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VOLTAMMETRIC BEHAVIOUR OF INSULIN-ZINC ON THE MERCURY INTERFACE

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SUMMARY

Insulin-zinc suspensions are more electroactive on the hanging mercury drop electrode (hmde) when the protein is in amorphous state. Reduction and reoxidation of disulphide bridges depend on the Zn(II) present in buffer solutions.

The influence of the insulin adsorption on the reduction process of zinc at the hmde, can be explained by variation of the exchange current density with a change in the surface fraction covered by the protein on the electrode.

INTRODUCTION

Insulin is found forming a monomer-dimer-hexamer system (1-3) in an aqueous solution. This type of association equilibria depends on its concentration, on the pH, on the temperature (4) and on the medium (5). The association constants which characterize the monomer-dimer and dimer-hexamer equilibria are $2.2 \times 10^4 \text{ M}^{-1}$ and $8.6 \times 10^5 \text{ M}^{-2}$

respectively(6). The polarographic reduction of insulin involves the breakage of disulphide bridges(7-9).

The structural changes of some proteins and the breaking of their disulphide bridges can be affected by the intervention in these processes by divalent metallic cations such as Ca^{2+} , Co^{2+} , Ni^{2+} , Hg^{2+} , etc(10-17).

We studied the behaviour of the insulin-zinc system on the hanging mercury drop electrode by cyclic voltammetry and on a dropping mercury electrode. We used Zn(II) as a test cation for the study of the adsorption kinetics of insulin.

EXPERIMENTAL

Cyclic voltammograms and coulometric determinations were made with AMEL equipment composed of an AMEL 551 potentiostat, an AMEL 567 function generator, an AMEL 563 coulometer, an HP-AMEL 862/0 recorder and an AMEL 448 oscilloscope. Also, a Belpor HQ-305 function generator, a Belpor HQ-105 potentiostat and a Riken Denshi F-35 recorder. We used a three-electrode system with thermostatted cell (25.0 ± 0.1 °C). The working electrode used in voltammetric experiments was a h.m.d.e.

METROHM EA 290. The area of the mercury pool electrode was 7 cm^2 . The Ag|AgCl (s) , KCl (sat) electrode was used as a reference electrode in Britton-Robinson buffers, and $\text{Hg|HgSO}_4(\text{sat.})$ in all other cases.

We used two suspensions of insulin complex (Laboratories Novo, Copenhagen) with an activity of 40 i.u./cm^3 . The first preparation was 70% crystallized porcine/bovine insulin-zinc. The second preparation was

100% amorphous state porcine insulin-zinc. A third preparation was porcine insulin protamine (Nordisk Gentoite) with 40 i.u./cm^3 .

Other products used to prepare the solutions were zinc chloride and zinc sulphate p.a. Merck.

Two buffer solutions have been used. The Britton-Robinson buffer was composed of acetic, boric and phosphoric acids in a 0.1 M concentration and different KOH and KCl concentrations. The other buffer media it has been made with acetic and phosphoric acids (0.1 M) and KOH and K_2SO_4 .

RESULTS

W. Lee and coworkers(9) found three cathodic peaks and one anodic in a non-buffered medium at $\text{pH} = 1$ using cyclic voltammetry (Fig.1). Diagram (a) shows the reduction (wave C) and re-oxidation (wave C*) of Zn(II) . Diagrams (b) and (c) show the effect caused by the addition of insulin, on successive scans, to the reduction of Zn(II) present in the solution. Diagram (c) is an amplification of (b) to show clearly the reduction (wave A) and re-oxidation (wave A*) of disulphide bridges of insulin.

In our experiments with Britton-Robinson buffer, we detected an anodic peak near -500 mV , only visible when the second cathodic peak was recorded. This phenomenon disappears at $\text{pH} > 7.5$ (Fig. 2).

