



## Biomimetic oxidation of catechol employing complexes formed *in-situ* with NH-pyrazole ligands and transition metallic salts

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### ABSTRACT

In the present paper, our main objective is to describe the catalytic properties of the complexes formed *in-situ* with the NH-pyrazole ligands:  $L_1$ - $L_7$  and different metallic salts ( $Cu(CH_3COO)_2$ ,  $CuSO_4$ ,  $Cu(NO_3)_2$ ,  $NiCl_2$ ,  $Co(NO_3)_2$ ,  $ZnCl_2$ ), which aimed to mimic the active site of catechol oxidase. In order to determine factors influencing the catecholase activity of these complexes, the effect of ligand concentration and the nature of solvent have been studied. The highest rate of catechol oxidation is given by the combination formed by one equivalent of ligand  $L_4$  and two equivalents of  $Cu(CH_3COO)_2$  in THF which equal to  $27,449 \mu mol.L^{-1}min^{-1}$ . The Michaelis-Menten model is applied to obtain the kinetic parameters of the best catalyst.

**Keywords:** catecholase, biomimetic oxidation, pyrazole, heterocyclic ligands, oxidation and metallic salts.

### INTRODUCTION

Oxidation of phenols to quinones has been the subject of many studies [1-5], and it is of industrial interest, because various quinones are used as intermediates in the synthesis of fine organic materials such as drugs, vitamins and perfume aromas [6], due to the importance of quinones in human life and the high reactivity of quinones, substantial research on the chemistry and toxicology of these compounds has taken place [7-10]. The two most common types of quinones are ortho- and para-quinones. Ortho-quinones are the products of catechols oxidation. This oxidation is often performed to metalloproteins containing copper, like catechol oxidase [11-12], which catalyzes the aerial oxidation of diphenols to corresponding quinones.

The catecholase is a type-III copper protein, in which the active site is constituted by a dinuclear copper, each Cu(II) is coordinated by three histidine nitrogens and a bridging  $OH^-$  ion [13-15], Nishida et al. [16] have found that several oxy-bridged binuclear Cu(II) complexes show catalytic activity if the Cu---Cu distance is less than 5 Å. Because the two atoms of copper should be close enough to facilitate the connexion between the hydroxyl groups of the catechol and the metal centers. The Cu---Cu distance has been determined to be 2.9-3.8 Å for the enzyme isolated from the spiny lobster *Panulirus interruptus* [17] and to be 4.6 Å for the enzyme isolated from the horseshoe crab *Limulus polyphemus* [18].

Numerous biomimetic approaches were devoted to the synthesis of ligands models based on iron [19-21], copper [22-29], manganese [30-34], and cobalt [35-36] complexes to reproduce catecholase activity. These studies aim to mimic the environment of the metal active site of this enzyme and also to better understand its properties to activate molecular dioxygen. In this context of modeling enzymes, the research of new catalysts in this area is always in progress [37-49]. In 2007, Bouabdallah et al. [25] have studied the catalytic activities of *in-situ* prepared complexes by stirring copper salts and new tridentate pyrazole ligands which differ between them in nature of junction, N-C-N

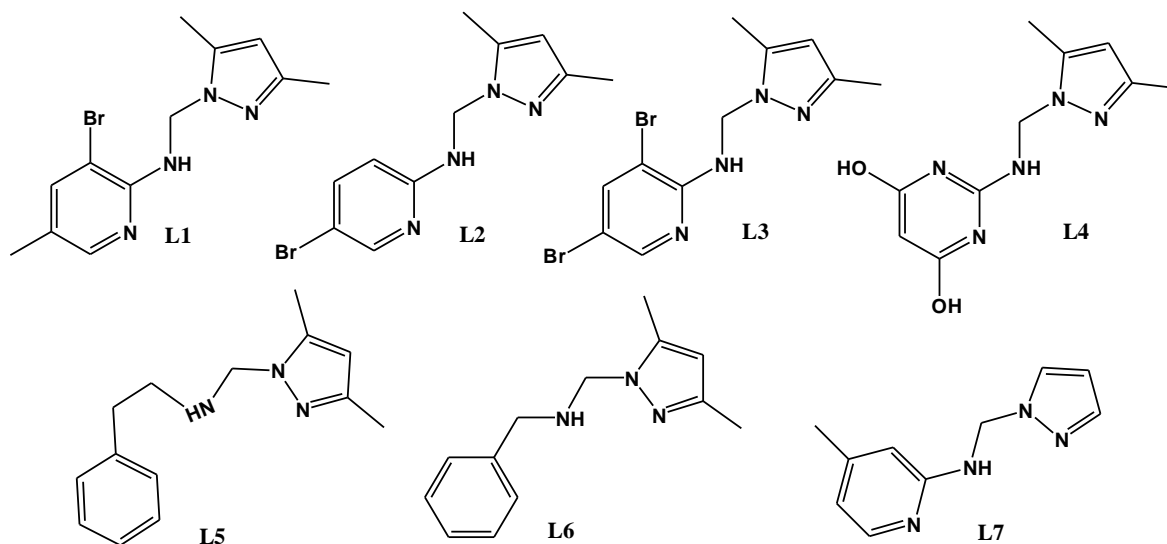
and N-C-C. They demonstrate that complexes with junction N-C-N have a stronger rate of the catecholase reaction than the complexes of the ligands with junctions C-C-N, and proved that the catalytic activity in the case, as of tripods with junction N-C-N, is controlled by the steric effect of the ligands and this probably because of the flexibility of this junction. In 2011, R. Marion *et al.* [50] have synthesized a family of tripodal pyrazole-based ligands by a condensation reaction between 1-hydroxypyrazoles and aminoalcohols. The corresponding copper(II) complexes have been generated *in situ* by reaction of the ligand with  $\text{CuCl}_2$  in THF. The influence of substituents and side chain of the tripodal ligands on the catecholase activity of the complexes was studied. They demonstrated that reaction rate depends on two factors. First, the presence of an oxygen atom in the third position of the side chain should be avoided to keep the effectiveness of the reaction. Second, the electronic and steric effects of substituent on the pyrazole ring strongly affect the catalytic activity of the complex.

For this purpose, and in continuation of our work in this field [22-29, 51], seven ligands **L1-L7** have been examined for their catecholase activities with different metallic salts, ( $\text{Cu}(\text{CH}_3\text{COO})_2$ ,  $\text{CuSO}_4$ ,  $\text{Cu}(\text{NO}_3)_2$ ,  $\text{NiCl}_2$ ,  $\text{Co}(\text{NO}_3)_2$ ,  $\text{ZnCl}_2$ ), and the effect of ligand concentration and nature of solvent have been studied.

## EXPERIMENTAL SECTION

### Ligands description

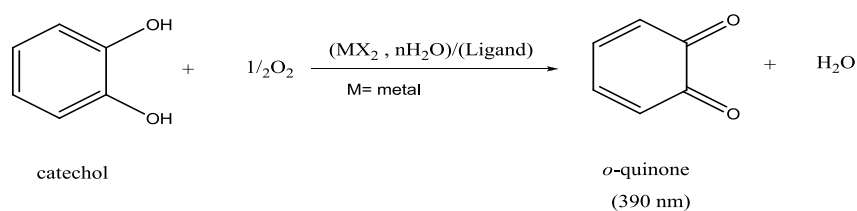
Pyrazolyl derivatives **L1-L7** were prepared by according to the literature procedure by condensation of one equivalent of 3,5-dimethyl-1H-pyrazol-1-yl)methanol with one equivalent of amine derivatives in acetonitril for 4 hours (**Scheme 1**). The reaction was carried out at refluxed solvent under stirring. The tested compounds were characterized by IR,  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  and mass spectrometry before using [52].



