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Interaction of Metal Porphyrins with Molecular Oxygen in Solutions

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The oxidation of divalent metal tetraphenylporphin complexes by molecular oxygen has been investigated in solutions. It was found that the one-electron oxidation of low-spin iron(II) complexes to yield high-spin iron(III) does not take place, while a low-to-low conversion proceeds with ease. It is suggested that the ready oxidation is due to the delocalization of the d_π electrons of iron(II) to the vacant π-orbital of the porphin ligand. Oxidative mechanisms of manganese(II) and cobalt(II) tetraphenylporphins were also discussed.

It is well known that iron porphyrin complexes take part in oxygen-carrying, electron transfer (redox reaction) and in decomposing hydrogen peroxide in biological processes. These subtle functions may be ascribable to both the iron porphyrin and the axial-ligand environment (protein), and they are quite informative in regard to catalysis.

In the present work, a much simpler reaction system is undertaken; the interaction of synthetic iron tetraphenylporphin (abbreviated to TPP) complexes (Fig. 1) with molecular oxygen is investigated in chloroform solutions, mainly by means of an ESR technique, with special attention paid to the electron-spin configurations of the central metal ion and its ligand environment. Since the spin state of iron in the porphin ring is changeable according to the coordinating capability of the axial ligand, the redox behavior of the iron will be affected more or less by its surroundings. Previous works[1-3]

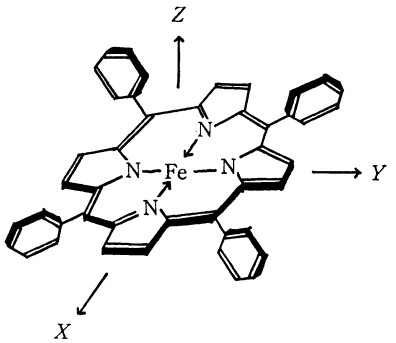

Fig. 1. Iron tetraphenylporphin. Four phenyl groups are bound perpendicular to the porphin plane.

1) K. Yamamoto, K. Marumo, K. M. Sancier and T. Kwan, "Recent Developments of Magnetic Resonance in Biological System," ed. by S. Fujiwara and L. H. Piette, Hirokawa Pub., Tokyo (1968), p. 164.

2) Y. Ogata, K. Marumo, and T. Kwan, *Chem. Pharm. Bull.*, **17**, 1194 (1969).

3) K. Yamamoto and T. Kwan, *J. Catalysis*, **18**, 354 (1970).

on cobalt phthalocyanine and cobalt TPP have, in fact, shown that the oxygenation and oxidation catalysis by these complexes are extensively influenced by the presence of axial ligands.

It is the purpose of the present paper to outline such a redox behavior of iron porphin complexes and to compare it with those of manganese and cobalt TPP complexes.

Experimental

Fe(III)-, Mn(III)-, and Co(II)-TPP complexes were prepared as usual[4] form metal(II) acetate and synthetic TPP. These complexes were dissolved in chloroform with or without a base which was expected to serve as an axial ligand (50—200 times or a saturated concentration). The axial bases used were tetrahydrofuran, quinoline, pyridine, 4-cyanopyridine, 4-methylpyridine, 4-aminopyridine, piperidine, imidazole, and benzimidazole.

Divalent iron and manganese complexes were prepared by reducing the corresponding trivalent metal TPP complexes with sodium dithionite($Na_2S_2O_4$). After the reduction treatment, the reducing reagent was removed from the solution by centrifugation. The concentrations of the metal complex usually ranged from 10^{-3} to 10^{-2}M. Throughout the procedure the complexes were kept in a dried nitrogen atmosphere.

The oxidation of metal(II) complexes was carried out by exposing their chloroform solutions to one atmospheric oxygen at room temperature. The ESR or optical absorption spectra were recorded before and after exposure to oxygen respectively. The ESR spectra were recorded at 77°K by means of a JEOL-P-10 (X-band) spectrometer with a 100-kcps field modulation.

