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Cyclohexane hydroxylation by iodosylbenzene and iodobenzene diacetate catalyzed by a new β-octahalogenated Mn–porphyrin complex: The effect of *meso*-3-pyridyl substituents

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Abstract

The synthesis of 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetrakis(3-pyridyl)porphyrinatomanganese(II) (Mn(II)Br_8T3PyP), a new compound, is described along with some of its electrochemical and catalytic properties. Relative to 5,10,15,20-tetrakis(3-pyridyl)porphyrinatomanganese(III) chloride (Mn(III)T3PyPCl, $E_{1/2} = -0.07$ V versus SCE, *N*,*N*-dimethylformamide) the Mn(III)/Mn(II) reduction potential of Mn(II)Br_8T3PyP shows anodic shift of 0.66 V. These compounds have been studied as catalysts in the hydroxylation of cyclohexane by iodosylbenzene (PhIO) and iodobenzene diacetate (PhI$(OAc)_2$). The roles of water and an exogenous axial ligand (imidazole) were also examined. The results show that whereas Mn(III)T3PyPCl performs much better with PhI$(OAc)_2$, Mn(II)Br_8T3PyP performs better with PhIO; no significant differences in selectivity were observed on changing the oxygen donor. Moderate to good catalytic efficiency may be achieved with the use of a low oxidation-state Mn–porphyrin catalyst, i.e. Mn(II)Br_8T3PyP, but the β-octabromination in this particular case neither increased overall catalyst performance (as compared to the non-brominated analogue), nor yielded a more oxidatively robust catalyst. Catalytic and electrochemical properties of these 3-pyridyl systems are in sharp contrast with their isomeric, 2-pyridyl counter-parts.
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1. Introduction

Synthetic metalloporphyrins (MP) have been extensively used as catalysts for hydrocarbon hydroxylation under mild conditions by single oxygen donors such PhIO [1–12], ClO^- [13–15], and H_2O_2 [16–20]. Their catalytic efficiency in these biomimetic systems is usually related to the metal-centered reduction potential [21–24]. The general effect of the presence of halogen atoms attached to tetrapyrrolic macrocycle on stabilizing and activating metalloporphyrin-based catalysts in oxidation reactions has been the driving-force to the synthesis of several β-substituted metalloporphyrins [3,21,23–42]. Moreover, these compounds exhibit unique optical, redox electrochemical and stereochemical features [22,43–75]. It has been often reported that β-octahalogenated metalloporphyrins are more active as catalysts and more resistant to oxidative degradation than their β-unsubstituted analogues [3,24,25,28,49,76–79]. There are, however, a few exceptions [80–83] to this general trend and the work described herein constitutes incidentally another example of such an "unusual" behavior.

Tetrapyridylporphyrins (TPyP) comprise an important class of simple synthetic *meso*-substituted porphyrins that have been extensively used for the synthesis of model compounds of interest in chemical [84,85], photochemical [86] and biological [87,88] studies. These compounds exist in three isomeric forms, according to the relative position of the pyridyl groups: the *ortho*- (T2PyP derivatives), the *meta*- (T3PyP derivatives), and the *para*-isomers (T4PyP derivatives). This class of compounds has

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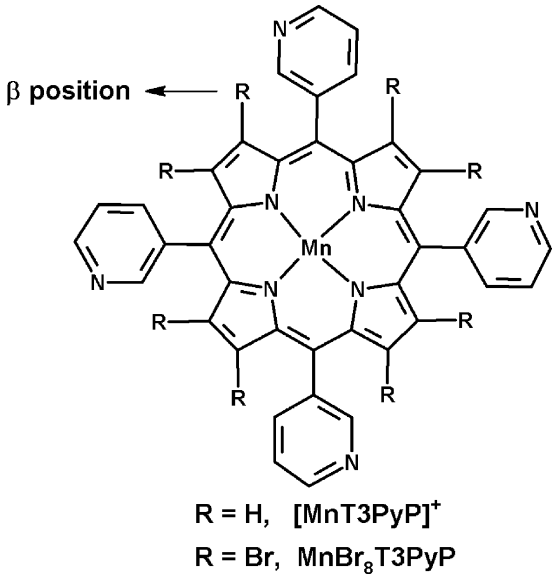

Fig. 1. Schematic structure of the manganese–porphyrins in study.

received considerable attention as derivatization of the pyridyl groups provides not only a simple entry to hydrophilic, cationic porphyrins (via quaternization of the nitrogen of the pyridyl groups) [86,87,89–92], but also to elegant, superstructured coordination compounds [93–96]. The possible biological/medicinal application of these compounds is noteworthy; for example, complexes of 5,10,15,20-tetrakis-(1-methyl-4-pyridyl)porphyrin (H_2T4MPyP) have been used as magnetic-resonance contrast-agents for imaging of tumor and liver in mice [97] and examined as mimics for superoxide dismutase [87,98,99]. The porphyrins derived from 5,10,15,20-tetrakis-(2-pyridyl)porphyrin (H_2T2PyP) have been established as useful precursors for the design of biomimetic catalysts [97,100–105].

Our group has been traditionally dedicated to the preparation and the study of the catalytic properties of *ortho*-substituted metalloporphyrins [12,21,100,101,103,106], especially those derived from T2PyP, and has recently reported on the Mn-complex of the perbrominated T2PyP as mimics for the enzymes SOD [106] and cytochromes P450 (cyclohexane oxidation) [21]. During these studies became evident that although works on T2PyP and T4PyP derivatives are abundant, the *meta*-isomer, T3PyP, remains the least studied. We describe here a contribution to the development of the chemistry of the T3PyP derivatives. Specifically, we report on the effect that the β-bromination of T3PyP exerts on both electrochemical and P450-like catalytic properties of a new manganese–porphyrin 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetrakis(3-pyridyl)-porphyrinatomanganese(II) (Mn(II)Br_8T3PyP) (Fig. 1). Hydroxylation of cyclohexane with PhIO and $PhI(OAc)_2$ was chosen as a P450 representative-reaction. The results are compared with those of the non-brominated analogue 5,10,15,20-tetrakis(3-pyridyl)porphyrinatomanganese(III) chloride (Mn(III)T3PyPCl) (Fig. 1), and with those of the T2PyP counterparts. Also included are synthetic protocols for the synthesis of these complexes, which are potential precursors for cationic, water-soluble, β-halogenated porphyrins.

