INDO AMERICAN JOURNAL OF PHARMACEUTICAL RESEARCH

SYNTHESIS AND CHARACTERIZATION OF NICKEL (II) COMPLEXES WITH 3-(2-HYDROXYPHENYL)-2-IMINO-1-THIAZOLIDIN-4-ONE AND 3-(2-HYDROXYPHENYL)-2-IMINO-1-OXAZOLIDIN-4-ONE

Lalisa Wakjira Duresa

Mettu University, Faculty of Natural and Computational Sciences, Department of Chemistry, P.O.Box: 318, Mettu, Ethiopia.

ARTICLE INFO

Article history

Received 31/03/2017

Available online 30/04/2017

Keywords

Synthesis;

Characterization;

Heterocyclic Ligands;

Ni (II) Complexes.

ABSTRACT

This paper focuses on synthesis and characterization of ligands and complexes. The ligands, 3-(2-hydroxyphenyl)-2-imino-1-thiazolidin-4-one ($C_9H_8O_2N_2S$) and 3-(2-hydroxyphenyl)-2-imino-1-oxazolidin-4-one ($C_9H_8O_3N$), synthesized by cyclocondensation of 2-chloro-N-(2-hydroxyphenyl) acetamide, obtained by reaction of o-aminophenol with chloroacetylchloride, with potassium thiocyanate and potassium cyanate respectively. The metal complexes were prepared by refluxing solutions containing each ligand and metal salt in hot ethanol in 1:1 molar ratio. Analyses and conductometric results revealed 1:2 metal-ligand ratio and nonelectrolytic nature of the complexes respectively. IR spectral data revealed that both heterocyclic ligands coordinate through their heterocyclic nitrogen and phenolic oxygen to the metal and act as anionic bidentate ligands. Magnetic susceptiblity studies indicated square planar geometry of $[NiL_2].2H_2O$ complex whereas other complex exhibiting magnetic moments less than spin-free d^8 geometry seemed to be equilibrium mixture of four coordinate tetrahedral and square planar geometries owing to high spin to low spin or vice versa spin crossover phenomenon. However, splitting patterns of d-d bands in the electronic spectra of the complexes in solutions are consistent with their square planar geometry; tetrahedral stereochemistry has most probably been changed to square planar form by interaction with the solvent molecules. Newly synthesized complexes of Ni(II) which were 1:2 metal-ligand ratio were nonelectrolytic and formed by coordination of the ligands through their heterocyclic atoms and phenolic oxygen.

Corresponding author

Lalisa Wakjira Duresa

Mettu University,

Faculty of Natural and Computational Sciences,

Department of Chemistry

P.O.Box: 318, Mettu, Ethiopia.

lelisawak@gmail.com

Please cite this article in press as ***Lalisa Wakjira Duresa*** *et al. Synthesis and Characterization of Nickel (II) Complexes with 3-(2-hydroxyphenyl)-2-imino-1-thiazolidin-4-one and 3-(2-hydroxyphenyl)-2-imino-1-oxazolidin-4-one. Indo American Journal of Pharmaceutical Research.2017:7(04).*

INTRODUCTION

The scope of coordination chemistry, indeed, is very broad and interdisciplinary. Coordination compounds play a very significant role in our lives; their study has contributed to the highest degree of understanding of the chemical bonding in inorganic chemistry. Some of the important types of coordination compounds occur in biological systems (like, heme and chlorophyll) and the catalytic properties of coordination compounds are worth mentioning [1].

Transition metal complexes of ligands containing nitrogen, sulphur or oxygen are becoming increasingly important because of their capacity of binding with different metal centers involving various coordination sites and allow successful synthesis of metallic complexes with interesting stereochemistry. Transition metal-Schiff's base complexes are used in electrochemical reduction of gels from styrene polymers, as catalyst in photo polymerization of printing plates and as dispersing agents in dyeing [2]. The complexes of Ni(II), Cu(II), Cd(II), Co(II), Mn(II) and Zn(II) with hydroxypyrazole or pyrazplane aldehyde Schiff bases are light stabilizers for plastics and fibres. Moreover Schiff base complexes of transition metal complexes are used as oxidation inhibitors for lubricating oils, in the manufacture of fluorescent brightener and liquid crystal compositions in optical display devices. An increase in the number of complexes with therapeutic value has witnessed in the field of medicine and interest on Schiff's base metal complexes has been growing in the area of bio-inorganic chemistry due to the role of such complexes in providing synthetic models for the metal containing sites in metalloprotiens and enzymes [3-4].

Even if ligands are divided into unidentate, bidentate and multidentate types; according to the number of donor atoms they contain, the stereochemistry of some ligands does not allow all the binding sites to be simultaneously bonded to the same metal, i.e. a ligand potentially tridentate, may function only as a bidentate ligand [5].

