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Mechanism of Electrochemical Reduction of the (5,10,15,20-Tetraphenylporphinato)dihydroxophosphorus(V) Cation

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The electrochemical reductions of the title complex are significantly different from those of the analogous dichloro species. As previously reported, reduction of the dichloro complex proceeds by two sequential one-electron steps. The first is chemically reversible and involves formation of the radical "anion". The second step leads initially to the porphyrin-ring dianion but reacts further to yield new products (phlorin anion and unmetalated tetraphenylporphine). In contrast, the reduction of the title complex by one electron initiates a series of complicated chemical steps, yielding a variety of porphyrin products, some of which have been identified. The cause for these differences upon electrochemical reduction has been traced to the presence of the weakly acidic hydroxyl protons in the hydroxy compound. The results of cyclic voltammetry, chronoamperometry, and bulk electrolysis investigations on the dihydroxy complex are described.

Introduction

Recently we have reported on the synthesis, characterization, and electrochemistry of (5,10,15,20-tetraphenylporphinato)dichlorophosphorus(V) chloride.[2,3] The analogous (tetraphenylporphinato)dihydroxophosphorus(V) hydroxide had been synthesized and characterized by us earlier.[4] Our interest in "metalloid" porphyrins stems from the fact that phosphorus is the first non-metal and, in the pentavalent state, the smallest ion to undergo insertion into a porphyrin ring. The recent crystal structure[5] reveals that the coordination of the small phosphorus(V) ion results in extensive ruffling of the porphyrin macrocycle as predicted by Hoard.[6] In addition, phosphorus can exist in two stable oxidation states, III and V, and both have been reported for its complexes with octaethylporphyrin.[7,8]

As part of our interest in the effects of structure on redox properties, we have previously examined the reductive electrochemistry of the dichloro complex and demonstrated that this was the easiest metalloporphyrin to reduce yet reported. Since it has been established that axial ligation can have a profound effect on porphyrin electrochemistry, we report herein the electrochemistry of the dihydroxy analogue, which is indeed strikingly different.

Experimental Section

The (tetraphenylporphinato)dihydroxophosphorus(V) cation was prepared by the modifications of the method of Carrano and Tsutsui[4] as described in ref 3. The general electrochemical procedures have also been previously described.[2,3] All potentials are recorded vs. the saturated calomel electrode and are uncorrected for junction potentials. Heterogeneous electron-transfer rate constants were measured in a specially designed cell, with the working electrode positioned very near a Luggin capillary tip, and solution resistance was compensated electronically by positive feedback.

Results

Cyclic Voltammetry. The reductive electrochemistry of the (tetraphenylporphinato)dihydroxophosphorus(V) cation,

hereafter referred to as P(OH)$_2$, is characterized by cyclic voltammetry at potential sweep rates greater than 100 V/s, as consisting of two sequential, chemically reversible waves (Figure 1A). At these fast sweep rates, the voltammograms of the dichloro and dihydroxy species are quite similar (see ref 2). The potential for the first reduction of P(OH)$_2$ ($E_1^{\circ\prime}$ = -0.64 V) is approximately 340 mV negative of the first reduction of the dichloro complex. This difference in reduction potential is adequately predicted by the inductive effect of the dihydroxophosphorus(V) center.[3] The calculated charge density at the porphyrin ring is larger for the dihydroxo complex than for the more electronegative dichloro complex, leading directly to the more negative reduction potential.[9] The second reduction appears 380 mV negative of the first reduction ($E_2^{\circ\prime}$ = -1.02 V) in P(OH)$_2$, similar to what is seen with the dichloro complex. Both reductions for P(OH)$_2$ are nearly electrochemically reversible,[10] k_{s^1} = 0.06 cm/s and k_{s^2} = 0.04 cm/s, again similar to the dichloro complex. Thus, the voltammogram at fast potential sweep rates (Figure 1A) probably represents two sequential one-electron ring reductions similar to those characterized for the dichloro complex, only shifted negatively by inductive effects.

The straightforward electrochemical behavior of P(OH)$_2$ observed at fast potential sweep rates disappears as the rate of potential sweep is lowered. A cyclic voltammogram at a potential sweep rate of 0.5 V/s is shown in Figure 1B. It consists of two chemically irreversible reductions labeled I and II and two oxidations labeled III and IV. At slow potential sweep rates the initially chemically reversible reductions in Figure 1A are now observed to be chemically irreversible. The lack of reoxidation waves for processes I and II indicates that a chemical reaction follows the initial electron transfers. This chemical irreversibility of waves I and II is better observed in Figure 2, where the products are built up at the electrode surface by continuous potential cycling. The rates of the chemical step/steps that follow the first and second reductions are not the same. As Figure 1B,C illustrates, the rate of the chemical step for the first reduction is slow enough so that upon potential sweep reversal the reoxidation of the initially reduced species, labeled V, is observed, while for the second reduction no such corresponding oxidation is observed. Two additional important features of the voltammograms in Figure 1B and C are (1) oxidations III and IV appear to be formed by *both* the first and the second reductions and (2) the reoxidation of I is totally absent when the potential limits include the second reduction.

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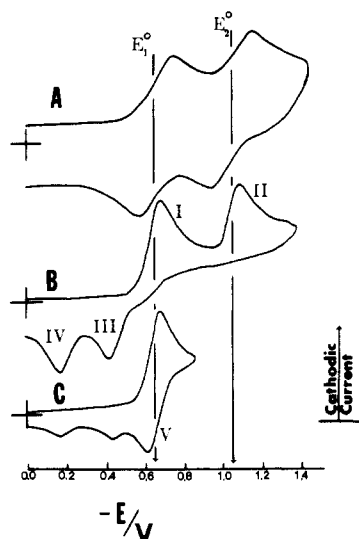(10) Nicholson, R. S. *Anal. Chem.* 1965, 37, 1351.

