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N,N'-bipyrazole compounds: Effect of concentration, solvent, ligand and metal anions on the catecholase properties

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Abstract

Six bidentate pyrazole ligands $\mathbf{L_1}$–$\mathbf{L_6}$ have been prepared, Bis(*1H*-pyrazol-1yl)methane $\mathbf{L_1}$, 3,5-Dimethyl-1-pyrazol-1-ylmethyl-*1H*-pyrazole $\mathbf{L_2}$, (bis(3,5-dimethyl-*1H*-pyrazol-1-yl)methane $\mathbf{L_3}$, Ethyl 1-((3,5-dimethyl-*1H*-pyrazol-1-yl)methyl)-5-methyl-*1H*-pyrazole-3-carboxylate $\mathbf{L_4}$, Ethyl 1-((*1H*-pyrazol-1-yl)methyl)-5-methyl-*1H*-pyrazole-3-carboxylate $\mathbf{L_5}$, Ethyl-1-((3,5-dimethyl-*1H*-pyrazol-1-yl)methyl)-5-phenyl-*1H*-pyrazole-3-carboxylate $\mathbf{L_6}$. Copper (II) complexes of these compounds were examined for their catalytic properties. The *in situ*-generated copper (II) complexes were suitable catalysts for the catalytic oxidation of catechol substrate to quinone with dioxygen at ambient condition. All complexes catalyze the oxidation reaction with the rate varying from a high of 25.0854µmol$L^{-1}$$min^{-1}$ for the $\mathbf{L_6/[Cu(CH_3CO_2)_2]}$ complex in THF to a weaker rate of 0.0645µmol$L^{-1}$$min^{-1}$ for $\mathbf{L_1/[CuCl_2]}$. The preliminary results show that the oxidation rate depends on different parameters such as the concentration, solvent and the metal anions.

Keywords: Bidentate ligands**,** N,N'bipyrazole, Catechol oxidation and Copper(II) metals.

