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FULL PAPER

Octabutylthiophthalocyaninatoiron(II): electrochemical properties and interaction with cyanide

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Received 14th December 2001, Accepted 14th February 2002
First published as an Advance Article on the web 15th March 2002

The preparation of the thiol-derivatised iron(II) phthalocyanine (FePc) complex, 2,3,9,10,16,17,23,24-octabutylthiophthalocyaninatoiron(II), $FePc(SC_4H_9)_8$, is described. Electrochemical data obtained by both cyclic voltammetry and Osteryoung square wave voltammetry in DMF showed four redox couples. Kinetics and equilibrium measurements for the interaction of cyanide with $FePc(SC_4H_9)_8$ at 25.0 ± 0.5 °C in both DMSO and DMF are reported. Gradual spectroscopic changes were only observed for the formation of the dicyano complex, $[(CN)_2FePc(SC_4H_9)_8]^{2-}$. This complex is formed with equilibrium constants, K, of $(6.8 \pm 0.8) \times 10^2$ $dm^3\ mol^{-1}$ in DMF and $(1.3 \pm 0.2) \times 10^3$ $dm^3\ mol^{-1}$ in DMSO. Pseudo-first-order rate constants, k_{4r}, were also estimated to be $(1.9 \pm 0.1) \times 10^{-2}$ and $(8.2 \pm 0.3) \times 10^{-2}$ $dm^3\ mol^{-1}\ s^{-1}$ in DMF and DMSO, respectively. These results agree with the weak electron-donating properties of the peripheral butylthio-substituents on the phthalocyanine ring and the O-bonded *trans* DMF.

Introduction

Metallophthalocyanines (MPcs) are well-known compounds which have found numerous applications including their use as catalysts,[1–3] sensors,[4–7] photosensitisers[8–11] and in photovoltaic cells.[12] In most of the applications of the MPc complexes, exchange of electrons occurs between them and electron-donors or electron-acceptors, hence a good understanding of the redox properties of MPc complexes is important.

Thiol-derivatised MPcs have not received much attention. To the best of our knowledge, the title complex containing an iron metal center has not been reported. Following our interest in the investigation of potential catalytic and photosensitization applications of thiol-derivatised MPc complexes, we report on the synthesis and electrochemistry of the complex, 2,3,9,10,16,17,23,24-octabutylthiophthalocyaninatoiron(II), $FePc(SC_4H_9)_8$, (Fig. 1), and its interaction with cyanide in both dimethyl sulfoxide and dimethylformamide.

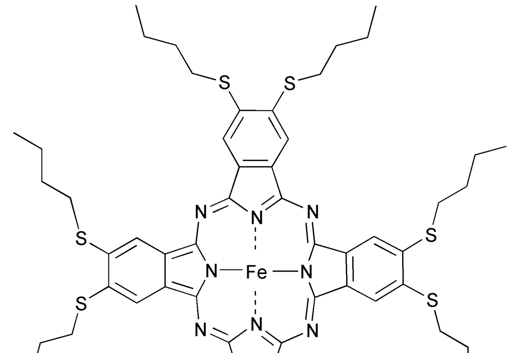

Fig. 1 Molecular structure of octabutylthiophthalocyaninatoiron(II), $FePc(SC_4H_9)_8$.

Iron(II) phthalocyanine (FePc) has a strong tendency to undergo axial ligation with different types of ligands including cyanide.[13–22] Cyanide poisoning partially occurs when cyanide binds to the iron(III) porphyrins in cytochrome oxidase[23] and prevents respiration. Because of their porphyrin-like structures, MPcs serve as useful models for investigating biological processes involving hemoprotein. FePc is usually considered analogous to the haem group of hemoglobin and myoglobin, hence the study of its axial coordination with cyanide is important in the search for anti-cyanide drugs. To this end we examined the equilibria and kinetics of the interaction of cyanide with $FePc(SC_4H_9)_8$ and compared the results with those previously reported for unsubstituted[20] and substituted FePc complexes.[21,22] Electron-donating and electron-withdrawing substituents are known to affect both the electrochemistry and axial exchange reactivity of MPc complexes.[24,25]

Experimental

Materials

Dimethyl sulfoxide (DMSO), dimethylformamide (DMF), butanethiol and dichlorophthalic acid were purchased from Sigma-Aldrich. DMSO and DMF were freshly distilled after drying over alumina, before use. All other reagents were of analytical grade and were used as received from the suppliers without further purification. Tetrabutylammonium perchlorate (TBAP) was recrystallized from ethanol and used as an electrolyte for all electrochemical measurements. Ferrocene was recrystallised from ethanol before being employed as an internal standard for electrochemical measurements.

