Available online at http://www.journalcra.com

International Journal of Current Research
Vol. 7, Issue, 07, pp.18340-18348, July, 2015

INTERNATIONAL JOURNAL OF CURRENT RESEARCH

ISSN: 0975-833X

RESEARCH ARTICLE

SYNTHESIS AND CHARACTERIZATION OF COPPER COMPLEX WITH 2-(2-(1H-1, 2, 4-TRIAZOL-3-YL) DIAZENYL)-4-(4, 5-DIHYDROOXAZOL-2-YL) PHENOL

*Bitew Kassaw Dessie

Department of Chemistry, College of Natural and Computational Sciences,
University of Gondar, Gondar, Ethiopia

ARTICLE INFO

Article History:
Received 22nd April, 2015
Received in revised form
30th May, 2015
Accepted 15th June, 2015
Published online 31st July, 2015

Key words:

Oxazoline, 2-(4-hydroxyphenyl)-2-oxazoline,
2-(2-(1H-1, 2, 4-triazol-3-yl)
diazenyl)-4-(4,5-dihydrooxazol-2-yl) phenol.

ABSTRACT

2-(2-(1H-1, 2, 4-triazol-3-yl) diazenyl)-4-(4, 5-dihydrooxazol-2-yl) phenol (L) is a ligand synthesized by the azo coupling reaction of 1, 2, 4-triazole-3-diazonium chloride with 2-(4-hydroxyphenyl)-2-oxazoline. The synthesis and characterization of di-nuclear Cu(II) complex derived from 'L' has been described. The complex was prepared in good yield by the reactions of 'L' with hydrated copper (II) chloride. IR, NMR and UV-Vis spectroscopy techniques were used to characterize the precursors: Methyl-4-hydroxybenzoate, N-2-hydroxyethyl-4-hydroxybenzamide, 2-(4-hydroxyphenyl)-2-oxazoline and the ligand, 'L'. The complex was characterized by magnetic susceptibility, UV-Vis spectroscopy, IR, conductance measurement and chloride estimation method. Distorted octahedral geometry was proposed for this bi-nuclear complex.

Citation: Bitew Kassaw Dessie, 2015. "Synthesıs and characterızatıon of copper complex wıth 2-(2-(1H-1, 2, 4-trıazol-3-yl) dıazenyl)-4-(4, 5-dıhydrooxazol-2-yl) phenol", *International Journal of Current Research*, 7, (7), 18340-18348.

INTRODUCTION

Oxazoline is highly reactive functional group in the field of organic chemistry (Frump, 1971) and it was discovered by Andreasch about 120 years ago (Andreasch, 1884). However, its synthetic application become attention-grabbing during the past two decades, especially in the areas of transition metal catalysis and asymmetric synthesis (Hoveyda *et al*., 1992). Metal complexes of oxazoline based ligands have been widely studied owing to four main motives (Miller *et al*., 2009): i) it is naturally available as part of microbial chelating agents. ii) Easily prepared from synthetic β-amino alcohols and naturally available chiral amino acids. iii) It forms kinetically inert chiral metal complexes. iv) It is conformational rigid and shows several coordinating modes such a smonodentate, bidentate, polydentate. Several industrial patents and scientific papers have been reported on the practical application and utilization of oxazoline based ligands and its metal complexes. For instance, starting materials for polymerization chemical reaction (Kobayashi, 1990; Gant and Meyers, 1994), synthetic intermediates and pharmacophores (Culbertson, 2002; Meyers and Mihelich, 1976), protecting groups especially for carboxylic functional groups (Meyers and Temple, 1970), chain extenders and chirality-transfer auxiliaries for catalysis reaction (Loontjens *et al*., 1993; Guillon *et al*., 2004), core molecules for dendrimer preparation (Lach *et al*., 1998), active functionalities for blending processes (Baker and Saleem, 1987), favor recycling of organic macromolecules (Cardi *et al*., 1993), biological activities with anti-inflammatory, antihypertensive, anticonvulsant and analgesic properties (Ishida *et al*., 1987; Rodríguez *et al*., 1999) and directing group for Directed ortho-metallation reactions (Frump, 1971) are some of the significant applications. In addition, catalyzing the cross-coupling reaction of alkyl halides with alkyl zinc halides (Zhou and Fu, 2003) via combination of tridentate pyridine–bis (oxazoline) and Ni(cod)$_2$) (Feth *et al*., 2003) or by means of organonickel(II) complexes of oxazoline derivatives are the widely used application of metal complexes of oxazoline based ligands. Cu(II) emerged as a promising organizational center with regard to both reactivity and selectivity owing to Irving and Williams series (Irving and Williams, 1953). It forms a thermodynamically stable complex with complex ligands. It is also kinetically labile with respect to more weakly bound ligands through Jahn-Teller distortion (Hathaway *et al*., 1987).

Most of the previous reports focused only on the ring closure of N-2-hydroxy-4-hydroxybenzamide to synthesize oxazoline ligands and its metal complexes to further understand the catalytic and other biological applications. So far, no researchers attempted the azo coupling reaction of 1, 2, 4-triazole-3-diazonium chloride with 2-(4-hydroxyphenyl)-2-

Corresponding author: Bitew Kassaw Dessie,
Department of Chemistry, College of Natural and Computational Sciences, University of Gondar, Gondar, Ethiopia.

oxazoline ligand to create -N=N- coordination center. The main objective of this study was therefore to synthesize and characterize 2-(2-(1H-1, 2, 4-triazol-3-yl) diazenyl)-4-(4, 5-dihydrooxazol-2-yl) phenol ligand and its copper complex.

Experimental

Chemicals and Reagents

All chemicals were used as received without further purification and most of them were of analytical grade. The reagents used were hydrated copper(II) chloride, amitrole, sodium nitrite, thionyl chloride, p-hydroxy benzoic acid.