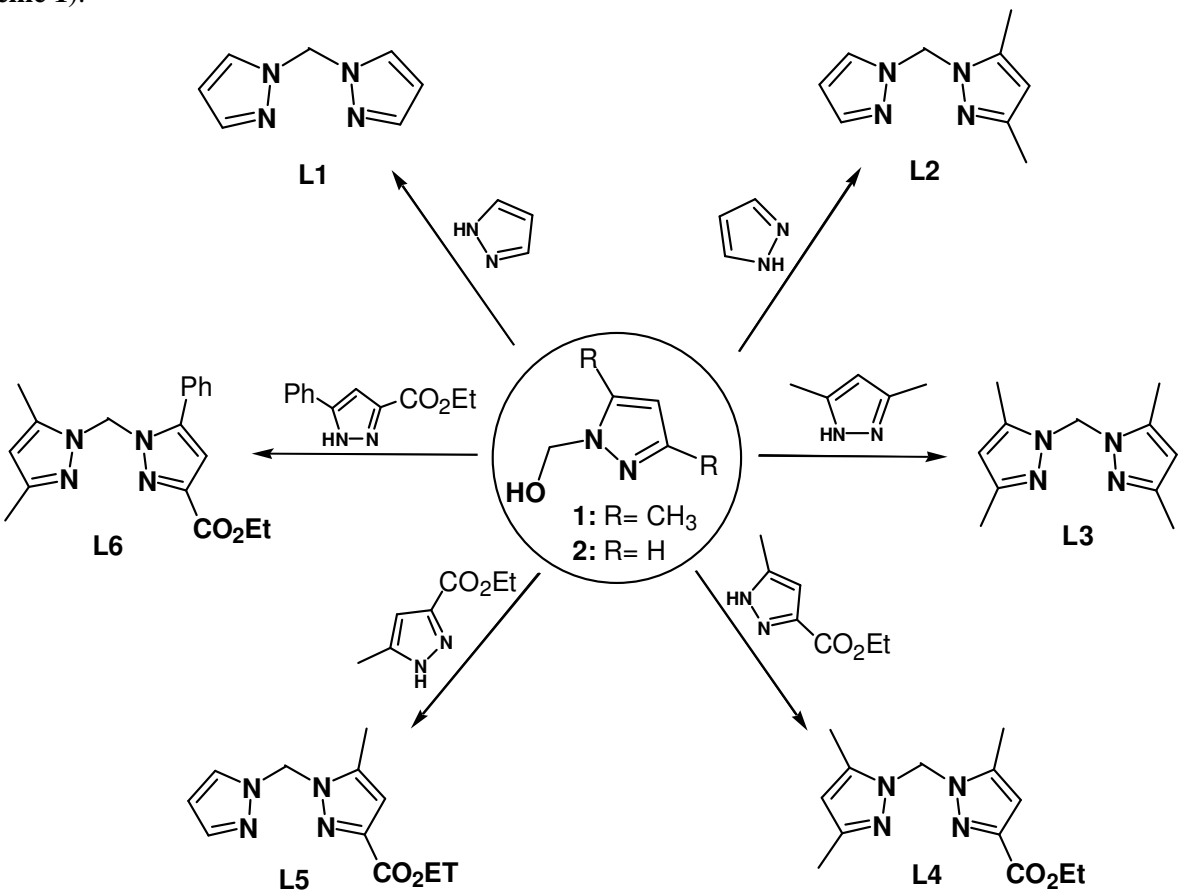
1. Introduction

The active center of type 3 copper (II) proteins have been the subject of extensive studies in recent years, such as tyrosinase [1], catechol oxidase [2-3] and hemocyanins [4]. Searching for the compounds able to bio mimic and reproduce this process, chemists have designed model complexes based on available spectroscopic data. New models can provide powerful tools to understand better natural systems [5-7]. Nitrogen compounds such as pyrazole are versatile building blocks for a variety of fascinating synthetic molecular and supramolecular assemblies [8], dendrimers [9], micelles [10] and proteins [11- 13]. The scope of accessible pyrazole side-chain functionalities has been reported by organic chemists who have developed different methods for the synthesis, for example, macrocycle [14], carbohydrate [15], or organic natural product [16] and catalyst [17]. In this paper, we are focused on the catecholase activity of copper (II) complexes towards oxidation of catechol to quinone using bidentate functional ligands and discussing all the parameters which can influence the rate of this reaction such as solvent, concentration, substituent, kinetics and the metal anions.

2. Experimental section

Materials and methods

The ligands $\mathbf{L_1}$-$\mathbf{L_6}$ are known compounds and have spectral data in according to the literature data [18-22] (**Scheme 1**).



Scheme 1: General structures of the six N,N'bidentate pyrazole ligands ($\mathbf{L_1}$–$\mathbf{L_6}$)

Catecholase Activity Measurements

Kinetic measurements were made spectrophotometrically on UV-Visible spectrophotometer (In the COSTE: Centre de l'Oriental des Sciences et Technologies de l'Eau), following the appearance of *o*-quinone over time at 25 °C (390 nm absorbance maximum, ε = 1600 M^{-1} cm^{-1} in methanol; ε = 1900 M^{-1} cm^{-1} in THF; ε = 1600 M^{-1} cm^{-1} in CH_3CN). The metal complex (prepared *in-situ* [23-34]; 0.3 mL of a 10^{-3}M methanol solution) and a solution (2 mL of a 10^{-1}M methanol solution) of catechol were mixed in the spectrophotometric cell (**Figure 2**).

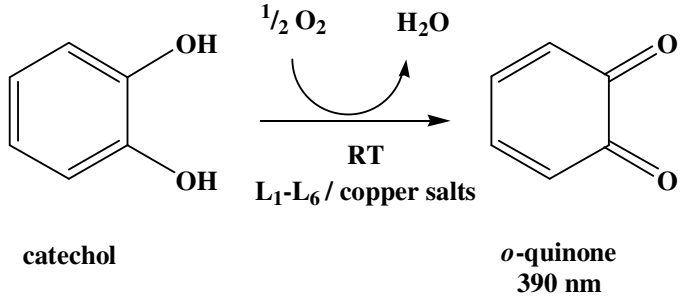


Figure 2: Biomimetic reaction model for catechol oxidation

3. Results and discussion

3.1. Synthesis

Six bidentate pyrazole ligands **L_1–L_6** have been prepared in good yield by condensation of one equivalent of 3,5-dimethyl-*1H*-pyrazol-1-yl)methanol **1** and *1H*-pyrazol-1-yl)methanol **2** with one equivalent of pyrazole starting material derivatives, in refluxed acetonitrile during 4 hours (**Figure 1**). All compounds were characterized by IR, ^{1}H-NMR and ^{13}C-NMR and mass spectrometry [35].

