trans-[Pt(PEt$_3$)$_2$Cl$_2$] with Br$^-$ in methanol. This particular reaction was studied earlier by Taylor and Hathaway[33] in absolute methanol and methanol–water (60% water) for which $\Delta V^{\ddagger}_{\text{exptl}}$ values of −27 ± 3 and −28 ± 3 cm^3 mol^{-1}, respectively, were reported, in obvious agreement with our datum. Although $\Delta V^{\ddagger}_{\text{intr}}$ for this reaction may be somewhat more negative than −4 cm^3 mol^{-1} because of the larger radius of the bromide ion, it must be assumed that $\Delta V^{\ddagger}_{\text{solv}}$ is mainly responsible for such a large negative $\Delta V^{\ddagger}_{\text{exptl}}$ value. We must conclude that in the partially formed Pt–Br bond the bulk of the negative charge resides on the bromide ligand thereby considerably enhancing the dipole moment of the activated species giving rise to a large negative $\Delta V^{\ddagger}_{\text{solv}}$ term. The loosely bound bromide presumably exerts an electrostrictive influence on the solvent comparable to that of the free ion. Otherwise, a reduction in the degree of electrostriction around the bromide would offset the large increase in the solvation of the substrate. This explanation of $\Delta V^{\ddagger}_{\text{exptl}}$ is preferred over the proposed argument[33] that the reaction mechanism involves simultaneous Pt–Br bond formation and strengthening of a Pt–MeOH bond. The latter postulate involves a six-coordinate transition state which, among other properties, would not show the same correlation with the Kirkwood treatment as was observed here; i.e., the formation of a Pt–py bond to give a six-coordinate transition state would not lead to a significant change in the dipole moment of the substrate or in any other property which could account for the solvent dependence of $\Delta V^{\ddagger}_{\text{exptl}}$.

A general feature of all these reactions is that $\Delta V^{\ddagger}_{\text{exptl}}$ is pressure independent at least up to 1.5 kbar. This is consistent with a process involving merely a contraction of the existing solvation layers rather than a complete rearrangement of the solvent as was the case in the Menschutkin reaction for example.[10,11]

Finally, although these Pt(II) complexes and their reaction products were generally too insoluble to allow accurate measurements of their partial molar volumes to be made, a value could be obtained for *trans*-[Pt(py)$_2$(Cl)(NO$_2$)] in dichloromethane of 196.8 ± 1.2 cm^3 mol^{-1} at 25 °C. Thus, with the measured partial molar volume of pyridine in CH$_2$Cl$_2$ at 25 °C of 80.8 ± 1.1 cm^3 mol^{-1} and the appropriate $\Delta V^{\ddagger}_{\text{exptl}}$ value, the partial molar volume of the transition state, [Pt(py)$_3$(Cl)(NO$_2$)], can be calculated[30] to be 255.4 ± 4.0 cm^3 mol^{-1}. Naturally it would be of considerable interest to obtain the partial molar volume of the transition state in the remaining solvents as we have proposed that the solvation effects are virtually all to be seen in the transition state. At the present time, it can only be stated that the partial molar volume of pyridine varies only slightly with the solvent; e.g., in CH$_3$NO$_2$, CH$_3$OH, C$_2$H$_5$OH, and CH$_2$Cl$_2$ the respective volumes are 78.0 ± 0.5, 78.6 ± 0.5, 79.0 ± 0.5, and 80.8 ± 1.1 cm^3 mol^{-1}.

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Registry No. *trans*-[Pt(py)$_2$(Cl)(NO$_2$)], 70774-90-2; *cis*-[Pt(py)$_2$(Cl)(NO$_2$)], 70812-17-8; *trans*-[Pt(PEt$_3$)$_2$Cl$_2$], 15692-07-6; [Pt(py)$_3$NO$_2$]ClO$_4$, 70749-51-8; *trans*-[Pt(py)$_2$Cl$_2$], 14024-97-6; *cis*-[Pt(py)$_2$Cl$_2$], 15227-42-6.

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ESCA and EPR Studies of Monomer, Dimer, and Polymer Iron Phthalocyanines: Involvements for the Electrocatalysis of O$_2$ Reduction

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Core- and valence-level X-ray photoemission spectra of three iron phthalocyanines (monomer, dimer, and polymer) are interpreted and related with the catalytic activity of these compounds in the electrochemical reduction of oxygen. EPR data are also reported for the three species. The iron spin and oxidation state, the electron delocalization in the organic ligand, and the covalent character of the Fe–O$_2$ bond are found to be important factors in the catalytic process.

I. Introduction

The questions raised by the reactivity with oxygen of phthalocyanine or hemoglobin structures are of interest to biochemistry as well as to electrochemistry concerned with air cathodes. In this way, Collman[1] reported that the free enthalpy change during oxygen adsorption on hemoglobin was 16 kcal

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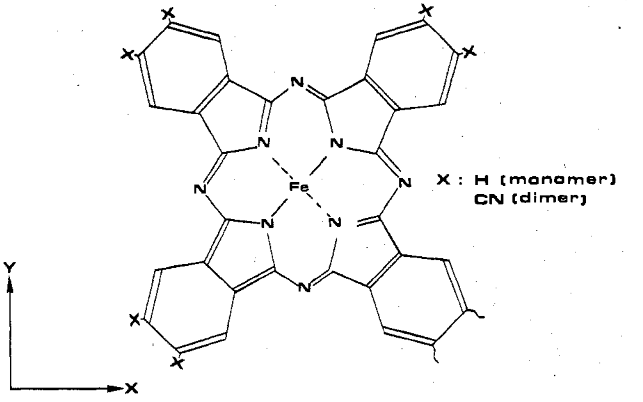


Figure 1. Structural formula of phthalocyanines.

mol^{-1}, a value which is close to those found by Boreskov[2] for the most active oxides in the homomolecular oxygen exchange reactions. The effects of molecular association on activity of iron porphyrins have been described by Wallace and Caughey:[3] the reduction rate of adsorbed oxygen by reaction with a water molecule increases with the transfer rate of the first two electrons from a donor molecule, leading to the formation of hydrogen peroxide.

