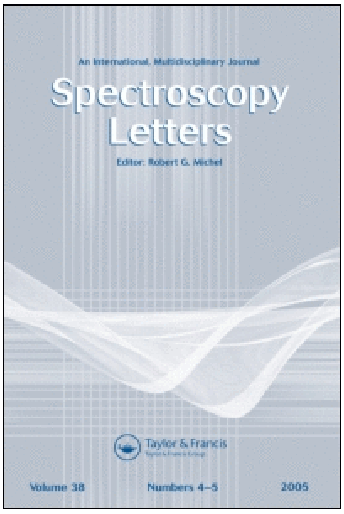

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Spectroscopic and Electrochromic Behavior of a Pentanuclear Cyanoiron(Ii)-Polyimine Supermolecule and Its Corresponding Prussian Blue Film

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SPECTROSCOPIC AND ELECTROCHROMIC BEHAVIOR OF A PENTANUCLEAR CYANOIRON(II)-POLYIMINE SUPERMOLECULE AND ITS CORRESPONDING PRUSSIAN BLUE FILM

Key words: cyanoiron-complex, iron-polyimine complex, electrochromism, Prussian blue film, spectroelectrochemistry

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ABSTRACT

A novel pentanuclear iron(II)-polyimine complex containing four pentacyanoferrate(II) groups attached to peripheral pyridine residues has been synthesized, exhibiting a characteristic iron-to-pyridine charge-transfer band at 395 nm, in addition to the iron-to-polyimine charge-transfer bands at 490 and 600 nm. The corresponding Mössbauer spectrum has been deconvoluted in terms of two symmetric doublets of 4:1 relative intensities, respectively, at IS = 0.345 and 0.021 mm/s and QS = 0.841 and 0.845 mm/s, associated with the pentacyanoferrate(II) and the iron(II)-polyimine centers. The peripheral groups can be reversibly oxidized at 0.38 V, in aqueous solution, leading to the decay of the 395 nm band. This process is not accessible in the corresponding Prussian-blue film; instead, the electrochromic behavior observed in this case reflects the changes in the intervalence-transfer band at 750 nm, accompanying the

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electrochemical process at 0.4 V associated with the $Fe^{III/II}$ redox couple in the matrix.

INTRODUCTION

Metal complexes containing multi-bridging ligands have been of great interest as building blocks in supramolecular chemistry.[1-3] Recently, we reported on the chemistry of an interesting iron(II)-polyimine system containing four pyridine groups available for interacting with transition metal complexes.[4] This multi-bridging system was obtained from the reaction of 2,6-diacetylpyridine with 4-aminomethylpyridine in the presence of iron(II) ions, exhibiting a rather stable and inert bis(triimine)iron(II) center. Here we describe a novel pentanuclear species generated from this complex, by attaching four pentacyanoferrate(II) groups at the pendant pyridine arms, as shown in Fig. 1. The binding of the pentacyanoferrate(II) groups was pursued with great interest, since their further reaction with Fe^{3+} ions can provide a good strategy for immobilizing the complex onto electrode surfaces, allowing one to exploit the electrochemical properties of the corresponding Prussian blue films.

EXPERIMENTAL

The $[Fe(dapipy)_2](PF_6)_2$ (dapipy = 2,6-diacetyl-4-methylpyridiliminepyridine) and $Na_3[Fe(CN)_5NH_3]\cdot 3H_2O$ complexes were prepared as previously reported.[4,5] The $Na_{10}[\mu_4\text{-}Fe(dapipy)_2\text{-}\{Fe(CN)_5\}_4]\cdot 30H_2O$ complex was synthesized by dissolving 63 mg (0.06 mmol) of $[Fe(dapipy)_2](PF_6)_2$ in 10 cm^3 of water and adding 76 mg (0.024 mmol) of $Na_3[Fe(CN)_5NH_3]\cdot 3H_2O$ and 0.4 g of sodium iodide, under an argon atmosphere. After 1 h, the solution was filtered, and treated with 15 cm^3 of ethanol. The blue solid was collected on a filter, washed with dry ethanol and diethyl ether. (Found: C, 33.6; H, 4.6; N, 18.2. $C_{62}H_{102}N_{30}Fe_5Na_{10}O_{30}$ requires C, 33.0; H, 4.6; N, 18.6).

