Article

New In Situ Catalysts Based on Nitro Functional Pyrazole Derivatives and Copper (II) Salts for Promoting Oxidation of Catechol to *o*-Quinone

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Abstract: Herein, new substituted ligands based on pyrazole (L_1–L_4) were synthesized via a one-step by condensing (1*H*-pyrazole-1-yl) methanol with different primary amine compounds. The present work utilized the catalytic properties of the in situ complexes formed by these ligands with various copper (II) salts viz. $Cu(CH_3COO)_2$, $CuSO_4$, $CuCl_2$, and $Cu(NO_3)_2$ for the oxidation of catechol to *o*-quinone. The studies showed that the catalytic activities depend on the nature and concentration of the ligand, the nature of the counterion, and the solvent. It was observed that the complex formed by L_2 and $Cu(CH_3COO)_2$ exhibited good catalytic activity in methanol with V_{max} of 41.67 μmol L^{-1} min^{-1} and K_m of 0.02 mol L^{-1}.

Keywords: pyrazole; copper; catalyst; oxidation reaction; catecholase; *o*-quinone

1. Introduction

Pyrazole-based compounds have gathered tremendous advancement in the last decade [1–10] toward numerous versatile applications in the field of bioinorganic and medical sciences. These compounds have been utilized as precursors in the synthesis of many compounds, including artificial metalloenzymes with important biological activities [11–13]. The pyrazole-based ligands have been employed in a wide range of applications, such as electronics [14], catalysis [15–28], and pharmacology [29]; they also exhibit anticorrosion [30], anticancer, antifungal, antiviral, and antibacterial behavior [31,32]. Additionally, they exhibit cytotoxic activities [33,34] and are used for the extraction of lithium and cesium cations [35,36].

Furthermore, the complexation chemistry of these ligands with transition metal ions shows great potential in catalysis, especially in mimicking enzyme activity [37]. One of the important metal ions is copper, which has the ability to combine with various organic ligands to catalyze diverse biological processes. In this regard, a variety of copper-based complexes are employed to study the oxidation reaction of catechol to quinone [19,32,35]. It is remarkable how these complexes can bind reversibly to oxygen under ambient conditions, thus, aiding the reaction [24–28]. Several studies have explored the catalytic activity of copper-based complexes, either in situ [28,32] or through isolated complexes [15–18,35].

Numerous studies have also investigated the catalytic activity of catechol oxidation using a variety of metal complexes, such as iron, cobalt, manganese-based complexes, etc. [22–24]. However, it has been recently reported that copper-based complexes exhibit excellent catalytic activity toward the oxidation reaction [35].

Thus, the present work aims to study the catalytic activity of in situ-prepared pyrazole-based ligands and copper complexes for the conversion of catechol to *o*-quinone in the presence of atmospheric oxygen (O_2). Four different pyrazole-based ligands (**L$_1$–L$_4$**) were synthesized and characterized using ^1H NMR, ^{13}C NMR, elemental analysis (EA (%)), and Fourier transform infrared (FT-IR) spectroscopy (please see supplementary information, Figures S1–S15).

2. Experimental Section

2.1. Materials and Characterization Techniques

Catechol, $Cu(NO_3)_2$, $Cu(CH_3COO)_2$, $CuSO_4$, $CuCl_2$, and solvents, such as methanol, tetrahydrofuran, acetonitrile, and chloroform, were purchased from Aldrich and used as received without further purification.

All compounds were characterized using the ^1H NMR, ^{13}C NMR, and IR spectroscopy techniques. ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded in CDCl$_3$ at room temperature (Varian Unity-Plus (400 MHz) spectrometer for NMR, and the elemental analyses were retrieved with the help of 2400 Series II CHNS/O elemental analyzer). Chemical shifts (δ) were recorded in parts-per-million (ppm) using tetramethylsilane (TMS) as the internal standard. FT-IR spectra were recorded on a Schimadzu 8201 PC FT-IR spectrophotometer (νmax in cm^{-1}) supported by pressed KBr pellets. The UV-vis absorbance was recorded on a JENWAY 7315-spectrophotometer, and the experiments concerning the oxidation of catechol to *o*-quinone were carried out at the Higher Institute of Nursing and Health Professions Techniques Laboratory, Oujda.

