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Catalytic Behaviors of Co^II and Mn^II Compounds Bearing α-Diimine Ligands for Oxidative Polymerization or Drying Oils

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The oxidative polymerization of linseed oil was investigated comparing the classical catalysts cobalt(II) 2-ethylhexanoate and manganese(II) 2-ethylhexanoate and their derivatives modified by the presence of chelating nitrogen ligands, i.e., 2,2'-bipyridyl, 2-(acetyl-2,6-diisopropylphenylimine)-pyridine and [*N*-(2,6-diisopropylphenyl)imine]acenaphthoquinone. The suitable stoichiometries between the two precursor complexes with the three ligands were determined by UV-visible spectroscopy. All complexes were characterized by infrared spectroscopy, and one complex was characterized also by X-ray diffraction. The apparent kinetic constants of oxidative polymerization of linseed oil was determined, for each catalytic system, via the periodic measurements of the oil viscosity during the oxidation reaction. The results indicated that the modifications of the classical two complexes with the chelating nitrogen ligands improved the catalytic efficiency at least to the manganese complex.

Keywords: oil oxidation, driers, drying oils, catalytic oxidative polymerization, metal carboxylates, nitrogen ligand

Introduction

One of the most important applications of controlled oxidative polymerization reaction of unsaturated oils is observed during the formation of alkyd films on the most different type of substrates. Indeed, this process is called oxidative curing or drying, and many studies about this subject have been carried out or supported by coating industries.[1] Alkyd resins exhibit excellent performance properties that make them one of the most employed materials obtained from a renewable source in the coatings industry.[2-4]

Unsaturated substrates, such as vegetable oils and their derivatives, can undertake a process known as oxidative polymerization. This process comprises several chemical reactions and starts from a hydrogen abstraction from the activated methylene group on the unsaturated chain, generating an organic radical (oxidative step). This radical is converted into a peroxy radical (ROO•) after reaction with molecular oxygen, forming a hydroperoxide

via H-abstraction. In this sequence, alkoxy or peroxy radicals (RO• and ROO•, respectively) are formed by hydroperoxide decomposition in the presence of metal species. The recombination of these radicals leads to a polymerization process, followed by a molecular weight increase due to crosslinking reactions, resulting in C–C, C–O–C and C–O–O–C bond formations. Another polymerization reaction mechanism involves an allylic radical formation via hydrogen abstraction and its addition to double bonds. This process is accompanied by the formation of volatile compounds, such as aldehydes or alcohols.[1-5]

The oxidative polymerization of unsaturated oils can occur without the use of catalyst, however, under this condition, this process is too slow for industrial and practical applications. Indeed, depending on the application, the oxidative polymerization reaction need to be more or less rapid, and this is the reason that different catalytic systems have been developed. Despite the large number of catalyst at our disposal, the development of new catalysts is still a subject of research interest at academic and industrial level.[1]

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The catalysts of oxidative polymerization of oil are normally named as driers at the coating industry. These catalytic systems use to be well dissolved or dispersed in the oily matrix and functions as a deactivator of natural antioxidants, diminishing the induction period and accelerating oxygen absorption and peroxide formation.[1-5] Cobalt carboxylate-based complexes are an important group of driers, but due to the carcinogenic effects of cobalt,[1,4] they are progressively been substituted. In this context, manganese-based driers are considered a good alternative to overcome the cobalt-based analogues in numerous applications, however, most of the manganese-based driers are less active.[1,6,7] One strategy to raise the catalytic performance of these catalytic systems is based on a modification of their coordination sphere, employing nitrogen ligands, since their ability to modify the steric and electronic properties can be used to change the behavior of the complexes for oxidative polymerization and to improve the compatibility of the driers in the reaction system.[1,6-11]

In former work, it was observed that the addition of nitrogen ligands *in situ* improved the reaction rate of the oxidative polymerization, in the presence of classical catalysts.[10] In order to extend the alternatives, in this work is established the influence of diverse nitrogen ligands on the catalytic performances of metal carboxylates in oxidative polymerization processes. Therefore, complexes bearing nitrogen ligands, i.e., 2,2'-bipyridyl (**a**), 2-(acetyl-2,6-diisopropylphenylimine)-pyridine (**b**) and [*N*-(2,6-diisopropylphenyl)imine]acenaphthoquinone (**c**), were systematically evaluated. Those ligands were employed to modify the complex precursors cobalt(II) 2-ethylhexanoate (**1**) and manganese(II) 2-ethylhexanoate (**2**).