The electronic spectra were recorded on a Guided-Wave fiber optics spectrophotometer. The Mössbauer spectra were recorded on a Wissel instrument,

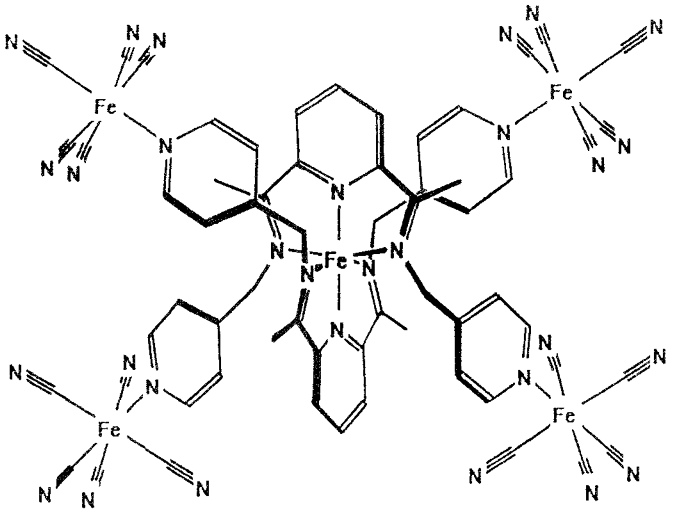

Fig.1. MM$^+$ structural representation of [μ_4-Fe(dapipy)$_2$-{Fe(CN)$_5$}$_4$]$^{10-}$, showing *the two orthogonal polyimine ligands and the four peripheral groups* symmetrically distributed around the iron center.

at room temperature, using a ^{57}Co(Rh) source and metallic iron for calibration. Cyclic voltammetry and spectroeletrochemical measurements were carried out using a Princeton Applied Research instrument. The experimental procedures were as outlined in previous studies.[6,7] The Prussian blue modified electrodes were prepared by immersing the bare platinum electrode into an aqueous solution containing 2 mmol dm^{-3} FeCl$_3$, 2 mmol dm^{-3} [μ_4-Fe(dapipy)$_2$-{Fe(CN)$_5$}$_4$]$^{6-}$ (freshly prepared by oxidizing the starting complex with aqueous bromine), 10 mmol dm^{-3} KCl and 10 mmol dm^{-3} HCl, and scanning the potential from 0.2 to 0.8 V. The electrode was washed with water and dried in air, exhibiting a homogeneous bluish film on its surface. Molecular mechanics calculations were carried out for illustrative purposes, using the MM$^+$ force field from Hyperchem 5.0, at a refinement level of 10^{-5} kcal.

RESULTS AND DISCUSSION

The reaction of the $[Fe(dapipy)_2]^{2+}$ complex with the pentacyanoferrate(II) ions leads to a symmetric pentanuclear species, as represented in Fig. 1. The proposed structure, based on molecular mechanics calculations, exhibits an iron(II)-polyimine center of D_{2d} symmetry and four peripheral groups oriented in an approximate tetrahedral arrangement, in order to minimize the steric and electrostatic repulsions.

The electronic spectrum of the starting $[Fe(dapipy)_2]^{2+}$ complex exhibits strong absorption bands in the visible region, ascribed[4] to metal-to-ligand charge-transfer transitions in iron(II)-polyimine complexes (Fig. 2, inset). According to previously reported ZINDO/S calculations for the iron(II)-bis(acetyliminepyridine) chromophore,[8] the highest occupied levels correspond to the d_{xy} and the degenerate d_{xz} and d_{yz} orbitals. The two lowest unoccupied molecular orbitals exhibit π-symmetry (here denoted π_1^* and π_2^*) and are mainly centered on the ligands, involving anti-bonding combination with the metal d_{xz}, d_{yz} orbitals. The $d_{xy}\rightarrow\pi_1^*$ and $d_{xz,yz}\rightarrow\pi_1^*$ transitions are theoretically expected around 650 nm, displaying oscillator strengths very close to zero. They have been ascribed[4] to the observed weak band at 660 nm. Two intense bands are theoretically expected around 490 and 590 nm, corresponding to the $d_{xy}\rightarrow\pi_2^*$ and $d_{xy,yz}\rightarrow\pi_2^*$ charge-transfer transitions, respectively. These transitions have been ascribed[4] to the observed bands at 504 and 600 nm, respectively. The last one exhibits a multiplet of vibronic components, as shown in Fig. 2 (inset).

