

## Full Length Research Paper

# Spectrophotometric study on the stability constants and thermodynamic parameters of $Zn^{2+}$ , $Cd^{2+}$ and $Hg^{2+}$ complexes with Imino Thiazolidinone

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The heterocyclic ligand (L), 3-(2-hydroxy phenyl)-2-iminothiazolidin-4-one, was synthesized by the cyclocondensation of o-hydroxy phenyl chloroacetamide with potassium thiocyanate. The stoichiometries of the title complexes were first determined by spectrophotometric mole ratio method which gave rise to the M:L ratio of 1:4 in case of Zn(II) and Cd(II) and 1:2 in case of Hg(II) ions respectively. Using these predetermined M:L ratios, complexes of the formulas  $[Zn-L_4]$ ,  $[Cd-L_4]$  and  $[Hg-L_2]$  were prepared accordingly using precursor of the corresponding metal salts with the title ligand in ethanol medium. The synthesized compounds were characterized by elemental analysis, FTIR,  $^1H$  and  $^{13}C$ NMR, UV-Vis and conductometric measurement. Stability constants ( $K_s$ ) of these complexes were investigated by spectrophotometric mole ratio method. The FTIR,  $^1H$  NMR and  $^{13}C$  NMR data revealed that the studied ligand function as monodentate ligand interacting through phenolic oxygen as donor with Zn(II) and Cd(II) and as bidentate ligand interacting through phenolic oxygen and nitrogen atom with Hg(II). The synthesized complexes show conductivity values in the range of 122-133  $\mu Smol^{-1}cm^2$  in DMSO at 298 K which confirms the electrolytic nature of the complexes. The stability constants decreased with increased temperature, confirming that these metal complexes are not stable at higher temperature. Sufficiently large negative values of  $\Delta G$  of complex confirm the spontaneous formation of the title complexes. Furthermore, it was noted that the spontaneity of the reaction increased with temperature. The stability constant of these complexes follow the sequence  $Zn(II) > Cd(II) > Hg(II)$ . Therefore, the overall result is complying very well with the Irving-William series of stability constants of metal complexes.

**Key words:** Stability constants, 3-(2-hydroxyphenyl)-2-iminothiazolidin-4-one, Irving-William series, thermodynamic parameters, mole ratio method.

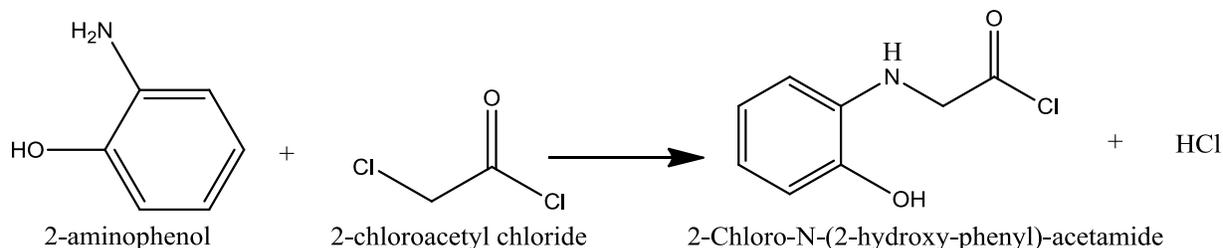
## INTRODUCTION

Thiazolidinones are thiazolidine derivatives and have an atom of sulfur at position 1, an atom of nitrogen at

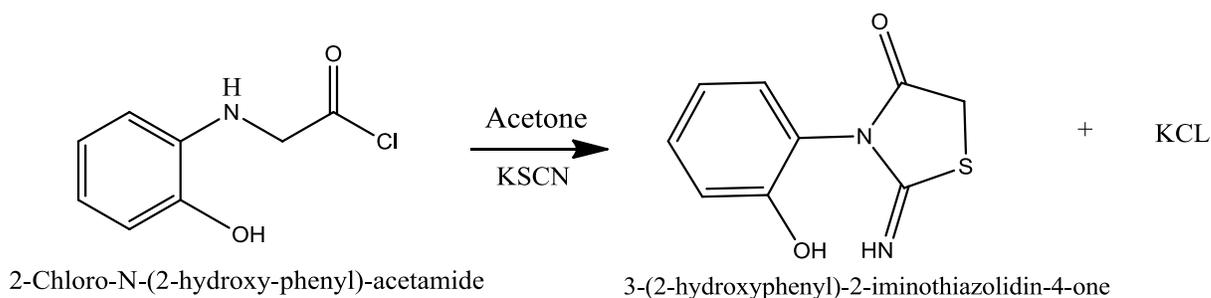
position 3 and a carbonyl group at position 2, 4 or 5. However, its derivatives belong to the most frequently

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**Figure 1.** Synthesis of 2-Chloro-N-(2-hydroxy-phenyl)-acetamide.