Experimental

Materials

Cobalt(II) 2-ethylhexanoate (**1**) and manganese(II) 2-ethylhexanoate (**2**) were provided by Miracema (Campinas, SP, Brazil). Synthetic air (20 % oxygen) was purchased from White Martins (Maceió, Alagoas State, Brazil). 2,2'-Bipyridyl (**a**, purity ≥ 99 %) was purchased from Sigma-Aldrich (Saint Louis, MO, USA) and used as received. The ligands 2-(acetyl-2,6-diisopropylphenylimine)-pyridyne (**b**) and [*N*-(2,6-diisopropylphenyl)imine]acenaphthoquinone (**c**) were synthesized according to procedures previously reported.[12] Linseed oil (purity 99%) was acquired from Pindorama (Panambi, RS, Brazil), with fatty acid composition of C16:0 (palmitic) = 4%, C18:0 (estearic) = 6%, C18:1 (oleic) = 21%,

C18:3 *cis/cis/cis* 9,12,15 (linolenic) = 16% and C18:2 *cis/cis* 9,12 (linoleic) = 53%.[13]

Characterization and synthesis of the modified complexes

To determine the number of nitrogen ligands bonded at the metal center expected for the formation of the complex containing the nitrogen ligands the Yoe-Jones method was adopted.[14] Briefly, different amounts of the ligands **a**, **b** or **c** (1.0×10^{-5}; 2.0×10^{-5}; 3.0×10^{-5}; 4.0×10^{-5}; 5.0×10^{-5}; 10×10^{-5}; and 15×10^{-5} mol) were added to a solution of the complex precursors **1** or **2** in dichloromethane (10 mL, 5×10^{-3} M). After 10 min, UV-visible spectra of the respective solutions were acquired, and the maximum absorption associated to the formation of the new complex was determined.

The respective complexes were synthesized, stirring for 24 h at room temperature in dichloromethane (15 mL) the suitable amount of the nitrogen ligand (5.0 or 2.5 mmol) and the precursor complexes (2.5 mmol). They were precipitated from the solutions by cooling at 6 °C, separated, washed rapidly with cold dichloromethane, and dried under vacuum. The diffuse reflectance infrared Fourier transform (DRIFT) spectra of the ligands and new complexes were acquired employing a Varian 660 spectrometer with 32 scans at a nominal spectral resolution of 4 cm⁻¹.

For the crystallographic study, a crystal fragment of **1b** was mounted on a goniometer in an Enraf-Nonius Kappa geometry CCD diffractometer with graphite monochromated Mo Kα (k = 0.71073 Å) radiation. The final unit cell parameters were based on all reflections. The data collection was made using the COLLECT program, and integration and scaling of the reflections were performed with the HKL Denzo-Scalepack system of programs. The structure was solved by direct methods, and the models were refined by a full-matrix least squares procedure on F2 with SHELXL-97. The programs SHELXL-97 and ORTEP-3 were used within WinGX.

Catalytic tests

For the catalytic tests, the complexes were generated *in situ* according to the stoichiometry determined above. Predetermined quantities of metal carboxylate and ligand (0.6 mmol of catalyst) and 150 g of linseed oil were placed in a 0.5 L glass reactor and heated at 80 °C. Synthetic air was bubbled into the reaction mixture (200 mL min⁻¹) under mechanical stirring (1100 rpm). During the reaction time (18 h), the kinematic viscosity was determined with an Ostwald viscometer (Cannon-Fenske) at 80 °C immediately

after collecting the aliquots. All oxidative polymerization experiments are run at least in duplicate and the maximum difference admitted for the same experimental point, in terms of viscosity, was 10%.
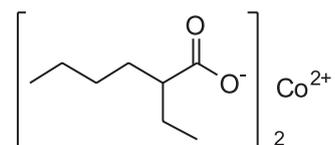
Results and Discussion

