Iron(III) Phthalocyanines: Oxidation and Spin States of Iron in Iron Phthalocyanines with Carboxyl Groups

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Mössbauer and e.s.r. spectroscopy have revealed that 2,3,9,10,16,17,23,24-octacarboxy- (1), 2,9,16,23-tetracarboxy- (2), and 2,9 (or 10)- and 2,16 (or 17)-bis(3′,4′-dicarboxybenzoyl)-phthalocyaninatoiron (3) are mixtures of high-spin iron(III) and low-spin iron(III) complexes and that intermediate-spin species may be present in (2) in the solid state. However, the low-spin component disappears when the phthalocyanines are immobilized on poly(styrene). The properties of these compounds in solution are described on the basis of e.s.r., m.c.d., and u.v. spectroscopy.

The oxidation state of iron in monomeric iron phthalocyanines is generally +II.[1] Quite recently, however, the first example of a mononuclear high-spin iron(III) phthalocyanine, *i.e.* 2,9,16,23-tetradecyloxycarbonylphthalocyaninatoiron was reported.[2]

In this work we have examined the oxidation and spin state of iron in 2,9,16,23-tetracarboxyphthalocyaninatoiron (2), and the related compounds (1) and (3). These compounds have been used for instance to initiate a polymerization reaction,[3] as catalysts for the decomposition of hydrogen peroxide[4,5] and oxidation of guaiacol,[6] and as a labelling reagent in immunoassay.[7] Although not well characterized spectroscopically, the oxidation state of iron in these compounds has been tentatively assigned as +III in order to explain, for example, the reaction mechanisms.

Experimental

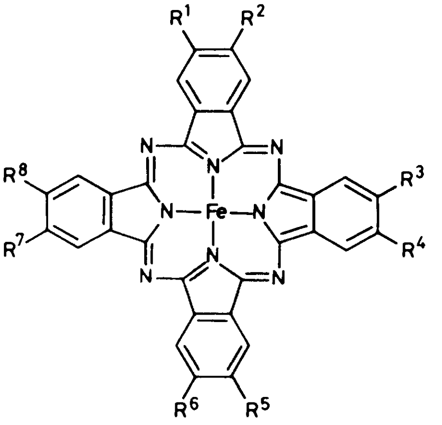
Materials.—Compounds (1)—(3) and (5) are those employed in previous papers.[4,5,8] Compound (4) was prepared from the 8 COCl derivative of (1) and poly(styrene) by the method similar to that for (5),[8] *i.e.* by a Friedel–Crafts reaction. The $x:y$ ratio in compound (4) was calculated from the average iron and nitrogen elemental analyses (0.70 and 1.45%, respectively). Compound (4) is soluble in benzene, tetrahydrofuran, and chloroform, while (5) is practically insoluble in most usual solvents, although slightly soluble in dimethyl sulphoxide (dmso) or in hot *N,N*-dimethylformamide (dmf).

Measurements.—E.s.r. spectra were recorded on a Varian E0112 *X*-band spectrometer equipped with tapered ring-shim tips and with an Oxford ESR 9 cryostat. The microwave frequencies were monitored by a Takedariken TR-5501 frequency counter with a TR-5023 frequency converter. Mössbauer spectra were obtained with a scanned velocity spectrometer operating in the time mode. The velocity scale was calibrated absolutely from an independent Mössbauer run using a thin metallic iron absorber and the centre of symmetry of the spectrum was taken as zero velocity. The velocity was determined to an accuracy of ±0.01 mm s^{-1}. The data were fit by a least-squares approximation assuming Lorenzian line shapes. Absorption spectra were measured with a JASCO UVIDEC-1 spectrophotometer. Magnetic circular dichroism (m.c.d.) spectra were obtained by use of a JASCO J-500 spectrodichrometer equipped with a data processor and an electromagnet which produced magnetic fields up to 1.17 T. Spectra of electrolysed solutions were obtained using an optically transparent thin-layer electrode which contained a platinum minigrid as working electrode, in conjunction with a potentiostat.[9]

