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Reactions of Metalloporphyrin π Radicals. 2. Thin-Layer Spectroelectrochemistry of Zinc Tetraphenylporphyrin Cation Radicals and Dications in the Presence of Nitrogenous Bases

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The oxidations of (TPP)Zn to radical cation and dication species in the presence of nitrogenous base ligands (substituted pyridines) are investigated in this work. Thin-layer spectroelectrochemistry is used to demonstrate the mechanistic pathway and reversibility of these reactions. Cyclic voltammetry and thin-layer spectra indicate that the first oxidation is simply the reaction

$$\text{(TPP)ZnL} \overset{e^-}{\leftrightharpoons} [\text{(TPP)ZnL}]^+$$

which is electrochemically and spectrally reversible. The mechanism for $[\text{(TPP)ZnL}]^+$ oxidation is EC by cyclic voltammetry, but $[(\text{TPP}(\beta\text{-py}))\text{Zn}]^{2+}(\text{ClO}_4^-)_2$ spectra show that this process too is spectrally reversible. Combined spectral and electrochemical characterizations rule out $[\text{(TPP)Zn}]^{2+}(\text{ClO}_4^-)_2$, $[\text{(TPP)ZnL}]^{2+}$, $[\text{(TPP)ZnL}_2]^{2+}$, and $[(\text{TPP}(\beta\text{-py}))\text{Zn}]^{2+}(\text{ClO}_4^-)_2$ as the product of the $[\text{(TPP)ZnL}]^+$ oxidation. The best remaining possibility is the formation of a pyridine–isoporphyrin derivative. Thin-layer cyclics for this compound show that the reverse reduction is a two-electron transfer back to (TPP)ZnL. However, on the time scale required to complete the experiment, a coproportionation reaction can occur between the isoporphyrin dication and TPPZnL to give spectral peaks for both $[\text{(TPP)ZnL}]^+$ and (TPP)ZnL. The $[\text{(TPP)ZnL}]^+$ formed is also ultimately reduced back to the starting (TPP)ZnL reactant.

Introduction

The mechanism of oxidized metalloporphyrin π-radical reactions with nucleophiles is a phenomena that is not well understood.[1] Previously, it had been believed that reaction with the cation radical did not occur,[2] but recent work has shown that nucleophilic substitution is possible at both the meso[3] and β-pyrrole positions.[4] In addition, reaction with the dication radical can lead to the formation of isoporphyrin[5] or meso-substituted porphyrin.[6]

Regardless of the actual mechanism involved, these reactions provide useful routes to new porphyrin compounds. However, synthetic considerations aside, the understanding of metalloporphyrin redox properties in the presence of nucleophiles, ligands, counterion, or solvent is most important from its parallel to photosynthetic or respiratory processes.[7-9] Only processes of a chemically reversible nature lend themselves to modeling of these more complicated biological systems, and it is in this light that the previously mentioned oxidized π-radical reactions were investigated.

In this paper reactions of the radical cation and dication of zinc tetraphenylporphyrin with nucleophiles were monitored by spectroelectrochemical techniques. This allows for determination of reaction reversibility in several minutes and also provides intermediate product spectra at all times. In short, this is a relatively easy method to follow in an exact manner the products and mechanistic pathways for this class of reactions. The (TPP)Zn system was picked as the test case for two reasons. It has been with this porphyrin that most of the β-pyrrole derivatives have been isolated.[4] In addition, previous studies in our laboratory have shown reversible electrochemistry for the cation radical reaction in the presence of ligand.[10] These apparent contradictions led us to reinvestigate this system to look for the causes of these alternate reaction pathways.

Experimental Section

Zinc tetraphenylporphyrin ((TPP)Zn) was prepared by the method of Adler et al.[11] and purified by chromatographay on neutral alumina. Ethylene chloride (EtCl_2) was Mallinckrodt reagent grade. Prior to use it was successively extracted from concentrated H_2SO_4, distilled water, and 5% KOH. The resultant extract was dried over anhydrous Na_2SO_4, distilled from P_2O_5, and stored in the dark over activated 4-Å molecular sieves. Acetonitrile was of spectral grade and stored over sieves. Tetrabutylammonium perchlorate (TBAP), used as supporting electrolyte, was obtained from Eastman Chemicals and recrystallized once from ethyl acetate/pentane. It was then stored until use under reduced pressure at 40 °C. The series of substituted pyridines used as ligands (L) in this study was obtined from Fisher Scientific and Aldrich Chemical Co. and was purified by standard literature methods. All other chemicals used were of reagent grade.

Cyclic voltammetric measurements were made in the conventional three-electrode configuration by applying a triangle wave input (Hewlett-Packard Model 3310B waveform generator) to a Princeton Applied Research (PAR) Model 364 polarographic analyzer. The resulting current–voltage curves were collected on a Houston Instruments Omnigraphic 2000 X–Y recorder at sweep rates of from 0.020 to 0.500 V/s. All solutions were 1.0×10^{-3} M in porphyrin and 1×10^{-1} M in supporting electrolyte. Ligand concentration ranged from 1×10^{-3} to 1 M.

