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Original Research Article

Synthesis, Spectral Characterization, Thermokinetics and Biological Studies of Co(II), Ni(II), Cu(II), Zn(II) and Zr(IV) Complexes Derived from Hydrazone Schiff Base

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Abstract

Mononuclear Co(II), Ni(II), Cu(II), Zn(II) and Zr(IV) complexes with new bidentate Schiff base ligand 2-hydroxy-N'-(2-oxoindolin-3-ylidene)benzohydrazide (LH₂) were synthesized and the complexes were characterized by elemental analysis, IR, FAB-mass, molar conductivities, magnetic measurements, electronic spectra and thermal analysis. The Cu(II) complex was additionally characterized by ESR study. The ligand behaves as a monobasic bidentate ligand, coordinating through azomethine Nitrogen and the deprotonated Oxygen atom. Analytical data suggested 1:2 (metal: ligand) mole ratio for all the complexes. The low molar conductance values of the all metal complexes in DMSO reveal their non-electrolytic nature. The physicochemical data suggested an octahedral geometry for Zn(II) and Zr(IV) complexes, distorted octahedral geometry for Cu(II), whereas square planar geometry for Co(II) and Ni(II) complexes. The thermodynamic analysis showed that the complexes loose hydrated and/or coordinated water molecules in the first step followed by decomposition of ligand moiety in the further steps leading to formation of stable metal oxide. The antibacterial as well as antifungal activities of the ligand and its metal complexes were evaluated.

Keywords: Salicyloyl hydrazide, Schiff base, Electronic Spectra, ESR, Thermal analysis, Antibacterial activity.

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INTRODUCTION

<u>Schiff bases</u> are extensively studied by researchers due to their admirable chelating ability with different metal ions and also their medicinal importance. The imine moiety present in the Schiff bases are responsible for a broad spectrum of applications in different fields and show pharmacology, antibacterial, antifungal, antianalgesic, anticonvulsant, antimalarial, antitumaral and antiviral activities [1, 2]. Hydrazones, an important class of Schiff bases, have been continuously studied due to their diverse and wide spectrum of biological properties and ability to act as flexidentate ligands in coordination chemistry [3-5]. As a result of significant biological applications of hydrazone metal complexes, they have received a great deal of attention [6]. Motivated by the above mentioned observations and in continuation of our keen interest in the synthesis and study of different hydrazone ligands and synthesis and characterization of their metal complexes [7], in the present work, we have synthesized a series of Co(II), Ni(II), Cu(II), Zn(II) and Zr(IV) complexes with new hydrazone Schiff base derived by the condensation of salicyloyl hydrazide and isatin. These compounds were characterizes by various spectroscopic techniques, thermal analysis and antibacterial activity against gram negative bacteria (*Escherichia coli* and *Pseudomonas*) and gram positive bacteria (*Staphylococcus aureus* and *Diplococcus pneumoniae*) & antifungal activity with two fungi (*Candida albicans* and *Trichophyton rubrum*) by disc diffusion method.

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EXPERIMENTAL SECTION

Materials

All the chemicals and reagents used in this work were of analytical grade (Aldrich) and used without further purification. The solvents were of analytical grade and purified by standard methods [8]. Isatin, salicyloyl hydrazide, acetate salts of Co(II), Ni(II), Cu(II) and Zn(II) and oxychloride salt of Zr(IV) were used in the synthesis of the complexes.

Analytical and Physical measurements

The elemental analyses (C, H and N) were performed at C. D. R. I., Lucknow. The infrared spectra of all the synthesized compounds were recorded in the region 4000-400 cm⁻¹ in KBr pellet on a Shimadzu spectrophotometer (L1280032) spectrophotometer at Central Instrumentation Cell, Shri Shivaji Science College, Amravati. The electronic spectra of all the compounds were recorded in DMSO on a Shimadzu (UV-1800 Series) spectrophotometer in the region 200-800 nm. Room temperature molar conductance of the complexes (DMSO) was recorded on the Equip-Tronic conductivity meter at a conc. of 10⁻³ M. The ¹H NMR spectrum of synthesized ligand was recorded using DMSO and TMS as an internal standard on Bruker DRX500 NMR spectrometer, National Chemical Laboratory (CSIR-NCL), Pune. The magnetic susceptibility values of complexes were recorded at room temperature by the Gouy method. Thermal analysis results of the complexes were obtained at a rate of 10°C per minute on a Shimadzu DTA-60 thermodilatometer.

