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Air Oxidation of catechol by in-situ copper (II) complexes with ligands containing benzyl groups

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Abstract

In order to mimic the function of catecholase activity, in-situ copper (II) complexes of three ligands containing different numbers of benzyl groups: (E)-4- methoxy-N-(4-methoxybenzylidene)aniline $\mathbf{L_1}$, (E)-N-(4-methoxybenzylidene) naphthalene-1-amine $\mathbf{L_2}$, (E)-N-(4-methoxybenzylidene)aniline $\mathbf{L_3}$, were reported and examined, in combination with different cupric salts, for their catecholase activities at ambient conditions. The highest rate activity was given by the combination of two equivalents of $\mathbf{L_3}$ and one equivalent of $Cu(CH_3COO)_2$ in methanol. The Michaelis - Menten model was applied to obtain the kinetic parameters of the best catalyst.

Keywords: catecholase, aniline, copper, oxidation reaction, aromatic imines.

1. Introduction

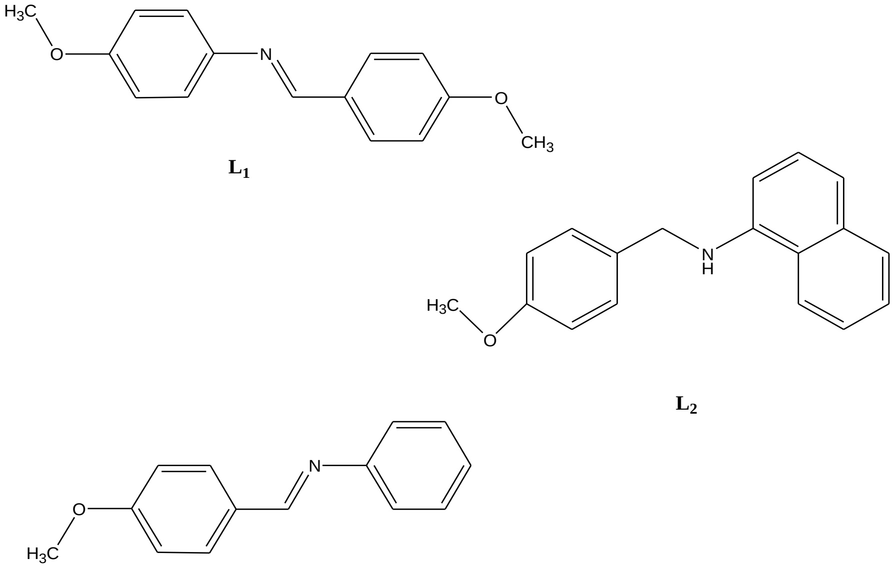
Development of biomimetic oxidation catalysts involving Cu(II) ion as the active metal center is really challenging [1-2]. As an important example, numerous biomimetic approaches were devoted to the synthesis of binuclear Cu(II) ion complexes with various ligands to reproduce catecholase activity [3-4]. These studies aim to mimic the environment of the metal active site of the enzyme catecholase, and also to better understand its properties to activate molecular dioxygen. Activation of dioxygen is a very important process in many living organisms, this function is often assigned to metalloproteines containing copper, like catechol oxidase [5-7], which is an enzyme that possess a binuclear copper center in its active site, and is known to have two copper Cu(II) ions joined by a bridging OH^-, each copper is coordinated by three histidine nitrogens [8-9], this enzyme catalyses the oxidation of catechol to corresponding ortho-quinone through the four-electron reduction of molecular oxygen to water [10-12]. In an attempt to mimic the active site function of catechol oxidase, much ligands models based on iron [13, 15], copper [16-24], manganese [25-29] and cobalt [30-31] complexes have been designed and extensively studied. The study of ‘biomimetic’ reactions, catalyzed by functional metalloenzyme models, helps understand the influencing factors of catalytic activity of these models toward the oxidation of catechol. In 2001 Neves et al. [32] have synthesized new copper (II) complexes with different numbers of N, O donor groups to correlate these modifications with the catecholase activity of the new complexes. In same year C.H.Kao et al. [33] found that the complexes with the bond distance of Cu(II)…Cu(II) located at 2.9-3.0 Å show higher catecholase activity. In the same context, the catecholase activity of binuclear copper (II) complexes models, and other different structural parameters, has been investigated, like nature of the ligand, nature of the ion salts, concentration of the complex and the solvent nature… [16-24] and [34-38].

The present work stems from our continued interest in the chemical modelling of catecholase [16-24], and continuation of our looking for other ligands, to be tested in same reaction, which concern imine or Schiff-base compounds. The imines are an important class of versatile synthetic intermediates for the preparation of nitrogencontaining compounds as building blocks [39], for biological activity [40-41], in catalysis area [42] and biochemistry [43]. In recent work they are used like Schiff-base complexes of transition metals as small synthetic analogs of metallobiosites [44]. However, to the best of our knowledge no systematic study of mononuclear copper (II) complexes of Schiff-base ligands is reported in the literature on this subject. Herein three ligands containing different numbers of benzyl groups are reported and studied for their catecholase activity. The results revealed that the trend of catecholase activity correlated to the sort of the ligands, and it was found that the complex, arising from two equivalents of L_3 which have sp^2 nitrogen, and one equivalent of $Cu(CH_3COO)_2$ in methanol, showed a higher catecholase activity.

