



Scholars Research Library

Der Pharma Chemica, 2014, 6(2):51-58
(<http://derpharmachemica.com/archive.html>)



ISSN 0975-413X
CODEN (USA): PCHHAX

Spectroscopic characterization and biological evolution of ortho vanillin pramipexole schiff base metal complexes

T. Noorjahan Begum, A. Jaya Raju, G. Nageswara Reddy and J. Sreeramulu*

Department of Chemistry, Sri Krishnadevaraya University, Anantapuramu, A.P, India

ABSTRACT

A novel and simple approach to the synthesis of Schiff base ligand resulted from the condensation of Pramipexole (N6-propyl-4,5,6,7-Tetrahydro-1,3-benzothiazole-2,6-diamine) with O-Vanillin (2-hydroxy-3-methoxy benzaldehyde). Using this bidentate ligand, complexes of Cu(II), Ru(II) with general formula ML_2 have been synthesized and characterized using different physico-chemical studies as elemental analysis, FT-IR, 1H NMR, conductivity, magnetic properties, thermal analysis, and their biological activities. The elemental analysis data suggest that stoichiometry to be 1:2 [M:L]. All the complexes are non electrolytic in nature as suggested by molar conductance measurements. Infrared spectral data indicate the co-ordination between ligand and central metal ion through deprotonated phenolic oxygen and azomethine nitrogen. In addition the authors have been screened the compounds for biological activity. It was found that the compounds have shown activity against the organisms like *Escherichia coli*, *Klebsiella* and *Bacillus subtilis*.

Keywords: Synthesis, Characterization, Schiff base (OVP), pramipexole, DNA binding Biological activity

INTRODUCTION

A large number of Schiff bases and their complexes have been investigated for their interesting and important properties, such as their ability to reversibly bind oxygen [1], catalytic activity in the hydrogenation of olefins [2], photo chromic properties [3,4] and complexing ability towards some toxic metals [5]. Schiff bases are a special class of ligands with a variety of donor atoms exhibiting interesting coordination modes towards various metals [6- 8]. The azomethine linkage in Schiff bases is responsible for the biological activities such as antitumor, antibacterial, antifungal and herbicidal activities [9]. Designing a suitable polydentate Schiff base ligand to combine with a metal ion along with pseudo halide anion has opened a new area of synthesizing metal complexes of particular choice [10]. Such complexes are readily assembled from diamines and various aldehyde derivatives and are amenable to combinatorial syntheses [11]. Metal Schiff base complexes have been well known for their easy synthesis, stability and wide application [12-14]. The study of structural and binding features of various Schiff base complexes can play an important role in better understanding of the complex biological process. Schiff bases derived from O-Vanillin are well known for their interesting ligational properties and exclusive applications in different fields. It is well known from the literature that Schiff bases derived from pramipexole have a strong ability to form metal complexes. The interaction of these donor ligands and metal ions gives complexes of different geometries, and literature survey reveals that these complexes are potentially more biologically active. Thus, in recent years Schiff bases and their metal complexes have attained much attraction because of their extensive biological activities [12, 13]. Keeping the above fact in our mind and in continuation of our earlier work on transition metal complexes with Schiff bases the

ligand OVP Schiff base(L) has been synthesized. In the present paper, the synthesis and characterization of the ligand and its complexes with Cu(II), Ru(III) are being reported.

MATERIALS AND METHODS

Instrumentation:

The percentage compositions of the elements (CHNO) for the compounds were determined using an element analyzer CHNO model Fison EA 1108. The Infra red spectra were recorded as potassium bromide (KBr) discs using a JASCO FT/IR-5300. The ¹H (400Hz) nuclear magnetic resonance spectra were recorded using the ACF200 Broker Germany Spectrometer. Ultraviolet Spectra were recorded using Perkin-Elmer lab India UV-Vis Spectrometer. The Electron spin resonance spectra were recorded using the JES-FA Series and TG-DTA spectra were recorded using the SPTQ600 PA, Thermo gravimetric analyses of the metal complexes were carried out by using the Perkin Elmer system in thermal analysis centre Stick Cochin. Melting points were measured on a unimelt capillary melting point apparatus. All materials used in this investigation were purchased from Sigma/Aldrich and AR (Merck). Solvents used were of reagent grade and purified before use by the standard methods.