**Figure 2.** Synthesis of 3-(2-hydroxy phenyl)-2-iminothiazolidin-4-one.

studied moieties and its presence in penicillin was the first recognition of its occurrence in nature (Singh et al., 1981; Brown, 1961; Pulici and Quartieri, 2005). The perusal of literature shows that thiazolidine-4-ones have many interesting activity profiles, namely COX-1 inhibitors, inhibitors of the bacterial enzyme MurB, which was precursor acting during the biosynthesis of peptidoglycan, nonnucleoside inhibitors of HIV-RT and antihistaminic agents (Look et al., 1996; Andres et al., 2000; Barreca et al., 2001). Thiazolidinones are also known to exhibit antibacterial, anticonvulsant, antifungal, amoebicidal, antioxidant, and anticancer activities (Diurno et al., 1992; Mulwad and Choudhari, 2005.). Thiazolidine derivatives containing nitrogen oxygen and sulfur donors are being popular as biologically significant species. However a little known regarding on metal complexes of imino-derivatives of thiazolidinones of their complex equilibria, stability constant and physico-chemical properties of metal ion complexes. In this paper, we describe the syntheses, characterization, and thermodynamic parameters of synthesized thiazolidin-4-one with transition metal ions

## EXPERIMENTAL

### Synthesis of the ligand: 3-(2-hydroxy phenyl)-2-imino-1-thiazolidin-4-one

o-hydroxy phenyl chloro acetamide was prepared by 2-hydroxy aniline (0.05 mol) in ice cold benzene followed by 8 ml chloroacetyl

chloride added in 1 ml installments with vigorous stirring. Precipitate obtained was filtered out, washed with benzene, dried in air and crystallized by ethanol (Figure 1).

2-chloro-N-(2-hydroxyphenyl)-acetamide obtained from the previous reaction (5.986 g) and potassium thiocyanate (2.91 g) in acetone in 1:1 molar ratio were mixed, refluxed for 5 h and the product 3-(2-hydroxyphenyl)-2-iminothiazolidin-4-one was obtained as precipitate after evaporation of the solvent. Then the precipitate washed with water to ensure complete removal of unreacted KSCN and finally washed with dry acetone and ether successively. All the products were recrystallized from ethanol and dried in dry air and the purity was checked by TLC plates. Then, the air dried product was collected for further steps (Figure 2).

### Synthesis of the title complexes (M:L complex formation)

A common procedure was followed to prepare all complexes. To the solution containing 0.015 mol of each M (II) ions in hot ethanol, the ligand solution (0.015 mol) in ethanol was added with stirring and the reaction mixture was refluxed for about 2 h. The reaction product on cooling at room temperature yielded precipitate of the particular complexes. The precipitate obtained as such was then filtered, washed with water and ethanol successively and dried in air.

### Determination of stoichiometry (M:L ratio) of complexes by spectrophotometric mole ratio method

This method was used to determine the number of complexes formed and for choosing a wavelength suitable for performing further experiments. Absorption experiments were performed with mixtures containing varying molar ratios of reactants and number of maxima on the extrapolation of optical density and wavelength for each mixture set, were recorded to be informative of the number of

complexes formed in a given system. The wavelength obtained corresponding to wavelength maxima ( $\lambda_{\max}$ ) of a particular system was selected for use in all other spectrophotometric experiments (Vosburgh and Cooper, 1941). From the standard solutions, 2 ml of  $1.0 \times 10^{-2}$  M metal (II) chloride solutions were pipetted into each of eight 50 ml volumetric flasks and aliquots (2, 4, 6 to 16 ml) of  $1.0 \times 10^{-2}$  M ligand solution were mixed with thoroughly shaking the flasks to get homogenous solutions. Then, the absorbance was measured at maximum wavelength of each sample against reagent blank (DMSO) both at room temperature (that is, 25°C) and at 40°C.

### Test of purity of the compounds

#### Chloride test

From each complex, 30 mg was weighted and digested in nitric acid to remove organic content and diluted to give a clear solution to which  $\text{AgNO}_3$  solution was added in a drop wise manner. Absence of a white precipitate which could be due to  $\text{AgCl}$  in any of the complexes prepared indicates the absence of chlorine neither as chloride nor as coordinated chlorine.

#### TLC test

The purity of the complexes were tested by using thin-layer chromatography (TLC) on silica gel thin layers using two component solvent systems, ethyl acetate and n-hexane (9:1 ratio). A single spot on thin layer chromatogram was indicated that the complex was pure.

