

## Synthesis, characterization and antimicrobial studies of Schiff base ligand and its Ru(III),Pd(II)and Pt(IV) complexes

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### Abstract

*The Schiff base ligand LE[3,3'-((1E,1'E)-(propane-1,3-diylbis(azanylydene)bis(ethan-1-yl-1-ylidone)bis(4-hydroxy-6-methyl-2H pyran-2-one).] and it's solid complexes of Ru(III),Pd(II)and Pt(IV) have been synthesized and characterized by elemental analysis, conductometry, magnetic susceptibility, UV-Visible, FTIR, , Powder X-ray diffraction, and mass spectral analysis. From the microanalytical data, the stoichiometry of the complexes has been found to be 1:1 (metal : ligand) ratio. The diffraction data suggests orthorhombic crystal system for Ru(II) and monoclinic crystal system for Pd(II) complexes. The ligand and their metal complexes were screened for antibacterial activity against staphylococcus aureus , Escherinchia coli and salmonella typhi. and fungicidal activity against Aspergillus flavus and candida albicans.*

**Keywords:** Schiff base ligand, Mass spectrum, FTIR Spectra, Biological activity and X-Ray Diffraction etc.

### INTRODUCTION

Transition metals plays a central role in the construction of molecular materials, which display magnetic properties and find applications in materials and supramolecular chemistry and biochemistry<sup>[1-4]</sup> In past two decades, the field of catalysis has been found to be boon with numerous applications associated with newer and better complexes. Each complex is having higher catalytic efficiency or lower loading ratio or lower toxicity when used in different chemical transformations. Transition metal complexes based on Schiff base ligands have received a bigger proportion of attention due to their diverse structural features. Imine or azomethine groups are present in various natural, naturally derived and non-natural compounds. The imine group present in such compounds has shown to be critical to their biological activities. Schiff bases are important compounds owing to their wide range of industrial applications.

The platinum-group metals are ruthenium, rhodium, palladium and platinum. They have similar physical and chemical peoperties, and tend to occur together in the same mineral deposits. The platinum group metals have many useful catalytic properties<sup>[5]</sup> They are highly resistant to water and tarnish, making platinum, in particular, well suited for fine jewellery. Other distinctive properties include resistance to chemical attack, excellent high-temperature characteristics and stable electrical properties. All these properties have been exploited for industrial applications.<sup>[6-8]</sup>

## EXPERIMENTAL WORK

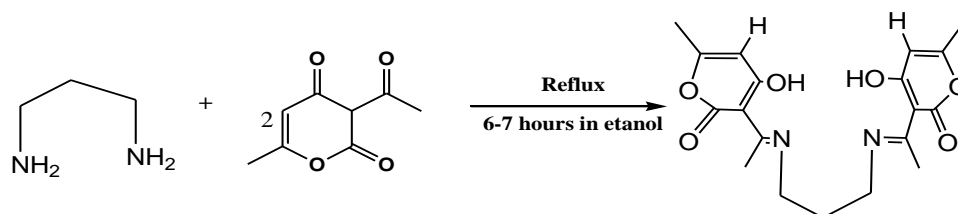
### Material and Method

DHA (dehydroacetic acid), 1,3-diaminopropane, super dry ethanol were used for the synthesis of ligand. AR grade metal chlorides were used for the complex preparation. The carbon, hydrogen and nitrogen contents were determined on Perkin Elmer (2400) CHN analyzer. FTIR spectra were recorded on Jasco FTIR-4100 spectrometer using KBr pellets and XRD were recorded on SDT Q600 V 20.9 build 20 respectively. Magnetic susceptibility measurements of the metal complexes were carried out on Gouy balance at room temperature using Hg [Co(SCN)<sub>4</sub>] as calibrant. Molar conductance of complexes was measured on Elico CM 180 conductivity meter using 10<sup>-3</sup> Solution in DMF.