A series of iron phthalocyanines (Figure 1) with different degrees of polymerization has been investigated for their electrocatalytic activity in aqueous media.[4] Under comparable conditions, the phthalocyanines show a decreasing activity in the following order: dimer > polymer ≫ monomer. The mechanism of this process is similar to the one described above for porphyrins, the electrons being supplied here from a metal electrode, through a charge-transfer process directed along the ligand–iron–oxygen–water axis. The reaction mechanisms found for the dimer[4] and for the monomer[5] catalysts show that HO_2 and OH radicals are formed on the dimer, rather than the O_2^- species which is formed on the monomer. On the active dimer compound, a series of chemical and electrochemical reactions, using the surface OH radicals, leads to reduction of the HO_2^- ions which are formed by fast transfer of two electrons from chemisorbed oxygen.

Following optical and Mössbauer spectroscopic studies, Appleby, Fleish, and Savy[4] concluded that the OH radicals involved in this mechanism are formed during a reaction step by which Fe^{3+} in the catalyst is reduced to Fe^{2+}; Fe^{3+} is then regenerated during another step associated with the desorption of a water molecule.

The role of structure (polymer or dimer) would be concerned not only with the rate of Fe^{2+} to Fe^{3+} conversion but also with the spin multiplicity of the Fe^{3+} formed. Mössbauer studies provide evidence for an intermediate spin (IS) state in the dimer, and this could explain the activation of electron-transfer kinetics by spin conversion.[6] In the active form, a small change in ligand field parameters allows a multiplicity change in the iron ion.[7]

In addition to these considerations, the π–d interaction with the π electrons in the conjugated rings can modify the $Fe^{II} \rightarrow Fe^{III}$ conversion rate; this effect is expected to be higher in the polymer, because of the larger number of delocalized electrons available.[4]

The EPR spectroscopy provides a way to determine the "free" electron density and the oxidation state of iron and its g value, which is related to the ligand field parameters. By X-ray photoelectron spectroscopy (ESCA, electron spectroscopy for chemical analysis), it is not only possible to detect the presence of surface oxygen and to estimate atomic charges on carbon and nitrogen but also to obtain direct information on the Fe d orbitals by looking at the valence band, at the Fe 2p shake-up satellites, and at the Fe 3s multiplet splitting.

The present work aims at showing how these techniques shed light on the relation between the nature of the $Fe–O_2$ bond and catalytic activity when they are applied to the three compounds (monomer, dimer, and polymer) which have provided the basis of the electrochemical studies.

II. Experimental Section

Iron phthalocyanine (PcFe) dimer was prepared by the reaction of tetracyanobenzene with iron dipivaloylmethane, following the method described by Appleby and Savy.[8] It was characterized by the N/Fe elemental ratio obtained by X-ray fluorescence.[9]

The polymer of iron phthalocyanine was prepared by the method of Drinkard and Bailar.[10] According to this paper, it would correspond to a hexamer, with six units either aligned or zigzag.

The monomer iron phthalocyanine was a commercial compound from Eastman Kodak.

An analysis of elemental composition has been obtained by proton-induced X-ray spectrometry (PIXE). This method is particularly appropriate for detecting even low concentrations of transition metals. No trace of transition metals other than Fe were found in the samples. For the dimer, the results indicate that Fe concentration is approximately the expected value. But for the polymer, only 25% of the expected value was found. This indicates a incomplete metalation of the complex.

X-ray photoelectron spectra were obtained on a Hewlett-Packard 5950 A ESCA spectrometer, using monochromatized Al Kα radiation ($h\nu = 1486.6$ eV). The samples were pressed as pellets and deposited on a gold-plated sample holder.

In order to prevent surface contamination, all measurements were performed with pressures in the preparation and analyzing chamber of at most 5×10^{-7} and $\sim 10^{-9}$ torr, respectively, before introducing the phthalocyanine samples. No problems were encountered in the case of the monomer and polymer, for which sample cleanliness was checked on the ESCA spectra. In the case of the most active compound (dimer), it was necessary to outgas the sample a few minutes in the preparation chamber.

In spite of this, the pressure in the analyzing chamber was larger than in the other two cases (10^{-8}–5×10^{-7} torr), indicating oxygen desorption. This could be followed very precisely by reading the residual gas pressure in the spectrometer chamber and identified by mass analysis with a quadrupole mass spectrometer (Balzers QMG 101 A) installed directly on the sample-handling chamber. Equilibrium was reached after 0.5 h with a pressure $\leq 10^{-8}$ torr.

The reproducibility of the different spectra was very good, and the estimated standard deviations on the binding energy values in Table I are smaller than 0.1 eV. We referenced binding energies by vacuum evaporating a thin gold layer over the sample, taking the Au $4f_{7/2}$ binding energy as reference at 84.0 eV. Gold decoration was achieved with a distance between the sample and the filament of about 15 cm, in order to prevent decomposition of the phthalocyanine by heat during evaporation. A slight modification was still observed in the core levels shape of the pure samples after calibration with gold; we therefore proceeded to a second comparative calibration, using a mixture of phthalocyanine (70% weight) and graphite (30%). The graphite C 1s line was determined at 284.2 eV.

All spectra presented below have been obtained by using signal averaging over typical times of 15 h for valence bands and Fe 2p levels (40 h for the polymer) and 40 h for Fe 3s levels. Stabilities of experimental conditions and of the sample itself have been verified on standard spectra (C 1s or N 1s) at regular intervals.

