

Research Article

Systematic investigation of the oxidative polymerization of linseed oil catalyzed by Co(II), Mn(II), and Fe(II) complexes with chelating nitrogen ligands

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Several metal catalysts, i.e., cobalt(II) 2-ethylhexanoate (1), manganese(II) 2-ethylhexanoate (2) and iron(II) 2-ethylhexanoate (3), and their complexes with the chelating nitrogen ligands, i.e., 1,10-phenanthroline (a), 4-methyl-1,10'-phenanthroline (b), and 5,6'-dimethyl-1,10'-phenanthroline (c), were tested for the oxidative polymerization of linseed oil. The stoichiometries of the complexes were determined, and the isolated complexes were characterized by IR spectroscopy to confirm that complexation had occurred. The evolution of the viscosity was evaluated for 18 h, and the results were expressed as apparent kinetic constants calculated from $\ln(\text{viscosity})$ versus time. The results indicate that the manganese and iron chelates exhibit higher catalytic efficiencies than their corresponding carboxylates and that their performances are comparable to that of the cobalt carboxylate.

Practical applications: The coordination of chelating nitrogen ligands to manganese and iron carboxylates improves their catalytic performance and is a promising strategy for substituting cobalt carboxylates in some applications in the coating industry.

Keywords: Catalyst / driers / Oxidative polymerization / Metal carboxylates / Drying oils

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1 Introduction

In the coatings industry, alkyd resins synthesized from polyols, dibasic acids, and fatty acids exhibit good performance properties that make them one of the most used materials in this field and represents a very good example of polymer obtained from renewable source [1–3]. Alkyd film formation on a substrate occurs via a series of chemical

reactions involved in oxidative polymerization, also called oxidative curing or drying.

This oxidative polymerization process (Fig. 1) starts by oxidative step, wherein take place the hydrogen abstraction from activated methylene group present in unsaturated chains, leading to organic radical formation (Eq. 1). The radical resulting is converted, after reaction with molecular oxygen, into peroxy radical $\text{ROO}\cdot$, which is converted into a hydroperoxide via H-abstraction (Eq. 2 and 3, respectively). In the sequence, the hydroperoxides decomposition, in the presence of metal catalyst, results into alkoxy or peroxy radicals $\text{RO}\cdot$ and $\text{ROO}\cdot$ (Eq. 4 and 5, respectively). The recombination of these radicals undergo a polymerization step in which the molecular weight grows due the crosslink reactions among free radicals issued from the hydroperoxide decomposition, resulting in C–C, C–O–C, and C–O–O–C bonds formation (termination step). The polymerization can also proceed through a hydrogen abstraction mechanism

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Abbreviations: UV–Vis, ultraviolet–visible spectroscopy; DRIFT, diffuse reflectance IR Fourier transform



Figure 1. Scheme of oxidative polymerization reactions in the presence of molecular oxygen (adapted from [2]).

producing allylic radicals or by addition of the hydroperoxide radicals to double bonds [2–5]. It is important to mention that is possible to observe the formation of lower molecular weight products such as aldehydes or alcohols [2, 4].

This very complex route can be accelerated by catalysts known as driers, which work via homogenous catalysis pathway by deactivation of natural antioxidants, decreasing the induction period, acceleration of oxygen absorption, and peroxide production [2–5]. Primary or surface driers promote drying from the top down, and cobalt, manganese, and iron carboxylates comprise a very important subset of this class of compounds. Cobalt 2-ethylhexanoate (1), manganese 2-ethylhexanoate (2) and iron 2-ethylhexanoate (3) are largely employed as drying catalysts, but due to the carcinogenic properties of cobalt [2, 4], it is desirable to minimize its use.

In this scenario, manganese and iron driers could replace cobalt in several paint formulations. However, some studies have indicated that these complexes are less effective in oxidative polymerization than cobalt carboxylates [4, 6–7]. To increase the catalytic performance of manganese and iron driers, one approach is to modify them with organic ligands. Several reports demonstrate the potential of nitrogen-containing ligands [6–9], and this area of research has been recently reviewed [4]. The potential of these ligands stems from their ability to alter steric and electronic effects that can impact the behavior of the complexes in oxidative polymerization and to enhance the compatibility of the catalysts in the reaction medium.

