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Synthesis, Characterization, and Electrochemistry of (5,10,15,20-Tetraphenylporphinato)dichlorophosphorus(V) Chloride

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The title complex has been prepared and characterized by optical, NMR, and IR spectroscopy and electrochemistry. The electrochemistry reveals that this material undergoes two reductive processes at the porphyrin ring. The potential of these processes demonstrates that these are the easiest porphyrin-ring reductions yet reported. The ease of these reductions is attributed to the inductive effects of the highly charged P(V) ion and perhaps structural factors as well. One-electron reduction of the complex leads to a stable ring-reduced radical, which has been isolated and characterized. Addition of a second electron leads to, among other products, free-base tetraphenylporphine via an internal electron transfer.

Introduction

Porphyrin complexes of nearly every metal in the periodic table are known.[1] Recently, this remarkable complexing ability has been found to extend even to the metalloids and non-metals.[2] Phosphorus porphyrins were first synthesized independently by Gouterman and co-workers$_3$ and Carrano and Tsutsui.[4] These phosphorus complexes have several unique characteristics that make them interesting points of study. These include the fact that the central "metal", phosphorus, can exist in two oxidation states, III and V. For the trivalent state, theory predicted and experiment has demonstrated an unusual "hyper" type spectrum.[3] The pentavalent form of phosphorus is the smallest ion found to undergo insertion into a porphyrin ring. Hoard has calculated that, if the radius of the central "hole" is less than 1.96 Å, the macrocycle must undergo some buckling and a deviation from planarity.[5] This has been borne out by the recent structure determination of (tetraphenylporphinato)dihydroxophosphorus(V) hydroxide dihydrate.[6] Thus, coordination of the small phosphorus(V) ion results in extensive ruffling of the porphyrin macrocycle. Considering the expectation that reduction of porphyrins and metalloporphyrins might lead to nonplanar species[7] (via a Jahn–Teller type distortion caused by odd-electron population of a degenerate e_g type orbital) and the potential redox activity of the phosphorus atom itself, we felt it would be illuminating to examine the redox properties of these unusual systems. The results of our electrochemical investigations, along with the synthesis and characterization of the title complex, are reported.

Experimental Section

(5,10,15,20-Tetraphenylporphinato)dichlorophosphorus(V) Chloride. The title compound was synthesized by a modification of the procedure of Tsutsui and Carrano.[4] After reaction of tetraphenylporphine (TPP) with an excess of $POCl_3$ in dry pyridine, the mixture was taken to dryness directly by evaporation under high vacuum rather than being hydrolyzed prior to this step. The resulting solid was taken up in chloroform and applied to a column of neutral alumina. Free-base TPP and a small amount of red material could be eluted. Addition of 2% methanol allowed for elution of the green-violet product. It was found advisable to repeat this chromatographic procedure to obtain pure material. When completely pure and dry, the product could be recrystallized from $MeCl_2$/heptane as long violet needles, which were dried under high vacuum for several hours. Conductivity measurements confirmed its formulation as a 1:1 electrolyte in acetonitrile solution. λ_{max} (ϵ) (acetonitrile): 437 nm (237 000), 567 nm (10 400), 610 nm (4800).

(5,10,15,20-Tetraphenylporphinato)dihydroxophosphorus(V) Hydroxide. The dihydroxo complex can be prepared from the dichloro by addition of aqueous silver nitrate to a methanolic solution of the latter. Filtration of the precipitated silver chloride followed by several crystallizations from $MeOH/H_2O$, washing with boiling water, and drying under vacuum gave pure crystalline (tetraphenylporphinato)dihydroxophosphorus(V) with IR, proton NMR, and visible spectra nearly identical with those previously reported.[4] We have also recorded the previously unreported ^{13}C and ^{31}P NMR spectra of this material for comparison to the dichloro species.

