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# Hydrogen bond controlled formation of *trans*-dihydroxo porphyrinato platinum(IV) complexes: Synthesis, characterization and catalytic activity in olefin epoxidation

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# ABSTRACT

A number of *trans*-dihydroxo porphyrinato platinum(IV) complexes, [(porp)Pt<sup>IV</sup>(OH)<sub>2</sub>] have been synthesized and characterized from their platinum(II)-porphyrin precursors by spectroscopic methods. The crystal structure of the platinum complex of *trans*-dihydroxo-*meso*-tetramesitylporphyrinato platinum(IV) *meta*-chlorobenzoic acid ([(TMP)Pt<sup>IV</sup>(OH)<sub>2</sub>](*m*-CBA)<sub>2</sub>) has also been determined. The porphyrin periphery is planar and the platinum atom has a slightly distorted octahedral environment. It must be noted that there is a very strong O–H···O hydrogen bond between the hydrogen atoms of *m*chlorobenzoic acids and the two hydroxo ligands coordinated to the platinum center. This crystal structure has been previously described by us as *trans*-dihydroxo-*meso*-tetramesitylporphyrinato platinum(VI) *meta*-chlorobenzoate ([(TMP)Pt<sup>VI</sup>(OH)<sub>2</sub>](*m*-CB)<sub>2</sub>), but the spectroscopic data has been reinterpreted due to the contradictory +6 oxidation state for platinum. The UV–Vis and NMR spectroscopic data suggest that the porphyrin skeleton is similar to that of normal porphyrins and are also indicative of the +4 oxidation state for platinum. Cyclic voltammetry studies also indicate that Pt<sup>II</sup>TMP can oxidize up to Pt<sup>IV</sup>(TMP<sup>+</sup>) species via three successive one-electron oxidation steps. The results of DFT studies and NBO analysis confirm that platinum has +4 oxidation state in both [(TMP)Pt(OH)<sub>2</sub>](*m*-CBA)<sub>2</sub> and [(TMP)Pt(OH)<sub>2</sub>](*m*-CB)<sub>2</sub> complexes. The catalytic activity of these porphyrin complexes has been investigated for the oxidation of various alkenes in the presence of iodosylbenzene.

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# 1. Introduction

Metalloporphyrins are known to mimic the activity of monooxygenase enzymes [1–5]. In this regard, an extensive amount of research has been focused on them, owing to the critical role they play in electron transfer [6] and photosynthesis [7] processes and also in catalytic oxygen atom transfer processes including hydroxylation [8–11] and epoxidation [12–15] of hydrocarbons. It is found that the reactivity of metalloporphyrin complexes depends on the central metal [13,16], the substituents on the porphyrin periphery [10,17,18], and the axially coordinated ligand [19–21]. Investigations in this area have been concentrated on the mechanism of the function of heme-containing enzymes such as cytochrome P-450 by designing metalloporphyrins as models [22– 24]. Considerable attention has been paid to the oxidation of hydrocarbons catalyzed by Fe-, Mn-, and Ru- porphyrins [1,15,25–29]. Although platinum porphyrins have been studied as oxygen sensing probes [30–32], photosensitizers [33–35], potential antitumor agents [36], and molecular conductors [37,38], there aren't any studies on platinum porphyrins as oxidation catalysts.

In addition, high oxidation states of Platinum are very rare [39]. PtF<sub>6</sub> complex is the only compound that represents +6 oxidation state of platinum [40,41] which is an extraordinarily powerful oxidizing agent.

Initial reports on Pt<sup>IV</sup>-oxo complex isolation were revisited to confirm that the repulsion between filled  $d_z^2$  electrons and an electron rich ligand such as the oxo ligand prevents Pt-oxo formation [42,43]. However, Pt<sup>IV</sup>(porp)X<sub>2</sub> (X = Cl, Br) has also been reported [44–47]. Kadish et al. also reported on the formation of Pt(IV) porphyrin and Pt(IV) porphyrin  $\pi$ -cation radical by spectroelectochemical methods [48,49] although, to the best of our knowledge, there is no report on Pt(IV) porphyrin complexes that contains hydroxo groups as the axial ligand.







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Porphyrin macrocycles and their metal complexes have rich redox chemistry. The macrocycle can have a versatile character; the most stable and abundant oxidation state of the macrocycle is the normal aromatic 18  $\pi$ -electron ring in which the macrocycle has a -2 oxidation state. Under reducing conditions, monoanion radical 19  $\pi$ -electron and anti-aromatic 20  $\pi$ -electron dianion systems have been recognized [50-53]. In the oxidative environment of the enzyme, porphyrin  $\pi$ -cation radical with 17  $\pi$ -electron system has been proposed [22,54,55]. Vaid et al. and Yamamoto et al. have reported anti-aromatic 16  $\pi$ -electron porphyrins and their Li<sup>+</sup> and Zn<sup>2+</sup> complexes [56–59]. All 20 or 16 anti-aromatic porphyrins have similar features, such as (i) alternating C-C bond distances along the 20 carbon periphery of their porphine ring system, (ii) highly saddle or ruffle distortion of the porphine from planarity, (iii) red shift in Soret band for 20  $\pi$ -elecron system and blue shift for 16  $\pi$ -electron system to that of normal porphyrin and (iv) strong paratropic shift in NMR for anti-aromatic porphyrins compared to that of diatropic shift normally seen in aromatic porphyrins.