Platinum buttons served as both the counterelectrode and working electrode for conventional cyclic voltammetric measurements. A 1000-lpi gold-minigrid working electrode sandwiched between two glass slides[12] and a platinum-gauze electrode were used in the thin-layer cell. In both cases a saturated calomel electrode (SCE), separated from the test solution by a fritted supporting electrolyte/solvent bridge, was used as the reference electrode.

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Table I. Ligand Concentrations Used To Provide >99% Complexation of $[(TPP)ZnL]^+$ [a]

ligand	pK_a [b]	$\log \beta_1^{+\,c,d}$	[L], M
3,5-dichloropyridine	0.67	1.64	1.0
4-cyanopyridine	1.86	2.23	5.8×10^{-1}
3-bromopyridine	2.84	2.87	1.3×10^{-1}
4-acetylpyridine	3.51	3.25	8.4×10^{-2}
pyridine	5.29	3.98	1.1×10^{-2}
3-picoline	5.79	4.00	1.0×10^{-2}
3,4-lutidine	6.46	4.59	1.0×10^{-2}
4-(dimethylamino)pyridine	9.71	5.60	1.0×10^{-2}

[a] Concentration of (TPP)Zn used was 1.0×10^{-3}. [b] K. S. Schoefield, "Hetero-Aromatic Nitrogen Compounds", Plenum Press, New York, 1967, p 146. [c] Reaction: $[(TPP)Zn]^+ + [L] \rightleftarrows [(TPP)ZnL]^+$. [d] Reference 10.

Spectrocoulometry was performed by both bulk electrolysis and thin-layer techniques. The bulk cell followed the design of Fajer et al.[13] and had an optical path length of 0.19 cm. The path length of the thin-layer cell was found to be 0.006 cm by both spectrophotometric and electrochemical calibration. In addition to spectrocoulometry, cyclic voltammetry (at sweep rates of from 1 to 4 mV/s) was performed in the thin-layer cell. The spectroelectrochemical cells were coupled with a Tracor Northern 1710 optical spectrometer/multichannel analyzer to obtain time-resolved spectra. The spectra result from the signal averaging of 100 5-ms spectral acquisitions. Each acquisition represents a single spectrum from 325 to 950 nm, simultaneously recorded by a diode-array detector with a resolution of 1.2 nm/channel.

Porphyrin concentrations were 1.0×10^{-4} M in the bulk cell and 2.5×10^{-4} and 1.0×10^{-3} M in the thin-layer cell. This allowed monitoring of the visible bands in both cells and of the Soret band in the thin-layer cell. Supporting electrolyte was 0.1 M in the bulk cell and 0.5 M in the thin-layer cell, and ligand concentrations were adjusted to at least the minimum value which would give greater than 99% complexation for the radical cation. These concentrations were calculated from the formation constants of the cation radicals as determined previously by Kadish et al.[10] and are listed in Table I.

Methoxy- and hydroxyisoporphyrin have been previously observed for the reaction of $[(TPP)Zn]^{2+}(ClO_4^-)_2$ with methanol or water.[5] Thin-layer cyclic voltammetry was used in this study to observe the spectral characteristics and the pathway of electrochemical formation and reversibility for these compounds. These results are compared with those for (TPP)Zn oxidations in the presence of nitrogenous base ligands.

The possibility for other than axial ligation to the cation radical and dication or isoporphyrin formation has been discussed in the literature.[3,4,6] A $[(TPP(\beta\text{-py}))Zn]^+(ClO_4^-)$ product has been isolated from the reaction of the radical cation with py in acetonitrile.[4] To further investigate this pathway, which disagrees with our electrochemical results,[10] we repeated the previous synthetic work. In addition, aliquots of the radical cation in $EtCl_2$ and acetonitrile were generated in the bulk coulometry cell, titrated with specific excess ligand, and monitored spectrally.

Finally, attempts were made to isolate the product of the dication product in the presence of py. A solution 7×10^{-3} M (TPP)Zn with a 10-fold excess of py in 0.1 M TBAP/$EtCl_2$ was electrolyzed at 1.25 V. The resultant product was rotovaped, extracted with benzene, and characterized by visible–near-IR spectra. These results are compared to those found in the thin-layer cell.

Results and Discussion

Previous spectroscopic[14–16] and electrochemical results[10] have shown that both the neutral and cation radical of (TPP)Zn are monoligated in the presence of sufficient nitrogenous base. In this study, using cyclic voltammetry, the oxidation to the ligated cation radical proceeds reversibly to quasireversibly with increased concentrations of low pK_a ligands. However, for ligands of $pK_a \geq 6.46$ the reverse scan at highest ligand concentrations shows a slight decay in the magnitude of the reduction process. This result is indicative of excess ligand oxidation by the radical as will be demonstrated later. The results for the oxidation to the dication species in the presence of two selected ligands are illustrated in Figure 1. An EC mechanism is indicated for curves 2 and 3 since there is no reduction process coupled to the oxidation peak at 1.1 V. In addition, for ligands of highest pK_a the current for dication formation is greater than a one-electron transfer when compared to the dication formation with no ligand present. This indicated either oxidation of excess ligand or a catalytic regeneration of previous species with subsequent reoxidation or some combination of both. The products for both the forward and reverse steps of the second oxidation are thus in question, and the mechanism operative cannot be quantitated solely on the basis of cyclic voltammetry.