III. ESCA Results and Discussion

1. Results. a. Wide-Range Spectra. A 1000-eV-wide scanning of the spectra of the three compounds provides a fast check of elemental composition. Besides the absence of any observable impurities, the most striking evidence is the lack of oxygen on the monomer, the O 1s line being strongest for the dimer and also present for the polymer.

b. Detailed Spectra. Detailed spectra of the C 1s (Figure 2), N 1s, Fe 2p (Figure 3), and Fe 3s lines (Figure 4) and of the valence regions (Figure 5) have been systematically recorded. The O 1s levels have been recorded as well; the width and structure of these peaks indicate the presence of different

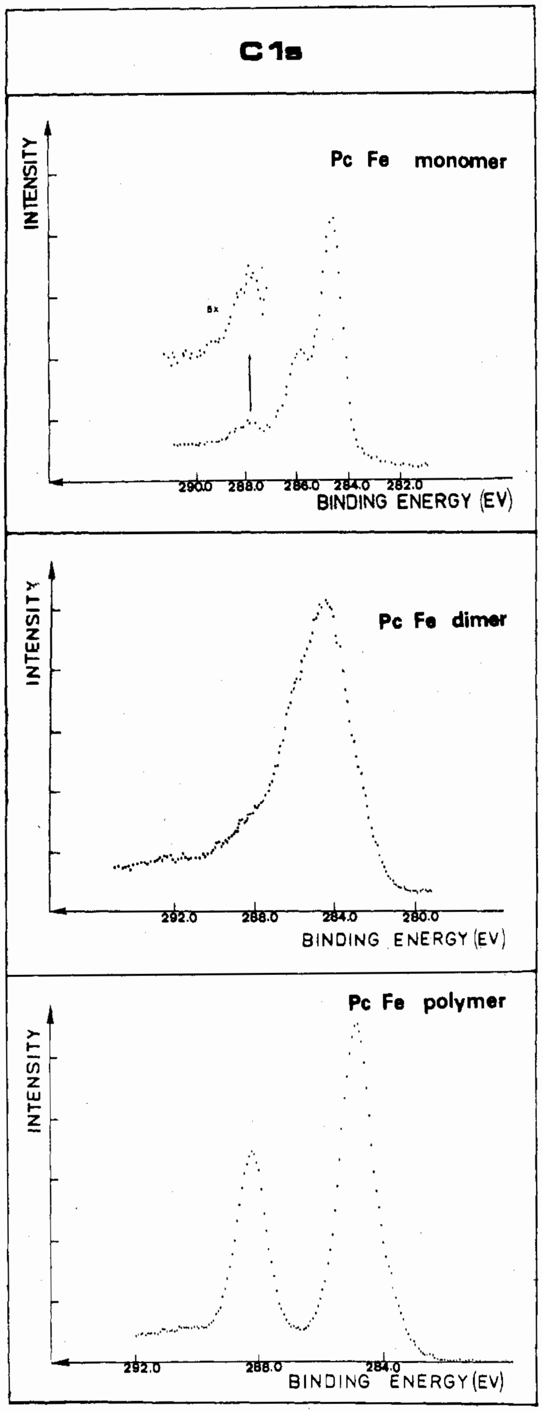


Figure 2. C 1s ESCA spectra.

types of oxygen. Their detailed identification, assisted by the present work, is a promising future perspective.

Observed binding energies, calibrated as described in the Experimental Section, are reported in Table I, together with the valence band data of the three compounds which are illustrated in Figure 5. The spectra have proven to be very reproducible over several independent measurements.

Low-intensity signals have been accumulated over appropriate times to improve counting statistics. The polymer Fe 2p lines, which are particularly weak, were obtained in this way after a 40-h run. Only the Fe 3s line of polymer phthalocyanine was too weak to be detected.

All spectra shown in the figures are unsmoothed; positions of photopeaks were specified by using the second derivative of smoothed spectra. The procedure usually used in our laboratory has been described elsewhere.[11]

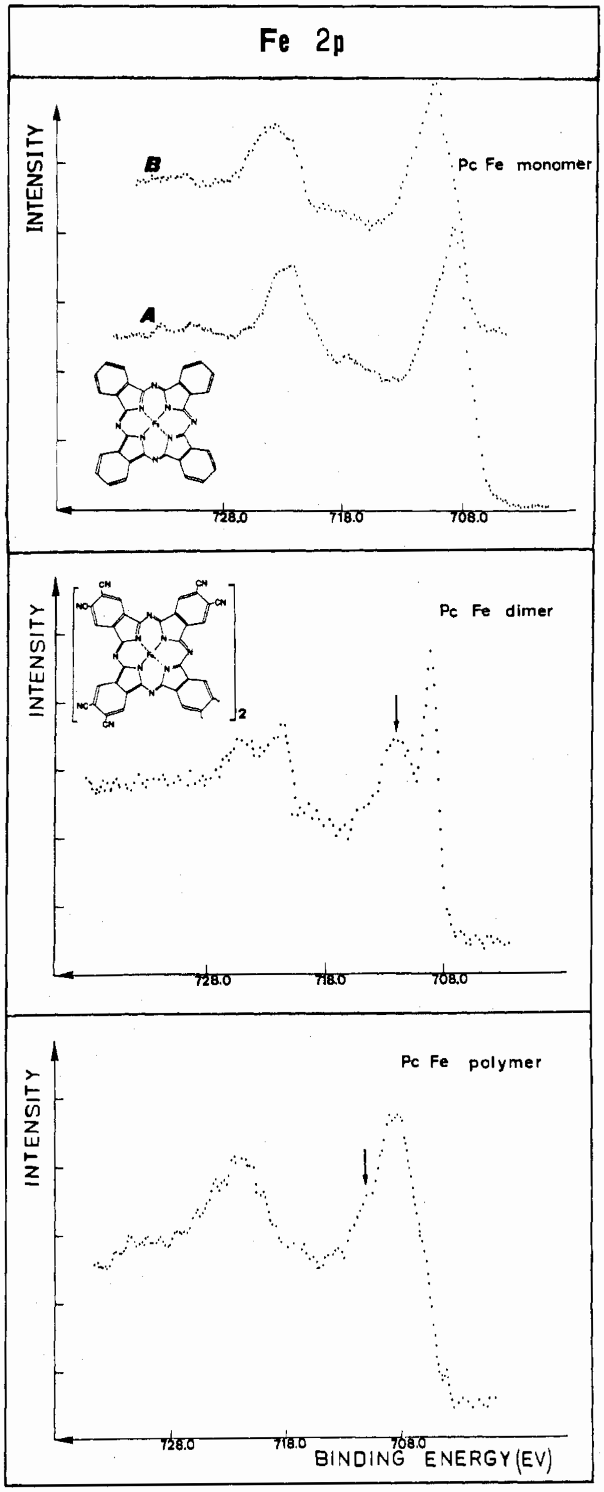


Figure 3. Fe 2p ESCA spectra (PcFe monomer: A, 10^{-9} torr O_2; B, 2.10^{-7} torr O_2); shake-up satellites are indicated by arrows.

