# Mössbauer and Electronic Absorption Spectra of Dicyano(*meso*(*p*-substituted)-tetraphenylporphinato)iron(III) Complexes

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## Abstract

Studies on a number of tetra *meso*-substituted porphyrinatoiron(III) complexes in both aqueous and non-aqueous solvents in the presence of excess cyanide are reported.

The Mössbauer data resulting from such frozen solutions all have small or zero quadrupole splitting. The presence or absence of these splittings are discussed in terms of the possible ground states of the iron atoms.

The electronic absorption spectra of the same complexes are found to be dependent on several factors including solvent, substituent in the porphyrin and the cyanide concentration.

## Introduction

There have been many studies on the binding of cyanide ion to iron(III) porphyrin complexes as model compounds for haemproteins [1–6]. The binding of strong field cyano ligands to iron(III) porphyrins can be described by two steps [4, 5, 7] (where P = porphyrin).

$$PFe(III) + CN^- \rightleftharpoons PFe(III)CN \qquad (1)$$

$$PFe(III)CN + CN^- \rightleftharpoons PFe(III)(CN)_2^- \qquad (2)$$
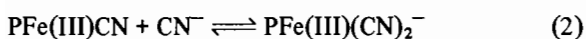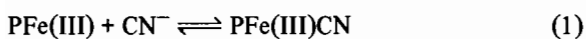
Such binding of a strong field ligand leads to the formation of low-spin ferric complexes. The latter fact has been used in a number of NMR studies on haemproteins [8, 9] and porphinato–iron(III) derivatives [10–13].

We have previously studied the binding of cyanide ions to protoporphyrin IX iron(III) (PPIXFe(III)) using conductiometric titrations [3]. We found evidence in Mössbauer spectra of frozen solutions for species of the type [PPIXFeCN(X)] where X = $OH^-$, $H_2O$ or CN [1, 3]. The structure of potassium dicyano(*meso*tetraphenylporphinato)iron(III) bis-(acetone) has essentially linear Fe–C–N groups with Fe–C bonds of 1.975(2) Å. We studied the complex sodium dicyano(protoporphyrinato)iron(III) bis-(dimethylformamide) using Mössbauer spectroscopy.

From the Mössbauer spectrum, a small quadrupole splitting 0.40 mm s$^{-1}$ at 298 K was observed. The small quadrupole splitting (*QS*) is primarily due to the presence of the strong field $CN^-$ ligands that act as both sigma donors and $\pi$ acceptors (better than nitrogen ligands) effectively nearly balancing the four pyrrole nitrogens of the porphyrin ring. There is a greater stabilisation along the Fe–CN coordinate due to $\pi$-backbonding from metal to ligand [1]. A major problem in the understanding of the dicyano(protoporphyrinato)iron(III) complexes is the assignment of the orbital ground state of the iron(III). We previously suggested [1] that the ground state for the NaPPIXFe(CN)$_2$ (I) complex arose from either (i) an equal spreading out of the 5d electrons across the three $d_{xy}$, $d_{yz}$ and $d_{xz}$ orbitals (such a state could arise from spin orbit coupling of the $^2B_{2g}$ and $^2E_g$ states); this would be seen as a small or zero *QS* with a large temperature dependence or (ii) the alternative explanation is that it is a $^2E_g$ ground state but the difference in energy between the ($d_{xy}$) and ($d_{xz}$, $d_{yz}$) orbitals is very small so that it is only a slightly distorted octahedral environment and thus only a *QS* with little temperature dependence will be observed.

As the temperature dependence of the *QS* was relatively large (20% in the 78–298 K range) in I compared to 5% in Fe(TPP)(Im)$_2$Cl [14], it might appear that (i) is the best description. However, as the overall splitting is so small, the latter explanation (ii) cannot be ruled out.

The aim of this work was to study other such complexes using Mössbauer spectroscopy to enable further understanding of the resulting electronic environments. We report here studies on a number of *meso*-substituted porphyrinatoiron(III) cyanide complexes both on solids and frozen solutions.

