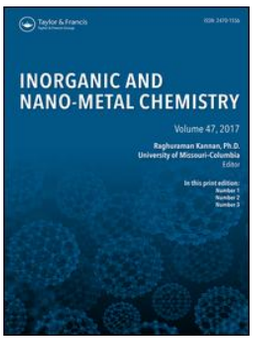

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Development of a new methodology for the synthesis of chloro(glycinato)1,10-phenanthroline copper(II) monohydrate and analogous complexes and study of their catalytic utility towards selective hydroxylation of phenol

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Abstract

A new simple and convenient method has been developed for the synthesis of copper(II)complexes using Proline and Glycine as ligand. The complexes were characterized by using conventional spectroscopic techniques and by determining structure. Methodology developed gives substantial yield of the products. Chloro(Glycinato) 1,10-Phenanthroline Copper(II) monohydrate and other complexes effectively catalyze the selective orthohydroxylation of phenol , in presence of Hydrogen peroxide, in water. Catechol formation was confirmed by IR and NMR spectroscopy. Hydroxylation reaction produces moderate to good yield of the product catechol. Longer time duration results in decrease of yield.

Keyword:

1,10-Phenanthroline,Glycine, Methodology, Hydroxylation, Phenol, Catechol, Regioselectivity.

1. Introduction

Copper(II) ions and its metal complexes have continued to attract attention of synthetic chemists due to its various interesting structural features, its usefulness as models of the active centers of various metallo-enzymes, magnetic, electronic, catalytic and biological properties.[1] Copper(II) can effectively coordinate with N-donor atom of 1,10-phenanthroline and N,O-donor atoms of many amino acids through chelation. Copper (II) formed a number of mixed ligand metal complexes, where two or more ligand coordinates with the metal center. Many mixed-ligand copper complexes containing 1,10-phenanthroline[2] or 2,2'-bipyridine[3] and other ligands such as Schiff bases derived from amino acid[4] have been reported. Herein we have reported the synthesis, characterization and catalytic activity of Chloro(glycinato) 1,10-phenanthroline copper(II) monohydrate and other few analogous complexes. Utility of such complexes towards hydroxylation reaction of phenol has also been studied.

Use of Copper(II) complexes for selective hydroxylation of aromatic compounds is industrially recognized as most challenging chemical reactions in synthetic organic chemistry. Selective hydroxylation of phenols has lots of industrial significance because phenol and catechol is widely used in industry as an important intermediate in manufacturing pesticides[5] and medicines[6] and can also be used to produce perfumes (e.g., piperonal)[7], dyes[8], photosensitive materials[9], insecticides[10] and many more. Catechol is used in the manufacture of the artificial flavors vanillin and ethyl vanillin.[11] Catechol also has wide applicability in pharmaceutical industry. The pharmaceuticals used in the treatment of Parkinson's disease and hypertension, L-dopa and methyl L-dopa, are manufactured from catechol.[12] Catechol is synthesized industrially from phenol with hydrogen peroxide.[13] The most common oxidizing agents used in phenol

hydroxylation are hydrogen peroxide, and alkyl hydroperoxides. For hydroxylation reactions, hydrogen peroxide is preferred over Organic peroxides because organic hydroperoxides are not eco friendly and at the same time they are explosive, corrosive and flamable too.[14] Hydrogen peroxide is usually not selective because of the further oxidation of the phenol ring due to the introduction of the activating -OH group which eventually causes formation of a mixture of acids and polymeric compounds.[15]The reaction yields hydroquinone and catechol. During catechol synthesis through hydroxylation, in most of the cases low selectivity towards catechol is a general problem. The industrial catalysts give selectivity on catechol from 50 to 70%.[16] Catechol synthesis using hydrogen peroxide often accompanies with the formation of hydroquinone and o-quinone as byproducts and product yield is also less.[17]