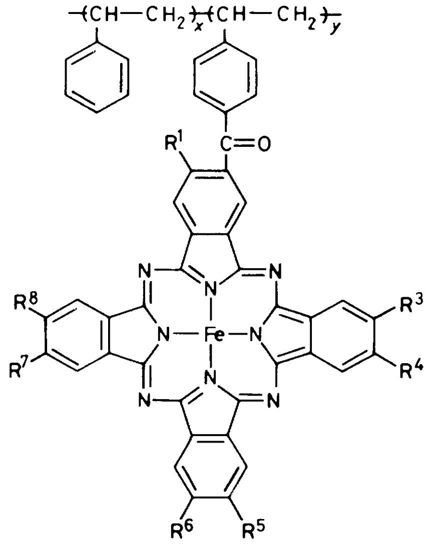
Results and Discussion

Spectral Behaviour in Solid State.—Figure 1 shows e.s.r. spectra of compounds (1)—(5) in the solid state at ambient temperature and at 7.5 K. Complexes (1)—(3) show very broad signals at around $g = 4$ and 2, while (4) and (5) reveal sharp signals at around $g = 2$ at room temperature. Thus, the line shapes and the g values of these compounds are different from those of ordinary high-spin (g *ca.* 6 and 2)[10] or low-spin (g *ca.* 1.7—2.8)[10,11] iron(III) complexes hitherto reported. Upon lowering the temperature the spectra change dramatically (especially below *ca.* 20 K) and at 7.5 K the curves shown as solid lines are obtained. Compounds (1) and (2) show both high-spin and low-spin iron(III) signals at around $g = 5.4$ and 2. In the case of (3), the spectral pattern is complicated with ill defined signals at g *ca.* 5.4, 4, and 2. Compounds (4) and (5), on the other hand, exhibit well known high-spin iron(III) spectra. In addition, for (5) another signal is observed at $g = 4.25$. Although the spectrum of compound (4) is a little peculiar in the context that the intensity of the signal at g *ca.* 5.7 is smaller than that at g *ca.* 2, the latter signal becomes relatively weaker with decreasing temperature. [For (1)—(5), signals at g *ca.* 5—6 can be detected at temperatures lower than *ca.* 15 K, and their intensities increase with decreasing temperature.] Thus, from the above spectral behaviour, especially at 7.5 K, it is suggested that (1)—(3) are mixtures of high-spin and low-spin iron(III) complexes and that the decrease in phthalocyanine–phthalocyanine interaction by dilution with poly(styrene) extinguishes the low-spin component. The signal at $g = 4.25$ of compound (5) may be from an intermediate-spin ($S = \frac{3}{2}$) component.[12]

Mössbauer spectra of compounds (1)—(3) at 77 K are shown in Figure 2. They are resolved into several components. Although it may not always be correct to analyse such spectra by use of previous knowledge on iron porphyrins, based on a report[13] which classified natural and synthetic iron porphyrins according to the magnitude of the isomer shift, δ/mm s^{-1}, and of the quadrupole splitting, ΔE_Q/mm s^{-1}, then the component designated as I appears to be that of low-spin iron(III); however, the possibility of intermediate-spin iron(II) is not ruled out completely. Likewise, the component II seems



(1) $R^{all} = CO_2H$
(2) $R^{odd} = CO_2H$, $R^{even} = H$
(3a) $R^1 = R^3 = OCC_6H_3(CO_2H)_2$-3,4
(3b) $R^1 = R^4 = OCC_6H_3(CO_2H)_2$-3,4
(3c) $R^1 = R^5 = OCC_6H_3(CO_2H)_2$-3,4
(3d) $R^1 = R^6 = OCC_6H_3(CO_2H)_2$-3,4
$R^{other} = H$



(4) $R^{all} = CO_2H$, $x : y = 98.51 : 1.49$
(5) $R^{odd} = H$, $R^{even} = CO_2H$, $x : y = 95.94 : 4.06$

most likely to be high-spin iron(III), albeit there are some possibilities of intermediate- or low-spin iron(II). Similarly, component III may be attributable to intermediate-spin iron(III). Therefore, (1) and (3) are mixtures of high- and low-spin iron(III) complexes, and (2) of high-, intermediate-, and low-spin iron(III) complexes, respectively. These results are essentially in accord with those obtained from e.s.r. (Figure 1).

