ESR STUDIES OF PORPHYRIN π-CATIONS:
THE $^2A_{1u}$ and $^2A_{2u}$ STATES*

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INTRODUCTION

Recent work has established that metalloporphyrins can be reversibly oxidized and that electrons can be abstracted from the organic moiety, from the chelated metal, or from both.\textsuperscript{1-7} ESR spectra of the radicals of zinc-meso-tetraphenylporphyrin (ZnTPP\textsuperscript{+}), and of magnesium octaethylporphyrin (MgOEP\textsuperscript{+}) provide clear evidence of electron removal from the porphyrin $\pi$ system but show marked differences in spin density distribution.\textsuperscript{5} Comparison\textsuperscript{6} of the optical spectra of several $\pi$ cations indicates that they fit into two classes represented by ZnTPP\textsuperscript{+} and MgOEP\textsuperscript{+}. The latter shows a major absorption band near 700 nm with a high energy shoulder, whereas the former exhibits several overlapping peaks in the region of 500–700 nm. We propose to review here the evidence for oxidation of the porphyrin $\pi$ system and to discuss the correlation between the experimental data and molecular orbital calculations which have led us to suggest the existence of two distinct ground states. These are typified by the radicals MgTPP\textsuperscript{+} or ZnTPP\textsuperscript{+} ($^2A_{2u}$) and MgOEP\textsuperscript{+} or ZnOEP\textsuperscript{+} ($^2A_{1u}$), which show remarkably different properties.

EXPERIMENTAL

Br\textsubscript{2}, Cl\textsubscript{2}, XeF\textsubscript{2}, ZnTPP\textsuperscript{+} ClO\textsubscript{4} (\(\varepsilon_{1/2} = 0.77\) V vs. sce) and (FeTPP)\textsubscript{2}O\textsuperscript{+} ClO\textsubscript{4} (\(\varepsilon_{1/2} = 0.84\) V) were used as oxidizing agents. Unless otherwise specified, (C\textsubscript{6}H\textsubscript{5})\textsubscript{4}NCl was the carrier electrolyte used for electrolysis. The techniques used for chemical oxidations, controlled potential electrolyses, coulometry, and optical and ESR measurements have been described.\textsuperscript{5-9}

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Deuterated Zinc Porphyrins

All the deuterated tetraphenylporphyrins were made by the same general procedure. 1.2 g of pyrrole were added to 1.8 g of benzaldehyde dissolved in ~80 ml of hot propionic acid – \(\text{d}_1\). This solution was refluxed for a half hour and then allowed to cool. The TPP was filtered out and crystallized from CHCl\(_3\)/MeOH. The crystals were chromatographed in CHCl\(_3\) on Merck alumina to remove chlorin, and recrystallized from CHCl\(_3\)/MeOH. Mass spectral analysis showed the following deuterium content: 2,4,6-dTPP = 98.8 %, 2,6-dTPP = 92.5 %, 3,5-dTPP = 98 %, 4-dTPP = 85.4 %. The zinc complexes were prepared by dissolving 50 mg of the TPP in ~10 cc of hot DMF. Excess ZnCl\(_2\) was added and the progress of the reaction was followed optically. Water was added, the solution cooled to room temperature, and ZnTPP collected by filtration, dried, and recrystallized from CH\(_2\)Cl\(_2\)/MeOH. This material was chromatographed twice on basic alumina and recrystallized from CH\(_2\)Cl\(_2\)/MeOH.

Magnesium Tetraphenylporphyrins

0.293 mmoles of TPP dissolved in 30 ml of benzene were slowly added (1.5 hr) at room temperature, and under argon, to a solution of 10 ml benzene containing 4.5 mmoles methyl-magnesium bromide. After 3 hr, excess Grignard was destroyed with 10 ml of 1 M ammonium chloride solution and 120 ml of benzene were added. The benzene layer was separated, washed three times with a 1M NH\(_4\)Cl solution, dried with anhydrous magnesium sulfate, filtered, and evaporated to 5 ml. The product was crystallized from CH\(_2\)Cl\(_2\)/CH\(_3\)OH.

