

# Transition Metal Complexes with Unsymmetrical Schiff Base Ligand: Synthesis, Spectroscopic, Thermal, Electrical and Biological Studies

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## ABSTRACT

Complexes of Co(II), Ni(II), Zn(II), Cd(II), Zr(IV) and UO<sub>2</sub>(VI) with an unsymmetrical tetra dentate Schiff base ligand 1-(5-chloro-2-hydroxyphenyl) ethylidene -1-(2-hydroxy-5-methylphenyl)- ethylidencarbohydrazide derived from 2-hydroxy 4-methylacetophenone, 2-hydroxy-4-chloroacetophenone and carbohydrazide have been prepared. All the complexes have been characterized by elemental analysis, UV-Vis and IR spectroscopy, magnetic measurements and thermal analysis. The complexes were found to be quite stable and decomposition of the complexes ended with respective metal oxides as an end product. The IR spectral data suggest that the ligand behaves as a dibasic tetradentate ligand with ONNO donor atoms sequence towards central metal ion. The solid-state electrical conductivity has been measured over 313-403 K temperature range and all the compounds showed semiconducting behavior as their conductivity increases with increase in temperature. Some complexes have been tested for the catalytic oxidation of styrene. The ligand and its complexes have also been screened for their antimicrobial activity using various micro-organisms and all of them were found to be moderately active against the organisms.

**KEYWORDS:** Unsymmetrical Schiff base, Transition metal complexes, d.c. conductivity, TGA, antimicrobial activity.

## INTRODUCTION

Unsymmetrical Schiff base ligands derived from substituted carbohydrazide have played an important part in revealing the preferred coordination geometries of metal complexes and have valuable importance in the coordination chemistry due to their preparative accessibility and structural variability [3, 4]. The preparation of the metal complexes of unsymmetrical Schiff base of carbohydrazide and substituted hydroxyl acetophenone has come from the desire to form simple unsymmetrical complexes for their physicochemical characterization and Recent interest has been growing in the synthesis and characterization of unsymmetrical Schiff basemetal complexes because of their physiological activity, biological capability and applications in analytical chemistry [1, 2]. structural elucidation. In this paper we report the synthesis and characterization of the unsymmetrical Schiff base derived from 2-hydroxy 4-methyl acetophenone, 2-hydroxy 4-chloro acetophenone and carbohydrazide and its metal complexes.

## MATERIALS AND METHODS

All the chemicals and solvents used as starting materials for the synthesis of ligand and its metal complexes were of analytical grade procured from SD's fine chemicals and Qualigens Chemicals. The metal salts used for preparation of complexes i.e, cobalt acetate dihydrate, nickel acetate dihydrate, zinc acetate dihydrate, cadmium chloride monohydrate, zirconyloxchlorideoctahydrateand uranyl acetate dihydrate were used as received.

### Synthesis of *N''*-[1-(5-chloro-2-hydroxyphenyl) ethylidene]-*N'''*- [(1-(2-hydroxy-5-methylphenyl) ethylidene) carbonohydrazide (H<sub>2</sub>L) [5]

An ethanolic solution of 2-hydroxy-5-methyl acetophenone (2.4 g, 0.016 M) was mixed with ethanolic solution of 2-hydroxy-5-chloro acetophenone (2.72 g, 0.016 M) and to this mixture a hot ethanol-DMF solution (60:40 v/v; 25ml) of carbohydrazide (1.44 g., 0.016 M) was added drop wise with continuous stirring. The resulting mixture was refluxed on sand bath for about 7 h. The solvent was then partially evaporated under air and faint yellow coloured compound formed was suction filtered, washed with ethanol, petroleum ether and then dried in vacuo. Yield: 72% ; m.p. 292°C.

12.78 (S, 1H, OH, phenolic), 12.48 (S, 1H, OH, phenolic), 11.16-11.41 (2H, S, imino, NH), 2.21 (S, 6H, CH<sub>3</sub>), 2.15 (S, 3H, Ar-CH<sub>3</sub>), 6.77-7.94 (6H, m, aryl-H).