3.2. Catecholase studies

The progress of the catechol oxidation reaction is conveniently followed monitoring the strong absorbance peak of quinone in the UV/Vis spectrophotometer. The metal complex [23-34] and a solution of catechol were added together in the spectrophotometric cell at 25°C. Formation of *o*-quinone was monitored by the increase in absorbance at 390 nm as a function of time. In all cases, catecholase activity was noted. **Table 1** shows the oxidation rates of different complexes**.**

3.2.1. Effect of concentration of Metal/Ligand (M/L):

3.2.1.a. Concentration of M/L: 1/1 in MeOH

As can be seen from **Table 1**, all of the complexes catalyze the oxidation reaction of catechol to *o*-quinone with the rate varying from a high of 15.5559 µmol L^{-1} min^{-1} for the **L_6/[$Cu(CH_3CO_2)_2$]** complex to a weaker rate of 0.0187 mol $L^{-1}min^{-1}$ for **L_1/ [$Cu(NO_3)_2$]** complex**.** The catalytic activities depend strongly on both the form of the nature of ligand and the type of inorganic copper anion.

Table 1: Oxidation rates (µmol $L^{-1}min^{-1}$) of catechol (M/L :1/1 in MeOH).

Ligand/Metallic salt	$Cu(CH_3COO)_2$	$CuSO_4$	$Cu(NO_3)_2$	$CuCl_2$
L_1	1.6322	0.3218	0.0187	0.6468
L_2	2.3343	0.0302	0,1271	0.0771
L_3	3.1458	0.2364	0.2583	0.2416
L_4	0.1656	1.0270	0.1656	1.4625
L_5	8.3885	3.5552	0.2958	2.9385
L_6	15.5559	6.6771	0.1281	2.0271

3.2.1.b. Concentration of M/L:1/2 in MeOH

As can be seen from **Table 2**, all of the complexes catalyze the oxidation reaction of catechol to quinone with the rate varying from a high of 6.6968 µmol L^{-1} min^{-1} for the **L_6/[$Cu(CH_3CO_2)_2$]** complex to a weaker rate of 0.0437 mol L^{-1} min^{-1} for **L_3/[$CuSO_4$]** complex**.** The catalytic activities depend strongly on both the nature of ligand and the type of inorganic copper anion.

Table 2: Oxidation rates (µmol. L^{-1}. min^{-1}) of catechol (M/L:1/2 in MeOH).

Ligand/metallic salt	$Cu(CH_3COO)_2$	$CuSO_4$	$Cu(NO_3)_2$	$CuCl_2$
L_1	0.3093	0.2385	0.0885	1.7625
L_2	1.2501	0.2958	0.2083	0.0971
L_3	1.9677	0.0437	0.3468	0.3458
L_4	0.2187	0.4011	0.2437	0.1375
L_5	6.3760	2.0751	0.2645	1.6187
L_6	6.6968	5.5447	2.7664	3.3801

3.2.1.c. Concentration of M/L: 2/1 in MeOH

Table 3: Oxidation rates (µmol.L^{-1}.min^{-1}) of catechol (M/L: 2/1 in MeOH)

Ligand/metallic salt	$Cu(CH_3COO)_2$	$CuSO_4$	$Cu(NO_3)_2$	$CuCl_2$
L_1	2.1135	1.3072	0.0521	1.4291
L_2	3.3479	1.2312	0.1501	2.4927
L_3	11.3906	1.3354	0.1229	4.3011
L_4	1.3761	2.5885	0.0035	1.2968
L_5	10.5104	3.5552	0.5771	3.7961
L_6	22.9729	4.3708	0.0239	1.8501

As can be seen from **Table 3**, all of the complexes catalyze the oxidation reaction of catechol to *o*-quinone with the rate varying from a high of 22.9729 µmol L^{-1} min^{-1} for the **L_6/ [$Cu(CH_3CO_2)_2$]** complex to a weaker

rate of 0.0035 mol L^{-1} min^{-1} for **L_4/ [$Cu(NO_3)_2$]** complex**.** The catalytic activities depend strongly on both the form of the lateral chains and the type of inorganic anion.

