ion proposed by Swift[7] is directly relevant to this study. From the temperature dependence of the concentration independent relaxation time ($\tau = 0.13$ sec at 25° in aqueous $Zn(NO_3)_2$), $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were estimated to be 3.8 kcal/mol and −42 eu, respectively. Swift attributed this process to the tetrahedral–octahedral conversion. The relaxation times we observed for the formation of the zinc monoglycinate complex were in the 10^{-4} sec region and those for the bis rearrangement were much longer. We propose, therefore, that the bis rearrangement may be due to a change in structure similar to that observed by Swift.

The structure of bis(glycinato)zinc monohydrate has been studied by infrared and X-ray methods.[8,25] Both studies are in agreement; the structure of this complex is octahedral. The glycine anions are in a trans configuration coplanar to the central metal ion, while the other two coordination positions are occupied by carboxyl oxygens of neighboring glycine ligands. Also the axial bond lengths are longer than those in an equatorial position, and in this instance are occupied by water molecules. It seems reasonable, therefore, to assign an octahedral structure[26] to the $Zn(gly)_{2aq}'$ species of scheme B, where the waters of hydration occupy axial positions and the glycine ligands are equatorial. An octahedral configuration is also consistent with the presence of three bidentate ligands in the tris complex. Although the structure of zinc monoglycinate is not known, some comment can be made about its probable structure. It is more common for zinc to have a coordination number of four than six.[24] X-Ray studies have demonstrated that tetrachloro-[27] and tetracyanozincates[24] are tetrahedral. Moreover, it is known that diamminedichlorozinc is tetrahedral while hexaamminezinc(II) is octahedral.[24] That is, in this case increased coordination converts zinc from a tetrahedral to an octahedral structure. These considerations suggest that the $Zn(gly)^{+}_{aq}$ species of scheme B is tetrahedral and that $Zn(gly)_2'$ is octahedral. Our kinetic data are consistent with a structural change occurring after the formation of the monoglycinate complex. We propose therefore that this process involves the $Zn(gly)^+$ complex (in a probably tetrahedral configuration) being converted to the bis complex $Zn(gly)_2'$ (octahedral). If the suggestion of Krishnan and Plane[26]—that the bis complex is tetrahedral—is correct, then it would be necessary to propose the other structure for the mono complex. Nevertheless, the sequence resulting from the latter assignment (octahedral $Zn^{2+} \rightarrow$ octahedral $Zn(gly)^+ \rightarrow$ tetrahedral $Zn(gly)_2 \rightarrow$ octahedral $Zn(gly)_2$ in solid) is much less satisfying than the sequence proposed above. Kinetic data of course cannot distinguish between these possibilities.

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Metalloporphyrin Redox Chemistry. Unusual Electron-Transfer Behavior in the Oxidation of Lead Porphyrins

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Lead(II) octaethylporphyrin (PbOEP) undergoes two electrochemically reversible one-electron oxidations in dichloromethane, acetonitrile, or *n*-butyronitrile. In the product of the first oxidation, $PbOEP^+$, Pb(II) is covalently bound to the ring-oxidized π cation radical. However, loss of a second electron gives $PbOEP^{2+}$ which from its lability and spectral properties contains Pb(IV) weakly bound to OEP^{2-}. The properties of $PbOEP^{2+}$ are very similar to those of the ionic Ba^{2+} porphyrin complexes. The unusual pattern of oxidation is apparently a consequence of the tendency of Pb(II) to undergo net two-electron oxidation.

Introduction

An interest in the redox chemistry of metalloporphyrins is warranted by the likely involvement of ring-oxidized chlorophyll in photosynthesis and by the electron-transfer chemistry of the cytochromes. Recent work in this area has revealed two general patterns of oxidation.[2-7] For divalent metal ion complexes in which the metal ion is nonoxidizable or oxidized only with difficulty—this includes complexes of Zn^{2+}, Mg^{2+}, Cd^{2+}, and Cu^{2+}—oxidation proceeds by two reversible one-electron steps

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$$M^{II}P \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} M^{II}P^{+} \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} M^{II}P^{2+}$$

Correlations can be made between the ease of oxidation and the size or electronegativity of the central metal ion,[4] but the available evidence clearly indicates that oxidation gives ring-oxidized π cation radicals and dications in the successive steps. Methanol reacts with the dication of zinc(II) tetraphenylporphyrin by nucleophilic attack at the *ring* at the carbon bridge between pyrrole rings giving the isolable zinc isoporphyrin.[8]