Figure 1. Cyclic voltammograms of $[P^V(OH)_2TPP]^+$ in aceto-nitrile/0.1 M tetrabutylammonium hexafluorophosphate ((TBA)PF$_6$) (conditions: $[P(OH)_2]$ = 0.73 mM): (A) v = 100 V/s; (B) v = 0.5 V/s; (C) v = 0.5 V/s.
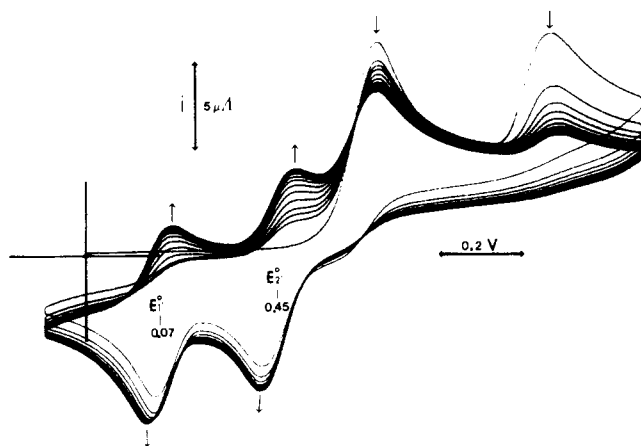

Figure 2. Continuous potential cycling of $P(OH)_2$ in acetonitrile/0.1 M (TBA)PF$_6$ (conditions: $[P(OH)_2]$ = 0.70 mM; v = 0.5 V/s).

When we attempted to quantify the rate of the chemical step by analysis of i_{pa} to i_{pc} ratios as a function of scan rate, as described by Nicholson and Shain,[11a] we observed a concentration dependence to the calculated rate constants. Since the Nicholson and Shain analysis assumes first-order behavior, which is not observed in this system, the quantitative results are not meaningful. However, the linear dependence of the calculated rate constants with porphyrin concentration suggests a second-order process may be involved. In light of the large number of mechanisms that may display such a concentration dependence,[11b] we did not attempt to analyze the data further. The concentration dependence on the rate of the chemical step was also observed in a number of other ways.

For example, we have observed that as the rate of the chemical step that follows the first reduction is increased, there is a concomitant decrease in the current for the second reduction. At high porphyrin concentrations, 3 mM, the rate of the chemical step for the first reduction appears to be relatively fast, and the current for the second reduction was almost unobservable. Similar trends were observed for lower porphyrin concentrations at very low potential sweep rate, 0.02 V/s. This observation of a decrease in current for the second reduction with increasing rate of the chemical step following
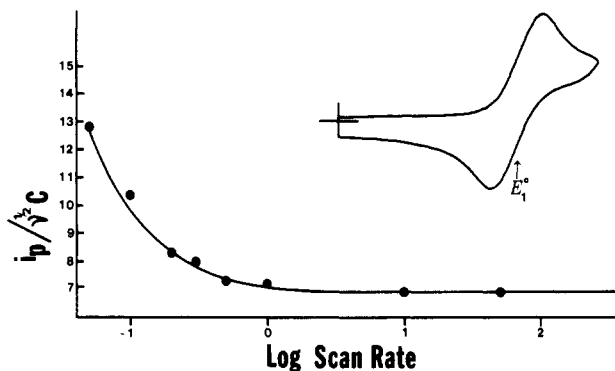

Figure 3. Dependence of CV current function on potential sweep rate ($[P(OH)_2]$ = 2.88 mM). Inset represents the CV for the first reduction at v = 50 V/s.

the first reduction is expected if the second wave represents the reduction of the radical "anion" to the "dianion", since the chemical step would deplete the concentration of the monoreduced species at the electrode surface, leaving little or none to be further reduced to the "dianion" (of course any fresh porphyrin diffusing to the electrode from the bulk solution can be reduced to the dianion of this potential, but the current will be much less than in the absence of the chemical step). The above results support the contention that the reductions were initially associated with the sequential reduction of the porphyrin ring, as evidenced at high potential sweep rates.

In addition unlike the dichloro complex, the first reduction of $P(OH)_2$ was not diffusion controlled. Plots of peak current vs. porphyrin concentration, and the square root of potential sweep rate, were not linear but deviated in a positive direction at high porphyrin concentrations, or at low potential sweep rates (not shown). As the concentration increased, the current under the first reduction wave became larger.

In order to better understand the above observations, we have analyzed the CV current function constant for a variety of $P(OH)_2$ concentrations. As expected, when the current function was constant, a stable, chemically reversible CV was obtained, indicating that the chemical step for the first reduction was outrun by the potential sweep rate, and the reduction was under diffusion control (Figure 3). By plotting these current function constants against $P(OH)_2$ concentration (not shown), we were able to calculate a diffusion coefficient for the starting material, D_0 = 1.35 × 10^{-5} cm^2/s. Incorporating the new diffusion coefficient into the current function constant

$$2.69 \times 10^5 n^{3/2} A D_0^{1/2}$$

where A is the electrode area in cm^2 and evaluating it for n = 1, we see that for a one-electron reduction the current function constant should be 6.92. As illustrated by Figure 3, the $P(OH)_2$ complex approached this value at high potential sweep rates. This suggested that at high potential sweep rates, when the chemical step was outrun, the $P(OH)_2$ complex was reduced by one electron, as expected for a porphyrin-ring reduction. At low potential sweep rates the chemical step was fast with respect to v and contributed to the current under the first wave.

The cyclic voltammetric data described above suggested that the initial reduction of $P(OH)_2$ by one electron was followed by a chemical step that produced a new porphyrin/porphyrins that also underwent reduction. These observations typify the ECE mechanism where the $E^{o'}$ for the second process is less negative than the $E^{o'}$ for the initial reduction of $P(OH)_2$.[12]

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We should note, however, that the chemical step for this ECE mechanism could be a disproportionation, which would also yield more current at slow sweep rates and which is a second-order process as well. Methods for distinguishing between these two mechanistic pathways have been given consideration by Saveant.[13] However, experimentally the distinction is difficult to observe. In practice we have been unable to distinguish between the two mechanisms by cyclic voltammetry, but product analysis (vide infra) will allow us to choose between these mechanisms.

Chronoamperometry. In the chronoamperometric technique the potential of the working electrode is suddenly changed from a potential where no reduction (or oxidation) takes place, i.e., $E_{work} \gg E^{\circ\prime}$, to a potential where the concentration of the oxidized (or reduced) species at the electrode surface is instantaneously driven to zero.[14] The observed current–time behavior for such a potential step is described by the Cottrell equation

$$i_t = nFAC_{ox} \qquad (1)$$

where n is the number of electrons transferred in the electrochemical step, F is the faraday, C_{ox} is the bulk concentration of oxidized species, and t is time in seconds. Plots of i_t vs. $t^{-1/2}$ are linear for diffusion-controlled systems, and $it^{1/2}$ is a constant. Stepping the potential onto the rising portion of a polarogram, i.e., the range where C_{ox}(surface) is controlled by the Nernst equation, and sampling the current at a specified time for each step produces, when i_t is plotted against E_{app}, a sampled current voltammogram, SCV, that is the envelope of a polarogram.[12]

