

## Journal of Advanced Scientific Research

ISSN **0976-9595** *Research Article* 

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# SYNTHESIS, SPECTRAL CHARACTERIZATION, THERMAL AND BIOLOGICAL STUDIES OF CU(II), CO(II), TH(IV) AND ZR(IV) COMPLEXES WITH SYMMETRIC THIOCARBOHYDRAZONE LIGAND

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#### ABSTRACT

The thiocarbohydrazone Schiff base ligand  $(LH_2)$  was synthesized by the condensation of thiocarbohydrazide and 1-(5bromo-2-hydroxyphenyl)ethanone. Such Schiff base ligand with heteroatoms such as nitrogen, oxygen and sulphur as donor atoms have unique tendency to conjugate with metal ion for the formation of metal complexes. By knowing this fact, a series of Cu(II), Co(II), Th(IV), and Zr(IV) metal complexes were synthesized from  $(H_2L)$  Schiff base ligand and characterized by using spectroscopic techniques.

IR spectra reveal that co-ordination of the ligand with metal ion resulting into mononuclear complexes. The ligand mainly coordinates through the hydroxyl oxygen and azomethine nitrogen to give five membered rings in some cases. Molar conductance values of synthesized metal complexes in DMF indicate the nonelectrolytic nature of the complexes. From the observed magnetic moment and electronic spectral data, probable structures for the complexes have been proposed. The thermal behavior of ligand and metal complexes shows the presence of lattice and the co-ordinate water around their co-ordination sphere. The synthesized Schiff base ligand and its complexes were also tested for their antimicrobial activity against *E. Coli, S. aureus, S. epidermis, and K. pneumoniae*.

Keywords: Thiocarbohydrazide, Metal Complexes, IR, Electronic Spectra, Freemann-Caroll

### 1. INTRODUCTION

Schiff base complexes of transition metals are of particular interest to inorganic chemists because of their structural, spectral and chemical properties are often strongly dependant on the nature of ligand structure. Study of compounds of oxygen, nitrogen and sulphur are extensive as it includes effects of donor sites and electron delocalisation in transition metal complexes [1]. Field of schiff base complexes is fast developing because of the wide variety of possible structures for the ligands [2]. Antimicrobial activities of thiosemicarbazones had been studied comparative to thiocarbohydrazones [3]. Thiocarbohydrazides can exist in thioenol and thioketo forms and as other sulphurs donors can act as bridging sites allowing various structural possibilities with different stereo-chemistries [4, 5]. There is no report on the synthesis of metal complexes with the schiff base derived from thiocarbohydrazide and 1-(5-bromo-2hydroxyphenyl)ethanone. As part of our investigation we have synthesized the Schiff base ligand LH<sub>2</sub> (Scheme 1) and its Cu(II), Co(II), Th(IV) and Zr(IV) complexes. The antimicrobial thermal analysis of compounds was examined in present study. Most Schiff bases are

chemically unstable and show 'tautomeric' interconversions therefore, successful application of Schiff bases requires a careful study of characteristics their metal complexes.





### 2. MATERIALS AND METHODS

### 2.1. Materials and physical measurements

All the chemicals were obtained from S D Fine and Aldrich and were used without further purification. The solvents were of analytical grade and purified by standard methods. The C, H, N elemental analyses were carried out at Sophisticated Analytical Instrumentation Facility (Chandigarh). The IR spectra of the ligand and complexes were recorded in the 4000-400 cm<sup>-1</sup> region in KBr disks. FT-IR instrument which was used during research work is of Perkin-Elmer spectrophotometer (L1280032). The electronic spectra of the ligand and complexes were recorded on a Shimadzu UV-1800 Series UV/Vis spectrophotometer in the region 200-800 nm. Room temperature molar conductance of the complexes in DMF was recorded on Equip-Tronic conductivity meter at a conc. of 10<sup>-3</sup> M. <sup>1</sup>H NMR spectra of the ligand and the complexes were recorded in DMSO-d6 solution on a Bruker 300-FT-NMR spectrophotometer. ESR spectra were recorded on a JES - FA200 ESR Spectrometer at IIT Mumbai. The magnetic susceptibilities were recorded at room temperature by Gouy method. Thermal analysis of complexes was carried out by heating in air at a rate of 10°C per minute on a Rijaku-Thermo plus EVO2 thermodilatometer.

