

THE REACTION OF CYANIDE WITH IRON(II) HEXADECACHLOROPHTHALOCYANINE

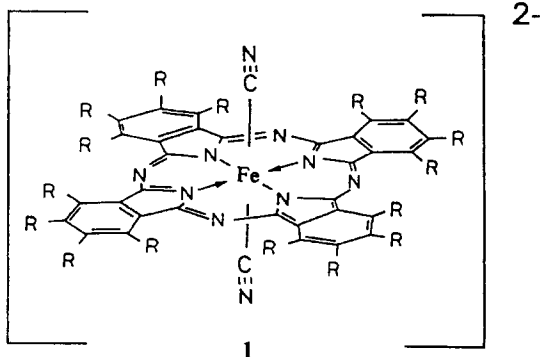
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Abstract—Kinetics and equilibria for the reaction between cyanide and iron(II) hexadecachlorophthalocyanine ((Cl)₁₆PcFe(DMSO)₂, where Pc(−2) = phthalocyanine dianion) in dimethyl sulphoxide (DMSO) are reported. Only the spectrophotometric changes due to the formation of the dicyano, [(Cl)₁₆PcFe(CN)₂]^{2−}, complex were observed. This complex is formed with the equilibrium constant, $K_3 = 1.6 \times 10^3 \text{ dm}^3 \text{ mol}^{-1}$ and a rate constant of $k_{3f} = 4.2 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. The K₂[(Cl)₁₆PcFe(CN)₂] complex dissolves in DMSO and dimethyl formamide (DMF) with $\epsilon = 110\,000$ and $92\,000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$, respectively.

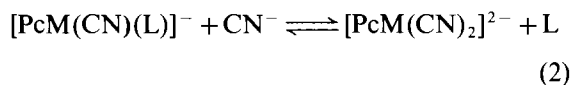
Hexadecachlorophthalocyanato metal complexes, (Cl)₁₆PcM, are under intense study^{1,2} due to their potential applications as optical recording substrates and as photoreceptors. Studies on (Cl)₁₆PcM complexes have shown that (Cl)₁₆PcCo and (Cl)₁₆PcZn complexes are aggregated in solution even at very low concentrations,¹ (Cl)₁₆PcFe was found to exist as a monomer.¹ The (Cl)₁₆PcM complexes have very low solubility in many solvents. Axial ligation is known to increase the solubility of unsubstituted metallophthalocyanine (MPc, where Pc = phthalocyanine dianion) complexes considerably.³ In this work we report on an axially ligated, [(Cl)₁₆PcFe(CN)₂]^{2−} complex 1:



R = H; [PcFe(CN)₂]^{2−}
 R = Cl; [(Cl)₁₆PcFe(CN)₂]^{2−}

Coordination of cyanide to MPc complexes is of great interest since there is a need to develop complexes that can coordinate cyanide in solution and hence act against its toxic effects.

Kinetic studies on Fe^{II}Pc and Ru^{II}Pc complexes have shown that the axial coordination of cyanide occurs in a stepwise manner, with the coordination of the first cyanide occurring much faster than that of the second,^{4,5} equations (1) and (2):



where L is the leaving ligand.

The coordination of the first cyanide to RuPc complexes occurred very fast and showed only minor spectrophotometric changes.⁴ The coordination of the first cyanide to FePc was accompanied by more pronounced spectrophotometric changes.⁵ Perchloro-substitution of the ring leads to complexes whose properties are modified by the electron withdrawing substituents. The kinetics and equilibria for the axial coordination of cyanide to (Cl)₁₆PcFe are reported in this paper and compared with the data for the non-substituted FePc derivative.