We have applied this method to the reduction of $P(OH)_2$. Stepping the potential in 50-mV increments from 0.0 V vs. SCE produced the corresponding current–time plots. Sampling the current 0.27 s after the potential step, and plotting this vs. the applied potential step, E_{app}, yielded a sampled current voltammogram. Since this is the envelope of polarogram, it can be analyzed on the rising portion of the SCV as in polarography.[15] A plot of $-E_{app}$ vs. log $[i/(i_d - i)]$ was linear with a slope of 0.058 V and an intercept of –0.627 V. Our slope of 0.058 V was indicative of electrochemical reversibility, and the intercept was close to that obtained by CV (–0.64 V). Thus, as seen in cyclic voltammetry, the first reduction is kinetically fast. However, information regarding the apparent n value cannot be obtained directly from the "diffusion", or limiting current, because the chemical step is of course time dependent. A more accurate treatment has been described by Shain[16] and Murray.[17]

If we analyze the current for an ECE process where the $E^{\circ\prime}$ for the product/products from the chemical step is higher than the $E^{\circ\prime}$ for $P(OH)_2$, then the current is described by eq 2,

$$i_t = FAC_{ox}\left(\frac{D_0}{\pi}\right)^{1/2} t^{-1/2}(n_1 + n_2[1 - \exp(-k_f t)]) \qquad (2)$$

where n_1 is the number of electrons transferred in the initial electrochemical step, n_2 is the number of electrons transferred in the product/products electrochemical step, k_f is the rate constant for the chemical step, and the other variables and constants have their usual meaning. The bracketed term of eq 2 is the apparent n value, n_{app}, which, for short enough
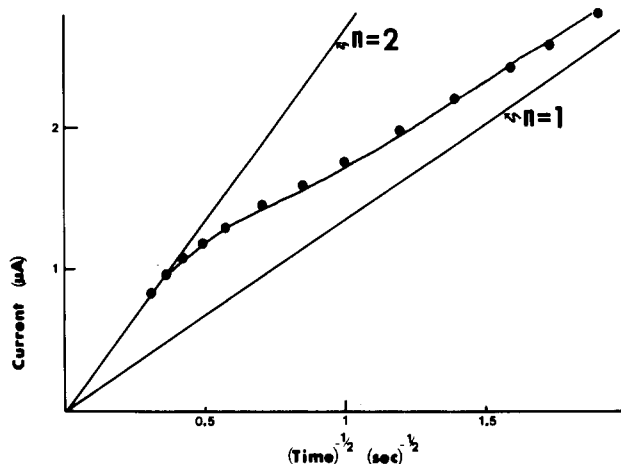
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Figure 4. Plot of the current–time behavior of $P(OH)_2$ obtained from a chronoamperometric potential step. Solid circles represent the experimental current; the solid line represents the calculated current from eq 2.
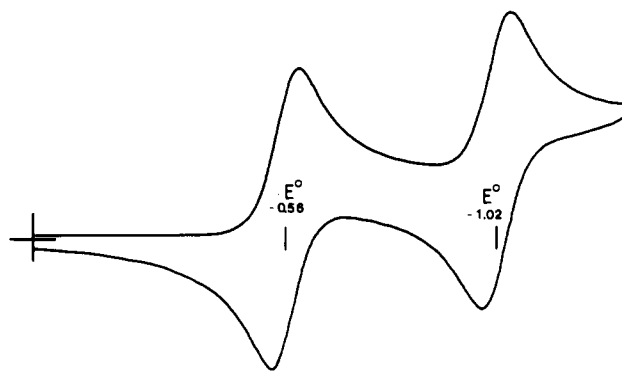

Figure 5. Cyclic voltammogram of O-trimethylsilyl phosphorus porphyrin in acetonitrile/0.1 M $(TBA)PF_6$ ($v = 0.1$ V/s).

sampling times, approaches n_1; i.e., the current has been sampled before the chemical step becomes important. At long enough sampling times, i.e., letting the chemical step go to completion, $n_{app} = n_1 + n_2$. Equation 2 thus predicts a transition from $n_{app} = n_1$ to $n_{app} = n_1 + n_2$, the rate of this transition being controlled by k_f.

We have analyzed the first reductive process of $P(OH)_2$ by the method described by Shain and Murray, outlined above. The rate constant for the chemical step was obtained by assuming $n_2 = 1$ and plotting ln $[-(n_{app} - 2)]$ vs. t, the slope of which was a direct measure of k_f. From the slope, $k_f = 0.38$ s^{-1}. Incorporating k_f into eq 2 and plotting the calculated current, i_c, against $t^{-1/2}$ gave the results shown in Figure 4. The calculated current tranverses the $n = 2$ plot to the $n = 1$ plot and is a good description of the actual measured current, as is evident by the close fit. This strongly suggests that n_2 is indeed 1 and that the chemical step produces a product or products that undergo reduction at a potential $>E^\circ$ of the first reduction of $P(OH)_2$.

The question arises as to the cause of the extreme difference in chemical reactivity of reduced $P(OH)_2$ as compared to the dichloro complex (which produced an exceptionally stable monoreduced ring radical). We believe it is undoubtedly due to the coordinated hydroxyl groups and their weakly acidic protons. In an attempt to better understand this reactivity, i.e., the nature of the chemical step in the proposed ECE mechanism, we have investigated the effect of excess acid, base, and N-(trimethylsilyl)imidazole on the cyclic voltammetry of $P(OH)_2$.

N-(trimethylsilyl)imidazole is an excellent silanizing reagent, thought to be specific for hydroxyl groups.[18] It reacts rapidly

and cleanly with a variety of –OH groups to yield the *O*-tri-methylsilyl derivatives. The addition of *N*-(trimethylsilyl)-imidazole produces dramatic changes in the voltammograms of the dihydroxy complex (Figure 5). Two chemically reversible (on the CV time scale) reductions separated by 450 mV have replaced the chemically irreversible reductions of $P(OH)_2$, recall Figure 1B. The observed electrochemical reductions are those of the *O*-trimethylsilyl phosphorus porphyrin, uncomplicated by any chemical steps, and are similar to what is observed with the dichloro complex. Therefore, these reductions probably represent the same sequential one-electron ring reductions. Because D_0 and C_0 are not known, a direct calculation of the *n* value is not possible. However, in situations where D_0 and C_0 are not known, the *n* value can be estimated by comparing the Cottrell constant, $it^{1/2}$, to the CV current function constant, $i_p/v^{1/2}$, during the same experiment.[19] Since conditions are identical, e.g., C_0, D_0, A, solvent, temperature, etc., one need only to evaluate the two constants[19]

$$i_p/v^{1/2}/it^{1/2} = 4.94n^{1/2}$$

where 4.94 is the result of collecting the constants of the Randell–Sevcik and Cottrell equations.[19] When the currents for the chronoamperometric experiment were corrected for charging currents, this ratio was 4.53, close to the expected value for a one-electron process. Plots of *i* vs. $t^{-1/2}$ for the first and second reduction of this species had identical slopes, indicating that the *n* value was the same. Thus, it appears that both reductions proceed by 1e/porphyrin molecule and do indeed represent ring reductions as expected. Thus, removal of the weakly acidic hydroxyl protons returns the $P(OH)_2$ complex to simple porphyrin electrochemistry. This was confirmed by bulk electrolysis at the first wave that gave an *n* value near to 1 and generated a species that had the characteristic visible spectrum of a monoreduced ring radical.[3]