Metal complexes are usually employed as catalyst for hydroxylation reaction and in such catalytic transformations structure of the ligands play a significant role. One of the most prominent method is silanol-directed, Pd-catalyzed C–H oxygenation of phenols into catechols.[18] This method is highly site selective and general, as it allows for oxygenation of not only electron-neutral but also electron-poor phenols. Copper(II) complexes are known to catalyze efficiently the hydroxylation reactions of phenol and numerous research publications are available. Copper alginate (dry beads and powder) catalysts showed highest conversions of phenol as 52.9% and 62.5% over dry beads and powder, respectively, with a catechol-to-hydroquinone ratio of 3:2.[19] Copper substituted mesoporous silica (Cu-SBA-15) also shows excellent catalytic activity towards hydroxylation of phenol using hydrogen peroxide with 62.4% selectivity for catechol (about 71% selectivity).[20]The catalytic reaction of cis-bisglycinato copper (II) monohydrate also catalyze hydroxylation of phenols in presence of hydrogen peroxide which

yields catechol and hydroquinone (in 1:1.2 ratio) in good yield.[21] Use of transition metal complexes as catalyst generally associated with side reactions, especially when the time lag is more.[16] In all reviewed literature, two types of byproduct, quinone and macromolecular tars, were formed due to over oxidation. The over oxidation problem is solved, in industry, by using high phenol/hydrogen peroxide ratios along with high concentrations of phenol.[16] It is expected that catechol should be formed at a higher rate in short time duration and that will help to avoid over oxidation because in that case high conversion of hydrogen peroxide will not be achieved. Development of efficient catalytic system for such selective conversion of phenol is an important research objective.

2. Experimental

2.1. Materials

Copper (II) sulphatepentahydrate, 1,10 – Phenanthroline, Glycine, Phenol, Hydrogen peroxide, Hydrochloric acid, sulphuric acid, Diethyl ether were procured from TCI, Japan and Sisco Research Laboratory and were used as received. Solvents are used after drying by standard procedure.

2.2. Instrumental

IR spectra of the products were recorded on a Perkin Elmer Spectrum-BX IR spectrometer. Cyclic Voltametry was recorded on a PAR 237A Potentiostate. Scan rate 20mV/S, electrolyte used 0.1M KCl solution. Elemental analysis were carried out on a Thermo finnigan, FLASH EA 1112 Elemental analyser. NMR spectra were recorded on a Varian make 400 NMR Spectrometer (Model: Mercury Plus).

2.1. Synthesis of Chloro(glycinato)(1,10 – Phenanthroline) Copper(II) monohydrate

$CuSO_4.5H_2O$ (0.249g, 0.001mol) was dissolved in 5.0 ml of 1N HCl. Glycine (0.750g, 0.001mol) and Phenanthroline (0.198g, 0.001mol) were dissolved separately in another 5.0ml of 1N HCl solution. The two solutions were then mixed properly in a 50.0ml round bottom flask to obtain a blue coloured solution. The resulting solution was then stirred continuously for 1 hour at 70^0C which results in the formation of a green coloured precipitate. The precipitate obtained was then filtered and washed with cold water (2 x 5.0ml) and then dried in the oven at 60^0Cfor 40 minutes to obtain a green coloured complex. Yield = 0.2563g, 69.0%, Anal. Calc. $C_{14}N_3O_2H_{11}Cl.H_2OCu$ (mol. Wt. 371): C, 45.28; H, 3.51; N, 11.32. Found C, 45.78; H, 2.89; N, 9.042. It is to be noted that for heterocyclic compounds containing nitrogen in the cycle or in the groups like azide, nitrile, nitro, etc. usually underestimated results are obtained for nitrogen due to incomplete conversion of different forms of nitrogen to elemental nitrogen. IR spectra of the complex 3368 cm^{-1} υ (NH), 3077 cm^{-1} υ (C-H, aromatic), 1635 cm^{-1} υ (c=o), 1582 cm^{-1} υ (C=N), 1553 cm^{-1}, 1513 cm^{-1}, 1420 cm^{-1} υ (C-C str), 1351 cm^{-1}, 1145 cm^{-1}, 1108 cm^{-1}, 853 cm^{-1}, 720 cm^{-1}, 610 cm^{-1} υ (M-N), 407 cm^{-1} υ (M-O).