The re-oxidation of SH-groups of the amorphous insulin formed when disulphide bridges are reduced, can show one or two anodic peaks depending on the potential cycled (Fig. 2). This demonstrates the

participation of free-Zn(II), reduced, in the re-oxidation process of previously reduced disulphide bridges. Such behaviour indicates that

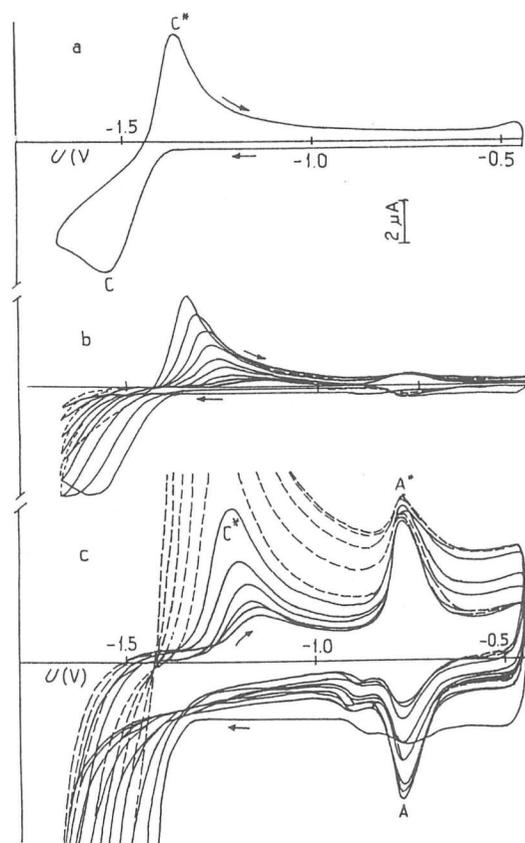


Fig. 1.- Effect of the insulin addition on Zn(II) solution. Successive potential scans. pH = 3.02; $C_{Zn} = 4 \times 10^{-4} M$, $\nu = 250 mV s^{-1}$. a) $C_p = 0$; b) $C_p = 0.63 \times 10^{-5} M$; c) amplification of b) recorded to observe the redox process of disulphide bridges. Reference electrode $Hg|Hg_2SO_4(s)|_2SO_4(aq)$.

reduced zinc in the second cathodic process remains adsorbed on the electrode, interacting successively with the SH-group. The process can be described as follows:



(This symbolism is expressed in accordance with Ref. 8).

According to some authors, insulin possesses a negative charge(8) which must contribute to the effect that Zn(O), generated from the reduction of Zn(II) free, re-oxidizes into Zn(II) complexed to compensate this charge. This could justify the detection of the anodic peak superimposed on the reoxidation of disulphides. The variation of the cathodic peak current intensity (wave A, fig. 2), with pH, is attributed to the distinct forms of molecular association in which insulin is found. The disulphide bonds reduction gives cathodic and anodic peaks which become smaller when the hydrogen ions concentration decreases. At pH= 4.3 (when insulin dimers are formed(8)), cathodic I_p falls suddenly, perhaps because the disulphide bonds dimer reduction becomes sterically more difficult than the insulin monomer. The U_p and $U_p/2$ dependence on the pH (fig.3) confirms that at $pH < 6$ the reduction begins by a protonation; however at greater pH a change of electrochemical mechanism occurs in the same way as in the cystine reduction(18).

On the other hand, the variation of peak and half-peak potentials of wave A with pH fulfills the following equations:

$$U_p (mV) = - 639.46 - 48.40 pH \quad (1)$$

$$U_{p/2} \text{ (mV)} = - 616.00 - 41.07 \text{ pH} \quad (2)$$

in the range $1 < \text{pH} < 6$.

Taking into account that equation (3)(19):

$$U_p - U_{p/2} = - \frac{47.4}{n\alpha} \quad (3)$$

holds true and combining equations (1), (2) and (3) we can relate the transfer coefficient, α , with the pH:

$$n\alpha = - \frac{47.7}{23.46 + 7.33 \text{ pH}} \quad (4)$$

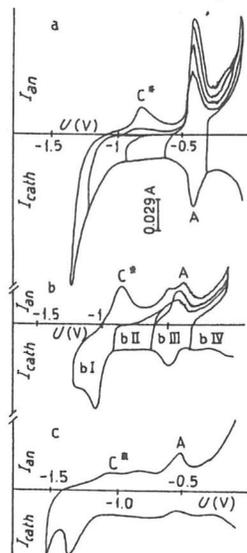


Fig. 2.- Cyclic voltammograms of insulin-zinc. $C_p = 0.63 \times 10^{-5} \text{ M}$; $C_o = 2.4 \times 10^{-5} \text{ M}$; $v = 250 \text{ mV s}^{-1}$. a) $\text{pH} = 3.5$; b) $\text{pH} = 6.8$; b-I with the potential cycled past the Zn(II) cathodic peak; b-II and b-III past the first cathodic peak; b-IV is not past the first cathodic peak; c) $\text{pH} = 9.5$. Reference electrode $\text{Ag/AgCl(s)/KCl (sat)}$. Britton-Robinson buffer.