Preparation of the ligand and its metal complexes: (Preparation of Pramipexole and O-Vanillin Schiff base (OVP)):

Pramipexole 4.22g (0.02mole) and O-Vanillin 3.043g (0.02mole) were dissolved in 25ml of methanol were taken in 250ml borosil reflection flask and 1 ml of triethylamine. The mixture was refluxed for 3 hour on water bath and then cooled to room temperature, dark cream colored sharp needles were separated out and washed with methanol and dried in vacuum desiccators over CaCl₂ anhydrous.

For the Preparation of Cu(II) and Ru (III) metal chloride salts were used. Dissolve 3.454g (0.01 Mole) of newly synthesized ligand in adequate of methanol. To this solution, aqueous solution of 1.3434 g(0.01Mole) and 1.718g (0.01Mole) metal chlorides, and 1 ml of Sodium acetate. The mixture was refluxed for 6hours in a water bath and then cooled to room temperature, Dark green colored, dark brown colored sharp needles were separated out. The coloured metal complexes were washed with water and then methanol, and were recrystallised from ether and dried in vacuum desiccators' over CaCl₂ anhydrous. The elemental analysis was carried out for the newly synthesized ligand metal complexes. The prepared metal complexes were in 1:2 ratio. Ligands and metal complexes analytical data was tabulated in Table-1.

Table-1: Analytical data of the ligand and their metal complexes.

		Complex			
		OVP	Cu(OVP) ₂ X ₂	Ru(OVP) ₂ X ₂	
Molecular weight		345.47	789.48	828.01	
Co lour		Light Yellow	Dark green	Dark brown	
Yield		74	72	73	
M.P		242-244	250-252	262-264	
Elemental Analysis	C %	Calculated	65.52	54.71	52.17
		Found	62.44	52.17	51.76
	H%	Calculated	6.65	6.33	6.03
		Found	6.36	6.03	5.89
	N %	Calculated	12.15	10.63	10.14
		Found	11.98	10.45	10.01
	O%	Calculated	5.079	8.764	8.342
		Found	4.999	8.223	8.001
	M%	Calculated	-	8.04	12.20
		Found	-	7.99	12.04

RESULTS AND DISCUSSION

Infrared spectral analysis:-

Infrared spectra were recorded with a JASCO FT/IR-5300 Spectrometer (4000-400cm⁻¹) using KBr pellets. By utilizing this spectroscopy, the presence of important functional groups in the compound can be identified. Table2 through light on the observation made in analyzing IR spectra of ligand and metal complexes. The typical IR spectra are presented in the Fig.1, 2 and 3.

Interpretation of OVP and Cu(II) and Ru(III) complexes:

The Infrared spectrum of the ligand was compared with the spectra of Cu(II) and Ru(III) complexes. The data was summarized in table along their assignment. The typical IR spectra were shown in Fig.1, 2 and 3. A strong band exhibited at 1649cm^{-1} [16] in the IR spectrum of the ligand has been assigned to the (C=N) Stretching vibration of the azomethine group. On complexation this band is shifted to 1604 and 1594cm^{-1} for Cu (II),and Ru (III) complexes respectively [17] . This shift to lower wave numbers supports the participation of the azomethine group of this ligand in binding to the metal ion. This was due to the reduction of electron density on Nitrogen. There by indicating the coordination of the metal in through the nitrogen atoms.

