Polyhedron 29 (2010) 1001–1006

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Peroxidase activity of dimanganese(III) complexes with the $[Mn_2(\mu\text{-}OAc)(\mu\text{-}OR)_2]^{3+}$ core

Hernán Biava, Sandra Signorella *

Instituto de Química Rosario – CONICET, Universidad Nacional de Rosario, Suipacha 531, S2002LRK Rosario, Argentina

ARTICLE INFO

Article history:
Received 20 October 2009
Accepted 2 December 2009
Available online 11 December 2009

Keywords:
Phenols oxidation
Dimanganese complexes
Lignin oxidation
Pulp beaching

ABSTRACT

Catalytic activity of three dinuclear Mn^{III} complexes of general formula $[Mn_2(\mu\text{-}OAc)(\mu\text{-}OMe)(L)]BPh_4$ (H_3L = 1,5-bis[(2-hydroxy-5-X-benzyl)(2-pyridylmethyl)amino] pentan-3-ol, **1**: X = H, **2**: X = OMe, **3**: X = Br) in the oxidation of phenol, 2,6-dimethoxyphenol and wood pulp by H_2O_2 has been investigated. The role of pH, electronic properties of the ligand and metal coordination environment on the ability of these complexes to activate H_2O_2 has been examined. The three catalysts showed similar activity independently of the aromatic substituent in the ligand and were found to be 2–3 times more active at pH 9.00 than at neutral pH. Bleaching of Kraft pulp by H_2O_2 activated by **1** in alkaline media decreased the kappa number of the pulp by 16%, at room temperature and low catalyst concentration, without damage of cellulose fibers. It was found that the exchange of the methoxo- and acetato-bridges by an oxo-bridge reduces the catalytic activity of these compounds, probably by direct binding of phenolate to a vacant site on the metal center.

1. Introduction

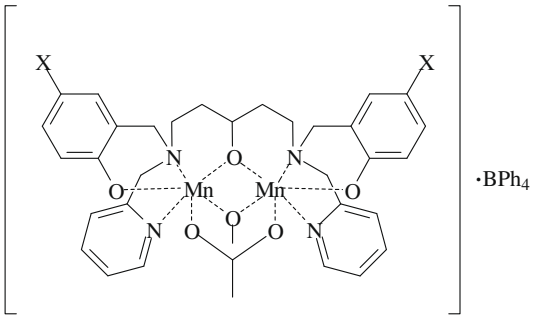
The oxidative degradation of lignin from wood pulp is a crucial step for paper manufacturing, which is usually referred as "pulp bleaching". Traditionally, this process has been accomplished by employing chlorine-based bleaches, but the generation of chlorinated organic pollutants as byproducts has led to develop alternative oxygen-based bleaching sequences that employ dioxygen, ozone or hydrogen peroxide [1].

Alkaline-H_2O_2 bleaching has been applied for large scale removal of lignin; however, it presents limited delignification capability [2,3]. For this reason, a number of activators (enzymes and metal complexes) have been tested to enhance the bleaching efficiency of H_2O_2; but due to cellulose degradation, catalyst instability and high costs, this field remains open to continuous research [2,4].

In nature, microorganisms such as *Phanerochaete chrysosporium* can oxidize lignin by means of a manganese peroxidase which catalyzes lignin oxidation by H_2O_2 [5]. A biomimetic approach to lignin degradation has shown that dimanganese complexes are good candidates to replace the enzyme [6]. Dimanganese complexes derived from 1,4,7-triazacyclononane (tacn) and its substituted derivatives [7–13], 1,2-bis(4,7-dimethyl-1,4,7-triazacyclonon-1-yl)ethane (dtne) [7–9,11–14] and tris(2-methylpyridyl)amine (tpa) ligands [15] have proven to be H_2O_2 activators in delignification chemistry. These catalysts possess different bridging motifs: $Mn(\mu\text{-}O)_3Mn^{2+/+}$, $Mn(\mu\text{-}O)_2Mn^{3+}$, $Mn(\mu\text{-}OAc)_2(\mu\text{-}O)Mn^{2+}$ or $Mn(\mu\text{-}O)_2(\mu\text{-}OAc)Mn^{2+}$, and their ability to catalyze the H_2O_2-based oxidation of lignin depends strongly on the reaction conditions (temperature, pH, H_2O_2 and catalyst concentration) and Mn oxidation states [6]. However, little is known about the role of the bridging-ligands on the catalytic activity or the structural and electronic features of the dimetal core that are responsible for the delignification activity. Examination of dimanganese complexes that possess other bridging motifs as catalysts in H_2O_2-based oxidation of phenolic compounds, can contribute to the future outline of the structural requirements that are essential for catalytic delignification activity. We report here the ability of three dimanganese complexes containing the $Mn(\mu\text{-}OR)_2(\mu\text{-}OAc)Mn^{3+}$ core, $[Mn_2L^{1-3}(\mu\text{-}OAc)(\mu\text{-}OR)]BPh_4$ (**1**–**3**), obtained with the heptadentate ligands 1,5-bis[(2-hydroxy-5-X-benzyl)(2-pyridylmethyl)amino]pentan-3-ol (L^1H_3: X = H, L^2H_3: X = OMe, L^3H_3: X = Br) [16], to catalyze the oxidation of two lignin models: phenol and 2,6-dimethoxyphenol with H_2O_2. Further, the pulp bleaching capability of complex **1** was examined and compared to that of complexes with the same triply bridged diMn core but with two labile coordination sites (one on each Mn ion), in order to gain insights on the structural factors affecting the peroxidase-like activity of this class of complexes.