Without considering the coulombic fields around the electrode, according to the theory of Devanathan(20), the second monoelectronic transfer is the determinant at $\text{pH} = 1$. The voltammogram shows a single cathodic peak and a single anodic peak. At $\text{pH} = 6$ the first monoelectronic transfer is the determinant one and it is possible to observe experimentally the separation of both monoelectronic transfers (Fig.4).

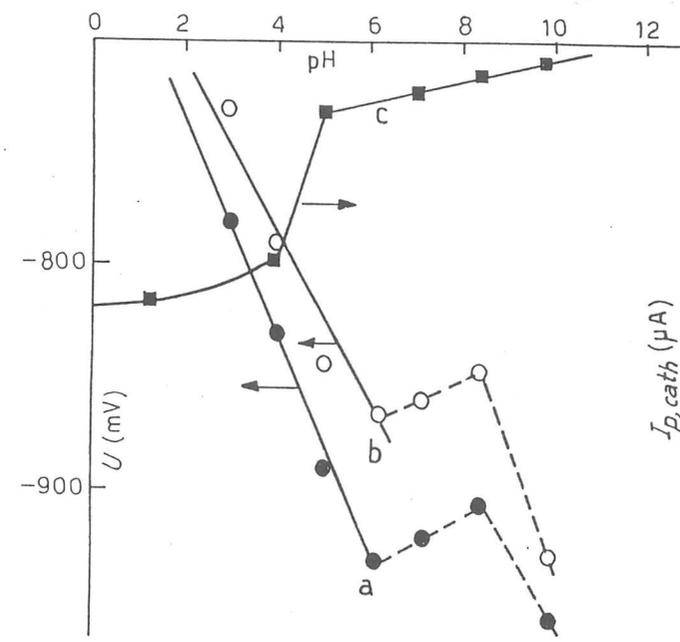


Fig. 3.- Variation of peak potentials U_p (a), half-peak potentials $U_{p/2}$; (b) and cathodic peak current intensities $I_{p,cath}$; (c) of reduction of disulphide bridges with pH. $C_p = 0.63 \times 10^{-5} \text{ M}$; $v = 250 \text{ mV s}^{-1}$. Reference electrode $\text{Hg/Hg}_2\text{SO}_4(\text{s})/\text{K}_2\text{SO}_4(\text{sat.})$.

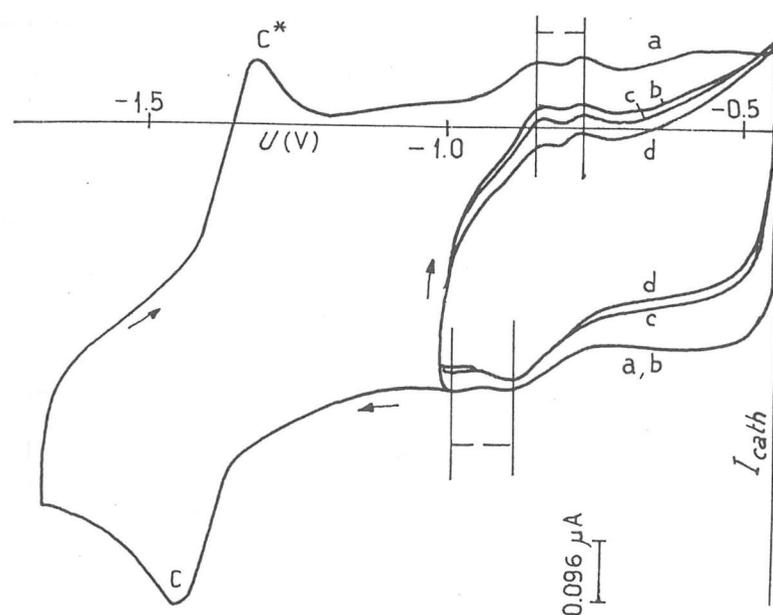


Fig. 4.- The redox resolution process of disulphide bridges in two cathodic and two anodic waves. a) first scan with the potential cycled past Zn(II) (peak C); b), c) and d) are the first, second and third scan respectively with the potential cycled past disulphide bridges waves. Reference electrode Ag/AgCl(s)/KCl(sat.).