To further test the importance of the hydroxyl protons in the electrochemical reductions of $P(OH)_2$, the effects of acid and base were examined. It has been reported that the hydroxyl protons of a number of phosphorus porphyrins can be titrated, and the pK_a's for the two protons of the dihydroxo-phosphorus(V)–mesoporphyrin IX complex are reported to be 9.52 and 12.20, respectively.[20] We have qualitatively examined the deprotonation behavior of the TPP complex as well. Addition of a solution of tetraethylammonium hydroxide in acetonitrile to an acetonitrile solution of $P(OH)_2$ leads to spectral changes similar to those seen in ref 20. The presence of two sequential sets of isosbestic points indicates the successive deprotonation of both hydroxyl groups. The blue shift in the spectra has been explained.[20] While no equilibrium constants have been extracted from this nonaqueous system, it seems clear that the hydroxyl protons on $P(OH)_2$ are weakly acidic and probably have similar pK_a values to those previously reported.

Electrochemically, the addition of small (much less than stoichiometric) quantities of hydroxide ion to $P(OH)_2$ has a significant effect on the chemical step following the first reduction. As hydroxide ion is added, the peak current for the first reduction increases while that of the second reduction decreases. Eventually the reverse oxidation of the first reduction can no longer be observed upon scan reversal. Before hydroxide ion was added, the peak current ratio, i_{pa}/i_{pc}, for the first reduction was 0.56 at 0.2 V/s. Since under the same conditions no reverse oxidation is observed upon addition of
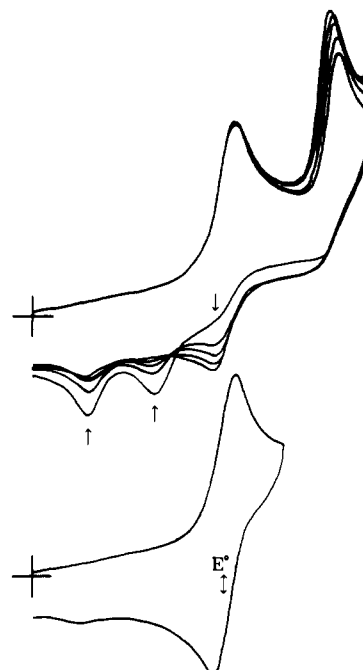

Figure 6. Changes in the cyclic voltammogram of $P(OH)_2$ upon additions of acetic acid. All voltammograms are at $v = 0.1$ V/s; arrows indicate direction of change.
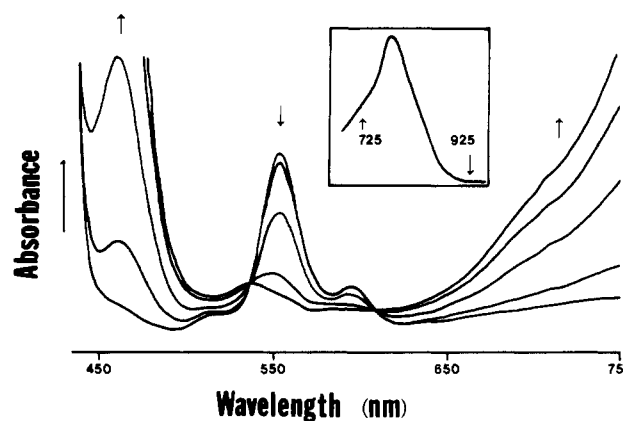

Figure 7. Changes in the visible spectrum of $P(OH)_2$ upon reduction in acetonitrile/1% acetic acid within an OTTLE cell. Inset represents the near-IR absorption of the phlorin anion. Arrows indicate the direction of change.

small amounts of the base solution, the rate of chemical step has clearly increased. Continued addition of hydroxide ion (1–2 equiv) deprotonates the $P(OH)_2$ complex and forms a new reductive process that occurs 143 mV negative of that of the initial species. It is interesting to note that the deprotonated porphyrin also leads to products with similar oxidative processes. The oxidation initially at –0.419 V appears to be little affected by base, while the most positive oxidation is shifted 94 mV in the negative direction.

In contrast, the addition of acetic acid to $P(OH)_2$ apparently retards the rate of the chemical step for the first reduction (on the CV time scale) (Figure 6). An important observation is the appearance of the oxidation corresponding to the first reduction upon subsequent additions of acetic acid. Also, as this oxidative process grows with each acetic acid addition, the normal product oxidations diminish. This implies that the product of the second reduction reacts preferentially with acetic acid rather than with starting porphyrin (vida infra). This phenomenon is not specific for acetic acid, in that small amounts of HCl produce the same result; therefore, the acid effect is a general one.

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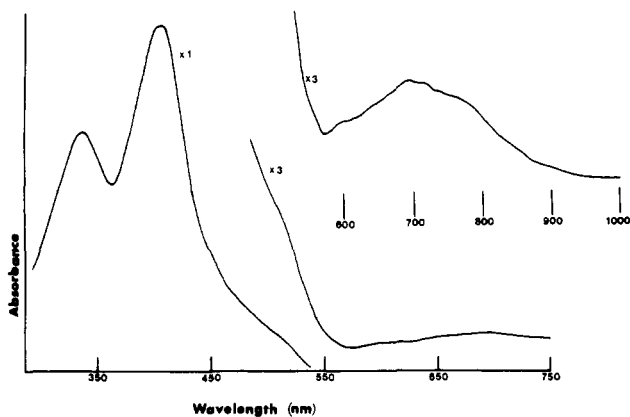(20) Gouterman, M.; Sayer, P.; Shankland, E.; Smith, J. P. *Inorg. Chem.* **1981**, *20*, 87.

Figure 8. Visible–near-IR spectrum of $P(OH)_2$ after bulk reduction in acetonitrile at -0.8 V.

