

Synthesis and structural elucidation of Ni(II), Cu(II), Zn(II) and Cd(II) metal complexes of oxazoline based ligands

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To cite this article:

Bitew Kassaw Dessie, Muluye Melak Zenebe, Atnafu Guadie Assefa. Synthesis and Structural Elucidation of Ni(II), Cu(II), Zn(II) and Cd(II) Metal Complexes of Oxazoline Based Ligands. *American Journal of Applied Chemistry*. Vol. 3, No. 2, 2015, pp. 40-47.

doi: 10.11648/j.ajac.20150302.12

Abstract: Synthesis of 2-(2'-hydroxyphenyl)-2-oxazoline(2-Phox) and 2-(4-hydroxyphenyl)-2-oxazoline(4-Phox) and their complexes with Ni(II), Cu(II), Zn(II) and Cd(II) have been done. They have been characterized by elemental analysis, magnetic susceptibility, NMR (HH-COSY, HSQC, HMBC), UV-vis, IR spectroscopy and conductance measurement. The complexes were formed in 1:2 (M:L) ratio. Their molar conductance of one millimolar solution measured in DMF indicated them to be non electrolyte. On the basis of these studies a tetrahedral geometry has been assigned for all the complexes.

Keywords: Oxazoline, Metal Complexes, Spectroscopy

1. Introduction

Transition-metal-catalyzed cross-coupling reactions of organic halides with organometallic reagents, for example, the Kumada, Negishi, Suzuki, and Stille reactions are reliable and versatile tools in organic synthesis [1]. Fu and co-workers reported that a combination of Ni(cod)₂ and a neutral tridentate pyridine-bis(oxazoline) ligand catalyzed the cross-coupling of a range of alkyl bromides and iodides with alkyl zinc halides [2]. One of the first benchmarks was the phosphane-nickel complexes used in the Shell Higher olefin Process [3].

The naturally occurring 2-oxazoline ring is present in siderophores. The affinity of siderophores for Fe(III) is due to the presence of 2-(2'-hydroxyphenyl)-2-oxazoline and 2-(2'-hydroxyphenyl)-2-thiazole derivatives which form stable Fe(III) complexes. Various methods have been developed for the synthesis of 2-oxazoline from carboxylic acids, carboxylic esters, aldehydes, aminoalcohols, isocyanides, amido alcohols, imino ether hydrochlorides, nitriles and iminoesters by heating or dehydrating [4, 5].

2-Oxazoline is used as starting materials for polymerization [6,7] synthetic intermediates [8] protecting groups for carboxylic functions [9], chain extenders [10], core molecules for dendrimer preparation [11] active functionalities for blending processes [12] and recycling of organic macromolecules [13]. Oxazolines are also used in

asymmetric synthesis, enantio-selective transition metal catalysis [14] oxidation and cycloaddition reactions with organic acids, anilines, phenols or thiols [15]. Most of them have a stereogenic center at the carbon atom adjacent to the coordinating nitrogen.

The chelating bis-(oxazoline) ligand affords a thermodynamically stable complex which is kinetically labile with respect to more weakly bound ligands. Importance of 2-oxazolines is based on their application as intermediates for functional structure [16] and wide biological activity [17]. The use of oxazoline type ligands as chirality-transfer auxiliaries has been largely developed in the recent years for a broad range of catalytic reactions based on a variety of metals [18].

The crystal structure of the Mn(III) complex with 2-(2'-hydroxyphenyl)-4,4-dimethyl-2-oxazoline was found to be unique in that the five-membered oxazoline ring of the 2-(2'-hydroxyphenyl)-4,4-dimethyl-2-oxazoline is partially hydrolyzed to give an open chain. The Mn(III) ion present in the complex is six-coordinate where two nitrogen atoms of 2-oxazoline rings and one carbonyl oxygen of the hydrolyzed oxazoline are coordinated to the metal ion in addition to the aryloxo groups.

It has been reported in the recent past [19] that oxorhenium(V) complex with 2-(2'-hydroxyphenyl)-2-oxazoline acts as an efficient catalyst for the reduction of perchlorate with R₂S even under very mild condition. It prompted us to undertake, in this communication the

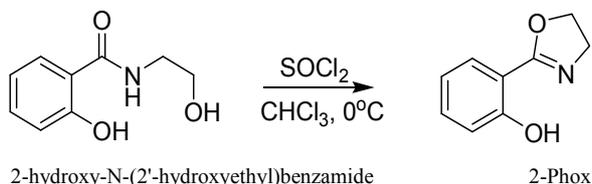
synthesis and characterization of Ni(II), Cu(II), Zn(II) and Cd(II) complexes of 2-phox and 4-phox to study the coordinating behavior of the ligand.

2. Experimental

2.1. Synthesis

2.1.1. Preparation of 2-(2'-Hydroxyphenyl)-2-Oxazoline(2-Phox)

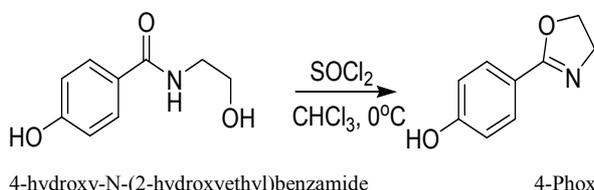
The 2-hydroxy-N-(2'-hydroxyethyl)benzamide (1.0 g, 0.0060 mol) solution in chloroform (10.5 ml) was cooled to 0 °C. Then thionyl chloride (2.07 g, 0.02 mol) was added dropwise over 45 min. This mixture was brought to room temperature and stirred for 22 h which yielded a white solid. The intermediate, 2-(2-hydroxyphenyl)-2-oxazolinium chloride (0.959 g, 97%), m.pt, 38-41 °C) was washed with chloroform and dried in vacuo. The product was dissolved in water (7.0 mL) and saturated aqueous NaHCO₃ (5%, 12 ml) was added. The pinkish solid was isolated (0.8 g, 90%), mpt, 41-42 °C (Scheme 1)