EXPERIMENTAL

Materials

Iron(II) hexadecachlorophthalocyanine, $(\text{Cl})_{16}\text{PcFe}$, was prepared according to published procedures.² The axially cyanated, $\text{K}_2[(\text{Cl})_{16}\text{PcFe}(\text{CN})_2] \cdot 8\text{H}_2\text{O}$, complex was prepared by methods reported^{6,7} for the preparation of other $\text{PcM}(\text{CN})_2$ complexes, by mixing 0.1 g of $(\text{Cl})_{16}\text{PcFe}$ with 0.1 g (excess) potassium cyanide and refluxing the mixture in dimethyl formamide (DMF) for 3 h. The resulting green solution was evaporated to dryness and the solid washed in water and recrystallized from absolute ethanol. Yield 60%. UV/Vis λ_{max} (dimethyl sulphoxide, DMSO): 685s ($\epsilon = 110\,000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$), 620sh, 480m, 450m, 415m, 380m nm. IR (KBr disks): 3420m, 2070m [$\nu_{(\text{C}=\text{N})}$], 1600w, 1540w, 1490m, 1455w, 1430m, 1355m, 1305s, 1275s, 1209w, 1160m, 1140s, 948s, 865w, 795w, 765s cm^{-1} . Found: C, 28.4, N, 10.2, H, 1.1. Calc. for $\text{K}_2\text{C}_{34}\text{N}_{10}\text{Cl}_{16} \cdot 8\text{H}_2\text{O}$ ($M_r = 1385.5$): C, 29.4; N, 10.1; H, 1.1%.

Electrochemical methods

Electrochemical data were collected with the BAS CV 27 Voltammograph connected to an HP 7047A X-Y recorder. For cyclic voltammetry, a platinum disc (1.6 mm diameter) was used as a working electrode and a platinum wire as an auxiliary electrode. A silver wire was used as a reference electrode. Potentials were referenced internally to the ferrocenium/ferrocene (fc^+/fc) couple,⁸ using published redox potential values [vs a saturated calomel electrode (SCE)]⁹ for the fc^+/fc couple. Platinum sheet working and auxiliary electrodes and a silver wire reference were employed for bulk electrolysis, the auxiliary electrode being separated from the compartment housing the reference and working electrode by a fine glass frit.

Kinetics and equilibria

Kinetic and equilibrium studies were run at 25°C and monitored with the Beckman UV 5240 spectrophotometer. Cyanide binding was followed by monitoring the increase in the intensity of the Q band of the $[(\text{Cl})_{16}\text{PcFe}^{\text{II}}(\text{CN})_2]^{2-}$ complex. The solubility of $(\text{Cl})_{16}\text{PcFe}$ in DMSO is very low.¹ The solubility increased slightly when this complex was dissolved in warm DMSO. The resulting solution was concentrated enough for kinetic and equilibrium studies. Typically a known volume of the DMSO solution of $(\text{Cl})_{16}\text{PcFe}$ was added to a spectrophotometric cell of 1 cm path length, then a

known volume of the DMSO solution of potassium cyanide was added to the cell and the absorption spectra monitored. Cyanide concentrations were determined by titration with silver nitrate. Cyanide concentrations ranging from 5.0×10^{-4} to 3.0×10^{-2} were employed.

All solvents were freshly distilled. Tetraethylammonium perchlorate [TEAP] was recrystallized and used as an electrolyte for electrochemical studies. Ferrocene was recrystallized from ethanol before use as an internal standard.

Infrared spectra (KBr disks) were collected with a Perkin-Elmer 180 IR spectrophotometer. Elemental analyses were performed by University of Natal.

RESULTS AND DISCUSSION

Spectroscopic studies

Axial ligation in metallophthalocyanine complexes often leads to an increase in the solubilities of these complexes,^{3,10} for example, $\text{K}_2[(\text{CN})_2\text{RuPc}]$ is soluble in water, while unligated RuPc is insoluble in most solvents.⁷ The reaction between $(\text{Cl})_{16}\text{PcFe}$ and potassium cyanide results in the complex, $\text{K}_2[(\text{Cl})_{16}\text{PcFe}(\text{CN})_2]$, which is highly soluble in DMF and DMSO, with extinction coefficients ($\epsilon_{\text{Q band}}$) of 92 000 and 110 000 $\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$, respectively. The Q bands are centred at 680 and 685 nm for DMF and DMSO solutions, respectively. The spectra shows an absorption band centred near 450 nm (Fig. 1a) as is typical of axially ligated $\text{Fe}^{\text{II}}\text{Pc}$ complexes. This band is associated with a metal-to-ligand charge transfer transition. The presence of this charge transfer band is a good indication that the Fe ion remains in the +2 oxidation state on addition of cyanide to $(\text{Cl})_{16}\text{PcFe}^{\text{II}}$. The electronic absorption spectra of the $[(\text{Cl})_{16}\text{PcFe}(\text{CN})_2]^{2-}$ species is typical of the non-aggregated MPc complexes;¹¹ $(\text{Cl})_{16}\text{PcFe}$ was also shown to be non-aggregated in DMF and in DMSO.¹ The spectra in Fig. 1(a), shows the split in the Soret band that is typical of cyano complexes of metallophthalocyanines.¹²