The IR spectra of metal chelates shows the disappearance of the $\nu(\text{OH})^{[16]}$ bond at 3413cm^{-1} . It indicates the proton displacement from the phenolic (OH) group on complexation. Thus bonding of the metal ions to the ligands under investigation takes place through a covalent link with oxygen of the phenolic group. The IR spectra of Cu(II) and Ru(III) metal complexes exhibit a broad band ^[17] around 3303cm^{-1} and 3419cm^{-1} respectively, which can be assigned to $\nu(\text{OH})$ of water molecules associated with complex formation.

New bands were observed in the complexes, which were not observed in ligand. The bands at 690cm^{-1} and 609cm^{-1} were assigned to stretching frequencies of (M-O), the band at 475cm^{-1} and 490cm^{-1} [18] were assigned to the stretching frequencies (M-N) respectively[19-21].

Table-2: The important IR bands of the Ligand and Their Metal Complexes

Compound	OH Water	OH Phenolic	C=N	N-H	M-O	M-N
OVP	----	3413	1648	3315	-	-
OVP-Cu	3303	-	1604	3303	690	475
OVP-Ru	3419	-	1594	3386	609	490

NMR Spectrum of OVP Ligand and its Metal complexes:

The ^1H NMR spectra of ligand and metal complexes in DMSO- d_6 as solvent were given in fig.4 and 5. The chemical shift values of the ligand and metal complexes were shown in Table-3.

A singlet observed at 6.9 ppm [21] for ^1H NMR spectrum of the OVP ligand is assigned to the proton attached to azomethine (C=N) group [16,17]. The another signal appeared at 1.557 ppm is attributed to the methylene protons of the cyclohexane ring. A singlet is observed in the region 7.1 ppm due to the aromatic -OH protons of phenolic hydroxy group. The multiplet observed at 6.9-7.2 ppm for ^1H NMR spectrum of the = C-H proton of the phenyl ring. A singlet is observed in the region 3.936 [18,19] due to the aromatic -OCH₃ protons of phenolic methoxy group. The another singlet appeared at 9.932 ppm due to N-H proton of ligand.

In the ^1H NMR spectrum of the OVP- Cu complex, a signal appeared due to protons attached to azomethine group at 7.1 ppm. This field shift indicates the deshielding of azomethine proton on coordination through nitrogen atom of azomethine group [27]. The signal observed at 2.3-1.9 ppm due to the methylene protons of cyclohexane ring for the (Cu) complex. . The multiplet observed in the region 6.6-6.9 ppm due to aromatic two C-H protons of phenyl ring for (Cu) complex may be due to the drifting of ring of electrons towards the metal ion. Another multiplet observed in the region of 7.9-8.2 ppm indicate two C-H protons of phenyl ring. A new signal is observed as a singlet at 4.70 ppm in the case of Cu(II) complex indicating the presence of water molecules coordinated to the metal atom. A signal observed at 9.932 ppm in ligand due to N-H proton is shifted to 8.5 ppm for Cu complex. In the ^1H NMR spectrum of the OVP- Ru complex, a signal appeared due to protons attached to azomethine group has been shifted to 7.2. ppm compared to 6.9 ppm in the case of ligand [21]. This downfield shift indicates the deshielding of azomethine proton on coordination through nitrogen atom of azomethine group [27]. The signal observed at 1.6-2.57 ppm due to the methylene protons of cyclohexane ring for the (Ru) complex.. The multiplet observed in the region 6.3-6.39 ppm due to aromatic two C-H protons of phenyl ring for (Ru) complex may be due to the drifting of ring of electrons towards the metal ion. Another multiplet observed in the region of 7.64-7.66 ppm indicate two C-H protons of phenyl ring.]

A new signal is observed as a singlet at 4.9. ppm in the case of Ru(III) complex indicating the presence of water molecules coordinated to the metal atom. A signal observed at 9.932 ppm in ligand due to N-H proton is shifted to 12.07 ppm for Ru complex .

