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Platinum(II) and platinum(IV) porphyrin complexes: synthesis, characterization, and electrochemistry†

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Abstract—Platinum(IV) porphyrins of the type $[Pt^{IV}(p\text{-}X)_4TPP]Cl_2$ where $(p\text{-}X)_4TPP$ is a *para*-substituted tetraphenylporphyrin have been synthesized by the direct oxidation of their Pt^{II} precursors with Cl_2. Both the Pt^{II} and Pt^{IV} complexes have been characterized by visible and ^1H NMR spectroscopy and their electrochemical properties. The Soret, α and β bands of the visible spectra are shifted to longer wavelengths upon oxidation of the Pt^{II}. All ^1H resonances experience a downfield shift upon oxidation of the Pt^{II} to Pt^{IV}. Each $[Pt^{II}(p\text{-}X)_4TPP]$ complex shows two oxidations and two reductions and their potentials are dependent upon the X substituent on the porphyrin ring. In general, the $[Pt^{IV}(p\text{-}X)_4TPP]Cl_2$ complexes show a similar oxidation and reduction pattern and a substituent effect is evident. There is an additional reduction that can be attributed to $Pt^{IV} \rightarrow Pt^{II}$. © 1997 Elsevier Science Ltd

Keywords: platinum(II); platinum(IV); porphyrins; tetraphenylporphyrins; electrochemistry; voltammetry.

Metal porphyrin complexes play important roles in many biological and catalytic systems. Their chemical reactivity is found to be dependent on the central metal as well as the substituents on the porphyrin ring. In particular, tetraphenylporphyrins (TPP), substituted tetraphenylporphyrins and phthalocyanines containing the transition metals Fe^{II}, Co^{II}, Ni^{II} and Pt^{II} have proven to be effective catalysts in the isomerization of quadricyclene to norbornadiene (a symmetry-forbidden reaction) [1], photoisomerization of azastilbene [2] and the homogeneous and heterogeneous oxidative dehydrogenation of cyclohexadiene [3]. Recent studies have found that Pd^{II} and Pt^{II} porphyrins act as photosensitizers capable of photochemical conversion and storage of solar-energy [4], as potential molecular conductors [5] and as photosensitizers for the *cis* to *trans* isomerization of stilbene [6]. Pt^{II} and Pd^{II} porphyrins display intense phosphorescence that has allowed their use as oxygen sensing probes [7].

Platinum(II) and palladium(II) in a square-planar coordination environment in porphyrins have displayed little tendency to bind axial ligands [8]. This is believed to be due to the low-spin d^8 electronic configuration $(d_{xz}d_{yz})^4$ $(d_{xy})^2$ $(d_{z^2})^2$ in which the filled d_{z^2} orbital repels axial ligands approaching the metal ion. However, Ni^{II} porphyrins will form five- and six-coordinate complexes in the presence of ligands in high concentration or with covalent attachment of axial ligand(s) [9]. All Pt^{IV} complexes characterized to date are in an octahedral environment and diamagnetic with the low-spin $(d_{xz}d_{yz}d_{xy})^6$ electronic configuration. It has been demonstrated by Buchler *et al.* that oxidation of $[Pt^{II}(TTP)]$ and $[Pt^{II}(OEP)]$ yields the corresponding $[Pt^{IV}(TTP)]Cl_2$ and $[Pt^{IV}(OEP)]Cl_2$ complexes [TTP = *meso*-tetra(*p*-tolyl)porphyrin and OEP = octaethylporphyrin], which are thermally stable to 200°C [10]. Recently Milgrom *et al.* have characterized $[Pt^{IV}(TPP)]Cl_2$ and several derivatives by NMR spectroscopy [11].

The redox chemistry of metalloporphyrins has

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received considerable attention. In most metal-porphyrin complexes, there are three and often four porphyrin-centered and one metal-centered sites of redox activity. For a variety of metalloporphyrins in which the metal is divalent, the porphyrin ring is reversibly oxidized in two one-electron steps to yield a π-cation radical and a π-dication and reversibly reduced to yield a π-anion radical and a π-dianion [12]. Two one-electron oxidation and two one-electron reduction steps have been identified for metal-free porphyrins as well. Cyclic voltammetry studies on [Pt^{II}(TPP)] and [Pd^{II}(TPP)] complexes indicate all observed oxidations and reductions are one-electron transfer processes [13]. Recent studies indicate that the electrochemical reduction of Ni^{II} porphyrins yields a Ni^{II} porphyrin π-anion radical, a Ni^{I} porphyrin anion, or a mixture of the two, and the process is highly dependent upon the substituents of the porphyrin system [14].

We have synthesized Pt^{IV} porphyrins of the type [Pt^{IV}(*p*-X)$_4$TPP]Cl_2 (Fig. 1) from their corresponding [Pt^{II}(*p*-X)$_4$TPP] counterparts, where X = Cl, H, CH_3 and OCH_3, through direct oxidative addition using Cl_2(g) or through the utilization of hydrogen peroxide as an oxidizing agent. The complexes have been characterized by ^1H NMR and UV–vis spectroscopy and by their electrochemical properties *via* cyclic voltammetry and constant-potential coulometry. The results of these studies are the focus of this report.