2. Discussion. a. Ligand Core Levels: **C 1s, N 1s.** A clear difference is observed between the C 1s levels in the three compounds (Table I and Figure 2).

For the monomer, two peaks are distinguished, in a 1:3 ratio corresponding to the ratio between benzenic and pyrrolic carbon atoms in the molecule. This result is in agreement with literature data.[12-14] A shake-up satellite is also observed, separated from the strongest C 1s peak by 3.3 eV; this will be interpreted below, together with similar phenomena related to the Fe 2p levels.

Table I. Electron Binding Energies in Iron Phthalocyanines (eV)

A. Core Levels

levels	monomer	dimer	polymer
C 1s	284.5	284.5 (asym;	284.8
	285.8 w	see sect III.2.a.)	288.1
satellite	287.5		
N 1s	399.1	398.9	398.6
			400.2 w
Fe $2p_{3/2}$	708.8	709.2	708.3 (Fe^{2+})
			710.5 (Fe^{3+})
satellite		711.8	713.1
Fe $2p_{1/2}$	722.2	721.8	723.7
satellite		724.5	
Fe $2p_{3/2}$[c]	708.8 (Fe^{2+})		
	710.6 (Fe^{3+})		
Fe $2p_{1/2}$[c]	722.2 (Fe^{2+})		
	723.7 (Fe^{3+})		
Fe 3s	94.5	94.5	unobsd

B. Valence Levels

monomer			dimer		
no.[b]	E_b obsd	identific[a]	no.[b]	E_b obsd	interpretn
1	2.0	$2b_{2g}$	1	0.9	Fe–O_2 (π_g)
2	2.8	$2a_{1g}$	2	3.7	Fe–N
3	4.3	$2e_g$	3	6.9	Fe–O_2 (π_g)
4	6.2	$1b_{2g}$			

[a] By comparison with the calculation by A. M. Schaffer, M. Gouterman, and E. R. Davidson, *Theor. Chim. Acta,* **30,** 9 (1973); see Figure 4. [b] See Figure 3. [c] With oxygen; see section III.2.b.

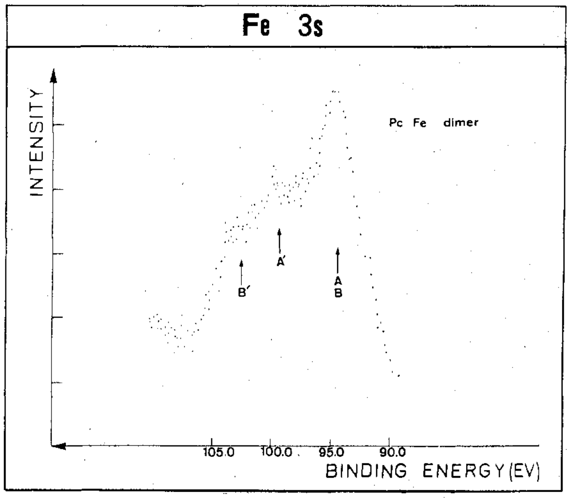
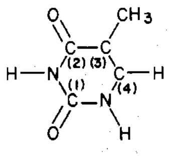


Figure 4. Fe 3s ESCA spectrum of iron phthalocyanine dimer: A,A′, doublet from Fe^{2+} (LS); B,B′, doublet from Fe^{3+} (IS).

The dimer shows only one C 1s peak, with a strong asymmetry indicating a shoulder at high binding energies. The present observation indicates charge equalization over the whole ligand carbon framework in the dimer.

The polymer C 1s spectrum is very different: two well-separated symmetric core levels, with intensity ratio 0.47/1 (highest/lowest binding energy), are observed. The hypothesis of a strong shake-up satellite is not very convincing, despite the energy separation of 3.3 eV between peaks. Such intense satellites have, indeed, never been reported for the C 1s level in any type of molecule. We found, however, that in the ESCA spectrum of thymin



a similar shift is reported[15] between the C(1) and C(3) 1s levels.

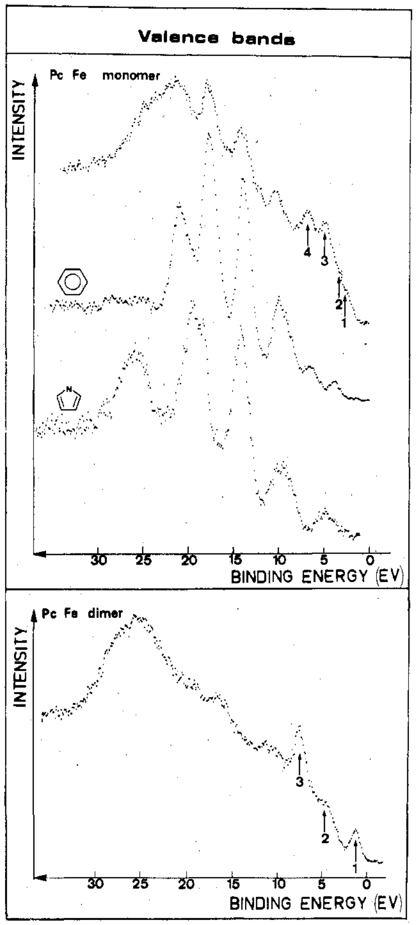
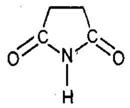


Figure 5. Valence-band ESCA spectra for iron phthalocyanine monomer and dimer (valence-band ESCA spectra of pyrrole and benzene are shown for comparison).

We conclude that a cyclic imide structure



similar to that observed by Inoue[16] may have been formed from the cyanated benzene groups, the imide carbon atoms giving rise to the C 1s peak at higher binding energy. This conclusion is supported by IR absorption spectra, which show an intense $\nu_{C=O}$ band at 1765 cm^{-1} and a ν_{N-H} band around 3400 cm^{-1}, whereas the dimer presents a strong absorption band at 2225 cm^{-1} ($\nu_{C\equiv N}$) which is totally absent here. The strong relative intensity of the high binding energy (E_b) peak is explained by considering the fact that a fraction of the benzenic carbon atoms, close to the imide rings, also have a higher positive charge in the polymer.

