



# Synthesis, Characterization and Inclusion Properties of an Iron(II) Polyimine Complex Derived from 2,6-Diacetylpyridine and an Aliphatic Polyamine

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**Abstract.** A novel multibinding species has been obtained by attaching four aliphatic polyamine chains to an iron(II)-polyimine centre, derived from 2,6-diacetylpyridine. Molecular simulations for the complex corroborate the evidence from  $^1\text{H}$  NMR spectroscopy of a symmetric structure, with the four polyamines displaying a tetrahedral arrangement around the metal centre. The protonated polyamine complex interacts with hexacyanoferrate(II) ions, leading to an inclusion compound which has been characterized based on vibrational and Mössbauer spectroscopy, and on cyclic voltammetry.

**Key words:** polyamine complex, iron(II)-polyimines, cyanoiron inclusion compound, Mössbauer spectra

## 1. Introduction

Transition metal polyimine complexes have been used as versatile structural units for building up supramolecular structures and devices [1–3]. By attaching coordinating groups to the metal-polyimine centre, a novel type of multi-bridging system can be devised for assembling polymetallic species [4] and for molecular recognition purposes. Here, we report on the synthesis and characterization of an iron(II) polyimine complex exhibiting four aliphatic polyamine arms (Figure 1). The basic idea pursued in this work is centred on a new structural unity containing four polyamine chains specially oriented for cooperative binding of the amino/ammonium groups to donor/acceptor substrates. In fact, molecular recognition of hexacyanometallates *via* outer-sphere association with protonated cyclic polyamine ligands has already been reported in the literature [5–7]. For this reason, a similar approach was attempted in this work by using the multi-

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binding polyamine complex to generate the corresponding inclusion compound with hexacyanoferrate(II) ions.

## 2. Experimental

The starting iron(II) complex,  $[\text{Fe}(\text{CH}_3\text{CN})_3(\text{H}_2\text{O})_3](\text{CF}_3\text{SO}_3)_2$ , was prepared as previously reported [4]. The  $[\text{Fe}(\text{dapipam})_2](\text{CH}_3\text{SO}_3)_2 \cdot 12\text{H}_2\text{O}$  (dapipam = 2,6-diacetylpyridineiminepolyamine) complex shown in Figure 1, was synthesized by mixing, under an argon atmosphere, 2.6 g (5 mmol) of the starting complex dissolved in 70 mL of water, with 10 mL of a methanol solution containing 1.63 g (10 mmol) of 2,6-diacetylpyridine (Aldrich), and heating at 70 °C. After 10 min, 14.0 mL of *N,N'*-bis(3-aminopropyl)ethylenediamine was added dropwise, and the solution was kept under argon at constant heating, for 12 h. After filtering through a fine filter, the solvent was removed by means of a rotary evaporator and the remaining solid was dissolved in 20 mL of ethanol, and treated with 50 mL of diethyl ether. The solid product was collected on a fine filter, washed with ether and dried under vacuum. Yield: 47%. The corresponding hexafluorophosphate salt was prepared by dissolving 1 g of the trifluoromethanesulfonate compound in 10 mL of 0.01 mol dm<sup>-3</sup> NaOH solution, and adding 50 mg of  $\text{NH}_4\text{PF}_6$  dissolved in 10 mL of water. The violet solid was collected on a filter, washed with a small volume of water, and finally with ether. Anal. Calcd for  $[\text{Fe}(\text{C}_{50}\text{H}_{98}\text{N}_{18})](\text{CF}_3\text{SO}_3)_2 \cdot 12\text{H}_2\text{O}$ : C, 37.9; N, 14.8; H, 6.4. Found: C, 37.3; N, 14.6; H, 6.3. Calcd for  $[\text{Fe}(\text{C}_{50}\text{H}_{98}\text{N}_{18})](\text{PF}_6)_2$ : C, 39.9; H, 6.3; N, 16.2. Found: C, 39.7; H, 6.5; N, 16.6.

The inclusion compound  $[\text{Fe}(\text{H}_3\text{dapipam})_2\{\text{Fe}(\text{CN})_6\}_2] \cdot 15\text{H}_2\text{O}$  was obtained by dissolving 0.2 g (0.11 mmol) of the trifluoromethanesulfonate complex in 20 mL of 0.05 mol dm<sup>-3</sup> HCl, and adding 5 mL of an aqueous solution containing 0.092 g (0.23 mmol) of  $\text{K}_4[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$ . The violet precipitate was collected on a filter, washed with water and finally with ether. Anal. Calcd for  $[\text{Fe}(\text{C}_{50}\text{H}_{104}\text{N}_{18})\text{FeC}_{12}\text{N}_{12}] \cdot 15\text{H}_2\text{O}$ : C, 43.4; H, 8.2; N, 24.5. Found: C, 42.5; H, 7.9; N, 25.2.