The Fe—CN vibration for the $[(\text{Cl})_{16}\text{PcFe}(\text{CN})_2]^{2-}$ complex, observed at 2070 cm^{-1} , is in the range reported for M—CN vibrations in $\text{MPc}(\text{CN})_2$ complexes.^{6,13-15} The Fe—CN vibration is observed at 2120 cm^{-1} for the $[(\text{CN})_2\text{FePc}]^{2-}$ complex.⁵

Electrochemical studies

Electrochemical properties of $\text{Fe}^{\text{II}}\text{Pc}$ complexes are well established.^{3,16-18} $\text{Fe}^{\text{II}}\text{Pc}$ shows redox

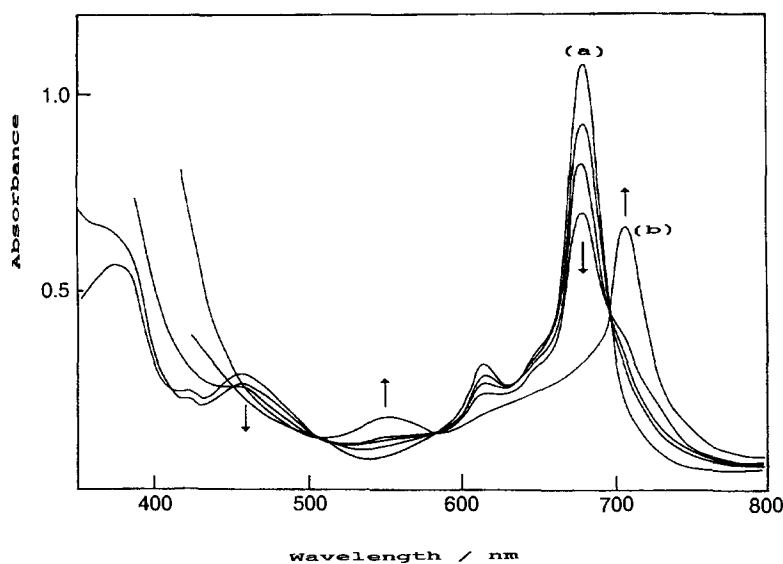


Fig. 1. The absorption spectra of (a) $[(\text{Cl})_{16}\text{PcFe}^{\text{II}}(\text{CN})_2]^{2-}$ in DMF, (b) $[(\text{Cl})_{16}\text{PcFe}^{\text{III}}(\text{CN})_2]^{-}$ in DMF, obtained by addition of bromine to (a).

activity at the central metal with oxidation to Fe^{III} Pc or reduction to Fe^{I} Pc. Perchloro-substitution of the phthalocyanine ring leads to a complex that is much easier to reduce and more difficult to oxidize,¹ due to the electro-withdrawing effect of the chlorine substituents. Redox potentials for the $[(\text{Cl})_{16}\text{PcFe}(\text{CN})_2]^{2-}$ complex are reported in Table 1. The redox potentials (vs SCE) were assigned by comparison with the non-cyanated $(\text{Cl})_{16}\text{PcFe}$ complex.¹ Hence, the first reduction at -0.79 V is assigned to the $[(\text{Cl})_{16}\text{Pc}(-2)\text{Fe}^{\text{I}}(\text{CN})_2]^{3-}/[(\text{Cl})_{16}\text{Pc}(-3)\text{Fe}^{\text{I}}(\text{CN})_2]^{4-}$ couple, the $\text{Fe}^{\text{II}}/\text{Fe}^{\text{I}}$ couple being observed as a broad shoulder to the positive side of the first reduction as reported before.¹ The reduction at -0.97 V is assigned to a further reduction of the ring (Table 1). Oxidation occurs at the metal first, as is typical of $\text{Fe}(\text{II})\text{Pc}$ complexes, giving $[(\text{Cl})_{16}\text{Pc}(-2)\text{Fe}^{\text{III}}(\text{CN})_2]^{-}$ with a half-wave potential ($E_{1/2}$) = 0.58 V. Chemical ox-