EXPERIMENTAL

General

^1H NMR spectra were recorded at 300.154 MHz with a General Electric QE300 instrument (reference δ7.26, $CHCl_3$). UV–vis spectra were obtained with a Beckman DU-7500 diode array instrument using quartz cells with a path length of 1.0 cm. Cyclic voltammetry was carried out with the conventional three-electrode method in CH_2Cl_2 (distilled from P_2O_5 or CaH_2) with Bu_4NPF_6 (0.10 M) as a supporting electrolyte. Electrochemical measurements were made with either a PAR 174A electrochemical analyzer or an Amel Model 551 potentiostat, a 567 function generator and a 731 digital coulometer. The concentration of the complex was usually between 0.5 and 1.0×10^{-3} M. Ferrocene was used as an internal standard and all potentials are referenced to the $E_{1/2}$ $\{=\frac{1}{2}(E_{pa}+E_{pc})\}$ for the $(C_5H_5)_2Fe/(C_5H_5)_2Fe^+$ couple; $E_{1/2}$ for ferrocene was typically $+0.48 \pm 0.02$ V *vs* the Ag | AgCl | NaCl (saturated) BAS reference electrode; this value is close to the 0.45 V reported [14b] for the ferrocene couple *vs* an SCE reference electrode.

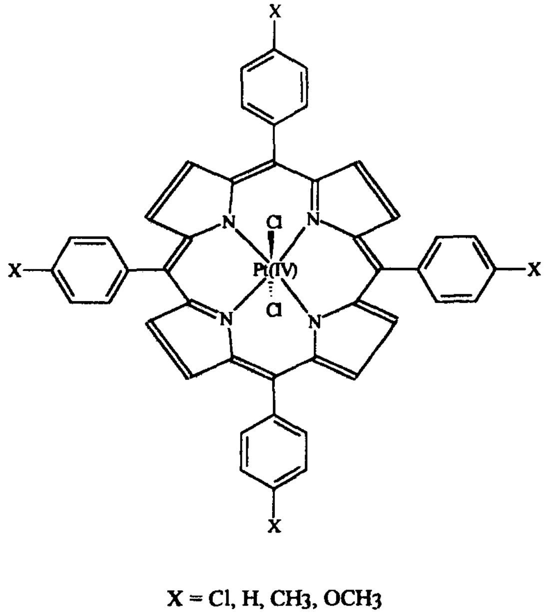

Fig. 1. [Pt^{IV}(*p*-X)$_4$TPP]Cl_2 (X = Cl, H, CH_3, OCH_3).

Reagent-grade chemicals and solvents were purchased from Aldrich Chemical Company, Fisher Scientific, Matheson Coleman & Bell and Mallinckrodt Chemical Company. Platinum(II) chloride was obtained from Johnson–Matthey Company. Chromatographic-grade aluminum oxide, activated neutral, standard grade 150 mesh, 58 Å, and Silica gel, Merckt grade 9385, 230–400, mesh 60 Å were purchased from Aldrich.

Elemental analyses were performed by Desert Analytics, Tucson, Arizona.

Synthesis of [Pt^{II}(*p*-X)$_4$TPP] (X = Cl, H, CH_3, OCH_3)

The *p*-substituted tetraphenylporphyrin free bases, H_2(*p*-X)$_4$TPP, were synthesized by the method of Adler *et al.* [15] and were purified by treatment with 2,3-dichloro-5,6-dicyanobenzoquinone, DDQ, then chromatographed on aluminum oxide prior to metallation [16]. Platinum was inserted into the porphyrin by the addition of platinum(II) chloride (0.75 mmol) to the porphyrin (0.75 mmol) in refluxing benzonitrile [10a]. The resulting [Pt^{II}(*p*-X)$_4$TPP] compounds were purified by chromatography on silica gel with typical isolated yields of 30–40%.

Synthesis of [Pt^{IV}(*p*-X)$_4$TPP]Cl_2 (X = Cl, H, CH_3, OCH_3)

[Pt^{IV}(*p*-X)$_4$TPP]Cl_2 complexes were synthesized by the oxidation of the corresponding [Pt^{II}(*p*-X)$_4$TPP] complexes by two routes. The first route involves direct-oxidative addition of $Cl_{2(g)}$ to the corresponding platinum(II) species. A saturated $Cl_{2(g)}/CHCl_3$ solution was prepared by bubbling $Cl_{2(g)}$ through 10 cm^3 of chloroform for approximately 15 s. Of the saturated $Cl_{2(g)}/CHCl_3$ solution, 0.6 cm^3 was added dropwise to [Pt^{II}(*p*-X)$_4$TPP] (0.022 mmol) dissolved in 20 cm^3 of chloroform at 0°C. Immediately upon addition of the first drops of the $Cl_{2(g)}/CHCl_3$ to [Pt^{II}(*p*-X)$_4$TPP], the solution changed from orange to red. The reaction was monitored by UV–vis spectroscopy over the course of 2.5 h, in which the Soret band of [Pt^{II}(*p*-X)$_4$TPP] at 403 nm gradually decreases and the Soret band associated with [Pt^{IV}(*p*-X)$_4$TPP]Cl_2 at 421 nm appears. The solution was concentrated to 5 cm^3 by rotary evaporation and an equal volume of cold methanol precipitated the red/purple [Pt^{IV}(*p*-X)$_4$TPP]Cl_2 crystalline solids. The products were dried under vacuum in a desiccator for 2 days. The compounds were found to be pure by ^{1}H NMR and no further purification was required. Obtained yields were in the range of 45%. Elemental analysis of [Pt(*p*-H)$_4$TPP]Cl_2 was performed. Found: C, 59.2; H, 3.2; N, 6.1; Cl, 7.2. Calc. for $C_{44}H_{28}PtN_4Cl_2$: C, 60.1; H, 3.2; N, 6.4; Cl, 8.1%. When this reaction was performed at room temperature, [Pt^{IV}(*p*-X)$_4$TPP]Cl_2 was produced but impurities were detected.