Synthesis

The synthesis of 2,3,9,10,16,17,23,24-octabutylthiophthalocyaninatoiron(II), $FePc(SC_4H_9)_8$, (Fig. 1) was adapted from a procedure similar to that used for the synthesis of the copper phthalocyanine complex, octa(hexylthio)phthalocyaninatocopper(II).[26] 1,2-Dibutylthio-4,5-dicyanobenzene was synthesized following the method of Wöhrle *et al.*[27] by reacting 1,2-dichloro-4,5-dicyanobenzene with butanethiol. However,

DOI: 10.1039/b111429h

the conversion of the 1,2-dichloro-4,5-dicyanobenzene to 1,2-dibutylthio-4,5-dicyanobenzene was achieved at lower temperature, 45 °C, instead of the usual 90 °C reported in literature,[27] resulting in a better yield of up to 86%. The 1,2-dibutylthio-4,5-dicyanobenzene gave similar spectroscopic characteristics as reported elsewhere.[28,29] A mixture of 1,2-dibutylthio-4,5-dicyanobenzene (0.10 g, 0.33 mM.), $FeCl_2 \cdot 4H_2O$ (0.02 g, 0.08 mM) and urea (0.032 g, 0.5 mM) was heated and stirred at 150 °C for 90 min under nitrogen atmosphere. After cooling to room temperature, the reaction mixture was treated with hot ethanol and filtered by centrifugation. The dark green crude product was purified by chromatography by first dissolving in chloroform and then eluting from a silica gel column with chloroform. The first band was collected and the solvent removed under reduced pressure. Yield: (0.09 g, 88%). Anal.: Calcd. for $C_{64}H_{80}N_8S_8Fe \cdot 8H_2O$: C, 54.24: H, 6.78: N, 7.91 %. Found: C, 54.58: H, 6.47: N, 7.91. IR [(KBr) ν_{max}/cm^{-1}]: 3447, 2958, 2863, 1589, 1500, 1455, 1412, 1375, 1325, 1263, 1215, 1185, 1073, 960, 865, 803, 746, 700. UV-Vis [(DMSO, λ_{max}/nm (log ε)]: 348 (5.88) and 676 (4.97); UV-Vis [(DMF, λ_{max}/nm (log ε)]: 356 (5.08), 449 (4.59), 620 (4.61), 684 (5.06).

The $FePc(SC_4H_9)_8$ dissolves very slowly in DMF, hence we synthesized the axially ligated complex, $(DMF)_2FePc(SC_4H_9)_8$, and employed it for the studies in this work. This was prepared by stirring $FePc(SC_4H_9)_8$ (0.05g) in DMF (10ml) at 100 °C for 3 h under nitrogen atmosphere. The resulting green solution was evaporated under vacuum, the dark green solid washed with water and acetone and then dried *in vacuo*. Yield: (0.046 g, 93%). Anal.: Calcd. for $C_{70}H_{94}N_{10}O_2S_8Fe \cdot 2H_2O$: C, 57.78: H, 6.47: N, 9.63%. Found: C, 57.63: H, 6.51: N, 9.52. IR [(KBr) ν_{max}/cm^{-1}]: 3425, 2927, 2867, 1688, 1593, 1500, 1460, 1413, 1378, 1325, 1215, 1189, 1120, 1073, 958, 880, 850, 781, 746 and 705. UV-Vis [(DMF, λ_{max}/nm (log ε)]: 356 (5.08), 449 (4.59), 620 (4.61), 684 (5.06).

The axially ligated dicyano complex, $K_2[(CN)_2FePc(SC_4H_9)_8]$, was prepared by the method reported for other dicyanometallophthalocyanine $(CN)_2MPc$ complexes[30,31] by mixing 0.05 g of $FePc(SC_4H_9)_8$ with 0.05 g (excess) of potassium cyanide and refluxing the mixture in DMF (5 ml) for 3 h under nitrogen atmosphere. The brilliant green solution was evaporated to dryness and the solid washed with hexane, and then recrystallised twice from acetone. The complex gave satisfactory spectroscopic (IR and UV-Vis) characteristics as evidenced, for example, by the Fe–CN vibration at 2169 cm^{-1} (see text for further discussion) as well as the elemental analysis result. Yield: (0.041 g, 82%). Anal.: Calcd. for $K_2C_{66}H_{80}N_{10}S_8Fe \cdot 10H_2O$: C, 50.02: H, 4.98: N, 8.83%. Found: C, 50.07: H, 5.06: N, 8.85. IR [(KBr) ν_{max}/cm^{-1}]: 3433, 2958, 2869, 2169 ($\nu_{Fe\text{–}CN}$), 1592, 1512, 1458, 1407, 1381, 1216, 1131, 1073, 960, 872, 804, 781, 747 and 701. UV-Vis [(DMSO, λ_{max}/nm (log ε)]: 368m, 408w, 445w, 468w, 620m and 686s (5.10); UV-Vis [(DMF, λ_{max}/nm (log ε)]: 366m, 408w, 445w, 468w, 620m and 686s (5.08).

UV-Vis spectra were recorded on a Varian 500 UV-Vis-Nir spectrophotometer. Routine infra red spectra (KBr discs) were obtained with the Perkin-Elmer spectrum 2000 FTIR spectrometer. ^1H NMR spectra 400 MHz) were recorded in $CDCl_3$ using the Bruker EMX 400 NMR spectrometer.

