



Meso-tetracinnamylporphyrin: Synthesis, characterization and the catalytic activity of its Mn(III) complex in olefin epoxidation with tetra-n-butylammonium hydrogen monopersulfate

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ABSTRACT

Meso-tetracinnamylporphyrin (H₂tcp) has been synthesized and characterized by UV–Vis, ¹H NMR and IR spectroscopies. Protonation of H₂tcp with HCl is accompanied by a blue shift (77 cm⁻¹) of the Q(0,0) band, probably indicating a decrease in the efficiency of the π-electron donation from the meso-substituents to the a_{2u} orbital in comparison with the corresponding dication of meso-tetraphenylporphyrin (H₂tpp). The unusual NH signal multiplicity observed in ¹H NMR spectrum of H₂tcp shows evidence of a long distance coupling between the vinyl protons and NH ones. This long range coupling can occur between the remote centers using the a_{2u} orbital as a connector. Mntcp(OAc) shows higher catalytic activity (ca. 1.2-fold higher) than Mntpp(OAc) in olefin epoxidation with tetra-n-butylammonium hydrogen monopersulfate (TBAO). The low ratio (~1.5) of *cis*- to *trans*-stilbene oxide, in competitive oxidation of *cis*- and *trans*-stilbene with TBAO, strongly suggests the involvement a common high-valent manganese oxo complex as the reactive intermediate responsible for oxygen atom transfer.

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1. Introduction

Metal complexes of porphyrins bearing different meso- and/or β-substituents have been extensively used as models for cytochrome P450 enzymes. Peripheral functionalization of porphyrins with the aim of obtaining more stable “second- and third-generation” porphyrins with halogen, nitro or sulfone substituents is an effective strategy for the development of novel porphyrin-based catalysts for oxidation reactions [1]. The stabilization of HOMO level of the so called electron-deficient porphyrins, leads to significantly improved catalytic activity and stability of their corresponding metalloporphyrins towards oxidative degradation [2–4]. For the a_{2u} orbitals, the electron densities are largest on meso-carbons and the central nitrogen atoms [5]. Accordingly, the a_{2u} orbital can be destabilized through resonance interactions between the meso-aryl and porphyrin π-systems [6]. Large dihedral angles between the porphyrin macrocyclic plane and the aryl substituents hinder the effective resonance interactions [7,8]. The introduction of bulky substituents at ortho-positions of meso-aryl substituents or/and pyrrole β-positions gives porphyrins with increased dihedral angles between the meso-substituted aryls and

the porphyrin mean plane such as meso-tetramesitylporphyrin (H₂tmp) and meso-tetra(2,6-dichlorophenyl)porphyrin (H₂tdcpp) [9,10]. [Mntmp]OAc has been found to show higher catalytic activity relative to Mn(tpp)OAc in the oxidation of sterically unhindered cycloalkanes and arylalkanes with periodate as oxidant [11]. In a recent work, similar catalytic activities for Ru(IV)(tmp)Cl₂ and Ru(IV)(tdcpp)Cl₂ have been reported [12]. Herein, we report the synthesis and characterization of H₂tcp (Fig. 1) as a porphyrin with weak electron-donating unsaturated substituents at meso positions. In addition, the catalytic activity of Mntcp(OAc) in olefins epoxidation with tetra-n-butylammonium hydrogen monopersulfate (TBAO) is presented and compared with that of Mntpp(OAc) in the same conditions.

2. Experimental

2.1. Instruments and materials

¹H spectra were obtained in CDCl₃ solutions with a Bruker FT-NMR 250 (250 MHz) spectrometer. The residual CHCl₃ in conventional 99.8% CDCl₃ gives a signal at δ = 7.26 ppm, which was used for calibration of the chemical shift scale. The absorption spectra were recorded on a double beam GBC-916 UV–Vis spectrophotometer. The reaction products of oxidation were analyzed by a

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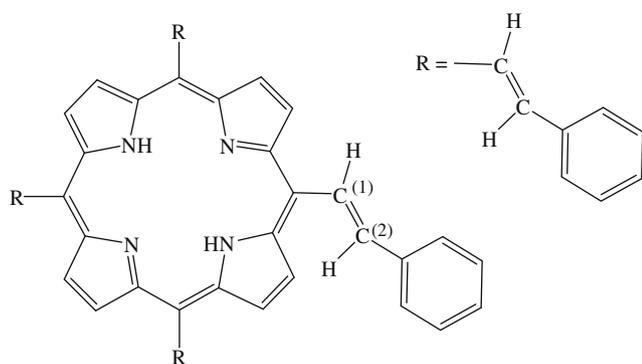


Fig. 1. Meso-tetracinnamylporphyrin, H₂tcp.