The second synthetic route previously reported by Buchler *et al.* utilizes H_2O_2 as an oxidizing agent and HCl(aq) as the source of chlorine [10a]. [Pt^{II}(*p*-X)$_4$TPP] (0.22 mmol) was refluxed for 2 h in 150 cm^3 of chloroform with 1 cm^3 of 30% hydrogen peroxide and 2 cm^3 of 18% hydrochloric acid. The solution changed in color from orange to red. After refluxing, the chloroform phase was washed three times with water and evaporated to dryness using a rotary evaporator. The residue was dissolved in a minimum amount of toluene and loaded onto a 10 cm silica gel column. Nonreacted [Pt^{II}(*p*-X)$_4$TPP] was eluted with toluene. [Pt^{IV}(*p*-X)$_4$TPP]Cl_2 was collected upon elution with chloroform. Concentration of the chloroform solution to 25 cm^3 and addition of an equal volume of cold methanol precipitated the red/purple [Pt^{IV}(*p*-X)$_4$TPP]Cl_2 crystalline solids. [Pt^{IV}(*p*-X)$_4$TPP]Cl_2 was collected by filtration then washed with cold methanol and water. For [Pt^{IV}(*p*-CH_3)$_4$TPP]Cl_2, the nonreacted [Pt^{II}(*p*-CH_3)$_4$TPP] was eluted first from the silica gel column using a toluene/petroleum ether (2 : 3 volume ratio) mixture as poor column separation was found between [Pt^{II}(*p*-CH_3)$_4$TPP] and [Pt^{IV}(*p*-CH_3)$_4$TPP]Cl_2 using toluene alone. Final yields of the [Pt(*p*-X)$_4$TPP]Cl_2 complexes were in the 50–60% range.

Table 1. Spectral data for the [Pt(*p*-X)$_4$TPP] and [Pt(*p*-X)$_4$TPP]Cl_2

	Wavelengths (nm)		
	Soret band	β-band	α-band
[Pt^{II}(*p*-Cl)$_4$TPP]	403	511	540
[Pt^{IV}(*p*-Cl)$_4$TPP]Cl_2	422	537	572
[Pt^{II}TPP]	402	510	540
[Pt^{IV}TPP]Cl_2	421	536	570
[Pt^{II}(*p*-CH_3O)$_4$TPP]	407	512	539
[Pt^{IV}(*p*-CH_3O)$_4$TPP]Cl_2	426	537	572
[Pt^{II}(*p*-CH_3)$_4$TPP]	405	511	539
[Pt^{IV}(*p*-CH_3)$_4$TPP]Cl_2	424	538	575

RESULTS AND DISCUSSION

The electronic spectra of the [Pt^{II}(*p*-X)$_4$TPP] complexes (Table 1) are dominated by the Soret band near 400 nm and the α and β bands near 540 nm and 510 nm, respectively. These bands are red-shifted approximately 20 nm for the [Pt^{IV}(*p*-X)$_4$TPP]Cl_2 complexes (Table 1). The electronic absorption bands for regular metalloporphyrins, those containing closed-shell metal ions (d^0 and d^{10}, e.g. Zn^{II}), have been attributed to the π-to-π^* electronic transitions of the porphyrin ring [17]. Platinum(II) porphyrins have been classified as *hypsoporphyrins* (irregular porphyrins) as the Soret, α, and β bands of Pt^{II} porphyrins undergo a shift to shorter wavelength (a hypsochromic shift) with respect to regular metalloporphyrin systems. The hypsochromic shift is interpreted as an indication of strong d_π (d_{xz}, d_{yz}) metal-based orbital interaction with the porphyrin $e_g(\pi^*)$ orbital (metal-to-ligand π-backbonding). This interaction increases the separation between the porphyrin $e_g(\pi^*)$ orbitals (the LUMOs) and the $a_{2u}(\pi)$ or $a_{1u}(\pi)$ orbitals (the HOMOs) causing the electronic transitions to occur at shorter wavelengths. The electronic spectra of the [Pt^{IV}(*p*-X)$_4$TPP]Cl_2 complexes with respect to their [Pt^{II}(*p*-X)$_4$TPP] precursors are similar in appearance but have undergone a bathochromic shift (Table 1); the presence of only two bands between 500 and 600 nm in the spectra is indicative of an uncharged porphyrin ring [12c]. Buchler *et al.* have interpreted the bathochromic shifts to indicate a decrease in metal d_π-porphyrin π^*-bonding resulting in a decrease in the HOMO–LUMO separation [10a]. Milgrom and coworkers [11] have offered an alternative explanation to the bathochromic shifts and have postulated, based on observed upfield ^{13}C chemical shifts (*ca* 2.5 ppm) of the α-carbons (*vide infra*), that upon oxidation of Pt^{II} to Pt^{IV}, the d_π-porphyrin π^*-backbonding is increased rather than decreased. The bathochromic shift is explained by suggesting upon oxidation, the porphyrin a_{2u} orbital is raised in energy to a larger extent, relative to the prophyrin a_{2u} orbital of the Pt^{II} precursor, than the π-backbonding raises the energy of the porphyrin e_g orbital; the result is a smaller energy separation between the porphyrin a_{2u} and e_g orbitals. We feel there are potentially many factors which could contribute to the enhanced shielding displayed in the ^{13}C NMR of the α-carbons. In particular, Pt^{IV} porphyrins may experience significant prophyrin ring ruffling due to the small ionic radius, 0.625 Å, of Pt^{IV}. Another factor which may slightly affect ^{13}C chemical shifts in metalloporphyrin systems are anisotropic contributions from the ring current and the manner in which it is affected by oxidation and coordination of axial ligands to the platinum center [18]. It is felt that in order to delineate factors affecting ^{13}C chemical shifts in these systems, additional work involving axial groups other than chloride are in order and we are presently pursuing this aspect.

