Comparison of U.V. –Visible Spectra of Iron(ɪ)–Porphyrin– and Iron(ɪɪ)–Porphyrin (thiolato)-(thiocarbonyl) and -(carbene) Complexes. Relevance to Ferrous Cytochrome P450 Complexes

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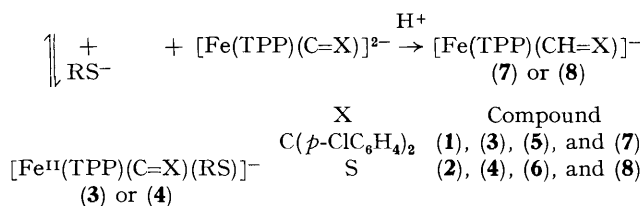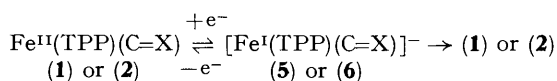
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Summary Addition of alkylthiolates to Fe^{II}(porphyrin)-(carbene or CS) complexes and the electrochemical one-electron reduction of these complexes has given, respectively, the Fe^{II}(porphyrin)(RS⁻)(carbene or CS) and

Fe^I(porphyrin)(carbene or CS) complexes which are stable enough to allow comparison of their u.v.–visible spectra.

Some peculiar spectral and chemical properties of cytochrome P450 have been related to the nature of its axial, endogenous ligand, which seems to be a cysteinate.[1] For instance, the unusual hyperporphyrin spectrum of the cytochrome P450–Fe^{II}–CO complex has been attributed[2] to a charge-transfer transition of the thiolate sulphur electrons to the porphyrin π^*-orbital, coupled with the normal porphyrin $\pi \rightarrow \pi^*$ transition. Similar spectra have been obtained from model compounds prepared by addition of thiolates to Fe^{II}(porphyrin)(CO) complexes.[3] The same method has been successful in obtaining models of nitrosyl–cytochrome P450,[4] but has failed, so far, to give models for cytochrome P450–Fe^{II}–RNO[5] or carbene[6]† complexes because of irreversible fast reactions between the thiolates and bound RNO or carbenes, like CCl$_2$,[7] even at low temperatures. Since (Fe^{I}RS·) is a likely mesomeric form of (Fe^{II}RS$^-$) it is of interest to compare ferrous cytochrome P450 complexes or their models with the corresponding Fe^I(porphyrin) complexes. However, presumably owing to the instability of the latter complexes and their poor affinity for ligands,[8] only one comparison of [Fe^{II}(porphyrin)(RS)(L)]$^-$ and [Fe^I(porphyrin)(L)]$^-$ complexes has been reported in the literature with L = CO).[9]

$$\text{Fe}^{II}(\text{TPP})(\text{C=X}) \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} [\text{Fe}^I(\text{TPP})(\text{C=X})]^- \rightarrow \textbf{(1)} \text{ or } \textbf{(2)}$$
$$\textbf{(1)} \text{ or } \textbf{(2)} \quad\quad \textbf{(5)} \text{ or } \textbf{(6)}$$

$$\begin{array}{c} \\ + \\ \text{RS}^- \end{array} + [\text{Fe(TPP)(C=X)}]^{2-} \xrightarrow{\text{H}^+} [\text{Fe(TPP)(CH=X)}]^- \quad \textbf{(7)} \text{ or } \textbf{(8)}$$

	X	Compound
[Fe^{II}(TPP)(C=X)(RS)]$^-$	C(p-ClC$_6$H$_4$)$_2$	**(1)**, **(3)**, **(5)**, and **(7)**
(3) or **(4)**	S	**(2)**, **(4)**, **(6)**, and **(8)**

Scheme

We report herein that the addition of alkylthiolates to porphyrin–iron^{II}–(carbene or CS) complexes which contain a strong iron–carbon bond and the electrochemical one-electron reduction of these complexes gave, respectively, the [Fe^{II}(porphyrin)(carbene or CS)(RS)]$^-$ and [Fe^I(porphyrin)(carbene or CS)]$^-$ complexes. These are stable enough to allow comparison of their u.v.–visible spectra.

Addition of Bu^{n}SNa (3—4 equiv.), dissolved in dimethylacetamide (DMA) (70 μl) in the presence of a stoicheiometric amount of a 15-crown-5 ether, to Fe[TPP][C=C-(C$_6$H$_4$Cl-p)$_2$] **(1)**[10]‡ or Fe(TPP)(CS) **(2)**[11] ($ca.$ 10^{-5} M in dry toluene (3 ml) at −75 °C, immediately gave the new entities **(3)** and **(4)**, characterised by their hyperporphyrin spectra (Figure), with Soret peaks, respectively, at λ 385 and 461 nm, and λ 380 and 453 nm. This formation does not
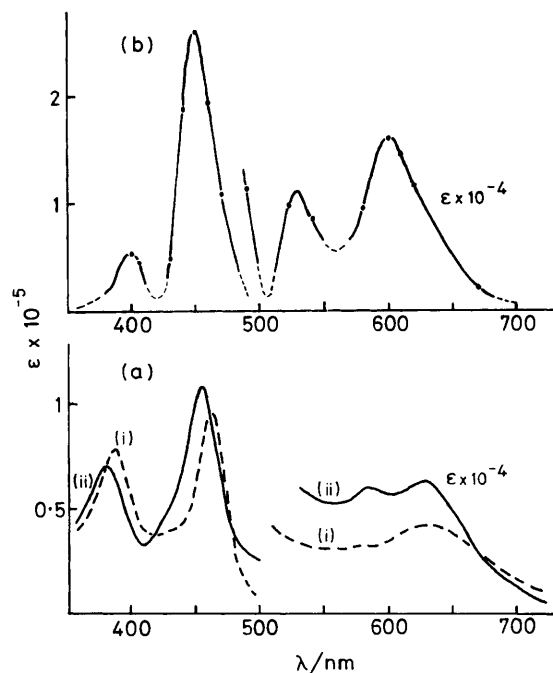

