

**RUTHENIUM(III) AND COPPER(II) METAL COMPLEXES AND THEIR ANTIOXIDANT, ANTIMICROBIAL ACTIVITIES.****Kumar Naik K. H.\***

\*Department of Chemistry, K.R.C.E.S., GGD Arts, BMP Commerce and SVS Science Degree College, Bailhongal-591102, Belagavi, Karnataka, India.

Article Received on  
22 Nov. 2017,  
Revised on 13 Dec. 2017,  
Accepted on 02 Jan. 2018  
DOI: 10.20959/wjpr20182-10246

**\*Corresponding Author****Kumar Naik K. H.**

Department of Chemistry,  
K.R.C.E.S., GGD Arts,  
BMP Commerce and SVS  
Science Degree College,  
Bailhongal-591102,  
Belagavi, Karnataka, India.

**ABSTRACT**

Present work emphasis the biological importance of Ruthenium(III) and Copper(II) metal complexes, we had approaches the synthesis of ligands (L1 & L2) and their respective metal complexes were characterized by elemental analysis, conductivity measurements, magnetic susceptibility, electronic spectral studies, infrared spectroscopy studies, <sup>1</sup>H NMR spectral studies, Mass spectral studies and thermogravimetric studies. This study highlights the biological activities such as antioxidant, antibacterial and antifungal activity of metal complexes and also compared with standard compounds.

**KEYWORDS:** Ruthenium(III) and Copper(II) metal complexes, DPPH activity, antibacterial activity, antifungal activity.

**INTRODUCTION**

Recently, the research relating with metal complexes of N/S/O functionalized ligands has expanded enormously and now comprising their interesting aspects in coordination chemistry with a special emphasis in bioinorganic chemistry. A use of organosilicon and organotin compounds as reagents or intermediates in the inorganic synthesis has further strengthened their applications.<sup>[1]</sup> On the other hand, N/S/O functionalized ligands and their transition metal complexes have been of great interest in view of their structural features such as ligand rigidity, type of donor atoms, their disposition and resemblance to natural systems of metalloenzymes.<sup>[2]</sup>

Recently Mishra and groups were studied on anti-HIV Ru(II) complexes, which they suggested that flavones complexes possess as a anti-HIV agent. Eilatin-containing octahedral ruthenium complexes inhibit HIV-1 replication in CD<sup>4+</sup> HeLa cells and in human peripheral

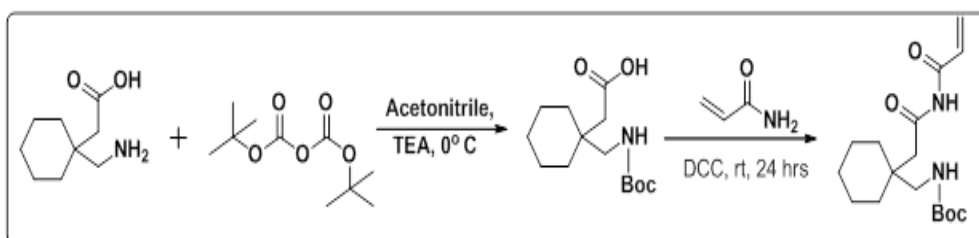
blood monocytes with IC(50) values of approximately 1  $\mu$ M. Similar metal complexes that lack eilatin display 15-100-fold lower anti-HIV activities.  $[\text{Ru}(\text{bpy})(\text{pre-eilatin})]^{2+}$  a complex that contains a nonplanar analogue<sup>[3]</sup> of eilatin, shows significantly lower nucleic acid binding and lower anti-HIV activity than eilatin complexes. Their interaction with aqueous buffered calf thymus DNA was measured.<sup>[4]</sup> These results prompted additional screening for anti-HIV (human immunodeficiency virus) activity against DNA replication in H<sub>9</sub> lymphocytes and cytotoxic activity against eight tumor cell lines.<sup>[5]</sup>

From above literature survey of Ruthenium(III) and Copper(II) metal complexes, we had approaches the synthesis of various ligands of having different organic moieties and their biological applications in various field. The synthesized ligands and their respective metal complexes were characterized by elemental analysis, conductivity measurements, magnetic susceptibility, electronic spectral studies, infrared spectroscopy studies, <sup>1</sup>H NMR spectral studies, mass spectral studies and thermogravimetric analysis.

## METHODOLOGY

### Synthesis of ligand (L1)

*Preparation of tert-butyl (1-(2-acrylamido-2-oxoethyl)cyclohexyl)methylcarbamate;* The Ligand *tert-butyl (1-(2-acrylamido-2-oxoethyl)cyclohexyl)methylcarbamate* prepared by the Methanolic solution of Boc protected gabapentine (0.01 mol) was added drop wise to a solution of 2-amino acetic acid (0.01 mol) dissolved in methanol (Scheme-6). The mixture was stirred for 24 h in 0°C then room temperature for 3 h and filtered. Yield was about 65%.<sup>[6,7]</sup>

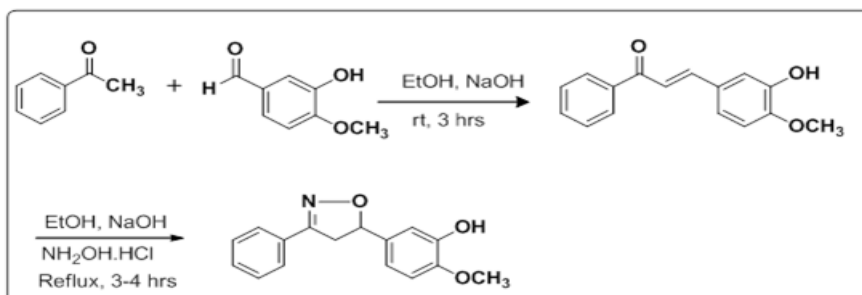


**Scheme-1: Synthesis of Ligand (L1).**

### Synthesis of ligand (L2)

*Preparation of 3,5-diphenyl-4,5-dihydroisoxazole and its derivatives;* A mixture of various chalcone derivatives (1 mmol) is taken in a 100 ml of round bottom flask was dissolved in 15 ml of ethanol. To this reaction mixture hydroxylamine hydrochloride is added (2 mmol)

shake well and then sodium hydroxide (1.5 mmol) was added (Scheme-1). The reaction mixture was stirred and reflux for 3-4 hrs. The progress of reaction is followed by TLC. After completion of the reaction, the mixture pours into 50ml of ice water. The separated product was filtered off and washed with cold water for several times and dried afforded ligand.<sup>[8]</sup>