2.2. Synthesis and Characterization

2.2.1. Preparation of Compounds L$_1$–L$_4$

The four pyrazole-based ligands (**L$_1$–L$_4$**) were synthesized via a one-step process by the condensation of primary amines and pyrazole derivatives reported in our previous work [38]. Briefly, (1*H*-pyrazol-1-yl) methanol derivatives (1.1eq.) were added to the solution of one equivalent of a primary amine in 10 mL of acetonitrile at room temperature (RT). The reaction was carried out under continuous stirring for 6 h at 60 °C. As the reaction progressed, the solid product separated from the clear and homogenous mixture of amine and (pyrazolyl-1-yl) methanol derivatives in acetonitrile. Thereafter, the unreacted starting material and solvent were removed from the mixture by the filtration process. Subsequently, the isolated product was washed with acetonitrile and ethyl acetate and dried at reduced pressure to remove all the volatile organic compounds. The synthesized pathway is depicted in Scheme 1.

2.2.2. Characterization

N-((1H-pyrazol-1-yl)methyl)-4-nitroaniline L$_1$: This compound was obtained as a yellow solid, yield 85%, M$_P$: 118–120 °C, **FT-IR:** (KBr, ν(cm^{-1}): 3256, 3165, 3114, 3023, 2985, 1722, 1605, 1545, 1384, 1214, 1106, 1020, 766; **^1H NMR** (400 MHz, CDCl$_3$): δH = 5.58 (d, 2H, CH$_2$), 6.26 (dd, 1H, CH$_{Py}$), 6.94 (dd, 1H, CH$_{Ar}$), 7.48 (dd, 1H, CH$_{Py}$), 7.87 (dd, 1H, CH$_{Py}$), 8.03 (dd, H, CH$_{Ar}$, 8.24 (t, H, NH);**^{13}C NMR** (100 MHz, CDCl$_3$): δC = 58.3 (CH$_2$), 106.5 (CH$_{Py}$), 113.8 (CH$_{Ar}$), 126.1 (CH$_{Ar}$), 130.4 (CH$_{Py}$), 139.7 (CH$_{Py}$), 138.1 (C$_{Ar}$), 153.2 (C$_{Ar}$). **EA(%):** Calcd: (55.04)C; (4.62)H; (25.68)N; Obsd: (55.10)C; (4.57)H; (25.63)N.

N-((3,5-dimethyl-1H-pyrazol-1-yl)methyl)-4-nitroaniline   **L$_2$:** This compound was obtained as a yellow solid, yield: 90%, M$_P$: 128–130 °C, **FT-IR:** (KBr, ν(cm^{-1}): 3224, 3316, 3230, 3135, 2993, 2920, 1591, 1580, 1487, 1340, 1246, 1230, 1087, 1048, 750; **^1H NMR** (400 MHz, CDCl$_3$): δH = 2.07 (s, 3H, CH$_3$), 2.29 (s, 3H, CH$_3$), 5.41 (d, 2H, CH$_2$), 5.81 (s, 1H, CH$_{Py}$), 6.94 (dd, 1H, CH$_{Ar}$), 8.03 (dd, H, CH$_{Ar}$), 8.12 (t, H, NH); **^{13}C NMR**

(100 MHz, CDCl$_3$): δC = 11.2 (CH$_3$), 14.5 (CH$_3$), 56.7 (CH$_2$), 106.1 (CH$_{Py}$), 112.6 (CH$_{Ar}$), 126.4 (CH$_{Ar}$), 138.5 (C$_{Py}$), 139.1 (C$_{Ar}$), 146.2 (C$_{Py}$), 153.3 (C$_{Ar}$). **EA(%):** Calcd: (58.53)C; (5.73)H; (22.75)N. Obsd. (58.62)C; (5.71)H; (22.65)N.

Ethyl 5-methyl-1-(((4-nitrophenyl)amino)methyl)-1H-pyrazole-3-carboxylate L$_3$: This compound was obtained as a yellow solid, yield: 90%, M$_P$: 125–127 °C, **FT-IR**: (KBr, ν(cm^{-1}): 3379, 3280, 3129, 2983, 2952, 2836, 1635, 1553, 1456, 1424, 1385, 1310, 1226, 1068, 1040, 805, 765, 702; **^{1}H NMR** (400 MHz, CDCl$_3$): δH = 1.26 (t, 3H, CH$_3$), 2.39 (s, 3H, CH$_3$), 4.24 (q, 2H, CH$_2$), 5.64 (d, 2H, CH$_2$), 6.53 (s, 1H, CH$_{Py}$), 6.95 (dd, H, CH$_{Ar}$), 8.04 (dd, H, CH$_{Ar}$), 8.27 (t, H, NH); **^{13}C NMR** (100 MHz, CDCl$_3$): δC = 11.7 (CH$_3$), 15.1(CH$_3$), 58.4(CH$_2$), 60.0 (CH$_2$), 109.4 (CH$_{Py}$), 112.7 (CH$_{Ar}$), 126.8 (CH$_{Ar}$), 138.5 (C$_{Py}$), 141.2(C$_{Ar}$), 142.3(C$_{Py}$), 153.5 (C$_{Ar}$), 162.6 (CO). **EA(%):** Calcd: (55.26)C; (5.30)H; (18.41N). Obsd. (56.01)C; (5.21)H; (18.56)N.

