Origin of the Electron Spin Resonance Signal in Diamagnetic Phthalocyanins

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Detailed analysis of the e.s.r. signal observed in some diamagnetic phthalocyanins and metal-free tetraphenylporphyrin suggests that the cause is various charge-transfer interactions between phthalocyanin or porphyrin cations and dioxygen anions stabilised by the surface of the diamagnetic host.

INVESTIGATIONS into the origin of the unpaired electron in metal-free phthalocyanins have had a long and chequered history. Electron spin resonance signals were first detected by Ingram and Bennett.[1] Since then, there have been many proposals as to their source. These included suggestions that they are the result of broken π bonds,[2] diradical structures,[3] defect structures,[4] and electronically active centres.[5,6] Others have studied the phenomenon, but are noticeably vague in their explanation.[7] Oxygen has been implicated in several of the studies, but firm evidence for its role is lacking.[4-7] Assour and Harrison,[5] using e.s.r. techniques, made a quantitative assessment of the surface concentration of radicals and found that it was *ca.* 10^{14} sites cm^{-2}. They observed that the number of radicals remained essentially constant *in vacuo*, increased with oxygen treatment, and decreased with exposure to hydrogen.

The purpose of this paper is to reconsider the evidence for the e.s.r. signal, to define the conditions under which it is formed, and to report on further experiments which we have carried out with a view to solving the problem. In so doing we have studied the interaction of metal-free and various diamagnetic metallated phthalocyanins and also the corresponding tetraphenylphorphyrins with a range of electron acceptors. The e.s.r. spectrum of the phthalocyanin cation is also discussed in some detail.

RESULTS

E.S.R. Spectra.—Powders with oxygen. The e.s.r. spectra of powdered samples of metal-free and zinc, nickel, pallad-

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ium, and platinum phthalocyanins and of metal-free tetraphenylporphyrin all showed strong signals (at 77 K and at room temperature) which in the case of the metal-free and zinc compounds consisted of a single line with widths *ca.* 4 G.* The metal-free and zinc phthalocyanins showed no apparent asymmetry, but the nickel, palladium, and platinum phthalocyanins showed marked asymmetry. Measurements at *Q*-band frequencies showed evidence of asymmetry in the metal-free and zinc phthalocyanins, and clear rhombic symmetry for the nickel, palladium, and platinum phthalocyanins (Figures 1 and 2). The *g* values are given in the Table. In metal-free phthalocyanin there was a broadening of the low-field component of the line suggesting an obscured $g_{\parallel}$ feature with $g_{\parallel} > g_{\perp}$. In zinc phthalocyanin, the reverse was true, suggesting $g_{\parallel} < g_{\perp}$. In platinum phthalocyanin the low- and high-field lines showed evidence of hyperfine structure which was interpreted as arising from coupling to ^{195}Pt ($I = \frac{1}{2}$, 33%). This was supported by computer simulation and yielded a coupling of *ca.* 30 ± 5 G for the low-field line and *ca.* 20 ± 5 G for the high-field line.

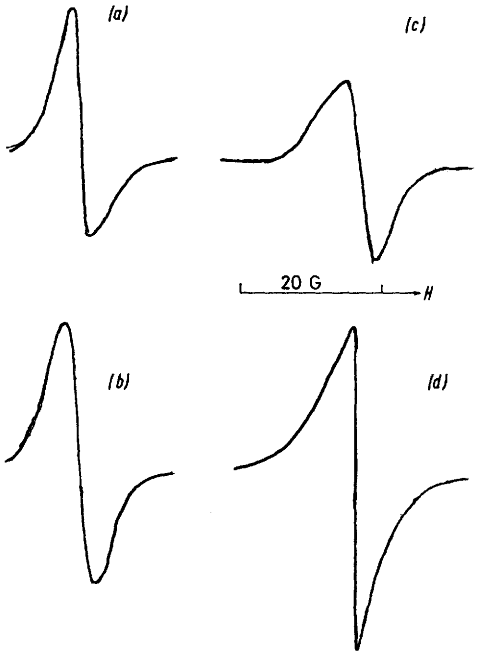

FIGURE 1 *Q*-Band e.s.r. spectrum of zinc phthalocyanin, (*a*) in air and (*b*) after hydrogen reduction, and metal-free phthalocyanin, (*c*) in air and (*d*) after hydrogen reduction