In our previous report [60], we proposed the formation of  $[(TMP)Pt^{VI}(OH)_2]^{2+}$  species on the basis of chemical and X-ray studies. Complementary spectroscopic and electrochemical studies motivated us to revisit our X-ray structure. In addition, the results of our DFT studies and NBO analysis confirm that platinum has +4 oxidation state in both  $[(TMP)Pt^{IV}(OH)_2](m-CBA)_2$  and  $[(TMP)Pt(OH)_2](m-CB)_2$  complexes. Furthermore, DFT studies helped us to revisit the crystal structure to find the exact position of protons and come up with the correct interpretation of our X-ray data.

#### 2. Experimental

#### 2.1. Material and instruments

All chemicals and solvents were purchased from Merck, Fluka or Aldrich chemical companies. The free bases, *meso*-tetraphenylporphyrin (H<sub>2</sub>TPP), *meso*-tetramesitylporphyrin (H<sub>2</sub>TMP) and *meso*-tetrakis(pentafluorophenyl)porphyrin (H<sub>2</sub>F<sub>20</sub>TPP or H<sub>2</sub>TPFPP), were prepared according to the literature [61]. Iodosylbenzene was obtained by the hydrolysis of iodosylbenzene diacetates [62].

The electronic absorption spectra were recorded on a SPECORD S600 spectrophotometer from Analytikjena. The reaction products were analyzed by gas chromatography using a Trace GC ultra from Thermo equipped with an FID Detector and Rtx<sup>®</sup> –1 capillary column. The chemical yields for the oxidation reactions were based on iodosylbenzene, the limiting reactant.

Table 1

Electronic absorptions and multi-nuclear NMR data for some platinum porphyrins.

A home-made three-electrode cell consisting of a glassy carbon working electrode, a platinum counter electrode and a silver chloride reference electrode (Ag/AgCl) was used for cyclic voltammetry experiments. Cyclic voltammetry was carried out by using a  $\mu$ Autolab Type III potentiostat/galvanostat from Metrohm in combination with the powerful GPES software at room temperature.

#### 2.2. Preparation of platinum porphyrins

Free base porphyrins were metalated with platinum(II) chloride, PtCl<sub>2</sub>, as described in the literature to give corresponding *meso*-tetraphenylporphyrinato platinum (PtTPP), *meso*-tetramesitylporphyrinato platinum (PtTMP) and *meso*-tetrakis(penta-fluorophenyl)porphyrin (PtTPFP) complexes [63]. A typical procedure was as follows: typical free base porphyrins (0.2 mmol) were dissolved in 50 ml of anhydrous benzonitrile, then PtCl<sub>2</sub> (0.4 mmol) was added to the porphyrin solution. The mixture was then purged with N<sub>2</sub> as it was slowly heated to 190 °C. The mixture was refluxed under N<sub>2</sub> until there were no free base porphyrins revealed by UV–Vis spectroscopy. The mixture was then cooled to room temperature and the solvent was removed by vacuum distillation. The crude product was washed with 5 ml of methanol and then purified by column chromatography. NMR and UV–Vis data for these platinum porphyrins are given in Table 1.

#### 2.3. Synthesis of [(TMP)Pt(OH)<sub>2</sub>](m-CBA)<sub>2</sub> complex

*meso*-Tetramesitylporphyrinato platinum(II) (PtTMP) (43 mg, 0.044 mmol) was dissolved in 10 ml  $CH_2Cl_2$ . To this solution, *meta*-chloroperbenzoic acid (*m*-CPBA) (21.6 mg, 0.088 mmol) was added. The color of the solution rapidly changed from orange to red. The reaction mixture was stirred for 5 min and then  $CH_2Cl_2$  was evaporated to dryness and then purified by passing through a column of activated basic alumina by elution with dichloromethane. The obtained product was crystallized from a dichloromethane solution by slow evaporation. Spectroscopic data for [(TMP)Pt(OH)<sub>2</sub>](*m*-CBA)<sub>2</sub> are given in Table 1.

## 2.4. General oxidation procedure

Stock solutions of the platinum porphyrins  $(3 \times 10^{-3} \text{ M})$  and alkenes (0.5 M) were prepared in CH<sub>2</sub>Cl<sub>2</sub>. In a 10 ml round-bottom flask, the reagents were added in the following order: alkene (0.5 mmol, 1 ml), catalyst  $(4 \times 10^{-4} \text{ mmol}, 0.14 \text{ ml})$  and odosylbenzene. PhIO ( $5 \times 10^{-3} \text{ g}$ ) was then added to the reaction mixture