2.2. Synthesis of Chloro (1,10 – Phenanthroline)(L-Prolinato) Copper(II) trihydrate

In an analogous manner $CuSO_4.5H_2O$ (0.249g, 0.001mol) was dissolved in 5.0ml of 1NHCl. L-Proline (0.115g, 0.001mol) and Phenanthroline (0.198g, 0.001mol) were dissolved separately in another 5.0ml of 1N HCl and both the solutions were mixed in a 50.0ml round bottom flask to obtain a blue coloured solution. The resulting solution was then stirred continuously for 1 hour at 70^0C. With progress of time the colour of the solution changes and a green colour precipitate is formed. The precipitate obtained was then filtered and washed with

cold water (2 x 5.0ml) and then dried in the oven for 40 minutes to obtain a green coloured complex. Yield, 0.2436g, 62.0%, Anal. Calc. $C_{17}N_3O_2H_{16}Cl.3H_2OCu$ (Mol. Wt. 447): C, 45.63; H, 3.57; N, 9.39. Found C, 45.59; H, 2.99; N, 8.71.For similar reasoning stated above, here also we have obtained underestimated results for percentage of nitrogen. IR spectra of the complex 3353 cm^{-1} υ (NH), 3053 cm^{-1} υ (C-H, aromatic), 1626 cm^{-1} υ (c=o), 1587 cm^{-1} υ (C=N), 1553 cm^{-1}, 1517 cm^{-1}, 1424 cm^{-1} υ (C-C str), 1354 cm^{-1} , 1226 cm^{-1}, 1104 cm^{-1}, 1047 cm^{-1}, 852 cm^{-1}, 720 cm^{-1}, 639 cm^{-1} υ (M-N), 408 cm^{-1} υ (M-O).

2.3. Synthesis of (glycinato)(1,10 – Phenanthroline)(Sulfonato) Copper(II) Monohydrate

A solution (5.0ml) of $CuSO_4.5H_2O$ (0.249g, 0.001mol) was prepared in 1N H_2SO_4. Glycine (0.750g, 0.001mol) and Phenanthroline (0.198g, 0.001mol) were dissolved separately in another 5.0ml of 1N H_2SO_4. The two solutions were then mixed properly to obtain a blue coloured solution. The resulting solution was then stirred continuously for 1 hour at 70^0C. The precipitate obtained was then filtered and washed with cold water (2 x 5.0ml) and then dried in the oven for 40 minutes to obtain a blue coloured complex. Yield = 0.3864g, 69.0% Anal. Calc. $C_{14}H_{13}N_3SO_6.H_2OCu$ (Mol. Wt. 432.5): C, 38.84; H, 3.01; N, 9.71, S, 7.40. Found C, 38.598; H, 3.273; N, 7.764; S, 8.772. Reason for underestimated result for nitrogen mentioned above. IR spectra of the complex shows absorption at 3442cm^{-1} υ (NH), 3049 cm^{-1} υ (C-H, aromatic), 1627cm^{-1} υ (c=o), 1586 cm^{-1} υ (C=N), 1549 cm^{-1}, 1517 cm^{-1}, 1424 cm^{-1} υ (C-C str), 1347 cm^{-1} υ (C-N str), 1213.47 cm^{-1} 1104cm^{-1} υ (C-O str), 1047cm^{-1}, 852cm^{-1}, 620cm^{-1}, 522 cm^{-1} υ (M-N), 407 cm^{-1} υ (M-O).

2.4. Synthesis of (L-Prolinato)(1,10 – Phenanthroline) (Sulfonato) Copper(II) Tetrahydrate

A solution (5.0ml) of $CuSO_4.5H_2O$ (0.249g, 0.001mol) was prepared in 1N H_2SO_4. L-Proline (0.115g, 0.001mol) and Phenanthroline (0.198g, 0.001mol) were dissolved separately in another 5.0ml of 1N H_2SO_4. The two solutions were then mixed properly. The resulting solution was then stirred continuously for 1 hour at 70^0C. The precipitate obtained was then filtered and washed with cold water (2 x 5.0ml) and then dried in the oven for 40 minutes to obtain a blue coloured complex. Yield, 0.2875g, 62.0%, Anal. Calc. $C_{17}H_{18}N_3SO_6.4H_2OCu$ (Mol. Wt.527.5): C, 38.67; H, 3.41; N, 7.96, S, 6.07. Found C, 38.61; H, 3.273; N, 7.764 S, 8.468. IR spectra of the complex shows absorption at 3434cm^{-1} υ (NH), 3020.42 cm^{-1} υ (C-H, aromatic), 1634.82 cm^{-1} υ (c=o), 1586.21 cm^{-1} υ (C=N), 1553.79 cm^{-1}, 1517.33 cm^{-1}, 1424.15 cm^{-1} υ (C-C str), 1347.17 cm^{-1} υ (C-N str), 1213.47 cm^{-1} 1106cm^{-1} υ (C-O str), 853cm^{-1}, 720cm^{-1}, 620 cm^{-1} υ (M-N), 405 cm^{-1} υ (M-O).