Synthesis of the Schiff base(LH₂)

2-hydroxy-N'-(2-oxoindolin-3-

ylidene)benzohydrazide (LH₂) was prepared by the method reported earlier [9]. The mixture of salicyloyl hydrazide (1.52 g, 0.01 mol) and isatin (1.47 g, 0.01 mol) (1:1 ratio) in absolute ethanol was refluxed in a waterbath for 4-6 h as shown in Scheme 1. The reaction mixture was then allowed to cool at room temperature for half an hour. The yellow precipitate of the ligand so

obtained was filtered off, washed with cold water and dried under vacuum. The product was recrystallized from ethanol and its purity was checked by thin layer chromatography (TLC).

Synthesis of metal complexes

An ethanolic solution of the ligand (LH_2) (0.002 was added to an ethanolic solution of mol) Co(OCOCH₃)₂.4H₂O, Ni(OCOCH₃)₂.4H₂O and Cu(OCOCH₃)₂.H₂O, Zn(OCOCH₃)₂.2H₂O (0.002 mol). The resulting mixture was refluxed for about 4 h on a water bath. In the preparation of Zr(IV) complex, oxozirconium(IV) diacetate was prepared by stirring a methanolic solution of ZrOCl₂.8H₂O (0.002 mol) with a methanolic solution of anhydrous sodium acetate (0.004 mol). The separated sodium chloride in the mixture was filtered off and an ethanolic solution of the ligand (0.002 mol) was added into the mixture (1:4 v/v) refluxed under water bath for 4-6 h. All the solid products obtained were filtered off, washed 2-3 times with an alcohol followed by petroleum ether to remove unreacted ligand and corresponding metal salts. Finally dried and stored in vacuum over fused calcium chloride (yield 50-55%).

Test organisms and determination of zone of inhibition

In present study, antibacterial and antifungal studies of synthesized compounds was carried out by disc diffusion method in which sterile Whatman filter paper disc were impregnated with 20µl of different samples. The test organism's cultures of gram negative bacteria (Escherichia coli and Pseudomonas) and gram positive bacteria (Staphylococcus aureus and Diplococcus pneumoniae) and two fungi (Candida albicans and Trichophyton rubrum) were obtained from the Samruddhi Microbiology Diagnostic Lab, Amravati, Maharashtra, India. The bacterial isolates were standardized by colony suspension and matching the strain's suspension with 0.5 McFarland standard to give a final concentration of 1.5 x 10⁸cfu/mL. The culture of each of the respective organism was spread on the

surface of sterile Mueller Hinton Agar plates. The impregnated discs with respective samples were then placed on the inoculated surface of the agar plates. The agar plates were incubated at 37^{0} C for one day. Antibacterial activity of each sample against the test species was measured by growth free "zone of inhibition" near the respective spots [10-11]. The assay was performed in triplicate.

RESULTS AND DISCUSSION

Scheme 1 represents formation of ligand (LH₂) by the reaction of salicyloyl hydrazide with isatin (1:1) in ethanol. The analytical and physical data of the ligand and its complexes are summarized in Table 1. All the synthesized complexes are colored and non-hygroscopic solids, stable in air, insoluble in water and common organic solvents but soluble in coordinating solvents like DMF and DMSO. The molar conductance values of all

the complexes in DMSO (10^{-3} M) are low (5.25-22.81 Ω^{-1} ¹cm²mol⁻¹) indicating their non-electrolytic nature. The mass spectra of all the compounds exhibited parent peaks due to formation of molecular ions (M⁺). The proposed molecular formulae of these complexes were confirmed by comparing their molecular formula weights with the m/z values. The molecular ion peaks obtained were as follows: *m*/*z* 282, 639, 693, 664, 715 and 706 for ligand, Co(II), Ni(II), Cu(II), Zn(II) and Zr(IV) complex respectively. The resultant mass spectral data are in good agreement with those calculated for the suggested molecular formula of the complexes. In addition to the molecular ion peaks, the spectra exhibited different peaks assignable to various fragments arising from the thermal cleavage of the complexes. From the analytical data, the stoichiometry of the complexes suggested as 1:2 (metal: ligand) for all the synthesized complexes in present work.