* Corresponding author. Tel./fax: +54 341 4350214.
E-mail address: signorel@infovia.com.ar (S. Signorella).

0277-5387/$ - see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.poly.2009.12.004



1: X = H; **2**: X = OMe; **3**: X = Br

2. Experimental

2.1. Materials

Eucalyptus grandis Kraft pulp was supplied by Celulosa Argentina S.A. Phenol stock solution (55 mM) was purchased from Wiener Lab. Whatman cellulose medium fibers CF11 were employed in viscosity determination. All other reagents were purchased from Aldrich and used without further purification. Solvents were purified by standard methods. The concentration of H_2O_2 stock solution was determined by iodometric titration. Phosphate (pH 7.00) and borate (pH 9.00) buffer solutions were prepared by partial neutralization of $NaH_2PO_4{\cdot}2H_2O$ or $Na_2B_4O_7{\cdot}10H_2O$ with concentrated HCl or NaOH in deionized water. Synthesis of complexes **1**–**3** was carried out as previously described [16].

2.2. Methods

2.2.1. Physical measurements

Electronic spectra were recorded with a JASCO V550 spectrophotometer with thermostated cells. IR spectra were recorded with a Perkin–Elmer Spectrum One FT-IR spectrophotometer on CsI pellets. ESI-mass spectra were recorded with a Perkin–Elmer SCIEX 365 LCMSMS mass spectrometer at a flow rate of 5 μL min^{-1}.

2.2.2. General procedure for phenol oxidation

The H_2O_2-based oxidation of phenol catalyzed by complexes **1**–**3** in the presence of excess of 4-aminoantipyrine (4-AAP), at 25 °C, was monitored spectrophotometrically by following the absorbance increase at 505 nm due to the formation of the quinoneimide adduct [17,18]. In a typical procedure, 10 μL of a 1.0 M solution of H_2O_2 in acetone were added to 2.5 mL of an aqueous buffered solution (pH 7 or 9) containing 0.0008 mmol of phenol and 0.00204 mmol of 4-AAP. The reaction was initiated by addition of 0.5 mL of a 0.016 mM solution of the catalyst in acetonitrile and left to react for 2 h. Reactant concentrations in the mixture were: [phenol] = 0.26 mM, [4-AAP] = 0.68 mM, [H_2O_2] = 3.3 mM, [catalyst] = 2.6 μM. Blank experiments without addition of catalyst did not show increase of absorbance at 505 nm. The molar absorbance coefficient of the product at 505 nm was determined by complete oxidation of phenol with horseradish peroxidase enzyme (200 UI/mL) under the same reaction conditions [19]. Found values were $\varepsilon = 7040\ M^{-1}\ cm^{-1}$ (pH 9.00) and $\varepsilon = 5940\ M^{-1}\ cm^{-1}$ (pH 7.00). The turnover number (t.o.n.) after 2 h of reaction was determined by applying Eq. (1).

$$\text{t.o.n.} = \text{Abs}_{505\text{nm,2h}} \times \left\{\varepsilon(M^{-1}\ cm^{-1})1\ (\text{cm})\ [\text{catalyst}]\ (M)\right\}^{-1} \quad (1)$$

2.2.3. General procedure for 2,6-dimethoxyphenol oxidation

The H_2O_2-based oxidation of 2,6-dimethoxyphenol catalyzed by complexes **1**–**3**, at 25 °C, was monitored spectrophotometrically by following the absorbance increase at 470 nm due to the formation of 3,3′,5,5′-tetramethoxydiphenoquinone [20–22]. In a typical procedure, 10 μL of a 1.0 M solution of H_2O_2 in acetone were added to 2.5 mL of an aqueous buffered solution (pH 7.00) containing 0.0026 mmol of 2,6-dimethoxyphenol. The reaction was initiated by addition of 0.5 mL of a 0.03 mM solution of catalyst in acetonitrile and left to react for 2 h. Reactant concentrations in the mixture were: [2,6-dimethoxyphenol] = 0.86 mM, [H_2O_2] = 3.3 mM, [catalyst] = 5.0 μM. Blank experiments without addition of catalyst did not show increase of absorbance at 470 nm over 2 h. The molar absorbance coefficient of the reaction product was determined from commercial 3,3′,5,5′-tetramethoxydiphenoquinone under the reaction conditions. The value found at pH 7 was $\varepsilon = 6645\ M^{-1}\ cm^{-1}$. The turnover number after 2 h of reaction was calculated by applying Eq. (2).

