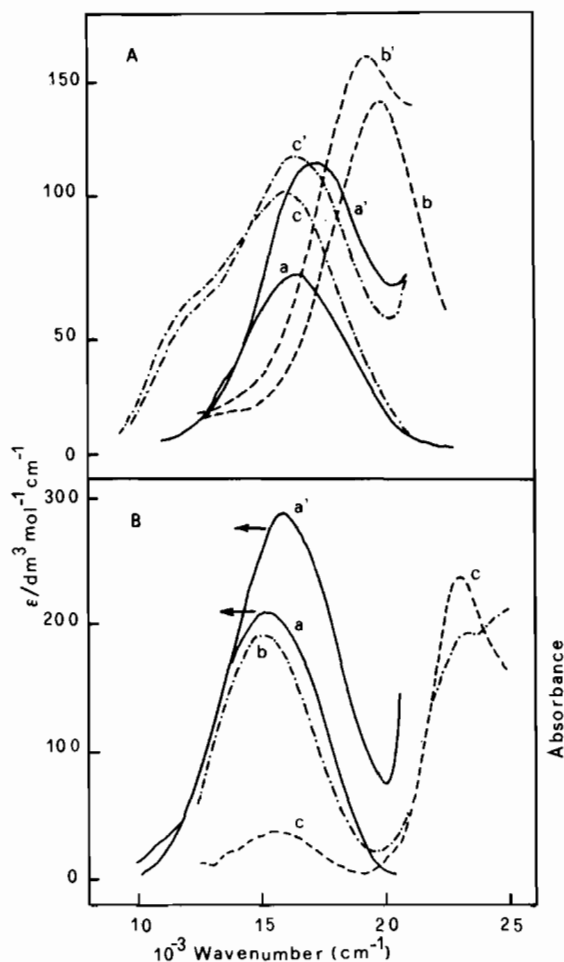


Fig. 1. (A) Absorption spectra of aqueous solutions of:  $[\text{Cu}(\text{dien})_2]^{2+}$  (a);  $[\text{Cu}(\text{trans-diene})_2]^{2+}$  (b); and  $[\text{Cu}(\text{dien})_2]^{2+}$  (c). Primed letters indicate the corresponding spectra after excess  $[\text{Fe}(\text{CN})_6]^{3-}$  addition. (B) Absorption spectra of aqueous solutions of  $[\text{Cu}(\text{dienMe}_5)_2]^{2+}$  in the absence (a) and in the presence of excess  $[\text{Fe}(\text{CN})_6]^{3-}$  (a'). Single crystal spectra of  $\text{K}_3[\text{Cu}(\text{dienMe}_5)(\text{OH})]_3[\text{Fe}(\text{CN})_6]_2 \cdot 6\text{H}_2\text{O}$  in two perpendicular light polarizations (b) and (c).

and assuming that  $[\text{Cu}(\text{dien})_2]^{2+}$  is the only species contributing to the EPR signal, the variations of the EPR amplitude with increasing amounts of  $[\text{Fe}(\text{CN})_6]^{3-}$  fit a theoretical curve when the equilibrium constants of the two reactions are  $K_1 = 12.0 \times 10^3$  and  $K_2 = 0.9 \times 10^3 \text{ dm}^3 \text{ mol}^{-1}$  respectively. The optical density changes at  $18,200 \text{ cm}^{-1}$  as a function of  $[\text{Fe}(\text{CN})_6]^{3-}$  concentration fit a theoretical curve calculated by using the same values of the equilibrium constants and the extinction coefficients  $\epsilon_0 = 38$  for  $[\text{Cu}(\text{dien})_2]^{2+}$ , in the absence of  $[\text{Fe}(\text{CN})_6]^{3-}$ ,  $\epsilon_0 = 102$  for the anionic 1:1 adduct, in the presence of excess  $[\text{Fe}(\text{CN})_6]^{3-}$ , and  $\epsilon_0 = 220 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  for the cationic 2:1 adduct (Fig. 3A).