E.s.r. *g*-factors of diamagnetic phthalocyanins (Pc) and tetraphenylporphyrins (TPP)

	Before H_2 reduction	After H_2 reduction	Frozen solution
H_2Pc	2.003	2.003	2.002 (dioxan) 2.002 (H_2SO_4)
ZnPc	2.002	2.002	*a*
NiPc	1.998, 2.002, 2.007	1.995, 2.002, 2.005	*a*
PdPc	1.977, 2.002, 2.008	1.978, 2.002, 2.008	1.978, 1.988, 1.995 (dioxan)
PtPc	1.993, 2.012, 2.032 *b*	1.995, 2.012, 2.032 *b* + line at 2.002	1.981, 2.009, 2.025 (naphthalene) + line at 1.990 1.979, 1.999, 2.024 (dioxan) + line at 1.990
H_2TPP	2.001	2.001	2.005 (chloroform) 2.005 (nitrobenzene) 2.004 5 (H_2SO_4)

a Not measured. *b* Hyperfine couplings 20, —, 30 (±5) G.

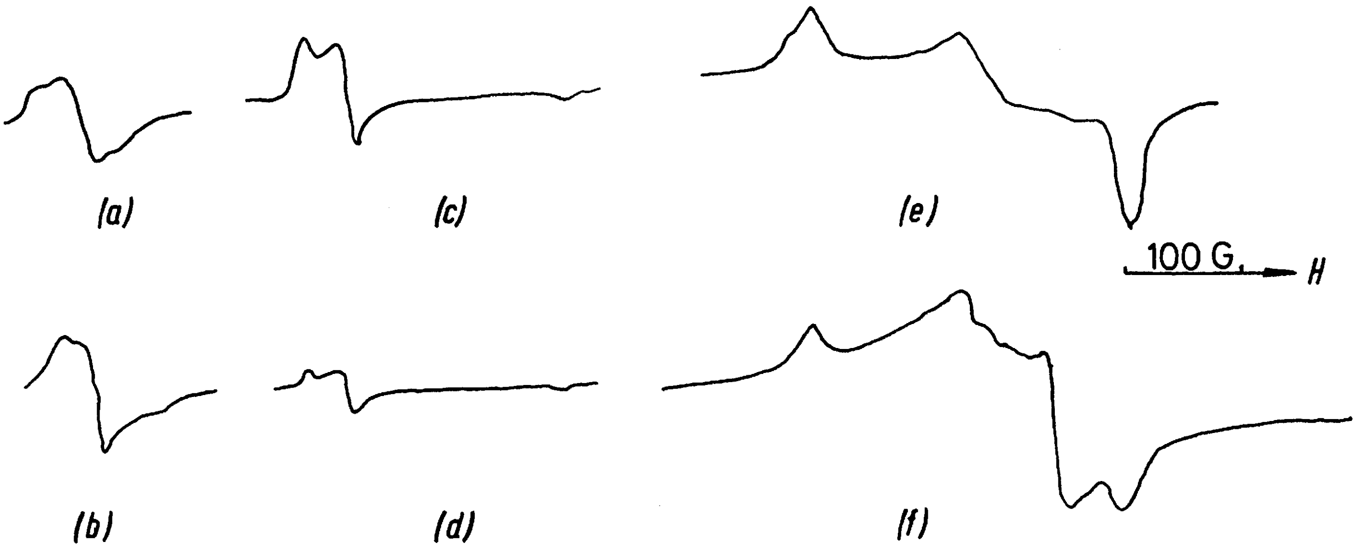

FIGURE 2 *Q*-Band e.s.r. spectrum of nickel phthalocyanin, (*a*) in air and (*b*) after hydrogen reduction, palladium phthalocyanin, (*c*) in air and (*d*) after hydrogen reduction, and platinum phthalocyanin (*e*) in air and (*f*) after hydrogen reduction

After the compounds had been heated to 650 K for 2 h *in vacuo* (10^{-5} Torr) the e.s.r. signal in all cases decreased in intensity by a factor of up to 2. Prolonged treatment caused no further change. In each case, admission of oxygen caused the signal to increase to its original intensity and shape. The whole cycle could be repeated several times on the same sample.