Scheme 1. Synthesis of 2-Phox

2.1.2. Preparation of 2-(4-Hydroxyphenyl)-2-Oxazoline (4-Phox)

To 4-hydroxybenzamide (5 g, 0.0276 mol) solution in methylene chloride at 0 °C a freshly distilled cold thionyl chloride (15 g, 0.126 ol) was added dropwise. The reaction mixture was kept at 0 °C for 30 min. and stirred at room temperature for 21 h. The product thus obtained was filtered, washed with CH₂Cl₂. Aqueous solution of NaHCO₃ (0.4 M, 50 ml) was added portion wise until effervescence ceases to continue. The mixture was stirred for additional 30 min and filtered. The solid product was dried in an oven at 60 °C (2.84g, 63%), m.pt, 197 - 200 °C.



Scheme 2. Synthesis of 4-phox

2.1.3. Preparation of Ni(II) and Cu(II) with 2-Phox

To a methanolic solution (2 ml) of 2-Phox (0.1 g, 0.6125 mmol) NiCl₂ (0.04 g, 0.306 mmol) and CuCl₂·2H₂O (0.05 g, 0.306 mmol) each in methanol (3 mL) in a separate round bottom flasks were added. The mixture was stirred for 18 h at room temperature. The pale green Ni(II) complex formed was filtered and washed with methanol and dried under

vacuo (0.26 g 60%), m.pt, 224-226 °C. In the case of Cu(II), the solution was concentrated under vacuum to give a green solid (0.38 g, 85%), m.pt, 190-192 °C.

2.1.4. Preparation of Zn(II) and Cd(II) Complexes

To a solution of 2-Phox (0.1 g, 0.6125 mmol) in methanol (2 ml) were added CdCl₂·2H₂O (0.08 g, 0.3 mmol) and ZnCl₂ (0.04 g 0.3 mmol) each in methanol (3 mL) in different flasks. The reaction mixture was stirred for 24 h at room temperature when a white solid was formed in both cases. It was filtered and dried under vacuo. Yield 0.042 g (90%) m.pt, 240- 243 °C for Cd(II) and 0.042 g (90%) m.pt, 210-212 °C for Zn(II).

2.1.5. Syntheses of Zn(II) and Cd(II) Complexes with 4-Phox

To a solution of 4-Phox (0.2 g, 1.225 mmol) in Acetone (15 mL) CdCl₂·2H₂O (0.08 g, 0.6 mmol) and ZnCl₂ (0.16 g, 0.6 mmol) each in acetone (10 mL) were added in separate flasks. The reaction mixtures were stirred for 24 h at room temperature. The complexes formed were filtered and dried under vacuum. Yields (0.4 g, 78.58%), m.pt, 270 - 273 °C for Zn(II), and (0.25 g, 49%), decomposes at 350 °C for Cd(II). Attempts to synthesize Ni(II) and Cu(II) complexes was unsuccessful.

2.2. Physical Measurements

¹H and ¹³C NMR spectra were recorded in CDCl₃ with Bruker Ultra-shield NMR. IR spectra were recorded using Perkin-Elmer FT-IR spectrophotometer with 4000-400 cm⁻¹ range. Electronic spectra were recorded with SPECTRONIC GENESY™ 2PC UV-visible spectrophotometer. The magnetic susceptibility was measured using MSB-AUTO Sherwood magnetic balance. Pascal constant was used for diamagnetic corrections Elemental analyses were carried out with Exeter Analytical CE 440 elemental analyzer. The metal contents were estimated on a Buck Scientific AAS model 210 VGP. The molar conductance was measured with Bench conductivity meter EC 214. The melting points were recorded using IA 9200 digital melting point apparatus.

3. Results and Discussion

3.1. 2-(2'-Hydroxyphenyl)-2-Oxazoline(2-Phox)

¹H NMR (CDCl₃, 400 MHz, ppm): δ 12.25(s, 1H, OH), 7.68(dd, 1H, ar.), 7.4(m, 1H, Ar), 7.0(d, 1H, Ar), 6.90(m, 1H, Ar), 4.45(t, 2H, O-CH₂), 4.2(t, 2H, N-CH₂) (Fig. 1).

¹³C NMR (Acetone-d₆, 100.6 MHz, ppm): δ 53.4(1C, N-CH₂), 66.77 (1C, O-CH₂), 110.73, 116.68, 118.59, 128.01, 133.27 and 159.78(6C, Ar), 166.18 (1C, N=C-O) (Fig. 2). The DEPT spectrum (Fig. 2) also shows four signals at δ 116.68, 118.59, 128.01 and 133.27 ppm for the four C-H protons in the benzene ring and two signals at 53.41 and 66.77 for N-CH₂ and O-CH₂ respectively. The absence of signals at 110.73, 159.78 and 166.18 ppm in the DEPT spectrum confirms the presence of three quaternary carbons as expected in the structure of 2-Phox.

Bi-dimensional correlation spectra were recorded. HH-COSY, HSQC and HMBC heteronuclear and homonuclear correlation techniques were used.