The schematic representation of the synthesis of ligand H<sub>2</sub>L is shown in figure 1.

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### Synthesis of Co(II), Ni(II), Zn(II), Cd(II) and UO<sub>2</sub>(VI) complex

To a hot DMF solution (25 ml) of ligand (1.0 mmol), a hot ethanolic solution of the appropriate metal salt solution (1.0 mmol) was added slowly with continuous stirring. The resulting mixture was refluxed for 4-5 h. On cooling to room temperature the precipitated solid was filtered, washed several times with ethanol, DMF and petroleum ether to remove unreacted ligand and metal salts. Finally all complexes dried under vacuum at room temperature (Yield: 65-70%).

### Synthesis of Zr(IV) complex

In case of Zr(IV) complex, zirconyloxochlorideoctahydrate (0.64 g, 0.002 mol) was dissolved in methanol (15 mL) and to this a solution of anhydrous sodium acetate (0.32 g, 0.004 mol in 15 mL) was added and stirred for 5 min. The separated sodium chloride was filtered off. The ligand was dissolved in minimum quantity of hot DMF. To this ligand solution, the solution containing oxozirconium (IV) diacetate was added with continuous stirring and the reaction mixture was refluxed on a sand bath for 5h. The colored solid complex obtained was filtered and washed with methanol, DMF and finally with petroleum ether. The products were dried in air at room temperature and stored in desiccators over CaCl<sub>2</sub>. (Yield :60-75 %).

### Biological Activity

The antibacterial activity of ligand H<sub>2</sub>L and its Co(II), Ni(II), Zn(II), Cd(II), Zr(IV) and UO<sub>2</sub>(VI) complexes was tested for their effect on the growth of microbial cultures. Solutions of 100, 200 and 300 ppm of the compounds in DMSO were used for the studies. These discs were placed on the already seeded plates and incubated at 35°C for 24h. The activity was determined by measuring the diameter (mm) of zones showing complete inhibition. For antifungal study Zapek-Dox agar (CDA) media was used.

### Physical measurements:

Elemental analysis carbon, hydrogen and nitrogen were obtained using Carlo Erba 1108 analyzer in micro analytical laboratory, CDRI, Lucknow. IR spectra were recorded on a Perkin-Elmer 597 spectrophotometer using KBr pellets at SAIF Punjab University, Chandigarh. <sup>1</sup>H NMR spectrum of ligand was obtained using a Bruker Avance-II 400 NMR spectrophotometer in DMSO solvent at SAIF Punjab University, Chandigarh. The Electronic spectra of the complexes were recorded on Varian SE UV-NIR spectrophotometer at RSIC, IIT, and Chennai using MgO as reference. Magnetic Susceptibility of complexes was measured by Gouy's method at room temperature and Hg[CO(NCS)<sub>4</sub>] as a calibrant. The diamagnetic corrections were made using Pascal's constants. The solid state d.c. electrical conductivity of compounds was measured by Zentech Electrometer in their compressed pellet form over 313-403 K temperature range. TG analysis of the complexes was carried out on Perkin Elmer TG-2 thermobalance in ambient air with a heating rate of 10°C per minute. Metal contents of the complexes were analyzed gravimetrically after decomposing the complexes with a mixture of HClO<sub>4</sub>, H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub> and then igniting to metal oxide. Biological activities of the ligand and its complexes were carried out against the bacteria *Escherichia Coli*, *Salmonella Abony*, *Staphylococcus Aureus*, *Pseudomonas Aeruginosa*, *Bacillus Subtilis*, *Aspergillus Niger* and *Candida Albicans* by the disc diffusion method [6].