### Physico-chemical characterization

UV-visible spectra of the ligands and complexes were recorded on Varian Cary 500 spectrophotometer in the range 200 to 800 nm in solution. The IR spectra were recorded in KBr pellets (4000 to 400  $\text{cm}^{-1}$ ) on a Perkin-Elmer spectrum 2000 FT-IR spectrometer equipped with a DTG detector, in a region 4000 to 400  $\text{cm}^{-1}$ .  $^1\text{H}$  and  $^{13}\text{C}$ -NMR spectra were obtained on an Avance Bruker AMX 400 MHz spectrometer. All samples were prepared using deuterated solvents. Chemical shifts are reported in parts per million (ppm) relative to an internal standard tetramethylsilane (TMS).

## RESULTS AND DISCUSSION

### Electronic spectra and solvent effect on UV/Vis spectral of complexes

$\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Hg}^{2+}$  complexes are diamagnetic d10 ions and the electronic spectra of these complexes do not show any d-d transition band (Suresh and Prakash, 2010). The UV-Vis spectrum of the synthesized ligand is characterized mainly by one absorption band at 440 nm which may be assigned to  $n \rightarrow \pi^*$  transition. This transition was also observed in the spectra of the complexes, but with a red shift towards lower frequency, confirming the coordination of the ligand to the metal ions. The ligand as well as its metal complexes were found to be more soluble in DMSO, but only slightly soluble in methanol and ethanol. A series of solutions were prepared having a constant concentration ( $1 \times 10^{-2}$  M) of the metal ion but in

excess of these for the ligand so that the M:L ratios could be determined from the relationship between the absorption at  $\lambda_{\max}$  and the mole ratio obtained for each respective complex.

The UV/Vis absorption spectra of the iminothiazolidinone ligand and its complexes were obtained at room temperature in three organic solvents (Methanol, Ethanol and DMSO) with different polarity. In general, with increasing polarity of solvent the spectra of the ligand as well as the complex shifted to lower energy, that is, bathochromic shift observed. The solvent effect on the UV/Vis absorption spectra of the ligand (iminothiazolidinone (L) and its complexes ( $\text{Zn-L}_4$ ,  $\text{Cd-L}_4$  and  $\text{Hg-L}_2$ ) were found to be strongly dependent on the nature of the substituent on the imino group. This phenomenon may possibly be because by the difference in the conjugational or migrating ability of the lone pair electrons on nitrogen atoms of the ligand. These results are in accordance with structure of this ligand, such that the electronic behavior of the nitrogen atom of the amide group is somewhat different from carbonyl group as an electron-donating substituent.

### Stoichiometric studies and synthesis of metal ligand complexes

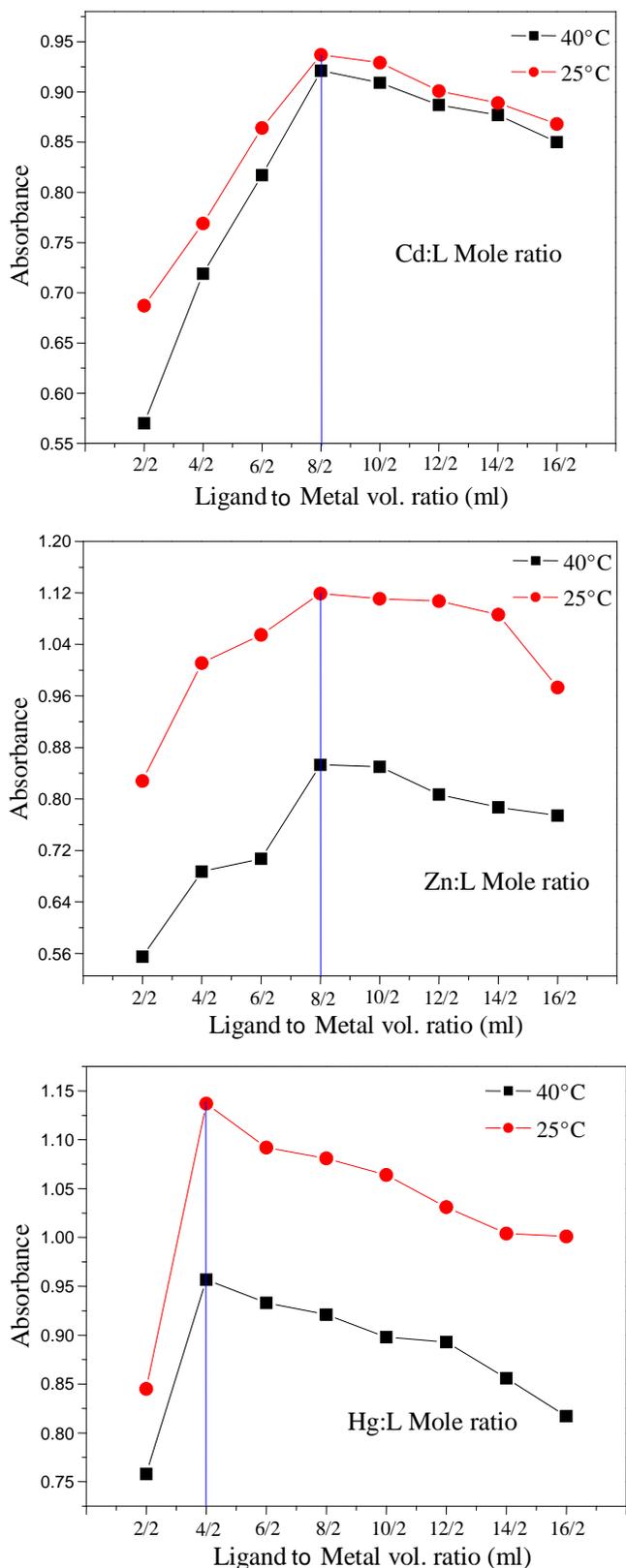
The stoichiometries of  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Hg}^{2+}$  complexes with the synthesized ligand were determined by the mole ratio method at constant metal ion concentration ( $1 \times 10^{-2}$  M) and varying ligand concentrations. The optical density of each complex solution was measured and the  $\lambda_{\max}$  occurs at 300, 305 and 295 nm in DMSO, respectively.