HH-COSY (CDCl_3 , 400 MHz, ppm): In the NMR spectrum of 2-Phox, the HH-COSY NMR spectrum (Fig. 3) shows that δ 4.1(2H, t) and δ 4.4(2H, t) protons are not interrelated with δ 6.8(1H, t), δ 7.0(1H, d), δ 7.38(1H, t) and

δ 7.68(1H, d) but each other. δ 6.8(1H, t) have proton-proton correlative signal in HH-COSY spectrum with δ 7.38(1H, t) and δ 7.38(1H, t). δ 7.0(1H, d) has correlation with δ 7.38(1H, t) only and δ 7.38(1H, t) has correlation with three types of protons such as δ 7.68(1H, d), δ 7.0(1H, d) and δ 6.8(1H, t). Finally, δ 7.68(1H, d) has correlation with δ 6.8(1H, t) and δ 7.38(1H, t) protons.

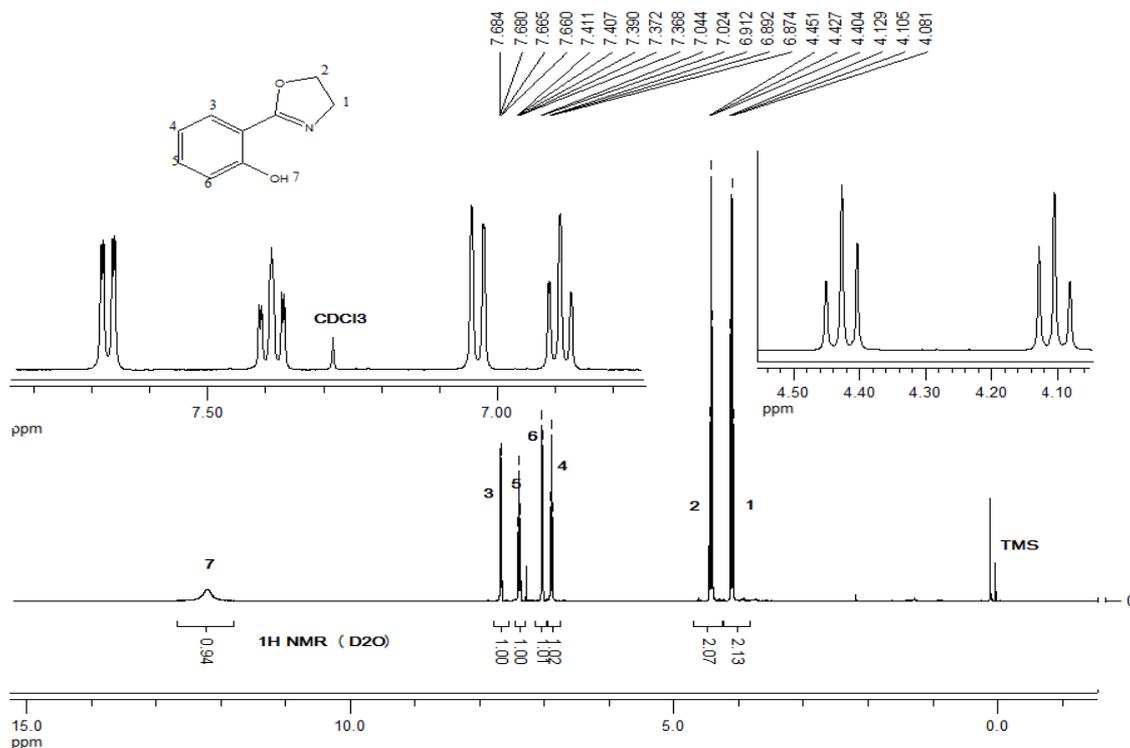


Fig. 1. ^1H NMR (CDCl_3 , 400 MHz, ppm) of 2-Phox.

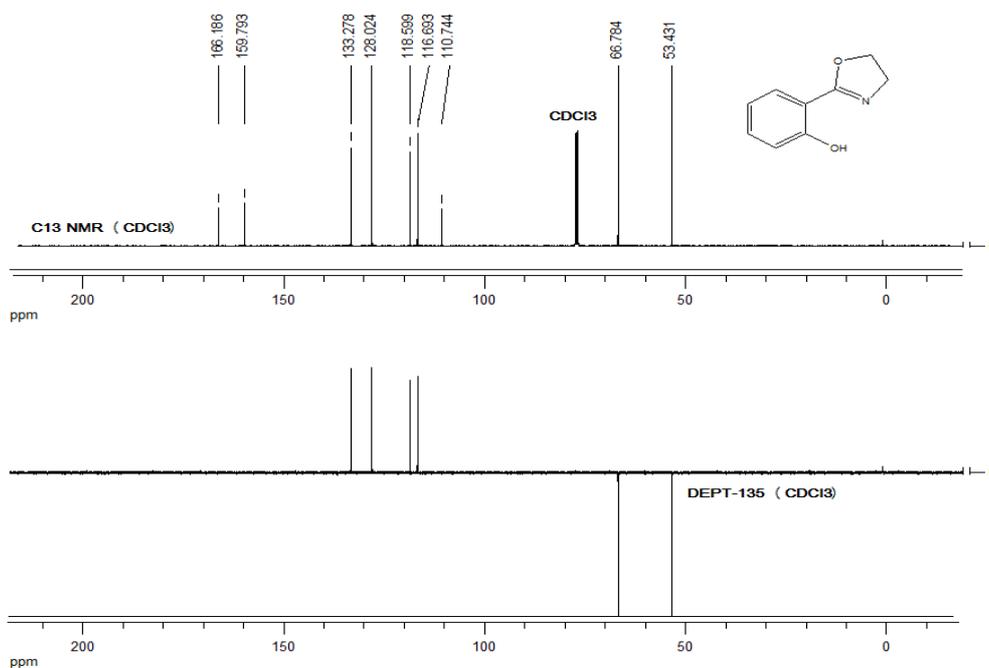


Fig. 2. DEPT-135 and ^{13}C NMR (CDCl_3 , 100.6 MHz, ppm) of 2-Phox.