The electronic spectra of the [Pt^{II}(p-X)$_4$TPP] and [Pt^{IV}(p-X)$_4$TPP]Cl$_2$ complexes in our studies appear to be nearly insensitive to the *para*-substituent on the phenyl rings. However, Atwater has detected slight shifts of *ca* 2 nm, except for X = NH$_2$ (19 and 15 nm shifts for the Soret and α bands, respectively) and X = OH (a 7 nm shift for the Soret band), for [Pt^{II}(p-X)$_4$TPP] complexes containing strong electron-releasing or strong electron-withdrawing substituents in both the absorption and phosphorescence spectra [7]. These trends were interpreted through the four-orbital model for metalloporphyrins developed by Gouterman [17].

Platinum insertion into the porphyrin ring and subsequent oxidation of the [Pt^{II}(p-X)$_4$TPP] compounds to [Pt^{IV}(p-X)$_4$TPP]Cl$_2$ were monitored by ^{1}H NMR. Platinum insertion results in all ^{1}H resonances exhibiting a small upfield chemical shift compared with the free-base porphyrin resonances (Table 2). ^{1}H NMR shifts upon metallation of porphyrins are typically small and may be either upfield or downfield depending upon the metal [18]. For platinum porphyrins, the slight upfield ^{1}H chemical shift is attributed to platinum to porphyrin π-backbonding [19]. All ^{1}H resonances experience a downfield chemical shift upon oxidation of Pt^{II} to Pt^{IV} due to decreased shielding (Table 2). The J_{Pt-H} pyrrole coupling of [Pt^{II}(TPP)] can be determined directly from the spectrum. In the case of the substituted porphyrin ring systems, the coupling constants were obtained by resolution enhancement of the F.I.D. by double exponential multiplication using the NICOLET/QE300 data processing software with DM = 5. The J_{Pt-H} coupling associated with the pyrrole proton ^{1}H resonances decreases from Pt^{II} to Pt^{IV} from *ca* 11Hz to *ca* 7 Hz, respectively. This decrease in J_{Pt-H} has previously been observed in other platinum porphyrins and in a variety of platinum compounds and is attributed to the relative decrease in platinum 6*s* character from dsp^2 to d^2sp^3 hybridization [10a,11,20]. For the Pt^{II} and Pt^{IV} porphyrins, no distinct trend in the pyrrole proton J_{Pt-H} coupling constants due to substituent effects is noted.

As is fairly typical of other [M^{II}(TPP)] complexes, the [Pt^{II}(p-X)$_4$TPP] complexes exhibit four ligand-based sites of redox activity (Table 3 and Fig. 2). The center two are quasireversible and involve a one-electron transfer as evidenced by their ΔE_p values. The

Table 2. ^{1}H NMR chemical shifts and coupling constants[a]

	H-pyr	H-*ortho*	H-*meta*	H-*para*	
H$_2$[(p-Cl)$_4$TPP]	8.85	8.12	7.75	—	(N—H = −2.83)
[Pt^{II}(p-Cl)$_4$TPP]	8.75 (J_{Pt-H} = 11)	8.09	7.73	—	
[Pt^{IV}(p-Cl)$_4$TPP]Cl$_2$	9.09 (J_{Pt-H} = 6)	8.20	7.80	—	
H$_2$(TPP)	8.85	8.22	7.76	7.77	(N—H = −2.76)
[Pt^{II}(TPP)]	8.76 (J_{Pt-H} = 12)	8.15	7.74	7.75	
[Pt^{IV}TPP]Cl$_2$	9.06 (J_{Pt-H} = 7)	8.27	7.79	7.81	
H$_2$[(p-CH$_3$O)$_4$TPP]	8.86	8.13	7.29	—	(—OCH$_3$ = 4.10, N—H = −2.75)
[Pt^{II}(p-CH$_3$O)$_4$TPP]	8.78 (J_{Pt-H} = 10)	8.05	7.26	—	(—OCH$_3$ = 4.13)
[Pt^{IV}(p-CH$_3$O)$_4$TPP]Cl$_2$	9.11 (J_{Pt-H} = 9)	8.18	7.32	—	(—OCH$_3$ = 4.11)
H$_2$[(p-CH$_3$)$_4$TPP]	8.86	8.10	7.56	—	(—CH$_3$ = 2.71, N—H = −2.77)
[Pt^{II}(p-CH$_3$)$_4$TPP]	8.76 (J_{Pt-H} = 11)	8.03	7.53	—	(—CH$_3$ = 2.69)
[Pt^{IV}(p-CH$_3$)$_4$TPP]Cl$_2$	9.08 (J_{Pt-H} = 7)	8.15	7.60	—	(—CH$_3$ = 2.72)

[a] Chemical shifts in ppm, coupling constants in Hz.