(2-(((3,5-dimethyl-1H-pyrazol-1-yl)methyl)amino)-nitrophenyl)(phenyl)methanone L$_4$: This compound was obtained as a yellow solid, yield: 84%, M$_P$: 94–96 °C, **FT-IR:** (KBr, ν(cm^{-1}): 3462, 3338, 3264, 3127, 2955, 2847, 1642, 1603, 1479, 1278, 1085, 1055, 766; **^{1}H NMR** (400 MHz, CDCl$_3$): δH = 2.08 (s,3H,CH$_3$), 2.23 (s, 3H, CH$_3$), 5.22 (d, 2H, CH$_2$), 5.81 (s, 1H, CH$_{Py}$), 7.31–8.32 (m, 8H, CH$_{Ar}$), 8.11 (t,1H, NH); **^{13}C NMR** (100 MHz, CDCl$_3$): δC = 11.3 (CH$_3$), 14.1 (CH$_3$), 71.5(CH$_2$), 106.2 (CH$_{Py}$), 115.5 (CH$_{Ar}$), 117.5 (CH$_{Ar}$), 129.3(CH$_{Py}$), 129.2 (CH$_{Ar}$), 129.1 (CH$_{Ar}$), 129.7 (CH$_{Ar}$), 130.3(CH$_{Ar}$), 130.5(CH$_{Ar}$), 132.3(CH$_{Py}$), 132.1 (CH$_{Ar}$), 135.8 (C), 139.1 (C), 139.4 (C), 157.6(C), 197.7 (CO). **EA(%):** Calcd: (62.75)C; (7.12)H; (30.13)N. Found: (62.81)C; (7.08)H; (30.21)N.
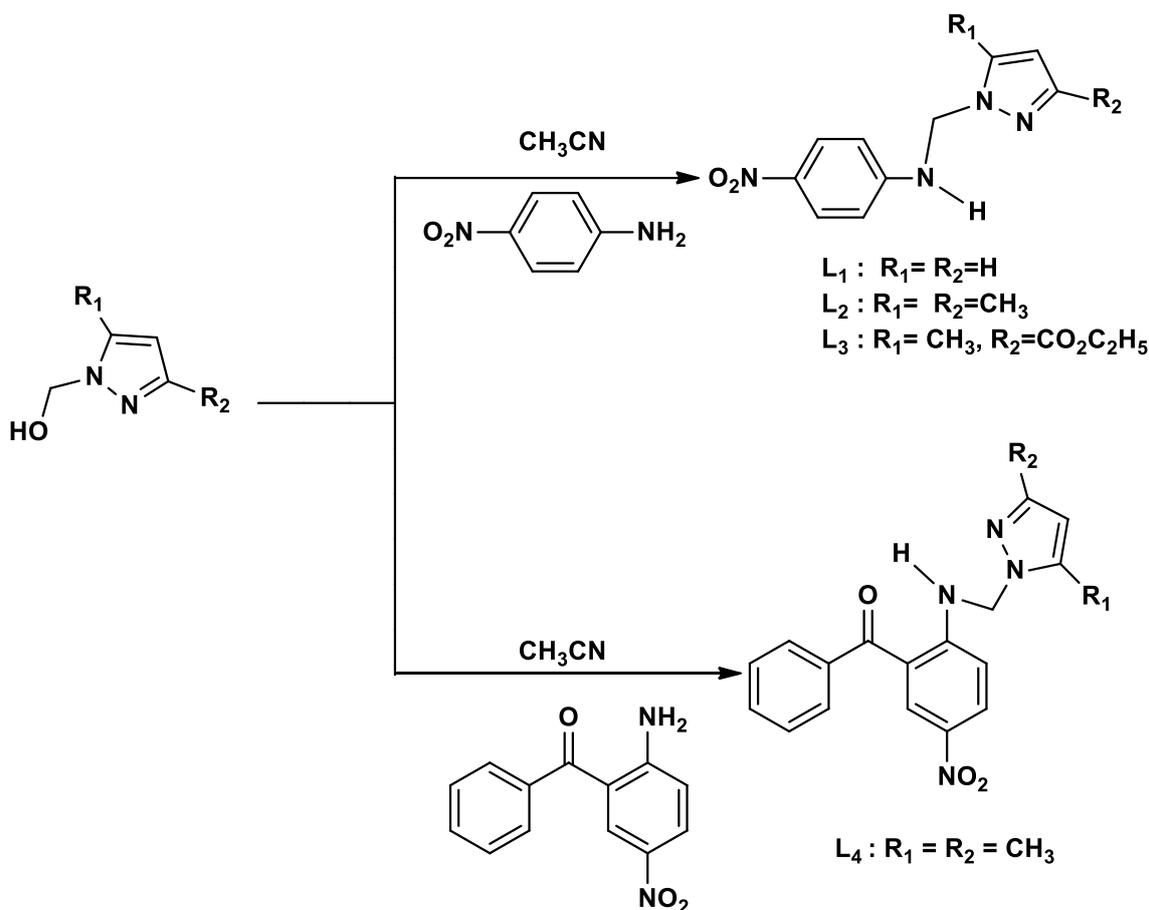