The binding of  $[\text{Fe}(\text{CN})_6]^{3-}$  to  $[\text{Cu}(\text{trans-diene})_2]^{2+}$  is reflected by the bathochromic shift of the main copper band in the optical spectrum

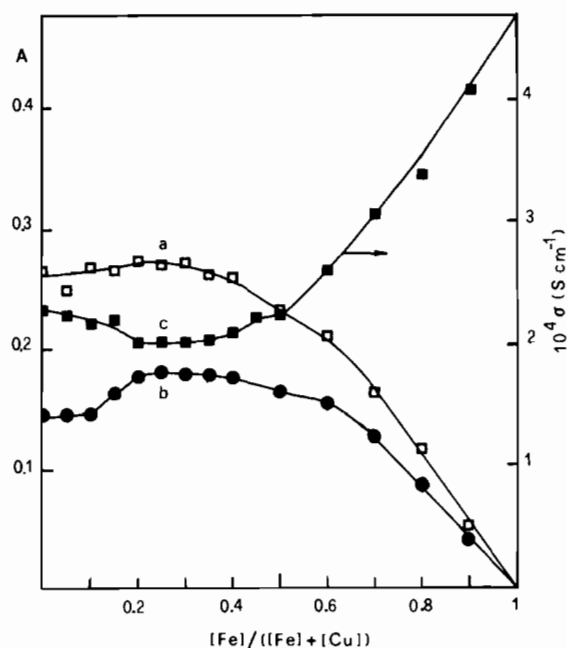


Fig. 2. Job plots for the reaction between  $[\text{Cu}(\text{dien})_2]^{2+}$  and  $[\text{Fe}(\text{CN})_6]^{3-}$  ( $[\text{Cu}(\text{dien})_2]^{2+} + [\text{Fe}(\text{CN})_6]^{3-} = 10^{-3} \text{ M}$ ) at  $18,200 \text{ cm}^{-1}$  (a); at  $19,200 \text{ cm}^{-1}$  (b); path length  $10 \text{ cm}$ . The corresponding conductivity changes at  $18^\circ \text{C}$  (c).

from  $19,700$  to  $19,100 \text{ cm}^{-1}$  and its small increase of intensity from  $\epsilon_0 = 130$  to  $150 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ . Both EPR and optical changes can be simulated as in the previous case (Fig. 3B) with  $K_1 = 1.24 \times 10^3$  and  $K_2 = 1.33 \times 10^2 \text{ dm}^3 \text{ mol}^{-1}$ . The extinction coefficients at  $18,000 \text{ cm}^{-1}$  were taken as  $90$ ,  $127$ , and  $310 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  for  $[\text{Cu}(\text{trans-diene})_2]^{2+}$ , the anionic 1:1 adduct, and the cationic 2:1 adduct, respectively.

Addition of hexacyanoferrate(III) to solutions where the ratio  $\text{dien}/\text{Cu}$  allows the species  $[\text{Cu}(\text{dien})_2]^{2+}$  to be present produces relatively minor changes of the optical spectrum (Fig. 1A), whilst the amplitude of the EPR copper signal varies as in the preceding two cases (Fig. 3B). The experimental EPR data can be fitted to a theoretical curve with  $K_1 \approx K_2 = 600 \text{ dm}^3 \text{ mol}^{-1}$ .

Titration with  $[\text{Fe}(\text{CN})_6]^{3-}$  of  $[\text{Cu}(\text{dienMe}_5)_2]^{2+}$  solutions were prevented by the formation of a precipitate. Nonetheless, by retarding the precipitation by addition of a large excess of  $[\text{Fe}(\text{CN})_6]^{3-}$  (50 fold the copper content) it was possible to measure the optical and EPR spectra. The former consists of an asymmetric band at  $15,800 \text{ cm}^{-1}$  ( $\epsilon_0 = 286 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ) in place of a band at  $16,000 \text{ cm}^{-1}$  ( $\epsilon_0 = 240 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ) of the parent compound (Fig. 1B). The EPR spectrum does not show any copper signal. Further information on the adduct was obtained from solid state studies on  $\text{K}_3[\text{Cu}(\text{dienMe}_5)(\text{OH})]_3[\text{Fe}(\text{CN})_6]_2 \cdot 2\text{H}_2\text{O}$ , the copper