4-Deuteriobenzaldehyde

\(\alpha\)-Bromotoluene (0.20 moles) in 50 ml of ether was added to 0.33 moles of Mg turnings in ether under N\(_2\). After the reaction had ceased, 45 ml of D\(_2\)O were added to the solution. The solid magnesium hydroxide was filtered off and washed with ether, and the combined ether-organic layer was dried and distilled to give 0.11 moles of 4-deuteriobenzene. The toluene was refluxed under white light while a stream of Cl\(_2\) was passed through it. The progress of the reaction was followed by NMR. The crude \(\alpha\)-\(\alpha\)-dichloro-\(p\)-deuteriobenzene was stirred with 50 ml of a slurry of 25 % Ca(OH)\(_2\) in water and heated to reflux. The product was extracted with CH\(_2\)Cl\(_2\) and distilled to give 0.02 mole of 4-deuteriobenzaldehyde.

2,6-Dideuteriobenzaldehyde

0.24 moles of \(\alpha\)-dichlorotoluene and 0.33 moles of Mg turnings were refluxed in 150 ml of THF; 20 ml of D\(_2\)O were added and the solution was stirred overnight under N\(_2\). After filtration and distillation, 0.19 moles of 2-chloro-6-dideuteriobenzaldehyde were recovered. This was dissolved in 100 ml of THF and refluxed for 24 hours with 0.25 moles of Mg turnings. After cooling, 20 ml of D\(_2\)O were added. Filtration and distillation gave 0.07 moles of 2,6-dideuteriobenzaldehyde. The procedure discussed was used to prepare the benzaldehyde.

3,5-Dideuteriobenzaldehyde

HCl was bubbled through a solution of 0.28 moles of \(p\)-toluidine in 300 ml of ether. When the reaction was complete the precipitate was filtered, giving 0.255 moles of \(p\)-toluidine HCl. This was dissolved in 100 ml of D\(_2\)O and refluxed for
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24 hr. The solvent was removed and the solid redissolved in 100 ml of D₂O and refluxed for another 24 hr. After repeating this procedure for a third time, the NMR showed essentially complete deuteration at the required positions. The dideuterotoluidine HCl was deaminated with hypophosphorous acid and NaNO₂ to give 0.064 moles of the 3,5-dideuteriotoluene. The benzaldehyde was prepared as discussed above.

2,4,6-Trideuteriobenzaldehyde

0.43 moles of aniline HCl were refluxed in 100 g of D₂O for 24 hr. The exchange with D₂O was carried out three times, until the NMR showed that the reaction was complete. The trideuterioaniline HCl was converted to the trideuteriobenzonitrile by diazotization followed by reaction with 36 g of CuCN and 30 g of KCN. After distillation 0.076 moles of the benzonitrile were recovered. The benzonitrile was converted to the benzaldehyde with SnCl₂, followed by hydrolysis.

Benzaldehyde-d₆

To a stirred solution of 0.11 moles of toluene-d₆ in 500 ml of 3.5N nitric acid at 75°C, under argon, was added 0.44 moles of ammonium hexanitro-cerate in 1200 ml of 3.5N nitric acid. The addition was carried out so that the reaction mixture stayed a pale yellow color (CeIV-solution). (This procedure requires 4–5 hours). The reaction mixture was then stirred at 75–85°C for another 2½ hr, cooled and extracted twice with chloroform. The combined organic layers were washed with sodium carbonate, water, and dried over magnesium sulfate. The solution was then filtered and the solvent removed on a rotatory evaporator. The crude benzaldehyde (11.8 g), contained minimal traces of unoxidized toluene and was used immediately without further purification.

Pyrrrole-d₅

0.747 moles of freshly distilled pyrrole, 0.82 moles of acetic acid-d₄ and 5.0 moles of deuterium oxide were equilibrated under argon for 6 hr at room temperature in the dark; 300 ml of dry CH₂Cl₂ were added and the aqueous suspension was neutralized by adding 0.835 moles of anhydrous potassium carbonate. The CH₂Cl₂ layer was separated, dried with anhydrous magnesium sulfate, filtered, and the solvent removed at room temperature and reduced pressure. The above exchange procedure was repeated twice to give 45 g of pyrrole-d₅ with greater than 95 mole % deuterium.