Complex characterization

The structure of the respective catalyst precursors and ligands employed in this work are presented in Scheme 1. The choice of such ligands in these studies were based in their affinity for Co^{II} and Mn^{II} complexes,[1,10,11] as well the aim to produce more stable complexes (chelate effect).[18] Of course, the reactivity of the complexes could be compromised, however, the life time of the complex can be improved, and side reactions that cause deactivation of the catalytic species can be suppressed or diminished.[18]

UV-visible spectroscopy was used to characterize all complexes and ligands, since all species present absorption bands in this region due to the presence of one of these bands: d-d, π-π* and/or n-π* electronic transitions. The maximum

absorption bands for all species are present in Table 1. The bands in the region 300-450 nm can be attributed to intraligand transitions and these bands are different when one compares the spectra of the free ligand and the respective after complexation. In the spectra of the complexes, the d-d transitions were weak and not very well defined.

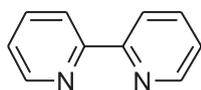**Table 1.** Selected signals from the UV-visible spectra of the compounds studied in this work

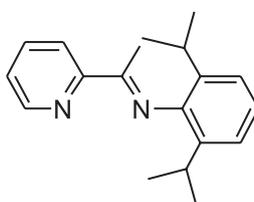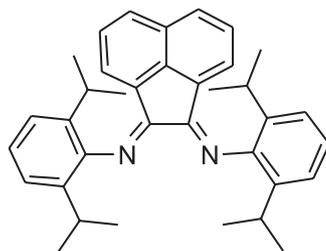| Complex precursor and ligand	λ_{max} / nm
1	579
2	300
a	300
b	340
c	310
Modified complex	λ_{max} / nm
1a	360
1b	400
1c	445
2a	410
2b	370
2c	425

cobalt(II) 2-ethylhexanoate (**1**)
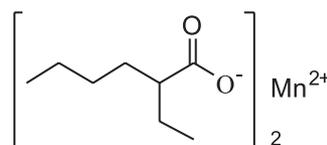
manganese(II) 2-ethylhexanoate (**2**)

2,2'-Bipyridyl (**a**)

2-(acetyl-2,6-diisopropylphenylimine)-pyridine (**b**)

[*N*-(2,6-diisopropylphenyl)imine]acenaphthoquinone (**c**)

Scheme 1. The structural formula of the ligands, and catalyst precursors employed in this work.

The complexes were also characterized by infrared spectroscopy, and from infrared spectra it is possible to identify the main bond vibration of each chemical species. All metal complexes studied here display bands related to the presence of carboxylate groups, and the frequencies of these bands are highly sensitive to their structure.[19] The modification of the complexes due the presence of nitrogen ligands was established based on the shift of the C=O stretching bands (strong asymmetric (νCO_{asym}) and weak symmetric (νCO_{sym})) vibrations[19] of the modified complexes in comparison to those of the carboxylates **1** and **2**. In order to illustrate, for **1**, the νCOO_{asym} and νCOO_{sym} absorptions appeared at 1749 and 1587 cm^{-1}, respectively, and are shifted in **1a** to 1758 and 1608 cm^{-1} and in **1b** to 1750 and 1537 cm^{-1}, respectively. In the case of **2** and **2a**, these absorption peaks shifted from 1591 and 1691 to 1705 and 1577 cm^{-1}, respectively.

Additionally, strong bands observed in the region from 3000 to 2850 cm^{-1} corresponding to CH$_3$, CH$_2$ and CH aliphatic stretching,[12] beyond the C=O stretching absorption, were present in all the spectra of the modified complexes indicating that at least one carboxylate ligand remained coordinated to the metal centers. Furthermore, the presence of absorption bands related to the vibrational ring modes (νC-C and νC-N) at ca. 1620, 1505, 1419, 1341, 1293 and 1217 cm^{-1} and the ring deformation near 765 cm^{-1} in the spectra of the complexes[20] confirmed the coordination of **a**, **b**, and **c** to the carboxylates.