2- Experimental section

2.1. Ligands description

The three imines (**Scheme 1**) were prepared by condensation between aromatic aldehydes [benzaldehyde and 4-methoxybenzaldehyde] and aromatic amines [aniline, 4-mothoxyaniline and naphthalene-2-amine] in the presence of $CeCl_3 \cdot 7H_2O$ (cerium chloride heptahydrate) as a Lewis base. The structures of all the products were unambiguously established on the basis of their spectral analysis (IR, ^1H NMR and MS mass spectral data [45-47].



L₁

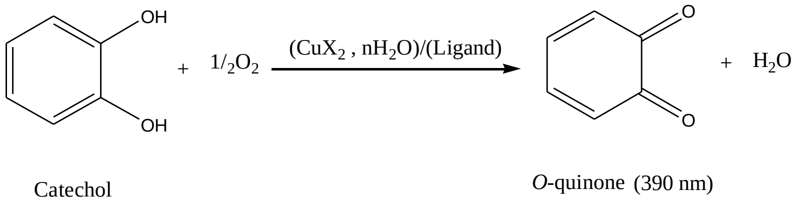
L₂

L₃

Scheme 1: Tested compounds

2.2. Catecholase activity measurements

The catecholase activities of the complexes formed *in-situ* by mixing successively 0,15 mL of a solution (2.10^{-3} mol/L) of copper salt CuX_2, nH_2O (with X = NO^{3-}, CH_3COO^-, SO_4^{2-}) with 0,15 mL of ligand solution (2.10^{-3}mol/L) were performed for the oxidation of catechol (10^{-1} mol/L) (**Scheme 2**) with O_2 of air in methanol (99,99 %) at ambient 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 (Catechol oxidation)

3. Results and discussion

3.1. Catalytic activity studies

3.1.1. Reaction of catechol oxidation catalyzed by copper complexes formed with ligands L_1-L_3

To get an estimation of the ability of the complexes formed *in-situ* from our ligands L_1-L_3 and cupric salts to catalyze the oxidation of catechol to ortho-quinone. 0,15 mL of a solution (2.10^{-3} mol/L) of copper salt CuX_2,

nH_2O (with X = NO^{3-}, CH_3COO^-, SO_4^{2-}) with 0,15 mL of ligand solution (2.10^{-3}mol/L) were treated with 2 mL of catechol (10^{-1} mol/L) under aerobic conditions.

As can be seen in **Figures 1-3**, the evolution of o-quinone absorbance showed considerable catecholase activity of studied complexes. The calculated reaction rates (**Table 1**), indicate that the catalytic activity varies from a complex to the other one, changes observed in the UV-Vis spectra recorded in methanol solution (**Fig.1-3**) can be explained by differences in the nature of the counter anion and the nature of our ligands, especially in the nature of the nitrogen atom in the ligand, combination between **L_2**, which have sp^2 nitrogen, and the metallic salt $Cu(CH_3COO)_2$, presents the highest rate activity in the reaction conditions. The increase of catalytic activity can be explained by an increase of the steric hindrance around the metallic ion resulting from mesomeric effect of the benzyl group.

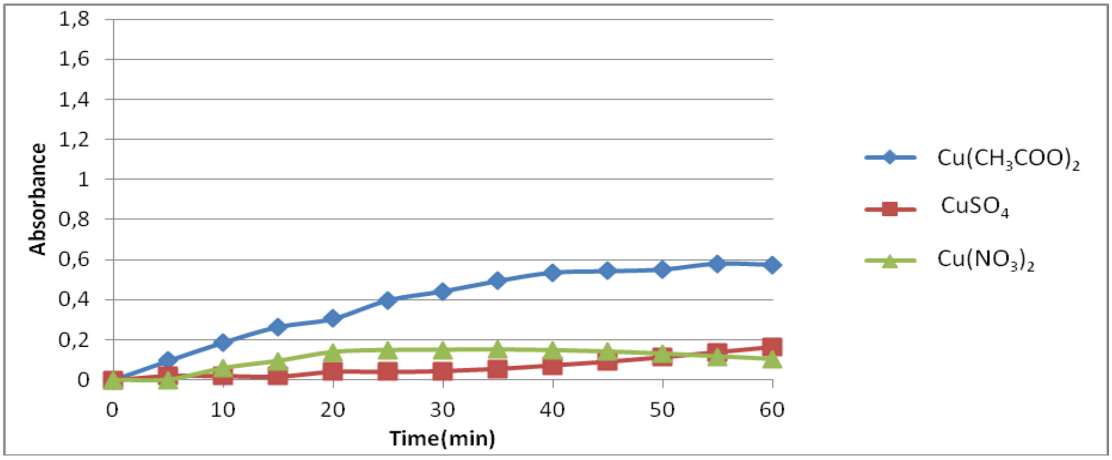


Fig.1: Catechol oxidation in the presence of copper complexes formed with **L_1**