The electronic spectra were recorded on a Hewlett-Packard model 8453 diode array spectrophotometer. FTIR spectra were recorded on a Midac instrument, in KBr pellets. The spectral data were analysed by means of the Grams-92 software. Mössbauer spectra were recorded on a Wissel instrument, at room temperature, using a <sup>57</sup>Co(Rh) source. Isomer shift data were given with reference to a metallic iron absorber. <sup>1</sup>H NMR spectra were recorded on a Bruker AC-200 FT instrument, in CD<sub>3</sub>CN. Cyclic voltammetry was carried out using a Princeton Applied Research model 173 potentiostat and a model 175 universal programmer. The conventional three electrode arrangement was employed, consisting of a platinum disc or a carbon paste working electrode, a platinum wire auxiliary electrode and a reference electrode of Ag/AgNO<sub>3</sub> (0.010 mol dm<sup>-3</sup>) in acetonitrile ( $E^0 = 0.503$  V [8]), or Ag/AgCl (1.00 mol dm<sup>-3</sup> KCl,  $E^0 = 0.222$  V [9]) in aqueous solution.

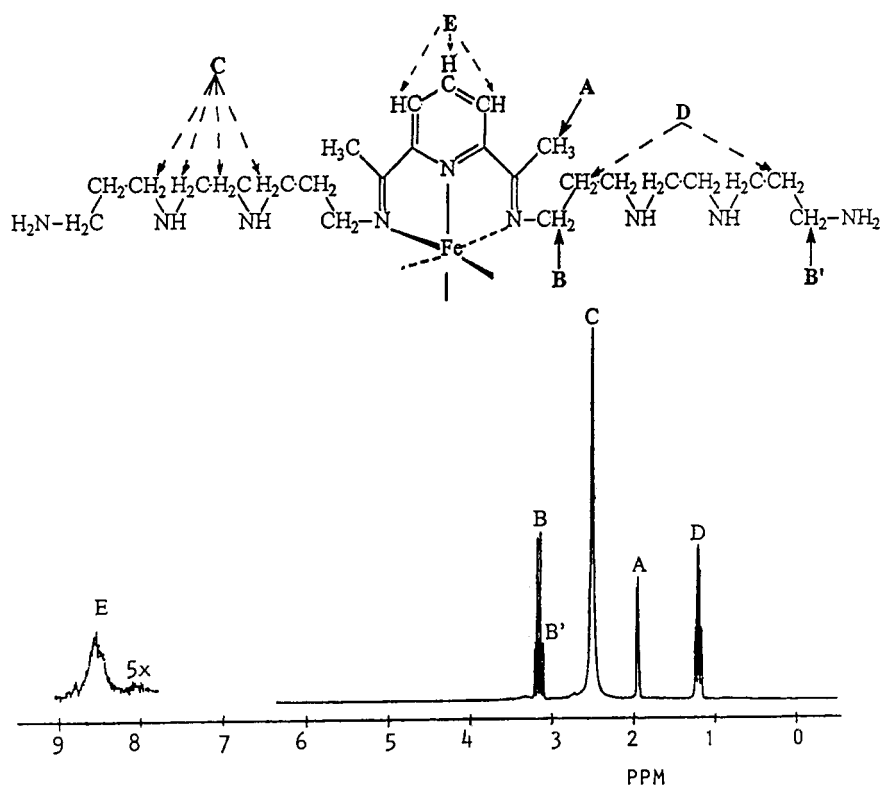


Figure 1. Structural representation and  $^1\text{H}$  NMR spectrum of the  $[\text{Fe}(\text{dapipam})_2]^{2+}$  complex in acetonitrile.

Molecular mechanics calculations were carried out using the  $\text{MM}^+$  force field from Hyperchem 5.0, at a refinement level of  $10^{-5}$  kJ.

### 3. Results and Discussion

#### 3.1. $^1\text{H}$ NMR SPECTRA

The proposed structure for the  $[\text{Fe}(\text{dapipam})_2]^{2+}$  complex can be demonstrated by the  $^1\text{H}$  NMR spectrum (Figure 1), from the presence of five sets of signals at 8.72 (multiplet, 3H), 3.17 (multiplet, 8H), 2.51 (singlet, 16H), 1.95 (singlet, 6H) and 1.20 ppm (multiplet, 8H), corresponding respectively, to the three pyridine protons, the eight terminal N- $\text{CH}_2$  groups, the sixteen N- $\text{CH}_2$  groups in the middle, the six methyl protons and the eight equivalent  $\text{CH}_2$  protons, as shown in Figure 1, for the dapipam ligand. The NMR data are also consistent with two equivalent ligands, and a global  $D_{2d}$  symmetry for the complex.

### 3.2. ELECTRONIC SPECTRA

The electronic spectrum of the complex is shown in Figure 2. Two main absorption bands can be observed at 509 ( $\varepsilon = 5700 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ ) and 600 nm ( $\varepsilon = 8300 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ ), in addition to a series of shoulders around the low energy band. According to ZINDO/S calculations and resonance Raman spectra for the iron(II)-polyimine centre [10], the two bands at 509 and 600 nm can be ascribed to charge-transfer transitions from the metal  $d_\pi$  orbitals of  $b_1$  and  $e$  symmetry to a  $\pi^*$  orbital of  $a_2$  symmetry of the polyimine ligand. The several shoulders can be ascribed to vibronic components of the 600 nm charge-transfer transition. The strong absorptions in the UV region, e.g. at 242 and 267 nm, can be ascribed to  $\pi \rightarrow \pi^*$  transitions in the polyimine ligand.