2. Experimental

2.1. Materials and methods

5,10,15,20-Tetrakis(3-pyridyl)porphyrin (H_2T3PyP) was purchased from MidCentury Chemicals and used as received. Anhydrous CH_3OH, CH_2Cl_2 and $CHCl_3$ of analytical grade were obtained from Aldrich Chemical Co. and freshly distilled prior to use. PhIO was prepared according to a literature procedure [107]. All other reagents and solvents were of analytical grade and used without further purification unless stated otherwise.

UV–vis spectra (190–800 nm) were recorded in an HP-8453A diode-array spectrophotometer. The ^{1}H NMR (proton nuclear magnetic resonance) spectra were recorded in $CDCl_3$ in a Bruker DRX-200 Avance spectrometer (200 MHz, tetramethylsilane, TMS as internal standard) at room temperature. Variable temperature ^{1}H NMR spectra were recorded in $CDCl_3$ in a Bruker DRX-400 Avance spectrometer (400 MHz, TMS as internal standard). Mass spectrometry (ESI: electronspray ionization and ESI-TOF: electronspray ionisation-time-of-flight) was performed in the Department of Chemistry at The University of British Columbia (Vancouver, Canada).

Cyclic voltammetry was conducted using Potenciostat BAS, model 100B, coupled to a PC computer At-486. A cell consisting of a Pt disk-working electrode, a Pt coil counter electrode and an Ag/AgCl wire conventional reference electrode was employed. *n*-Tetrabutylammonium perchlorate ($TBAClO_4$, Aldrich, 99%) was used as electrolyte. *N*,*N*-Dimethylformamide (DMF) was dried over KOH, followed by distillation over P_2O_5 and maintained over 4 Å molecular sieves prior to use. Electrochemical measurements were carried out in dry DMF solutions containing 0.1 M of $TBAClO_4$, 2.0×10^{-3} M of manganese–porphyrin, and ferrocene (as internal standard) in N_2 atmosphere. Scan rates were 10–300 mV s^{-1}. Potentials measured against the ferrocenium/ferrocene couple (Fc^+/Fc) were converted to values relative to the saturated calomel electrode (SCE) using a reported $E_{1/2}$ for Fc^+/Fc of +0.47 V (versus SCE; DMF/$TBAClO_4$) [108]. Literature $E_{1/2}$ values (versus Fc^+/Fc) for the T2PyP system measured in CH_2Cl_2/$TBAPF_6$ were converted to the SCE scale using a $E_{1/2}$ for Fc^+/Fc of +0.46 V (versus SCE; CH_2Cl_2/$TBAPF_6$) [108].

Gas chromatographic analyses were performed on a Shimadzu GC-17A, flame ionization detector, with a Carbowax capillary column (30.0 m × 0.32 mm and film thickness 0.25 μm) using *n*-octanol as internal standard.

The ultrasound used was a Minisson-Thorthon laboratory cleaner ultrasound (40 W, 50–60 Hz).

2.2. Syntheses

2.2.1. Preparation of Mn(II)Br_8T3PyP

This fully β-brominated complex was prepared from H_2T3PyP by the following three steps.

2.2.1.1. Cu(II)T3PyP. 5,10,15,20-Tetrakis(3-pyridyl)porphyrinatocopper(II) was prepared by metallation of H_2T3PyP

(50.00 mg, 0.081 mmol) with $CuCl_2{\cdot}2H_2O$ (80.67 mg, 0.40 mmol) in refluxing chloroform/methanol [109] (20 mL) via an adaptation of a method described by do Nascimento et al. [24] for a related porphyrin. After 30 min of reflux, the solvent was completely removed in a rotary evaporator and $CHCl_3$ was added. The solution was washed twice with water to remove the excess of $CuCl_2{\cdot}2H_2O$, and dried over anhydrous Na_2SO_4. The product was then subjected to chromatography in a neutral alumina column using a $CHCl_3$:CH_3OH (80:1) mixture as eluent. The red fraction was collected, the solvent was removed, and the resulting solid (with no fluorescence under long-wavelength UV lamp) was dried over P_2O_5 (yield: 99%). UV–vis in $CHCl_3$, λ_{max}, nm (log ε): 416 (5.71), 540 (4.35).

2.2.1.2. H_2Br_8T3PyP. 2,3,7,8,12,13,17,18-Octabromo-5,10,15,20-tetrakis(3-pyridyl)porphyrin was synthesized by Br_2-bromination of Cu(II)T3PyP using an adaptation of a literature procedure for a related porphyrin [43]. A Br_2 solution (0.9 mL, 17.5 mmol, in 10 mL of DMF) was added dropwise (over 30 min) to a solution of Cu(II)T3PyP (301.64 mg, 0.44 mmol) in DMF (20 mL), and the mixture was left to stand at room temperature for 48 h. A saturated aqueous solution of sodium metabisulfate was then added and the solvent was completely removed in a rotary evaporator. $CHCl_3$ was added and the resulting solution was washed twice with a solution of $NaHCO_3$ to remove excess H^+, and dried over anhydrous Na_2SO_4. The product was then purified by column chromatography on neutral alumina using a $CHCl_3$:CH_3OH (20:1) mixture as eluent. The green fraction was collected and the solvent was removed to yield Cu(II)Br_8T3PyP (with no fluorescence under long-wavelength UV lamp), which was further dried over P_2O_5 (yield: 70%). The Cu(II)Br_8T3PyP complex (65.60 mg, 0.050 mmol) was demetallated with trifluoroacetic acid (TFA, 10 mL) and $HBr_{(conc.)}$ (1 mL) [24]. The color of the reaction mixture changed immediately to yellow due to the formation of $H_8Br_8T3PyP^{6+}$ (UV–vis in $CHCl_3$, λ_{max}, nm: 501, 733). To this reaction mixture were added a H_2O:TFA mixture (10:1, 50 mL) and a $CHCl_3$:TFA mixture (10:1, 40 mL). This biphasic mixture was washed with small amounts of aqueous NaOH solution (3.0 M) and the organic layer separated, dried over anhydrous Na_2SO_4 and the chloroform evaporated. The product was purified by column chromatography on neutral alumina using a $CHCl_3$:CH_3OH (1:1) mixture as eluent. The green fraction corresponding to H_2Br_8T3PyP was collected, the solvent evaporated, and the resulting solid was further dried over P_2O_5 (yield: 83%). UV–vis in $CHCl_3$, λ_{max}, nm (log ε): 465 (5.19), 566 (4.04), 613 (3.98), 726 (3.76). ^{1}H NMR (200 MHz, $CDCl_3$, TMS, room temperature): δ 9.58 (d; 4H; *p*-H pyridyl), 9.20 (s; 4H; *o*-H pyridyl), 8.74 (d; 4H; *o*-H pyridyl), 7.93 (t; 4H; *m*-H pyridyl). ^{1}H NMR (400 MHz, $CDCl_3$, TMS, −40 °C): δ 9.37 (d; 4H; *p*-H pyridyl), 9.10 (s; 4H; *o*-H pyridyl), 8.73 (d; 4H; *o*-H pyridyl), 7.80 (t; 4H; *m*-H pyridyl), −1.50 (s, 2H, pyrrole–NH). ESI-MS (positive mode): *m/z* 1251 $[P+H]^+$.

