



## SYNTHESIS, SPECTROSCOPIC CHARACTERIZATION AND BIOLOGICAL EVOLUTION OF AZOMETHINE LIGAND AND IT'S THEIR METAL COMPLEXES LIKE CU(II) AND LA(III)

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### ARTICLE INFO

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### ABSTRACT

The present paper deals with the synthesis and characterization of Azomethine derived from p-Toulic Hydrazide metal complexes. The bidentate ligand was obtained by the condensation reaction between p-Toulic Hydrazide with 4-Hydroxy-3-Methoxy Benzaldehyde (Vanillin) in a 1:1 molar ratio. The complexes of Cu (II) and La (III) with general formula  $ML_2$  have been synthesized by using this bidentate ligand. The synthesized complexes were characterized by various spectroscopic techniques like Elemental analysis, IR spectroscopy, NMR spectroscopy, UV-Visible spectroscopy, ESR spectroscopy, VSM. The thermal stability was analyzed by TG-DTA techniques and the conductivity of the synthesized metal complexes was measured. 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. In addition, the compounds were screened for its biological activity and from the results it was found that the compounds have shown activity against the organisms like Escherichia coli, Enterococcus faecalis and Bacillus subtilis.

### INTRODUCTION

The synthesis of new ligands was the most important step in the development of metal complexes which exhibit unique properties. Since the electron donor and electron acceptor properties of the ligands, functional groups and the position of the ligand in the coordination sphere are responsible for the reactivity of coordination compounds<sup>[1]</sup>. Schiff bases are an important class of ligands, the ligands and their metals complexes having potential applications including biological, clinical, analytical,

industrial and catalysis and organic synthesis<sup>[2-5]</sup>. Schiff bases are a special class of ligands with a variety of donor atoms exhibiting interesting coordination modes towards various metals<sup>[6- 8]</sup>. The key factor responsible for the activities in Schiff bases are due to the presence of azomethine linkage which exhibits biological activities such as antitumor, antibacterial, antifungal and herbicidal activities<sup>[9]</sup>. 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<sup>[10]</sup>. Such complexes are readily assembled from diamines and various aldehyde derivatives and are amenable to combinatorial synthesis<sup>[11]</sup>. Metal Schiff base complexes have been well known for their easy synthesis, stability and wide application<sup>[12-14]</sup>. The study of structural and binding features of various Schiff base complexes can play an important role in the better understanding of the complex biological process. In the present paper, the synthesis and characterization of the ligand and its complexes with Cu (II) and La (III) were reported.

## EXPERIMENTAL:

### Methods:

The percentage compositions of synthesized ligands and their metal complexes were determined using an element analyzer CHNO model Fison EA 1108. The Infrared spectra were recorded by using KBr pellets using Perkin-Elmer Spectrum 100. The <sup>1</sup>H (400Hz) nuclear magnetic resonance spectra were recorded using the ACF200 Bruker Germany Spectrometer. The 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, Thermogravimetric analyses of the metal complexes were carried out by using the Perkin Elmer STA 6000 system. Melting points were measured on an unmelt 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 method.

**Synthesis of p-Toluic Hydrazide and 4-Hydroxy 3-methoxy benzaldehyde Schiff Base (VPTH):**

The equimolar concentrations (0.01 moles) of p-Toluic Hydrazide and 4-Hydroxy 3-methoxy benzaldehyde (Vanillin) were

dissolved in 50 ml of methanol in a round bottom refluxing flask. To the above mixture a few drops of Conc. HCl acid were added. Then the mixture was refluxed for about 4 hours in a water bath. On cooling the above mixture light yellow color VPTH crystal products were obtained. The obtained compound was recrystallized by using methanol. The yield and the melting point of the compound is 86% and 186-188°C respectively.

### Synthesis of Cu(II) and La(III) metal complexes of VPTH:

The ligand (VPTH) and metal salts (Cu, La) of 0.01 moles were dissolved separately in 50ml methanol in 2:1 ratio. The content of the mixture was refluxed for half an hour on a water bath. To the mixture 5ml sodium acetate solution was added and refluxed for 7 hours. The reaction mixtures were poured in excess amount of cold water. Dark green (VPTH-Cu), pale yellow (VPTH-La) colored precipitates of metal complexes were obtained with good yield. It was separated by filtration and washed several times with hot water and methanol to free unreacted metal salt ligand respectively and finally dried with ether and in vacuum desiccators. Ligands and metal complexes analytical data was tabulated in Table-1.

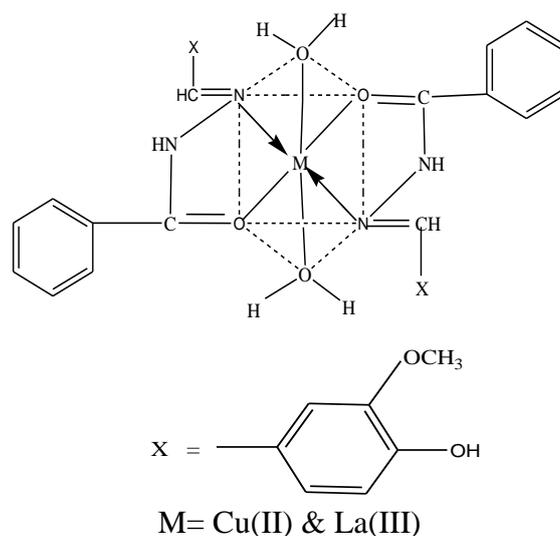


Fig.VPTH metal Complexes

## RESULTS AND DISCUSSION:

### Interpretation of IR spectrum VPTH ligand and its metal complexes:

The Infrared spectra of the VPTH ligand were compared with the spectra of its Cu (II) and La (III) complexes and it is given in Figure1-3. The important and specific IR spectral frequencies along with their assignments are given in Table 2.