### 3.3. VIBRATIONAL SPECTRA

A typical FTIR spectrum of the  $[\text{Fe}(\text{dapipam})_2](\text{PF}_6)_2$  complex can be seen in Figure 3. The broad band around  $3400 \text{ cm}^{-1}$  is characteristic of  $\nu(\text{NH})$  and  $\nu(\text{OH})$  vibrations from the polyamines and the water residues in the KBr pellets. The bands at  $2926$  and  $2856 \text{ cm}^{-1}$  can be ascribed to  $\nu(\text{CH})$  vibrations. The asymmetric band at  $1630 \text{ cm}^{-1}$  can be ascribed to  $\delta(\text{HOH})$  and aromatic  $\nu(\text{C}=\text{C})$  vibrations, while the peaks at  $1460$  and  $1391$  can be associated with composite  $\nu(\text{C}=\text{C})$  and  $\nu(\text{C}=\text{N})$  vibrations, as reported in the literature [10, 11]. The weak peaks at  $1321$ ,  $1291$ ,  $1247$ ,  $1118$  and  $1031$  correspond to  $\delta(\text{CH})$  and to  $\nu(\text{C}-\text{C}, \text{C}-\text{N})$  vibrations. The strong peaks at  $840$  and  $556 \text{ cm}^{-1}$  are characteristic of  $\nu(\text{PF}_6^-)$  and  $\delta(\text{PF}_6^-)$  vibrations [12]

In the presence of acid, the protonated  $[\text{Fe}(\text{dapipam})_2]^{2+}$  complex reacts with two mol of  $[\text{Fe}(\text{CN})_6]^{4-}$  forming a precipitate which can be isolated as  $[\text{Fe}(\text{H}_3\text{dapipam})_2\{\text{Fe}(\text{CN})_6\}_2] \cdot 15\text{H}_2\text{O}$ . The solid is not soluble in the conventional solvents, but dissolves in the presence of  $\text{OH}^-$  ions. Under similar conditions, the protonated polyamine ligands do not precipitate with  $[\text{Fe}(\text{CN})_6]^{4-}$  ions [4–6]. The most plausible hypothesis is that the hexacyanoferrate(II) ion interacts, *via* hydrogen bonding with the protonated polyamine arms, forming a stable inclusion compound.

The infrared spectrum of the  $[\text{Fe}(\text{H}_3\text{dapipam})_2\{\text{Fe}(\text{CN})_6\}_2] \cdot 15\text{H}_2\text{O}$  compound is shown in Figure 3, for comparison purposes. The presence of protonated  $\text{N}-\text{H}^+$  groups is responsible for the new peaks at  $1410 \text{ cm}^{-1}$  and  $1100 \text{ cm}^{-1}$  due to  $\delta(\text{NH}_2^+)$  and  $\rho(\text{NH}_2^+)$ , respectively. In addition, the strong peaks of the  $[\text{Fe}(\text{CN})_6]^{4-}$  complex can be observed at  $2080$ ,  $590$ , and  $498 \text{ cm}^{-1}$ , corresponding to the  $\nu(\text{CN})$ ,  $\delta(\text{FeCN})$  and  $\nu(\text{Fe}-\text{C})$  vibrations, respectively [12]. It is interesting to note that the  $\nu(\text{CN})$  peak for the  $\text{K}_4[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$  complex occurs at  $2046 \text{ cm}^{-1}$ . The observed shift of  $34 \text{ cm}^{-1}$  and the broadening of the  $\nu(\text{CN})$  band indicate a different environment around the  $[\text{Fe}(\text{CN})_6]^{4-}$  ion, as expected for an inclusion compound.