Different results were, however, obtained when the compounds were heated to 650 K under 1 atm of hydrogen for

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* Throughout this paper: 1 G = 10^{-4} T; 1 Torr = (101 325/760) Pa; 1 atm = 101 325 Pa.

15 h. The signals in each case shrank to *ca.* one-sixth of their original size and peak positions changed slightly. In the case of hydrogen and platinum phthalocyanins an additional narrow and stronger line appeared at $g = 2$. Figures 1(*d*) and 2(*f*) allow comparison between the spectra of the untreated and hydrogen-reduced phthalocyanins and show the magnitude of the change. In each case admission of oxygen caused the signal to revert to its original intensity and shape but only when heated to 600 K in oxygen.

These results strongly suggest oxygen is the cause of a substantial part of the signal, but that there remains some signal which is either caused by a species involving oxygen and which is resistant to reduction by hydrogen or by some other radical or interaction. If oxygen is implicated as a cause of the signal, perhaps as $[O_2]^-$ or O^-, as is well established for the absorption of oxygen on various metal oxide surfaces,[8] then this would be readily confirmed by using oxygen enriched in the ^{17}O isotope ($I = \frac{5}{2}$, natural abundance 0.04%). This was tested by taking each of the phthalocyanins and the tetraphenylporphyrin and subjecting them to pressures ranging from 10^{-1} to 20 Torr of 54% enriched $^{17}O_2$ at 650 K (after reduction in hydrogen at 650 K or after simple pumping at 10^{-5} Torr for 1 h at 650 K). In each case the e.s.r. spectrum at 77 K and at room temperature was identical to that before treatment.

These results show that the species responsible for the e.s.r. signal is not a simple radical with the unpaired electron localised on the oxygen as $[O_2]^-$, O^-, or as a hyperoxo-adduct {known to be present in $[Co(pc)(O_2)]$ [9] (pc = phthalocyaninate)} as has been postulated by some workers.[4-7] Such radicals would have manifested themselves by characteristic g values and hyperfine coupling to ^{17}O. Our interpretation of these e.s.r. results will be given later in this paper after consideration of some measurements in solution.

Solutions with oxygen. Phthalocyanins are insoluble in most solvents except concentrated sulphuric acid in which they are very soluble, and naphthalene and dioxan in which there is slight solubility. Tetraphenylporphyrins are soluble in most of the polar and aromatic organic solvents, as well as H_2SO_4. The e.s.r. spectra of the metal-free tetraphenylporphyrin in nitrobenzene and in chloroform, and of metal-free phthalocyanin in dioxan or concentrated H_2SO_4, each gave a weak single narrow line varying from 3 to 5 G wide in frozen solutions at 77 K. For phthalocyanin, $g = 2.0020$, and for tetraphenylporphyrin, $g = 2.0045$. When the solutions were degassed the e.s.r. signal almost disappeared, but returned again on oxygenation. With palladium phthalocyanin in dioxan and platinum phthalocyanin in dioxan or naphthalene (at 77 K) the spectrum resembled that in the solid and was characterised by three g values. The signal in degassed solution was very weak, increasing in intensity on contact with air. With platinum phthalocyanin, admission of oxygen caused a new narrow line to appear at $g = 1.990$ which became dominant in the presence of excess of oxygen. All these effects were reversible. The reversible character of the signals which are dependent on the presence of oxygen, and having similar g values and linewidths to the solid, suggests that the signals arise from the same or closely related radical(s) or species. Furthermore, it strongly suggests that we are dealing with a molecular rather than a solid-state effect, *i.e.* the unpaired electron is associated with a single phthalocyanin or porphyrin molecule (as is presumed to exist in solution) rather than associated with conduction bands, or radicals in defects or grain boundaries, *etc.*, as has been suggested by other workers.[1-7]