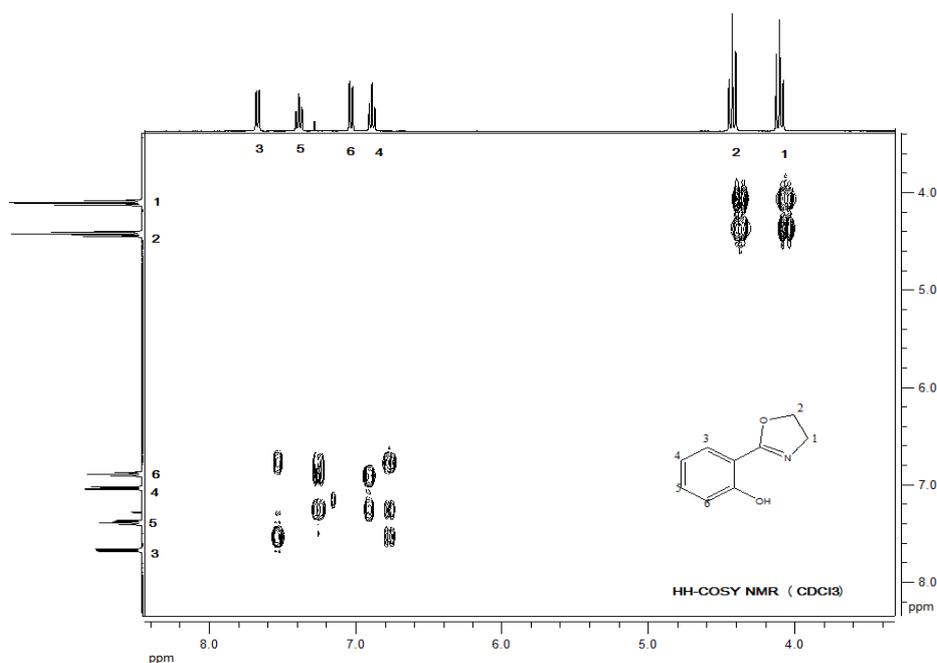


Fig. 3. HH-COSY NMR spectrum of 2-Phox.

HSQC (CDCl₃): The protons at δ 4.1 (2H, 1) and δ 4.4 (2H, t) have correlation with δ 53.4 carbon(C-1) and δ 66.77 carbon(C-2) respectively. HSQC spectra (Fig. 4), shows the protons at δ 6.8(1H, t), δ 7.0(1H, d), δ 7.38(1H, t) and δ 7.68(1H, d) corresponds to δ 118.59 carbon(C-6), δ 116.68 Carbon(C-4), δ 133 carbon (C-3) and δ 128.01 carbon (C-5) respectively.

HMBC (CDCl₃): By HMBC spectrum (Fig. 5) the specific assignment of protons and carbons are made as follows: H-1 protons correlative in HMBC with δ 66.77 carbon(C-2), δ 110.73 carbon(C-7), δ 166.18 carbon (C-9) and δ H-2 with δ

53.41 carbon(C-1) and δ 166.18 carbon(C-9).

H-4 protons with δ 116.68 carbon(C-4), δ 110.73 carbon(C-7), δ 118.59 carbon(C-6), δ 128.01 carbon(C-5), δ 133.27 carbon(C-3), δ 159.78 carbon(C-8) and δ 166.18 carbon(C-9). H-6 with δ 110.73 carbon(C-7), δ 118.59 carbon(C-6), δ 159.78 carbon(C-8), δ 128.01 carbon(C-5) and δ 166.18 carbon(C-9). H-5 with δ 128.01 carbon(C-5), δ 110.73 carbon(C-7) and δ 159.78 carbon(C-8). H-3 with δ 116.68 carbon(C-4), δ 133.27 carbon(C-3), δ 159.78 carbon(C-8) and δ 166.18 carbon(C-9).

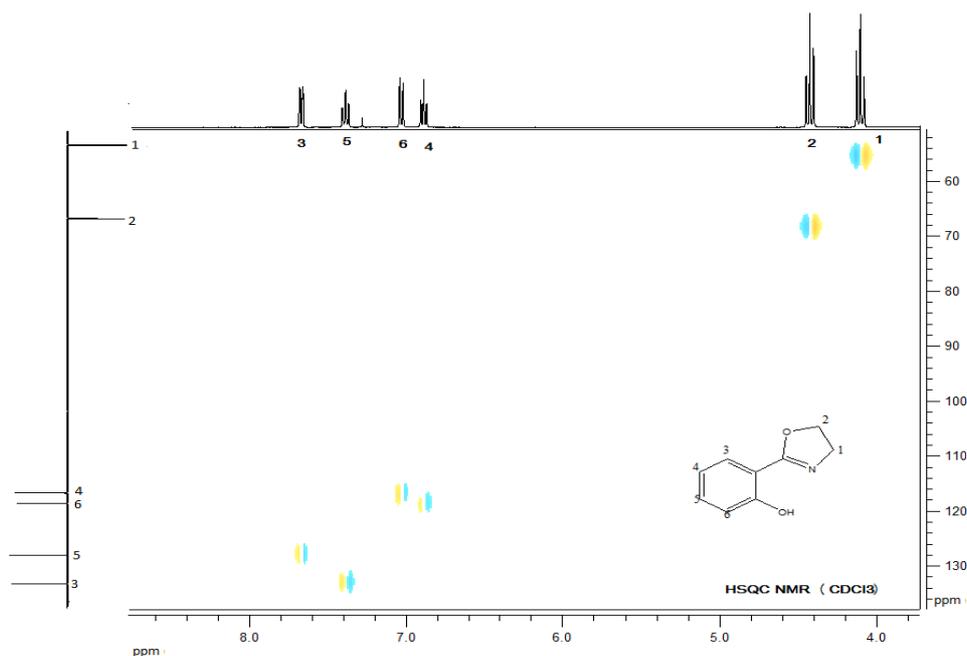


Fig. 4. HSQC NMR spectrum of 2-Phox.