As shown in Figure 3, the intercepts of tangents on both arms of the graphs plotted between optical density and varying concentrations of ligand indicate 1:4, 1:4 and 1:2 metal to ligand interaction ratios of the complexes  $[\text{Zn-L}_4]$ ,  $[\text{Cd-L}_4]$  and  $[\text{Hg-L}_2]$ , respectively. The stoichiometric studies showed that there is a similar pattern of complexation with optical density (or absorbance) of each complex showing specific values at the two selected temperatures, that is, at 298 and 313K (Harvey and Manning, 1950). Therefore, results of the stoichiometric studies conducted on the prepared complexes using DMSO as a solvent suggested that the metal-ligand interactions may be expressed by the following complex equilibria forms:



### Thermodynamic parameters

The thermodynamic parameters were obtained spectrophotometrically by measuring the absorbance of



**Figure 3.** A graph plotted absorbance versus a function of VL/VM mole ratios of  $Zn^{2+}$ ,  $Cd^{2+}$  and  $Hg^{2+}$  complex with the ligand 3-(2-hydroxyphenyl)-2-iminothiazolidin-4-one at room (298 K) and 313 K temperatures.

solution of ligand and metal mixtures. The degree of formation of each complex was obtained according to the relationship indicated in Equations (1) and (2). The thermodynamic parameter of the metal ion complexes at five different temperatures 298, 303, 313, 323, 333 and 343 K were studied. The calculated  $\ln K_s$ ,  $\Delta G$ ,  $\Delta H$  and  $\Delta S$  values for the prepared complexes are recorded as follows:

$$\Delta G = -RT \ln K_s \quad (1)$$

$$\ln K_s = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad (2)$$

The value of  $\alpha$  (degree of dissociation) obtained by measuring the  $E_m$  (Maximum absorbance) and  $E_s$  (Absorbance found at correct Stoichiometry) from the maximum wavelength can be calculated using Equation 3.

$$\alpha = \frac{E_m - E_s}{E_m} \quad (3)$$

The free energies of formation ( $\Delta G$ ) of all metal complexes have negative values indicating spontaneity of the reaction process in all cases. In line with this, as the temperature increases, from 298 K to 343 K, the stability of complexes decreases.

### Effect of temperature

A perusal of data (Tables 2) shows that, the stability constant ( $K_s$ ) values decreases with an increase in temperature. Thus, higher temperature is not favorable for dissociation of proton from the carbonyl group of the ligand in these compounds implying that the values of metal-ligand stability constant decrease with increase in temperature. Thus, rise in temperature is not favorable for the formation stable complexes in these systems. As evidenced from Equation (2), the relationship between  $K_s$  and  $\Delta G$ , the values of free energies of formation of the complexes were become more and more negative with rise in temperature. This indicates that the complex formation is a spontaneous process and spontaneity increases with temperature. The observed entropy changes of the complex formation are positive in the range between 0.227 and 0.535  $\text{kJmol}^{-1}\text{K}^{-1}$ . Through the binding of ligand with the metal ions leads to more ordered system and this should lead to decrease entropy ( $-\Delta S$ ) yet the observed positive change in entropy may be due to the dissociation of ligand with ionic species that predominantly makes the net entropy change positive. As indicated in Table 1, the endothermic  $\Delta H$  values for all

**Table 1.** UV-Vis spectral data of Ligand and complexes in various solvents.

Solvents	Ligand $\lambda_{\text{max}}$ (nm)	[Zn-L <sub>4</sub> ] $\lambda_{\text{max}}$ (nm)	[Cd-L <sub>4</sub> ] $\lambda_{\text{max}}$ (nm)	[Hg-L <sub>2</sub> ] $\lambda_{\text{max}}$ (nm)
Methanol	280	246	241	234
Ethanol	278	237	233	230
DMSO	440	320	310	305

**Table 2.** Analytical data of metal-ligand stability constants, change in free energy, enthalpy and entropy of [Zn-L<sub>4</sub>], [Cd-L<sub>4</sub>] and [Hg-L<sub>2</sub>] complexes at various temperatures (298-343 K).