2.5. Hydroxylation of Phenol

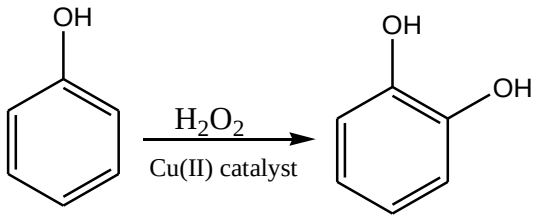
1.0 ml of Phenol (~10 mmol) was taken in a 25 ml round bottom flask. Specific amount of (refer to table-1) Chloro(glycinato) 1,10-phenanthroline copper(II) monohydrate was dissolved separately in 2.0ml of distilled water and the resulting solution was transferred to the above round bottom flask and mixed properly to obtain a homogeneous solution. 2.0 ml of 30% $H_2O_2$was then added to the reaction mixture. An instantaneous reaction takes place. The reaction mixture was then stirred at 60^0C for about 15 minutes. Product of the reaction mixture was then extracted with 3 x 10 ml of diethyl ether. Progress of the reaction was monitored by using thin layer chromatography. For all the four cases comparison of the product with authentic catechol sample indicated exclusive formation of catechol from all the reactions. Final solvent was

removed to obtain the final product. Reaction yields 63% of product Catechol. IR spectra of the compound shows absorption at 3450.91 cm^{-1} ,3326.72 cm^{-1} υ (O-H stretching) , 3052 cm^{-1} , 2961.52 cm^{-1} , 2924 cm^{-1} , 2851 cm^{-1} υ (C-H, aromatic), 2740 cm^{-1} , 2621 cm^{-1}, 2465 cm^{-1}, 2049 cm^{-1},1993 cm^{-1} , 1881.99 cm^{-1}, 1746.04 cm^{-1}, 1718.44 cm^{-1}, 1602.00 cm^{-1}, 1514.09 cm^{-1}, 1363.93 cm^{-1}, 1280 cm^{-1}, 1241.81 cm^{-1}, 849.13 cm^{-1}, 802.68 cm^{-1}, 754 cm^{-1}, 636.96 cm^{-1}, 564 cm^{-1}, 499.17 cm^{-1} ^{1}H NMR ($CDCl_3$) δ,5.52 (s, 2H) δ, 6.74 - 6.79 (m, 4H); $^{13}C\{^{1}H\}$($CDCl_3$) 116, 120, 149.

3. Results and discussion

3.1. Mixed Ligand Cu- Complex

Copper(II) complexes with N,N bonded and N,O bonded ligands have attracted significant scientific interest for their industrial significance as efficient catalytic system. Many of such complexes catalyze hydroxylation reaction of phenol. The mixed ligand Copper (II) complexes were found to be useful for selective *ortho*-hydroxylation of phenol using water as solvent. Reaction of Phenol with hydrogen peroxide in presence of catalytic amount of Chloro(Glycinato) 1,10-Phenanthroline Copper(II) monohydrate results in exclusive formation of catechol (equation 1). As stated above that was confirmed by comparison of the product with authentic catechol sample in thin layer chromatography. Similar results were also obtained with other three mixed ligand copper(II) complexes in water produces exclusively Catechol.



