

The copper dopants in the zinc ap3d compounds show a rather large rhombic distortion, as deduced from the g values of the ESR spectra. The differences observed in A_{\parallel} for the Cu and Cu-doped Zn compounds must originate from small differences in coordination geometry for the Cu^{2+} ions.

Concluding Remarks

The ligand ap3d appears to be a pentadentate nitrogen donor ligand toward first-row transition-metal ions.

In all compounds studied the coordination geometry is close to octahedral, the coordination being completed by a water molecule. The constraint of the propylene bridge is much less than that of the ethylene bridge, as is deduced from the amine-

Co-amine bond angle. In this way the elongation of the bridge was a successful attempt. This means that with aptd (the tetrakis(pyrazole) derivative of 1,3-diaminopropane) an octahedral coordination geometry can be expected (if the synthesis of aptd is ever successful).

Future research on ap3d and analogous ligand systems will be directed to determine which factors are responsible for the incompleteness of the amine substitution.

Acknowledgment. We are indebted to S. Gorter for the collection of the crystallographic data.

Supplementary Material Available: Listings of fractional coordinates of the hydrogen atoms, interatomic distances and bond angles and anisotropic thermal parameters of the non-hydrogen atoms, observed and calculated structure factors, and analytical data (9 pages). Ordering information is given on any current masthead page.

(12) *Chem. Eng. News* 1983, 61 (Dec 5), 4.

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Redox Chemistry of Tetrakis(3,5-di-*tert*-butyl-4-hydroxyphenyl)porphine and Its Zinc(II) Complex in Dimethylformamide

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Received May 31, 1985

In dimethylformamide both the free ligand tetrakis(3,5-di-*tert*-butyl-4-hydroxyphenyl)porphine and its zinc(II) complex exhibit electrochemistry that is characteristic of a combination of porphyrin and a hydroquinone (or catechol). Thus, the aromatic character of the tetraphenol derivative stabilizes the one-electron-oxidation products of the porphine anion and of the anion for the zinc(II) porphyrin and results in reversible electron transfer. The zinc(II)-porphyrin complex catalyzes the two-electron reduction of dioxygen.

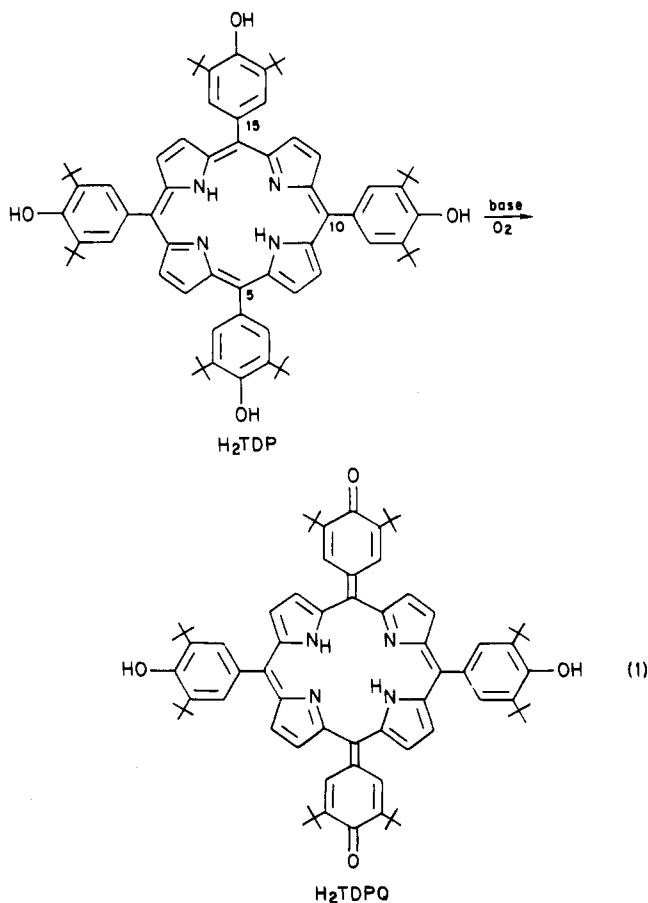
There have been several recent reports of the chemical oxidation of tetrakis(3,5-di-*tert*-butyl-4-hydroxyphenyl)porphine (H_2TDP) to a stable quinone-like product (H_2TDPQ),¹⁻⁵ similar to a 5,15-dioxoporphodimethene.⁶ One example of such a reaction is its autoxidation under alkaline conditions (eq 1). Oxidation products of metalloporphyrins derived from H_2TDP also have been reported, but their quinone character is less firmly established.¹⁻⁵