Figure 9. Changes in the visible spectrum of $P(OH)_2$ upon reduction in DMF within an OTTLE cell. Arrows indicate direction of change.

It has been demonstrated by Wilson et al.[21] that acid promotes disproportionation and protonation in the electrochemical reductions of ZnTPP. It was possible that the same phenomenon was occurring with $P(OH)_2$ in acid media. By employing an OTTLE cell, we were able to observe the direct formation of the phlorin anion of $P(OH)_2$ from the first reduction process in ~1% acetic acid/acetonitrile. Figure 7 illustrates the changes of the visible bands upon potential stepping of the gold minigrid. As is indicated by the isosbestic points, the changes in the visible spectrum are due to two species, the starting material and the phlorin anion (identified by its characteristic optical spectrum λ_{max} = 445 and 773 nm). This is consistent with initially reduced "anion" radical disproportionating to the dianion, which rapidly protonates to form the phlorin anion.

The effects we have observed in 1% acetic acid, i.e., disproportionation and disappearance of the normal products formed in the *absence* of acid, implies that a new reductive mechanism was operating. These results are similar to those observed for ZnTPP.[21]

Bulk Reductions of $P(OH)_2$. When the dihydroxo complex was reduced at the first wave, by bulk electrolysis methods, the amount of electricity consumed was indicative of a two-electron reduction; Q/FN_0 = 2.0 ± 0.1, where Q is the number of coulombs consumed and N_0 equals the total number of moles $P(OH)_2$. Thus, bulk electrolysis confirms the cyclic and chronoamperometric results. The purple-pink color of the original $P(OH)_2$ complex turned yellow-brown upon reduction. The visible–near-IR spectrum of the reduced material is shown in Figure 8. As can be seen, the normal visible bands (550 and 600 nm) of $P(OH)_2$ have been replaced by a weak broad absorption, extending into the near-IR region, and the intense Soret band (λ_{max} = 427 nm) of $P(OH)_2$ has been replaced with two weaker bands at 339 and 408 nm. The cyclic voltammogram of the reduced material revealed two oxidative processes at $E_1^{\circ\prime}$ = -0.19 V and $E_2^{\circ\prime}$ = -0.39 V, respectively. These oxidations are nearly identical with those obtained by continuous potential cycling; recall Figure 2.

While most of the bulk reductions were done in acetonitrile, bulk reductions on the first wave in DMF generally gave similar results. For example, the optical absorption spectrum of a reduction in DMF is nearly superimposable on that obtained in acetonitrile. The cyclic voltammogram of the reduced material also revealed redox couples similar to those in acetonitrile.

Due to the long time required to completely electrolyze the samples (>30 min) and their extreme air sensitivity when reduced, a number of minor species were also formed in ad-
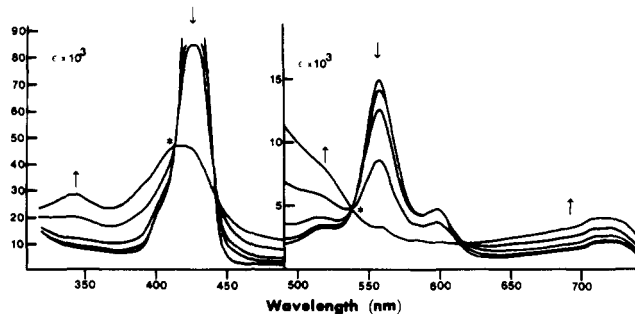
dition to the major product.[22] By employing an OTTLE cell, we were able to do complete electrolyses in seconds and to monitor the optical spectrum in a completely sealed system, which served to eliminate decomposition problems. It should also be noted that in order to observe the $P(OH)_2$ visible bands in the OTTLE cell, the concentration of $P(OH)_2$ was very high, ca. 20 times the average concentration used in bulk and CV experiments. These high concentrations, ca. 10 mM, cause the rate of the chemical step following the first reduction to be very fast. The experiments reported here are for DMF, which gave better thin-layer voltammograms. However, the optical results in acetonitrile were the same as those in DMF. Stepping the potential in 50-mV increments and recording the visible spectrum after each potential step yielded the visible spectroscopic changes illustrated in Figure 9. After the fourth potential step, the visible spectrum no longer changes, indicating depletion of the $P(OH)_2$ complex in the grid area. The final visible spectrum is very similar to that obtained by bulk reductions in either acetonitrile or DMF. The existence of two isosbestic points indicates that when the spectra were recorded *only two species* were present. Thus, the OTTLE experiments indicate that under these conditions a clean reduction of the starting $P(OH)_2$ to the 2e-reduced product is achieved and that this product is identical with the major product found upon bulk electrolysis.

The properties of the reduced material in DMF or acetonitrile such as CV and visible spectra *are not* similar to those seen for other metalloporphyrins. Hence, the nature of the reduction product is unclear. It is reasonable to assume, however, that the major electrochemical activity *is not* due to any reduced, and subsequently protonated, metallo or free-base porphyrin because these species normally undergo reduction at a potential negative of the original porphyrin.[23] Thus, it seems likely that the electrochemical activity is due to a new species with an intact porphyrin skeleton.

Since the reduction product was extremely air sensitive, it was felt a better characterization could be achieved by reoxidation of product to an air-stable material. Cyclic voltammetric oxidation of the reduced product had already implied chemically reversible oxidation on the bulk scale. We therefore attempted the bulk oxidation of the reduced product at 0.0 V in acetonitrile. The yellow-brown color of the reduced product changed to a deep forest green, and the amount of electricity consumed was generally 80–85% of the number of coulombs needed to reduce it. Because of the incomplete recapture of the number of coulombs for reduction, we could not ascertain the n value for the oxidation. However, based

(22) One of the minor products had EPR and optical characteristics similar to porphyrin monoreduced ring radical species. This probably arises from one-electron oxidation of the major reduced species by adventitious oxygen. The amounts are small (ca. 10%) and vary depending on solvent and other factors and are not observed when the electrolyses are fast (i.e., thin layer).

