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# Catecholase Activites Studies of Bis-Tripodale Pyrazolyl N-Donor Ligands, With Different Copper (II) Salts.

**Rabab Boyaala[a] , Rafika El Ati[a], Farid Abrigach[a], Mohamed El Kodadi[a,b*], Rachid Touzani[a,c], and Belkheir Hammouti[d]**

[a] LCAE, Faculté des Sciences, Oujda, Morocco.
[a] COSTE, Université Mohammed 1er, BP524, 60 000 Oujda, Morocco.
[b] CRMEF Oriental, Oujda, Morocco.
[c] FPD, Nador, BP300, Selouane, 62700 Nador, Morocco.
[d] LC2AME Faculté des Sciences, Oujda, Morocco.

**ABSTRACT**

The complexes XCubisTiCuX (i=1-9) (with X = ($CH_3COO^-$), ($Cl^-$), ($NO_3^-$), $SO_4^{2-}$) prepared in situ were tested for their reactivity towards the oxidation of catechol to o-quinine by following the appearance of quinine spectrophotometrically. The complexes show differing rates of reaction depending on the nature the junction between bis-tridentate ligand and ion nature in three solvents ethanol, methanol and tetrahydrofuran.

**Keywords**: Copper (II), Pyrazole, Catalysis, Oxidation, Bis-Tripodal, Catecholase Activites.

***Corresponding author***

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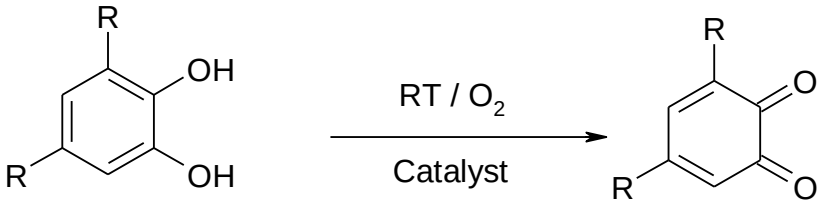
## INTRODUCTION

Copper(II) is one of the important metals in the chemistry of life. It has been detected in about 20 metalloenzymes, which are all involved in the redox chemistry in cellular life. So the coordination chemistry of diazoles acting as ligands in copper(II) compounds in the context of modelling the active site of hemocyanin, azurin, plastocyanin or blue oxidases gained much interest in the past dacades [1-3].

There in considerable interest in the synthesis of multidentate organic ligands which have donor atoms of biological relevance and their resultant metal complexes.many of these compounds are prepared in attempts to mimic the behaviour of various metalloproteins, such as the copper containing proteins hemocyanin and tyrosinase[4-8].

Notable progress has been made to mimic tyrosinase activity using copper complexes coordinated to multidentate heterocyclic amine ligands. several catechol derivatives were used in the literature as models for these kinds of studies [9-12] (Scheme 1).



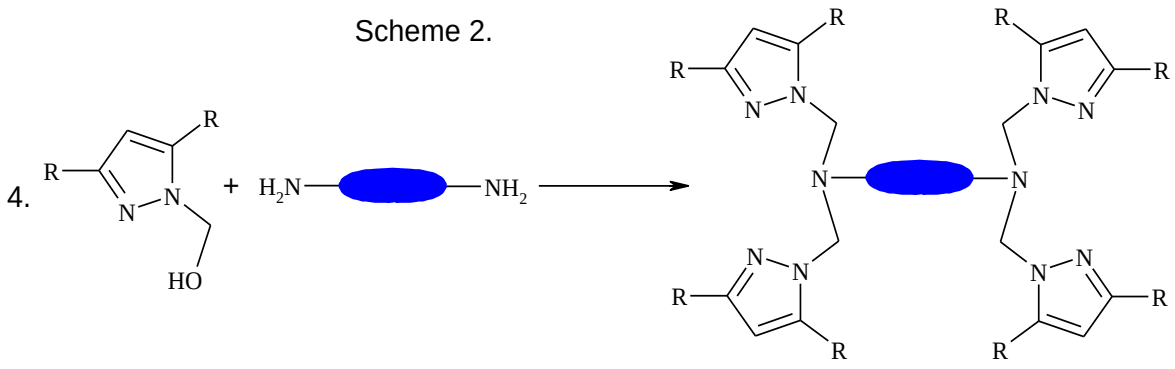

1 : R = H
2 : R = $^{t}$Bu
3 : R = $SO_3$

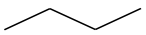
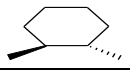
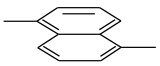
Catalyst = Ligand / Copper (II) salt

Scheme 1.

We have reported the oxidation reaction of the copper(II) complex with the oxidation bis-tridentates ligands $L_1$-$L_9$ obtained from the condensation of 1-hydroxymethyl-3,5-dimethylpyrazole and 1-hydroxymethylpyrazole with different diamine [13]. This bis-tridantates ligands provides four pyrazole nitrogen $sp^2$, two amine nitrogen $sp^3$, form two coordinates, each site capable of coordinating two atoms of copper [14-18]. (Schema 2).