RESULTS AND DISCUSSIONS

The ²A₂₅ State

One-electron oxidations of selectively deuterated MgTPP, carried out electrochemically or by electron transfer from ZnTPP⁺ClO₄⁻ or (FeTPP)₂O⁺ClO₄⁻, yield the ESR spectra shown in Figure 1. The partially resolved 9-line spectrum of MgTPP⁺ does not change when the β pyrrole positions are deuterated in MgTPPₐ₈. On the other hand, a significant spectral narrowing does occur when the phenyl groups are deuterated, as illustrated for MgTPPₐ₂₀. In further agreement with the results obtained for MgTPPₐ₈, little difference is observed between MgTPPₐ₂₀ and the perdeutero compound MgTPPₐ₂₈. Additional resolution is obtained with
FIGURE 1. Second derivative ESR spectra of MgTPP$^+$ClO$_4^-$, MgTPP$_{d_{20}}^+$, MgTPP$^+$ d$_{20}$ (deuterated phenyls) and MgTPP$_{d_{28}}^+$ (perdeutero) in chloroform at room temperature. Computer simulation (dashed lines), gaussian line shapes, with the splitting constants shown, are overlapped on the top and bottom curves.

MgTPP$^+$ or MgTPP$_{d_{6}}^+$ at lower temperatures, as shown in Figure 2. In contrast to this behavior, the spectra exhibited by MgTPP$_{d_{20}}^+$ or MgTPP$_{d_{28}}^+$ do not vary with temperature. These data lead to the following interpretation: (1) The major nine lines are caused by the four equivalent nitrogens, since they are observed in all deuterated and nondeuterated species and, therefore, cannot be due to protons. (2) The additional small splittings observed at low temperature in MgTPP$^+$ cannot be due to the protons on the $\beta$ pyrrole positions, since the same splittings are observed in MgTPP$_{d_{28}}^+$. (3) The small splittings must be due to protons on the phenyl groups because of the above argument and because these splittings disappear upon deuteration of the phenyl groups.

A computer simulation which assumes four equivalent nitrogens with $a_N = 1.40$ G and eight equivalent hydrogens $a_H = 0.28$ G yields reasonable agreement with the room temperature spectrum of MgTPP$^+$, as demonstrated in Figure 1. (The values of $a_N$ and $a_H$ are determined directly from the experimental data at 25° and $-55^\circ$C). The better resolved spectra obtained at low temperatures can be simulated with the splitting constants shown in Figure 2, but an additional variable is required. Two spectra of a ratio of approximately 50:1 are used, the dominant one being the broad room temperature spectrum, the other having very narrow, well-resolved linewidths. (We have previously observed$^5$ a similar, very solvent dependent effect with ZnTPP$^{2-}$). The increased resolution normally obtained at low temperatures may be counter-
acted by weak aggregation effects of which the MgOEP⁺⁺ dimer is an extreme example.) Finally, the spectrum of the deuterated species MgTPPd₂₈ can be simulated as shown in Figure 1, by invoking four equivalent nitrogens, a₀ = 1.40 G and eight equivalent deuterons, with a₀ = 0.043 G (a₀ = 0.1535 a₉ because of the magnetic properties of the two isotopes).

The deuteration experiments described above clearly establish that in the MgTPP⁺⁺ radical the unpaired electron interacts with protons on the phenyl rings. We have previously observed the same effect in ZnTPP⁺⁺ and ZnTPPd₂₀ and postulated then that the main spin delocalization mechanism is the σ-π interaction due to overlap of the ortho protons of the phenyl group into the π cloud of the porphyrin which has a very high spin density, calculated and observed, at the meso positions. To test this suggestion further, we have prepared a series of partially deuterated ZnTPP⁺⁺ radicals. The results for ZnTPP⁺⁺, ZnTPPd₈ (meta), ZnTPPd₈ (ortho), ZnTPPd₁₂ (ortho and para) and ZnTPPd₂₀ at room temperature are shown in Figure 3. Clearly, although a significant line narrowing occurs by deuterating the ortho positions, the meta and to a lesser extent, even the para positions contribute to the overall line shape of ZnTPP⁺⁺. A splitting constant of 0.3 G (at -50°C) is still observed when the meta positions are deuterated and is therefore assigned to the ortho protons. (Preliminary ENDOR results on ZnTPP⁺⁺ in toluene also show proton splittings of -0.3 G.) The INDO treatment of benzyl radicals by Pople and Beveridge, modified for the case at hand, yields results compatible with the above observations. In addition, the observed splitting constants agree best with those values calculated for a dihedral angle of ~90° between the porphyrin and phenyl rings.