## 2.2.Synthesis

## 2.2.1. Synthesis of the thiocarbohydrazone ligand (LH<sub>2</sub>)

The mixture of thiocarbohydrazide (0.01mole, 0.91g) and p-bromoacetophenone and (0.02mol, 4.3g) in absolute ethanol (20 mL) was refluxed for 2 h. The reaction mixture was allowed to cool to room temperature for half an hour. Then, yellow precipitate was filtered off and washed several time with absolute ethanol. The crystalline yellow solid obtained was purified by re-crystalization from hot absolute ethanol and dried (yield 73%). The analytical and physical data for the LH<sub>2</sub> ligand and its metal complexes are listed in Table 1.

## 2.2.2. Synthesis of the Cu(II), Co(II), Th(IV) and Zr(IV) complexes of ligand (LH<sub>2</sub>)

An ethanolic solution of the ligand  $LH_2$  (0.002 mol) was added to ethanolic solution of  $Cu(CH_3COO)_2.H_2O$ ,  $Co(CH_3COO)_2.4H_2O$ ,  $Th(NO_3)_4.4.H_2O$ , and  $ZrOCl_2.8H_2O$  (0.002 mol). The resulting mixture was refluxed for about 4 h on a water bath. The solid product obtained on cooling was filtered, washed thoroughly with ethanol and finally with petroleum ether to remove unreacted ligand and metal salts. Finally dried and stored in vacuum over fused calcium chloride (yield 71-75%).

## 2.3. Antimicrobial activity

In the disc diffusion test sterile Whatman filter paper (number-01) disc were impregnated with  $20\mu$ l of different samples [6]. At 24 h, broth culture of each of the respective species mentioned above 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  $37^{\circ}$ C for 24hr. Antimicrobial activity of each sample against the test species was measured by growth free "zone of inhibition" near the respective discs. The assay was performed in triplicate. The bacterial strains, *E. coli* (ATCC 14948), *K. pneumoniae* (MTCC 4030), *S. aureus* (ATCC 33591) and *S. epidermis* (MTCC 3086) were used in the study.

## 3. RESULTS AND DISCUSSION

Condensation of thiocarbohydrazide and 1-(5-bromo-2-hydroxyphenyl) ethanone in ethanol yields the Schiff base (LH<sub>2</sub>). All the complexes derived from LH<sub>2</sub> are colored, non-hygroscopic solids and stable in air. They are insoluble in water, but soluble in coordinating solvents like DMF and DMSO. The molar conductance values of  $10^{-3}$ M solutions of complexes lie in the range 5-10  $'\Omega^{-1}$  cm<sup>2</sup>mol<sup>-1</sup>, indicating the non-electrolytic nature of the complexes shown in **Table 1**.

Compound	Color	Yield		%Found (calcd.)				
Compound	COIOI	(%)	С %	Н%	N %	M %	Mass	
LH <sub>2</sub>	Yellow	72	40.82 <b>(40.82)</b>	3.22 <b>(3.22)</b>	11.20 <b>(11.20)</b>	-	501	
$[Co(L)].H_2O$	Brown	72	32.42 <b>(35.50)</b>	3.06 <b>(2.80)</b>	9.45 <b>(9.74)</b>	9.94 <b>(10.25)</b>	575	
$[Cu(L)(H_2O)_2]$	Pale brown	74	35.22 <b>(34.16)</b>	2.78 <b>(3.04)</b>	9.66 <b>(9.37)</b>	10.96 <b>(10.63)</b>	597	
$[Th(L)(NO_3)_2].2H_2O$	Brown	71	23.90 <b>(25.81)</b>	1.65 <b>(1.66)</b>	9.84 <b>(8.85)</b>	27.16 <b>(29.33)</b>	890	
[Zr(L)O].H <sub>2</sub> O	Brown	73	32.75 <b>(33.73)</b>	2.59 (2.33)	8.99 <b>(9.25</b> )	14.63 <b>(15.07)</b>	623	

