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Research Article

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Synthesis, characterisation, antimicrobial activity, DNA cleavage studies on binary complexes of Cu(II), Ni(II), Co(II) and Ru(II) with (*R*)-*N*-(phenyl)ethyl-5-chloro-2-hydroxy-1-salicylaldimine schiff base

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ABSTRACT

A series of binary complexes of Co(II), Ni(II), Cu(II) and Ru(II) with (R)-N-(phenyl)ethyl-2-hydroxy-1salicylaldimine (L or NPEHS) have been synthesised. The Ligand (NPEHS) is co-ordinated to the metal ion with the N, O donor atoms in 1:2 (metal : ligand) ratio and it is determined by spectrophotometric studies. The resulting metal complexes of NPEHS were characterised by the FT-IR, UV-Vis, TGA, elemental analysis, conductivity measurements and ESR spectral studies. Conductometric measurements confirm all the metal complexes were nonelectrolytic in DMSO. Based on spectral and analytical data octahedral geometry is assigned to the complexes with two coordinated water molecules. The stoichiometry of the resulting complexes have been found to be $[M(L)_2(H_2O)_2]$, here M = Co(II), Ni(II), Cu(II) and Ru(II). The in-vitro antimicrobial studies performed through the Disc Diffusion Method revealed that the complexes have shown better antimicrobial activity than free ligand. DNA cleavage of metal complexes are also confirmed through the gel electrophoresis technique. It is found that these complexes effectively cleave the DNA.

Key words: Binary metal complexes, spectral analysis, antimicrobial activity, spectrophotometry and DNA cleavage.

INTRODUCTION

In the coordination chemistry of transition, inner transition and main group elements, Schiff bases have been used as an important class of ligands [1,2]. It is due to the azomethine linkage present in them and is responsible for various biological actions like antibacterial, antifungal, herbicidal and clinical activities [3-5]. For the past few decades transition metal complexes have been receiving much attention in homogeneous asymmetic catalysis [6-8]. The importance of these chiral based ligands is to synthesize the metal complexes of single isomer, which are required to develop the large number of potential applications in cancer therapy [9], DNA targeting [10,11], molecular sensors [12,13], recognition of anion [14,15] and supramolecular chemistry [16,17].

Schiff base ligands like bis(*N*-alkyl-salicylideneimine) incorporated into some Cu(II), or Ni(II) metal complexes are known to exhibit flexible structural changes [16]. Many metal complexes based on salicylidenimine derivatives are useful bidentate ligands containg N,O- donor atoms. These complexes have been investigated for their physical, chemical and catalytic properties. Some structural features of Cu(II), Co(II) and Ni(II) complexes of salicylidenimine ligands have recently reviewed by the Blagus *et al.* [17]. Due to the promotion of chelation and extra stability to the metal centers given by these salicylidene Schiff bases, considerable importance has been given to them. In the present work synthesis and characterisation of some novel binary octahedral metal complexes was carried out using the ligand (R)-N-(phenyl)ethyl-2-hydroxy-1-salicylaldimine (L or NPEHS). Metal complexes have shown a very good antimicrobial activity than free ligand.

EXPERIMENTAL SECTION

Chemicals: The chemicals used in the present work were of analytical grade. The metal salts used were in their hydrated form.

Synthesis of ligand (*R*)-*N*-(phenyl)ethyl-2-hydroxy-1-salicylaldimine: (NPEHS or L):

A mixture of (*R*)-1-phenylethylamine (0.45 mL, 3.3 mmol) and 5-chloro-2-hydroxy-1-salicylaldehyde (0.48 g, 2.8 mmol) in dichloromethane (DCM) (20 mL) was stirred at room temparature for 8 h. After removal of the solvent the residue was chromatographed on silica gel using diethyl ether/hexane as an eluent to give the required ligand L (0.74 g, 96%) as a yellow precipitate (Scheme 1).



Scheme 1: Synthesis of NPEHS ligand (L)

Synthesis of metal complexes: Metal(II) chloride hydrates (1.0 mmol) dissolved in methanol (2 mL) was added slowly to the solution of the (*R*)-*N*-(phenyl)ethyl-2-hydroxy-1-salicylaldimine (LH) (1.0 mmol) in methanol (100 mL) with continuous stirring. The pH of the solution was slowly raised to obtain the required pH for the formation of the metal complexes by drop-wise addition of triethyl amine in methanol solution. The resulting mixture was stirred for 4-6 hours at reflux temperature. The complexes thus formed were filtered out, washed with methanol followed by water and dried under vacuum over fused $CaCl_2$.