Schiff's bases, products of primary amines and an aldehyde or a ketone, possessing azomethine (-C=N-) group, are most popular organic ligands in past few decades. A large number of Schiff's bases and their complexes may exhibit the properties like to reversibly bind oxygen, transfer an amino group, as nanoprecursors and varied complexing/redox agents. Many Schiff bases owing to their high affinity to chelate with the transition metal ions, have potential applications in biology, catalysis, thermal, electrical, optical , magnetic etc fields [6].

Heterocycles containing sulfur, oxygen and nitrogen atoms in addition to carbon in the ring are useful as components of functional materials since heteroatoms in their rings are helpful to stabilize ions or ion radical species, and extended π-conjugation decreases coulombic repulsion. In addition, intermolecular interactions caused by heteroatom contacts can be expected to form novel molecular assemblies [7]. Recently, meta-methoxythiazolidinone and para-nitro thiazolidinone have been studied among some of the attractive compounds due to their high antimicrobial potential [8].

Transition metal complexes with nitrogen and oxygen donor containing ligands stimulated interest due to their vast variety of biological activities ranging from pharmacological, antitumour, fungicidal, bactericidal, anti-inflammatory, and antiviral activities [9,10].

Transition metal complexes containing heterocyclic compounds have been of considerable interest in terms of structural chemistry, catalysis and biological functions. The field has undergone spectacular growth due to the synthesis of multidentate ligands from heterocyclic compounds to synthesize chelates with metal ions [11].

There are a number of multidentate ligands that play important roles in coordination chemistry and catalyst designing. The degree of interaction between the metal center and the neutral ligand atom can exert a profound influence on the reactivity of the resulting complexes. A large number of multidentate ligands have been synthesized and investigated [12, 13] for their metal binding character including Ni(II).

Although a large number of complexes of transition metals with different heterocyclic ligands have been studied for their structures and biological properties, use of oxazolidinone and thiazolidinone derivatives as ligands for complexation has been scarcely done [14,15] and there is no report on the study of the complexes of 3-(2-hydroxyphenyl)-2-imino-1-thiazolidin-4-one and 3-(2-hydroxyphenyl)-2-imino-1-oxazolidin-4-one. In view of little knowledge in the chemistry of complexes of oxazolidinones and thiazolidinones in general and non-availability of any report on complexes of mentioned heterocyclic ligands in particular it has been thought worthwhile to synthesize and characterize Ni(II) complexes with 3-(2-hydroxyphenyl)-2-imino-1-thiazolidin-4-one and 3-(2-hydroxyphenyl)-2-imino-1-oxazolidin-4-one.

Therefore this study is generally conducted to undertake synthesis and characterization of 3-(2-hydroxyphenyl)-2-imino-1-thiazolidin-4-one and 3-(2-hydroxyphenyl)-2-imino-1-oxazolidin-4-one ligands and their Ni(II) complexes. And specifically the study is intended to:

- Synthesize 3-(2-hydroxyphenyl)-2-imino-1-thiazolidin-4-one and 3-(2-hydroxyphenyl)-2-imino-1-oxazolidin-4-one, and their Ni(II) complexes.
- Elucidate the structure of the ligands and their Ni(II) complexes by physico-chemical techniques, viz., elemental analyses, conductometric and magnetic measurements, as well as IR, and UV-Visible , ^{1}H NMR and ^{13}CNMR spectroscopy.

MATERIALS AND METHODS

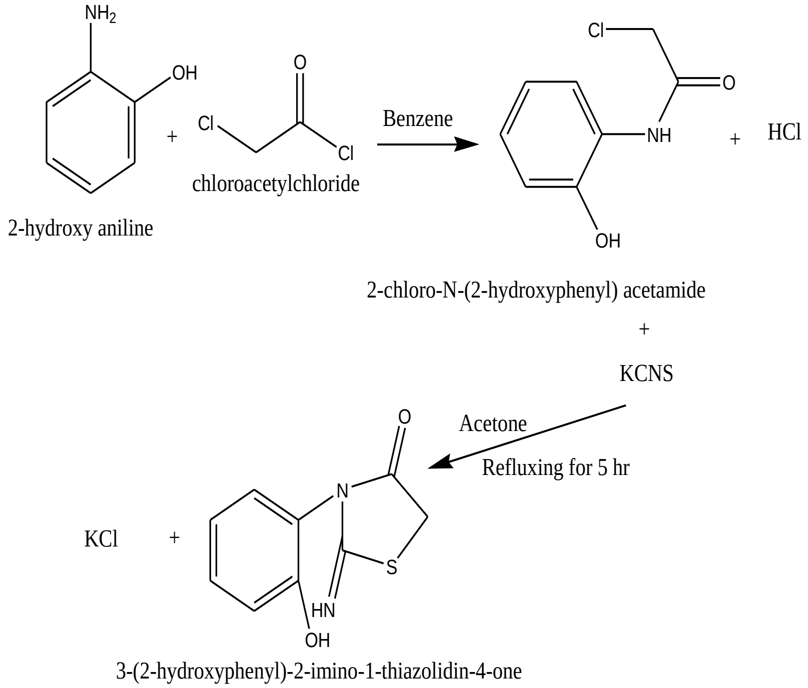
All the chemicals used in the synthetic work were analytical grade except solvents which were laboratory reagents. In spectroscopic and thin layer chromatographic works all solvents were HPLC grade. The chemicals used were; Ni(II) nitrate hexahydrate ($Ni(NO_3)_2.6H_2O$), Ni(II) chloride hexahydrate, 2-hydroxy aniline, chloroacetyl chloride, potassium cynate (KCNO), potassium thiocyante (KCNS), PDA (potato dextrose agar), MHA (Mueller Hinton agar), nitric acid, and organic solvents such as benzene, acetone, ethanol, methanol, DMSO (dimethyl sulfoxide).