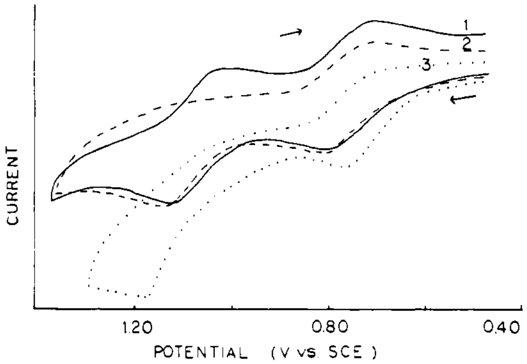

Figure 1. Cyclic voltammograms for (TPP)Zn oxidations in the presence of nitrogenous bases: (1) none (—); (2) 3,5-dichloropyridine (- - -); (3) 4-(dimethylamino)pyridine (···).

Thin-layer coulometry was performed by aspirating the porphyrin/ligand solution into the slide assembly and electrolyzing with spectral monitoring. As opposed to bulk coulometry, which required 30–45 min for a complete electrolysis, the thin-layer oxidations produced by voltage steps required only 30 s for complete conversion from (TPP)ZnL to $[(TPP)ZnL]^+$ and a maximum of 150 s for conversion from (TPP)ZnL to the dication species. For oxidations from (TPP)ZnL to $[(TPP)ZnL]^+$, it was found that 1.0 ± 0.1 electron was transferred with use of ligands of pK_a less than that of 3,4-lutidine. For oxidations from (TPP)ZnL to the dication product 2.0 ± 0.2 electrons were transferred for ligands of pK_a less than that of 3-picoline. Complexation of ligands above these values showed increased oxidative behavior which thin-layer blanks verified as ligand oxidation. The resultant uncertainty in the coulometry precludes the reporting of *n* values for these species. The reverse reductive coulometry was as expected within the described pK_a limits. However, above these limits less than 1 and 2 electrons were transferred to obtain the original (TPP)ZnL spectra. This suggests that the cation radical and dication had been spontaneously reduced by oxidizing the excess ligand. This was tested in the thin-layer cell by forming the dication product and then placing the working electrode at open circuit. Results are shown in Figure 2 for pyridine and 3,4-lutidine. It is quite apparent that reduction of the dication species by pyridine proceeds to only a limited extent in 5 min while that by 3,4-lutidine proceeds reversibly back to (TPP)ZnL in 2 min. Thus, the coulometry trends and spectral results are consistent. This trend for autoreduction of an oxidized porphyrin by a complexed nitrogenous base ligand has been observed previously[17,18] and is

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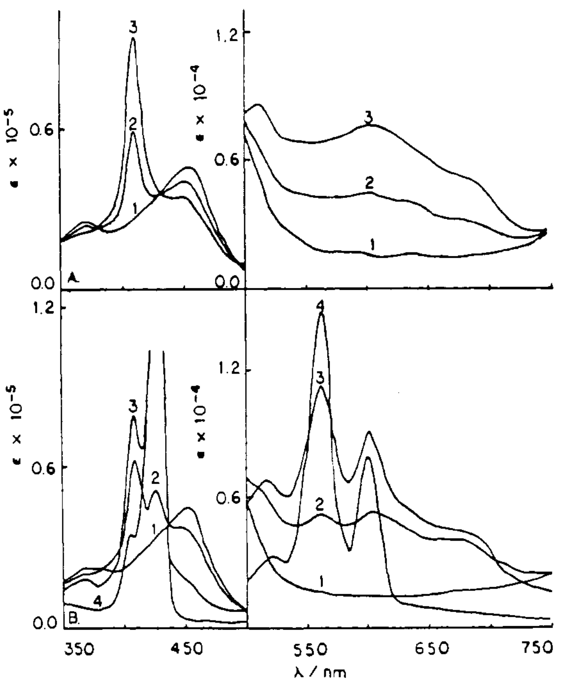

Figure 2. Time-resolved thin-layer spectra for the reduction of the dication species by ligand at open circuit. (A) Pyridine: (1) 0; (2) 150; (3) 300. (B) 3,4-Lutidine: (1) 0; (2) 30; (3) 60; (4) 120. Times are listed in seconds.

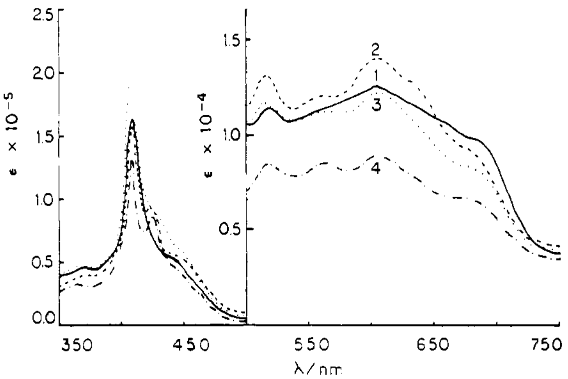

Figure 3. Thin-layer spectra for cation radical species in the presence of ligand: (1) none (—); (2) 3-bromopyridine (- - -); (3) pyridine (···); (4) 3,4-lutidine (-·-).

certainly reasonable at these potentials.