## RESULTS AND DISCUSSIONS

The reaction of 2-hydroxy-5-methyl acetophenone and 2-hydroxy-5-chloro acetophenone with carbohydrazide in hot DMF-ethanol yields Schiff base (H<sub>2</sub>L), the formation of which is supported by its analytical and spectral data. The signal for -OH is obtained at a down field due to possibility of the formation of intramolecular hydrogen bonding with azomethinenitrogen. The reaction of H<sub>2</sub>L in DMF with appropriate metal salts in ethanol gives the complexes. The analytical data for the ligand and complexes are given in table 1. All the complexes are coloured solids, air stable, non-hygroscopic and insoluble in common organic solvents but sparingly soluble in DMSO. The elemental analysis shows 1:1 metal to ligand stoichiometry for all the complexes.

### IR spectra

The IR spectra of the complexes were interpreted by comparing the spectra with that of the free ligand. The IR spectrum of the ligand shows a medium intensity band at 2982 cm<sup>-1</sup> due to intramolecular hydrogen bonding vibrations (O-H...N) [7]. The absence of this band in the spectra of the complexes indicates the breakdown of H-bonding followed by deprotonation of the phenolic OH group and subsequent involvement of phenolic oxygen atom towards coordination [7]. This is further supported by the upward shifting of this ν(C-O) phenolic band by 9-26 cm<sup>-1</sup> from 1246 cm<sup>-1</sup>, suggesting the coordination of phenolic oxygen via deprotonation to the metal ion [8]. The ligand exhibits bands at 1633 cm<sup>-1</sup> and 999 cm<sup>-1</sup> due to azomethine ν(C=N) and ν(N-N) stretches respectively and these bands shifted their positions on complexation. The ν(C=N) band shows red shift by 5-40 cm<sup>-1</sup> while ν(N-N) band shows a blue shift of 12-25 cm<sup>-1</sup> thereby implying the coordination of

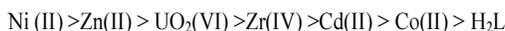
azomethine nitrogen atom to the metal ion [9-12]. The consistent appearance of the  $\nu(\text{C}=\text{O})$  band at  $1702\text{ cm}^{-1}$  in both the ligand and its complexes rules out the involvement of amido oxygen in the coordination. The coordination of  $\text{H}_2\text{O}$  in the Co(II) and Ni(II) complexes is indicated by the appearance of bands at  $3218\text{-}3392$ ,  $1508\text{-}1538$  and  $831\text{-}860\text{ cm}^{-1}$  assignable to  $\nu(\text{OH})$ ,  $\delta(\text{H}_2\text{O})$  and  $\rho\omega(\text{H}_2\text{O})$  modes respectively. The spectrum of Zr(IV) complex shows new bands at around  $975$  and  $1133\text{ cm}^{-1}$  due to  $\nu(\text{Zr-OH})$  vibrations. The  $\text{UO}_2(\text{VI})$  complex also shows band at  $919\text{ cm}^{-1}$  due to  $\nu_{\text{asym}}(\text{O}=\text{U}=\text{O})$  stretches and this indicates the *trans*- $\text{UO}_2$  structure for complex. The appearance of new bands in the complexes in far-infrared regions  $514\text{-}537$  and  $444\text{-}489\text{ cm}^{-1}$  suggests  $\nu(\text{M-O})$  and  $\nu(\text{M-N})$  vibrations respectively [13].