Alkyl substitutions in radical ions derived from benzene cause perturbations due partly to hyperconjugation and partly to inductive effects. In order to probe the spin density at the meso position of porphyrins, we have prepared the radical of zinc meso tetra( tert-propyl) porphyrin, Zn(Pr)₄P by oxidation with (FeTPP)₂⁺ClO₄⁻.
The results are illustrated in Figure 4. A reasonable computer fit requires four nitrogens $a_N = 1.47$ G and eight protons, $a_H = 2.94$ G. Although deuteration of the propyl groups is required to verify the assignment, these values of $a_H$ are close to the calculated value of 4–5 G for the CH$_2$ groups, whereas the β-CH$_2$ groups should show $a_H$ at least an order of magnitude smaller.\textsuperscript{20}

Delocalization of spin onto the metal was determined by incorporating zinc 67 (89.5\%) into ZnTPP$_{10}$. The spectrum of the radical produced by oxidation with (FeTPP)$_2$O$^+$ClO$_4^-$ is shown in Figure 5. A computer analysis yields $a_N = 1.45$ G, which is consistent with a previously determined value in CH$_2$Cl$_2$ and a value of $a_Zn = 1.22$ G for zinc 67 (I = §).

The charge of the cation radicals considered up to now was balanced by a perchlorate anion, which is an inert, noncomplexing ion. We consider now the effect of other counterions on the properties of these radicals. Oxidation of ZnTPP with bromine, chlorine or xenon difluoride leads to the corresponding radicals ZnTPP$^+$Br$^-$, ZnTPP$^+$Cl$^-$ and ZnTPP$^+$F$^-$, all of which exhibit absorption...
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**Figure 4.** Second derivative ESR spectrum of Zn(n-C\(_3\)H\(_7\))\(_4\)P\( ^{++} \)ClO\(_4^-\) in CH\(_2\)Cl\(_2\) with a simulation at the bottom.

**Figure 5.** First derivative ESR spectra of ZnTPP\( ^{++} \)ClO\(_4^-\) containing 90% \(^{67}\)Zn. Top: experimental; bottom: simulation using the constants shown.

spectra similar to that of ZnTPP\( ^{++} \)ClO\(_4^-\). Their ESR spectra are, however, quite different from the usual 9-line spectrum (Figure 3) of the ClO\(_4^-\) species, and can be interpreted\(^9\) in terms of an additional interaction of the ZnTPP\( ^{++} \) radical with the nuclear spin of the halide ions\(^1\) (I = \( \frac{1}{2} \) for F\(^-\), \( \frac{3}{2} \) for Cl\(^-\) and Br\(^-\)). These effects are

\(^1\) Similar hyperfine interactions of halide ions have been observed in chelated diimin radicals.\(^{21}\)
FIGURE 6. Second derivative ESR spectra. A (a) ZnTPP$^{+}$Br$^{-}$, (b) simulation 4 nitrogens, 1 bromine, (c) ZnTPP$^{2+}$Br$^{-}$ with nitrogens splitting partially resolved. B and C, CdTPP$^{+}$Br$^{-}$ and CdTPP$^{+}$Cl$^{-}$. D, MgTPP$^{+}$Cl$^{-}$ prepared by electrolysis in CH$_2$Cl$_2$ with 0.1 M (C$_2$H$_5$)$_4$NCl. Bottom curves in B, C and D are simulations: 4 nitrogens and one halogen. (See TABLE 1 for splitting constants.)
illustrated in Figure 6 for ZnTPP+·Br− and ZnTPP+·Br−, as well as for CdTPP+·Br−, CdTPP+·Cl− and MgTPP+·Cl−. In each case, a reasonable computer match is obtained by assuming the interaction of four nitrogens with one halide nucleus. (Note that the nitrogens remain magnetically equivalent.)