Scheme 1. Synthesis pathway for preparing ligands **L$_1$–L$_4$**.

3. Study of Conversion Reaction of Catechol to *o*-Quinone

The in situ complexes were formed by mixing the organic pyrazole-based ligands with the different copper (II) salts, which were utilized for the oxidation reaction by adding to

the catechol solution under ambient conditions. The oxidation of catechol to *o*-quinone was carried out following the reaction shown in Scheme 2. The oxidation activity was determined directly by recording the absorbance of the *o*-quinones at 390 nm (maximum absorption of *o*-quinone) using UV-Visible absorbance spectroscopy. Firstly, the catechol oxidation reactions were performed without the in situ catalysts in order to validate their effect on the catechol to *o*-quinone conversion reaction under the experimental conditions. It was observed that the absorbance vs. time was almost unchanged, suggesting the role of the in situ catalysts in the oxidation reaction rates.
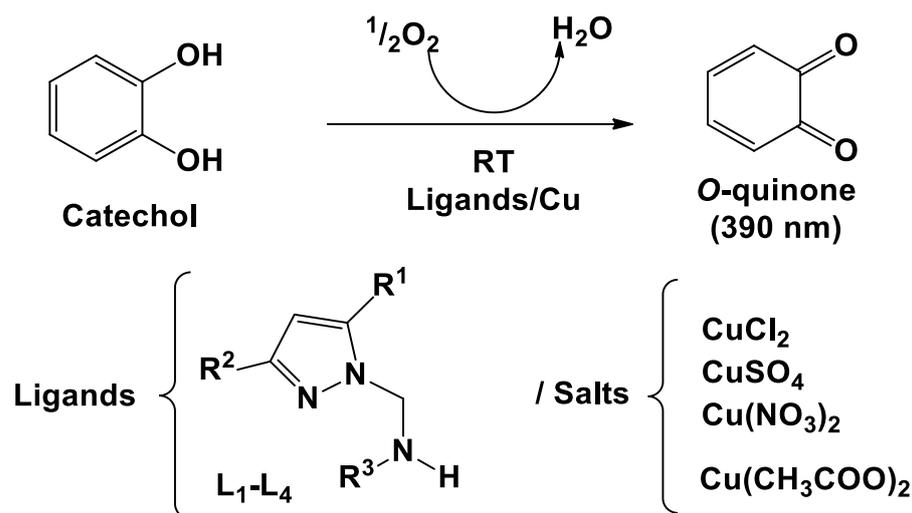
Scheme 2. General reaction for the oxidation of catechol to *o*-quinone.