A strong band exhibited at  $1640\text{ cm}^{-1}$  in the IR spectrum of the ligand has been assigned to the stretching vibration of C=N bond of azomethine group. On complexation, this band is slightly shifted to the range of  $1606\text{ cm}^{-1}$  and  $1612\text{ cm}^{-1}$ , for Cu(II) and La(III) complexes respectively<sup>[15]</sup>. This shift to lower wavenumbers confirms the interaction of the azomethine group of the ligand and the metal ion. The coordination of azomethine nitrogen to the metal atom would be expected to reduce the electron density in the azomethine group and thus cause for a reduction in C=N stretching frequency. The Bands appeared near  $3612$  and  $1373\text{ cm}^{-1}$  are due to the stretching<sup>[16]</sup> and bending vibrations of phenolic -OH group respectively. In complexes the bands were disappeared due to the deprotonation of phenolic -OH. This is further confirmed by the appearance of new bands in the region  $625\text{-}638\text{ cm}^{-1}$  and  $420\text{-}435\text{ cm}^{-1}$ , which are assigned to the stretching frequencies of M-N and M-O bonds of Cu(II) and La(III) metal complexes<sup>[17]</sup>.

The IR spectrum of the ligand has shown a band in the region  $1462\text{-}1554\text{ cm}^{-1}$  due to the C=C stretching vibrations. The weak band observed around  $3078\text{ cm}^{-1}$  in ligand and the bands at  $3032\text{ cm}^{-1}$ ,  $3022\text{ cm}^{-1}$  in complexes were ascribed to the aromatic C-H stretching vibration. A broadband exhibited at  $3336\text{ cm}^{-1}$  in the IR spectrum of the ligand due to N-H stretching vibration. On complexation, this band shifted to  $3360\text{ cm}^{-1}$  and  $3372\text{ cm}^{-1}$  for Cu(II) and La (III) complexes respectively. The IR spectrum of the ligand has shown a sharp

band at  $1710\text{ cm}^{-1}$  due to C=O stretching vibration. On complexation, this band shifted to  $1705\text{ cm}^{-1}$  and  $1699\text{ cm}^{-1}$  for Cu(II) and La(III) complexes respectively. These results indicate the formation of the complex.

The IR spectra of Cu(II) and La(III) complexes exhibited broad bands at  $3425\text{ cm}^{-1}$  and  $3420\text{ cm}^{-1}$  respectively which can be assigned to the OH stretching vibration of the coordinated water molecules<sup>[18]</sup>. These results indicate that the ligand coordinate with the metal ion through the azomethine nitrogen and the oxygen of the deprotonated hydroxyl group.

### Interpretation of NMR spectra of VPTH ligand and its metal complexes:

The NMR spectra of the VPTH ligand and its Cu(II) and La(III) complexes are shown in the Fig.(4-6) The chemical shift values of ligand and its metal complexes are assignments in Table.3.

A typical NMR Spectra of VPTH ligand was presented in the Fig.4., a singlet observed at  $2.39\text{ ppm}$  for  $^1\text{H}$  NMR spectrum of the VPTH ligand is assigned to the azomethine (H-C=N) proton<sup>[19]</sup>. The singlet appeared at  $0.98\text{ ppm}$  is due to the methyl protons of the phenyl ring. Another singlet observed at  $3.89\text{ ppm}$  for  $^1\text{H}$  NMR spectrum of the methoxy protons of the phenyl ring. A multiplet is observed in the region  $6.86\text{-}7.73\text{ ppm}$ <sup>[20]</sup> due to the aromatic protons of phenyl rings. A singlet appeared at  $11.08\text{ ppm}$  is attributed to the hydroxyl proton attached to the phenyl ring in the ligand. The singlet appeared at  $8.58\text{ ppm}$  due to N-H proton of ligand.

In the  $^1\text{H}$  NMR spectrum of the VPTH-Cu complex as shown Fig.5., a signal appeared due to azomethine proton has been shifted to  $2.33\text{ ppm}$  when compared to the peak observed in ligand at  $2.39\text{ ppm}$ . This downfield shift indicates the deshielding of azomethine proton on coordination through the nitrogen atom of the azomethine group. The signal observed at

0.98 ppm due to the methyl protons in the ligand is shifted to 1.00 ppm for the Cu complex. The signal observed at 3.89 ppm due to the methoxy protons in the ligand is shifted to 3.55 ppm for the Cu complex. The singlet appeared at 11.08 ppm due to phenolic hydroxyl proton is absent in the NMR spectrum of Cu complex indicating the deprotonation of the hydroxyl group and the involvement of that oxygen in coordination<sup>[21]</sup>. A new signal is observed as a singlet at 4.42 ppm in the case of Cu (II) complex indicating the presence of water molecules coordinated to the metal atom. The multiplet observed in the region 6.86-7.73 ppm due to aromatic protons for the ligand showed a shift to 6.54-7.71 ppm for Cu complex may be due to the drifting of the ring of electrons towards the metal ion.