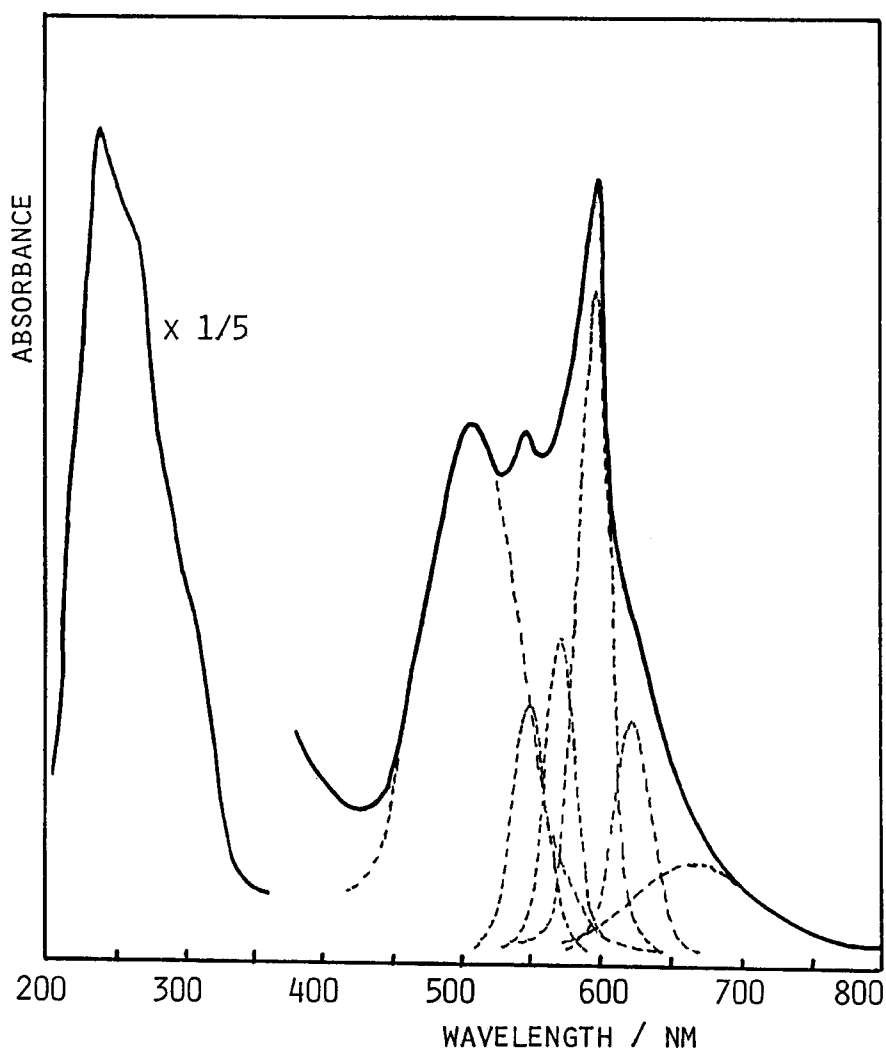


Figure 2. Deconvoluted electronic spectrum of  $[\text{Fe}(\text{dapipam})_2]^{2+}$  ( $0.10 \text{ mol dm}^{-3}$ ) in acetonitrile, based on Gaussian analysis.

#### 3.4. MÖSSBAUER SPECTRA

Mössbauer spectra of the  $[\text{Fe}(\text{dapipam})_2](\text{PF}_6)_2$ ,  $\text{K}_4[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$  and  $[\text{Fe}(\text{H}_3\text{dapipam})_2\{\text{Fe}(\text{CN})_6\}_2] \cdot 15\text{H}_2\text{O}$  compounds are shown in Figure 4. The spectrum of the  $[\text{Fe}(\text{dapipam})_2](\text{PF}_6)_2$  complex exhibits a doublet of linewidth  $\Gamma = 0.482 \text{ mm s}^{-1}$ . The observed isomer shift,  $\text{IS} = 0.154 \pm 0.004 \text{ mm s}^{-1}$ , and quadruple splitting,  $\text{QS} = 0.900 \pm 0.008 \text{ mm s}^{-1}$ , are consistent with a low spin iron(II) complex displaying axial symmetry [13, 14]. The spectrum of  $\text{K}_4[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$  is shown for comparison purposes, and is typical of a cubic