Electrochemical methods

Electrochemical data were obtained under purified nitrogen gas with BioAnalytical System (BAS) 100 B/W Electrochemical Workstation. Cyclic voltammograms (CVs) and Osteryoung square wave voltammograms (OSWVs) were collected using a conventional three-electrode set-up with a glassy carbon electrode (GCE, 3.00mm diameter) as a working electrode, a platinum wire counter electrode, and a silver wire pseudo-reference electrode. All potentials were referenced internally to the ferrocinium/ferrocene (fc^+/fc) redox couple. The fc^+/fc couple has been reported[32] to be 0.46 V *vs.* saturated calomel electrode (SCE) in DMF, hence potentials are reported *versus* SCE. TBAP (0.1 mol dm^{-3}) was used as supporting electrolyte. The concentration of the $(DMF)_2FePc(SC_4H_9)_8$ was maintained at 1×10^{-4} mol dm^{-3} in DMF. The parameters for the OSWV were: step potential 4 mV; square wave amplitude 25 mV at a frequency of 15 Hz.

Equilibria and kinetics

Equilibrium and kinetic studies were run at constant temperature (25.0 ± 0.5 °C) and monitored with the Varian 500 UV-Vis-Nir spectrophotometer. The solubility of $FePc(SC_4H_9)_8$ in DMSO is poor but was good enough for the low concentration (~3×10^{-6} mol dm^{-3}) required for this study. However, its solubility in DMF is extremely slow; hence the complex, $(DMF)_2FePc(SC_4H_9)_8$, was used for the studies in DMF. Cyanide binding was followed by monitoring the increase in the intensity at 686 nm following the addition of cyanide to a DMSO solution of $FePc(SC_4H_9)_8$ or DMF solution of $(DMF)_2FePc(SC_4H_9)_8$. The later is, of course, equivalent to studying cyanide binding to $FePc(SC_4H_9)_8$ in DMF. Typically, a known volume of the DMSO or DMF solution of the phthalocyanine complex was added to a 1cm pathlength spectrophotometric cell, then a known volume of the DMF or DMSO solution of the potassium cyanide was added to the cell and the changes in absorption spectra monitored with time. For the kinetic studies the concentration of the MPc complex was maintained at ~3×10^{-6} mol dm^{-3}. The concentration was determined from the extinction coefficients of the Q band of $(DMF)_2FePc(SC_4H_9)_8$ in DMF {$\varepsilon_{684} = (1.2 \pm 0.1) \times 10^5$ dm^3 mol^{-1} cm^{-1}} and $FePc(SC_4H_9)_8$ in DMSO {$\varepsilon_{676} = (9.4 \pm 0.1) \times 10^4$ dm^3 mol^{-1} cm^{-1}}. The cyanide concentrations, determined by titration with silver nitrate, were varied from 1.8×10^{-4} to 3.0×10^{-3} mol dm^{-3}. Since the concentrations of cyanide were larger than those for the phthalocyanine complexes, pseudo-first-order conditions were assumed for the kinetic studies.

Results and discussion

Synthesis and spectral characterization

The formation of the 2,3,9,10,16,17,23,24-octabutylthiophthalocyaninatoiron(II), $FePc(SC_4H_9)_8$, was accomplished by a simple direct reaction of 1,2-dibutylthio-4,5-dicyanobenzene with $FeCl_2 \cdot 4H_2O$ in good yield. Both $FePc(SC_4H_9)_8$ and $(DMF)_2FePc(SC_4H_9)_8$ are readily soluble in the common organic solvents (such as chloroform, tetrahydrofuran, benzene and toluene). Whereas the solubility of $FePc(SC_4H_9)_8$ in DMF is extremely poor at room temperature, $(DMF)_2FePc(SC_4H_9)_8$ is soluble in both DMF and DMSO. This is not surprising since axial ligation often leads to an increase in the solubility of MPc.[33,34] The O-bonding of DMF is evidenced by the presence of the distinct Fe–O vibrations[35,36] at 850 cm^{-1} in the IR spectra of $(DMF)_2FePc(SC_4H_9)_8$ but absent in $FePc(SC_4H_9)_8$ and $K_2[(CN)_2FePc(SC_4H_9)_8]$, complexes.

UV-Vis spectra of $FePc(SC_4H_9)_8$ in DMSO (Fig. 2a) and DMF (Fig. 2b) with two strong absorption regions, 348–356 nm (Soret or B band) and 676–684 nm (Q band) are typical of MPc complexes with D_{4h} symmetry.[37] The spectrum in DMF showed an absorption band centered near 450 nm as is typical of low-spin six-coordinate $Fe^{II}Pc$ species.[36,38–43] This band is usually associated with Fe^{II}-to-ligand charge-transfer transitions,[38,41–43] hence its presence is a good indication that the central metal ion remains in the +2 oxidation state.[21,37] This band has also been observed to become more intense as the σ donor strength of the axial ligand increases.[37] Both B and Q bands of these complexes are slightly shifted to longer wavelengths when compared to unsubstituted FePc (330 and 659 nm in DMF). Such a red shift is an indication that the energy gap between the highest occupied molecular orbital (HOMO) and lowest unoccupied