3.1. Effect of Concentration

3.1.1. Catalytic Studies Using Ligand/Metal Ratio as 1L/1M in MeOH

The experiments were conducted at room temperature (RT) in methanol (99.99%, MeOH). The complexes were synthesized in situ by successively mixing 0.15 mL of copper (II) salt solution (2×10^{-3} mol L^{-1}; CuCl$_2$, Cu(CH$_3$COO)$_2$, CuSO$_4$, and Cu(NO$_3$)$_2$) with 0.15 mL of the ligand solution (2×10^{-3} mol L^{-1}). This step was followed by the addition of 2 mL of a catechol solution (0.1 mol L^{-1}) to the mixture. Finally, the oxidation reaction kinetics was studied by observing the changes in the absorbance of *o*-quinone at 390 nm as a function of time. The results obtained using the ligands (**L$_1$**–**L$_4$**) and various copper (II) salts are presented in Figures S16–S19 (see SI).

It is important to study the changes in the absorbance of *o*-quinone when various combinations of the ligands (**L$_1$**–**L$_4$**) with the copper (II) salts (CuCl$_2$, Cu(CH$_3$COO)$_2$, CuSO$_4$, and Cu(NO$_3$)$_2$) were used as the catalysts. It was observed that the changes in the absorbance during the oxidation of catechol in the presence of the complex formed by the ligand **L$_1$** and CuSO$_4$ were greater than those with other copper (II) salts. In the case of **L$_2$** as the ligand with CuCl$_2$, very low absorbance was recorded for the oxidation reaction. On the other hand, the absorbance of the *o*-quinone exceeded 1.5 times for all the complexes formed between ligand **L$_3$** and four copper (II) salts, Cu(NO$_3$)$_2$, Cu(CH$_3$CO$_2$)$_2$, CuSO$_4$, and CuCl$_2$, respectively. While in the case of the complexes formed between ligand **L$_4$** and all four copper (II) salts, the absorbance exceeded 0.8 times (Figure S16). It should be mentioned here that the oxidation rates for the transformation in the presence of in situ complexes formed by the combination of ligands(**L$_1$**–**L$_4$**) and copper (II) salts in MeOH in the ratio (1L/1M) are tabulated in Table 1 and calculated by the following expression

$$V = \frac{\Delta A}{\varepsilon \cdot \text{L}.\Delta t}$$

where A is the absorbance of o-quinone measured by UV-vis spectrophotometer at 390 nm, ε is the linear molar extinction coefficient expressed in L/mol/cm, L is the optical distance of the cuvette, generally equal to 1 cm, and t is time in min.

Table 1. The reaction rate of catechol oxidation in methanol (μmol L^{-1} min^{-1}) (1L/1M).

L/M	Cu(NO$_3$)$_2$	Cu(CH$_3$COO)$_2$	CuSO$_4$	CuCl$_2$
L_1	0.6667	1.9167	3.0104	0.1458
L_2	12.5521	14.010	14.115	4.1042
L_3	1.1875	0.5625	4.5833	4.5729
L_4	0.1562	1.4166	0.7292	1.7083

The results presented in Table 1 revealed that all the copper complexes formed in situ with the ligands L_1–L_4 showed catalytic activity toward the oxidation reaction of catechol to o-quinone. However, the oxidation rates differ drastically from 0.1458 μmol L^{-1} min^{-1} to 14.115 μmol L^{-1} min^{-1} for the complexes formed between ligand L_1 and CuCl$_2$ (weak catalyst) and L_2 and CuSO$_4$ (strong catalyst), respectively.

3.1.2. Catalytic Studies Using Ligand/Metal Ratio as (2L/1M) in Methanol

These complexes were synthesized in situ by successively mixing one equivalent (0.15 mL, 10^{-3} mol L^{-1}) of copper (II) salt solution (CuCl$_2$, Cu(CH$_3$COO)$_2$, CuSO$_4$, and Cu(NO$_3$)$_2$) with two equivalents of a ligand solution (0.15 mL, 2 $\times$ 10^{-3} mol L^{-1}). The resultant mixture was added with 2 mL of catechol solution (0.1 mol L^{-1}). The evolution of absorbance of o-quinone at 390 nm with respect to time is shown in Figures 2 and 3, while the oxidation rates are summarized in Table 2.

Table 2. The rate of oxidation of catechol in methanol (μmol·L^{-1}·min^{-1}) (2L/1M).