$$\text{t.o.n.} = \text{Abs}_{470\text{nm,2h}} \times 2(\text{phenol/quinone}) \times \left\{\varepsilon(M^{-1}\ cm^{-1})\ 1\ (\text{cm})\ [\text{catalyst}]\ (M)\right\}^{-1}. \quad (2)$$

2.2.4. Pulp bleaching experiments

Bleaching experiments were performed in a 250 mL glass vessel with continuous stirring. Kraft pulp (0.7 g) was dispersed in 90 mL of aqueous buffer of pH 9.00. Then, 0.05 mL of 10 M H_2O_2 was added, followed by addition of 10 mL of a 0.001 M solution of complex **1** in acetonitrile. The reaction was left with mechanical stirring for 2 h, at room temperature. The pulp was filtered and successively washed with acetonitrile (3 × 10 mL) and deionized water (3 × 10 mL), and dried at 105 °C. Finally, the kappa number of the treated pulp was determined.

2.2.5. Catalyzed lignin oxidation

A sample of 0.1 g of alkali lignin was dispersed in 90 mL of aqueous buffer solution (pH 9.00). Then, 0.05 mL of 10 M H_2O_2 was added, followed by addition of 10 mL of a 0.001 M solution of complex **1** in acetonitrile. The mixture was left to stir at room temperature for 30 min. The mixture was filtered, washed with acetonitrile (3 × 10 mL) and deionized water (3 × 10 mL), and then dried at 105 °C. The FT-IR spectrum of the solid was recorded and compared to those of untreated lignin and H_2O_2-treated lignin without addition of catalyst.

2.2.6. Cellulose treatment

Cellulose fibers (1.50 g) were dispersed in 180 mL of aqueous buffer of pH 9.00. Then, 0.1 mL of 10 M H_2O_2 was added, followed by addition of 20 mL of a 0.001 M solution of complex **1** in acetonitrile. The reaction was left with mechanical stirring for 2 h, at room temperature. Cellulose was filtered, washed with acetonitrile (3 × 10 mL) and deionized water (3 × 10 mL), and dried at 105 °C. From this sample, a series of solutions of increasing concentration were prepared in CuEn (copper ethylenediamine solution) as solvent and kept under nitrogen atmosphere for viscosity determinations. The obtained average degree of polymerization (DP) was compared to that of untreated cellulose.

2.2.7. Determination of kappa number of pulp and cellulose viscosity

The kappa number of pulp was determined according to international procedures [23]. Intrinsic cellulose viscosity (η_i) was measured viscosimetrically in CuEn 0.5 M [24], and the obtained intrinsic viscosities were converted into the respective values of DP by applying the Staudinger equation $[\eta_i] = 8.07 \times 10^{-3}$ (DP) [25].

3. Results and discussion

3.1. Phenol oxidation with H_2O_2 catalyzed by complexes **1**–**3**

Co-oxidation of phenol with H_2O_2 in the presence of 4-APP catalyzed by peroxidases has been widely used in the analysis of biological samples [26,27], phenols quantification [28,29] and phenols oxidative removal [17]. We employed this method to evaluate the capability of complexes **1**–**3** to activate H_2O_2, replacing peroxidase by one of these complexes. Essays were performed using the catalyst dissolved in acetonitrile, MeOH, acetone, DMF or H_2O, and the best results were obtained when the catalyst was dissolved in acetonitrile. It has been previously shown that complexes **1**–**3** catalyze H_2O_2 disproportionation (catalase-like activity) in non-protic solvents. However, this activity is very low in protic solvents [16]. In the media used in this work to evaluate the peroxidase activity of complexes **1**–**3**, the proportion of water was high and the competitive H_2O_2 disproportionation was minimal. Additionally, H_2O_2 solutions were prepared in acetone where the formation of 2-hydroxy-2-hydroperoxypropane stimulates gradual availability of the oxidant, avoiding its decomposition [30,31]. In the absence of metal complex, the mixture of phenol, 4-APP and H_2O_2 did not show any color development, even after 24 h. However, when complexes **1**–**3** were added, an increment of the absorbance at 505 nm was observed, providing a clear indication that these complexes catalyze phenol oxidation. Sequential spectra registered during the reaction catalyzed by **1** at pH 7.00, are shown in Fig. 1.

It has been reported that the redox potential (E) of complexes **1**–**3** increases with the electron withdrawing ability of the substituent on the phenolato arms, resulting in ΔE of 160 mV from **2** (X = OMe) to **3** (X = Br) [16]. However, the similar kinetic profiles observed for phenol oxidation with H_2O_2 catalyzed by the three complexes (Fig. 2) indicate that the nature of the aromatic substituent on the ligand has little influence on activity. This result suggests that catalysis is not critically dependent of the redox potential of the $diMn^{III}$ center.