The halide interaction results in an increase in aN and a gradual shift in g values due to spin orbit coupling with the heavy counterions, as shown in Table 1. The explanation for the observed effects is twofold: first, we have already demonstrated that the nitrogens and the chelated zinc in ZnTPP+ carry some spin density, secondly, ZnTPP itself is complexed by a large number of anions such as F−, Cl−, Br−, I−, OH−, CN−, N3− and NO3− in the solvents used here. An example of this is shown in Figure 7, which compares the absorption spectra of ZnTPP (and ZnOEP).

<table>
<thead>
<tr>
<th>MTPP+·X−</th>
<th>aX/G*</th>
<th>aN/G*</th>
<th>g value</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnTPP+·Br−</td>
<td>8.11</td>
<td>1.60</td>
<td>2.006(±0.0003)</td>
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<tr>
<td>ZnTPP+·Cl−</td>
<td>8.78</td>
<td>1.61</td>
<td>2.0027(±0.0001)</td>
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<td>ZnTPP+·ClO4−</td>
<td>—</td>
<td>1.45</td>
<td>2.0025(±0.0001)</td>
</tr>
<tr>
<td>CdTPP+·Br−</td>
<td>3.81</td>
<td>1.90</td>
<td>2.005(±0.0003)</td>
</tr>
<tr>
<td>CdTPP+·Cl−</td>
<td>1.82</td>
<td>1.85</td>
<td>2.0030(±0.0002)</td>
</tr>
<tr>
<td>CdTPP+·ClO4−</td>
<td>—</td>
<td>1.61</td>
<td>2.0026(±0.0001)</td>
</tr>
<tr>
<td>MgTPP+·Cl−</td>
<td>1.51</td>
<td>1.52</td>
<td>2.0031(±0.0002)</td>
</tr>
<tr>
<td>MgTPP+·ClO4−</td>
<td>—</td>
<td>1.41</td>
<td>2.0028(±0.0001)</td>
</tr>
<tr>
<td>Zn(Pr)+·P+·Br−</td>
<td>8.8</td>
<td>1.5</td>
<td>2.0045(±0.0003)</td>
</tr>
<tr>
<td>Zn(Pr)+·P+·ClO4−</td>
<td>—</td>
<td>1.47</td>
<td>2.0026(±0.0001)</td>
</tr>
</tbody>
</table>

* Obtained from computer simulations.
† aB,79/aB,81 = 0.928.
‡ ac,35/ac,37 = 1.20.

in the presence of ClO4− and Cl− ions. CdTPP and MgTPP are similarly complexed but to varying degrees: for chloride ion, the relative equilibria are CdTPPCl− ≫ ZnTPPCl− ≫ MgTPPCl−. Stronger interactions between the charged MgTPP+ radical and the halide ion are, therefore, not surprising. (This can be demonstrated by cyclic voltammetry. ZnTPP is more easily oxidized in the presence of Cl− than ClO4−, ε1/2(ClO4−) − ε1/2(Cl−) is almost 0.2 V. These data indicate that the ZnTPP+·Cl− complex is more stable than the ZnTPP+·Cl− one.) The relative order of complexing constants of the parent molecule seems to be maintained in the corresponding radicals. Whereas the ESR spectra shown for CdTPP+·Cl− and ZnTPP+·Cl− are fully developed at 1:1 ratios of chloride to porphyrin, the MgTPP+·Cl− spectrum shown is only obtained at high chloride concentrations (0.01–0.1 M Cl−). We therefore ascribe the additional hyperfine interaction to the fact that the metal is complexed by the halide ion and that there exists a detectable spin density on the metal.

Finally, we call attention to another effect of an additional "ligand." Addition of oxygen to any of the radicals discussed here results in loss of hyperfine structure. This is illustrated in Figure 8, which shows the ESR spectra of ZnTPP+·ClO4− with and without oxygen. The effect is reversible: outgassing the solution, or simply
bubbling argon through it, will remove the oxygen and regenerate the original spectra. Thus, the oxygen is only weakly complexed to the cation radical.

