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# Spectral and kinetic investigation on oxidation and reduction of water soluble porphyrin-manganese(III) complex

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#### ABSTRACT

In this work the oxidation and reduction reactions of  $Mn^{III}$ –Coproporphyrin-I ( $Mn^{III}$ –CPI) have been studied and four forms of manganese–CPI complexes have been characterized. This complex was observed to be highly reactive (at basic pH) towards Mn(II), hypochlorite, hydrogen peroxide and oxone, forming  $[Mn^{IV}(O)CPI(OH)]^-$  that was unstable and, after a short time, formed again  $[Mn^{III}CPI(OH)_2]^-$ . With an excess of NaClO, a further oxidation of the complex  $[Mn^{IV}(O)CPI(OH)]^-$ , provoked a significant spectral change for the  $[Mn^V(O)CPI(OH)]$  formation that showed, in the time, a partial polymerization.  $[Mn^{III}CPI(OH)_2]^-$  was reduced by sodium dithionite to form the very unstable complex of  $[Mn^{II}CPI(OH)]^-$  that successively degraded with Mn(II) release.

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#### 1. Introduction

The ability of porphyrins to form complexes with numerous metal ions has been the object of many studies [1-5]. Special attention was devoted to manganese, iron and chromium, that are essential metal ions in some biological systems involved in the reactions of electrons transfer. Because the manganese-porphyrin complexes were found to be similar to the biologically active compounds, they have more extensively studied [6-9]. These compounds were also used as catalysts for the oxygenation of alkanes, alkenes and compounds containing nitrogen and sulfur [10-12]. The reactivity of the Mn(III)-porphyrin concerns the changes in the oxidation states of Mn in the complexes for its high reactivity with  $O_2$ . [13]; it is known that this reaction and those with reactive nitrogen, particularly involved in many pathological processes including inflammation, ischemia, hemorrhagic shock, neurological disorders, carcinogenesis and age. The most important properties of manganese in complex biological systems is the flexibility, resulting from highly variable oxidation states of the metal, that can be easily obtained in aqueous solutions. The complexes of manganese - porphyrins are known to have in fact the central metal with formal oxidation number +2, +3, +4, +5 [14]. Manganese, in the complexes obtained by the reaction of Mn(II) with the porphyrins, has oxidation number +3, so the complex of Mn(II) can be obtained only by reduction, while those of Mn(IV) and Mn(V) for the oxidation of Mn(III)-complexes. All these compounds can be easily spectrophotometrically distinguished among them because they have different absorption spectra [15] from which is possible to know the oxidation number of Mn. High valent manganese species with porphyrins, in aqueous solutions, form metal-oxo complexes that are very reactive and several of these species are employed catalytically in synthesis and in the oxygen production [16]. Several oxo-manganese(V) porphyrin complexes have been prepared and characterized by different authors [17–21].

Interest in the reactions of the acid 2,7,12,17 tetrapropionic of 3,8,13,18 tetramethyl-21H, 23H-porphyrin called Coproporphyrin-I (CPI) with manganese in the various oxidation states is motivated by its biological importance because CPI is a product of the metabolism of glutamate together with protoporphyrin IX, Coproporphyrin, uroporphyrin III [22]. Numerous works have been made in our laboratory on the reactions of CPI with different metal ions with the aim to determine the kinetic and equilibrium constants, and the reaction mechanisms [23–26].

In the present work we have studied the oxidation and reduction reactions of manganese(III)–CPI by spectrophotometric measurements in different experimental conditions and in the presence of oxidant and reducing agents, in order to characterize the Mn–CPI complexes in the different oxidation states of the central metal ion; the kinetics of all reactions have been studied and the constant rates of these have been calculated. For better investigate on the reactivity of Mn<sup>III</sup>CPI in neutral and basic pH, the reaction with Mn(II) excess and with several oxidant and reducing agents have been performed.