Table 1 Comparison of redox potentials of $(DMF)_2FePc(SC_4H_9)_8$ with those of FePc and $FePc(Cl)_{16}$ complexes. Pc(−2) = phthalocyanine dianion

	$E_{1/2}$ (V *vs.* SCE)			
$(L)_2Fe^{II}Pc$ complexes	I $[Fe^{III}Pc(-1)]^{2+}/[Fe^{III}Pc(-2)]^{+}$	II $[Fe^{III}Pc(-2)]^{+}/[Fe^{II}Pc(-2)]$	III $[Fe^{II}Pc(-2)]/[Fe^{I}Pc(-2)]^{-}$	IV $[Fe^{I}Pc(-2)]^{-}/[Fe^{I}Pc(-3)]^{2-}$
FePc[a]	—	0.37	−0.55	−1.17
$FcPc(Cl)_{16}$[b]	—	0.73	—	−1.11
$(DMF)_2FePc(SC_4H_9)_8$[c]	0.91	0.26	−0.49	−1.00

[a] Ref. 49 (data obtained in dimethylacetamide, DMA). [b] Ref. 49 (data obtained in DMF). [c] This work (data obtained in DMF).

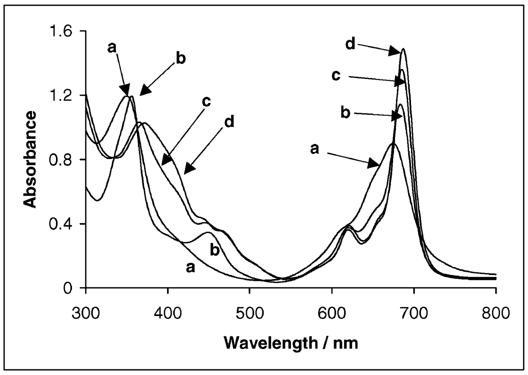

Fig. 2 Electronic absorption spectra of (a) $FePc(SC_4H_9)_8$ (9.64×10^{-6} mol dm^{-3}) in DMSO, (b) $FePc(SC_4H_9)_8$ (1.00×10^{-5} mol dm^{-3}) in DMF, (c) $[(CN)_2FePc(SC_4H_9)_8]^{2-}$ (1.12×10^{-5} mol dm^{-3}) in DMF and (d) $[(CN)_2FePc[(SC_4H_9)_8]^{2-}$ (1.21×10^{-5} mol dm^{-3}) in DMSO.

molecular orbital (LUMO) of the complex are narrower than those of the FePc.[37] The Q band of $FePc(SC_4H_9)_8$ is broad in DMSO and in apolar solvents such as $CHCl_3$ (not shown), even at low concentrations (~10^{-6} mol dm^{-3}). Behaviour of this nature has been observed before[26] and was attributed to some intermolecular interactions of the central metal ion of one molecule with the thioether groups of another. These Fe–thioether interactions seem to be less favoured in DMF than in DMSO or apolar solvents. Since the behaviour was not observed in the zinc analogue, $ZnPc(SC_4H_9)_8$,[28,44] the involvement of the Fe^{II} ion may also be assumed.

The ligation of cyanide was confirmed by the IR spectrum of the solid complex, $K_2[(CN)_2FePc(SC_4H_9)_8]$. Because of steric constraints a six-coordinate species is not likely to exhibit aggregation in solution. The electronic absorption spectra of this dicyano complex in both DMF and DMSO (Fig. 2c and d, respectively) are typical of a non-aggregated MPc complex.[37] Its spectrum showed a split in the Soret band in either of the two solvents, which is typical of such dicyano complexes.[45] The Fe–CN vibration is observed at 2169 cm^{-1}, a value in the range reported for M–CN vibrations in $(CN)_2MPc$ complexes.[21,46–48] For example, the Fe–CN vibrations for $[(CN)_2FePc]^{2-}$ and $[(CN)_2FePc(Cl)_{16}]^{2-}$ have been reported[20,21] as 2120 and 2070 cm^{-1}, respectively. Indeed, it is interesting to see how the two different peripheral substituents, chloride (an electron-acceptor) and butylthio (an electron-donor) affect the Fe–CN vibrations with equal but opposite magnitudes (~ ± 50 cm^{-1}).

Electrochemical studies

Because of good solubility in DMF and high concentration (~10^{-4} mol dm^{-3}) required for the electrochemical investigation, $(DMF)_2FePc(SC_4H_9)_8$ was chosen in preference to $FePc(SC_4H_9)_8$ for this investigation. The redox properties of FePc complexes are well established.[49] The redox properties of $(DMF)_2FePc(SC_4H_9)_8$ were studied using both CV and OSWV in DMF containing 0.1 mol dm^{-3} TBAP (Fig. 3). The purity of the complex is evident in the well-defined voltammograms. The redox potential values are listed in Table 1. In comparison with other $Fe^{II}Pc$ complexes,[49] the weak couple **I** observed near 1.0V *vs.* SCE is assigned to the ring oxidation couple $[Fe^{III}Pc(-1)]^{2+}/[Fe^{III}Pc(-2)]^{+}$. Couple **II** is assigned to the metal-based oxidation, $[Fe^{III}Pc(-2)]^{+}/[Fe^{II}Pc(-2)]$, while the two reduction processes **III** and **IV** are assigned to $[Fe^{II}Pc(-2)]/[Fe^{I}Pc(-2)]^{-}$ and $[Fe^{I}Pc(-2)]^{-}/[Fe^{I}Pc(-3)]^{2-}$, respectively.