In summary, the ground state under consideration here is characterized by: (1) high spin density at the *meso* position from which charge can overlap onto *meso* substituents such as phenyl or propyl groups; (2) enough spin density at the nitrogens to result in $a_n \approx 1-2 \text{ G}$; (3) no detectable spin density at the $\beta$ pyrrole positions, i.e., at the outer periphery; (4) enough spin density on the metal to yield values ranging from $1 \text{G}$ for $a_n$ to $6 \text{G}$ for $a_e$ [in $\text{Co_{III}}\text{TPP}^{2+}$ (Reference 5)]; and finally, spin density can be transmitted to an axial ligand as shown for $\text{MTPP}^{+}X^-$. We now contrast this behavior with that of the $^2A_{1g}$ state, which is typified by $\text{MgOEP}^{+}$ or $\text{ZnOEP}^{+}$. 

![Optical absorption spectra of ZnTPP and ZnOEP](image)

**Figure 7.** Optical absorption spectra of ZnTPP and ZnOEP in $\text{CH}_2\text{Cl}_2$ with 0.1M $(\text{C}_2\text{H}_5)_4\text{NClO}_4$ (----), after addition of 0.1M $(\text{C}_2\text{H}_5)_4\text{NCl}$ (-----).
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FIGURE 8. First derivative ESR spectra of ZnTPP· ClO$_4^-$ in CH$_2$Cl$_2$ with (0.2 atm) and without oxygen.

The $^2A_{1u}$ State

One-electron oxidations, chemical or electrochemical, of ZnOEP and MgOEP result in radicals with characteristic visible absorption spectra and singlet ESR signals.\(^{2,5}\) In methanol, at $-50^\circ$, the ESR spectrum of MgOEP$^+$ resolves\(^{5}\) into five lines, as shown in FIGURE 9. If the compound is deuterated at the meso positions, the singlet shown in FIGURE 9 is observed instead. The five lines of the MgOEP$^+$ can therefore be assigned to the four protons at the meso positions. The simplest simulations of the observed spectra require 4 protons, $a_H = 1.48$ G and 4 deuterons, $a_D = 0.227$ G for the deuterated species (FIGURE 9).

These results provide a direct measure of the spin density at the meso positions because the McConnell equation\(^{22}\) $a_H = Q_H a_C$ relates the proton hyperfine splitting to the spin density on the carbon to which the proton is attached. For aromatic cation radicals,\(^{22}\) $Q_H \approx 27$. If $a_H = 1.48$ G, then the spin density at each meso position equals $\approx 0.055$ and the four meso carbons account for $\approx 22\%$ of the unpaired spin density. Where is the remaining spin? Only two regions of the molecule would give rise to hyperfine interactions; these are the nitrogens and the ethyl groups on the β pyrrole positions. Since interactions with these nuclei are not obvious from the experimental data, we attempt a series of computer simulations in order to obtain some insight into the spin distribution in the radical.

We consider the nitrogens first. An assumed splitting constant of $a_N = 0.3$ G for the four nitrogens and the observed $a_H = 1.48$ G still reasonably account for the experimental spectrum elicited from MgOEP$^+$ as shown in FIGURE 10a. This is accomplished by narrowing all linewidths. If, however, the nitrogen splitting is increased by $50\%$, changing the linewidths no longer yields satisfactory simulation (FIGURE 10b,c) and a value of $a_N < 0.45$ G becomes an upper limit for the nitrogen constants.
When we consider the β pyrrole positions, delocalization of spin over the eight CH₂ groups would result in interactions with sixteen protons. A splitting constant of \( a_{H1} = 0.3 \) G added to the \( a_{H\text{meso}} = 1.48 \) G can again be reconciled with the experimental results by narrowing linewidths as shown in Figure 10d. The next simulations show the effects of a 50% increase in the methylene splitting constant. Clearly, these spectra do not resemble the experimental ones and therefore \( a_{H2} < 0.45 \) G.