Results and Discussion

Spin State of Iron(III) Complexes. Magnetic susceptibility measurements have served to provide information on the electronic configuration of ferrous or ferric ions. ESR methods have also provided supplementary information. Thus, theoretical analyses[5,6] have shown that high-spin iron(III) porphyrin complexes should exhibit ESR spectra with an axial symmetry at $g_\perp \sim 6$ and $g_{//} \sim 2$, while in low-spin complexes the anisotropic spectra of the three different g components are to be found near $g \sim 2$. The spin state of iron(III) porphin may thus be judged qualitatively from the shape of the obtained spectra.

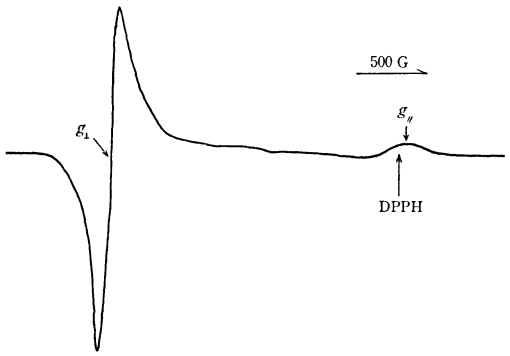

Fig. 2. ESR spectrum of Fe(III)-TPP-Cl in chloroform at 77°K. $g_\perp \sim 6$, $g_{//} \sim 2$.

A typical ESR spectrum of the Fe(III)–TPP complex in chloroform is shown in Fig. 2. It is apparent from the spectral shape of Fig. 2 that the complex is high-spin. The spin configuration is consistent with that determined by the magnetic susceptibility measurements.[7] When excess imidazole was added to this solution, the spectrum of Fig. 2 appeared to change greatly into that shown in Fig. 3 or into that characteristic of low-spin iron. The weak absorption around $g \sim 6$ is probably due to the contamination of high-spin iron.

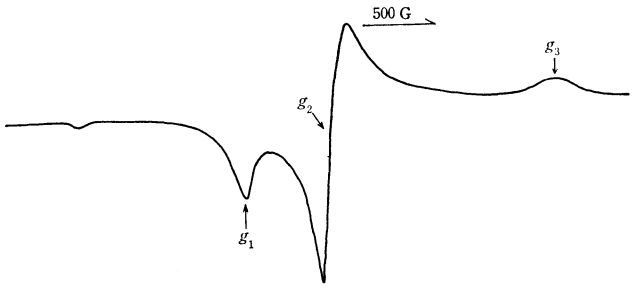

Fig. 3. ESR spectrum of [Fe(III)-TPP-2Im]Cl in chloroform at 77°K.
$g_1=2.98$, $g_2=2.31$, $g_3=1.52$.

A crystalline sample was then found to be isolable when repeated partial evaporation and centrifugation were carefully done. An elementary analysis of the isolated crystal indicated that its composition was consistent with [Fe–TPP–2Im]Cl(imidazole is abbreviated to Im); $C_{50}H_{36}N_8FeCl$, anal. (%), calcd., C: 71.47, H: 4.33, N: 13.34; found, C: 71.29, H: 4.47, N: 14.99. The sample redissolved in chloroform gave almost the same spectrum as that shown in Fig. 3. The diimidazole complexes may, hence, be regarded as stable in chloroform. Their formation may be expressed by:

$$\text{Fe(III)-TPP-Cl} + n\ \text{Im} \longrightarrow \text{[Fe(III)-TPP-2Im]Cl} + (n-2)\text{Im}$$

The ESR spectra of Fe(III)–TPP complexes coordinated with the other axial bases were further investigated; most complexes were found to be high-spin except that coordinated with 4-aminopyridine, which

Table 1. Electron spin states of Fe(III)-TPP complexes

Complex	ESR Spectra	Spin States
Fe(III)-TPP-Cl	$g_\perp=6.10$, $g_{//}=1.98$	high-spin
[Fe(III)-TPP-2B]Cl		
B: 4-cyanopyridine		
pyridine	$g \sim 6$	high-spin
4-methylpyridine		
4-aminopyridine	anisotropic	low-spin
B: imidazole	$g_1=2.98$, $g_2=2.31$, $g=1.52$	low-spin

4) P. Rothemund and A. R. Menotti, *J. Amer. Chem. Soc.*, **70**, 1808 (1948).

