

# Association of Keggin-type anions with cationic *meso*-substituted porphyrins: synthesis, characterization and oxidative catalytic studies

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## Abstract

New compounds based on the association of polyoxometalates and cationic porphyrins or metalloporphyrins were prepared with the aim of obtaining new bi-functional catalysts. A combined study on the syntheses, characterization and catalytic activity of these compounds was performed. The new compounds have the general formula (porphyrin)<sub>x</sub>H<sub>y</sub>[XM<sub>12</sub>O<sub>40</sub>]<sub>z</sub> solv,  $x=0.75$  or  $1$ ,  $X=P$  or  $Si$  and  $M=W$  or  $Mo$ . The porphyrins used were 5,10,15,20-tetrakis(4-pyridyl)porphyrin, 5,10,15,20-tetrakis(1-methyl-4-pyridinio)porphyrin, 5,10,15-tris(2,6-dichlorophenyl)-20-(4-pyridyl)porphyrin, and 5,10,15-tris(2,6-dichlorophenyl)-20-(1-methyl-4-pyridinio)porphyrin, either as free bases or complexed with Mn<sup>III</sup> (one case with Zn<sup>II</sup>). A few compounds with metal substituted Keggin anions ([PW<sub>11</sub>Y(H<sub>2</sub>O)O<sub>39</sub>]<sup>n-</sup>, Y = Mn, Fe, Ni, Zn) were also prepared. All compounds were characterized by spectroscopic and analytical techniques. The oxidation of *cis*-cyclooctene, geraniol and (+)-3-carene by hydrogen peroxide catalysed by the polyoxometalate/Mn<sup>III</sup>porphyrin associations and co-catalysed by ammonium acetate was examined. Some of the associations significantly increased the percentage of conversion of the substrates relatively to the respective metalloporphyrin alone. However, the regio-, chemo- and stereoselectivity of the oxidation reactions catalysed by metalloporphyrins were globally preserved: *cis*-cyclooctene was selectively epoxidised to epoxycyclooctane; geraniol gave 6,7-epoxygeraniol as the major product and (+)-3-carene was preferably oxidised to the  $\alpha$ -3,4-epoxycarene. In the conditions studied, the polyoxoanions seem to contribute mainly to stabilise the metalloporphyrin against deactivation during catalytic cycles.

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**Keywords:** Polyoxometalates; Cationic porphyrins; Metalloporphyrins; Manganese(III); Oxidation; Hydrogen peroxide; Monoterpenes; Cyclooctene

## 1. Introduction

The interest on possible developments of mixed organic/inorganic materials with diverse properties that may lead to new applications has been continuously increasing. In particular, polyoxometalates have been recently associated with a variety of organic molecules in order to prepare new compounds with interesting optical, magnetic or electric properties [1,2]. Keggin-type heteropolyanions have been frequently referred, associated with, among others, benzo-

triazole [3], 2,2'-biquinoline [4], 8-hydroxyquinoline [5,6], urea [7], glycine [8], and other *N*-containing molecules. Compounds with Keggin-type polyoxometalates and metalloporphyrins have been rarely considered [9,10]. Nevertheless, these compounds can be envisaged as potential new bi-functional catalysts, as they may be expected to originate systems in which the catalytic abilities of the two species reinforce each other. Also, these associations may provide ways of stabilising the metalloporphyrins against deactivation during the catalytic cycles.

The search for new catalysts for the selective and efficient oxidation of organic compounds under clean mild conditions still remains a challenge [11,12]. In this context both

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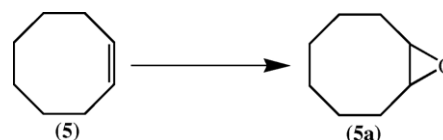
metalloporphyrins and polyoxometalates have been extensively investigated. A wide variety of oxidative reactions catalysed by metalloporphyrins have been studied [13–17]. Several strategies have been devised to overcome the difficulties arising from the frequently encountered destruction of the porphyrin ring during the course of reaction, namely the use of selected electron-withdrawing substituents on the porphyrin ring. Thus, metal complexes based on 5,10,15,20-tetra-arylporphyrins with electron-withdrawing groups on the aryl substituents and on the  $\beta$ -pyrrolic positions were described as robust catalysts in oxidation reactions [17]. Another approach involved the immobilization of metalloporphyrins on solid supports. These systems could prevent the self-oxidation of the catalyst, allowing better selectivity due to the local environment of the support and facilitating the recovery and re-use of the catalyst [18–20]. Cationic metalloporphyrins with methylpyridinio groups on the *meso*-positions have been electrostatically adsorbed on silica supports, showing a catalytic performance superior to their homogeneous analogues [21–24].

The use of polyoxometalates in homogeneous oxidative catalysis has been extensively reviewed [25–30]. In particular, the Keggin-type polyoxotungstates have been used as homogeneous catalysts for several epoxidation reactions [27,29,31,32], including the oxidation of naturally occurring alkenes with hydrogen peroxide [33–34].

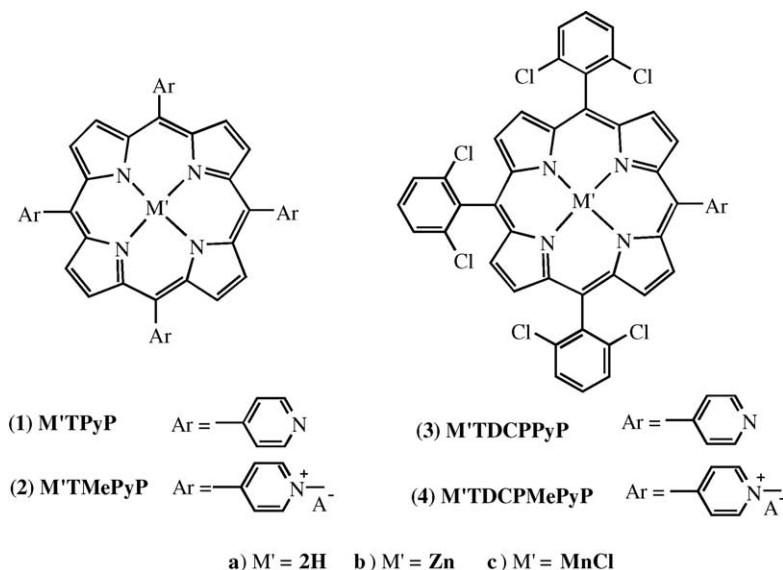
A few studies can be found involving polyoxometalates and porphyrins simultaneously. Attanasio and Bachechi referred the preparation and properties of charge transfer compounds with the  $Zn^{II}$  complex of 5,10,15,20-tetra-phenylporphyrin and Keggin heteropolyanions [9]. Others described homogeneous photocatalytic oxidations in the presence of an iron<sup>III</sup> porphyrin and  $[PW_{12}O_{40}]^{3-}$  [35–37] or  $[W_{10}O_{32}]^{4-}$  [38]. During the course of our studies

[39–42], the preparation of compounds with the tetracationic 5,10,15,20-tetrakis(1-benzyl-4-pyridinio)porphyrin and the anion  $[SiW_{12}O_{40}]^{4-}$  was reported [10]. Also, modified glassy carbon electrodes with metalloporphyrins and Keggin anions have been devised and studied to be used in the electrocatalytic reduction of dioxygen [10,43–45].