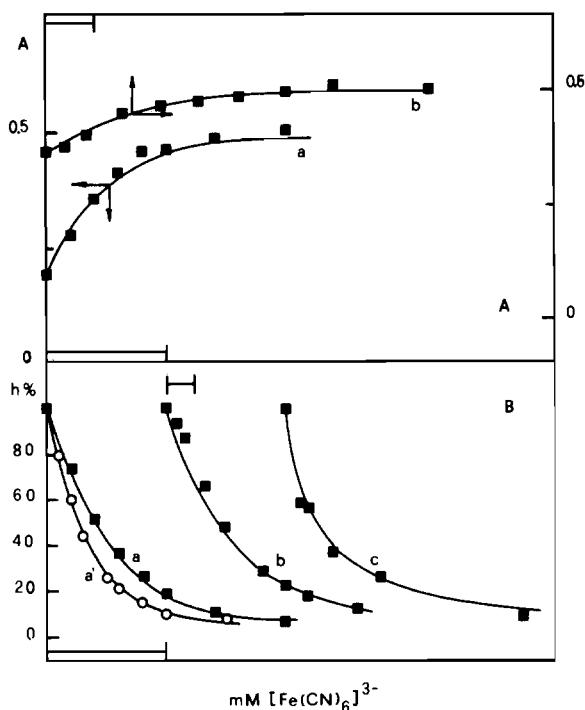


Fig. 3. (A) Absorbance variations on  $[\text{Fe}(\text{CN})_6]^{3-}$  addition.  $[\text{Cu}(\text{dien})]^{2+}$  1.0 mM, path length 5 cm,  $\nu = 18,200 \text{ cm}^{-1}$  (a);  $[\text{Cu}(\text{trans-diene})]^{2+}$  4.0 mM, path length 1 cm,  $\nu = 18,000 \text{ cm}^{-1}$  (b). (B) EPR amplitude changes on  $[\text{Fe}(\text{CN})_6]^{3-}$  addition.  $[\text{Cu}(\text{dien})]^{2+}$  1.0 mM (a) and 0.5 mM (a');  $[\text{Cu}(\text{trans-diene})]^{2+}$  4.0 mM (b);  $[\text{Cu}(\text{dien})_2]^{2+}$  1.0 mM (c). Solid lines were computed as described in the text. The bars along the abscissa represent 1.0 mM  $[\text{Fe}(\text{CN})_6]^{3-}$  units.

chromophore of which is not substantially different from that present in solution, as inferred by the similarity of solution, powder reflectance, and single crystal spectra. The EPR spectrum, measured with polarized light along the diagonals of the largest crystal face, *i.e.* along the extinction directions, is given in Fig. 1B. Two bands, one at  $15,000 \text{ cm}^{-1}$  and a much less intense one at  $15,800 \text{ cm}^{-1}$ , were observed. The EPR spectrum shows an isotropic line with  $g = 2.16$  with an intensity only accounting for a small percentage of the spins present. The compound prepared by substituting  $[\text{Fe}(\text{CN})_6]^{3-}$

with  $[\text{Co}(\text{CN})_6]^{3-}$  gives an anisotropic spectrum, accounting for most of the spins present, with  $g_{\perp} = 2.065$  and  $g_{\parallel} = 2.230$ , compatible with a copper ion still in a tetragonal environment. The IR spectra of the two latter adducts are indicative of  $\text{CN}^-$  bridges between iron or cobalt and copper [2], as bands due to CN stretching are found at 2122, 2138 and  $2167 \text{ cm}^{-1}$  for the hexacyanoferrate(III) complex and at 2138, 2145 and  $2177 \text{ cm}^{-1}$  for the hexacyanocobaltate(III) complex.

No change in the EPR amplitude signal is observed when  $[\text{Fe}(\text{CN})_6]^{3-}$  is added (even up to a tenfold excess) to a solution of  $[\text{Cu}(\text{titriplex})]^{2-}$ , the optical spectrum of the mixture being exactly the sum of that due to the copper complex and that of hexacyanoferrate(III).

Volume magnetic susceptibility measurements were performed at room temperature on 50 mM  $\text{K}_3[\text{Fe}(\text{CN})_6]$  and  $\sim 2\text{--}5 \text{ mM}$   $\text{Cu}^{2+}$  complex solutions. The high ratio between iron and copper ensures the formation of 1:1 adducts; a low content of copper had to be used because of the low solubility of the compounds. The experimental values of  $\sum_i \mu_i^2 c_i$  ( $c_i$  = concentration of each paramagnetic species) are reported in Table I, together with those calculated by assuming either a perfect antiferromagnetic coupling between iron and copper or a complete absence of interaction between the unpaired electrons of the two metals.