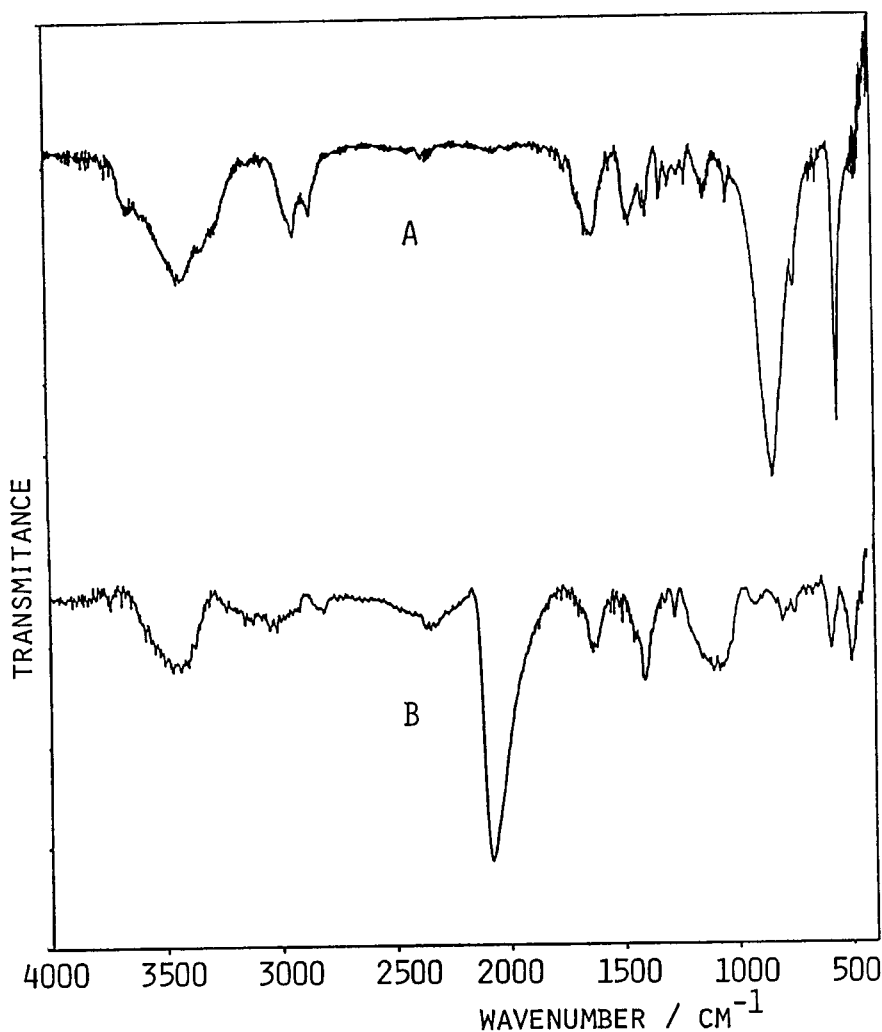


Figure 3. FTIR spectra of the  $[\text{Fe}(\text{dapipam})_2](\text{PF}_6)_2$  complex (A) and of the inclusion compound  $[\text{Fe}(\text{H}_3\text{dapipam})_2\{\text{Fe}(\text{CN})_6\}_2] \cdot 15\text{H}_2\text{O}$  (B), in KBr pellets.

symmetry, with  $\text{IS} = -0.069 \pm 0.001 \text{ mm s}^{-1}$ ,  $\text{QS} = 0$  and  $\Gamma = 0.330 \text{ mm s}^{-1}$ . The  $[\text{Fe}(\text{H}_3\text{dapipam})_2\{\text{Fe}(\text{CN})_6\}_2] \cdot 15\text{H}_2\text{O}$  compound exhibits a composite Mössbauer spectrum, which can be deconvoluted in terms of a doublet at  $\text{IS} = 0.279 \pm 0.021$ ,  $\text{QS} = 0.825 \pm 0.047$  and  $\Gamma = 0.479 \text{ mm s}^{-1}$ , and a broad singlet at  $\text{IS} = -0.198 \pm 0.004 \text{ mm s}^{-1}$ , and  $\Gamma = 0.585 \pm 0.033 \text{ mm s}^{-1}$ . The relative areas exhibit a 1 : 2 ratio, in harmony with the proposed composition. The doublet peaks belong to the  $[\text{Fe}(\text{H}_3\text{dapipam})_2]$  moiety; however, the corresponding IS is shifted by  $+0.125 \text{ mm s}^{-1}$  with respect to the non-protonated complex, reflecting the influence of the positive charges at the neighbourhood of the metal centre. More significantly, however, is the shift of the IS values by  $-0.129 \text{ mm s}^{-1}$ , and the substantial broadening