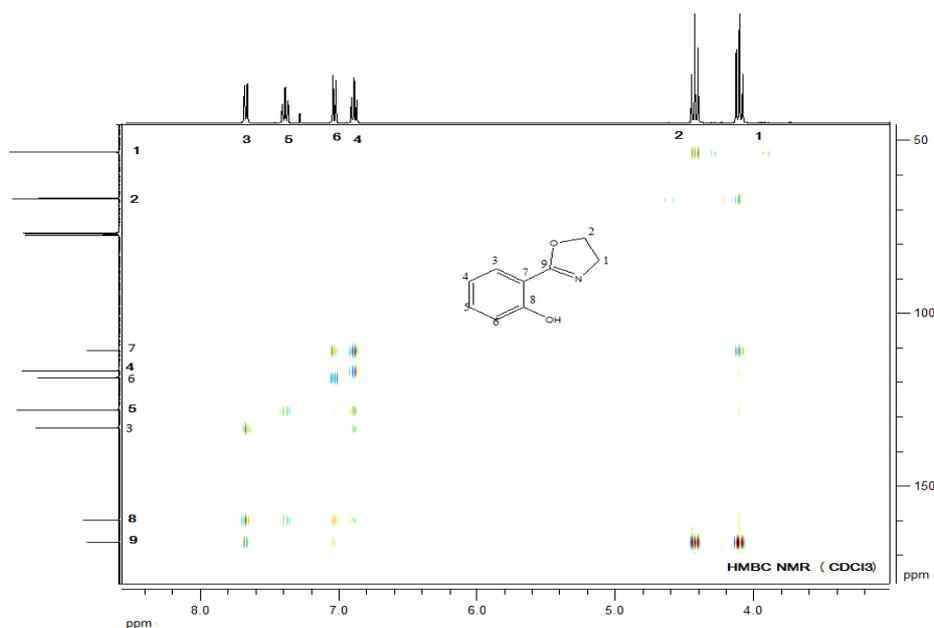


Fig. 5. HMBC NMR spectrum of 2-Phox.

IR (KBr) spectrum of 2-Phox: 3555-3342 cm^{-1} (ν_{OH}); 3044 cm^{-1} (ν_{CH} , Ar); 2995-2912 cm^{-1} (ν_{CH} aliphatic); 1643 cm^{-1} ($\nu_{\text{C=N}}$ oxazoline); 1607 cm^{-1} and 1510 cm^{-1} ($\nu_{\text{C=C}}$); 1495 cm^{-1} , and 1371 cm^{-1} (ν_{CH} aliphatic). ^1H NMR, ^{13}C NMR and IR spectrum justify the formation of 2-Phox [14].

3.2. 2-(4-Hydroxyphenyl)-2-Oxazoline(4-Phox)

^1H -NMR (Acetone- d_6 , 400 MHz, ppm): δ 9.10(s, 1H, $\text{C}_6\text{H}_4\text{-OH}$); 7.85(d, 1H, Ar), 6.8(d, 1H, Ar); 4.4(t, 2H, (N- CH_2), 3.8(t, 2H, O- CH_2) (Fig. 6).

^{13}C -NMR (Acetone- 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) (Fig. 7). The DEPT spectrum (Fig. 7) also shows two signals at δ 115.00 and 129.79 ppm for the two C-H groups in the benzene ring. The absence of signals at 119.59, 160.07 and 163.43 ppm confirms the presence of three quaternary carbons in the compound. IR (KBr) spectrum : 3555-3342 cm^{-1} (ν_{OH}); 3044 cm^{-1} (ν_{CH} , Ar); 2995-2912 cm^{-1} (ν_{CH} , aliphatic); 1634 cm^{-1} ($\nu_{\text{C=N}}$, oxazoline); 1590 cm^{-1} and 1511 cm^{-1} ($\nu_{\text{C=C}}$); 1369 cm^{-1} , 1289 cm^{-1} and 1248 cm^{-1} (ν_{CH} , aliphatic).