Varian-3800 gas chromatograph equipped with a HP-5 capillary column (phenylmethyl siloxane 30 m × 320 μm × 0.25 μm) and flame-ionization detector. IR spectra were taken with KBr pellets on a Perkin Elmer RXI Spectrophotometer. Pyrrole, imidazole, cinnamaldehyde and benzaldehyde were obtained from Fluka and Merck. Pyrrole was distilled before use and the others were used without further purification. Alkenes were obtained from Fluka and Merck. Styrene, α -methylstyrene, and cyclohexene were purified with a short alumina column before use. Tetrabutylammonium hydrogen sulfate and Oxone were purchased from Merck and Acros, respectively.

2.2. Synthesis and metallation of H₂tcp

H₂tcp was synthesized and purified according to the method reported by Neya et al. for the synthesis of meso-tetraalkylporphyrins, with some modifications in the procedure as detailed hereinafter [13]. Pyrrole (4.2 ml, 0.0605 mole) and cinnamaldehyde (3 ml, 0.0238 mole) were added at 2.5: 1 molar ratios to an Erlenmeyer flask containing 300 ml of propionic acid, 12 ml of water and 1 ml of pyridine. The mixture stirred at reflux temperature of the solvent (ca. 140 °C) for 30 min. Then, a supplementary amount of cinnamaldehyde (1.2 ml, 0.0095 mole) was added and the solution was stirred for another 2 h under reflux conditions. Chloroform (300 ml) was added to the cooled solution, and the mixture was washed with water (300 ml × 2), 50 mM sodium hydroxide (300 ml × 2), and water (300 ml) to remove propionic acid. The chloroform solution was evaporated to dryness. Purification with soxhlet extraction (methanol) was carried out before washing the residue with methanol (5 ml × about 10) on a centrifuge (5000 rpm, 3 min). The solid was chromatographed (three times) on a neutral alumina column with dichloromethane. H₂tcp (275 mg, 4.5%) was obtained after recrystallization from dichloromethane/methanol. UV–Vis in CH₂Cl₂, λ_{max} (log ϵ): 417 (5.50) (Soret), 516 (4.25), 552 (4.14), 590 (4.01), 654 (3.99). ¹H NMR (Bruker FT-NMR 250) (δ ppm): –2.43 to –2.73 (2H, br, sextet, NH); 9.49 (8H, β , br); 8.85 (quintet, 4H, CH(1)); 8.19 (4H, br d, CH(2)); 7.78 (8H, br s, H_o); 7.39–7.60 (12H, multiplet, H_{m,p}). IR spectrum shows N–H stretching band at 3311 cm^{–1}. Pattern in the CH stretching region is similar to that of vinyl benzene and observed in the range of 2852–2956 cm^{–1}. Mntcp(OAc) (λ_{max} = 479 nm in dichloromethane) has been prepared and purified according to the the method of Adler et al. [14].

2.3. Preparation and metallation of H₂ttp

The preparation and metallation of H₂ttp was carried out following the literature methods [14,15].

2.4. General oxidation procedure

Stock solution of Mntcp(OAc) (0.0006 M) and imidazole (0.5 M) were prepared in CH₂Cl₂. In a 10 ml round-bottom flask were added successively: alkene (0.06 mmol), catalyst (0.0006 mmol, 1.0 ml), imidazole (0.012 mmol, 24 μl). Tetrabutylammonium oxone (0.15 mmol, 0.060 g) was then added to the reaction mixture at room temperature. The solution was stirred thoroughly for 2 min at ambient temperature. Formation of epoxide was detected by GC analysis. In the case of *cis*- and *trans*-stilbene, the products were analyzed by ¹H NMR.