It is important to point out that experimental conditions determine these phenomena; however the role of chloride, phosphate ions and especially sulphate ions, has not been clarified. The number of electrons per molecule involved in the potentiostatic reduction of

electrons needed for reducing the three disulphide bonds of insulin is observed, since in the coulometric reduction both Zn(II) and hydrogen ions are discharged. At pH= 6.85, a value of $n = 6.3$ is calculated, which is close to the six electrons theoretically required to reduce all disulphide bonds in amorphous protein at the mercury pool electrode, while at pH= 9.48, only two disulphide bonds are reduced.

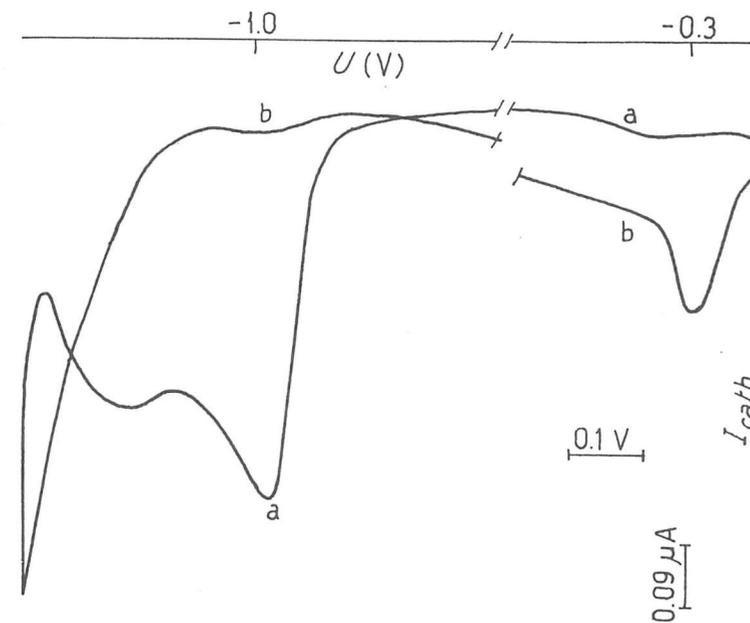


Fig. 5.- Differential pulse polarographic waves of insulin-zinc. pH = 3.2; $t_{drop} = 0.4$ s. $\Delta U_p = -20$ mV; a) $C_p = 0.63 \times 10^{-5}$ M, $C_o = 2.4 \times 10^{-5}$ M; b) $C_p = 3.8 \times 10^{-5}$ M, $C_o = 1.5 \times 10^{-4}$ M. Reference electrode Ag/AgCl(s)/KCl(sat.).

When we subtract the theoretical number of electrons associated with the first wave ($n=6$ at neutral or acid pH, and $n=4$ at basic pH) from the whole number of electrons determined in coulometric reduction at the potential of the second wave, the number of electrons determined experimentally is near 2, i.e. close to the number of electrons required for the reduction of Zn(II).

In amorphous state, insulin-zinc presents less steric impediments and its disulphide bridges are more electroactive than those of insulin-zinc in crystalline form(21). Reduction processes are strongly affected by insulin adsorption. The increase of the insulin concentration on the surface of the electrode (Γ_t) favours the reduction of disulphide bridges (wave A) and makes the reduction of Zn^{2+} difficult (wave C Figs. 1 and 5). Figs. 6 and 7 show the shift of anodic peak potential and anodic peak current due to the adsorption time for different insulin concentrations.