On the other hand, complexes of divalent iron, cobalt, and nickel bound to tetraphenylporphyrin[3,9] undergo an initial, reversible oxidation at the metal ion which for cobalt and nickel is followed by succes-

$$M^{II}P \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} M^{III}P$$

sive one-electron oxidations at the porphyrin ring.

$$M^{III}P \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} M^{III}P^{+} \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} M^{III}P^{2+}$$

It was reported recently[10] that the second oxidation step for a variety of iron porphyrins leads to iron(IV) porphyrins instead of a trivalent iron-ring-oxidized dication as suggested previously.[3]

The redox chemistry of divalent tin porphyrins is rather more complicated, largely because of the inability of the large Sn(II) ion to fit squarely into the central hole of the porphyrin. A reactivity scheme for tin(II) porphyrins is

$$\begin{tikzcd}
Sn^{II}P \arrow[d, "\Delta \text{ or } h\nu"'] \arrow[rrrrd, "O_2"] & & & & \\
Sn^{IV}P^{2-} \arrow[rr, shift left, "-e^-"] & & Sn^{IV}P^{-} \arrow[ll, shift left, "+e^-"] \arrow[rr, shift left, "-e^-"] & & Sn^{IV}P \arrow[ll, shift left, "+e^-"]
\end{tikzcd}$$

The tin(II) complexes are thermally or photolytically converted into a more stable isomeric form in which Sn(IV) is bound to the porphyrin dianion.[11] This isomer can also be prepared by the electrochemical or light induced chemical reduction of Sn(IV) porphyrins.[11,12] In contrast to Sn(II), tetravalent tin is small enough to fit into the central cavity of the porphyrin; that this is the case for the Sn(IV) porphyrins is indicated by their high stability as well as by spectral evidence. For the tin(II) complexes, the metal ion is probably severely out of the porphyrin plane.[11,13] Theoretical calculations[13] predict that both Sn(II) and Pb(II) porphyrins should have the metal out of plane; from consideration of the spectra of the latter complexes it is estimated that the Pb is out-of-plane by *ca.* 1 Å.[13] However, in contrast to the Sn(II) porphyrins the Pb(II) complexes are isolable and oxidatively stable. No evidence for thermal or photochemical isomerizations has been found.

Our interest in the redox chemistry of lead porphyrins, and here specifically of lead(II) comes partly from a desire to make comparisons with the tin complexes. In addition we felt that our work might lead to heretofore unreported complexes of Pb(IV) with the metal ion in the plane of the porphyrin. Interestingly, the theoretical treatment of Schaffer and Gouterman[13] predicts that the highest filled orbital in both Sn(II) and Pb(II) porphyrins is a metal $A_1(p_z)$ orbital. What we in fact find is an unusual pattern of reactivity in which the redox chemistry of PbOEP is controlled both by the ligand and by the tendency for Pb(II) to undergo net two electron transfer. Initial oxidation occurs at the ring to yield a more-or-less normal π cation radical of $Pb^{II}OEP$ while removal of the second electron yields a dicationic complex, $PbOEP^{2+}$, which remarkably contains Pb(IV) weakly bound to the unoxidized porphyrin.

Experimental Section

Measurements.—Ultraviolet–visible spectra were recorded on a Cary Model 14 spectrophotometer and epr spectra on a Varian E-3 spectrometer. All electrical measurements were *vs.* the saturated sodium chloride calomel electrode (ssce) at 22 ± 2° and are uncorrected for junction potentials. In all electrochemical experiments standard three electrode operational amplifier circuitry was used as described previously.[14] Values of n, where n is the total number of electrons transferred in exhaustive electrolyses at constant potential, were calculated after measuring the total areas under current *vs.* time curves for complete reaction. Reactions were judged to be complete when the current had fallen below 1% of its initial value. The n values reported here are averaged values for at least three separate experiments. All voltammetric measurements were carried out at platinum bead electrodes.