3. Results and discussion

3.1. UV–Vis spectra

UV–Vis spectrum of H₂tcp is shown in Fig. 2. Although the Soret band of H₂tcp shows no observable shift with respect to that of H₂ttp, the Q(0,0) band is red-shifted (165 cm^{–1}) relative to the latter (Fig. 2, Table 1). According to the general belief that only a large red shift in the UV–Vis bands is indicative of a very nonplanar porphyrin macrocycle, an essentially planar conformation is expected for H₂tcp in solution [16]. Due to the distribution of the a_{2u} electron densities on the meso positions and the central nitrogen atoms, the Q(0,0) band is more sensitive to the electronic properties of the meso-substituents than the a_{1u} orbital [5,17]. Diprotonation of H₂tcp with HCl leads to the red shift (1414 cm^{–1}) of the

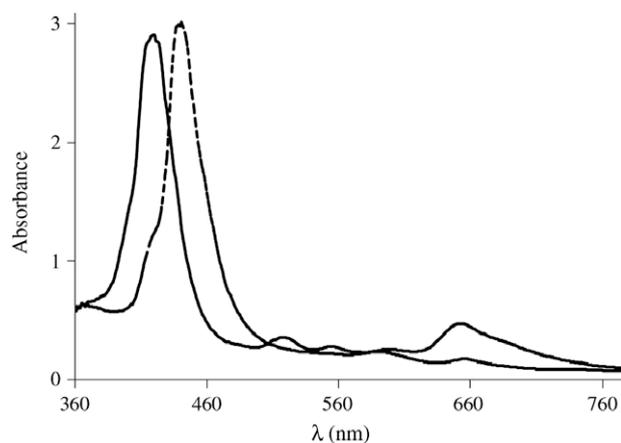


Fig. 2. UV–Vis spectra of H₂tcp (full line) and H₂tcp(HCl)₂ (dot line) in CH₂Cl₂.

Table 1

UV–Vis spectral data of H₂tcp, H₂ttp and the diacids in dichloromethane.^a

Porphyrin	Soret (λ /nm)	Q (λ /nm)			
		IV	III	II	I ^b
H ₂ tcp	416	516	552	590	654
H ₂ tcp(HCl) ₂	442			596.7	651
$\Delta\nu$ (cm ^{–1})	–1414				77.5 ^c
H ₂ ttp	417	514	548	590	647
H ₂ ttp(HCl) ₂	444				656
$\Delta\nu$ (cm ^{–1})	–1458				–212 ^c
H ₂ t(n-Pr)p	416	520	557	602	661
H ₂ t(n-Pr)p(HCl)	434				643
$\Delta\nu$ (cm ^{–1})	–997				423.5 ^c

^a Acid treatment of H₂tcp gave the green porphyrin diacation. Concentrated HCl was added to a solution of porphyrin in CH₂Cl₂ and the mixture was stirred for 10 min.

^b Q(0,0).

^c Shift of the Q(0,0) band.

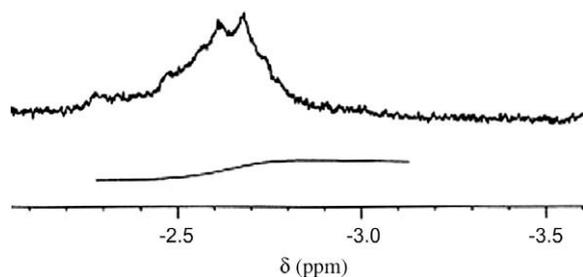


Fig. 3. ^1H NMR spectra of H_2tcp in NH region.

Soret band and the blue shift (77.5 cm^{-1}) of the Q(0,0) band. The observed blue shift of the Q(0,0) band may be attributed to the decreased π -donation from the *meso*-cinnamyl substitution to the porphyrin core in comparison with that of *meso*-phenyl groups of H_2tpp and other *meso*-tetraarylporphyrins [6–8,18]. It should be noted that the adduct formation of *meso*-tetraalkylporphyrins (with primary and secondary alkyl residues) with Lewis or protic acids also causes the blue shift of the Q(0,0) band [18,19]. Accordingly, the title porphyrin may be considered as an electron-deficient one with respect to *meso*-tetraphenylporphyrin.

3.2. ^1H NMR spectrum

In ^1H NMR spectrum of H_2tcp , the NH protons appear as a broad multiplet between 2.43 and -2.73 ppm which suggests a long distance coupling between the vinyl protons and NH ones (Fig. 3). The a_{2u} electron densities which are largest on the *meso*-carbon atoms and pyrrole nitrogen atoms connect the nitrogen atoms to the

