A Mononuclear High-spin Iron(III) Phthalocyanine

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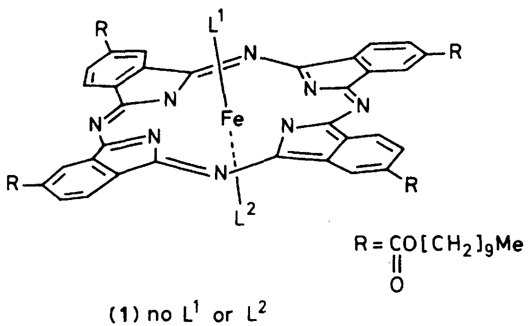
Magnetic susceptibility, e.s.r., u.v. absorption, and m.c.d. spectroscopy have revealed that 4,4′,4″,4‴-tetradecyloxycarbonylphthalocyaninatoiron (**1**), its monoimidazole adduct (**2**), and its di-imidazole adduct (**3**) are high-spin iron(III), low-spin iron(III), and low-spin iron(II) complexes, respectively.

It is generally accepted that the oxidation state of iron in iron porphyrins, both synthesized[1] and extracted from hemoproteins,[2] is +III, but that in iron phthalocyanines is +II,[3] notwithstanding their structural similarity. Accordingly, iron(III) phthalocyanines have rarely been identified, having been obtained in tetrasulphonated low-spin form[4] and in binuclear μ-oxo-species.[5,6] We present here the first example of a high-spin iron(III) phthalocyanine, *i.e.* (**1**), which undergoes a high-spin to low-spin transition and reduction from iron(III) to iron(II) on ligation of one and two imidazole molecules, respectively. Complex (**1**) was obtained from 4,4′,4″,4‴-tetracarboxy-chlorinated iron phthalocyanine[7] by esterification with decyl alcohol and subsequent purification by silica gel chromatography.† It had an effective magnetic moment



$R = \underset{\underset{O}{\|}}{C}O[CH_2]_9Me$

(**1**) no L^1 or L^2

(**2**) L^1 = imidazole, no L^2

(**3**) L^1 = L^2 = imidazole

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† Although (**1**) is a high-spin iron(III) complex no counter-anion (in our case halide) was detected in the combustion analysis. It is possible that the atomic charge density at iron is reduced markedly.[8] Calculations indicate a charge density of +1.33 for iron(II), though a figure is not available for iron(III). In connection with this problem, we found that the interaction between iron(III) in porphyrins and halide counter-anion depends on the porphyrin skeleton, decreasing markedly in the order, *meso*-tetraphenylporphyrin > tetrabenzoporphyrin > (**1**) (to be published).

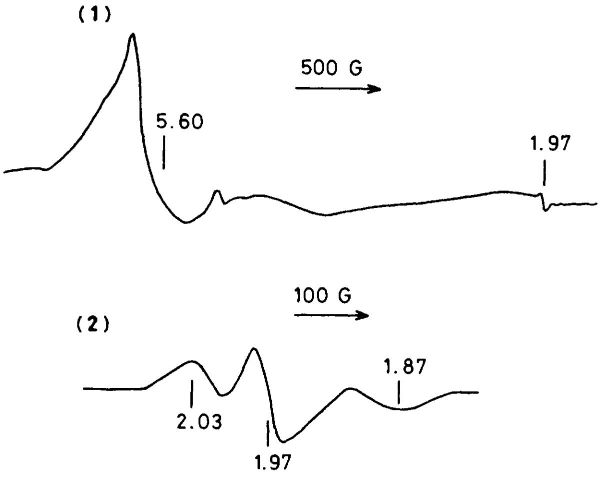

Figure 1. E.s.r. spectra of (**1**) and (**2**) in dichloromethane at 10 K, showing *g*-values. [(**1**)] = [(**2**)] = *ca.* 1 × 10^{-2} M.

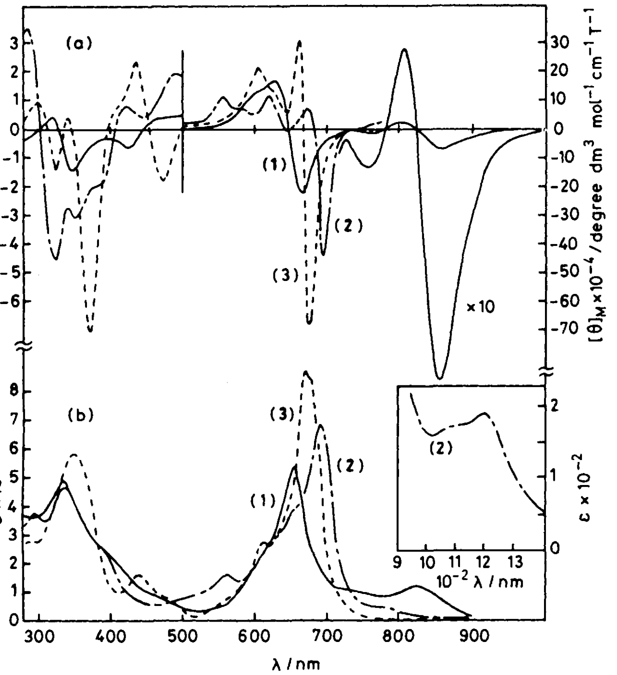

Figure 2. (a) Magnetic circular dichroism and (b) absorption spectra of (**1**), (**2**), and (**3**) in dichloromethane at *ca.* 20 °C. [(**1**)] = [(**2**)] = [(**3**)] = 2.65 × 10^{-5} M; magnetic field 1.1 T; path length of cell 10 mm.