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### 2. Experimental

#### 2.1. Materials

All chemicals were of analytical-reagent grade and used without further purification. All the solutions were prepared with Milli-Q water. Stock solution of free ligand CPI  $4.18 \times 10^{-4}$ mol dm<sup>-3</sup> was prepared by dissolving 76.1 mg of CPI-dihydrochloride in 500 ml of  $0.61 \times 10^{-4}$  mol dm<sup>-3</sup> sodium hydroxide solution. Stock solutions containing  $1.06 \times 10^{-2}$  mol dm<sup>-3</sup> of Mn(II), were prepared by solving weighted suitable quantities of MnCl<sub>2</sub> in water and standardized by Inductively Coupled Plasma (JY24R).

#### 2.2. Methods

For absorbance measurements, all the reactions have been carried out in the dark because of the photosensitivity of CPI [26] and were studied and monitored, for the required time and at 20 °C, by a Hewlett–Packard 8452A diode array spectrophotometer with a 1-cm quartz cell well-stoppered and connected to Lauda K2R thermostat. A Metrohm 655 pH-meter with a combined electrode (Inlab 413) was used for pH determination.

#### 3. Results and discussion

Aqueous solutions of Mn<sup>III</sup>CPI have been obtained by the reaction of CPI with Mn(II) at neutral pH. The color of the solution changed slowly from pink to deep orange and a great transformation of the CPI spectrum [23] with the formation of five bands has been observed: three more intense, one of which in the UV at 242 nm. two in the Soret band at 366 and 458 nm and two other less intense in the O zone at 542 and 572 nm. Three other small bands at 300, 414 and 800 nm have been observed (Fig. 1). The spectrum obtained showed a d-type hyperporphyrin character and the reason of this remarkable spectral difference [27,28], was attributable to a greater interaction between Mn(III) and porphyrin. Spectra of metal-porphyrin complexes with these characteristics are not common and are generated by the charge transfer of  $\pi$ orbitals of porphyrin into those empty of manganese. In this metal, the electrons 3d are all of fairly high energy and are therefore all used in the bond; for this reason, manganese in this type of complexes takes usually the oxidation state of Mn(III) with high-spin d<sup>4</sup> configuration, as demonstrated by other authors with measures of magnetic susceptibility [29]. Manganese in the complex with the CPI, at neutral pH, was coordinated with two water molecules and is in the form  $[Mn^{III}CPI(H_2O)_2]^+$ , therefore the reaction between the CPI and Mn(II) in aqueous solution could be represented with the equilibrium:

$$CPI + Mn(II) + 2H_2O \xrightarrow{\kappa_1} [Mn^{III}CPI(H_2O)_2]^+$$

The inset of Fig. 1 shows a typical "d-type-hyper" spectrum [28] of  $[Mn^{III}CPI(H_2O)_2]^+$  obtained. In order to clarify the mechanism of the reaction, kinetic studies of the complexation reaction have been carried out measuring the absorbances as a function of time at various wavelengths (Fig. 1). Plotting  $ln([Mn(II)]_t[CPI]_0)$ - $\ln([Mn(II)]_0[CPI]_t)$  versus time t, a good straight line has been obtained, confirming a second order kinetic with respect to reagent concentrations, as previously observed for other CPI-metal complexes [23–26]. The  $k_1$  value obtained from the slope of this straight line was  $10.60 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  slightly lower than that previously obtained at basic pH [23]. In this complex, the two water molecules in the axial position could be deprotonated by pH increase with a corresponding spectral change. The pH change involved only the coordinated water molecules in the complex because the spectrum of porphyrin free base did not change by pH increase: the equilibria are:

$$[\mathbf{Mn}^{\mathrm{III}}\mathbf{CPI}(\mathbf{OH}_2)_2]^+ \stackrel{\kappa_{a1}}{\leftrightarrow} [\mathbf{Mn}^{\mathrm{III}}\mathbf{CPI}(\mathbf{OH}_2)(\mathbf{OH})] + \mathbf{H}^+$$
(1)

$$[Mn^{III}CPI(OH_2)(OH)] \stackrel{\kappa_{a2}}{\leftrightarrow} [Mn^{III}CPI(OH)_2]^- + H^+$$
(2)