Equation - 1

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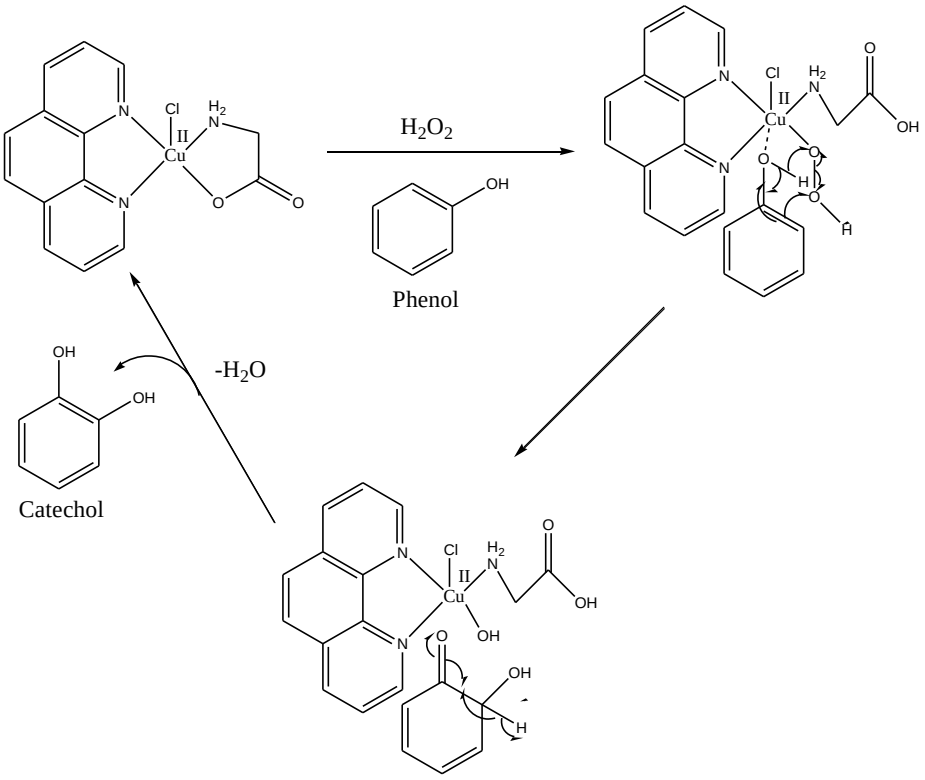
Maximum yield obtained for such reaction is 63% with Chloro(glycinato)(1,10 – phenanthroline) copper(II) monohydrate as the catalyst. Yield of this reaction for different catalysts are tabulated in table-1.

Yield of the product was found to be influenced by nature of the ligand and also it depends on the reaction time. Allowing the reaction for longer time duration results in tar formation and consequently decreases the yield of the product catechol.

Complexes of copper containing N,N (e.g., bipyridil[16,22]) or N,O ligands (Salen type and bis(2-hydroxybenzyl) ethylenediamine type[16]) have been active in hydroxylation of aromatic compounds by oxygen or hydrogen peroxide. These ligands form the (μ-v2:v2-peroxo) dicopper(II) complexes that prove to be active toward selective hydroxylation of phenol[23]. Copper ions can increase the selectivity of hydroxylation.

Catalytic decomposition of hydrogen peroxide by copper(II) complexes containing phenanthroline and imidazole ligands were found to generate $Cu(I)O_2Cu(I)$ superoxide ion as intermediate through catalytic decomposition of hydrogen peroxide[24] Copper(I)regenerates copper(II) again by the reaction with O_2 and H_2O_2. The reaction of copper(II) and H_2O_2 also generates peroxodicopper(II) [-Cu(II)-O-O-Cu(II)-].[25,23] Based on these facts and keeping in view the exclusive formation of catechol from the reactions, the following reaction mechanism

can be depicted for selective hydroxylation of phenol (scheme-1). It can be observed from scheme-1 that formation of hydroquinone from the reaction is only a rare possibility.



Scheme - 1

Formation of Catechol from the reactions was confirmed from FT-IR and NMR spectroscopic data. The two broad absorption peaks observed in the region 3326.72cm^{-1} – 3450 cm^{-1} in FT-IR spectra of the product corresponds to the two –OH groups in the compound. The ^{1}H-NMR spectra of the compounds shows one strong absorption at δ,5.52 which can be attributed to the two –OH protons. Absorption due to the aromatic ring protons were observed as complex multiplet in the region δ, 6.74 - 6.79. The ^{1}H-NMR spectra of catechol is given below in figure-1.