For oxidations from (TPP)ZnL to $[(\mathrm{TPP})\mathrm{ZnL}]^+$ at the ligand concentrations listed in Table I, the spectra of Figure 3 resulted. The primary differences between the $[(\mathrm{TPP})\mathrm{Zn}]^+(\mathrm{ClO}_4^-)$ spectrum (no. 1) and the $[(\mathrm{TPP})\mathrm{ZnL}]^+$ spectra (no. 2–4) lies in the different intensities of the Soret bands at 409 nm and the broad bands of the visible region. Over the time scale of this experiment, that is 1 min to step from (TPP)ZnL to $[(\mathrm{TPP})\mathrm{ZnL}]^+$ and back again, spectral reversibility is noted for all solutions.

At the same solution concentrations the spectra shown in Figure 4 were obtained for the second oxidation. These spectra could be obtained by oxidation from either (TPP)ZnL or from $[(\mathrm{TPP})\mathrm{ZnL}]^+$. $[(\mathrm{TPP})\mathrm{Zn}]^{2+}(\mathrm{ClO}_4^-)_2$ (no. 1) is essentially a featureless low-intensity spectrum in the visible–near ir region and agrees with the published spectra of this complex.[5] However, in the presence of ligand a peak is found at 454 nm for the final product of the cation radical oxidation. That this

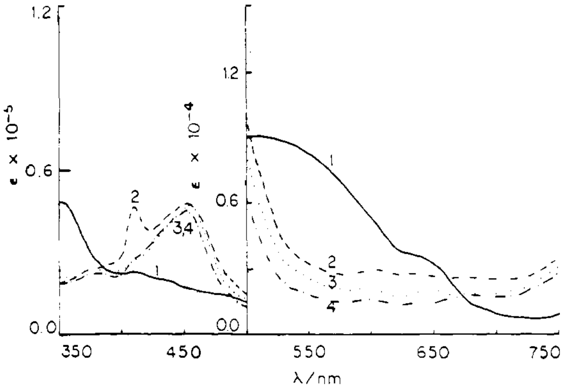

Figure 4. Thin-layer spectra for dication species in the presence of ligand: (1) none (—); (2) 3-bromopyridine (- - -); (3) pyridine (···); (4) 3,4-lutidine (-·-)

peak was not in fact due to excess ligand oxidation was verified by thin-layer blanks. Similar to $[(\mathrm{TPP})\mathrm{ZnL}]^+$, these dication spectra are also not too sensitive to the specific ligand present. This lack of sensitivity for both species with nitrogenous bases is not surprising considering that the differences for (TPP)Zn spectra with counterions (ClO_4^-, Br^-, Cl^-, F^-) are rather striking,[14] while the spectra for the cation radical complexed with these same counterions are essentially identical.[19]

The peak at 454 nm for the dication product is somewhat similar in intensity and position to the literature Soret peaks for methoxy and hydroxy zinc isoporphyrins (~440 nm).[5] Comparitive thin-layer cyclics and dication product spectra are shown for (TPP)Zn with methanol and pyridine in Figure 5. If in fact the dication–pyridine adduct is some form of isoporphyrin, its ratio of Soret to near-IR bands is much greater than that for the cation isoporphyrins. In addition, over the time scale for the thin-layer cyclics (15 min), the solutions with substituted pyridines were spectrally reversible. This was not the case for methoxyisoporphyrin as it could not be reversibly reduced to the starting (TPP)Zn compound.

The thin-layer cyclics of Figure 5A make one fairly obvious point. While theory predicts the same peak potentials for the forward and reverse scans of a reversible redox couple[20] (i.e., eq 1) in practice there is a finite peak separation. This is

$$(\mathrm{TPP})\mathrm{Zn} \overset{e^-}{\rightleftharpoons} (\mathrm{TPP})\mathrm{Zn}^+ \tag{1}$$

caused by a voltage drop due to the solution resistance in the thin-layer slide and results in a lag of the effective applied voltage to the actual applied voltage. This effect must be remembered in interpreting all thin-layer experiments as the effective voltage only catches up as the current goes to zero.

While a pyridine–isoporphyrin derivative has been implicated as the possible dication product, the question still remains as to by what pathway it reversibly returns to (TPP)ZnL. So that this question could be answered, thin-layer cyclic voltammetry with spectral monitoring was performed. Results are shown in Figure 6 for (TPP)Zn oxidations and reverse reductions in the presence of pyridine. The forward oxidations show the expected behavior. However, the reverse reduction is quite interesting. There is only minimal reversal of the dication spectra until the foot of the reduction peak at point 2 of Figure 6A. At this point spectral peaks due to $[(\mathrm{TPP})\mathrm{ZnL}]^+$ begin to appear. These grow through approximatley