The Table summarizes the Mössbauer parameters at various temperatures. Owing to instrumental limitations, the data were collected only above 77 K. As shown, the spectra at room temperature (*ca.* 293 K) and 195 K do not differ significantly from those at 77 K.

Spectral Behaviour in Solution.—Compounds (1)—(3) are soluble in water at alkaline pH. When a solution of pH 9.0 (0.1 mol dm^{-3} carbonate buffer) containing 0.1 mmol dm^{-3} of compound (1), (2), or (3) was cooled to 7.5 K it showed e.s.r. signals as clear and sharp as those revealed by (4) at 7.5 K (Figure 1) at $g = 5.55$, 5.47, and 5.78, respectively (as for the solid samples, e.s.r. signals at $g = 5$—6 in water are discernible only at temperatures lower than *ca.* 15 K). They also produce small poorly defined signals in the region of $g = 2.35$—2.11. From the spectral changes below 30 K, however, the $g_{\parallel}$ signals of the high-spin iron(III) component of compounds (2) and (3) are judged to be at $g_{\parallel} = 2.16$ and 2.22, respectively. No signals are found in other regions. Thus, compounds (1)—(3) appear to exist as a mixture of high- and low-spin iron(III) in solution.

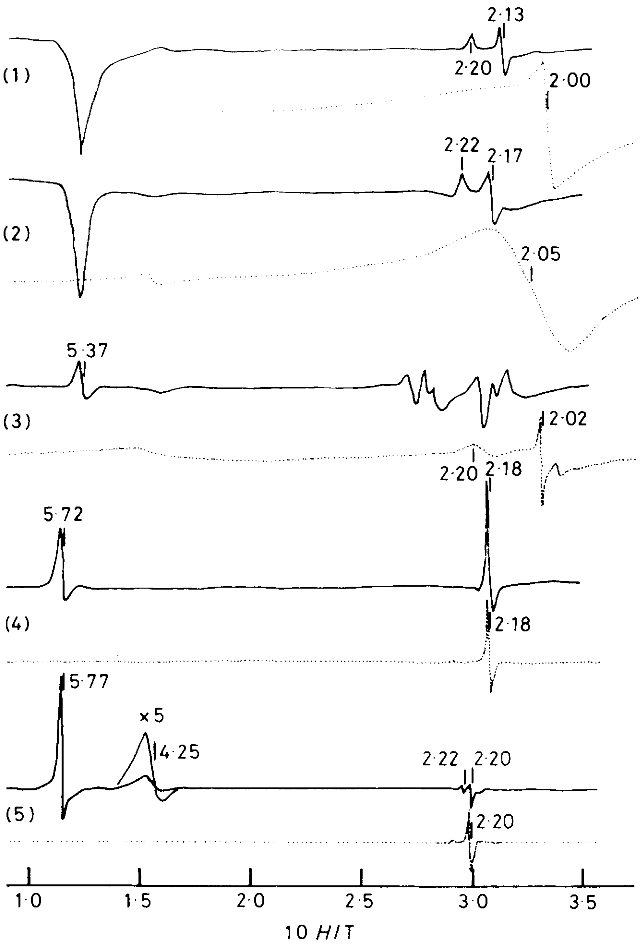


Figure 1. E.s.r. spectra of compounds (1)—(5) in the solid state at ambient temperature (dotted line) or 7.5 K (solid line), showing the main g values