2.2.1.3. Mn(II)Br_8T3PyP. 2,3,7,8,12,13,17,18-Octabromo-5,10,15,20-tetrakis(3-pyridyl)-porphyrinatomanganese(II) was prepared by metallation of H_2Br_8T3PyP (95.00 mg, 0.076 mmol) with $Mn(OAc)_2{\cdot}4H_2O$ (198.50 mg, 0.80 mmol) carried out in refluxing chloroform/methanol [109]. After the end of this reaction (24 h), the solvent was completely removed in a rotary evaporator and $CHCl_3$ was added. The solution was washed twice with water to remove excess of $Mn(OAc)_2{\cdot}4H_2O$, and dried over anhydrous Na_2SO_4. The product was then purified by column chromatography on silica using initially a $CHCl_3$:$(CH_3)_2CO$ (10:1) mixture and later "neat" $(CH_3)_2CO$ as eluent. The red fraction was collected (with no fluorescence under long-wavelength UV lamp), the solvent was removed, and the resulting solid was further dried over P_2O_5 (yield: 43%). UV–vis in $CHCl_3$, λ_{max}, nm (log ε): 492 (4.76), 577 (3.83), 661 (3.26). ESI-MS (positive mode): *m/z* 1304 $[MnP+H]^+$.

2.2.2. Preparation of Mn(III)T3PyPCl

5,10,15,20-Tetrakis(3-pyridyl)porphyrinatomanganese(III) chloride was prepared and purified using a procedure adapted from that described for the *ortho*-isomer Mn(III)T2PyPCl (5,10,15,20-tetrakis(2-pyridyl)porphyrinatomanganese(III) chloride) [21]. The acetate counter-ion of the isolated Mn(III)T3PyPOAc was exchanged to chloride by percolation through an ion-exchange resin column (Dowex 2X8, Cl^-) using CH_3OH as eluent (yield: 90%). UV–vis in $CHCl_3$, λ_{max}, nm (log ε): 376 (4.69), 478 (5.00), 579 (4.13), 616 (4.12).

2.3. Oxidation reactions

All catalytic reactions were performed in 2 mL Wheaton vials sealed with Teflon-faced silicon septa at 0 or 25 °C under ultrasound or magnetic stirring for 90 min, using procedures adapted from de Sousa et al. [12]. The oxidation of cyclohexane was carried out in air using either $PhI(OAc)_2$ or PhIO as oxygen donor. Reaction mixtures contained 4.0×10^{-7} mol of catalyst (Mn(III)T3PyPCl or Mn(II)Br_8T3PyP), 4.0×10^{-6} mol of oxidant (PhIO or $PhI(OAc)_2$), 200 μL of cyclohexane (1.9×10^{-3} mol), and 400 μL of CH_2Cl_2 or CH_3CN. The molar ratio of catalyst:oxidant:substrate was of 1:10:5000. The reaction mixtures were directly analyzed by capillary gas chromatography using authentic product samples for comparison and *n*-octanol as internal standard. The yields were based on either initial PhIO or initial $PhI(OAc)_2$. Each reaction was performed at least three times and the reported data represent the average of these reactions; errors in yields and selectivities were calculated based on the reproducibility of these reactions. The degree of destruction of the manganese–porphyrin (bleaching) was determined by UV–vis spectroscopy in the end of the catalytic run. Control reactions, in the absence of the catalyst, were carried out under the same conditions as the catalytic runs.

The effect of imidazole was studied with the addition of a 20 μL aliquot of a 1.0×10^{-2} M imidazole (Im) solution in dichloromethane. The effect of water was studied with the addition of 0.5 μL of water.

Control experiments carried out under N_2 atmosphere gave almost identical results to those obtained under aerobic conditions, indicating that molecular oxygen does not significantly affect these systems; this is in agreement with previous works [24,100,110].

3. Results and discussion

3.1. Syntheses

The preparation of the free-base H_2Br_8T3PyP was accomplished via the β-octabromination of Cu(II)T3PyP by using Br_2 as brominating agent, followed by acidic Cu-demetallation. Subsequent Mn-metallation of this free-base yielded the corresponding Mn-complex, $Mn(II)Br_8T3PyP$.