The ^{1}H and ^{13}C NMR spectra of the ligands were recorded in DMSO on Bruker Ultra shield TM 400 spectrometer using TMS as internal standard at Addis Ababa University. The Infrared spectra were recorded on Fourier Transform Infrared (FT-IR) spectrometer (prestige-21) in the range 4000 cm^{-1}- 400 cm^{-1} in KBr medium; Elemental analyses of C, H, N and S were done at IIT, Roorkee (India). The melting points of the synthesized compounds were determined in open glass capillaries using BibbySterilin LTD, ST150SA, UK melting point apparatus. Electronic spectral measurements were conducted on UV/Vis-SP65 SYANO spectrophotometer in 200-900 nm range. Magnetic susceptibility measurements were done on MSB AUTO, (Sherwood Scientific) magnetic balance at Addis Ababa University. The molar conductivity measurements were carried out using Jenway digital conductivity meter (UK) at Haramaya University. ^{1}H and ^{13}C NMR, FT-IR, magnetic susceptibility measurements and elemental analysis were done outside Haramaya University whereas; all other instrumental and synthetic works were carried out in the Chemistry Department research laboratories of Haramaya University.

Synthesis of 3-(2-hydroxyphenyl)-2-imino-1-thiazolidin-4-one

It is a two steps preparation. In the first step, 2-chloro-N-(2-hydroxyphenyl) acetamide was prepared which on subsequent treatment with potassium thiocyanate yielded iminothiazolidinone. For synthesis of 2-chloro-N-(2-hydroxyphenyl) acetamide, to the solution of 2-hydroxy aniline (0.05mol) in ice cold benzene 8 ml chloroacetyl chloride was added in 1 ml installments with vigorous stirring. Precipitate obtained was filtered out, washed with benzene, dried in air and crystallized from alcohol.

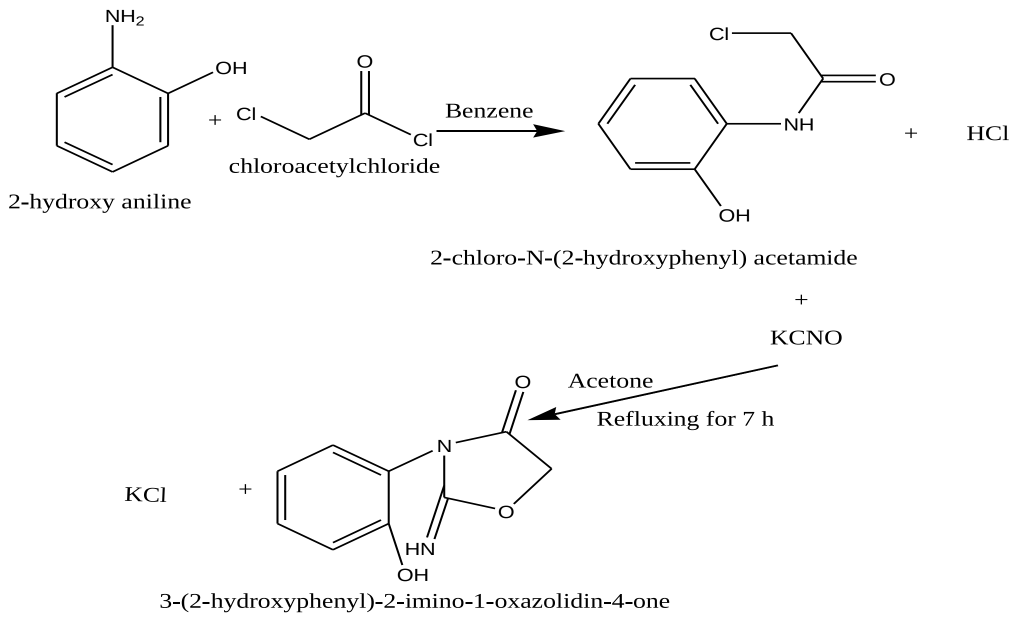
A mixture containing 2-chloro-N-(2-hydroxyphenyl) acetamide (5.985 g) and potassium thiocyanate (2.91 g) in acetone in 1:1 molar ratio was refluxed for 5 h and filtered. Filterate was evaporated on water bath and residue after stirring with excess water was filtered, washed with water and crystallized from alcohol. Air dried product was collected [16].