Therefore, at pH 7  $[Mn^{III}CPI(H_2O)_2]^+$  was prevalent, while at pH 13,  $[Mn^{III}CPI(OH)_2]^-$  predominated. The loss of one or two protons from  $[Mn^{III}CPI(H_2O)_2]^+$  in the reaction with NaOH, as already observed by other authors for other complexes of this type [30,31], allowed to carry out a spectrophotometric acid – base titration for determining the dissociation constants. The titration was performed in the pH range from 6.77 to 13.36 by adding NaOH to a solution of  $[Mn^{III}CPI(H_2O)_2]^+$  and measuring the absorbance values at 348 and 366 nm after each addition. The gradual decrease, during the titration, of the bands at 366, 458, 542 and 572 nm with the increase of two new bands at 348 and 556 nm has been observed (Fig. 2); simulta-



**Fig. 1.** Time resolved UV–Vis spectrum for the reaction between Mn(II)  $4.56 \times 10^{-5}$  mol dm<sup>-3</sup> with CPI  $1.48 \times 10^{-5}$  mol dm<sup>-3</sup> at 20 °C. The spectra was recorded at 20 min intervals; in inset the final spectrum of the complex [Mn<sup>III</sup>CPI(H<sub>2</sub>O)<sub>2</sub>].



Fig. 2. Spectral change of  $[Mn^{III}CPI(H_2O)_2]^+ 0.75 \times 10^{-5}$  mol dm<sup>-3</sup> in the pH range 6.7–13.4.

neously the solution showed a color change from orange to yellow always more deep. During this titration a well-defined isosbestic point at 353 nm has been observed that was a proof of the presence of only two absorbent species, or that, if in the presence of three species, two of these had similar spectral characteristics; in the inset of Fig. 2 the titration plot is showed.

For the calculation of  $pK_a$ 's, the adsorbance values at pH > 10 have been used. Knowing that  $A_{348} = \varepsilon_{348}[Mn^{III}CPI(OH)_2]^+$  and  $A_{366} = \varepsilon_{366}[Mn^{III}CPI(H_2O)_2]$ , in the point corresponding to the intersection of two curves of Fig. 2,  $A_{348} = A_{366}$ , and therefore  $\varepsilon_{348}[Mn^{III}CPI(OH)_2]^+ = \varepsilon_{366}[Mn^{III}CPI(H_2O)_2]^+$ , that replaced in the Eqs. (1) and (2) gave:

$$K_{a1} \times K_{a2} = \frac{[\mathrm{H}^+]^2 [\mathrm{Mn}^{\mathrm{III}} \mathrm{CPI}(\mathrm{OH})_2]^-}{[\mathrm{Mn}^{\mathrm{III}} \mathrm{CPI}(\mathrm{H}_2\mathrm{O})_2]^+} = \frac{[\mathrm{H}^+]^2 \varepsilon_{366}}{\varepsilon_{348}}$$

From the values of  $\varepsilon_{366} = (7.90 \pm 0.03) \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$  and  $\varepsilon_{348} = (5.46 \pm 0.02) \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$  calculated at pH 7 and 13, respectively, an estimated value of  $(25.60 \pm 0.02)$  for p $K_{a1} + pK_{a2}$  has been obtained. This value was comparable with those of Mn complexes with other porphyrins [32] and depended by the force with which the water molecules was linked to the axial ion central.

#### 3.1. Reactions of Mn<sup>III</sup>CPI with Mn(II)

When an excess of Mn(II) was added to a basic solution (pH > 10.5) of  $[Mn^{III}CPI(OH)_2]^-$ , it has been observed in few minutes that the solution color changed from deep yellow to yellow-green with a corresponding decrease of the absorbance at 366, 458 542 and 572 nm and with the simultaneous formation of new bands at 348, 400, 562 and 610 nm (Fig. 3). After few minutes, the band at 400 nm disappeared and the spectrum of  $[Mn^{III}CPI(OH)_2]^-$  was restored. In anaerobic solutions, obtained under Argon atmosphere, this reaction did not occur and for this reason the band at 400 nm could be attributed to the probable formation of  $[Mn^{IV}(O)CPI(OH)]^-$  derived from the reaction of  $[Mn^{IV} \circ O(OH)_2]$  with the complex. In fact it is well-known that Mn(II) ions, in basic aqueous solution and in the presence of O<sub>2</sub> give rise to the formation of Mn(IV) ions according to the following reaction:

 $2Mn^{2+} + 4OH^- + O_2 \iff 2Mn^{IV}O(OH)_2$ 

The excess of  $Mn^{IV}O(OH)_2$  promoted the formation of the complex  $[Mn^{IV}(O)CPI(OH)]^-$  through the reaction:

$$\begin{split} &Mn^{IV}(O)(OH)_2 + [Mn^{III}CPI(OH)]^- \\ &\stackrel{k_2}{\rightarrow} [Mn^{IV}(O)CPI(OH)]^- + Mn^{3+} + 2OH^- \end{split}$$

The complexes of Mn(IV) with several porphyrins are known to have a short lifetime and decayed back to reform  $[Mn^{III}CPI(OH)_2]^-$ [33]. In order to clarify the mechanism of this reaction, kinetic studies of this reaction have been carried out measuring the absorbance changes as a function of time at various wavelengths (Fig. 3). Plotting  $ln([Mn^{III}CPI(OH)_2]_t[Mn^{IV}CPI(O)(OH)]_0)-ln([Mn^{III}$  $CPI(OH)_2]_0 [Mn^{IV}CPI(O)(OH)]_t) versus$ *t*, a good straight line hasbeen obtained, confirming a second order kinetic with respect to $reagent concentrations. The <math>k_2$  value obtained from the slope of this straight line was 15.28 dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>.

## 3.2. Reactions of Mn<sup>III</sup>CPI with oxone

Oxone (potassium peroxy mono persulfate) is one of the most powerful oxidants available, is stable in the pH range from 1 to 7 showing only a very slow hydrolysis to form hydrogen peroxide, while, in basic solution, the product of decomposition is  $O_2$ . At neutral pH,  $[Mn^{III}CPI(H_2O)_2]^+$  reacted only in the excess of oxone with a fast disappearance of the spectrum for likely decomposition of the complex. At basic pH, the same reaction showed an initial spectral variation, involving a slow decrease of the absorbance at 366, 458 542 and 572 of the complex with the simultaneous formation of three new bands at 348, 400, 502 and 610 nm (Fig. 4) corresponding to the formation of  $[Mn^{IV}(O)CPI(OH)]^-$  as in the reaction with Mn(II) above described.

In this case the reaction occurred because oxone in the basic solutions released molecular  $O_2$  removing two electrons from the metal porphyrin. Under these conditions, these two reactions occurred:

$$2[\mathrm{Mn^{III}CPI}(\mathrm{OH})_2]^- + \mathrm{OH}^- \rightarrow [\mathrm{Mn^{IV}}(\mathrm{O})\mathrm{CPI}(\mathrm{OH})]^- + e^- + \mathrm{H}_2\mathrm{O}$$

$$1/2O_2 + 2e^- + H_2O \rightarrow 2OH^-$$

That summed give:

 $[Mn^{III}CPI(OH)_2]^- + 1/2O_2 \xrightarrow{K_3} 2[Mn^{IV}(O)CPI(OH)]^- + H_2O$ 

Successively the decrease of the spectrum obtained for likely oxidative degradation of  $[Mn^{IV}(O)CPI(OH)]^-$  has been observed. In order to explain the kinetic mechanism of the formation of various species during the reaction, the absorbance changes as a function of



Fig. 3. Time resolved UV–Vis spectrum for the reaction at basic pH between Mn(II) 4.44 × 10<sup>-5</sup> mol dm<sup>-3</sup> and  $[Mn^{II}CPI(OH)_2]^-$  1.48 × 10<sup>-5</sup> mol dm<sup>-3</sup> at 20 °C; the spectra was recorded at 30 s intervals.