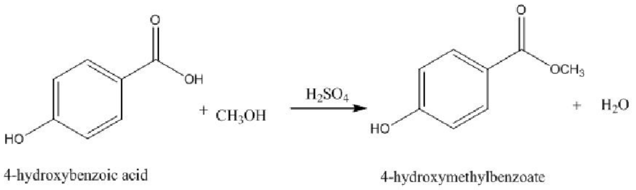
Instrumentation

^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ by using Bruker Ultra-shield NMR (400 and 100.6 MHz for ^{1}H and ^{13}C respectively). IR spectra were recorded using Perkin-Elmer FT-IR spectrophotometer in the range of 4000-400 cm^{-1}. Electronic spectra of the ligands and the metal complexe were recorded in the region in the range of 200-800 nm by SPECTRONIC GENESY^{TM} 2PC UV-Visible spectrophotometer. The magnetic susceptibility of the complex was measured using MSB-AUTO, Sherwood magnetic balance. The metal estimation was done using BUCKER Scientific 210 VGB atomic absorption spectrophotometer. Elemental analyses of CHN were carried out by using Exter Analytical CE 440 elemental analyzer. The conductivity of the complex was obtained on Bench conductivity meter (EC 214). The melting point was recorded using IA 9200 digital melting point apparatus.

Syntheses of precursors and Ligand

Synthesis of Methyl-4-hydroxybenzoate

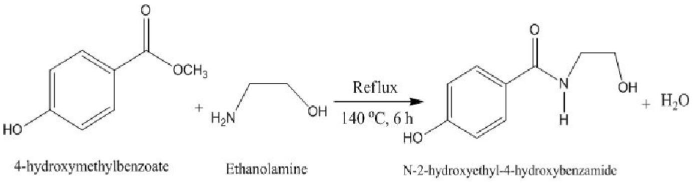
To a 100 mL round bottom flask containing 4-hydroxybenzoic acid (0.5 g, 0.0036 mol), methanol (20 mL) and concentrated sulfuric acid (3 mL) were added (Srividhya *et al*., 2009; Dinku *et al*., 2003). The reaction mixture was refluxed for 12 h, cooled to room temperature and was poured into ice cooled water. The resulting white solid was washed several times with water to remove the traces of acid and was crystallized from aqueous ethanol to afforded white crystalline solid (0.43 g, 78.12%), mpt, 133-135 ^{0}C.



Scheme 1. Esterification reaction of 4-hydroxybenzoic acid

Synthesis of N-2-hydroxyethyl-4-hydroxybenzamide

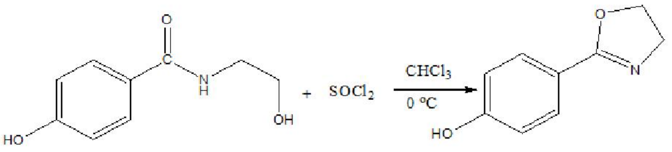
A mixture of methyl-4-hydroxybenzoate (5 g, 0.031 mol) and ethanolamine (7.5 mL, 0.064 mol) was refluxed at 140 °C for 6 h (Lustoň *et al*., 2006). Excess of ethanolamine and ethanol released in the reaction were removed using rotary evaporator where yellowish oil was obtained (4.76 g, 80%), which was directly used (Scheme 2) for a ring closure reaction to obtain the intended 2-(4-hydroxyphenyl)-2-oxazoline.



Scheme 2. Preparation of N-2-hydroxy-4-hydroxybenzamide

Synthesis of 2-(4-hydroxyphenyl)-2-oxazoline

4-hydroxybenzamide (5 g, 0.0276 mol) was dissolved in methylene chloride and cooled to 0 °C and a cold freshly distilled thionyl chloride (15 g, 0.126 mol) was added dropwise. The reaction mixture was kept at 0 °C for 30 min. and stirred at room temperature for additional 21 h. The product obtained was filtered, washed four times with CH_2Cl_2 and then aqueous solution of solution of $NaHCO_3$ (0.4 M, 50 mL) was added portionwise where effervescence was observed. The mixture was stirred for additional 30 minutes and filtered. The solid product was dried in an oven at 60 ^{0}C (2.84 g, 63%), mpt, (197 - 200 ^{0}C) (Lustoň *et al*., 2006).

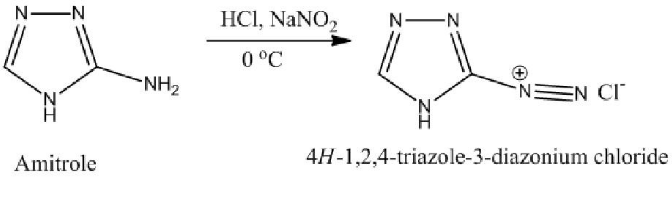


Scheme 3. Synthesis of 2-(4-hydroxyphenyl)-2-oxazoline

Synthesis of 2-(2-(1H-1, 2, 4-triazol-3-yl) diazenyl)-4-(4,5-dihydro-oxazol-2-yl) phenol (Srividhya *et al*., 2009)

Diazotization of 3-Amino-1, 2, 4-triazol

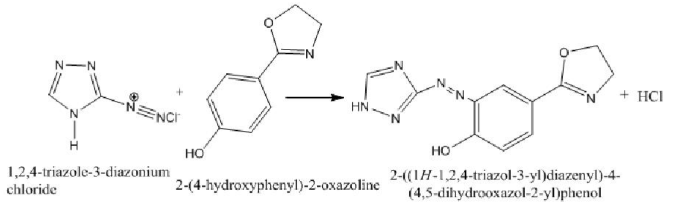
3-Amino-1,2,4-triazol (amitrole) (0.21 g, 0.0025 mol) and concentrated hydrochloric acid (0.3015 g, 0.0025 mol) were mixed in 100 mL round bottomed flask. The reaction mixture was cooled to 0 ^{o}C on ice bath. Sodium nitrite (0.1725 g, 0.0025 mol) was dissolved in distilled water (10 mL) and was added to the acidic solution of 3-amino-1, 2, 4-triazol dropwise.



Scheme 4. Diazotization reaction of 3-amino-1, 2, 4-triazol

Azo coupling reaction of 1,2,4-triazole-3-diazonium chloride with 2-(4 hydroxyphenyl)-2-oxazoline

2-(4-hydroxyphenyl)-2-oxazoline (0.408 g, 0.0025 mol) was dissolved in ethanol (10 mL) and NaOH solution (10 ml, 2.5 M, 13.6 pH) and the mixture was cooled to 0 ^{o}C. Ethanolic solution of 2-(4-hydroxyphenyl)-2-oxazoline was added dropwise to the diazonium salt solution with vigorous stirring at 0^{o}C. The red solution was dried under reduced pressure and the residue was dissolved in acetone. The precipitated red solid was dried in oven at 50 °C (0.51 g, 80.6%), decomposes above 296 °C.