Table 3. Electrochemical data for H$_2$(TPP) and the [Pt^{II}(p-X)$_4$TPP] complexes

	Potentials[a]
H$_2$(TPP)	*+1.01*, +0.55 (85), −1.67 (70), −2.00 (80)
[Pt^{II}(p-Cl)$_4$TPP]	*+1.29*, +0.79 (80), −1.75 (80), *−2.28*
[Pt^{II}(TPP)]	*+1.23*, +0.72 (80), −1.79 (85), *−2.36*
[Pt^{II}(p-CH$_3$)$_4$TPP]	*+1.16*, +0.65 (70), −1.82 (80), > *−2.38*
[Pt^{II}(p-CH$_3$O)$_4$TPP]	*+1.08*, +0.63 (70), −1.82 (85), *−2.37*

[a] Scan rates were 100 mV s^{-1}. Potentials referenced to the ferrocene/ferrocinium redox couple. Values in italics are peak potentials due to poor reversibility of the wave. Values in parentheses are ΔE_p values in mV.

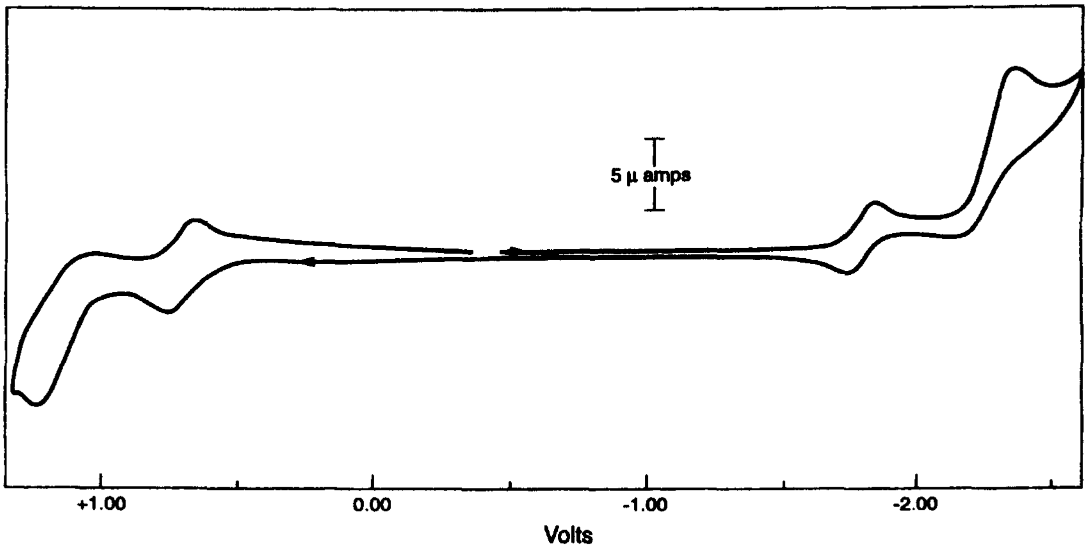

Fig. 2. Cyclic voltammogram of [Pt^{II}(TPP)] in CH_2Cl_2 at 100 mV s^{-1}. Potentials referenced to the ferrocene/ferrocinium redox couple.

second oxidation and second reduction occur near the anodic and cathodic limits of the solvent-supporting electrolyte system and the waves are not as well defined but are discernible in most voltammograms. The four electrochemical process can be described as:

$$[Pt(p\text{-}X)_4TPP]^{2+} + e^- \rightarrow [Pt(p\text{-}X)_4TPP]^+ \quad (1)$$

$$[Pt(p\text{-}X)_4TPP]^+ + e^- \rightarrow [Pt(p\text{-}X)_4TPP] \quad (2)$$

$$[Pt(p\text{-}X)_4TPP] + e^- \rightarrow [Pt(p\text{-}X)_4TPP]^- \quad (3)$$

$$[Pt(p\text{-}X)_4TPP]^- + e^- \rightarrow [Pt(p\text{-}X)_4TPP]^{2-}. \quad (4)$$

For all electrochemical experiments, the starting point is the [Pt^{II}(p-X)$_4$TPP] complex. When allowances are made for the different reference electrodes used in the two studies, the $E_{1/2}$ values for reactions (1) and (2) for [Pt^{II}(p-CH_3)$_4$TPP] reported in Table 3 compare favorably with those reported earlier [10a]. However, the cyclic voltammogram for [Pt^{II}(TPP)] is not similar to that previously described [13] as these authors report three oxidations and at least four reductions. Instead, our [Pt^{II}(TPP)] results resemble their [Pd(TPP)] results.

An effect in the oxidation and reduction potentials of the [Pt^{II}(p-X)$_4$TPP] complexes due to the substituent on the phenyl portion of the ligand is evident (Table 3). The electron-withdrawing substituent (Cl) shifts the first oxidation more positive by *ca* 70 mV and the first reduction less negative by *ca* 40 mV relative to the [Pt^{II}(TPP)]. The effect is most pronounced for the quasireversible oxidation and reduction, but is evident for both oxidations and both reductions. Electron-donating groups (CH_3 and CH_3O) shift the potentials in the opposite directions with the oxidations *ca* 80 mV less positive and the reductions *ca* 30 mV more negative than those of [Pt^{II}(TPP)]. This trend has also been observed in the metal-free porphyrin and other metalloporphyrin systems [21]. Half-wave potentials of the electrochemical redox reactions can be related to the Hammett linear free-energy relationship [21b–f] through the expression:

$$E_{1/2} = 4\sigma\rho \quad (5)$$

where the reaction constant, ρ, is a measure of the polar effects the substituents have on the electrochemical process and σ, the substituent constant [22], is multiplied by four due to the combined effects of the four substituents in the porphyrin system. A plot of $E_{1/2}$ *vs* 4σ should provide a linear relationship with the slope equal to the reaction constant. The value of ρ has been taken to indicate the point of redox activity, i.e. values of 0.061 ± 0.007 for the first ring oxidation [reaction (2)] and 0.068 ± 0.021 for the first reduction [reaction (3)] for [Ni^{II}(p-X)$_4$TPP] have been used to suggest the π-system of the porphyrin ring is the site of redox activity [1]. For reactions (1) and (2), plots of $E_{1/2}$ *vs* 4σ (Fig. 3) gave ρ values of 0.102 and 0.084, respectively, considerably higher than those for the similar Ni^{II} systems, but near those reported for similar electrochemical reactions for [Co^{III}(p-X)$_4$TPP]$^+$ complexes [21d]. In lieu of other evidence for the [Pt(p-X)$_4$TPP] complexes, we suggest that the oxidations are from the π-system of the porphyrin ring, presumably from either the a_{1u} or a_{2u} π-orbital of the formally (p-X)$_4$TPP^{2-} ligand of [Pt^{II}(p-X)$_4$TPP]. The ρ value for reaction (3) is considerably less than those for (1) and (2), but is close to that of the [Co^{II}(p-X)$_4$TPP] described by [21d]:

$$[Co^{II}(p\text{-}X)_4TPP] + e^- \rightarrow [Co^{I}(p\text{-}X)_4TPP]^-. \quad (6)$$

However, there is no evidence to suggest that the

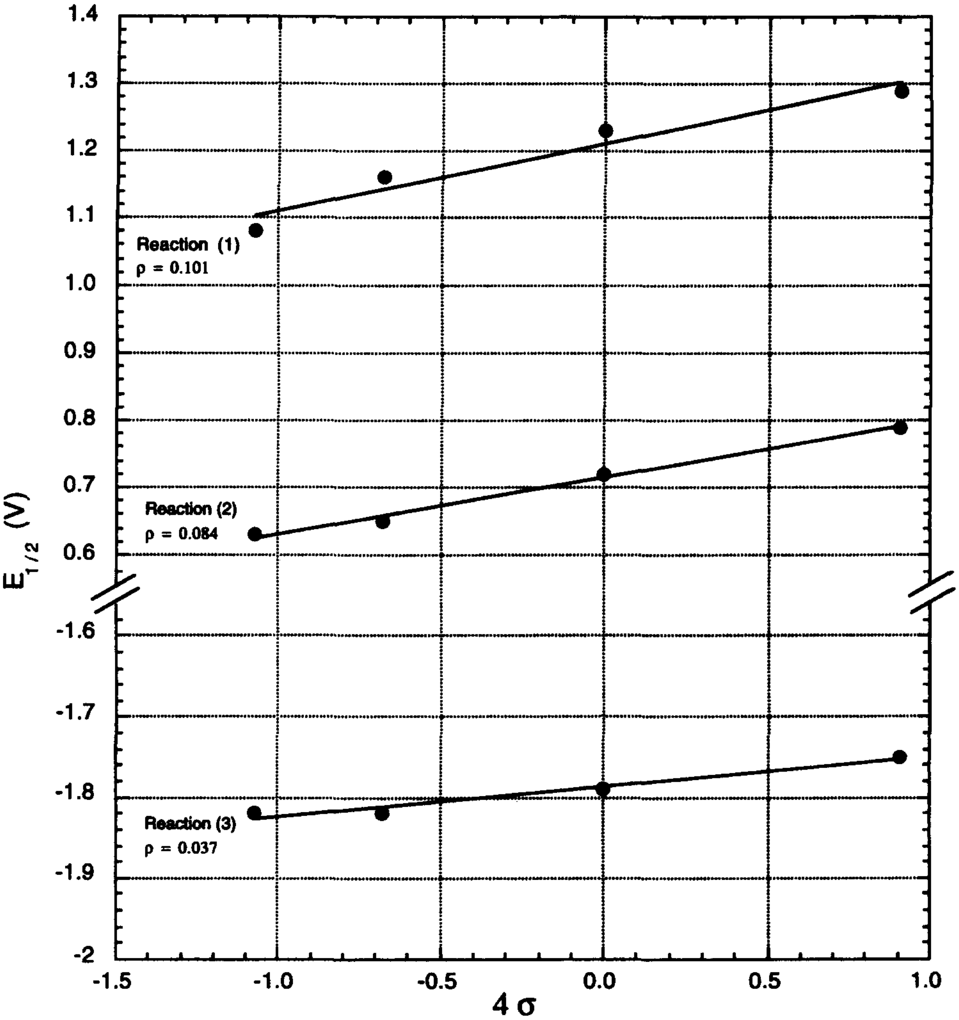

Fig. 3. Plot of $E_{1/2}$ *vs* 4σ for electrode reactions (1)–(3).

Pt^{II} is reduced and rather than attempt to relate the reaction constants to the site of redox activity, we prefer to view these as a measure of the influence of the central metal on the π-system of the porphyrin ring. Certainly, extensive π-bonding between the Pt^{II} and the porphyrin e_g orbital should influence the reaction constant for the reduction more so than for the oxidations as the electron is added directly to the e_g orbital.