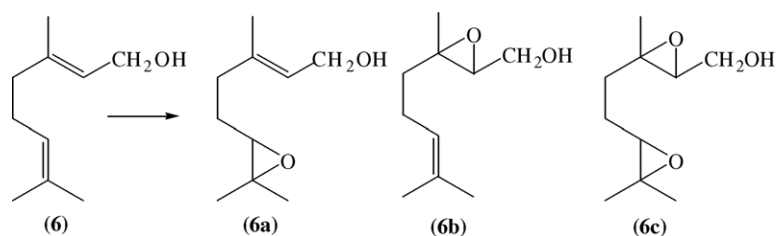
A combined study on the preparation, characterization and catalytic application in homogeneous oxidation of organic substrates of new polyoxometalate/porphyrin and polyoxometalate/metalloporphyrin associations is described in this paper. New compounds were prepared by reaction of the heteropolyacids  $H_3[PM_{12}O_{40}] \cdot zH_2O$  and  $H_4[SiM_{12}O_{40}] \cdot zH_2O$  ( $M = Mo, W$ ) or salts of  $[PW_{11}Y(H_2O)O_{39}]^{n-}$ ,  $Y = Mn, Fe, Ni, Zn$ , with porphyrins carrying one or four 4-pyridyl or 1-methyl-4-pyridinio groups in the *meso*-positions (Scheme 1). The polyoxometalate/ $Mn^{III}$  porphyrin associations were used as catalysts in the oxidation of terpenes, following our recent studies on the catalytic functionalization of these naturally occurring compounds with other  $Mn^{III}$  porphyrins [46–48] and with Keggin-type anions [33,49,50], in search of efficient transformations of cheap and readily available compounds into more valuable ones. The catalytic conversion of terpenes into fine chemicals was recently reviewed [51,52]. In the work here described, the catalytic performance of the new associations was tested in the oxidation of *cis*-cyclooctene (5), geraniol (6) and (+)-3-carene (7) in acetonitrile with hydrogen peroxide (Schemes 2–4). The same substrates were oxi-



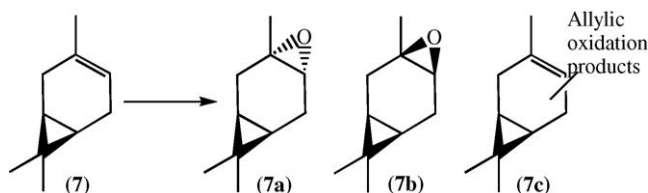
Scheme 2.



Scheme 1.



Scheme 3.



Scheme 4.

dised in the presence of the non-associated  $\text{Mn}^{\text{III}}$  porphyrins for comparison. Compounds with the polyoxometalates and the porphyrins in the free base form or complexed with zinc were synthesised for comparison, in order to contribute to the characterization of these new type of organic–inorganic materials.

## 2. Experimental

### 2.1. Reagents and synthetic procedures

All chemicals were used as received from the suppliers. Solvents were used as received or distilled and dried using standard procedures. Hydrogen peroxide (30 wt.% aqueous solution) was purchased from Riedel-de Haën. Geraniol, (+)-3-carene, *cis*-cyclooctene, *n*-octane and undecane were purchased from Aldrich. Other commercial reagents used were  $\text{H}_3[\text{PW}_{12}\text{O}_{40}] \cdot z\text{H}_2\text{O}$ ,  $\text{H}_3[\text{PMo}_{12}\text{O}_{40}] \cdot z\text{H}_2\text{O}$ ,  $\text{H}_4[\text{SiW}_{12}\text{O}_{40}] \cdot z\text{H}_2\text{O}$ ,  $\text{H}_4[\text{SiMo}_{12}\text{O}_{40}] \cdot z\text{H}_2\text{O}$  and ammonium acetate.  $(\text{TBA})_3[\text{PW}_{12}\text{O}_{40}]$  and  $\text{TBA}_x\text{H}_y[\text{PW}_{11}\text{Y}(\text{H}_2\text{O})\text{O}_{39}] \cdot z\text{H}_2\text{O}$ , TBA = tetrabutylammonium, Y =  $\text{Mn}^{\text{III}}$ ,  $\text{Fe}^{\text{III}}$ ,  $\text{Ni}^{\text{II}}$  or  $\text{Zn}^{\text{II}}$ ,  $y = 0$  or  $1$ , were prepared as reported previously [53–55]. 5,10,15,20-Tetrakis(4-pyridyl)porphyrin (**1a**), 5,10,15,20-tetrakis(1-methyl-4-pyridinio)porphyrin (**2a**), 5,10,15-tris(2,6-dichlorophenyl)-20-(4-pyridyl)porphyrin (**3a**), 5,10,15-tris(2,6-dichlorophenyl)-20-(1-methyl-4-pyridinio)porphyrin (**4a**), the corresponding  $\text{Mn}^{\text{III}}$  complexes (**1c–4c**) and the zinc complex **1b** were prepared according to known procedures [56–58]. All the synthetic procedures were performed protected from light.  $\text{O}_2(\text{g})$  was bubbled for ca. 30 min through solutions of  $\text{Mn}^{\text{III}}$  porphyrins prior to their use in the synthesis of the new compounds. Consistent analyses (see supplementary material) were obtained for all prepared polyoxometalate/porphyrin and polyoxometalate/metalloporphyrin associations (Table 1).

*Associations type 1XM:*  $[(\text{M}'\text{TPyP})\text{H}_4]_n[\text{XM}_{12}\text{O}_{40}] \cdot z$  solv,  $\text{M}' = 2\text{H}$ ,  $\text{Zn}^{\text{II}}$ ,  $\text{Mn}^{\text{III}}\text{Cl}$ ,  $\text{M} = \text{Mo}$ ,  $\text{W}$ ,  $\text{X} = \text{P}$  ( $n = 0.75$ ) or  $\text{Si}$  ( $n = 1$ ). Solutions of porphyrins **1a**, **1b** or **1c** (2 ml,  $0.02 \text{ mol dm}^{-3}$ ) in  $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$  (5:1) and of  $\text{H}_3[\text{PM}_{12}\text{O}_{40}] \cdot z\text{H}_2\text{O}$  or  $\text{H}_4[\text{SiM}_{12}\text{O}_{40}] \cdot z\text{H}_2\text{O}$  in absolute ethanol (2 ml,  $0.04 \text{ mol dm}^{-3}$ ) were prepared and mixed with stirring. The formation of a dark precipitate was immediately observed. The reaction was stirred overnight and the precipitate was filtered, washed with ethanol and dried in a vacuum desiccator.

*Associations type 1PWY:*  $[(\text{M}'\text{TPyP})\text{H}_4]_m[\text{PW}_{11}\text{Y}(\text{H}_2\text{O})\text{O}_{39}] \cdot z$  solv,  $\text{M}' = 2\text{H}$ ,  $\text{Mn}^{\text{III}}\text{Cl}$ ,  $\text{Y} = \text{Mn}^{\text{III}}$ ,  $\text{Fe}^{\text{III}}$ ,  $\text{Ni}^{\text{II}}$ ,  $\text{Zn}^{\text{II}}$ . Solutions of porphyrins **1a** or **1c** (10 ml,  $0.008 \text{ mol dm}^{-3}$ ) in  $\text{CH}_3\text{CN}$  were acidified with trifluoroacetic acid.