Physical Measurements. Optical spectra were recorded on either a Perkin-Elmer 552 or Cary 14 spectrophotometer. Infrared spectra, as KBr pellets, were obtained on a Nicolet 6000 FT IR system. A Bruker WH-250 NMR spectrometer operating in a pulsed FT mode was utilized for all NMR experiments. All spectra were recorded in $CDCl_3$ solution. ^{31}P NMR spectra were collected at 30 °C and referenced to an external standard of phosphoric acid.

EPR spectra were run on a modified Varian E-4 spectrometer operating at 9.125 GHz. Spectra were recorded either in toluene (pure monoreduced product) or in acetonitrile (other electrolysis products) in a quartz flat cell at room temperature. Diphenylpicrylhydrazide (DPPH) was used as a standard.

Electrochemistry. Acetonitrile (Burdick-Jackson) was used without further purification. Tetrabutylammonium hexafluorophosphate ($(TBA)PF_6$) was recrystallized three times from distilled ethanol and vacuum dried at 100 °C. All potentials were referenced to the saturated calomel electrode (SCE) and are uncorrected for junction potentials. Solutions were purged with prepurified nitrogen and kept under a blanket of the gas during each experiment.

Cyclic voltammograms were generated with a PAR Model 173 potentiostat/galvanostat and PAR Model 175 universal programmer. A conventional three-electrode cell with Luggin probe was employed. Voltammograms were routinely recorded on an HP-7004B X-Y recorder. Permanent recordings of voltammograms employing sweep rates >0.5 V/s were made on a Boscom-Turner series 4000 data acquisition recorder.

For electrolysis experiments, a conventional "H" type cell, with separated (fine-porosity glass frits) auxiliary and reference compartments, was used. The number of electrons per molecule passed was determined either by manual integration of current–time plots or by direct digital readout using a PAR 179 coulometer. All exhaustive electrolysis experiments, utilizing a Pt-gauze working electrode, were carried out inside a Vacuum Atmospheres Corp., inert-atmosphere box. Samples for EPR and optical spectra were obtained by transferring part of the electrolysis solution (still in the drybox) into cells of the appropriate type, which were well capped.

The optically transparent thin-layer electrochemical cell (OTTLE) was of conventional design and was the generous gift of Dr. C. M. Elliott. It was constructed with a fine-mesh gold minigrid and had a measured path length of 0.0044 cm.

Results and Discussion

Synthesis and Characterization. The dichloro compound was originally reported to be the mixed-ligand chloro–hydroxo

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Table I. NMR Data for (Tetraphenylporphinato)dichlorophosphorus(V) and (Tetraphenylporphinato)dihydroxophosphorus(V)

	chemical shifts, ppm	
assignt	dihydroxo	dichloro
	^{1}H NMR	
pyrollic β-hydrogen	8.87 (d) (J_{P-H} = 2.5 Hz)	9.14 (d) (J_{P-H} = 4.7 Hz)
ortho phenyl hydrogens	7.9 (m)	8.0 (m)
meta and para phenyl hydrogens	7.7 (m)	7.8 (m)
hydroxyl hydrogen	−1.8 (d) (J_{P-H} = 22 Hz)	
	^{31}P NMR	
central phosphorus	−192.3	−176.7
	^{13}C NMR^a	
C_α	139.3	140.2
C-1″	136.6	134.4
C-2″, C-6″	133.5	133.4
C_β	132.6 (J_{P-C} = 6.8 Hz)	133.1 (J_{P-C} = 6.7 Hz)
C-4″	129.0	130.5
C-3″, C-5″	127.8	128.9
C_{meso}	115.5 (J_{P-C} = 2.6 Hz)	117.9 (J_{P-C} = 2.8 Hz)

[a] Number scheme used is that of Katz et al.[10]

complex.[4] However, detailed NMR analysis and fluorescence measurements on several batches of material convinced us that this formulation was in error. In fact the product was probably a mixture of the dichloro and dihydroxo complexes (vide infra). Utilizing a modification of the literature procedure, which dispenses with the hydrolysis step and hence avoids contamination with the dihydroxo complex, we have been able to isolate and crystallize the pure dichloro complex.