**Fig. 4.** Time resolved UV–Vis spectrum for the reaction between oxone and  $[Mn^{III}CPI(OH)_2]^-$  1.48 × 10<sup>-5</sup> mol dm<sup>-3</sup> at 20 °C. The spectra was recorded at 30 s intervals; in inset the final spectrum of the complex  $[Mn^{IV}(O)CPI(OH)]^-$ .

time at various wavelengths, were measured. Plotting  $ln([Mn^{III} CPI(OH)_2]_t[O_2]_0)-ln([Mn^{III} CPI(OH)_2]_0[O_2]_t)$  as a function of time *t*, a good straight line has been obtained, confirming a second order kinetic with respect to reagent concentrations. The  $k_3$  value obtained from the slope of this straight line was 229.36 dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>.

#### 3.3. Reactions of $Mn^{III}CPI$ with $H_2O_2$

In the reaction of  $[Mn^{III}CPI(H_2O)_2]^+$  with  $H_2O_2$ , at neutral pH, no spectral change was observed. The same reaction conducted at basic pH in the stoichiometric ratio, initially caused the decrease of the absorbances at 366, 458, 542 and 572 of  $[Mn^{III}CPI(OH)_2]^-$  with the simultaneous formation of the characteristic bands of  $[Mn^{IV}(O)CPI(OH)]^-$  (as previously observed in the reactions with Mn(II) and oxone) that was instable and decayed back to  $[Mn^{III}CPI(OH)_2]^-$  (Fig. 5). The formation of  $[Mn^{IV}(O)CPI(OH)]^-$  occurred because  $H_2O_2$  at basic pH decomposes into  $H_2O$  and molec-

ular O<sub>2</sub>.Kinetic studies of this reaction have been carried out measuring the absorbance changes as a function of time at various wavelengths. Plotting  $\ln([Mn^{III}CPI(OH)_2]_t[O_2]_0)-\ln([Mn^{III}CPI$  $(OH)_2]_0[O_2]_t)$  as a function of time *t*, a good straight line has been obtained, confirming a second order kinetic with respect to reagent concentrations. The  $k_4$  value obtained from the slope of this straight line was 155.34 dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>. The same reaction conducted with an excess of H<sub>2</sub>O<sub>2</sub> led, after the formation of [Mn<sup>IV</sup>(O)CPI(OH)]<sup>-</sup>, to the final disappearance of all bands for likely oxidation of porphyrin ring.

#### 3.4. Reactions of Mn<sup>III</sup>CPI with hypochlorite

In the reaction of  $[Mn^{II}CPI(H_2O)_2]^+$  with NaClO at neutral pH, the decrease of all bands of the spectrum, for likely oxidative transformation of porphyrin ring, has been observed. The same reaction conducted at basic pH, with NaClO in stoichiometric ratio, caused a



Fig. 5. Time resolved UV–Vis spectrum for the reaction at basic pH between  $H_2O_2$  and  $[Mn^{III}CPI(OH)_2]^- 1.48 \times 10^{-5}$  mol dm<sup>-3</sup> at 20 °C. The spectra was recorded at 30 s intervals.

spectral change corresponding to the  $[Mn^{IV}(O)CPI(OH)]^-$  formation that slowly reverted to  $[Mn^{III}CPI(OH)_2]^-$  (Fig. 6). The semireactions in this case were:

 $[Mn^{III}CPI(OH)_2]^- + OH^- \rightarrow [Mn^{IV}(O)CPI(OH)]^- + e^- + H_2O$ 

 $CIO^- + H_2O + 2e^- \rightarrow Cl^- + 2OH^-$ 

The overall reaction was:

$$2[Mn^{III}CPI(OH)_2]^- + CIO^- \rightarrow 2[Mn^{IV}(O)CPI(OH)]^- + CI^- + H_2O$$

Also in this case this reaction showed a second order kinetic with respect to the reagent concentrations: in fact, plotting  $ln([Mn^{III}CPI(OH)_2]_t[CIO^-]_0)-ln([Mn^{III}CPI(OH)_2]_0[CIO^-]_t)$ , as a function of time *t*, a good straight line has been obtained the slope of which represented the  $k_5$  value of 148.29 dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>. The same reaction conducted in the excess of reagent, initially caused the formation of  $[Mn^{IV}(O)CPI(OH)_{-}]_{-}$ , that after at least 12 h evolved, with a