In this work, the oxidative polymerization of linseed oil, which was used as a model alkyd resin [5], was investigated in the presence of cobalt(II) 2-ethylhexanoate (1), manganese(II) 2-ethylhexanoate (2), iron(II) 2-ethylhexanoate (3), and complexes obtained by modifying these metal carboxylates with chelating nitrogen ligands, i.e., 1,10-phenanthroline (**a**), 4-methyl-1,10'-phenanthroline (**b**), and 5,6'-dimethyl-1,10'-phenanthroline (**c**). The aim of this work was to systematically establish the influence of the different ligands on the catalytic behavior of the metal carboxylates in oxidative polymerization.

Table 1. Fatty acid composition (%) of linseed oil

Fatty acid	(%)
C16:0 (palmitic)	4
C18:0 (stearic)	6
C18:1 (oleic)	21
C18:2 cis/cis 9,12 (linoleic)	16
C18:3 cis/cis/cis 9,12,15 (linolenic)	53

2 Materials and methods

2.1 Materials

Linseed oil (purity 99%) was purchased from Pindorama (Panambi, RS, Brazil) and their fatty acid composition (Table 1) is in according with the literature [10]. The metal salts (cobalt(II) 2-ethylhexanoate, manganese(II) 2-ethylhexanoate, and iron(II) 2-ethylhexanoate) were purchased from Miracema (Campinas, SP, Brazil). Synthetic air (20% oxygen) was obtained from White Martins. The 1,10-phenanthroline (purity ≥99%), 4-methyl-1,10'-phenanthroline (purity = 99%) and 5,6'-dimethyl-1,10'-phenanthroline (purity = 99%) ligands were acquired from Sigma-Aldrich.

2.2 Determination of the stoichiometry of the modified complexes

The stoichiometry of the modified complexes was determined by the Yoe–Jones method [11]. Various amounts of selected ligand **a**, **b**, or **c** (1.0×10^{-5} mol; 2.0×10^{-5} mol; 3.0×10^{-5} mol; 4.0×10^{-5} mol; 5.0×10^{-5} mol; 1.0×10^{-4} mol; 1.5×10^{-4}), corresponding to different molar ratios, were added to flasks containing 10 mL of the metal carboxylate (1, 2, or 3) dichloromethane solutions (5×10^{-3} mol/L). The UV–Vis spectra of these solutions were obtained, and the absorption maximum corresponding to complex formation was determined and subsequently measured. This analytical signal increases with an increase in the ligand molar ratio until a maximum is reached. After this point, the absorbance remains constant and indicates the stoichiometry of the complex.

2.3 Synthesis and characterization of the modified complexes

The complexes were synthesized with the stoichiometry determined in Section 2.2 in dichloromethane under stirring for 24 h at 25°C. The solutions were then cooled to 6°C, and the precipitate was isolated, washed with cold dichloromethane and dried under vacuum. The IR spectra (DRIFT) were obtained using a Varian 660 spectrometer with 32 scans at a nominal spectral resolution of 4 cm^{-1} .

2.4 Catalytic assays

For the catalytic assays, the modified complexes with the stoichiometry determined in Section 2.2 were generated *in situ*. Specifically, 150 g of linseed oil and the predetermined amounts of metal carboxylate and ligand (0.6 mmol of catalyst) were placed in a 0.5 L glass reactor and heated to 80°C. Synthetic air was bubbled into the reaction mixture (200 mL/min) under mechanical stirring (1100 rpm). During the 18-h reaction, samples were collected and analyzed to determine the viscosity. The kinematic viscosity was measured with an Ostwald viscosimeter (Cannon-Fenske) at 80°C immediately after the sample collection.