Temp (K)	$E_s$	$E_m$	$\alpha$	$\ln K_s$	$-\Delta G_0$ kJ/mol	$\Delta H$ kJ/mol	$\Delta S$ kJ/molK
<b>[Zn-L<sub>4</sub>]</b>							
298	2.066	2.174	0.049678	27.84	68.96	68.90	0.463
303	1.92	2.009	0.044301	28.41	71.58	71.52	0.472
313	1.86	1.925	0.033766	29.78	77.50	77.44	0.495
323	1.786	1.841	0.029875	30.40	81.63	81.57	0.505
333	1.722	1.764	0.02381	31.54	87.32	87.26	0.524
343	1.721	1.758	0.021047	32.16	91.71	91.65	0.535
<b>[Hg-L<sub>2</sub>]</b>							
298	1.95	2.397	0.186483	21.07	52.19	52.10	0.350
303	1.9	2.204	0.137931	22.63	57.01	56.92	0.376
313	1.84	2.035	0.095823	24.50	63.76	63.67	0.407
323	1.794	1.929	0.069984	26.10	70.09	70.00	0.434
333	1.752	1.838	0.04679	28.14	77.90	77.81	0.468
343	1.724	1.776	0.029279	30.50	86.98	86.89	0.507
<b>[Cd-L<sub>4</sub>]</b>							
298	2.063	2.386	0.135373	13.68	33.89	33.84	0.227
303	1.925	2.159	0.108384	14.38	36.21	36.16	0.239
313	1.851	2.009	0.078646	15.37	40.00	39.95	0.255
323	1.82	1.941	0.062339	16.09	43.20	43.15	0.267
333	1.759	1.841	0.044541	17.11	47.38	47.33	0.284
343	1.742	1.786	0.024636	18.91	53.93	53.87	0.314

L=3-(2-hydroxyphenyl)-2-iminothiazolidin-4-one.

complexes at the five different temperatures are comparable suggesting that, enthalpy is dependent on temperature in the given range (298 to 343 K). The variation in  $\Delta H$  values for all complexes provides clear evidence to the assumption that  $\Delta H$  value is dependent on the chemical structure of the complexes, that is, on strength of the M-L coordination. The observed positive entropy change and negative Gibbs energy change suggest that the complex formation is favored both by Gibbs energy as well as entropy gain. Therefore, based on the calculated values of thermodynamic parameters, order of stability of the title complexes is found to be [Zn-L<sub>4</sub>] > [Cd-L<sub>4</sub>] > [Hg-L<sub>2</sub>]. Thus, divalent Zn<sup>2+</sup> complex of imino thiazolidinone ligand has the highest value of stability constant. Generally, this order is found to be in good agreement with Irving-Williams order of stability.

## Elemental analysis

Physical properties and elemental analyses data of ligands and their complexes are presented in Tables 3 and 4. The proposed molecular formulae of the newly synthesized compounds are consistent with their analysis data of C, H, N, S and metal contents. For Zn<sup>2+</sup> and Cd<sup>2+</sup> complexes the metal-ligand ratios of 1:4 were established, whereas for Hg<sup>2+</sup> complex, 1:2 stoichiometry was recognized.

## Determination of metal contents by atomic absorption spectroscopy (AAS)

The atomic absorption spectroscopy (AAS) measurements

**Table 3.** Formula weight, % yield, melting point and elemental analyses data of the ligand and its complexes, with metals.

Compound	Mol. mass	% yield	Color	M.P ( $\pm 10^\circ\text{C}$ )	Elemental analysis calculated (experimental) %				
					C	H	N	S	M(II)
$\text{C}_9\text{H}_8\text{O}_2\text{N}_2\text{S}$	208.00	81	Pale yellow	120	51.92(51.87)	3.37(3.34)	13.46(13.39)	15.38(15.31)	-
[Zn-L <sub>4</sub> ]	893.38	74	Yellow	235	48.36(48.23)	3.13(3.08)	12.54(12.64)	14.33(14.21)	7.32(7.26)
[Cd-L <sub>4</sub> ]	940.41	77	White	244	45.94(45.44)	2.98(2.59)	11.91(12.01)	13.61(13.48)	11.95(11.88)
[Hg-L <sub>2</sub> ]	614.59	73	Yellowish brown	201	35.15(35.43)	2.28(2.34)	9.11(9.25)	10.41(10.28)	32.64(32.85)

L= 3-(2-hydroxyphenyl)-2-iminothiazolidin-4-one).