The N 1s peaks provide only limited information concerning the ligand. In the polymer, a shoulder at lower binding energy indicates that two different types of nitrogen atoms are present (pyrrolic and imidic). It should be noted that the presence of a single peak in the dimer is an additional evidence for the delocalization of charges already mentioned for the carbon atoms.

b. Fe 2p Levels. The large differences in Fe 2p core-level spectra can be immediately observed in Figure 3. Several details are directly related to the catalytic activity of the compound: less active compounds (monomer and polymer) show broader lines; the intensity of the shake-up satellite relative to the Fe 2p peak coincides with activity (zero for the monomer, strong for the dimer, weak for the polymer).

Also, the oxidation state of the iron ion and, to some extent, its spectroscopic state can be determined from these spectra. Core levels indeed provide a threefold source of information: (i) chemical shifts of their binding energies, which are related to the species electronic environment (oxidation state, nature of surrounding atoms), (ii) multiplet splitting, which arises from the exchange interaction of unpaired valence electrons with core electrons becoming unpaired because of the departure of the photoelectron, and (iii) shake-up satellites, at higher E_b values (or lower electron kinetic energies). In the final state of the system, a valence electron is excited to a partly (or completely) vacant orbital, following the monopole selection rule.[17] The energy required for this transition appears in the energy balance of the photoemission process, lowering the photoelectron kinetic energy.

Chemical shifts between Fe^{2+} and Fe^{3+}, particularly for the oxides, are of the order of 2 eV.[34-36] Looking at the Fe 2p spectra obtained in the present work (Figure 3), one observes that the monomer and dimer phthalocyanines contain only one dominant type of iron, while the polymer contains a mixture of two species. Knowing that the monomer contains Fe^{2+}, we have admitted a pressure of 2×10^{-7} torr of O_2 into the analyzing chamber of the spectrometer. Some of the iron ions were thereby oxidized to Fe^{3+}, showing a distinct chemical shift on the ESCA spectrum (1.7 eV; see Table I and Figure 3).

Using this information, the chemical shift observed for the Fe 2p doublet in the dimer being intermediate, we conclude that the Fe oxidation state is between +2 and +3; a simple, linear interpolation yields an estimate of +2 with a 20% additional electron transfer to the oxygen ligand, the remaining ligand atoms being identical with those in the monomer. This result is very close to the recent theoretical values proposed by Dedieu et al.[18] for $Fe(porph)O_2$ (porph = porphyrin) and related systems. These authors conclude that, in the case of organometallic complexes such as $Fe(porph)O_2(Im)$ (Im = imidazole) and $Fe(C_2N_3H_4)_2O_2(Im)$, total charges are, respectively, 15.98 and 16.06 electrons, meaning a very small charge transfer in $Fe-O_2$ bonding.

Finally, in the polymer, we find a mixture of Fe^{2+} and Fe^{3+}.

Turning now to the shape of the Fe 2p spectra, we note that they differ in their widths and/or the presence of satellites. These features are commonly observed in transition-metal 2p levels, and they are associated with multiplet splitting[19] and shake-up processes.[17] Multiplet splitting is simple only for s core holes, where only two final states are observed; for 2p levels, it generally results in a line broadening, due to the large number of mixed spectroscopic terms, and in variations in the $2p_{1/2}-2p_{3/2}$ line separation in the spectra.

The principal information in this case is contained in the satellites which are present for the dimer and polymer compounds: they are typical shake-up satellites. To interpret them, as well as to understand the valence electron spectra, we need to use a molecular energy level diagram. The choice of this model and the characteristics of the $Fe-O_2$ bond will be examined in detail in a later section devoted to the interpretation of the valence bands. Among the available calculations, a convenient model for the monomer is given by Schäffer et al.;[20] a schematic MO energy level diagram for the iron-ligand system is reproduced in Figure 8A.

Recalling the monopole selection rule, pertaining to shake-up satellites,[17] by which—simultaneously to core photoemission—a valence electron is excited from an occupied to an empty or partly occupied level of same symmetry, we explain the absence of satellites for the monomer by the lack of orbitals satisfying this condition in D_{4h} symmetry.

The C 1s shake-up satellite mentioned earlier, however, should correspond to an $e_g(\pi)$ to $e_g(\pi^*)$ transition (ligand levels, not shown in Figure 8) from an occupied to the first unoccupied ligand level according to the calculation by Schäffer et al.[20] It must also be noted that ESCA spectra of similar compounds (tetraphenylporphyrin[13]) present the same characteristic shake-up satellites which are similarly interpreted.

In the case of the dimer, on the other hand, the presence of an oxygen molecule as an additional ligand brings a change to this situation. The formation of the $Fe-O_2$ bond is followed by the generation of new molecular levels, some of which are likely to permit monopole transitions. The energy levels concerned are shown in Figure 8B, regardless of the symmetry lowering which necessarily follows the oxygen bonding. It should be noted that the Fe 2p satellite can be explained with reference to the valence-band spectra. Another interesting confirmation of the relation between shake-up process, oxygen ligand, and catalytic activity should be provided by the study of an oxygen-free dimer sample, which will be prepared under appropriate conditions.

We explain the lower intensity of the shake-up satellite in the polymer by the smaller number of active sites (Fe^{2+} ions), the model presented for the dimer phthalocyanine still being applicable. This is in good agreement with the observed difference in activity.[8]

c. Fe 3s Levels. When unpaired electrons are present in the valence shell of an ion or complex, the photoemission of a core s electron gives rise to two final states of different energies. The extent of multiplet splitting as well as the intensity ratio of the two terms are related to the number of unpaired electrons, i.e., to the spin multiplicity of the species and to the appropriate exchange integral between atomic (or molecular) shells.

The Fe 3s levels could only be observed for the monomer and dimer phthalocyanines. The low photoelectric cross section, combined with poorer iron content, made it impossible to obtain this spectrum for the polymer.