5) J. S. Griffith, "Molecular Biophysics", ed. by B. Pullman and M. Weissbluth, Academic Press, New York (1965), p. 191.

6) J. S. Griffith, Nature, **180**, 30 (1957).

7) H. Kobayashi, M. Shimizu, and I. Fujita, This Bulletin, **43**, 2335, 2342 (1970).

was low-spin. The inspection of these spectra permitted us to confirm that a large basicity of the axial ligand favors a low-spin configuration of iron. The electronic features of the Fe(III) complexes are illustrated in Table 1. It is interesting to note in the Table that the dipyridine iron(III) complex[8] is high-spin, whereas the diimidazole complex is low-spin. This somewhat remarkable difference between pyridine and imidazole ligands can probably be ascribed to the stronger basicity[9] and π-donating capability of imidazole as compared with those of pyridine.[10]

Spin State of Iron(II) Complexes. Low-spin iron(II) complexes have six *d* electrons in the t_{2g} (d_π) orbital, hence, they are diamagnetic. The ESR absorption for high-spin iron(II) complexes is difficult to measure, probably because of the short spin-lattice relaxation time. Fe(II)-TPP coordinated with various bases has, in fact, shown no ESR spectrum, indicating that this technique is inadequate as far as ferrous iron is concerned.

On the other hand, magnetic susceptibility data were available for Fe(II)-TPP complexes,[7] as is illustrated below:

	μ Bohr magneton
Fe(II)-TPP	4.75
Fe(II)-TPP-2THF	2.75
Fe(II)-TPP-2Py	0

Accordingly, the dipyridine iron(II) complex can be said to be low-spin, while Fe(II)-TPP is high-spin. Unfortunately, no information is available on the diimidazole iron(II) complex. However, it seems very probable, in view of the stronger coordinating capability of imidazole as compared with that of pyridine, that the diimidazole iron(II) complex is also low-spin.

Interaction of Oxygen with Iron(II) Complexes. The oxidative behavior of Fe(II)-TPP complexes has been investigated in the light of both ESR and optical absorption spectra before and after exposure to oxygen at room temperature respectively. Generally speaking, the reactivity of Fe(II)-TPP complexes appeared to vary extensively from one complex to the other. Here, we shall confine ourselves to some extreme cases.

The high-spin Fe(II)-TPP was readily oxidized to yield Fe(III)-TPP upon exposure to oxygen, whereas this was not the case with the low-spin Fe(II)-TPP-2Py. Since the latter complex is hexacoordinated, the fact that oxidation did not occur for Fe(II)-TPP-2Py would, at first sight, indicate that the axial pyridine can not be displaced by oxygen. This interpretation is not correct, however; the hexacoordinated Fe(II)-TPP-2Im complex appeared to be readily and reversibly oxidized under exactly the same reaction conditions as in the case of Fe(II)-TPP-2Py. Such interesting oxidative behavior of Fe(II)-TPP complexes is compared below, together with their electron-spin states (in parentheses).

$$\text{Fe(II)-TPP (high)} \longrightarrow \text{Fe(III)-TPP (high)}$$

$$\text{Fe(II)-TPP-2Py (low)} \dashrightarrow \text{Fe(III)-TPP-2Py (high)}$$

$$\text{Fe(II)-TPP-2Im (low)} \rightleftharpoons \text{Fe(III)-TPP-2Im (low)}$$

where $\longrightarrow$ indicates "oxidized", and $\dashrightarrow$, "not oxidized". In other words, "oxidized" means the formation of a Fe(III) complex when the corresponding Fe(II) complex is brought into contact with oxygen, while "not oxidized" means no spectral change.