Table 1

Molecular formula and abbreviations for the compounds resulting from the association of polyoxometalates and porphyrins or metalloporphyrins<sup>a</sup>

$[(\text{H}_2\text{TPyP})\text{H}_4]_{0.75}[\text{PW}_{12}\text{O}_{40}] \cdot 6\text{H}_2\text{O} \cdot \text{C}_2\text{H}_5\text{OH}$	<b>1aPW</b>
$[(\text{H}_2\text{TPyP})\text{H}_4][\text{PW}_{11}\text{Fe}(\text{H}_2\text{O})\text{O}_{39}] \cdot \text{CH}_3\text{CN}$	<b>1aPWFe</b>
$[(\text{H}_2\text{TPyP})\text{H}_4][\text{PW}_{11}\text{Ni}(\text{H}_2\text{O})\text{O}_{39}]$	<b>1aPWNi</b>
$[(\text{H}_2\text{TPyP})\text{H}_4][\text{PW}_{11}\text{Zn}(\text{H}_2\text{O})\text{O}_{39}]$	<b>1aPWZn</b>
$[(\text{MnClTPyP})\text{H}_4][\text{PW}_{11}\text{Mn}(\text{H}_2\text{O})\text{O}_{39}] \cdot 2\text{CH}_3\text{CN}$	<b>1cPWNm</b>
$[(\text{MnClTPyP})\text{H}_4]_{0.75}[\text{PW}_{12}\text{O}_{40}] \cdot 10\text{H}_2\text{O} \cdot \text{CH}_2\text{Cl}_2$	<b>1cPW</b>
$[(\text{ZnTPyP})\text{H}_4]_{0.75}[\text{PW}_{12}\text{O}_{40}] \cdot 10\text{H}_2\text{O}$	<b>1bPW</b>
$[(\text{H}_2\text{TPyP})\text{H}_4]_{0.75}[\text{PMo}_{12}\text{O}_{40}] \cdot 9\text{H}_2\text{O}$	<b>1aPMo</b>
$[(\text{MnClTPyP})\text{H}_4]_{0.75}[\text{PMo}_{12}\text{O}_{40}] \cdot 8\text{H}_2\text{O}$	<b>1cPMo</b>
$[(\text{H}_2\text{TPyP})\text{H}_4][\text{SiW}_{12}\text{O}_{40}] \cdot 10\text{H}_2\text{O} \cdot \text{CH}_2\text{Cl}_2$	<b>1aSiW</b>
$[(\text{MnClTPyP})\text{H}_4][\text{SiW}_{12}\text{O}_{40}] \cdot 10\text{H}_2\text{O} \cdot 2\text{C}_2\text{H}_5\text{OH}$	<b>1cSiW</b>
$[(\text{H}_2\text{TPyP})\text{H}_4][\text{SiMo}_{12}\text{O}_{40}] \cdot 10\text{H}_2\text{O} \cdot \text{C}_2\text{H}_5\text{OH}$	<b>1aSiMo</b>
$[(\text{MnClTPyP})\text{H}_4][\text{SiMo}_{12}\text{O}_{40}] \cdot 8\text{H}_2\text{O}$	<b>1cSiMo</b>
$[\text{H}_2\text{TMePyP}]_{0.75}[\text{PW}_{12}\text{O}_{40}] \cdot 6\text{H}_2\text{O}$	<b>2aPW</b>
$[\text{MnClTMePyP}]_{0.75}[\text{PW}_{12}\text{O}_{40}] \cdot 9\text{H}_2\text{O}$	<b>2cPW</b>
$[\text{H}_2\text{TMePyP}]_{0.75}[\text{PMo}_{12}\text{O}_{40}] \cdot 5\text{H}_2\text{O}$	<b>2aPMo</b>
$[\text{MnClTMePyP}]_{0.75}[\text{PMo}_{12}\text{O}_{40}] \cdot 8\text{H}_2\text{O}$	<b>2cPMo</b>
$[\text{H}_2\text{TMePyP}][\text{SiW}_{12}\text{O}_{40}] \cdot 8\text{H}_2\text{O}$	<b>2aSiW</b>
$[\text{MnClTMePyP}][\text{SiW}_{12}\text{O}_{40}] \cdot 11\text{H}_2\text{O}$	<b>2cSiW</b>
$[\text{H}_2\text{TMePyP}][\text{SiMo}_{12}\text{O}_{40}] \cdot 14\text{H}_2\text{O}$	<b>2aSiMo</b>
$[\text{MnClTMePyP}][\text{SiMo}_{12}\text{O}_{40}] \cdot 10\text{H}_2\text{O}$	<b>2cSiMo</b>
$[(\text{H}_2\text{TDCPPyP})\text{H}][\text{PW}_{12}\text{O}_{40}] \cdot 4\text{H}_2\text{O} \cdot 2\text{CH}_3\text{OH}$	<b>3aPW</b>
$[(\text{MnClTDCPPyP})\text{H}][\text{PW}_{12}\text{O}_{40}] \cdot 4\text{H}_2\text{O} \cdot 3\text{CH}_3\text{OH}$	<b>3cPW</b>
$[(\text{H}_2\text{TDCPPyP})\text{H}][\text{SiW}_{12}\text{O}_{40}] \cdot 5\text{H}_2\text{O} \cdot \text{CH}_3\text{OH}$	<b>3aSiW</b>
$[(\text{MnClTDCPPyP})\text{H}][\text{SiW}_{12}\text{O}_{40}] \cdot 6\text{H}_2\text{O} \cdot 3\text{CH}_3\text{OH}$	<b>3cSiW</b>
$[\text{H}_2\text{TDCPMePyP}][\text{PW}_{12}\text{O}_{40}] \cdot 5\text{H}_2\text{O} \cdot 2\text{CH}_3\text{OH}$	<b>4aPW</b>
$[\text{MnClTDCPMePyP}][\text{PW}_{12}\text{O}_{40}] \cdot 3\text{H}_2\text{O} \cdot \text{CH}_3\text{OH}$	<b>4cPW</b>
$[\text{H}_2\text{TDCPMePyP}][\text{SiW}_{12}\text{O}_{40}] \cdot 7\text{H}_2\text{O} \cdot 3\text{CH}_3\text{OH}$	<b>4aSiW</b>
$[\text{MnClTDCPMePyP}][\text{SiW}_{12}\text{O}_{40}] \cdot 4\text{H}_2\text{O} \cdot \text{CH}_3\text{OH}$	<b>4cSiW</b>

<sup>a</sup> Porphyrin and metalloporphyrin abbreviations are presented in Scheme 1.

acid (TFA) (26  $\mu\text{l}$ ). Solid  $\text{TBA}_x\text{H}_y[\text{PW}_{11}\text{Y}(\text{H}_2\text{O})\text{O}_{39}] \cdot z\text{H}_2\text{O}$  (0.14 mmol) was added with stirring. The formation of a dark precipitate was immediately observed. The reaction was stirred overnight and the precipitate was centrifuged, washed with acetonitrile and dried under vacuum.

*Associations type 2XM:*  $[\text{M}'\text{TMePyP}]_n[\text{XM}_{12}\text{O}_{40}] \cdot z$  solv,  $\text{M}' = 2\text{H}$ ,  $\text{Mn}^{\text{III}}\text{Cl}$ ,  $\text{M} = \text{Mo}$ ,  $\text{W}$ ,  $\text{X} = \text{P}$  ( $n = 0.75$ ) or  $\text{Si}$  ( $n = 1$ ). Aqueous solutions (0.02 mol  $\text{dm}^{-3}$ ) of the cationic porphyrin **2a** (iodide salt) or **2c** (chloride salt) and of  $\text{H}_3[\text{PM}_{12}\text{O}_{40}] \cdot z\text{H}_2\text{O}$  or  $\text{H}_4[\text{SiM}_{12}\text{O}_{40}] \cdot z\text{H}_2\text{O}$  (0.04 mol  $\text{dm}^{-3}$ ) were prepared and mixed in equal volumes with stirring. The formation of a precipitate was immediately observed. The reaction was stirred overnight and the precipitate was filtered, washed with water and ethanol and dried under vacuum.

*Associations type 3XW:*  $[(\text{M}'\text{TDCPPyP})\text{H}]_n[\text{XW}_{12}\text{O}_{40}] \cdot z$  solv,  $\text{M}' = 2\text{H}$ ,  $\text{Mn}^{\text{III}}\text{Cl}$ ,  $\text{X} = \text{P}$  ( $n = 2$ ) or  $\text{Si}$  ( $n = 3$ ). Solutions of porphyrins **3a** or **3c** (5 ml, 0.02 mol  $\text{dm}^{-3}$ ) in 1,2- $\text{C}_2\text{H}_4\text{Cl}_2/\text{CH}_3\text{OH}$  (5:2) and of  $\text{H}_3[\text{PM}_{12}\text{O}_{40}] \cdot z\text{H}_2\text{O}$  or  $\text{H}_4[\text{SiM}_{12}\text{O}_{40}] \cdot z\text{H}_2\text{O}$  in absolute ethanol (5 ml, 0.04 mol  $\text{dm}^{-3}$ ) were prepared and mixed with stirring. The formation of a dark precipitate was immediately observed. The reaction was stirred overnight and the precipitate was separated by centrifugation, washed with ethanol and dried under vacuum.