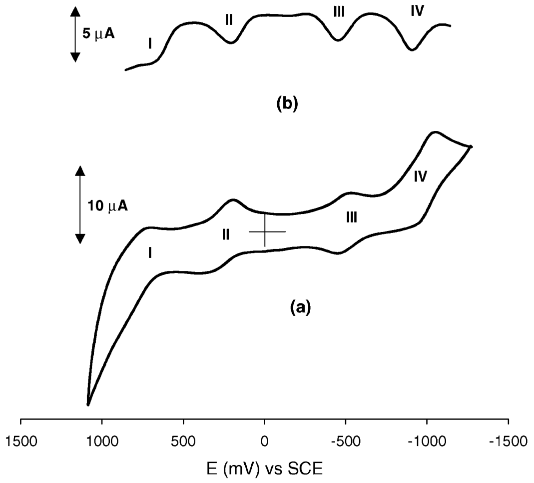

Fig. 3 The cyclic voltammogram (a) and Osteryoung square wave voltammogram (b) of 1×10^{-4} mol dm^{-3} of $(DMF)_2FePc(SC_4H_9)_8$ in DMF containing 0.1 mol dm^{-3} TBAP. Scan rate = 100 mV s^{-1}.

Introduction of electron-donating substituents (such as the SC_4H_9–) to the MPc ring should lead to an increase in the electron density of the central metal ion thereby making the MPc complex more easily oxidized and less easily reduced.[24,25] Table 1 shows that $(DMF)_2FePc(SC_4H_9)_8$ is more easily oxidized than either the unsubstituted FePc or chloro-substituted complex, $FePc(Cl)_{16}$. It is surprising that the $E_{1/2}$ values for the reduction processes **III** and **IV** do not show a corresponding difficulty in the reduction process. The reason for this behaviour is not yet understood. However, available reports on alkylthio-derivatived MPcs show little or no difference in their reduction potentials when compared to the unsubstituted MPcs. For example, the first reduction potentials ($E_{1/2}$) for the CoPc in DMF is −0.37V *vs.* SCE,[49] while it is −0.38V *vs.* SCE for $CoPc(SC_4H_9)_8$[50] and −0.38V *vs.* SCE for $(SC_2H_4OH)_8CoPc$ in DMSO.[51] These data indicate the weak electron-donating influence of the alkythio-substituents on the average electron density of the MPc molecule.

The anodic to cathodic peak separations ($\Delta E\text{p} = E_{pa} - E_{pc}$) were found to range between 60 and 140mV. Couples **II** and **IV** showed quasi-reversible behaviour (ΔE_p values 140 and 110mV, respectively) and cathodic to anodic peak currents (i_{pc}/i_{pa}) greater than unity. For couples **II** and **IV**, the peak currents were found to increase linearly with the square root of the scan rates (for scan rates ranging from 10 to 800 mV s^{-1}, indicating that the electrode processes are purely diffusion-controlled. The reduction process **III** showed excellent reversible behaviour at high scan rates (> 100 mV s^{-1}) in that i_{pc}/i_{pa} equals unity and ΔE_p = 60 mV. The ΔE_p value for the ferrocene internal standard was observed at 70 mV.

Kinetics and equilibrium studies

On addition of DMSO solutions of cyanide to a DMSO solution of $FePc(SC_4H_9)_8$, the Q band first shifts from 676 nm to 684 nm, then to 686 nm and increases in intensity with time (Fig. 4a). In the DMF system, on the other hand, the Q band shifts from 684 to 686 nm and then increases with time (Fig. 4b). In each solvent system, the B band splits and shifts to lower energy (Fig. 5). The band at 450 nm region in the DMF system also splits. The splitting of the B bands in the UV region and their shifts to lower energy is typical of cyanide coordination.[37] The final spectra for both DMSO and DMF systems are similar to the spectra of the dicyano complex discussed above (Fig. 2c and 2d). The new spectra are formed with isosbestic points at 368, 524 and 706 nm for the DMSO system, and 365, 430, and 536 nm for the DMF system. Further addition of cyanide had no effect on the position of the maxima. These data indicate that the final spectrum obtained on addition of cyanide to a DMSO or DMF solution of $FePc(SC_4H_9)_8$ is that of the dicyano complex, $[(CN)_2FePc(SC_4H_9)_8]^{2-}$.