Scheme 2.




| Compound |  | R |
|---|---|---|
| bis**T1** |  | H |
| bis**T2** |  | $CH_3$ |
| bis**T3** |  | $CH_3$ |
| bis**T4** |  | $CH_3$ |
| bis**T5** |  | H |

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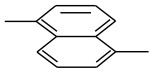
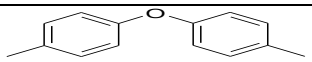
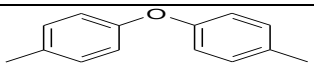
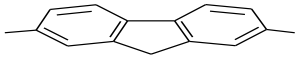
| | | |
|---|---|---|
| bis**T6** |  | $CH_3$ |
| bis**T7** |  | H |
| bis**T8** |  | $CH_3$ |
| bis**T9** |  | $CH_3$ |

Here we report the catalytic activity of the copper(II) complex prepared *in situ* in the reaction of catechol by molecular oxygen. We have compared this results obtained between complex of different ligand bisTi (i=1-9) bis-tripodal and three solvent effect methanol, ethanol and tetrahydrofurane.

In this work, and in continuation of our works in this field [14, 19-27], nine ligands have been examined for there catecholase activites with different metallic salts $Cu(CH_3COO)_2$, $CuCl_2$, $Cu(NO_3)_2$ and $CuSO_4$ and the effect nature of three solvent (methanol, ethanol and tetrahydrofuran) have been studied.

## EXPERIMENTAL SECTION

we have studied the oxidation of catechol to o-quinone by the complexes prepared *in situ* according to the following reaction route. (Schema 1).

### CATECHOLASE ACTIVITY MEASUREMENTS

Kinetic measurements were made spectrophotometrically using UV-Visible Digital Spectrophotometer Shimadzu (UV-1650 PC), following the appearance of quinone over time at room temperature. The metal complexes prepared *in situ* [28] by mixing successively 0.20 ml of a solution ($2.10^{-3}$ mol/l) of four metallic salts with 0.10 ml of bis-tripodal ligands solution ($2.10^{-3}$ mol/l) and a 2 ml solution ($10^{-1}$ mol/l solvent solution) of catechol was added together in the spectrophotometric cell.

## RESULTS AND DISCUSSION

### SYNTHESIS OF BIS-TRIPODAL LIGAND:

Pyrazole derivatives ligands bis-tripodal **bisTi** (i=1-9) were prepared according to the literature procedure by condensation of four equivalent of the 1-hydroxymethyl-3,5-dimethylpyrazole or 1-hydroxymethylpyrazol with one equivalent a series of primary diamines as ethane-1,2-diamine, propan-1,3-diamine, cyclohexane-1,2-diamine, benzene-1,2-diamine, naphthalene-1,5-diamine, 4,4'-oxydianiline and 9H-fluorene-2,7-diamine respectively (Schema 2) [13].

### CATECHOLASE STUDIES:

The progress of the catechol oxidation reaction is conveniently followed the strong absorbance peak of o-quinone in the UV/Vis spectra. The metal complex (prepared *in situ* from copper salts and the bis-tripodal ligands) [28] and a solution of catechol were placed together in the spectrophotometer cell at room temperature. Formation of quinone was monitored by the increase in absorbance at 390 nm as a function of time. In all cases, catecholase activity was noted. Figs. 1-12, show the absorbance versus time for the first 60 min of the reaction for the copper (II) complexes while the activities are shown in (Table 1-3).

### CATECHOLASE STUDIES IN METHANOL SOLVENT.

As can be seen from (Table 1 and the Fig. 1-4), all of the complexes catalyze the oxidation reaction of catechol to quinone in the methanol solvent with the activity varying from a high of 39.37 and 36.97 µmol substrate per mg catalyst per min for the bisT2($CuSO_4$) and bisT6($Cu(NO_3)_2$) complexs respectively to a low of 0.05 µmol substrate per mg catalyst per min for the bisT7($Cu(NO_3)_2$ complex.

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**Table 1: Kinetic data for the oxidation of catechol by bisTripods copper (II) complexes in the methanol solvent [V:rate (µmol $dm^{-3}min^{-1}$), a:activity (µmol $mg^{-1}min^{-1}$), T: turnover rate ($min^{-1}$)]**