*Associations type 4XW:*  $[(\text{M}'\text{TDCPMePyP})\text{H}]_n[\text{XW}_{12}\text{O}_{40}] \cdot z$  solv,  $\text{M}' = 2\text{H}$ ,  $\text{Mn}^{\text{III}}\text{Cl}$ ,  $\text{X} = \text{P}$  ( $n = 2$ ) or  $\text{Si}$  ( $n = 3$ ). The method used for associations 3XW was applied, using porphyrins **4a** (iodide salt) or **4c** (chloride salt) in place of **3a** or **3c**.

## 2.2. Analysis

Elemental analyses for P, W, Mo, Mn and Zn were performed by ICP spectrometry (JY 70 plus) at the Central Laboratory of Analysis of the University of Aveiro. Solutions for analysis were prepared on a closed microwave system by heating the compounds during 30 min in a mixture of HCl (2 ml),  $\text{HNO}_3$  (2 ml) and HF (1 ml), followed by further heating after addition of 2 ml of HCl and 0.1 ml  $\text{HClO}_4$ . C, H, N elemental analyses were performed on a Leco CHNS-932 apparatus. Thermogravimetric analyses were carried out in air at  $5^\circ\text{C min}^{-1}$  on a TGA-50 Shimadzu thermobalance. The values of the total weight loss (TG) were calculated from thermogravimetric analysis performed up to  $700^\circ\text{C}$ , assuming decomposition to a mixture of oxides. GC-FID analyses were performed using a Varian Star 3400CX chromatograph and hydrogen as the carrier gas (55 cm/s). GC-MS analyses were performed using a Finnigan Trace GC/MS (Thermo Quest CE Instruments) using helium as the carrier gas (35 cm/s). In both cases fused silica Supelco capillary columns SPB-5 (30 m  $\times$  0.25 mm i.d.; 25  $\mu\text{m}$  film thickness) were used. The chromatographic conditions were as follows: initial temperature,  $80^\circ\text{C}$  (2 min); temperature rate,  $20^\circ\text{C/min}$ ; final temperature,  $200^\circ\text{C}$ ; injector temperature,  $220^\circ\text{C}$ ; detector temperature,  $220^\circ\text{C}$ , for *cis*-cyclooctene oxidation reactions; ini-

tial temperature,  $80^\circ\text{C}$  (2 min); temperature rate,  $25^\circ\text{C/min}$ ; final temperature,  $155^\circ\text{C}$ ; temperature rate,  $5^\circ\text{C/min}$ ; final temperature,  $200^\circ\text{C}$ ; injector temperature,  $220^\circ\text{C}$ ; detector temperature,  $220^\circ\text{C}$ , for geraniol and (+)-3-carene oxidation reactions. The values of conversion and selectivity are based on the chromatographic peak areas, using *n*-octane or undecane as internal standards.

## 2.3. Catalytic procedures

In a typical experiment, the substrate (0.3 mmol), the catalyst (according to the chosen substrate/catalyst ratio), ammonium acetate (15 mg) and the internal standard (0.3 mmol) (*n*-octane for *cis*-cyclooctene and undecane for (+)-3-carene and geraniol oxidations) were dissolved in acetonitrile (2 ml) and the reaction was stirred at 22 or  $60^\circ\text{C}$ . Aqueous hydrogen peroxide (30 wt.%) diluted in acetonitrile (1:10) was gradually added to the reaction mixture in 150  $\mu\text{l}$  aliquots every 15 min. The course of the reactions was followed by GC. The products had been previously isolated and characterized in our laboratory [48]. GC-MS was used to confirm the identity of the reaction products.

During the oxidation reactions, the absorbance of the Soret band on the visible spectra of the solution (150  $\mu\text{l}$  of the reaction medium diluted with DMSO up to 5 ml) decreased progressively. The metalloporphyrin stability was determined by the ratio between the intensities of the Soret band at a certain time and at the beginning of the reaction.

The reuse of 4cPW was done in two successive reactions. The reaction was carried out in the conditions described above, using a substrate/catalyst ratio (S/C) of 60. After 1 h of reaction the catalyst was filtered from the reaction medium, washed with  $\text{CH}_3\text{CN}$  and reused.

## 2.4. Physical measurements

Electronic absorption spectra were recorded on a Jasco V-560 spectrophotometer or on an Uvikom 922, Kontrom Instruments.  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectra were recorded on a Bruker AMX 300, using tetramethylsilane (TMS) as internal reference or 85% aqueous  $\text{H}_3\text{PO}_4$  as external reference, respectively. Diffuse reflectance and infrared absorption spectra, powder X-ray diffraction patterns and magnetic moments were obtained as described previously [4].

## 3. Results and discussion

### 3.1. Synthesis and characterization of the associations

The association of the Keggin anions  $[\text{XM}_{12}\text{O}_{40}]^{n-}$  ( $\text{M} = \text{Mo}$ ,  $\text{W}$ ;  $\text{X} = \text{P}$ ,  $\text{Si}$ ) with large cations leads frequently to the precipitation of insoluble compounds. This behaviour was explored in this work in order to obtain the desired associations of cationic porphyrins or metalloporphyrins with polyoxometalates (Table 1). The solvent or mixture of solvents



used were chosen in such a way that the precipitation of the compounds occurred by simple mixing. In the presence of the strong heteropolyacids  $H_3[PM_{12}O_{40}] \cdot zH_2O$  or  $H_4[SiM_{12}O_{40}] \cdot zH_2O$  ( $M = Mo, W$ ) the porphyrins with 4-pyridyl substituents (**1a** and **3a**) and the corresponding metal complexes were expected to protonate at the pyridyl residues, thus providing the necessary cations for salt formation. The results of the elemental analysis confirmed this supposition in many cases. Trifluoroacetic acid (TFA) was added to ensure protonation of the pyridyl residues in synthesis starting with TBA salts of the metal substituted heteropolyanions. The obtained compounds were soluble in dimethylsulphoxide (DMSO) and *N,N'*-dimethylformamide (DMF), slightly soluble in water and  $CH_3CN$  and insoluble in other common organic solvents. They were generally dark green or dark brown-green solids, amorphous or with low crystallinity.

The formulas presented in Table 1 were determined by elemental and thermal analyses. The stoichiometric porphyrin/polyoxometalate ratio was never larger than 1. Magnetic moments were determined for some Mn-containing solids ( $\mu = 4.0 \mu_B$  for **1cPW** and  $4.6 \mu_B$  for **2cPW**). The value  $\mu = 4.3 \mu_B$ , obtained for the  $Mn^{III}$  complex of 5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrin, was used comparatively in this work as indication of the presence of  $Mn^{III}$ . Magnetic moments of  $Mn^{III}$  porphyrins usually fall in the range  $4.2\text{--}4.9 \mu_B$  [59,60]. Thus, the obtained values suggested the presence of  $Mn^{III}$  in the prepared associations.

Several spectroscopic techniques were used to characterize the new compounds. All the results seem to indicate that they are salts of heteropolyanions with the porphyrins or metalloporphyrins as the cations.