Scheme 1. Tested compounds

### Catecholase activity

To determine the catecholase activities of the complexes formed *in-situ* by mixing successively 0,5 mL of a solution ( $2.10^{-3}$  mol/L) of different metallic salts ( $\text{Cu}(\text{CH}_3\text{COO})_2$ ,  $\text{CuSO}_4$ ,  $\text{Cu}(\text{NO}_3)_2$ ,  $\text{NiCl}_2$ ,  $\text{Co}(\text{NO}_3)_2$ ,  $\text{ZnCl}_2$ ) with 0.15 mL of ligand methanolic solution ( $2.10^{-3}$ mol/L), complexes were treated with 100 equivalents of catechol in methanol (99.99 %) under aerobic conditions, the evolution of product absorbance was followed at 390 nm according to time after regulation in zero on a spectrometer UV-Vis UV 1650 PC Shimadzo (In COSTE: Centre Oriental des Sciences et Technologies de l'Eau).



Scheme 2. Reaction model oxidation of catechol to the *o*-quinone.

## RESULTS AND DISCUSSION

## Catalytic activity studies

Reaction of catechol oxidation in the presence of copper complexes formed with ligands **L**<sub>1</sub>–**L**<sub>7</sub>

In order to investigate the ability of the copper complexes formed *in-situ* to act as catalysts for catecholase-like activity, the catalytic oxidation of the substrate catechol by the a combination of ligands **L**<sub>1</sub>–**L**<sub>7</sub> and different metallic salts ( $\text{Cu}(\text{CH}_3\text{COO})_2$ ,  $\text{CuSO}_4$ ,  $\text{Cu}(\text{NO}_3)_2$ ,  $\text{NiCl}_2$ ,  $\text{Co}(\text{NO}_3)_2$ ,  $\text{ZnCl}_2$ ), was evaluated in dioxygen saturated at room temperature. Before realizing the catalysis of the oxidation reaction, no absorbance of product (ortho-quinone) was observed in absence of catalysts, which explains that the catechol does not oxidize in absence of catalysts. After that, methanolic solution of a complex formed *in-situ* by the ligands **L**<sub>1</sub>–**L**<sub>7</sub> and different metallic salts was treated with 100 equivalents of catechol under aerobic conditions. The evolution of absorbance of ortho-quinone, which is highly stable and shows a maximum absorption at about 390 nm in methanol, was followed by UV–Vis spectroscopy, and the time dependent spectral scans of the seven combinations are depicted in **Fig.1- Fig.7**, and the reaction rates are showed in **table.1**. As can be seen, the results reveal that all complexes showed activity towards the oxidation of catechols. But with different rates which vary from  $0,0635\mu\text{mol.L}^{-1}.\text{min}^{-1}$  for the complex arising from ligand **L**<sub>3</sub> and metallic salt  $\text{ZnCl}_2$  (weak catalyst) to  $18,9219\mu\text{mol.L}^{-1}.\text{min}^{-1}$  for the complex formed from ligand **L**<sub>4</sub> and the metallic salt  $\text{Cu}(\text{CH}_3\text{COO})_2$  (best catalyst). This can be related to the nature of ligands and metallic salts, all ligands are produced by the reaction of amine and a pyrazol unit, but are different in the size and the nature of the organic chain bound to the amine which reacts with the pyrazol to produce these ligands. The ligand **L**<sub>4</sub> which presents the best catecholase activity is characterized by the existence of 2 OH<sup>-</sup> which can participate in the coordination of the metallic ion, thus the ligands **L**<sub>4</sub> presents a suitable environment of coordination and facilitates the formation of the *in-situ* complex, thus increasing the reaction rate of oxidation.

It is important to mention that no significant absorbance is observed when oxidation reaction is catalyzed by combinations formed by ligands **L**<sub>1</sub>–**L**<sub>7</sub> and  $\text{NiCl}_2$ ,  $\text{Co}(\text{NO}_3)_2$ ,  $\text{ZnCl}_2$ , and copper appears a better metallic ion to catalyze the oxidation of catechol. On the other hand the effect of the nature of the counter anion on the catalytic activity has been noted, this allowed us to observe that the counter anion participates in the coordination environment and its nature influences well the catalytic activity.

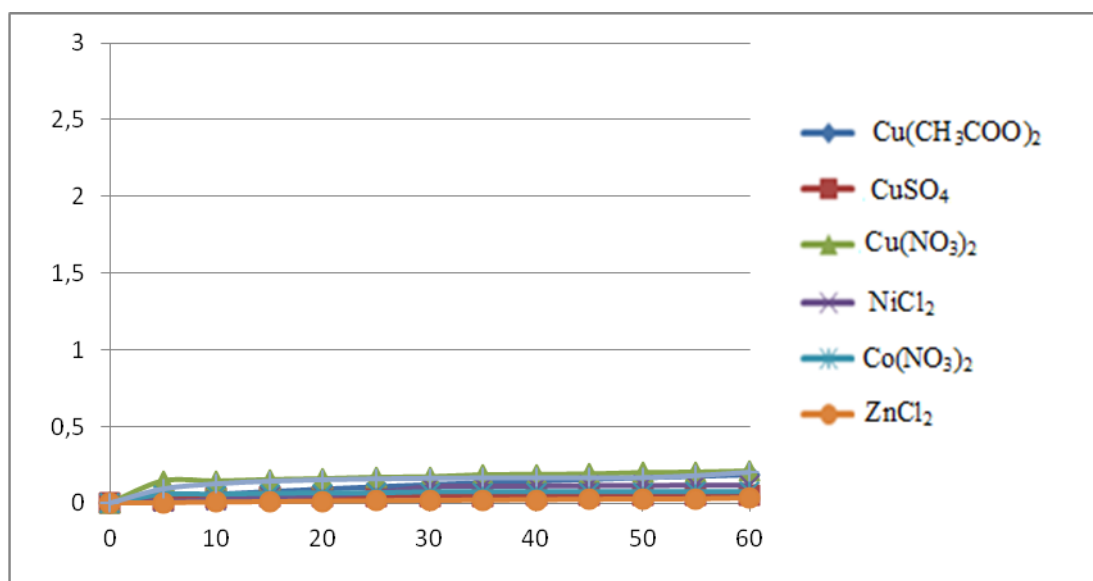


Figure 1. Absorbance of o-quinone in presence of complexes formed by **L**<sub>1</sub> and different metallic salts versus time.