We previously noted that in ZnTPP⁺⁺, which represents the \( ^{2}A_{2g} \) state, interaction with the metal can be established by incorporating \( ^{67}\text{Zn} \) into the molecule. Further delocalization of the electron on the gegenion is observed by substituting chloride or bromide ions for perchlorate. In contrast to these results, substitution of \( ^{67}\text{Zn} \) into ZnOEP, oxidation with bromine to yield ZnOEP⁺⁺Br⁻ or electrolytic oxidation in 0.1M \((\text{C}_3\text{H}_5)_2\text{NCI}\) carrier electrolyte to give ZnOEP⁺⁺Cl⁻ show very little effect on the ESR spectrum of ZnOEP⁺⁺. Although the spectra displayed in Figure 11 exhibit some linewidth variations, clearly no strong interactions with \( ^{67}\text{Zn} \) or the halide ions exist. Note that neutral ZnOEP is complexed by chloride ion as shown in Figure 7. In addition, cyclic voltammetry data indicate that it is easier to oxidize ZnOEP in the presence of \( \text{Cl}^- \) than with \( \text{ClO}_4^- \); the ZnOEP⁺⁺Cl⁻ radical is more stable, therefore, than the complex \([\text{(C}_3\text{H}_5)_2\text{N}]^+\text{ZnOEP}\text{Cl}^-\). The presence (and effect) of the halide ion on the radical is thus established. Conditions for observing hyperfine interaction between the radical and the halide ions seem to require that the metal be initially complexed and, secondly, that there exist a sufficiently large spin density at the metal and presumably at the nitrogens.

The question now arises what is the spin density distribution in these radicals. The meso positions account for only \( \sim 22\% \) of the unpaired electron. If we accept the computer estimates of 0.45 G for \( a_{N} \) and \( a_{H\text{meso}} \) (obviously these represent inflated
Figure 10. Second derivative ESR spectra of MgOEP\textsuperscript{2+} Cl\textsubscript{4}\textsuperscript{-} in methanol at \(-50^\circ C\): (a) experimental and simulated, assuming 4 meso protons and 4 nitrogens; (b) and (c) 50\% increase in \(a_N\) with different gaussian linewidths; (d) experimental and simulated, assuming 4 meso protons and 16 protons from the methylene groups; (e) and (f) 50\% increase in \(a_{\text{CH}_2}\) with different gaussian linewidths.

Figure 11. First derivative ESR spectra, in CH\textsubscript{2}Cl\textsubscript{2} of ZnOEP\textsuperscript{2+} Br\textsuperscript{-}, of ZnOEP\textsuperscript{2+} Cl\textsuperscript{-} (by electro-oxidation in 0.1 M (C\textsubscript{2}H\textsubscript{5})\textsubscript{4}N Cl) and of \(^{67}\text{ZnOEP}^{2+}\) Cl\textsubscript{4}\textsuperscript{-} (90\%\(^{67}\))Zn.
limits because the computer values were obtained for one or the other), and if we use reported McConnell-like equations, the four nitrogens and eight \( \beta \) pyrrole carbons account for, at best, another 20\% of the spin. The remaining 60\% can only be on the positions adjacent to the nitrogens. (This number represents a lower limit, since \( a_N \) and \( a\beta_H \) are overestimated.) We have now mapped the \( ^2A_{1u} \) state. More than 60\% of the spin is distributed among the eight C-1 carbons, 22\% is found on the four meso positions. The rest is divided among the nitrogens, the \( \beta \) pyrrole carbons and the metal.

**Correlations with the MO Calculations**

We have previously applied the self-consistent field molecular orbital method of Pariser, Parr and Pople to doublet states and used the \( \pi \) orbital model of Weiss, Kobayashi and Gouterman to predict absorption and ESR spectra of porphyrin radicals. Results of these calculations show that the energetic order of one-electron orbitals is the same as in the neutral porphyrin. For \( D_{4h} \) symmetry, the ground state configuration is \( (2e)^4(2a_{2u})^2(2b_{2g})^2(3e)^4(1a_{1u})^2(3a_{2u})^1 \), i.e., an electron has been removed from the \( a_{2u} \) orbital and the ground electronic state is \( ^2A_{2u} \). Spin density distributions after configuration interaction are listed in TABLE 2. The main feature of this state is the localization of spin on the meso-carbons and the nitrogens. If the electron is removed from the \( a_{1u} \) orbital instead, then the ground electronic state becomes \( ^2A_{1u} \). The energy separation between the two states is sensitive to changes in the MO parameters used and ranges between 1,500–2,000 cm\(^{-1}\). A change from \(-11.22 \text{ eV} \) to \(-11.90 \text{ eV} \) in \( \alpha_c \) for the meso carbon favors the \( ^2A_{1u} \) state by more than 1,100 cm\(^{-1}\) and leads to drastic changes in spin densities (TABLE 2). A characteristic of the \( ^2A_{1u} \) state is the low spin density on the nitrogens and the high localization on the C-1 carbons. Again, we emphasize the sensitivity of the predicted spin distribution to the choice of semi-empirical parameters. The calculations described here do yield the general features of the experimental optical absorption spectra and the different spin densities.