A complete bromination of copper porphyrin was successfully introduced by Bhyrappa and Krishnan [44]. This method results in good yields of the β-octabrominated complexes, when compared to the direct use of free-base porphyrins. However, attempts to brominate Cu(II)T3PyP in solvents such as $CHCl_3$ or CH_3OH using the standard protocol led to an incomplete bromination; similar results have also been noted on the bromination of $Cu(II)T4MPyP^{4+}$ by Richards et al. [43], who suggested the use of DMF as solvent as a means to avoid an incomplete bromination. Accordingly, $Cu(II)Br_8T3PyP$ was successfully prepared via the Br_2/DMF adaptation. The reaction is marked by an immediate color-change from red to green upon addition of Br_2. The use of the pyridine (an additive in the original protocol [44]) was found not appropriate in this particular case because it led to a very slow reaction and an incomplete bromination of the β-pyrrole positions; a similar situation was also observed by Richards et al. [43] in a related system. The use of DMF as solvent favors a fast and complete per-bromination of the porphyrin ring as noted by Bocchi and Palla [111]. The isolated $Cu(II)Br_8T3PyP$ has spectral data in agreement with those previously reported for a family of other β-octabrominated derivatives [24,44,112]. Of note, β-octabromination of T3PyP derivatives, such as Cu(II)T3PyP or Zn(II)T3PyP using NBS was also attempted but with no success.

H_2Br_8T3PyP was obtained by the demetallation of $Cu(II)Br_8T3PyP$ using $TFA/HBr_{(conc.)}$ following a procedure adapted from that described for other brominated Cu-porphyrins by do Nascimento et al. [24]. The removal of Cu(II) from $Cu(II)Br_8T3PyP$ was marked by dramatic color changes and was conveniently monitored by UV–vis spectroscopy. Immediately upon addition of acid, the $Cu(II)Br_8T3PyP$ solution turned from green to yellow; the UV–vis spectrum of this yellow solution showed the appearance of characteristic bands [43,113,114] for fully (pyrrole and pyridyl) N-protonated species, which is consistent with the in situ formation of $H_8Br_8T3PyP^{6+}$ (yellow, UV–vis in $CHCl_3$, λ_{max}, nm: 501, 733). The addition of the mixtures H_2O:TFA (10:1) and $CHCl_3$:TFA (10:1) to this yellow solution allowed the physical separation of the Cu^{2+} ions and the porphyrin species into the aqueous and the organic phase, respectively. The neutralization of the organic phase yielded the new β-octabrominated free-base H_2Br_8T3PyP, which is green (UV–vis in $CHCl_3$, λ_{max}, nm: 465, 566, 613, 726). Noteworthy is that the aqueous phase needs to be regularly separated and discarded to remove the extracted Cu^{2+} ions from the system and, thus, prevent Cu-reinsertion into the macrocycle during the neutralization process. Of note, under acidic conditions the protonated species, such as $H_8Br_8T3PyP^{6+}$, prevails and these species do not undergo metallation [45].

The ^1H NMR spectrum of H_2Br_8T3PyP did not show any β-pyrrole hydrogen signals in the δ 8.80–9.00 region, confirming the β-octabromination (the β-pyrrole resonance for H_2T3PyP appears at δ 8.90). The signals for the *para*-, the two inequivalent *ortho*-, and the *meta*-pyridyl protons were not appreciably shifted upon bromination and showed the expected multiplicity and integration ratio (4:4:4:4, respectively). The electron-deficiency of perbrominated porphyrins, induced by an electron-withdrawing effect of the bromine substituents, results in an increased acidity of these compounds and a faster exchange of the pyrrole–NH protons with residual water protons, which commonly broadens the pyrrole–NH resonance into the baseline [24,43,46–52,115]; accordingly, the pyrrole–NH resonance for H_2Br_8T3PyP was not observed at room temperature, but at −40 °C the pyrrole–NH resonance of H_2Br_8T3PyP appeared as a sharp singlet at δ −1.50 that integrated for two protons. This resonance is deshielded by 1.26 ppm relative to the parent compound, H_2T3PyP, as a result of the introduction of the electron-withdrawing, bromine substituents on the macrocycle. Whereas the UV–vis spectrum of H_2T3PyP showed four Q bands consistent with Gouterman's four-orbital model [116], only three bands were discernible in the spectrum of H_2Br_8T3PyP, which can be explained by the overlap of two Q transitions; identical behavior has been observed in other brominated systems [44]. The positive-mode ESI mass spectrum of H_2Br_8T3PyP was characterized by abundant cluster centered at m/z 1251, corresponding to $[P+H]^+$.

The preparation of the Mn-complexes, Mn(III)T3PyPCl and $Mn(II)Br_8T3PyP$, was achieved by metallation of the corresponding free-bases H_2T3PyP and H_2Br_8T3PyP, respectively, using a standard metallation procedure [21,109]. Whereas Mn(II) porphyrins are generally air-sensitive, giving rise to Mn(III)-compounds (e.g. Mn(III)T3PyPCl), the large Mn(III)/Mn(II) reduction potential associated with the Mn-complex derived from H_2Br_8T3PyP (see Section 3.2, below) stabilizes the central metallic-ion in a low oxidation state even in the presence of air. This behavior has precedents among perhalogenated Mn–porphyrins [21,25,46,83] and is attributed to the electron-withdrawing effect of the halogen, which, being in direct conjugation with the π system of the porphyrin, reduces the electronic density of both the central metal and the conjugated π-system itself [22,44,52,117]; this stabilizes, consequently, the Mn(II) oxidation state in $Mn(II)Br_8T3PyP$. Treatment of $Mn(II)Br_8T3PyP$ with HBr/TFA overnight, followed by neutralization with $NaHCO_3$(aq), yielded the corresponding free-base, which had spectral (UV–vis) and TLC characteristics identical to that of an authentic H_2Br_8T3PyP sample. The positive-mode ESI-TOF mass spectrum of $Mn(II)Br_8T3PyP$ was characterized by abundant cluster centered at m/z 1304, corresponding to $[MnP+H]^+$.