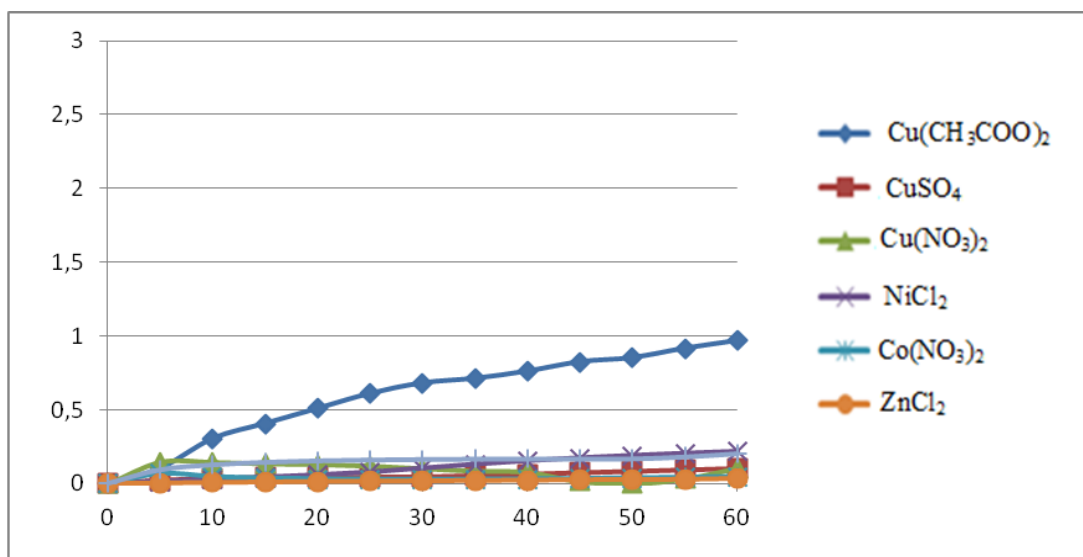


Figure 2. Absorbance of o-quinone in presence of complexes formed by  $L_2$  and different metallic salts versus time.

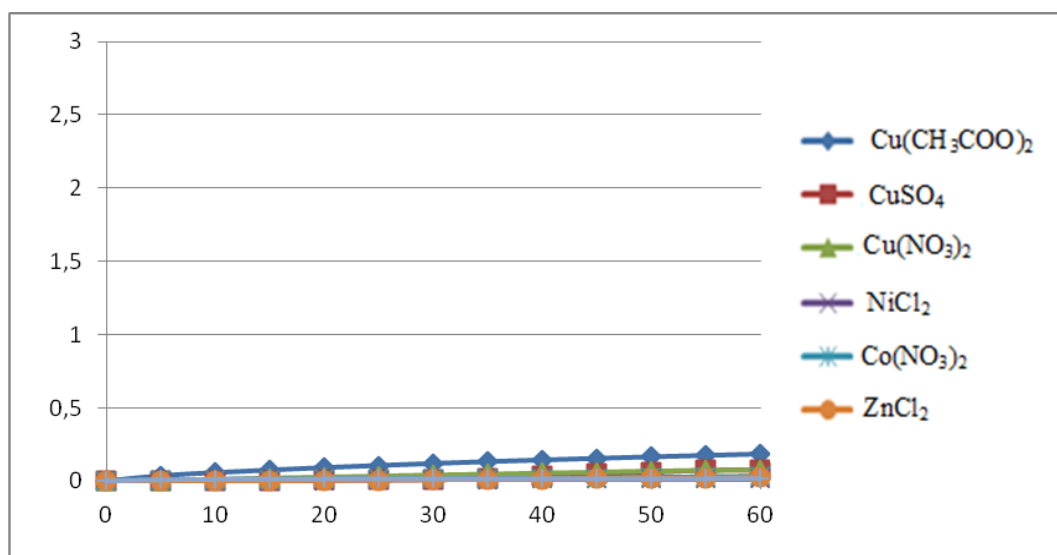


Figure 3. Absorbance of o-quinone in presence of complexes formed by  $L_3$  and different metallic salts versus time.

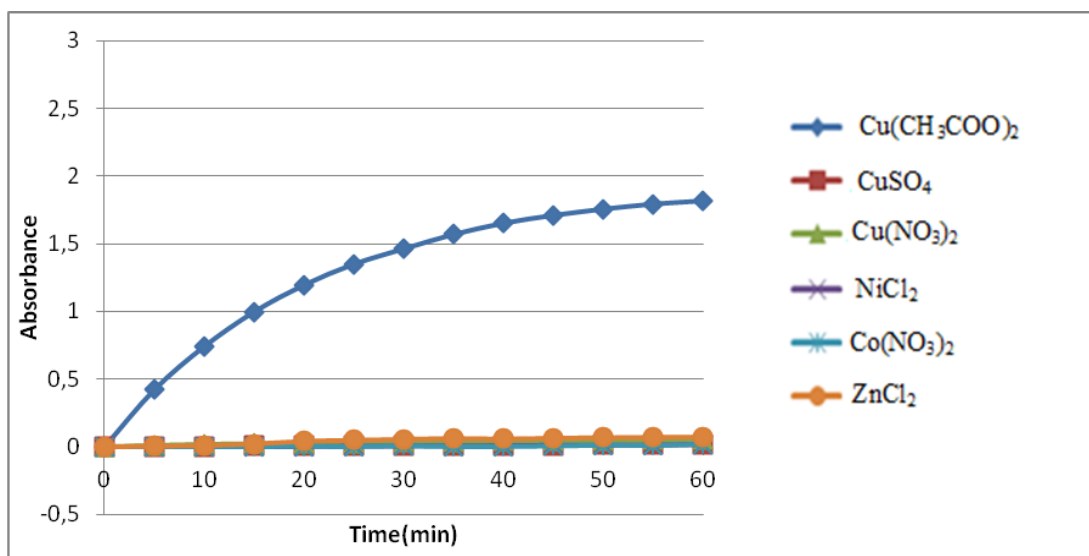


Figure 4. Absorbance of o-quinone in presence of complexes formed by  $L_4$  and different metallic salts versus time.

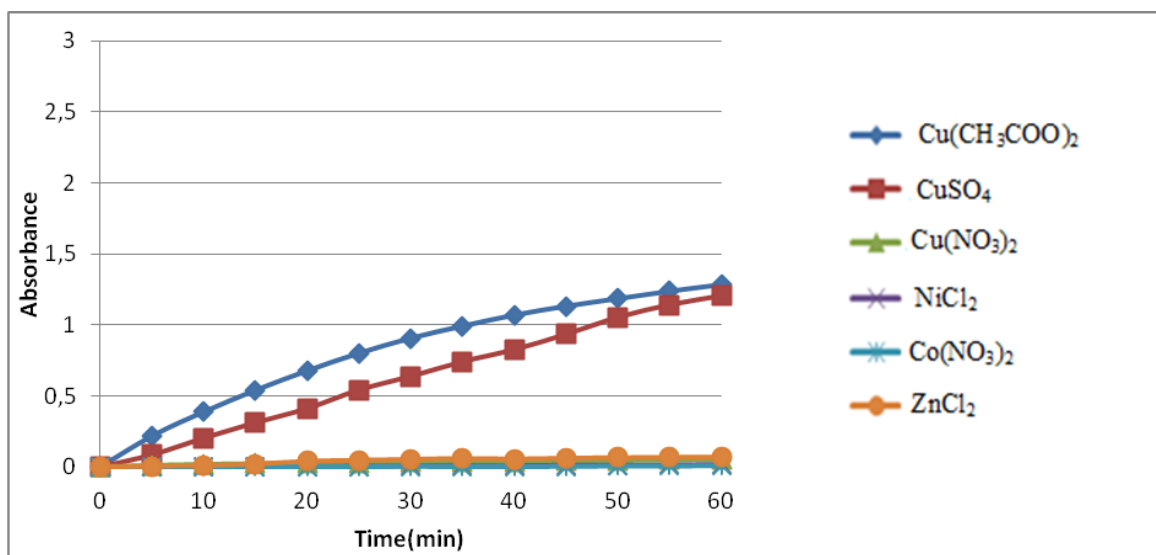


Figure 5. Absorbance of o-quinone in presence of complexes formed by  $L_5$  and different metallic salts versus time.

