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Polyhedron 19 (2000) 1057-1062



Platinum(IV) tetraphenylporphyrin dibromide complexes: synthesis, characterization, and electrochemistry

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Received 6 December 1999; accepted 15 February 2000

Abstract

Platinum(IV) porphyrins of the type $[Pt^{IV}(p-X)_4TPP]Br_2$ where $(p-X)_4TPP$ is a *para*-substituted tetraphenylporphyrin have been synthesized by direct oxidation of their Pt(II) precursors with Br_2. Both the Pt(II) and Pt(IV) complexes have been characterized by visible and ¹H NMR spectroscopy and their electrochemical properties. In both the oxidation and reduction processes, a substituent effect is evident, and the reduction of $Pt^{IV} \rightarrow Pt^{II}$ is identified. The oxidation and reduction potentials of the $[Pt^{IV}(p-X)_4TPP]Br_2$ complexes are compared to those of the $[Pt^{II}(p-X)_4TPP]$ precursors and $[Pt^{IV}(p-X)_4TPP]Cl_2$ analogs. Addition of I_2 or I^- to Pt(II) porphyrins does not result in oxidative-addition to form Pt(IV) porphyrins. Instead, the addition of I^- to $[Pt^{IV}(p-X)_4TPP]Br_2$ results in the reduction of the platinum to form the corresponding $[Pt^{II}(p-X)_4TPP]$. ©2000 Elsevier Science Ltd All rights reserved.

Keywords: Platinum(II); Platinum(IV); Bromide; Porphyrins; Electrochemistry; Voltammetry

1. Introduction

An extensive amount of research has focused on metalloporphyrins owing to the critical roles they play in electron transfer, photosynthesis, and oxygen transfer processes [1]. Their reactivity is found to be dependent upon the central metal, the substituents on the porphyrin ring, and the axially coordinated ligands. Platinum porphyrins have been investigated as oxygen sensing probes [2-6], photosensitizers [7–9], potential antitumor agents [10], and molecular conductors [11,12]. Most of the recent studies have focused on Pt(II) porphyrins. Pt(IV) porphyrins of the type [$Pt^{IV}(p X_{4}$ TPP]Br₂, where X = CN, H, CH₃, and OCH₃, have been synthesized from the corresponding $[Pt^{II}(p-X)_4TPP]$ precursors through direct oxidative-addition of $Br_{2(1)}$. Stable $[Pt^{IV}(p-X)_4TPP]Br_2$ complexes are formed with axial Br⁻ ligands that generate large Δ splitting values in the Pt(IV) $(5d, t_{2g}^6 e_g^0)$ through σ donation [13]. Considerable attention has recently been devoted to the development of platinum(IV) dichloride complexes as pro-drug antitumor agents [14–18], whereas relatively few reports have involved the study of platinum(IV) dibromide compounds [19–21]. The compounds in this paper are prepared in a fashion similar to $[Pt^{IV}(p-X)_4TPP]Cl_2$ complexes previously reported [22]. The chemical and electrochemical reactivity of Pt(II) and Pt(IV) tetraphenylporphyrins with the halogens chlorine, bromine, and iodine is discussed in this research.

2. Experimental

2.1. General

¹H NMR spectra were recorded at 270.167 MHz with a JEOL ECLIPSE spectrometer (reference δ 7.24, CHCl₃). 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 by the conventional three-electrode method in CH₂Cl₂ (distilled from CaH₂) with Bu₄NPF₆ (0.10 M) as a supporting electrolyte. Electrochemical measurements were made with either a PAR 174A electrochemical analyzer or an Amel model 551 potentiostat and a model 567 function generator. The concentration of the complex was usually between $(0.5-1.0) \times 10^{-3}$ M. Ferrocene was used as an internal standard. All potentials are

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referenced to the $E_{\frac{1}{2}} (E_{\frac{1}{2}} = \frac{1}{2}(E_{pa} + E_{pc}))$ for the $(C_5H_5)_2$ Fe/ $(C_5H_5)_2$ Fe⁺ couple; $E_{\frac{1}{2}}$ for ferrocene was typically + 0.48 ± 0.02 V versus the Ag|AgCl|NaCl(saturated) BAS reference electrode, near the 0.45 V reported for the ferrocene couple versus an SCE reference electrode [23].