The present electrochemical and spectroscopic results provide a more complete characterization of the redox chemistry available to H_2TDP and its zinc derivative, ZnTDP , as a consequence of their dual functionality: porphyrin and polyphenol. The electrochemistry of aromatic diols and quinones in aprotic media is well characterized and generally follows the sequence diol anion \rightleftharpoons semiquinone anion \rightleftharpoons quinone.⁷ Electrochemical formation of π -cations and π -anions in porphyrins also has been studied extensively and is the subject of a recent review.⁸ The goal of this study has been to determine how the well-defined redox behavior of the phenolic and porphyrin functions is manifested in H_2TDP and its zinc derivative.

Experimental Section

Equipment. The cyclic voltammetric (CV) and controlled-potential electrolysis (CPE) measurements were made with a three-electrode potentiostat that was equipped with a Universal programmer and digital coulometer (Princeton Applied Research Model 173-175/179). Cyclic voltammograms were recorded on a Houston Instruments Series 100 X-Y recorder.

The cell for cyclic voltammetry consisted of a Bioanalytical Systems Microcell Assembly (BAS-MF 1065) modified to accommodate a platinum-button or glassy-carbon (GCE) working electrode, a platinum-flag auxiliary electrode, and an Ag/AgCl reference electrode filled with aqueous tetramethylammonium chloride and adjusted to 0.000 V vs. SCE.⁹ The reference electrode was contained in a Pyrex tube with a



cracked soft-glass tip. This assembly was placed inside a Luggin capillary that contained 0.1 M electrolyte in the appropriate aprotic solvent. A

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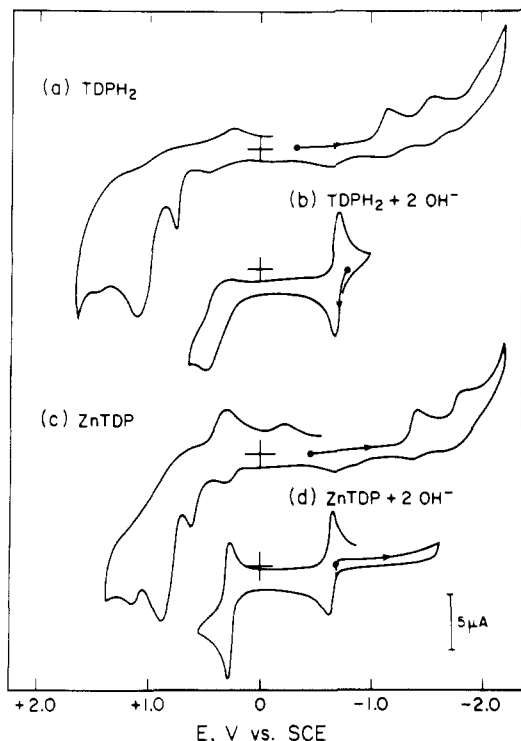


Figure 1. Cyclic voltammograms in DMF (0.1 M TEAP) of (a) 1.0 mM H_2TDP , (b) 1.0 mM H_2TDP plus 2 equiv of hydroxide ion (tetraethylammonium hydroxide in water), (c) 1.04 mM $ZnTDP$, and (d) 1.04 mM $ZnTDP$ plus 2 equiv of hydroxide ion (scan rate 0.1 V s^{-1} ; Pt electrode surface area 0.11 cm^2).

platinum-mesh working electrode was used for the controlled-potential electrolysis experiments. The cell was closed with a Teflon cap that included holes for purging with high-purity argon and the introduction of samples.