**Scheme-1: Synthesis of Ligand (L2).**

## RESULTS AND DISCUSSION

### a) Stoichiometry

The stoichiometries of Ru(III) and Cu(II) complexes were concluded from their elemental analysis. All the synthesized complexes are coloured and are stable in air, non-hygroscopic, have high melting points and are insoluble in water, but soluble in coordinating solvents such as DMF, DMSO, THF as well as acetonitrile. The analytical data are depicted in Table-1. Suggest that the metal: ligand ratio was 1: 2, they can be represented by the general formulae;  $[M(L1 \& L2)_2XY]$ ,

Where M = Ru(III), Cu(II). X = Cl, Y = H<sub>2</sub>O.

### b) Conductometric studies

All the complexes were anhydrous in nature and insoluble in methanol, ethanol, acetone and benzene. They are soluble in dimethyl sulphoxide and in dimethyl formamide. The general structures of the metal complexes were shown in Fig.1. The 10<sup>-3</sup> M solution of the complex in dimethyl sulphoxide (DMSO) was used to determine the molar conductance. The conductivity data reveals that the complexes are non-electrolytic in nature. The metal and anions are estimated using standard procedure (Vogel A. I., 1962).

### c) Magnetic susceptibility measurements

The magnetic susceptibility measurements of the complexes were obtained at room temperature using Gouy balance. Pure Hg[Co(SCN)<sub>4</sub>] was synthesized is used as calibration standard. The transition element of ruthenium having electronic configuration [Kr] 4d<sup>6</sup> 5s<sup>2</sup>

and Ru(III) ion being a  $d^5$  system has five unpaired electron in 4d shell and its complexes are expected to have magnetic moments close to the spin only value of about 5.91 BM, irrespective of the bond type involved. The magnetic moment of mononuclear Ru(III) complexes usually lies in the range 5.12-5.95 BM have no major interaction between the unpaired electron on different manganese ions and essentially temperature independent.

And in the copper complexes having electronic configuration  $[Ar] 3d^{10} 4s^1$  and Cu(II) ion being a  $d^9$  system has one unpaired electron in 3d shell and its complexes are expected to have magnetic moments close to the spin only value of about 1.91 BM, irrespective of the bond type involved. The magnetic moment of Cu(II) complexes usually lies in the range 1.75-1.91 BM have no major interaction between the unpaired electron on different manganese ions and essentially temperature independent.<sup>[9]</sup>

#### d) Electronic spectral measurements

The spectrum of the Ru(III) complexes (5,6 and 8) are represented in Fig-5,6,8 respectively, the electronic spectrum shows that the dominated by one strong MLCT  $[Ru(L1 \& L2)_2XY]$  transition at  $20000 \text{ cm}^{-1}$  due to the HOMO-LUMO excitation. There are two weak transitions in the  $20000-225000 \text{ cm}^{-1}$  region due to HOMO-LUMO and HOMO-LUMO excitations of Ru(III). ruthenium(III) ion which has five d electrons and The ground term arising from the  $t^3_{2g} e^2_g$  configuration in an octahedral field is  $^4T_{1g}$  and having three spin allowed d-d transitions,  $\nu_1 = ^4T_{1g} (F) \rightarrow ^4T_{2g} (F)$ ,  $\nu_2 = ^4T_{1g} \rightarrow ^4A_{2g} (F)$ ,  $\nu_3 = ^4T_{1g} (F) \rightarrow ^4T_{1g} (P)$ .<sup>[10,11]</sup>

The lowest energy transition  $^4T_{1g} (F) \rightarrow ^4T_{2g}$  was assigned near infrared region and the band in visible region near  $20000-22300 \text{ cm}^{-1}$  is assigned to the  $^4T_{1g} (F) \rightarrow ^4T_{1g} (P)$ . The  $^4T_{1g} \rightarrow ^4A_{2g}$  transition is due to a band near  $20000 \text{ cm}^{-1}$ . The  $^4A_{2g}$  state is derived from a  $t^3_{2g} e^4_g$  configuration. The  $^4T_{1g} \rightarrow ^4A_{2g} (F)$  essentially a two electron process and for this region it should be weaker than the other transition. This weakness combined with closeness of the  $^4T_{1g} (F) \rightarrow ^4T_{1g} (P)$  band results in the  $^4T_{1g} \rightarrow ^4A_{2g}$  transition being unobserved. the band located in the region  $20250-22150 \text{ cm}^{-1}$  are assigned to  $^4T_{1g} \rightarrow ^4A_{2g} (F)$  and  $^4T_{1g} (F) \rightarrow ^4T_{1g} (P)$  transition respectively.<sup>[12]</sup> These results reveals that the ruthenium(III) ion complexes is in octahedral field with ligands. The copper element having the ground term arising from the  $t^5_{2g} e^2_g$  configuration in an octahedral field is  $^4T_{1g}$  and having three spin allowed d-d transitions are,  $\nu_1 = ^4T_{1g} (F) \rightarrow ^4T_{2g} (F)$ ,  $\nu_2 = ^4T_{1g} \rightarrow ^4A_{2g} (F)$  and  $\nu_3 = ^4T_{1g} (F) \rightarrow ^4T_{1g} (P)$ . The lowest energy transition  $^4T_{1g} (F) \rightarrow ^4T_{2g}$  was assigned near infrared region and the band in visible region near  $17100-17700 \text{ cm}^{-1}$  is assigned to the  $^4T_{1g} (F) \rightarrow ^4T_{1g} (P)$ . The  $^4T_{1g} \rightarrow ^4A_{2g}$

transition is due to a band near  $14000\text{ cm}^{-1}$ . The  ${}^4\text{A}_{2g}$  state is derived from a  $t^3_{2g} e^4_g$  configuration. The  ${}^4\text{T}_{1g} \rightarrow {}^4\text{A}_{2g}$  (F) essentially a two electron process and for this region it should be weaker than the other transition. This weakness combined with closeness of the  ${}^4\text{T}_{1g}$  (F)  $\rightarrow$   ${}^4\text{T}_{1g}$  (P) band results in the  ${}^4\text{T}_{1g} \rightarrow {}^4\text{A}_{2g}$  transition being unobserved.