| bisTi Salt | | bisT1 | bisT2 | bisT3 | bisT4 | bisT5 | bisT6 | bisT7 | bisT8 | bisT9 |
|---|---|---|---|---|---|---|---|---|---|---|
| $Cu(CH_3COO)_2$ | V | 6,81 | 13,09 | 10,43 | 8,36 | 11,09 | 10,03 | 9,56 | 18,39 | 14,97 |
| | a | 18,17 | 28,52 | 21,47 | 17,34 | 25,19 | 19,46 | 20,42 | 33,86 | 27,69 |
| | T | 10218,75 | 19640,63 | 15646,88 | 12534,38 | 16640,63 | 15037,50 | 14343,75 | 27590,63 | 22453,13 |
| $CuCl_2$ | V | 0,55 | 0,44 | 0,14 | 12,36 | 0,84 | 0,84 | 4,80 | 2,44 | 2,39 |
| | a | 1,60 | 1,04 | 0,32 | 27,44 | 2,05 | 1,73 | 10,98 | 4,77 | 4,70 |
| | T | 825,00 | 665,63 | 215,63 | 18543,75 | 1256,25 | 1256,25 | 7200,00 | 3665,63 | 3590,63 |
| $Cu(NO_3)_2$ | V | 0,33 | 0,84 | 0,18 | 2,61 | 0,66 | 19,19 | 0,03 | 0,30 | 12,90 |
| | a | 0,86 | 1,81 | 0,36 | 5,36 | 1,48 | 36,97 | 0,05 | 0,55 | 23,69 |
| | T | 487,50 | 1256,25 | 262,50 | 3909,38 | 984,38 | 28790,63 | 37,50 | 450,00 | 19350,00 |
| $CuSO_4$ | V | 4,18 | 17,50 | 9,71 | 12,48 | 1,39 | 5,99 | 1,89 | 1,66 | 4,19 |
| | a | 11,60 | 39,37 | 20,61 | 26,71 | 3,26 | 11,98 | 4,16 | 3,13 | 7,97 |
| | T | 6271,88 | 26250,00 | 14568,75 | 18712,50 | 2081,25 | 8990,63 | 2831,25 | 2484,38 | 6290,63 |

It is noted that all the bistripodal-based complexes and the acetates and sulfate ions exhibit good activities, on the other hand, when chloride and nitrate ions are used except for the complexes based on bisT4 and bisT7 and the chloride which gives respectfully to activities 27.44 and 10.98 µmol $mg^{-1}$ $min^{-1}$ with the chloride ion, and the complexes based on bisT6 and bisT9 suitably gives catalytic activities 36.97 and 23.69 µmol $mg^{-1}$ $min^{-1}$ with the nitrate ion.

It is noted that the catalytic activity depends on the nature of the ligand for the same anion, the catalytic activity varies from ligand to ligand, and also depends on the nature of the metal salt used, for example in the case of ligand bisT1, the catalytic activity has values of 1.6, 18.17, 0.86 and 11.60 µmol $mg^{-1}$ $min^{-1}$ respectively with metallic $CuCl_2$, $Cu(CH_3COO)_2$, $Cu(NO_3)_2$ and $CuSO_4$. The results obtained by complexes based on copper (II) acetate and copper (II) sulfate are comparable to the values reported in literature [20, 29-30] for similar tripod ligands.

**CATECHOLASE STUDIES IN ETHANOL SOLVENT.**

As can be seen from (Table 2 and the Fig. 5-8), all of the complexes catalyze the oxidation reaction of catechol to quinone with the activity varying from a high of 121.99 , 87.78 , 65.53 and 65.14 µmol substrate per mg catalyst per min for the bisT1($CuCl_2$), bisT5($CuCl_2$), isT2($Cu(CH_3COO)_2$) and bisT6($CuCl_2$) complexs respectively to a low of 0.03 µmol substrate per mg catalyst per min for bisT7($Cu(NO_3)_2$) complex. All the complexes based on the bis-tripodal ligands with the different metal ions represent good catalytic activities except the ligands bisT3 and bisT8 with the chloride ion which gives respectively 0.40 and 0.81, and the ligands bisT5 and bisT7 with the ion of one another, acetate catalysts which exhibit catalytic activities of 2.20 and 0.44, and also complexes based on nitrate ions which exhibit low catalytic activity with respect to the other ions. The catalytic activities depend strongly on the nature of the bis-tripodal ligands and on the type of inorganic anion used.

**Table 2: Kinetic data for the oxidation of catechol by bis-Tripods copper (II) complexes in the ethanol solvent [V: rate (µmol $dm^{-3}$ $min^{-1}$), a:activity (µmol $mg^{-1}$ $min^{-1}$), T: turnover rate ($min^{-1}$)].**

| bisTi Salt | | bisT1 | bisT2 | bisT3 | bisT4 | bisT5 | bisT6 | bisT7 | bisT8 | bisT9 |
|---|---|---|---|---|---|---|---|---|---|---|
| $Cu(CH_3COO)_2$ | V | 9,40 | 30,09 | 7,41 | 31,09 | 0,97 | 17,33 | 0,21 | 20,63 | 15,29 |
| | a | 25,07 | 65,53 | 15,24 | 64,52 | 2,20 | 33,63 | 0,44 | 37,97 | 28,28 |
| | T | 14100,00 | 45131,25 | 11109,38 | 46631,25 | 1453,13 | 25987,50 | 309,38 | 30937,50 | 22931,25 |

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| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| $CuCl_2$ | V | 41,92 | 11,83 | 0,18 | 20,11 | 35,91 | 31,52 | 8,43 | 0,41 | 5,41 |
| | a | 121,99 | 27,64 | 0,40 | 44,65 | 87,78 | 65,14 | 19,29 | 0,81 | 10,62 |
| | T | 62878,13 | 17737,50 | 271,88 | 30168,75 | 53859,38 | 47278,13 | 12646,88 | 618,75 | 8109,38 |
| $Cu(NO_3)_2$ | V | 0,51 | 0,63 | 0,27 | 1,91 | 3,44 | 1,81 | 0,01 | 2,14 | 2,94 |
| | a | 1,35 | 1,36 | 0,55 | 3,92 | 7,75 | 3,48 | 0,03 | 3,92 | 5,41 |
| | T | 768,75 | 946,88 | 403,13 | 2859,38 | 5165,63 | 2709,38 | 18,75 | 3215,63 | 4415,63 |
| $CuSO_4$ | V | 4,67 | 11,69 | 5,36 | 10,38 | 3,86 | 7,87 | 3,16 | 4,48 | 15,45 |
| | a | 12,96 | 26,31 | 11,38 | 22,21 | 9,07 | 15,72 | 6,96 | 8,48 | 29,38 |
| | T | 7003,13 | 17540,63 | 8043,75 | 15562,50 | 5793,75 | 11803,13 | 4734,38 | 6721,88 | 23175,00 |