The UV–vis data presented in this work are in agreement with the literature, where B (Soret) and Q (visible) transition energy bands of perhalogenated porphyrins are red-shifted relative to those of the unsubstituted analogues [25,44,51–55,114]. Electron-withdrawing substituents in the porphyrin ring stabilize both HOMO and LUMO. Bulky groups, however, cause severe distortions to the macrocycle and destabilize the HOMO

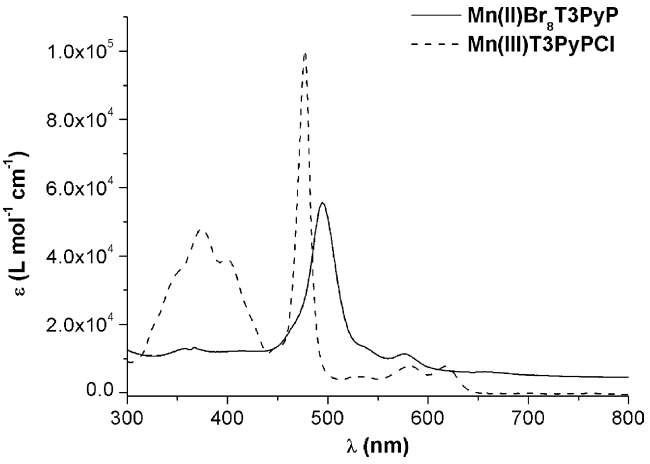

Fig. 2. The UV–vis spectra of Mn(III)T3PyPCl and Mn(II)Br_8T3PyP in $CHCl_3$.

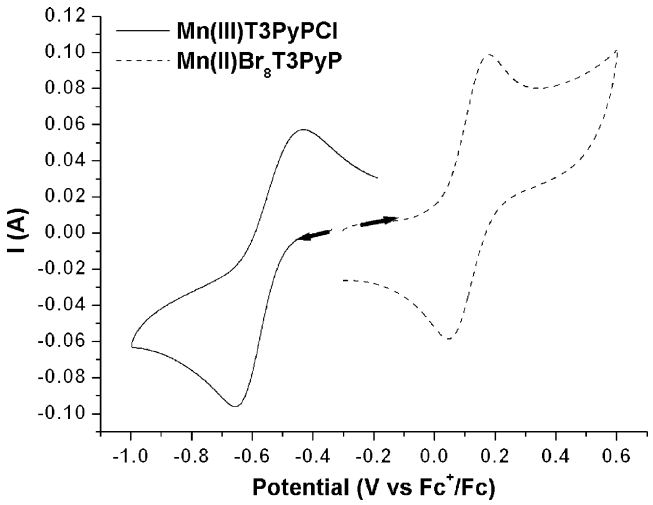

Fig. 3. Cyclic voltammograms of Mn(III)T3PyPCl and Mn(II)Br_8T3PyP (DMF, MnP = 2.0×10^{-3} M, $TBAClO_4$ = 0.1 M, scan rate 0.1 V s^{-1}).

more than the LUMO. In consequence, the HOMO–LUMO energy gap decreases [22,25,44,48–55,118–122] and the Soret band is considerably shifted to lower energy; the Q bands are also shifted to lower energy but to a smaller extent. The bathochromic shift was a function not only of the substituent on the periphery of the porphyrin ring but also of that in the N_4-porphyrin core: the Soret bands of Cu(II)Br_8T3PyP (λ_{max} 449 nm) and H_2Br_8T3PyP (λ_{max} 465 nm) exhibited a bathochromic shift of 4.0 and 5.8 nm/Br relative to the Cu(II)T3PyP (λ_{max} 416 nm) and H_2T3PyP (λ_{max} 419 nm), respectively. For the free-base *ortho*-isomers H_2T2PyP (λ_{max} 416 nm) and H_2Br_8T2PyP (λ_{max} 462 nm) a shift of 5.8 nm/Br is also observed [21]. In the case of the β-brominated manganese–porphyrin the bathochromic shift was 6.9 nm/Br for Mn(II)Br_8T3PyP (λ_{max} 492 nm) relative to Mn(II)T3PyP (λ_{max} 437 nm). Such a bathochromic shift is much larger than those previously reported (4.0 nm/Br [123]) and, in particular, larger than that of 3.0 nm/Br reported for the brominated *ortho*-isomer, Mn(II)Br_8T2PyP (λ_{max} 464 nm), relative to the parent Mn(II)T2PyP (λ_{max} 440 nm). This evidences the greater influence of the bromine atoms and 3-pyridyl substituents in the electronic properties of the Mn complex. The molar absorptivity (ε) of the Soret bands of the β-brominated derivatives was smaller than that of the non-brominated analogue [24] (Fig. 2).

3.2. Electrochemistry

Representative cyclic voltammograms for Mn(III)T3PyPCl and Mn(II)Br_8T3PyP in DMF (0.1 M $TBAClO_4$) are presented in Fig. 3, and the redox potential data for the one-electron process associated with the Mn(III)/Mn(II) couple is summarized in Table 1. The half-wave potentials ($E_{1/2}$) for the Mn(III)/Mn(II) couple of Mn(III)T3PyPCl and Mn(II)Br_8T3PyP were located, respectively, at −0.07 and 0.59 V (versus SCE) in DMF. Whereas these values were relatively independent of the scan rate (from 10 to 100 mV s^{-1}), an increase of the peak–peak separation associated with these processes was observed with the increase of the scan rate (Table 1); this influence of the scan rate on the reversibility of the metal-centered process was not investigated in detail in the present work, but has been noted before for other porphyrin systems [124]. At higher potentials, the Mn(III)T3PyPCl system showed also an additional, irreversible process (E_{pa} = 1.16 V versus SCE), to which a corresponding process was not observed for Mn(II)Br_8T3PyP, at least up to 1.47 V (versus SCE).

A 0.66 V anodic shift the metal-centered potential of Mn(II)Br_8T3PyP (as compared to that of Mn(III)T3PyPCl) is observed. The shift is comparable to the values associated with the β-halogenation of other metalloporphyrins [22,24,46,125], but it is, to our knowledge, one of the greatest shifts observed so far. Attempts to oxidize Mn(II)Br_8T3PyP to its Mn(III) analogue using either peroxides or ferricyanide were unsuccessful. Noteworthy is that Mn(II)Br_8T3PyP shows a Mn(III)/Mn(II) potential shift (relative to its non-brominated parent complex) higher than that found for its *ortho*-isomer counter-part (Table 2); this indicates that the electronic properties of the metal center in the *meta*-isomer derivatives are more susceptible to modulation via peripheral ring-substitution than the *ortho*-isomers are.