	UV-Vis <sup>a</sup>		<sup>1</sup> H NMI	<sup>1</sup> H NMR <sup>b</sup>			<sup>13</sup> C NMR <sup>c</sup>			<sup>195</sup> Pt NMR <sup>d</sup>	Refs.
	Soret	Q-bands	H <sub>β</sub>	H <sub>o</sub> <sup>e</sup>	H <sub>m</sub>	$H_p^{f}$	Cm	Cα	C <sub>β</sub>		
Pt <sup>II</sup> TMP	402	510, 540	8.56	1.85	7.25	2.6	-	-	-	2553.8	tw <sup>g</sup>
Pt <sup>II</sup> TPP	402	510, 539	8.77	8.14	7.72	7.72	-	-	-	-	tw
Pt <sup>II</sup> TPFPP	392	508, 539	8.83	-	-	-	-	-	-	-	tw
$[Pt^{IV}(TMP)(OH)_2](m-CBA)_2$	423	536	8.84	1.88	7.28	2.62	119.1	138	129.7	4395	tw
[Pt <sup>(IV)</sup> (TMP)(OH) <sub>2</sub> ](MeOH) <sub>2</sub>	421	534	8.79	1.91	7.29	2.62	-	-	-	-	tw
[Pt <sup>(IV)</sup> (TPP)(OH) <sub>2</sub> ](CF <sub>3</sub> COOH) <sub>2</sub>	417	532	9.09	8.16	7.74	7.74	-	-	-	-	tw
Pt <sup>IV</sup> (TMP)(Br) <sub>2</sub>	427	536	8.79	1.89	7.3	2.65	119.1	138.5	131	4019	tw
Pt <sup>II</sup> TPP	402	510,540	8.74	8.14	7.7	7.7	122.3	140.9	130.7	1235	[69]
Pt <sup>IV</sup> (TPP)(Cl) <sub>2</sub>	421	538,575	9.06	8.27	7.8	7.8	121.4	138.3	132.1	4215	[69]

<sup>a</sup>  $\lambda$  (in nm) and in CH<sub>2</sub>Cl<sub>2</sub> solution.

<sup>b</sup> Chemical shifts in ppm from impurity of CHCl<sub>3</sub> (7.26 ppm) in CDCl<sub>3</sub> solvent.

<sup>c</sup> Chemical shift in ppm referenced to TMS.

<sup>d</sup> Pt referenced to  $PtCl_6^{2-} = 4522 \text{ ppm}.$ 

e Ortho-H or Me.

f Para-H or Me.

g This work.

at room temperature. The mixture was stirred for 24 h and then was analyzed by gas chromatography. The yields were calculated by the internal standard method.

#### 2.5. DFT calculations

The computational study performed on  $[(TMP)Pt(OH)_2](m-CBA)_2$  and  $[(TMP)Pt(OH)_2](m-CB)_2$  complexes was accomplished with DFT using the GAUSSIAN 98 A.9 program suite [64]. The energies and geometries of different complexes were calculated and optimized with the B3LYP hybrid functional method [65,66]. The 6-31G (*d*,*p*) basis set was applied to the nonmetal atoms (hydrogen, carbon, nitrogen and oxygen) while the LANL2DZ effective core potential (ECP) and corresponding basis set functions [67] were used for the platinum atom.

Full optimizations of the studied compounds in singlet spin states, without any symmetry constraint, have been performed with the FOPT keyword. The optimized structures for all species are presented in the Supplementary materials. Harmonic



Fig. 1. UV-Vis spectra for (—) PtTMP ( $5.3 \times 10^{-6}$  M), (—) Pt(TMP)(OH)<sub>2</sub> ( $2.4 \times 10^{-6}$  M) and (—) Pt(TMP)Br<sub>2</sub>( $3.4 \times 10^{-6}$  M) in CH<sub>2</sub>Cl<sub>2</sub> solution.

vibrational frequencies were systematically computed to confirm whether an optimized geometry correctly corresponds to a local minimum that has only real frequencies. Atomic charge and spin density studies were based on Mulliken calculations. The natural bond orbital (NBO) analysis is used to explain electron distribution in the *d*-orbitals of platinum and the macrocycle ring as well as to assign the atomic charges. The molecular orbital analyses were performed by Gauss View applied to the respective Gaussian output file.

### 3. Results and discussion

# 3.1. UV-Vis spectra

The electronic spectra of the  $CH_2Cl_2$  solution of  $Pt^{II}TMP$  complex and the final Pt-complex product of its titration with 2.0 equivalents of *m*-CPBA have been shown in Fig. 1.

According to Fig. 1, the Soret band of the Pt-complex has significant red shift (21 nm) relative to that of PtTMP, with no evidence of an absorption band at 600–700 nm indicative of a porphyrin  $\pi$ -cation ring [18]. This significant red shift that is in contrast to the blue shift observed for the 16  $\pi$ -electron metalloporphyrins [57] is indicative of the oxidation of Pt<sup>II</sup> to Pt<sup>IV</sup> as seen in previous reports [44,45,49]. This electronic spectrum resembles the Pt<sup>IV</sup>(TMP)Br<sub>2</sub> spectrum. As explicitly shown in Fig. 1, there is only a slight shift (5 nm) in the Soret band of Pt<sup>IV</sup>TMP(Br)<sub>2</sub> compared to that of Pt(TMP)(OH)<sub>2</sub> which can be attributed to change occurring in the axial ligand; this again provides another indication for the existence of Pt<sup>IV</sup> in the latter Pt-complex [45].

The reaction of Pt<sup>II</sup>TMP with two equivalents of iodosylbenzene caused no dihydroxo formation after several days, but the addition of a few drops of methanol to the above solution exclusively formed Pt(TMP)(OH)<sub>2</sub> after 6 h at room temperature. Furthermore, no new products were achieved with the reaction of PtTPP and iodosylbenzene after 7 days while upon the addition of 2.0 equivalents of trifluoroacetic acid, the corresponding species formed and stabilized rapidly. Consequently, it seems that the formation of hydrogen bonding between *m*-chlorobenzoic acids and hydroxo groups is absolutely essential for the formation and stabilization of such dihydroxo platinum complexes (Scheme 2). Electronic and multi-nuclear NMR data for some Pt<sup>II</sup>(porp) and [(porp)Pt(OH)<sub>2</sub>)] complexes have been given in Table 1.