Reagent grade chemicals and solvents were purchased from Aldrich Chemical Company, Fisher Scientific, and Spectrum. Platinum(II) chloride was obtained from Alfa Aesar, chlorine, from Matheson Gas Products, and bromine from Janssen Chimica. Chromatographic grade aluminum oxide, activated neutral, standard grade 150 mesh, 58 Å and silica gel (Merck grade 9385, 230-400, mesh 60 Å) were purchased from Aldrich Chemical Company. Elemental analyses were performed by Desert Analytics, Tucson, AZ.

2.2. Synthesis of $[Pt^{IV}(p-X)_4TPP]Br_2$ (X = CN, H, OCH₃, CH₃)

The synthesis of the $[Pt^{II}(p-X)_4TPP]$ complexes has been previously reported [22]. The $[Pt^{IV}(p-X)_4TPP]Br_2$ complexes were synthesized through direct addition of Br₂ to the corresponding [Pt^{II}(p-X)₄TPP] complexes. A Br₂₍₁₎/CHCl₃ solution was prepared by the addition of 12 drops of $Br_{2(1)}$ to 10 cm³ of CHCl₃, and 50 drops of the mixture were added slowly to $[Pt^{II}(p-X)_4TPP]$ (0.022 mmol) dissolved in 20 cm³ of CHCl₃ at 0°C. The reaction was monitored by UV-Vis spectroscopy and judged complete in 2 h by the gradual decrease of the Soret band near 403 nm associated with $[Pt^{II}(p-X)_4TPP]$ and the appearance of the Soret band near 421 nm associated with $[Pt^{IV}(p-X)_4TPP]Br_2$. The solution was concentrated to 5 cm^3 by rotary evaporation, and an equal volume of cold methanol precipitated the $[Pt^{IV}(p-$ X)₄TPP]Br₂ crystalline solid. The complex was dissolved in a minimum amount of toluene and loaded onto a 3 cm×18 cm silica gel column. Non-reacted $[Pt^{II}(p-X)_4TPP]$ was eluted as a light orange band with toluene. [$Pt^{IV}(p-$ X)₄TPP]Br₂ was collected upon elution with 2% trifluoroacetic acetic acid (TFA) in chloroform and appeared as a dark red-purple band. Concentration of the TFA/chloroform solution to 25 cm³ and addition of an equal volume of cold methanol precipitated the red-purple $[Pt^{IV}(p-X)_4TPP]Br_2$ crystalline solid. $[Pt^{IV}(p-X)_4TPP]Br_2$ was collected by filtration and then washed with cold methanol and water. $[Pt^{IV}(p-CN)_4TPP]Br_2$ was not purified by column chromatography owing to limited solubility. Final yields were in the range of 75%. Elemental analyses gave the following results. Calc. for [Pt(*p*-H)₄TPP]Br₂ (C₄₄H₂₈PtN₄Br₂): C, 54.62; H, 2.92; N, 5.79; Br, 16.52. Found: C, 53.95; H, 2.81; N, 5.57; Br, 16.09%. Calc. for $[Pt(p-OCH_3)_4TPP]Br_2$ (C₄₈H₃₆Pt-N₄O₄Br₂): C, 53.00; H, 3.34; N, 5.15; Br, 14.69. Found: C, 52.64; H, 3.01; N, 4.89; Br, 14.60%.

3. Results and discussion

As reported for the $[Pt^{IV}(p-X)_4TPP]Cl_2$ complexes, the UV–Vis spectra of the $[Pt^{IV}(p-X)_4TPP]Br_2$ complexes are