### Electronic spectra and magnetic properties

The electronic spectral data and magnetic moment values have been studied to obtain the geometry of the metal complexes. The Co(II) complex shows three bands at  $10391$ ,  $16388$  and  $23928\text{ cm}^{-1}$ , due to  ${}^4\text{T}_{1g}(\text{F}) \longrightarrow {}^4\text{T}_{2g}(\text{F})$ ,  ${}^4\text{T}_{1g}(\text{F}) \longrightarrow {}^4\text{T}_{1g}(\text{P})$  and  ${}^4\text{T}_{1g}(\text{F}) \longrightarrow {}^4\text{A}_{2g}(\text{F})$ , transitions, respectively in an octahedral environment around the Co(II) ion [14]. The ligand field parameters, Dq, Racah interelectronic repulsion parameter ( $B'$ ), nephelauxetic ratio ( $\beta$ ) and  $\nu_2/\nu_1$  of metal-ligand bond have been calculated for Co(II) complex and the values for Dq,  $B'$ ,  $\beta$  and  $\nu_2/\nu_1$  are  $535\text{ cm}^{-1}$ ,  $610\text{ cm}^{-1}$ ,  $0.64$  and  $1.59$ . The interelectronic repulsion parameter B for the Co(II) complex is  $610$  and it is found to be lower than the free Co(II) ion value ( $B'$ ) of  $971\text{ cm}^{-1}$ , which indicates orbital overlap and delocalization of d-orbitals. The magnetic moment value for the Co(II) complex is found to have  $4.88\text{ B.M.}$ , which is in good agreement with high spin octahedral geometry. Since spin only value for three unpaired electrons is only  $3.94\text{ B.M.}$ , the slight high value in the present case may be attributed to orbital contribution. The Ni(II) complex exhibits three bands at  $10616$ ,  $16950$  and  $25978\text{ cm}^{-1}$  due to spin allowed transitions  ${}^3\text{A}_{2g}(\text{F}) \longrightarrow {}^3\text{T}_{2g}(\text{F})$ ,  ${}^3\text{A}_{2g}(\text{F}) \longrightarrow {}^3\text{T}_{1g}(\text{F})$  and  ${}^3\text{A}_{2g}(\text{P}) \longrightarrow {}^3\text{T}_{1g}(\text{P})$ , respectively, in an octahedral symmetry [15]. The ligand field parameters, Dq, Racah interelectronic repulsion parameter ( $B'$ ), nephelauxetic ratio ( $\beta$ ) and % covalency of metal-ligand bond have been calculated for Ni(II) complex and the values obtained are Dq,  $B'$ ,  $\beta$ ,  $\nu_2/\nu_1$  and % covalency  $1063\text{ cm}^{-1}$ ,  $740\text{ cm}^{-1}$ ,  $0.73$ ,  $1.61$  and  $28.48$ . The value of  $\beta$  observed for the complex is lower than the Ni(II) free ion value which indicates the covalent character in the metal-ligand bonds. The  $\nu_2/\nu_1$  ratio for Ni(II) complex is  $1.60$  and this lies in the usual range reported for majority of octahedral Ni(II) complexes. The Ni(II) complex has a magnetic moment of  $3.10\text{ B.M.}$  which lie in normal range expected for magnetically dilute octahedral Ni(II) complexes. The Zn(II) and Cd(II) complexes under present study are found to be diamagnetic. This is in accordance with the  $d^{10}$  (i.e. completely filled  $d'$  sub shells) configurations of Zn(II) and Cd(II) ion and both complex may have tetrahedral geometry. The Zr(IV) and  $\text{UO}_2(\text{VI})$  complex are found to be diamagnetic as expected from their electronic configurations and may have octahedral geometry.

### Thermogravimetric study

An examination of the thermograms of  $\text{H}_2\text{L}$  and its metal complexes (fig. 2) indicates that they are with varying thermal stability undergoing decomposition at different temperatures. The Co(II), Ni(II), Zn(II), Cd(II) and  $\text{UO}_2(\text{VI})$  complexes show that these complexes undergo two stage decomposition pattern whereas Zr(IV) complex shows three stage decomposition patterns. The TG curve of Zr(IV) complex shows elimination of one water molecule takes place between  $80\text{-}125^\circ\text{C}$  indicating the presence of lattice water molecule whereas in Co(II), Ni(II) and Zr(IV) complexes water eliminated in between  $140\text{-}225^\circ\text{C}$  indicating the presence of these water molecules as coordinated one [% wt. loss, obs./calcd. Zr(IV):  $3.60/3.37$  for lattice water and Co(II) :  $3.98/3.68$ ; Ni(II)  $3.82/3.74$  and Zr(IV) :  $3.54/3.37$  for coordinated water]. In the TG curve of Zn(II), and Cd(II) complex, there is no weight loss up to  $245^\circ\text{C}$ , and this rules out the presence of any water molecule in these complexes.  $\text{UO}_2(\text{VI})$  complex are almost stable up to  $160^\circ\text{C}$  indicating that absence of lattice or coordinated water molecule. The continuous and rapid weight loss has been observed above  $250^\circ\text{C}$  corresponding to thermal degradation of free part of the coordinated ligand along with the other groups present there in. A gradual weight loss above  $\sim 430^\circ\text{C}$  corresponding to the degradation of actual coordination part of the ligand. The percent weight loss as compared from thermograms of the metal complexes suggests that the final product of decomposition in them corresponds to respective metal oxide. The half decomposition temperature of the compounds decreases in the order:



From the thermal decomposition data various kinetic parameters have been evaluated by using Horowitz-Metzger method [16]. The negative values of  $\Delta S$  suggest a more ordered activated state than the individual reactants and may be possible through the chemisorption of oxygen and other decomposition products. No definite trend in the values of  $E_a$  is observed. The activation energies of decomposition are found to be in the range  $11.35\text{-}57.36\text{ kJmol}^{-1}$ . The thermal decomposition data of the compounds is given in table 2.

### Electrical conductivity measurements

The values of solid state d.c. electrical conductivity of the ligand and its complexes is given in table 1. The solid state d.c. electrical conductivity was measured in their compressed pellet form from room temperature to 403 K. The solid state d.c. electrical conductivity increases with increasing the temperature [17]. The electrical conductivity ( $\sigma$ ) varies experimentally with the absolute temperature according to the relation  $\sigma = \sigma_0 \exp(E_a/kT)$  where  $\sigma_0$  is constant,  $E_a$  is the activation energy of electrical conduction,  $T$  is the absolute temperature and  $k$  is Boltzmann constant. In the solid state d.c. electrical conductivity measurements the plot of  $\log \sigma vs 1/T$  are found to be linear over studied ranged temperature indicates their semiconducting behavior [18]. The values of electrical conductivity lie in range  $1.68 \times 10^{-11}$  to  $2.61 \times 10^{-5}$  eV.

### Biological Activity

Minimum inhibitory concentrations of these compounds were determined by literature method [19, 20]. The results for antibacterial study are interpreted by measuring the zones of inhibition of growth of the bacterial culture. Antibacterial screening of ligand and its complexes against *E. Coli*, *S. abnoy*, *S. aureus*, *P. aeruginosa* and *B. Subtilis* strains were carried out. The results show (figure 3 and table 3) that the ligand exhibit good biocidal behavior towards all the bacterial streams. Co(II), UO<sub>2</sub>(VI), Zn(II), Ni(II) and Zr(IV) complexes show higher antibacterial activity against *P. aeruginosa* as compared to other bacterial strains. Co(II), UO<sub>2</sub>(VI), Ni(II), Cd(II) complexes are highly active against *E. Coli* than *C albicians*. Other metal complexes show moderate activity against all the bacterial and fungal culture. UO<sub>2</sub>(VI), Zr(IV) and Zn(II) complexes has maximum antibacterial activity whereas UO<sub>2</sub>(VI), Ni(II) and Zn(II) complexes has maximum antifungal activity. All the compounds were sensitive towards the micro organism screened in the present study. In general the results reveal that the antimicrobial activity of the ligand found to be enhanced on complexation with metal ions. It has been observed that the metal complexes show enhanced antibacterial activity as compared to the free ligand. The same microorganism under identical experimental conditions, this is due to complexation [6]. This may be explained by chelation theory, according to which chelation or complexation reduces the polarity of central metal atom because of partial sharing of its positive charge with the donor group within the whole chelate ring system. This chelation increases the lipophilic nature of the central atom, which favor the permeation of the complexes through the lipid layer of the cell membrane and results in enhancement of activity.