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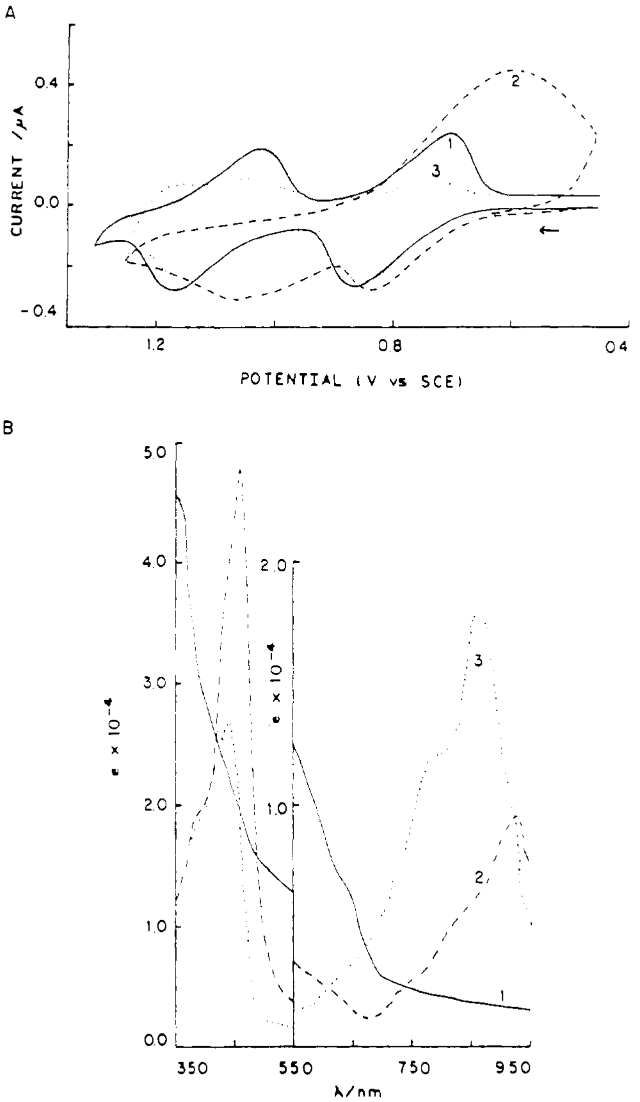

Figure 5. (A) Thin-layer cyclics for TPPZn oxidations in the presence of (1) no nucleophile (—), (2) 10:1 py:(TPP)Zn (---), and (3) 10:1 MeOH:(TPP)Zn (···). (B) Corresponding thin-layer spectra for the dication species with (1) no nucleophile (—), (2) 10:1 py:(TPP)Zn (---), and (3) 10:1 MeOH:(TPP)Zn (···).

40% of the reduction peak and then begin to disappear as (TPP)ZnL peaks grown. There are two possible explanations for this effect. The first is that two successive one-electron transfers of slightly differing potentials are melded into one peak. The slight IR losses then allow some of the $[(TPP)ZnL]^+$ to be reduced to (TPP)ZnL before all of the dication is reduced to $[(TPP)ZnL]^+$. The other possibility is a two-electron transfer of the dication product resulting directly in (TPP)ZnL. This then coproportionates with the dication to give $[(TPP)ZnL]^+$ spectral peaks. The relative concentrations of the three species would implicate the latter mechanism, but the result is not completely conclusive.

As a further check of this point, bulk coulometry was performed by stepping from 0.0 to +1.20 V and back again. The dication product formed was similar but not identical with to that found in the thin-layer cell. However, upon reverse reduction it returned greater than 90% to the starting (TPP)ZnL reactant. In this case a two-electron reduction should occur. However, once again peaks were observed for $[(TPP)ZnL]^+$ in the approximate concentrations required to describe a coproportionation reaction.

Finally, an aliquot of the dication product was generated at +1.20 V in the bulk cell and placed at open circuit. This species was titrated with aliquots of (TPP)Zn and monitored spectrally. Again the coproportionation mechanism is indicated as the (TPP)ZnL peaks disappear, the dication peaks decrease in intensity, and the $[(TPP)ZnL]^+$ peaks appear and grow in intensity. Further electrochemical reduction of this species at 0.0 V regenerates the (TPP)ZnL spectra.

This explains the pathway but not the exact identity of the dication product. Attempts at preparative-scale coulometry provided for synthesis of similar isoporphyrins, but these do not match those found in the thin-layer cell (Figure 7). It is probable that the 5-h time scale required for this preparation resulted in some formation of hydroxyisoporphyrin as well as the pyridine adduct.

Thus, we believe that the mechanism for the oxidative electrochemistry of (TPP)Zn in the presence of nitrogenous base ligands can be explained by Scheme I.