### Procedure

#### Synthesis of ligand

A hot ethanolic solution (25 ml) of DHA (0.02) and 1,3-diaminopropane (0.01) were mixed slowly with constant stirring. This reaction mixture was refluxed at 80-90°C for 6-7 hours on cooling a solid dark yellow crystalline precipitate appeared, which was filtered, washed with cold EtOH and dried under vacuum over P<sub>4</sub>O<sub>10</sub><sup>[9-12]</sup>



#### Synthesis of complexes:

A hot methanolic (30ml) solution of the ligand (0.001mol) and hot methanolic (30ml) solution of the corresponding metal chlorides (0.001mol) were mixed together with constant stirring. The pH of reaction mixture was adjusted in the range 3-4 by adding 10% methanolic ammonia solution. The reaction mixture was refluxed for 10-12 h at 70-80°C. On cooling, the reaction mixture, colored precipitate was formed. It was filtered, washed with cold ethanol and dried under vacuum over P<sub>4</sub>O<sub>10</sub><sup>[13-15]</sup> (Yield 55-57%).

## RESULTS AND DISCUSSION

Physical characterization, micro analytical, molar conductance data of ligand and its metal complexes are given in Table 1. The analytical data of complexes reveals 1:2 molar ratio (metal : ligand). The presence of water molecules and chloride ions was confirmed by FTIR spectroscopy. The X-ray diffraction data suggest monoclinic crystal system for Pd(II) and orthorhombic crystal system for Ru(III) complexes. The metal chelate solutions in DMSO showed low conductance which supports the non-electrolyte nature of metal chelates.

#### Mass Spectrum of Ligand

Mass Spectral data confirmed the structure of the ligand (L<sub>E</sub>) as indicated by the peak corresponding to its molecular mass (Fig.1)