The IR spectrum of the dichloro complex shows no bands at 895–900 cm^{-1}, where P–O stretching vibrations are found for the dihydroxo complex. The lack of hydroxo ligands is further confirmed by the proton NMR spectrum, which shows no peaks at ∼−2 ppm where the hydroxyl hydrogens appear in the dihydroxo complex. The rest of the NMR spectrum is unexceptional with peaks at 9.14 (d, pyrollic protons, J_{H-P} = 4.7 Hz), 8.0 (m, ortho phenyl hydrogens), and 7.8 ppm (m, meta and para phenyl hydrogens). The NMR reported in ref 4 can now be understood as a ca. 3:1 mixture of (tetraphenylporphinato)dichlorophosphorus(V) and (tetraphenylporphinato)dihydroxophosphorus(V) on the basis of the ratio of the 9.14 and 8.9 ppm peaks reported, which we can now confidently assign to these species respectively. The NMR results for both complexes are summarized in Table I.

The ^{31}P spectra gave single peaks for both species in the range previously reported for the phosphorus(V) complexes of octaethyl- and mesoporphyrin.[8] The downfield shift on going from the dihydroxo to the dichloro complex is consistent with the relative electronegativities of the Cl vs. the OH ligands.[9]

The ^{13}C spectra of both compounds have been assigned by comparison to the available literature on porphyrin systems and are compiled in Table I. There are several noteworthy features of these spectra. The first is a considerable (∼6–10 ppm) high-field shift of the C_α and C_{meso} carbon resonances in the phosphorus TPP complexes relative to other diamagnetic metalloporphyrins (i.e., Zn, Cd, Hg, Tl) or TPP itself.[10] The phenyl and C_β carbon resonances are relatively unaffected, with small (1–3 ppm) shifts to lower field. In general, it has been found that metal incorporation into the porphyrin ring has little or no effect on the ^{13}C spectra.[10] It seems reasonable to attribute the substantial shifts seen upon P(V) incorporation into the TPP macrocycle to unusual structural and/or electronic effects associated with this small highly charged cation. It has previously been suggested that structural effects are of minimal importance in the interpretation of porphyrin ^{13}C spectra.[10] A search through the literature would seem to confirm this. The diacid and Tl(III) complexes of TPP, both of which are extensively distorted (S_4 "ruffling" in the diacid[10] and "doming" in the highly expanded core of the Tl(III) complex[11]), show unexceptional ^{13}C spectra. The electronic effects are hard to estimate, because, although the P(V) cation has a strong inductive effect on the ring (vide infra), it has proven difficult to correlate ^{13}C shifts with substituent electronegativity.[12]

Table II. Reduction Potentials of [(TPP)P^{V}Cl$_2$]$^+$ in Several Solvents

	potential vs. SCE^a		
solvent	E(I), V	E(II), V	$\Delta E°$ = E(II) − E(I), mV
acetonitrile	−0.30	−0.68	380
dimethylformamide	−0.20	−0.64	440
methylene chloride	−0.33	−0.84	510

[a] At the Pt electrode.

Central atom–carbon-13 couplings are observable in these systems, as has been seen in the case of Tl(III) porphyrins.[13] The phosphorus–meso carbon couplings are 2.6 and 2.8 Hz for the dihydroxo and dichloro complexes, respectively. Values of 6.8 and 6.7 Hz are seen for the β-carbons. No coupling is observed with the α-carbons. This pattern is in contrast to the case of the Tl(III) porphyrins where $J_{Tl-^{13}C_\beta} < J_{Tl-^{13}C_{meso}}$. Also interesting are the nearly identical P–^{13}C coupling constants for the dichloro and dihydroxo complexes while the monochloro- and monomethylthallium(III) species show very large differences in their central metal–^{13}C coupling constants. However, in the proton NMR the dichloro complex does have a $J_{H_\beta-P}$ that is about twice as large as that in the dihydroxo complex. We have no satisfactory explanation for all these effects, but a careful NMR study of some of the related metalloid (As, Sb, Bi) porphyrins may shed some light on the relative importance of structural and electronic effects in the ^{13}C spectra.