dominated by the Soret, α , and β bands near 420, 573, and 536 nm, respectively (Table 1). These bands exhibit 20-25 nm bathochromic shifts (to longer wavelengths) with respect to the precursor $[Pt^{II}(p-X)_4TPP]$ complexes and are similar in absorption values to their $[Pt^{IV}(p-X)_4TPP]Cl_2$ analogs [22]. A slight bathochromic shift of ~ 4 nm is detected for the Soret band for the $[Pt^{IV}(p-X)_4TPP]Br_2$ complexes compared to their chloride counterparts. Thus, there is a substantial effect on the electronic spectra of the complexes as a result of the $Pt^{II} \rightarrow Pt^{IV}$ oxidation but little effect due to variance in the halogens at the axial positions. The bathochromic shifts resulting from $Pt^{II} \rightarrow Pt^{IV}$ have been interpreted as being indicative of a decrease in metal d to porphyrin π^* -bonding [24]. As was observed for $[Pt^{II}(p-X)_4TPP]$ and $[Pt^{IV}(p-X)_4TPP]$ X)₄TPP]Cl₂, the Soret, α , and β bands of the [Pt^{IV}(p- $X_{4}TPPBr_{2}$ complexes do not display any pronounced substituent effect.

In the ¹H NMR spectra, a distinct decrease in shielding of all proton resonances is evident upon oxidation of $[Pt^{II}(p-$ X)₄TPP] to $[Pt^{IV}(p-X)_4TPP]Br_2$ (Fig. 1), and a similar trend was observed for the analogous $[Pt^{IV}(p-X)_4TPP]Cl_2$ complexes [22]. In comparing the ¹H NMR of the [Pt^{IV}(p- $X_{4}TPP$ Br₂ to the [Pt^{IV}(*p*-X)₄TPP] Cl₂ complexes, the bromide complexes display a slight upfield chemical shift of all ¹H NMR resonances (~ 0.02 ppm). The upfield chemical shift may be indicative of increased electron density about the platinum center for the dibromide complexes. Increased electron density about the platinum center would allow for increased platinum-porphyrin π^* -backbonding resulting in increased shielding of the porphyrin proton resonances. This would be anticipated as Pt(IV) forms a weaker bond with the bromide than with the chloride ion [25], and this feature is evident in the electrochemical results. As was the case for the $[Pt^{IV}(p-X)_4TPP]Cl_2$ complexes, the J_{Pt-H} pyrrole coupling decreases from ca. 11 Hz for Pt(II) to ca. 8 Hz for Pt(IV) owing to the relative decrease in platinum 6s character (Table 2).

A porphyrin ring generally shows three or four well defined, quasireversible sites of redox activity. The LUMO of the porphyrin ring is considered to be the $e_g(\pi^*)$ orbital and the HOMO either an $a_{2u}(\pi)$ or $a_{1u}(\pi)$ orbital. In earlier

Table I					
Spectral data for	$[Pt^{II}(p-X)_{4}TPP]$	and [Pt ^{IV} (p	-X) ₄ TPP]	Br ₂ complexes	a

	Soret band	β band	α band
$Pt^{II}(p-CN)_4TPP$	403	511	541
$[Pt^{IV}(p-CN)_4TPP]Br_2$	427	538	573
[Pt ^{II} (TPP)]	402	510	540
[Pt ^{IV} (TPP)]Br ₂	426	535	b
$[Pt^{II}(p-CH_{3}O)_{4}TPP]$	407	512	539
$[Pt^{IV}(p-CH_3O)_4TPP]Br_2$	430	537	573
$[Pt^{II}(p-CH_3)_4TPP]$	405	511	539
$[Pt^{IV}(p-CH_3)_4TPP]Br_2$	427	535	b

^a Wavelengths in nanometers.

^b Not observed.



Fig. 1. NMR spectra of the aromatic region (270 MHz, reference δ 7.24, CHCl₃): (a) [Pt^{II}(*p*-CH₃O)₄TPP], (b) [Pt^{IV}(*p*-CH₃O)₄TPP]Br₂.