These observed anodic shifts following β-bromination could be ascribed to effects of the bulky and electron-withdrawing bromine substituents in the β-pyrrole positions of the porphyrin ring. In fact, several electrochemical studies have reported that the type and number of β-halogen atoms in a porphyrin ligand as well as the nature of the metal cen-

Table 1
Anodic (E_{pa}), cathodic (E_{pc}), and half-wave ($E_{1/2}$) potentials (V vs. Fc^+/Fc) for the Mn(III)/Mn(II) couple of Mn(III)T3PyPCl and Mn(II)Br_8T3PyP in DMF, 0.1 M $TBAClO_4$

Scan rate (V s^{-1})	Mn(III)T3PyPCl			Mn(II)Br_8T3PyP		
	E_{pa}	E_{pc}	$E_{1/2}$	E_{pa}	E_{pc}	$E_{1/2}$
0.010	−0.49	−0.64	−0.56	0.16	0.06	0.11
0.015	−0.49	−0.66	−0.57	0.17	0.06	0.11
0.020	−0.48	−0.65	−0.57	0.17	0.05	0.11
0.025	−0.47	−0.66	−0.56	0.18	0.05	0.12
0.100	−0.43	−0.66	−0.54	0.19	0.05	0.12

Table 2
Half-wave potential data for the Mn(III)/Mn(II) couple of Mn–porphyrins

Mn–porphyrins	$E_{1/2}$, V vs. Fc^+/Fc	$E_{1/2}$, V vs. SCE
$[Mn(III)T3PyP]^+$	−0.54[a]	−0.07
$Mn(II)Br_8T3PyP$	+0.12[a]	+0.59
$[Mn(III)T2PyP]^+$	−0.65[b]	−0.19
$[Mn(III)Br_8T2PyP]^+$	−0.25[b]	+0.21

[a] In DMF, 0.1 M $TBAClO_4$, 0.1 V s^{-1}.
[b] In CH_2Cl_2, 0.1 M $TBAPF_6$, 0.1 V s^{-1}; Ref. [21].

ter crucially affect the redox behavior of these systems [21–24,26,46,47,51,53,55,57,58,111,126–131].

3.3. Catalytic studies

The hydroxylation of cyclohexane by PhIO or $PhI(OAc)_2$ was carried out at room temperature, using Mn(III)T3PyPCl or $Mn(II)Br_8T3PyP$ as catalysts. Alcohol (cyclohexanol, C-ol) was obtained as the major product along with small amounts of ketone (cyclohexanone, C-one) and, unless otherwise indicated, oxidation experiments were run for 90 min ("standard conditions") to allow direct comparison to other literature systems [24,12]. To the best of our knowledge, there has been only two reports on good hydroxylation yields for reactions catalyzed by manganese(II) porphyrins [83,123]. The data for $Mn(II)Br_8T3PyP$ presented here represent an additional contribution to the investigation of these low-oxidation-state compounds as catalysts in reactions of hydroxylation of alkanes. The results are shown in Tables 3–5.

A common and important feature among these hydroxylation reactions is that per-bromination of T3PyP did not yield an oxidatively robust catalyst: whereas $Mn(II)Br_8T3PyP$ was always completely destroyed during the catalytic run, Mn(III)T3PyPCl was still partially recovered (∼50%). This low oxidative stability of the perbrominated catalyst was an unexpected finding given that (i) porphyrin halogenation is generally assumed to yield more oxidatively robust catalyst, (ii) the oxidant:MnP molar ratio used was rather low (10:1), and (iii) hydroxylation reactions catalyzed by the corresponding *ortho*-isomer was completely bleached only at much higher oxidant:catalyst ratio (70:1). Indeed, complete bleaching of a third-generation catalyst in hydroxylation reactions by such a low excess of oxidant seems unprecedented. It is worth noting, however, that hydroxylation reactions are chemically more demanding than epoxidations, and complete destruction of a third-generation catalyst during epoxidation reactions has been reported [81,82]. The bleaching of the $Mn(II)Br_8T3PyP$ may be ascribed to the low stability of Mn(II)-porphyrins compared to their Mn(III) counter-parts [46,132]. Furthermore, due to the high Mn(III)/Mn(II) reduction potential of $Mn(II)Br_8T3PyP$, the access of this compound to higher-oxidation states is probably limited, and the catalytic species may likely involve a Mn(IV)-porphyrin. Mn(IV)-porphyrins could support radical-based pathways [110,133], which may result in the in situ generation of hydroxyl radicals that could attack, therefore, the porphyrin ring in a process similar to that invoked in related systems [134,135].

Table 4
Oxidation of cyclohexane by PhIO in CH_3CN, catalyzed by Mn(III)T3PyPCl, Mn(III)T2PyPCl, $Mn(II)Br_8T3PyP$ and $Mn(III)Br_8T2PyPCl$[a]

Mn–porphyrin	Yields (%)[b] and selectivity (C-ol, %)[c]		
	C-ol	C-one	Selectivity
Mn(III)T2PyPCl[d]	14	7	67
Mn(III)T3PyPCl	22	9	71
$Mn(III)Br_8T2PyPCl$[d]	41	26	61
$Mn(II)Br_8T3PyP$	13	3	81

[a] Conditions: MnP = 5×10^{-4} M, PhIO = 5×10^{-3} M, catalyst:oxidant:substrate molar ratio of 1:10:5000, 0 °C, magnetic stirring, 90 min.
[b] Yields based on the starting PhIO. Average error = ± 1%.
[c] C-ol selectivity [=100%$C_{C\text{-ol}}/(C_{C\text{-ol}} + C_{C\text{-one}})$].
[d] From Ref. [21].