Table -3 NMR Spectral DATA of OVP Ligand and Its Metal complexes

Compound	H-C=N	Ar-H	CH ₂	Ar-OH	N-H	H ₂ O-OH
OVP	6.9	6.9-7.22	1.557	7.1	9.932	-----
OVP-Cu	7.1	6.6-8.2	1.9-2.3	-----	8.5	4.70
OVP-Ru	7.2	6.3-7.66	1.6-2.57	-----	12.07	4.9

Conductivity measurements:

The molar conductance of complexes in DMF ($\sim 10^{-3}$ M) was determined at 27+20C using Systronic 303 direct reading conductivity bridge. A known amount of solid complexes is transferred into 25ml standard flask and dissolved in dimethyl formamide (DMF). The contents are made up to the mark with DMF.

The complex solution is transferred into a clean and dry 100ml beaker. The molar conductances of the complexes were less than 20 $\text{Ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ indicating the Non-electrolytic nature. These values suggest non-electrolytic nature of the present complexes. The molar conductance values of these metal complexes are given in the Table 4.

Table-4: Conductance data for Metal-OVP Complexes: Cell constant: 1.00

S. No.	Metal Complex	Molar Conductance $\text{Ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$
1.	Cu(OVP) ₂	18
2.	Ru(OVP) ₂	21

Electronic spectra:

In UV-Visible electromagnetic radiation, the transitions are associated with the electronic energy levels of the compound under investigation. The electronic spectra were recorded on a Thermo Spectronic Heylosa spectrophotometer. The transition metal ions occur in a variety of structural environments. Because of this, the electronic structures are extremely varied. The electronic structures have been identified with UV-Visible spectroscopy OVP and its metal complexes:

The electronic spectral of ligand and its metal complexes were given in the transitions were reported in the Table-5. Ligand shows signal band at 310 nm, assigned to $\pi-\pi^*$ transition. In complexes this band was shifted to higher wavelength regions. New bands were observed in the complexes at corresponding to the charge transfer transitions. In high concentration spectra of complexes d-d transitions were observed in visible region.

Table-5 : Electronic spectral data

Compound	λ_{max} of compound
OVP	318
OVP-Cu	329
OVP-Ru	345

Magnetic susceptibility measurements of copper (II) and Ruthenium (III) complexes:

The effective magnetic moment values for all the complexes are represented in the Table.6. There are considerable orbital contribution and effective magnetic moments for octahedral complex at room temperature. The magnetic moments of the present (OVP)₂ Cu complex is 4.82 B.M. and the value is less than the spin only value, it shows reduced Para magnetism, which suggest the formation of low-spin complex having octahedral geometry. The magnetic moments of the present (OVP)₂ Ru complex is 1.40 B.M. and this value is less than the spin-only value, showing reduced para magnetism, which suggest the formation of low-spin complex having square planar.

Table-6: Magnetic moments of copper and Ruthenium

S.No.	Metal Complexes	Effect. In B.M.		Number of unpaired electron
		Theoretical	Observed	
1.	Cu(OVP) ₂	4.90	4.82	4
2.	Ru(OVP) ₂	1.80	1.40	1

Thermal analysis:

The thermal studies of these complexes are carried out to know the stability of the complexes on thermal decomposition, as well as to know the different final products that are obtained in thermal decomposition having novel catalytic properties.

Study of OVP and its Cu (II) and Ru (III) metal complexes by TGA-DTA spectra:

Thermo analytical data of metal complexes were given in the Table.8. The representative thermo grams were shown in the fig.8 and 9. The Cu complexes are thermally stable up to 1000°C.

The Copper complex of OVP shows three main decomposition stages, and the first stage with small endothermic dehydration step in the range of 160°C to 180°C was due to loss of two water molecules coordinated to the metal. The Second step involves two sub steps which involves decomposition of the ligand moiety, Exothermic decomposition of the ligand moiety takes place around 210–380°C, to give the stable intermediate M (OVP)₂ and this was stable up to 700°C, which on further undergoes exothermic decomposition in the above 710 in the third stage forming Copper Oxide (CuO) as final residual product.