Electrochemistry. The electrochemistry of dichlorophosphorus(V) tetraphenylporphine is characterized by cyclic voltammetry (CV) as consisting primarily of two sequential reductions. The potentials for these processes as determined by CV in various solvents are given in Table II. For chemically reversible one-electron processes (vide infra), these values are interchangeable with the classical polarographic $E_{1/2}$ and in these cases the thermodynamically significant $E°$. The general features of the cyclic voltammograms are typical for porphyrin complexes.[14] The differences between $E_{1/2}^{(ox)}$ and $E_{1/2}^{(red)}$ and between the first and second reductions of 2.1 and 0.38 V, respectively, are near the values of 2.25 ± 0.15 and 0.42 ± .05 V reported by Kadish for a series of metalloporphyrins and indicate that the electrochemistry is occurring at the porphyrin ring rather than at the central "metal".[14] A notable difference however is the very high reduction potential

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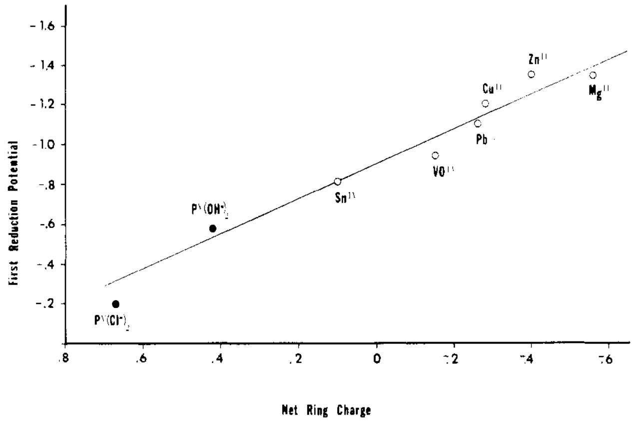

Figure 1. Plot of first "ring" reduction potential vs. net ring charge. Potentials are referenced to an SCE. Solvents are DMF or Me_2SO: ○, data taken from ref 7 and 14; ●, this work (net ring charge calculated from data of Gouterman et al.[3,9]).

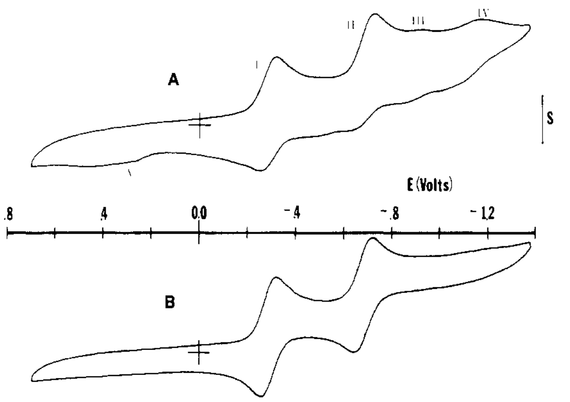

Figure 2. Steady-state cyclic voltammograms of (tetraphenylporphinato)dichlorophosphorus(V) in acetonitrile/0.1 M $(TBA)PF_6$ (potential sweep rate 0.1 V/s; $S = 1.25 \times 10^{-4}$ A/cm^2): A, room-temperature voltammogram; B, low-temperature voltammogram (−3 °C).

observed for this complex. In fact, this is the most easily reduced porphyrin complex yet reported, most porphyrins not undergoing reduction until ca. −1.0 V.[7] This high reduction potential probably has its origin in two factors, the inductive effects of the highly charged P(V) and the structural deformations associated with binding the very small P(V) atom.