## Experimental

*Preparation of Sodium Dicyano(p-tetrasulphophnyl)porphyrin Iron(III) bis DMF, Na[FeTPPS(CN)$_2$] · 2DMF*

FeTPPS was prepared according to the Fleischer method [15]. 300 mg of FeTPPS were dissolved in

100 ml of DMF (Aldrich). The insoluble particles were separated by filtration. 10 ml of a saturated solution (at 15 °C) of sodium cyanide in DMF was added to the iron porphyrin solution and mixed. A solid product was obtained by adding 100 ml of diethyl ether and filtered. No further purification was carried out. This was identified as Na[FeTPP-$(CN)_2$]·2DMF.

### Preparation of K[Fe(TPP)(CN)₂]·2(CH₃)₂CO and K[Fe(TTP)(CN)₂·2(CH₃)₂CO

Two hundred mg of FeTPPCl [16] or FeTTPCl were dissolved in a mixture of 70 ml dry methanol + 30 ml dry chloroform; excess of KCN = 400 mg was added to the solutions. As the KCN was added, the colour changed from red to green. The solvent was distilled by rotary evaporation and the resulting solid was extracted with acetone saturated with KCN. The acetone was removed and the solid was obtained. K[Fe(TPP)(CN)$_2$]·2(CH$_3$)$_2$CO has been prepared previously [7]. K[Fe(TTP)(CN)$_2$·2(CH$_3$)$_2$-CO was seen to be similar and characterised by its spectral similarity to K[Fe(TPP)(CN)$_2$]·2(CH$_3$)$_2$CO.

The preparations of Fe(III)TNP and Fe(III)TNPS have been described previously [17].

### Mössbauer Spectroscopic Experiments

The solids used for Mössbauer spectroscopy were formed as above. For frozen solutions, 150 mg of each of the iron(III) porphyrins (the following

porphyrins were used: Fe(III)TPPCl, Fe(III)TTPCl, Fe(III)PPIX (haematin purchased from Aldrich) and Fe(III)TPPS) were dissolved in 2 ml DMF (or 2 ml H$_2$O for sulphonated porphyrins). Excess KCN was then added while the solution was stirred for a few minutes. Finally, the solution was transferred to a nylon cell and frozen under liquid nitrogen at 78 K.

The spectrophotometer was calibrated with a 25 $\mu$M thick natural iron reference absorber at 298 K (as zero chemical shift) to which all chemical shifts are referred. Details of the spectrometer have been previously described [18].

### Electronic Spectra

The electronic absorption spectra of iron(III) porphyrins were recorded in DMF, acetone and H$_2$O on a Lambda 5G-spectrophotometer at 15 °C. Concentrations of iron(III) porphyrin were in the range of $1-3 \times 10^{-5}$ M. Dicyano—iron(III) porphyrin complexes were prepared by adding excess cyanide ion to iron(III) porphyrin solutions.

## Results and Discussion

### Electronic Absorption Spectra of Iron(III) Porphyrins with Cyanide

The electronic absorption spectra of iron(III) porphyrins with cyanide ion were obtained in organic solvents. The data are listed in Table 1.

TABLE 1. Electronic Absorption Spectra of Iron(III) Porphyrins with Cyanide[a]

| Sample | Solvent | γ-band (nm) | Γ[b] (nm) of Soret band | β-band (nm) | α-band (nm) |
|---|---|---|---|---|---|
| 1 FeTTPCl + excess KCN | DMF | 431, 445[c] (120) (76) | 48 | 569 | 612 (11) |
| 2 FeTPPCl + KCN 1:2.5 | DMF | 416.4 (90) | 26 | 553 (7.6) | 605 |
| 3 FeTPPCl + KCN 1:4 | DMF | 430 (91) | 32 | 575 (7.7) | 612 (8.2) |
| 4 K[FeTPP(CN)₂]· 2(CH₃)₂CO + 100 excess KCN | DMF | 431 (92) | 33 | 570 (7.85) | 612 (8.25) |
| 5 Na[FeTPPS(CN)₂]· bis DMF + excess NaCN | DMF | 432 (52.3) | 47 | 572.4 (5.36) | 613 (5.48) |
| 6 FeTTPCl + excess KCN | DMF:H₂O 1:1 | 428.8, 445[c] | 47 | 570 | 608 |
| 7 Na[FeTPPS(CN)]₂· bis DMF + excess NaCN | DMF:H₂O 1:1 | 424 (59.2) | 48 | 557 (6.5) | 602, 732 (5.4, 1.4) |
| 8 K[FeTPP(CN)₂]· 2(CH₃)₂CO + excess KCN | DMF:H₂O 1:1 | 426.8 (45.3) | 20 | 570 (5.35) | 608.4 (2.9) |