In the <sup>1</sup>H NMR spectrum of the VPTH-La complex are shown in the Fig .6., a peak appeared at due to azomethine proton at 2.39ppm in ligand is shifted to 2.79 ppm due to the formation of complex. This downfield shift indicates the deshielding of azomethine proton on coordination through the nitrogen atom of the azomethine group. The signal observed at 0.98 ppm due to the methyl protons in the ligand is shifted to 0.92 ppm for the La complex. The signal observed at 3.89 ppm due to the methoxy protons in the ligand is shifted to 3.63 ppm for the La complex. The singlet appeared at 11.08 ppm due to phenolic hydroxyl proton is absent in the NMR spectrum of La complex indicating the deprotonation of the hydroxyl group and the involvement of that oxygen in coordination<sup>[21]</sup>. A new signal is observed as a singlet at 4.48 ppm in the case of La (III) complex indicating the presence of water molecules coordinated to the metal atom. The multiplet observed in the region 6.86-7.73 ppm due to aromatic protons for the ligand showed a shift to 6.79-7.74 ppm for La complex may be due to the drifting of the ring of electrons towards the metal ion.

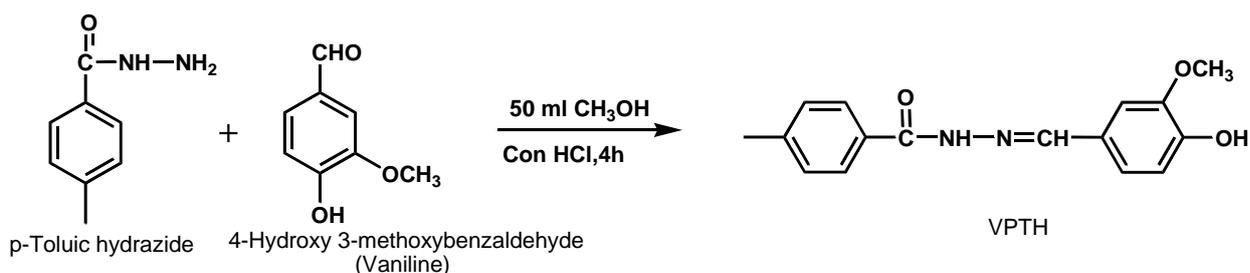
### **Study of Copper and Lanthanum complexes through UV Spectrophotometer:**

The UV-Visible spectra of Cu(II) and La(III) complexes of Schiff base compounds were recorded. The electronic spectra of the aqueous solutions of Cu<sup>+2</sup> and La<sup>+3</sup> individual ions are compared with the corresponding ligand nature. The data is given in table .4 and Fig .(7-9). The data indicates that the energy of the d-d transitions in the complexes is slightly less when compared to the corresponding aqua ions either<sup>[22]</sup> because of slight covalent interaction of the 3d vacant orbitals with ligands, leading to some delocalization with consequent reduction in interelectronic repulsion, or by increased nuclear shielding of the orbitals due to slight covalent ligand-metal electron drift.

The transition for the ligand occurred at 300 nm. But on complexation with the different metal ions like Copper and Lanthanum new bands appeared at 388 nm and 410 nm respectively corresponding to the transitional charge transfer from the ligand to the different metal ions. Bands occurred in the region of 388-410 nm for all complexes are assigned to charge transfer transition (L→M). Based on the results octahedral structure is proposed for Cu<sup>+2</sup> and La<sup>+3</sup> complexes.

### **ESR Spectral studies of VPTH-Cu complex:**

ESR spectra of Cu metal complexes give useful information regarding the stereochemistry and nature of metal-ligand bonding. A broad signal is exhibited in the ESR spectra of the complexes in a polycrystalline state, which is due to dipolar broadening and enhanced spin-lattice relaxation. Anisotropic spectra obtained for the synthesized complexes in DMF at liquid nitrogen temperature and corresponding ESR spectra are given in Fig.10. In this low-temperature spectrum, four peaks of small intensity have been identified which are considered to originate from  $g_{||}$  component.



**Synthesis of p-Toluic Hydrazide and 4-Hydroxy 3-methoxy benzaldehyde Schiff Base (VPTH)**

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

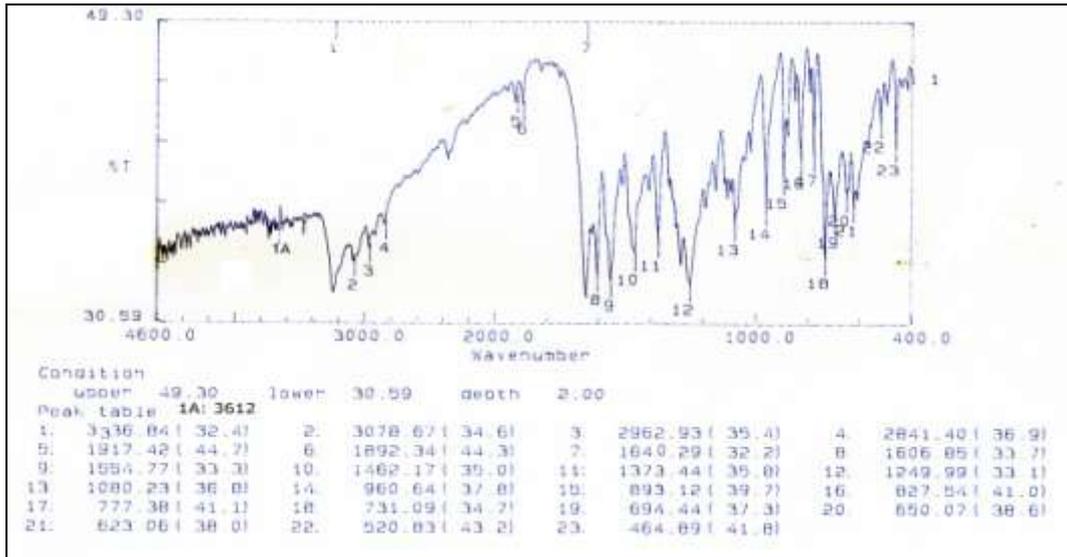
		Complex			
		VPTH	Cu(VPTH) <sub>2</sub> X <sub>2</sub>	La(VPTH) <sub>2</sub> X <sub>2</sub>	
<b>Molecular weight</b>		284.33	668.206	743.56	
<b>Colour</b>		Light yellow	Dark green	Pale yellow	
<b>Yield</b>		86	80	76	
<b>M.P</b>		186-188	298-300	240-242	
<b>Elemental Analysis</b>	<b>C %</b>	<b>Calculated</b>	67.52	57.46	51.64
		<b>Found</b>	67.48	57.39	51.59
	<b>H%</b>	<b>Calculated</b>	5.62	5.38	4.84
		<b>Found</b>	5.56	5.31	4.71
	<b>N %</b>	<b>Calculated</b>	9.85	8.38	7.53
		<b>Found</b>	9.81	8.27	7.45
	<b>O%</b>	<b>Calculated</b>	16.88	19.15	17.21
		<b>Found</b>	16.91	19.07	17.30
	<b>M%</b>	<b>Calculated</b>	-	9.51	18.68
		<b>Found</b>	-	9.42	18.59