Adopting the values given by Kowalczyk[19] for 3s multiplet splitting in Fe ions, the splitting energy (eV units) is given by the formula in eq 1 where S is the total spin of the ion.

$$\Delta E(3s) = 1.0(2s + 1) + 0.6 \qquad (1)$$

Attempting to identify the species from our spectra, we observe in the monomer a dominant splitting of ~3.0 eV, corresponding to $S = 1$. This is in good agreement with the theoretical model of Schäffer et al.[20]

For the dimer (Figure 4), we observe three peaks, whereof the lowest binding energy component can be regarded as built up from two contributions (A,B).

Because of other arguments related to the valence-band analysis, discussed in the next section, we conclude that the preferred hypothesis for the (A,A′) doublet is $S = 1$ (low spin, LS) in the MO diagram of the $Fe-O_2$ complex. The two unpaired electrons are then in the a_{1g} (d_{z^2}) orbital and in an antibonding $Fe-O_2$ orbital. The second contribution (B,B′) is best explained as due to Fe^{3+} (intermediate spin, IS), i.e., $S = {}^3/_2$, which the EPR spectra confirms the existence of in very small concentration in the sample.

The whole analysis of Fe 3s multiplet splittings is in agreement with the results of previous Mössbauer spectrometric studies.[4]

d. Valence Levels. Valence-band spectra of Fe phthalocyanines are illustrated in Figure 5, together with the corresponding spectra of solid benzene[21] and pyrrole,[22] which are the cyclic constituents of the ligand. In this way, it will be easier to distinguish the peculiarities of the Fe-N central unit. The ligand σ orbitals, with binding energies from ~8 to 30 eV, do not interfere with these bonds; below ~8 eV the π-

Table II. Percent Composition of Top Filled and Lowest Empty Orbitals in the PcFe Monomer[a]

molec levels	occupancy[c]	N_α $2p_\sigma$[b]	N 2s	N $2p_\sigma$	N $2p_\pi$	Fe $3d_{x^2-y^2}$	Fe $3d_{z^2}$	Fe $3d_{xy}$	Fe $3d_\pi$ ($3d_{xz}$, $3d_{yz}$)	Fe 4s
$2b_{1g}$	0	1	3.5	41.8		49.7				
$2b_{2g}$	2	8.3					73.1			4.4
$2a_{1g}$	1	38.6		9.9				42.5		
$2e_g$	3				14.9				85.1	
$1b_{2g}$	2	36.0		5.1				55.3		

[a] Reference 20. [b] N_α = bridging nitrogen between two pyrrolic cycles (see Figure 1). [c] Numbers of electrons.

orbital contributions of very low photoelectric cross section[23] are masked by the background resulting from the stronger peaks with Fe 3d character.

Our results are in excellent agreement with the XPS spectra of Höchst et al.[12] and the UPS data of Battye et al.[24]

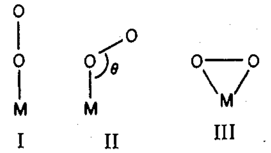
There are numerous theoretical models available for porphyrin-related systems but only one for complete phthalocyanine systems.[20] This semiempirical extended Hückel calculation has been used to produce the energy level diagram shown in Figure 8A. The atomic orbital contributions are summarized in Table II. According to this calculation, separation between LUMO ($2b_{1g}$) and HOMO ($2b_{2g}$, lying very close to $2a_{1g}$ and $2e_g$) is ~2 eV. The next occupied level is $1b_{2g}$.

We should mention here that the ordering of the three highest occupied levels is a matter of controversy between theoreticians and experimentalists: on the basis of magnetic susceptibility measurements, Dale[25] has suggested $2a_{1g} > 2e_g > 2b_{2g}$ (in eigenvalues).

The observation of four peaks in the spectrum fits this theoretical model, with three electrons occupying the $2e_g$ orbital and one in the $2a_{1g}$ orbital. The respective peak intensities, according to Gelius[23] are dominated by their relative Fe 3d character (the Fe 3d/N 2p photoelectric cross section ratio is 26.3[26]). Using the data of Table II for the only metal character, we find that the ratio of the $2e_g/2b_{2g}/2a_{1g}$ intensities approachs 100/33/29. This is reasonable when peaks 3, 2, and 1 in Figure 5 are examined (uppermost curve). Indeed, we have experimentally determined that the ratio of peak heights 3/2/1 is 100/38/30, very close to the theoretical prediction. Peak 4 is then $1b_{2g}$.

There are two peaks of particular interest in the valence band of the dimer which are not present for the monomer: a sharp peak at 6.9 eV (binding energy, E_b) and a small one at 0.9 eV, near the Fermi level. In agreement with our interpretation of the Fe 2p levels and their shake-up satellites, we attribute them to a highly covalent Fe–O_2 bond. The following reasons support this view. (i) Comparison with other nitriles studied in the solid phase[22] precludes the interpretation of the lowest E_b peak as lone pair or π electrons from the peripheral –CN groups, which are present in our sample (see Figure 1). (ii) The observed features are consistent with the changes expected with the bonding of an oxygen molecule.

This last statement requires a detailed analysis of the Fe–O_2 bond. Three geometries have been proposed for such synthetic oxygen carriers in general: linear (I),[27] bent (II),[28] and sideways perpendicular (III).[29]



Systems with central Fe^{2+} or Co^{2+} ions have been characterized crystallographically as belonging to structure type II, with 124° ≤ θ ≤ 155°.[30] Within this model, there are still two possible ways of interaction between O_2 and the metal ion: (A) $1\pi_g{}^a(O_2)$ with $2a_{1g}$ (mainly d_{z^2}) of PcFe (Figure 6), (B) $1\pi_g{}^{a,b}(O_2)$ with $2e_g$ (mainly d_{yz} and d_{xz}) of PcFe (Figure 7). The $1\pi_g(O_2)$ orbital being doubly degenerate, its contributions are noted with a and b superscripts. The first results from the $2p_x$ and $2p_z$ atomic orbitals combination and the second from the $2p_y$.[31]

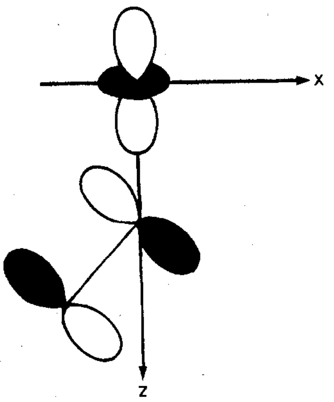


Figure 6. $2a_{1g}$ (d_{z^2})–dioxygen $1\pi_g$ interaction in the bent structure.