3.2.2. Effect of solvent

3.2.2.a. Concentration of M/L: 1/1 in THF

Table 4: Oxidation rates (μmol.L^{-1}.min^{-1}) of catechol (M/L: 1/1 in THF)

Ligand/metallic salt	$Cu(CH_3COO)_2$	$CuSO_4$	$Cu(NO_3)_2$	$CuCl_2$
L_1	5.0541	0.6125	0.4760	1.1916
L_2	8.0552	0.7593	0.6489	1.2833
L_3	2.3979	0.0281	0.1541	2.3979
L_4	1.4156	0.5635	0.0614	1.3521
L_5	14.1401	20.0067	0.1916	0.6645
L_6	21.6802	17.4001	0.1656	1.4395

As can be seen from **Table 4**, all of the complexes catalyze the oxidation reaction of catechol to *o*-quinone with the rate varying from a high of 21.6802 μmol.L^{-1}.min^{-1} for the **L_6/ [$Cu(CH_3CO_2)_2$]** complex to a weaker rate of 0.0614 μmol.L^{-1}.min^{-1} for **L_4/ [$Cu(NO_3)_2$]** complex**.** The catalytic activities depend strongly on both the form of the lateral chains and the type of inorganic anion.

3.2.2.b. Concentration of M/L: 1/2 in THF

Table 5: Oxidation rates (μmol. L^{-1}. min^{-1}) of catechol (M/L:1/2 in THF)

Ligand/metallic salt	$Cu(CH_3COO)_2$	$CuSO_4$	$Cu(NO_3)_2$	$CuCl_2$
L_1	5.8302	0.8843	0.2906	0.2322
L_2	8.0750	1.0250	0.8354	0.5187
L_3	0.4052	7.2312	0.2958	1.8479
L_4	6.2718	6.0937	0.2437	0.7239
L_5	9.6218	16.3895	0.1911	1.0406
L_6	15.9812	15.3427	0.2437	0.6645

As can be seen from **Table 5**, all of the complexes catalyze the oxidation reaction of catechol to *o*-quinone with the rate varying from a high of 16.3895 μmol L^{-1} min^{-1} for the **L_5/[$CuSO_4$]** complex to a weaker rate of 0.1911 μmol L^{-1} min^{-1} for **L_5/[$Cu(NO_3)_2$]** complex**.** The catalytic activities depend strongly on both the form of the lateral chains and the type of inorganic anion.

3.2.2.c. Concentration of M/L: 2/1 in THF

Table 6: Oxidation rates (μmol. L^{-1}. min^{-1}) of catechol (M/L :2/1 in THF)

Ligand/metallic salt	$Cu(CH_3COO)_2$	$CuSO_4$	$Cu(NO_3)_2$	$CuCl_2$
L_1	7.9843	4.1458	0.2135	0.0645
L_2	10.2229	1.9604	0.7385	0.9271
L_3	0.6166	0.0843	0.0937	0.9708
L_4	6.1864	1.2927	1.4416	6.1864
L_5	15.7697	18.4781	1.2333	0.8166
L_6	25.0854	20.8333	0.1843	0.1333

As can be seen from **Table 6**, all of the complexes catalyze the oxidation reaction of catechol to *o*-quinone with the rate varying from a high of 25.0854 μmol$L^{-1}$$min^{-1}$ for the **L_6/[$Cu(CH_3CO_2)_2$]** complex to a weaker rate of 0.0645 μmolL^{-1} min^{-1} for **L_1/[$CuCl_2$]** complex**.** The catalytic activities depend strongly on both the form of the lateral chains and the type of inorganic anion.