#### e) FT-IR spectral studies

The structure of ligand confirmed by using IR spectral analysis. The imported infrared spectral data of prepared Ligand and their metal complexes are represented in Table-3. the IR discussions of ligand and metal complexes are as follows,

*Ligand (L1 & L2)*; IR spectra of all the complexes of ligand (L1 & L2) exhibited a broad band around  $3280\text{-}3540\text{ cm}^{-1}$  and a sharp peak in the range of  $1640\text{-}1550\text{ cm}^{-1}$ , These peaks can be assigned to N-H and aromatic C-H stretching vibration which are present in free ligand. In the low-frequency region, two bands were observed for complexes at  $\sim 445$  which were attributed to  $\nu(\text{M-N})$  in ligand (L1 & L2) These bands were not found in the spectra of the ligand<sup>[13]</sup>, suggesting that coordination of the ligand with the metal ions takes place via the nitrogen atoms and via oxygen. It was found that the characteristic band of the C-N group in the free ligand at  $1360\text{-}1250\text{ cm}^{-1}$  was shifted to lower frequency of  $1348\text{-}1350\text{ cm}^{-1}$  in the complexes. This alter indicates coordination of the nitrogen to the metals in the complexes. This shift also indicates that bonding in the complexes occurred through the nitrogen atom.

#### f) ${}^1\text{H}$ NMR spectral studies

The  ${}^1\text{H}$  NMR data the ligands and metal complexes are presented in Table-7.5. The  ${}^1\text{H}$ -NMR spectra were recorded in DMSO- $d_6$  in a multiplet from  $\delta(7.89\text{-}8.01)$  ppm for aromatic protons (Ar-H) in ligand (L1 and L2). For L1, L2 ligands the signals within the range of  $\delta(3.85\text{-}3.89)$  ppm due to O- $\text{CH}_3$  protons.<sup>[14,15]</sup> The spectra of ligands (L1, L2) is shown in Fig-3 & 4 respectively.

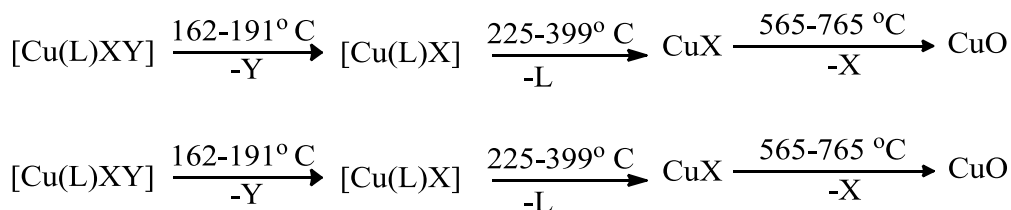
#### g) Thermal Analysis

Thermal decomposition of newly synthesized complexes were carried out to observe the thermal behavior and to determine the decomposition temperature of the metal(III)/(II) complexes. The decomposition temperatures of these complexes obtained from their thermograms are recorded in Table-5 and some important TGA/DTA curves are reproduced in Fig-8.

In the first stage of degradation the newly synthesized ruthenium(III) complexes start decomposition in the range 184-210. The weight loss was 1.32-1.51% very gradual is termed as first stage of degradation. The weight loss corresponds due to dehydration of water molecules. The DTG peak of this stage is observed in the range 172-189°C and the height of the DTG peak at above temperature gives the rate of mass change is agreement with the theoretical values of the complexes. Where in  $[\text{Cu}(\text{L1} \ \& \ \text{L2})(\text{X})(\text{H}_2\text{O})]$  complexes shows the weight loss in the temperature range 80-97°C and DTG peak at 95-101°C, it suggest that water molecule present inside the coordination sphere.

The second and third stages of degradations are at 225-399°C and 353-470°C respectively. The percentage of weight loss in the range 40.51-54.25%, 31.60-37.27%, which may be attributed to loss of thermally stable organic moiety i.e., ligands is termed as second stage and third stage of degradations. In Third stage of degradation occurs in range 482-756°C, the weight loss 5.21-7.42% in the TGA curve of complexes. The percentage of weight loss may be attributed to the inorganic ligand, after this stage the TGA curve become a constant and the black residue obtained has been chemically identified as pure ruthenium oxide.<sup>[16,18]</sup>

The four significant steps of thermal degradation can be formulated as,



[Where, L=ligand, X = Cl<sup>-</sup>, Y= H<sub>2</sub>O]

In all the thermal degradation stages the experimental value of weight loss are in well agreement with the expected TGA values. The final decomposition product was left above as respective oxide, which has been chemically identified.

## Biological evolution

### Antioxidant activity

All the synthesized ligands and their respective metal complexes exhibited effective antioxidant scavenging activities. From all the synthesized compound of ligand (L1 & L2) and their respective metal complexes (2, 3) with hydroxyl and methoxy with electron withdrawing nitrogen moiety promotes scavenging of Free radical activity and also the

scavenging of Free radical increases after complexation with above said ligands because the metal moiety was in electron deficient state this property make the complexes to scavenge the free radical very effectively than the free ligand as well as standard drug. Except these ligands and their metal complexes other ligands and metal complexes are exhibits somewhat moderate activity because these compounds are also contain withdrawing groups.<sup>[19,20]</sup> Finally the complexes 6 and 7 shows normal antioxidant activity and complexes remain complexes shows moderate activity, all the tested ligand and metal complexes responds against the free radical scavenging strain significantly these data are reproduced in Table-6. and graphical representation in Fig-9.

### Antimicrobial activity

The new Complexes were assayed *in vitro* to assess their ability to inhibit the growth of selected species of bacteria and fungi. The data is summarized in Table-7. and graphical representation in Fig-10, for antibacterial and Table-8, and graphical representation in Fig-11 for antifungal studies. On the basis of observed zones of inhibition, it was found that, in general, all the prepared ligands and their metal complexes responded against all the tested bacterial and fungal strains significantly.<sup>[20,27]</sup> The investigation of antibacterial screening data revealed that the tested compounds showed moderate to good antibacterial and antifungal activities against *Escherichia coli*, *Staphylococcus aureus*, *Pseudomonas aeruginosa* and *Aspergillus flavus*, *Chrysosporium keratinophilum* and *Candida albicans* respectively. The compounds 2,3, 5 and 6 displayed excellent antibacterial activity while remaining compounds shows moderate antibacterial activity as compare to standard drug Chloramphenicol.