idation of $[(\text{Cl})_{16}\text{Pc}(-2)\text{Fe}^{\text{II}}(\text{CN})_2]^{2-}$ with bromine gave spectrophotometric changes that are typical^{3,19} of metal oxidation in MPC complexes (Fig. 1b). There was no spectrophotometric evidence for the loss of the cyanide ligands during oxidation. Reduction of the oxidized species with sodium borohydride resulted in more than 95% re-generation of the original species. Attempts to produce the $\text{Fe}(\text{III})$ complex by bulk electrolysis at potentials of the first oxidation from DMF solutions resulted in decomposition of the starting complex.

The oxidation couple observed at 1.06 V is assigned to the oxidation of the ring in comparison with $\text{Fe}(\text{II})\text{Pc}$ complexes.¹⁶ The ring oxidation couple was not observed for the $(\text{Cl})_{16}\text{PcFe}$ in DMF solutions.¹ Table 1 shows that, as expected, $[(\text{Cl})_{16}\text{PcFe}(\text{CN})_2]^{2-}$ is more difficult to oxidize and easier to reduce than the $[\text{PcFe}(\text{CN})_2]^{2-}$ species. This is due to the electron-withdrawing properties

Table 1. Half-wave potentials of the FePc complexes in DMSO containing TEAP

Complex	$E_{1/2}$ (V vs SCE)	Assignment
$[(\text{Cl})_{16}\text{PcFe}(\text{CN})_2]^{2-}$	1.06	$[(\text{Cl})_{16}\text{Pc}(-1)\text{Fe}^{\text{III}}(\text{CN})_2]/[(\text{Cl})_{16}\text{Pc}(-2)\text{Fe}^{\text{III}}(\text{CN})_2]^{-}$
	0.58	$[(\text{Cl})_{16}\text{Pc}(-2)\text{Fe}^{\text{III}}(\text{CN})_2]^{-}/[(\text{Cl})_{16}\text{Pc}(-2)\text{Fe}^{\text{II}}(\text{CN})_2]^{2-}$
	-0.79	$[(\text{Cl})_{16}\text{Pc}(-2)\text{Fe}^{\text{I}}(\text{CN})_2]^{3-}/[(\text{Cl})_{16}\text{Pc}(-3)\text{Fe}^{\text{I}}(\text{CN})_2]^{4-}$
	-0.97	$[(\text{Cl})_{16}\text{Pc}(-3)\text{Fe}^{\text{I}}(\text{CN})_2]^{4-}/[(\text{Cl})_{16}\text{Pc}(-4)\text{Fe}^{\text{I}}(\text{CN})_2]^{5-}$
$[\text{PcFe}(\text{CN})_2]^{2-}$	0.98	$[\text{Pc}(-1)\text{Fe}^{\text{III}}(\text{CN})_2]/[\text{Pc}(-2)\text{Fe}^{\text{III}}(\text{CN})_2]^{-}$
	0.14	$[\text{Pc}(-2)\text{Fe}^{\text{III}}(\text{CN})_2]^{-}/[\text{Pc}(-2)\text{Fe}^{\text{II}}(\text{CN})_2]^{2-}$
	-0.72	$[\text{Pc}(-2)\text{Fe}^{\text{II}}(\text{CN})_2]^{2-}/[\text{Pc}(-2)\text{Fe}^{\text{I}}(\text{CN})_2]^{3-}$
	-1.15	$[\text{Pc}(-2)\text{Fe}^{\text{I}}(\text{CN})_2]^{3-}/[\text{Pc}(-3)\text{Fe}^{\text{I}}(\text{CN})_2]^{4-}$

of the chloride ligands. These ligands reduce the electron density on the metal, making the metal more difficult to oxidize and easier to reduce.