**Table .2. Important IR Spectral bands of VPTH ligand and its metal complexes**

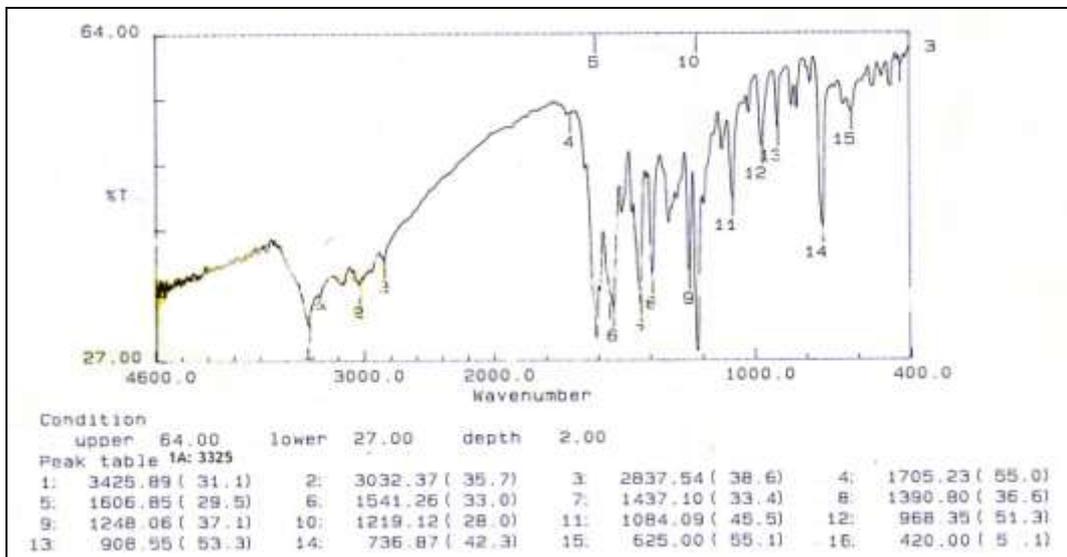
S. No.	Compound	$\nu_{\text{OH Water}}$	$\nu_{\text{OH Phenolic}}$	$\nu_{\text{C=N}}$	$\nu_{\text{N-H}}$	$\nu_{\text{C=O}}$	$\nu_{\text{M-O}}$	$\nu_{\text{M-N}}$
1	VPTH	-	3612	1640	3336	1710	-	-
2	VPTH-Cu	3425	-	1606	3360	1705	420	625
3	VPTH-La	3420	-	1612	3372	1699	435	638

**Table .3. <sup>1</sup>H NMR spectral data of VPTH ligand and its metal complexes**

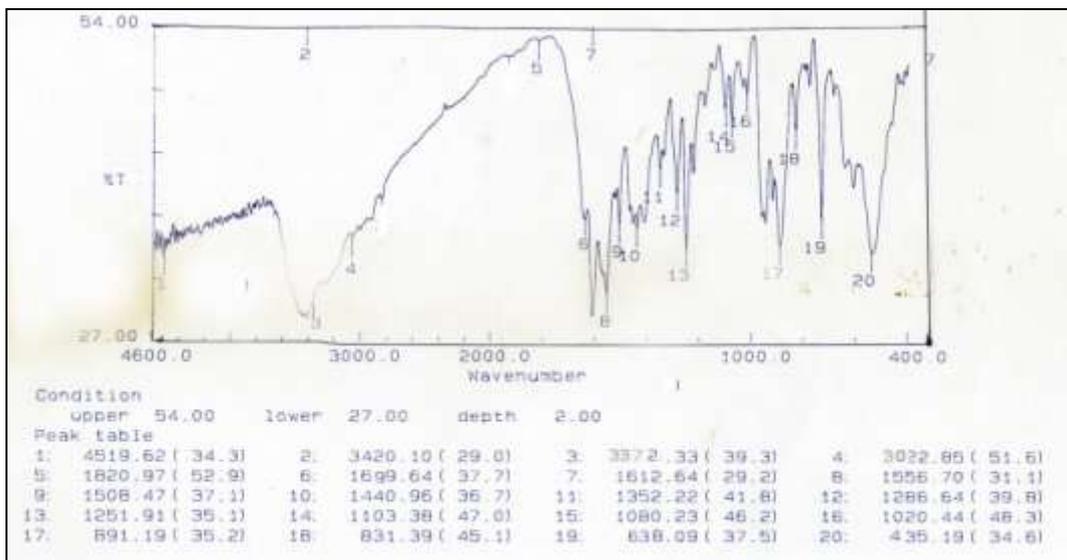
S. No.	Compound	H-C=N	Ar-H	-CH <sub>3</sub>	N-H	Ar-OH	H <sub>2</sub> O-OH	-OCH <sub>3</sub>
1	VPTH	2.39	6.86-7.73	0.98	8.58	11.08	-	3.89
2	VPTH-Cu	2.33	6.54-7.71	1.00	8.48	-	4.42	3.55
3	VPTH-La	2.79	6.79-7.74	0.92	8.40	-	4.48	3.63