3.2.2.d. Concentration of M/L: 1/1 in acetonitrile (CH_3CN)

As can be seen from **Table 7**, all of the complexes catalyze the oxidation reaction of catechol to *o*-quinone with the rate varying from a high of 4.6802 μmol L^{-1} min^{-1} for the **L_6/[$Cu(CH_3CO_2)_2$]** complex to a weaker

rate of 0.0281 µmol L^{-1} min^{-1} for **L_3/[$CuSO_4$]** complex**.** The catalytic activities depend strongly on both the form of the lateral chains and the type of inorganic anion.

Table 7: Oxidation rates (µmol. L^{-1}. min^{-1}) of catechol (M/L :1/1 in CH_3CN)

Ligand/metallic salt	$Cu(CH_3COO)_2$	$CuSO_4$	$Cu(NO_3)_2$	$CuCl_2$
L_1	0.8875	0.0916	0.3343	1.8166
L_2	3.8885	0.3906	0.0531	1.2833
L_3	2.3291	0.0281	0.1541	0.9291
L_4	4.3458	0.3685	0.0614	1.3520
L_5	3.7239	1.7114	0.0635	0.0479
L_6	4.6802	0.5666	0.0635	1.4395

3.2.2.e. Concentration of M/L: 1/2 in CH_3CN

Table 8: Oxidation rates (µmol. L^{-1}. min^{-1}) of catechol (M/L :1/2 in CH_3CN)

Ligand/metallic salt	$Cu(CH_3COO)_2$	$CuSO_4$	$Cu(NO_3)_2$	$CuCl_2$
L_1	1.8979	0.4343	0.0895	0.3343
L_2	1.8979	0.0565	0.7531	0.5187
L_3	2.5791	0.9697	1.4416	1.8479
L_4	2.4062	1.4354	0.0204	1.9156
L_5	3.7281	2.0145	0.2104	1.0197
L_6	4.3270	2.3218	0.2437	0.9958

As can be seen from **Table 8**, all of the complexes catalyze the oxidation reaction of catechol to *o*-quinone with the rate varying from a high of 4.3270 µmol L^{-1} min^{-1} for the **L_6/[$Cu(CH_3CO_2)_2$]** complex to a weaker rate of 0.0204 µmol L^{-1} min^{-1} for **L_4/[$Cu(NO_3)_2$]** complex**.** The catalytic activities depend strongly on both the form of the lateral chains and the type of inorganic anion.

3.2.2.f. Concentration of M/L: 2/1 in CH_3CN

Table 9: Oxidation rates (µmol. L^{-1}. min^{-1}) of catechol (M/L :2/1 in CH_3CN)

Ligand/metallic salt	$Cu(CH_3COO)_2$	$CuSO_4$	$Cu(NO_3)_2$	$CuCl_2$
L_1	0.7947	0.3239	3.3385	0.0645
L_2	1.6489	0.6218	0.1489	0.9270
L_3	0.3250	0.0281	0.0937	0.0645
L_4	2.6687	1.2635	0.0427	0.3822
L_5	0.8239	1.3385	0.1260	1.3479
L_6	3.1572	1.1010	0.0104	0.2447

As can be seen from **Table 9**, all of the complexes catalyze the oxidation reaction of catechol to *o*-quinone with the rate varying from a high of 3.3385 µmol L^{-1} min^{-1} for the **L_1[$Cu(NO_3)_2$]** complex to a weaker rate of 0.0104 µmol L^{-1} min^{-1} for **L_6[$Cu(NO_3)_2$]** complex**.** The catalytic activities depend strongly on both the form of the lateral chains and the type of inorganic anion. We can conclude that, the oxidation rate depends strongly on the concentration of both combination of M/L, the best one is 2/1. The nature of the solvent affects the copper complex; THF is the best solvent for this reaction model. The order of reactivity for the oxidation of catechol by $Cu(CH_3COO)_2$ complexes is **L_6 >L_5>L_2>L_1>L_4>L_3** (**Table 6**). The nature of the anion in the metal salts and the nature of the ligand have a big effect on the coordination properties of the center nitrogen donor site [36-37].