It is also of interest to compare the redox values of $[Pt^{II}(TPP)]$ to those of the unmetallated free base, $H_2(TPP)$; the oxidation processes of $[Pt^{II}(TPP)]$ relative to $H_2(TPP)$ are found at more positive potentials, while the reduction processes for $[Pt^{II}(TPP)]$ are found at more negative potentials than those for $H_2(TPP)$. This implies a larger energy difference between the HOMO and the LUMO of the Pt^{II} complexes than in $H_2(TPP)$ itself and is consistent with the position of the Soret band in the complex (403 nm) relative to comparable bands in $H_2(TPP)$ at 419 and 446 nm. It is postulated that for the majority of metalloporphyrins, the metal 2+ ion affects the ring oxidation and reduction potentials largely through electrostatic forces [12b–d] and a rough linear relationship between the electronegativity of the metal and the first oxidation or reduction potential exists. It has also been observed in many complexes containing a 2+ metal that a rather constant difference of 2.25 ± 0.15 V exists between the first ring oxidation and the first ring reduction process in which the π-cation radical and π-anion radical are formed [12b,c]. For the $[Pt^{II}(p\text{-}X)_4TPP]$ complexes, this difference is larger and is 2.49 ± 0.05 V. Enhanced π-bonding between the Pt^{II} and the porphyrin ring is a reasonable explanation for this observation, especially if the π-bonding is responsible for pushing the reduction to a more negative potential. Furthermore, many metalloporphyrins display a constant difference in $E_{1/2}$ values between the first and second ring oxidations, 0.29 ± 0.15 V, and first and second ring reductions, 0.42 ± 0.05 V [12b,c]. For the $[Pt^{II}(p\text{-}X)_4TPP]$ complexes the differences in the $E_{1/2}$ values between the first and second ring oxidations are 0.46 ± 0.04 V and the differences in the $E_{1/2}$ values between the first and second ring reductions

Table 4. Electrochemical data for the [Pt^{IV}(p-X)$_4$TPP]Cl$_2$ complexes

	Potentials[a]
[Pt^{IV}(p-Cl)$_4$TPP]Cl$_2$	+1.02 (90), *−0.85*, −1.75 (70), −2.19 (120)
[Pt^{IV}(TPP)]Cl$_2$	+0.91 (80), *−0.93*, −1.79 (50), *−2.36*
[Pt^{IV}(p-CH$_3$)$_4$TPP]Cl$_2$	+0.86 (90), *−1.11*, −1.84 (100), −2.4
[Pt^{IV}(p-CH$_3$O)$_4$TPP]Cl$_2$	+1.16 (120), +0.08 (90), *−1.03*, −1.84 (90), *−2.41*

[a] Scan rates were 200 mV s^{-1}. Potentials referenced to the ferrocene/ferrocinium redox couple. Values in italics are peak potentials due to poor reversibility of the wave. Values in parentheses are ΔE_p values in mV. The wave near −1.0 V (also in italics) is the Pt^{IV} → Pt^{II} reduction.

are 0.51±0.03 V. These differences for the [Pt^{II}(p-X)$_4$TPP] complexes are actually the differences in the peak potentials due to the poor reversibility of the second oxidation and second reduction.

Electrochemical data for the [Pt^{IV}(p-X)$_4$TPP]Cl$_2$ complexes (Table 4) are similar to their Pt^{II} counterparts. Only the [Pt^{IV}(p-CH$_3$O)$_4$TPP]Cl$_2$ complex shows all four ligand-based waves; in the other cases, the second oxidation is presumably outside the electrochemical window of this system. A substituent effect as displayed by the [Pt^{II}(p-X)$_4$TPP] compounds is again evident for the first oxidation of the [Pt^{IV}(p-X)$_4$TPP]Cl$_2$ complexes. A plot of $E_{1/2}$ *vs* 4σ for this oxidation gave a value of 0.107 for the reaction constant, essentially the same value as for the first oxidation of the Pt^{II} complexes. As expected, the Pt^{IV} complexes are more difficult to oxidize than their Pt^{II} counterparts, in part due to the higher charge of the central metal. The first reduction that is observed is an irreversible one near −1.0 V that corresponds to the Pt^{IV} → Pt^{II} reduction. This wave is not as well-defined as most of the ligand-based ones and tends to decrease in intensity if cycled through several times. Constant potential coulometry cathodic to this reduction for [Pt^{IV}(p-CH$_3$O)$_4$TPP]Cl$_2$, indicated 1.90 electrons per molecule were consumed. During electrolysis of the [Pt^{IV}(p-X)$_4$TPP]Cl$_2$ complexes, a color change in the solution is immediately evident and the visible spectrum of the electrochemically generated product is identical to the authentic [Pt^{II}(p-X)$_4$TPP] complex. In studies of the redox potentials of other [M^{II}(p-X)$_4$TPP] complexes, it has been observed that the potentials are largely reflective of the energy of the porphyrin orbitals as opposed to the metal d-orbitals [12b–d]. However, a distinguishable substituent effect is observed for the Pt^{IV} → Pt^{II} reduction and as expected, the electron withdrawing p-chloro substituent causes the Pt^{IV} to undergo reduction at potentials less negative than that of those unsubstituted TPP or the CH$_3$O and CH$_3$ derivatives. The reductions for the [Pt^{IV}(p-X)$_4$TPP]Cl$_2$ complexes occur, within experimental uncertainties, at the same potentials as the reductions for the corresponding [Pt^{II}(p-X)$_4$TPP] complexes. This is consistent with the explanation that the Pt^{IV} is being reduced to the Pt^{II} complex. There is a larger difference between the first oxidation and the first reduction in the voltammogram of the Pt^{IV} complexes (2.70±0.07 V) than in the Pt^{II} complexes. This is primarily due to the effect of the Pt^{IV} on the HOMO of the porphyrin (either the a_{2u} or a_{1u}) orbital.