Fuhrhop, Kadish, and Davis have shown that the redox behavior of metalloporphyrins can be associated simply with the inductive effects of the central metal on the porphyrin ring.[14] The importance of inductive over conjugative effects of the central metal has been given theoretical backing as well.[14] While these inductive effects can only be quantitated by the electronegativity of the central metal for simple 2+ cations, they are also manifested by the total porphyrin-ring charge as determined by MO calculations. As might be expected, plots of reduction potential vs. net ring charge are nearly linear.[14] Such a plot is shown in Figure 1. As can be seen, the phosphorus(V) complexes show first reduction potentials consistent with what might be expected on the basis of ring charge, although the dichloro species is slightly easier to reduce than predicted. In contrast, the Sb(III) and -(V) complexes of OEP are much harder to reduce, although they have nearly the same net ring charge as the dichlorophosphorus(V) complex.[15] The potential for reduction of the P(V) OEP complex has not been reported. The ease of reduction of the P(V) TPP complexes *relative* to the Sb(V) OEP complexes may be due to structural deformations associated with the P(V) ion. The structure of the Sb(V) OEP complex has been determined, and a planar porphyrin macrocycle[16] is seen while a strongly ruffled macrocycle is seen in (tetraphenylporphinato)dihydroxophosphorus(V) hydroxide.[6] The effects of ring distortion on the redox potential of the diacid of TPP have been considered by Murray.[17] This strongly distorted species also has a high redox potential (ca. −0.45 V vs. SCE in benzonitrile). However, once again it is difficult to sort out the structural effect from the electrostatic effect of the dipositive charge.

A typical cyclic voltammogram of $(TPP)PCl_2^+$ in acetonitrile is shown in Figure 2A. Upon scanning to negative potentials, two well-defined voltammetric waves, labeled I and II, and two smaller waves, III and IV, are observed. Reversing the direction of the potential sweep reveals the chemical irreversibility of II and the appearance of an oxidative process, labeled V.

Waves I and II are diffusion controlled as indicated by the linearity of peak current (i_{pc}) vs. $v^{1/2}$ plots. These waves are also *electrochemically* reversible on the basis of their heterogeneous electron-transfer rate constants[18] as determined by the method of Nicholson.[19] Plots of peak current vs. concentration are linear over the range from about 3×10^{-4} to 30×10^{-4} M and indicate no obvious equilibrium processes. From these data we have calculated a diffusion coefficient for the cation of 4.8×10^{-6} cm^2/s.

As was previously mentioned, these processes are consistent with two sequential ring reductions based on the electrochemical criteria set forth by Fuhrhop, Kadish, and Davis. Thus, these waves correspond to the processes

$$[(TPP)P^{V}Cl_2]^+ + e^- \rightleftharpoons [(TPP)P^{V}Cl_2]^0 \qquad (1)$$

$$[(TPP)P^{V}Cl_2]^0 + e^- \rightarrow [(TPP)P^{V}Cl_2]^- \qquad (2)$$

As indicated, the second process is not *chemically* reversible. However, at scan rates ≥5 V/s or at low temperature (Figure 2B) the chemical process is outrun or slowed down. Analysis of the i_{pa} to i_{pc} ratio with scan rate as described by Nicholson and Shain,[20] assuming a first-order decay, yields a rate constant of ca. 0.91 s^{-1} for this chemical step, which we believe is a combination of ring protonation and internal electron transfer (vide infra). This compares with a value of 1 s^{-1} found by Wilson for a similar ring protonation.[21]

The nature of waves III, IV, and V has not been investigated in detail, but on the basis of an analogy to the results of the closed shell, ZnTPP[21] electrochemistry and our spectral and coulometric studies probably represent two one-electron reductions of the phlorin anion (vide infra) and its corresponding oxidation, respectively.[22] It is also noted that these Faradaic processes disappear at fast sweep rates or low temperatures, consistent with an ECE type mechanism.