The Yoe-Jones method[14] was applied to determine the ligand:metal mol ratio to determine the conditions for the formation of the new complexes **1a**, **1b**, **1c**, **2a** and **2c**. When the suitable absorption band at the UV-visible region becomes constant, the ligand:metal mol ratio is defined. Figure 1 presents, as an example, a plot of absorbance at 400 nm as a function of the amount of ligand **b** in the
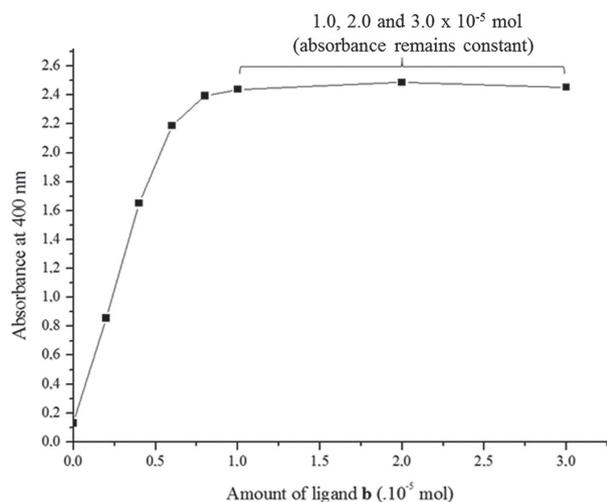
presence of **1** to form **1b**. In the UV-visible region, the absorption bands observed are attributed to the coordinated ligands (π-π* transitions of the aromatic structure or n-π* transitions of isolated electron pairs localized on the nitrogen atoms)[15,16] or transitions due to charge transfer[17,18] involving the metal and ligand.

Table 2 presents the results of the mol ratios of ligands coordinated to the metal center after Yoe-Jones essays. From the data, one can verify that the Co^{II} carboxylate compound **1** is able to add one chelating ligand on its coordination sphere. On the other hand, Mn^{II} carboxylate compound **2** is able to coordinate two of the chelating ligands on its coordination sphere. A priori, this tendency could be expected since Mn^{II} has less electrons than Co^{II}, and more ligands are necessary to reach their maximum electron valence.

Table 2. The stoichiometry found between ligand and catalyst precursor, via Yoe-Jones method

Species	Mol ratio between ligand:metal for the new catalysts
1a	1:1
1b	1:1
1c	1:1
2a	2:1
2b	2:1
2c	2:1

The stoichiometries determined for complexes **1a**, **1b** and **1c** and **2a**, **2b** and **2c** agree with the literature.[8] The **1b** structure was confirmed by XRD analysis of a single crystal of the complex, as a six-fold coordination, and Figure 2
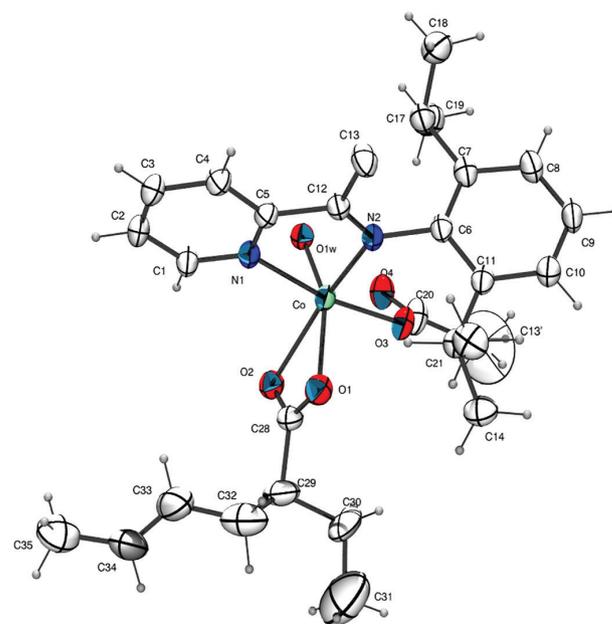

Figure 1. Plot of the absorbance at 400 nm as a function of the amount of ligand **b** to form **1b.**

Figure 2. ORTEP diagram of **1b**.