The binding of the four pentacyanoiron(II) groups to the iron(II)-dapipy center leads to a new strong band at 395 nm (log ε = 4.92) in addition to the absorption bands at 600 (3.80) and 490 nm (4.00), as shown in Fig 2. This band is similar to that observed in the $[Fe(CN)_5py]^{3-}$ complex,[5] and can be ascribed to an iron-to-pyridine charge transfer transition involving the peripheral groups. The strong absorption at 240 nm can be associated with $\pi\rightarrow\pi^*$ (dapipy) and $d_\pi\rightarrow p_\pi^*$ (Fe-CN) charge transfer transitions expected in this region.

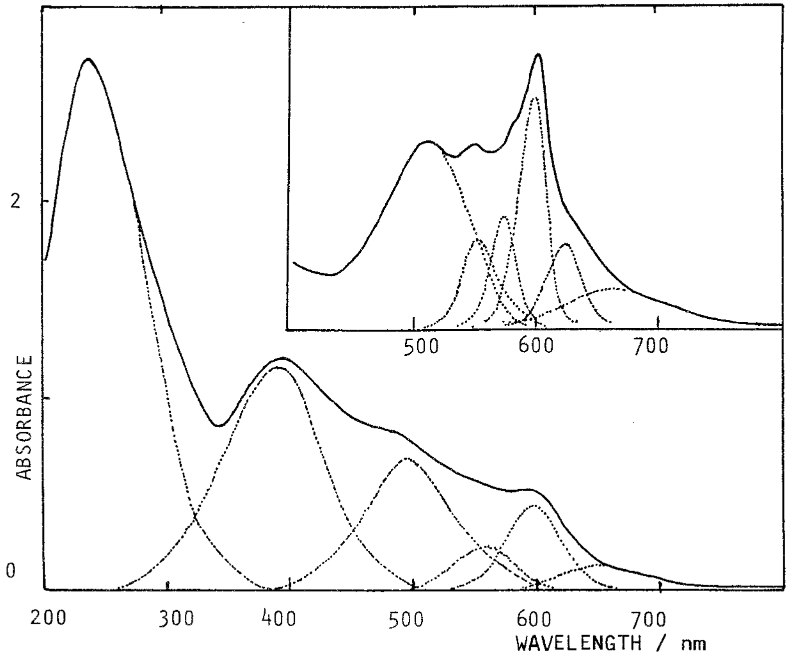

Fig. 2. Electronic spectra of the $[Fe(dapipy)_2]^{2+}$ (inset) and $[\mu_4\text{-}Fe(dapipy)_2\text{-}\{Fe(CN)_5\}_4]^{10-}$ (10 μmol dm^{-3}) complexes, in aqueous solution (.... Gaussian components).

The Mössbauer spectrum of the $[Fe(dapipy)_2]^{2+}$ complex consists of a doublet of peaks at IS = 0.145 ± 0.003 mm and QS = 0.962 ± 0.005 mm, characteristic of a low-spin iron(II) complex.[9,10] In the case of the pentanuclear complex, the Mössbauer spectrum exhibits a doublet with two symmetric shoulders, which can be deconvoluted in terms of two pair of peaks of 4:1 intensities. The strongest peaks at IS = 0.345 and Q = 0.841 mm, correspond to the four $[Fe(CN)_5py]^{3-}$ moieties, while the shoulders can be associated with the central iron(II)-polyimine complex, exhibiting IS = 0.021 and Q = 0.845 mm. It is interesting to note that, in spite of occupying remote positions, the pentacyanoferrate(II) ions do exert some influence on the central ion, decreasing its corresponding IS by 0.124 mm.