As is shown above, the diimidazole Fe(II) and Fe(III) complexes were both low-spin. On the other hand, the dipyridine Fe(II) was low, with its oxidized form high. The change in the spin state of iron is remarkable for the one-electron oxidation of the dipyridine Fe(II) complex when compared with that for the diimidazole complex. According to X-ray analysis,[11] there exists a substantial difference in structure between the low-spin-iron-porphyrin and high-spin-iron-porphyrin complexes. For high-spin iron porphyrins, the iron atom is known to lie 0.40—0.50 Å out-of-plane from the four porphin-nitrogens, whereas for low-spin iron porphyrins it lies nearly in-plane, hence bringing about rather long bonds between the iron and the porphin-nitrogen, for high-spin iron porphyrins. Thus, a large energy is required for the one-electron oxidation of the Fe(II) complex accompanied by a change in the spin state. The structural difference may arise from the electronic difference that two electrons must be transferred from the nonbonding $t_{2g}(d_\pi)$ to the antibonding $e_g(d_\sigma)$ orbital for the high-spin complex (Fig. 4).

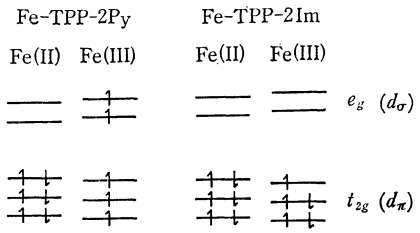

Fig. 4. Electron configuration of Fe-TPP complexes.

The ready oxidation of the diimidazole Fe(II) complex by molecular oxygen to yield Fe(III) is worthy of note, for the mechanism is perhaps associated with that in biological processes, for example, the effective electron transfer by hexacoordinated Cytochrome C. Mössbauer studies[12] of the Fe(II)-porphyrin bond has indicated that the electron of low-spin Fe(II) is extensively delocalized to the porphyrin ligand. Porphyrin itself is known to undergo facile reduction and

8) We were unable to isolate a crystalline dipyridine iron(III) because of some stickiness of the complex, unlike the case of diimidazole iron(III). On the other hand, the dipyridine protoporphyrin iron(III) complex has been isolated by us from a benzene-pyridine solution; $C_{44}H_{42}N_6FeCl$, anal. (%), calcd., C: 65.22, H: 5.24, N: 10.37; found, C: 64.71, H: 5.18, N: 9.69 (unpublished data). The ESR absorption lines of this complex were consistently explained if two pyridine molecules were assumed to be coordinated with the iron atom.[1]

9) pK_a-values: 5.18(pyridine), 1.80(4-cyanopyridine), 6.10(4-methylpyridine), 9.18(4-aminopyridine), 11.12(piperidine), 7.12-(imidazole).

10) L. M. Epstein, D. K. Straub, and C. Maricondi, *Inorg. Chem.*, **6**, 1720 (1967).

11) R. Countryman, D. M. Collins, and J. L. Hoard, *J. Amer. Chem. Soc.*, **91**, 5166 (1969).

12) T. H. Moss, A. J. Bearden, and W. S. Caughey, *J. Chem. Phys.*, **51**, 2624 (1969).

oxidation thus forming a variety of molecular complexes.[13,14]

It may be suggested, therefore, that the oxidation of the diimidazole Fe(II) complex by molecular oxygen takes place by means of a *long-range* interaction mechanism. One electron of the $t_{2g}(d_\pi)$ orbital of Fe(II) is delocalized to the vacant π-orbital of the porphin ligand. Electrons may thus be transferred to molecular oxygen close to the porphin ligand, although the position of the oxygen is still undetermined.