Table-1: Elemental analysis, melting point, molecular weight and molar conductance data of ligand and their metal complexes.

Sl. No.	Compounds	Yield (%)	Mel.point (°C)	Molecular Weight	Elemental analysis Calc. (found) (%)						Molar conduct.(Ohm <sup>-1</sup> cm <sup>-2</sup> mol <sup>-1</sup> )
					M	C	H	N	O	anion	
1	L1 (C <sub>16</sub> H <sub>15</sub> NO <sub>3</sub> )	75	184-185	269	--	71.26 (71.30)	5.58 (5.61)	5.20 (5.22)	17.71 (17.78)	--	16.41
2	[Ru(C <sub>16</sub> H <sub>15</sub> NO <sub>3</sub> ) <sub>2</sub> (Cl)(H <sub>2</sub> O)]	72	198-201	693	14.48 (14.52)	55.31 (55.35)	4.53 (4.55)	4.01 (4.04)	16.06 (16.10)	14.51 (14.53)	18.67
3	[Cu(C <sub>16</sub> H <sub>15</sub> NO <sub>3</sub> ) <sub>2</sub> (Cl)(H <sub>2</sub> O)]	79	194-195	655	8.61 (8.64)	58.61 (58.64)	4.85 (4.88)	4.21 (4.23)	16.95 (16.99)	9.61 (9.64)	22.86
4	L2(C <sub>8</sub> H <sub>7</sub> N <sub>3</sub> OS)	68	171-172	193	--	49.55 (49.57)	3.61 (3.64)	21.76 (21.76)	8.28 (8.31)	-	19.31
5	[Ru(C <sub>8</sub> H <sub>7</sub> N <sub>3</sub> OS) <sub>2</sub> (Cl)(H <sub>2</sub> O)]	67	196-198	540	18.20 (18.24)	35.48 (35.50)	2.89 (2.91)	15.48 (15.49)	8.67 (8.67)	11.81 (11.85)	17.51
6	[Cu(C <sub>8</sub> H <sub>7</sub> N <sub>3</sub> OS) <sub>2</sub> (Cl)(H <sub>2</sub> O)]	76	186-188	503	12.54 (12.55)	38.15 (38.19)	3.19 (3.20)	16.81 (16.85)	9.41 (9.45)	12.65 (12.71)	21.05



Table-2: Electronic spectral and magnetic susceptibility data of metal complexes.

Sl.No.	Complexes	Electronic spectra (cm <sup>-1</sup> )				Magnetic moment[BM]
1	L1 (C <sub>16</sub> H <sub>15</sub> NO <sub>3</sub> )	14806	16324	25254	34726	--
2	[Ru(C <sub>16</sub> H <sub>15</sub> NO <sub>3</sub> ) <sub>2</sub> (Cl)(H <sub>2</sub> O)]	20903	22284	29315	35749	5.90
3	[Cu(C <sub>16</sub> H <sub>15</sub> NO <sub>3</sub> ) <sub>2</sub> (Cl)(H <sub>2</sub> O)]	15858	16356	26156	35706	1.89
4	L2(C <sub>8</sub> H <sub>7</sub> N <sub>3</sub> OS)	14846	16360	25451	34842	--
5	[Ru(C <sub>8</sub> H <sub>7</sub> N <sub>3</sub> OS) <sub>2</sub> (Cl)(H <sub>2</sub> O)]	20887	22644	29225	35741	5.88
6	[Cu(C <sub>8</sub> H <sub>7</sub> N <sub>3</sub> OS) <sub>2</sub> (Cl)(H <sub>2</sub> O)]	15125	17765	27350	35642	1.85

Table-3: Important IR spectral data of Ligand and their metal complexes.

Sl.No.	Compounds	Frequencies (cm <sup>-1</sup> )						
		O-H	N-H	C=N	C=O	M-N	M-O	M-X
1	L1 (C <sub>16</sub> H <sub>15</sub> NO <sub>3</sub> )	3380-3500	3380-3450	2473	-	477-490	460-467	-
2	[Ru(C <sub>16</sub> H <sub>15</sub> NO <sub>3</sub> ) <sub>2</sub> (Cl)(H <sub>2</sub> O)]	3350-3550	3350-3450	2469	-	465-485	448-464	274
3	[Cu(C <sub>16</sub> H <sub>15</sub> NO <sub>3</sub> ) <sub>2</sub> (Cl)(H <sub>2</sub> O)]	3340-3450	3400-3450	2468	-	477-498	455-456	285
4	L2(C <sub>8</sub> H <sub>7</sub> N <sub>3</sub> OS)	-	3360-3450	2460	-	480-500	445-450	
5	[Ru(C <sub>8</sub> H <sub>7</sub> N <sub>3</sub> OS) <sub>2</sub> (Cl)(H <sub>2</sub> O)]	-	3385-3550	2468	-	475-486	465-470	268
6	[Cu(C <sub>8</sub> H <sub>7</sub> N <sub>3</sub> OS) <sub>2</sub> (Cl)(H <sub>2</sub> O)]	-	3410-3550	2450	-	470-495	472-485	271

Table-4: Important <sup>1</sup>H NMR spectral data of ligand and their metal complexes.