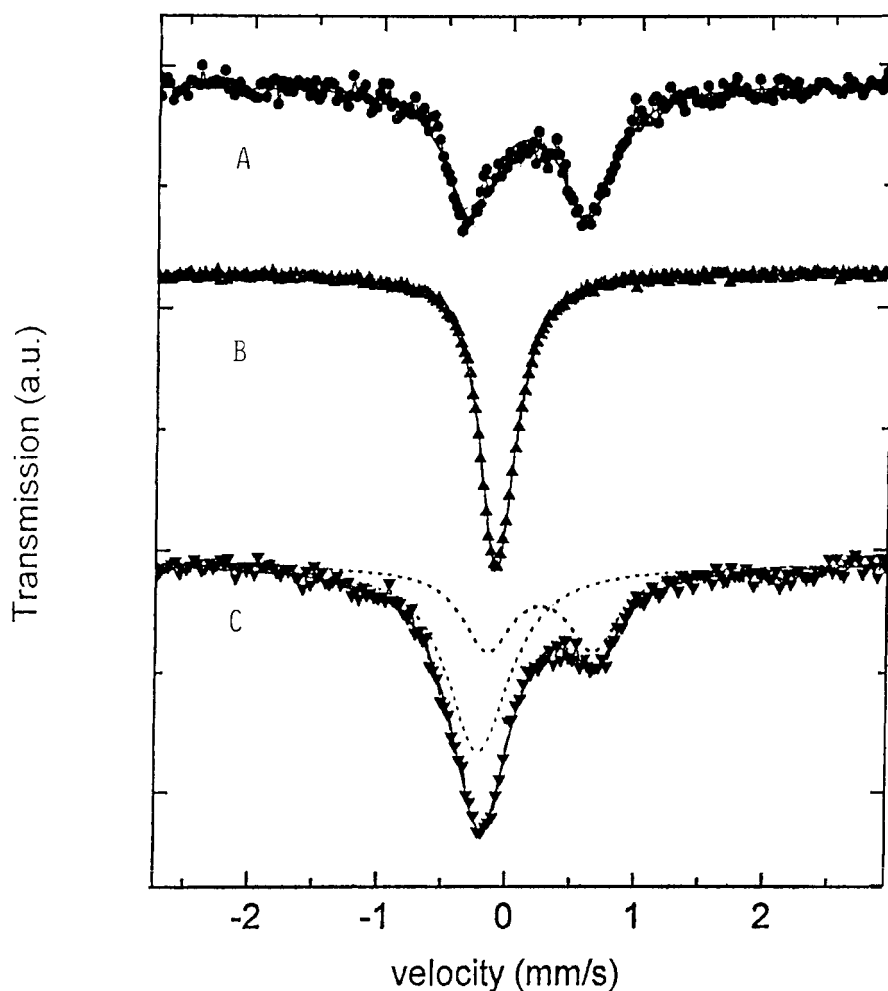


Figure 4. Mössbauer spectra of  $[\text{Fe}(\text{dapipam})_2](\text{PF}_6)_2$  (A),  $\text{K}_4[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$  (B) and  $[\text{Fe}(\text{H}_3\text{dapipam})_2\{\text{Fe}(\text{CN})_6\}_2] \cdot 15\text{H}_2\text{O}$  (deconvoluted) (C).

( $\Delta\Gamma = 0.255 \text{ mm s}^{-1}$ ) of the Mössbauer signals for the  $[\text{Fe}(\text{CN})_6]^{4-}$  ion in the associated compound. The decrease of IS can be explained in terms of increasing  $\pi$ -backbonding effects from the coordinated cyanide ligands, as they interact with the protonated amino groups of the  $[\text{Fe}(\text{H}_3\text{dapipam})_2]$  complex. The broadening of the singlet peak suggests that the environment around the hexacyanoferrate(II) unity is not rigid, reflecting the influence of the several conformations and binding site distributions along the polyamine chains.

### 3.5. CYCLIC VOLTAMMETRY

A typical cyclic voltammogram of the  $[\text{Fe}(\text{dapipam})_2]^{2+}$  complex in acetonitrile solution can be seen in Figure 5. By starting at 0.5 V, the reduction of the polyimine ligand [15] proceeds according to two quasi-reversible steps, at  $-1.00$  and  $-1.15$  V, while the oxidation of the iron(II) centre is quite irreversible, exhibiting an oxidation peak at 1.3 V. A similar irreversible anodic peak is obtained by starting at 0.5 V and going in the direction to more positive potentials. The oxidation of the iron(II)-centre leads to a very reactive complex, highly susceptible to the nucleophilic attack of the amino residues. In the absence of the amino groups, as in the methyl and furfuryl derivatives previously reported in the literature [15], the oxidation of the iron(II) centre proceeds in a reversible way, according to a well behaved monoelectronic process.

The cyclic voltammogram of the  $[\text{Fe}(\text{H}_3\text{dapipam})_2\{\text{Fe}(\text{CN})_6\}_2]\cdot 15\text{H}_2\text{O}$  compound was obtained with the solid directly mixed with carbon paste at the electrode surface. The measurements carried out in aqueous solution, are shown in Figure 6. In contrast to the measurements for the  $[\text{Fe}(\text{dapipam})_2]^{2+}$  complex in solution, the redox waves of the iron(II)/(III) polyimine complex appear quasi-reversible, and shifted to lower potentials, i.e., at  $E_{1/2} = 1.10$  V. The redox waves of the  $[\text{Fe}(\text{CN})_6]^{3-/4-}$  couple occur at 0.40 V, exhibiting reversible characteristics. The relative intensities are very close to 1:2, in agreement with the proposed composition.

### 3.6. MOLECULAR SIMULATIONS

Molecular mechanics calculations for the  $[\text{Fe}(\text{dapipam})_2]^{2+}$  complex led to a very symmetric structure, with the four polyamine arms adopting a distorted tetrahedral arrangement around the iron(II) centre, as illustrated in Figure 7A.

The binding of the hexacyanoferrate(II) ions allows several possibilities, involving 1 to 4 binding sites along the two vicinal polyamine arms. According to the molecular mechanics calculations, the participation of more than 4 binding sites can be ruled out, since it would greatly enhance the distortion and decrease the stability of the inclusion compound. By assuming four binding sites, as shown in Figure 7B, the final structure is quite stable, with the three metal centres aligned symmetrically, keeping a metal-metal distance of 7.75 Å. In each hexacyanoferrate(II) ion, two cyanide ligands remain available for molecular interactions, e.g. *via* hydrogen bonding with the free NH groups of the neighbouring molecules, facilitating the formation of an extended structure. A similar case has been reported for the interaction of hexacyanocobaltate(III) and protonated polyamines [7].