The magnetic moments used were determined as  $\mu = 2.30 \text{ B.M.}$  for  $\text{K}_3[\text{Fe}(\text{CN})_6]$  and  $1.90 \text{ B.M.}$  for the copper complexes. No result could be obtained for  $[\text{Cu}(\text{dienMe}_5)]^{2+}$  because of the formation of a precipitate during the course of the magnetic measurement. For the latter case only magnetic susceptibility measurements on the solid adduct could be considered. Values of  $1/\chi(\text{Fe}^{3+})$  vs.  $T$  of the solid  $[\text{Cu}(\text{dien})]^{2+}$  and  $[\text{Cu}(\text{dienMe}_5)]^{2+}$  hexacyanoferrate(III) adducts are reported in Fig. 4. The data were obtained by subtracting from the experimental susceptibility values those due to the copper complexes, and were corrected for possible diamagnetic contributions. For the susceptibility of  $[\text{Cu}(\text{dien})]^{2+}$  in the solid adduct it was assumed a Curie behaviour and  $\mu = 1.80 \text{ B.M.}$ , as suggested by the measurements performed on  $[\text{Cu}(\text{dien})]_2$

TABLE I. Magnetic Susceptibility of 50 mM  $\text{K}_3[\text{Fe}(\text{CN})_6]$  and  $c$  (mM) Copper Complexes.

Complex	$c$	$T$ (K)	exp.	$\sum \mu_i^2 c_i$ ( $\pm 6$ ) coupled	$\sum \mu_i^2 c_i$ ( $\pm 6$ ) uncoupled
$[\text{Cu}(\text{dien})]^{2+}$	1.88	289	285	254	272
	3.75	286	300	243	279
$[\text{Cu}(\text{trans-diene})]^{2+}$	5.00	306	293	238	283
$[\text{Cu}(\text{dien})_2]^{2+}$	5.00	297	298	238	283

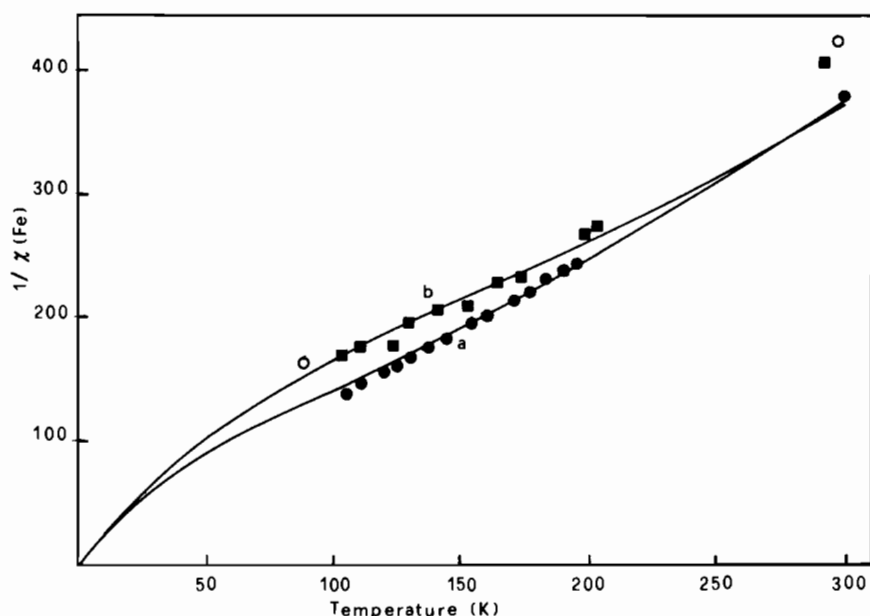


Fig. 4.  $1/\chi$  ( $\text{Fe}^{3+}$ ) vs.  $T$  (K) for  $[\text{Cu}(\text{dien})]_3[\text{Fe}(\text{CN})_6]_2 \cdot 6\text{H}_2\text{O}$  (●);  $\text{K}_3[\text{Cu}(\text{dienMe}_5)(\text{OH})]_3[\text{Fe}(\text{CN})_6]_2 \cdot 6\text{H}_2\text{O}$  (■) and  $[\text{Fe}(\text{CN})_6]^{3-}$  from ref. 3 (○). Curves (a) and (b) were calculated for  ${}^2T_2$  term in  $O_h$  with  $\lambda = -200$  and  $-300 \text{ cm}^{-1}$  respectively.

$[\text{Fe}(\text{CN})_6] \cdot 6\text{H}_2\text{O}$  where the paramagnetism is only due to the copper part. The same value was also used for  $[\text{Cu}(\text{dienMe}_5)]^{2+}$  [10]. Comparison was made with the data relative to the  ${}^2T_2$  term, the ground term of  $d^5$  in a strong octahedral field, for the two values  $\lambda = -300$  and  $-200 \text{ cm}^{-1}$  of the spin-orbit coupling constant. No account was taken of low symmetry components in spite of their presence as revealed by the splitting of  $\nu(\text{CN})$  multiplets in the IR spectra. On the same plot  $1/\chi$  values of free  $[\text{Fe}(\text{CN})_6]^{3-}$  from literature data [3] are reported. No substantial difference was found if the susceptibility of the copper part of the adduct was taken as 1.90 B.M.