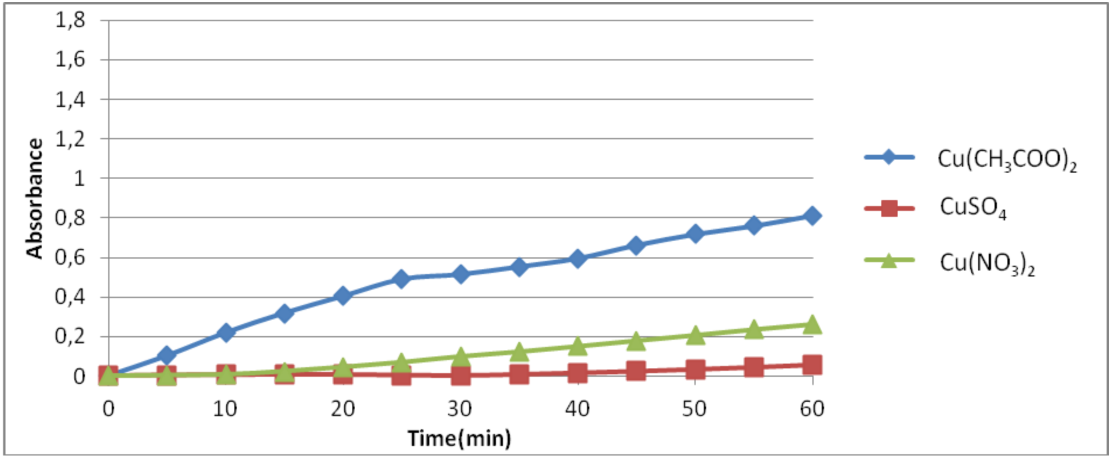


Fig. 2: Catechol oxidation in the presence of copper complexes formed with **L_2**

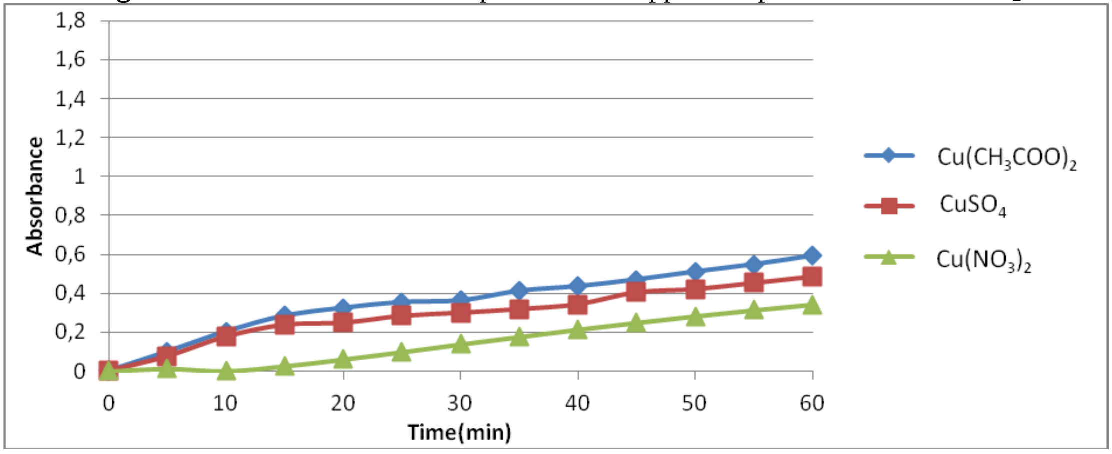


Fig.3: Catechol oxidation in the presence of copper complexes formed with **L_3**

3.1.2. Effect of the ligand concentration on the catecholase activity

In order to determine the effect of ligand concentration on the catecholase activity of resultant complexes, ligand concentration is varying to be two equivalents for one equivalent of metallic salt. The reactivity studies were performed in methanol solution under ambient conditions, the evolution of product absorbance versus time is collected in **Fig.4-6**. This study aims to correlate the concentration modifications with the catecholase activity. Obtained results show that the ligand concentration has an observable effect on the rate of catechol oxidation; this is previously confirmed in the literature [21, 24] which was explained by the nature of coordination environment.

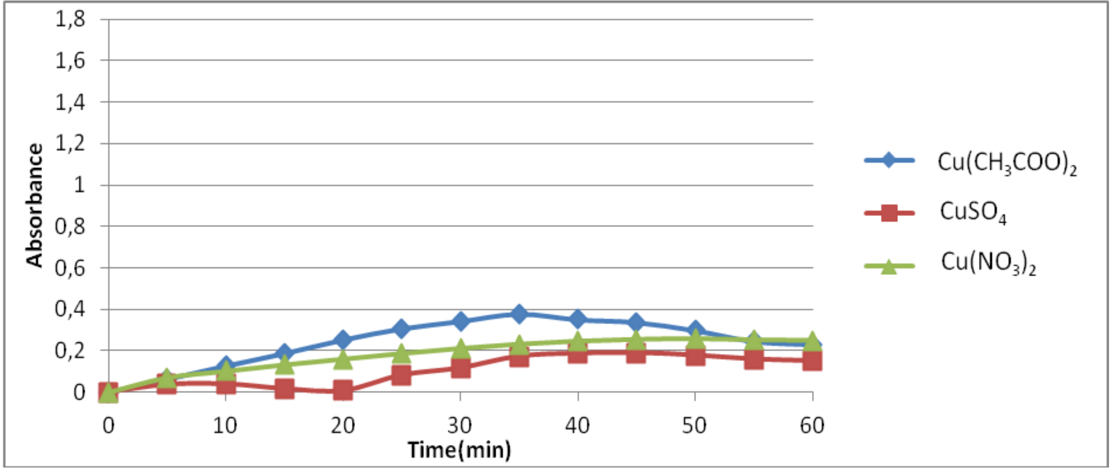


Fig.4: Catechol oxidation in the presence of copper complexes formed with $\mathbf{L_1}$
(2 equivalents of ligand for 1 equivalent of metallic salt in methanol)