spectral change (inset of Fig. 6), forming a band at 384 nm with lower absorbance and two weaker bands in the area Q, respectively, at 526 ( $\beta$  band) and 562 nm ( $\alpha$  band) [28]. The obtained compound was very stable and its spectrum is typical of a porphyrin metal complex. The low and large absorption band in the Soret region is characteristic of an aggregate form, while the bands in the Q zone confirmed that the complex obtained is very stable because  $\alpha$  band is greater than  $\beta$  [28]. For these reasons it has been hypothesized that this behavior corresponded to a complex obtained for the further oxidation of Mn(IV) into Mn(V) through the reactions:

$$[\mathrm{Mn}^{\mathrm{IV}}(\mathrm{O})\mathrm{CPI}(\mathrm{OH})]^{-} \to [\mathrm{Mn}^{\mathrm{V}}(\mathrm{O})\mathrm{CPI}(\mathrm{OH})] + e^{-}$$

$$CIO^- + H_2O + 2e^- \rightarrow Cl^- + 2OH^-$$

that summed:



Fig. 6. Time resolved UV–Vis spectrum for the reaction at basic pH between NaClO and  $[Mn^{III}CPI(OH)_2]^- 1.48 \times 10^{-5}$  mol dm<sup>-3</sup> at 20 °C. The spectra was recorded at 30 s intervals; in inset the final spectrum of the complex  $[Mn^V(O)CPI(OH)]$ .

$$\begin{split} &2[Mn^{IV}(O)CPI(OH)]^- + CIO^- + H_2O \\ &\rightarrow 2[Mn^V(O)CPI(OH)] + CI^- + 2OH^- \end{split}$$

The complex [Mn<sup>V</sup>(O)CPI(OH)], having neutral character, showed easily an arrangement into aggregate form. In fact, slowly, part of the complex polymerized with formation of a precipitate that was instable in strongly acidic solution likewise to other Mn<sup>V</sup>–porphyrin complexes [17–21]. The kinetic of this reaction was of second order with respect to reagent concentrations, the  $k_6$  value obtained was 6.88 dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>.

#### 3.5. Reactions of Mn<sup>III</sup>CPI with dithionite

In the reaction of  $[Mn^{III}CPI(H_2O)_2]$ , at neutral pH, with an excess of Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>, the decrease of the complex bands due to the demetallation with the formation the dimeric form of CPI has been observed. It is probable that Mn(III) in the complex was reduced to Mn(II) that leaving the porphyrin core, restored CPI, that, in the presence of Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>, dimerized for the salt effect. The same reaction conducted at basic pH, caused the formation of  $[Mn^{II}CPIOH]^$ with a spectral variation involving a slow decrease of the absorbance at 348 nm, the simultaneous formation of a new band at 414 nm and two bands of lower intensity at 544 ( $\beta$  band) and 574 nm ( $\alpha$  band) (Fig. 7). The obtained spectrum successively decreased up to the complete disappearance, for probable decomposition of  $[Mn^{II}CPIOH]^-$  without release of CPI free ligand.

$$\begin{split} 2[Mn^{III}CPI(OH)_2]^- + S_2O_4^{2-} &\rightarrow 2[Mn^{II}CPIOH]^- + 2HSO_3^- \\ & [Mn^{II}CPIOH]^- &\rightarrow decomposition \end{split}$$

Also in this case the reaction of  $[Mn^{II}CPIOH]^-$  formation was of the second order respect to reagent concentrations, in fact, plotting  $ln([Mn^{III}CPI(OH)_2]_t[S_2O_4^{-}]_0)-ln([Mn^{III}CPI(OH)_2]_0[S_2O_4^{-}]_t)$  as a function of time *t*, a good straight line has been obtained the slope of which represented the  $k_7$  value of 55.23 dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>.

In the Fig. 8 is showed a summary of all the complexes obtained in the reaction of  $[Mn^{III}CPI(OH)_2]^-$  with several reagents in different conditions while in Tables 1 and 2 are reported all spectral characteristics and kinetic constants.



Fig. 8. Summary of all studied Mn-CPI complexes.

 Table 1

 Summary of the spectral characteristics of Mn-CPI complexes.