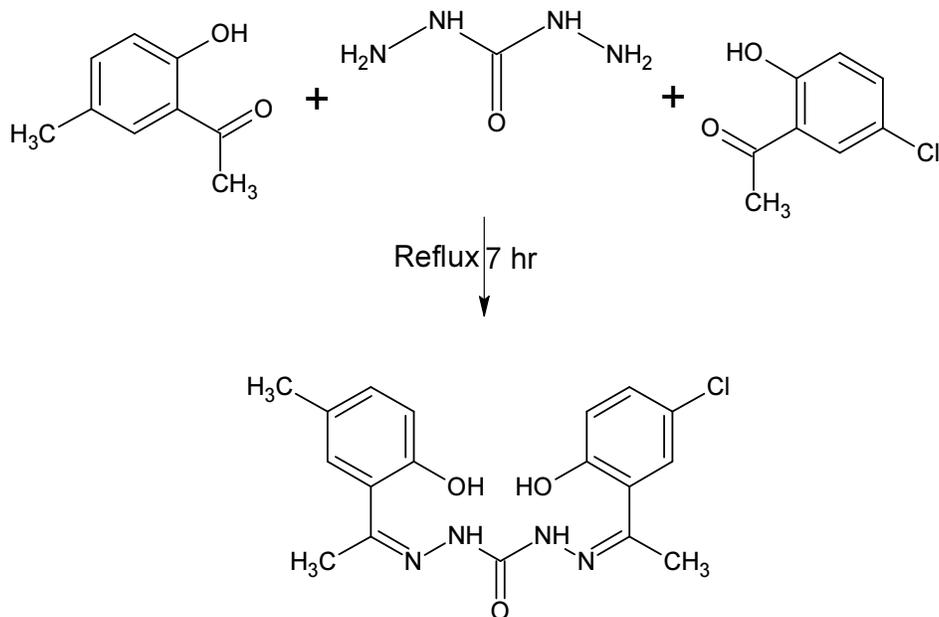


Fig 1: Synthesis of ligand (H<sub>2</sub>L)