Scheme 5. Azo coupling reaction of 1, 2, 4-triazole-3-diazonium chloride with 2-(4-hydroxyphenyl)-2-oxazoline

Synthesis of metal ion complex

Syntheses of Complex of Cu(II) with 'L'

To solution of 'L' (0.2 g, 0.77 mmol) in methanol (15 mL), a solution of $CuCl_2 \cdot 2H_2O$ (0.26 g, 0.0016 mmol) in methanol (5 mL) was added in a round bottomed flask. The resulting violet solution was refluxed for 5 h at 80 °C. The violet solution formed was filtered and washed with methanol and dried under vacuum to give a brownish solid (0.24 g, 82.8%). The complex was found to decompose at > 350 °C.

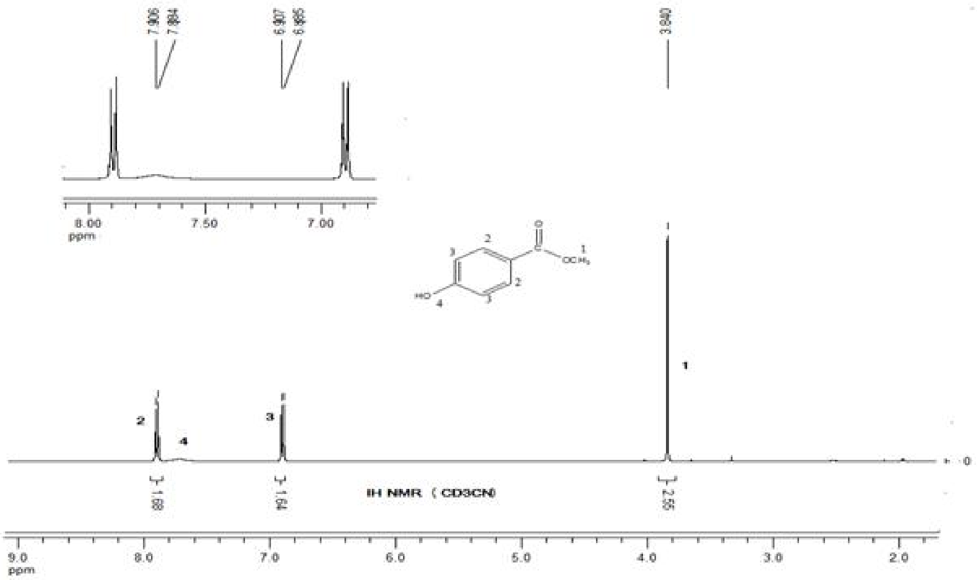


Fig.1. 1_H NMR (CD_3CN, 400 MHz, ppm) of methyl-4-hydroxybenzoate

RESULTS AND DISCUSSION

Characterization of Precursors and Ligand

Methyl-4-hydroxybenzoate

^1H NMR (CD_3CN, 400 MHz, ppm): δ 7.90(d, 2H, Ar), 6.86(d, 2H, Ar), 7.7(s, 1H, OH), 3.82(s, 3H, CH_3) (Figure 1). ^{13}C-NMR (CD_3CN, 100.6 MHz): δ = 166.51(1C, C=O), 161.23(1C, C-OH), 131.92, 121.85, 115.14 and 51.35(4C, Ar), (1C, C-OCH_3) (Figure 2). The DEPT spectrum (Figure 2) also shows three signals at δ 131.54, 115.14 and 51.35 ppm for the three C-H groups in the benzene ring. The disappeared signals at 121.85, 161.23 and 166.51 ppm confirm the presence of three quaternary carbons and all the above NMR data) are in agreement with literature report (Srividhya *et al*., 2009; Dinku *et al*., 2003).

2-(4-hydroxyphenyl)-2-oxazoline

^1H-NMR (Acetone-d_6, 400 MHz, ppm): δ 9.10(s, 1H, C_6H_4-OH); 7.85(d, 1H, Ar), 6.8(d, 1H, Ar); 4.4(t, 2H, (N-CH_2), 3.8(t, 2H, O-CH_2) (Figure 3). ^{13}C-NMR (Aceton-d_6, 100.6 MHz, ppm): δ 54.57(1C, N-CH_2), 67.10(1C, O-CH_2), 115.00, 119.59 and 129.79(3C, Ar), 160.07(1C, C-OH) and 163.43(1C, N=C-O) (Figure 4). The DEPT spectrum (Figure 4) also shows two signals at δ 115.00 and 129.79 ppm for the two C-H groups in the benzene ring. The disappeared signals at 119.59, 160.07 and 163.43 ppm confirm the presence of three quaternary carbons in the compound.

Elemental analysis data found (calculated) values are: C, 63.97 (66.265), H, 5.54 (5.552) and N, 8.18 (8.582) are in a good agreement. IR (KBr) spectrum (Figure 5): 3555-3342 cm^{-1} (ν_{OH}); 3044 cm^{-1} (ν_{CH}, Ar); 2995-2912 cm^{-1} ($\nu_{CH,}$ aliphatic); 1634 cm^{-1} ($\nu_{C=N,}$ oxazoline); 1590 cm^{-1} and 1511 cm^{-1} ($\nu_{C=C}$); 1369 cm^{-1}, 1289 cm^{-1} and 1248 cm^{-1} (ν_{CH}, aliphatic).

All spectral data of the ligand (1H NMR (Figure 3), 13C NMR (Figure 4), IR (Figure 5) and elemental analysis data support the preparation of the precursor, (2-(4-hydroxyphenyl)-2-oxazoline), and are in agreement with literature report (Lustoň *et al*., 2006).