### 3.1.1. Spectroscopic characterization of the solids (IR, DRS)

Keggin-type polyoxometalates originate characteristic infrared bands in the  $700\text{--}1000\text{ cm}^{-1}$  region of the spectra, assigned to  $M=O$  and  $M-O-M$  stretching vibrations [54,61,62]. These bands were observed in the spectra of the prepared compounds without significant changes. Frequency values for compounds with  $[XM_{12}O_{40}]^{n-}$  differed slightly from those of the original acids, as described for other salts of large counter-cations [54]. Bands obtained for solids with  $[PW_{11}Y(H_2O)O_{39}]^{n-}$  are identical to those of analogous TBA salts [63]. The bands with lower intensities observed at  $1100\text{--}1600\text{ cm}^{-1}$  and near  $3000\text{ cm}^{-1}$  confirmed the presence of the organic moieties in the compounds (Fig. 1).

Diffuse reflectance spectra of the prepared solids showed the bands corresponding to the porphyrins and to the polyoxometalates in the visible and UV region, respectively. The visible spectra in solution ( $CHCl_3$ ,  $CH_3CN$ , DMSO, DMF) of the non-metallated porphyrins **1a–4a** were characterized by a strong Soret band at about  $420\text{--}426\text{ nm}$  and four Q-bands of decreasing intensities between  $500$  and  $650\text{ nm}$  [64,65]. Diffuse reflectance spectra of these free bases were similar, showing the same five bands observed in solution spectra but with the relative intensity of the Soret band comparatively

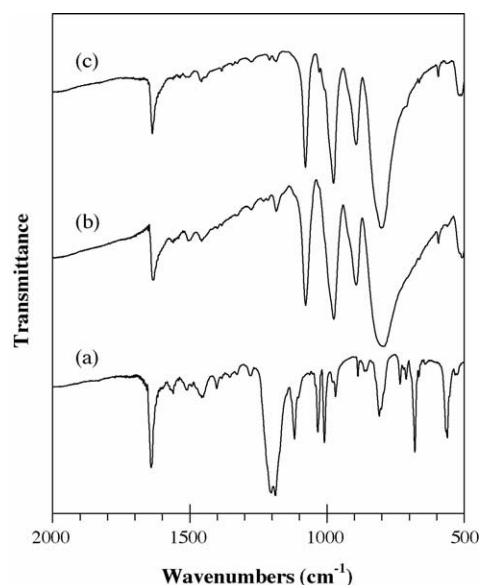


Fig. 1. Infrared spectra of: (a) **2a**; (b) **2aPW**; (c) **2cPW**.

diminished. Similar patterns were observed for the associations of porphyrins **1a–4a** with the polyoxometalates (Fig. 2). Similarly, the diffuse reflectance spectra of the metalloporphyrins **1c–4c** and **1b** were identical to the corresponding spectra in solution and were not significantly altered by the associations with polyoxometalates.

These results indicate that both the Keggin anions and the cationic porphyrins and metalloporphyrins used are present in the solid compounds obtained without noticeable changes. The fact that the spectroscopic properties described for the anions and the cations have not been substantially altered seems to point out simple ionic interactions between them. The protonation of the pyridyl residues needed for the formation of some of these compounds could not be observed by any of these techniques.

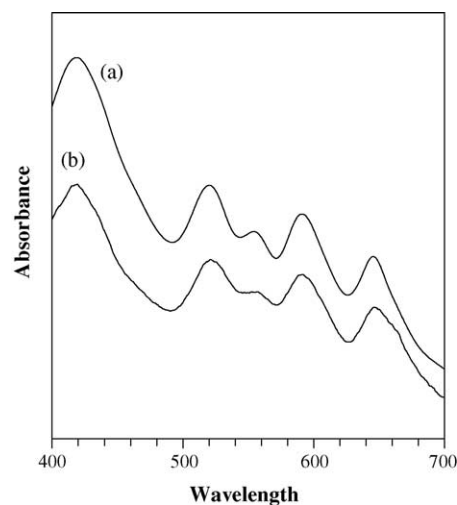


Fig. 2. Diffuse reflectance spectra of: (a) **1a**; (b) **1aSiMo**.

### 3.1.2. Spectroscopic characterization of the compounds in solution (UV–vis, NMR)

The electronic spectra of the new compounds in DMSO presented the bands characteristic of the porphyrinic moieties in the visible region [64,65]. Comparison of these spectra with those of the corresponding free porphyrins or metalloporphyrins in the same solvent provided evidence for the following facts: (a) the protonation of the inner nitrogen atoms of the porphyrinic ring of porphyrins **1a–4a** did not occur; (b) the central metals of the metalloporphyrins **1c–4c** and **1b** were still present. These conclusions were based on the absence of modification of the visible spectra [65,66]. The protonation of the pyridyl residues did not change the visible spectra of the porphyrin. The UV spectra presented a band near 250 nm characteristic of the polyoxometalates used [67].

<sup>1</sup>H NMR spectra were obtained for all diamagnetic compounds in DMSO-d<sub>6</sub>, unless when other solvents are indicated (Table 2). The spectrum of **1a** in CDCl<sub>3</sub> presented four signals: one singlet, corresponding to the β-pyrrolic protons, two multiplets, due to the protons of the pyridyl residues and one singlet at negative values of δ due to the NH protons of the porphyrin ring [68]. The spectrum of the same compound in DMSO showed a complicate pattern that could not be assigned. This behaviour was probably due to the aggregation of the porphyrin molecules in this media. Addition of TFA to the DMSO solutions restored the expected four signal spectra, but the multiplets corresponding to the pyridyl protons were

not as well resolved as in CDCl<sub>3</sub> (two doublets were observed instead). Aggregation was thus destroyed by the protonation of the pyridyl residues. The positions of the peaks changed with the amount of acid used. When this porphyrin was dissolved in pure TFA (no DMSO added) the singlet observed at negative values (around –3 ppm) shifted to near 1 ppm (entry b, Table 2). This shift corresponded to the protonation of the inner nitrogen atoms of the porphyrin ring, only observed in this highly acidic media.

The same type of spectra was obtained for the compounds **1aPW**, **1aPMo**, **1aSiW** and **1aSiMo** (Table 2). In all cases the signal of the protons bonded to pyrrole nitrogen atoms was observed near –3 ppm, suggesting that protonation only occurred at the pyridyl groups. The addition of acid to the DMSO solutions of the compounds shifted slightly the position of the peaks (entries e and i, Table 2). This may indicate that an equilibrium between protonated and deprotonated pyridyl groups was probably established in solution.

The zinc complex of porphyrin **1a** was synthesised to allow the study by NMR spectroscopy of the association of polyoxotungstates with metalloporphyrins. Except for the peak near –3 ppm (absent for the zinc complex), the spectra of the zinc porphyrin (**1b**) and of the association **1bPW** (entries k–m, Table 2) were identical to the spectrum of **1a**.