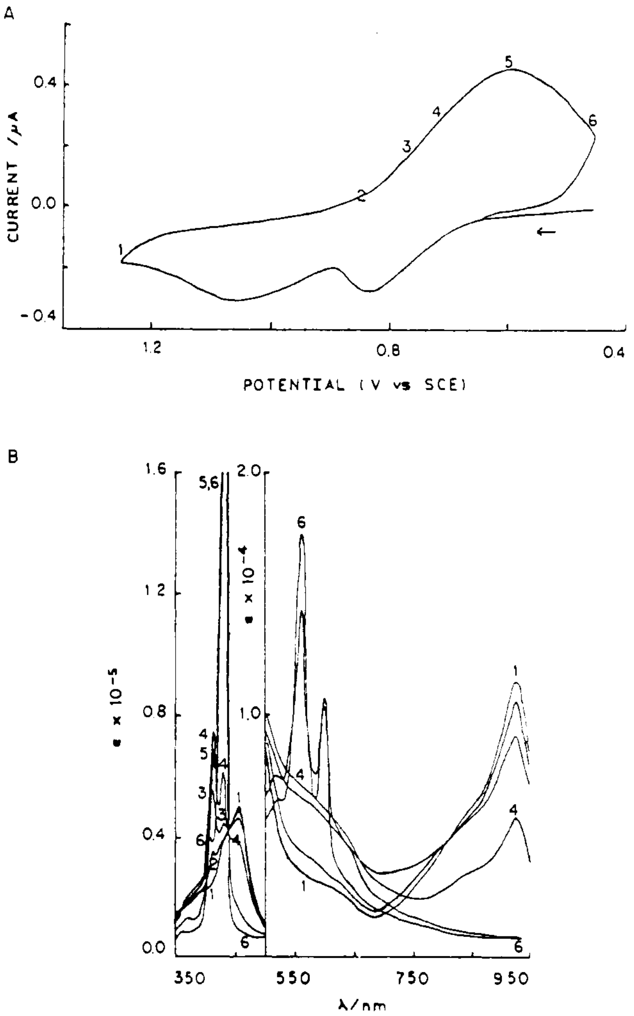

Figure 6. (A) Thin-layer cyclic for (TPP)Zn oxidations in the presence of pyridine and (B) voltage-resolved thin-layer spectra for the same oxidations: (1) +1.25 V; (2) +0.85 V; (3) +0.77 V; (4) +0.72 V; (5) +0.60 V; (6) +0.45 V.

Scheme I

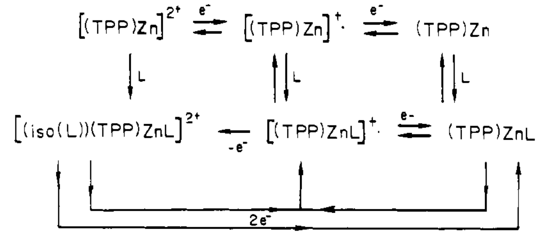

Table II. Spectral Characterization of (TPP)Zn and $[(TPP(\beta\text{-py}))Zn]^+(ClO_4^-)$ with and without 1×10^{-2} M Pyridine[a]

	Soret		β		α			
compd	λ, nm	ε/10⁵	λ, nm	ε/10⁴	λ, nm	ε/10⁴	β/α	ref
(TPP)Zn	419	5.7	548	2.5	586	0.5	5.14	this work
(TPP)Zn + py	427	6.0	562	2.4	601	1.1	2.24	this work
$[(TPP(\beta\text{-py}))Zn]^+(ClO_4^-)$	427	2.7	555	1.7	594	1.3	1.30	21
$[(TPP(\beta\text{-py}))Zn]^+(ClO_4^-)$	427	1.7	558	1.3	596	1.0	1.32	this work
$[(TPP(\beta\text{-py}))Zn]^+(ClO_4^-)$ + py	437	1.9	571	0.9	615	0.9	1.10	this work

[a] Spectra taken in $EtCl_2$ at total porphyrin concentration of 5.0×10^{-5} M.

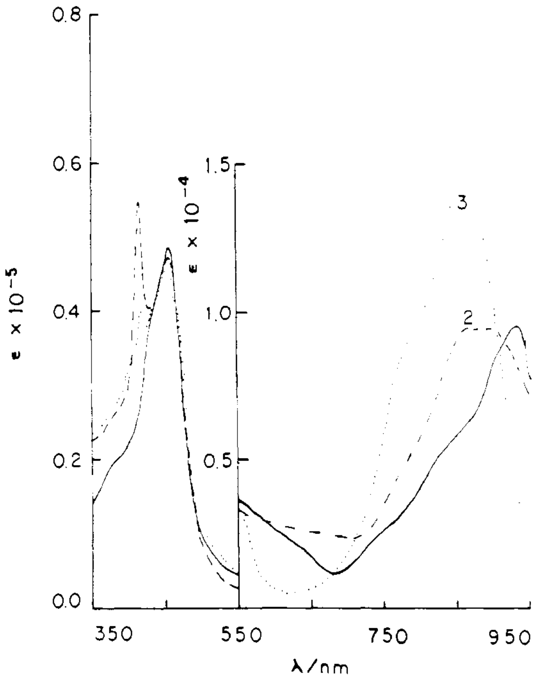

Figure 7. Dication species spectra in the presence of pyridine for (1) thin-layer oxidation (2.5 min) (—), (2) bulk coulometry oxidation (1 h) (- - -), and (3) preparative scale coulometry (5 h) (···).