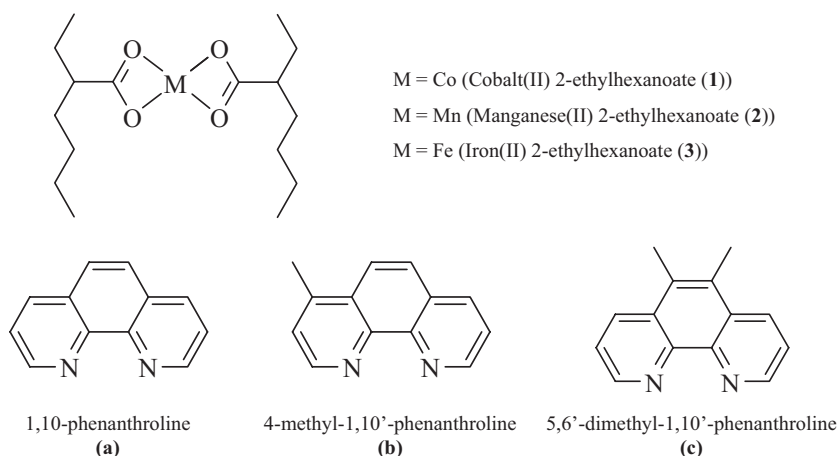
3 Results and discussion

3.1 Complex characterization

Scheme 1 presents the chemical structures and nomenclatures of the precursor complexes and nitrogen ligands used in

this work. The modification of the **1**, **2**, and **3** precursors by the selected ligands generate the complexes **1a**, **1b**, **1c**, **2a**, **2b**, **2c**, **3a**, **3b**, and **3c**.

Initially, the stoichiometries of the **1a**, **1b**, **1c**, **2a**, **2b**, **2c**, **3a**, **3b**, and **3c** complexes were evaluated in a dichloromethane solution using UV–Vis spectroscopy. The method developed by Yoe and Jones [11] was used as described in the experimental section. In the Fig. 2, an example is presented for **1b** complex, in order to illustrate the procedure employed. In the UV–Vis region, the absorption band observed for the ligand might correspond to the $\pi\text{--}\pi^*$ transitions of the aromatic structure and the $n\text{--}\pi^*$ transitions of isolated electron pairs localized on nitrogen [12, 13]. The absorption bands observed for the metal carboxylates and new complexes can be attributed to the coordinated ligands ($\pi\text{--}\pi^*$ or $n\text{--}\pi^*$), transitions between the metal and ligand or vice versa (charge transfer) and $d\text{--}d$ transitions on the metal center [14, 15]. For **1b** complex these transitions can be observed at 330 nm (absorption maxima) and in the 450 and 700 nm region, respectively.



Scheme 1. Chemical structures and nomenclatures of the precursor complexes and nitrogen ligands.

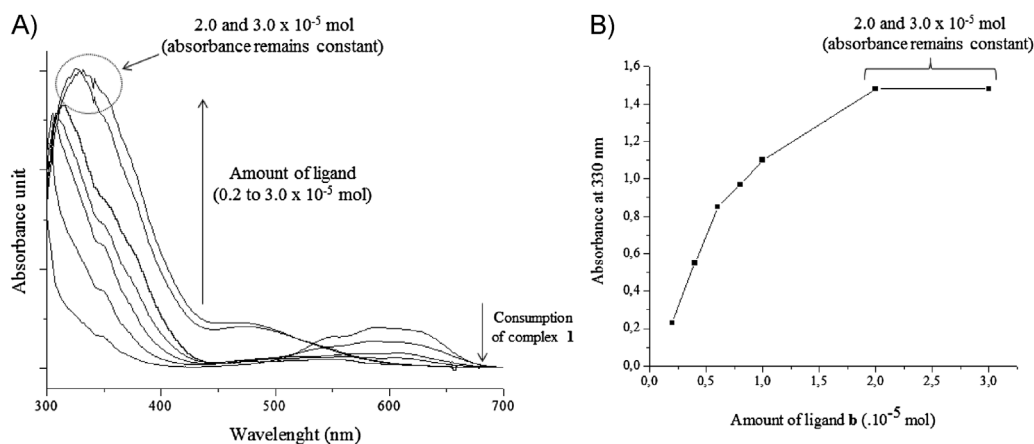


Figure 2. UV–Vis spectra for different amounts of ligand **b** (A) and graphical of absorbance at 330 nm as function of ligand amount (B) for **1b**.