Results for other polyoxometalate/porphyrin associations were similar (Table 2). For **2a** in DMSO, the <sup>1</sup>H NMR spectra showed the signals of pyrrole and pyridyl protons at 9.19,

Table 2  
<sup>1</sup>H and <sup>31</sup>P NMR chemical shifts<sup>a</sup>

Entry	Compound <sup>b</sup>	H <sub>β</sub> <sup>c</sup>	H <sub>2,6</sub> <sup>d</sup>	H <sub>3,5</sub> <sup>d</sup>	NH	CH <sub>3</sub>	P
a	<b>1a</b> (CDCl <sub>3</sub> )	8.87 s	9.06 m	8.17 m	–2.92 s	–	–
b	<b>1a</b> (TFA)	9.00 s	9.41 d	9.10 d	1.05 s	–	–
c	<b>1a</b> + TFA <sup>e</sup>	9.06 s	9.23 d	8.83 d	–3.03 s	–	–
d	<b>1aPW</b>	9.01 s	9.19 d	8.51 d	–3.06 s	–	–14.5 s
e	<b>1aPW</b> + TFA <sup>f</sup>	9.16 s	9.44 d	8.86 d	–3.00 s	–	–14.5 s
f	<b>1aPWZn</b>	9.04 s <sup>g</sup>	9.23 d	8.60 d	–3.08 s	–	–11.0 s
g	<b>1aPMo</b>	9.09 s	9.31 d	8.72 d	–3.07 s	–	–3.0 s
h	<b>1aSiW</b>	9.09 s	9.30 d	8.73 d	–3.08 s	–	–
i	<b>1aSiW</b> + TFA <sup>f</sup>	9.12 s	9.40 d	8.89 d	–3.02 s	–	–
j	<b>1aSiMo</b>	9.04 s	9.21 d	8.59 d	–3.07 s	–	–
k	<b>1b</b>	8.82 s	9.01 d	8.21 d	–	–	–
l	<b>1b</b> + TFA <sup>f</sup>	9.00 s	9.32 d	8.86 d	–	–	–
m	<b>1bPW</b>	8.87 s	9.05 d	8.29 d	–	–	–14.5 s
n	<b>2a</b>	9.19 s	9.48 d	8.99 d	–3.11 s	4.72 s	–
o	<b>2aPW</b>	9.19 s	9.48 d	8.99 d	–3.11 s	4.74 s	–14.5 s
p	<b>2aSiW</b>	9.20 s	9.47 d	9.01 d	–3.10 s	4.75 s	–
q	<b>3a</b>	8.75 s; 8.81 d; 8.89 d	9.36 d	9.01 d	–2.84 s	–	–
r	<b>3aPW</b>	8.77 s; 8.80 d; 8.89 d	9.39 d	9.04 d	–2.85 s	–	–14.5 s
s	<b>3aSiW</b>	8.77 s; 8.82 d; 8.90 d	9.40 d	9.07 d	–2.84 s	–	–
t	<b>4a</b>	8.81 s; 8.90 d; 9.01 d	9.46 d	9.08 d	–2.83 s	4.70 s	–
u	<b>4aPW</b>	8.78 s; 8.86 d; 9.00 d	9.41 d	9.04 d	–2.83 s	4.70 s	–14.5 s
v	<b>4aSiW</b>	8.78 s; 8.87 d; 9.05 d	9.42 d	9.05 d	–2.86 s	4.69 s	–

<sup>a</sup> ppm relatively to TMS or conc. H<sub>3</sub>PO<sub>4</sub>, s: singlet, d: doublet, m: multiplet.

<sup>b</sup> DMSO-d<sub>6</sub> solutions, except when indicated (solvent in brackets).

<sup>c</sup> Pyrrole protons.

<sup>d</sup> Pyridyl ring protons.

<sup>e</sup> TFA/porf = 4.

<sup>f</sup> Addition of 3–4 drops of TFA to the DMSO solutions in the NMR tube.

<sup>g</sup> Low intensity peaks at 9.02 are also observed.

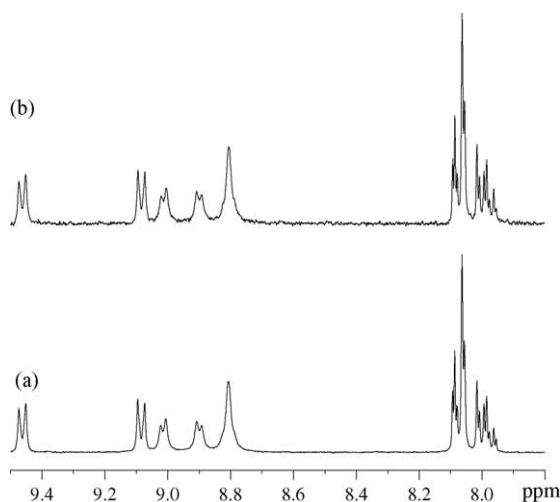


Fig. 3.  $^1\text{H}$  NMR spectra in DMSO of: (a) **4a**; (b) **4aPW**.

9.48 and 8.99 ppm ( $\text{H}_\beta$ ,  $\text{H}_{2,6}$  and  $\text{H}_{3,5}$ , respectively [64]). Two other singlets, with  $\delta$  equal to  $-3.12$  and  $4.72$  ppm, were assigned to the N–H and methyl protons. The compounds with this cation (**2aPW** and **2aSiW**) gave the same type of spectra almost without changes in the position of the peaks. For **3a** and **4a** and their associations **3aXW** and **4aXW** in DMSO, the  $^1\text{H}$  NMR spectra also showed, apart from the signals referred in Table 2, the signals of the 2,6-dichlorophenyl residues between 7.93 and 8.06 ppm (Fig. 3).

$^{31}\text{P}$  NMR spectra of the associations with P-containing anions in DMSO presented one singlet at  $-14.5$  or  $-3.0$  ppm characteristic of the  $[\text{PW}_{12}\text{O}_{40}]^{3-}$  and  $[\text{PMo}_{12}\text{O}_{40}]^{3-}$  anions, respectively [4]. These studies confirmed that the various cations or anions were present in solution without major alterations, as expected for solids with ionic bonding between the organic cationic moieties and the heteropolyanions.

### 3.2. Catalytic studies

#### 3.2.1. Oxidation of *cis*-cyclooctene

The  $\text{Mn}^{\text{III}}$  metalloporphyrins **1c**, **2c**, **3c**, **4c** and the compounds resulting from their association with the polyoxometalates (**1cPW**, **1cPMo**, **1cSiW**, **1cSiMo**, **1cPWMn**, **2cPW**, **2cSiW**, **3cPW** and **4cPW**) were used as catalysts in the oxidation of *cis*-cyclooctene with  $\text{H}_2\text{O}_2$ , in  $\text{CH}_3\text{CN}$  at different temperatures up to  $60^\circ\text{C}$ . In all cases the epoxycyclooctane was obtained as the only product (Scheme 2).

The results obtained in the oxidation of *cis*-cyclooctene in the presence of the metalloporphyrin (**1c**) or of the corresponding associations **1cPW**, **1cPMo**, **1cSiW** and **1cSiMo** are summarized in Table 3. With these catalysts comparatively low conversions were found and quite similar results were obtained at 22 and  $60^\circ\text{C}$ . The best results were obtained with the association **1cPW**. The stability of the metalloporphyrin was controlled by visible spectroscopy. Total bleaching had occurred after 1 h of reaction.

Table 3  
Oxidation of *cis*-cyclooctene with  $\text{H}_2\text{O}_2$  in the presence of catalysts based on metalloporphyrin (**1c**)<sup>a</sup>

Entry	Catalyst	Conversion (%) <sup>b</sup>	
		22 $^\circ\text{C}$	60 $^\circ\text{C}$
1	<b>1cPW</b>	19	21
2	<b>1cPMo</b>	8	–
3	<b>1cSiW</b>	3	6
4	<b>1cSiMo</b>	2	3
5	<b>1c</b>	14	17
6	$[\text{PW}_{12}\text{O}_{40}]^{3-}$ <sup>c</sup>	0	0
7	No catalyst	0	0

<sup>a</sup> Reaction conditions: substrate:catalyst:co-catalyst = 100:1:65, in acetonitrile (2 ml) and progressive addition of 0.5 equiv. of  $\text{H}_2\text{O}_2$  every 15 min, during 1 h. At the end of reaction,  $[\text{H}_2\text{O}_2]/[\text{substrate}] = 2$ .

<sup>b</sup> Determined by GC analyses using *n*-octane as the internal standard.

<sup>c</sup>  $\text{TBA}_3[\text{PW}_{12}\text{O}_{40}]$  and  $\text{H}_3[\text{PW}_{12}\text{O}_{40}] \cdot z\text{H}_2\text{O}$ .