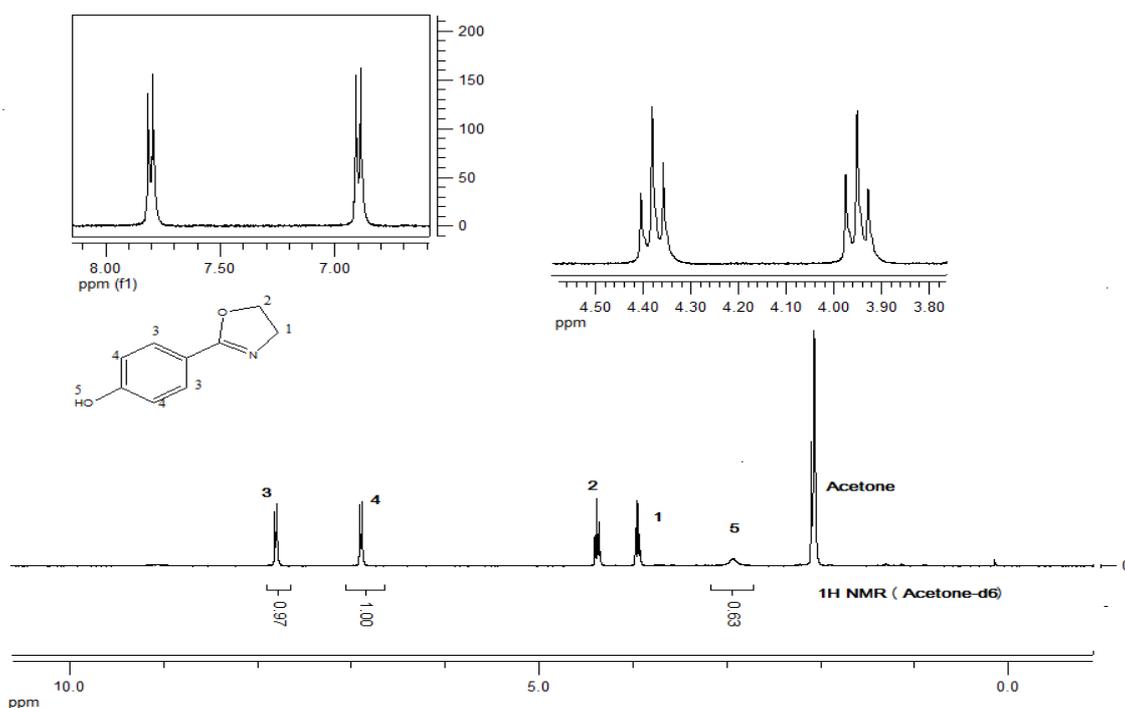


Fig. 6. ^1H NMR (Acetone- d_6 , 400 MHz, ppm) of 4-Phox.

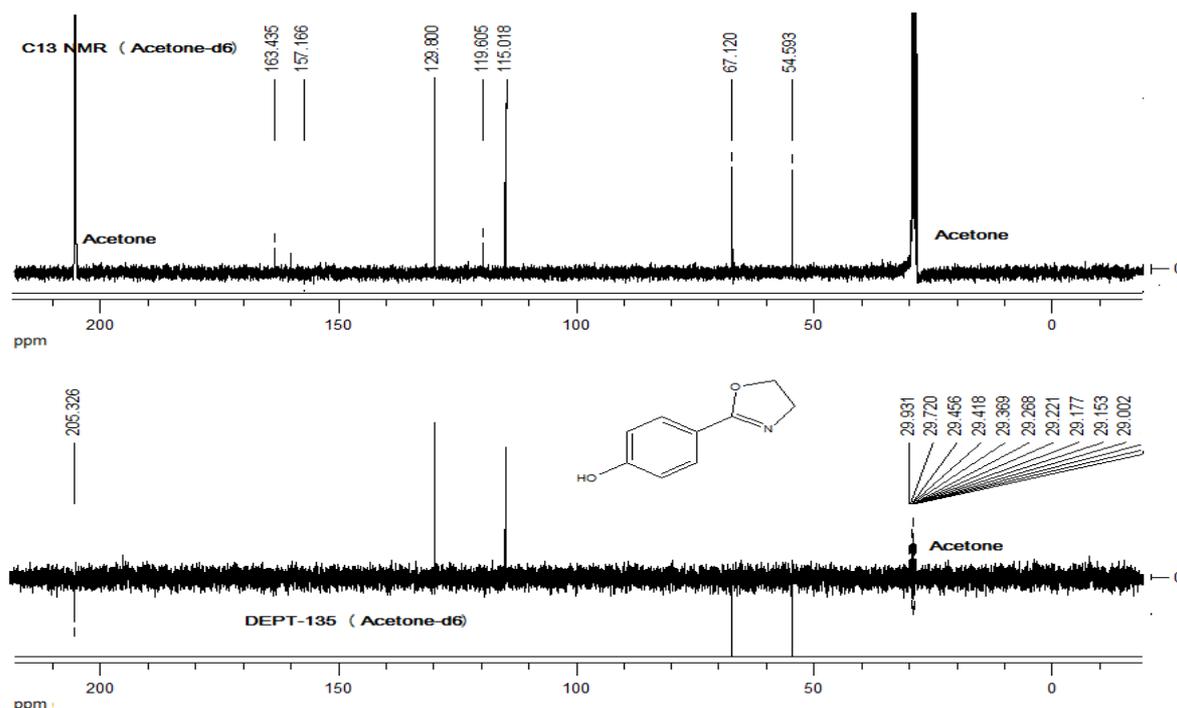


Fig. 7. DEPT-135 and C-13 NMR (Acetone-d6, 100.6 MHz, ppm) of 4-Phox.

3.3. IR Spectra

The elemental analysis (Table 1) suggests that the complexes are formed in 1:2 (M:L) ratio.

Table 1. Elemental Analysis of the ligands and Complexes.

Formula	Found (Calcd), %		
	Carbon	Hydrogen	Nitrogen
2-Phox	64.90(66.26)	5.41(5.55)	8.34(8.58)
[Ni(2-Phox) ₂]	55.67(56.44)	4.12(4.18)	6.62(7.31)
[Cu(2-Phox) ₂]	54.67(55.81)	4.15(4.13)	6.44(7.23)
[Zn(2-Phox) ₂]	54.46(55.47)	4.00(4.10)	6.98(7.19)
[Cd(2-Phox) ₂]	47.99(49.49)	3.11(3.66)	6.00(6.41)
4-Phox	63.97(66.26)	5.54(5.55)	8.18(8.58)
[Zn(4-Phox) ₂ Cl ₂]	44.68(46.71)	3.33 (3.89)	5.76(6.05)
[Cd(4-Phox) ₂ Cl ₂]	42.10 (42.40)	3.03(3.53)	4.76(5.49)

The IR spectrum of 2-Phox showed characteristic band for the $\nu(\text{C}=\text{N})$ of oxazoline at 1643 cm^{-1} which shifted to lower frequencies in the complexes (Table 2). These shifts are indicative of coordination of the 2-Phox to metal ions through nitrogen of the oxazoline ring. The shifting of $\nu(\text{C}-\text{O})$ band confirms deprotonation of phenolic proton and subsequent coordination to metal ion. The IR spectra of all the 2-phox complexes show two absorption bands in 530-585 cm^{-1} and 430-471 cm^{-1} region, which are assignable to (M-O) and (M-N) vibrations, respectively [20].