U.v. and m.c.d. spectra of these complexes are displayed in Figure 3. These spectra can be interpreted with the aid of knowledge of the spectra of typical high-spin iron(III)-, low-spin iron(III)-, intermediate-spin iron(II)-, and low-spin iron(II)-phthalocyanines.[2,14] From the lack of the band at around 440 nm which has been considered to be the charge-transfer (c.t.) transition from iron(II) to axial ligands,[15] at least the possibility of a low-spin iron(II) species is eliminated. In addition, from the shape of the m.c.d. spectra in the Soret region, intermediate-spin iron(II) species appear to be unlikely. Although it is difficult to rule out completely high-spin iron(II) complexes and some aggregated forms, the spectra can be rationalized as mixtures of high- and low-spin iron(III)

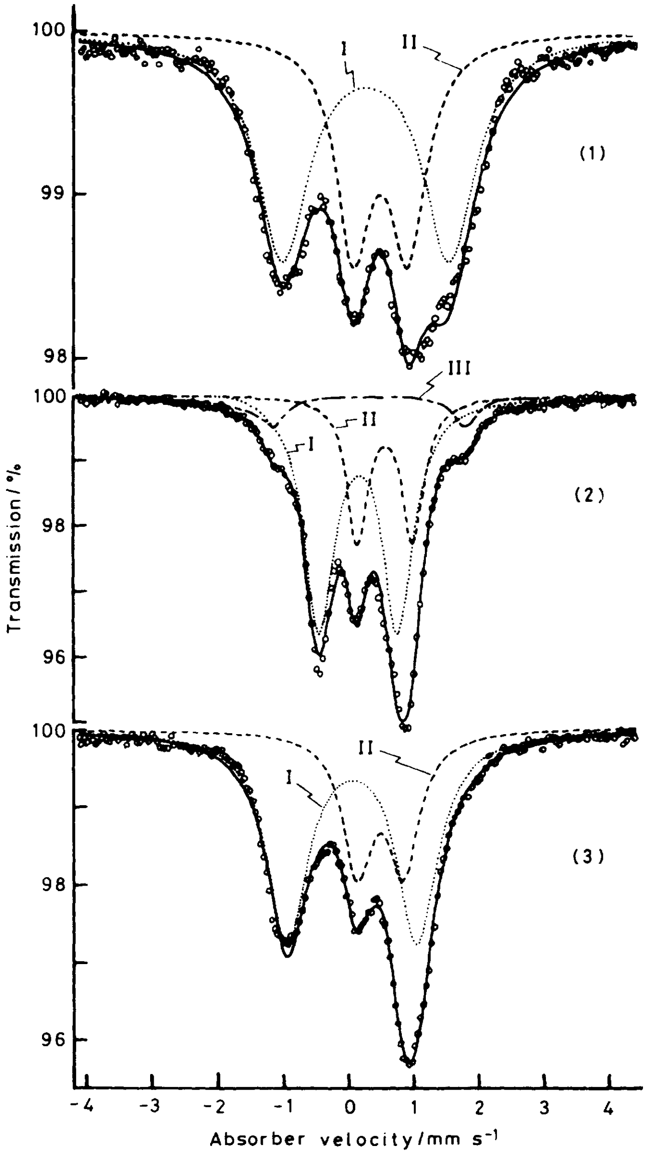


Figure 2. Mössbauer spectra of compounds (1)–(3) at 77 K. For components I—III see text

Table. Mössbauer parameters for iron(III) phthalocyanine complexes

Complex	T/K	ΔE_Q	δ [a]	Γ	Assignment [b]
		mm s⁻¹			
(1)	293	2.498	0.137	0.450	I
		0.793	0.352	0.308	II
	195	2.564	0.198	0.474	I
		0.815	0.421	0.336	II
	77	2.554	0.238	0.483	I
		0.834	0.470	0.339	II
(2)	195	1.225	0.126	0.349	I
		0.825	0.521	0.206	II
		2.906	0.251	0.249	III
	77	1.236	0.170	0.326	I
		0.816	0.557	0.202	II
		2.923	0.297	0.233	III
(3)	195	2.026	0.017	0.351	I
		0.729	0.429	0.291	II
	77	2.008	0.046	0.376	I
		0.716	0.478	0.287	II

[a] The isomer shift is relative to metallic iron. [b] One possibility is as follows: I, Fe^{III} ($S = \frac{1}{2}$) > Fe^{II} ($S = 1$); II, Fe^{III} ($S = \frac{5}{2}$) > Fe^{II} ($S = 0$), Fe^{II} ($S = 1$); III, Fe^{III} ($S = \frac{3}{2}$) > Fe^{III} ($S = \frac{1}{2}$).