Figure. (a) U.v.–visible spectra of complexes **(3)** (i) and **(4)** (ii) obtained as described in the text. Further addition of DMA gave a red-shift of the peaks and an increase of the intensity of the λ 380 nm band relative to that of the λ 450 nm band. (b) U.v.–visible spectrum of the complex **(6)**, calculated from the spectra obtained during the electrochemical reduction of complex **(2)** as described in the text.

imply any irreversible modification of the Fe$\leftarrow$C=X bond [X = C(C$_6$H$_4$Cl-p)$_2$ or S] since protonation of Bu^{n}S$^-$ by the addition of AcOH (10 equiv.) to the solution at −75 °C gave compounds which produced spectra typical of the hexaco-ordinated Fe^{II}(TPP)(CX)(Bu^{n}SH) complexes. Moreover, the starting Fe(TPP)(CX) complexes were quantitatively recovered, after the solution was warmed to room temperature, by thin-layer chromatography. Since the new compounds were formed immediately and reversibly at −75 °C, they are likely to have derived from the binding of Bu^{n}S$^-$ $trans$ to the CX ligand. The corresponding complexes **(3)** and **(4)** were quantitatively formed at −75 °C and were stable for at least 1 h at this temperature. Complexes **(1)** and **(2)** were electrochemically reduced in dimethylformamide at 25 °C in a one-electron reversible step at −1·28 and −1·25 V ($vs.$ standard calomel electrode), respectively. The corresponding products **(5)** and **(6)** were stable within the time scale ($ca.$ 1 s) of low-sweep cyclic voltammetry.[12] However, for longer time ranges such as those of spectroelectrochemistry in thin-layer cells (1—10 mm), compounds **(5)** and **(6)** were unstable. Complex **(5)** underwent a disproportionation reaction to give compound **(1)** and [Fe(TPP){C=C(Ar)$_2$}]$^{2-}$ which was itself rapidly protonated to give, finally, the σ-vinyl[Fe^{II}(TPP)(CH=CAr$_2$)]$^-$ complex **(7)**.[12] Though the disproportionation requires energy (by 0·3 eV), the overall

† Partial and transient formation of the [Fe(porphyrin)(1,3-benzodioxole-2-carbene)(Bu^{n}S)]$^-$ complex has been detected by visible spectroscopy (D. Mansuy, J. P. Battioni, J. C. Chottard, and V. Ullrich, $J. Am. Chem. Soc.$, 1979, **101**, 3971).

‡ TPP is the dianion of mesotetraphenylporphyrin.

reaction is assisted by the following protonation which results in a lifetime of a few minutes for the Fe^I–carbene complex. Similar results were obtained with compound (2); the lifetime of compound (6) was, however, somewhat longer than that of (5). During the reduction of (2) in the spectro-electrochemical cell, compounds (6), (2), and (8) are simultaneously present in relative proportions which depend upon the electrolysis time. It was, however, possible to extract the spectrum of compound (6) from the overall spectral pattern, taking into account the known spectra of compounds (2)[11] and (8),[12] and also to evaluate the rate constant for decomposition of (6). The spectrum of compound (5) appears to be of the same type as that of (6), although more difficult to determine because of the faster decomposition of compound (5).

Complex (3) is the first† reported stable (at -75 °C) carbene complex of an iron(II)-porphyrin with a thiolate group in the *trans*-position to the carbene ligand. Along with complex (4) and the previously reported [Fe(porphyrin)-(RS)(CO or NO)]⁻ complexes,[3,4] it exhibits a hyperporphyrin spectrum. The position of its red-shifted Soret peak is similar to that reported for cytochrome P450–Fe^{II}–carbene complexes[6] (*ca.* 460 nm) which confirms that the

endogeneous cysteinate axial ligand is present in these complexes.

Although the spectrum of compound (6) has a less pronounced hyperporphyrin character than those of compounds (3) and (4), they all display two common, distinctive features; (i) a red-shifted Soret peak (λ 450—460 nm) and (ii) a band in the λ 600—650 nm region. In the same manner, the complex obtained upon CO addition to $[Fe^I(TPP)]^-$ was reported to display a peak at λ 455 nm,[9] as does $[Fe^{II}(TPP)(CO)(MeS)]^-$ (λ *ca.* 450 nm), though the spectra of these two complexes were different apart from the unusually long wavelength position of the Soret peak. The similarity of the spectra of the carbene (or thio-carbonyl) complexes of iron(I)- and iron(II)-thiolato-porphyrins suggests that these complexes have similar electronic structures and, therefore, that there is a significant contribution of the $[Fe^IRS^{\bullet}]$ mesomeric form to the electronic structure of some ferrous cytochrome P450 complexes and their synthetic models.

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