Copper is a very good coordinating metal which coordinates to a number of N (e.g. phenanthroline) and O (e.g. carboxyls and hydroxyl groups) atoms. The reported Chloro(Glycinato) Copper(II) monohydrate and other analogous mixed ligand Copper(II) complexes were characterized by using CHN analysis and FT-IR spectroscopy as detailed in experimental section. FT-IR Spectra of the complexes exhibits broad absorption in the region 3200-3363 cm^{-1}which can be attributed due to N-H stretching in the complexes. The absorptions around 3050-3053 cm^{-1} is due to aromatic C-H stretching, which indicates the presence of aromatic ring i.e. phenanthroline, The presence of C=O group is evident from the observed peaks around 1640 - 1690 cm^{-1}. Absorption peaks due to Cu-O bond stretching was observed in the region in the region 426-450 cm^{-1}. Similarly absorption peak due to Cu-N bond stretching was observed in the region 620-644 cm^{-1}. Elemental analysis of the complexes also shows good conformity to the structure assigned. However for heterocyclic compounds containing nitrogen in the cycle or in the groups like azide, nitrile, nitro, etc. usually underestimated results are obtained for nitrogen due to incomplete conversion of different forms of nitrogen to elemental nitrogen. Due to this fact we have obtained underestimated results for the values of nitrogen in elemental analysis. Thermogravimetric study of the complexes also supports the structures assigned for the complexes.

3.2. Electroanalytical study of the complexes

Cyclic voltamograms for the four complexes were recorded and analyzed. For Chloro(glycinato)(1,10 – Phenanthroline) Copper(II) monohydrate (1) [Figure 2(a)] and Chloro (1,10 – Phenanthroline)(L-Prolinato) Copper(II) trihydrate (2) [figure-2(b)], the nature of the voltamograms were found to be similar where one pair of current peaks is observed for both the

cases. For (1) the pair of current peak observed in the range -0.77 to 0.53V and for (2), the pair of peak observed in the range -0.65 to 0.35 V. The observed current peaks can be attributed to the Cu(II) / Cu(I) redox process. However in case of (Glycinato))(1,10 – Phenanthroline)(Sulfonato) Copper(II) Monohydrate [Figure 2(c)] (3) pair of peak was observed in the range -0.53 to 0.19 V and for (L-Prolinato)(1,10-phenanthroline)(sulfonato) copper(II) [Figure 2(d)] (4) we have not observed any significant anodic current peak. Absence of significant anodic peak for (4) can be ascribed as irreversible reduction of Cu(II) center to Cu(I) in the complex. The data obtained from the cyclic voltamograms for the four complexes(1), (2), (3) and (4) from -1.0V to +1.0V are summarized in table-2.

For complexes(1) and (2), where only amine ligand was changed, comparison of the potential values indicates that significant differences in the potential values of anodic peak potential. Whereas for (3) and (4), where chloro ligands were exchanged for sulphonato ligand in (1) and (2) respectively, marked differences in the redox behavior was observed. No significant redox behavior is shown by (3) and (4). Therefore complexes (3) and (4) exhibit lesser catalytic activity towards phenolic hydroxylation with maximum 'Turn Over Number' (TON) of 26.25 for complex (3). In contrast complexes (1) and (2) which exhibit redox behavior shows better catalytic activity towards phenolic hydroxylation with maximum TON of 78.25 for complex (1). (1) and (2) exhibit one more cathodic current peak at around -0.2V for which corresponding anodic current peaks were not observed. This might corresponds to some irreversible reduction (Cu(II)/Cu(I).

4. Conclusion

This study demonstrates that mixed ligand copper (II) complexes are efficient catalyst for ortho hydroxylation of phenol by hydrogen peroxide in water. Particularly the regioselectivity aspect of the catalytic system is an important point to emphasize. As far as yield is concerned, Chloro(glycinato)(1,10 – Phenanthroline) Copper(II) monohydrate is the best among the four catalysts. Apart from these facts, these reactions can be carried out in an ecofriendly solvent i.e. water using again ecofriendly hydrogen peroxide as the oxidant. Therefore it can be concluded that we have developed an environmentally benign catalytic system for synthesis of catechol.