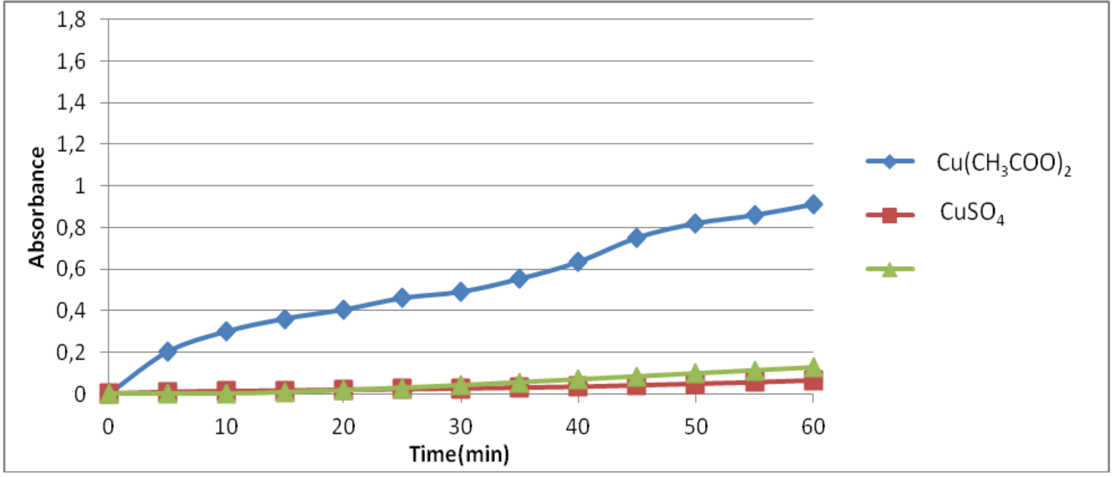


Fig.5: Catechol oxidation in the presence of copper complexes formed with $\mathbf{L_2}$
(2 equivalents of ligand for 1 equivalent of metallic salt in methanol)

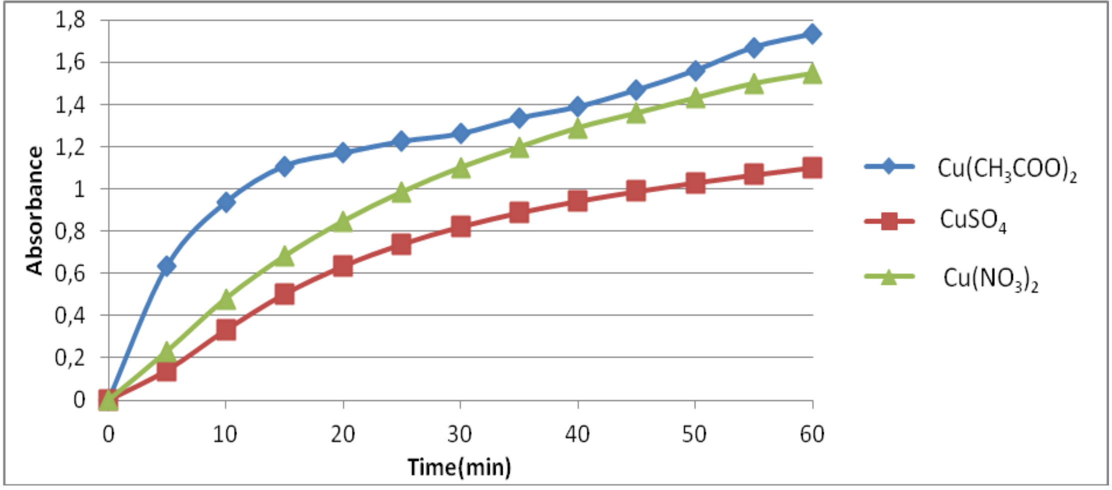


Fig.6: Catechol oxidation in the presence of copper complexes formed with $\mathbf{L_3}$
(2 equivalents of ligand for 1 equivalent of metallic salt in methanol)

Table 1: Activity rate of catechol oxidation in methanol (µmol.L^{-1}.min^{-1})

Ligand - metallic salt	$Cu(CH_3COO)_2$		$CuSO_4$		$Cu(NO_3)_2$	
	Mol-mol	2mol-1mol	Mol-mol	2mol-1mol	Mol-mol	2mol-1mol
L_1	5,992	2,406	1,680	1,562	1,071	2,593
L_2	8,473	9,516	0,609	0,703	2,740	1,343
L_3	6,200	18 ,062	5,062	11,488	3,567	16,101

3.1.3. Solvent effect

The catalysis oxidation reaction of catechol were performed in methanol as well as in acetonitrile under same thermodynamic conditions, in order to more understand the effect of solvent on the evolution the reaction rate, the absorbance variation of *O*-quinone with time was continuously monitored at 390 nm, as can be seen from **Fig.7-8**, catechol oxidation rate in the presence of the copper complexes with ligands **L_2-L_3** in the acetonitrile (**L_1** was not soluble in the acetonitrile) was determined (**Table 2**).