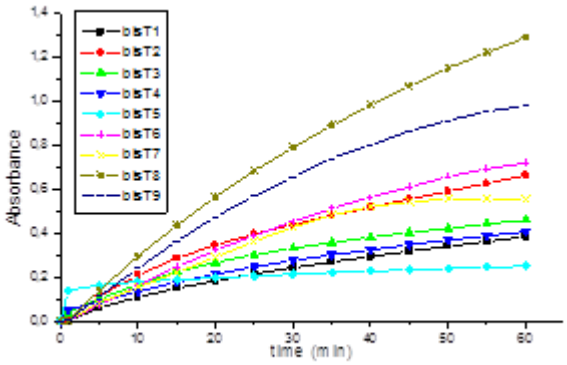

Fig. 1. Oxidation of catechol by complexes of $CH_3COO^-$ in MeOH

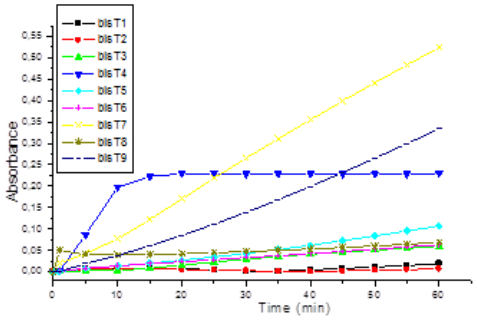

Fig. 2. Oxidation of catechol by complexes of $Cl^-$ in MeOH

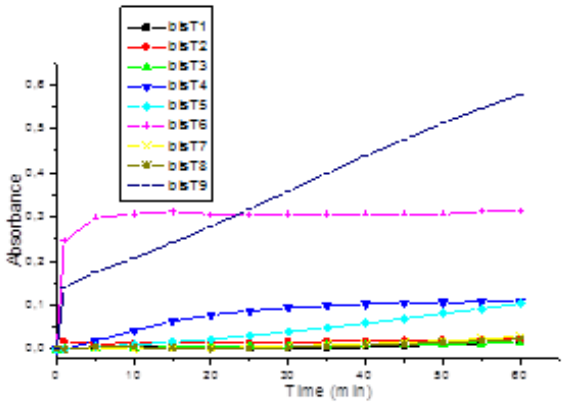

Fig. 3. Oxidation of catechol by complexes of $NO_3^-$ in MeOH

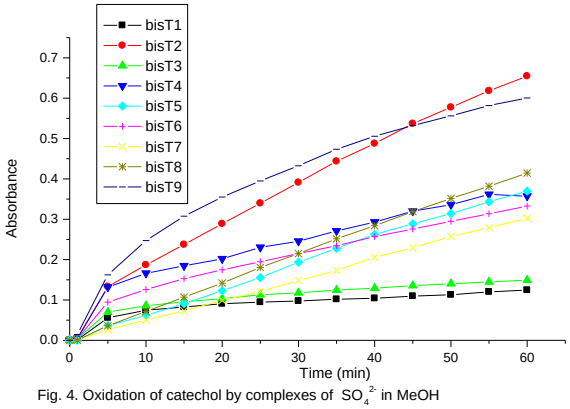

Fig. 4. Oxidation of catechol by complexes of $SO_4^{2-}$ in MeOH

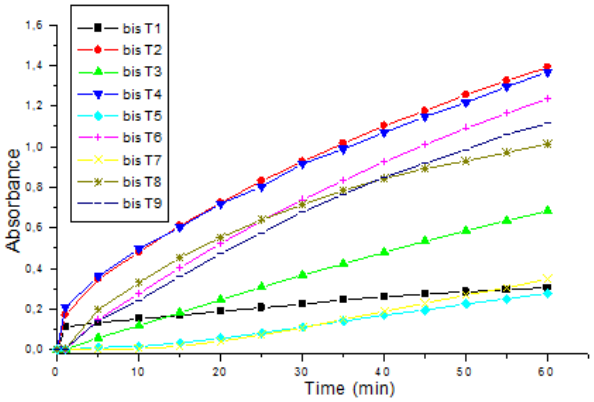

Fig.5. Oxidation of catechol by complexes of $CH_3COO^-$ in EtOH

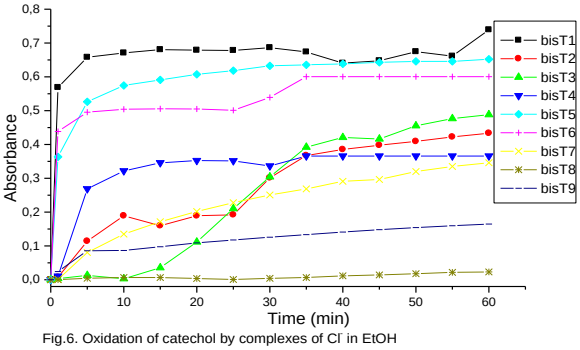

Fig.6. Oxidation of catechol by complexes of $Cl^-$ in EtOH

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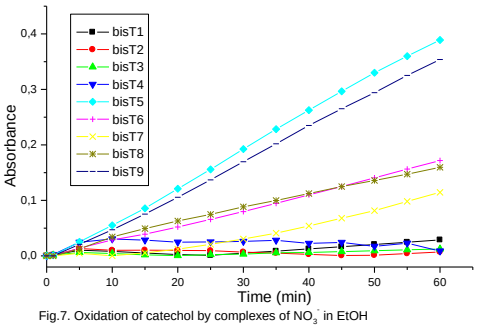


Fig.7. Oxidation of catechol by complexes of $NO_3^-$ in EtOH

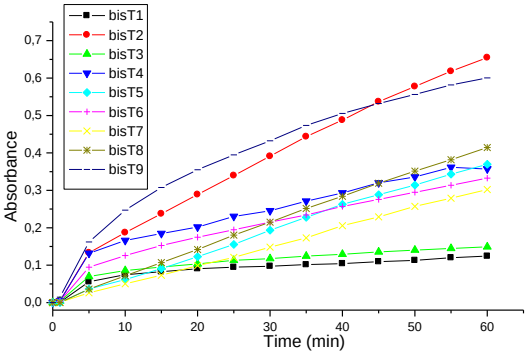


Fig.8. Oxidation of catechol by complexes of $SO_4^-$ in EtOH

**CATECHOLASE STUDIES IN THF SOLVENT.**

As can be seen from (Table 3 and the Fig. 9-12), all of the complexes catalyze the oxidation reaction of catechol to quinone with the activity varying from a high of 31.06, 24.39, 23.36 and 22.57 µmol substrate per mg catalyst per min for the bisT9($CuCl_2$), bisT1($CuSO_4$), bisT1($CuCl_2$) and bisT4($Cu(NO_3)_2$) complexs respectively to a low of 0.27 µmol substrate per mg catalyst per min for bisT2($CuSO_4$) complex. It is noted that almost all the ligand-based complexes and the metal chloride and sulfate ions give good catalytic activities with respect to the abase of the acetate and nitrate ions which exhibit low catalytic activities except with complexes based on the ligands bisT4 and bisT9 and the nitrate ions which