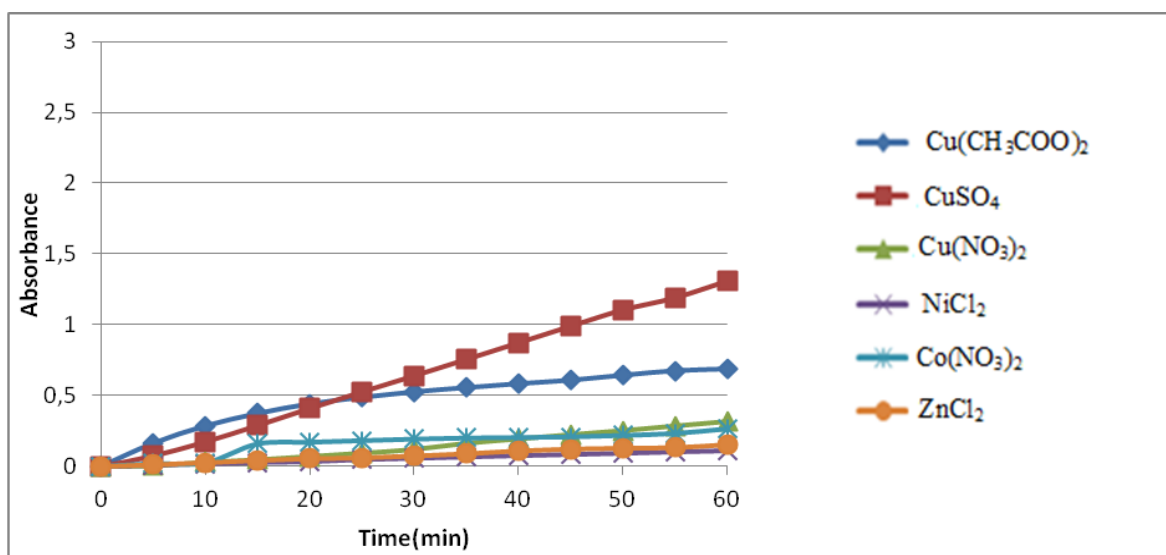


Figure 6. Absorbance of o-quinone in presence of complexes formed by  $L_6$  and different metallic salts versus time.

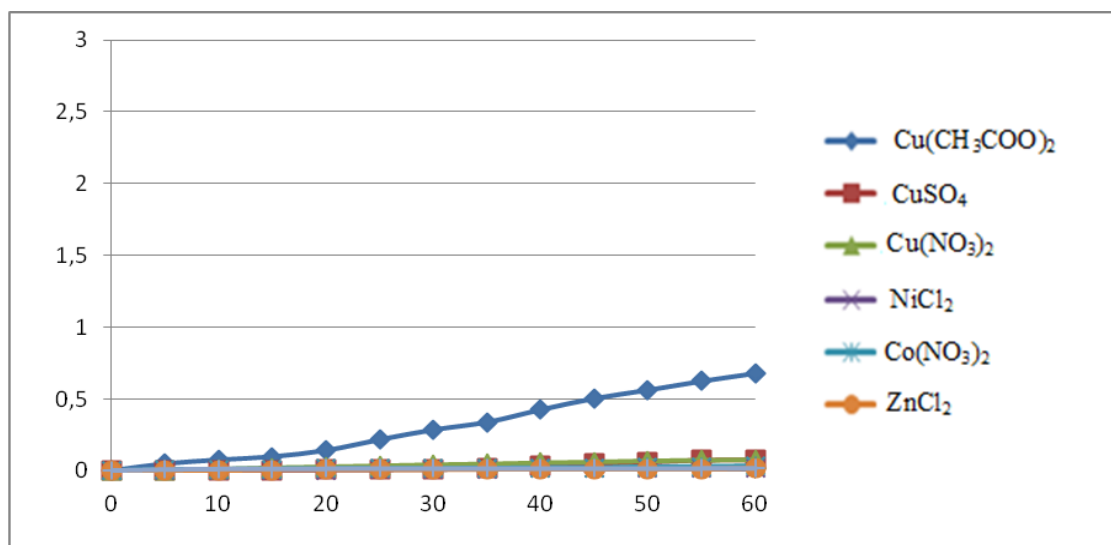


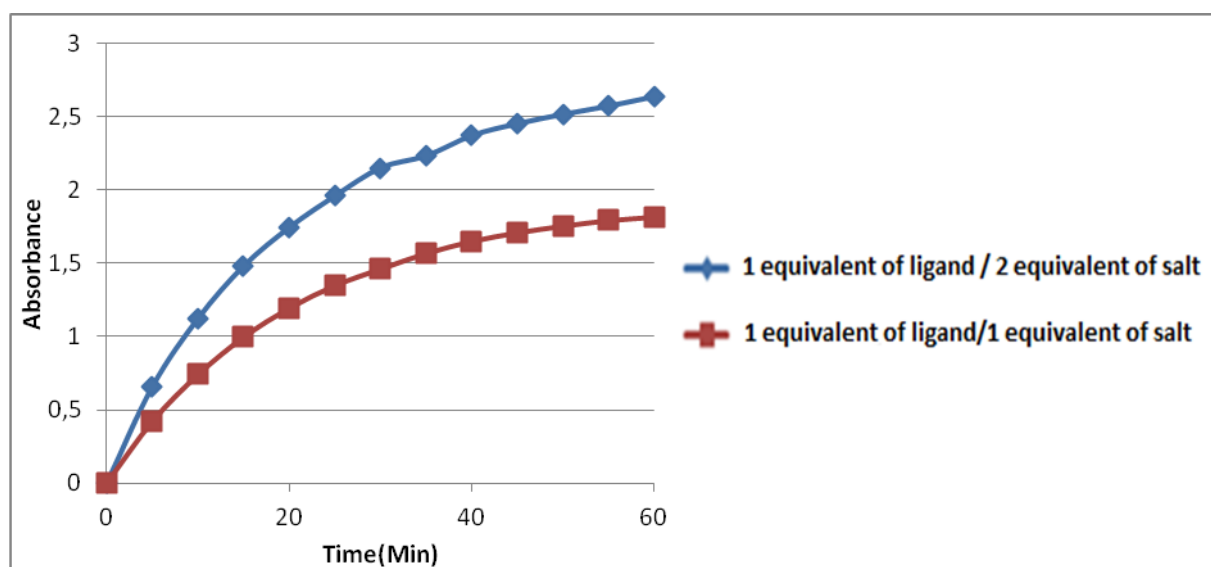
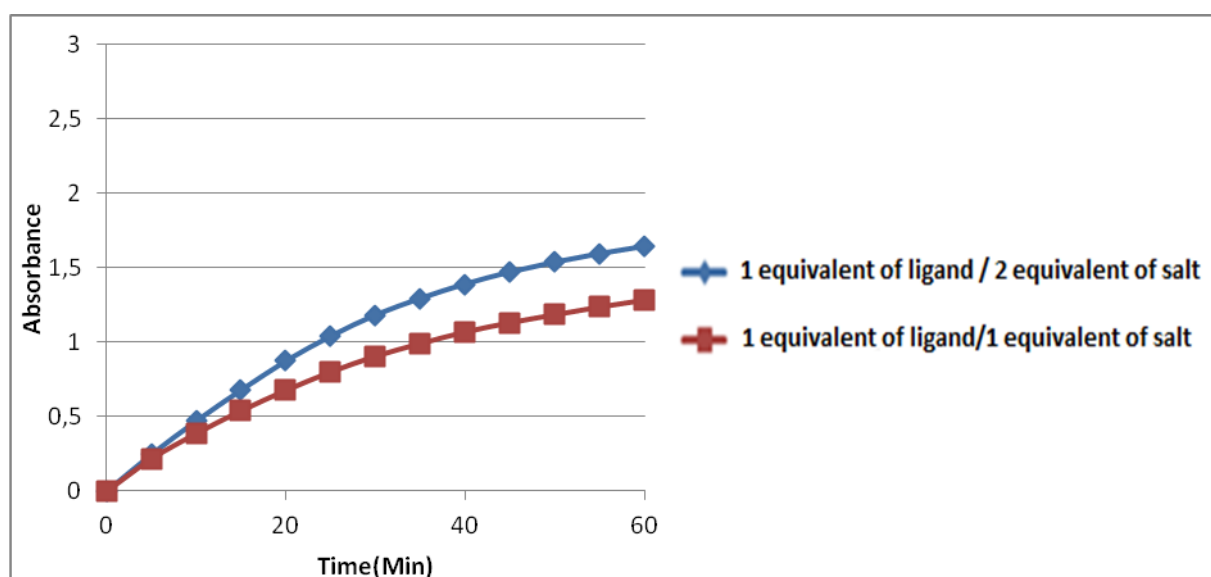
Figure 7. Absorbance of o-quinone in presence of complexes formed by  $L_7$  and different metallic salts versus time.