Compound	Color	Molar cond.	Yield (%)	% Found (calcd.)				Formula Weight		
		$(\Omega^{-1} \text{ cm}^2 \text{mol}^{-1})$		M %	С%	Н%	N %			
LH ₂	Yellow	-	79	-	60.87	6.05	17.41	281		
					(64.05)	(4.94)	(14.94)			
$[Co(LH)_2].H_2O$	Brown	22.81	54	9.19	56.49	3.59	13.02	637		
				(9.24)	(56.52)	(3.48)	(13.18)			
$[Ni(LH)_2].4H_2O$	Brown	12.54	63	8.45	52.03	4.16	12.03	691		
				(8.39)	(52.12)	(4.08)	(12.16)			
$[Cu(LH)_2(H_2O)_2]$	Brown	5.32	61	9.60	54.52	3.41	12.80	660		
				(9.63)	(54.59)	(3.66)	(12.73)			
$[Zn(LH)_2(H_2O)_2].3H_2O$	Orange	5.25	59	9.16	50.29	4.29	11.81	715		
	-			(9.13)	(50.33)	(4.22)	(11.74)			
$[Zr(LH)_2(OH)_2].H_2O$	Yellow	5.62	64	12.89	51.05	3.36	11.79	703		
				(12.96)	(51.20)	(3.44)	(11.94)			

 Table-1: The analytical and physical data of the compounds

¹H NMR spectrum of the ligand



The ¹H NMR spectrum of ligand showed signals at 5.15 ppm corresponding to proton of phenolic OH. The signals observed at 7.00 and 8.32 ppm may be due to the -NH (hydrazide) and -NH (secondary amide) respectively. The aromatic protons showed signals in the range 6.58-7.78 ppm [7] as shown in Figure 1.

IR spectra

The IR spectra data of Schiff base ligand and its complexes are presented in Tables 2. To study the binding modes of ligand toward metal ion, the data of the ligand was compared with those of respective metal complexes. The important IR frequencies appeared in the spectrum of the ligand at 3171, 1666, 1612 and 1311cm⁻ ¹ correspond to v(N-H), v(C=O), v(C=N) and v(C-O)phenolic stretching vibration respectively [12, 13]. The band at 3275 cm⁻¹ due to intramolecular H-bonded v(O-H) group in the spectrum of free ligand disappeared in spectra of all the complexes and the v(C-O phenolic)band at 1305 cm⁻¹, shifted to higher frequency by 6-10 cm cm⁻¹, suggest the coordination of ligand through phenolic oxygen via deprotonation [14-17]. In all the complexes, a new band appeared in the region 1248-1254cm⁻¹ due to the destruction of carbonyl moiety as a result of the enolisation [18-22].

IR spectra of all the complexes exhibited v(N-H) and v(C=O) vibrations of the indole ring system almost at the same frequency as that of the free ligand, indicating non involvement of this groups in

coordination with metal ion [23-24]. The v(C=N) band in the spectrum of ligand is found to be shifted to lower frequencies by 31-38 cm⁻¹ in the spectra of all the complexes, indicating the coordination via azomethine nitrogen [16, 20]. This coordination is further supported by the shift of v(N-N) vibration of ligand from 1008 cm⁻ ¹ to a higher frequency by 24-37cm⁻¹ in the spectra of complexes [7, 16, 20]. The far IR spectra of the complexes showed new bands in the region 477-498cm⁻¹, corresponding to v(M-N) vibrations, which supports complexation of the azomethine nitrogen. Also in addition to the above bands, the spectra of complexes displayed the bands in the region at 576-591cm⁻¹ assigned to v(M-O) vibrations [7, 12]. The IR spectra of Cu(II) and Zn(II) complexes exhibited characteristic bands of coordination water in the range 3430-3495, 1612, 820-879 and 740-756 cm⁻¹ assigned to v(OH), $\delta(H_2O)$, $\rho_r(H_2O)$ and $\rho_w(H_2O)$ vibrations respectively [15, 16]. The IR spectra of Co(II), Ni(II) and Zr(IV) complexes exhibited the bands 3464, 3554 and 3439cm⁻ ¹ corresponds v(OH) respectively. Non-appearance of $\rho_r(OH)$ and $\rho_w(OH_2)$ bands the spectra of these complexes suggested only presence of water of hydration and not that of coordinated water molecules in them. The spectrum of Zr(IV) complex displayed new band at 1103 cm^{-1} due to v(Zr-OH) vibrations [15]. Thus, the IR spectral data suggests monobasic bidentate (ON) nature of the ligand towards these metal ions.