Materials.—Tetra-*n*-butylammonium hexafluorophosphate (TBAH) was prepared by standard techniques,[15] recrystallized three times from hot ethanol–water mixtures, and vacuum dried at 70° for 10 hr. Octaethylporphyrinlead(II), PbOEP, was prepared from octaethylporphyrin[16] in the free base form by the metalation procedure reported previously.[17] Acetonitrile (MCB "Spectrograde") was dried over activated alumina before use. *n*-Butyronitrile was first vacuum distilled from sodium carbonate–potassium permanganate and then dried over activated alumina. Solutions of Pb^{4+} ion in 0.1*M* TBAH–*n*-butyronitrile were generated by suspending a 1 × 2 cm piece of 99.98% lead foil (analytical grade) from a platinum wire and oxidizing it at +1.80 V *vs.* the ssce. The concentration of Pb^{4+} in solution was calculated from the measured number of coulombs passed during the oxidation. All other chemicals were reagent, spectral, or polarographic grade and were used without further purification.

Solutions and Reactions.—All experiments were carried out under an atmosphere of dry, deaerated nitrogen.

1. **$PbOEP^+$.**—Solutions of $PbOEP^+$ in acetonitrile, *n*-butyronitrile, and dichloromethane were generated electrochemically. From 5 to 10 mg of the neutral porphyrin complex was dissolved in the appropriate solvent which was 0.1 *M* in TBAH. The solutions were electrolyzed at +0.75–0.85 V *vs.* the ssce at a platinum electrode until oxidation was complete (20–30 min).

2. **$PbOEP^{2+}$.**—In 20 ml of a deaerated solution of 0.1 *M* TBAH–*n*-butyronitrile (in a volumetric flask fitted with a tightly fitting serum cap) was added 2 mg of octaethylporphyrin dissolved in a few milliliters of a deaerated 0.1 *M* TBAH–*n*-butyronitrile solution. An excess of electrolytically generated Pb^{4+} was added using a syringe, and the solution was diluted to a known volume. The ultraviolet–visible spectrum of an aliquot of the solution was recorded. To another aliquot was added excess hydrazine (0.1 g). From the ultraviolet–visible spectrum of this aliquot, the products of the hydrazine reaction were shown to be PbOEP and H_2OEP in approximately equal amounts.

3. **Cyclic Voltammograms in the Presence of Added Nucleophiles.**—The neutral porphyrin complex, PbOEP (6–8 mg), was

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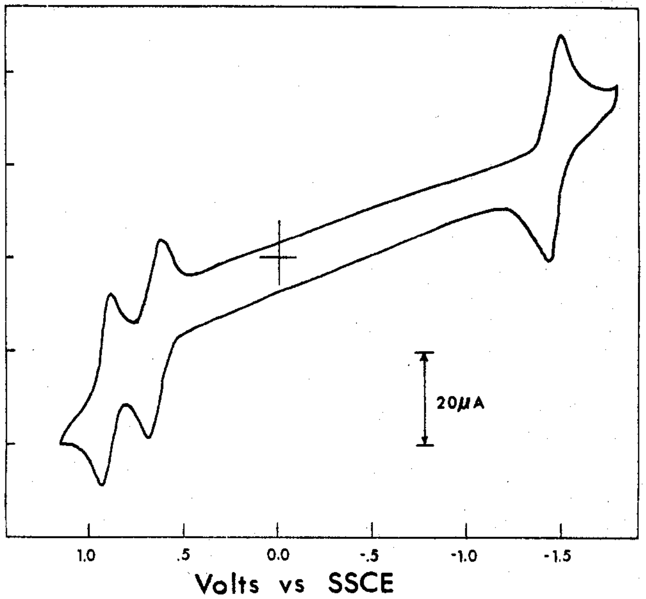


Figure 1.—Cyclic voltammogram of PbOEP in *n*-butyronitrile.

dissolved in 20 ml of a 0.1 *M* TBAH–acetonitrile solution. A cyclic voltammogram of the solution from 0 to +1.50 V (*vs.* the ssce at a platinum bead electrode) was recorded at a sweep rate of 200 mV/sec. Water (or pyridine) was added to the solution in 0.05 ml aliquots using a microliter syringe. Cyclic voltammograms were recorded at the same scan speed after the addition of each aliquot.

Results

Electrochemistry.—A cyclic voltammogram (200 mV/sec) of PbOEP (1.0×10^{-3} *M*) in 0.1 *M* TBAH–*n*-butyronitrile solution is shown in Figure 1. From the cyclic voltammogram it is apparent that on the cyclic voltammetry time scale, the neutral porphyrin complex undergoes reversible oxidations at waves 1 and 2 (giving $PbOEP^+$ and $PbOEP^{2+}$) and a reversible reduction at wave 3 (giving $PbOEP^-$).