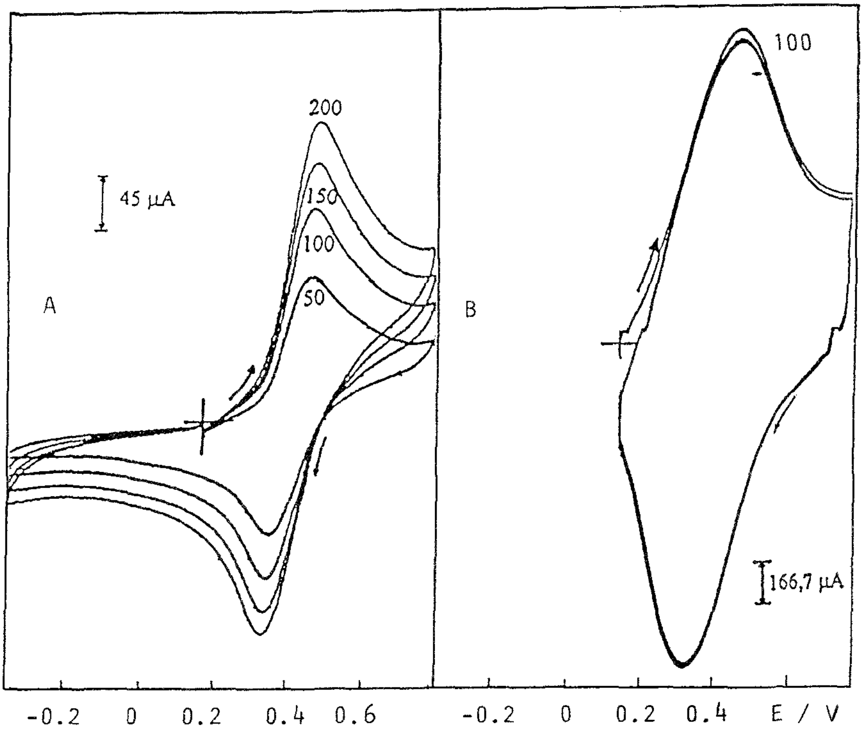

Figure 3. Cyclic voltammograms of the $[\{Fe(CN)_5\}_4\text{-}\mu_4\text{-}Fe(dapipy)_2]^{10-}$ complex (A) at several scan rates ($mV\ s^{-1}$) and of the corresponding Prussian blue film onto platinum electrode (B), in aqueous solution, KCl = 0.10 mol dm^{-3}, E / V *vs* SHE.

In aqueous solution, the cyclic voltammogram (Fig. 3.A) of the pentanuclear complex consists of a reversible wave at $E_{1/2}$ = 0.38 V, ascribed to the $[Fe(CN)_5py]^{2-/3-}$ redox couple. The redox waves associated with the iron-polyimine center are not accessible in aqueous solution[4,7]. Starting from the oxidized pentanuclear complex in the presence of ferric ions, the formation of Prussian blue films onto the electrode surface can be induced by scanning the potential in the 0.2 - 0.8 V range. The modified electrode is quite stable, displaying a reversible wave at 0.4 V when immersed in the aqueous electrolyte solutions, as shown in Fig. 3. B.