Scheme 1: Synthesis of 3-(2-hydroxyphenyl)-2-imino-1-thiazolidin-4-one.

Synthesis of 3-(2-hydroxyphenyl)-2-imino-1-oxazolidin-4-one

Equimolar solutions of the reactants, 2-chloro-N-(2-hydroxyphenyl) acetamide (5.985 g) and potassium cyanate (2.43 g) in dry methanol were mixed together in 1:1 molar ratio and reaction mixture was refluxed for about 7 h and filtered to remove KCl. Solvent of filtrate was evaporated on water bath, and residue was washed with water repeatedly to ensure complete removal of KCl, dried and crystallized from ethanol. Crystals of product were dried in air [17].



Scheme 2: Synthesis of 3-(2-hydroxyphenyl)-2-imino-1-oxazolidin-4-one.

Synthesis of the metal complexes

A common procedure was followed to prepare both complexes. To the solutions containing 0.015 mol of Ni(II) salts in hot ethanol, each ligand solution (0.015 mol) in ethanol was mixed and reaction mixtures were refluxed for about 2 h. Reaction mixtures on cooling at room temperature yielded precipitates of complexes. Products were filtered, washed with water and alcohol successively and dried in air.

Test for Purity of the Compounds

The purity of the complexes was tested by using thin-layer chromatography (TLC) on silica gel thin layers using two component solvent systems, ethyl acetate and n-hexane (9:1 & 4:1 v/v ratio). A single spot in all samples indicate that the complexes were pure.

Chloride Test

A 30 mg of each chloro complex was digested in nitric acid to remove organic content and diluted and $AgNO_3$ solution was added. Absence of AgCl white precipitate indicates that there is no chlorine in the complexes, neither as chloride nor as coordinated chlorine.

Metal Determination

Atomic absorption spectroscopic measurements on the complexes were done to know the metal contents. 30 mg of each of Ni(II) complex was placed in a clean and dry beaker and 10 mL of 69% conc. HNO_3 was added and the contents were heated gently in a hood until a few drops remained in each beaker. Then 5 mL of additional 69% conc. HNO_3 was added to each beaker and heated slowly until a few drops remained. After three repetitions of this process, each time with the organic portions of the complexes were decomposed the solution was then diluted with deionized water in a 100 mL volumetric flask. These solutions were subjected to AAS studies after appropriate dilutions. Based on the absorbance data the concentrations of Ni(II) in the complexes were calculated using the following formula:

$$\mathrm{M}(\%) = \mathrm{Concentration}(\mathrm{PPm})\,\mathrm{x}\,\frac{volume\ diluted\ to}{massofsampletaken}\,x\,\frac{100}{1000}$$

Fourier Transform Infrared (FT-IR) spectra

Fourier Transform Infrared (FT-IR) spectra of ligands and their complexes recorded in 4000-400 cm^{-1} in KBr medium were used to obtain information regarding the coordinating sites of the ligands in the metal complexes.

Molar conductance measurements

Conductometric measurements on the complexes were done on their solutions in DMSO/Me_2CO at room temperature to know the electrolytic nature of the complexes.

Magnetic susceptibility measurements

Magnetic susceptibility measurements on the complexes were done at 22^0C to know their magnetic nature and stereochemistry.
The following equations were used to calculate the magnetic parameters of the complexes.

$$\chi_M = \chi_g \text{ x M.W} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{ (i)}$$

Where, χ_M, molar magnetic susceptibility (cm^3 mol^{-1}), χ_g, gram magnetic susceptibility (cm^3 g^{-1}), M.W, molecular weight (g mol^{-1}).

$$\chi_{Meff=}\ \chi_M\text{-Diamagnetic correction-------- (ii)}$$

$$\mu_{eff} = 2.84(\chi_{Meff}T)^{1/2}\text{--------------------- (iii)}$$

Where, μeff = effective magnetic moment and T = temperature in K.

^{1}H and ^{13}C NMR spectral studies

^{1}H and ^{13}C NMR spectra of the ligands were studied to elucidate the structures of the ligands, 3-(2-hydroxyphenyl)-2-imino-1-thiazolidin-4-one and 3-(2-hydroxyphenyl)-2-imino-1-oxazolidin-4-one.