It is interesting that there appeared to be no formation of the previously reported $[(TPP(\beta\text{-py}))Zn]^+(ClO_4^-)$ from this oxidative sequence. Since the structures are somewhat similar, the possibility of spectral overlap needed to be ruled out. To do this, $[(TPP(\beta\text{-py}))Zn]^+(ClO_4^-)$ was synthesized and characterized spectrally and electrochemically. The electrochemistry in $EtCl_2$ for $[(TPP(\beta\text{-py}))Zn]^+(ClO_4^-)$ showed a reversible oxidation/reduction at 0.92 V and an irreversible process at 1.27 V. Addition of 1×10^{-2} M py made the first process irreversible and obliterated the second process. The thin-layer spectroelectrochemistry reflected this chemical irreversibility in 1×10^{-2} M py by only returning about 60% of the spectra of the starting porphyrin reactant.

The maximum wavelengths and extinction coefficients for both (TPP)Zn and $[(TPP(\beta\text{-py}))Zn]^+(ClO_4^-)$ in $EtCl_2$ and $EtCl_2/1 \times 10^{-2}$ M py are shown in Table II. Elemental analysis of our product showed some inclusion of solvated py and explains the slight spectral differences between our work and the previous work. Mixtures of (TPP)Zn and $TPP(\beta\text{-py})Zn^+ClO_4^-$ in pyridine show that formation of the complexed β-pyrrole species will be reflected more in the loss of intensity for the (TPP)Zn(py) spectra than in the appearance of the $[(TPP(\beta\text{-py}))Zn(py)]^+(ClO_4^-)$ spectra. This can be seen more clearly in Figure 8 for the addition of py at open circuit to electrochemically generated $[(TPP)Zn]^+(ClO_4^-)$ in $EtCl_2$ and acetonitrile. In $EtCl_2$ only $[(TPP)ZnL]^+$ and (TPP)ZnL are present until enough py is added to entirely reduce the radical. In acetonitrile the (TPP)ZnL spectra and the final spectra are not the same and indicate a final mixture of approximately 50% (TPP)Zn(py) and 50% $[(TPP(\beta\text{-py}))Zn(py)]^+(ClO_4^-)$. Thus, a change in oxidative mechanism occurs with change in the solvent system.

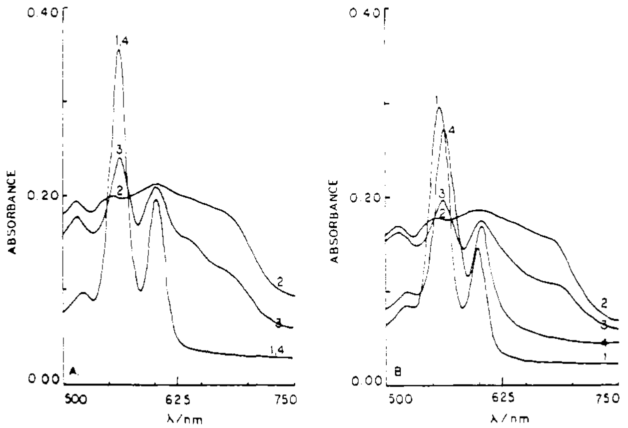

Figure 8. Spectral monitoring of the addition of pyridine to $[(TPP)Zn]^+(ClO_4^-)$ in (A) $EtCl_2$ and (B) acetonitrile: (1) standard (TPP)ZnL spectra; (2) $[(TPP)Zn]^+(ClO_4^-)$; (3) $[(TPP)Zn]^+(ClO_4^-)$ + 10L; (4) $[(TPP)Zn]^+(ClO_4^-)$ + 1000L.

Conclusions

The oxidative mechanism of (TPP)Zn + L in ethylene dichloride is not straightforward. For ligands of pK_a less than that of 3,4-lutidine the first oxidation process occurs in an electrochemically quasi-reversible fashion. At ligands of higher pK_a, the slight loss of peak current for the reverse reduction is nothing more than partial reduction of the ligated cation radical by excess ligand. However, for all ligands the process is chemically reversible.

The mechanisms for the cation radical oxidation and the dication reduction are classified as EC by conventional cyclic voltammetry. Questions as to the identity of the dication species and the eventual products of its reduction need to be answered. Thin-layer spectroelectrochemistry shows that the dication species is reversibly reduced to the starting reactant (TPP)ZnL. Thin-layer cyclics with spectral monitoring shows the reduction peak to probably be a two-electron transfer; the dication species being first reduced to (TPP)ZnL which can coproportionate with the remaining dication to give $[(TPP)ZnL]^+$. This ligated cation radical is then further reduced back to (TPP)ZnL.

In identifying the dication species, combined spectral and electrochemical evidence rules out the loss of a ligand to form the uncomplexed dication. This same information also rules out the possible formation of either a (β-py) substituted pyrrole or bis-liganded dication. The shift from 350 to 454 nm for the Soret peak indicates an interruption in the conjugation of the porphyrin π system, most likely due to the formation of a pyridine–isoporphyrin dication derivative. Attempts at preparative scale coulometry result in compounds of isoporphyrin character. However, the time-scale stability of these compounds result in slightly different species than those found in the thin-layer cell.

While the chemical reversibility of the oxidations of (TPP)ZnL in $EtCl_2$ seen here is interesting, it is at variance with previously reported work in acetonitrile. It is surprising that no measurable quantity of the (β-py) derivative is formed and suggests that the solvent system plays an important role in the intermediate stablization of two possible oxidative pathways. Since the isolation of the (β-py) derivative was easily repeated and the $[(TPP)ZnL]^+$ titration showed mixed species spectra, this solvent effect must indeed be operative. It should be noted, however, that even with the 500-ms time scale of our spectral acquisitions we cannot determine the exact nature of the intermediates in these pathways. Spectral changes were instantaneous with ligand addition.