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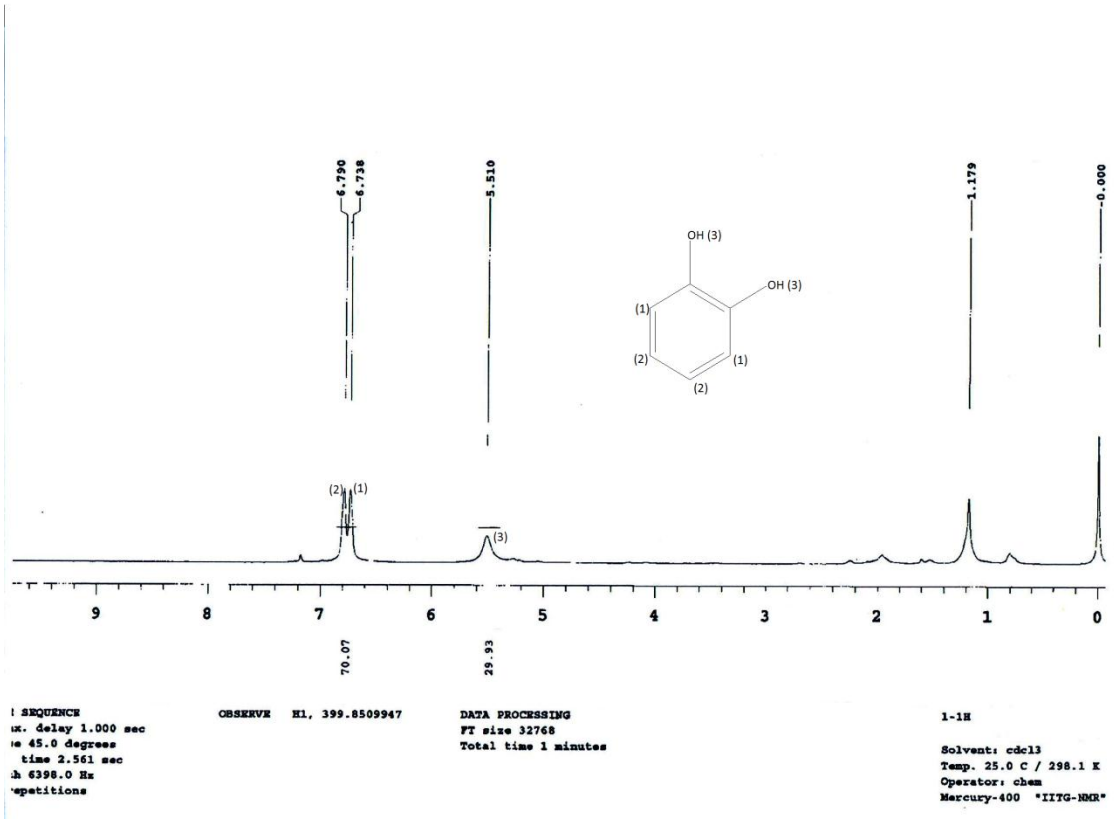

