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New imines bearing alkyl armed for catecholase activity

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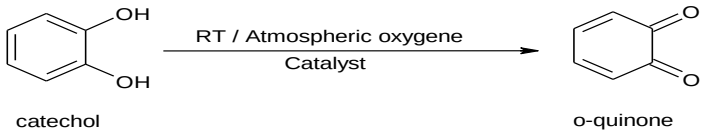
Abstract
A comparative study of new activity catecholase using complex based on three compounds type pentylidene-(4-vinyl-phenyl)-amine **L1**, butylidene-(4-vinyl-phenyl)-amine **L2**, sopentylidene-(4-methoxy-phenyl)-amine **L3** has been reported. This study was performed to examine the catalytic effect of the *in situ*-generated copper (II) complexes towards catechol oxidation reaction with atmospheric dioxygen at room temperature. All complexes catalyze the studied reaction with the rate varying from a higher 9.5625 µmol $L^{-1}min^{-1}$ for the **L2**[$Cu(CH_3CO_2)_2$] to a weaker of 0.2500 µmol L^{-1} min^{-1} for **L2**[$Cu(NO_3)_2$]. The duplicating of ligand concentration influences in different way the oxidation rates. Against with an excess of catechol, the oxidation rate becomes very low.

Keywords: Catechol, oxidation, copper, quinone, Schiff base.

1. Introduction
Interest in synthetic metal complexes is partially derived from their existence in biological systems and their capacity to act as catalysts for numerous chemical reactions [1]. Copper (II) complexes coordinated to multidentate heterocyclic amine ligands have found extensive use as models for the type III copper proteins hemocyanin and tyrosinase [2]. A notable advance in the understanding of the protein properties has been achieved through the comparison of synthetic models to the naturally occurring molecules [3]. The catechol is among common substrate used in catecholase enzyme research (Scheme 1).

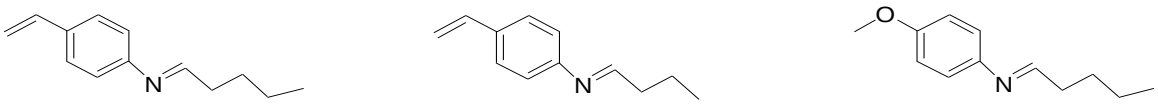


Scheme 1

Several copper (II) complexes containing ligands such as amino acid [4], benzoylacetonate [5], 2-pyridilpropanol [6], phenol Schiff base [7], 4,6-O-ethylidene-β-D glucopyranosyl-amine derived Schiff base [8], chiral steroid [9], phenoxy, alkoxo, oxo-bridged and l-alkoxo-l-carboxylato bridged [10], bis benzimidazole diamide [11], double bridged l-phenoxo-l-carboxylate and l-phenoxo-bis(l-carboxylate) [12], heterobridged systems containing both the phenoxo and azide/cyanate bridges [13], diclofenac complexes with pyridine [14] are used to catalysis this reaction. Other materials based on tripodal ligands showing in their structures fused pyrazolic rings have been the subject of many investigations [15-19]. Studies using the *in situ* generated complexes have been reported in recent works [20, 21]. Schiff base ligands and their metal complexes can be easily synthesized and are extensively used as catalysts in oxidation [22]. Synthesis of Schiff base complexes containing copper (II) are the aim of many investigations [23-26]. As continuation of our interest in developing compounds that mimic the catecholase activity, we report in this paper the catalytic effect study of the *in situ*-generated copper (II) complexes based on some alkyl Schiff base containing aromatic ring towards the oxidation of catechol to o-quinone using atmospheric dioxygen at room temperature.

2. Experimental section
2.1. Synthesis
The investigated materials **L1-L3** were prepared according to the literature procedure by stiring aliphatic aldehydes and aromatic amines in MeOH at room temperature (figure 1) [27]. Then solution of $CeCl_3{\cdot}7H_2O$ was added. The structures of

all products were unambiguously established on the basis of their spectral analysis (IR, ^{1}H NMR and MS data) before using.



L1 **L2** **L3**

Figure 1: Structure of the tested ligands

2.2. Catechol oxidation measurements

Kinetic measurements were made on the UV-Visible spectrophotometer (COSTE: Centre de l'Oriental des Sciences et Technologie de l'Eau, Oujda), following the appearance of o-quinone over time at 25°C using the 390 nm peak (ε = 1600 M^{-1} cm^{-1}). The *in-situ* generated (0.3 mL, 10^{-3}M, CH_3OH) copper (II) complexes prepared from copper salts (0.15 µmol) and ligand (0.15 µmol) were mixed in the spectrophotometric cell with catechol solution (2 mL, 10^{-1}M, CH_3OH).