3.3. Kinetic studies

To gain better understand of the influence of solvent on the oxidation rates of catechol, we carried the following study. Kinetic study determined by the initial rate method was performed with the best catalysts [**L_6/$Cu(CH_3CO_2)_2$**], in booth MeOH and THF solvents (**Figures 3-4**). Solutions containing different concentrations of substrate were prepared from a concentrated stock solution. To determine the dependence of the rates on the substrate concentration, solutions of *in-situ* generated complex were treated with increasing amounts of catechol. Initial rates were determined from the slope of the tangent of the absorbance vs time curve after the induction period of 20 min (**Figures 3-5**). The parameters that we have determined are K_M and

V_{max} [38]. The Michaelis kinetic parameter K_M represents the dissociation constant of the intermediate compound *catechol-Cat* (**Table 10**). More K_M is smaller; more the catalyst has the affinity for catechol substrate. V_{max} corresponds to the maximum initial rate of reaction when the catalyst is linked to the substrate. The experimental kinetic parameters are presented in (**Table 10**).

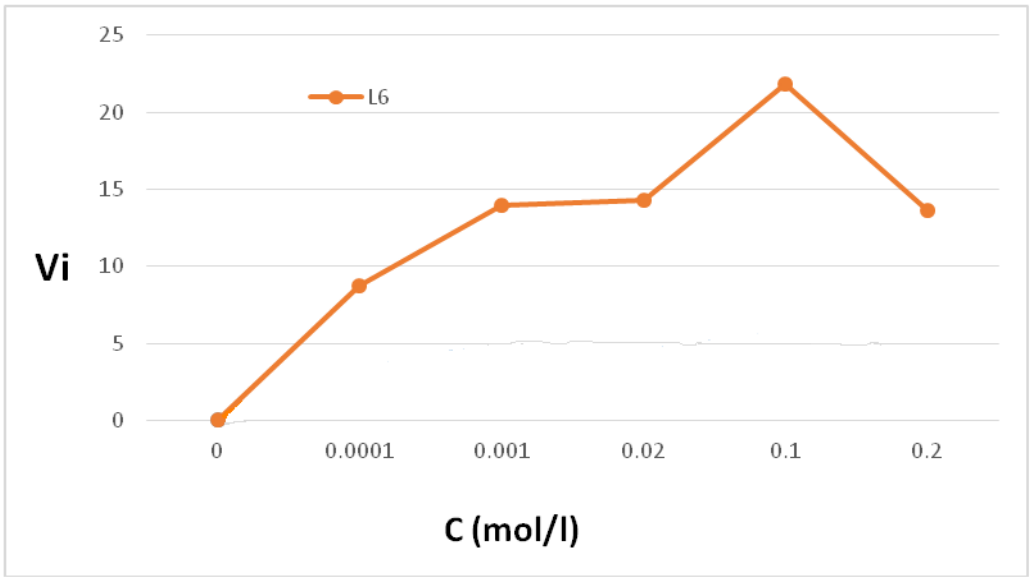


Figure 3: Reaction dependence on the concentration of catechol using **L_6/[$Cu(CH_3COO)_2$]** in MeOH