Temperature dependence. Other workers have shown that solid metal-free phthalocyanins interact with chloranil (2,3,5,6-tetrachloro-*p*-benzoquinone) [10] and iodine [11] and that magnesium phthalocyanin interacts with iodine.[12] In each case a strong e.s.r. signal appeared and measurements of its intensity as a function of temperature were shown to obey singlet–triplet statistics. The species responsible for the signal was thought to be a surface-adsorbed charge-transfer complex having a thermally accessible triplet state. We have measured the intensity of the e.s.r. adsorption in solid oxygenated metal-free, zinc, and nickel phthalocyanins and in metal-free tetraphenylporphyrin and in the same compounds after reaction with hydrogen for 15 h at 650 K. Spectra were recorded at 20-K intervals from 120 to 500 K.

Bijl *et al.*[13] first considered the temperature dependence of e.s.r. signal intensities, I, of solid charge-transfer complexes. If the ground state is a doublet, then the simple Curie law is obeyed and we obtain expression (1). If there is pairwise

$$I \propto 1/T \qquad (1)$$

spin interaction with a ground singlet state and an associated excited triplet state separated by the exchange interaction J then (2) is applicable. Since all our spectra were Lorentzian

$$I \propto \frac{1}{T(e^{J/kT} + 3)} \qquad (2)$$

in shape, the intensity was taken to be proportional to the product of the square of the separation of the points of maximum gradient of the absorption and the amplitude of the derivative curve. By plotting log IT against $1/T$, the gradient equals $-J/\mathbf{k}$, except at the highest temperatures.

Plots of log IT against $1/T$ for all the compounds in air showed irregular and irreproducible behaviour as the temperature was increased and decreased between 120 and 500 K, although in general terms there was a decrease in intensity as the temperature was decreased. However, corresponding plots for the metal-free and zinc phthalocyanins in particular, after hydrogen treatment, consisted of a pair of intersecting straight lines (Figure 3). We interpret this as arising from pairwise spin interaction with a ground singlet and an excited triplet state. The two straight lines show that two different types of interaction are taking place with a sharp transition temperature. For the metal-free phthalocyanin, when $T < 295$ K, $J = 422$ J, and when $T > 295$ K, $J = 4\,582$ J. With zinc phthalocyanin, for $T < 245$ K, $J = 66$, and for $T > 245$ K, $J = 1\,870$ J. The values of J derived from e.s.r. measurements are accurate to *ca.* ±10%.

These results strongly suggest that the cause of this part of the single e.s.r. absorption in at least the metal-free and zinc phthalocyanins, and possibly in the nickel phthalocyan-

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in and metal-free tetraphenylporphyrin, is a charge-transfer complex between the phthalocyanin and oxygen, where electron transfer has taken place from the phthalocyanin to the oxygen molecule with the probable formation of a phthalocyanin radical cation and a hyperoxide anion.

The expected zero-field splittings for our complexes in the triplet state are not observed over our temperature range (>77 K). As the temperature is increased the components normally observed at low temperatures broaden and move together, eventually collapsing into a single line which becomes progressively sharper. This process is characteristic of an exchange interaction, a process which first removes fine structure (exchange broadening) and then sharpens up the single remaining resonance line (exchange narrowing). Furthermore, temperature-dependent exchange effects which remove the dipolar-induced zero-field splitting will also remove dipolar-induced mixing of states, resulting in the vanishing of the $\Delta m = \pm 2$ transition. Our inability to detect such transitions lends support to our theory that the spectra arise from a thermally accessible triplet state. Likewise, the exchange rate is fast enough to remove any hyperfine structure from the separate radicals which might be present.