attain 22.57 and 15.78 µmol substrate per mg catalyst per min respectively. The different catalytic activity in all combinations of bis-tripodal ligand and metal salts, the activity depends strongly on the nature of the metal salts and also on the nature of the bis-tripod ligands.

**Table 3: Kinetic data for the oxidation of catechol by bisTripods copper (II) complexes in the tetrahydrofuran solvent [V: rate (µmol $dm^{-3}$ $min^{-1}$), a: activity (µmol $mg^{-1}$ $min^{-1}$), T: turnover rate ($min^{-1}$)].**

| bisTi Salt | | bisT1 | bisT2 | bisT3 | bisT4 | bisT5 | bisT6 | bisT7 | bisT8 | bisT9 |
|---|---|---|---|---|---|---|---|---|---|---|
| $Cu(CH_3COO)_2$ | V | 1,44 | 0,81 | 2,07 | 2,10 | 2,90 | 0,75 | 6,57 | 3,76 | 0,58 |
| | a | 3,83 | 1,75 | 4,26 | 4,36 | 6,59 | 1,46 | 14,03 | 6,93 | 1,07 |
| | T | 2155,26 | 1207,89 | 3102,63 | 3150,00 | 4350,00 | 1128,95 | 9860,53 | 5644,74 | 868,42 |
| $CuCl_2$ | V | 8,03 | 6,68 | 1,57 | 2,80 | 6,43 | 2,61 | 9,12 | 5,47 | 15,82 |
| | a | 23,36 | 15,62 | 3,46 | 6,22 | 15,72 | 5,40 | 20,87 | 10,68 | 31,06 |
| | T | 12039,47 | 10026,32 | 2360,53 | 4200,00 | 9647,37 | 3915,79 | 13681,58 | 8202,63 | 23723,68 |
| $Cu(NO_3)_2$ | V | 0,24 | 1,69 | 0,83 | 10,96 | 1,16 | 1,61 | 1,49 | 2,03 | 8,59 |
| | a | 0,64 | 3,66 | 1,69 | 22,57 | 2,62 | 3,09 | 3,15 | 3,70 | 15,78 |
| | T | 363,16 | 2542,11 | 1239,47 | 16444,74 | 1744,74 | 2407,89 | 2234,21 | 3039,47 | 12892,11 |
| $CuSO_4$ | V | 8,79 | 0,12 | 3,13 | 0,55 | 4,72 | 3,28 | 4,04 | 3,28 | 4,98 |
| | a | 24,39 | 0,27 | 6,64 | 1,18 | 11,09 | 6,56 | 8,90 | 6,21 | 9,48 |
| | T | 13184,21 | 181,58 | 4689,47 | 828,95 | 7081,58 | 4926,32 | 6055,26 | 4926,32 | 7476,32 |