Table 2

¹H NMR chemical shifts and coupling constants ^a

	H-pyr	H-ortho	H-meta	H-para	
$Pt^{II}(p-CN)_{4}TPP \\ [Pt^{IV}(p-CN)_{4}TPP]Br_{2}^{b} \\ [Pt^{IV}(TPP)] \\ [Pt^{IV}(TPP)]Br_{2} \\ [Pt^{IV}(p-CH_{3}O)_{4}TPP] \\ [Pt^{IV}(p-CH_{3}O)_{4}TPP]Br_{2} \\ [Pt^{II}(p-CH_{3})_{4}TPP] \\ [Pt^{IV}(p-CH_{3})_{4}TPP] \\ [Pt^{IV}(p-CH_{3})_{4}TPP]Br_{2} \\ [Pt^{IV}(p-CH_{3})_{4}TPP] \\ [Pt^{IV}(p-CH_{3})$	8.68 $(J_{Pt-H} = 11)$ 9.10 $(J_{Pt-H} = 8)$ 8.76 $(J_{Pt-H} = 12)$ 9.03 $(J_{Pt-H} = 8)$ 8.78 $(J_{Pt-H} = 10)$ 9.05 $(J_{Pt-H} = 8)$ 8.76 $(J_{Pt-H} = 11)$	8.26 8.38 8.15 8.25 8.05 8.16 8.03 8.12	8.07 8.21 7.74 7.78 7.26 7.30 7.53 7.53	7.75 7.79	$(-OCH_3 = 4.13)$ $(-OCH_3 = 4.10)$ $(-CH_3 = 2.69)$

^a Chemical shifts in ppm, coupling constants in Hz.

^b NMR in acetonitrile solvent.

work, we were able to observe the four redox waves for $H_2(TPP)$, but the oxidation at the most positive potential was distorted and did not display good redox characteristics [22]. Substitution of the *para* protons by –CN to give $H_2(p-CN)_4TPP$ provides a ligand that does exhibit all four well defined sites of redox activity (Table 3). The substituent effect observed in other $H_2(p-X)_4TPP$ ligands is evident for $H_2(p-CN)_4TPP$ as the first oxidation is shifted by +0.23 V and the first reduction by +0.16 V relative to $H_2(TPP)$.

These are substantially larger changes than observed in other $H_2(p-X)_4$ TPP ligands as, for example, the first oxidation of $H_2(p-Cl)_4$ TPP relative to H_2 (TPP) is only +0.09 V.

In several instances, the electrochemistry of the $[Pt^{II}(p-X)_4TPP]$ complexes also shows four sites of redox activity attributable to the porphyrin ring, and the substituent effect is observed in the complexes as well as the free ligands. Reaction of the $[Pt^{II}(p-X)_4TPP]$ complexes with Cl₂ produced the $[Pt^{IV}(p-X)_4TPP]$ Cl₂ complexes. The four sites of

Table 3	
Electrochemical data for the $[Pt^{IV}(p-X)_4TPP]Br_2$ complexes	

H ₂ (TPP) ^a	+1.01	+0.55(85)		-1.67(70)	-2.00(80)
H ₂ (p-CN) ₄ TPP ^a	+1.02(93)	+0.78(88)		-1.51(105)	-1.83(110)
$[Pt^{II}(p-CN)_4TPP]^{a}$		+0.91(80)		-1.64(70)	-2.04(90)
[Pt ^{IV} (p-CN) ₄ TPP]Br ₂ ^b		+1.14(80)	-0.50	-2.04(90)	
$[Pt^{IV}(TPP)]Br_2^{a}$		+0.89(100)	-0.75	-1.84(100)	
$[Pt^{IV}(p-CH_3)_4TPP]Br_2^{a}$		+0.85(90)	-0.80	-1.87(80)	
[Pt ^{IV} (p-CH ₃ O) ₄ TPP]Br ₂ ^a		+0.76(95)	-0.81	-1.86(95)	

^a Electrochemistry performed in CH₂Cl₂. Scan rates were 200 mV s⁻¹. Potentials (mV) are referenced to the ferrocene/ferrocinium redox couple. Numbers in parentheses are ΔE_p (mV) and the numbers in italics are the Pt^{IV} \rightarrow Pt^{II}(V) reductions.