Voltammetric scans were initiated near 0.0 V. When the scan is in a positive direction (Fig. 4), the oxidations are relatively clean. However, if the voltammogram is cycled several times, small additional oxidations occur prior to those initially observed. Likewise, if the scan is initiated toward negative potentials, the small oxidations are evident on the first scan in the positive direction. The origin of these oxidations is not known, but they are clearly associated with the reduction of the Pt^{IV} complex. The potentials do not match the oxidations of the [Pt^{II}(p-X)$_4$TPP] complexes. We are continuing our investigation with other Pt^{IV} complexes.

CONCLUSIONS

[Pt^{IV}(p-X)$_4$TPP]Cl$_2$ complexes are readily accessible through a direct oxidative-addition reaction of Cl$_2$(g) on the corresponding [Pt^{II}(p-X)$_4$TPP] complex. Insertion of the Pt^{II} into the free-base porphyrin results in a hypsochromic shift of the Soret, α and β absorption bands while oxidation of the Pt^{II} to Pt^{IV} results in a bathochromic shift. All Pt^{IV} porphyrin ^{1}H NMR resonances exhibit downfield shifts between 0.07 and 0.34 ppm due to decreased shielding and the $J_{Pt\text{-}H}$ coupling associated with the pyrrole protons are observed to decrease by *ca* 5 Hz. Pt^{II} and Pt^{IV} porphyrins generally display four ligand-based one-electron redox processes. An effect for both Pt^{II} and Pt^{IV} complexes in which an electron-withdrawing group on the phenyl position of TPP shifts the oxidation potentials to more positive values and electron-donating groups shift the reduction potentials to more negative values is observed. A linear Hammett relationship is observed between $E_{1/2}$ and the substituent constant σ. An irreversible reduction corresponding to Pt^{IV} → Pt^{II} also shows a substituent effect. We are currently pursuing the preparation of Pt^{IV} containing other substituted porphyrins and axial ligands in order to probe the feasibility of using Pt^{IV} porphyrins as potential activators of small molecules.

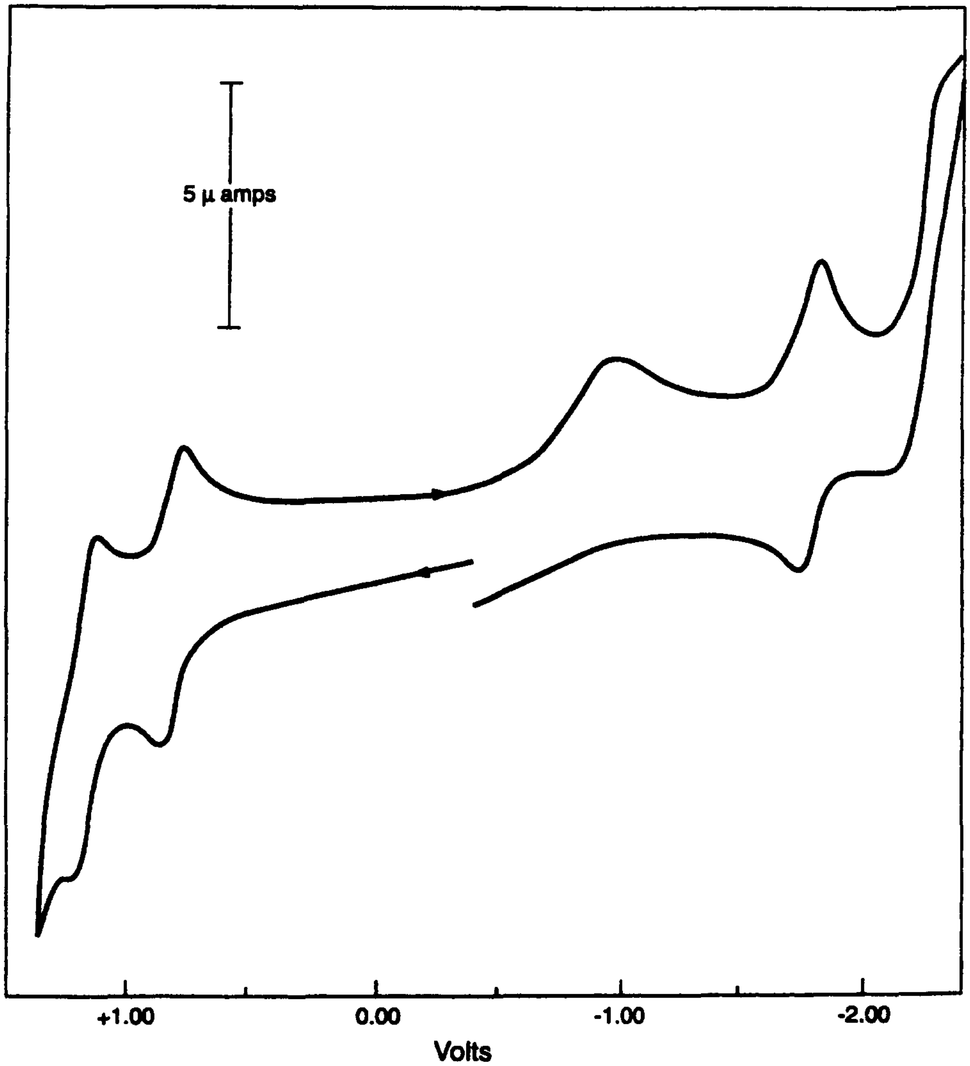

Fig. 4. Cyclic voltammogram of $[Pt^{IV}(p\text{-}CH_3O)_4TPP]Cl_2$ in CH_2Cl_2 at 200 mV s^{-1}. Potentials referenced to the ferrocene/ferrocinium redox couple.

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