**TABLE 2**

<table>
<thead>
<tr>
<th>Atom</th>
<th>(^2A_{2u}) Calc.</th>
<th>(^2A_{2u}) &quot;Found&quot;</th>
<th>(^2A_{1u}) Calc.</th>
<th>(^2A_{1u}) &quot;Found&quot;</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-1</td>
<td>-0.0094</td>
<td>(&lt;0.02^*)</td>
<td>0.0981</td>
<td>&gt;0.075^*</td>
</tr>
<tr>
<td>C-2</td>
<td>0.0134</td>
<td>(&lt;0.01)</td>
<td>0.0262</td>
<td>(&lt;0.018)</td>
</tr>
<tr>
<td>C-5</td>
<td>0.1932</td>
<td>(~0.12^\dagger)</td>
<td>0.0012</td>
<td>0.055</td>
</tr>
<tr>
<td>N</td>
<td>0.049</td>
<td>0.05-0.08^\ddagger</td>
<td>0.000</td>
<td>(&lt;0.019)</td>
</tr>
</tbody>
</table>

* Leftover after allowances for other positions.
\^\dagger In Zn(C\(_5\)H\(_7\))\(_4\)P\(_4^+\) for \( a\beta_{H2} = 25 \text{ pc.} \)
\^\ddagger \( a_N = 24\rho N. \) \( a_N \) ranges from 1.2–1.9G.
What are the consequences of the two states, and can changes from one to the other be induced? We have previously noted that the cation radicals of cobaltic octaethyl-(or etio-)porphyrins exhibit optical spectra characteristic of either the $^2A_{1u}$ and $^2A_{2u}$ states, depending on the gegenions. The radicals with weak complexing anions such as $F^-$, $BF_4^-$, $CF_3COO^-$, $CF_3SO_3^-$ or $ClO_4^-$ show the $^2A_{2u}$ absorption spectra, whereas $[\text{Co}_{III}\text{Etio}]^{2+}2\text{Br}^-$ and $[\text{Co}_{III}\text{OEP}]^{2+}2\text{Br}^-$ display $^2A_{1u}$ absorption with concomitant differences in ESR characteristics. The primary compounds of horseradish peroxidase and catalase (those forms of the porphyrin-bearing enzymes that have lost two electrons) exhibit optical features which certainly suggest that the two states exist in these natural porphyrins as well. If that is true, the spin distribution in the two states may provide an explanation for the very different reactivities of the two enzymes.

ACKNOWLEDGMENTS

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DISCUSSION

DR. FUHRHOP (Braunschweig): Your evidence is almost complete and supports the formulation we made that all soft cations or all soft anions are polarizing the porphyrin π-cation radical ring. The cation is reacting to make a phlorin type of compound. For all the soft ligands, e.g., chloride and bromide, you get strong bands in the long wavelength region with the magnesium compound. We also find that when you do the same reactions in very dry methylene chloride, there is a strong absorption at 680 nm with the magnesium porphyrin radical giving only a third of its original extinction.

How did you make the silver complex radical? We found you can oxidize the silver porphyrin to get the trivalent silver complex which is diamagnetic and, therefore, is not a radical.

Dr. FAJER: The silver OEP complex does oxidize to silver III, and the ESR spectrum disappears entirely. The changes in the visible spectrum were small, which supports the theory that it is silver III. One can then oxidize that species and get the usual 2A1u radical. This requires potentials of about 1.4 volts in methylene chloride. I have not done the ESR of that species.

Concerning the phlorin postulate, the ESR evidence shows the four nitrogens or the four meso positions to be equivalent. If there were an addition at those positions, as you seem to suggest, this would certainly result in at least one proton being inequivalent, and should show up in the ESR spectrum.

Dr. FUHRHOP: No, I don't think it makes a covalent linkage, but I think the radical is just polarized by the soft ligands, making a phlorin type spectrum.