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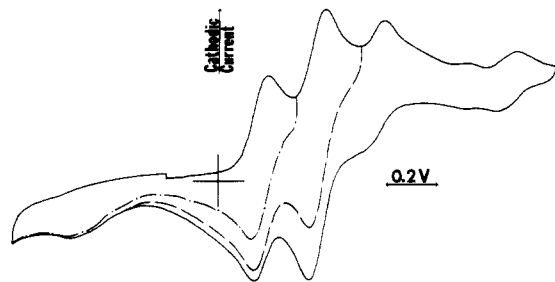
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Figure 10. Cyclic voltammogram of the bulk oxidized solution ($v =$ 0.1 V/s; conditions as described in text).
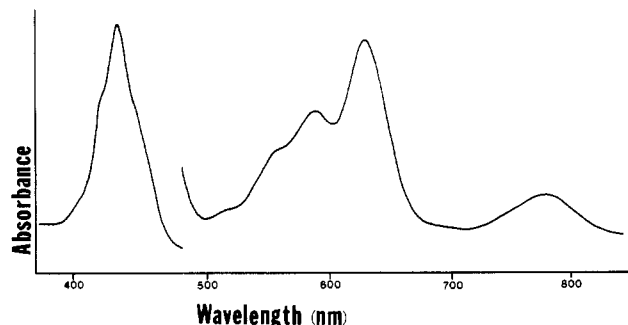

Figure 11. Visible–near-IR spectrum of the bulk oxidized solution (conditions as described in text).

on the cyclic voltammetric oxidations and the closeness of the number of recaptured coulombs for bulk oxidation, these probably represent two successive one-electron oxidations. Figures 10 and 11 illustrate the cyclic voltammetry and visible–near-IR spectrum of a bulk oxidation experiment. As can be seen from Figure 10, bulk oxidation produced the oxidized form of the reduced product, confirming the suggested chemical reversibility from cyclic voltammetry. The visible–near-IR spectrum was distinctly different from that of the reduced product. Several features of the spectrum revealed the presence of some identifiable porphyrins. The shoulders near 410 and 510 nm are identified as belonging to unmetalated tetraphenylporphine. The near-IR absorption at 773 nm is identified as the phlorin anion of $P(OH)_2$. The phlorin anion is frequently observed as a minor component. However, if the solvent and electrolyte are absolutely free of protons, then the phlorin anion is absent. The remaining portion of the spectrum must be due to the oxidized form of the product (λ_{max} (nm) 427, 589, 629).

The results of the oxidation encouraged us to attempt the isolation of the product by column chromatography, in order to better characterize it. Application of the bulk oxidized solution to a silica gel column (1×10 cm) and elution with $CHCl_3$ resulted in the separation of the original green solution into two fractions. The initial minor band contained free TPP and a small amount of another unknown material. The second and major band was a deep green color and appeared to be the desired product. Unfortunately, isolation by chromatography apparently produced a new porphyrinic species, as the major band had optical and CV properties distinctly different from that observed prior to column application. We did not, however, pursue the characterization of this material. Since chromatography appeared to be destructive, we attempted to isolate the oxidized product by slow crystallization. In every attempt, pure unmetalated TPP was the only crystallized material to be isolated. It seems therefore, that the major product after bulk oxidation is sufficiently unstable to prevent its isolation by conventional methods.
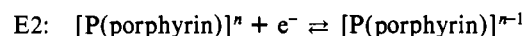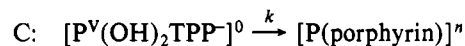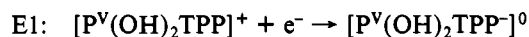
While the second reductive process of $P(OH)_2$ has not been studied in as great detail as the first, upon bulk reduction, similar products appear to be produced. An exhaustive

electrolysis at -1.3 V yields $Q/FN_0 = 2.13$ (N_0 = total number of moles of $P(OH)_2$, present before electrolysis). The cyclic voltammetry of the reduced solution is reminiscent of what was seen upon bulk reduction at the first wave except that the amount of "familiar" products produced is considerably less. It is reasonable to imagine that reduction at -1.3 V leads to the formation of less stable species that can degrade to give a variety of products, some of which may not be electroactive. What is significant is the number of electrons passed and the resemblance of the products obtained to the product of the first reduction, in agreement with the cyclic voltammetric experiments.

Discussion

As the results herein have indicated, the dihydroxo complex, $P(OH)_2$, is initially reduced in two sequential one-electron steps, as observed by CV at rapid sweep rates, in a manner very similar to that observed for the dichloro complex and for other metalloporphyrins. However, an examination of these reductions at slower potential sweep rates (CV), at longer times (chronamperometry), or upon bulk reductions (including thin-layer voltammetry) revealed that both reductions are chemically irreversible. We have demonstrated that this instability upon reduction is due to the coordinating hydroxyl groups, specifically the weakly acidic hydroxyl protons. The chemical steps that follow both reductions appear to lead to the same porphyrinic product. These points are illustrated below as we discuss each reductive process.
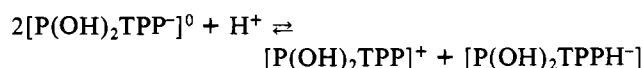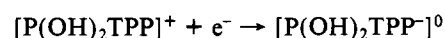
The first reduction of the $P(OH)_2$ complex can be best described by an ECE mechanism, where the product is easier to reduce than the original material.

E1: $[P^V(OH)_2TPP]^+ + e^- \rightarrow [P^V(OH)_2TPP^-]^0$

C: $[P^V(OH)_2TPP^-]^0 \xrightarrow{k} [P(porphyrin)]^n$

E2: $[P(porphyrin)]^n + e^- \rightleftharpoons [P(porphyrin)]^{n-1}$

The initial reduction leads to the radical "anion" that then, in an unknown chemical step, is converted to a new porphyrin, P(porphyrin), which is futher reduced. The chemical reaction is accelerated by small amounts of base. Larger amounts of OH^- deprotonate the original $P(OH)_2$ complex, and new electrochemical reductions are observed. The product $[P(porphyrin)]^{n-1}$ can be reversibly oxidized in two sequential, one-electron steps, i.e.

$[P(porphyrin)]^{n-1} \rightleftharpoons [P(porphyrin)]^n + e^-$

$[P(porphyrin)]^n \rightleftharpoons [P(porphyrin)]^{n+1} + e^-$
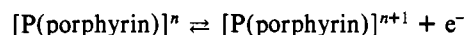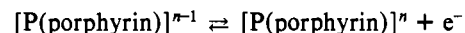
The above mechanism is operative in ostensibly proton-free solutions. However, in acid media, the normal oxidations of $[P(porphyrin)]^{n-1}$ disappear, suggesting a different mechanism. The OTTLE experiments in 1% acetic acid have shown that the new product after reduction of $P(OH)_2$ at the first wave was the phlorin anion of $P(OH)_2$. Phlorin anion production has been observed upon reduction of other metalloporphyrins.[21] Formation of this product is believed to arise from protonation of the porphyrin-ring dianion. While the phlorin anion is observed after reduction at the first wave of $P(OH)_2$ in the presence of acetic acid, where the dianion is not expected to be formed ($E^{o'} = -1.02$ V), its presence can arise from a disproportionation of the anion radical produced at the first wave by