The epoxidation of *cis*-cyclooctene in the presence of the tetramethylated porphyrin **2c** proceeded with quite low conversion ( $<5\%$ ) and this result was not altered in the presence of compounds **2cPW** and **2cSiW**. Also in the case of **1cPWMn**, where the  $\text{Mn}^{\text{III}}$  is present in both the porphyrin and the polyoxometalate, very low conversion ( $<1\%$ ) was obtained. The polyoxometalate PWMn (and also PWNi and PWZn) was found to catalyse the epoxidation of *cis*-cyclooctene with  $\text{H}_2\text{O}_2$  in acetonitrile with significant conversion at higher temperature (ca.  $80^\circ\text{C}$ ) [50]. At this temperature, reactions performed in the presence of PWMn or **1cPWMn** yielded similar results.

The poor efficiency of the metalloporphyrins **1c** and **2c** can be attributed to the highly deprotected macrocycle that contributes to their low stability in the catalytic conditions. Other factors can be implicated in the superior reactivity of porphyrin **1c** when compared with **2c**, as the possible formation of *N*-oxides on pyridyl residues of the porphyrin **1c** [69] or the fact that the presence of positive charges on porphyrin substituents may result in stable oxo $\text{Mn}^{\text{V}}$  species [70,71] and, consequently, less reactivity. This effect may be more important in the case of the tetracationic metalloporphyrin **2c**. The electrostatic association with the polyoxometalates did not generally improve the efficiency of these metalloporphyrins. Some results seem to indicate that this interaction may even prevent the catalytic action of the metalloporphyrin Mn centre.

Metalloporphyrins **3c** and **4c** and the corresponding associations with  $[\text{PW}_{12}\text{O}_{40}]^{3-}$  (**3cPW** and **4cPW**) gave rise to good catalytic performance (Table 4 and Fig. 4). A clear positive effect of the association could be observed when the catalytic studies were performed at  $60^\circ\text{C}$ . At this temperature, after 1 h, the conversion of *cis*-cyclooctene when **3cPW** was used was almost twice than that due to metalloporphyrin **3c**. A similar behaviour was observed with the pair **4c** and **4cPW**, where the conversion increased from 25 to 41%. The polyoxoanion seems to have a protective effect on the metalloporphyrin against its deactivation during catalytic cycles, since an improvement on the porphyrin stability was also

Table 4  
Oxidation of *cis*-cyclooctene with H<sub>2</sub>O<sub>2</sub> in the presence of catalysts based on metalloporphyrins **3c** and **4c**<sup>a</sup>

Entry	Catalyst	Conversion (%) <sup>b</sup>		Porphyrin (%) <sup>c</sup>
		22 °C	60 °C	
1	<b>3c</b>	37	30	29
2	<b>3cPW</b>	32	61	53
3	<b>4c</b>	22	25	0
4	<b>4cPW</b>	17	41	8
5	<b>4cPW</b> <sup>e</sup>	–	100	100
6	First reuse <sup>f</sup>	–	100	100
7	Second reuse <sup>f</sup>	–	82	0
8	TBA <sub>3</sub> [PW <sub>12</sub> O <sub>40</sub> ]	0	0	–
9	H <sub>3</sub> [PW <sub>12</sub> O <sub>40</sub> ].23H <sub>2</sub> O	0	0	–
10	<b>3c</b> + TBA <sub>3</sub> [PW <sub>12</sub> O <sub>40</sub> ]	32	29	–
11	No catalyst	0	0	–

<sup>a</sup> Reaction conditions: substrate:catalyst:co-catalyst = 600:1:390, in acetonitrile (2 ml) and progressive addition of 0.5 equiv. of H<sub>2</sub>O<sub>2</sub> every 15 min, during 1 h. At the end of reaction, [H<sub>2</sub>O<sub>2</sub>]/[substrate] = 2.

<sup>b</sup> Determined by GC analysis, using *n*-octane as the internal standard.

<sup>c</sup> Percentage of metalloporphyrin remaining in solution, determined by the ratio between the intensities of the Soret band at 15 min and at the beginning of the reaction.

<sup>d</sup> Molar ratio [H<sub>2</sub>O<sub>2</sub>]/[substrate] = 0.5.

<sup>e</sup> Substrate:catalyst:co-catalyst = 60:1:39.

<sup>f</sup> See Section 2.

observed (Table 4 and Fig. 5). This is possibly due to a stereo effect resulting from the electrostatic interaction between the porphyrin cation and the heteropolyanion.

When the catalysts were replaced by TBA<sub>3</sub>[PW<sub>12</sub>O<sub>40</sub>] or H<sub>3</sub>[PW<sub>12</sub>O<sub>40</sub>].23H<sub>2</sub>O, no reaction occurred at either 22 or 60 °C. Fast reactions at room temperature are generally characteristic of metalloporphyrin catalysed reactions, while catalysis by polyoxometalates may require more time and/or higher temperature. These results seem to indicate that, in this case, the metalloporphyrin is the active catalyst, which is protected against oxidation by the polyoxometalate.

The performance of the non-associated metalloporphyrins **3c** and **4c** was not affected by the change in reaction temperature (22–60 °C), as typically occurs with homogeneous catalysts based on heme chemistry. This was not the case with the associated metalloporphyrins, which almost doubled their

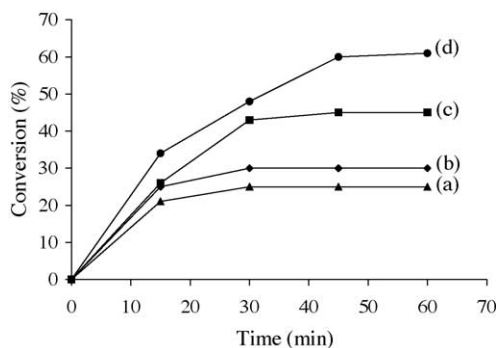


Fig. 4. Oxidation of *cis*-cyclooctene using some associations and porphyrins alone at 60 °C: (a) **4c**; (b) **3c**; (c) **4cPW**; (d) **3cPW**.

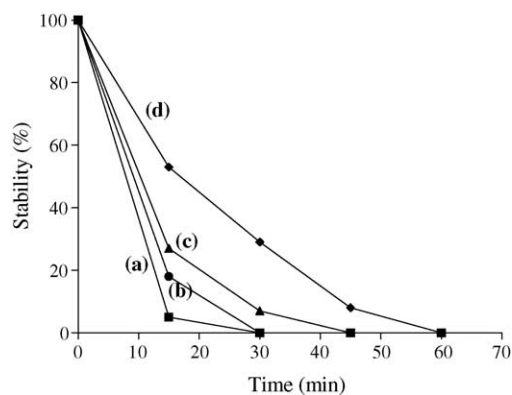


Fig. 5. Stability of Mn<sup>III</sup>porphyrins during the oxidation of *cis*-cyclooctene with H<sub>2</sub>O<sub>2</sub> at 60 °C, using the catalysts: (a) **4c**; (b) **3c**; (c) **4cPW**; (d) **3cPW**. The metalloporphyrin stability was determined by the ratio between the intensities of the Soret band at a certain time and at the beginning of the reaction.

performance from 22 to 60 °C. This may be due to several reasons, including higher solubility of the catalyst at higher temperature, higher stability of the associated metalloporphyrin (allowing its use at 60 °C for a longer period without decomposition) and possible influence of the temperature on the reaction medium.

Porphyrins **3c** and **4c** were devised to combine the high protection due to the bulky electron-withdrawing groups with a positively charged group, allowing the possibility of electrostatic bonding to a polyoxoanion. They were expected to afford better catalytic performances when compared with **1c** and **2c**, as it was experimentally found. The relative reactivity of the non-associated metalloporphyrins (**3c** > **4c**) may be explained by their relative stabilities (Fig. 5) together with the fact that the ionic charges may contribute to deactivate the final oxidant species Mn<sup>V</sup> = O, as referred before [70,71]. It can be observed that **3cPW** is more active than **4cPW**, reflecting the behaviour of the respective metalloporphyrins. It may also happen that the polyoxoanion in **3cPW** displays a more efficient protective effect than in **4cPW**, what may be related to the different type of interactions expected: (–N<sup>+</sup>–H) ···(PW)<sup>3–</sup> versus (–N<sup>+</sup>–CH<sub>3</sub>) ···(PW)<sup>3–</sup>, respectively.