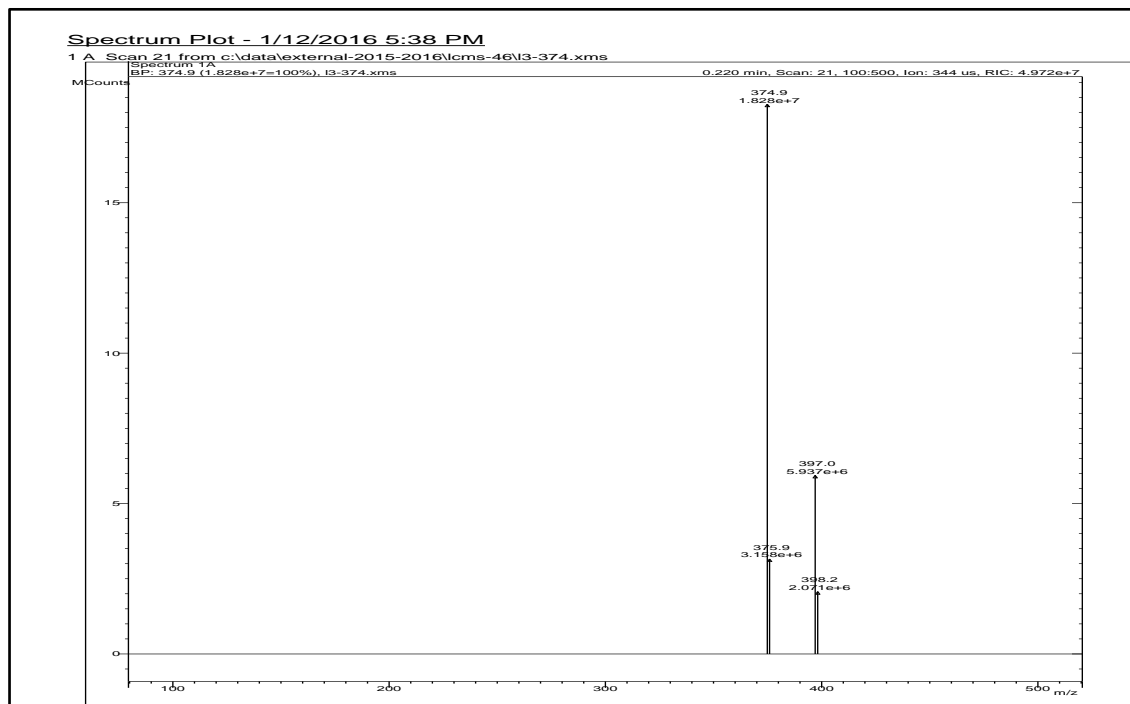


Fig. 1. Mass spectrum of Ligand

### FTIR spectrum

The spectrum of ligand ( $L_E$ ) shows a  $\nu$  (C=N) peak at 1694 and absence of  $\nu$  (C=O) peak at around  $1710\text{ cm}^{-1}$  is indicative of Schiff base condensation. The IR spectra of all complexes shows  $\nu$  (C=N) band at  $1543\text{-}1600\text{ cm}^{-1}$  [16-17] and which have been shifted by about  $40\text{-}29\text{ cm}^{-1}$  to lower energy region compared to that of free ligand ( $L_E$ ). This phenomenon appears to be due to the co-ordination of azo-methine nitrogen to the metal ion [18-19]. The  $\nu$  (OH) vibration of phenolic proton appears in the region  $3200\text{-}3600\text{ cm}^{-1}$ , probably due to the overlapping of the symmetric and antisymmetric OH stretching vibrations of lattice water [20]. The presence of co-ordinated water is also established and supported by TG-DSC analysis of these complexes. The band in the  $450\text{-}470\text{ cm}^{-1}$  region may be assigned to  $\nu$  (M-N) vibration [21]. The IR spectra of the complexes are characterized by the appearance of a broad band in the region at  $3400\text{-}3450$  due to OH group [22-24]. The infrared spectra of the complexes exhibited band in the range  $426\text{-}568\text{ cm}^{-1}$ , assignable to  $\nu$  (M-Cl) stretching vibration [25]. Also the new band in the region  $585\text{-}632\text{ cm}^{-1}$  in the spectra of complexes indicate the vibration  $\nu$  (M-O) bonds respectively [26].

On the basis of above discussion six and four coordinated structure is proposed for Ru(III), Pt(IV) and Pd(II) complexes respectively in which the ligand is coordinated *via* ON donor atoms (Table 2).

### Magnetic measurements:

The magnetic measurements were carried out at room temperature with a Gouy's balance using  $[\text{HgCo}(\text{SCN})_4]$  as a calibrant. Results are as shown in Table.1

**Table 1. Physical characterization, analytical and molar conductance data of ligand and its metal complexes**

Ligand/complexes	F.W.	M.P. ( <sup>o</sup> C)	Magnetic moment (B.M.)	Molar conduc. Mho (cm <sup>2</sup> mol <sup>-1</sup> )	% Found (Calcd.)			
					C	H	N	M
C <sub>19</sub> H <sub>22</sub> N <sub>2</sub> O <sub>6</sub>	373	220	---	-----	60.92(60.74)	5.62(5.64)	5.13(5.00)	-----
[C <sub>19</sub> H <sub>22</sub> ClN <sub>2</sub> O <sub>7</sub> Ru]	527.91	>300	1.43	17.6	43.19 (44.00)	4.21 (4.97)	5.32 (5.12)	19.18 (18.00)
[C <sub>19</sub> H <sub>24</sub> N <sub>2</sub> O <sub>8</sub> Pd]	514.05	>300	Diamagnetic	13.4	44.33 (44.00)	4.71 (3.97)	5.44 (4.92)	20.67 (20.00)
[C <sub>19</sub> H <sub>20</sub> Cl <sub>2</sub> N <sub>2</sub> O <sub>6</sub> Pt]	638.1	>300	Diamagnetic	12.8	35.73 (35.75)	3.16 (3.97)	4.39 (3.99)	30.52 (30.99)

**Table 2. FTIR spectra of the ligand (L<sub>E</sub>) and its complexes (cm<sup>-1</sup>).**

Ligand/complexes	(OH)	(C=N)	(C-O)	(C=O)	(C=C)	(M-N)	(M-O)	(M-Cl)
[L <sub>E</sub> ]	3100	1714	1660	1574	1359	-----	-----	-----
[ RuL <sub>2</sub> Cl H <sub>2</sub> O]	3139	1557	1476	1695	1471	444	---	515
[Pd L <sub>2</sub> ].2H <sub>2</sub> O	3272	1640	1456	1643	1567	538	480	---
[ PtL <sub>2</sub> Cl <sub>2</sub> ]	3020	1643	1446	1695	1518	538	---	426