Kinetics and equilibria

Figure 2 shows absorption spectrophotometric changes observed when DMSO solutions of potassium cyanide were added to solutions of $(\text{Cl})_{16}\text{PcFe}$ in de-aerated DMSO. The solution of this complex in DMSO is most likely the $(\text{Cl})_{16}\text{PcFe}(\text{DMSO})_2$ complex; PcFe complexes dissolve in DMSO to give the six coordinate $\text{PcFe}(\text{DMSO})_2$.¹² The presence of the charge transfer band in the 400–500 nm region of the spectra of $(\text{Cl})_{16}\text{PcFe}(\text{DMSO})_2$ is characteristic of an axially coordinated iron(II) phthalocyanine.^{12,20} Upon addition of cyanide to $(\text{Cl})_{16}\text{PcFe}(\text{DMSO})_2$ in DMSO, the Q band shifts from 678 nm to 685 nm and increases gradually in intensity with time. The final spectra, with the Q band centred at 685 nm, is similar to the spectra of the dicyano $[(\text{Cl})_{16}\text{PcFe}(\text{CN})_2]^{2-}$ complex (Fig. 1a). The new spectra is formed with isosbestic points at 718 and 545 nm. Further addition of cyanide had no effect on the position of the maxima. Thus the final spectra observed on addition of cyanide to $(\text{Cl})_{16}\text{PcFe}(\text{DMSO})_2$ is that of the dicyano complex. Cyanide is known to act as a bridging ligand in some metal phthalocyanine complexes;^{6,21} there was, however, no spectrophotometric evidence for aggregation in $[(\text{Cl})_{16}\text{PcFe}(\text{CN})_2]^{2-}$. Aggregation

in MPc complexes is accompanied by considerable broadening of the Q band.¹

Axial ligand substitutions in MPc complexes occur in a stepwise manner and are preceded by the formation of a highly reactive five-coordinate intermediate.^{5,22–26} Spectrophotometric changes in Fig. 2 show no evidence for the formation of the monocyano $[(\text{Cl})_{16}\text{PcFe}(\text{CN})(\text{DMSO})]^-$ complex prior to the formation of $[(\text{Cl})_{16}\text{PcFe}(\text{CN})_2]^{2-}$. The former should be formed as the first step in the axial ligand exchange. The coordination of the first axial ligand in MPc complexes generally causes only very minor spectrophotometric changes that are often difficult to observe.²⁶ Coordination of the first pyridine ligand to $\text{PcFe}(\text{DMSO})_2$ for example, caused only a 2 nm shift in the wavelength.²⁵ Hence, the lack of clear spectrophotometric changes associated with the formation of $[(\text{Cl})_{16}\text{PcFe}(\text{CN})(\text{DMSO})]^-$ is most likely due to the fact that the spectra for this complex are quite similar to the spectra of the original species.

Equilibrium data for the formation of the $[(\text{Cl})_{16}\text{PcFe}(\text{CN})_2]^{2-}$ complex were analysed by standard spectrophotometric techniques using equation (3):

$$\log [(A_{\text{eq}} - A_0)/(A_{\infty} - A_{\text{eq}})] = \log K + n \log [\text{CN}^-] \quad (3)$$

where A_{eq} is the equilibrium absorbance at 685 nm corresponding to the formation of the $[(\text{Cl})_{16}\text{PcFe}(\text{CN})_2]^{2-}$ complex, A_0 is the absorbance