The performance of these catalysts (in terms of t.o.n., Fig. 3) is comparable to that reported for the oxidation of phenol with H_2O_2 catalyzed by Mn tetrasulfophtalocyanines (t.o.n. = 8), Cu tetraazamacrocycle (t.o.n. = 27) and Mn Schiff base (t.o.n. = 15) complexes, in aqueous solution [17,32,33].

3.2. Effect of pH

Stability of the catalyst in alkaline aqueous media is one of the main challenges to be overcome by catalysts suitable for pulp bleaching. Therefore, we performed phenol oxidation assays at different pH. Catalysts **1**–**3** showed activity and did not decompose in the 7.00–9.00 pH range, such as revealed by the ESI-mass spectra. At pH >10, a rapid inactivation was observed concomitantly with the formation of a precipitate, probably indicating catalyst decomposition. At pH <7.00, these complexes were not active.

The kinetic profiles of the H_2O_2-based phenol oxidation catalyzed by complexes **1**–**3**, at pH 9, are shown in Fig. 3. Again, at this pH, all the three complexes show similar reactivity, with little influence of the substituent on the reaction rate. A comparison of the catalytic efficiency at pH 7.00 and 9.00, shows that the reactivity of these complexes is 2–3 times higher in alkaline medium than at neutral pH. Since at both pH values, the protonated form of phenol is predominant ($pK_{a\ phenol}$ = 9.9) [34], reactivity enhancement cannot be attributed to a higher phenolate concentration, but, possibly, to a higher concentration of hydroperoxide anion (HOO^-), which has previously been proposed to be the active form of the oxidant [2].

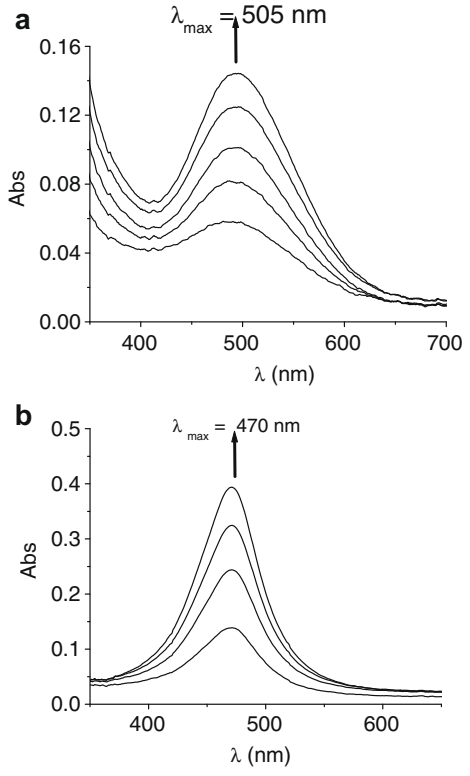


Fig. 1. Electronic spectra taken during H_2O_2 oxidation of phenol (a) and 2,6-dimethoxyphenol (b) catalyzed by **1**, at pH 7.00. Conditions: (a) [phenol] = 0.26 mM, [4-APP] = 0.68 mM, [H_2O_2] = 3.3 mM, [**1**] = 0.0026 mM. (b) [2,6-Dimethoxyphenol] = 0.85 mM, [H_2O_2] = 3.3 mM, [**1**] = 0.005 mM.

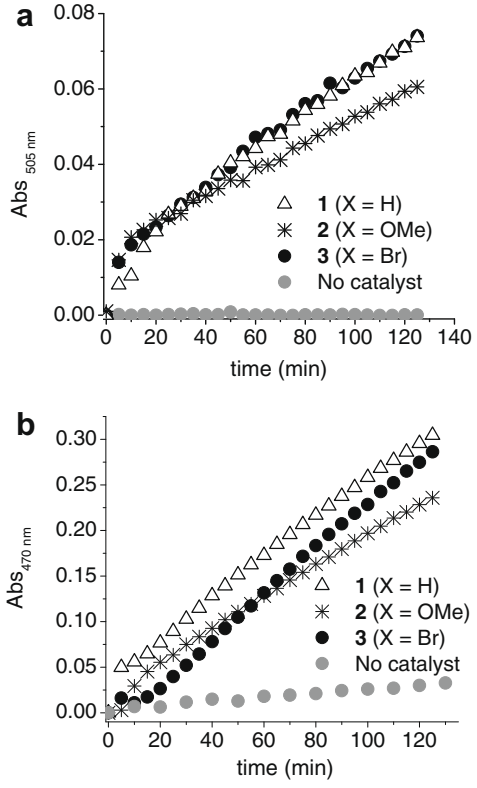


Fig. 2. Time course for product formation in the oxidation of phenol and 2,6-dimethoxyphenol by H_2O_2 catalyzed by complexes **1**–**3**, at pH 7.00. (a) [Phenol] = 0.26 mM, [4-AAP] = 0.68 mM, [H_2O_2] = 3.3 mM, [catalyst] = 0.0026 mM. (b) [2,6-Dimethoxyphenol] = 0.85 mM, [H_2O_2] = 3.3 mM, [catalyst] = 0.005 mM.