Table 1. Reaction rate of catechol oxidation in methanol ( $\mu\text{mol. L}^{-1}. \text{min}^{-1}$ ).

Ligand/salt	Cu(CH <sub>3</sub> COO) <sub>2</sub>	CuSO <sub>4</sub>	Cu(NO <sub>3</sub> ) <sub>2</sub>	NiCl <sub>2</sub>	Co(NO <sub>3</sub> ) <sub>2</sub>	ZnCl <sub>2</sub>
L <sub>1</sub>	1,926	1,799	0,5281	0,2583	0,2698	0,4343
L <sub>2</sub>	1,7520	0,1427	0,4541	0,3323	0,1770	0,2427
L <sub>3</sub>	1,3999	1,1999	0,2031	0,5416	0,2146	0,0635
L <sub>4</sub>	18,9219	0,1594	0,5698	0,2187	0,1375	0,7562
L <sub>5</sub>	13,3802	12,5427	0,5593	0,2396	0,1448	0,7917
L <sub>6</sub>	7,1427	14,3646	3,2925	1,1100	2,7750	1,5975
L <sub>7</sub>	6,1698	5,5469	5,5237	0,4312	0,1427	0,3510

### Effect of ligand concentration on the catecholase activity

In order to obtain accurate predictions of effect of ligand concentration on the catecholase activity, the concentration of ligands L<sub>1</sub>-L<sub>7</sub> was decreased to be 1 equivalent for 2 equivalents of metallic salt to form the catalyst, some results of evolution of ortho-quinone absorbance are given in Fig.8-Fig.10, and values of the oxidation rate are showed in table (2), these results confirm that there is a difference in catecholase activity in comparison with obtaining results from 1:1 metal salt: ligand ratio. This difference may be related to the effect of the ligand concentration, which can be explained by the mode of coordination of the ligand to the metal center.

Figure 8. Absorbance evolution of o-quinone in presence of complexes formed by L<sub>4</sub>/Cu(CH<sub>3</sub>COO)<sub>2</sub>Figure 9. Absorbance evolution of o-quinone in presence of complexes formed by L<sub>5</sub>/Cu(CH<sub>3</sub>COO)<sub>2</sub>

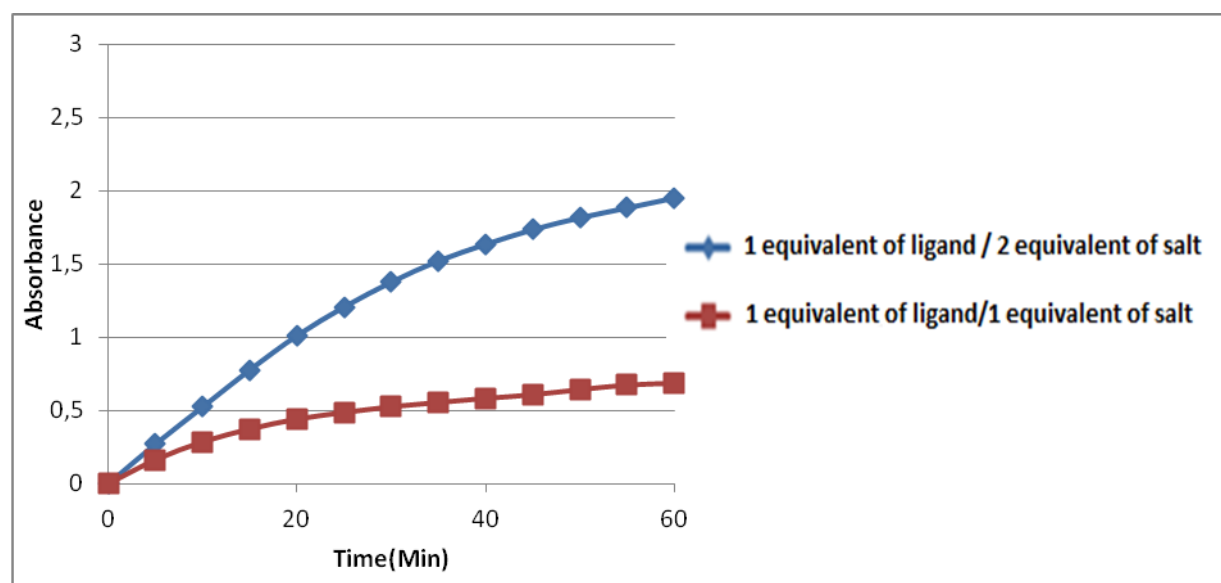


Figure 10 . Absorbance evolution of o-quinone in presence of complexes formed by  $L_6/Cu(CH_3COO)_2$

Table 2. Reaction rate of catechol oxidation in methanol ( $\mu\text{mol. L}^{-1}. \text{min}^{-1}$ ) in presence of complexes formed by one equivalent legend and two equivalents of metallic salt.