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Registry No. (TPP)Zn, 14074-80-7; $[(TPP(\beta\text{-py}))Zn]^+(ClO_4^-)$, 60165-30-2; py, 110-86-1; 3,4-lutidine, 583-58-4; 3,4-dichloropyridine, 55934-00-4; 4-(dimethylamino)pyridine, 1122-58-3; 3-bromopyridine, 626-55-1; MeOH, 67-56-1.

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Molecular Structure of Phosphaferrocene and Charge Density Distribution at Low Temperature

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X-ray diffraction measurements have been performed at 74 K on the sandwich complex dimethylphosphaferrocene. The molecular geometry is discussed and compared to room-temperature results. A qualitative study of the charge density distribution (X–X method) shows an analogy with ferrocene in the metal region. A strong peak in the phosphorus region is indicative of a localized lone pair. This is in apparent contradiction with the electrophilic character of phosphorus, deduced from chemical and spectral properties.

A chemical and spectroscopic (NMR and mass spectra) study of phosphaferrocene has demonstrated the aromaticity of the phospholyl group in this complex, in sharp contrast to uncomplexed phospholes C_4H_4PR.[1] Thus, whereas phosphole acetylation takes place at the P atom, phosphaferrocene is exclusively acetylated on the C atoms of the phospholyl nucleus. The question was asked whether the electrophilic character of phosphorus in the complex implied a delocalization of the P lone pair.

In an attempt to answer this question, we performed low-temperature X-ray diffraction measurements in order to determine experimentally the charge density distribution in dimethylphosphaferrocene (X–X method). The crystal structure of the same compound had already been determined at room temperature.[2]

Experimental Section

A crystal of the title compound has been grown by sublimation under vacuum at 40 °C and ground into a sphere. A few general and crystallographic data are given in Table I. There is no phase change between room temperature and 74 K. The low-temperature cell dimensions were determined by accurate centering of 12 reflections and their Friedel equivalents at $+2\theta$ and -2θ (Mo $K\alpha_1$, $65° < 2\theta < 70°$).

Details of the experimental conditions are given in Table II. The measurements were performed on a Picker diffractometer equipped with a beryllium cryostat. A stable temperature of 74 K was maintained by circulation of liquid nitrogen under depression.

Table I. General and Crystallographic Characteristics for (η^5-Cyclopentadienyl)[η^5-(3,4-dimethyl-1-phosphacyclopentadienyl)]iron

formula $(\eta^5\text{-}C_5H_5)[\eta^5\text{-}PC_4H_2(CH_3)_2]Fe$ or $C_{11}H_{13}PFe$; $M_r = 232.04$

monoclinic, space group $P2_1/n$;[a] $Z = 4$

cell dimensions at 293 K:[2] $a = 12.292$ (4) Å, $b = 10.824$ (3) Å, $c = 7.831$ (2) Å, $\beta = 91.60$ (4)°, $V = 1041.5$ Å^3, $\rho_{calcd} = 1.48$

cell dimensions at 74 K: $a = 12.092$ (1) Å, $b = 10.667$ (1) Å, $c = 7.767$ (1) Å, $\beta = 91.73$ (1)°, $V = 1001.4$ Å^3, $\rho_{calcd} = 1.54$

[a] In ref 2, the space group was mistakenly reported as $P2_1/c$.

Table II. Diffraction Measurements and Data Processing

wavelength = 0.709 30 Å (Mo $K\alpha_1$)
temp = 74.0 ± 0.5 K
sample size: diameter = 0.24 ± 0.01 mm
absorptn: $\mu = 16.10$ cm^{-1}; transmission factor between 0.751 and 0.758
monochromator: graphite; $2\theta_{min} = 11.66°$
continuous $\omega/2\theta$ scan; speed in $2\theta = 2°$/min
scan interval in 2θ: $2.3° + \alpha_1\alpha_2$ separation
bkgd measurement: during 20 s at each end of the scan interval
no. of measured reflctns: 14853 (2 crystallographically equivalent sets); 3635 independent reflections with $(\sin\theta)/\lambda < 0.76$ Å^{-1}; 3976 independent reflections with $(\sin\theta)/\lambda > 0.76$ Å^{-1}
agreement between equivalent reflections: $R = \Sigma\langle|I - \langle I\rangle|\rangle/\Sigma\langle I\rangle = 0.046$ (0.023 for $(\sin\theta)/\lambda < 0.76$ Å^{-1})

Three standard reflections were measured after every 60 regular measurements. The variation of their intensity as a function of time was used to determine an overall time-dependent scale factor. A locally written Fortran program (STANDARD) was used for this purpose. Values of the scale factor (and its esd) are obtained by averaging over groups of ten consecutive standard reflection intensities. Linear interpolation is then used to determine the scale factor of any given reflection and to modify accordingly the esd of its intensity. This procedure also enables to estimate the variance σ^2 of individual intensities before scaling from the observed dispersion within each group

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