**Fig .1:** IR Spectra of VPTH Ligand



**Fig .2:** IR Spectra of VPTH-Cu Complex

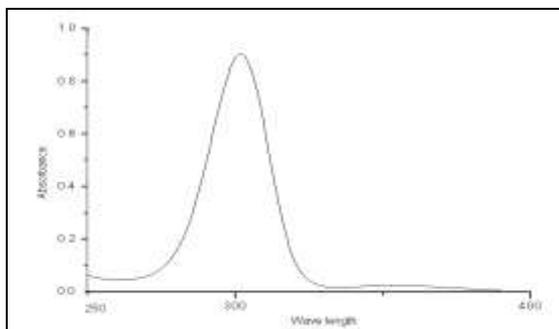


**Fig .3:** IR Spectra of VPTH-La Complex

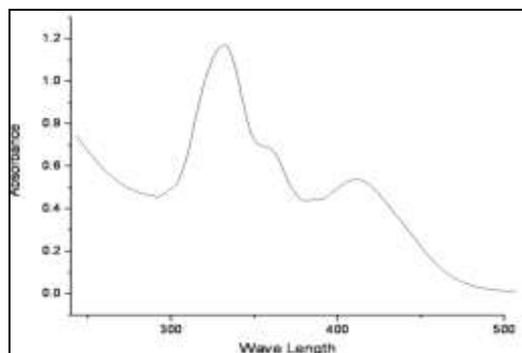
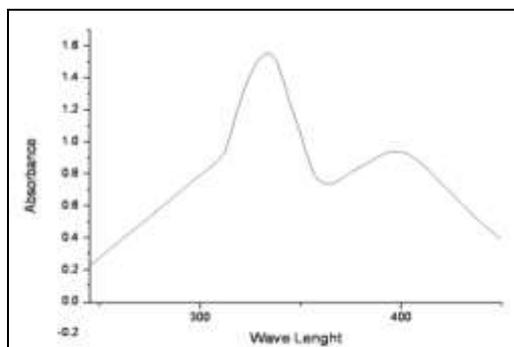


**Table-4. Electronic Spectral data of VPTH ligand and its metal complexes**

S. No.	Compound	$\lambda_{\text{max}}$ of compound
1	VPTH	300
2	VPTH-Cu	388
3	VPTH-La	410



**Fig.V.7:** UV spectra of VPTH ligand



**Fig.V.8&9:** UV spectra of VPTH-Cu & VPTH-La Complexes

**Table:5. Spin-Hamiltonian and orbital reduction parameters of VPTH-Cu complex and VPTH-La in DMF solution**

S.No.	Parameters	VPTH-Cu	VPTH-La
1	$g_{\parallel}$	2.24766	2.04569
2	$g_{\perp}$	2.06121	1.99000
3	$g_{\text{ave}}$	2.1233	2.00856
4	G	4.0460	4.5690
5	$A_{\parallel}^*$	0.01915	0.01922
6	$A_{\perp}^*$	0.00428	0.00582
7	$A_{\text{ave}}^*$	0.00781	0.01068
8	d-d	16222	17472
9	$K_{\parallel}$	0.614	0.614
10	$K_{\perp}$	0.752	0.749
11	$P^*$	0.0172	0.0184
12	$\alpha^2$	0.582	0.616

\* Values are given as  $\text{cm}^{-1}$  units.