UV-visible absorption spectra were obtained with a Cary Model 219 or a Kontron 820 spectrophotometer, and IR spectra with a Nicolet Model 4000 or Nicolet Model 5000 FTIR spectrometer. ESR spectra were obtained on a Bruker Model ER 200D spectrometer.

A Vacuum Atmospheres drybox that employed a Model HE-43 DriTrain was used for experiments with air-sensitive compounds.

Reagents. Dichloromethane, *N,N*-dimethylformamide (DMF), and acetonitrile (Burdick and Jackson Laboratories "distilled in glass") were used as received. Tetraethylammonium perchlorate (TEAP) and tetrabutylammonium perchlorate (TBAP) (both G. Frederick Smith) were crystallized from methanol and stored in vacuo before use as the supporting electrolyte. Tetraethylammonium hydroxide ((TEA)OH, 25% in methanol, Eastman) was used as received after the molarity had been determined by acid-base titration.

Porphyryns. Tetrakis(3,5-di-*tert*-butyl-4-hydroxyphenyl)porphine (H_2TDP) was synthesized by the Adler method¹⁰ (equimolar 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde (Aldrich) and pyrrole in refluxing propionic acid).^{5,11} The zinc complex ($ZnTDP$) was prepared by reacting an excess of $Zn(OAc)_2 \cdot H_2O$ with the porphyrin in $CHCl_3/MeOH$.¹² Both porphyrin compounds were purified by low-pressure

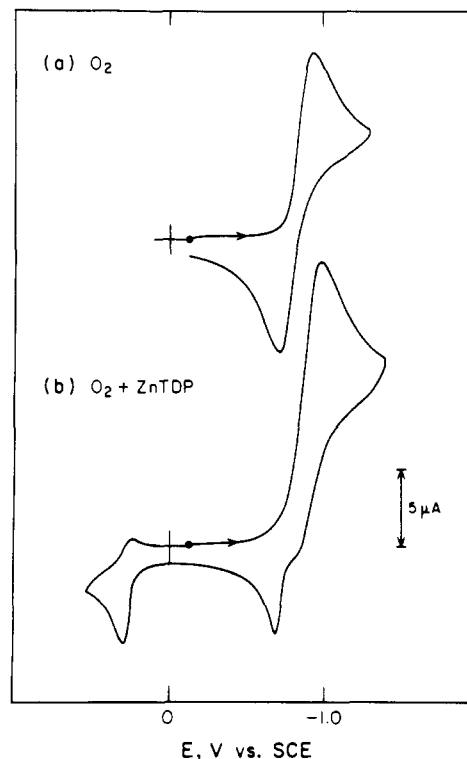


Figure 2. Cyclic voltammograms in DMF (0.1 M TEAP) of (a) 0.9 mM O_2 (air saturated) and (b) 1.0 mM $ZnTDP$ and 0.9 mM O_2 (scan rate 0.1 V s^{-1} ; Pt electrode surface area 0.11 cm^2).

Table I. UV-Visible Spectral Data for Basic Solutions of 0.1 mM H_2TDP and $ZnTDP$ and for Their One-Electron-Oxidation Products in MeCN (0.1 M TEAP) under N_2

soln	wavelength, nm (ϵ , $\text{mM}^{-1} \text{ cm}^{-1}$)			
	$TDPH_2 + 2OH^-$	280 (21)	410 (86)	481 (30)
$ZnTDP + 2OH^-$	280 (21)	404 (80)	478 (84)	755 (38)
$TDPH_2 + 2OH^- - e^-$	294 (22)	415 (34)	555 (52)	715 (51)
$ZnTDP + 2OH^- - e^-$	255 (39), 292 (17)	448 (52)	570 (52)	760 (52)

HPLC (silica gel PF, toluene), recrystallized from chloroform by slow evaporation of the solvent, and characterized by their visible and IR spectra.^{5,5}

Electrochemical experiments for air-sensitive compounds were carried out in the drybox under nitrogen. Samples for the UV-visible and ESR measurements (anions formed by the addition of base and redox products formed by electrolysis) were prepared in the drybox.