3.3.1. Oxidation of cyclohexane by PhIO

Table 3 displays the results for cyclohexane hydroxylation in which PhIO was used as oxygen donor. The yields of the products and the alcohol selectivity, in the absence of additives, are largely not influenced by the bromination of the T3PyP-macrocycle, which is consistent with high-valent manganese-oxo porphyrin as the oxidizing species [110,133]. Such species are often invoked as the active species responsible for oxygen insertion into the substrate C–H bond, via a rebound mechanism, in alkane hydroxylations catalyzed by Mn–porphyrins using different oxygen donors; discussions on the mechanism of metalloporphyrin-catalyzed hydroxylations have been thoroughly reviewed [110,133,136,137].

Nitrogenous organic-base ligands, such as imidazole, may play major roles as co-catalysts in oxidation reactions catalyzed

Table 3
Oxidation of cyclohexane by PhIO in CH_2Cl_2, catalyzed by Mn(III)T3PyPCl and $Mn(II)Br_8T3PyP$[a]

Mn–porphyrin	System yields (%)[b] and selectivity (C-ol, %)[c]								
	PhIO			$PhIO/H_2O$			PhIO/Im		
	C-ol	C-one	Selectivity	C-ol	C-one	Selectivity	C-ol	C-one	Selectivity
Mn(III)T3PyPCl	26	10	72	25	10	71	40	15	73
$Mn(II)Br_8T3PyP$	29	9	76	37	9	80	48	13	79

[a] Conditions: MnP = 5×10^{-4} M, PhIO = 5×10^{-3} M, catalyst:oxidant:substrate molar ratio of 1:10:5000, 25 °C, ultrasound stirring, 90 min.
[b] Yields based on the starting PhIO. Average error = ± 1%.
[c] C-ol selectivity [=100%$C_{C\text{-ol}}/(C_{C\text{-ol}} + C_{C\text{-one}})$].

Table 5
Oxidation of cyclohexane by $PhI(OAc)_2$ in CH_2Cl_2, catalyzed by Mn(III)T3PyPCl and Mn(II)Br_8T3PyP[a]

Mn–porphyrin	Systems yields (%)[b] and selectivity (C-ol, %)[c]								
	$PhI(OAc)_2$			$PhI(OAc)_2/H_2O$			$PhI(OAc)_2$/Im		
	C-ol	C-one	Selectivity	C-ol	C-one	Selectivity	C-ol	C-one	Selectivity
Mn(III)T3PyPCl	40	17	70	35	16	69	27	10	76
Mn(II)Br_8T3PyP	15	5	75	32	9	78	19	6	76

[a] Conditions: MnP = 5×10^{-4} M, $PhI(OAc)_2 = 5 \times 10^{-3}$ M, catalyst:oxidant:substrate molar ratio of 1:10:5000, 25 °C, ultrasound stirring, 90 min.
[b] Based on the starting $PhI(OAc)_2$. Average error = ± 2%.
[c] C-ol selectivity [=100%$C_{C\text{-ol}}/(C_{C\text{-ol}} + C_{C\text{-one}})$].

by metalloporphyrins [1,83,138,139]. Whereas the use of imidazole as co-catalyst in epoxidation reactions has been extensively investigated [1,138,139], in hydroxylation reactions this remains ill explored [83,140,141]. The present work illustrates the beneficial effect of imidazole on the PhIO-oxidation of cyclohexane (Table 3); the addition of imidazole improved the efficiency of both catalysts, Mn(III)T3PyPCl and Mn(II)Br_8T3PyP. The alcohol selectivity, however, was unaffected, which suggests that the overall mechanism remains the same with or without imidazole. Of note, a similar behavior has been described by Assis and co-workers [83] in a related Mn-system.

The addition of water, motivated by the reactions with $PhI(OAc)_2$ (see below), had no effect on the PhIO-hydroxylations catalyzed by the first-generation catalyst, but was beneficial on the reactions catalyzed by Mn(II)Br_8T3PyP. This may be related to the higher Lewis-acidity of porphyrins bearing electron-withdrawing substituents on the β-pyrrolic positions of macrocycle.

Oxidation of cyclohexane by PhIO catalyzed by Mn(III)-T3PyPCl and Mn(II)Br_8T3PyP was also carried out in MeCN, at 0 °C, under magnetic stirring to allow direct comparison with literature data for the *ortho*-isomer Mn–porphyrin analogues (Table 4). When the first-generation catalysts Mn(III)T2PyPCl and Mn(III)T3PyPCl are compared (Table 4), it is observed that the latter is slightly more efficient and selective. With respect to the third-generation compounds, Mn(III)Br_8T2PyPCl [21] and Mn(II)Br_8T3PyP, however, it is verified that the *meta* isomer derivative is more selective, but significantly less efficient, which may likely be associated with their considerably different oxidative stability (the brominated *meta*-isomer is completely bleached during the reaction, whereas the brominated *ortho*-isomer is essentially stable under the catalytic conditions). Although ultrasound may promote radical formation and porphyrin destruction [8], no significant effect of the stirring mode (ultrasound versus magnetic stirring) on the reactions catalyzed by Mn(III)T3PyPCl or Mn(II)Br_8T3PyP was observed (Tables 3 and 4).

3.3.2. Oxidation of cyclohexane by PhI(OAc)$_2$

We decided to use $PhI(OAc)_2$ as an alternative oxygen donor since this is a stable compound, soluble in most organic solvents, and commercially available. In addition, there has been a great deal of interest recently on the use of $PhI(OAc)_2$ instead of PhIO [140,142–145]. The only work in the literature involving cyclohexane oxidation by $PhI(OAc)_2$ catalyzed by a manganese–porphyrin was presented by Li and Xia [140]. These authors reported that the low hydroxylation yields (actual values not given) for the reactions carried out in CH_2Cl_2 were associated with the decomposition of the first-generation catalyst used [140]. Table 5 presents the results for the $PhI(OAc)_2$-hydroxylation of cyclohexane catalyzed by Mn(III)T3PyPCl and Mn(II)Br_8T3PyP. It is worth noting that, as for the PhIO reactions, Mn(II)Br_8T3PyP was completely destroyed during the catalytic runs, whereas ∼45% of Mn(III)T3PyPCl was recovered at the end of the runs. Regardless of the presence or absence of additives (imidazole, H_2O), the Mn(III)T3PyPCl complex was more an efficient catalyst in $PhI(OAc)_2$-hydroxylations than its brominated congener, Mn(II)Br_8T3PyP. This is in sharp contrast to the PhIO-oxidation, where Mn(III)T3PyPCl showed lower (or, at best, comparable) catalytic efficiency than Mn(II)Br_8T3PyP. The higher efficiency of Mn(III)T3PyPCl (versus Mn(II)Br_8T3PyP) in $PhI(OAc)_2$-hydroxylations is accompanied, however, by lower selectivity.