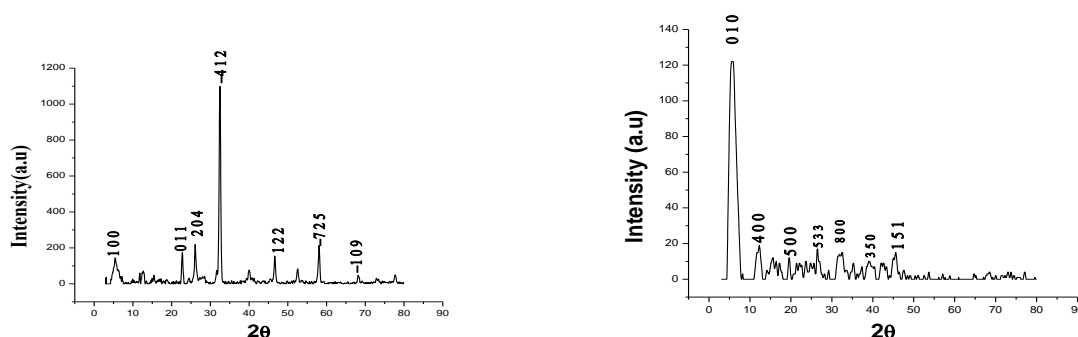
#### Powder X-ray diffraction :

The X-ray diffraction of representative metal complexes were scanned in the range 20-80° at wavelength 1.540 Å. The diffractogram and associated data depict the 2θ value for each peak, relative intensity and inter-planer spacing (d-values). The X-ray diffraction patterns of these complexes with respect to major peaks having relative intensity greater than 10% has been indexed by using computer programme .

The diffractogram of Ru(III) complex showed 11 reflections with maxima at 2θ = 5.84° and it's intensity 122a.u corresponding to d value 15.10 Å. The observed & calculated densities are 2.02 and 1.36 respectively. Unit cell of Ru(III) complex yielded values of lattice constants a = 22.65 Å, b = 15.0995 Å, c = 2.715 Å and unit cell volume V = 945.90 (Å<sup>3</sup>). The standard deviation observed

0.012% is within permissible range. In concurrence with these cell parameters, the conditions such as  $a \neq b \neq c$  and  $\alpha = \beta = \gamma = 90^\circ$  required for sample to be orthorhombic were tested and found to be satisfactory. Hence it can be concluded that Ru (III) complex have orthorhombic crystal system<sup>[27]</sup>.

The diffractogram of Pd(II) complex showed 13 reflections with maxima at  $2\theta = 32.47^\circ$  and its intensity 1099 a.u corresponding to d value  $2.577 \text{ \AA}$ . The standard deviation observed for Pd(II) complex is 0.021 % which is within permissible limit. The observed and calculated densities of complexes are 1 and  $0.7 \text{ g cm}^{-3}$  respectively. The unit cell of Pd(II) complex yielded values of lattice constants  $a = 16.441 \text{ \AA}$ ,  $b = 4.0598 \text{ \AA}$ ,  $c = 1.29 \text{ \AA}$  with unit cell volume  $V = 945.90 \text{ \AA}^3$ . In concurrence with these cell parameters, the conditions such as  $a \neq b \neq c$  and  $\alpha = \gamma = 90^\circ$ ,  $\beta \neq 90^\circ$  required for sample to be monoclinic were tested and found to be satisfactory. Hence, it can be calculated that Pd(II) complexes of have monoclinic crystal system<sup>[28]</sup>.