The oxidation of PbOEP was also studied by voltammetry in dichloromethane, acetonitrile, and *n*-butyronitrile. $E_{1/2}$ values obtained from the voltammetric oxidation waves in each of the three solvents are given in Table I. The potential values, which are given in Table I, are reduction potentials and refer to the reactions

TABLE I

$E_{1/2}$ VALUES FOR OXIDATION OF PbOEP AND H_2OEP

Compound	Solvent[a]	$E_{1/2}(1)$,[b] V	$E_{1/2}(2)$,[b] V
PbOEP	CH_2Cl_2	0.68	1.03
	CH_3CN	0.61	0.92
	$CH_3(CH_2)_2CN$	0.68	0.87
H_2OEP	CH_2Cl_2	0.83	1.39
	CH_3CN	0.80	1.42
	$CH_3(CH_2)_2CN$	0.86	1.35

[a] In all three solvents the supporting electrolyte was 0.1 *M* TBAH. [b] At 22 ± 2° *vs.* the ssce uncorrected for junction effects, ±0.02 V. The measurements were made at platinum electrodes.

$$PbOEP^+ + e^- \longrightarrow PbOEP \qquad (1)$$

$$PbOEP^{2+} + e^- \longrightarrow PbOEP^+ \qquad (2)$$

For the first oxidation ($E_{1/2}(1)$), *n* values determined by coulometry varied between 0.97 and 1.01. For both voltammetric waves in all three solvents plots of log $(i_l - i)/i$ *vs.* *E* (where i_l is the limiting current for the voltammetric wave) had slopes in the range of 59 to 67 mV showing that the waves are electrochemically reversible. The $E_{1/2}$ values are somewhat solvent dependent, but this is not unexpected since medium effects of the magnitude seen in Table I have been observed for other metalloporphyrin oxidations.[2]

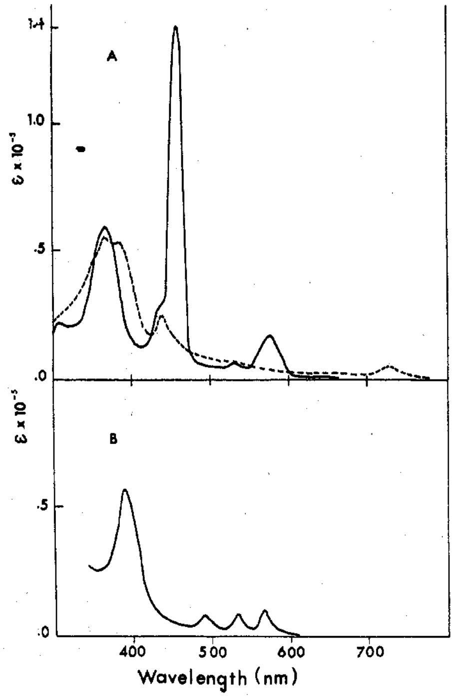


Figure 2.—Spectra of lead porphyrin complexes. A: ——, PbOEP; - - - - - - - -, $PbOEP^+$. B: ——, $PbOEP^{2+}$. Solvent is *n*-butyronitrile in each case.

For purposes of comparison, $E_{1/2}$ values for the two oxidation waves of the neutral, uncomplexed porphyrin are also given in Table I. The binding of Pb(II) ion to the porphyrin (in place of the two protons in H_2OEP) makes both oxidation steps energetically more favorable. This appears to be a general result for divalent metal ion–porphyrin complexes.[2,3] The diprotonated porphyrin, H_4OEP^{2+}, has no anodic waves in the region 0 to + 1.60 V.

$PbOEP^+$.—From the electrochemical data, the neutral porphyrin complex can be reversibly oxidized giving the monocation, $PbOEP^+$

$$PbOEP \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} PbOEP^+$$

n values, measured coulometrically, for both the forward and reverse steps were essentially unity (0.97–1.01) as expected.

Solutions of $PbOEP^+$ in dichloromethane, acetonitrile, or *n*-butyronitrile were prepared by the exhaustive electrolysis of PbOEP as described in the Experimental Section. In all cases the oxidized solutions were stable for at least 1 hr.