2-(2-(1H-1, 2,4-triazol-3-yl) diazenyl)-4-(4,5-dihydrooxazol-2-yl) phenol

^1H NMR (D_2O, 400 MHz, ppm): δ 3.75(t, 2H, O-CH_2); 4.4(t, 2H, N-CH_2), 4.75(s, 1H, OH exchanged D_2O); 6.55(d, 1H, Ar), 7.5(d, 1H, Ar), 8.05(s, 1H, -CH of 1,2,4-triazol), 8.25(s, 1H, NH of 1, 2, 4-triazol) (Figure 6). ^{13}C NMR (D_2O, 100.6 MHz,

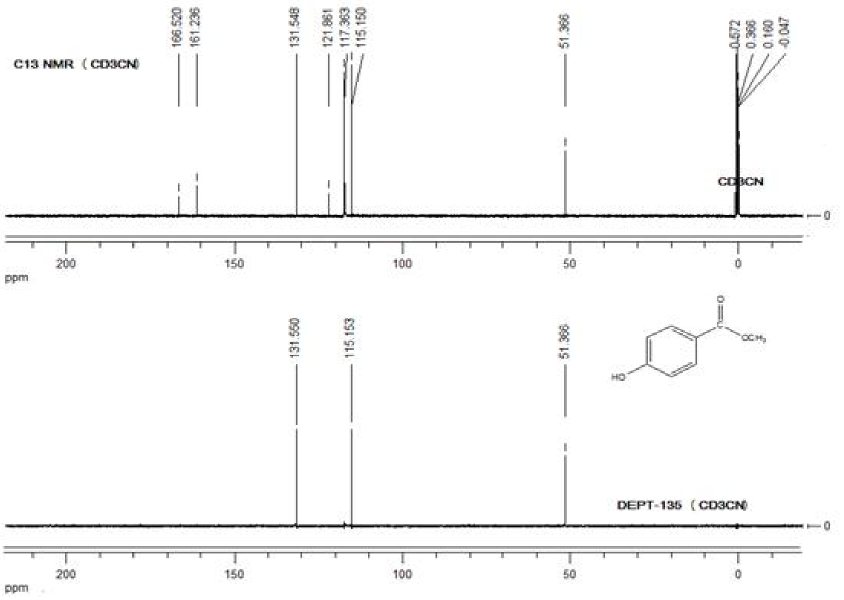


Fig. 2. DEPT-135 and C-13 NMR (CD_3CN, 100.6 MHz, ppm) of methyl-4-hydroxybenzoate

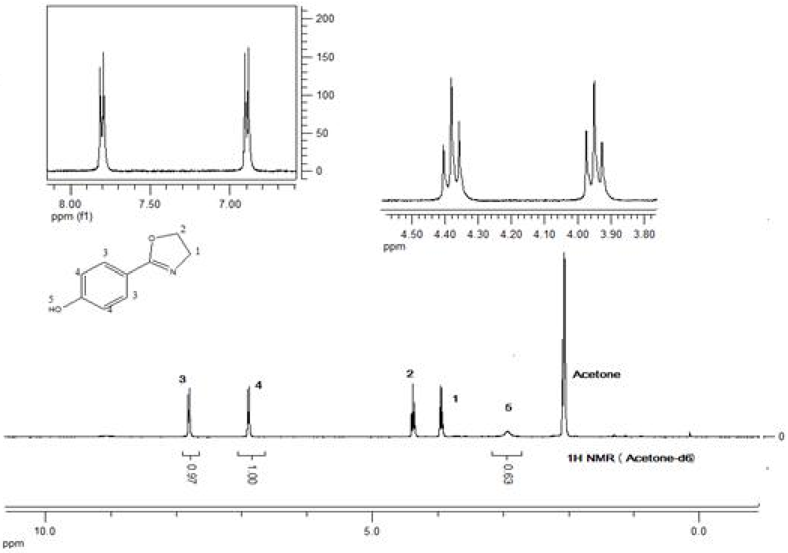


Fig. 3. 1_H NMR (Acetone-d6, 400 MHz, ppm) of 2-(4-hydroxyphenyl)-2-oxazoline

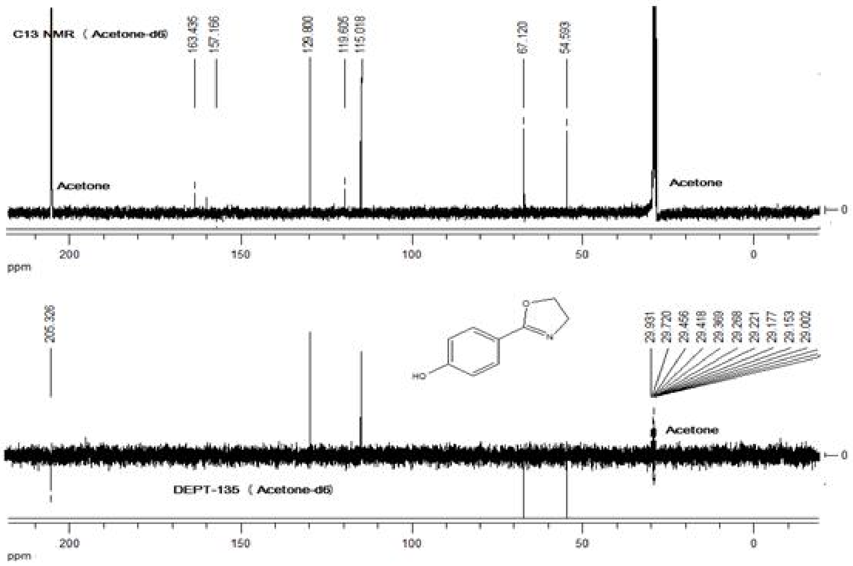


Fig.4. DEPT-135 and C-13 NMR (Acetone-d6, 100.6 MHz, ppm) of 2-(4-hydroxyphenyl)-2-oxazoline

ppm): δ 52.55, 67.78, 111.48, 116.71, 118.88, 123.51, 130.26, 150.23, 167.07, 167.43 and 171.25 ppm (Figure 7). The DEPT spectrum (Figure 7) also shows four signals at δ 118.88, 123.51, 130.25 and 150.22 ppm for the three C-H groups C-atoms in the benzene ring and one C-H of C-atom in the amitrole moiety. The absence of signals at 111.48, 116.71 and 167.07, 167.43 and 171.25 ppm in the DEPT confirm the presence of five quaternary carbons.