Table 3. Selected geometric parameters to **1b**

Bond distance / Å			
Co–O3	2.012 (4)	Co–O2	2.256 (4)
Co–O1W	2.065 (4)	O1–C28	1.259 (7)
Co–N1	2.120 (4)	O2–C28	1.261 (7)
Co–N2	2.120 (4)	O3–C20	1.285 (8)
Co–O1	2.153 (5)	O4–C20	1.248 (9)
Angle / degree			
O3–Co–O1W	90.89 (17)	O1W–Co–O1	154.96 (16)
O3–Co–N1	169.78 (17)	N1–Co–O1	90.54 (17)
O1W–Co–N1	87.52 (17)	N2–Co–O1	97.50 (17)
O3–Co–N2	94.50 (16)	O3–Co–O2	93.88 (17)
O1W–Co–N2	106.25 (16)	O1W–Co–O2	95.97 (15)
N1–Co–N2	76.29 (16)	O1–C28–O2	120.4 (5)
O4–C20–O3	124.7 (6)		
Dihedral angle / degree			
Co–N2–C6–C11	−80.4 (6)	Co–N1–C1–C2	178.9 (5)

presents the proposed structure. In Table 3, selected bond distances and angles are presented.

It is clearly seen that, even if there are difficulties in refining the structure due to disordered alkyl chains of 2-ethylhexanoate, one nitrogen ligand (**b**) is coordinated to the complex, confirming the 1:1 nitrogen ligand:metal. Both carboxylate ligands are coordinated to the metal center, in which one is bonded as monodentate and the other as bidentade ligand at solid state. A water molecule is also coordinated at the metal center, at least at the crystal structure. This must be the reason to observe one mono and one bidentade carboxylate ligands. Complex **1b**, must be a high spin, with 19 valence electrons on the metal center. This electronic condition helps the complex to act as catalyst since it is able to generate free radicals on the reagents.[1,10,11] Similar structures to **1b** can be found in the literature.[8,23,24]

Tables S1 to S5 (in the Supplementary Information (SI) section), contain the primary data. It is important to mention that no suitable monocrystals were obtained for the other complexes studied here.

Catalytic reactions

With the aim of evaluating the catalytic behavior of **1**, **2**, **1a**, **1b**, **1c**, **2a**, **2b** and **2c** in oxidative polymerization, the evolution of the kinematic viscosity over time was examined (Figure 3). As described in the literature[3,10] the viscosity increases exponentially over time in the presence of driers, and no change in the viscosity is observed without a catalyst.
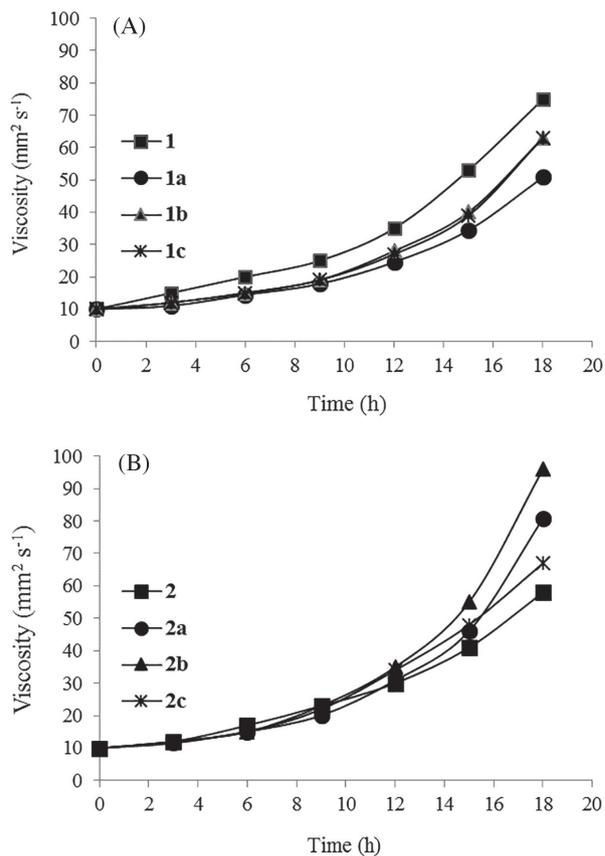

Figure 3. Evolutions of the kinematic viscosity over time for the complexes (0.6 mmol of catalyst at 80 °C): (A) Co complexes and (B) Mn complexes.