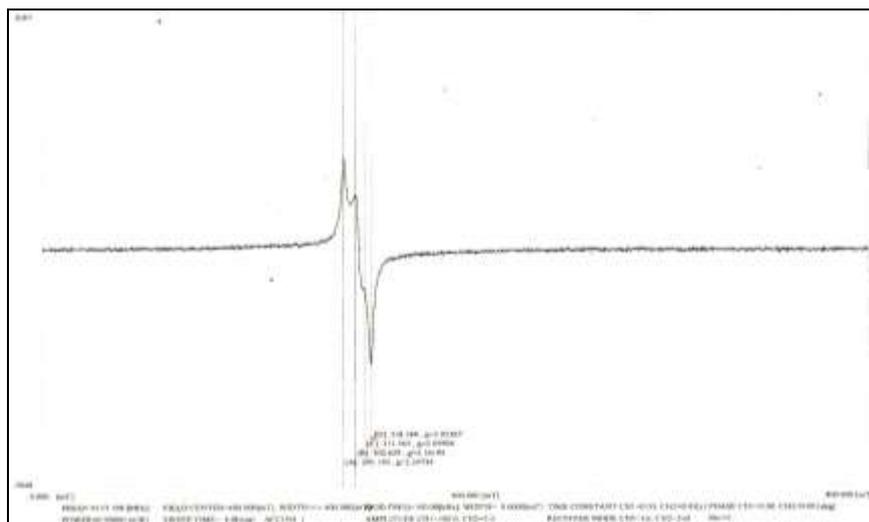


Fig.10: ESR Spectra of VPTH-Cu complex

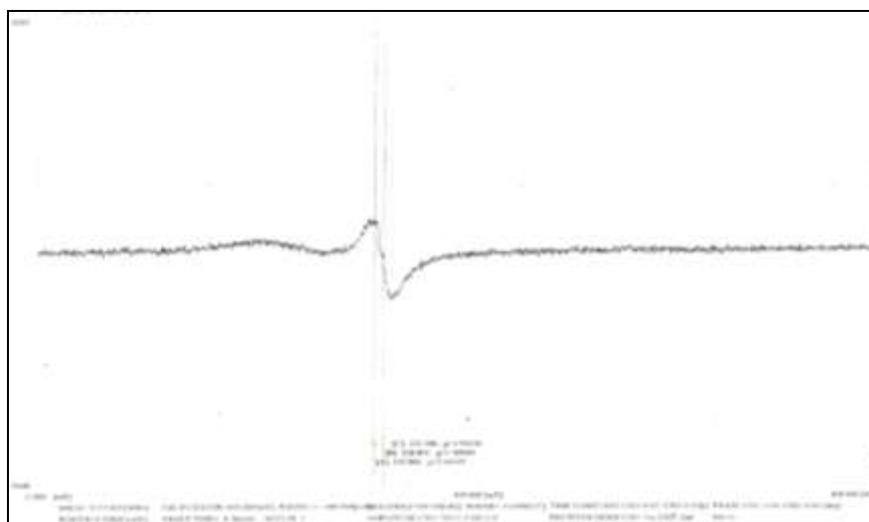


Fig.11: ESR Spectra of VPTH-La complex

Table .6. Magnetic moments of Copper and Lanthanum complexes

S. No.	Complex	Copper in (B.M)	Lanthanum in (B.M)
1	(VPTH) <sub>2</sub>	2.08	5.41

Table 7. Thermal Analytical Data of the VPTH Ligand metal complexes

Complex X=H <sub>2</sub> O	Molecular Wt. in gm	Wt. of the complex taken in mg	Temperature range in °C	Probable assignment	Mass loss (%)	Total mass loss (%)
[Cu L <sub>2</sub> .2X] L=C <sub>16</sub> H <sub>16</sub> O <sub>3</sub> N <sub>2</sub>	668.206	13.57	110 to 220	Loss of 2H <sub>2</sub> O molecules	5.3875	95.025
			260 to 440	Loss of 2L molecules	81.8101	
			Above 440	Corresponds to CuO	11.9044	
[La L <sub>2</sub> .2X] L=C <sub>16</sub> H <sub>16</sub> O <sub>3</sub> N <sub>2</sub>	743.56	12.08	120 to 260	Loss of 2H <sub>2</sub> O molecules	4.841	75.51
			300 to 420	Loss of 2L molecules	73.5192	
			Above 430	Corresponds to LaO	20.8322	