Sl. No.	Compounds	Chemical shift(δ ppm)						
		Aromatic-H	O-H	N-H	CH <sub>2</sub> -O	CH <sub>3</sub> -O	CH <sub>2</sub> -N	cyclohexane
1	L1 (C <sub>16</sub> H <sub>15</sub> NO <sub>3</sub> )	6.72-8.01	5.37	-	5.23	3.79	-	-
2	[Ru(C <sub>16</sub> H <sub>15</sub> NO <sub>3</sub> ) <sub>2</sub> (Cl)(H <sub>2</sub> O)]	6.69-7.89	5.38	-	5.18	3.75	-	-
3	[Cu(C <sub>16</sub> H <sub>15</sub> NO <sub>3</sub> ) <sub>2</sub> (Cl)(H <sub>2</sub> O)]	6.58-7.78	5.37	-	5.19	3.81	-	-
4	L2(C <sub>8</sub> H <sub>7</sub> N <sub>3</sub> OS)	6.91-7.81	-	7.98-8.01	5.18	-	-	-
5	[Ru(C <sub>8</sub> H <sub>7</sub> N <sub>3</sub> OS) <sub>2</sub> (Cl)(H <sub>2</sub> O)]	6.89-7.85	-	8.14-8.17	5.21	-	-	-
6	[Cu(C <sub>8</sub> H <sub>7</sub> N <sub>3</sub> OS) <sub>2</sub> (Cl)(H <sub>2</sub> O)]	6.90-7.79	-	8.03-8.16	5.20	-	-	-

Table-5: Thermogravimetric characteristics of metal complexes.

Complexes	Process of degradation	Temp. Range(°C)	DTG Peaka Temp.	Product Degradised	No. of moles	Weight		Residue(MO)		
						Cal.	Expt.	Cal.	Expt.	Nature
[Ru(C <sub>16</sub> H <sub>15</sub> NO <sub>3</sub> ) <sub>2</sub> (Cl)(H <sub>2</sub> O)]	Dehydration	155-216	177	H <sub>2</sub> O	1	04.46	04.18	09.28	08.75	RuO
	Decomposition of L <sub>8</sub>	283-325	316	L <sub>8</sub>	1	40.20	38.83			
	Decomposition of Cl <sup>-</sup>	475-656	586	Cl <sup>-</sup>	1	15.37	14.19			
[Cu(C <sub>16</sub> H <sub>15</sub> NO <sub>3</sub> ) <sub>2</sub> (Cl)(H <sub>2</sub> O)]	Dehydration	160-211	174	H <sub>2</sub> O	1	04.62	04.26	09.62	09.25	CuO
	Decomposition of L <sub>8</sub>	278-322	312	L <sub>8</sub>	1	41.65	40.31			
	Decomposition of Cl <sup>-</sup>	488-655	577	Cl <sup>-</sup>	1	12.33	11.65			

**Table-6: Antioxidant activity ( $IC_{50}$ ) of the ligand and their metal complexes.**

Sl.No.	Compounds	DPPH activity $IC_{50}^a$ ( $\mu$ M /mL)
1	L <sub>8</sub> (C <sub>16</sub> H <sub>15</sub> NO <sub>3</sub> )	82±0.11
2	[Ru(C <sub>16</sub> H <sub>15</sub> NO <sub>3</sub> ) <sub>2</sub> (Cl)(H <sub>2</sub> O)]	108±0.31
3	[Cu(C <sub>16</sub> H <sub>15</sub> NO <sub>3</sub> ) <sub>2</sub> (Cl)(H <sub>2</sub> O)]	127±0.01
4	L <sub>9</sub> (C <sub>8</sub> H <sub>7</sub> N <sub>3</sub> OS)	65±0.41
5	[Ru(C <sub>8</sub> H <sub>7</sub> N <sub>3</sub> OS) <sub>2</sub> (Cl)(H <sub>2</sub> O)]	70±0.17
6	[Cu(C <sub>8</sub> H <sub>7</sub> N <sub>3</sub> OS) <sub>2</sub> (Cl)(H <sub>2</sub> O)]	72±0.16

<sup>a</sup> $IC_{50}$  = the concentration ( $\mu$ M/mL) exhibiting 50% inhibition of DPPH radical.

**Table-7: Antibacterial activity of the ligand and its metal complexes. Inhibitory zone (diameter in mm) of the synthesized compounds against tested bacterial strains by well plate method.**

Sl. No.	Compounds	Escherichia coli	Staphylococcus aureus	Pseudomonas aeruginosa
1	L <sub>8</sub> (C <sub>16</sub> H <sub>15</sub> NO <sub>3</sub> )	07±0.19	06±0.21	07±0.12
2	[Ru(C <sub>16</sub> H <sub>15</sub> NO <sub>3</sub> ) <sub>2</sub> (Cl)(H <sub>2</sub> O)]	08±0.26	04±0.19	02±0.01
3	[Cu(C <sub>16</sub> H <sub>15</sub> NO <sub>3</sub> ) <sub>2</sub> (Cl)(H <sub>2</sub> O)]	08±0.04	06±0.17	05±0.34
4	L <sub>9</sub> (C <sub>8</sub> H <sub>7</sub> N <sub>3</sub> OS)	06±0.14	08±0.10	03±0.24
5	[Ru(C <sub>8</sub> H <sub>7</sub> N <sub>3</sub> OS) <sub>2</sub> (Cl)(H <sub>2</sub> O)]	07±0.15	07±0.09	02±0.14
6	[Cu(C <sub>8</sub> H <sub>7</sub> N <sub>3</sub> OS) <sub>2</sub> (Cl)(H <sub>2</sub> O)]	07±0.28	06±0.03	01±0.08
Std.	chloramphenicol	07.0± 0.09	06.0± 0.14	04.0± 0.21

**Table-8: Antifungal activity of the ligand and its metal complexes. Inhibitory zone (diameter in mm) of the synthesized compounds against tested bacterial strains by well plate method.**

Sl.No.	Compounds	Aspergillus flavus	Chrysosporium keratinophilum	Candida albicans
1	L <sub>8</sub> (C <sub>16</sub> H <sub>15</sub> NO <sub>3</sub> )	10±0.12	07±0.09	06±0.19
2	[Ru(C <sub>16</sub> H <sub>15</sub> NO <sub>3</sub> ) <sub>2</sub> (Cl)(H <sub>2</sub> O)]	06±0.14	07±0.04	07±0.15
3	[Cu(C <sub>16</sub> H <sub>15</sub> NO <sub>3</sub> ) <sub>2</sub> (Cl)(H <sub>2</sub> O)]	07±0.14	09±0.45	08±0.06
4	L <sub>9</sub> (C <sub>8</sub> H <sub>7</sub> N <sub>3</sub> OS)	11±0.02	10±0.24	09±0.25
5	[Ru(C <sub>8</sub> H <sub>7</sub> N <sub>3</sub> OS) <sub>2</sub> (Cl)(H <sub>2</sub> O)]	12±0.21	12±0.06	11±0.35
6	[Cu(C <sub>8</sub> H <sub>7</sub> N <sub>3</sub> OS) <sub>2</sub> (Cl)(H <sub>2</sub> O)]	13±0.41	11±0.25	09±0.24
Std.	Nystatin	8±0.13	7±0.11	5±0.21