The elemental analysis data found (calculated) values: C, 46.4 (50.1), H, 2.8 (3.9), and N, 28.04 (32.5) are in a good agreement. However, a small variation showing the synthesis of the desired compound has impurities due to recrystallization problem and due to instrumental defect as the number of nitrogen atom increases. The IR (KBr) spectrum of 'L' (Figure 8) shows a very broad and strong band in the region 3600-3200 cm^{-1} assignable to $\nu_{(NH)}$ of amitrole moiety and $\nu_{(OH)}$ of the phenolic group.

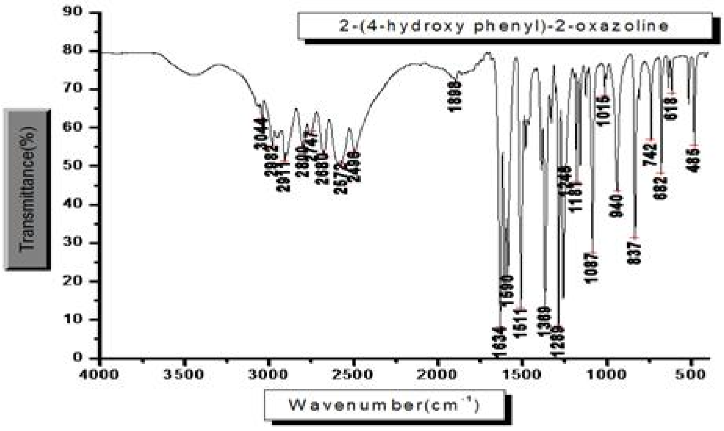


Fig.5. IR spectrum of 2-(4-hydroxyphenyl)-2-oxazoline

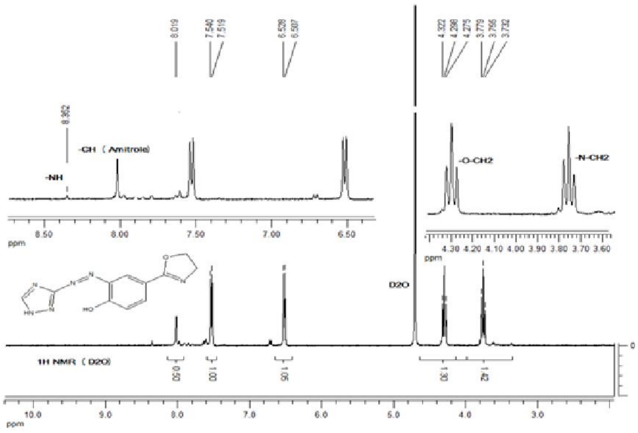


Fig.6. 1_H NMR (D_2O, 400 MHz, ppm) of 'L'

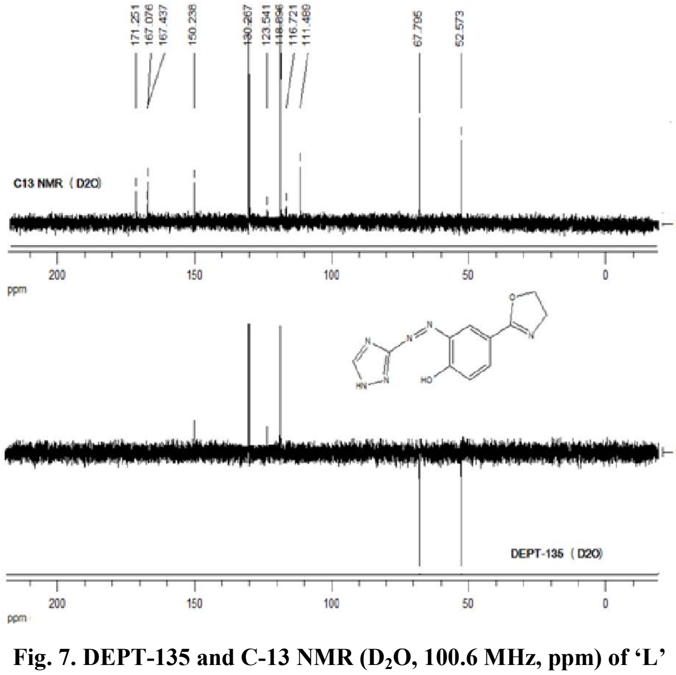


Fig. 7. DEPT-135 and C-13 NMR (D_2O, 100.6 MHz, ppm) of 'L'

The observed broad band may be attributed to involvement of the functional groups in the molecules in intermolecular as well as intramolecular hydrogen bonding interactions (Scheme 6). Multiple bands at 1636 cm^{-1}, 1594 cm^{-1} and 1545 cm^{-1} are due to ring $\nu_{(N=C)}$ and $\nu_{(NH,\ OH)}$ vibrations. The bands at 1368 cm^{-1} and 1289 cm^{-1} are may be due to $\nu_{(CH)}$ (aliphatic). Other characteristics are the medium band at 1165 cm^{-1}, 1087 cm^{-1} and weak intensity band at 945 cm^{-1} are assignable to $\nu_{(C\text{-}O)}$ (phenolic) and $\nu_{(N=N)}$ in amitrole ring. A strong intensity band at 866 cm^{-1} indicates the $\nu_{(C=N)}$.

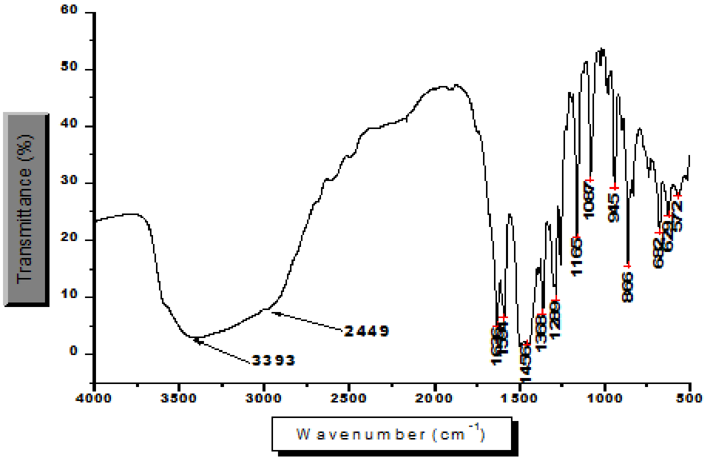
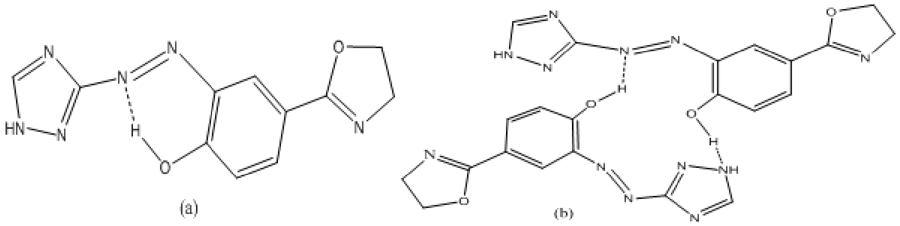