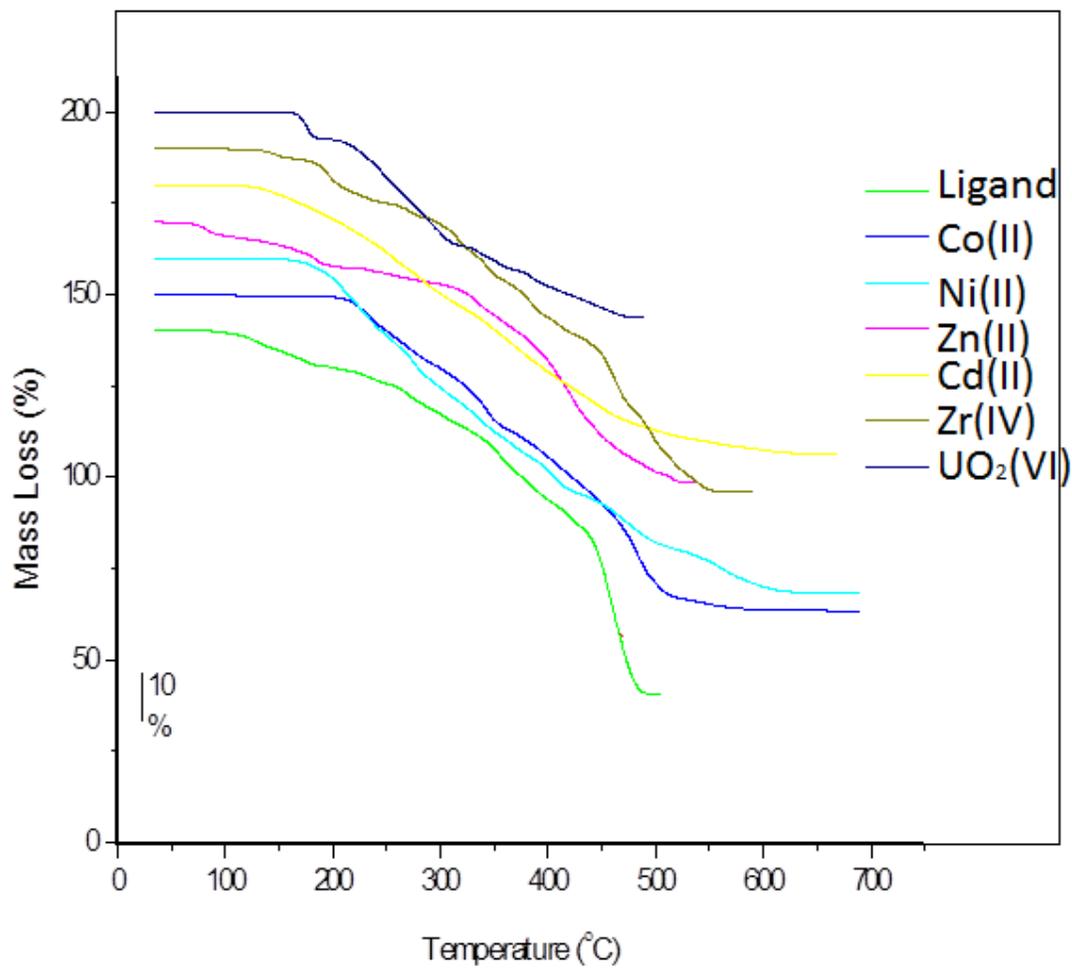


Fig. 2: Thermograms of ligand and its complexes

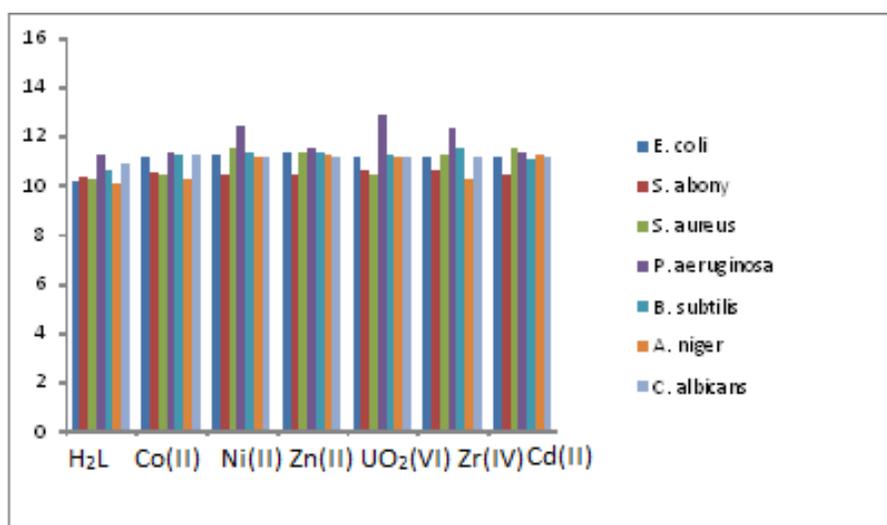


Figure 3: Antimicrobial activity of H<sub>2</sub>L and its complexes

Table 1: Analytical and Physical data of ligand and its complexes

Sr. No.	Compound	Formula Weight (gmol <sup>-1</sup> )	Colour	Elemental analyses % found (calcd.)				Electrical Conductivity $\sigma$ ( $\Omega^{-1}\text{cm}^{-1}$ ) at 373 K	Activation energy (eV)
				C	H	N	M		
1	H <sub>2</sub> L	374.82	Avocado	57.32 (57.68)	5.02 (5.11)	14.12 (14.95)	--	1.68 x 10 <sup>-11</sup>	0.9961
2	[Co L (H <sub>2</sub> O) <sub>2</sub> ]	465.75	Light brown	46.42 (46.38)	4.11 (4.27)	12.03 (12.36)	12.65 (12.82)	3.84 x 10 <sup>-6</sup>	0.8453
3	[Ni L (H <sub>2</sub> O) <sub>2</sub> ]	465.51	Copper leaf	46.44 (46.59)	4.11 (4.25)	12.04 (11.39)	12.61 (12.58)	6.53 x 10 <sup>-8</sup>	0.8342
4	[Zn L]	436.19	Leaf brown	49.56 (49.67)	3.47 (3.65)	12.84 (12.98)	15.00 (15.32)	2.61 x 10 <sup>-5</sup>	0.7231
5	[CdL]	483.20	Mid buff	44.74 (44.82)	3.13 (3.42)	11.59 (11.84)	23.23 (23.93)	4.20 x 10 <sup>-10</sup>	0.6720
6	[Zr L(OH) <sub>2</sub> H <sub>2</sub> O] H <sub>2</sub> O	532.06	Yellow Gold	40.63 (40.15)	5.01 (4.34)	11.27 (10.49)	17.14 (17.08)	2.97x 10 <sup>-9</sup>	0.6007
7	[UO <sub>2</sub> L]	642.83	Khaki	32.84 (33.63)	1.89 (2.67)	7.68 (8.72)	36.39 (37.03)	4.18 x 10 <sup>-7</sup>	0.5519

Table 2: Thermal decomposition data of ligand and its complexes