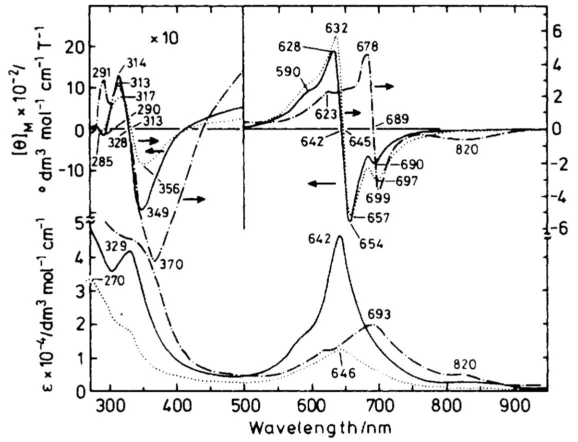


Figure 3. M.c.d. (top) and u.v. (bottom) spectra of compounds (1) (— · —), (2) (——), and (3) (· · ·) in water at pH 9.0 (0.1 mol dm⁻³ carbonate buffer); $[\theta]_M$ = molar ellipticity

complexes as follows. (*i*) Compound (1) shows an absorption peak at 820 nm and a corresponding negative trough which are often observed for high-spin iron(III) porphyrins.[2,16] Compounds (2) and (3) do not have any corresponding absorption peak in the 800—1 000 nm region. However, this does not necessarily mean that the complex is not in a high-spin iron(III) state, since this band [c.t. from $a_{1u}(\pi)$, $a_{2u}(\pi)$ to $e_g(d_\pi)$] [16,17] has been shown to diminish with increasing dissociation of axial ligands from high-spin iron(III).[18] (*ii*) Although the m.c.d. spectra of iron phthalocyanine differ greatly upon changing the oxidation and spin states of iron,[2,14] the shape of the m.c.d. spectra of compounds (1)—(3) in the u.v.-visible region is quite similar to that of typical high-spin iron(III) phthalocyanine, for example, showing dispersion-type spectra of approximately equal intensity and of opposite signs at the position of the *Q* absorption peaks. Thus, the m.c.d. troughs at 690 and 697 nm may be attributable to the small amount of low-spin iron(III) of (2) and (3), respectively.

In Figure 4 is shown the spectrum of the first electrochemical reduction product of compound (2) in pH 9.0 buffer [applied potential, −0.45 V *vs.* saturated calomel electrode (s.c.e.)]. From the presence of a peak at around 440 nm, the spectrum is that of low-spin iron(II) phthalocyanine. Similarly, aqueous solutions of (1) and (3) also produce spectra of low-spin iron(II) phthalocyanines when electrolysed at the same potential (not shown). As mentioned above, solutions of compounds (1)—(3) at pH 9 produce e.s.r. signals of iron(III) complexes in the absence of an applied potential. Hence the spectra of their first electrochemical reduction products are those of iron(II) phthalocyanines, indicating that an electron is transferred to iron and not to the phthalocyanine skeleton; this provides further support for the spectra in Figure 3 being those of iron(III) species, notwithstanding their complexity. Thus, the oxidation state of iron in compounds (1)—(3) in water is considered to be +III.