According to Table 1 and with respect to the <sup>1</sup>H-NMR evidence of very weak paratropic ring current effects [44,45] the involvement of an 18  $\pi$ -electron porphyrin ligand is supported.



**Scheme 1.** Three cartoons representing the different electronic aspects of the  $[(porp)Pt(OH)_2]^0$  and  $[(porp)Pt(OH)_2]^{2+}$ .



Scheme 2. Hydrogen bond controlled formation of [Pt(porp)(OH)<sub>2</sub>]. 2X, (X = OMe, m-CB) and its proposed intermediate.

Moreover, <sup>195</sup>Pt chemical shift confirms the oxidation of Pt<sup>II</sup>(porp) to corresponding Pt<sup>IV</sup>(porp)X<sub>2</sub> complexes [68,69]. In spite of some positive indications resulting from the X-ray analysis of the crystal structure and stoichiometric titration in which two mole ratios of *m*-CPBA were consumed [60], our spectroscopic data do not confirm the formation of  $[Pt(TMP)(OH)_2]^{2+}$  nor  $[(TMP^0) Pt^{IV}(OH)_2]^{2+}$  species, Scheme 1.

## Table 2

Half-wave potentials ( $E_{1/2}$ , V vs. Ag/AgCl) of platinum porphyrins in CH<sub>2</sub>Cl<sub>2</sub> containing 0.05 M of TBAP.

Compound	Ox1	Ox2	Red1	Red2	Refs.
Pt <sup>II</sup> TMP	1.19	1.67	-1.48	-	tw
Pt <sup>II</sup> TPP	1.23	1.60	-1.3	-	tw
Pt <sup>II</sup> TPFPP	-	1.7	-0.85	-1.3	tw
Pt <sup>II</sup> TPP	1.20	1.52	-1.3	-	[49]



Fig. 2. Voltammogram of a  $Pt^{II}TMP$  solution in  $CH_2Cl_2$  containing 0.05 M TBAP as supporting electrolyte at a scan rate of 0.1 V/s.

# Table 3

Half-wave oxidation potentials ( $E_{1/2}$ , V vs. Ag/AgCl) of platinum porphyrins in the presence of three axial ligands in CH<sub>2</sub>Cl<sub>2</sub> solution containing 0.05 M of TBAP.

Compound	Oxidation potential							
	Perchlor	ate	Methano	ol	Bromide			
Pt <sup>II</sup> TPP Pt <sup>II</sup> TMP Pt <sup>II</sup> TPFPP	1.23 1.19 -	1.59 1.67 1.7	1.23 1.19 -	1.53 1.55 1.7	1.44 1.37 v.b <sup>a</sup>			

<sup>a</sup> Very broad peak.

The consumption of 2.0 equivalents of oxidant may be an indication that PtTMP would initially be oxidized to the  $[Pt(TMP)(OH)_2]^{2+}$  or  $[Pt^{IV}(TMP^{+.})(OH)_2]$  species, but these species have an extremely short life time and hence rapidly reduce to a  $[Pt^{IV}(TMP)(OH)_2]^0$  complex as confirmed by its UV–Vis and NMR data. Hydrogen bond formation between two axial hydroxo groups and hydrogen atoms of *meta*-chlorobenzoic acids or any other protic species such as methanol and trifluoroacetic acid enables the formation and stabilization of such species (Scheme 2).



**Fig. 3.** Intermolecular  $O-H\cdots O$  hydrogen bonds between benzoic acid molecules and OH-Pt-OH hydroxyl groups. Some of hydrogen atoms are omitted for better clarity.

#### 3.2. Cyclic voltammetry studies

Electrochemical behavior of three  $Pt^{II}(porp)$  complexes including  $Pt^{II}TPP$ ,  $Pt^{II}TMP$  and  $Pt^{II}TPFPP$  was investigated to find a clue about what takes place during the stoichiometric titration. The results have been summarized in Table 2. Cyclic voltammogram of  $Pt^{II}TMP$  in  $CH_2Cl_2$  in the presence of 0.05 M tetra-*n*-butylammonium perchlorate (TBAP) as supporting electrolyte has been shown in Fig. 2.

There are two reversible oxidation peaks in this voltammogram. As expected [48], the first reversible oxidation of  $Pt^{II}TMP$  occurs at slightly less positive potential than that of  $Pt^{II}TPP$  (Table 2), which indicates that the first oxidation is macrocycle centered and leads to the formation of  $Pt^{II}(TMP^{+})$  and  $Pt^{II}(TPP^{+})$  respectively. This is further confirmed by the absence of  $\pi$ -cation formation for

Pt<sup>II</sup>TPFPP due to the electron withdrawing effect of 20 fluorine atoms (Table 2, Fig. S1).

The second oxidation peak takes place at around 1.6–1.7 V and its position is independent of the macrocycle structure and shows that it is a metal centered one. The current for the second peak (19.2  $\mu$ A) is approximately double that of the first peak (10  $\mu$ A) which indicates the involvement of a two-electron transfer process in the second step. It seems that in total, three electrons are abstracted from the initial Pt<sup>II</sup>TMP to form the Pt<sup>IV</sup>(TMP<sup>+.</sup>) species. Kadish et al. previously reported the formation of  $\pi$ -cation Pt<sup>IV</sup> by the spectroelectrochemical method [44,48,49].