Sr. No.	Compound	MP*/Half Decomp. Temp. (°C)	Activation Energy 'Ea' (K J mol <sup>-1</sup> )	Frequency factor 'Z' (s <sup>-1</sup> )	Entropy Change 'ΔS' (J mol <sup>-1</sup> K <sup>-1</sup> )	Free Energy Change 'ΔG' (K J mol <sup>-1</sup> )
1.	H <sub>2</sub> L	308	11.35	20.42	-27.16	28.06
2.	[Co L (H <sub>2</sub> O) <sub>2</sub> ]	380	15.83	12.33	-27.64	32.14
3.	[Ni L (H <sub>2</sub> O) <sub>2</sub> ]	428	54.63	60.56	-26.19	71.23
4.	[ZnL]	442	28.76	33.46	-26.80	48.10
5.	[CdL]	385	39.96	40.63	-26.51	56.81
6.	[Zr L(OH) <sub>2</sub> H <sub>2</sub> O] H <sub>2</sub> O	425	48.51	62.61	-26.17	66.78
7.	[UO <sub>2</sub> L]	422	57.36	52.90	-26.33	75.61

Table 3. Antimicrobial Activity of compounds

Sr. No.	Name of ligand and complex	Antimicrobial activity					Antifungal activity	
		Zones of inhibition (in mm)						
		<i>E.coli</i>	<i>S. abony</i>	<i>S. aureus</i>	<i>P. aruginosa</i>	<i>B. subtilis</i>	<i>A. niger</i>	<i>C. albicans</i>
1	H <sub>2</sub> L	11.13	11.32	11.23	12.24	11.58	11.10	11.92
2	[Co L (H <sub>2</sub> O) <sub>2</sub> ]	12.11	11.48	11.40	12.31	12.20	11.20	12.22
3	[Ni L (H <sub>2</sub> O) <sub>2</sub> ]	12.22	11.42	12.50	13.42	12.32	12.12	12.12
4	[ZnL]	12.32	11.41	12.30	12.52	12.30	12.22	12.15
5	[CdL]	12.12	11.62	11.42	11.82	12.27	12.11	12.12
6	[Zr L(OH) <sub>2</sub> H <sub>2</sub> O] H <sub>2</sub> O	12.12	11.60	12.20	13.32	12.50	11.22	12.12
7	[UO <sub>2</sub> L]	12.12	11.42	12.50	12.32	12.10	12.24	12.12

Concentration: 100 µg/ml

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