*(continued)*

TABLE 1. *(continued)*

| Sample | Solvent | $\gamma$-band (nm) | $\Gamma^b$ (nm) of Soret band | $\beta$-band (nm) | $\alpha$-band (nm) |
|---|---|---|---|---|---|
| 9 FeTPPCl + excess KCN | acetone | 412 (112.5) | 25 | 568 (7.08) | 612$^d$ |
| 10 FeTNPCl + excess KCN | acetone: DMF 10:1 | 435.6 (60) | 19 | 542.4 (5.3) | 636 (3.0) |
| 11 FeTNPS + excess KCN | DMF | 438 (53.5) | 40 | 541.6 (3.7) | 622 (1.06) |
| 12 FeTNPCl + excess KCN | DMF: acetone:$H_2O$ 1:10:30 | 432 (52) | 20 | 538 (5.3) | 660 (2.0) |
| 13 FeTNPS + excess KCN | DMF:$H_2O$ 1:1 | 432.4 (71.5) | 38 | 542.8 (8.0) | 661 (4.0) |

$^a \epsilon$ (mM) values are in parentheses. $^b \Gamma$ = bandwidth. $^c$These bands appear as a shoulder on the main Soret band. $^d$This band is very weak.

There are two different kinds of spectra observed. These are dependent on the substituent at the methine carbon, solvent and concentration of cyanide ion.

The first type of spectrum was characterised by three bands in DMF solvent. They are from shorter to longer wavelength $431 \pm 1$, $570 \pm 2$ and $612 \pm 3$ nm (samples no. 1 and 3–5, Table 1). The Soret bands in these complexes moved to shorter wavelength when a water–DMF mixture was used as solvent (samples no. 6–8). The broad Soret band in samples no. 1 and 6 (TTP was used) suggests more than one species was present.

Sample no. 2 is a mono cyanide Fe(III)TPP, but samples no. 3 and 4 are better assigned to dicyano Fe(III)TPP complexes (see Fig. 1). Sample no. 9 is a dicyano Fe(III)TPP complex, where the Soret band at 412 nm is very different to the others in Table 1. This spectrum is thus obviously very solvent-dependent.

The second type of spectrum (samples no. 10 and 11) is very different from the first type. This spectrum type also has three bands, the Soret band in the range of 435–438 nm, $\beta$-band around 542 nm and an $\alpha$-band in the range of 622–636 nm (samples no. 10 and 11, Table 1). Adding water to these samples caused the Soret bands and the $\alpha$-bands to move to shorter and longer wavelengths respectively (samples no. 12 and 13). This type of spectrum is found for the *meso* tetranaphthyl porphyrins (see Fig. 2). Samples 1, 3, 4, 5, 9, 10 and 11 are therefore assigned to dicyano iron(III) complexes, but samples 6, 7, 8, 12 and 13 are explained as a replacement of one molecule of cyanide by a $H_2O$ molecule, giving [PFe(III)(CN)($H_2O$)] complexes (where P = porphyrin).