Figure 4 includes also the spectrum of compound (4) in dichloromethane. Although this compound gave an e.s.r. signal in the solid state (Figure 1) typical of high-spin iron(III),

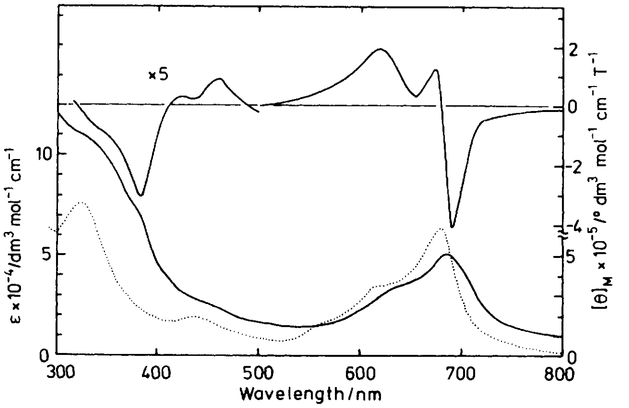


Figure 4. M.c.d. (top) and u.v. (bottom) spectra of compound (4) in dichloromethane (solid line) and (2) in water at pH 9.0 under an applied potential of -0.45 V *vs.* s.c.e. (dotted line). $[(4)] = 1.60 \times 10^{-5}$ mol dm^{-3} on the basis of the phthalocyanine unit

both the m.c.d. and u.v. spectra are those of low-spin iron(III) complexes.

From the results in Figures 1—3, compounds (1)—(3) are found to be iron(III) complexes both in the solid state and when dissolved in solution. As shown by using (4) and (5), compounds (1)—(3) appear predominantly to contain high-spin iron(III) when axial ligands are absent or the phthalocyanine–phthalocyanine interaction is weakened. However, the presence of iron(III) species was always recognized in the spectra of compounds (1)—(3). The reason for the co-existence of high- and low-spin iron(III) species may be the facile transition from high-spin to low-spin iron(III) as observed in related compounds. For example, the octaester derivative,[19] (6), of (1) exhibits an effective magnetic moment which is highly sensitive even to solvents of low donor ability, as also with the tetradecyl ester, (7), of compound (2).[2] Compounds (6) and (7) show m.c.d. and u.v. spectra which are exemplary for high-spin iron(III) phthalocyanines in solvents such as dichloromethane, chloroform, benzene, and monochlorobenzene, but produce spectra of low-spin iron(III) phthalocyanines in 1,2-dichloroethane, chloroform–methanol (24 : 1, v/v), and acetonitrile. Also, upon addition of a small amount of tetra-alkylammonium chloride or bromide (electrolytes) to chloroform or benzene solutions containing (6) or (7) the spectra are transformed from those of high-spin iron(III) to those of low-spin iron(III) phthalocyanines. Hence, it is quite probable that the originally high-spin iron(III) complexes, (1) and (2), change in part to low-spin iron(III) complexes, for example, in the purification process which is carried out in water containing species capable of co-ordination, *e.g.* OH^- and CO_2^-.[3-8] [That (1) and (2) are originally high-spin iron(III) complexes in the absence of axial ligands is revealed by the e.s.r. spectra of (4) and (5) at 7.5 K (Figure 1).] An easy alternation of spin state upon change of environment is suggested also for compound (4). The iron in (4) is mainly in the trivalent high-spin state in the solid (Figure 1), but in the trivalent low-spin state when dissolved in dichloromethane (Figure 4). In this way, a facile transition of spin state appears to be a characteristic of high-spin iron(III) phthalocyanines, and may be relevant to the failure to detect axial ligands (in our case, halide) in the combustion analyses [no counter anion has been detected for compounds (1)—(7)[2-8,19]]. If axial ligands are absent, the co-ordination of ligand(s) to iron would become easier, thereby facilitating the spin-state change.

In conclusion, compounds (1)—(3) are found to be rare examples of monomeric iron(III) phthalocyanines. As shown using compounds (4) and (5), (1)—(3) appear predominantly to contain high-spin iron(III). However, they are generally obtained as mixtures of at least high- and low-spin iron(III) complexes, since the tendency to become low-spin iron(III) is extraordinarily marked.

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