Fig. 8. IR Spectrum of 'L



Scheme 6. Possible intramolecular (a) and intermolecular (b) hydrogen bonding in 'L'

Spectral data: ^{1}H NMR (Figure 6), ^{13}C NMR (Figure 7) and IR (Figure 8) for 'L' confirm the synthesis of the ligand is achieved and the data are also in an excellent agreement with literature report (Srividhya *et al.*, 2009).

Physical properties of ligand and its copper complex

Some of the physical properties of the ligand and its complex are presented in Table 1.

Table 1.Physical properties of the ligand and its copper complex

Compound	Yield (%)	Color	mpt (ºC)	Physical Appearance
L = $(C_{11}H_{10}N_6O_2)$	80.6	red	> 296	Powder
$[(Cu)_2(L)_2(Cl_2)(H_2O)_4]$	82.8	Brownish	> 350	....

Characterization of metal complex of the synthesized ligand

IR spectra of Cu(II) complex with 'L'

The most important peaks of the IR spectra have been assigned for the ligand and the binding sites of the ligand to the metal ions in complex was determined by comparison of the spectra of the ligand to their metal complex. The strong broad band of the ligand (Figure 8) in the region 3600-3000 cm^{-1} is modified into a relatively narrow band and appeared in the region 3400-3200 cm^{-1} in IR spectrum of the complex (Figure 9). This may be owing to the presence of coordinated water molecule in the complex. The absence of the phenolic OH group in the complex can be justified by the absence of band structure in the region 3000-3200 cm^{-1} and 3450-3600 cm^{-}1. This can be due to the deprotonation of phenolic O-H group and its subsequent involvement in coordination to Cu(II) centre. This is also confirmed from the a positive shifting of $\nu_{(C\text{-}O)}$ bands from 1165 to 1168 cm^{-1}, 1289 to 1303cm^{-1} , 1368 to 1384 cm^{-1} and 1087 to 1090 cm^{-1} (Dinku *et al.*, 2003).

The downward shift of $\nu_{(C=N)}$ of the 2-oxazoline ring in 'L' from 1638 cm^{-1} in the ligand (Figure 8) to 1607 cm^{-1} in the complex (Figure 9) can be attributed to the involvement of cyclic nitrogen of the 2-oxazoline in coordination. A positive shift of the azo group $\nu_{(N=N)}$ stretching frequency of the complex from 1503 cm^{-1} in the free ligand to 1516 cm^{-1} in the complex indicates coordination of the ligand to the Cu(II) via the N=N group. Appearance of new or non-ligand bands in the spectra of the complex are assignable to rocking ($\rho_r(H_2O)$ at 745, 839 and 945 cm^{-1}) and wagging ($\rho_w(H_2O)$ at 664 cm^{-1}) modes of coordinated water. A new band at 483 cm^{-1} may be due to M-N vibrations which confirm the coordination of the ligand through N-atom of the ligand (Aly, 2011). The assignments of the IR spectral data of the ligand and its Cu(II) complex is summarized in Table 2.

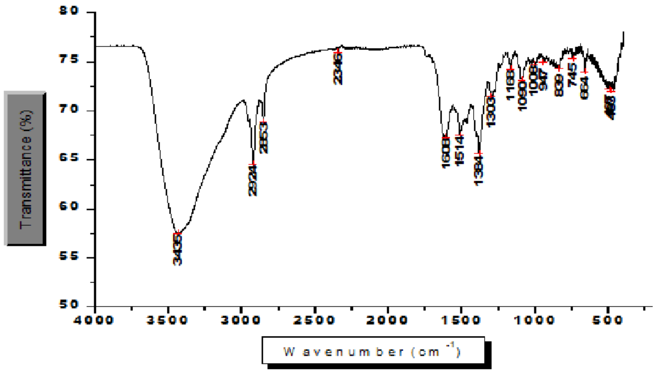


Fig. 9. IR spectrum of Cu-L Complex

Table 2. Assignments of the IR frequencies (cm^{-1}) of 'L' and its Cu(II) complex

Compound	$\nu_{(O-H, N-H)}$	$\nu_{(C=N)}$	$\nu_{(N=N)}$)	$\nu_{(C-O)}$)	New bands
Ligand (L)	3600-3200	1636	1503	1165,1289, 1368,1087	……
Complex	3400-3200	1607	1516	1168,1303 ,1384, 1090	745, 839, 945,664, 483

Electronic spectra (UV-Vis) of ligand and its metal complex

The ligand (L) is a red colored compound and shows well resolve absorption bands in the visible region. Its electronic spectrum was recorded in DMF and four main absorption bands were observed: 294, 311, 357 and 516 nm (Figure 10). The first band (294 nm) may be attributed to phenyl moiety of the ligand π→π* and intra-ligand π→π* transitions. The second band (311 nm), is attributed n→π∗ electronic transition of the -N=N- group. The band at 357 nm and 516 nm, can be assigned to π→π* transition involving the whole electronic system of the azo-dyes (Kirkan and Gup, 2008).