Electrooxidation of Pt<sup>II</sup>TMP in the presence of methanol, which has a weak coordinating ability, caused no change in the first oxidation potential, however it shifted the second one to a less positive potential (Table 3). This is an indication that the first



**Fig. 4.** The observed out-of-plane displacement of the porphyrin core atoms from the mean plane of the porphyrin for the experimental and calculated structures of (A)  $[(TMP)Pt^{V}(OH)_{2}](m-CBA)_{2}$  (blue and red, respectively) and (B)  $[(TMP)Pt^{V}(OH)_{2}TMP](m-CB)_{2}$  (orange and green, respectively) in units of Å. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



**Fig. 5.** The porphyrin core-superimposed of experimental and calculated structures of  $[(TMP)Pt^{IV}(OH)_2](m-CBA)_2$  (blue and red, respectively) and  $[(TMP)Pt^{VI}(OH)_2](m-CB)_2$  (orange and green, respectively). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

oxidation is ring-centered and the second oxidation peak is a metal-centered one. Electrochemistry studies were also performed in the presence of 2.0 equivalent of bromide anion. In the presence of bromide ion, a stronger coordinating ligand, only one reversible oxidation peak at the less positive potential of 1.37 V was observed which was assigned to the  $[Pt^{IV}(TMP)]Br_2$  species (Table 3 and Figs. S2–S4).

Electrochemistry shows that Pt<sup>II</sup>TMP can be oxidized by a maximum of three electrons and forms the Pt<sup>IV</sup>(porp<sup>+</sup>) species, but this species is very unstable and tends to reduce to a six coordinate Pt<sup>IV</sup>(porp) X<sub>2</sub> complex in the presence of an axial ligand even in electrochemical conditions. In our chemical conditions, hydrogen bonding formation between hydrogen atoms of *meta*-chlorobenzoic acids and hydroxo groups coordinated to platinum provides very favorable conditions for reducing the [Pt<sup>IV</sup>(TMP<sup>+</sup>.)(OH)<sub>2</sub>] intermediate to the [(TMP)Pt(OH)<sub>2</sub>)] complex. Therefore, the reaction only progresses in the presence of a protic agent.

# 3.3. X-ray crystal structure of [(TMP)Pt(OH)<sub>2</sub>]·2metachlorobenzoic acid

In the present report, for Pt-complexes, two different structures, either  $[Pt^{VI}(OH)_2TMP](m-CB)_2$  or  $[Pt^{IV}(OH)_2TMP](m-CBA)_2$  can be refined. While the difference between these two structures is in two hydrogen atoms, finding the correct structure from X-ray diffraction data is too difficult (Figs. S9–S10 and Tables S5–S7). Electron density can be measured by X-ray diffraction. Thus, the heavier atoms have a stronger effect on the diffraction pattern. This also means that, especially in the presence of heavy atoms, the localization of the light atoms is more difficult. Here, in the presence of a heavy atom such as platinum, light atoms such as hydrogen, are somewhat more difficult to localize. On the other hand, the treatment of hydrogen atoms in an X-ray structure depends on many things, such as the geometry of the hydrogen atom containing moiety and the element type of the atom bound to hydrogen.

Table 4

The average bond lengths of 16  $\pi$ -, 18  $\pi$ -electron porphyrin rings in comparison with those of  $[(TMP)Pt(OH)_2](m-CBA)_2$ .

	beta N N <sub>py</sub> N beta 24e - 16 pi meso 16 π-electron References: 1. Li <sup>+</sup> /BF <sub>4</sub> 2. Zn <sup>2+</sup> /Cl <sup>-</sup> /ZnCl <sub>3</sub> 3. Octaethyl-Phenyl-Free	NH N 22e - 18 pi N HN 18 π-electron	[(TMP)Pt(OH) <sub>2</sub> ]( <i>m</i> -CBA) <sub>2</sub>
$C_{\beta}-C_{\beta}$ (Å)	1.352	~1.350	1.352
$C_{\beta}$ – $C_{\alpha}$ (Å)	1.466	~1.441	1.442
$C_{\alpha}\text{-}C_{meso}~(\text{\AA})$	1.362 1.472	~1.393	1.395 -
$C_{\alpha}\text{-}N_{py}\left(\text{\AA}\right)$	1.312 1.412	~1.378 -	1.366 1.380



Fig. 6. Comparison between the structures of the Pt-complex as obtained with (A) X-ray, (B) (B3LYP/LANL2DZ)  $[(TMP)Pt(OH)_2](m-CBA)_2$  and (C) (B3LYP/LANL2DZ)  $[(TMP)Pt(OH)_2](m-CBA)_2$   $[(TMP)Pt(OH)_2](m-CBA)_2$  [(TMP)Pt

Therefore, complementary studies must be used to distinguish these structures. In our previous report, the two hydroxo groups were considered axial ligands coordinated to the  $Pt^{VI}$  center, and two *m*-chlorobenzoate anions bound to it by a very strong hydrogen bonding, according to stoichiometric titration and primary electronic spectral changes [60]. It should be noted, in our previous report, the structure was reported as  $[Pt^{VI}(OH)_2TMP](m-CB)_2$ . Here, our complementary work such as more completed spectroscopic studies and electrochemistry results as well as theoretical calculations show that the metal center must be considered as  $Pt^{IV}$ .