Table 2. Stoichiometries of the modified complexes (molar ratio of the nitrogen ligand coordinated to the metal carboxylate) and absorption maxima (λ_{max} , nm) for the ligands, precursor complexes and modified complexes

Species	λ_{max} (nm)	Modified complex stoichiometry (ligand/precursor)
1	579	
2	300	
3	326	
a	303	
b	299	
c	299	
1a	380	2:1
1b	330	2:1
1c	400	2:1
2a	410	1:1
2b	400	1:1
2c	500	1:1
3a	470	1:1
3b	470	1:1
3c	470	1:1

Likewise, it is important to mention that between 450 and 700 nm it is possible to observe the complex **1** consumption (Fig. 2A), due the formation of new complex (**1b**).

In Table 2, the stoichiometries of the complexes in terms of the molar amount of ligand coordinated to the metal carboxylate and the absorption maxima (λ_{max} (nm)) for the ligands, precursor complexes, and modified complexes are given.

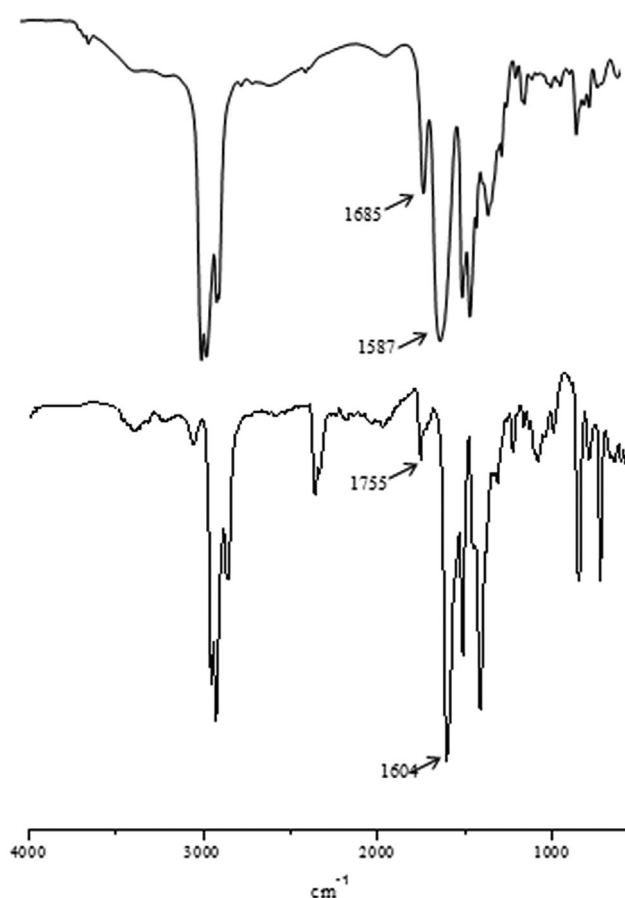
It is important to highlight that (i) the stoichiometries of the new manganese and iron complexes are 1:1 and that for the new cobalt complex is 2:1 and (ii) this characterization method does not detect any coordinated 2-ethylhexanoate ligands, which might still be attached to the metal center after the formation of the new complexes (modified complexes).

After the stoichiometries were determined, the complexes were synthesized according to the information presented in Table 2, isolated and characterized using IR spectroscopy to obtain more details about the complex structures. Table 3 presents the IR data for the C=O stretching bands of the carboxylates.