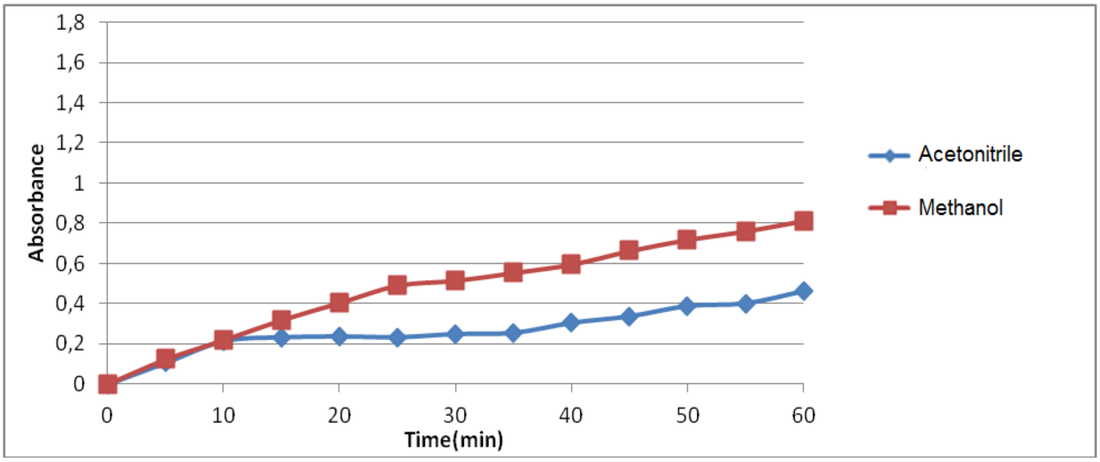


Fig.7: Catechol oxidation in presence of copper complexes formed with **L_2**

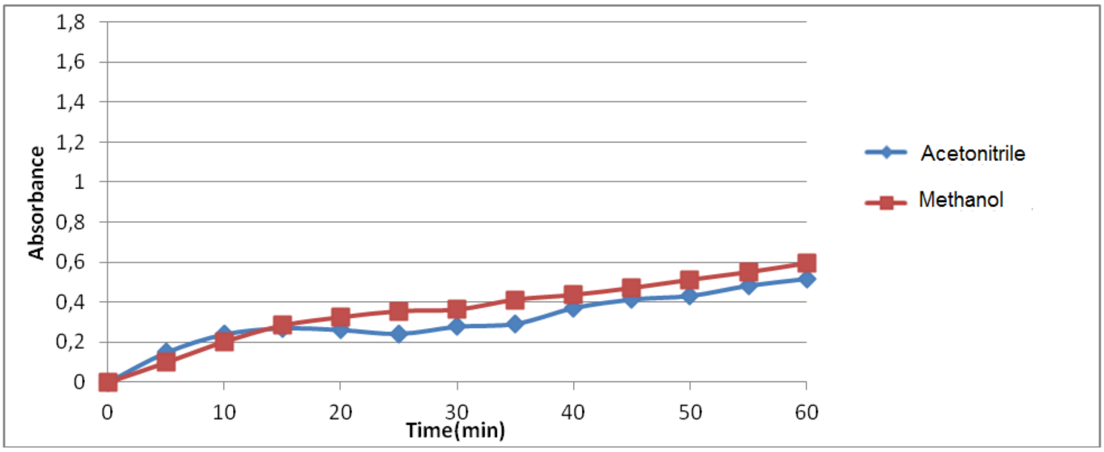


Fig.8: Catechol oxidation in the presence of copper complexes formed with **L_3**

Table 2: Activity rate of catechol oxidation in acetonitrile (µmol.L^{-1}.min^{-1})

Ligand - metallic salt	$Cu(CH_3COO)_2$		$CuSO_4$		$Cu(NO_3)_2$	
	Mol-mol	2mol-1mol	Mol-mol	2mol-1mol	Mol-mol	2mol-1mol
L_2	5,4912	0,3561	0,6351	0,9807	2,4587	4,5807
L_3	4,2982	5,2456	1,0263	0,3359	5,2780	2,9438

Absorbance evolution of reaction product obtained by the spectrometer UV-Vis and reaction rate values, illustrate well the importance of the solvent effect on the catalytic activities. Methanol appears a better solvent than the acetonitrile. Methanol and acetonitrile are two solvents which differ in several physical parameters like dielectric constant, dipole moment, polarity, etc... These physical parameters bring not much information about the capacity of the solvent molecules to interact at short distances with the molecules of solutes. Which explains that is the coordination power or protic nature of the solvents that play the key role in changing the activity of the complexes [24, 48]. According to this reasoning, we can propose that the reaction of catechol oxidation is more quickly with polar and protic solvents (like methanol), and more slowly with the dipolar and aprotic solvents (like acetonitrile) To confirm that the methanol is a better solvent than the acetonitrile for the catechol oxidation reaction, this oxidation was carried out by monitoring the increase of the intensity of *o*-quinone band at 390 nm with time (**Fig.9**), the concentration of the substrate catechol was always kept at least 100 times larger than the catalyst formed *in-situ* by mixing of two equivalents of **L_3**, and one equivalent of $Cu(CH_3COO)_2$ in methanol as well as in acetonitrile, and the *o*-quinone absorbance was recorded at a time interval of 20 min at constant temperature of 25 °C.