(μ_{eff}), determined by the use of Evans method,[9] of 4.4 and 5.0 μ_B in CH_2Cl_2 and $CHCl_3$ at 35 °C, respectively. Along with its characteristic e.s.r. spectrum[10] (Figure 1), these values indicate that (**1**) is a high-spin iron(III) complex.

When imidazole was added to solutions of (**1**),[11] the formation of complexes (**2**) and (**3**) was confirmed from the u.v. spectral changes. Under the same conditions as for (**1**), (**2**) has a μ_{eff} value of 2.28 μ_B and the e.s.r. spectrum shown in Figure 1; these are typical of low-spin iron(III) porphyrin derivatives.[2,10] In contrast, complex (**3**) gave no e.s.r. signal.

Figure 2 shows the u.v. absorption and m.c.d. spectra of (**1**), (**2**), and (**3**). Although, it is not always correct to judge the oxidation- and spin-states only from u.v. absorption and m.c.d. spectra, these spectra can be rationalized as follows. Complex (**1**) shows near-i.r. bands at 825 and *ca.* 740 nm. If we consider the fact that $a_{1u}(\pi)$, $a_{2u}(\pi)$ to $e_g(d\pi)$ charge-transfer (CT) transitions in high-spin iron(III) porphyrin derivatives appear in the 800—1000 nm region,[12–14] and compare the energy of the $a_{1u}(\pi)$ orbital in porphyrins, tetrabenzoporphyrins, and phthalocyanines,[15] the 825 nm band can be ascribed to the $a_{1u}(\pi)$ to $e_g(d\pi)$ CT transition. Further, its m.c.d. pattern in the 700—1000 nm region (*i.e.* − to + from the lower-energy side for the 825 nm absorption peak and a negative trough corresponding to the band at 740 nm) is that which has been observed commonly among high-spin iron(III) porphyrin species.[13,14] Complex (**2**) has no absorption peak in the 800—1000 nm region, but shows peaks at 1085 (ε 170) and 1195 (190) nm. This may correspond to a CT transition from phthalocyanine to iron by analogy with low-spin iron(III) porphyrins.[12,13] Complex (**3**) shows a new band at 440 nm, absent from the spectra of (**1**) and (**2**), which can be assigned to CT from iron to imidazole expected in low-spin iron(II) phthalocyanines[16,17] and porphyrins.[18] Also, the m.c.d. spectrum is quite similar in shape to that of the diamagnetic bispyridine phthalocyanine.[19]

From these observations, we deduce that (**1**), (**2**), and (**3**) are high-spin iron(III), low-spin iron(III), and low-spin iron(II) complexes, respectively.

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References

1 M. Gouterman, in 'The Porphyrins,' ed. D. Dolphin, Academic Press, New York, London, 1979, vol. 3, p. 1.
2 E. Antonini and M. Brunori, 'Hemoglobin and Myoglobin in their Reactions with Ligands,' North-Holland, Amsterdam, 1971.
3 A. B. P. Lever, *Adv. Inorg. Chem. Radiochem.*, 1965, **7**, 27.
4 J. H. Weber and D. H. Busch, *Inorg. Chem.*, 1965, **4**, 469.
5 C. Ercolani and G. Rossi, *Inorg. Chim. Acta*, 1980, **44**, L215.
6 A. B. P. Lever, S. Licoccia, and B. S. Ramaswamy, *Inorg. Chim. Acta*, 1982, **64**, L87.
7 H. Shirai, A. Maruyama, K. Kobayashi, and N. Hojo, *Makromol. Chem.*, 1980, **181**, 575.
8 N. H. Sabelli and C. A. Melendres, *J. Phys. Chem.*, 1982, **86**, 4342.
9 D. F. Evans, *J. Chem. Soc.*, 1959, 2003.
10 G. Palmer, in ref. 1, vol. 4, p. 313.
11 N. Kobayashi, K. Funayama, M. Koshiyama, T. Osa, H. Shirai, and K. Hanahusa, *J. Chem. Soc., Chem. Commun.*, 1983, following communication.
12 D. W. Smith and R. J. P. Williams, *Struct. Bonding* (*Berlin*), 1970, **7**, 1.
13 T. Yamamoto, T. Nozawa, N. Kobayashi, and M. Hatano, *Bull. Chem. Soc. Jpn.*, 1982, **55**, 3059, and references 13—19 therein.
14 N. Kobayashi, M. Koshiyama, and T. Osa, *Chem. Lett.*, 1983, 163.
15 L. K. Lee, N. H. Sabelli, and P. R. LeBreton, *J. Chem. Phys.*, 1982, **86**, 3926, and references cited therein.
16 A. M. Schaffer, M. Gouterman, and E. R. Davidson, *Theor. Chim. Acta* (*Berlin*), 1973, **30**, 9.
17 B. W. Dale, *Trans. Faraday Soc.*, 1969, **65**, 331.
18 H. Kobayashi and Y. Yanagawa, *Bull. Chem. Soc. Jpn.*, 1972, **45**, 450.
19 M. J. Stillman and A. J. Thomson, *J. Chem. Soc., Faraday Trans.* 2, 1974, **70**, 790.