## FIGURES (SPECTRUM AND BAR GRAPHS AND IMAGES)

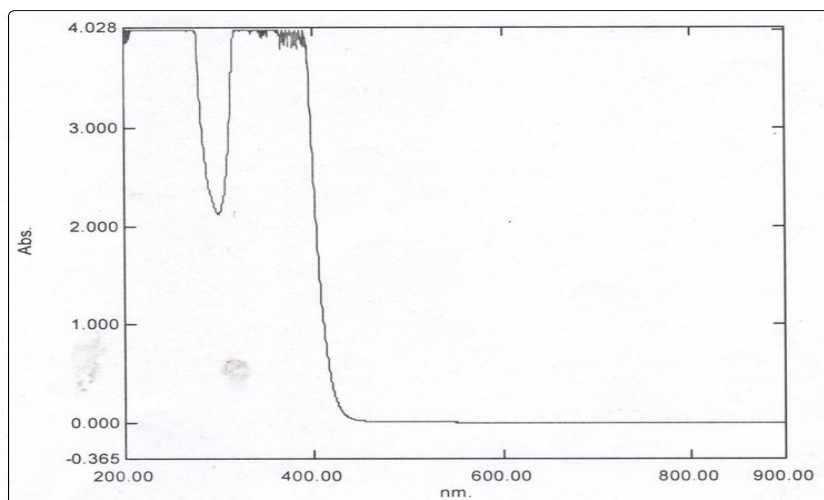
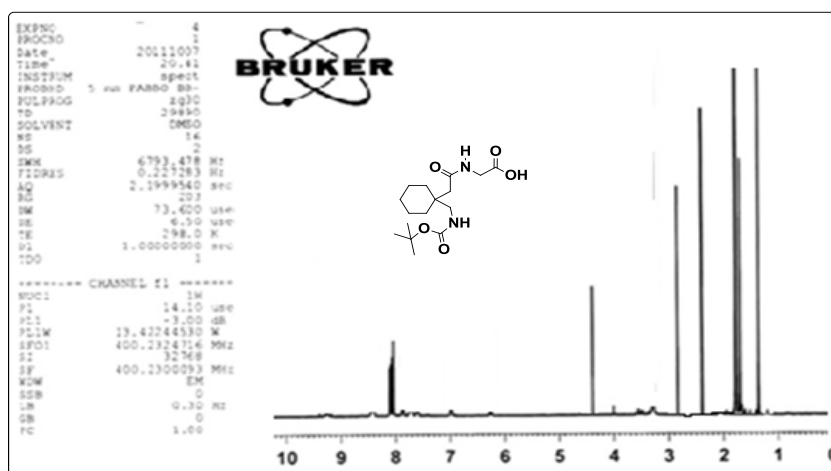
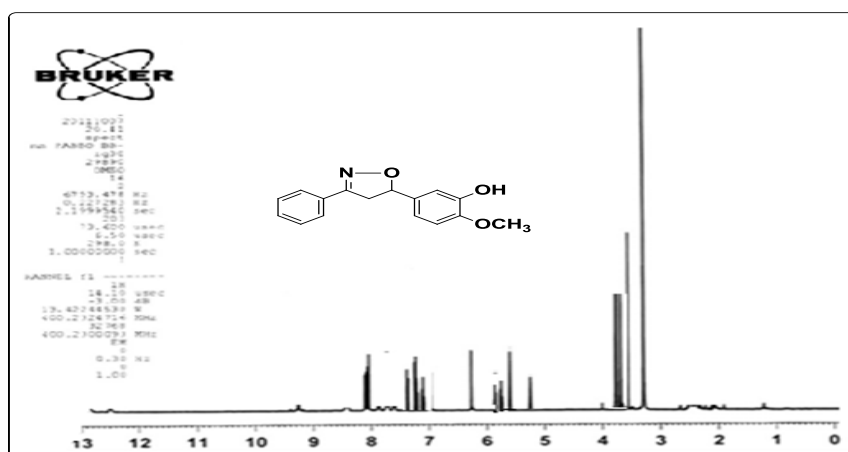
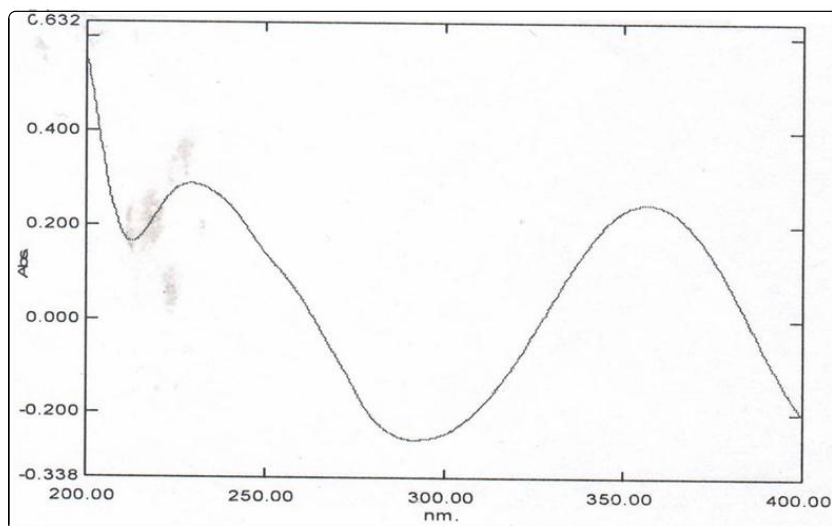
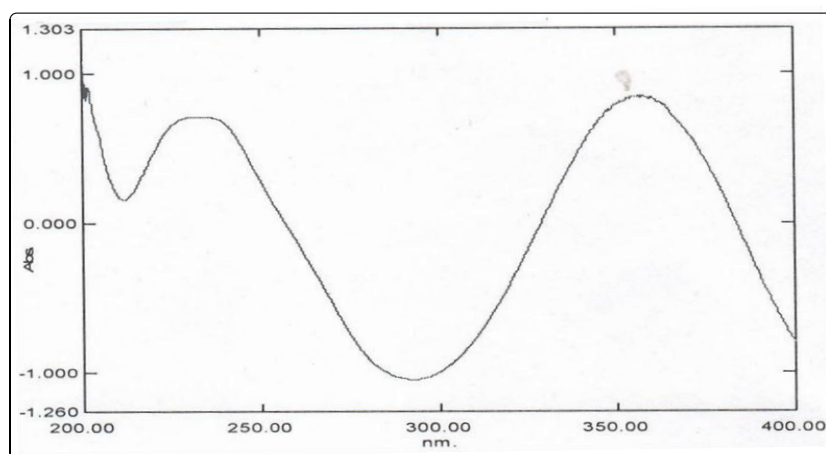


Fig-2: Electronic spectra of Ligand (L2).