Compound	v(O-H) hydrogen bonded	v(N-H)	Coordinated water v(OH)	v(C=N)	v(C-O) phenolic	v(C-O) enolic	v(N-N)	v(M-O)	ບ(M- N)
LH ₂	3275	3171	-	1612	1305	-	1008	-	-
$[Co(LH)_2].H_2O$	-	3170	3464	1581	1311	1252	1029	576	482
[Ni(LH) ₂].4H ₂ O	-	3171	3554	1577	1314	1254	1025	578	498
$[Cu(LH)_2(H_2O)_2]$	-	3171	3495	1576	1313	1251	1027	582	494
$[Zn(LH)_2(H_2O)_2].3H_2O$	-	3171	3430	1574	1315	1248	1024	591	490
$[Zr(LH)_2(OH)_2].H_2O$	-	3171	3439	1580	1311	1251	1045	580	477

Table-2: Infrared frequencies (cm⁻¹) of the ligand LH₂ and its metal complexes

Electronic absorption spectra and magnetic moments

The electronic absorption spectral data and magnetic moments of the metal complexes are listed in Table-3. The electronic spectrum of the Co(II) complex exhibited two bands at 368 and 565 nm assigned to LMCT and ${}^{1}A_{1g} \rightarrow {}^{1}B_{1g}$ transitions respectively. These bands significantly suggest square planar geometry for Co(II) complex [25]. The measured magnetic moment at 3.05 B.M. also supports the expected square planar geometry for Co(II) ion [26]. The electronic spectra of Ni(II) complex exhibited three d-d bands at 540, 742 and 778 nm due to ${}^{1}A_{1g} \rightarrow {}^{1}A_{2g}$, ${}^{1}A_{1g} \rightarrow {}^{1}B_{2g}$ and ${}^{1}A_{1g} \rightarrow {}^{1}E_{g}$ transitions in favour of square planar geometry around Ni(II) ion [27, 28]. The electronic spectrum of the Cu(II) complex showed the first band at 565 nm assigned to the $^{2}E_{g}\rightarrow^{2}T_{2g}$ transition which suggests a distorted octahedral arrangement around the metal ion [29]. The distortion may be due to the Jahn-Teller effect since the transition indicates the further splitting of both ${}^{2}E_{\sigma}$ and ${}^{2}T_{2g}$ due to deviation of symmetry from O_{h} to D_{4h} symmetry. The ESR spectrum of Cu(II) complex (Figure 2) supports the absence of any metal-metal interaction with the neighboring molecules, also confirmed by the magnetic moment 1.74 B.M which is at the expected normal range for Cu(II) monomeric complex [7, 30]. The Zn(II) complex exhibited two bands at 284 and 370 nm correspond to charge transfer transition. The metal atom in Zn(II) complex suggests to be six coordinated by two hydrazone ligands to form octahedral coordination [31]. The electronic spectrum of Zr(IV) chelate displayed absorption band at 383 nm due to charge transfer transition [15, 32-33]. The magnetic susceptibility measurements reveals the both Ni(II), Zn(II) and Zr(IV) complexes are diamagnetic as expected.

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Compound	v(nm)	d-d transition	$\mu_{\rm eff}({ m BM})$
LH ₂	380	$n \rightarrow \pi^*$	-
	285	$\pi \rightarrow \pi^*$	
$[Co(LH)_2].H_2O$	368	LMCT	3.05
	565	${}^{1}A_{1g} \rightarrow {}^{1}B_{1g}$	
[Ni(LH) ₂].4H ₂ O	540	$^{1}A_{1g} \rightarrow ^{1}A_{2g}$	Diamagnetic
	742	${}^{1}A_{1g} \rightarrow {}^{1}B_{2g}$	
	778	${}^{1}A_{1g} \rightarrow {}^{1}E_{g}$	
$[Cu(LH)_2(H_2O)_2]$	565	$^{2}E_{g}\rightarrow ^{2}T_{2g}$	1.74
	410	LMCT	
[Zn(LH) ₂ (H ₂ O) ₂].3H ₂ O	370	СТ	Diamagnetic
	284	CT	
$[Zr(LH)_2(OH)_2].H_2O$	383	LMCT	Diamagnetic