**Table 4.** FAAS analysis data for the metal-ligand complexes.

Complexes	Mol.wt	[M(II)] (ppm)	A	M(II) contents(%)	
				Calculated	Found
[Zn-L <sub>4</sub> ]	893.38	23.67	0.493	7.89	7.27
[Cd-L <sub>4</sub> ]	940.41	36.03	0.510	12.01	12.08

L= 3-(2-hydroxyphenyl)-2-iminothiazolidin-4-one; A = Absorbance.

**Table 5.** Observed IR frequencies ( $\text{cm}^{-1}$ ) of the ligand and its metal complexes.

Vibrational mode	$\text{C}_9\text{H}_8\text{O}_2\text{N}_2\text{S}$	[Zn-L <sub>4</sub> ]	[Cd-L <sub>4</sub> ]	[Hg-L <sub>2</sub> ]
$\nu\text{C}=\text{N}$	1547	1538	1546	1546
$\nu\text{C}=\text{O}$	1646	1638	1645	1645
2 <sup>o</sup> amine $\nu\text{N}-\text{H}$	3383	3380	3382	3382
$\nu\text{C}-\text{N}$ ring	1371	1362	1371	1370
$\nu\text{C}-\text{S}$	639	626	638	638
Phenol $\nu\text{OH}$	3169	-	-	-
Phenol $\nu\text{C}-\text{O}$	1040	1030, 968, 1121	1041, 968, 1131	1040, 969, 1131
$\nu\text{C}=\text{C}$ Benz	1458, 1597	1587, 1450	1595, 1458	1595, 1458
$\nu\text{C}-\text{H}$ Arom	2979	3113	3116	3115
$\nu\text{M}-\text{O}$	-	587	578	446
$\nu\text{M}-\text{N}$	-	-	-	541

L= 3-(2-hydroxyphenyl)-2-iminothiazolidin-4-one).

on the synthesized complexes were conducted to know the metal contents and the results obtained were given in Table 4. The metal to ligand ratio for  $\text{Zn}^{+2}$  and  $\text{Cd}^{+2}$  complexes were found to be 1:4 and these coincide with the elemental analysis results.

### FTIR spectral analysis results

The IR data of the spectra for the Schiff base ligand and its metal complexes were presented in Table 5. Accordingly, the IR spectra of the complexes were compared with that of pure ligand in order to determine the coordination sites that could be involved in complex formation. The perusal of Table 5 reveals that absorption

bands corresponding to two weak bands at 2979 and 2929  $\text{cm}^{-1}$ , may be attributed to aromatic and aliphatic  $\nu(\text{C}-\text{H})$  peaks respectively. These showed very small red shift in position in all three chelate complexes. The spectra of the free ligand shows a strong peak at 3383  $\text{cm}^{-1}$ , which can be attributed to secondary  $\nu(\text{N}-\text{H})$  stretching vibration in the ligand and in all its complexes. Band of the free ligand at 1646  $\text{cm}^{-1}$ , assignable to stretching vibration due to  $\nu(\text{C}=\text{N})$  groups of imino thiazolidinone, did not shift in any of the complexes, suggesting that there was no involvement of the imine nitrogen atom of the ligand in complex formations with any of the metal ions. Disappearance of the  $\nu\text{OH}$  (phenolic) band of the ligand (3169  $\text{cm}^{-1}$ ) peak size and/or appearance of new band(s) of  $\nu\text{C}-\text{O}$  (phenolic