Thus, with the help of theoretical studies, the original crystallographic data were re-refined as Pt<sup>IV</sup> central metal. This was done by adding the contribution of two hydroxo axial ligands that are bound to two *m*-chlorobenzoic acids via a very strong hydrogen bond. The resulting crystal unit cell is almost the same as the original one (see Table S5) meaning that an X-ray crystal structure determination alone is not sufficient to decide which oxidation state should be assigned to the metal center.

It is notable that two benzoic acid molecules are directed toward hydroxo groups of OH–Pt–OH and form some very strong O–H···O hydrogen bonds. Coordinated hydroxyl groups to platinum center act as hydrogen bond acceptor from the hydroxyl group of benzoic acid (O<sub>benzoic acid</sub>–H···O<sub>hydroxy</sub>), [O2–H2B = 0.96(3), H2B···O1 = 1.59(4), O2···O1 = 2.522(5) Å and O2-

#### Table 5

NBO analysis of electron distribution for Pt in  $[(TMP)Pt(OH)_2](m-CBA)_2$  and  $[(TMP)Pt(OH)_2](m-CB)_2$ .

[(TMP)Pt(OH) <sub>2</sub> ](1	n-CBA) <sub>2</sub>	$[(\text{TMP})\text{Pt}(\text{OH})_2](m-\text{CB})_2$				
Occupancy	Orbital	Occupancy	Orbital			
1.91	LP $(d_{xy})$ Pt	1.85	LP $(d_{xy})$ Pt			
1.95	LP $(d_{yz})$ Pt LP $(d_{yz})$ Pt	1.95	LP $(d_{xz})$ Pt LP $(d_{yz})$ Pt			

 $H2B \cdots O1 = 164(5)^\circ$ ], Fig. 3. It seems that the formation of such a hydrogen bonding plays an extremely important role in the formation and stabilization of the crystal packing of this complex.

Comparison of out-of-plane displacement of the porphyrin core atoms from the mean plane of the porphyrin for experimental and optimized structures shows that there is much better fit between the experimental and optimized structure of  $[Pt^{IV}(OH)_2TMP](m-CBA)_2$ , Fig. 4. Moreover, this is confirmed by porphyrin core-superimposed between experimental and calculated structures, Fig. 5.

The alternative for  $[(TMP^{2-})Pt^{VI}(OH)_2](m-CB)_2$  might be considered as  $[(TMP^0)Pt^{IV}(OH)_2](m-CB)_2$  in which the porphyrin core is a dication 16  $\pi$ -electron system. The bond lengths for 16  $\pi$ -electron [50,56,58] and 18  $\pi$ -electron [46,51–53] porphyrin rings in comparison with those of the Pt-complex obtained from X-ray analysis are listed in Table 4. From this table, it is found that there is much similarity in the values of bond distances of 18  $\pi$ -electron rings and the Pt-complex reported here. However, the most important feature evident in the structure of the Pt-complex is that such C $_{\alpha}$ -C<sub>meso</sub> and C $_{\alpha}$ -N<sub>py</sub> single and double bond alternation seen in 16  $\pi$ -electron rings cannot be observed here. Furthermore, the observed bond lengths of the Pt-complex can be completely fitted with the normal valent porphyrin bond lengths obtained from the average of hundreds of crystal structures. Thus, the pi-system of the Pt-complex should be an aromatic 18  $\pi$ -electron system.

#### 3.4. Theoretical studies

The X-ray structure obtained for the Pt-complex was optimized with B3LYP with the LANL2DZ basis set. Platinum was set to have oxidation states of IV and VI and oxygen atoms coordinated to platinum atom were supposed to be hydroxo or oxo forms. Fig. 6 shows the optimized structures. Structure A belongs to the X-ray determined structure, and structure B and C are for the same structure optimized by DFT studies,  $[(TMP)Pt^{IV}(OH)_2](m-CBA)_2$  and  $[(TMP)Pt^{VI}(OH)_2](m-CB)_2$  respectively. The bond distances and



**Fig. 7.** MO, KS, relevant to interaction between macrocycle and  $d_{xy}$  Pt orbital. (a)  $a_{2u}$  molecular orbital of porphyrin ring; (b)  $d_{xy}$  orbital of Pt and (c) resulting molecular orbital from their overlap.



Fig. 8. Kohn-Sham orbitals and their occupations in [(TMP)Pt(OH)<sub>2</sub>](m-CB)<sub>2</sub>.

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overall conformations resulted from X-ray structure studies are similar to those of optimized structure of [(TMP)Pt<sup>IV</sup>(OH)<sub>2</sub>](*m*-CBA)<sub>2</sub> with close approximation (Figs. S5–S8 and Tables S1–S4).

To further confirm the electronic structures, we have performed NBO analysis for form B and C. The results of NBO analysis are presented in Table 5. These data show that the occupancy numbers of  $d_{xy}$ ,  $d_{xz}$  and  $d_{yz}$  orbitals for platinum of form B are 1.91, 1.95 and 1.96 respectively and for form C are 1.85, 1.93 and 1.95. Form C has two less electrons than form B, as obvious from the NBO analysis, three paired electrons are presented for *d*-orbitals in form C to make the whole system Pt(IV)  $d^6$  (See Fig. 8).