meso-carbon atoms and consequently to the unsaturated bonds conjugated to the porphyrin ring [5]. Therefore, long range couplings between the NH protons and those of the peripheral substituents can be created using the a_{2u} orbital as a connector. It should be noted that non-bulky unsaturated chains or rings are able to lie coplanar with the porphyrin nucleus and form extended delocalized π systems [17,20]. Very broad signals observed for NH protons (also for β -protons) may be possibly due to the existence of various isomers resulting from different orientations of cinnamyl groups. It should be noted that the common broadening of NH signal of free base porphyrins has been rationalized by the intramolecular N–H...N hydrogen bonds between the adjacent pyrrole rings [21]. The β protons appear as an unusual broad signal at δ 9.49 ppm. The broadening of signal indicates that β protons are subject to a range of different chemical environments which is probably the result of different interactions of cinnamyl groups with the protons of pyrrole rings (see Fig. 1). A broad quintet at 8.85 ppm and a broad signal at 8.19 ppm with very similar integrations (considering 8 for β protons give ca. 4 for the two signals) were assigned to the CH(1) and CH(2) protons, respectively. The proton adjacent to the porphyrin macrocycle, CH(1), is more deshielded than CH(2) one by the porphyrin ring current. ^1H NMR spectrum of cinnamaldehyde, shows a quintet at δ 6.7 ppm for CH(1) and a broad doublet signal at 7.55 for CH(2) protons [22,23].

3.3. Catalytic studies

3.3.1. Oxidation of alkenes

$\text{Mntcp}(\text{OAc})$ has been used as a catalyst for oxidation of different alkenes (Table 2). It is observed that the conjugated double bonds and unstrained cyclic alkenes are more reactive than simple ones. It has been shown by quantum-chemical calculations that

Table 2
Oxidation of olefins with TBAO in the presence of $\text{Mntcp}(\text{OAc})$ and imidazole at room temperature in dichloromethane (for 20 min).^a

Entry	Alkene	Conversion ^b (%)	Epoxide	Selectivity (%)
1		84		100
2		80		65 ^c
3		99		100
4		70		70
5		98		100
6		27		100
7		59 ^d		96.6
				3.4
8		44 ^d		100

^a The molar ratios for alkene:oxidant:ImH:catalyst are 100:250:20:1, all were used in concentrations 0.2 times lower than that have been used for catalytic oxidation of alkenes with TBAO in the presence of other metalloporphyrins, for controlling the reaction rate [26,29–32].

^b Analyzed by GC. Authentic samples were prepared according to the literature for entries 2, 5, 6, 7 and 8 [27].

^c Acetophenone is the by-product.

^d Analyzed by ^1H NMR.

the strained double bonds, which already deviate from planarity, have a destabilized HOMO with respect to the planar ones and should form particularly strong bonds to transition metals [24]. This may explain the higher reactivity of the strained double bond of indene relative to that of styrene, although the nearly planar structure of indene which can diminish the steric hindrance about the reaction center may be also involved. Contrary to other reports, a significant difference between the reactivity of cyclohexene and cyclooctene has been observed [25–27]. The observed pattern of reactivity agrees with that reported for metalloporphyrin catalyzed epoxidation of alkenes with tetrabutylammonium periodate [28]. This observation may possibly reveal the nonplanar orientation of cinnamyl groups with respect to the porphyrin mean plane in the active oxidant (vide infra) which in turn leads to a decrease in the reactivity of more bulky alkenes such as cyclooctene.

3.3.2. Comparison of catalytic activity of Mntcp(OAc) and Mntpp(OAc)

Comparative oxidation of indene and α -methyl styrene have been carried out in the presence of Mntcp(OAc) and Mntpp(OAc) (Table 3). It is observed that Mntcp(OAc) shows higher catalytic activity (ca. 1.2 fold higher) than Mntpp(OAc). This may again show the enhanced electron-deficient character of porphyrin core due to the substitution of cinnamyl groups for phenyl ones.

3.3.3. Stability of Mntcp(OAc)

The title porphyrin possesses extended π -conjugation with four cinnamyl substituents at its periphery. This extended π -conjugation is expected to enhance the stability of Mntcp(OAc) towards oxidation with different intermediates such as radicals or/and high valent oxo-species through the delocalization of radical or carbocation centers which may form in oxidative conditions. The UV–Vis spectrum of a solution containing catalyst, alkene, ImH and TBAO has been recorded at 30 s intervals (Fig. 4). It is observed that Mntcp(OAc) has been degraded ca. 36% (compare curve a and curve e) after 2 min. After 2.5 min (curve e), the rate of degradation de-

Table 3

Comparative oxidation of indene and α -methyl styrene with TBAO in the presence of imidazole, catalyzed by Mntcp(OAc)(1) and Mntpp(OAc)(2) in dichloromethane.^a

Alkene	Conversion (% for 1)	Conversion (% for 2)	Time (min)
α -Methyl styrene	80 \pm 3	59 \pm 2	20
Indene	98 \pm 4	80 \pm 3	20

^a See the footnote of Table 2 for reaction conditions; all experiments were repeated three times.