The ultraviolet–visible spectra of PbOEP and of $PbOEP^+$ in 0.1 *M* TBAH–*n*-butyronitrile are shown in Figure 2. In order to verify that oxidation of PbOEP to $PbOEP^+$ and reduction of $PbOEP^+$ to PbOEP involve simple electron transfer to the electode, both reactions were carried out stepwise by incremental electrolyses, and the spectra of the solutions were recorded at each step. In all three solvents interconversion between PbOEP and $PbOEP^+$ occurred smoothly and the appearance of characteristic isosbestic points (for example at 600, 547, and 425 nm in 0.1 *M* TBAH–*n*-butyronitrile) verified that only PbOEP and $PbOEP^+$ were present in appreciable concentrations during the stepwise reactions. From the similarity of its epr and electronic spectra to those for other porphyrin π-cation radicals, $PbOEP^+$ is probably also best described as a π-cation radical. The room temperature epr spectrum of $PbOEP^+$ in a 0.1 *M* TBAH–dichloromethane solution yields a g value of 1.0158. This is very near to the g value of 1.0161 for the π-cation radical obtained by electrochemical oxidation of free-base octaethylporphyrin at +1.00 V *vs.* ssce in the same medium. The electronic absorption spectrum of $PbOEP^+$ closely resembles in dispersion those of $MgOEP^+$ [4,6] and $Co^{III}OEP^{2+}$ [5] where it has been well established that a single electron has been removed from the ring. However, for $PbOEP^+$ the transitions have somewhat lower oscillator strength (ϵ_{max} values *ca.* one-third of those for $MgOEP^+$) and they occur at slightly longer wavelengths (λ_{max} 725 nm for $PbOEP^+$ for the long wavelength band compard to 683 nm for $MgOEP^+$ [4] and 675 nm for $Co^{III}OEP^{2+}$ [5]). The red shifts and lower oscillator strengths are also observed for neutral $Pb^{II}OEP$ and $Sn^{II}OEP$[11] compared to other metal complexes of the porphyrins where the metal is in the plane. Theoretical calculations indicate that transition probabilities for porphyrin π–π^* transitions should be lowered as the metal is moved out of the porphyrin plane.[13] The spectrum of $PbOEP^+$ suggests therefore that the one-electron oxidation product is a ring-oxidized π-cation radical in which the lead is considerably out-of-plane.

$PbOEP^{2+}$.—From Figure 1 the loss of a second electron from the porphyrin complex (giving the dication, $PbOEP^{2+}$) is reversible, at least on the time scale

$$PbOEP^+ \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} PbOEP^{2+}$$

(seconds) of the cyclic voltammetry experiment. However, attempts to prepare solutions of $PbOEP^{2+}$ in dichloromethane, acetonitrile, or *n*-butyronitrile by the exhaustive electrolysis of $PbOEP^+$ (at +1.20 V *vs.* the ssce at a platinum gauze electrode) were unsuccessful. *n* values were nonintegral and greater than 1, and the ultraviolet–visible spectra of the completely oxidized solutions showed that the only porphyrin-containing product was the unoxidized, diprotonated porphyrin H_4OEP^{2+}. The latter result shows that the dication is unstable with respect to demetalation on the time scale for electrolysis (minutes). A possible origin for the demetalation reaction is nucleophilic attack by water since water is present in trace amounts in all of the solvents used.

To see if the demetalation reaction was caused by nucleophiles, cyclic voltammograms of PbOEP (200 mV/sec; 0 to +1.5 V) were recorded in 0.1 *M* TBAH–acetonitrile to which water or pyridine had been added. The experiments were carried out as described in the Experimental Section. In pure acetonitrile the wave heights (peak currents) for both the oxidation

$$PbOEP^+ \xrightarrow{-e^-} PbOEP^{2+}$$

and the reduction

$$PbOEP^{2+} \xrightarrow{+e^-} PbOEP^+$$

reactions are the same (see wave 2 in Figure 1) showing that the dication once formed is completely recaptured by reduction at the electrode. Water was then added in 0.05 ml increments using a microliter syringe, and cyclic voltammograms were recorded after each addition. The wave height for reduction of $PbOEP^{2+}$ decreased more or less directly as the concentration of water increased, while the wave height for the oxidation of $PbOEP^+$ was unaffected. Water clearly reacts with the dication, and in the cyclic voltammetry experiment, this reaction becomes more competitive with the electrode reduction of $PbOEP^{2+}$ as the water concentration is increased.