The observed lower occupancy for  $d_{xy}$  with respect to the  $d_{xz}$ and  $d_{yz}$  orbitals may be interpreted due to the effective overlap between  $d_{xy}$  and  $a_{2u}$  molecular orbital of the porphyrin macrocycle. The major molecular orbitals responsible for overlaps between  $d_{xy}$ and porphyrin macrocycles are seen in Fig. 7a–c. These interactions might be responsible for delocalizing macrocycle  $\pi$  electrons to the  $d_{xy}$  or vice versa. In the valance bond approach two resonance forms are possible:  $\pi^{16} d_{xy}^2 d_{xz}^2 d_{yz}^2 (Pt^{IV}(porp^0)) = \pi^{18} d_{xy}^0 d_{xz}^2 d_{yz}^2$  $(Pt^{VI}(porp^{-2}))$  and so the latter form prevents the anti-aromatic behavior of the porphyrin ring. Calculated Mulliken charges presented in Table 6 indicate that the axial hydroxo groups are also contributing to these molecular orbitals and have less negative charges than those of  $[(porp)Pt(OH)_2]^0$ .

The NBO findings have been corroborated by the results obtained from molecular calculations. Fig. 8 shows Kohn-Sham

orbitals for the last three doubly occupied molecular orbitals of platinum in ([(TMP)Pt(OH)<sub>2</sub>](*m*-CB)<sub>2</sub>). Based on this figure, paired electrons are placed on  $d_{xy}$ ,  $d_{xz}$  and  $d_{yz}$ . Calculated charges show that in [(TMP)Pt(OH)<sub>2</sub>](*m*-CB)<sub>2</sub> the charges on the macrocycle and platinum are 1.34 and 1.20 respectively, while in [(TMP)Pt(OH)<sub>2</sub>](*m*-CBA)<sub>2</sub>, the charges on the macrocycle and platinum are -0.45 and 1.18 respectively. Therefore the ring in [(TMP)Pt(OH)<sub>2</sub>](*m*-CB)<sub>2</sub> has  $\pi$ -dication nature. This shows that two electrons can transfer from the ring to the platinum center and the charge on the ring decreases from -0.45 in ([(TMP)Pt(OH)<sub>2</sub>](*m*-CBA)<sub>2</sub>) to 1.34 in ([[(TMP)Pt(OH)<sub>2</sub>](*m*-CB)<sub>2</sub>), while the charge density on the platinum going from ([(TMP)Pt(OH)<sub>2</sub>](*m*-CBA)<sub>2</sub>) to ([(TMP)Pt(OH)<sub>2</sub>](*m*-CBA)<sub>2</sub>) to ([(TMP)Pt(OH)<sub>2</sub>](*m*-CBA)<sub>2</sub>) remains fixed at around 1.20; consistent with the formation of the platinum(IV) oxidation state.

Our DFT study and bond NBO analysis show that Pt<sup>II</sup>TMP can be oxidized by two electrons to form the Pt<sup>IV</sup>TMP species. Further

Table 6											
Calculated	Mulliken	charges	for	the	Pt,	macrocycle,	pyrrolic	nitrogen	and	two	OH
groups.											

Compounds	Pt	Ring	20H	Ν
Form B	1.18	-0.45	-0.70	-0.65
Form C	1.20	1.34	-0.52	-0.63

#### Table 7

			% Yield <sup>a</sup>		
Entry	Alkene	Product(s)	PtTPP	PtTMP	PtTPFPP
1	Cyclooctene	Epoxy cyclooctene	32	35	58
2	Cyclohexene	Cyclohexene oxide 2-Cyclohexene- 1-ole 2-Cyclohexene-	4 40 17	7 50 21	24 32 47
3	<i>cis</i> -Stilbene <sup>b</sup>	1-one <i>cis</i> -Stilbene oxide <i>trans</i> -Stilbene oxide	Not detected Not detected	46 Not detected	100 Not detected
4	Styrene	Epoxy styrene Benzaldehyde	Not detected 30	Not detected 24	40 20
5	α- Methylstyrene	α-Methylstyrene oxide	38	37.5	52
6	4- Chlorostyrene	4-Chlorostyrene oxide	9.8	20.2	57.6
7	4-Methoxy styrene	4-Methoxy styrene oxide	40	55	81.3
8	1-Octene	1-Octene oxide	5	2.3	18.7

Oxidation of various alkenes with iodosylbenzene in the presence of various Pt(II)-porphyrin complexes.

 $^a$  Conditions: Catalyst  $4\times 10^{-4}$  mmol, PhIO  $2\times 10^{-2}$  mmol, Alkene 0.5 mmol, 25 °C, stirring for 24 h.

<sup>b</sup> Epoxidation was performed in the absence of light.

#### Table 8

Epoxidation of cis-stilbene in the presence of trace amounts of methanol.