As can be seen in **Fig.9**, the absorbance of the *o*-quinone does not exceed 1,6 nm after three hours of the reaction in the acetonitrile, on the other hand in the methanol the absorbance affects 2 after the same duration of the reaction, which confirms that the methanol remains a better solvent than the acetonitrile to catalyze this type of reactions.

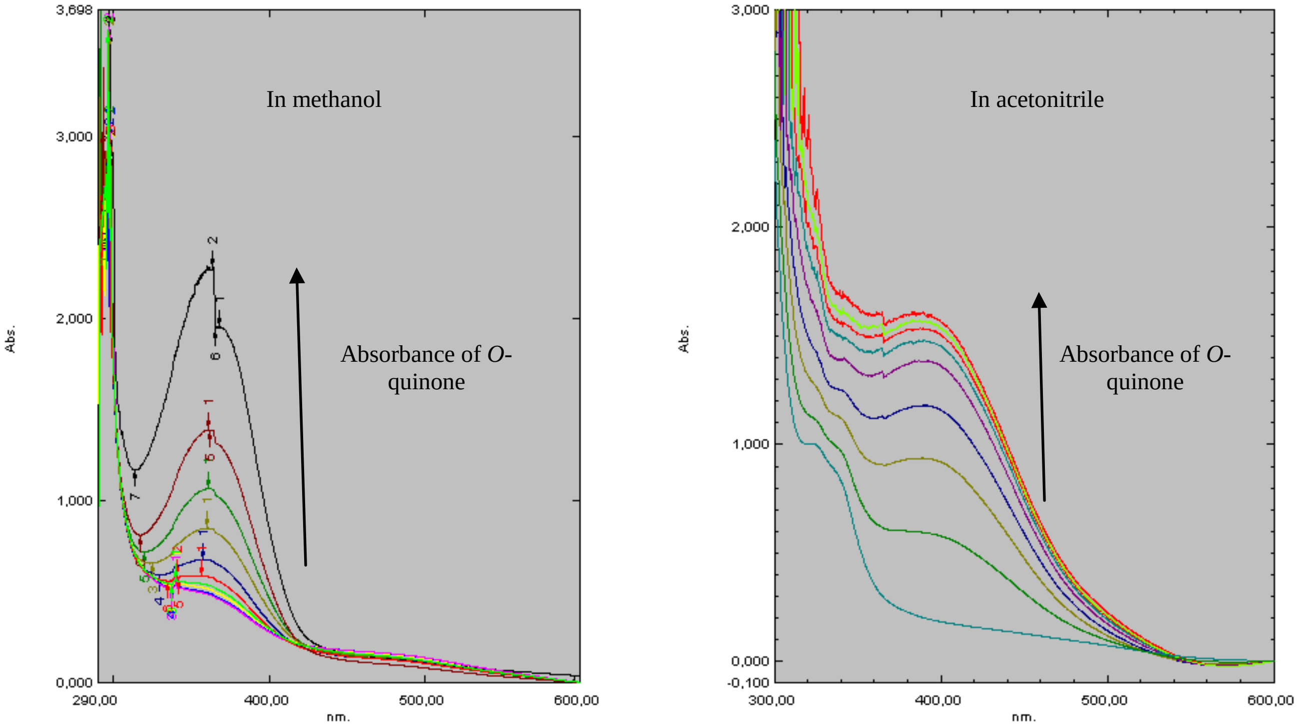


Fig.9: Increase in the *O*-quinone absorbance at 390 nm for the combination **L_3**/$Cu(CH_3COO)_2$

3.2. Kinetic study

The kinetics of formation of *o*-quinone, in the presence of the combination **L_3**/$Cu(CH_3COO)_2$, was determined by the method of initial rates by monitoring the increasing absorbance of the 390 nm band of the product in methanol as well as in acetonitrile, with a concentration of substrate varies in the range 2.10^{-1} to 10^{-3} mol/L, and the concentration of **L_3/**$Cu(CH_3COO)_2$, which formed the best catalyst, was fixed in 10^{-3} mol/L. The evolution of absorbance of ortho-quinone was monitored for the first 5 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. The concentration dependence of reaction rate in the presence of the catalyst arising from **L_3** and $Cu(CH_3COO)_2$ (**Fig.10-11**) shows two regions, the region of the first order dependence in substrate concentrations at low concentration of substrate and zero order in substrate at high concentrations. Basing on the information which confirms that the small **K_m** means tight binding between substrate and catalyst, and high **K_m** corresponds to weak binding, The **K_m** values for combination formed by **L_3**/$Cu(CH_3COO)_2$ in methanol as well as in acetonitrile showed in **Table 3** are in excellent agreement with the above results which confirm that the methanol is a better solvent for the oxidation reaction of catechol than the acetonitrile.