3. Results and discussion

3.1. Catecholase activity kinetic studies

To compare the activity of the catecholase copper (II) complexes, we studied their ability to catalyze the oxidation reaction of catechol to quinone. This reaction has been widely used for the study of the catecholase activity. The oxidized product presents a strong absorption band at 390 nm in methanol, allowing UV monitoring of the reaction. The kinetic study in the presence of complexes prepared in situ from ligands **L1-L3** and the corresponding copper (II) salts, was carried out in methanol. The catalyst and a solution of catechol were added together in the spectrophotometric cell at 25 °C and the absorbance was continually monitored at 390 nm for 60 min. The progress of the catechol oxidation reaction with atmospheric dioxygen is conveniently followed by colorimetric assay via monitoring the formation of *o*-quinone. In all cases, the catalysis of catechol oxidation reaction was noted. Figures 2-4 shows the absorbance versus time spectrum for the first 60 min of the reaction for the copper (II) complexes while the oxidation rates are shown in Table 1.

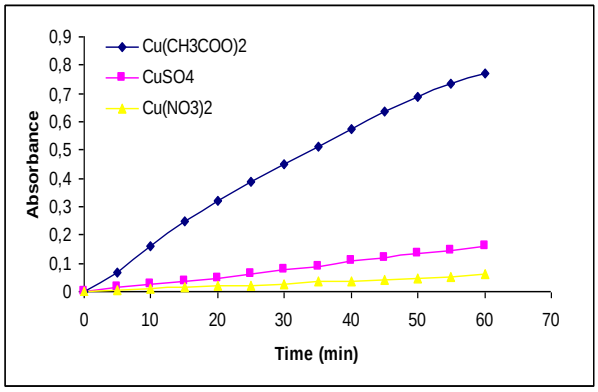


Figure 2. Plot of absorbance vs. time for the oxidation of catechol by complexes of ligand **L1**

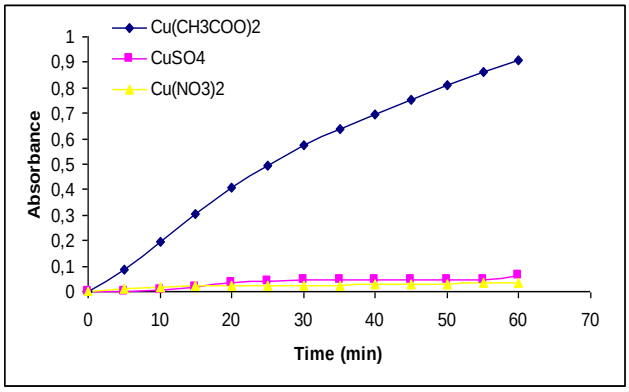


Figure 3. Plot of absorbance vs. time for the oxidation of catechol by complexes of ligand **L2**

Table 1: Oxidation rates (µmol L^{-1} min^{-1}) of catechol

Ligand / Salt	$Cu(CH_3CO_2)_2$	$CuSO_4$	$Cu(NO_3)_2$
L1	8.1875	1.6875	0.5625
L2	9.5625	0.6250	0.2500
L3	5.0625	1.0000	2.3125

Table 1 shows that all complexes catalyze the oxidation reaction of catechol to quinone with the rate varying from a high of 9.5625 µmol $L^{-1}min^{-1}$ for the **L2**[$Cu(CH_3CO_2)_2$] to a weaker rate of 0.2500 mol L^{-1} min^{-1} for **L2**[$Cu(NO_3)_2$]. The oxidation rates change depending on two parameters (ligand and inorganic anion).

3.2. Ligand and inorganic anion effects

The nature of ligand and anion affects considerably the copper complex geometries and this factor can contribute to explain the dependence between the oxidation rates and complexes. Indeed, the order of reactivity

for the oxidation of catechol by $Cu(CH_3COO)_2$ complexes is **L2>L1>L3**. Also, **L1** and **L2** whose the structures are very similar provide identical oxidation rates. But the elongation of the lateral arms in **L1** causes an increase of the oxidation rate in both sulphate and nitrate cases. As against the presence of methoxy group in **L3** causes a decreasing of catalytic activity. The complex **L2**[$Cu(NO_3)_2$] is less effective than its analogous **L2**[$CuSO_4$]. The change of methoxy moiety in **L3** by vinyl group in **L1** causes an increasing of oxidation rate for copper sulphate and acetate.