Amount of methanol (µl)	0	50	100	200	400
% Yield <sup>a</sup>	100	55	56	58	30

 $^a$  Conditions: PtTPFPP  $4\times 10^{-4}$  mmol, PhIO  $2\times 10^{-2}$  mmol, Alkene 0.5 mmol, 25 °C, stirring for 24 h.

oxidation led to ring oxidation, the  $[(\text{TMP})\text{Pt}(\text{OH})_2](m-\text{CB})_2$  complex has a Pt<sup>IV</sup> center along with the two-electron oxidation of the 18  $\pi$ -electron porphyrin to make an anti-aromatic 16  $\pi$ -electron porphyrin, but the effective overlap between the  $d_{xy}^2$  and the 16  $\pi$ -electron system of the ring prevents the anti-aromatic nature of the ring. In the present work, DFT studies solved the contradiction between X-ray diffraction and other spectroscopic data which indicates the intrinsic limitation of X-ray diffraction techniques for characterization of the compounds alone.

#### 3.5. Alkene epoxidation

The  $[(TMP)Pt(OH)_2]$  complex was formed from the addition of 2.0 equivalents of iodosylbenzene to a dichloromethane solution of PtTMP in the presence of a few drops of methanol and used as catalyst for the oxidation of cyclooctene. Isolated  $[(TMP)Pt(OH)_2]X$  (X = *m*-CBA, OMe) can convert two molecules of triphenylphosphine to triphenylphosphine oxide, but is not capable in oxidizing alkenes. Similar results were obtained by Gross et al. [70] in the oxidation of different alkenes using the  $[(TMP)Os^{VI}(O)_2]$  complex. Both  $[(TMP)Pt(OH)_2]$  and PtTMP are able to catalyze the oxidation of olefins in the presence of iodosylbenzene as an oxygen source. Table 7 shows the results for the oxidation of various alkenes with iodosylbenzene in the presence of different Pt-porphyrin catalysts.

The cyclohexene oxidation led to both epoxidation and allylic oxidation whereas cyclooctene is clearly selective for epoxidation [13].

*Cis*-stilbene was catalytically isomerized to *trans*-stilbene in the presence of light and Pt-porphyrins, therefore the exclusion of light is necessary to obtain *cis*-stilbene oxide as a product. To note, PtTPP has no catalytic activity for *cis*-stilbene while it can catalyze the oxidation of other alkenes which are less electron-rich than *cis*-stilbene.

Since alkenes should be considered nucleophiles in the oxidation reaction, the olefins with electron donating substituent on the aryl positions show better activity. In the case of 4-chlorostyrene, the  $\pi$ -electron donation effects of chlorine to the double bond may be balanced with its  $\sigma$ -electron acceptation effects. Greater reactivity of  $\alpha$ -methylstyrene with respect to styrene, 4-



Scheme 3. Proposed catalytic cycle.

chlorostyrene and 4-methoxystyrene may be due to the  $\sigma$ -electron donation effects of the methyl group to the double bond. Terminal double bond (Table 7, entry 8) is less reactive than the conjugated double bonds and shows lower activity.

The results of *cis*-stilbene epoxidation in the presence of PtTPFPP as catalyst and trace amounts of methanol are shown in Table 8. These data provide an indication that the coordinating ligand favors the formation of inactive six-coordinate  $Pt^{IV}(porp)(OH)_2$  versus  $Pt^{IV}(porp^{+})(OH)_2$  and reduces the yield of products.

#### 3.6. Proposed mechanism

In the catalytic cycle, PhIO can lead to the  $Pt^{IV}(porp^{+})(OH)_2$  complex which initiates a catalytic cycle as shown in Scheme 3. Formation of such an intermediate in the catalytic cycle was confirmed by cyclic voltammetry studies. Groves et al. also reported such a route in the hydroxylation of alkanes by ruthenium porphyrins [71]. In the absence of substrate and in the presence of coordinating ligands,  $Pt^{IV}(porp^{+})(OH)_2$  rapidly reduced to a more stable  $Pt^{IV}(porp)(OH)_2$  which is unreactive toward alkenes which were capable of oxidizing PPh<sub>3</sub> to PPh<sub>3</sub>(O).

#### 4. Conclusion

Oxidation of Pt<sup>II</sup>TMP consumes 2.0 equivalents of *m*-CPBA and forms a new Pt-complex that we have previously reported as  $[Pt^{VI}(TMP)(OH)_2](m-CB)_2$  based on stoichiometric titration and Xray analysis. Complementary spectroscopic, electrochemical and theoretical studies suggested +4 oxidation state for the platinum center. DFT studies were employed to find the correct position of hydrogen atoms and hence, the correct structure. Finally, we reformulated the crystal structure as  $[(TMP)Pt^{IV}(OH)_2](m-CBA)_2$  corresponding to DFT results, which shows Pt-oxo and dioxo species are not stable and tend to form platinum dihydroxo species.

It is notable that there is a strong hydrogen bonding between two hydroxo groups coordinated to platinum and hydrogen atoms of *m*-chlorobenzoic acids (or trifluoroacetic acid or methanol) that is a crucial factor for the formation and stabilization of this species.

While the  $[(porp)Pt(OH)_2]$  complexes are not active oxidants toward the oxidation of olefins, they can oxidized two molecules of triphenylphosphine. These complexes and their corresponding Pt<sup>II</sup>(porp) complexes showed catalytic activity toward olefin epoxidation in the presence of iodosylbenzene. Catalytic oxidation reactions also indicate the involvement of a Pt<sup>IV</sup>(porp<sup>+</sup>·) intermediate in catalytic cycle confirmed by electrochemistry studies.

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# Appendix A. Supplementary material

CCDC 1043896 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac. uk/data\_request/cif. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10. 1016/j.ica.2015.05.023.

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