$[P(OH)_2TPP]^+ + e^- \rightarrow [P(OH)_2TPP^-]^0$

$2[P(OH)_2TPP^-]^0 + H^+ \rightleftharpoons$
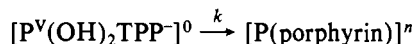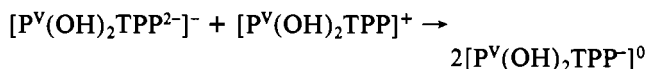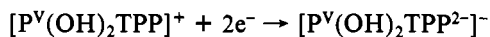$\qquad\qquad [P(OH)_2TPP]^+ + [P(OH)_2TPPH^-]$

The importance of protons for the disproportionation step was demonstrated quite clearly by the acetic acid and OH^-

additions on the cyclic voltammetry of $P(OH)_2$. When protons are not present, as in the case when small amounts of OH^- were present, the normal product oxidations were observed. The appearance of these oxidations implies that the ECE mechanism is operative and not the disproportionation. Thus, we conclude that H^+ promotes the disproportionation of the anion radical of $P(OH)_2$ while small amounts of OH^-, i.e., insufficient amounts to deprotonate the $P(OH)_2$ complex, accelerate the chemical step of the first reduction. Because the $[H^+]$ in the nonaqueous solvent, acetonitrile, is difficult to control, it is reasonable to assume that the disproportionation of the anion radical could occur (albeit to a lesser extent) without the addition of acid, due to the presence of small amounts of proton sources such as H_2O. The disproportionation, and subsequent protonation, would be competing with the ECE mechanisms. Experimentally, this competition has been verified by the small amounts of phlorin anion frequently present after bulk reduction.

Data on the second reduction of $P(OH)_2$ are limited. However, the cyclic voltammetric and bulk experiments indicate that the second reduction proceeds, initially by 1e/porphyrin and that the dianion thus formed eventually leads to the same product that results from reduction at the first wave. Any mechanism for what is occurring at the second wave must explain two prominent features: first, the n value observed from bulk experiments is 2; second, the product must be the same as the one obtained by the first reduction of $P(OH)_2$. Two mechanistic pathways come to mind for the second reduction of $P(OH)_2$. The first mechanism is an acid–base reaction between the initially formed dianion and starting material $P(OH)_2$ to form a phlorin anion and deprotonated $P(OH)_2$. The deprotonated complex would then be reduced and rearrange to the product by some unknown pathway. The major problem with the above mechanism is that it indicates the production of 50% phlorin anion, which is not observed. However, the stability of the phlorin anion under our conditions is unknown, and it may have undergone further decomposition.

The mechanism for the second reduction that we feel best describes the results is that of a conproportionation. That is, a redox reaction between the initially formed dianion and the starting material $P(OH)_2$, to form the anion radical of $P(OH)_2$, which must very rapidly convert to the typical product since no reoxidation of the anion radical is observed on cyclic voltammetry.

$$[P^V(OH)_2TPP]^+ + 2e^- \rightarrow [P^V(OH)_2TPP^{2-}]^-$$

$$[P^V(OH)_2TPP^{2-}]^- + [P^V(OH)_2TPP]^+ \rightarrow$$
$$2[P^V(OH)_2TPP^-]^0$$

$$[P^V(OH)_2TPP^-]^0 \xrightarrow{k} [P(porphyrin)]^n$$

Since the last step is the same as that invoked for the first reduction, the ultimate product is the same. The product will then undergo an electrochemical reduction to the reduced form, $[P(porphyrin)]^{n-1}$. This mechanism explains both the n value of 2e/porphyrin and the nature of the product resulting from the second reduction of $P(OH)_2$. Redox reactions such as in the above mechanism have been considered by Hawley in the first of a series of publications on the "Nuances of the ECE Mechanism".[24] The overall reductive mechanism of $P(OH)_2$ is shown in Figure 12.

Unfortunately, while a mechanism has been proposed that accounts for the electrochemical results, the nature of the product remains obscure. The observation that the product is reduced at a higher potential than the starting $P(OH)_2$
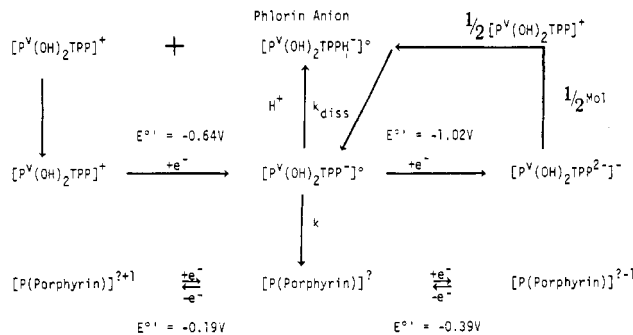

Figure 12. Overall mechanism of electrochemical reduction of $P(OH)_2$ in acetonitrile.

complex implies that it experiences a larger inductive effect and/or structural changes of such a nature that the reduction is thermodynamically easier ($\Delta G = -nFE$). This mitigates against the formation of ring-reduced and subsequently protonated materials such as phlorins or chlorins, which reduce at lower potentials than the parent porphyrin complex.[23]

The possibility of forming a phosphorus porphyrin with a greater inductive effect is attractive in light of the recent results with cyclenphosphine oxide.[25] This species exists in equilibrium with the hydroxyphosphorane:
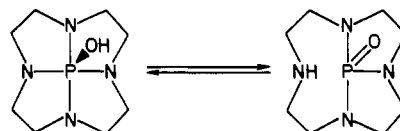
The $P(OH)_2$ complex does not exhibit this equilibrium in the original oxidized form but upon reduction the porphyrin ring becomes a stronger base and a similar equilibrium may be established.
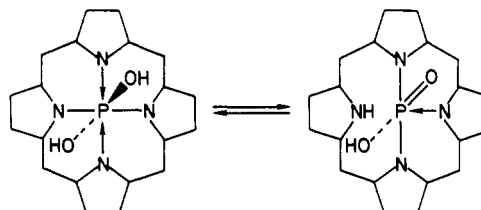
We have also demonstrated that the hydroxyl protons are critically important for the chemical step, and thus proton transfers must be involved. While we have not reported the very preliminary results of electrochemical reductions of $P(OH)_2$ in the nonpolar solvent methylene chloride, it is interesting that an equilibrium between the original $P(OH)_2$ complex and another porphyrinic species occurs. This "new" species also has a relatively high reduction potential, $E^{o\prime} = -0.20$ V and may represent the oxidized form of the reduced product of $P(OH)_2$ obtained in acetonitrile. Further experimentation in methylene chloride may eventually lead to the elucidation of this porphyrinic product. The relative inductive effect of the $P(OH)_2$ center vs. the $P=O(OH)$ center is not known. However, the formation of a phosphoryl center that would contain a protonated pyrrole nitrogen would cause significant structural changes in the planarity of the porphyrin ring, as is seen for the dication of TPP and N-alkylated porphyrins.[26] Possible changes in the planarity of the porphyrin ring are evidenced in the visible spectrum of the oxidized product, which resembles the spectra seen for the distorted nonplanar species referred to above. The general red shifting of the visible bands, which gives rise to the green

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coloration of these complexes, is thought to be due to an increased resonance interaction between the phenyl groups and the macrocyclic ring.[27] Further work on identifying the products of the reduction and the possible equilibria are in progress.