^b Electrochemistry performed in CH₃CN.

redox activity remain, and a fifth irreversible reduction attributable to $Pt^{IV} \rightarrow Pt^{II}$ that showed a substantial substituent effect was observed. With the preparation of the corresponding $[Pt^{IV}(p-X)_4TPP]Br_2$ and $[Pt^{IV}(p-X)_4TPP]Cl_2$ complexes, the effect of the axial ligand as well as the substituents on the porphyrin ring can be studied. As was found for the $[Pt^{IV}(p-X)_4TPP]Cl_2$ complexes, only the first oxidation and first reduction waves of the ligand were always well defined. Replacement of the two axial Cl^{-} ligands on the [Pt^{IV}(p-X)₄TPP]Cl₂ complexes with Br⁻ caused only a slight negative shift (<0.05 V) in both of these waves. However, a substantial positive shift (between 0.19 and 0.31 V) in the $[Pt^{IV}(p-X)_4TPP]Br_2$ complexes relative to the $[Pt^{IV}(p-X)_4TPP]Br_2$ X)₄TPP]Cl₂ complexes is observed for the irreversible $Pt^{IV} \rightarrow Pt^{II}$ reduction (Table 3). Thus, the axial ligands, which are directly coordinated to the Pt(IV), have a pronounced effect on that reduction, and the effect is in the direction expected as Cl^{-} should form the stronger bond to Pt(IV), making $[Pt^{IV}(p-X)_4TPP]Cl_2$ more difficult to reduce [25]. The reduction process for both the Cl⁻ and Br⁻ complexes can be described by:

$$[Pt^{IV}(p-X)_{4}TPP]X_{2}+2e^{-} \rightarrow [Pt^{II}(p-X)_{4}TPP]+2X^{-}$$
(1)

To illustrate, for the [Pt^{IV}TPP]Br₂ complex, if the potential scan is initiated at 0.00 V in the anodic direction (Fig. 2, scan A), the first porphyrin oxidation and, upon reversal of the potential scan the subsequent reduction, is observed at +0.89 V. The Pt^{IV} \rightarrow Pt^{II} reduction is then observed at -0.75V, followed by the reduction, and upon reversal of the potential scan, the subsequent oxidation of the porphyrin ring at -1.84 V. When the scan is initiated at 0.00 V in the cathodic direction (Fig. 2, scan B), the $Pt^{IV} \rightarrow Pt^{II}$ reduction and first reduction and subsequent oxidation of the porphyrin ring are again observed. However, a new irreversible oxidation at +0.25 V appears as do some small impurities associated with the porphyrin oxidation-reduction at +0.89 V. If scan A is repeated but allowed to go through two cycles (Fig. 2, scan C), the first cycle is identical to scan A but the second cycle has the oxidation at +0.25 V and the small impurities associated with the +0.89 V peak. When scan A is repeated and allowed to go through the $Pt^{IV} \rightarrow Pt^{II}$ reduction, but not the ring reduction and subsequent oxidation at -1.84 V (Fig. 2, scan D), the oxidation at +0.25 V, and impurities on the porphyrin peak are present. The cyclic voltammograms clearly indicate that the oxidation at +0.25 V and the small impurities on the +0.89 V oxidation and reduction are associated with the reduction of the Pt^{IV} and can be described by the overall process:

$$[Pt^{IV}(TPP)]Br_2 + 2e^{-} \rightarrow [Pt^{II}(TPP)] + 2Br^{-}$$
(2)

Either simultaneously or in a subsequent step, once the Pt(IV) is reduced, the Br⁻ becomes non-coordinating and is irreversibly oxidized at +0.25 V. The small peaks associated with the porphyrin ring at +0.89 V are due to the small quantity of [Pt^{II}(TPP)] formed near the electrode surface. Cyclic voltammetry of the [Pt^{IV}(*p*-CH₃O)₄TPP]Br₂ complex gave similar results. Proof that the +0.25 V peak was due to Br⁻ was obtained when a cyclic voltammogram of tetra(*n*-butyl) ammonium bromide gave the same peak.

An attempt was made to determine whether a six-coordinate Pt(II) species might at least temporarily result from the reduction above. If reaction (2) is a two-step process:

$$[Pt^{IV}(TPP)]Br_2 + 2e^{-} \rightarrow [Pt^{II}(TPP)]Br_2$$
(3)

$$[Pt^{II}(TPP)]Br_2 \rightarrow [Pt^{II}(TPP)] + 2Br^{-}$$
(4)

the addition of a large excess of Br^- may retard reaction (4) and reaction (3) may become partially reversible. The sup-