The reduction centered at $E_{1/2} = -0.30$ V has been confirmed by exhaustive electrolysis and coulometry to proceed by one electron per molecule and to correspond to process 1. When the reduction is carried out at −3 °C, the reduced (now

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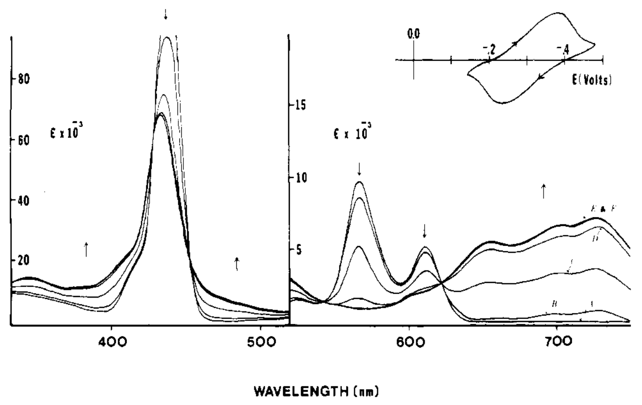

Figure 3. Variation in the visible spectrum of (tetraphenylporphinato)dichlorophosphorus(V) with degree of reduction. Inset: thin-layer cyclic voltammogram in acetonitrile/0.1 M (TBA)PF_6 at a gold-minigrid working electrode (potential sweep rate 0.004 V/s). The large ΔE_p is due to the high cell resistance in the OTTLE. Potential steps vs. SCE (V): A, 0.0; B, −0.25; C, −0.30; D, −0.35; E, −0.40; F, −0.45. Arrows indicate direction of change.

a neutral species) product crystallizes from solution. The crystalline material was isolated by washing with degassed acetonitrile followed by drying under an inert atmosphere. The product, as expected of a radical species, is paramagnetic and exhibits a room-temperature EPR spectrum consisting of a single line at $g = 2.0027$, devoid of any hyperfine splitting with a peak to peak width of 7 G. These values are similar to those that have been found for a variety of mono-ring-reduced metalloporphyrin complexes.[23a] The visible spectrum of this green solution (toluene) reveals bands at λ_{max} ($\epsilon \times 10^3$) 434 nm (68.0), 645 nm (5.2), 701 nm (6.3), 726 nm (6.8), and 830 nm (2.2). Once again, the presence of relatively intense bands in the near-IR region is consistent with the one-electron reduction of the TPP ring.[7] Such a visible spectrum can also be generated by chemical reduction of the complex with hydrazine.

That the visible spectrum is due to a single species and corresponds to the process at $E_{1/2} = -0.30$ V was confirmed by employing an OTTLE cell (Figure 3). Stepping the potential by −0.05 increments from −0.2 V causes a decrease in both the visible and Soret bands and a concomitant increase in the 625–750-nm region. The existence of four isosbestic points implies the presence of only two species, the starting material and the one-electron-reduced radical. The final spectrum is precisely the same as that obtained for the pure crystalline reduced product. Stepping the potential back to 0.0 V regenerates the original spectrum with no observable decrease in intensity, confirming the chemical reversibility of the process.

Our isolation of the one-electron-ring-reduced complex represents only the second time that such material has been crystallized and characterized.[23b] The solid-state stability of the radical is remarkably high with no detectable decomposition observed in samples exposed to the air for over 6 months. It is also stable for days in undegassed toluene solution but reverts back to starting material within several hours in chlorinated solvents. Attempts to prepare single crystals suitable for X-ray diffraction are in progress and would be helpful as no structure for a ring-reduced porphyrin species has been reported.

As is evident from Figure 2A, the addition of a second electron to the dichloro complex is chemically irreversible. This irreversibility is accentuated by the addition of water or other proton sources to the solution. Addition of 0.01-mL aliquots of water cause an increase in the peak current of wave II and a shift in potential of approximately +6 mV/aliquot. The peak current levels off at about 3% v/v water content to a value nearly twice its original. Since the peak height of the original wave II was the same as that of wave I, known to be a one-electron process, we can infer that the addition of water leads to a multielectron process at potentials around −0.68 V. This concept is supported by bulk electrolysis and spectral studies that indicate that in slightly "wet" acetonitrile more than two electrons per molecule are passed at −0.68 V and the products are TPP and a yet unidentified ring-protonated material.