## Discussion

The present results suggest that addition of  $[\text{Fe}(\text{CN})_6]^{3-}$  to aqueous solutions of copper complexes abolishes the Cu(II) EPR signal, provided a direct interaction in 1:1 or 1:2 adducts is possible, whatever the coordination site. In  $[\text{Cu}(\text{dien})]^{2+}$  and  $[\text{Cu}(\text{trans-diene})]^{2+}$  this occurs in the equatorial and axial direction respectively, as indicated by the isochromic and bathochromic shifts of the main copper d-d band.  $[\text{Cu}(\text{dien})_2]^{2+}$ , which by the presence of one band at  $15,900 \text{ cm}^{-1}$  and a 30% less intense shoulder at  $12,400 \text{ cm}^{-1}$  has a  $\text{CuN}_5\text{X}$  ( $\text{X} = \text{H}_2\text{O}$ ) chromophore, reacts with  $[\text{Fe}(\text{CN})_6]^{3-}$ , probably replacing X. This gives a less tetragonally-distorted chromophore, as inferred by the reduction of intensity of the shoulder relative to the

more intense d-d transition ( $\approx 50\%$ ), in close agreement with Hathaway observations [5].

$[\text{Cu}(\text{dienMe}_5)]^{2+}$  is expected to have a more distorted geometry compared with  $[\text{Cu}(\text{dien})]^{2+}$ , because of the steric requirements of its ligand [9]. The higher intensity of the solution spectrum substantiates the expectation; however, this complex behaves similarly to the dien compound when reacted with  $[\text{Fe}(\text{CN})_6]^{3-}$ , as the main copper transition also moves to higher energy and increases in intensity. This suggests that the chromophore retains  $d_{x^2-y^2}$  as the ground state for the unpaired electron in spite of the distortion. The EPR spectrum of the analogous hexacyanocobaltate(III) adduct (see Results) supports this suggestion, which also allows the rationalization of the single crystal spectrum of  $\text{K}_3[\text{Cu}(\text{dienMe}_5)(\text{OH})]_3[\text{Fe}(\text{CN})_6]_2 \cdot 6\text{H}_2\text{O}$ , by assigning the transitions at  $15,800$  and  $15,000 \text{ cm}^{-1}$  to  $d_{yz} \rightarrow d_{x^2-y^2}$  and  $d_{xz} \rightarrow d_{x^2-y^2}$  respectively [2]. The difference with respect to the analogous  $[\text{Cu}(\text{dien})]^{2+}$  hexacyanoferrate(III) adduct is probably related to a marked N-Cu-N angular deviation from  $180^\circ$ , in the form of a Berry twist [10], though insufficient to produce a trigonal bipyramidal species.

In the case of  $[\text{Cu}(\text{titriplex})]^{2+}$  hexacyanoferrate(III) is not allowed to penetrate the copper coordination sphere, as both the optical and EPR spectra are unaffected.

The decrease of the EPR signal of copper solutions by  $[\text{Fe}(\text{CN})_6]^{3-}$  addition, at room temperature, indicates an interaction between the two paramagnetic species. However, this does not affect the

value of the magnetic moments of the two metals in the adduct, measured in solution at room temperature. The same behaviour is also observed in the magnetic measurements carried out on the solid compounds as a function of temperature. As the chemical exchange of  $[\text{Fe}(\text{CN})_6]^{3-}$  among copper centres is likely to be slow on the EPR time scale, the decrease without broadening of the line amplitude may be attributed to a dipole-dipole interaction between the spins of the paramagnetic metal ions within each adduct [3]. In the light of the above and other findings [3, 11], while the reported disappearance of the copper EPR signal of  $[\text{Cu}(\text{glygly})]^{2+}$  by  $[\text{Fe}(\text{CN})_6]^{3-}$  addition in solution at room temperature can be justified, the diamagnetism of the copper(II)-glygly and other copper(II)-peptide- $[\text{Fe}(\text{CN})_6]^{3-}$  adducts is not easy to explain, the more so upon considering that oxidation of the copper ion was excluded [4].

As far as the problem of GaO is concerned, the disappearance of the copper signal by  $[\text{Fe}(\text{CN})_6]^{3-}$  addition, if not attributable to copper oxidation, is in line with the present results. Thus the availability of the copper first coordination sphere to hexacyanoferrate(III) can produce the disappearance of the EPR signal without affecting the value of the magnetic moment of the two metals.

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