Figure-1: ^{1}H NMR spectra of product Catechol in $CDCl_3$

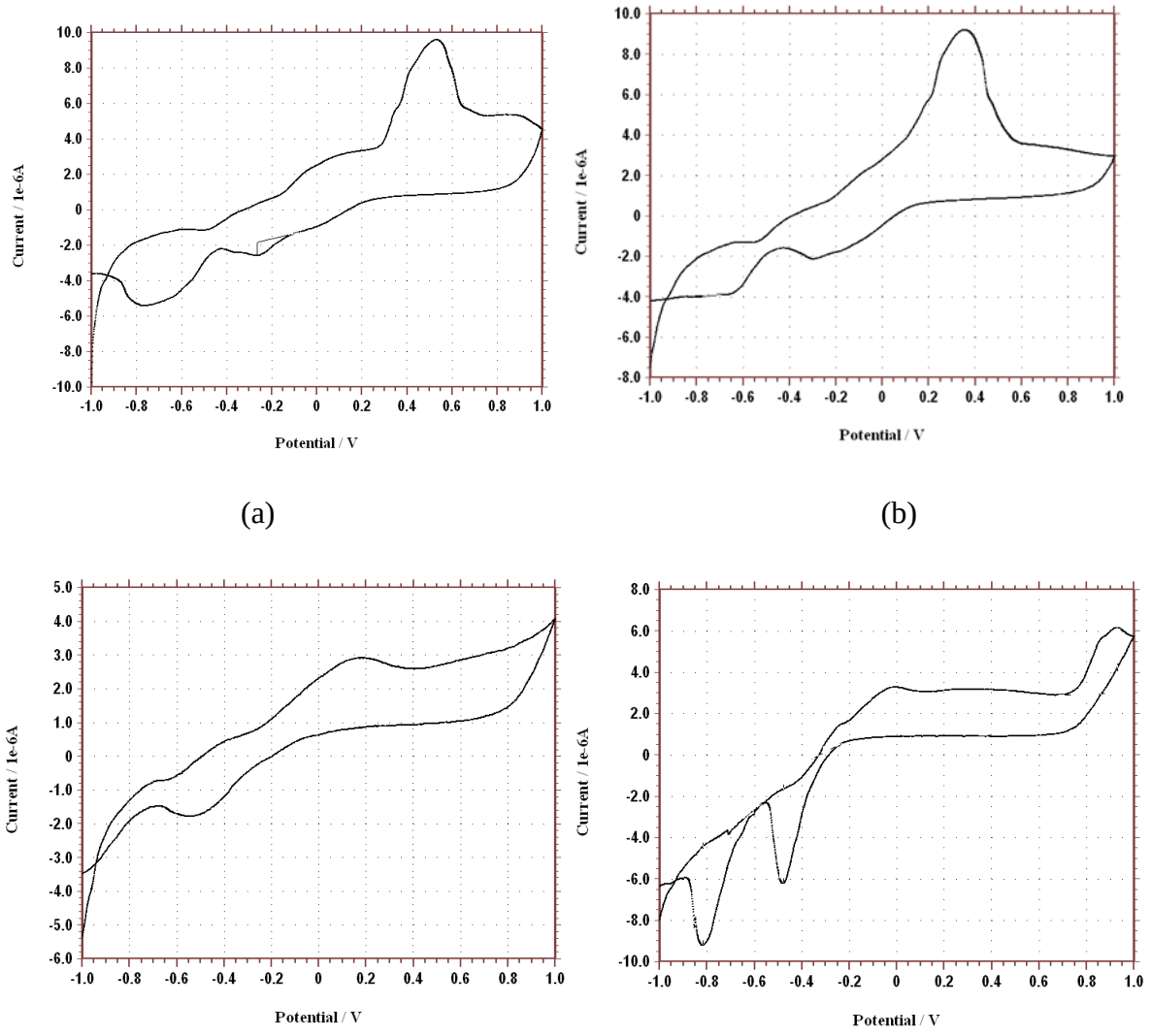

Figure-2: Cyclic voltamograms of the complexes in acetonitrile solution containing 0.1M tetraethyl ammonium tetrafluoroborate in the range of 1.0 to -1.0 with a current 1mA and a scanning voltage of 50mV/s.

Table-1: Yield of this reaction for different catalysts

S. No.	Name of the catalyst	Phenol/catalyst (mmol)	% yield of catechol
1.	Chloro(glycinato)(1,10 – Phenanthroline) Copper(II) monohydrate	10/0.08	63.0
2.	Chloro(glycinato)(1,10 – Phenanthroline) Copper(II) monohydrate	10/0.11	52.0
3.	Chloro(glycinato)(1,10 – Phenanthroline) Copper(II) monohydrate	10/0.16	49.0
4.	Chloro (1,10 – Phenanthroline)(L-Prolinato) Copper(II) trihydrate	10/0.08	44.0
5.	(glycinato)(1,10 – Phenanthroline)(Sulfonato) Copper(II) Monohydrate	10/0.08	21.0
6.	(L-Prolinato)(1,10 – Phenanthroline) (Sulfonato)Copper(II) Tetrahydrate	10/0.08	20.0
7.	Cis-bisglycinato copper(II) monohydrate	10/0.23	22.0

Table-2: Data obtained from the Cyclic Voltamograms of the four complexes

Complex	E_{pc1}(V)	E_{pa1}(V)	ΔE_p	I_{pa}/I_{pc}
(1)	-0.77	0.53	-1.3	-1.75
(2)	-0.65	0.35	-1.0	-2.4
(3)	-0.53	0.19	-0.72	-1.7
(4)	-0.82	0.92	-1.74	-0.7