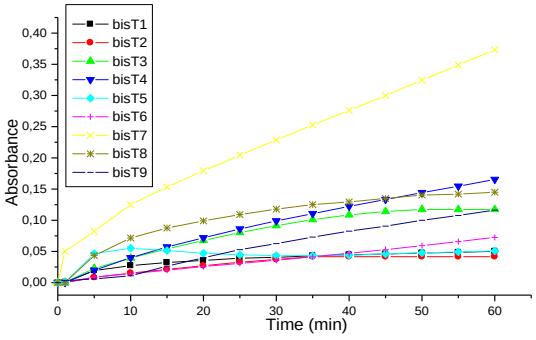


Fig.9. Oxidation of catechol by complexes of $CH_3COO^-$ in THF

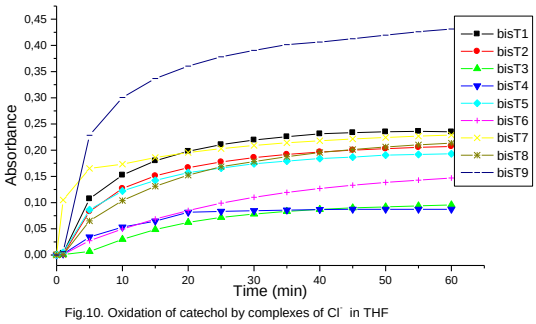


Fig.10. Oxidation of catechol by complexes of $Cl^-$ in THF

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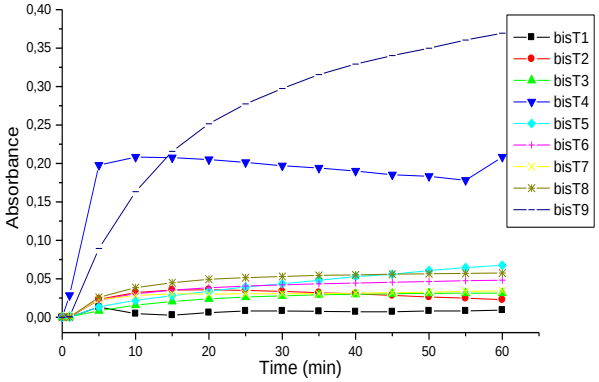


Fig.11. Oxidation of catechol by complexes of $NO_3^-$ in THF

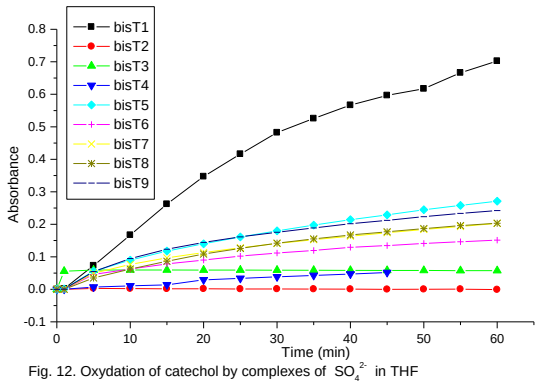


Fig. 12. Oxydation of catechol by complexes of $SO_4^{2-}$ in THF

**KINETIC STUDIES.**

The kinetic studies on the oxidation of catechol were carried out by the method initial rate by monitoring the increase in the characteristic quinone absorption band at 390 nm under air as a function of time. the metal complex (0.3 ml of $2x10^{-3}$ M solvent solution (MeOH, EtOH or THF)) and a 2.0 ml solution of catechol (0.005; 0.01; 0.05; 0.1; 0.2; 0.4 and 0.6 M) were equilibrated separately to 25°C and then added together in a spectrophotometric cell at 25°C. In this study we chose to study the oxidation of catechol in the presence of three complexes bisT6Cu$(NO_3)_2$, bisT1Cu$Cl_2$ and bisT9Cu$Cl_2$ which gives good results for the three solvents MeOH, EtOH and THF.

Figures 13, shows the dependence of the reaction rates on the catechol concentration for the oxidation reaction catalyzed by three copper (II) complexes in three solvent different (MeOH, EtOH and THF) while the activities are shown in table 4. An analysis of the data based on the Michaelis-Menten model, originally developed for enzyme kinetic, was applied. The results evaluated from curve in the Fig. 13 are Vmax = $6.3 \times 10^{-5}$ mol $dm^{-3}$ $min^{-1}$ Km = 0.063 mol $dm^{-3}$ for complexe formed by bisT1 and metallic salt ($CuCl_2$, $2H_2O$) in the EtOH is the best results with good turnover rate of 62878.13 $min^{-1}$ .