Table 1. Analytical and physical data of ligand and metal complexes

### 3.1.IR spectra

The characteristic bands of the compounds are assigned in **Table 2**. The infrared spectrum of  $LH_2$  shows bands at 3267 and in the lower ranges of 3161 and 3241cm<sup>-1</sup> assigned for vNH groups, the lower appearance of the second NH group may support its participation in hydrogen bonding [7]. The two bands at 1643 and 1084 cm<sup>-1</sup> for v(C=N) and v(N-N) vibrations, respectively [8]. The careful comparison between IR spectra of  $LH_2$  and each complex spectrum reflects the following observations:

(i) The negative shift (06-54 cm<sup>-1</sup>) observed on v(C=N) band,

(ii) The positive shift (01-33 cm<sup>-1</sup>) observed for v(N-N) band,

(iii) The coordination of azomethine nitrogen is also consistent with the presence of new band at the range

(446-488 cm<sup>-1</sup>) assignable to the v(M-N) vibration [9, 10],

(iv) The coordination via thiolate sulphur is indicated by the absence of v(C=S) vibration with the simultaneous appearance of new bands. Such vibration was not observed in synthesized complexes. In the IR spectra of the ligands, the band at 1281cm<sup>-1</sup> is ascribed to the stretching vibration of the phenolic (C-O). This band is shifted to lower frequency (1230–1251 cm<sup>-1</sup>) in IR spectra of the metal complexes indicating that the metal ions are coordinated through the oxygen atoms of the phenolic groups after deprotonation [11]. Such observations proposed the coordination feature of the ligand with Cu(II), Co(II), Th(IV) and Zr(IV) investigated metal ions in a mononuclear structure (**Table 2**).

Compound	H bonded- OH stretching	ט(N-H)	Coordinated water ບ(OH)	υ(C=N)	υ(C-O) phenolic	υ(N-N)	υ(M-O)	υ(M-N)
LH <sub>2</sub>	2726	3267	-	1643	1281	1084	-	-
$[Co(L)].H_2O$	-	3161	-	1637	1230	1085	588	472
$[Cu(L)(H_2O)_2]$	-	3195	-	1589	1252	1087	577	488
[Th(L)(NO <sub>3</sub> ) <sub>2</sub> ] .2H <sub>2</sub> O	-	3241	3357	1617	1249	1071	565	468
$[Zr(L)O].H_2O$	-	3206	3515	1598	1248	1117	581	446



3.2. <sup>1</sup>H NMR spectrum of ligand

Fig. 1: <sup>1</sup>H NMR spectrum of LH<sub>2</sub> Ligand

## 3.3.Electronic absorption spectra and magnetic moments

The electronic spectrum of Co(II) complex shows band in the region 378 and 515 nm ascribe to INCT and  ${}^{1}A_{1}g$  $\rightarrow$  <sup>1</sup>B<sub>1</sub>g transition. The values are matched to the square planar geometry for Co(II) complex. The magnetic moment values i.e. 3.88 also suggest the square planar geometry for Co(II) complex [12]. The electronic spectrum of the Cu(II) complex shows band at 560 nm assigned to the  ${}^{2}E_{\sigma} \rightarrow {}^{2}T_{2}g$  transition which may suggest a distorted octahedral arrangement around the metal ion. The distortion may be due to Jahn Teller effect. The broadness of band clearly indicates the further splitting of both  ${}^{2}E_{g}$  and  ${}^{2}T_{2g}$  due to departurate of symmetry from O<sub>h</sub> to D<sub>4h</sub> symmetry. Clear resolution of ESR spectrum supported absence of any metal-metal interaction with the neighboring molecules which is confirmed by normal magnetic moment 1.84BM corresponding to one unpaired electron [13-16]. Th(IV) complex exhibited only a broad band around 322 nm which was assigned to  $L \rightarrow M$  charge transfer transition and are not of help in deciding the geometry around the central thorium metal ion [17]. The electronic spectrum of Zr(IV) chelate displays two absorption bands at 250 nm and 340 nm due to charge transfer transition [18]. Overall Electronic and magnetic data of compounds is shown in **Table 3**.