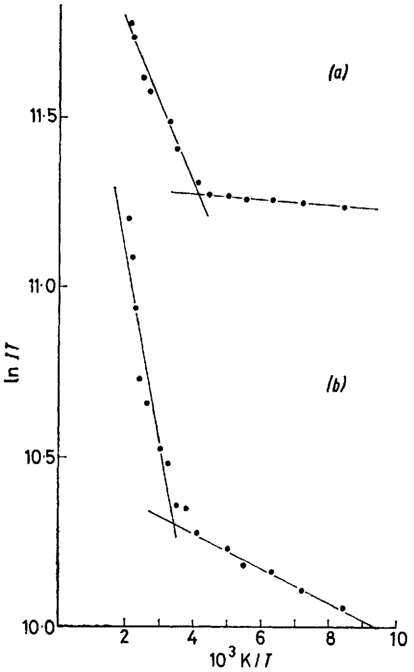

FIGURE 3 Plots of lnIT against $1/T$ for (*a*) zinc phthalocyanin and (*b*) metal-free phthalocyanin

Useful temperature-dependence studies on the palladium and platinum phthalocyanins could not be carried out because of the anisotropy, shape, and overlap of the lines.

Related charge-transfer studies. In order to gain further evidence to substantiate our proposal that charge-transfer interactions are responsible for the e.s.r. signal in the phthalocyanin–oxygen system, we added other electron acceptors to the phthalocyanins and recorded their e.s.r. spectra. Addition of iodine or tetracyanoethylene to metal-free tetraphenylporphyrin in chloroform or nitrobenzene, or to metal-free phthalocyanin in dioxan, or to the pure solids, yielded (at 77 K for solutions) a single narrow signal which was very strong in the case of iodine but relatively weak (about the same strength as the oxygen signal) in the case of tetracyanoethylene (tcne) (although the solution became green). Aoyagi *et al.*[11] obtained the same result in studies of metal-free phthalocyanin and iodine and also found that J = 3 570 J. Kearns *et al.*[10] used chloranil and obtained a signal as did Sharoyan *et al.* with iodine.[12] In all these cases the evidence points to a charge-transfer complex of the type $P^+I_2^-$ or P^+tcne$^-$ (where P^+ represents the phthalocyanin or porphyrin radical cation).

In the case of palladium phthalocyanin in dioxan with added iodine the spectrum at 77 K was similar to that with oxygen except that the signal was very strong. The g values were 1.994, 1.986, and 1.975. With the platinum analogue the g values were 2.026, 1.997, and 1.979, but no hyperfine coupling was detected. An additional symmetrical line at $g = 1.991$ was also seen. In each case, the signals were stronger than with oxygen.

Optical Spectra.—The optical spectrum of each phthalocyanin and the metal-free tetraphenylporphyrin was recorded in each of the solvents used for the e.s.r. measurements. The spectra were recorded with pure degassed solvents, and with the solvents saturated with dry oxygen. No difference in the optical spectrum of the phthalocyanin or the porphyrin was detectable, showing that any interaction of the oxygen with the solute was, at the most, very weak. This contrasts with the large effects seen in the spectra of many organic solvents with and without oxygen.[14]

DISCUSSION

We have presented evidence which strongly suggests that the e.s.r. signal in the phthalocyanins and tetraphenylporphyrin arises from a charge-transfer interaction with oxygen. However, there appear to be several different interactions responsible. For all the compounds there is an underlying e.s.r. absorption which cannot be removed by reaction with hydrogen at 650 K. However, there are two other coincident but stronger lines, one which cannot be removed by evacuating to 10^{-5} Torr, and the other present in air at ambient temperatures and pressures. We believe that these signals result from oxygen adsorbed on the surface of the phthalocyanin crystals, interacting in different manners with surface phthalocyanin molecules and with those near dislocations and other defect sites. In each case the strength of the interaction can vary very considerably because of the local effects at surface kinks, steps, terraces, vacancies, and adatoms.[15] The surfaces of phthalocyanins and related molecules have been studied by low-energy electron-diffraction methods.[16] Such studies have shown the clear effects of different surface sites on the reactivity of adsorbed molecules. Hence it is perfectly reasonable for some oxygen molecules to be adsorbed more strongly than others and thus have different strengths of charge-transfer interactions. Also, hydrogen reduction of the