The demetalation reaction presumably involves nucleophilic attack on $PbOEP^{2+}$ at *lead*

$$PbOEP^{2+} \xrightarrow{+H_2O} Pb(IV) + H_2OEP$$

followed by protonation of the free base porphyrin

$$2H^+ + H_2OEP \longrightarrow H_4OEP^{2+}$$

by protons released when water molecules associate with lead(IV). Pyridine is even more efficient at demetalating the dication. With the addition of just 0.05 ml of redistilled pyridine (per 20 ml of acetonitrile), the reduction wave for $PbOEP^{2+} \rightarrow PbOEP^+$ disappears completely at scan speeds of 200 mV/sec and cannot be observed even at scan speeds as high as 20 V/sec.

The nucleophilic demetalation reactions are remarkable in that they indicate that $PbOEP^{2+}$ contains Pb(IV) weakly bound to the unoxidized porphyrin. The long term instability of electrochemically generated solutions of $PbOEP^{2+}$ can be explained by the presence of traces of water in the solvents used.

Solutions of the dication can be prepared and stabilized in carefully dried *n*-butyronitrile by adding electrolytically generated Pb^{4+} to solutions of the free porphyrin

$$Pb^{4+} + 2H_2OEP \longrightarrow PbOEP^{2+} + H_4OEP^{2+}$$

The stepwise addition of Pb^{4+} to H_2OEP was followed by cyclic voltammetry. As Pb^{4+} was added, waves corresponding to the uncoordinated porphyrin decreased in peak height ($E_{1/2}$ at 0.86 and 1.35 V) and finally disappeared after excess Pb^{4+} had been added.

Waves for the dication ($E_{1/2}$ at 0.68 and 0.87 V) appeared and grew in height, leveling off after excess Pb^{4+} had been added. The existence of H_4OEP^{2+} in the solution was shown by spectrophotometry (λ_{max} values at 589, 544, and 400 nm). That $PbOEP^{2+}$ prepared by this route is identical with that produced by the electrochemical oxidation of PbOEP is shown by the fact that cyclic voltammograms of the two solutions are identical. Also the addition of excess hydrazine to $PbOEP^{2+}$ prepared in this way gives the

$$PbOEP^{2+} \xrightarrow{N_2H_4} PbOEP$$

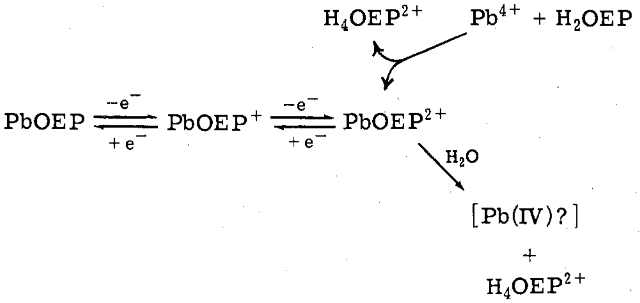
starting complex, PbOEP, as verified spectrophotometrically. The dication forms rapidly when Pb^{4+} and H_2OEP are mixed which also indicates the labile nature of the complex.

The electronic spectrum of $PbOEP^{2+}$ is given in Figure 2. The spectrum was obtained by adding excess Pb^{4+} to H_2OEP and then subtracting out the spectral contributions due to H_4OEP^{2+}. The spectrum is unlike those reported for other metalloporphyrin dications in which both electrons have been removed from the ring. In fact the spectrum of $PbOEP^{2+}$ resembles most closely that of normal unoxidized metalloporphyrin[11] with an intense near-uv (Soret) peak and relatively sharp, but weaker bands in the visible.

Discussion

The results presented in the preceding section are summarized in Chart I. From evidence previously cited (*vide supra*), the product of the one-electron oxidation of PbOEP is best described as a ring-oxidized π cation radical bound to Pb(II). Spectral evidence suggests that the Pb(II) is out-of-plane, but covalently bound, in $PbOEP^+$, as it is in the unoxidized complex. Although calculations[13] suggest that the highest occupied orbital in lead(II) porphyrins is a metal p_z orbital, in the first oxidation clearly an electron has been removed from an orbital that is basically a porphyrin π_{MO} giving a π cation. This is not an especially surprising result because the same calculations suggest that the metal p_z and porphyrin π orbitals are close together in energy and that changes in orbital occupation can cause inversion of these levels.