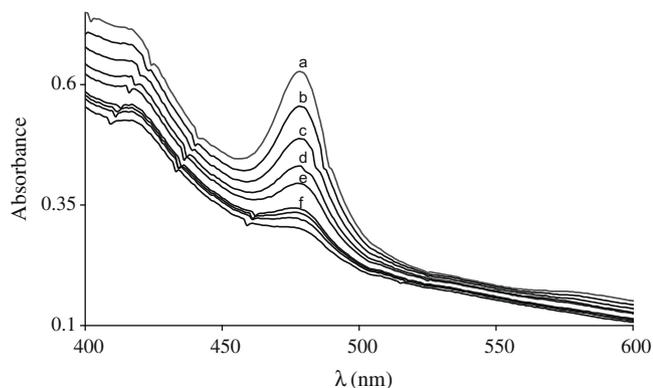


Fig. 4. UV–Vis monitoring of the degradation of Mntcp(OAc) in a dichloromethane solution containing TBAO, ImH and cyclooctene within 30 s intervals (see footnote of Table 1 for the molar ratios).

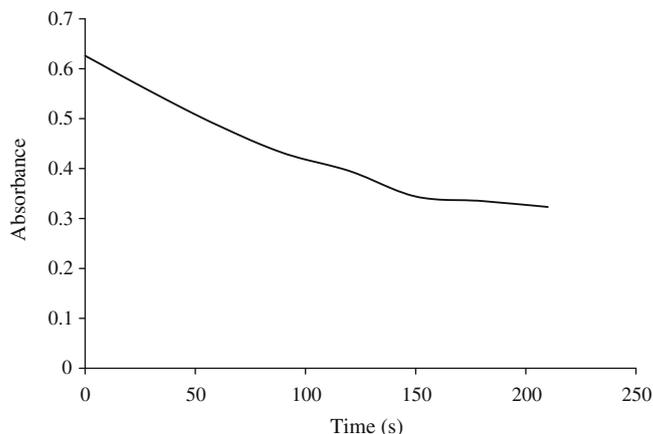


Fig. 5. Absorbance versus time for the degradation of Mntcp(OAc).

Table 4

Competitive oxidation of *cis*- and *trans*-stilbene with TBAO in the presence of Mntcp(OAc) and imidazole in dichloromethane.^{a,b}

Cis-oxide (%)	Trans-oxide (%)	Cis/trans ratio	Time (min)
12.8 \pm 0.4	8.7 \pm 0.5	1.47 \pm 0.2	20

^a The molar ratios for alkene:oxidant:ImH:catalyst are: (500,500):250:20:1.

^b Analyzed by ¹H NMR.

creases so that the reaction seems to proceed in the presence of a nearly constant catalyst concentration (Fig. 5).

3.3.4. The nature of active oxidant

Epoxidation of *cis*- and *trans*-stilbene, in a competitive reaction, has been shown to be a useful probe to elucidate the nature of active oxidant in the metalloporphyrin catalyzed epoxidation of olefins in the absence of nonbulky *ortho*-substituents on the phenyl groups of *meso*-tetraphenylporphyrins [28,29]. Competitive oxidation of *cis*- and *trans*-stilbene with TBAO in the presence of Mntcp(OAc) (Table 4) has been performed and yielded a ratio of 1.47 for *cis*- to *trans*-stilbene oxide. This ratio suggests a high valent Mn–Oxo species as the sole active oxidant.

4. Conclusions

In summary, the synthesis, characterization and metalation of H₂tcp are reported. UV–Vis studies imply that H₂tcp may be considered as an electron-deficient porphyrin in comparison with *meso*-tetraphenylporphyrin. The presence of CH=CH spacer in H₂tcp seems to cause a decrease in π -donation from phenyl groups to the porphyrin core. Mntcp(OAc) shows higher catalytic activity than Mntpp(OAc) in olefin epoxidation with TBAO. Competitive oxidation of *cis*- and *trans*-stilbene indicates the involvement of a high valent manganese oxo intermediate in the catalytic cycle.

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