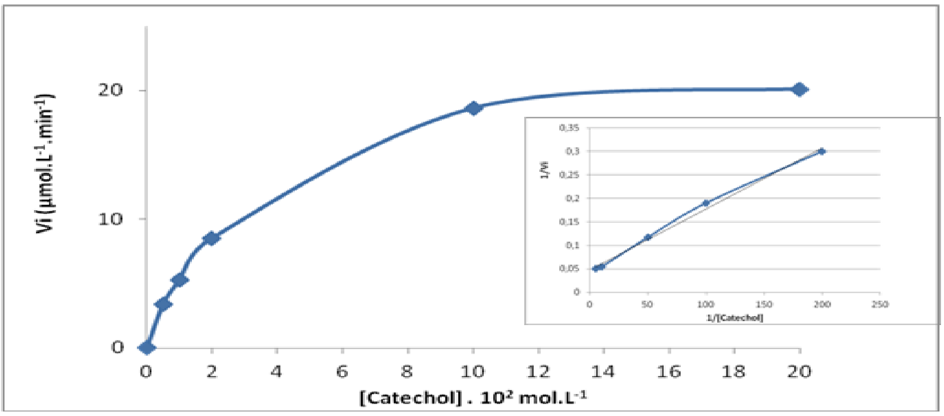


Fig.10: Dependence of the reaction rates on the catechol concentrations for the oxidation reaction catalyzed by complex arising from one equivalent of $\mathbf{L_3}$ and two equivalents of $Cu(CH_3COO)_2$ (in methanol)

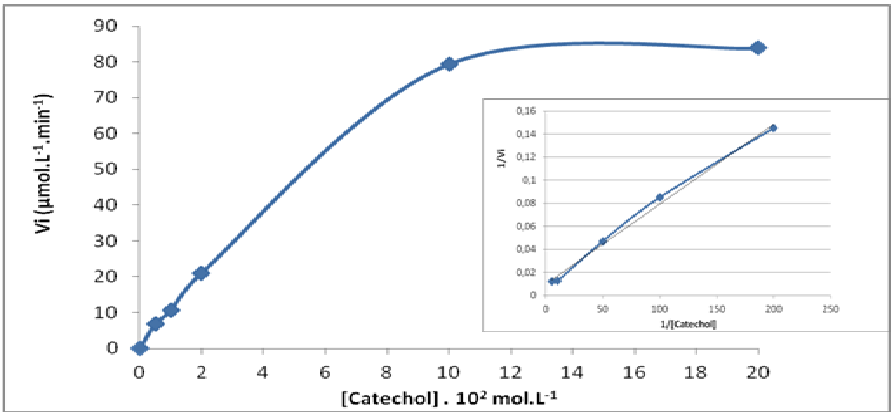


Fig.11 : Dependence of the reaction rates on the catechol concentrations for the oxidation reaction catalyzed by complex arising from one equivalent of $\mathbf{L_3}$ and two equivalents of $Cu(CH_3COO)_2$ (in acetonitrile)

Table 3: Kinetic parameters for the oxidation of catechol catalyzed by complex arising from one equivalent of $\mathbf{L_3}$ and two equivalents of $Cu(CH_3COO)_2$

	methanol	acetonitrile
V_m (µmol.L^{-1}.min^{-1})	20	80
K_m(mol.L^{-1})	2,6.10^{-2}	7,1.10^{-2}

Conclusion

The present study describes the investigation of the catechol oxidase employing the copper complexes, arising from ligands containing benzyl groups and Cu(II) salts. The results obtained show that all the complexes catalyze the aerobic oxidation of catechol to the corresponding *O*-quinone. To more understand the parameters influencing the catalytic activity of the studied complexes and to understand the key properties of solvents which have a controlling role in the catecholase activity, the effect of ligand concentration and the effect of the solvent are studied.

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References

1. Gamez P., Aubel P.G., Driessen W.L., Reedijk J., *Chem. Soc. Rev.* 30 (2001) 376.
2. Punniyamurthy T., Rout L., *Coord. Chem. Rev.* 252 (2007) 134.
3. Sreedaran S., Bharathi K., Rahiman A., Rajesh K., Nirmala G., Narayanan V., *J. Coord. Chem.* 61 (2008) 3594.
4. Allam A., Dechamps-Olivier I., Behr J.-B., Dupont L., Plantier-Royon R., *Inorg. Chim. Acta* 366 (2011) 310.
5. Cheng S.C., Wei H.H., *Inorg. Chim. Acta* 340 (2002) 105.
6. Rompel A., Karentzopoulos K.B., Molitor C., Krebs B., *Phytochem.* 81 (2012) 19.
7. Yu Z.L., Zeng W.C., Lu X.L., *Ultrason. Sonochem.* 20 (2013) 805.
8. Klabunde T., Eiken C., Sacchettini J.C., Krebs B., *Nat. Struct. Biol.* 5 (1998) 1084.