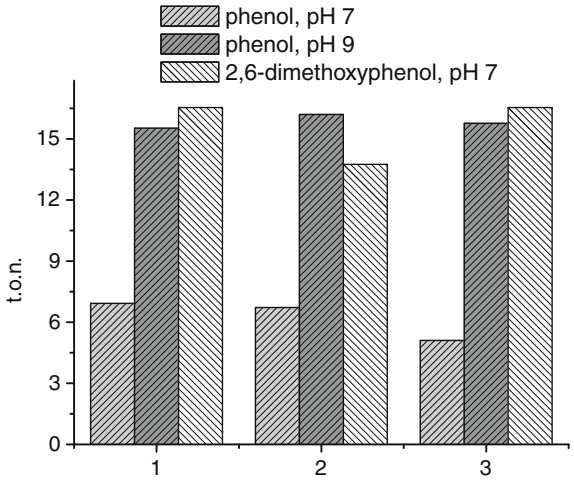


Fig. 3. Catalytic oxidation of phenol and 2,6-dimethoxyphenol by **1**–**3**. Conditions as described in Section 2. Reaction time = 2 h.

3.3. 2,6-Dimethoxyphenol oxidation with H_2O_2 catalyzed by complexes **1–3**

In order to evaluate the ability of complexes **1**–**3** to catalyze the oxidation of substituted phenol by H_2O_2, we investigated the oxidation of 2,6-dimethoxyphenol as a model of the guaiacol/syringol residues of lignin. In this reaction, the oxidation product, 3,3′,5,5′-tetramethoxydiphenoquinone, could be followed spectrophotometrically by monitoring the absorption growth at 470 nm. In the absence of catalyst, no increase of absorbance was observed, even after 24 h. Nonetheless, after addition of complexes **1**–**3**, the color of the solution rapidly intensified concomitantly with the growth of the absorption band at 470 nm, indicating the oxidation of 2,6-dimethoxyphenol (Fig. 1b). Also in this case, comparable kinetic profiles were obtained with the three catalysts, showing little influence of the phenol-substituent of the ligand on the catalytic activity (Fig. 2b). The rapid non-selective aerobic oxidation of 2,6-dimethoxyphenol at pH $\geqslant$9 disabled the evaluation of the influence of the basic medium on the H_2O_2-based oxidation.

Comparison of H_2O_2 oxidation of phenol and 2,6-dimethoxyphenol catalyzed by complexes **1**–**3**, under the same reaction conditions (pH 7.00, for 2 h, Fig. 3), proved that these complexes are better to catalyze the oxidation of the *o*-disubstituted phenol. This observation means that the reaction is not controlled by steric factors; rather, the higher conversion observed for the substituted phenol should result from the fact that it is oxidized easier than phenol as a consequence of the electron-donating effect of the methoxy groups [35].

3.4. Pulp bleaching

Given the ability shown by complexes **1**–**3** to catalyze oxidation of phenol and 2,6-dimethoxyphenol by H_2O_2, we decided to evaluate their ability to activate H_2O_2 in wood pulp bleaching experiments. Owing to the similar reactivity profiles of the oxidation of phenols with H_2O_2 catalyzed by the three complexes, these experiments were performed only with complex **1**.

The pulp bleaching ability of **1** was evaluated by determining the kappa number. Kappa number is the parameter used to measure the degree of delignification obtained in a bleaching process, and is defined as the number of milliliters of 0.1 N $KMnO_4$ that reacts with the lignin contained in 1 g of moisture-free pulp under specific conditions [23]. By these means, the decay in Kappa number is directly related to the bleaching capacity of the catalyst employed. Kraft pulp was treated with H_2O_2 and catalytic amounts of complex **1** at pH 9.00, for 2 h and room temperature, and the kappa number was determined before and after treatment. Under these conditions, the presence of 100 ppm of complex **1** causes kappa number to decrease from 15.6 to 13.1. Without addition of complex **1**, kappa number of wood pulp treated with H_2O_2 at room temperature for 2 h, decreases from 15.6 to 14.1. These results evidence that pulp bleaching is favorable (16% kappa number lowering) at low temperature and low catalyst concentration. With the most efficient diMn complexes known so far: $[Mn_2(\mu\text{-}O)_3(tmtacn)_2]^{2+}$ and $[Mn_2(\mu\text{-}O)_3(tmdtne)_2]^{2+}$, a 44% and 38% lowering of kappa number was achieved after 2 h, but at pH 11.5 and at 60 °C [11,12]. A decrease of 71% of kappa number was observed for the Kraft pulp treated with H_2O_2 in the presence of $[Mn_2(\mu\text{-}O)_2(tpa)_2]^{2+}$; but in this case, high temperature (80 °C), low pH (3.5) and longer time (3 h) were employed [36].