CHART I
REDOX REACTIONS OF PbOEP



In view of the fact that the first oxidation occurs at the ring, it is surprising to find that the product of the second oxidation, $PbOEP^{2+}$, is a complex of tetravalent lead bound to unoxidized porphyrin. This formulation is based on comparative $E_{1/2}$ values, the chemical properties of the complex, and spectral evidence.

The difference in $E_{1/2}$ values between the first

$$M^{II}(\text{porphyrin}) \underset{+e}{\overset{-e}{\rightleftharpoons}} M^{II}(\text{porphyrin})^+ \qquad E_{1/2}(1)$$

and second

$$M^{II}(\text{porphyrin})^+ \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} M^{II}(\text{porphyrin})^{2+} \qquad E_{1/2}(2)$$

oxidations for a large number of etio-, octaethyl-, and deuteroporphyrin complexes is

$$\Delta E_{1/2} = E_{1/2}(2) - E_{1/2}(1) \approx 0.5 \text{ V}$$

in cases where it is clear that both oxidations occur at the porphyrin ring. For PbOEP, $\Delta E_{1/2}$ is ~0.3 V (Table I) and for lead(II) etioporphyrin(I) only 0.26 V (in 0.1 *M* $LiClO_4$–*n*-butyronitrile).[2] Since the first oxidation for PbOEP occurs by the normal path giving $Pb^{II}OEP^+$, the smaller $\Delta E_{1/2}$ values for the lead complexes suggest that the second oxidation may be more complicated than simple loss of an electron from the ring.[18] $PbOEP^{2+}$ is quite reactive toward nucleophiles such as water and pyridine as has been observed previously for the dications of MgOEP[8] and zinc tetraphenylporphyrin.[6] However, for $PbOEP^{2+}$ nucleophilic attack occurs at the metal while for the zinc and magnesium dications nucleophilic attack occurs at the ring giving divalent metal isoporphyrins.[6,8] For $PbOEP^{2+}$ nucleophilic attack results in rapid demetalation giving unoxidized porphyrin (H_4OEP^{2+} where water is the nucleophile). That $PbOEP^{2+}$ is a loosely bound complex of OEP^{2-} with Pb(IV) is also suggested by the rapid formation of $PbOEP^{2+}$ when Pb^{4+} is mixed with free base porphyrin. Characteristically, metalloporphyrins are produced and demetalated only *via* the mono- or divalent metal ion forms and usually under moderately vigorous conditions.[19,20] The instability of the complex and the relative ease of metalation and demetalation are uncharacteristic of ter- and tetravalent metalloporphyrins (compare especially tin(IV))[11] and suggest that $PbOEP^{2+}$ is not a "normal" complex with the metal ion in the porphyrin plane.

The absorption spectrum of $PbOEP^{2+}$ is clearly unlike the spectra of most other doubly oxidized metalloporphyrins. In both dispersion and oscillator strength the spectrum of $PbOEP^{2+}$ resembles the spectra of nonoxidized metalloporphyrins with an intense Soret peak and weaker bands in the visible region. The spectrum and lability properties of $Pb^{IV}OEP$ are perhaps most similar to those of the barium porphyrins.[17,21,22] Although barium(II) is clearly too large to fit into the porphyrin central cavity, the spectra of barium porphyrins are strikingly similar to those of the smaller magnesium and disodium complexes,[17,22] and not at all like those of the "covalent" complexes of other large metals such as Hg(II) and Pb(II). Barium(II) porphyrins are readily demetalated by treatment with even such weak nucleophiles as methanol.[4] It has been suggested[21,22] that due to its large size and low electronegativity, barium forms an "ionic" complex in which the deprotonated porphyrin is perturbed by the barium cation. From the present results a similar ionic structure is indicated for Pb^{IV}-OEP. A rationale for the contrast in binding properties between Sn(IV) and Pb(IV) when bound to porphyrins may be that Pb(IV), with an ionic radius of *ca.* 0.94 Å,[23] is enough larger than Sn(IV) (ionic radius 0.69–0.71 Å)[23] to preclude or destabilize a covalent structure with the metal in the 2 Å or less[24] porphyrin central cavity.