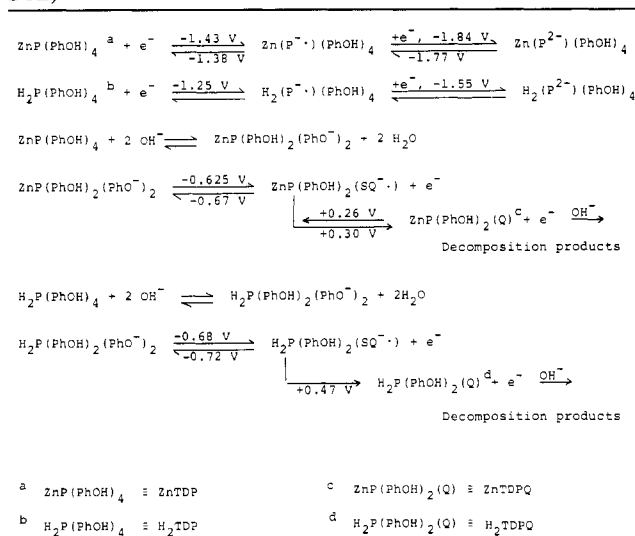
Results

Electrochemistry. Curves a and c of Figure 1 illustrate the cyclic voltammograms for tetrakis(3,5-di-*tert*-butyl-4-hydroxyphenyl)porphine (H_2TDP) and its zinc(II) complex ($ZnTDP$) in dimethylformamide (DMF). Their redox processes are similar to those for tetraphenylporphine (H_2TPP) and its zinc(II) complex ($ZnTPP$), with two porphyrin-ring oxidations at positive potentials and two porphyrin-ring reductions at negative potentials.¹³ Addition of base to H_2TDP shifts the ring reductions negatively by approximately -0.4 V (Figure 1b) and results in the appearance of a reversible oxidation at $E_{1/2} = -0.72 \text{ V}$ vs. SCE and an irreversible oxidation at $E_{pa} = +0.47 \text{ V}$. Addition of base to $ZnTDP$ shifts the ring reductions well past the solvent limit (Figure 1d). Two reversible oxidations are observed at $E_{1/2} = -0.65 \text{ V}$ and $E_{1/2} = +0.27 \text{ V}$. The oxidations at $E_{1/2} = -0.72 \text{ V}$ for H_2TDP and $E_{1/2} = -0.65 \text{ V}$ for $ZnTDP$ are one-electron transfers on the basis of controlled-potential electrolysis at -0.50 V .

The reversible reduction of dioxygen in air-saturated DMF ($[O_2] = 0.9 \text{ mM}$) is shown in Figure 2a. Addition of 1 mM

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Table II. Redox Reactions for ZnTDP and H₂TDP under Basic Conditions in Dimethylformamide (DMF) (0.1 M TEAP) (V vs. SCE)

ZnTDP to this solution increases the O₂-reduction current by a factor of 2 and results in the loss of the anodic peak at -0.6 V upon scan reversal (Figure 2b). Similar behavior is observed when H₂TDP is added to an O₂ solution.

Optical Spectroscopy. The UV-visible spectral parameters for basic solutions of ZnTDP and H₂TDP and their one-electron-oxidation products are summarized in Table I. The spectra for basic solutions of ZnTDP and H₂TDP after controlled-potential oxidation at -0.5 V exhibit a decrease in the molar absorptivity for their Soret bands, accompanied by a shift of the β-band to lower energy. The cyclic voltammetry for these solutions is identical with that illustrated in Figure 1b,d, except that the rest potential is shifted to -0.5 V. Neither of the two-electron-oxidation products (from electrolysis at +0.5 V) is stable within the time scale of the controlled-potential electrolysis experiment.