Ligand/salt	$Cu(CH_3COO)_2$	$CuSO_4$	$Cu(NO_3)_2$	$NiCl_2$	$Co(NO_3)_2$	$ZnCl_2$
$L_1$	2,0302	0,0812	0,0843	0,2562	0,2594	0,2656
$L_2$	1,8562	0,1531	0,4572	0,3427	0,1833	0,2323
$L_3$	0,2385	0,2771	0,2073	0,5312	0,2093	0,0739
$L_4$	27,4490	0,6219	0,2073	0,2083	0,1271	0,7667
$L_5$	17,1250	7,3312	2,6948	0,7510	1,8187	1,3760
$L_6$	20,3198	7,0812	4,1239	2,0406	1,6008	1,6648
$L_7$	12,1677	5,5125	5,5250	0,4406	0,1427	0,1635

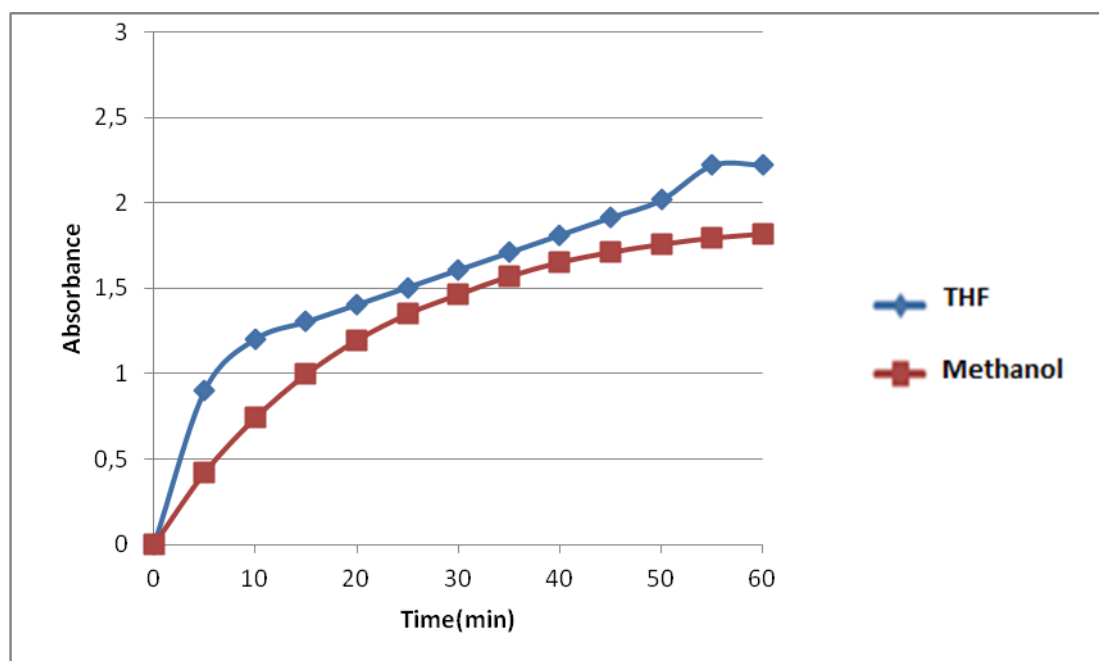


Figure 11. Absorbance evolution of o-quinone in presence of complexes formed by  $L_4$

### Solvent effect

Another important factor for catecholase activity is the nature of solvent used in reaction. In general the reaction rate of catechol oxidation will be influenced by solvent. In recent years, work of various groups has shown that the nature of solvent has a large effect on the catecholase activity [51, 53-55] and it is found that protic and polar

solvents, appears to be better solvent than aprotic and polar solvents. From the study of catecholase activity in methanol and in THF, it is clear that it is the nature of the solvent that plays a crucial role in catecholase activity of studied complexes. For the whole catalytic process, a  $2.10^{-3}$  mol/L solution of the catalyst was treated with 100 equivalents of the substrate catechol under aerobic conditions. Time dependent UV-Vis spectral scans were carried out in methanol and THF.

**Fig.11** and **table.3** clearly indicate that the conversion of catechol to ortho-quinone, catalyzed by systems formed *in-situ* by ligands **L<sub>1</sub>-L<sub>7</sub>** and different metallic salts, was significant when THF was employed as the solvent.

**Table 3.** Reaction rate of catechol oxidation ( $\mu\text{mol. L}^{-1} \cdot \text{min}^{-1}$ ) (mol-mol in THF).

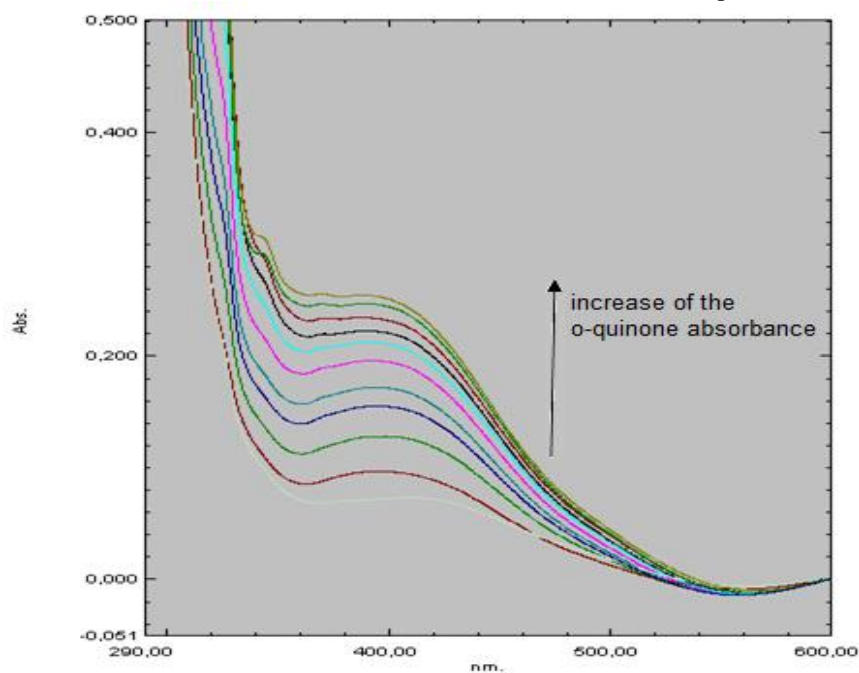
	Cu(CH <sub>3</sub> COO) <sub>2</sub>	CuSO <sub>4</sub>	Cu(NO <sub>3</sub> ) <sub>2</sub>
<b>L<sub>1</sub></b>	9,1432	10,6323	11,0931
<b>L<sub>2</sub></b>	13,5676	4,2667	2,4686
<b>L<sub>3</sub></b>	4,7608	0,3196	0,8294
<b>L<sub>4</sub></b>	21,7911	0,3725	0,2402
<b>L<sub>5</sub></b>	12,1010	15,5450	0,8284
<b>L<sub>6</sub></b>	7,2568	14,5813	0,3088
<b>L<sub>7</sub></b>	6,2176	5,7304	4,8245

**Table 4.** Reaction rate of catechol oxidation in presence of complexes formed by one equivalent ligand and two equivalents of metallic salt (in THF) ( $\mu\text{mol.L}^{-1} \cdot \text{min}^{-1}$ ).