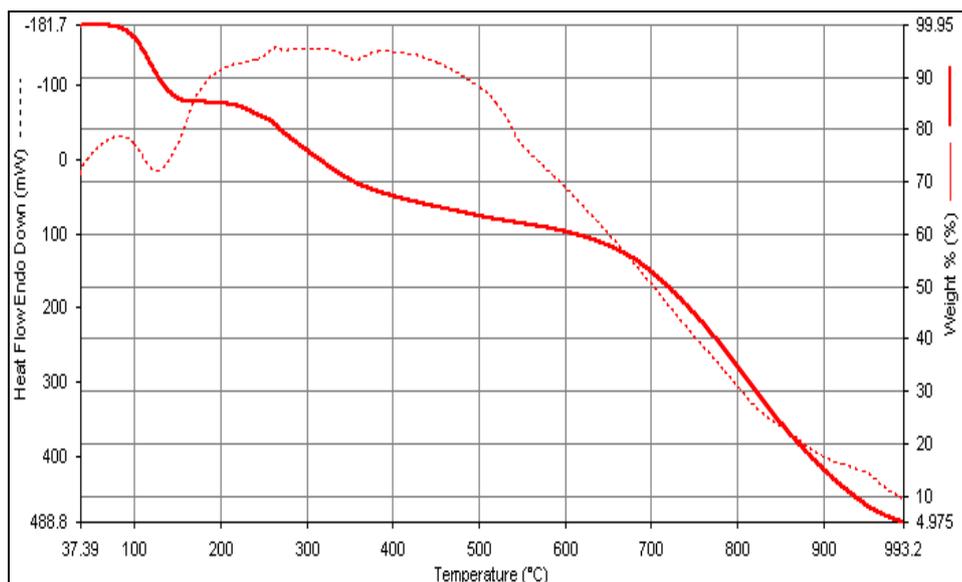


Fig.12: TG/ DTA of VPTH-Cu complex

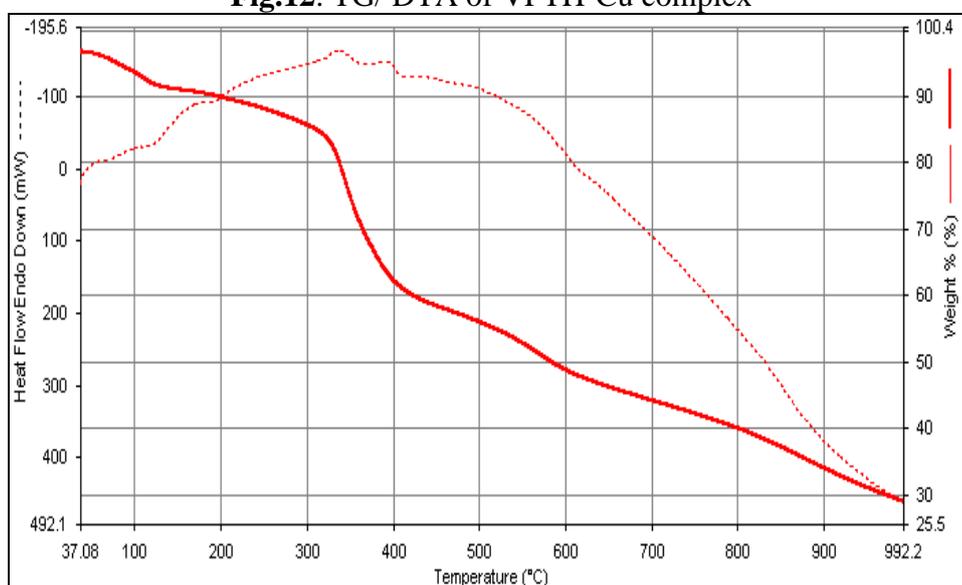


Fig.13: TG/ DTA of VPTH-La complex

Table:8. The molar conductivity of Cu and La complexes

S. No.	Metal complexes	Molar conductance ( $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ )
1	VPTH-Cu	11.12
2	VPTH-La	12.95

Table:9. Antibacterial activities of ligands and their transition metal complexes (Zone formation in mm)

Compound	<i>Escherichia coli</i>	<i>Bacillus subtilis</i>	<i>Enterococcus faecalis</i>
VPTH	8	12	12
(VPTH) <sub>2</sub> Cu	15	10	11
(VPTH) <sub>2</sub> La	9	12	10

The spin Hamiltonian, orbital reduction and bonding parameters of VPTH-Cu complex are presented in table .5.

The  $g_{\parallel}$  and  $g_{\perp}$  are computed from the spectrum using DPPH free radical as g marker. Kivelson & Neiman<sup>[23]</sup> have reported that  $g_{\parallel}$  value is less than 0.08 for covalent character and is greater than 2.3 for the ionic character of the metal-ligand bond in complexes. Applying this criterion, the covalent bond character can be predicted to exist between the metal and the ligand complexes. The trend  $g_{\parallel} > g_{ave} > g_{\perp} > 2.0023$  observed for the complex suggests that the unpaired electron is localized in the  $d_{x^2-y^2}$  or  $d_z^2$  orbital of the Cu (II) ions for the complexes. The G value for the Copper complex is given in table V.8. It is observed that the G value of the present complex is greater than four and suggests that there are no interactions between Copper-Copper<sup>[24]</sup> centers in DMF medium.

The ESR parameters  $g_{\parallel}$ ,  $g_{\perp}$ ,  $A_{\parallel}^*$  and  $A_{\perp}^*$  of the complexes and the energies of d-d transitions are used to evaluate the orbital reduction parameters ( $K_{\parallel}$ ,  $K_{\perp}$ ), the bonding parameters ( $\alpha^2$ ), the dipolar interaction (P). The observed  $K_{\parallel} < K_{\perp}$  indicates the presence of out of plane  $\pi$  bonding. The  $\alpha^2$  value for the present chelate is 0.582. It indicates that the complex has covalent character. This shows an appreciable covalency in the in-plane 'σ' bonding. Girdano and Bereman suggested the identification of bonding groups from the values of dipolar term P. The reduction of P values from the free ion value ( $0.036 \text{ cm}^{-1}$ ) might be attributable to the strong covalent bonding<sup>[25]</sup>. The value of P obtained for the present complex is  $0.0172 \text{ cm}^{-1}$  and remain consistent with the bonding of Copper ions to oxygen and nitrogen donor atoms respectively. The shape of ESR lines, ESR data together with the electronic spectral data suggest an octahedral geometry for VPTH-Cu complex.

### ESR Spectral studies of VPTH-La complex:

ESR spectra of La metal complexes give useful information regarding the stereochemistry and nature of metal-ligand bonding. A broad signal observed the ESR spectra of the complexes in a polycrystalline state, which is attributed to dipolar broadening and enhanced spin-lattice relaxation. Anisotropic spectra obtained for all complexes in DMF at LNT and representative ESR spectra of VPTH-La(III) ion complex is presented in Fig.12. In this low-temperature spectrum, four peaks of small intensity have been identified which are considered to originate from  $g_{\parallel}$  component.

The spin Hamiltonian, orbital reduction and bonding parameters of VPTH-La complex are presented in table .5.

The  $g_{\parallel}$  and  $g_{\perp}$  are computed from the spectrum using DPPH free radical as g marker. Kivelson & Neiman<sup>[23]</sup> have reported that  $g_{\parallel}$  value is less than 0.08 for covalent character and is greater than 2.3 for the ionic character of the metal-ligand bond in complexes. Applying this criterion, the covalent bond character can be predicted to exist between the metal and the ligand complexes. The trend  $g_{\parallel} > g_{ave} > g_{\perp} > 2.0023$  observed for the complex suggests that the unpaired electron is localized in  $d_{x^2-y^2}$  or  $d_z^2$  orbital of La (III) ions for the complexes. The G value for Lanthanum complex is given in table V.8. It is observed that the G value of the present complex is greater than four and suggests that there are no interactions between Lanthanum-Lanthanum<sup>[24]</sup> centers in DMF medium.