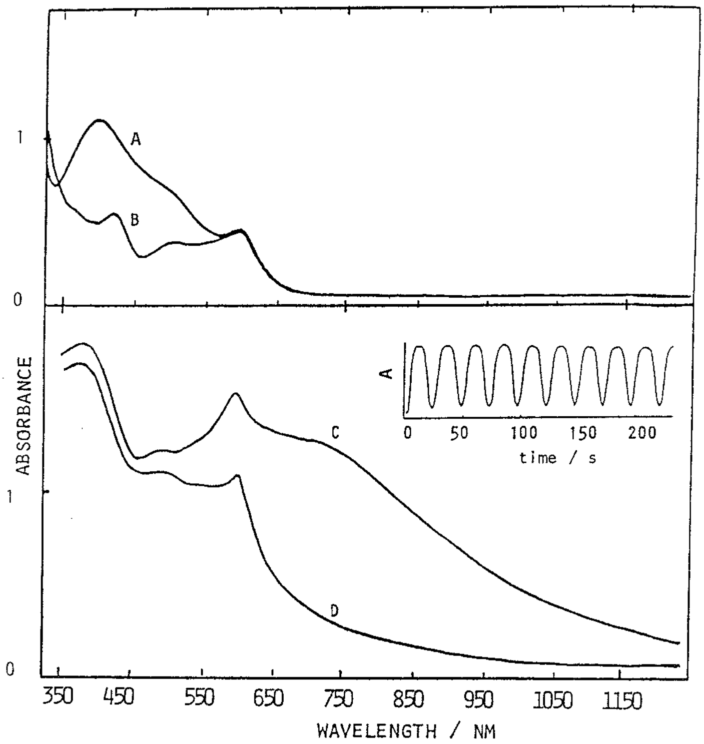

Fig. 4. Spectroelectrochemical behavior of the $[\{Fe(CN)_5\}_4\text{-}\mu_4\text{-}Fe(dapipy)_2]^{10-}$ complex at 0.2 V (A) and at 0.8 V *vs* SHE (B); and of the corresponding Prussian blue film at 0.2 V (C) and 0.8 V (D). Inset: typical electrochromic response of the film at 750 nm, during the repetitive cyclic scans from 0.2 to 0.8 V.

The *in-situ* spectroelectrochemical behavior of the pentanuclear complex and of its corresponding Prussian blue film onto a platinum electrode is shown in Fig. 4. The oxidation of the pentanuclear complex at 0.6 V leads to the decay of the 395 nm band, leaving unchanged the iron-to-polyimine charge transfer bands at 490 and 600 nm (Fig. 4.A). A new band appears at 416 nm, associated with a ligand-to-metal charge-transfer transition in the pentacyanoferrate(III) species.[11]

In contrast to the spectroelectrochemical behavior in solution, the oxidation of the Prussian blue film at 0.6 V does not affect the electronic spectra of the pentanuclear complex, as shown in Fig. 4.B. The main changes observed are associated with a broad band at 750 nm, typical of the intervalence transfer transitions in Prussian blue complexes.[12] Therefore, the redox wave observed at 0.4 V for the film should be ascribed to the $Fe^{III/II}$ redox couple in the Prussian blue matrix, rather than to the pentacyanoferrate(II)/(III) species. In fact, the redox potentials of the cyanometallate species are shifted above 1.0 V in the Prussian blue films, as a consequence of the strong electronic effects in this type of compound.[6]

As shown in Fig. 4, the redox behavior of the films containing the pentanuclear species is quite reversible, leading to reproducible electrochromic changes, by cycling the potentials from 0.2 to 0.8 V. This well behaved response suggests a potential usefulness of the modified Prussian blue films for applications in electrochromic devices.

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REFERENCES

1. Lehn J.-M., *Supramolecular Chemistry*, Weinheim: VCH, 1995.
2. Balzani V. and Scandola F., *Supramolecular Photochemistry*, Chichester: Ellis Horwood, 1991.
3. Vögtle F., *Supramolecular Chemistry*, Chichester: John Wiley, 1991.
4. Toma H. E. and Chavez-Gil T. E., Inorg. Chim. Acta 1997; **257:** 197.
5. Toma H. E. and Malin J. M., Inorg. Chem. 1973; **12**: 1039
6. Matsumoto F. M., Temperini M. L. and Toma H. E., Electrochimica Acta 1994; 39: 385.
7. Kuwabara I. H., Comminos F. C. M., Pardini V. L., Viertler H., and Toma H. E., Electrochimica Acta 1994; *16:* 2401.

8. Toma H. E., Kuwabara I. H. and deFaria D. L. A., J. Braz. Chem. Soc. 1996; 7: 391.

9. Bancroft G. M. and Platt R. H., Adv. Inorg. Chem. Radiochem. 1972; **15**: 59.

10. Parish V. R., *NMR, NQR, EPR and Mössbauer Spectroscopy in Inorganic Chemistry*, New York: Ellis Horwood, 1990.

11. Toma H. E. and Malin J. M., J. Am. Chem. Soc. 1975; **97**: 288.

12. Toma H. E., J. Inorg. Nucl. Chem. 1976; 38: 431.

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