Lukas and Silver [1] have reported the visible absorption spectra of Fe(II)PPIX in DMF with NaCN; they found the Soret band at 434 nm (which
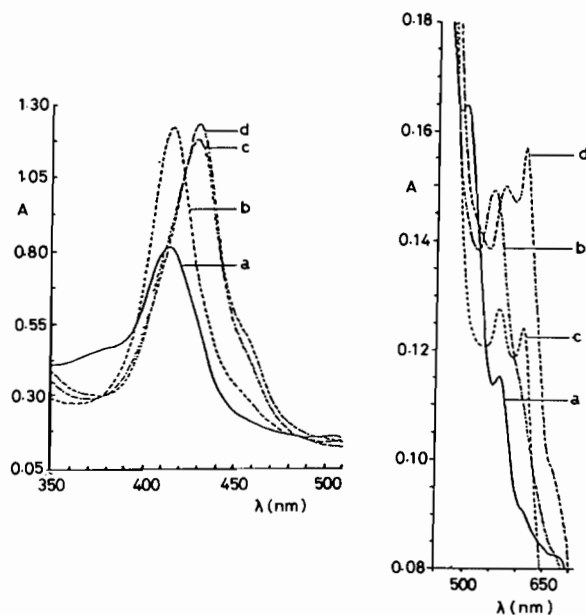


Fig. 1. Visible absorption spectra of Fe(III)TPPCl at concentration $1.3 \times 10^{-5}$ M in DMF with KCN at concentrations: (a) zero; (b) $3.06 \times 10^{-5}$ M; (c) $2.4 \times 10^{-4}$; (d) $5.5 \times 10^{-4}$ M.

is similar to this work) moves to 424 nm when $H_2O$ was added, but there is no similarity with the other peaks. It is likely that the substituent on the porphyrin (PPIX is vinyl substituted) affects the visible spectrum.

Scheidt *et al.* [7] have reported the visible absorption spectra of K[Fe(TPP)(CN)$_2$]·2(CH$_3$)CO dissolved in methanol; they found peaks at 424, 539, 560 and 596 nm. The Soret band at 424 nm was found both by Lukas and Silver [1] and in this work, when the samples are mixed with water, and is obviously a mono cyano species.
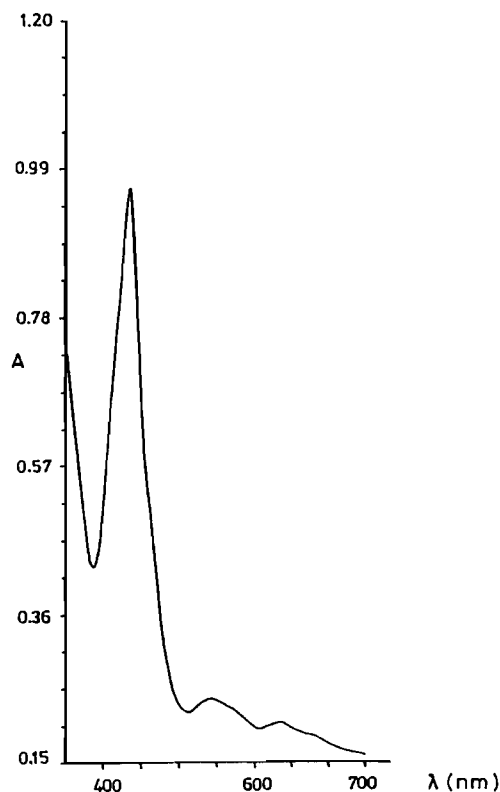
Fig. 2. Electronic absorption spectra of Fe(III)TNPCl (1.7 × $10^{-5}$ M) in acetone and DMF (10:1) solvent with excess KCN present.

## Mössbauer Parameters of Iron(III) Porphyrins with Cyanide Ion at 78 K

The Mössbauer data of the iron(III) porphyrins (solids and frozen solutions) are presented in Table 2. Small quadrupole splittings were obtained for many of the solid complexes (samples 1 to 4, Table 2), compared to those of known low-spin haemichromes with nitrogen axial ligands [19]. Such a small quadrupole splitting was observed by Silver and Lukas [1] for Fe(III)PPIX(CN)$_2^-$, ($\delta$ = 0.2 and

$\Delta$ = 0.53 mm/s at 80 K) and was explained as set out in the 'Introduction'. A similar explanation is suggested here for the complexes in samples 1 to 3; these are dicyano—iron(III) porphyrins. The spectra of sample 3 also shows the presence of a second iron(III) species. This species has a larger quadrupole splitting and its Mössbauer parameters are within the range expected for iron(III) complexes. An iron(III) porphyrin complex containing one cyanide and a $H_2O$ molecule as axial ligands would be consistent with such Mössbauer parameters (cf. those reported by Lukas et al. [3]).