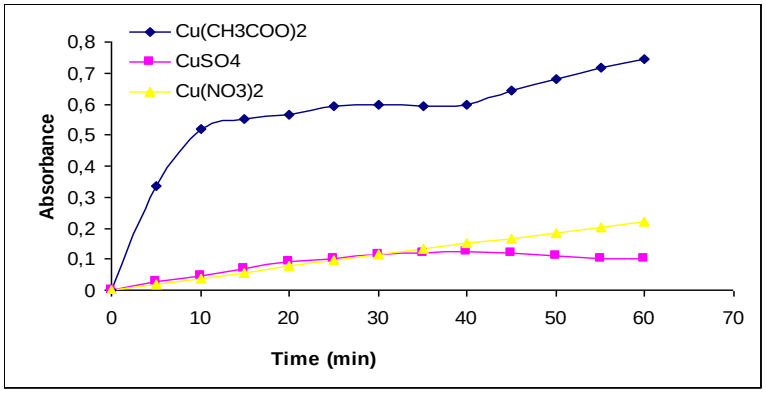


Figure 4. Plot of absorbance vs. time for the oxidation of catechol by complexes of ligand **L3**

3.3. Effect of ligand concentration duplicating

To optimize the catecholase activity, we decided to study the effect of ligand concentration duplicating (2.10^{-3}M) on the oxidation rate. Results summarized in Table 2, demonstrate that the increasing of this quantity has different effects towards the studied reaction rate.

Table 2: Oxidation rates (µmol $L^{-1}min^{-1}$) of catechol

Ligand / Salt	$Cu(CH_3CO_2)_2$	$CuSO_4$	$Cu(NO_3)_2$
L1	11.5000	2.0000	2.5000
L2	14.0000	0.5625	0.1875
L3	04.1250	8.3750	0.7500

(i) The oxidation rate increase with a high ratio from 1.5 to 8 in three cases. This result is due to the formation of free complex able to react easily with the catechol substrate [28]. (ii) The reaction rate remains unchanged in most cases. The increasing ligand concentration has a negligible effect due probably to the formation of mono complexes. (iii) The oxidation rate decrease with a ratio of 3. The experimental situation required the difficulty of catechol to come into contact with the obtained complex, justified by the coordination at least two ligands with one metallic center, leading to the very stable complex [29-31].

3.4. Effect of substrate concentration

In order to study the effect of substrate concentration on the oxidation rate of catechol, we chose the ligand **L2** that presents the highest oxidation rate value. To determine the dependence of the rates on the substrate concentration, solutions of *in situ* generated complex were treated with increasing amounts of catechol. The initial reaction rates have been determined from the slope of trace in the first 25 minutes of the reaction (Fig. 5).

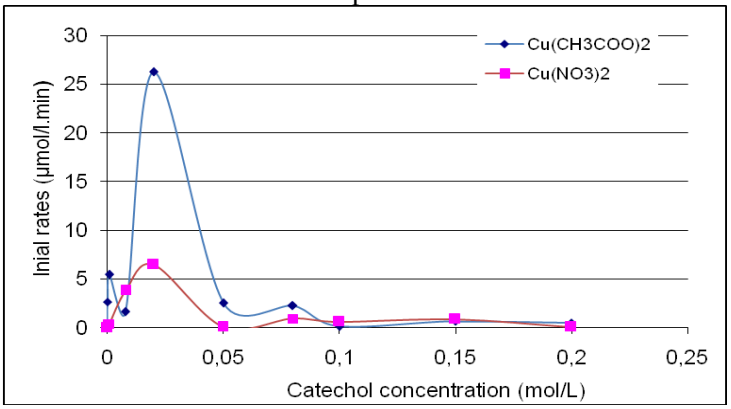


Figure 5. Plot of initial rate vs concentration of catechol for **L2**[$Cu(NO_3)_2$] and **L2**[$Cu(CH_3COO)_2$]

Under these experimental conditions, maximal kinetic parameters were found for the initial rates of 26.25 µmol $L^{-1}min^{-1}$ versus the catechol concentration. The initial maximal rate decrease four times when changing the acetate anion by nitrate. The reaction rate decreases from 2.10^{-2} M and takes a value from zero when the concentration becomes higher than 5.10^{-2} M. The reaction is probably hampered by adduct or a secondary product that would be formed directly after addition of an excessive amount of catechol. The explanation is abebooks web can advance the likely degradation of copper complex when adding catechol as has been observed in the literature [32] considering competition between the bridge connecting the metal cations and the bridge when the catechol concentration increases. Indeed, Koval et al [33] note that the steric hindrance of the complex is an important factor that influences the binding of catechol with the complex. So the distortions existing in the complex increases the catalytic activity, so that a complex which is energetically favored conformation will be inactive towards the catechol substrate

Conclusion

Our results show that the in situ complexation of Cu (II) by a family of Schiff base ligand generated the entities able to act as catalyst for oxidation of catechol to the corresponding light absorbing o-quinone. The best complex is obtained with the association of **L2** butylidene-(4-vinyl-phenyl)-amine with $Cu(CH_3CO_2)_2$. The increasing of ligand concentration influences in different way the oxidation rates. Against with an excess of catechol, the oxidation rate becomes very low.

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