2L/1M	Cu(NO$_3$)$_2$	Cu(CH$_3$COO)$_2$	CuSO$_4$	CuCl$_2$
L_1	1.1041	——	1.3854	——
L_2	22.3956	32.2917	16.6563	1.3021
L_3	6.8333	4.4895	——	——
L_4	0.4375	1.5104	0.0937	——

As shown in Figure 3, the absorbance of o-quinone is more significant when the catechol oxidation reaction was catalyzed by the complexes formed by the ligand L_1 and Cu(NO$_3$)$_2$ and CuSO$_4$, while the other two copper (II) salts led to precipitation, thereby gave the unstable absorbance values. As observed from Figure 1, the absorbance evolution of o-quinone was significant when the copper complexes formed by the ligand L_2 and Cu(NO$_3$)$_2$, Cu(CH$_3$COO)$_2$, and CuSO$_4$ were used as the catalyst. In contrast, the absorbance remained constant when CuCl$_2$ was used as the metal salt for the complex formation with ligand L_2. Furthermore, the absorbance value of o-quinone for the complex formed by ligand L_3 and Cu(NO$_3$)$_2$ and Cu(CH$_3$COO)$_2$ was significant, as shown in Figure S21. In contrast, unstable absorbance values were observed in the case of the other two copper salts (CuSO$_4$ and CuCl$_2$) due to the precipitation in the reaction. Additionally, the absorbance value for the complex formed by the ligand L_4 with CuSO$_4$ was greater than those for Cu(CH$_3$CO$_2$)$_2$ and Cu(NO$_3$)$_2$, as shown in Figure S20 (see SI). It was noted that the presence of CuCl$_2$ led to precipitation in the reaction system, which gave unstable absorbance values. Thus, according to the results summarized in Table 2, it was noted that all copper complexes formed in situ with the ligands L_1–L_4 showed catalytic activity toward the oxidation reaction of catechol to o-quinone. However, the oxidation rates differ from 0.0937 μmol L^{-1} min^{-1} to 32.2917 μmol L^{-1} min^{-1} for the complexes formed by the ligand L_4 and CuSO$_4$ (weak catalyst), and L_2 and Cu(CH$_3$CO$_2$)$_2$ (strong catalyst), respectively.

A comparison of the results presented in Tables 1 and 2 revealed the difference in the oxidation rates of catechol to o-quinone. This difference may be related to the effect

of ligand and its concentration which can be explained by the nature of the coordination environment due to the electronic effect of the group. The geometry imposed by the ligand on the metal ion and the characteristics of the steric effect of the ligand may have impacted the coordination and, thus, the activity. Therefore, the effect of the counter anion on the catalytic activity was noted, and the best results were obtained with CH_3COO^- as the anion in the reaction mixture.

3.2. Solvent Effect

To study the effect of the solvent on the rate and efficiency of the catechol oxidation reaction, the experiments were performed under the same reaction conditions with ligand **L₂**, using methanol (MeOH), tetrahydrofuran (THF), acetonitrile (CH_3CN), and chloroform ($CHCl_3$) as the solvents. The oxidation reaction was carried out using the complexes formed in situ by the combinations of two equivalents of ligand **L₂** and one equivalent of various copper (II) salts solution in four different solvents. The results summarized in Table 3 showed that a significant change in the absorbance of *o*-quinone was observed when MeOH was used as a solvent to conduct the oxidation reactions using the complexes formed between $2\mathbf{L_2}$ and $Cu(NO_3)_2$ and $CuSO_4$. However, the maximum change in the absorbance was recorded when $2\mathbf{L_2}$ was complexed with $Cu(CH_3COO)_2$ in MeOH with the oxidation rate of 32.2917 $\mu mol\ L^{-1}\ min^{-1}$. In contrast, the absorbance showed lower values when THF, CH_3CN, and $CHCl_3$ were used as the solvents, as shown in Figures S22–S25 (see SI).

Table 3. Catechol oxidation rates for combinations (2L/1M) in different solvents.

2L₂/Copper (II) Salt	Solvents	V ($\mu mol \cdot L^{-1} \cdot min^{-1}$)
2L₂/Cu(NO₃)₂	MeOH	22.3958
	THF	1.1667
	CH₃CN	0.0417
	CHCl₃	0.3021
2L₂/Cu(CH₃COO)₂	MeOH	32.2917
	THF	5.5625
	CH₃CN	0.0417
	CHCl₃	0.1458
2L₂/CuSO₄	MeOH	16.6563
	CH₃CN	0.1458
	CHCl₃	0.2604
2L₂/CuCl₂	MeOH	0.1302
	THF	0.1812
	CH₃CN	0.0021
	CHCl₃	0.0208