The main characteristic bands of metal carboxylates are strong asymmetric and weak symmetric CO₂ stretching vibrations ($\nu\text{CO}_{\text{asym}}$ and $\nu\text{CO}_{\text{sym}}$, respectively) [16]. The results show that the C=O stretching bands of the modified compounds are shifted relative to those of the precursor compounds, indicating that the new complexes have coordinated nitrogen ligands. Additionally, Fig. 3 presents an example of spectra for complexes **1** and **1b**, displaying that the CO₂ stretching vibrations of **1** (at 1587 and 1685 cm⁻¹) were shifted to 1604 and 1755 cm⁻¹ in **1b**.

Table 3. Wavenumbers (cm⁻¹) of the asymmetric and symmetric CO₂ stretching vibrations for the complexes

Complex	$\nu\text{CO}_{\text{asym}}-\nu\text{CO}_{\text{sym}}$ (cm ⁻¹)
1	1587–1749
2	1591–1691
3	1594–1697
1a	1597–1749
1b	1604–1755
1c	1592–1708
2a	1577–1705
2b	1593–1604
2c	1589–1702
3a	1657–1705
3b	1574–1712
3c	1569–1712

**Figure 3.** IR spectroscopy spectra for complexes **1** and **1b**.

Indeed, an intense absorption band between 3000 and 2850 cm⁻¹ related to CH₃, CH₂, and CH aliphatic stretching [12] is present in all spectra of the modified complexes (**1a**, **1b**, **1c**, **2a**, **2b**, **2c**, **3a**, **3b**, and **3c**). The presence of this absorption band along with those due to C=O stretching

shows that at least one carboxylate ligand remains coordinated to the metal center for the isolated complexes.

The coordination of **a**, **b**, and **c** to the metal center is also confirmed by the presence of absorption bands related to vibrational ring modes ($\nu\text{C}=\text{C}$ and $\nu\text{C}=\text{N}$) at ca. 1620, 1505, 1419, 1341, 1293, and 1217 cm^{-1} and ring deformation near 765 cm^{-1} in the spectra of the complexes [17].

3.2 Catalytic assays of the oxidative polymerization

The precursor (**1**, **2**, and **3**) and modified (**1a**, **1b**, **1c**, **2a**, **2b**, **2c**, **3a**, **3b**, and **3c**) complexes were tested for oxidative polymerization, and the evolution of the kinematic viscosity over time was monitored to evaluate the catalytic activities. Reports in the literature show that it is possible to correlate an increase in the kinematic viscosity to an increase in the molecular weight in oxidative polymerization reactions [5, 18]. As already mentioned in the introduction part, oxidative polymerization process occurs via a series of complex chemical reactions, also called oxidative curing or drying [2, 5, 7].

Figure 4 presents the evolution of the viscosity over time for precursors **1**, **2**, and **3** and in the absence of catalyst. As described in the literature [3] and confirmed by results, the viscosity increases exponentially over time in the presence of metal complexes. In the absence of catalysts, no evolution in the viscosity values is observed.

Consequently, the logarithms of the data were determined and the apparent rate constants ($k_{\text{oxi-pol}}$) were calculated from the logarithmic curves [5, 19, 20]. The same methodology was applied to the reactions catalyzed by **1a**, **1b**, **1c**, **2a**, **2b**, **2c**, **3a**, **3b**, and **3c**, and all results are presented in Table 4. For more details about these calculations see “Supporting Information.”

The evolution of the viscosity presented in Fig. 4 and apparent kinetic constants obtained for **1**, **2**, and **3** (Table 4)

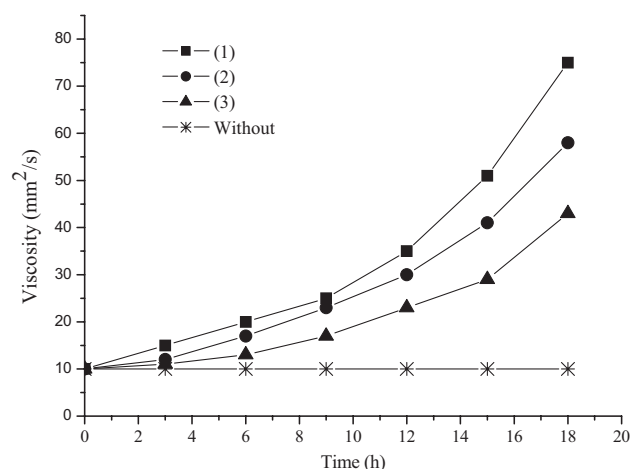


Figure 4. Evolution of the kinematic viscosity values over time for **1**, **2**, and **3** (0.6 mmol of catalyst, 80°C).