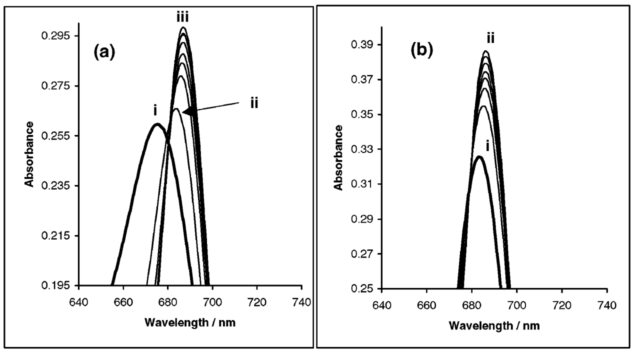

Fig. 4 Absorption spectral changes observed on addition of (a) cyanide (4.8×10^{-4} mol dm^{-3}) to $FePc(SC_4H_9)_8$ (2.8×10^{-6} mol dm^{-3}) in DMSO, (i) $[(DMSO)_2FePc(SC_4H_9)_8]$, (ii) $[(DMSO)(CN)FePc(SC_4H_9)_8]^-$, (iii) $[(CN)_2FePc(SC_4H_9)_8]^{2-}$, and of (b) cyanide ($5.4 \times 10^{-4}$ mol dm^{-3}) to $(DMF)_2FePc(SC_4H_9)_8$ (2.8×10^{-6} mol dm^{-3}) in DMF (i) $(DMF)_2FePc(SC_4H_9)_8$ (ii) $[(CN)_2FePc(SC_4H_9)_8]^{2-}$.

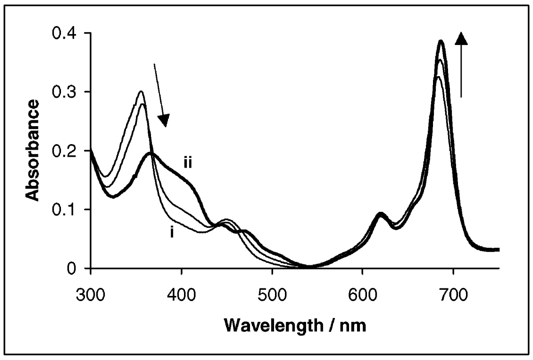

Fig. 5 Absorption spectral changes observed (i) before and (ii) 15 minutes after addition of cyanide (5.4×10^{-4} mol dm^{-3} to a solution of $(DMF)_2FePc(SC_4H_9)_8$ (2.8×10^{-6} mol dm^{-3}) in DMF.

Axial ligand substitutions in MPc (including porphyrin) complexes occur in a step-wise manner with the coordination of the first cyanide occurring much faster than that of the second.[20,21,52] The shift in the Q band from 676 to 684 nm before the final shift to 686 nm in the DMSO system shows the step-wise nature of the cyanide coordination. The first shift to 684 nm is most probably due to the formation of the monocyano species, $[(CN)(DMSO)Fe^{II}Pc(SC_4H_9)_8]^-$ and the second to 684 nm due to the dicyano complex, $[(CN)_2FePc(SC_4H_9)_8]^{2-}$. The coordination of the first axial ligand in MPc complexes generally occurs at a fast rate causing very minor spectroscopic changes that are difficult to observe.[16,21] This may explain why Fig. 4b does not show the stepwise change in wavelength observed in Fig. 4a. It is also most likely that the monocyano species, $[(CN)(DMF)Fe^{II}Pc(SC_4H_9)_8]^-$ absorbs at about the same wavelength (684 nm) as the original species, $(DMF)_2FePc(SC_4H_9)_8$. Spectral changes for the formation of the monocyano complexes in both solvent systems could not be followed using the techniques employed in this work since the changes occurred very fast. Hence, equilibria and kinetics could only be determined for the formation of the dicyano complex, $[(CN)_2Fe^{II}Pc(SC_4H_9)_8]^{2-}$.

Equilibrium data were determined by the standard spectrophotometric technique using the Hill equation[13] (eqn. 1).

$$\log [(A_{eq} - A_0)/(A_\infty - A_{eq})] = n \log [CN^-] + \log K \qquad (1)$$

where A_{eq} is the equilibrium absorbance at 686 nm, A_0 is the absorbance before the addition of cyanide and A_∞ is the absorbance for the complete formation of the dicyano complex. From the plots of $\log [(A_{eq} - A_0)/(A_\infty - A_{eq})]$ *vs.* $\log [CN^-]$ (Fig. 6) equilibrium constants [$K = (1.3 \pm 0.2) \times 10^3$ with $n = 1.01 \pm 0.04$ in DMSO and $K = (6.8 \pm 0.8) \times 10^2$ dm^3 mol^{-1} with $n = 0.99 \pm 0.05$ in DMF] were obtained. A value of $n = 1$ is an indication of the step-wise nature of the coordination of the second cyanide to these complexes. $K = K_4$ (equation below), thus corresponds to the coordination of the second cyanide and formation of the $(CN)_2Fe^{II}Pc(SC_4H_9)_8$, eqns. 4 and 5.