	Cu(CH <sub>3</sub> COO) <sub>2</sub>	CuSO <sub>4</sub>	Cu(NO <sub>3</sub> ) <sub>2</sub>
<b>L<sub>1</sub></b>	2,5951	0,7117	0,0829
<b>L<sub>2</sub></b>	1,6539	0,8843	0,1245
<b>L<sub>3</sub></b>	0,2651	0,2802	0,3245
<b>L<sub>4</sub></b>	33,2451	1,3588	0,1515
<b>L<sub>5</sub></b>	15,6216	1,8431	2,1559
<b>L<sub>6</sub></b>	20,0343	6,9235	4,0147
<b>L<sub>7</sub></b>	11,7667	6,0127	5,7411

To confirm that the THF is a better solvent than the methanol for the catecholase activity, the oxidation of catechol were carried out by monitoring the increase of the intensity of ortho-quinone bande at 390 nm with time (**Fig.12- Fig.13**) after mixing of 0,15 mL of **L<sub>4</sub>**,

0.15 mL of Cu(CH<sub>3</sub>COO)<sub>2</sub> and 2 mL of catechol, and the o-quinone absorbance was recorded at a time interval of 15 min. the oxidation reaction was carried out in methanol and THF at constant temperature of 25 °C.



**Figure 12.** Increase of o-quinone band at 390 nm after addition of 100 equivalents of catechu to a solution containing one equivalent of ligand **L<sub>4</sub>** and two equivalents of Cu(CH<sub>3</sub>COO)<sub>2</sub> (in methanol). The spectra were recorded after every 15 min.



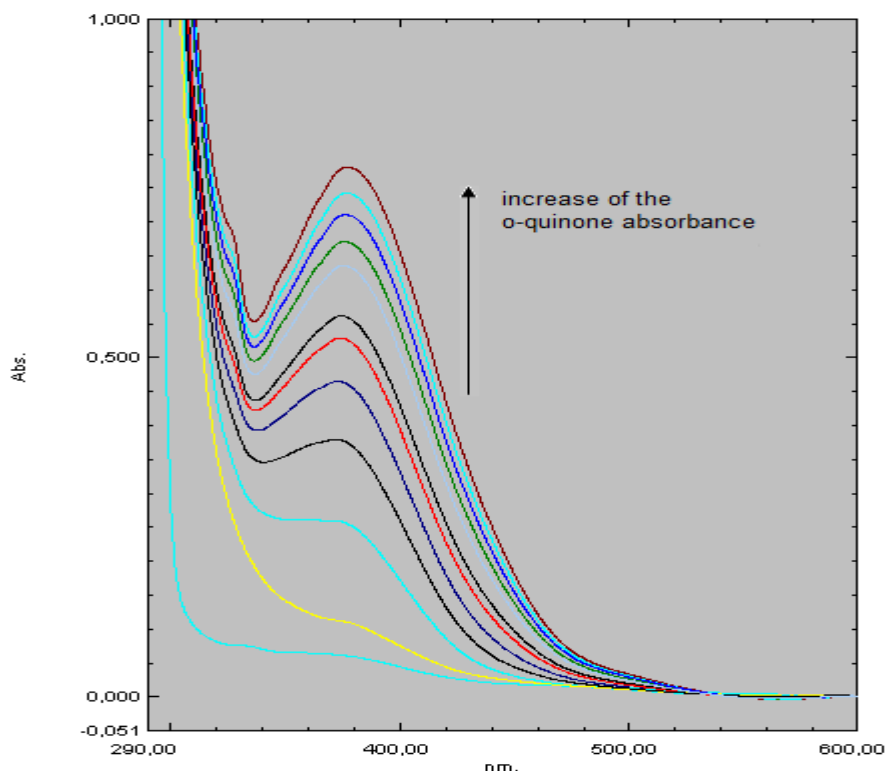


Figure 13. Increase of o-quinone band at 390 nm after addition of 100 equivalents of catechu to a solution containing one equivalent of ligand **L4** and two equivalents of  $\text{Cu}(\text{CH}_3\text{COO})_2$  (in THF). The spectra were recorded after every 15 min.

The **Fig.12** and **Fig.13** clearly show that band centered at around 390 nm is observed when reaction is realized in methanol as well as in THF, which explain that combination arising from ligand **L4** and copper salt  $\text{Cu}(\text{CH}_3\text{COO})_2$  catalyzes the oxidation of catechol to o-quinone smoothly.

In the methanol, the absorbance of the ortho-quinone does not exceed 0.3 after two hours of the reaction, on the other hand in the THF the absorbance affects 0.8 after the same duration of the reaction which confirms that the THF remains the best solvent to catalyse this type of reactions.

#### Kinetic study

The kinetics of the oxidation of catechol was determined by the method of initial rates by monitoring the increasing absorbance of the 390 nm band of the product ortho-quinone in methanol as well as in THF, the ligand **L4** and metallic salt  $\text{Cu}(\text{CH}_3\text{COO})_2$ , which formed the best catalyst for the catechol oxidation, were fixed in  $10^{-3}$  mol/L and the substrate (catechol) concentration was varied in the range  $10^{-1}$  to  $2 \cdot 10^{-2}$  mol/L. The evolution of absorbance of ortho-quinone at 390 nm was monitored for the first 05 minutes of the reaction time, and linear relationship for the initial rates and the substrate concentration was obtained. The Michaelis-Menten model, which developed for enzyme kinetics, is applied to obtain the kinetic parameters of the best catalyst. **Fig.14** and **Fig.16** represent the dependence of initial rate on the concentration of catechol for complex arising from **L4** and  $\text{Cu}(\text{CH}_3\text{COO})_2$ . A first order dependence was observed at low concentration of substrate. However, complex formed from **L4** and  $\text{Cu}(\text{CH}_3\text{COO})_2$  showed a saturation kinetic at higher concentration of catechol.

**Fig.15** and **Fig.17** show the Lineweaver-Burk plots for the best catalyst. The **K<sub>m</sub>** values **Table(5)** for combination formed by **L4** and  $\text{Cu}(\text{CH}_3\text{COO})_2$  in methanol as well as in THF are in excellent agreement with the above results which confirm that the THF is a better solvent for the oxidation reaction of catechol.

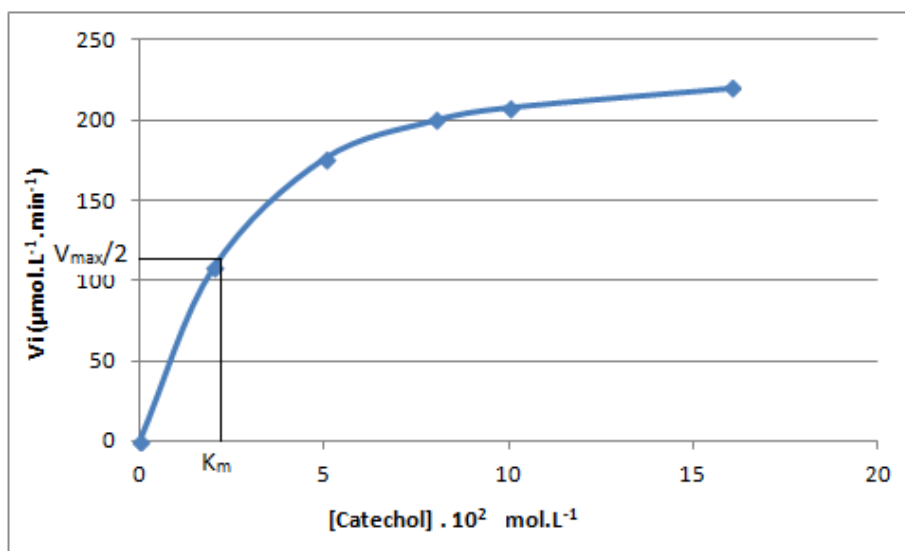


Figure 14. Dependence of the reaction rates on the catechol concentrations for the oxidation reaction catalyzed by complex arising from one equivalent of  $L_4$  and two equivalent of  $\text{Cu}(\text{CH}_3\text{COO})_2$  (in THF).