Uv-visible absorption spectra

Uv-visible absorption spectra on the solutions of the complexes in 200-900 nm regions were recorded to identify and determine energy of d-d electronic transitions and electronic charge transfers.

RESULTS AND DISCUSSION

Physico-chemical Characteristics of the Ligands and Their Complexes

Physical properties and elemental analyses data of ligands and their complexes are noted in Tables 1 and 2. The proposed molecular formulae of the newly synthesized compounds are consistent with their analyses data of C, H, N, S and metal contents. In all the complexes a metal-ligand ratio of 1:2 is established.

Table 1: Formula, Melting point and elemental analyses data of the ligands and their Complexes.

Compounds	**Mol.Wt**	*Colour*	**M.P (^{0}C)**	**Elemental Analysis Calculated(Found) %**				
				C	**H**	**N**	**S**	**Ni(II)**
$C_9H_8O_2N_2S$	208	Yellowish brown	120-121	51.92 (51.66)	3.85 (3.80)	13.46 (13.34)	15.38 (16.10)	-
$[NiL_2].2H_2O$	508.7	Gray brown	215-216	42.46 (42.29)	3.54 (3.28)	11.00 (10.77)	12.58 (12.79)	11.54 (11.74)
$C_9H_8O_3N_2$	192	Bronze	89-91	56.25 (56.59)	4.17 (4.19)	14.58 (14.72)	-	-
$[NiL'_2]$	440.7	Dark brown	122-123	49.01 (49.74)	3.18 (3.56)	12.71 (12.58)	-	13.32 (13.30)

Where, L= $C_9H_7O_2N_2S$ and L′= $C_9H_7O_3N$.

Determination of Metal Contents by AAS

The data obtained from AAS (Table 2) shows that the metal to ligand ratio for all Ni(II) complexes is 1:2.

Table 2: AAS data for the M-L complexes.

Complex	**Mol.wt**	**[Ni(II)] (ppm)**	**A**	**Ni(II) contents(%)**	
				Calulated	**Found**
$[NiL_2].2H_2O$	508.7	33.5	0.067	11.54	11.17
$[NiL'_2]$	440.7	39	0.078	13.32	13

Where, L= $C_9H_7O_2N_2S$ and L′= $C_9H_7O_3N_2$, A = Absorbance.

Conductometric study

Conductometric measurements on the complexes were conducted on their respective solutions in DMSO/ acetone at room temperature. Molar conductance values of complexes lying in 1.78-1.82 Ω^{-1} cm^2mol^{-1} range in acetone and 8.95-9.25 Ω^{-1} cm^2mol^{-1} range in DMSO reveal their non-electrolytic nature.

Table 3: Conductometric data.

Compounds	Conductance of complex (µS)	Specific conductance x10^6 ($ohm^{-1}cm^2mol^{-1}$)	Molar conductance ($\Omega^{-1}cm^2\ mol^{-1}$)	Electrolytic nature
$[NiL_2].2H_2O$	4.6	4.56	8.95	Non electrolyte
$[NiL'_2]$	0.81	0.80	1.82	Non electrolyte

Cell constant (k) = 0.99
Conductance of DMSO =4.28µS
Acetone = 0.27 µS

FT-IR spectral studies

Table 4: Principal IR frequencies with their assignments for ligands and their complexes.

Compound	*v* C=O ring	*v*C-O-C ring	*v* C-S-C ring	*v* C=N	Secondary ammine *v* N-H	*v* C-N-C ring	Phenol		Benzene		Ortho disubstitution	*v*M-O	*v* M-N
							v OH	*v* C-O	*v* C=C	*v* C-H			
$C_9H_8O_2N_2S$ (L)	1659	-	686d	1548	3338	1329	3185 3410	1039 1105	1456 1597	2983	750	-	-
$[NiL_2].2H_2O$	1647	-	703	1543	3382	1283	-	968 1040 1106 1131	1456 1595	3115	750	544	457
$C_9H_8O_3N_2$ (L′)	1653d	1106	-	1554	3341	1372	3341 3445	1041	1455 1600	2983	749	-	-
$[Ni\ L'_2]$	1653d	1112	-	1551	3368	1278d	-	923 1050 1152	1455 1502 1602	3082 2986	748	525	468d

Where, d= doublet.