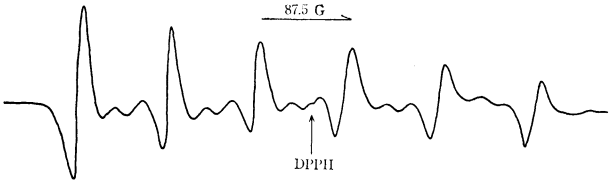

Fig. 5. ESR spectrum of Mn(II)-TPP in chloroform-imidazole solution at 77°K.

Interaction of Oxygen with Manganese(II) Complexes. The Mn(II)-TPP complex dissolved in chloroform gave rise to no ESR spectrum, but when excess amounts of imidazole are added it showed a resonance absorption near $g\sim2$. The spectrum consisted of six hf lines ($I=5/2$) and was characteristic of the high-spin state, provided that the zero field splitting parameters, D and E, are very small.[15,16] The signal is illustrated in Fig. 5. No ESR absorption was observed for most Mn(II)- and Mn(III)-TPP complexes on the addition of axial bases other than imidazole. However, since the magnetic moments have been reported to be in the range of 4.8—5.0 B.M. for a number of Mn(III) porphyrin complexes,[17] it would be highly probable that the Mn-TPP complexes are generally of the high-spin state.

No spectral change was observed when the imidazole Mn(II) complex was exposed to oxygen at room temperature, indicating that the complex was not susceptible to oxidation; we would expect the spectrum of Fig. 5 to disappear if the imidazole Mn(II) complex is oxidized. On the other hand, the Mn(II)-TPP complex was found to be readily oxidized in the absence of a base, because, on adding imidazole to the *oxidized* solution, we found no perceptible ESR spectrum; we should expect that type of spectrum (Fig. 5) to appear if the Mn(II)-TPP complex is not perceptible to oxidation.

Further observations were carried out on the Mn(II)-TPP complexes in the presence of other axial base, mainly by an optical technique. Some representative results are shown below. It is assumed that a dipyridine or diimidazole Mn(II)-TPP complex was formed in chloroform, although the complex was not isolated.

Mn(II)-TPP (high) ⟶ Mn(III)-TPP (high)

Mn(II)-TPP-2Py (high) —x→ Mn(III)-TPP-2Py (high)

Mn(II)-TPP-2Im (high) —x→ Mn(III)-TPP-2Im (high)

Interaction of Oxygen with Cobalt(II) Complexes. All of the Co(II)-TPP complexes coordinated with the axial ligand gave rise to ESR spectra characterized by eight hf lines, as is familiar in the case of cobalt ($I=7/2$). Some of them yielded three shf lines due to ligand nitrogen ($I=1$). The presence of the three shf lines suggests that the cobalt complex is coordinated with a *single* ligand molecule on its z-axis, unlike Fe(II)-TPP or Mn(II)-TPP

$$\text{Co(II)-TPP} + n\text{Py} \longrightarrow \text{Co(II)-TPP-Py} + (n-1)\text{Py}$$

A crystalline sample was isolated from the chloroform-pyridine solution on evaporation, and its composition was consistent with monopyridine complex, or $C_{49}H_{33}N_5Co$; calcd, C: 78.38, H: 4.44, N: 9.32; found, C: 78.38, H: 4.22, N: 9.63. This pentacoordinated form is probably due to the d^7 low-spin electronic configuration of Co(II).[3] The ESR spectrum for Co(II)-TPP coordinated with pyridine is shown in Fig. 6a.