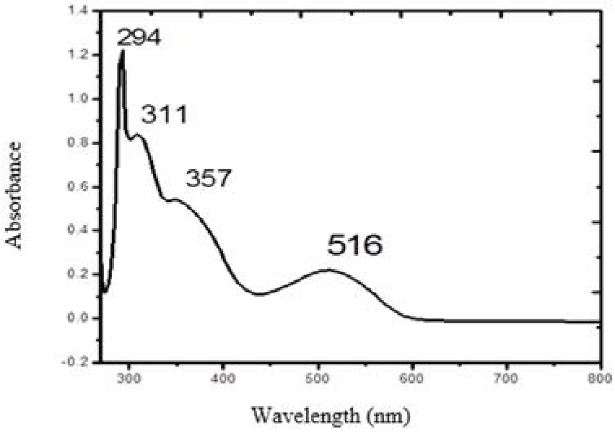


Fig. 10. UV-Vis spectrum of 'L'

The complex (Figure 11) showed a single broad band 555 nm in the visible region which can be identified as d-d band of the central ion, that is, an electronic transition localized on Cu(II) ion. The spectra of tetragonality distorted complexes should consist of three bands corresponding to the transitions $^2B_{1g}\rightarrow^2A_{1g}$, $^2B_{1g}\rightarrow^2B_{2g}$ and $^2B_{1g}\rightarrow^2E_g$. But generally, such complexes exhibit (Gup, 2006), a broad structure less band with or without shoulder between14000-1800cm^{-1} depending upon strength of axial and in-plane ligands. Since only single d-d broad band at 555 cm^{-1} has been observed in the complex reported here in, it is conclude that all the three transitions be within this broad envelope and the complex shows distorted octahedral geometry.

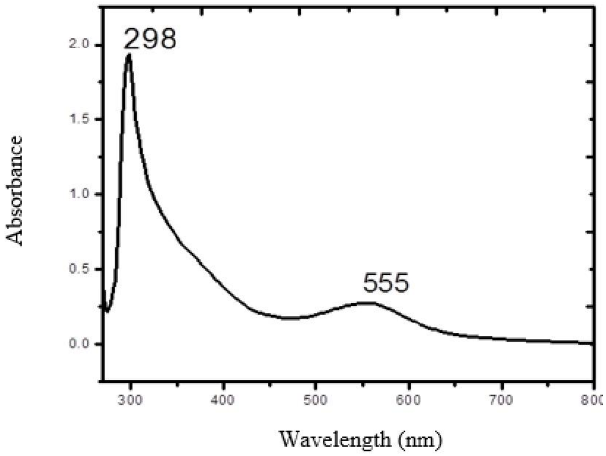


Fig. 11. UV-Vis spectrum of Cu-L Complex

Magnetic susceptibility measurement of Cu(II) complex of 'L'

The magnetic moment values of the Cu(II) complex is 2.5BM at 292 K. It is seen that these magnetic moment values of copper complex is slightly higher than the theoretical value of 1.73 BM for one d^9 copper ion, while they are also lower than that expected for di-nuclear copper(II) complexes. These subnormal magnetic moment values of the di-nuclear complexes may be explained by a weak antiferromagnetic intramolecular interaction since this situation can occur when 2 equivalent metal ions are coupled via an exchange interaction in a polynuclear complex and it is in expected range for distorted octahedral geometry (Iqbal *et al*., 2005).

Determination of composition of the metal in the complex

Metal ion determination in the complex gave 0.31 ppm (15.7%). These information reveal that Cu(II) complex of the ligand is 1:1 metal to ligand ratio. The experimental and calculated data obtained from the AAS analysis are presented in Table 3.

Table 3. Determination of metal ions in the complex using AAS

Metal complex	Concentration of metal ion (ppm)	Percentage of metal in the complex (%)		M: L ratio
		Calculated	Found	
$[(Cu)_2(L)_2(Cl_2)(H_2O)_4]$	0.31	16.16	15.7	1:1

Chloride Test

The formation of the white precipitate is a clear indication for the presence of chloride ions in the complex. The percentage of chloride found was 8.7%. These values demonstrate the presence of two chloride ions per molecule of the complex. The analytical result for the determination of the chloride ions in the complex is summarized in Table 4.

Table 4. Percentage of Chloride in the complex

Complex	Mass of Cl (g)	% of chloride	
		Found	Calculated
$[(Cu)_2(L)_2(Cl_2)(H_2O)_4]$	8.7×10^{-4}	8.7	9.03

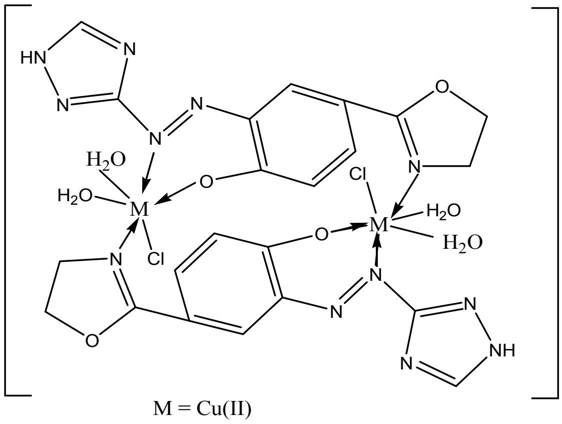


Fig.12. Proposed structures of Cu(II)-L complex

Conclusion

The ^1H and ^{13}C NMR, IR, UV-Vis and elemental analysis data established the correct synthesis of 2-(4-hydroxyphenyl)-2-oxazoline. IR and NMR and elemental analysis data clearly indicate the preparation of 'L'. These analytical methods as well as magnetic susceptibility and conductivity measurements synergetic with determination of amount of metal ion in AAS and chloride determination in the complex evidence the syntheses of metal complex. The IR and UV-Vis data confirm that 'L' binds to the metal centers via C=N of 2-oxazoline, -N=N- of the azo group and O-H of the oxazoline group has been demonstrated. The non-electrolytic nature of the complex and presence of chloride ions reveal the coordination of the chloride ion in the inner sphere. The magnetic susceptibility measurement data are also supportive evidence for the geometry of this complex. Based on collective analytical data, the proposed structure of the complex is represented by Figure 12.

REFERENCES

Aly, S. A. 2011. Copper (II), Nickel (II), Cobalt (II), Lithium (I) Complexes of thiosemicarbazide derivatives and Antibacterial activity, *J. Chem. Pharm. Res.*, *3*(6), 1028-1036.

Andreasch, R. 1884. To the knowledge of Allylharnstoffs. Monatshefte fur Chemie/Chemical Monthly, 5 (1), 33-46.

Baker, W. E., and Saleem, M. 1987. Coupling of reactive polystyrene and polyethylene in melts. *Polymer*, *28*(12), 2057-2062.