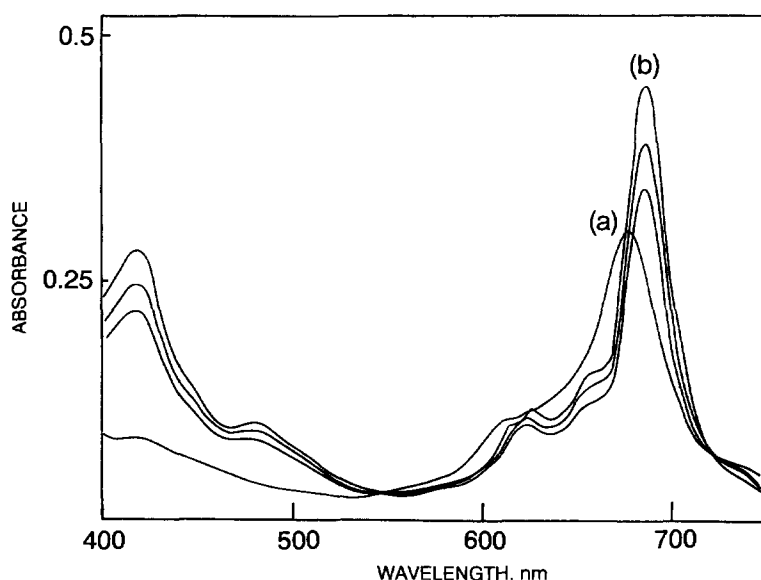
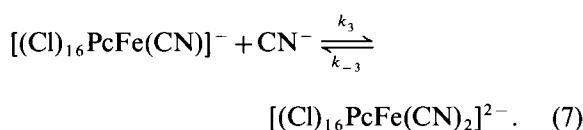
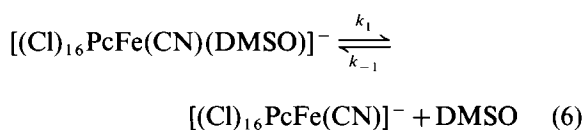
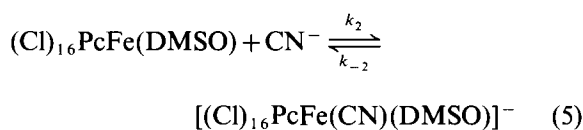
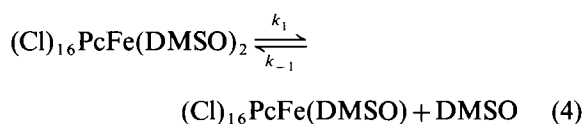


Fig. 2. Absorption spectrophotometric changes observed on addition of CN^- (7×10^{-4} M) to solutions of $[(\text{Cl})_{16}\text{PcFe}^{\text{II}}(\text{DMSO})_2]^-$ in DMSO.

at 685 nm corresponding to the zero per cent formation of this complex and A_∞ is the absorbance for the complete formation of the complex. Figure 3 shows a plot of $\log [(A_{\text{eq}} - A_0)/(A_\infty - A_{\text{eq}})]$ vs $\log [\text{CN}^-]$. A straight line plot with unit slope ($n = 1.00 \pm 0.05$) was obtained. An equilibrium constant of $K_3 = 1.6 \pm 0.5 \times 10^3 \text{ dm}^3 \text{ mol}^{-1}$ was obtained. A unit value for n confirms the stepwise nature for the coordination of cyanide to $(\text{Cl})_{16}\text{PcFe}(\text{DMSO})_2$, K_3 thus corresponds to the coordination of the second cyanide and the formation of $[(\text{Cl})_{16}\text{PcFe}(\text{CN})_2]^{2-}$, equations (6) and (7):



The formation of the monocyano complex, equations (4) and (5), precedes the formation of the dicyano complex. The former, however, does not show significant spectrophotometric changes, hence equilibria and kinetics could only be determined for the dicyano complex.

The equilibrium constant of $K_3 = 1.6 \pm 0.5 \times 10^3 \text{ dm}^3 \text{ mol}^{-1}$ is slightly higher than the equilibrium constant for the coordination of the second cyanide

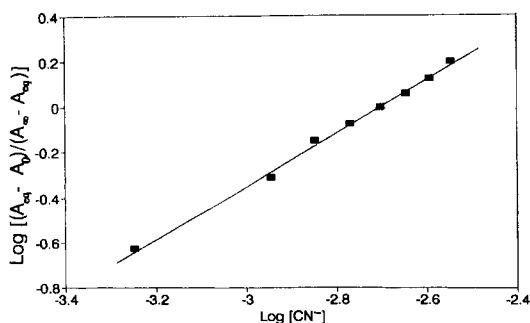


Fig. 3. Plot of $\log [(A_{\text{eq}} - A_0)/(A_\infty - A_{\text{eq}})]$ vs $\log [\text{CN}^-]$ for the formation of $[(\text{Cl})_{16}\text{PcFe}(\text{CN})_2]^{2-}$, equations (6) and (7).