The Ruthenium complex of OVP shows three main decomposition stages, and the first stage with small endothermic dehydration step in the range of 120°C to 160°C was due to loss of two water molecules coordinated to the metal. The Second step involves two sub steps which involves decomposition of the ligand moiety, Exothermic decomposition of the ligand moiety takes place around 180–360°C, to give the stable intermediate M (>C=N)₂ and this was stable up to 520°C, which on further undergoes exothermic decomposition in the above 520°C in the third stage forming Ruthenium Oxide (RuO) as final residual product.

All the experimental mass loss has shown Table.8. At high temperatures, the corresponding metal oxides were formed, as stable products. All the experimental percentage mass loss was compared with the calculated weights. Based on thermal data it was shown that the stability order of the complexes was Cu (II) > Ru (III).

Table 8 : Thermal analytical data of the Ligand and their metal complexes

Complex X=H ₂ O	Temperature range in °C	Probable assignment	Mass loss (%)	Total mass loss (%)
CuL ₂ X ₂ L=C ₁₈ H ₂₃ N ₃ SO ₂	160-180	Loss of 2H ₂ O molecules	9.53	84.87
	210-380	Decomposition of L	67.46	
	Above-710	Formation of CuO	7.88	
RuL ₂ X ₂ L=C ₁₈ H ₂₃ N ₃ SO ₂	120-160	Loss of 2H ₂ O molecules	12.89	79.64
	180-360	Decomposition of L	58.53	
	Above-520	Formation of RuO	8.22	

DNA Binding studies:

The interactions of all the newly synthesised complexes were monitored by UV–Visible spectral studies. Disodium salt of calf thymus DNA was stored at 5°C. Solution of DNA in the buffer 45 mM NaCl/5 mM Tris HCl (pH, 7.1) in water gave a ratio 1:9 of UV absorbance at 260 and 280 nm, A₂₆₀/A₂₈₀, indicating that the DNA was sufficiently free from protein [28]. The concentration of DNA was measured by using its coefficient at 260 nm (6600 Cm⁻¹) after 1:100 dilutions. Concentrated stock solutions of the complexes were prepared by dissolving in DMSO and diluting suitably with the corresponding buffer to the required concentrations for all the experiments.

The absorption spectra of complexes were compared in the absence and presence of CT–DNA. In the presence of increasing amounts of DNA, the spectra of complexes showed a strong decrease (hypochromicity) in intensity with shift in absorption maxima towards higher (red–shift) wavelengths. The binding of intercalative molecules to DNA has been well characterized by large hypochromism and significant red–shift due to strong stacking interaction between the aromatic chromospheres of the ligand and DNA base pairs with the extent of hypochromism and red shift commonly consistent with the strength of intercalative interaction.

To enable quantitative comparison of the DNA binding affinities the intrinsic binding constants K_b of the complexes for binding with CT DNA were obtained by using the equation.

$$[\text{DNA}]/(\epsilon_a - \epsilon_f) = [\text{DNA}] / (\epsilon_b - \epsilon_f) + 1 K_b (\epsilon_b - \epsilon_f)$$