Complex	Soret band $\lambda$ (nm)	Q band ( $\beta$ , $\alpha$ ) $\lambda$ (nm)
[Mn <sup>II</sup> CPIOH] <sup>-</sup>	414	544, 574
$[Mn^{III}CPI(H_2O)_2]^+$	366, 458	542, 572
$[Mn^{III}CPI(OH)_2]^-$	348, 458	556
[Mn <sup>IV</sup> OCPI(OH)] <sup>-</sup>	400	502, 610
[Mn <sup>V</sup> OCPI(OH)]	384	526, 562

#### 4. Conclusions

The studies reported in this work have highlighted that manganese in the CPI complexes can assume four oxidation degrees by oxidation or reduction of the central metal ion in the complex [Mn<sup>III</sup>CPI(OH)<sub>2</sub>]<sup>-</sup>. All the results indicated that this complex reacted with oxone, hydrogen peroxide and hypochlorite forming [Mn<sup>IV</sup>OCPI(OH)]<sup>-</sup> with kinetic constants of the second order respect to reagent concentrations and with comparable values



**Fig. 7.** Time resolved UV–Vis spectrum for the reaction at basic pH between  $Na_2S_2O_4$  with  $[Mn^{III}CPI(OH)_2]^- 1.48 \times 10^{-5}$  mol dm<sup>-3</sup> at 20 °C. The spectra was recorded at 30 s intervals; in inset the final spectrum of the complex  $[Mn^{II}CPIOH]^-$ .

Table 2			
Second order rate	constants	for Mn-CPI	complexes.

- • • •

Reagents		Product	$k (\mathrm{dm^3}\;\mathrm{mol^{-1}}\;\mathrm{s^{-1}})$
Mn(II) [Mn <sup>III</sup> CPI(OH) <sub>2</sub> ] <sup>-</sup> [Mn <sup>III</sup> CPI(OH) <sub>2</sub> ] <sup>-</sup>	CPI Mn(II) oxone H <sub>2</sub> O <sub>2</sub> NaCIO NaCIO excess	$ \begin{array}{l} [Mn^{III}CPI(H_2O)_2]^* \\ [Mn^{IV}OCPI(OH)]^- \\ [Mn^{IV}OCPI(OH)]^- \\ [Mn^{IV}OCPI(OH)]^- \\ [Mn^{IV}OCPI(OH)]^- \\ [Mn^{V}OCPI(OH)] \end{array} $	$10.60 \pm 0.04 \\ 15.28 \pm 0.08 \\ 229.36 \pm 0.13 \\ 155.34 \pm 0.11 \\ 148.29 \pm 0.11 \\ 6.88 \pm 0.02$
$[Mn^{III}CPI(OH)_2]^-$	$Na_2S_2O_4$	[Mn <sup>II</sup> CPIOH] <sup>-</sup>	55.23 ± 0.05

The first reaction has been carried out at neutral pH, while all others at pH 10.5.

decreasing in the order: oxone, hydrogen peroxide and hypochlorite relatively to their oxidation powers. With Mn(II), the same reaction was about 10 times slower because this was a displacement reaction of Mn(III) with Mn(IV) formed from Mn(II) in alkaline solution. Further oxidation has been obtained only with an excess of hypochlorite for the probable formation of the complex [Mn<sup>V</sup>OCPI(OH)] and presented a kinetic constant value of about 20–30 times lower respect to oxidation reaction. This complex was very stable, uncharged and for this reason, in the time slowly polymerized forming a precipitate.

The reduction reaction of  $[Mn^{II}CPI(OH)_2]^-$  with dithionite gave the formation  $[Mn^{II}CPIOH]^-$  that showed a kinetic constant of the second order respect to reagent concentrations, lower respect to the oxidation reactions; this complex was very instable and successively degraded with Mn(II) release. The spectral characteristics have confirmed the different stabilities of the obtained complexes decreasing in the order:  $[Mn^{V}(O)CPI(OH)] > [Mn^{II}CPI(H_2O)_2]^+ \approx$  $[Mn^{II}CPI(OH)_2]^- > [Mn^{IV}(O)CPI(OH)]^- > [Mn^{II}CPI(OH)]^-.$ 

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