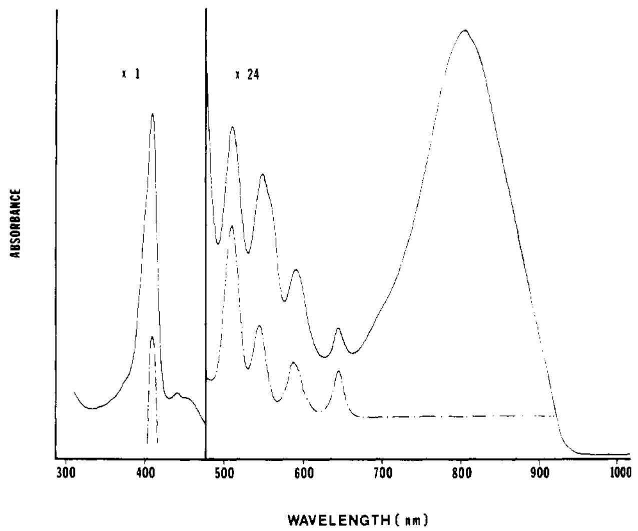

Figure 4. Visible and near-IR spectrum of (tetraphenylporphinato)dichlorophosphorus(V) after two-electron reduction in acetonitrile/0.1 M (TBA)PF_6. The dotted line represents a spectrum of TPP in the same solvent system.

The reduction at −0.68 V at low temperature or room temperature under *dry* conditions has been confirmed by exhaustive electrolysis to proceed by two electrons per molecule. Although a number of minor products are produced, there are only two major products. These products have been identified by optical spectroscopy (Figure 4) as the P^V phlorin anion and free-base tetraphenylporphine. On the basis of the known extinction coefficients of TPP in acetonitrile and estimated values for typical phlorin anions such as the Zn phlorin anion, we can calculate the ratio of TPP to phlorin anion produced as ca. 3:1. The spectrum of the electrolysis mixture clearly shows the four-banded TPP visible region and its characteristic Soret band. The remaining strong near-IR peak at 800 nm and the weak Soret-like band at 445 nm are characteristic of phlorin anions such as that seen in the reduction of ZnTPP. Cyclic voltammetry of this solution also shows a phlorin anion oxidation at $E_p = +0.36$ V.

The production of free TPP upon overall two-electron reduction is interesting and deserves comment. This can best be rationalized as an internal electron transfer between the direduced porphyrin ring and the central phosphorus atom, yielding a P(III) TPP complex.

Phosphorus(III) complexes of the porphyrins are known to be extremely unstable and to decompose to yield free-base porphyrin.[3] The phlorin anion, the other major product, seems to be formed competitively with the internal-electron-transfer product via protonation of the initially formed two-electron-ring-reduced species. There is no evidence that an internal electron transfer occurs in the phosphorus(V) phlorin anion. Allowing the electrolysis mixture to stand does not result in any obvious change in products other than a small amount of oxidation of the phlorin anion back to starting material. Thus, once the direduced monoanion is protonated, it has no further tendency toward internal electron transfer. Internal electron

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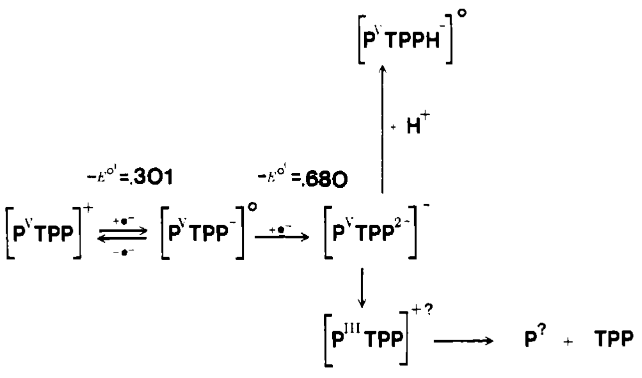
Scheme I



transfers such as that described here can be both irreversible and in one remarkable case reversible and have been reported for three other porphyrin systems.[24-26] All of the other reported examples have involved oxidative reactions, this being the first example to our knowledge of a reductive reaction. The overall electrochemistry is depicted in Scheme I.