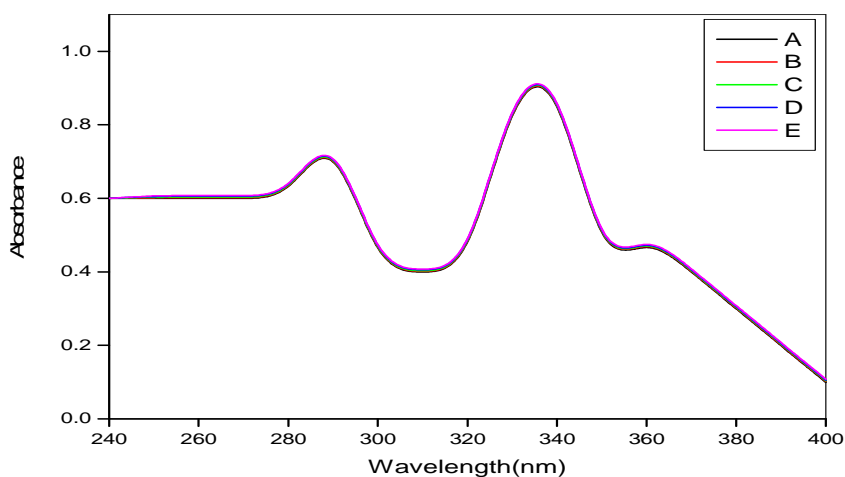
Where [DNA] is the concentration of DNA in base–pairs, ϵ_a is the apparent extinction coefficient obtained by calculating $A_{\text{obs}} / [\text{complex}]$, ϵ_f corresponds to the extinction coefficient of the complex in its free form and ϵ_b refers to the extinction coefficient of the complex in the bound form. Each set of data, when fitted to the above equation, gave a straight line with a slope of $1/(\epsilon_a - \epsilon_f)$ and a y–intercept of $1/K_b (\epsilon_b - \epsilon_f)$ and K_b was determined from the ratio

of the slope to intercept. The intrinsic binding constants K_b , obtained for the complexes.

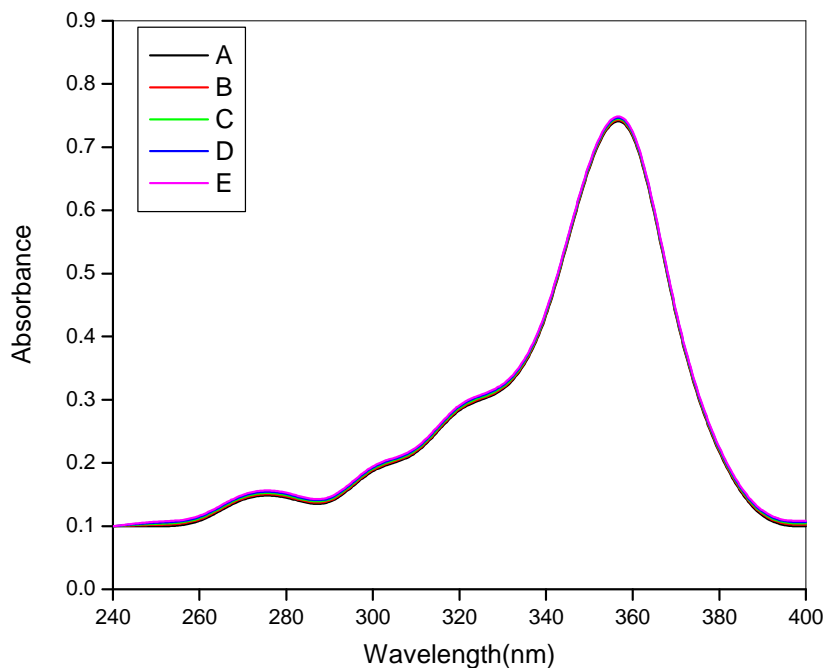
Absorption spectra were recorded 240–400 ranges. The ranges were selected where maximum absorption change observed on addition of DNA. Electronic absorption spectral data upon addition of CT–DNA and binding constants were given in Table 10 it was evident that these complexes bind with DNA with high affinities and the estimated binding constants are in the range of 10^5 – 10^6 M^{-1} . This may due to the presence of pi–stacking of the pyridine ring present in the ligand moiety.