**Table 6.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectral data for ligand and its metal complexes.

Compounds	$\delta$ (ppm)	$^1\text{H}$ NMR assignment	$\delta$ (ppm)	$^{13}\text{C}$ NMR assignment
$\text{C}_9\text{H}_8\text{O}_2\text{N}_2\text{S}$	3.85	Methylene ( $\text{CH}_2\text{-S}$ )	31.5	Aliphatic $\text{CH}_2$ S
	6.7-7.9	Aromatic H	119-125	Aromatic C
	10	Imine H ( $=\text{NH}$ )	126.5	Phenolic C( $\text{C-OH}$ )
	6.78	Phenolic H( $-\text{OH}$ )	148	Imine C( $\text{C=NH}$ )
			167.9	Carbonyl C( $\text{C=O}$ )
[Zn- $\text{L}_4$ ]	3.85	Methylene ( $\text{CH}_2\text{-S}$ )	42.90	Aliphatic $\text{CH}_2$ S
	6.7-7.9 and 9.5	Aromatic H	115.82-125	Aromatic C
			126.5	Phenolic C( $\text{C-OH}$ )
			151.2	Imine C( $\text{C=NH}$ )
			167.4	Carbonyl C( $\text{C=O}$ )
[Cd- $\text{L}_4$ ]	3.85	Methylene ( $\text{CH}_2\text{-S}$ )	42.91	Aliphatic $\text{CH}_2$ S
	6.7-7.85 and 9.4	Aromatic H	115.78-125	Aromatic C
			126.45	Phenolic C( $\text{C-OH}$ )
			149	Imine C( $\text{C=NH}$ )
			167.45	Carbonyl C( $\text{C=O}$ )
[Hg- $\text{L}_2$ ]	3.85	Methylene ( $\text{CH}_2\text{-S}$ )	42.92	Aliphatic $\text{CH}_2$ S
	6.75-7.85 and 9.4	Aromatic H	115.8-125	Aromatic C
			126.50	Phenolic C( $\text{C-OH}$ )
			147.5	Imine C( $\text{C=N}$ )
			167.41	Carbonyl C( $\text{C=O}$ )

L= 3-(2-hydroxyphenyl)-2-iminothiazolidin-4-one.

group) on complexation, and the appearance of new band at  $587\text{ cm}^{-1}$  for [Zn- $\text{L}_4$ ] complex and at  $578\text{ cm}^{-1}$  in [Cd- $\text{L}_4$ ] complex can be due to  $\nu(\text{M-O})$  band. This indicate the formation of  $\nu(\text{M-O})$  band. The other new bands appearing at  $446$  and  $541\text{ cm}^{-1}$  in the Hg complex can also substantiate the formation of  $\nu(\text{M-O})$  and  $\nu(\text{M-N})$ , respectively. These shifts of absorption bands to lower wave numbers in the complexes, strongly suggest the possible coordination of the heterocyclic nitrogen and phenolic oxygen to the metal centers. Infrared spectral studies clearly reveal that binding modes of the ligand is through deprotonated phenolic oxygen and heterocyclic nitrogen atoms and there is no role of anions from the  $\text{M}^{2+}$  salts in the inner coordination spheres of the complexes.

Therefore the ligand behaves as a neutral bidentate ligand coordinated, to Hg (II) ions, through the nitrogen atoms of the ring, and oxygen atoms of the phenolic groups to give a four membered chelate ring complexes (Viñuelas-Zahinos et al., 2011). However, the ligand acting as monodentate coordinating through phenolic oxygen in case of Zn(II) and Cd(II) complexes.

### NMR ( $^1\text{H}$ and $^{13}\text{C}$ ) spectra analysis

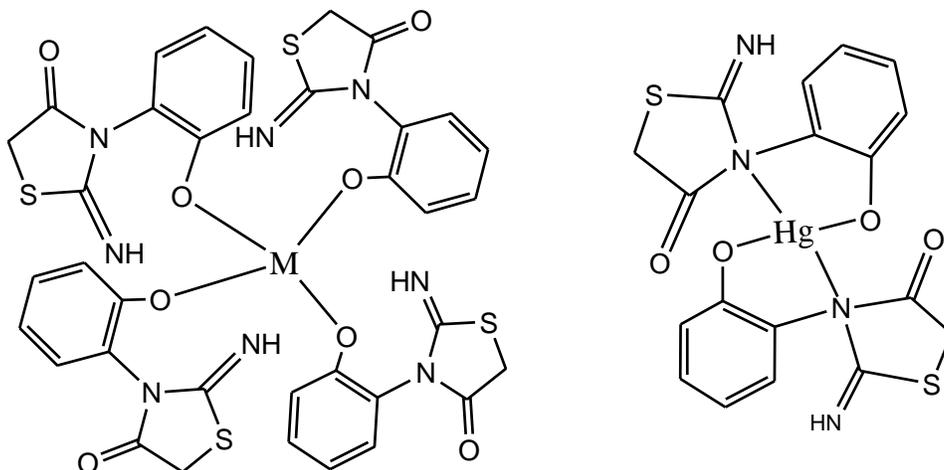
The  $^1\text{H}$ NMR and  $^{13}\text{C}$ NMR data of the 3-(2-hydroxyphenyl)-2-iminothiazolidin-4-one ligand and its complexes recorded in DMSO solvent as shown on Table 6. The  $^1\text{H}$

NMR spectral data (Table 6) of 3-(2-hydroxyphenyl)-2-iminothiazolidin-4-one displayed chemical shifts at  $\delta 3.85$  is attributed to heterocyclic (2H) between carbonyl group and heterocyclic sulfur, at  $\delta 10$  to imine (1H), at  $\delta 6.7-7.9$  and  $9.45$  to benzene ring (4H) and at  $\delta 6.78$  corresponding to phenolic (1H). On the other hands, the  $^{13}\text{C}$  NMR spectrum displays the aliphatic  $\text{CH}_2\text{-S}$  band at  $\delta 31.5$ , the HC (aromatic ring) band in the range (119-125), phenolic C( $\text{C-OH}$ ) band at  $\delta 126.5$ , imine C( $\text{C=NH}$ ) band at  $\delta 148$  Carbonyl C( $\text{C=O}$ ) display band at  $\delta 167.9$ .