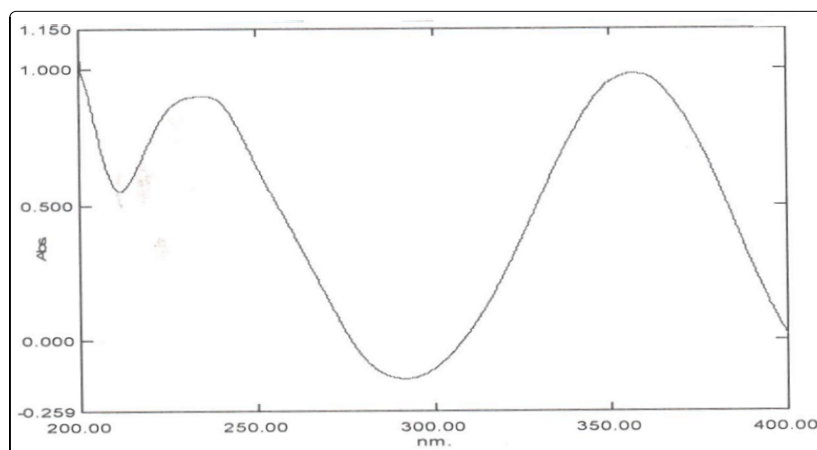
Fig-3:  $^1\text{H}$  NMR spectra of Ligand (L1).Fig-4:  $^1\text{H}$  NMR spectra of Ligand (L2).



**Fig-5: Electronic spectra of complex (5).**



**Fig-6: Electronic spectra of complex (6).**



**Fig-7: Electronic spectra of complex (8).**

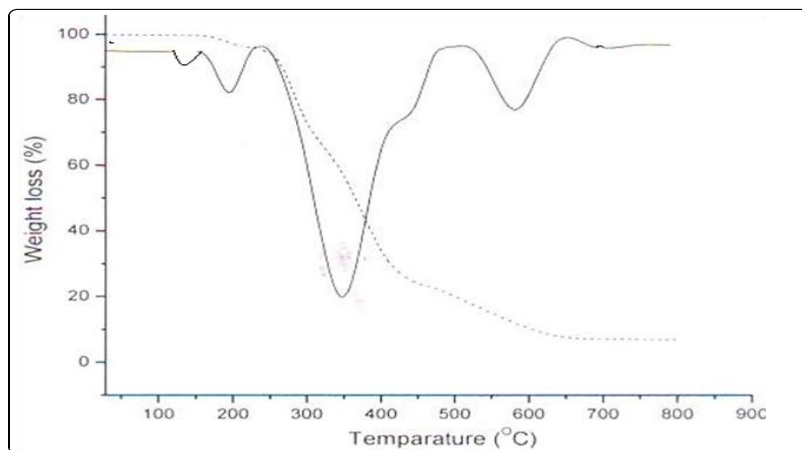


Fig-8: (.....)TGA and (——) DTA curve of complex (8).

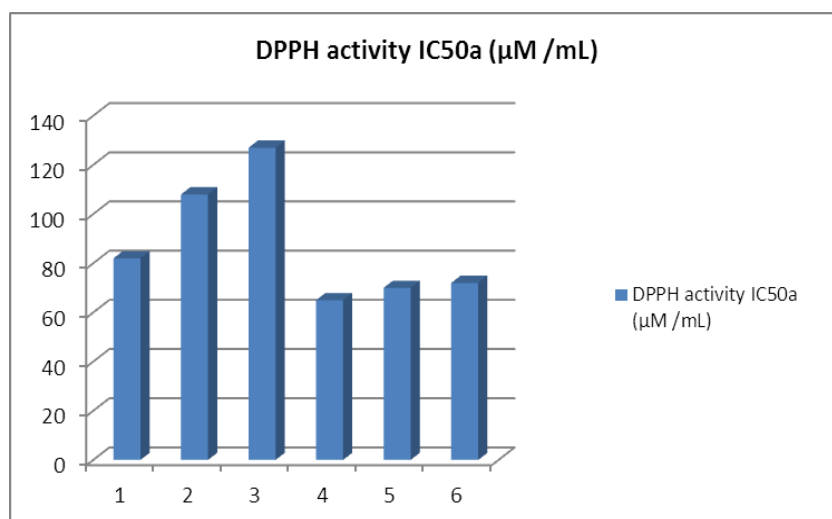
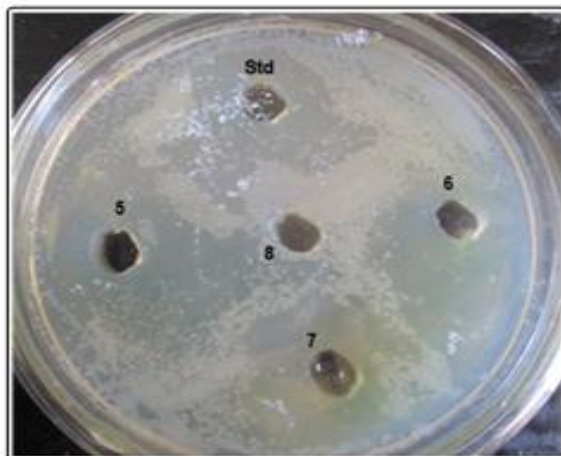


Fig-9: Antioxidant activity ( $IC_{50}$ ) of the ligand and their metal complexes.