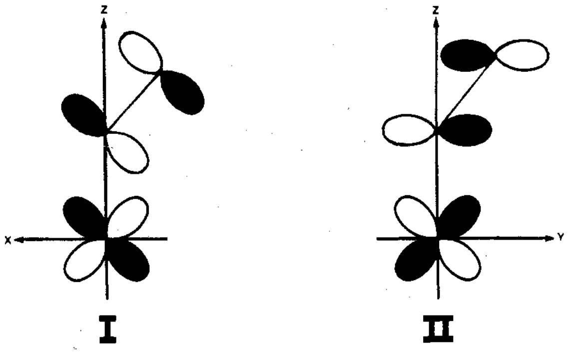


Figure 7. $2e_g$ (d_{xz},d_{yz})–dioxygen $1\pi_g$ interaction in the bent structure: I = $2e_g$ (d_{xz})–dioxygen $1\pi_g{}^a$, II = $2e_g$ (d_{yz})–dioxygen $1\pi_g{}^b$.

In complexes with highly ionic metal–oxygen bonds (such as oxygenated Co^{2+} Schiff base complexes, for which experimental data are available[32]), theoretical calculations[33] show that type A is predominant. On the contrary, when the bond is covalent (e.g., Fe(porph)O_2), mainly type B is found.[18] The present situation for PcFe dimer is very similar (see Fe 2p Levels section).

Recalling that the PcFe $2e_g$ orbital is triply occupied,[20] we have shown the filling of molecular orbitals arising from the overlap with oxygen $1\pi_g$ in Figure 8B. This diagram now permits an explanation of all pecularities reported for the active compound spectra, i.e., valence band, Fe 2p shake-up satellites, and EPR spectra (next section).

The two additional peaks in the valence bands are explained as due to the bonding and antibonding combinations of $2e_g$ and $1\pi_g$, the latter being simply occupied and close to the Fermi level. This electron, being in an orbital having d_π character (because of the Fe $3d_{xz}$ and d_{yz} overlap with the N $2p_\pi$ orbitals of the ligand), can be delocalized within the molecule through the π-electron system. The observation of a quasi-free electron in the EPR spectrum (described below)

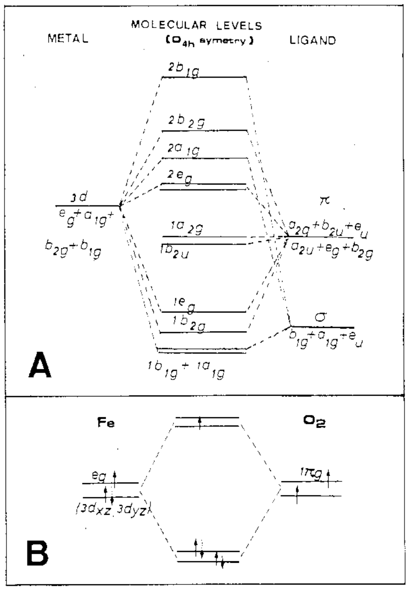


Figure 8. (A) Qualitative molecular energy levels for iron phthalocyanine monomer (after the EHMO calculation of A. M. Schaffer, M. Gouterman, and E. R. Davidson, *Theor. Chim. Acta*, **30**, 9 (1973)). For clarity, only the levels of the Fe–N central unit are mentioned. (B) Molecular energy levels concerned by Fe–O_2 bond in iron phthalocyanine dimer (schematic) (e_g level occupancy is taken from the same EHMO calculation).

supports this interpretation of the valence peak at 0.9 eV.

Finally, the Fe 2p shake-up satellite is better understood when the covalent Fe–O_2 bonding is taken into account. Here two possible explanations are suggested. (i) The electron jumps from the bonding to the antibonding $2e_g$–$1\pi_g$ combination; both belong to the same irreducible representation, and the antibonding orbital has a vacancy. This interpretation, however, requires a strong difference in relaxation energies for both orbitals, as the shake-up separation from the main Fe 2p peak is 4.2 eV smaller than the observed separation between the valence peaks under discussion. There is presently no evidence nor comparison in the literature to support this model. (ii) The shake-up satellite is due to the excitation of the least tightly bound electron to an unoccupied level. The D_{4h} symmetry of the active center is indeed broken by the bent bonding to O_2, and it should be possible to find an acceptor level having appropriate symmetry for the monopole selection rule. The present situation of theoretical models is too little advanced to provide the basis for a precise attribution.

Nevertheless, one thing is clear: the shake-up satellite is present only for the active compound, which forms a highly covalent bond with the oxygen molecule.

IV. EPR Results

Electron paramagnetic resonance spectra have been obtained for monomer, dimer, and polymer iron phthalocyanines on a Brücker B-ER-400 instrument operating in the X band at 9.5 GHz. Under the operating conditions, Fe^{2+} ions are not detected; they have only been observed at nearly liquid helium temperature. (See Table III.)

Iron phthalocyanine monomer examined in the atmosphere exhibits resonance signals corresponding to a small amount low-spin Fe^{3+}. At low temperature (110 K) we detect two Fe^{3+} species; one of the signals is very weak and is interpreted as the result of a small distortion around the paramagnetic center. (The iron atom is not perfectly coplanar with the four nitrogens.) On the other hand, oxygen stands in the O_2^- form, indicating a complete oxidation of a few sites.