($K_3 = 5.7 \times 10^2$) to $\text{PcFe}(\text{DMSO})(\text{CN})^-$ (Table 2). This implies that the substitution of the second DMSO ligand by cyanide is more favoured in the perchloro-substituted complex. DMSO behaves as a π acceptor ligand and gains some extra stability by π back bonding.²⁵ It is likely that this extra stability of DMSO is reduced in $[(\text{Cl})_{16}\text{PcFe}(\text{CN})(\text{DMSO})]^-$ since the chloride ligands pull the electron density away from the metal, thus reducing the available electron density for π back bonding with DMSO.

Rate constants for the formation of $[(\text{Cl})_{16}\text{PcFe}(\text{CN})_2]^{2-}$ were obtained by monitoring the absorption changes at 685 nm with time and at various cyanide concentrations. Since an excess of cyanide was employed, pseudo-first-order conditions were assumed in calculating the rate constants. Equation (8) gives the rate law for the dissociative mechanism shown by equations (6) and (7)

$$k_{\text{obs}} = \frac{k_1 k_3 [\text{CN}^-]}{k_{-1} [\text{DMSO}]} + k_{3r} \quad (8)$$

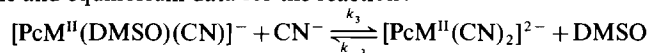
The rate constant for the forward reaction, k_{3f} , is given by $k_1 k_3 / k_{-1} [\text{DMSO}]$ and k_{3r} , the rate constant for the reverse reaction is equal to k_{-3} .

Plots of k_{obs} vs cyanide concentration were linear (Fig. 4), showing that the reaction is first order in cyanide. Least square analysis gave $k_{3f} = 4.2 \pm 0.3 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and from the intercept, k_{3r} was estimated to be $2.3 \pm 0.5 \times 10^{-6} \text{ s}^{-1}$. The ratio of k_{3f}/k_{3r} gives a value of $1.8 \times 10^3 \text{ dm}^3 \text{ mol}^{-1}$ for the equilibrium constant, K_3 . This value is in good agreement (within experimental error) with the value of $1.6 \pm 0.5 \times 10^3 \text{ dm}^3 \text{ mol}^{-1}$ obtained directly from experiment.

Table 2 shows that the rate of coordination of the second cyanide to $(\text{Cl})_{16}\text{PcFe}(\text{DMSO})_2$ is slower than the rate for the coordination of the second cyanide to $\text{PcFe}(\text{DMSO})_2$, by a factor of approximately 50. This is a consequence of the presence of the electron-withdrawing chloride substituents in the chloro-substituted complex. The chloride ligands reduce the electron density from the central metal, making it difficult for π acceptor ligands, such as cyanide, to coordinate.

All the reported data on the reaction of MPC complexes with cyanide have been based on non-aqueous solvents due to the insolubility of MPC complexes in water. The rate constants reported in Table 2 are in general lower than those for the formation of dicyano complexes of metalloporphyrins; the latter are, however, reported in water.²⁷ For example a rate constant of $3 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ has been reported for the formation of dicyano

Table 2. Kinetic and equilibrium data for the reaction:



$\text{M}^{\text{II}}\text{Pc}$	$K_3(\text{dm}^3 \text{ mol}^{-1})$	$k_3(\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1})$	$k_3(\text{s}^{-1})$	Ref.
RuPc		7.2×10^{-2}		4
FePc	5.7×10^2	0.2	3.5×10^{-4}	5
FePc(Cl) ₁₆	1.6×10^3	4.2×10^{-3}	2.3×10^{-6}	This work

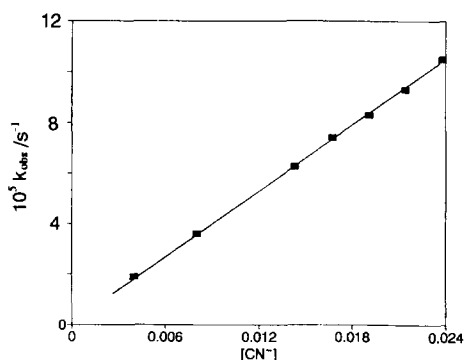


Fig. 4. The variation of observed rate constant with cyanide concentration for the formation of $[(\text{Cl})_{16}\text{PcFe}^{\text{II}}(\text{CN})_2]^{2-}$.

cobalt tetraphenyl porphyrin.²⁷ Work on the reaction of cyanide with water-soluble MPc complexes is underway.

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