In order to evaluate whether complex **1** damages cellulosic fibers, the cellulose intrinsic viscosity was determined before and after treatment with H_2O_2/complex. These experiments showed that the DP number of cellulose changed from 156 to 151 for untreated and H_2O_2/catalyst-treated cellulose. The degree of viscosity loss of cellulose is very low, indicating that pulp bleaching without concomitant cellulose damage can be achieved with this class of catalysts.

3.5. Lignin oxidation sites

Infrared spectroscopy is a very useful tool for characterization of lignins, especially for identification of diverse functional groups present in the polymeric chain [37,38]. We used IR spectroscopy to infer possible reaction sites of lignin during H_2O_2 oxidation catalyzed by complex **1**, under the same reaction conditions used in the wood pulp bleaching experiments described above. In order to avoid extended depolymerization and loss of the spectral pattern, the time of treatment was shortened to 30 min. FT-IR spectra of untreated, H_2O_2-treated and H_2O_2/catalyst-treated lignin are shown in Fig. 4.

The IR spectrum of untreated lignin displays a broad band between 3700 and 3050 cm^{-1} attributed to aliphatic and phenolic hydroxyl groups, and two absorptions at 2960 and 2856 cm^{-1} corresponding to CH stretching modes of the polymeric chain (not shown in Fig. 4), that remain unchanged after treatment with H_2O_2 and complex **1**. Besides, untreated and oxidized lignin show two bands at 1600 and 1705 cm^{-1}, associated to unconjugated/conjugated carbonyl stretching vibrations, and three absorptions at 1515, 1462 and 1426 cm^{-1} typical of the aromatic skeleton

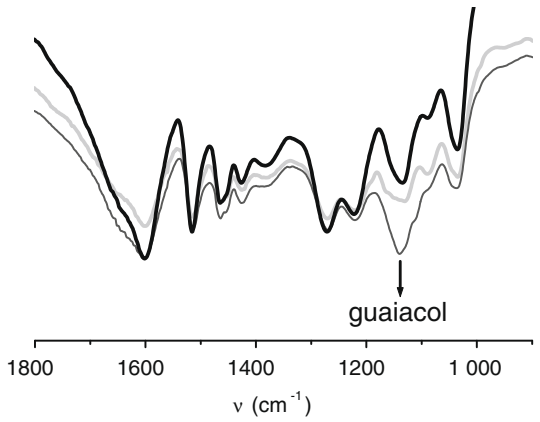


Fig. 4. FT-IR spectra of lignin (▬), H_2O_2-treated lignin (▬) and H_2O_2/catalyst-treated lignin (—).

vibrations that remain unaltered after oxidation, indicating the retention of the polymeric structure. The spectral region below 1400 cm^{-1}, although complex, provides information on different monomers, such as guaiacyl (1269 cm^{-1}, aromatic ring; 1130 cm^{-1}, C=O stretching) and syringyl units (1320 cm^{-1}, aromatic ring). After oxidative treatment of lignin with H_2O_2 and catalyst, the relative intensity of the band at 1130 cm^{-1} increased (as observed in Fig. 4). This observation can be interpreted in terms of a higher proportion of oxidized guaiacyl units upon oxidation of the phenol OH group, indicating that the phenol groups of guaiacol monomers are possible reaction sites in the H_2O_2-mediated oxidation of lignin catalyzed by **1**. This fact is consistent with the ability shown by the complex to catalyze the oxidation of phenol and 2,6-dimethoxyphenol with H_2O_2.

3.6. Effect of reaction medium on catalyst composition

With the aim of determining the effect of water on catalysts composition, ESI-mass spectra of complex **3** in acetonitrile were registered after addition of increasing amounts of water. In acetonitrile, the main peak of the positive mode ESI-mass spectrum is observed at m/z = 867 and originates from the $[Mn_2(OAc)(OMe)L^3]^+$ monocation. Addition of water results in decreasing intensity of the species at m/z = 867 concomitantly with the growth up of the $[Mn_2(OH)(OAc)L^3]^+$ monocation (m/z = 853). The methoxo-/hydroxo-exchange is favored when an aqueous basic solution of pH 9.00 is added. The same behavior had been observed when Bu_4NOH or acetate was added to a DMF or DMSO solution of these complexes [16]. The ESI-mass spectrum taken 1 h after preparation of a solution of **3** in acetonitrile containing 40% H_2O, is dominated by the peak corresponding to the $[Mn_2(O)L^3]^+$ monocation (m/z = 793) (Fig. 5), where the two exogenous bridging-ligands have been substituted by an oxo-bridge.