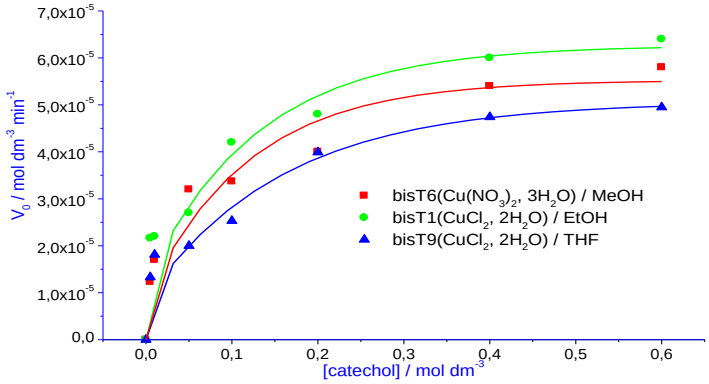


Fig. 13: Dependence of the initial rate of the quinone production on the concentration of substrate, catechol, at constant concentration of catalyse ($2x10^{-3}$M) in MeOH, EtOH and THF.

**Table 4. Kinetic data for the oxidation of catechol by three copper complexes (bisT1($CuCl_2$,$2H_2O$), bisT9($CuCl_2$,$2H_2O$) and bisT6($Cu(NO_3)_2$,$3H_2O$).**

| Complex/solvent | Activity (µmol substrate/mg catalyst per min) | Turnover ($min^{-1}$) | Km (mol $dm^{-3}$) | Vmax (mol $dm^{-3}$ $min^{-1}$) |
|---|---|---|---|---|
| bisT6Cu$(NO_3)_2$/MeOH | 36.97 | 28790.63 | 0.078 | $6.0 \times 10^{-5}$ |
| bisT1Cu$Cl_2$/EtOH | 121.99 | 62878.13 | 0.063 | $6.3 \times 10^{-5}$ |
| bisT9Cu$Cl_2$/THF | 31.06 | 23723.68 | 0.064 | $5.0 \times 10^{-5}$ |

The oxidation of catechol were carried out by monitoring the invrease of the intensity of o-quinone bande at 390 nm with time after mixing of 0.3 mL of bisT1Cu$Cl_2$ and bisT9Cu$Cl_2$ complexs and 2 mL of catechol,

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and the o-quinone absorbance was recorded at a time interval of 10 min, the oxidation reaction was carried out in EtOH and THF respectively at room temperature.

According to Fig. 14 it is clear show that the band at around 390 nm is observed when the oxidation reaction of catechol to o-quinone in the presence of the complex prepared in situ based on bisT1 ligand with copper (II) salt $CuCl_2$ is achieved.

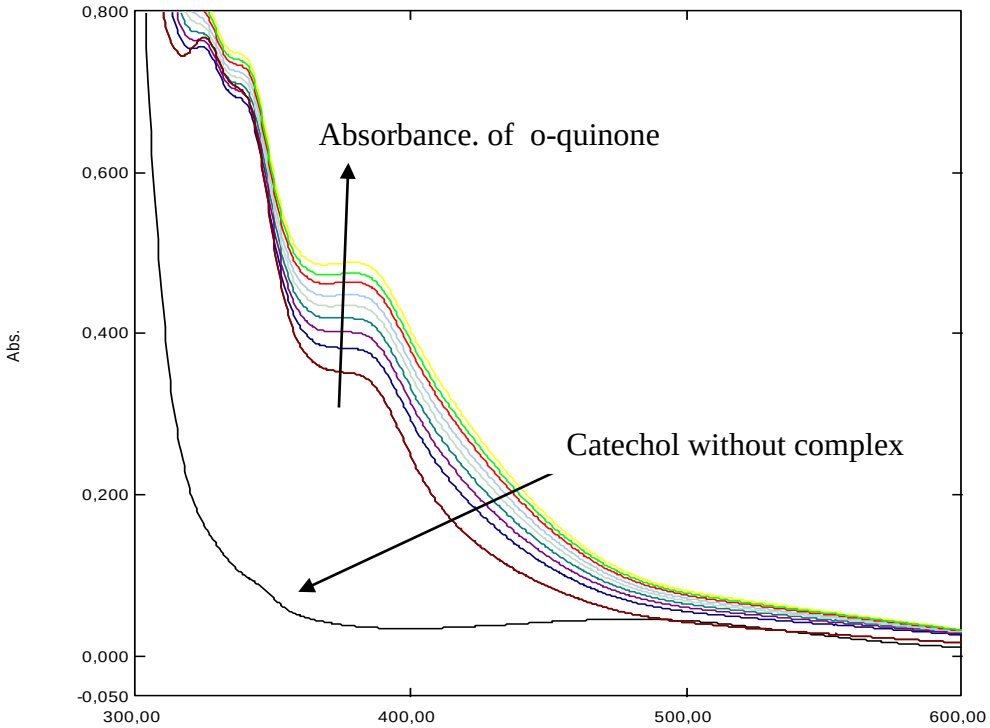


**Fig. 14: Increase of o-quinone band at 390 nm after addition of 2 mL of catechol ($1x10^{-1}$M) to a solution containing one equivalent of ligand bisT1 (0.1 mL, $2x10^{-3}$M) and two equivalents of $CuCl_2$ (0.2 mL, $2x10^{-3}$M) in ethanol. The spectra were recorded after every 10 min.**

**SOLVENT EFFECT**

The nature of solvent used in reaction is important factor for catecholase activity. in general the reaction rate of catechol oxidation will be influenced by solvent. in recent years, work of various groups has shown that nature of solvent has a large effect on the catecholase activity [31-33].