9. Quinjano M.R.M., Sueta G.F., Alamo M.F., Alcalde N.A., Vidales V.G., Sadivar V.M., Gasque L., *Dalton Trans.* 41(2012) 4985.
10. Rompel A., Fischer H., Karenzopoulos K.B., Meiwes D., Zippel F., Nolting H.F., Hermes C., Krebs B., Witzel H., *J. Inorg. Biochem.* 59 (1995) 715.
11. Born K., Comba P., Daubinet A., Fuchs A., Wadepohl H., *J. Biol. Inorg. Chem.* 12 (2007) 36.
12. Rompel A., Fischer H., Meiwes D., Karenzopoulos K.B., Dillinger R., Tuczek F., Witzel H., Krebs B., *J. Biol. Inorg. Chem.* 4 (1999) 56.
13. Singh R., Banerjee A., Rajak K.K., *Inorg. Chim. Acta* 363 (2010) 3131.
14. Megyes T., May Z., Schubert G., Grósz T., *Inorg. Chim. Acta* 359 (2006) 2329.
15. May Z., Simándi L.I., Vértes A., *J. Mol. Catal. A* 266 (2007) 239.
16. Boussalah N., Touzani R., Bouabdallah I., El Kadiri S., Ghalem S., *J. Mol. Catal. A* 306 (2009) 113.
17. Zerrouki A., Touzani R., El Kadiri S., *Arab. J. Chem.* 4 (2011) 459.
18. El Kodadi M., Malek F., Touzani R., Ramdani A., *Cata. Commun.* 9 (2008) 966.
19. Bouabdallah I., Touzani R., Zidane I., Ramdani A., *Cata. Commun.* 8 (2007) 707.
20. Toubi Y., Touzani R., Radi S., El Kadiri S., *J. Environm. Mater. Sc.*, 3 (2012) 328.
21. Mouadili A., Zerrouki A., Herrag L., Hammouti B., El Kadiri S., Touzani R., *Res. Chem. Intermed.* 38 (2012) 2427.
22. Saddik R., Khoutoul M., Benchat N., Hammouti B., El Kadiri S., Touzani R., *Res. Chem. Intermed.* 38 (2012) 2457.
23. Saddik R., Abrigach F., Benchat N., El Kadiri S., Hammouti B., Touzani R., *Res. Chem. Intermed.* 38 (2012) 1987.
24. Mouadili A., Attayibat A., El Kadiri S., Radi S., Touzani R., *Appl. Cata. A: Gen.* 454 (2013) 93.
25. Majumder A., Goswami S., Batten S.R., *Inorg. Chim. Acta* 359 (2006) 2375.
26. Kaizer J., Baráth G., Csonka R., Speier G., Korecz L., Rockenbauer A., Párkányi L., *J. Inorg. Biochem.* 102 (2008) 773.
27. Blay G., Fernández I., Pedro J.R., Ruiz-García R., Temporal-Sánchez T., Pardo E., Lloret F., Muñoz M.C., *J. Mol. Cata. A* 250 (2006) 20.
28. Guha A., Banu K.S., Banerjee A., Ghosh T., Bhattacharya S., Zangrandoc E., Das D., *J. Mol. Cata. A: Chem.* 338 (2011) 51.
29. Seth P., Drew M.G. B., Ghosh A., *J. Mol. Cata. A: Chem.* 365 (2012) 154.
30. Panja A., *Polyhedron* 43 (2012) 22.
31. Mandal S., Mukherjee J., Lloret F., Mukherjee R., *Inorg. Chem.* 51 (2012) 13148.
32. Neves A., Rossi L.M., Bortoluzzi A.J., Mangrich A.S., Haase W., Werner R., Braz J., *Chem. Soc.* 12 (2001) 747.
33. Kao C.H., Wei H.H., Liu Y.H., Lee G.H., Wang Y., Lee C.J., *J. Inorg. Biochem.* 84 (2001) 171.
34. Solomon E.I., Sundaram U.M., Mackonkin T.E., *Chem. Rev.* 96(1996) 2563.
35. Kitajima N., Moro-Oka Y., *Chem. Rev.* 94 (1994) 737.
36. Ryan S., Adams H., Fenton D.E., Becker M., Schindler S., *Angew. Chem. Int.* 37 (1998) 2134.
37. Holland P.L., Tolman W.B., *Coord. Chem. Rev.* 190–192 (1999) 855.
38. Decker H., Dillinger R., Tuczek F., *Angew. Chem. Int. Ed.* 39(2000) 1591.
39. He L.-P., Chen T., Gong D., Lai Z., Huang K.-W., *Organometallics* 31 (2012) 5208.
40. Bhattacharya P., Parr J., Ross A.T., *J. Chem. Soc. Dalton Trans* 19 (1998) 3149.
41. Djebbar-Sid S., Benali B.O., Deloume J.P., *Polyhedron* 16 (1997) 2175.
42. Liu C.-M., Xiong R.-G., You X.-Z., Liu Y.-J., Cheung K.-K., *Polyhedron* 15 (1996) 4565.
43. Curtis N.F., *Coord. Chem. Rev.* 3 (1968) 3.
44. Chattopadhyay T., Mukherjee M., Mondal A., Maiti P., Banerjee A., Banu K.S., Bhattacharya S., Roy B., Chattopadhyay D.J., Mondal T.K., Nethaji M., Zangrando E., Das D., *Inorg. Chem.* 49 (2010) 3121.
45. Yumei Z., Minghu H., *J. Chem. Res.* 35 (2011) 568.
46. Guzen K.P., Guarezemini A.S., Órfão A.T.G., Cella R., Pereira C.M.P., Stefani H.A., *Tetrahedron Lett.* 48 (2007) 1845.
47. Huang J., Yu L., He L., Liu Y.-M., Cao Y., Fan K.-N., *Green Chem.* 13 (2011) 2672.
48. Banu K.S., Mukherjee M., Guha A., Bhattacharya S., Zangrando E., Das D., *Polyhedron* 45 (2012) 245.

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