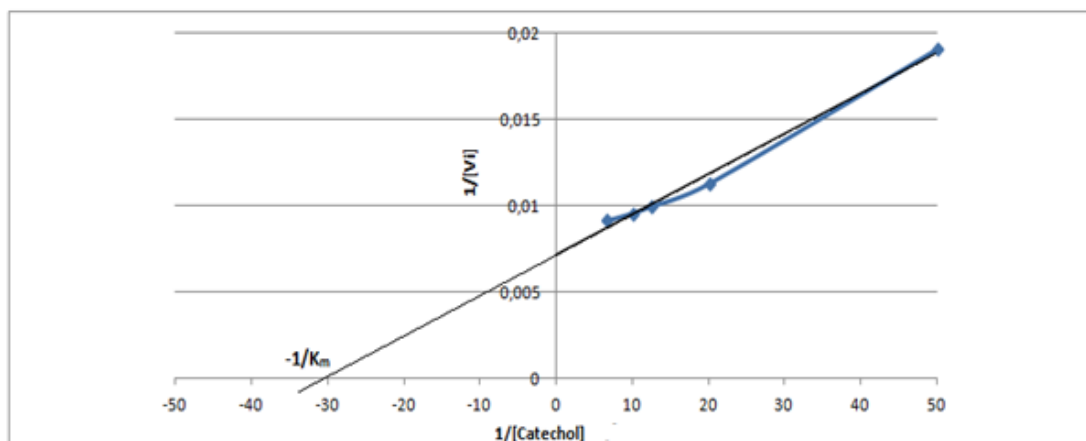


Figure 15. Lineweaver-Burk plot for the catalysis by complex arising from one equivalent of  $L_4$  and two equivalent of  $\text{Cu}(\text{CH}_3\text{COO})_2$  (in THF).

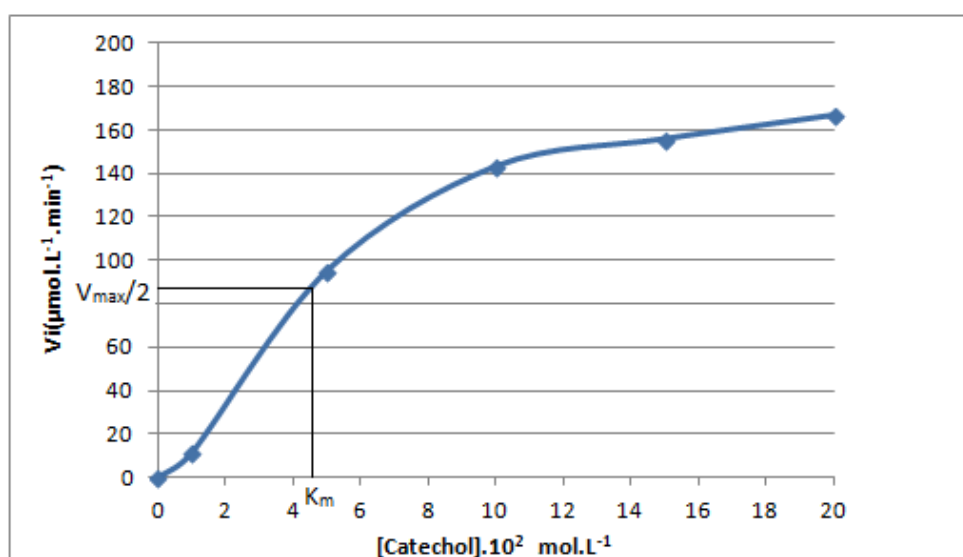


Figure 16. Dependence of the reaction rates on the catechol concentrations for the oxidation reaction catalyzed by complex arising from one equivalent of  $L_4$  an equivalent of  $\text{Cu}(\text{CH}_3\text{COO})_2$  (in methanol).

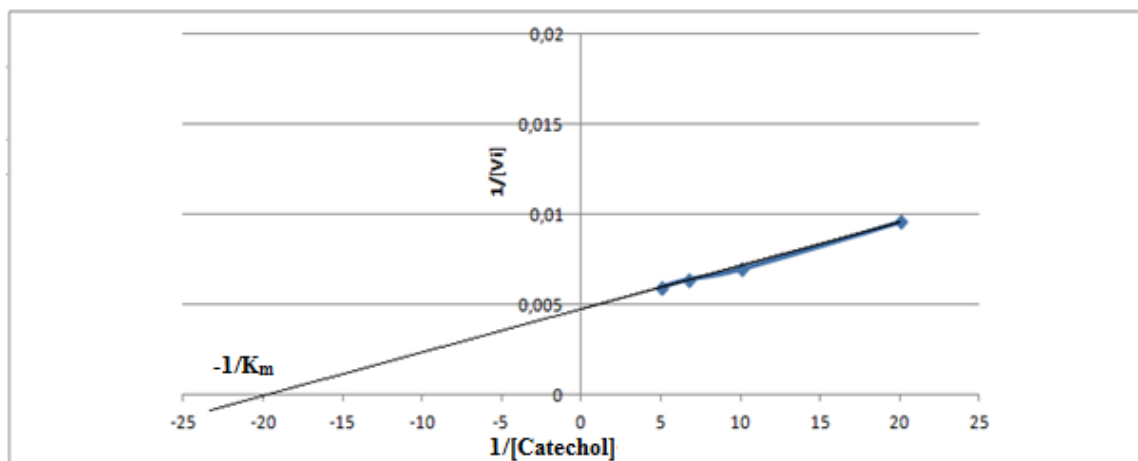


Figure 17. Lineweaver–Burk plot for the catalysis by complex arising from one equivalent of  $L_4$  and two equivalent of  $Cu(CH_3COO)_2$  (in methanol).

Table 5. Kinetic parameters for the oxidation of catechol catalyzed by complex arising from one equivalent of  $L_4$  and two equivalents of  $Cu(CH_3COO)_2$

	THF	methanol
$V_m$ ( $\mu\text{mol. L}^{-1} \cdot \text{min}^{-1}$ )	220	166
$K_m$ ( $\text{mol. L}^{-1}$ )	$3,33 \cdot 10^{-2}$	$5 \cdot 10^{-2}$

## CONCLUSION

In this paper, complexes, arising from pyrazole based ligands and different metallic salts, are reported and studied for their catecholase activities, all complexes are able to catalyze the oxidation reaction of catechols to o-quinones at ambient conditions using the oxygen of atmosphere as oxidant (catecholase activity), but are not able to oxidize the phenols to catechols (tyrosinase activity). Although the reaction rate is determined using different combinations of pyrazole based ligands and some metallic salts, oxidation rate varying from  $27,449 \mu\text{mol.L}^{-1} \text{min}^{-1}$  for the  $L_4[Cu(CH_3COO)_2]$  complex, generated in situ by 1:2 ligand: metallic salt ratio, in THF to  $0,0635 \mu\text{mol.L}^{-1} \text{min}^{-1}$  for complex resulting from one equivalent of  $L_3$  and one equivalent of  $ZnCl_2$  in methanol. The results of this work show that the catalytic activity of these complexes is influenced by many factors (the nature of ligand, the nature of counter anion and metallic ion, the ligand concentration, and the nature of solvent).

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