In order to identify coordinating groups of the ligands in their complexes, the infrared spectra of the ligands were separately measured and compared with the spectra of the particular complexes. The perusal of Table 4 reveals that absorption bands corresponding to *v* C=O, *v* C-S-C, *v* C=N, *v* N-H (secondary amine), *v* C=C &*v* C-H (benzene ring) and orthodisubstitution of ligand(L) observed at 1659 cm^{-1}, 686 cm^{-1}, 1548 cm^{-1}, 3338 cm^{-1}, 1456 & 1597 cm^{-1}, 2983 cm^{-1} and 750 cm^{-1} respectively for 3-(2-hydroxyphenyl)-2-imino-1-thiazolidin-4-one. These are almost undisturbed in its Ni(II) complex, whereas *v* C-N-C (ring) peak of the ligand at 1329 cm^{-1} shifted to 1283 cm^{-1} in the complex; the lowering in the frequency (bathochromic shift) of this band and appearance of a new band at 457 cm^{-1} in the complex which may be attributed to *v* Ni-N are suggestive of possible coordination of the heterocyclic ring nitrogen with the Ni(II). Disappearance of *v* OH (phenolic) bands of ligand (3185 & 3410 cm^{-1}) and drastic disturbance, lowering and /or appearance of new band(s) of *v* C-O (phenolic group) on complexation, and appearance of another new band at 544 cm^{-1} in the spectra of a complex ascertains coordination of deprotonated phenolic oxygen with the metal. Similarly, during the complexation of 3-(2-hydroxyphenyl)-2-imino-1-oxazolidin-4-one (L′) with the metal, the ligand band at 1372 cm^{-1} corresponding to the *v* C-N-C (ring) occurred at about 1278 cm-1 in a complex spectra and *v* OH (phenolic) bands of ligand (3341 & 3445 cm^{-1}) disappeared; the lowering in C-N-C ring frequency and disappearance of phenolic OH band of ligand in its complex indicates coordination of heterocyclic nitrogen and deprotonated phenolic oxygen of ligand. This inference gets strong support with the appearance of new bands at 525 and 468 corresponding to *v* M-O and *v* M-N appeared in the complex spectra.

Infrared spectral studies clearly reveal that binding modes of the ligands are identical; deprotonated phenolic oxygen and heterocyclic nitrogen and there is no role of anions of Ni(II) salts in coordination.

NMR (^{1}H and ^{13}C) spectral studies

Table 5: ^{1}H and ^{13}C NMR spectral data for ligands.

Compounds	^{1}H NMR (δ, ppm)	Assignment	^{13}C NMR (δ, ppm)	Assignment
$C_9H_8O_2N_2S$ (L)	4.35	CH_2 H	34	CH_2 C
	12.6	Azomethine H	157.5	Azomethine C
	6.6-7.9	Aromatic H	116-129	Aromatic C
		Carbonyl H	166	Carbonyl C
	4.8	Phenolic H	148	Phenolic C
$C_9H_8O_3N_2$ (L′)	2.5	CH_2 H	67	CH_2 carbon
	10.7	Azomethine H	167	Azomethine C
	6.7-8.0	Aromatic H	116-127	Aromatic C
		Carbonyl H	171	Carbonyl C
	4.2	Phenolic H	147.5	Phenolic C

The ^{1}H NMR (Table 5) of 3-(2-hydroxyphenyl)-2-imino-1-thiazolidin-4-one displays chemical shifs at δ4.35 attributed to heterocyclic (1H) between carbonyl group and heterocyclic sulfur, δ12.6 attributed to azomethine (1H), δ6.6-7.9 to benzene ring (4H) and δ4.8 corresponding to phenolic (1H) whereas ^{13}C NMR spectrum H_2C display its bands at δ34, for azomethine C, at δ157.5, for HC (aromatic) in the range (116-129), carbonyl C at 166 and phenolic groups carbon display their bands at 148.^{1}H NMR of 3-(2-hydroxyphenyl)-2-imino-1-oxazolidin-4-one displays chemical shifts at δ2.5 of heterocyclic (1H) between carbonyl group and heterocyclic oxygen, δ10.7 of azomethine (1H) δ(6.7-8.0), of benzene ring (4H) and δ4.2 of phenolic (1H) whereas in ^{13}C NMR spectrum H2C display its band at δ67, azomethine C at δ167, HC (aromatic) in the range (116-127), carbonyl C at 171 and phenolic group carbon display its bands at 147.5. These results of ^{1}H and ^{13}C NMR analyses also support the infrared inferences regarding the structure of 3-(2-hydroxyphenyl)-2-imino-1-thiazolidin-4-one and 3-(2-hydoxyphenyl)-2-imino-1-oxazolidin-4-one.

Magnetic susceptibility and electronic spectral studies

Magnetic susceptibility and magnetic moment values are depicted in Table 6. The results revealed diamagnetic nature of the $[NiL_2].2H_2O$ complex proving that all d-orbitals of Ni(II) are spin paired and this leads to suggest a four-coordinate square planar geometry for this particular complex. Given that the other complex is also tetra coordinated, it appeared to be displaying abnormal magnetic moment 1.13 BM. This value is, however, neither corresponding to the spin-only value (2.83) of tetrahedral spin-free mononuclear species nor to that of polynuclear ligand bridged complexes involving metal-metal interactions. Rather this abnormal magnetic moment indicates occurrence of spin crossover of low-spin (spin paired) square planar stereochemistry to high-spin tetrahedral geometry or vice versa.