As indicated in  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectral data of the ligand and its complexes, the changes with each chemical shift for the complexes were the same as the ligand. However, in the  $^1\text{H}$  NMR spectra of [Zn- $\text{L}_4$ ] and [Cd- $\text{L}_4$ ] complexes absence shifts at  $\delta 10$  were attributed to imine hydrogen. Whereas there was no  $^1\text{H}$  spectra shifts of [Hg- $\text{L}_2$ ] at  $\delta 10$  attributed to imine (1H) and  $\delta 6.78$  substantiate a phenolic H( $-\text{OH}$ ). Therefore, these results of  $^1\text{H}$  and  $^{13}\text{C}$  NMR analyses for the ligand and its complexes also support the inferences made based on the IR regarding the structure of 3-(2-hydroxyphenyl)-2-iminothiazolidin-4-one and its [Zn- $\text{L}_4$ ], [Cd- $\text{L}_4$ ] and [Hg- $\text{L}_2$ ] complexes.

### Conductivity measurements

Complexes prepared in this work showed molar



**Figure 4.** The proposed structural formula of [Zn-L<sub>4</sub>], [Cd-L<sub>4</sub>] and [Hg-L<sub>2</sub>] complexes with 3-(2-hydroxyphenyl)-2-iminothiazolidin-4-one ligand. M is Zn(II) and Cd(II).

conductance with values of 133, 125 and 122  $\mu\text{Smol}^{-1}\text{cm}^2$  for [Zn-L<sub>4</sub>], [Cd-L<sub>4</sub>] and [Hg-L<sub>2</sub>], respectively (all measured in DMSO at room temperature). These values indicate high conductivity nature of the complexes, and the molar conductance values suggested that all the complexes are electrolytes.

### Proposed structures of the synthesized complexes

Based on the inferences made from C, H, N, S and metals analyses, chloride test, conductometric, IR spectroscopy and UV/Vis or electronic spectral studies, the following general structures can be proposed for [Zn-L<sub>4</sub>], [Cd-L<sub>4</sub>] and [Hg-L<sub>2</sub>] complexes with the ligand, L, being, 3-(2-hydroxyphenyl)-2-iminothiazolidin-4-one, as presented in Figure 4.

### Conclusion

This paper reports spectrophotometric study of the metal complex of Zn<sup>2+</sup>, Cd<sup>2+</sup>, and Hg<sup>2+</sup> with heterocyclic ligand of 3-(2-hydroxyphenyl)-2-iminothiazolidin-4-one. The stoichiometric studies showed that there is a similar pattern in the optical density or absorbance of each of these complexes showing similar specific values at two temperatures giving rise to 1:4, 1:4 and 1:2 metals to ligand ratios in the complexes of [Zn-L<sub>4</sub>], [Cd-L<sub>4</sub>] and [Hg-L<sub>2</sub>], respectively. The metal-ligand complex stability constants (K<sub>s</sub> values) have been found to be in the order: [Zn-L<sub>4</sub>] > [Cd-L<sub>4</sub>] > [Hg-L<sub>2</sub>]. This order is found to be in good agreement with the Irving-Williams order of stability for divalent metal ion complexes. The conductometric study indicates the electrolytic nature of all synthesized complexes. All complexes were formulated as

mononuclear compounds involving 1:4 for Zn<sup>2+</sup> and Cd<sup>2+</sup> whereas Hg<sup>2+</sup> complex shows 1:2 metal to ligand ratio derived from elemental and metal analyses. Based on the infrared results, it is concluded that the ligand behaves as a neutral bidentate ligand coordinated to the metal ions through the nitrogen atoms of hetero cyclic groups, and oxygen atoms of the phenolic groups to give a chelating complexes. <sup>1</sup>H and <sup>13</sup>C NMR justified theoretically proposed structure of complexes from their stoichiometry. Magnetic studies indicated four coordinate tetrahedral geometry of [Hg-L<sub>2</sub>] and distorted geometries of [Zn-L<sub>4</sub>], [Cd-L<sub>4</sub>] complexes having a charge transfer transitions. The values of stability constants and negative sign of free energy changes of the complexes in the solvent used indicate that metal-ligand reactions are spontaneous and complexes are stable at room temperatures. Stability constant results suggest that ligand used is a good chelating agent for all the three metals.

### Conflict of Interest

The authors have not declared any conflict of interest

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