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adsorbed oxygen layer will be effective to varying degrees depending on the site of adsorption.[15]

Our measurement of the characteristic exchange energies, $J = ca.$ 422 and 4 852 J for metal-free phthalocyanin over different temperature ranges, supports this. At higher temperatures the stronger interaction is of a similar magnitude to those found[11,17] in $[PMePh_3]^+$-$[tcnq]_2^-$ (5 790 J), $[NHEt_3]^+[tcnq]_2^-$ (tcnq = tetracyanoquinodimethane) (3 281 J), and metal-free phthalocyanin–iodine (3 570 J). These figures represent relatively small interactions compared with, for example, the value of 39 561 J for the morpholinium–tcnq complex.[18] We obtained similar results with zinc phthalocyanin. In the case of metal-free and platinum phthalocyanin an additional symmetrical sharp line was generated on reduction with hydrogen. This must represent a different type of interaction.

The asymmetry of the e.s.r. spectra arises from the strong asymmetry of the phthalocyanin–oxygen interaction and is rather similar to that found by Singer and Kommandeur[18] with perylene–iodine where $g_{\parallel} = 2.003\,48$ and $g_{\perp} = 2.002\,38$. The increasing deviation, Δg, from $g = 2.003$ on going from metal-free to nickel, palladium, and platinum phthalocyanin must arise from progressively stronger spin–orbit interactions of the unpaired electron on the cation with the metal. In the case of nickel, palladium, and platinum phthalocyanins the values of Δg seem too large to be explained simply by asymmetry of the phthalocyanin–oxygen interaction. We suggest that they arise from species which are simply radical cations with the counter anion $[O_2]^-$ sufficiently remote to have effective dipolar coupling with the cation. The cation is likely to be stabilised by surface effects.

In the case of platinum phthalocyanin the outer lines are sufficiently well separated and resolved to detect hyperfine coupling to the metal. This is small, however, and probably arises from a polarisation mechanism. The value, *ca.* 20 G, is of the right order of magnitude for this process, since it represents *ca.* 0.54% *s* character (taking[19] 100% $a_{Pt}{}^s$ 3 709 G) and is very similar to that in the zinc (0.27%)[20] and cobalt tetraphenylphorphyrin cations (0.46%).[19] The coupling to palladium would be small and is not expected to be seen. With the palladium and platinum phthalocyanin a single line at $g = 2$ is also seen which comes from a strongly interacting charge-transfer complex. The e.s.r. spectrum in solution is in all cases very weak, and we were unable to detect any change in the optical spectra in solution when oxygen was bubbled through a degassed solution of the phthalocyanin.

The unpaired electron in the cations is in an a_{2u} orbital (assuming D_{4h} symmetry) by analogy with the results for magnesium and zinc tetraphenylporphyrin cations. This orbital is characterised by small hyperfine splitting to nitrogen and hydrogens, and coupling to the metal, in contrast to the alternative possibility shown by zinc, magnesium, and cobalt octaethylporphyrin cations where the unpaired electron has been shown to be in an a_{1u} orbital characterised by hyperfine splitting to protons only.

Our inability to see hyperfine coupling is not unusual. Systems where hyperfine coupling has been seen are usually very strongly interacting systems in good single crystals,[21] and always in the strict absence of oxygen.[22] A range of interacting sites or, in the case of oxygen, a dynamic surface would easily smear out any hyperfine coupling.

EXPERIMENTAL

The metal-free and zinc and nickel phthalocyanins were supplied by I.C.I., the platinum and palladium phthalocyanins by Johnson, Matthey Ltd., and the metal-free tetraphenylporphyrin by the Mad River Chemical Company, Yellow Springs, Ohio. All the phthalocyanins and the tetraphenylporphyrin were purified by sublimation before use. Solvents were dried over molecular sieves. E.s.r. spectra were recorded on a Varian E3 spectrometer, and optical spectra on a Unicam SP 8000 spectrophotometer.

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