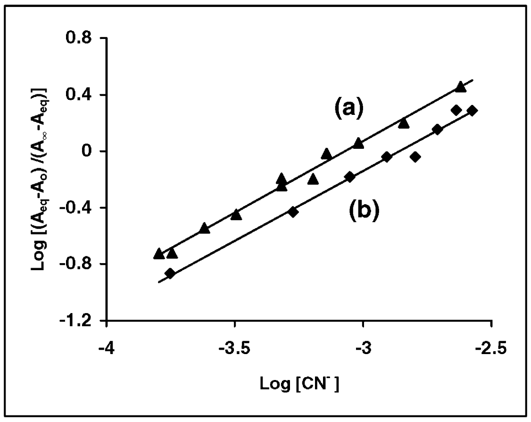

Fig. 6 Plots of $\log [(A_{eq} - A_0)/(A_\infty - A_0)]$ *vs.* $\log [CN^-]$ for the formation of $[(CN)_2FePc(SC_4H_9)_8]^{2-}$ in (a) DMSO and (b) DMF.

$$(L)_2Fe^{II}Pc(-2)(SC_4H_9)_8 \xrightleftharpoons[k_{-1}]{k_1} (L)Fe^{II}Pc(-2)(SC_4H_9)_8 + L \qquad (2)$$

$$(L)Fe^{II}Pc(-2)(SC_4H_9)_8 + CN^- \xrightleftharpoons[k_{-2}]{k_2} [(L)(CN)Fe^{II}Pc(-2)(SC_4H_9)_8]^- \qquad (3)$$

$$[(L)(CN)Fe^{II}Pc(-2)(SC_4H_9)_8]^- \xrightleftharpoons[k_{-3}]{k_3} [(CN)Fe^{II}Pc(-2)(SC_4H_9)_8]^- + L \qquad (4)$$

$$[(CN)Fe^{II}Pc(-2)(SC_4H_9)_8]^- + CN^- \xrightleftharpoons[k_{-4}]{k_4} [(CN)_2Fe^{II}Pc(-2)(SC_4H_9)_8]^{2-} \qquad (5)$$

where L is either DMSO or DMF.

The equilibrium constants obtained in both solvent systems are in the range (within experimental error) for those obtained for the coordination of the second cyanide in FePc complexes[20–22] (Table 2). The smaller K_4 value of $(6.8 \pm 0.8) \times 10^2$ dm^3 mol^{-1} in DMF in comparison to the value of $(1.3 \pm 0.2) \times 10^3$ dm^3 mol^{-1} in DMSO is most likely to be due to

Table 2 Kinetics and equilibrium data for the axial exchange reaction of cyanide with iron(II) phthalocyanine complexes

$$[(CN)(L)Fe^{II}Pc(-2)(SC_4H_9)_8]^- + CN^- \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} [(CN)_2Fe^{II}Pc(-2)(SC_4H_9)_8]^{2-} + L$$

MPc Complex	K_4/dm^3 mol^{-1}	k_{4f}/dm^3 mol^{-1} s^{-1}	k_{4r}/s^{-1}	Ref.
$[(DMSO)(CN)FePc]^-$	5.7×10^2	0.20	3.5×10^{-4}	20
$[(DMSO)(CN)FePc(Cl)_{16}]^-$	1.6×10^3	4.2×10^{-3}	2.3×10^{-6}	21
(CO)(DMSO)FePc	$(6.7 \pm 0.5) \times 10^2$	0.34 ± 0.12	5.9×10^{-4}	22
$[(DMSO)(CN)FePc(SC_4H_9)_8]^-$	$(1.3 \pm 0.2) \times 10^3$	$(8.2 \pm 0.3) \times 10^{-2}$	5.5×10^{-5}	This work
$[(DMF)(CN)FePc(SC_4H_9)_8]^-$	$(6.8 \pm 0.8) \times 10^2$	$(1.9 \pm 0.1) \times 10^{-2}$	2.5×10^{-5}	This work

the stronger O-bonded DMF in comparison to the weaker S-bonded DMSO, hence resulting in the lower lability of the DMF ligand. DMSO is known as a labile ligand because of the weak S–Fe σ-bond.[15] As a π acceptor ligand, DMSO gains extra stability by π back bonding. It has been suggested[21] that this extra stability is reduced in the presence of the electron-withdrawing ring substituents {*cf.* $K_4 = 1.6 \times 10^3$ dm^3 mol^{-1} for $[(DMSO)(CN)FePc(Cl)_{16}]^-$ and $K_4 = 5.7 \times 10^2$ dm^3 mol^{-1} for $[(DMSO)(CN)FePc]^-$} since these ligands pull electron density away from the metal. It would be expected that electron-donating substituents (such as the SC_4H_9) would result in the increase in stabilization of the Fe–DMSO bond by π back bonding. However, the electron-donating butylthio group in $[(DMSO)(CN)Fe^{II}Pc(SC_4H_9)_8]^-$ results in a similar K_4 value to the electron-withdrawing $[(DMSO)(CN)FePc(Cl)_{16}]^-$, again pointing to the weak electron-donating influence of the alkythio groups.