## 3.4. Mass Spectral studies of Schiff base and its complexes

The mass spectra of newly investigated compounds were recorded and investigated. The molecular ion peaks confirmed the proposed formulae. The mass spectrum of the studied Schiff base show the Fragment at m/z = 501 is due to the original molecular weight of the free Schiff base (H<sub>2</sub>L).

Compound	v(nm)	d-d transition	$\mu_{\rm eff}({ m BM})$	Geometry	Molar cond.
					$(\Omega^{-1} \operatorname{cm}^2 \operatorname{mol}^{-1})$
TTT	215	$\pi { ightarrow} \pi^*$			
Ln <sub>2</sub>	350	$n \rightarrow \pi^*$	-	-	-
	515	$^{1}A_{1}g \rightarrow ^{1}B_{1}g$	3.88	Square	7 18
$[CO(L)].\Pi_2O$	365	INCT	5.00	Planer	7.10
$[Cu(L)(H_2O)_2]$	560	$^{2}E_{g}\rightarrow ^{2}T_{2}g$	1.84	Octahedral	6.92
$(Tb(I)(NO)) \downarrow 2HO$	377	L→M	Diamagnetic	Octobodral	8 56
[III(L)(IVO <sub>3</sub> ) <sub>2</sub> ].2II <sub>2</sub> O	522	Charge Transfer	Diamagnetie	Octanedia	0.50
$[7r(I) \cap ] H \cap$	250	Charge Transfer	Diamagnetic	Octahedral	5 10
$[21(1)0].11_{2}0$	330	Charge Transfer	Diamagnetic	Octaileurai	5.10

Table 3: Electronic and magnetic data of LH2 and its complexes

The mass spectrum of  $[Co(L)]\cdot H_2O$  complex has been recorded. The spectrum of the Co(II) complex exhibited the molecular ion (M<sup>+</sup>) peak at m/z 575 suggesting the monomeric nature of the chelate. The fragments (Fig.2) at m/z values 501, 484, and 356 are analogous to the loss of C<sub>4</sub>H<sub>2</sub>NOBr<sub>2</sub>Co molecules from chemical formula of the complex and fragments at m/z 315 may be due to C<sub>2</sub>H<sub>2</sub>O ion. For Cu (II) chelate, the spectrum exhibits a fragment at m/z 599 due to the original molecular weight of the chelate. The mass spectrum exhibits fragments at m/z values 580, 562, 544, 525, and 431 suggesting different fragmentations and the final fragment at m/z 159 is corresponding to the loss of Copper(II) ion from chemical formula. The mass spectrum of [Th(L)  $(NO_3)_2$  · 2H<sub>2</sub>O complex exhibited the molecular ion (M<sup>+</sup>) peak at m/z 897 suggesting the monomeric nature of the chelate having fragments at m/z values 682, 611, 504 and 325 are analogous to the loss of successive molecules chemical formula of the from complex. For  $[ZrO(L)].(H_2O)$  complex, the spectrum exhibits a Fragment at m/z = 617 is due to the original molecular weight of respective metal complexes. Fragment at m/z= 608 is analogous to the loss of one water molecule. The fragments at m/z = 431 assigned to the loss of zirconium ion. The above fragmentations illustrate the formation of the Schiff base and the formation of the chelates in 1:1 [M: L] ratio.