Perusal of Table 7 comprising frequencies of electronic spectral bands of the complexes reveals the d-d transition bands and their splitting pattern corresponding to that of spin-paired square planar geometry. It is very interesting to observe that square planar and tetrahedral geometries which usually exist in equilibrium in solid state have been turned to square planar stereochemical form in solution, most probably arising from interaction with the solvents. Both complexes displayed 2 low energy bands in 16611 cm^{-1} - 23696cm^{-1} region. These bands in the order of increasing energy, are assigned to $^1A_{1g}$ (D) $\rightarrow ^1A_{2g}$ (G), $^1A_{1g}$ (D) $\rightarrow ^1B_{1g}$ (G),d-d transitions in square planar stereochemistry. One or two bands occurring in 31847 cm^{-1} - 42735 cm^{-1} rangeare attributed to ligand to metal charge transfer transitions.

Table 6: Magnetic Susceptibility and magnetic moment measurement Data.

Compounds	Mol.Wt	χ_g(x10^{-6}) (cgs)	X_M (x 10^{-6}) (cgs)	Diamagnetic correction x10^{-6} (cgs)	(X_{Meff}) x10^{-6}	(μ_{eff}) (BM)
$[NiL_2].2H_2O$	508.7	-	-	-	-	Diamagnetic
$[NiL'_2]$	440.7	0.93	409.85	-127.28	537.13	1.13

Where, L= $C_9H_7O_2N_2S$
L’= $C_9H_7O_3N$

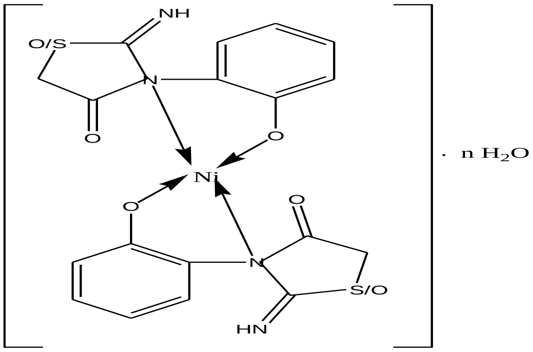
Table 7: The electronic spectra bands and their assignment.

Compound	Absorption bands (cm^{-1})	Band assignment
$[NiL_2].2H_2O$	16611	$^1A_{1g}(D)\rightarrow{}^1A_{2g}(G)$
	23696	$^1A_{1g}(D)\rightarrow{}^1B_{1g}(G)$
	34246	LMCT
	42735	LMCT
$[NiL'_2]$	18248	$^1A_{1g}(D)\rightarrow{}^1A_{2g}(G)$
	22522	$^1A_{1g}(D)\rightarrow{}^1B_{1g}(G)$
	31847	LMCT
	39062	LMCT

Where, L= $C_9H_7O_2N_2S$, L'= $C_9H_7O_3N_2$.

Proposed Structure of Ni(II) Complexes

Based on inferences arrived from C, H, N, S and Metal analyses, chloride test, conductometric, infrared and electronic spectral and magnetic studies, the following general structure canbe proposed for both complexes of Ni(II) with both 3-(2-hydroxyphenyl)-2-imino-1-thiazolidin-4-one and 3-(2-hydroxyphenyl)-2-imino-1-oxazolidin-4-one ligands.



Where n= 0 or 2.

Figure 1: Proposed structure of Ni(II) complexes with both 3-(2-hydroxyphenyl)-2-imino-1-thiazolidin-4-one and 3-(2-hydroxyphenyl)-2-imino-1-oxazolidin-4-one.

CONCLUSION

Syntheses of the metal complexes were conducted by refluxing solutions containing each ligand and metal salt in hot ethanol in 1:1 molar ratio. From the collective results of Analyses and conductometric results, 1:2 metal-ligand ratio and nonelectrolytic nature of the complexes were respectively obtained. Both heterocyclic ligands coordinate through their heterocyclic nitrogen and phenolic oxygen to the metal and act as anionic bidentate ligands. The geometry of the complexes $[NiL_2].2H_2O$ were found to be Square planar in whereas $[NiL'_2]$ which exhibited spin-free d^8 geometry seemed to be equilibrium mixture of four coordinate tetrahedral and square planar geometries owing to high spin to low spin or vice versa spin crossover phenomenon. Other metals complexes with these ligands and their microbial activities study are recommended next to this work.