The question arises, where did the $H_2O$ come from? The structure of K[FeTPP(CN)$_2$]·2CH$_3$CO-CH$_3$ is known to lose acetone easily in air. This acetone could either be replaced by water from vapour in the air, or the loss of acetone could cause the remaining acetone and/or the K$^+$ ions to interact with the CN axial ligands, generating a different field gradient at the iron(III) centre. Obviously it is not easy to decide what has happened, but if water replaces the acetone it is easy to imagine it either H-bonding to the CN ligands (thus effectively weakening their bonding to the iron(III)) or even replacing one of them.

Samples 4 and 5 are frozen solutions and they have very small isomer shifts and large linewidths. Such broad lines are usually found when a number of similar iron sites are present or when some kind of diffusion (or other dynamic process) occurs. Here the former suggestion is preferred, i.e. a number of similar species are present arising from the solvent interacting with the CN$^-$ ligands probably via hydrogen bonding. Support for this suggestion is found in the crystal structure of Fe(III)TPP(CN)(Py)·$H_2O$ [20]. In this a $H_2O$ molecule was found to be attached to the CN molecule via a hydrogen bond. Thus, these complexes (4 and 5) are most likely to be dicyano iron(III) porphyrins with hydrogen bonds between the cyanide and the solvents ($H_2O$ or DMF).

TABLE 2. $^{57}$Fe Mössbauer Parameters of Iron(III) Porphyrins with Cyanide Ions

| Sample | $\delta$ (mm/s) | $\Delta$ (mm/s) | $\Gamma$ (mm/s)[a] | A (%) |
|---|---|---|---|---|
| 1 Na[Fe(III)TPPS-(CN)$_2$]·bis DMF | 0.30(1) | 0.50(1) | 0.25(1) | 100(5) |
| 2 K[Fe(III)TPP-(CN)$_2$]·2(CH$_3$)$_2$C=O | 0.31(1) | 0.63(2) | 0.25(1) | 100(5) |
| 3 K[Fe(III)TTP-(CN)$_2$]·2(CH$_3$)$_2$C=O | 0.30(1) | 0.69(1) | 0.20(1) | 56(3) |
| | 0.06(2) | 1.79(5) | 0.43(4) | 43(4) |
| 4 Fe(III)TPPS + excess KCN in DMF/frozen | 0.07(1) | ca. 0 | 0.51(2) | 100(5) |
| 5 Fe(III)TPPCl + excess KCN in DMF/frozen | 0.06(1) | ca. 0 | 0.53(1) | 100(3) |

[a]Half width at half height.

The low chemical shifts of complexes 4 and 5 and the monocyanide complex of sample 3 suggests that these iron(III) porphyrin cyanide electronic environments have greater 's' electron density at the nucleus. This 's' electron density arises either from less 's' electron density being used in the bonding or from greater involvement of iron 3d electrons in the bonding causing less shielding of the s electrons from the nucleus. The latter explanation seems to us to be the more likely explanation.

From this work the nature of the ground state in the dicyano complexes can still not be unambiguously assigned. Though from the fact that only broad singlets were observed for compounds 4 and 5, it is not unreasonable to suggest that postulation (i), *i.e.* an equal spreading out of the 5d electrons across the three $d_{xy}$, $d_{yz}$ and $d_{xz}$ orbitals (*i.e.* spin orbit coupling of the $^2B_{2g}$ and $^2E_g$ states) is an adequate explanation of the ground state.

## Conclusions

Electronic absorption spectra of cyanide ions with iron(III) porphyrins are very dependent on the solvent, substituent on the porphyrin and its position and also the cyanide concentrations.

The Mössbauer data shows that the dicyano-(porphinato)iron(III) species have small quadrupole splittings in the solid state generated by an imbalance in the $t_{2g}$ orbitals. In frozen solutions single broad lines are found and have been tentatively explained.

## Acknowledgement

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