Fig. 2. Cyclic voltammograms for $[Pt^{IV}(TPP)]Br_2$ in CH_2Cl_2 at a scan rate of 100 mV s⁻¹; scan A initiated at 0.0 V in an anodic direction; scan B initiated at 0.0 V in a cathodic direction; scan C initiated at 0.0 V in an anodic direction, multiple cycles; scan D initiated at 0.0 V in an anodic direction, reversed after the Pt(IV) to Pt(II) reduction.

porting electrolyte tetra(*n*-butyl)ammonium hexafluorophosphate was replaced with tetra(*n*-butyl)ammonium bromide so that the [Br⁻] was 0.10 M. The electrochemical results at scan rates to 500 mV s⁻¹ were identical to the previous results and failed to reveal any evidence of a reversible nature to the Pt^{IV} \rightarrow Pt^{II} reduction.

For the $[Pt^{IV}(p-X)_4TPP]Br_2$ complexes, the data of Table 3 illustrate that the first oxidation and the first reduction of the porphyrins do exhibit a substituent effect similar to that found for the $[Pt^{IV}(p-X)_4TPP]Cl_2$ complexes. The electrondonating CH₃O- and CH₃- groups shift the first oxidation and the first reduction to a more negative potential, and the electron-withdrawing –CN group shifts them toward a more positive potential. As has been observed with other Pt(II) systems, the addition of I_2 or I^- in the presence of the oxidizing agent hydrogen peroxide, H₂O₂, to Pt(II) porphyrins does not result in oxidative-addition generating Pt(IV) porphyrins [26–29]. The addition of I⁻ to [Pt^{IV} $(p-X)_4$ TPP]Br₂ results in reduction of the platinum to form the corresponding Pt(II) porphyrins, $[Pt^{II}(p-X)_{4}(TPP)]$. However, addition of iodide to $[Pt^{IV}(p-X)_4TPP]Cl_2$ does not result in platinum reduction. This reduction process of Pt(IV) complexes by iodide has previously been observed and is believed to proceed through iodide-halide bond formation prior to the reduction in which the halogen acts as a bridging ligand [30–33]. The fact that iodide effectively reduces $[Pt^{IV}(p-X)_4TPP]Br_2$ and not $[Pt^{IV}(p-X)_4TPP]Cl_2$ is attributed to the more positive reduction potentials (by ca. 0.2 V) of the bromide species compared to their chloride counterparts. The enhanced ease of reduction of Pt(IV) bromide complexes compared to analogous Pt(IV) chloride complexes has previously been attributed to a weaker Pt(IV)-Br bond, and bromide being a good bridging ligand during the reduction process [25,28,29,34-38].

4. Conclusions

 $[Pt^{IV}(p-X)_4TPP]Br_2$ complexes are readily accessible through direct oxidative-addition of Br₂ to $[Pt^{II}(p-X)_4TPP]$. The $[Pt^{II}(p-X)_4TPP]$ porphyrins are non-reactive toward I₂ or iodide in the presence of an oxidizing agent. Iodide effectively reduces the $[Pt^{IV}(p-X)_4TPP]Br_2$ complexes whereas the $[Pt^{IV}(p-X)_4TPP]Cl_2$ complexes are unaffected. Replacement of axial Cl⁻ ligands on the Pt(IV) by Br⁻ has little effect on the electrochemistry of the complex other than to move the reduction of the Pt(IV) to considerably more positive potentials. The reduction results in the loss of the axial ligands and is described by:

 $[Pt^{IV}(p-X)_{4}TPP]Br_{2}+2e^{-} \rightarrow [Pt^{II}(p-X)_{4}TPP]+2Br^{-}$

Cyclic sweep voltammetry of the Pt(IV) complex shows the appearance of the corresponding Pt(II) complex. Use of a large excess of Br^- failed to make this reduction reversible.

Acknowledgements

Partial support for this work was provided by the National Science Foundation's Division of Undergraduate Education through grant DUE 9452076 for the purchase of the nuclear magnetic resonance spectrometer and by a Cottrell College Science Award of Research Corporation (LM). The authors thank Alfa Aesar, a Johnson Matthey Company, for their metal loan program, and CSUSB Associated Students, Inc. RKB wishes to acknowledge support by a Cottrell College Science Award by Research Corporation and the National Science Foundation (TFI-802595) for funds to purchase the electrochemical equipment.

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