The above-mentioned results indicated the notable effect of solvent on the catalytic activity of the in situ catalysts. Methanol, a polar protic solvent, was considered the best solvent among all, as better catalytic activity was shown by the complexes in this solvent. Moreover, it showed improved results when compared to THF, which is a polar aprotic solvent. Assuming that the general physical parameters of the solvents, including dielectric constant, dipole moment, and polarity, have no significant effect on the activity of the complexes in oxidizing catechol, as a consequence, it can be hypothesized that the coordination power or the protic nature of the solvents are the most important factors that can alter the catalytic activity of the system [39–41]. It has been widely reported that polar protic solvents can strongly solvate X anions (X = Cl^-, CH_3COO^-, SO_4^{2-}, and NO_3^-) by forming hydrogen bonding with them. Hence, the hydrogen bonding keeps the anions isolated, resulting in the least reactivity in this solvent system, whereas the counterion also solvated the cationic copper ions. However, due to the absence of hydrogen bonding in the case of cations, the solvation is comparatively less strong, leaving the cations to be more reactive. This reactivity, in turn, facilitated the formation of the complexes between the

ligands and cations, which overall increased the rate of oxidation of catechol to *o*-quinone. To validate the effect of solvent on the catalytic activity, the ligand combination (2L/1M) was tested using $2L_2/Cu(CH_3COO)_2$, $2L_2/Cu(NO_3)_2$, and $2L_2/CuSO_4$ in MeOH. The kinetic experiments were performed at room temperature, and the absorbance evolution of *o*-quinone was recorded every 5 min, as shown in Figures 1–3. The appearance of an intense band at 390 nm for the three combinations, $2L_2/Cu(CH_3COO)_2$, $2L_2Cu(NO_3)_2$, and $2L_2CuSO_4$ in MeOH confirmed that the catechol could be successfully oxidized to *o*-quinone with these combinations of catalysts.
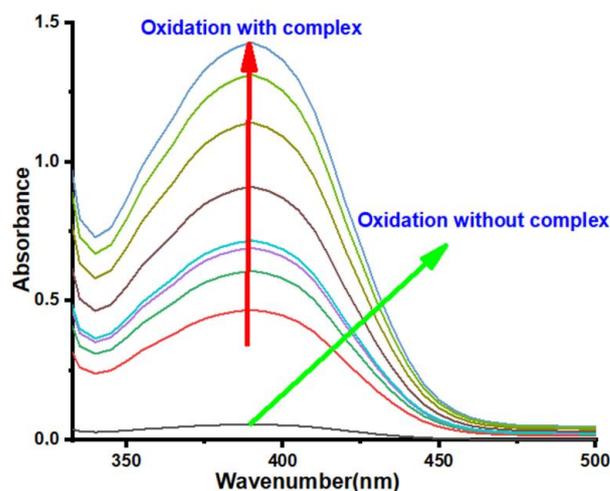
Figure 1. Absorbance spectrum of *o*-quinone as a function of time for the $2L_2/CuSO_4$ combination.
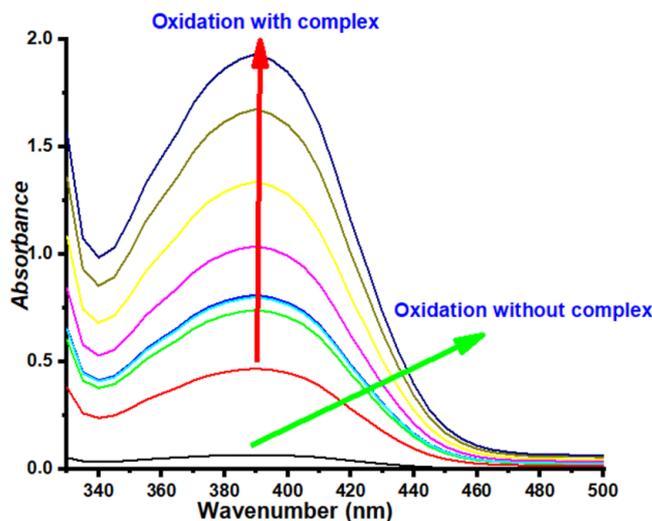
Figure 2. Absorbance spectrum of *o*-quinone as a function of time for the combination $L_2/Cu(CH_3COO)_2$.
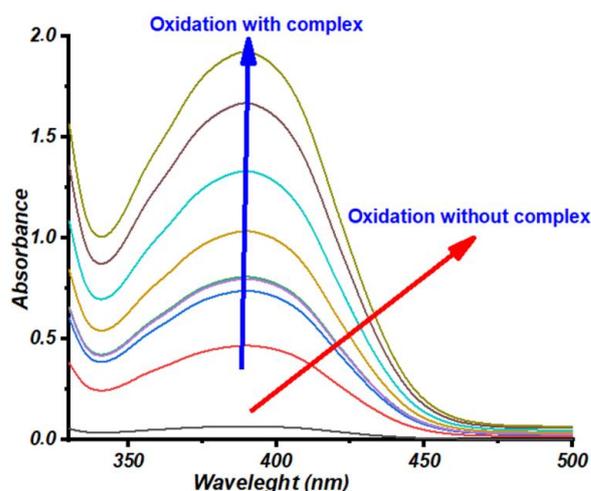
Figure 3. Absorbance spectrum of *o*-quinone as a function of time for the combination $2L_2/Cu(NO_3)_2$.