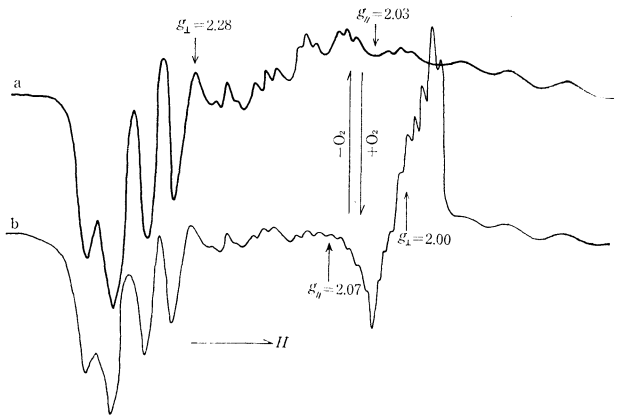

Fig. 6. ESR spectra of Co(II)-TPP-Py in chloroform at 77°K.
(a) evacuated; (b) exposed to O_2 for 10 min at room temperature.

When the Co(II)-TPP-Py complex was exposed to oxygen, the original signal due to Co(II) more or less decayed, while a new signal developed in the vicinity of $g\sim2$ (Fig. 6b). The spectral change was reversible as the oxygen pressures varied. The new signal near $g\sim2$ showed eight shf lines, suggesting that the molecular oxygen ion is formed and combined with cobalt.

An oxygenation took place irreversibly with the Co(II)-TPP coordinated with imidazole. In this case, no ESR signal was detectable after the irreversible oxygenation. The 3 d_{z^2} orbital energy of Co(II) rises especially when a strong base such as imidazole is coordinated. As a consequence, the unpaired electron of Co(II) may readily be transferred to the oxygenated cobalt complex, resulting in a diamagnetic, binuclear cobalt complex.[3] The complexing of oxygen is then no longer reversible.

13) H. A. O. Hill, A. J. Macfarlane, and R. J. P. Williams, *J. Chem. Soc.*, (A) **1969**, p. 1704.
14) J. Fajer, D. C. Borg, A. Forman, D. Dolphin, and R. H. Felton, *J. Amer. Chem. Soc.*, **92**, 3451 (1970).
15) M. Kotani, *Rev. Mod. Phys.*, **35**, 717 (1963).
16) R. D. Dowsing and J. F. Gibson, *J. Chem. Phys.*, **50**, 294 (1969).
17) L. J. Boucher, *J. Amer. Chem. Soc.*, **92**, 2725 (1970).

Summary

So far we have dealt with the oxidation of tetra-, penta-, and hexacooridnated transition metal(II) complexes differing in the spin state. In order to bring about a rapid oxidation, (1) the complexes should provide empty sites for oxygen, and (2) the activation energy should be low. These conditions seem to be fulfilled at least in the oxidation of Mn(II)-TPP, Fe(II)-TPP, and Co(II)-TPP-Py. Conversely, the oxidation will be slow or will be inhibited if empty sites are not available and if significant energy is required for electron transfer. Such a case is the oxidation of Fe(II)-TPP-2Py. These examples are obviously two extreme cases.

We have found an *intermediary* situation in the oxidation of the Fe(II)-TPP-2Im complex, where no more empty sites are available, but where the activation energy must be low enough because of the rapid oxidation that takes place. We have presented a *long-range* interaction mechanism between oxygen and the Fe(II) ion through a conjugated porphin ring. Kinetic data for the oxidation were only qualitative, but the interpretation was consistent with the electronic and structural properties of the complex.

Electron transfer *via* the so-called outer-sphere activated complex has been observed in the electron exchange reaction for $[Fe(CN)_6]^{4-} \rightleftharpoons [Fe(CN)_6]^{3-}$, $[Fe(phenantroline)_3]^{2+} \rightleftharpoons [Fe(phenantroline)_3]^{3+}$, and so on.[18] A net chemical reaction is not involved here. The electron transfer reaction demonstrated above between oxygen and Fe(II)-TPP-2Im thus constitutes a new aspect of the problem of electron transfer.

18) W. L. Reynolds and R. W. Lumry, "Mechanism of Electron Transfer," The Ronald Press, New York (1966), p. 13.