According to Nam and co-workers [144] epoxidation reactions catalyzed by Fe-porphyrins using $PhI(OAc)_2$ as oxygen donor (molar ratio 1:50, FeP:$PhI(OAc)_2$) are faster when water is added to the system. This has been ascribed to the involvement of water in the process of hydrolysis of $PhI(OAc)_2$, which could result in an in situ generation of reactive, non-polymeric PhIO and an increase in the reaction rate [144]. Such a rationale would imply that $PhI(OAc)_2$ hydrolysis is involved in the rate-determining step.

In the present Mn systems, the addition of water had very little effect in the Mn(III)T3PyPCl-catalyzed $PhI(OAc)_2$-oxidations (Fig. 4), but marked effects were observed with the use of Mn(II)Br_8T3PyP as catalyst (Table 5). Additionally, a comparison between the results for the PhIO- and the $PhI(OAc)_2$-systems (without additives or in the presence of H_2O (Tables 3 and 5)) reveals that whereas Mn(III)T3PyPCl performs much better with $PhI(OAc)_2$, Mn(II)Br_8T3PyP performs better with PhIO; no significant differences in selectivity were observed on changing the oxygen donor. The results seem to suggest that the intermediacy of an in situ generated PhIO in the $PhI(OAc)_2$ reactions may not be imperative. Collman et al. [142] showed that the formation of an oxygen-donor–MP adduct is fundamental to generate active species. It may be envisioned that the planar conformation of the Mn(III)T3PyPCl macrocycle permits a more effective interaction with the bulkier $PhI(OAc)_2$, whereas the distorted conformation of Mn(II)Br_8T3PyP may accommodate better the less-bulky PhIO.

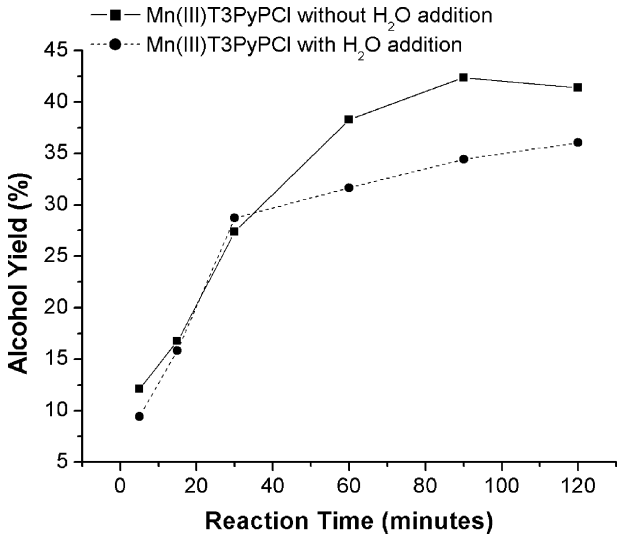

Fig. 4. Time course for the Mn(III)T3PyPCl-catalyzed hydroxylation of cyclohexane by $PhI(OAc)_2$ in the presence and absence of H_2O. Yields are calculated with respect to $PhI(OAc)_2$ used.

As the catalytic ability of manganese–porphyrins may be influenced by the use of nitrogen bases as co-catalysts, the effects of imidazole upon hydroxylation of cyclohexane by $PhI(OAc)_2$ were investigated. Comparison of the data in Tables 3 and 5 shows that the effect of axial ligand on the $PhI(OAc)_2$ systems is different from that of PhIO. In the $PhI(OAc)_2$ systems, the efficiency of Mn(III)T3PyPCl dropped significantly upon the addition of imidazole, whereas the Mn(II)Br_8T3PyP-catalyzed reactions were little affected; the addition of imidazole in the PhIO systems was accompanied by an increase in the efficiency of both catalyst. This may be associated with an stronger competition of imidazole (versus $PhI(OAc)_2$) for the axial coordination site of the manganese–porphyrin, which would interfere with and ultimately hinder the formation of catalytically active species. Of note, while studying the Mn–porphyrin-catalyzed cyclohexane oxidation by $PhI(OAc)_2$ in a 1,2-dichloroethane/ionic liquid mixture, Li and Xia [140] observed also a decrease in catalytic efficiency upon addition of imidazole to the catalytic system.

4. Conclusions

The synthesis of Mn(II)Br_8T3PyP, which may be of interest in designing water-soluble biomimetic models, is described. The redox potential of the Mn(III)/Mn(II) couple is remarkably high (0.59 V versus SCE), being about 0.66 V higher than that of the parent Mn(III)T3PyPCl. Additionally, it is observed that Mn(II)Br_8T3PyP has a Mn(III)/Mn(II) potential 0.37 V higher than that of the corresponding *ortho*-isomer, Mn(III)Br_8T2PyPCl, which contrasts to the 0.09 V difference between Mn(III)T3PyPCl and Mn(III)T2PyPCl. This indicates the greater influence of per-bromination on the *meta*- (versus *ortho*-)isomer.

The catalytic results show that the overall efficiency of T3PyP-based Mn–porphyrin catalysts is influenced by a combination of factors such as peripheral substitution pattern, redox properties, oxidative stability, and choice of oxidants and additives. In general, the complexes carried out the catalytic hydroxylation of cyclohexane by PhIO or $PhI(OAc)_2$ with good selectivity. As opposed to the *ortho*-isomer analogue, β-octabromination of T3PyP did not afford, however, an oxidatively robust catalyst, Mn(II)Br_8T3PyP being completely destroyed during the catalytic runs.

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