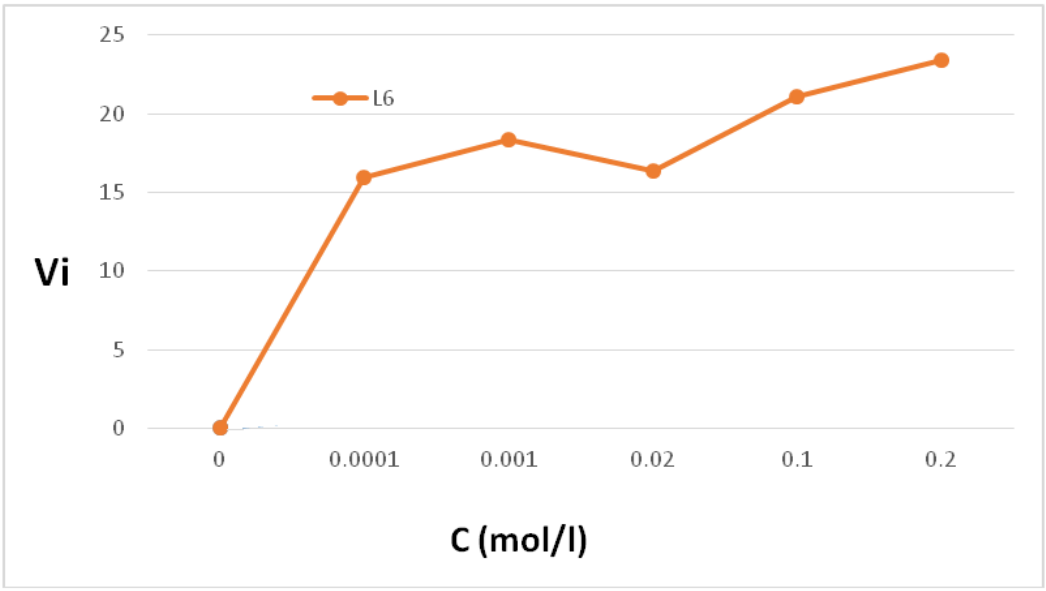


Figure 4: Reaction dependence on the concentration of catechol using **L_6/[$Cu(CH_3COO)_2$]** in THF

Table 10: Kenitic parameters of the oxidation of catechol using **L_6/$Cu(CH_3COO)_2$** in MeOH and THF

	MeOH	THF
V_m ($\mu mol.L^{-1}.min^{-1}$) L_6	15.7333	22.4691
K_M($mol.L^{-1}$) L_6	0.0001	0.00009

3.3. Proposed mechanistic hypothesis

For this oxidation reaction of catechol, important questions remain unanswered concerning the catalytic mechanisms. They mainly concern: in the first hand the control of the catalytic activity (pH, electronic

properties), in the second hand the coordination mode of the substrate: does it consist of a bridging catecholate between the two copper centers rather than a coordination centered to one metal ion (bridging bidentate coordination) in the third hand the reactive intermediate involved in the dioxygen activation [39]. In this context various mechanisms are proposed [40-43]. Our part we have proposed a mechanism (**Figure 5**) by considering that a homogeneous catalyst reacts with the reagent (catechol) than with the second reactants (O_2). However the catalyst is fully regenerated in the final stage.

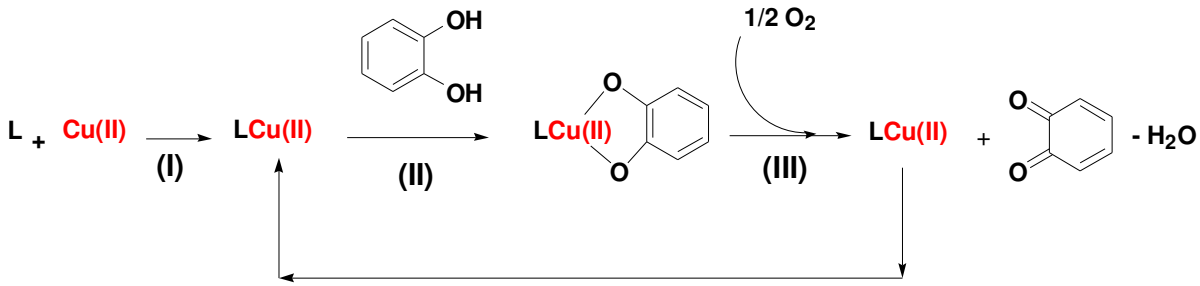


Figure 5: Proposed mechanism for the catechol oxidation using **L**[$Cu(CH_3CO_2)_2$] system

If we can suggest this pathway, which has three part: **(I)** the ligand **L** coordinate the Cu(II) according to the literature [44-49]. **(II)** The reaction with the catechol leads to an intermediate catecholate complex with the {Cu(L)(catecholate)} center [50-51]. **(III)** The oxidation of the catecholate by electron transfer from the oxygen to the Cu^{2+} center yields the corresponding orthoquinone which is released. The catalytic cycle in **Figure 5** is proposed and need more spectroscopic data to be validate.

4. Conclusion

We report the oxidation of catechol to give *o*-quinone by complexes of copper (II) with six bidentate bispyrazole ligands. The complexes of copper (II) were generated *in-situ*. We have demonstrated that the nature of ligand, metal anions, solvent and concentration have a large effect on the oxidation reaction rates.

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