According to the tables, it is noted that the oxidation catalytic activity of catechol to o-quinone varies in use the complexes prepared in situ based on the same ligands and the same copper (II) salt, with the change of the reaction solvent.

**PROPOSED REACTION PATHWAY**

Previous studies of the catecholase copper complex model, present reaction mechanisms in the oxidation of catechol to o-quinone [34-38], We try to present an oxidation mechanism of catechol, according to the Fig.15, the mechanism of catecholase activity (outer circle) starts from the complexe. catechol binds to the complexe (for example), followed by the oxidation of the substrate to the first quinone and the formation of the reduced of the copper. Oxidation to the second quinone forms the met state again and closes the catalytic cycle. Or two catechol substrates bind to the copper atoms, followed by the oxidation of two substrates to o-quinone and reduction of two copper atoms at the same time or one after the other.

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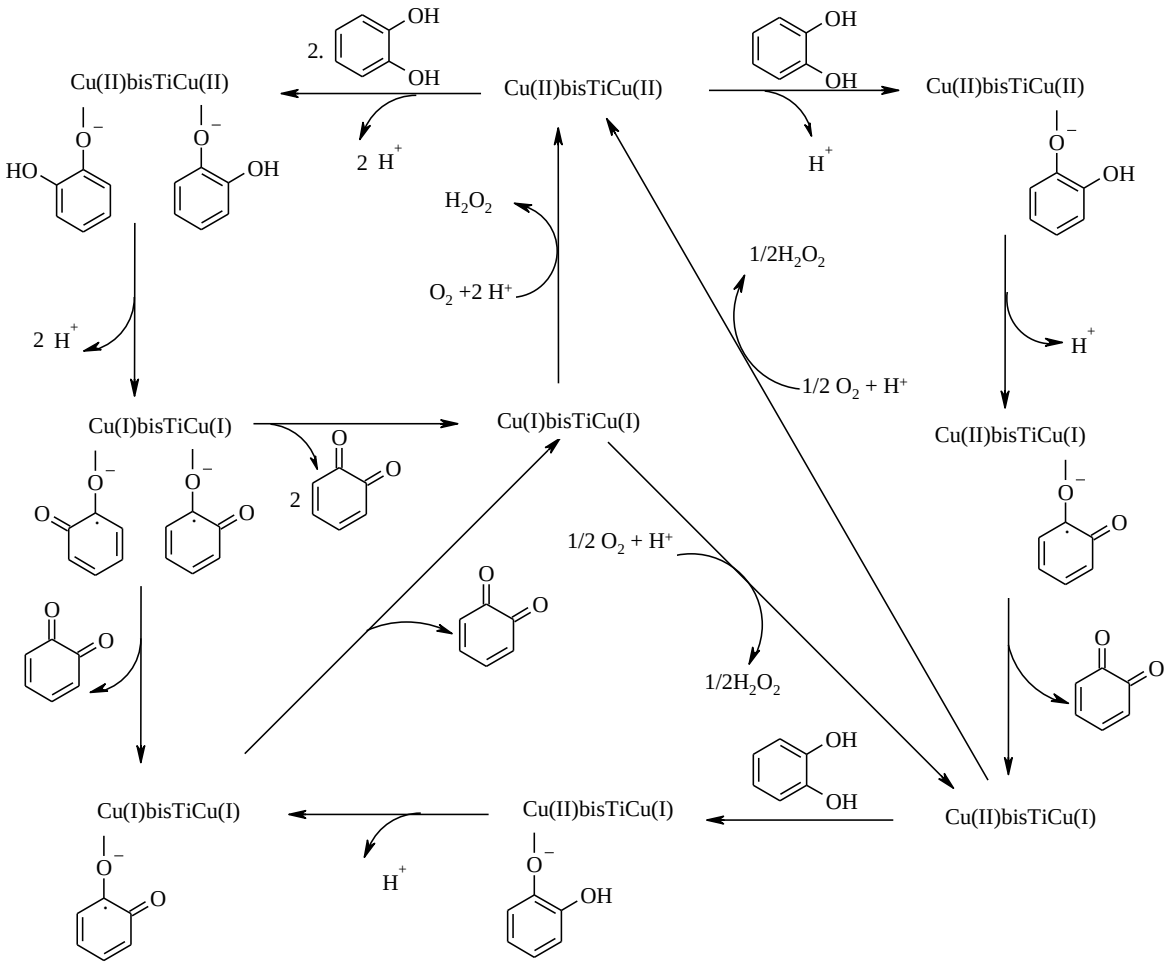


**Fig. 15: Proposed mechanistic pathway of the catalytic oxidation of catechol by Cu(II)bisTiCu(II) with (i = 1-9)**

## CONCLUSION

We report in this work that the oxidation of catechol is very efficient to give o-quinone by complexes of copper (II) with bis-tripodal pyrazole ligands present two site of coordination. the complexes of copper (II) were prepared in situ. In this study, we investigated the effect of nine bis-tridentate ligand. The results obtained show that the nature of the ligands, the metal salts and the nature of the solvent have a great effect on the combinations studied in the catecholase activity. The ligands studied have two coordination sites, so the complexes formed have important capacities to catalyze the oxidation reaction of catechol to o-quinone, explains the high values of the catalytic activities.

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