**Fig.2** Xray diffractogram of Ru (III) complex X-raydiffractogram of Pd(II) complex

### Antimicrobial activity

The antibacterial activity of ligand and its metal complexes were evaluated in vitro against bacteria such as gram +ve bacteria (*staphylococcus aureus*) and gram -ve bacteria (*Escherichia coli*) by agar diffusion method<sup>[29]</sup>. Wells were made on petriplates containing solidified 20 ml Muller Hinton agar medium (250 ppm and 500ppm) in DMF These plates were inoculated for 20-24 hours culture of bacterial strains. Different concentrations of the test samples were filled in the wells and incubated at  $37^\circ \text{C}$  for 24 hours. Control plates with Gentamycin and solvent were maintained. The antibacterial activity was assayed by measuring the diameter of the inhibition zone formed around the well. The results obtained were compared with known standard Gentamycin<sup>[30]</sup> Three replicates were tested at the concentration 250 ppm and 500ppm in DMF and compared with control. The culture of fungi purified by single pore isolation technique. The wells were made on petriplates containing solidified 20 ml sabouroud dextrose agar medium. These plates were inoculated with 36-40 hours. Control plates with Amphotericin B and solvent was maintained. The antifungal activity was assayed by measuring the diameter of the inhibition zone formed around the well. Three replicates of each treatment were repeated in all experiments. From Table 3 and 4, it is clear that the ligand does not show any antibacterial and antifungal activity. Only ruthenium and palladium complex show selective antibacterial and antifungal activity towards the test organism. The platinum complexes showed no appreciable activity which may be due to low solubility of complex<sup>[31-35]</sup>

**Table 3. Antibacterial activity of ligand and its metal complexes.**

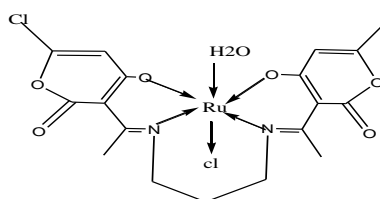
Ligand/complexes	Inhibition zone diameter (mm)					
	E. coli		Staphylococcus aureus		Sallmona typhi	
	250ppm	500ppm	250ppm	500ppm	250 ppm	500ppm
Gentamycin	29	31	26	30	26	27
(LE)	00	00	00	00	00	00
[ RuL <sub>2</sub> Cl H <sub>2</sub> O]	00	00	00	00	00	00
[Pd L <sub>2</sub> ].2H <sub>2</sub> O	00	00	00	00	11	14
[ PtL <sub>2</sub> Cl <sub>2</sub> ].H <sub>2</sub> O	00	00	00	00	00	00

**Table 4. Antifungal activity of ligand and its metal complexes.**

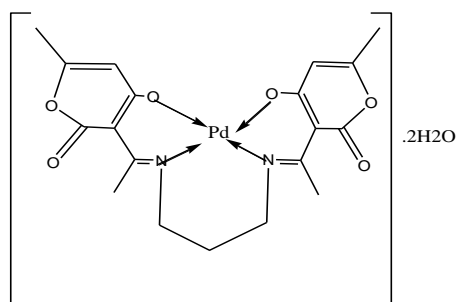
Ligand/complexes	Aspergillus Flavus		Candida albicans	
	250ppm	500ppm	250ppm	500ppm
Control	9	10	9	10
(L <sub>E</sub> )	00	00	00	00
[RuL <sub>2</sub> Cl H <sub>2</sub> O]	00	10	08	09
[Pd L <sub>2</sub> ].2H <sub>2</sub> O	00	00	00	00
[PtL <sub>2</sub> Cl <sub>2</sub> ]	00	00	00	00

## CONCLUSIONS

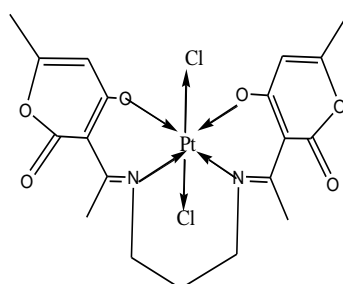
Based on analytical, conductance, magnetic, infrared, electronic spectral data, and X-ray powder patterns of Ru(III), Pt(IV) complexes exhibit six coordination number and Pd(II) complex exhibits four coordination number. A tentative proposed structure of Ru(III), Pd(II) and Pt(IV) complexes is given in Fig. 3. Biological studies of these complexes reveals that these complexes shows negligible activity compared to their respective ligand. The FTIR spectral data suggest that the ligand behaves as a tetradentate ligand with ON donar atoms towards central metal ion. The X-ray diffraction data reveals orthorhombic crystal system for Ru(III) and Monoclinic crystal system for Pd(II) complexes.



**(A) Ru (III)**



(B) Pd (II)



(C) Pt (IV)

Fig 3. Structure of metal complexes.

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