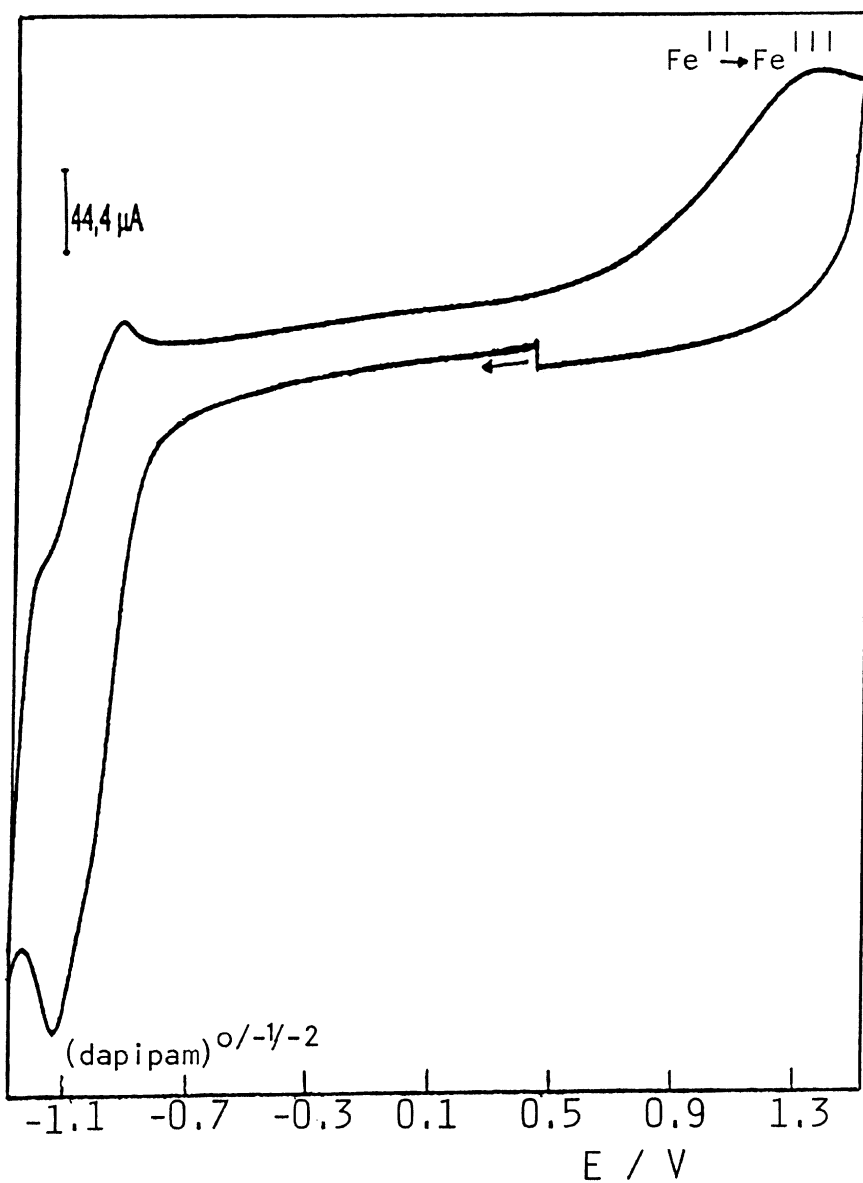


Figure 5. Cyclic voltammogram of the [Fe(dapipam)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> complex (5 mmol dm<sup>-3</sup>), at 100 mV s<sup>-1</sup>, in acetonitrile containing 0.1 mol dm<sup>-3</sup> *t*-butylammonium perchlorate.