Thus, the apparent rate constants ($k_{oxi-pol}$) were calculated from the logarithmic curves of the viscosity,[5,21,22] and these results are presented in Figure 4 for the reactions using **1**, **2**, **1a**, **1b**, **1c**, **2a**, **2b** and **2c**. It is important to mention that an increase in the kinematic viscosity can be related to an increase in the molecular weight due to the polymerization processes.[5,25]
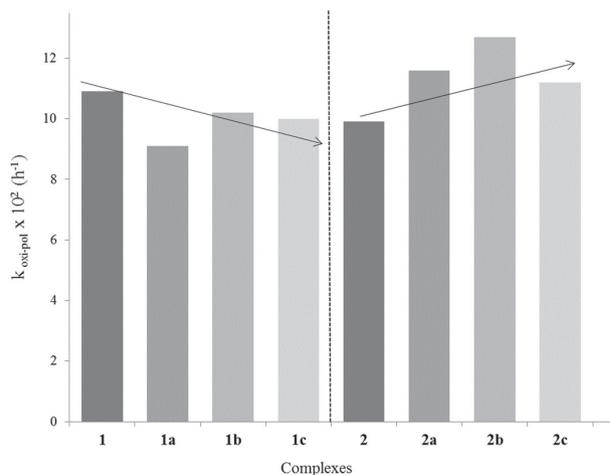

Figure 4. Apparent rate constants for the evolution of the viscosity ($k_{oxi-pol}$) in oxidative polymerization.

In the oxidative polymerization process, the apparent kinetic constants, which were related to the evolution of the viscosity, obtained for **1** and **2** show that the cobalt complex (**1**) is more active than the manganese complex (**2**), in accordance with previously reported results.[2,4,11] As can be observed from Figures 3 and 4, the modifications of cobalt 2-ethylhexanoate (**1**) by **a**, **b** and **c** diminished its catalytic effect. However, for the manganese carboxylate modified by the nitrogen ligands (**2a**, **2b** and **2c**), the catalytic effect was improved compared to that of the carboxylate (**2**), and in some cases, this activity was better than the cobalt carboxylate (**1**). The increase of the catalytic activity of manganese 2-ethylhexanoate (**2**) in the presence of the bipyridyl ligand has already been reported, and in this example, the carboxylates were not removed from the metal center.[7,10,11,25,26]

In this context, we suggest that the addition of the nitrogen ligands must stabilize both type of complexes. Nevertheless, in the case of the modified Co[II] complexes the coordination of nitrogen ligands provide the formation of very stable complexes that compromise their catalytic activity for oxidative polymerization reaction of drying oils. On the other hand, the addition of the nitrogen ligands on Mn[II] complex **2**, despite of the stabilization, do not compromise their catalytic activity. Indeed, the modified active species are stabilized and remain active in the reaction medium for longer times. Furthermore, the addition of the nitrogen ligands increase the compatibility of the complex with the reaction medium, since these kinds of nitrogen ligands provide more solubility of the complex into the oil.

It is also important to mention, that no significant effects were observed on the improvement of the catalytic performance among the modified Mn[II] complexes. This feature prompted us to suggest that the main reason to improve the catalytic activity is indeed the addition of the nitrogen ligands, and no particular electronic and steric effects were observed.

Conclusions

The manganese complex (**2**), Mn[II] 2-ethylhexanoate, was less efficient than Co[II] 2-ethylhexanoate (**1**) in oxidative polymerization. Nevertheless, the catalytic performance of **2** was improved by nitrogen ligand coordination. In some cases, the modified complexes presented better efficiencies for the oxidative polymerization reaction in comparison to the cobalt complex (**1**). For **1**, the modifications with chelating nitrogen ligands did not improve the catalytic performance. In addition, it was not possible to clearly distinguish the effects of the types of ligands, i.e., pyridine or symmetrical or unsymmetrical α-diimine, on the

catalytic performance due to the intricate set of reactions occurring in the oxidative polymerization process.

Supplementary Information

Supplementary information is available free of charge at http://jbcs.sbq.org.br as PDF file.

Acknowledgments

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