ACKNOWLEDGMENT

First of all I glorify my savior Almighty God for enabling me to complete this work. I appreciate the Department of Chemistry, Haramaya University and AAU the laboratory and instrumentation facilities for characterizing the samples during this study. In addition; I express deep sense of gratitude to Prof. R.K. Upadhyay and Dr. Abi Taddesse for their endless help and encouragement. Finally, my heartfelt appreciation extends to all members of my family especially for their love and follow-up during my study. May God bless them all!

LIST OF ABBREVIATIONS

AAS	Atomic Absorption Spectroscopy
BM	Bohr Magneton
DMSO	Dimethyl sulfoxide
FT-IR	Fourier Transforms Infrared
Me_2CO	Acetone
NMR	Nuclear Magnetic Resonance
TLC	Thin Layer Chromatography
UV-Vis	Ultra Violet and Visible

There is no conflict of interest.

REFERENCES

1. House, J. E. Synthesis and Reactions of Coordination Compounds. Inorganic chemistry.Elsevier Inc. 2008; 151: 568-695.
2. Theoder, S. Azomethine and diazomethane pigments preparation.J. Chemical Abstract. 1975; 84: 6481.
3. K.S. Abou-Melha and H. Faruk. Bimetallic Complexes of Schiff Base Bis-[4-hydroxycuomarin-3-yl]-1N,5N-thiocarbohydrazone as a Potentially Dibasic Pentadentate Ligand. Synthesis, Spectral, and Antimicrobial Properties. J. Iran. Chem. Soc. 2008 : 5 (1) : 122-134.
4. Gehad Geindy Mohamed, Mohamed Mohamed Omar, Ahmed Mohamed Hindy. Ahmed Mohamed Hindy. Metal Complexes of Schiff Bases: Preparation, Characterization, and Biological Activity. Turk J Chem. 2006; 30: 361 – 382.
5. Houghton, R.P. Metal Complex in Organic Chemistry, 1st Ed. Cambridge University Press; 1979. pp 335.
6. Soliman, A.A. and G.G, Mohamed. Spectroscopic and Biologacal activity studies on tridentate Schiff base.ThermochimActa. 2004; 421: 151.
7. Kumagai, T., M, Tomura., J, Nishida., and Y, Yamashita.1,3-dithiol-2-ylidene derivatives containing bis(ethynylpyridine) units. Tetrahedron Letters. 2003; 44 (36): 6845-6848.
8. Desta Gebretekle. Synthesis and Antimicrobial Evaluation of Novel Isomeric 1,4-thiazolidinones. “M.Sc Thesis”, Harmaya University, Ethiopia. 2012.
9. Chaudhary, A., A. Phor and R.V. Singh. Potentially biodynamic tetraazamacrocycles and their manganese complexes: antiandrogen, antimicrobial and PDI studies. Bioinorganic Chemistry and Applications, 2005; 3: 161–177.
10. Prasad, S. and R. K. Agarwal. Cobalt(II) complexes of various thiosemicarbazones of 4-aminoantipyrine: syntheses,spectral, thermal and antimicrobial studies. Transition Metal Chemistry. 2007; 32(2): 143–149.
11. Anacona, J. R., T. Martell and I.Sanchez. Metal complexes of a new ligand derived from 2, 3-quinoxalinedithiol and 2, 6-bis(bromomethyl) pyridine. J.chil.chem.soc. 2005; 1: 50.
12. Premlata, S.V. and S. Gita. Synthesis, Characterization and Antimicrobial Activity of Ni(II) Complexes with 2-substituted Benzothiazole Ligands & Amino acids. Research Journal of Pharmaceutical, Biological and Chemical Sciences: 2012; 0975-8585
13. Xian-He, B.,D.Miao., Z.Lei., L.Dai-Zheng., T.Jin-Kui., Ruo-Hua., Zhang. and S. Mitsuhiko. Novel nickel(II) complexes with diazamesocyclic ligands functionalized by additional phenol donor pendant(s): synthesis,characterization, crystal structures and magnetic properties. J. Chem. Soc., Dalton Trans. 2001; 593–598.
14. Mulay, A., G. Mangesh and A. P. Nikalje. Exploring potential of 4-thiazolidinone. International Journal of pharmacy and pharmaceutical Science. 2009; 1. (1): 47-64.
15. Krishna c. Majumdar, SanjuktaMuhuri, RafiqueUl Islam, and BuddhadebChattopadhyay. Synthesis of five- and six-membered heterocyclic compounds by the application of the metathesis reactions. The Japan Institute of Heterocyclic Chemistry. 2009; 78: 1109 - 1169.
16. Ilhan, E. and N.Ergent. Synthesis and evalution of substituted aryl thia-and oxazolidines for biological dieng properties. Arch.pharm (weinheim). 1992; 325:4625.
17. Swati Jain. Synthesis and evaluation of substituted aryl thia- and oxazolidinones for biological and dyeing properties. “Ph.D Thesis” CCS University, India. 2009.

54878478451**170429**