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Synthesis, Spectra, and Structure of af-Dibromo-b-ethoxo-d-oxo-ce-bis(4-nitropyridine)technetium(V) and Related Complexes

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Compounds of the type [O(RO)X$_2$L$_2$Tc^V], where X = Cl or Br, L = 4-cyanopyridine or 4-nitropyridine, and RO = OCH$_3$ or OCH$_2$CH$_3$, have been synthesized by the direct combination of [*n*-Bu$_4$N][TcOX$_4$] with the appropriate pyridine ligand in the corresponding alcohol as solvent. A complete crystal and molecular structure determination was performed on [O(CH$_3$CH$_2$O)Br$_2$(4-nitropyridine)$_2$Tc^V], which crystallized in the triclinic space group, P$\bar{1}$, with cell constants *a* = 10.820 (1) Å, *b* = 11.146 (2) Å, *c* = 9.006 (1) Å, α = 102.82 (1)°, β = 108.11 (1)°, and γ = 64.53 (1)°. The unit cell volume is 927.1 (4) Å^3 with Z = 2. The geometry of the molecule involves trans halides, trans pyridines, and trans alkoxo and oxo moieties. A high infrared stretching frequency (939 cm^{-1}) and short Tc-O bond length (1.684 Å) indicate a bond order of approximately 2.5 for the technetium(V)-oxo moiety. Similarly, the short Tc-OCH$_2$CH$_3$ bond length of 1.855 Å suggests a bond order of approximately 1.5 for the ethoxo bond. The average Tc-Br bond distance of 2.56 Å is the first reported for a Tc(V) complex, and the average Tc-N bond distance of 2.14 Å is now typical for Tc(V). Infrared and ^{1}H NMR spectra are reported with Tc-Cl and Tc-N stretching frequencies occurring at 309-344 and 220-270 cm^{-1}, respectively, and ring proton resonances being shifted somewhat downfield. All but the oxo ligands appear to be easily substituted in a variety of solvents.

Introduction

Complexes of Tc^V with π-donor ligands such as halides, thiolates, and alcoholates tend to form square-pyramidal complexes[2,3] containing the technetyl group, [Tc=O]$^{3+}$, while coordination with nitrogen ligands generally yields octahedral complexes[4-6] containing *trans*-[O$_2$Tc]$^+$. Davison has recently reported the synthesis of [O(EtO)Cl$_2$(bpy)Tc^V], which presumably contains the alcoholate trans to the oxo ligand with the halides in cis positions.[7] On the other hand, analogous rhenium complexes with monodentate pyridine ligands exhibit a trans geometry with respect to both the pyridine and halide ligands, so that it appeared likely that the corresponding Tc^V complexes should adopt a similar geometry.[8] We now report the synthesis, molecular structure, and spectroscopic characterization of a number complexes of the type [O-(RO)X$_2$L$_2$Tc^V], where L = 4-cyanopyridine (Cpy) or 4-nitropyridine (Npy), X = Cl or Br, and RO = methoxo or ethoxo.

Experimental Section

Synthesis. Compounds of the type [O(RO)X$_2$L$_2$Tc^V], where RO = MeO- or EtO-, X = Cl or Br, and L = 4-cyanopyridine or 4-

nitropyridine, were prepared by dissolving the pyridine ligand (1.6 mmol) together with [*n*-Bu$_4$N][TcOX$_4$] (0.2 mmol) at an 8/1 (ligand/metal) molar ratio in 35 mL of the appropriate alcohol. The solution was stirred for 2-3 min and then filtered (through filter paper) to obtain a green filtrate, which was loosely covered and allowed to stand. Green crystals usually began to precipitate within 1 h, and the product was normally collected by filtration after 24 h. Elemental analyses are summarized in Table I.

Caution! All syntheses were performed with ^{99}Tc, which is a β-emitting isotope with a half-life of 2.15 × 10^5 yr. Precautions for handling this material are described elsewhere.[4]

Compound Characterization. All elemental analyses (except for ^{99}Tc) were performed by the Stanford Microanalytical Laboratory, Stanford, CA (Table I). Technetium analyses were performed by dissolving a known quantity of the compound in 8 mL of acetone and adding approximately 2 mL of a 30% solution of H$_2$O$_2$ to oxidize the metal to TcO$_4^-$. Calibration standards were similarly prepared by dissolving [NH$_4$][TcO$_4$], which had been recrystallized from 0.1 M ammonia with the addition of a few drops of H$_2$O$_2$ and then dried in a vacuum desiccator at 25 °C for 10 h. Aliquots of 25-125 μL were then combined with 10 mL of Fischer Scintiverse scintillation cocktail and Tc determinations made on an LKB-1217 scintillatin counter. Counting was done for 60 s over a ^{3}H window (channels 8-110), with 10^4-10^5 counts usually being obtained for samples and standards. Unknown samples were determined from a linear least-squares fit to the standards. Infrared spectra were taken on a Perkin-Elmer Model 599B grating spectrophotometer in CsI pellets. UV-visible spectra were obtained on a Perkin-Elmer Model 575 equipped with a digital background corrector and a thermostated sample cell. ^{1}H NMR spectra were recorded on a Varian FT-80A Fourier transform spectrometer. All spectra were recorded at room temperature with a spectral width of 2000 Hz.

Structure Determination. Single crystals of [O(CH$_3$CH$_2$O)Br$_2$-(Npy)$_2$Tc^V][9] were obtained on slow evaporation of the ethanol reaction

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(8) Lock, C. J. L.; Turner, G. *Can. J. Chem.* **1977**, *55*, 333-339.
(9) *af*-Dibromo-*b*-ethoxo-*d*-oxo-*ce*-bis(4-nitropyridine)technetium(V).