In $[Mn_2(O)L^3]^+$, oxo and $L^{3(3-)}$ ligands occupy five coordination positions around each Mn ion leaving one labile site, probably occupied by the solvent, for reaction with the substrate. The decrease in catalytic activity observed when the proportion of this species increases, suggests that it corresponds to an inactive form of the catalyst. Inactivation could be probably related to the binding of phenolate to Mn by substitution of a labile solvent molecule, thus blocking the H_2O_2 access. This is not the case for $[Mn_2(\mu\text{-}OH)(\mu\text{-}OAc)L^3]^+$, with no coordinated solvent molecules, where peroxide binding can take place through hydroxo or carboxylato shift. This conclusion is consistent with the observation that complexes of the pentadentate 1,5-bis(salicylidenamino)pentan-3-ol (L^4H_3) family, $[Mn_2(\mu\text{-}OMe)(\mu\text{-}OAc)(X\text{-}L^4)(solvent)_2]^+$ [39,40], also containing the triply bridged bis(alkoxo)(carboxylato)dimanganese(III) core, but with two labile solvent molecules in axial positions, one on each Mn ion, are unable to catalyze phenols oxidation by H_2O_2 under the experimental conditions used here.

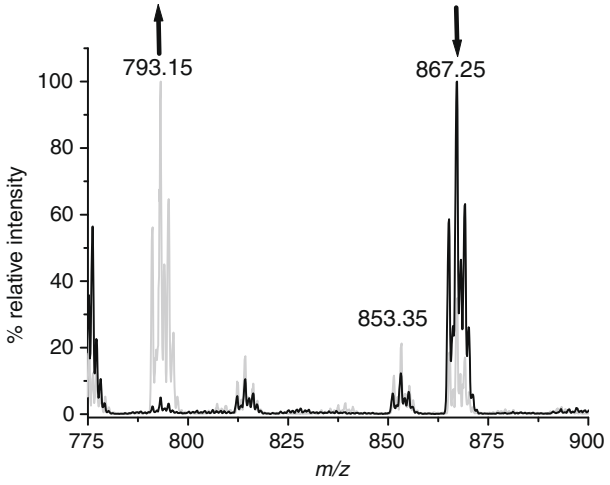


Fig. 5. ESI-MS spectra of complex **3** in 6:4 acetonitrile:H_2O mixture, immediately (▬) and 1 h (▬) after preparation.

4. Conclusions

The results presented in this study show that dimanganese complexes with $Mn^{III}_2(\mu\text{-}OAc)(\mu\text{-}OR)_2^{3+}$ core (where OR = L and OMe in complexes **1**-**3**) transform into $Mn^{III}_2(\mu\text{-}OAc)(\mu\text{-}OH)(\mu\text{-}OR)^{3+}$ (OR = L) in aqueous medium and are able to catalyze phenols oxidation and pulp bleaching with H_2O_2, at neutral and basic pH. Reactivity seems not to be critically dependent of the redox potential of the metal center, which is regulated by the nature of the phenol-arm substituent of the ligand. FT-IR spectroscopy showed that guaiacol units in the polymer are likely to be the oxidation sites of lignin. Although less efficient than $[Mn_2(\mu\text{-}O)_3(tmtacn)_2]^{2+}$ and $[Mn_2(\mu\text{-}O)_3(tmdtne)]^{2+}$ for wood pulp bleaching, complexes **1**–**3** have the advantage of being active at room temperature and selective, as no appreciable damage of cellulose fibers was observed. Substitution of the methoxo- and acetato-bridges by an oxo-bridge reduces the catalytic activity of these compounds, probably through binding of phenolate to the vacant site on the metal center. This suggests that the use of a non-labile bridging-ligand in place of the labile bridging acetate should be a critical feature for delineating selective and more active catalysts for pulp bleaching at room temperature.

Acknowledgments

We thank the National University of Rosario, CONICET and the National Agency for Sciences Promotion for financial support.