The 4-Phox shows observable changes in $\nu(\text{C}=\text{N})$ from 1634 cm^{-1} in the free ligand to 1623 cm^{-1} and 1618 cm^{-1} after its coordination with Zn(II) and Cd(II) respectively. This downward shift is consistent with metal binding through nitrogen of 2-oxazoline [21]. The phenolic-OH frequency

appears at 3340 cm^{-1} which remains unchanged even after complexation suggesting the non involvement of the group in coordination [22]. Furthermore, new bands at 475 cm^{-1} and 504 cm^{-1} for Zn(II) and Cd(II) complexes, respectively, may be assigned to M-N stretching [20]. New absorption bands at 569 cm^{-1} and 572 cm^{-1} have been assigned to (M-O) vibrations of Zn(II) and Cd(II) complexes, respectively.

Table 2. Important IR bands of 2-Phox, 4-phox and their complexes.

Complexes and ligands	$\nu(\text{C}=\text{N})$	$\nu(\text{OH})$	$\nu(\text{C}-\text{O})$	$\nu(\text{M}-\text{N})$	$\nu(\text{M}-\text{O})$
2-Phox	1643	3555-3342	1282
[Ni(2-Phox) ₂]	1634	3400	1259	461	532
[Cu(2-Phox) ₂]	1635	3435	1251	457	585
[Zn(2-Phox) ₂]	1619	3434	1266	471	580
[Cd(2-Phox) ₂]	1639	3500	1268	430	577
4-Phox	1634	3340	1289
[Zn(4-Phox) ₂ Cl ₂]	1623	3340	1278	475	569
[Cd(4-Phox) ₂ Cl ₂]	1618	3340	1276	504	572

3.4. Electronic Spectra of Complexes with 2-Phox

The UV-vis spectrum of 2-phox recorded in DMF (Fig. 8a) shows two intense bands centered at 262 nm and 301 nm due to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions. The Ni(II) complex (Fig. 8b) shows three bands at 271, 305 and 358 nm (Table 3). The peaks at high-energy region shifted to lower frequencies as a consequence of coordination of the ligand to metal ions. The bands at 305 and 358 nm have been attributed to transitions ${}^3\text{A}_2(\text{F}) \leftarrow {}^3\text{T}_1(\text{F})$, ${}^3\text{T}_1(\text{P}) \leftarrow {}^3\text{T}_1(\text{F})$ and ${}^3\text{T}_2(\text{F}) \leftarrow {}^3\text{T}_1(\text{F})$ respectively. They are characteristic of tetrahedral Ni(II) ion [23].

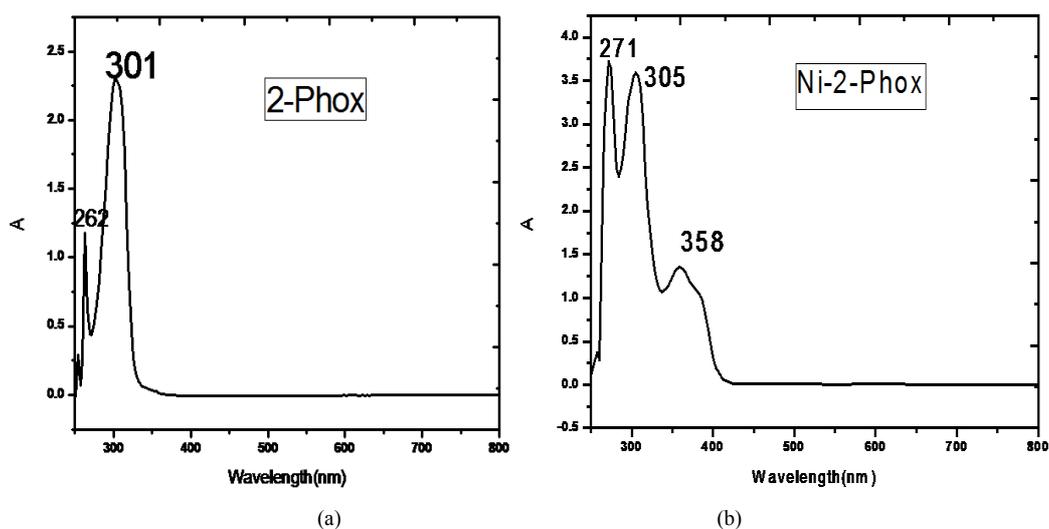


Fig. 8. UV-vis spectrum of 2-Phox and Ni-2-Phox Complex

It is known that a single broad band corresponding to (${}^2E \leftarrow {}^2B_2$, ${}^2B_1 \leftarrow {}^2B_2$ and ${}^2A_1 \leftarrow {}^2B_2$) transitions appear in the near IR region for tetrahedral geometry, three absorption bands corresponding to the transition ${}^2A_{1g} \leftarrow {}^2B_{1g}$, ${}^2B_{2g} \leftarrow {}^2B_{1g}$ and ${}^2E_g \leftarrow {}^2B_{1g}$ for distorted octahedral and three d-d bands corresponding to ${}^2B_{2g} \leftarrow {}^2B_{1g}$, ${}^2A_{1g} \leftarrow {}^2B_{1g}$ and ${}^2E_g \leftarrow {}^2B_{1g}$ transitions for square planar geometry are expected for Cu(II) complexes. Cu(II) complex in our case (Fig. 9b) shows a single broad band at 350 nm in addition to two intense bands

(262, 301 nm) at higher energies. The peak at 262 nm is assigned to the (N) \rightarrow Cu(II) LMCT [24] whereas the one at 301 nm is assigned to Cu(II) $\rightarrow \pi^*$ metal to ligand charge transfer. It has been reported [25] that the Cu(II) \rightarrow phenolate complex shows MLCT at 300 nm. In the present case we have observed a single broad band at 350 nm corresponding to d-d (${}^2E \leftarrow {}^2B_2$, ${}^2B_1 \leftarrow {}^2B_2$ and ${}^2A_1 \leftarrow {}^2B_2$) transitions which suggest a tetrahedral geometry for Cu(II) ion.