Table.10 DNA binding constants of metal complexes

S.No	Complex (X= H ₂ O)	λ_{max} nm		$\Delta\lambda$ nm	H%	$K_b(M^{-1})$
		Free	Bound			
1	[Cu (OVP) ₂ X ₂]	331	337	6	6.65	3.33×10^6
2	[Ru (OVP) ₂ X ₂]	351	356	5	6.33	4.25×10^6



DNA Binding interaction of Cu [OVP]



DNA Binding interaction of Ru [OVP]

Biological activity:

The author in this present investigation attempted to find out antibacterial activity of ligand and their metal complexes against *Escherichia coli*, *Klebsiella* and *Bacillus subtilis* choosing serial paper disc method Table 9. The results of the biological activity of the metal complexes indicated the following facts. A comparative study of the ligand and their complexes indicates that the metal chelates exhibited higher antibacterial activity than that of the free ligand. The increase in the antibacterial activity of metalchelates was found due to the effect of metal ion on the metal chelates which could be explained on the basis of overtones concept and chelation theory. On chelation the polarity of the metal ion reduced to a greater extent due to the overlap of the ligand orbital and partial sharing of positive charges of metal ion with donor groups. It was further noted that the delocalization of electrons over the whole chelate ring enhanced the lipophilicity of the complexes.

This increase in lipophilicity^[31] enhanced the penetration of the complexes into lipid membrane and blocking the metal sites on enzymes of microorganism. The zones of inhibition of the ligand metal complexes were in the Table.9. The activity was compared with zone of inhibition was measured in mm and reported in of Cu (II) and Ru(III) Complexes of Schiff, is found to be more.

Table 9: Antibacterial Activity of the Metal complexes Total Area of Zone of clearance in mm

S.No.	Compound	<i>Salmonella Typhi</i>	<i>Enterococcus Faecalis</i>	<i>Escherichia coli</i>
1	OVP	15	15	14
2	Cu(OVP) ₂	11	13	11
3	Ru(OVP) ₂	13	14	14

CONCLUSION

The outcome of the above results confirms the stoichiometry of the complexes to be 1 : 2 [M: L] as indicated by elemental analysis and conductometric measurements. IR spectra suggest that the ligand behaves as bidentate and coordinates to the central metal ion through azomethine nitrogen and phenolic –OH group. This has been further confirmed on the basis of NMR spectral studies. Thus, on the basis of above physicochemical and spectral studies the complexes are found to have higher biological activities as compared to the respective ligand and the parent drug that, somehow, justifies the purpose of the research work. The present work will be further extended to the synthesis of metal complexes using other biologically active metals and evaluation of their biological activities. All the metal complexes carry on charge and are thermally stable. As such no single technique is independent of predicting final structures of the complexes.

Acknowledgement

The authors gratefully acknowledge the financial support provided by UGC. They are also indebted to CDRI, Lucknow, for providing the facilities of elemental analysis. The authors are thankful to the Director, Central Instruments Laboratory, University of Hyderabad for the help rendered in obtaining ESR and VSM graphs. They are thankful to IIT Madras for providing IR and NMR. They are also thankful to Sri Krishnadevaraya University, Anantapur for providing TG&DTA, UV and Biological activity.

REFERENCES

- [1] N. Raman, V. Muthuraj, S. Ravichandran, and A. Kulandaisamy *Journal of Chemical Sciences*, **2003**, 115(3) 161–167,
- [2] C. Briickner, S. J. Rettig, and D. Dolphin, *Inorganic Chemistry*, **2000**, 39(2)6100–6106,
- [3] Y. Prashanthi, K. Kiranmai, Ira. Kumar, S. Chityala, and V. K. Shivraj, *Bioinorganic Chemistry and Applications*, **2012**, 12(2)394–403,
- [4] N. Raman, S. J. Raja, J. Joseph, A. Sakthivel, and J. D. Raja, *Journal of the Chilean Chemical Society*, **2008**, 53(3)1599–1604,
- [5] E. Malhotra, N. K. Kaushik, and H. S. Malhotra, *Indian Journal of Chemistry*, **2006**, 45(2) 370–376.
- [6] V. Muresan, L. S. Sbirna, S. Sbirna, C. I. Lepadatu, and N. Muresan, *Acta Chimica Slovenica*, **2001**, 48(3)439–443.
- [7] A. Choudhary, R. Sharma, M. Nagar, and M. Mohsin, *Journal of Enzyme Inhibition and Medicinal Chemistry*,

2011 26(3) 394–403.