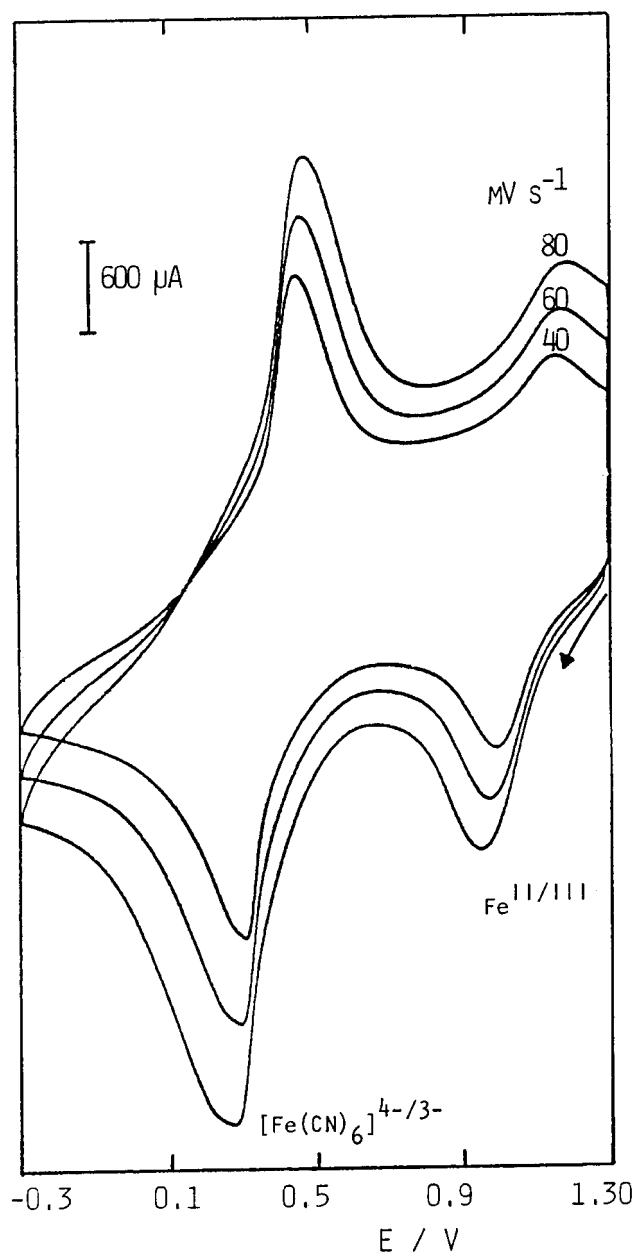


Figure 6. Cyclic voltammogram of the solid  $[\text{Fe}(\text{H}_3\text{dapipam})_2\{\text{Fe}(\text{CN})_6\}_2] \cdot 15\text{H}_2\text{O}$  complex dispersed into carbon paste, in the presence of  $0.10 \text{ mol dm}^{-3}$  KCl, at several scan rates.

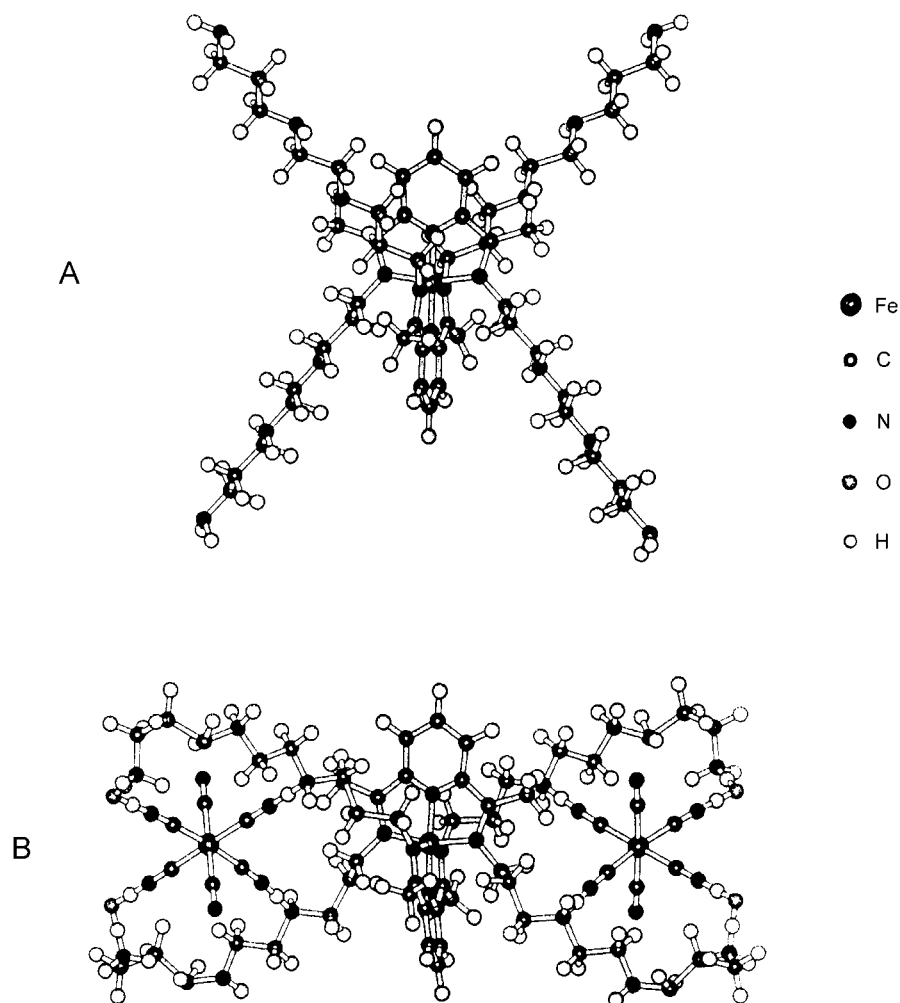


Figure 7. Molecular simulations (MM<sup>+</sup>/Hyperchem 5.0) for [Fe(dapipam)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> (A) and [Fe(H<sub>3</sub>dapipam)<sub>2</sub>Fe(CN)<sub>6</sub>]<sub>2</sub>·15H<sub>2</sub>O (B).

#### 4. Conclusions

By attaching four aliphatic polyamine chains to the iron(II)-polyamine complex, a new multibinding system, capable of interacting with hexacyanometallate anions, was successfully obtained in this work. In agreement with the <sup>1</sup>H NMR spectrum, the molecular simulations for the complex reproduced a highly symmetric structure, with the four polyamine arms displaying a tetrahedral arrangement around the iron(II)-polyimine centre. The proposed binding modes, based on molecular mechanics calculations, involve hydrogen bonding of four cyanide groups of the hexacyanoferrate(II) ion with the protonated amines, leaving two cyanide ligands

for intermolecular interactions. This model is in agreement with the observations from Mössbauer and vibrational spectroscopy. The occurrence of intermolecular interactions is reflected in the low solubility of the inclusion compound in conventional solvents, as expected for a polymeric structure.

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