When the association **3cPW** was replaced by **3c** and TBA<sub>3</sub>[PW<sub>12</sub>O<sub>40</sub>] in identical molar quantities, the catalytic performance of this mixture was identical to that of metalloporphyrin **3c** alone (Table 4, entries 1 and 10). Thus, the prepared associations were found to have better catalytic performances than the equivalent mixtures of the used metalloporphyrin and heteropolyanion. This is probably due to the fact that these mixtures have other species in solution that may interfere with any interaction between the porphyrin and the anion (for instance, ion pair formation in acetonitrile). If this happens, the protective effect of the polyoxometalate may be absent or diminished.

An important feature in catalysis is to develop methods for the recovery and the reuse of the catalyst. Some exper-



Table 5  
Oxidation of geraniol with H<sub>2</sub>O<sub>2</sub> catalysed by **3cPW** and **3c**<sup>a</sup>

Entry	Catalyst	Conversion (%) <sup>b</sup>	Selectivity (%) <sup>b</sup>		
			<b>6a</b>	<b>6b</b>	<b>6c</b>
1	<b>3cPW</b>	54	68	19	13
2	<b>3c</b>	16	63	37	0
3	[PW <sub>12</sub> O <sub>40</sub> ] <sup>3-c</sup>	0	–	–	–
4	No catalyst	0	–	–	–

<sup>a</sup> Reaction conditions: temperature 60 °C, substrate:catalyst:co-catalyst = 600:1:390 in acetonitrile (2 ml) and progressive addition of 0.5 equiv. of H<sub>2</sub>O<sub>2</sub> every 15 min, during 1 h. At the end of the reaction, [H<sub>2</sub>O<sub>2</sub>]/[substrate] = 2.

<sup>b</sup> Determined by GC analysis using undecane as the internal standard.

<sup>c</sup> TBA<sub>3</sub>[PW<sub>12</sub>O<sub>40</sub>] and H<sub>3</sub>[PW<sub>12</sub>O<sub>40</sub>]·zH<sub>2</sub>O.

iments were performed with the association **4cPW** using a substrate/catalyst ratio (S/C) equal to 60. In this condition, complete conversion of the substrate was observed and it was possible to perform two other reutilizations of the catalyst with high efficiency (Table 4). In spite of the best conversion obtained, the lower S/C ratio led to lower turnover numbers and to the use of a larger amount of catalyst.

### 3.2.2. Oxidation of geraniol and (+)-3-carene

In view of the results described above, the catalyst that afforded the best results (**3cPW**) were tested in the oxidation of geraniol (Scheme 3) and (+)-3-carene (Scheme 4). In the oxidation of geraniol no other products but the epoxides presented in Scheme 3 were found (Table 5). A much higher percentage of conversion was observed with catalyst **3cPW** (54%) than with porphyrin **3c** (16%). Geraniol was preferably epoxidised at the 6,7-position, as was previously reported with other metalloporphyrins [48]. It is noteworthy that in the reactions catalysed by polyoxometalates alone, the epoxidation of geraniol occurred preferably at the 2,3-position, at room temperature [33,49,50]. In the particular conditions used in this work, TBA<sub>3</sub>[PW<sub>12</sub>O<sub>40</sub>] or H<sub>3</sub>[PW<sub>12</sub>O<sub>40</sub>] did not catalyse the epoxidation of geraniol. However, the large increase on conversion observed when the heteropolyanion is present suggests that the participation of the heteropolyanion cannot be completely ruled out.

Table 6  
Oxidation of (+)-3-carene with H<sub>2</sub>O<sub>2</sub> catalysed by **3cPW** and **3c**<sup>a</sup>

Entry	Catalyst	Conversion (%) <sup>b</sup>	Selectivity (%) <sup>b</sup>			
			<b>7a</b>	<b>7b</b>	<b>7c</b>	<b>7a/7b</b>
1	<b>3cPW</b>	49	42	16	42	2.6
2	<b>3c</b>	26	42	15	43	2.8
3	<b>3cPW</b> <sup>c</sup>	68	41	16	44	2.6
4	[PW <sub>12</sub> O <sub>40</sub> ] <sup>3-d</sup>	0	–	–	–	–
5	No catalyst	0	–	–	–	–

<sup>a</sup> Reaction conditions: temperature 60 °C, substrate:catalyst:co-catalyst = 600:1:390, in acetonitrile (2 ml) and progressive addition of 0.5 equiv. of H<sub>2</sub>O<sub>2</sub> every 15 min, during 1.5 h. At the end of the reaction, [H<sub>2</sub>O<sub>2</sub>]/[substrate] = 3.

<sup>b</sup> Determined by GC analysis using undecane as the internal standard.

<sup>c</sup> Substrate:catalyst:co-catalyst = 300:1:195.

<sup>d</sup> TBA<sub>3</sub>[PW<sub>12</sub>O<sub>40</sub>] and H<sub>3</sub>[PW<sub>12</sub>O<sub>40</sub>]·zH<sub>2</sub>O.

In the case of (+)-3-carene, higher values of conversion were also obtained with catalyst **3cPW** (49%) when compared with the catalyst **3c** (26%). A better percentage of conversion was obtained with **3cPW** at a lower S/C ratio (Table 6). In all cases the product stereo- and chemoselectivities were similar. These results agree with the assumption that in this case the metalloporphyrin is the active catalyst, which is protected from degradation by the polyoxoanions. The oxidation of (+)-3-carene with H<sub>2</sub>O<sub>2</sub> catalysed by other Mn<sup>III</sup> metalloporphyrins led also to the  $\alpha$ -epoxide (**7a**) in high selectivity [48].

## 4. Conclusions

New compounds were prepared by reaction of Keggin-type polyoxometalates with porphyrins and metalloporphyrins bearing appropriate positively charged substituents at the *meso*-positions. The porphyrins used had one or four positive groups (1-methyl-4-pyridinio or pyridyl residues that could protonate in the reaction conditions). Preparative methods were devised for the different polyoxometalate/porphyrin combinations. The obtained salts, with a porphyrin/polyoxometalate stoichiometric ratio of 0.75 or 1, were characterized by different techniques.

The oxidation of *cis*-cyclooctene, geraniol and (+)-3-carene with hydrogen peroxide was examined in the presence of the compounds incorporating Mn<sup>III</sup> porphyrins, using ammonium acetate as the co-catalyst. In the conditions studied, the association **3cPW** showed the best performance, affording (at 60 °C) conversions significantly higher than those obtained with the corresponding porphyrin alone, without significant change in the region-, chemo- and stereoselectivity of the oxidation reactions. The polyoxoanions contributed to the stabilisation of the metalloporphyrin against deactivation during the catalytic cycles, and their effect as catalysts was not clearly observed. For all substrates studied, no reaction was observed in the presence of TBA<sub>3</sub>[PW<sub>12</sub>O<sub>40</sub>] or H<sub>3</sub>[PW<sub>12</sub>O<sub>40</sub>], possibly as consequence of the reaction conditions (slow addition of the oxidant, presence of co-catalyst, comparatively low temperature) noticeably different from those normally used in polyoxometalate catalysis. Due to the useful protective effect of the polyoxometalate on the stability of the porphyrin, the associated metalloporphyrins could be used at a higher temperature than those usually described and the polyoxometalate/metalloporphyrin associations were more efficient catalysts than the correspondent metalloporphyrins alone.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at 10.1016/j.molcata.2004.12.021.

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