#### 3.5. ESR Spectra

ESR spectra of complex were recorded in solid state at 298 K as shown in **Fig. 2** and in DMF solution at 77 K as shown in **Fig. 3**. The spectral parameters are summarized in **Table 4**. The room temperature solid-state ESR spectrum of copper complex exhibits axially symmetric *g*-tensor parameters with  $g_{||} > g_{\perp} > 2.0023$ . The g values reflect that, the Cu(II) center has a tetragonal distorted octahedral geometry with  $dx^2$ -  $y^2$  orbital as a ground state [19]. No band corresponding to the forbidden magnetic dipolar transition for the complex was observed at half-field (ca. 1500 G, g = 4.0). This reveals the absence of any Cu–Cu interaction which supporting the mono nuclear complex. In axial symmetry the *g*-values are related to the *G*-factor by the expression,

 $G = (g_{||}-2)/(g_{\perp}-2) = 4$ , which measures the exchange interaction between copper centers in the solid. 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, whereas when it is less than 4, a considerable exchange interaction exists in the solid complex [20]. In hexacoordinated complex, tetragonal distortion from the octahedral symmetry due to the Jahn–Teller distortion is very common. The low *g*-value (g = 2.19) obviously corresponds to regular octahedral Cu(II) complex. Superhyperfine structures for these complexes are not seen at higher fields excluding any interaction of the nuclear spins of the nitrogen (I = 1) with the unpaired electron density on Cu(II).

Table 4. Spectral parameters of powder Cu(II) Complex

Complex	g∥	g⊥	g	$A_{  } \times 10^{-4}$	$g_{\parallel}/A_{\parallel}$	A	$A_{\perp}$
Cu(II)	2.19	2.05	2.13	175.508	124.78	0.123	0.00188



Fig. 2: ESR spectra of Cu(II)complex (RT)



Fig. 3: ESR spectra of Cu(II)complex (LNT)

#### 3.6. Thermogravimetric Analysis

Thermal analysis of metal complexes is an important method as it provides useful information about thermal stability of complexes as well as coordination ability of water whether it is inside the coordination sphere or outside. Thermal data have been analyzed for all metal complexes as shown in **Fig. 4**.



## Fig. 4: Thermal graph of LH<sub>2</sub> and metal complexes.

The half decomposition temperature, activation energy, frequency factor, apparent entropy of activation and free energy change of compounds were calculated by employing Freemann Caroll and Sharp Wentworth method [21]. The TGA thermal curves of ligand and complexes were obtained in nitrogen environment with heating rate 10°C min<sup>-1</sup> are given in fig. 3 while the kinetic parameters are assigned in **Table 5**. All the compounds are stable upto 40°C and further decompose in three stages while Ligand decomposes in two steps. In Co(II) and Zr(IV) complexes decomposition of one lattice water molecule respectively observed at 120°C with a mass loss of **Obs**./Calc:**3.34**/3.14 & **4.39**/4.05. Further decomposition above 220°C indicates the loss of coordinate part of ligand. For Cu(II) complex, absence of lattice water molecule was confirmed as no weight loss recorded at120°C and at 220°C **Obs**./Calc:**6.66**/6.03 shows the removal of two coordinate water molecule. Further loss above 420°C observed for the decomposition of coordinate part of ligand and finally formation of metal oxides occurs. In Th(IV) complexes weight loss Obs./Calc: 4.39/4.05 upto 120°C observed for the removal of two lattice water molecule. There is no weight loss further upto 220°C indicates the absence of coordinate water molecule. The further loss above 460°C observed for decomposition of coordinate part of ligand. It has been observed that complexes are not decomposed completely and finally converted into their respective metal oxides.