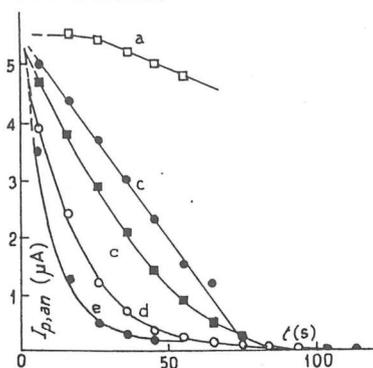


Fig. 6.- Variation of the anodic peak current intensity of Zn(II) with adsorption time of insulin. $C_{\infty} = 4 \times 10^{-4} M$; pH = 3.2; $v = 250 \text{ mV s}^{-1}$. a) $C_p = 0.126 \times 10^{-5} M$; b) $C_p = 0.315 \times 10^{-5} M$; c) $C_p = 0.378 \times 10^{-5} M$; d) $C_p = 0.504 \times 10^{-5} M$; e) $C_p = 0.63 \times 10^{-5} M$. Reference electrode $Hg|Hg_2SO_4(s)|K_2SO_4(sat)$.

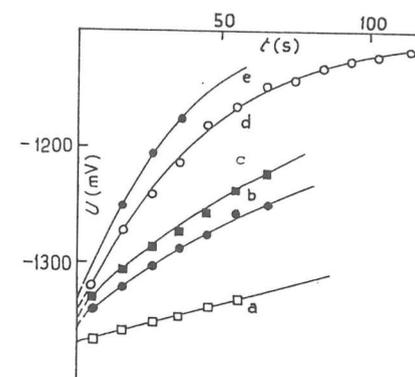


Fig. 7.- Variation of the anodic peak potential of Zn(II) with the insulin adsorption time. $C_{\infty} = 4 \times 10^{-4} M$; pH = 3.02; $v = 250 \text{ mV s}^{-1}$. a) $C_p = 0.126 \times 10^{-5} M$; b) $C_p = 0.31 \times 10^{-5} M$; c) $C_p = 0.378 \times 10^{-5} M$; d) $C_p = 0.504 \times 10^{-5} M$; e) $C_p = 0.630 \times 10^{-5} M$. Reference electrode $Hg|Hg_2SO_4(s)|K_2SO_4(sat)$.

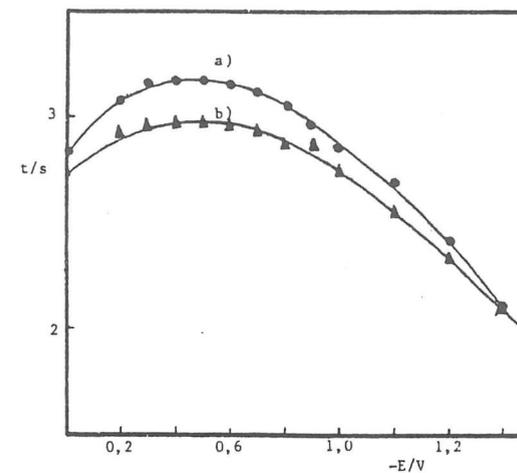


Fig. 8.- Electrocapillary curve of the insulin-zinc on Britton-Robinson buffer. pH = 2.07. a) $C_p = 0$; b) $C_p = 1.260 \times 10^{-5} M$.

DISCUSSION

From the electrocapillary curves (Fig. 8), it can be concluded that insulin is adsorbed in a wide interval of potentials. The surface concentration of insulin (Γ_t) for small values of the coverage (θ) can be calculated from Koryta's equation(14):

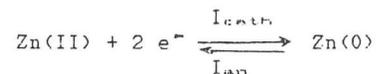
$$\Gamma = 7.36 \times 10^{-4} C_p D_p^{1/2} t^{1/2} \quad (5)$$

In buffer solutions where chloride ions are not present, we can consider that the area of the electrode can be divided in two parts. One part is occupied by adsorbed insulin and the other is free of insulin, namely:

$$A_{\text{electrode}} = A_{\text{occupied}} + A_{\text{free}} \quad (6)$$

Through the free part, Zn(II) is diffused toward the electrode before Zn(II) becomes reduced.