Internal electron transfers such as that described here may be important in biological electron transfers involving hemes.[27] It has been suggested that axial ligation can have a strong influence on these internal electron transfers.[26,27] This seems to be the case with these phosphorus systems as well; a report on the electrochemistry of the analogous dihydroxo complex, which is strikingly different, will be forthcoming. We should also add that protonation reactions, as demonstrated here, can also have a substantial effect on the internal electron transfer of reductive processes.

Acknowledgment. We wish to thank Prof. W. E. Geiger for the generous loan of his electrochemical equipment without which this work could not have been carried out. We also wish to acknowledge Prof. Geiger and Prof. C. M. Elliott for many helpful discussions concerning various aspects of this work and to thank K. Baptie for assistance with the synthesis and purification of the title compound.

Registry No. [(TPP)P^VCl_2]Cl, 84896-72-0; [(TPP)$P^V(OH)_2$]OH, 85565-87-3; [(TPP)P^VCl_2], 84896-73-1; [(TPP)P^VCl_2]$^-$, 84880-35-3.

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Cadmium Diethyl Phosphate: Structure Determination and Comparison to Cation Phospholipid Complexes

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X-ray diffraction analysis refined to residuals $R_1 = 0.026$ and $R_2 = 0.031$ has shown the structure of $Cd[(EtO)_2PO_2]_2$ to be polymeric with one-dimensional chains of cadmium atoms bridged by oxygen atoms from the phosphates. The compound crystallizes in space group $P\bar{1}$ with $a = 5.316$ (1) Å, $b = 12.867$ (4) Å, $c = 12.963$ (4) Å, $\alpha = 67.93$ (3)°, $\beta = 77.07$ (2)°, $\gamma = 79.13$ (2)°, $Z = 2$, and $V = 795.5$ Å^3. In comparison to existing polymeric structures for barium and magnesium analogues, this compound has an unusually short metal–metal distance of 3.50 Å. The concomitant compression of the phosphate–phosphate distances along the chain axis is even more pronounced. Aside from general implications for cadmium coordination chemistry, the variation in these distances is suggested to play a role in selective stimulation of membrane transformations by structurally similar complexes of Ca^{2+} and Cd^{2+} with anionic phospholipids.

Introduction

Complexes of divalent cations with phosphate esters are important entities in many biological systems. In particular, divalent cations are believed, in several cases, to mediate fusion of natural and artificial membranes with Ca^{2+} often showing enhanced activity over other divalent ions.[1] Correlation of activity with ion size is well documented in at least one model system, a mixed phosphatidylcholine–phosphatidic acid vesicle system.[2] High fusion activities of similar magnitudes were observed for the equivalent-sized ions Ca^{2+} and Cd^{2+}. By comparison, lower activities were observed for the larger and smaller ions Ba^{2+} and Mg^{2+}. This correlation suggests that structural aspects of the cation–phosphate ester complexes formed may provide a key to understanding ion selectivity in the fusion process.

X-ray crystal structures of the simple phosphate ester–cation complexes formed by Mg^{2+} and Ba^{2+} with diethyl phosphate have been published.[3,4] A structure of the Ca^{2+} or Cd^{2+} salt should provide a series in which structural correlations with activity could be sought. We present here the structure of the Cd^{2+} salt. Cd^{2+} has been used as a substitute ion for Ca^{2+} in a number of biochemical NMR studies.[5,6] It provides a useful spectroscopic probe in that the ^{113}Cd and ^{111}Cd isotopes are spin 1/2 with reasonably high NMR receptivity. Thus, in addition to completing a structural series useful in analyzing a possible structural basis for variation in membrane fusion activity, the cadmium–diethyl phosphate structure will provide the basis of solid ^{113}Cd NMR studies, which can extend structural characterization to less ordered membrane phases.

Experimental Section

$Cd[(EtO)_2PO_2]_2$ was crystallized from a solution of potassium-diethyl phosphate and $Cd(NO_3)_2$. KNO_3, which precipitates first,

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