Compound	Decomposition	Ea(kj/	mole)	$\Delta S^{-}$	$\Delta \mathbf{F}$	Ζ	S*	Order of
_	Temp (°C)	FC	SW	(Kj/mole)		(S <sup>-1</sup> )		Reaction
LH <sub>2</sub>	160	18.66	19.21	7.93	36.44	112	-10.90	0.97
$[Co(L)].H_2O$	360	17.82	18.72	7.77	71.17	120	-11.04	0.94
$[Cu(L)(H_2O)_2]$	310	20.56	19.68	7.71	65.71	132	-10.96	0.92
$[Th(L)(NO_3)_2].2H_2$ O	380	11.73	12.91	7.71	76.22	105	-11.11	0.93
[Zr(L)O].H <sub>2</sub> O	370	18.66	19.35	7.76	72.90	128	-11.02	0.96

Table 5. Thermal analysis data of metal complexes

Table 6. Ant	ibacterial activity	of the ligand LH <sub>2</sub>	and its metal complexes
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Compound	E. coli (ATCC 14948)	S. aureus (ATCC 33591)	S. epidermis (MTCC 3086)	K. pneumoniae (MTCC 4030)
LH <sub>2</sub>	S10	S11	S08	\$06
$[Co(L)].H_2O$	S12	S10	R	S07
$[Cu(L)(H_2O)_2]$	S11	S10	S12	S12
$[Th(L)(NO_3)_2].2H_2O$	R	S11	S11	R
$[Zr(L)O].H_2O$	R	S09	R	R

## 3.7. Antibacterial Activity

The thiocarbohydrazone ligand and their transition metal complexes were screened against antimicrobial activity against *E. Coli, S. aureus, S. epidermis, and K. pneumoniae.* **Table 6** shows that the ligands have lower activity against *K. pneumoniae.* Activity of compound 5 was comparatively less. The values in mm of inhibition of bacteria growth show that the complexes are more active than their thiocarbohydrazone ligand. The Cu(II) and Co(II) complexes were found to show almost high to moderate bacteriocidal (sensitive) nature against all the bacterial strains. Moderate activity of Zr(IV) complexes was found against *S. typhi* and *S. aureus*, respectively.

## 4. CONCLUSION

The synthesized ligand act as neutral, monobasic or dibasic tridentates ligand through azomethine nitrogen and phenolic oxygen atom to the metal ions. The bonding of the ligand to metal was confirmed by the elemental and thermal analyses, IR and electronic spectra as well as conductivity and magnetic susceptibility measurements. All the metal complexes exhibited octahedral geometry except Co(II) complex which exhibits square planer geometry. The activation energy calculated by the Freemann-Caroll and Sharp-Wentworth methods are in good agreement with each other. Thermodynamic parameters have been calculated on the basis of thermal activation energy and values are given in Table 5. The thermal stability of the compounds can be correlated with the substituent group attached to the ligands.

The probable structures are shown below, **Fig. 5-6**. The ligand as well as some metal complexes showed antibacterial activity against selected kind of bacteria.



$$\label{eq:metric} \begin{split} &\mathsf{M}{=}\mathsf{Co}(\mathbf{II}), \ &\mathsf{X}{=}\mathsf{Y}{=}\cdots \text{ and } Z{=}\ &\mathsf{H}_2\mathsf{O}.\\ &\mathsf{M}{=}\mathsf{Cu}(\mathbf{II}), \ &\mathsf{X}{=}\mathsf{Y}{=}\mathsf{H}_2\mathsf{O} \text{ and } Z{=}\cdots \\ &\mathsf{M}{=}\mathsf{Th}(\mathbf{IV}), &\mathsf{X}{=}\mathsf{Y}{=}\ &\mathsf{NO}_2 \text{ and } Z{=}2\mathsf{H}_2\mathsf{O}. \end{split}$$

Fig. 5: Probable structure for Cu(II), Co(II) and Th(IV) metal complexes



Fig. 6: Probable structure for Zr(IV) metal complex

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