When there is not insulin on the hmde, the current intensity recorded corresponds to the overall process:



and the anodic current intensity can be expressed⁽¹⁰⁾ as :

$$I_{\text{diff}} = k A_{\text{electrode}} \quad (7)$$

where

$$k = C_0 2 n (\alpha D_0 v)^{1/2} C_0 \pi^{1/2} \chi(bt) + 0.16 \frac{D_0^{1/2}}{r_0 (\alpha v)^{1/2}} \psi(bt) \quad (8)$$

If there is insulin on the electrode, only the free area will be useful to reduce, and re-oxidize, Zn(II). The intensity of reoxidation of Zn(0), corresponding to this fraction of area, is expressed as :

$$I_{\text{lim}} = k A_{\text{free}} \quad (9)$$

Combining equations (6), (7), (8), and (9) results :

$$\frac{I_{\text{lim}}}{I_{\text{diff}} - I_{\text{lim}}} = \frac{1 - \theta}{\theta} \quad (10)$$

where $\theta = A_{\text{occupied}}/A_{\text{electrode}} = \Gamma_t/\Gamma_0$ and the ratio

$[(I_{\text{diff}} - I_{\text{lim}}) / I_{\text{lim}}]$ is equivalent to the non-corrected coefficient of inhibition of the re-oxidation of Zn(0) (22-23). If the concentration of molecules of insulin on h.m.d.e. is very small after a long time, it can be considered that they do not interact among themselves so that equations (5) and (10) are sufficient to describe results:

$$7.36 \times 10^{-4} C_p D_p^{1/2} t^{1/2} = \Gamma_0 \left(1 - \frac{I_{\text{lim}}}{I_{\text{diff}}} \right) \quad (11)$$

Accepting the value of 724 \AA^2 for the area of one insulin molecule (24), and therefore $\Gamma_m = 2.29 \times 10^{-11} \text{ mol cm}^{-2}$, and giving C_p and D_p the values $0.126 \times 10^{-5} \text{ M}$ and $16.1 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ respectively (25), equation (10) can be summarized as :

$$k' t^{1/2} = \left(1 - \frac{I_{lim}}{I_{diff}}\right) \quad (11)$$

where $k' = 7.36 \times 10^{-4} C_p D_p^{1/2} \Gamma_m^{-1} = 0.051 \text{ s}^{-1/2}$.

Experimentally we find $k = 0.047 \text{ s}^{-1/2}$ which is in accordance with the aforesaid result.

Although the equation (11) is in agreement with the results obtained at low concentrations of the protein, it should be taken as an approximative equation.

ADDITIONAL SYMBOLS

- | | |
|---|---|
| A : electrode area (cm^2) | n : number of transferred electrons |
| C_{Zn} : Zn(II) concentration (M) | $U_{p/2}$: half peak potential (V) |
| C_p : insulin concentration (M) | α : transfer coefficient |
| D_{Zn} : Zn(II) diffusion coefficient ($\text{cm}^2 \text{ s}^{-1}$) | θ : covered surface |
| D_p : insulin diffusion coefficient ($\text{cm}^2 \text{ s}^{-1}$) | $\chi(bt)$: current function |
| I_{diff} : diffusion current intensity | $\beta(bt)$: current function correction |
| $I_{p,an}$: anodic current peak intensity (μA) | |
| $I_{p,cath}$: cathodic current peak intensity (μA) | |
| Γ_t : insulin surface concentration (mol cm^{-2}) | |
| Γ_m : maximum insulin surface concentration (mol cm^{-2}) | |

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ELECTROCHROMISM IN PRUSSIAN BLUE

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SUMMARY

Prussian blue (PB) has been electrodeposited on ITO-glass coated electrode. Electrochromism effect, stability of the film against continued ciclation of potential and influence of nitrate and chloride ions has been studied.

INTRODUCTION

As well-known, PB (Ferric Ferrocyanide) is an important member of the family of metal hexacyanometalates. In the past few years, interest in these mixed-valency compounds was renewed due to the easiness for coating it as thin-films on electrodes (1-4), allowing its use in electrochromic devices (5-7). The deposition can be carry out chemically (1-3) or electrochemically (1, 2) on different substrates: Pt (1-3), glassy Carbon (2), Au (2, 3) or transparent electrodes like ITO (Indium Tin Oxide) (4) and FTO (Fluorine Tin Oxide) (6).

PB has been described in two different formulas: soluble PB $KFe^{III}[Fe^{II}(CN)_6]$ and insoluble PB $Fe^{III}_4[Fe^{II}(CN)_6]_3$, owing the