Table 4. Apparent rate constants calculated from $\ln(\text{viscosity})$ versus time for the oxidative polymerization process ($k_{\text{oxi-pol}}$) catalyzed by various complexes

Entry	Complex	$k_{\text{oxi-pol}} \times 10^2 \text{ (h}^{-1}\text{)}$
1	1	11.5
2	1a	9.0
3	1b	9.5
4	2	9.9
5	2a	11.2
6	2b	11.0
7	2c	13.2
8	3	9.1
9	3a	12.8
10	3b	13.9
11	3c	14.4

show that the cobalt complex (**1**) is more efficient than the manganese (**2**) and iron (**3**) complexes in both the oxidation and polymerization steps of the oxidative polymerization reaction (entries 1, 4, and 8). These results are consistent with those in the literature [2, 4] and justify the strategy of modifying manganese and iron carboxylate complexes with organic ligands to enhance their catalytic performance.

As demonstrated by entries 2 and 3 in Table 3, the coordination of chelating nitrogen ligands to cobalt 2-ethylhexanoate (**1**) as in the **1a** and **1b** complexes does not improve its catalytic performance. It is important to remember that the stoichiometries of the modified complexes determined in this work indicate that two chelating nitrogen ligands are coordinated to the metal center. The modified complexes are most likely thermodynamically and kinetically stable due the chelate effect, making the systems inefficient in the oxidative polymerization. Furthermore, as reported in the literature for 1,10-phenanthroline (**a**), the complex between cobalt 2-ethylhexanoate and **a** forms via ligand exchange in the reaction medium, meaning the carboxylates are no longer coordinated to the metal center [21]. Therefore, it is likely that the same behavior occurs in the systems employed in the present work, leading to a decrease in the compatibility between the catalyst and reactants.

In contrast, the catalytic performances of the manganese and iron carboxylates with nitrogen ligands (entries 5, 6, and 7 and 9, 10, and 11, respectively) are enhanced compared to those of the corresponding carboxylates (entries 4 and 8, respectively) and comparable to that of the cobalt carboxylate (**1**). In these cases, the coordination of chelating nitrogen ligands improves the catalytic performance, which might be explained by the following reasons. First, the complex stoichiometries, which were determined experimentally, show that only one chelating ligand is coordinated to the metal center, making the resulting complex less thermodynamically and kinetically stable and therefore more suitable for oxidative polymerization reactions. Additionally, if only

one chelating ligand is coordinated to the metal center, it is more probable that at least one carboxylate ligand remains attached to the metal, increasing the compatibility of the catalytic system with the reactant.

The manganese and iron complexes with ligand **c**, which contains two methyl substituents (Fig. 1), have the highest rate constants. In this case, it is possible that these substituents enhance the compatibility of the complex formed in the reaction medium or the electron-donating properties of the methyl groups improve the catalytic properties of the complexes in the oxidative polymerization.

4 Conclusions

The cobalt complex (**1**) (cobalt 2-ethylhexanoate) is more efficient than the manganese (**2**) and iron (**3**) complexes in both the oxidation and polymerization steps of the oxidative polymerization of linseed oil. For the cobalt carboxylate, the coordination of chelating nitrogen ligands does not improve its catalytic performance.

In contrast, the catalytic performances of the manganese and iron carboxylates are enhanced when they are modified with nitrogen ligands. The modified complexes exhibit similar efficiencies in the oxidative polymerization reaction to the cobalt complex. In these cases, the coordination of chelating nitrogen ligands improves the catalytic performance effectively. These modified complexes are promising for substituting cobalt carboxylates in some applications in the coating industry.

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