The rate constants for the formation of the $[(CN)_2Fe^{II}Pc(-2)(SC_4H_9)_8]^{2-}$ equations were determined by monitoring the absorption changes at 686 nm. The rate law for the dissociative mechanism is generally given by (eqn. 6)[13–22]

$$k_{obs} = k_{4f}[CN^-] + k_{4r} \qquad (6)$$

where k_{4f}, the rate constant for the forward reaction, is given by $k_1k_4/k_{-1}[L]$ (L = DMSO or DMF) and k_{4r} is the rate constant for the reverse reaction. From the least square analysis of the data presented in Fig. 7 (summarized in Table 2) the values of k_{4f} (from the slopes) were $(1.9 \pm 0.1) \times 10^{-2}$ dm^3 mol^{-1} s^{-1} in DMF and $(8.2 \pm 0.3) \times 10^{-2}$ dm^3 mol^{-1} s^{-1} in DMSO while k_{4r} (from the intercepts) were 2.5×10^{-5} s^{-1} in DMF and 5.5×10^{-5} s^{-1} in DMSO. From these values, the equilibrium constants could be estimated from the relationship, $K_4 = k_{4f}/k_{4r} = 7.6 \times 10^2$ dm^3 mol^{-1} in DMF and 1.5×10^3 dm^3 mol^{-1} in DMSO. These values are in good agreement (within experimental error) with the value of $(6.8 \pm 0.8) \times 10^2$ dm^3 mol^{-1} and $(1.3 \pm 0.2) \times 10^3$ dm^3 mol^{-1} determined directly from eqn. 1 for DMF and DMSO systems, respectively.

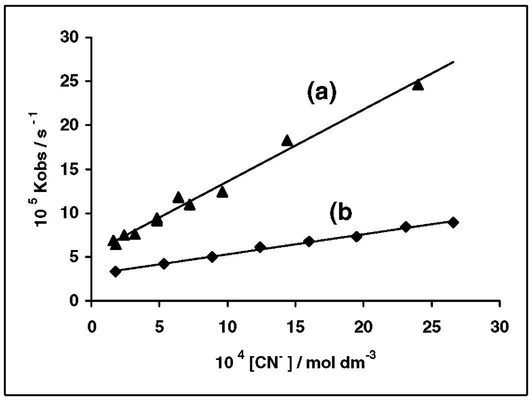

Fig. 7 The variation of observed rate constants with concentration changes for the formation of $[(CN)_2FePc(SC_4H_9)_8]^{2-}$ in (a) DMSO and (b) DMF.

It is apparent from Table 2 that the rate of coordination of the second cyanide, k_{4f}, to $[(DMSO)(CN)Fe^{II}Pc(-2)(SC_4H_9)_8]^-$ is greater than that for $[(DMF)(CN)Fe^{II}Pc(-2)(SC_4H_9)_8]^-$ by a factor of 4. This is of course due to the higher lability of the DMSO than the DMF ligand. However, the k_{4f} value for the coordination of cyanide to $[(DMSO)(CN)Fe^{II}Pc(-2)]^-$ or $(DMSO)(CO)Fe^{II}Pc(-2)$ is approximately three times greater than that for its coordination to $[(DMSO)(CN)Fe^{II}Pc(-2)(SC_4H_9)_8]^-$ but about ten times greater than that for the coordination to $[(DMF)(CN)Fe^{II}Pc(-2)(SC_4H_9)_8]^-$. The reason for the discrepancy may not be unconnected to the combined effects of the weak electron-donating influence of the eight peripheral butylthio-substituents and the stronger O–Fe σ-bond arising from DMF ligation. This is consistent with our discussion on electrochemistry concerning the small influence of the alkythio-substituents on the reduction potentials.

Conclusion

The presence of eight peripheral butylthio-substituents on FePc results in a striking decrease of the oxidation potential of this new complex, $FePc(SC_4H_9)_8$. This is a great advantage as this implies a low voltage window in any potential catalytic application of this complex. Already, this complex is being investigated for use as an electrochemical sensor in our laboratory.

The equilibrium and kinetic data of $FePc(SC_4H_9)_8$ for the binding with cyanide are comparable with those reported in literature. The formation of the dicyano species $[(CN)_2Fe^{II}Pc(-2)(SC_4H_9)_8]^{2-}$ is limited in DMF solution by the weak dissociation of the *trans* DMF from the central metal, iron. Although a direct comparison cannot be made between the rates of cyanide coordination by FePc complexes and the structurally similar iron porphyrin complexes because of differences in experimental conditions, especially with regard to solvent systems, it is worth noting that the rate constant for cyanide binding to iron(II) myoglobin (0.1 dm^{-3} mol^{-1} s^{-1})[53] is approximately the same as cyanide binding to the $[(DMSO)(CN)Fe^{II}Pc(-2)(SC_4H_9)_8]^-$. This suggests that this complex may offer substantial advantages over the similar analogues reported in the literature. We are extending this investigation to a wider selection of ligands.

Acknowledgements

We thank the National Research Foundation (NRF) of South Africa for supporting this work. K.O. is very grateful to the Andrew Mellon Foundation for a graduate scholarship.

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