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ESR Spectra

X-Band ESR spectrum of Copper(II) complex was recorded at 299 K (solid state) and at 77 K (Figure 2 and 3). The spectral parameters are summarized in Table 4. It exhibited an axially symmetric *g*-tensor parameters with $g_{\parallel} = 2.27 > g_{\perp} = 2.06 > 2.0023$. The g values reflect tetragonally distorted octahedral geometry for Cu(II) center with the presence of $d_x 2_{-y} 2$ ground state [34, 35]. The tetragonally distorted octahedral geometry of complex is supported from an index of tetragonal distortion, impirical factor $f = g_{\parallel}/A_{\parallel}$ cm⁻¹ was found to be 137 cm⁻¹ [36]. For a covalent complex, $g_{\parallel} < 2.3$, and for the ionic environment, normally $g_{\parallel} = 2.3$ or more. For

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present Cu complex, $g_{\parallel} > 2.3$ (i.e. 2.26 in solid-state) indicating covalent nature of M-L bond in this complex. In axial symmetry the *g*-values are related to the *G*-factor by the expression, $G = g_{\parallel} - 2.002/g_{\perp} - 2.002=4$ which measures the exchange interaction between Copper centers in the solid complex [37]. According to Hathaway, if the value of *G* is greater than 4, the exchange interaction between Copper(II) centers in the solid state is negligible. The calculated G=4.18 in present work supports the absence of exchange coupling between Copper(II) centers in the solid state.

Table-4: ESR data of Cu(II) Complex

Complexes		Spectr	Spectral Parameters							
		g_{\parallel}	g_{\perp}	g	A_{\parallel}	A_{\perp}	A	α^2	β^2	
Cu(II)	RT	2.261	2.061	2.12	-	-	-	-	-	
	LNT	2.278	2.068	2.13	166.5	24.1	71.56	0.465	0.341	



Fig-2: ESR spectrum of Cu(II)complex (RT)



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Fig-3: ESR spectrum of Cu(II)complex (LNT)

Thermal analysis

Thermal decomposition of metal complexes is an important study as it provides useful information about the thermal stability of complexes as well as the coordination ability of water whether it is inside the coordination sphere or outside. The half decomposition temperature, Entropy Change (Δ S), Free Energy Change (ΔF) and Frequency Factor (Z) of compounds were calculated by employing Freeman-Caroll and Sharp-Wentworth method [38, 39]. The thermal curves of ligand and its complexes were obtained with heating rate 10° C min⁻¹ are provided in Figure 4, while the kinetic parameters are assigned in Table 5. The ligand showed two-step decomposition pattern with the lowest half decomposition temperature. The Co(II), Ni(II), Cu(II) complexes showed a three-stage and Zr(IV) decomposition pattern whereas Zn(II) complex indicate a four-stage decomposition pattern. The Co(II) and Zr(IV) complexes showed the elimination of one lattice water molecule whereas, Zn(II) and Ni(II) complexes exhibit loss of three and four water molecules respectively up to 140°C indicates the presence of noncoordinated water molecules in the complexes. On the other hand, Cu(II) and Zn(II) complexes exhibited loss of two water molecules between 140- 220°C which indicates the presence of coordinated water molecules in the complexes. [% wt. loss, obs./calcd.] Co(II):3.00/2.82, Ni(II):10.80/10.41, Zn(II):7.32/7.54, Zr(IV):2.76/2.54 for lattice water while Cu(II):5.36/5.45 and Zn(II):5.23/5.02 for coordinated water. Further weight loss was been observed above 250°C, which may be due to the thermal degradation of the free part of the ligand moiety along with some other side chain present in the complexes. A gradual weight loss observed above 450° C, due to the degradation of the actual coordination part of the ligand and TG curves attain a horizontal level above 580° C suggesting the formation respective stable metal oxides. From the half decomposition temperature, the relative thermal stability of the compounds is found to be Co(II)>Cu(II)>Zr(IV)>Zn(II)>Ni(II) > LH_2.

Fig-4: Thermal graph of LH₂ and its metal complexes

Compounds	Half Decomposition	Activation Energy		Order of Reaction	Entropy Change	Free Energy Change	Apparent Entropy Change
	(°C)	FC	SW	(11)	(J/mol/K)		S^* (kJ)
LH ₂	310	19.72	20.67	0.95	-152.31	108.62	-25.41
$[Co(LH)_2].H_2O$	410	15.23	16.98	0.97	-192.11	131.23	-25.54
[Ni(LH) ₂].4H ₂ O	330	17.97	18.37	0.95	-139.58	84.18	-25.44
$[Cu(LH)_2(H_2O)_2]$	400	17.23	19.01	0.98	-134.10	90.27	-25.67
$[Zn(LH)_2(H_2O)_2].3H_2O$	370	15.85	16.74	0.99	-123.95	79.71	-25.63
$[Zr(LH)_2(OH)_2].H_2O$	382	19.10	20.43	0.97	-147.85	96.86	-25.51