ESR. The one-electron-oxidation products from electrolysis of H₂TDP and ZnTDP (see optical spectral data in Table I) are ESR-silent. Their two-electron oxidation under basic conditions yields a complex mixture that for H₂TDP is ESR-silent and for ZnTDP exhibits a triplet (*g* = 2.005, *A_H* = 1.8 G) (characteristic of a phenoxy radical). This triplet is reversibly quenched by cooling to 77 K and has been observed as a product of chemical oxidation.^{2,3}

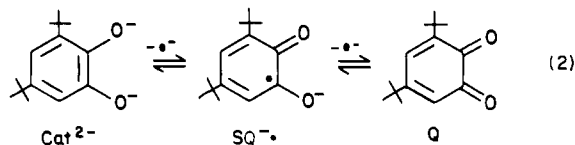
Discussion and Conclusions

A self-consistent set of redox reactions of ZnTDP and H₂TDP is outlined in Table II on the basis of the electrochemical and spectroscopic results. Neutral ZnTDP and H₂TDP are oxidized and reduced in a pattern consistent with their porphyrin character. The irreversibility of their oxidations, in contrast to reversible π-cation formation observed in the corresponding TPP systems,¹³ implies the formation of secondary oxidation states that involve the phenol groups.

The negative shift for the porphyrin-ring reductions of ZnTDP and H₂TDP upon addition of OH⁻ (ca. -0.40 V) is significantly larger than it is for neutral substituents in TPP reductions (ca. -0.20 V from *p*-CN to *p*-OCH₃).¹³ This is consistent with substantial charge delocalization from the anion to the porphyrin ring. The change in the visible spectrum upon anion formation (Table I) also implies strong resonance interaction. A study of unsym-

metrically substituted Fe^{III}(TPP)Cl provides further evidence for the direct conjugation between porphyrin and phenyl ring.¹⁴

In the reduction of anionic ZnTDP²⁻, the shift is further enhanced by axial binding of OH⁻ to Zn.¹⁵ The two reversible oxidation couples for ZnTDP²⁻ at *E*_{1/2} = -0.65 V and *E*_{1/2} = +0.27 V are not observed with ZnTPP in the presence of base and must be due to the polyphenol functionality of ZnTDP²⁻. This electrochemistry resembles the behavior of transition-metal complexes of 3,5-di-*tert*-butylcatechol¹⁶ and of aromatic diols derived from biphenyl.¹⁷ The general reaction sequence is



The present results indicate that similar redox behavior is observed when a porphyrin has been placed between the two phenolate groups of ZnTDP²⁻. The semiquinone-like anion from the oxidation of ZnTDP²⁻ is stable on the basis of electrochemistry. The similarity of the optical spectra for ZnTDP^{·-} and H₂TDP^{·-} (Table I) indicates similar electronic structures and that zinc ion has a minor effect. Aggregation via spinpairing may account for the lack of an ESR signal. The one-electron-reduction product of a related dioxoporphodimethene also is ESR-silent.⁶

The second oxidation for H₂TDP²⁻ is irreversible in the absence of the central metal ion (Figure 1b) and probably is due to the rearrangement or ionization of the product upon oxidation. The central zinc ion appears to limit the structural adjustments available to the porphyrin as the semiquinone form is oxidized, and more reversible behavior is observed. The initially formed semiquinone anions are stabilized by delocalization through the other phenol groups. Further oxidation leads to the stable quinone.

Previous work^{3,4} has noted that ZnTDP can act as a catalyst, and the present study confirms this for the electroreduction of O₂. As shown in Figure 2b, the addition of ZnTDP increases the O₂ reduction current and eliminates the oxidation peak upon scan reversal. The superoxide ion that initially is formed from O₂ reduction abstracts a phenolic proton (note the similar oxidation peak potentials in Figures 1d and 2b and the absence of an O₂⁻ oxidation peak), which promotes disproportionation to oxygen and hydrogen peroxide.¹⁸ The net result is an increase in the effective concentration of O₂ at the electrode and the observed increase in reduction current.

In summary, the redox chemistry of ZnTDP and H₂TDP under basic conditions is due solely to their polyphenol functionality, which is attenuated by the electronic and steric requirements of the porphyrin, and their behavior is analogous to that of simple aromatic diols. The anionic semiquinone-like and the quinone-like products for H₂TDP and ZnTDP appear to be similar. Both complexes react with superoxide ion via proton transfer, which is the basis for their electrocatalytic reduction of O₂.

Acknowledgment. This work was supported by the National Science Foundation under Grant Nos. CHE82-12299 (D.T.S.) and CHE 81-20969 (T.G.T.) and by the National Institutes of Health under Grant Nos. GM-22761 (D.T.S.) and HL 13581 (T.G.T.).

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