[8] L. Tatar, D. Ulku, and O. Atakol, *Acta Crystallographica C*, 199 55(4)508–510.

[9] P. Piotr, H. Adam, P. Krystaian, B. Bogemil, and B. Franz, “*Current Organic Chemistry*, **2009** 13(2)124–148.

[10] F. Shabani, L. A. Saghatforoush, and S. Ghammamy, “*Bulletin of the Chemical Society of Ethiopia*, **2010** 24(2)193–199.

[11] C. T. Supuran, “*Metal-Based Drugs*, 1996 3(1) 25–30.

[12] S. Jain, N. K. Jain, and K. S. Pitre, *Journal of Pharmaceutical and Biomedical Analysis*, **2002**, 29(5) 795–801.

[13] S. Chandra, D. Shukla, and L. K. Gupta, “*Journal of Indian Chemical Society*, **2008**, 85, 800–806, [14] S. Malik, S. Ghosh, and L. Mitu, “*Journal of the Serbian Chemical Society*, **2011** 76(10)1387–1394.

[15] S. Ghosh, S. Malik, B. Jain, and M. Gupta, *Journal of Indian Chemical Society*, **2012**, 89, 471–478, .

[16] R. Sreenivasulu, J. Sreeramulu, K. Sudhakar Babu, *J. Electro.chem. Soc.*, India, **2005**, 54, 11

[17] M. E. Hossain, M. N. Alam, J. Begum, M. Akbar Ali, M. Nagimuddin, F. E. Smith, R. C. Hynes; *Inorganic chimica Acta*, **1996**, 249, 207–213.

[18] T. J. Mabry, K. R. Markham; in the *Flavonoids*, edited by J. B. Harborne, T. J. Mabry, H. Mabry, Chapman and Hall, London p. 78 (**1975**).

[19] W. Heiber, P. John; *J. Chem. Ber.*, **1970** 103, 2161–2167

[20] Z. Jawarska, C. Jose, J. Urbanski; *J. Spectrochim. Acta*, **1974**. 30, 1161–1166

[21] B. Singh, R. D. Singh; *Ind. J. Chem.*, **1982**, 21, 648–652.

[22] Tarek M. A. Ismail; *J. of Coordination Chem.*, (**2006**).

[23] A. H. Maki, B. R. Mcgarvey; *J. Chem. Phys.*, 29, 31–35 **1958**, 59(3) 255–270

[24] M. A. Halcrow, L. M. L. Chia, X. Liu, E. J. L. McInnes, J. E. Davies, et al.; *Chem. Commun.*, 2465 (**1998**).

[25] M. R. Wagner, F. A. Walker; *J. Inorg. Chem.*, **1983**, 22, 3021

[26] S. Kumar and S. Rahang. *Journal of Chemical and Pharmaceutical Research*. **2013**, 5(1):4548. [27] UI Singh; RK Singh; WR Devi; CH Singh, *J. Chem. Pharm. Res.*, **2012**, 4(2), 1130.

[28] S. Prakash; V. P. Vaidya; K. M. Mahadevan; M. K. Shivananda; P. A. Suchetan; B. Nirmala; M. Sunitha, *J. Chem. Pharm. Res.*, **2012**, 4(2), 1179.

[29] IO Adeoye; OO Adelowo; OO Onawumi, *J. Chem. Pharm. Res.*, **2012**, 4(1), 1.

[30] AK Mapari; KV Mangaonkar, *Int. J. ChemTech Res.*, **2011**, 3(1), 477.

[31] M. Rajan; V. Kishor Kumar; P. Satheesh Kumar; K. Reddy Swathi, and S. Haritha, *J. Chem. Pharm. Res.*, **2012**, 4(6), 2860

[32] P. Patel; D. Gor and P. S. Patel, *J. Chem. Pharm. Res.*, **2012**, 4(6):2906–2910