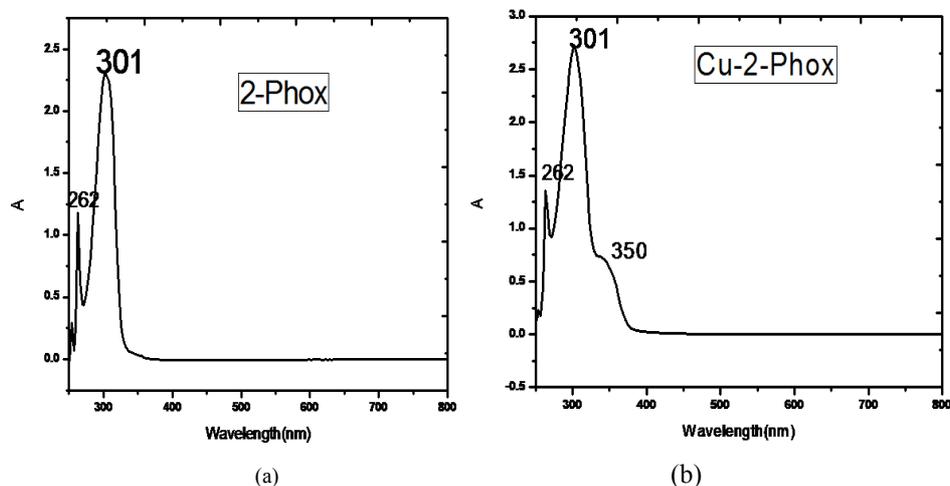


Fig. 9. UV-vis spectrum of 2-Phox and Cu-2-Phox Complex.

3.5. Magnetic Susceptibility Measurement

The observed magnetic moment is far higher (3.67 BM) than the expected spin-only value (2.828 BM) for tetrahedral Ni(II) ion. It may be due to orbital contribution. It is also reported that fairly regular tetrahedral complexes have moments between 3.52-4.0 BM and for the more distorted tetrahedral geometry; the magnetic moment is 3.02-3.5 BM [21]. It is, therefore, suggested that the geometry around the metal ion is regular tetrahedral. The observed magnetic moment for Cu(II) complex (1.76 BM) is very close to the

spin only value (1.73 BM) for one unpaired electron. A distorted tetrahedral geometry [26] is, therefore, suggested for the complex.

Table 3. Electronic spectra and magnetic moments of Ni(II)-2-Phox and Cu(II)-2-Phox complexes.

Complexes	Effective magnetic moment Electronic spectra	
	μ_{eff} (B.M.)	λ_{max} (nm)
$[(\text{Ni}(\text{2-Phox})_2)]$	3.67	271, 305, 358
$[(\text{Cu}(\text{2-Phox})_2)]$	1.76	262, 301, 350

3.6. Molar Conductance of the Complexes

The molar conductance of the complexes measured in

DMF at ambient temperature indicates that they are non electrolyte (Table 4).

Table 4. Conductivity data of the complexes ($\mu\text{s cm}^{-1}$)

Complexes	Molar conductance	Complexes	Molar Conductance
[Ni(2-Phox) ₂]	14.7	[Cd(2-Phox) ₂]	8.0
[Cu(2-Phox) ₂]	60	[Zn(4-Phox) ₂ Cl ₂]	9.0
[Zn(2-Phox) ₂]	7.0	[Cd(4-Phox) ₂ Cl ₂]	9.0

4. Conclusion

The composition of the ligand and the complexes has been established by ¹H and ¹³C NMR, IR, UV-Vis and elemental analysis. The IR and UV-Vis data confirm that 2-Phox binds to the metal centers via N-atom of the 2-oxazoline ring and O-H group of the phenolic moiety. The non electrolytic nature and the negative test for the chloride ions in the 2-Phox complexes prove the absence of chloride ion. The chloride test confirms the presence of coordinated chloride to Zn(II) and Cd(II)-4-phox complexes. The magnetic susceptibility and the conductance measurement data also support the proposed geometry. The proposed structures of the complexes Zn(II) and Cd(II) with 4-Phox and Ni(II), Cu(II), Zn(II) and Cd(II) with 2-Phox are represented by Fig. 10 and 11 respectively.

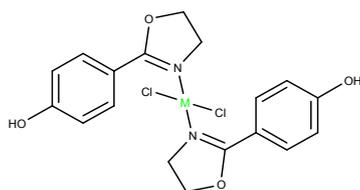


Fig. 10. Proposed structure for [M(4-phox)₂Cl₂], M = Zn(II) and Cd(II)

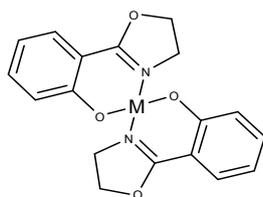


Fig. 11. Proposed structure for [M(2-phox)₂], M = Ni(II), Cu(II), Zn(II) and Cd(II)

Acknowledgements

The University of Gondar, Gondar, Ethiopia is thanked for providing financial assistance for this work.

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