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Biological Activity

The Schiff base and its complexes were screened for their biological study. The test organism's cultures of gram negative bacteria (*Escherichia coli* and *Pseudomonas*) and gram positive bacteria (*Staphylococcus aureus* and *Diplococcus pneumoniae*) and two fungi (*Candida albicans* and *Trichophyton rubrum*). Both Co(II) and Ni(II) complexes showed very good activity towards *Pseudomonas*, *S. aureus*, *D. pneumonia* and *C. albicans*. The ligand and metal complexes showed good activity in the order Co(II) >

 $Ni(II) > Zn(II) > LH_2 > Cu(II) > Zr(IV)$. According to the chelation theory of coordination chemistry, the polarity of central metal atom descends after complexation, which results in ascending lipophilic nature of the central atom and enhanced permeation of the complexes through the lipid layer of the cell membrane [40, 41]. It has been observed that the metal complexes show enhanced antibacterial activity for Co(II), Ni(II) and Zn(II) complex as compared to the LH₂ against the same microorganism under identical experimental conditions, this is due to complexation.

Table-6: Antibacterial activity of the ligand LH₂ and its metal complexes

Sr. No.	Ligand and its complexes	Inhil	bition Zone (mm				
		Gram - ve		Gram	+ ve	Fungus	
		<i>E</i> .	Pseudomonas	<i>S</i> .	<i>D</i> .	C. albicans	Т.
		coli		aures	pneumoniae		rubrum
1	LH_2	-	-	-	02	02	03
2	Co- LH ₂	04	10	12	14	12	02
3	Ni- LH ₂	-	06	14	12	12	01
4	Cu-LH ₂	-	03	02	03	03	-
5	Zn-LH ₂	-	02	07	04	02	02
6	Zr- LH ₂	-	-	-	-	-	09

CONCLUSION

The Schiff base, 2-hydroxy-N'-(2-oxoindolin-3-ylidene)benzohydrazide coordinates to the Co(II), Ni(II), Cu(II), Zn(II) and Zr(IV) metal ions acted as monobasic bidentate (ON) donor ligand. The assignment of distorted octahedral geometry for Cu(II) complex, octahedral geometry for Zn(II) and Zr(IV) complexes while square planer to Co(II) and Ni(II) complexes is substantiated by magnetic, thermal, infrared and electronic spectral measurements. The observed hyperfine splitting constant (A) and (g) parameters from the ESR spectra of complex confirmed the distorted octahedral geometry for the Cu(II) complex. The presence of lattice and coordinated water molecules was confirmed from the IR frequencies and thermograms of complexes. The activation energy calculated by the Freeman-Caroll and Sharp-Wentworth methods are in good agreement with each other. The ligand as well as some metal complexes showed antibacterial activity against selected kind of bacteria. The probable structures of complexes are shown below, Fig-5.

 $\begin{array}{l} \mathsf{M}{=}\mathsf{Co}(\mathsf{II}), \ \mathsf{X}{=}\mathsf{Y}{=}\mathsf{nil}, \ \mathsf{Z}{=}\mathsf{H}_2\mathsf{O}.\\ \mathsf{M}{=}\mathsf{Ni}(\mathsf{II}), \ \mathsf{X}{=}\mathsf{Y}{=}\ \mathsf{nil}, \ \mathsf{Z}{=}4.\mathsf{H}_2\mathsf{O}.\\ \mathsf{M}{=}\mathsf{Cu}(\mathsf{II}), \ \mathsf{X}{=}\mathsf{Y}{=}\ \mathsf{H}_2\mathsf{O}, \ \mathsf{Z}{=}\mathsf{nil}.\\ \mathsf{M}{=}\mathsf{Zn}(\mathsf{II}), \ \mathsf{X}{=}\mathsf{Y}{=}\ \mathsf{H}_2\mathsf{O}, \ \mathsf{Z}{=}3.\mathsf{H}_2\mathsf{O}.\\ \mathsf{M}{=}\mathsf{Zr}(\mathsf{VI}), \ \mathsf{X}{=}\mathsf{Y}{=}\mathsf{OH}, \ \mathsf{Z}{=}\mathsf{H}_2\mathsf{O}. \end{array}$

Fig-5: The probable structure for Co(II), Ni(II), Cu(II), Zn(II) and Zr(IV) metal complexes

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