The ESR parameters  $g_{\parallel}$ ,  $g_{\perp}$ ,  $A_{\parallel}^*$  and  $A_{\perp}^*$  of the complexes and the energies of d-d transitions are used to evaluate the orbital reduction parameters ( $K_{\parallel}$ ,  $K_{\perp}$ ), the bonding parameters ( $\alpha^2$ ), the dipolar interaction (P). The observed  $K_{\parallel} < K_{\perp}$  indicates the presence of out of plane  $\pi$  bonding. The  $\alpha^2$  value for the present

chelate is 0.616. It indicates that the complex has covalent character. This shows an appreciable covalency in the in-plane ' $\sigma$ ' bonding. Girdano and Bereman suggested the identification of bonding groups from the values of dipolar term P. The reduction of P values from the free ion value ( $0.036 \text{ cm}^{-1}$ ) might be attributable to the strong covalent bonding<sup>[25]</sup>. The value of P obtained for the present complex is  $0.0184 \text{ cm}^{-1}$  and remain consistent with the bonding of Lanthanum ions to oxygen and nitrogen donor atoms respectively. The shape of ESR lines, ESR data together with the electronic spectral data suggest an octahedral geometry for VPTH-La complex.

#### **Magnetic Susceptibility Measurements of Copper and Lanthanum complexes:**

The magnetic susceptibility measurement of ligand and their Cu(II) and La(III) complexes are given in table .6. The Copper complexes at room temperature were observed the magnetic moment range is 2.08 B.M.<sup>[26]</sup>. This magnetic momentum value indicates the presence of unpaired electrons as expected for Cu (II) complex. The magnetic moment value also revealed that the complex is monomeric in nature and metal-metal interaction along the axial positions is absent. It was observed that there was a considerable orbital contribution and effective magnetic moments for an octahedral complex at room temperature around the range 5.0-5.2 B.M for high spin octahedral complexes, the magnetic moment was observed 2.08 B.M for Cu(II) complexes. Thermal analysis showed that the Copper complexes involved the loss of two water molecules at about 110-220°C. This suggests that two water molecules coordinated with the central metal ion, which is further confirmed by their characteristic IR spectrum.

The magnetic susceptibility values are given in table .6. The Lanthanum complexes at room temperature were observed the magnetic

moment is 5.41 B.M.<sup>[26]</sup>. This magnetic momentum value indicates the presence of unpaired electrons as expected for La (III) complex. This magnetic momentum suggests an octahedral geometry. Thermal analysis showed that the Lanthanum complex involved the loss of two water molecules at about 120-260°C. This suggests that two water molecules coordinated with the central metal ion, which is further confirmed by their characteristic IR spectrum.

#### **Thermal behavior of Cu (II) and La(III) Metal complexes of VPTH:**

The Thermogravimetric studies of all the complexes were carried out in the air at a heating rate of 10° C per minute. The thermal analysis curves of the complexes are given in Fig. (12-13) and the data are listed in table .7. The thermal decomposition of the complexes follows three steps degradation. The Cu (II) and La(III) complexes are thermally stable up to 110 and 120°C respectively. The first stage of decomposition corresponding to endothermic dehydration of complexes by the loss of two water molecules occur<sup>[27]</sup> in the temperature range 110-220°C and 120-260°C respectively. The intermediates formed are stable up to 260°C and 300°C. The second decomposition with exothermic peak by the loss of ligand moiety occur in the temperature range 260-440°C and 300-420°C. The solid residues above 440 and 430°C were identified as Cu(II) and La(III) metal oxides respectively. In all the complexes, the final products are metal oxides.

#### **Conductivity Measurements of VPTH metal complexes:**

The molar conductance of complexes in DMF ( $\sim 10^{-3} \text{ M}$ ) was determined at 27+2°C using systronic 303 reading conductivity bridge Cu (II) and La(III) complexes of azomethine compound formed due to the condensation of Vanillin with P-Toluic hydrazide ligands is prepared. The complexes of VPTH ligand are highly soluble in dimethylformamide (DMF).

Therefore these metal chelates are dissolved in DMF to perform conductivity measurements. A known amount of solid complex was transferred into 25 ml standard flask and dissolved in DMF. The contents were made up to the mark with DMF. The complex solution is transferred into a clean and dry 100 ml beaker. The molar conductance values of these metal complexes which are residual are given in Table 8. These values suggest non-electrolytic nature<sup>[28]</sup> of the present complexes.

#### **Biological activity:**

The author in this present investigation attempted to find out the antibacterial activity of ligand and their metal complexes against *Escherichia coli*, *Bacillus subtilis* and *Enterococcus faecalis* choosing serial paper disc method Table 11. 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 metal chelates 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 the 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 increased lipophilicity 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 Table.9.

#### **CONCLUSION**

The Schiff bases of 4-Hydroxy 3-methoxy benzaldehyde with alkalamine namely

p-Toulic Hydrazide and their Cu(II) and La(III) metal complexes were synthesized. The ligand and the metal complexes were characterized using spectral studies and the ligand behaves bidentate during complexation. The obtained metal complexes carry no charge and they are thermally stable.

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