The overall electron transfer sequence for PbOEP

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[18] The difference in $E_{1/2}$ values for the oxidation of Pb(II) tetraphenylporphyrin (0.33 V) is about the same as those observed for a variety of metal tetraphenylporphyrin complexes[2] suggesting that the second wave here may give $Pb^{II}TPP.^{2+}$

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is summarized by eq 3 in terms of the oxidation states

$$\mathrm{Pb^{II}OEP} \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} \mathrm{Pb^{II}OEP^+} \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} \mathrm{Pb^{IV}OEP} \qquad (3)$$

of porphyrin and Pb. That loss of the second electron gives Pb^{4+} bound to unoxidized porphyrin is at first glance surprising. However, it is reasonable in terms of the expected instability of a Pb(III) complex and it is consistent with the known tendency of lead to undergo net two-electron transfer.

The formation of a stable, covalent metalloporphyrin *via* reduction of a labile, easily formed ionic complex is noteworthy. This heretofore unobserved

$$\mathrm{Pb^{IV}OEP} \xrightarrow{+2e^-} \mathrm{PbOEP}$$

type of reaction may have important consequences both in the laboratory and biosynthesis of metalloporphyrins.

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Uni- and Bimetallic Complexes Derived from a Substituted Pyrazine Ligand

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An attempt has been made to synthesize a substituted pyrazine molecule that would be capable of complexing simultaneously with two metal ions such that there exists an isolated bimetallic species. Of the Co^{2+}, Ni^{2+}, and Cu^{2+} complexes prepared, only the copper complex formed a compound with the desired stoichiometry. Low-temperature magnetic data indicated little metal–metal interaction in the system. It is believed that both nitrogens of the pyrazine are not involved in coordination in the bimetallic species.

Introduction

The purpose of synthesizing and studying this series of compounds was to investigate the possibility of there being metal–metal interaction between two isolated metal centers when bridged by pyrazine. With this type of ligand it was hoped to obtain the coordination shown in Figure 1. Some of the early work[1,2] with pyrazine was concerned with its ability to utilize both of its nitrogen atoms as donors and form polymers. This work came into sharp focus in a series of papers by Lever, Lewis, and Nyholm[3–6] dealing with the Co^{2+}, Ni^{2+}, and Cu^{+} complexes of pyrazine. They were able to demonstrate the ability of pyrazine and its methyl-substituted derivatives to form monomeric, dimeric, and polymeric species. Recently there has been evidence that pyrazine can act as a bridging ligand such that there is spin–spin interaction between the metal centers.[7–9] Since most of the previous work with pyrazine–metal complexes had dealt with polymeric systems, it was thought desirable to synthesize a substituted pyrazine ligand such that the substituents would wrap around two metal ions and form a bimetallic system bridged by the pyrazine moiety. Cotton and Gibson's[9] epr work suggested that metal–metal interaction in a bimetallic species might be present. It has also been demonstrated that there is enhanced basicity of the second nitrogen in pyrazine when complexed with pentaammineruthenium(II)[10,11] and that there was interaction between the two ruthenium ions in the pentaamminepyrazineruthenium mixed oxidation state species reported by Creutz and Taube.[12] These papers suggest a pathway through the aromatic base for metal–metal interaction.

Attempts to synthesize substituted pyrazines and study their transition metal chemistry have resulted in compounds analogous to 2,3,5,6-tetrakis(α-pyridyl)-pyrazine[13–15] which show only the ability to be tridentate and not bis tridentate. This paper describes the synthesis of bis(*N*-2-(2-ethylpyridyl))-2,3-pyrazinedicarboxamide (Figure 1) using as a starting material 2,3-pyrazinedicarboxylic acid. Of the transition metal complexes prepared with the new ligand, only the copper(II) compound was bimetallic. It is believed that both nitrogens of the pyrazine ring are not involved in coordination in the bimetallic species.

Experimental Section

Preparation of Ligand.—2,3-Pyrazinedicarboxylic acid from Aldrich Chemical Co. was the starting material. The dimethyl ester was prepared by refluxing 50 g of the diacid in 500 ml of methanol with 7 ml of H_2SO_4 for at least 15 hr. The methanol was evaporated to 250 ml and 1 l. of water was then added. The solution was neutralized over $NaHCO_3$ and extracted six times with 250 ml of ether. The ether was dried over Na_2SO_4. A yellowish oil remained when the ether was evaporated which yielded white crystals when placed in the refrigerator. The yield was 82%. The product was recrystallized from ether, mp 50–51°.

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