Cardi, N., Po, R., Giannotta, G., Occhiello, E., Garbassi, F., and Messina, G. 1993. Chain extension of recycled poly (ethylene terephthalate) with 2, 2′-Bis (2-oxazoline). *Journal of Applied Polymer Science*, *50*(9), 1501-1509.

Culbertson, B. M. 2002. Cyclic imino ethers in step-growth polymerizations. *Progress in Polymer Science*, *27*(3), 579-626.

Dinku, W., Megersa, N., Raju, V. J. T., Solomon, T., Jönsson, J. Å., and Retta, N. 2003. Studies on transition metal complexes of herbicidal compounds. II: Transition metal complexes of derivatized 2-chloro-4-ethylamino-6-isopropylamino-s-triazine (atrazine). *Bulletin of the Chemical Society of Ethiopia*, *17*(1).

Feth, M. P., Klein, A., and Bertagnolli, H. 2003. Investigation of the Ligand Exchange Behavior of Square-Planar Nickel (II) Complexes by X-ray Absorption Spectroscopy and X-ray Diffraction. *European Journal of Inorganic Chemistry*, *2003*(5), 839-852.

Frump, J. A. 1971. Oxazolines. Their preparation, reactions, and applications. *Chemical Reviews*, *71*(5), 483-505.

Gant, T. G., and Meyers, A. I. 1994. The chemistry of 2-oxazolines (1985–present). Tetrahedron, 50(8), 2297-2360.

Guillon, H., Daniele, S., Hubert-Pfalzgraf, L. G., and Letoffe, J. M. 2004. Synthesis, characterisation and thermal decomposition study of cerium (IV) 2-(2′-hydroxyphenyl)-2-oxazoline derivatives. *Polyhedron*, *23*(8), 1467-1472.

Gup, R. 2006. A new unsymmetrical vic-dioxime bearing salicylaldehyde 4-aminobenzoylhydrazone and its homo- and heterotrinuclear complexes with copper (II) and nickel (II) ions. *Russian Journal of Coordination Chemistry*, *32*(2), 99-108.

Hathaway, B. J., Wilkinson, G., Gillard, R. D., and McCleverty, J. A. 1987. Comprehensive coordination chemistry. *The synthesis, reactions, properties and applications of coordination compounds*, *5*, 533-774.

Hoveyda, H. R., Karunaratne, V., Rettig, S. J., and Orvig, C. 1992. Coordination chemistry of 2-(2'-hydroxyphenyl)-2-oxazolines with aluminum, gallium, and indium: first tris (ligand) metal (III) complexes of this naturally occurring binding group. *Inorganic Chemistry*, *31*(26), 5408-5416.

Iqbal, M. S., Bukhari, I. H., and Arif, M. 2005. Preparation, characterization and biological evaluation of copper (II) and zinc (II) complexes with Schiff bases derived from amoxicillin and cephalexin. *Applied Organometallic Chemistry*, *19*(7), 864-869.

Irving, H. M. N. H. and Williams, R. 1953. The stability of transition-metal complexes. *Journal of the Chemical Society (Resumed)*, 3192-3210.

Ishida, T., Inoue, M., Hamada, Y., Kato, S., and Shioiri, T. 1987. X-ray crystal structure of ascidiacyclamide, a cytotoxic cyclic peptide from ascidian. *Journal of the Chemical Society, Chemical Communications*, (5), 370-371.

Kirkan, B., and Gup, R. 2008. Synthesis of new azo dyes and Copper (II) complexes derived from barbituric acid and 4-aminobenzoylhydrazone. *Turkish Journal of Chemistry*, *32*(1), 9.

Kobayashi, S. 1990. Ethylenimine polymers. *Progress in Polymer Science*, *15*(5), 751-823.

Lach, C., Hanselmann, R., Frey, H., and Mülhaupt, R. 1998. Hyperbranchedcarbosilaneoxazoline-macromonomers: polymerization and coupling to a trimesic acid core. *Macromolecular Rapid Communications*, *19*(9), 461-465.

Loontjens, T., Belt, W., Stanssens, D., and Weerts, P. 1993. Synthesis of 1, 2-bis (2-oxazolinyl-2) ethane and its application as chain extender for poly (ethylene terephthalate). *Polymer Bulletin*, *30*(1), 13-18.

Lustoň, J., Kronek, J., and Böhme, F. 2006. Synthesis and polymerization reactions of cyclic imino ethers. I. Ring-opening homopolyaddition of AB-type hydroxyphenyl-substituted 2-oxazolines. *Journal of Polymer Science Part A: Polymer Chemistry*, *44*(1), 343-355.

Meyers, A. I., and Mihelich, E. D. 1976. The Synthetic Utility of 2-Oxazolines. *Angewandte Chemie International Edition in English*, *15*(5), 270-281.

Meyers, A. I., and Temple Jr, D. L. 1970. Syntheses via 2-oxazolines. II. Versatile synthesis of aliphatic carboxylic acids and esters. Mono-and dialkylation of acids masked by a simple protecting group. *Journal of the American Chemical Society*, *92*(22), 6644-6646.

Miller, J. J., Rajaram, S., Pfaffenroth, C., and Sigman, M. S. 2009. Synthesis of amine functionalized oxazolines with applications in asymmetric catalysis. *Tetrahedron*, *65*(16), 3110-3119.

Rodríguez, A. D., Ramírez, C., Rodríguez, I. I., and González, E. 1999. Novel Antimycobacterial Benzoxazole Alkaloids, from the West Indian Sea Whip Pseudopterogorgia e lisabethae. *Organic Letters*, *1*(3), 527-530.

Srividhya, D., Manjunathan, S., Nithyanandan, S., Balamurugan, S., and Senthil, S. 2009. Synthesis and characterization of triazole containing liquid crystalline polymers through 1, 3-dipolar cycloaddition polymerization. *Chinese Journal of Polymer Science*, *27*(06), 761-770.

Zhou, J., and Fu, G. C. 2003. Cross-couplings of unactivated secondary alkyl halides: room-temperature nickel-catalyzed Negishi reactions of alkyl bromides and iodides. *Journal of the American Chemical Society*, *125*(48), 14726-14727.

****