For the **iron phthalocyanine dimer**, four resonance signals are obtained at g values of 2.0265, 4.2554, 5.2197, and 2.0038; the latter is much stronger than the three others. These first three lines can be identified, from recent theoretical calculations by Caro et al.,[7] as being due to intermediate-spin Fe^{3+}, present in low concentration. The strong line at $g = 2.0038$ is therefore explained as being due to quasi-free electrons. This is supported not only by the g value and by the symmetrical line shape but also by the ESCA valence peak observed at very low binding energy and by the charge delocalization over the whole molecule as deduced from the C 1s peak. We conclude that the quasi-free electron, originally localized in the Fe–O_2 antibonding orbital (see Figure 8B), is in fact delocalized over the whole molecule, through the conjugated π orbitals of the ligands (pyrrolic and benzenic rings).

Table III. EPR Spectroscopy Results[a]

samples	g values	explanation	temp, K
PcFe monomer	$g_\perp$, 2.2026	Fe^{3+} LS	298
	$g_\parallel$, 1.9432		
	g_{iso}, 2.0997	O_2^-	298
	$g_\perp$, 2.2093	Fe^{3+} LS	110
	$g_\parallel$, 1.9481		
	$g_\perp$, 2.0007	Fe^{3+} LS (less abundant)	110
	$g_\parallel$, 2.0530		
	g_1, 2.0969	O_2^- (better resolved signal)	110
	g_2, 2.1591		
	disappearance of less abundant Fe^{3+}		160
PcFe dimer	g_1, 2.0265; g_2, 4.2554; g_3, 5.2197	Fe^{3+} IS	298[b]
	g, 2.0038	≃ free electron	298[b]
PcFe polymer	g, 2.0041	≃ free electron	298[b]

[a] LS = low spin; IS = intermediate spin. [b] Low temperature measurements (liquid nitrogen) do not improve the signals.

Iron phthalocyanine polymer also exhibits a quasi-free electron signal, about 10 times weaker than the dimer. On the other hand, the electrocatalytic activity of the polymer[4] is also lower than that of the dimer. Both observations can be explained by a smaller number of active sites (i.e., covalent Fe–O_2 bonds, with an electronic structure as described in Figure 8B).

This interpretation provides a second relation between electrocatalytic activity and the intensity of a spectral line, together with that of the Fe 2p shake-up satellite discussed above.

V. Conclusions

From ESCA and EPR investigations of three iron phthalocyanines (monomer, dimer, and polymer), we have learned that the nature of the Fe species and its bonding with oxygen can be deduced from the Fe 2p photoelectron peaks, the presence or absence of oxygen being monitored by the O 1s peak, that details on the Fe–O_2 bond are observable in the valence-band spectra, and that the spin multiplicity can be confirmed by the Fe 3s spectra.

Other important results are relevant to the ligand electronic structure. In the dimer, particularly, charge delocalization is observed over the whole molecule.

Considering previous results obtained by Mössbauer spectroscopy[4] and crystal field calculations[7] on the same system, we can now conclude that the electrocatalytic behavior of iron phthalocyanine dimer is favored by the high degree of covalency of the Fe–O_2 bond, by the ease of dynamic electron transfer processes by the high π–d interactions,[4] as indicated by charge delocalization over the phthalocyanine ring, and by the readiness of the LS to HS (high spin) transition of iron, as deduced from the observation of some IS Fe^{3+} ions and from the multiplicity maps by Caro et al.[7]

The lower activity of the polymer corresponds both to different bonding characteristics (see Fe 2p shake-up satellites) and to poorer iron content. Crystal field parameters are probably such that the iron ions are less strongly bound to the lattice. This would explain the lower iron content found by ESCA.

In compounds where the $Fe–O_2$ is more ionic, the O_2^- radical which is formed is at the origin of other reactions, in particular the irreversible formation of hydrogen peroxide.

Looking at the results reported here, we anticipate that further studies on the initial or model compounds of these systems will shed light on these mechanisms.

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Registry No. PcFe monomer, 132-16-1; PcFe dimer, 70728-85-7; PcFe polymer, 70728-87-9; O_2, 7782-44-7.

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Reduction of the Bis(2,9-dimethyl-1,10-phenanthroline)copper(II) Ion by Substituted Hydroquinones

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Anaerobic stopped-flow kinetic studies of the reduction of the bis(2,9-dimethyl-1,10-phenanthroline)copper(II) ion ($Cu(dmp)_2^{2+}$) by 16 monosubstituted hydroquinones (H_2Q-X) have been performed ($\mu = 0.2$ M (acetate)). In each case, the rate law was found to be $d[Cu(dmp)_2^+]/dt = (k_1 + (k_2/[H^+]))[H_2Q\text{-}X][Cu(dmp)_2^{2+}]$ within the range pH 4–6 at 25 °C. The data are consistent with a mechanism involving reduction of $Cu(dmp)_2^{2+}$ by both the un-ionized and monoionized forms of H_2Q-X. For hydroquinone, rate constants (25 °C) and activation parameters associated with reduction of $Cu(dmp)_2^{2+}$ by H_2Q and HQ^- are 1.2×10^2 M^{-1} s^{-1} ($\Delta H^{*} = 15.6$ kcal/mol, $\Delta S^{*} = +3$ cal/(mol deg)) and 2.5×10^7 M^{-1} s^{-1} ($\Delta H^{*} = 12.5$ kcal/mol, $\Delta S^{*} = +18$ cal/mol deg), respectively. It is shown that Marcus theory for outer-sphere electron transfer accounts reasonably well for the dependence of rate on thermodynamic driving force in the reactions of both H_2Q-X and $(HQ\text{-}X)^-$ with $Cu(dmp)_2^{2+}$. Marcus theory calculations further demonstrate that the 10^5-fold reactivity difference between H_2Q-X and $(HQ\text{-}X)^-$ is entirely attributable to the more favorable standard free energy exchange for the latter substrate. Finally, comparisons are made between the electron-transfer reactivities of substituted hydroquinones with $Cu(dmp)_2^{2+}$ and the type 1 copper site in the metallo enzyme laccase.

Introduction

We have recently been interested in the factors governing the electron-transfer reactivity of substituted hydroquinones with copper-containing metallo enzymes and with low molecular weight transition-metal ion oxidants. Of particular interest is the relationship between rate and thermodynamic driving force in these systems. According to Marcus theory for outer-sphere electron transfer, the excess free energy of

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