3.3. Kinetic Study

The kinetics of the oxidation reaction was studied to get more information on the catalytic efficiency of the complexes. This study was conducted to determine the kinetics parameters, such as V_{max} (maximum reaction rate) and K_m (reaction constant), using the initial rate method. The experiments were conducted in MeOH using the ligand-metal combinations as $2L_2/Cu(NO_3)_2$, $2L_2/Cu(CH_3COO)_2$, and $2L_2/CuSO_4$ under ambient conditions. This was treated with various concentrations of catechol substrate ranging from 4×10^{-2} mol L^{-1} to 4×10^{-1} mol L^{-1}. The evolution of the absorbance of *o*-quinone at 390 nm was observed and recorded as a function of time, and then the relationship between initial rates, V_i (μmol L^1 min^{-1}), and the substrate (catechol) concentration was established (mol L^{-1}).

As shown in Figures S26–S28 (see SI), a linear relationship between the initial velocities and substrate concentration was obtained; thus, the Michaelis–Menten model was applied to obtain the kinetic parameters in the reaction, summarized in Table 4. The results showed that the reactions rates, V_{max}, varied from 41.67 μmol L^{-1} min^{-1} to 33.56 μmol L^{-1} min^{-1} to 32.86 μmol L^{-1} min^{-1} when the combination $2L_2/Cu(CH_3COO)_2$, $2L_2/CuSO_4$, and $2L_2/Cu(NO_3)_2$ was used for the catalysis, respectively. Furthermore, a low value of K_m was obtained for the combination $2L_2/Cu(CH_3COO)_2$, demonstrating that MeOH is the suitable solvent for this catalytic study. It should be mentioned here that the smaller value of K_m results in the greater affinity of the catalyst toward the catechol substrate [42]. Thus, the best results were obtained in the case of $2L_2/Cu(CH_3COO)_2$, which achieved the highest catalytic efficiency.

Table 4. Values of the V_{max} and K_m constants.

$2L_2$/Cu(II) Salt	V_{max} (μmol·L^{-1}·min^{-1})	K_m (mol·L^{-1})
$2L_2/Cu(NO_3)_2$	32.86	0.04
$2L_2/Cu(CH_3COO)_2$	41.67	0.02
$2L_2/CuSO_4$	33.56	0.06

4. Conclusions

In summary, the catalytic activity of complexes formed by pyrazole-based ligands and different copper (II) salts were studied for the oxidation reaction of catechol. It was found that all combinations could catalyze the oxidation of catechol to *o*-quinone; however, their reaction rates varied under ambient conditions in the presence of atmospheric oxygen as the oxidant. It was also demonstrated that the reaction rates and catalytic efficiency of the particular combination were influenced by the nature and concentration of ligands with the combination (2L/1M) as an excellent catalyst. In addition, the nature of the

solvent significantly affected the catalytic activity of the in situ complexes. Furthermore, the combinations of $Cu(CH_3COO)_2$ with the pyrazole-based ligands in methanol were found to be more effective in catalyzing the oxidation reaction, suggesting the significant role of the counterion on the activity. The kinetics of the oxidation reaction was also studied using the Michaelis–Menten model and demonstrated that the results were in agreement with this model. It was reported that the combinations $2\mathbf{L_2}/Cu(CH_3COO)_2$, $2\mathbf{L_2}/CuSO_4$, and $2\mathbf{L_2}/Cu(NO_3)_2$ in MeOH were considered the best catalysts for the oxidation reaction of catechol.

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