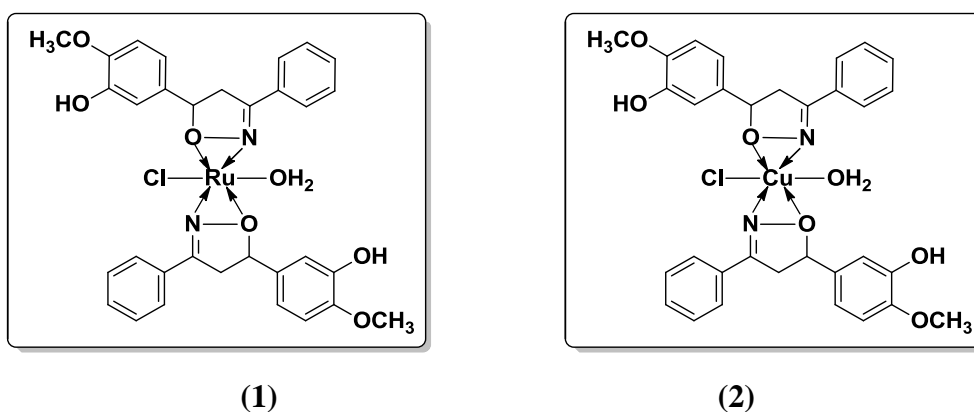
Fig-10: Antibacterial studies of ligands and their metal complexes.



**Fig-11: Antifungal studies of ligands and their metal complexes.**

## CONCLUSION

Metal complexes are having very effective biological properties, work described in this Chapter involved the synthesis and spectroscopic characterization ruthenium(III) and copper(II) complexes with a new N/O/S functionalized ligands. These complexes were characterized by using different physicochemical techniques. These complexes are all neutral and found to have an octahedral geometry with the six donor atoms. The synthesized compounds have *in vitro* antimicrobial screening effects evaluated against three bacterial strains and fungal strains by disc diffusion method using nutrient agar medium for antibacterial studies and potato dextrose agar medium for antifungal studies. And also these synthesized complexes reveal effective antioxidant activity by DPPH assay. From the above said spectral characterization of synthesized compounds, the proposed geometry of metal complexes is as follows,



M = Ru(III), Cu(II). X = Cl, Y = H<sub>2</sub>O.

**Fig-1: Proposed geometry of metal complexes.**

## REFERENCES

1. Pereyre M.J.P., Quintard A.R. *Tin* in Organic Synthesis. *Butterworths. London. UK. 1987.*
2. Chandra S., Monika T., Agrawal S. J. *Serb. Chem. Soc.*, 2010; 75(7): 935.
3. Xu H., Liang Y., Zhang P., Du F., Zhou B.R., Wu J., Liu J.H., Liu Z.G., Ji L.N. *J. Bioinorg. Chem.*, 2004; 10(5): 529.
4. Foote C.S. *Mechanism of Photooxygenation in Porphyrin Localization and Treatment of Tumors.* New York., 1984.
5. Mishra L., Singh A.K., Trigun S.K., Singh S.K. Pandey S.M. *Ind. J. Expt. Biolo.*, 2004; 42: 660.
6. Ott I., Kircher B., Gust R.J. *Inorg. Biochem.*, 2004; 98: 485.
7. Nuhn P., Hirtzel S. *Stuttgart. Nat. chemie.*, 1997; 157.
8. Bekhit A.A., Ashous H.M., Guemei A.A. *Arch. Pharm.*, 2005; 167: 338.
9. Novakova O., Malina J., Suchankova T., Kasparikova J., Bugarcic T., Sadler P.J. *Brabec V. Chem. Euro. J.*, 2010; 16: 5744.
10. Gryz M., Starosta W., Leciejewicz J.J. *Coord. Chem.*, 2007; 60: 539.
11. Karvembu R., Natarajan K. *Polyhedron.*, 2002; 21: 219.
12. Natarajan K., Poddar R.K., Agarwala U. *J. Inorg. Nucl. Chem.*, 1977; 39: 431.
13. Zerner M.C., Lipkowitz K.B., Boyd D.B. (Eds.) (chapter.2), *Reviews in Comp. Chemistry*, VCH, New York., 1991; 8: 313.
14. Stavrev K.K., Zerner M.C., Meyer T.J. *J. Am. Chem. Soc.*, 1995; 117: 8684.
15. Zerner M.C., Russo N., Salahub D.R. (Eds.), *Metal–Ligand Interactions*, Kluwer Academic, Amsterdam, 1996; 493.
16. Sanchez G.O., Lopez S.H., Sanchez B.F., Gracia M.I., Barba B.N. *J. Inorg. Biochem.*, 2009; 103: 1204.
17. Murukan B., Mohanan K.J. *Enz. Inh. Med. Chem.*, 2007; 22: 65.
18. Kalsi P.S. *Spectroscopy of Organic Compounds*, 4<sup>th</sup> edition, New Age International Limited Publishers, New Delhi. 2002.
19. Coats A.W., Redfern J.P., *Nature.*, 1964; 20: 68.
20. Sama B.D., Bailer Jr J.C. *J. Am. Chem. Soc.*, 1955; 77: 5476.
21. Nagaraja Naik., Ramappa P.G. *Asian J. Chem.*, 1995; 4: 860.
22. Johri K.N., Hemminger W. (Ed.), *Thermal Analysis*, Proc. VI ICTA, Birkhauser-Verlag. Basei, 1980; 2: 129.



23. Rangaswamy J., Vijay Kumar H., Harini S.T., Nagaraja Naik. Bioorg. Med. Chem. Lett., 2012; 22: 4773.
24. Harini S.T., Vijay Kumar H., Peethambar S.K., Rangaswamy J., Nagaraja Naik. Med. Chem. Res. DOI 10.1007/s00044-013-0793.
25. Boyd R.F. General microbiology, 2<sup>nd</sup> Int. Edn., Times Mirror/Mosky College, 1998; 441.
26. Harini S.T., Vijay Kumar H., Rangaswamy J., Nagaraja Naik., Bioorg. Med. Chem. Lett., 2012; 22: 7588.
27. Al-Amiery A.A., Kadhun A.A.H., Mohamad A.B. Bioinorg. Chem. Appl., 2012, doi:10.1155/2012/795812.