References

[1] H. Sixta, H.-U. Süss, A. Potthast, M. Schwanninger, A.W. Krotscheck, in: H. Sixta (Ed.), Handbook of Pulp, Wiley VCH, Wienheim, 2006, pp. 609–932.
[2] M. Suchy, D. Argyropoulus, in: D. Argyropoulus (Ed.), Oxidative Delignification Chemistry. Fundamentals and Catalysis, ACS Symposium Series, vol. 785, Oxford University Press, Washington, 2006, pp. 2–43.
[3] C.W. Jones, Applications of Hydrogen Peroxide and Derivates, Royal Society of Chemistry, Cambridge, UK, 1999.
[4] J. Dannacher, J. Mol. Catal. A: Chem. 251 (2006) 159.
[5] T.K. Kirk, R.L. Farrel, Annu. Rev. Microbiol. 41 (1987) 465.
[6] R. Hage, A. Lienke, Angew. Chim., Int. Ed. 45 (2006) 206.
[7] V. Alves, E. Capanema, C.L. Chen, J. Gratzl, J. Mol. Catal. A: Chem. 206 (2003) 37.
[8] K. Sibbons, K. Shastri, M. Watkinson, Dalton Trans. (2006) 645.
[9] R. Hage, A. Lienke, J. Mol. Catal. A: Chem. 251 (2006) 150.
[10] R. Hage, J. Iburg, J.E. Kershner, J.H. Koek, E.L.M. Lempers, R.J. Martens, U.S. Racherla, S.W. Rusell, T. Swarthoff, M.R.P. Van Vllet, J.B. Warnaar, L. Van Der Wolf, B. Krijnen, Nature 369 (1994) 637.
[11] C.-L. Chen, E.A. Capanema, H.S. Gracz, J. Agric. Food Chem. 51 (2003) 1932.
[12] C.-L. Chen, E.A. Capanema, H.S. Gracz, J. Agric. Food Chem. 51 (2003) 6223.
[13] V.B. Romakh, B. Therrien, L. Karmazin-Brelot, G. Labat, H. Stoeckli-Evans, G.B. Shul'pin, G. Süss-Fink, Inorg. Chim. Acta 359 (2006) 1619.
[14] Y. Cui, C.-L. Chen, J.S. Gratzl, R. Patt, J. Mol. Catal. A: Chem. 144 (1999) 411.
[15] T. Tzedakis, Y. Benzada, M. Comtat, Ind. Eng. Chem. Res. 40 (2001) 3435.
[16] H. Biava, C. Palopoli, C. Duhayon, J.-P. Tuchagues, S. Signorella, Inorg. Chem. 48 (2009) 3205.
[17] N. Rajendiran, J. Santhanalakshmi, J. Mol. Catal. A: Chem. 245 (2008) 185.
[18] R.R. Carballo, V. Campodall' Orto, I.N. Rezzano, J. Mol. Catal. A: Chem. 280 (2008) 156.
[19] S. Sgalla, G. Fabrizi, S. Cacchi, A. Macone, A. Bonamore, A. Boffi, J. Mol. Catal. B: Enzym. 44 (2007) 144.
[20] F. Xu, Biochemistry 35 (1996) 7608.
[21] C. Johannes, A. Marjcherczyc, J. Biotechnol. (2000) 193.
[22] S. Kobayashi, H. Higashimurab, Prog. Polym. Sci. 28 (2003) 1015.
[23] ISO 302:2004, Pulps – Determination of Kappa Number.
[24] R.S. Hatch, Ind. Eng. Chem., Anal. Ed. 16 (1944) 104.
[25] E.H. Immergut, B.G. Ranby, H.F. Mark, Ind. Eng. Chem. 45 (1953) 2483.
[26] P. Trinder, J. Clin. Pathol. 22 (1969) 158.
[27] J. Lott, K. Turner, Clin. Chem. 21 (1975) 1754.

[28] E. Emerson, J. Org. Chem. 8 (1943) 417.
[29] Y.C. Fiamegos, C.D. Stalikas, G.A. Pilidis, M.I. Karayannis, Anal. Chim. Acta 403 (2000) 315.
[30] P. Knops-Gerrits, D. De Vos, P. Jacobs, J. Mol. Catal. A: Chem. 117 (1997) 57.
[31] É. Balogh-Hergovich, G. Speier, J. Mol. Catal. A: Chem. 230 (2005) 79.
[32] V.K. Bansal, R. Kumar, R. Prasad, S. Prasad, J. Mol. Catal. A: Chem. 284 (2008) 69.
[33] J. Zhang, Y. Tang, J.-Q. Xie, J.-Z. Li, W. Zeng, C.W. Hu, J. Serb. Chem. Soc. 70 (2005) 1137.
[34] A. Labudzinska, K. Gorczynska, J. Mol. Struct. 349 (1995) 469.
[35] B.C. Gilbert, N.W.J. Kamp, J.R.L. Smith, J. Oakes, J. Chem. Soc., Perkin Trans. 2 (1997) 2161.
[36] T. Tzedakis, Electrochim. Acta 46 (2000) 99.
[37] G. Boeriu, D. Bravo, R.J.A. Gosselink, J.E.G. van Dam, Ind. Crop. Prod. 20 (2004) 205.
[38] S. Kubo, J.F. Kadla, Biomacromolecules 6 (2005) 2815.
[39] H. Biava, C. Palopoli, S. Shova, M. De Gaudio, V. Daier, M. González-Sierra, J.-P. Tuchagues, S. Signorella, J. Inorg. Biochem. 100 (2006) 1660.
[40] V. Daier, H. Biava, C. Palopoli, S. Shova, J.P. Tuchagues, S. Signorella, J. Inorg. Biochem. 98 (2004) 1806.