Instruments used: FT-IR spectra of the ligand and its complexes were recorded by using KBr pellets in the range 4000-400 cm⁻¹ on Prestige-21 IR instrument. The UV-Visible spectra of the Schiff base ligand and its metal complexes were carried out in DMSO using a SHIMADZU UV- 2600 spectrophotometer. By using micro analytical methods on Perkin Elmer 240C (USA) elemental analyzer, the percentage composition of C, H and N of metal complexes were determined. The ¹H NMR spectra were recorded at 200 MHz and 300 MHz on Varian Gemini Unity Spectrometer using TMS as an internal standard. ¹³C NMR spectra was recorded at 100 MHz on Varian Gemini Spectrometer. By using ESI technique on VG AUTOSPEC mass spectrometer, the mass spectra of the compounds were analysed. To record the X-band ESR spectra EPR VARIAN-E-112 at RT instrument was used. The TG and DT analysis of complex was carried on Mettler Toledo Star system in the temperature range 50-1000°C. The heating rates were controlled by 15 °C min⁻¹. Magnetic measurements were carried out on a Gouy balance model 7550 using Hg[Co(NCS)₄] as standard. By using Elico Electronic Digital conductivity meter conductivity measurements were carried out in DMSO (10⁻³M) and 0.01M KCl solution is used for calibration. The decomposition temperature of complexes and the melting points of the ligand were determined on Polmon instrument (model No.MP-96).

In Vitro Antimicrobial Studies: The anti bacterial assessment of the ligand and its metal complexes were analysed by disc diffusion method [18]. The complexes were screened against four bacterial strains.(i) Bacillus subtilis (Bs) is a gram-positive bacterium. (ii) Pseudomonas putida(P.putida) is a gram negative bacteria. The gram positive bacterium (iii) Staphylococcus aures (Sa) and (iv) Escherichia coli (E.coli) is a gram-negative bacterium. Antimicrobial activity of the complexes were tested through the disc diffusion technique involving the cultures of the selected organisms for 24h. Mueller Hinton agar number 2 (HiMedia, India) was used as the bacteriological medium. The saturation of the paper discs were carried out with 10µl of the compound dissolved in DMSO solution. These papers were placed in Petri dishes containing nutrient agar media and inoculated with the all the four bacterial strains separately. The zone of inhibition of the compounds were measured in millimetres after one day incubation at 37 $^{\circ}$ C.

DNA CLEAVAGE STUDIES

The compounds were dissolved in DMSO and added separately to the pUC18 DNA sample. The samples mixtures were incubated at 37°C for 1 hour. The electrophoresis of the samples was done according to the following procedure. Weigh 0.25grams of agarose and dissolve it in 25 ml of 1x TAE buffer (121.1g Tris base, pH 8.0, 0.5 M EDTA, 57.1ml of Glacial acetic acid for 1 ltr) by boiling. When the gel attains approximately 55°C, pour it into the gel cassette fitted with comb. Let the gel to solidify. Carefully remove the comb, place the gel in the electrophoresis

chamber flooded with TAE buffer. Load DNA sample with bromophenol blue carefully into the wells, along with standard DNA marker and pass the constant 100 V of electricity till the dye front reaches the end of gel. Remove the gel and carefully stain with ETBR solution (10 μ g/ml) for 10-15 min and destain the gel and observe the bands under UV transilluminator.

RESULTS AND DISCUSSION

Physical characteristics of the complexes: The metal complexes were colored, stable at room temperature and non-hygroscopic in nature. On heating, they melt at high temperatures. The complexes were insoluble in water and are soluble in DMSO.

Elemental analysis

The analytical data of the complexes were represented in **Table-1**. The data reveals that the experimental values have shown for each of the complexes were similar to that of their theoretical values. These values were confirmed the metal to ligand ratio is 1:2.

Molar conductance

The observed molar conductance values of complexes were measured at a concentration of 0.001M in DMSO. The conductance values fall in the range of 1-20 $\text{ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$, indicates that the complexes were non electrolyte in nature and are tabulated in **Table-2**.

Formula	M.Wt.	С	Н	Ν	Μ	
	259.5	69.06	5.19	5.24		
		(69.36)	(5.39)	(5.39)	-	
	617	58.14	4.76	4.34	10.09	
		(58.34)	(4.86)	(4.53)	(10.29)	
	612	58.62	4.79	4.36	9.53	
$[C_{30}\Pi_{30}\Pi_{2}O_{4}C_{12}C_{0}]$		(58.72)	(4.89)	(4.56)	(9.64)	
	612	58.43	4.66	4.38	9.49	
$[C_{30}\Pi_{30}N_2O_4C_12N_1]$		(58.72)	(4.89)	(4.56)	(9.64)	
	654	54.83	4.48	4.17	15.14	
		(54.96)	(4.58)	(4.27)	(15.44)	
*Found (Calculated)						

Table-1: Elemental analyses of synthesized metal complexes

*Found (Calculated)

Table-2: Molar conductance and magnetic moment values of ligand L and metal complexes.

Compound	Colour	M.P (°C)	Conductance (ohm ⁻¹ cm ² mol ⁻¹)	Magnetic moment (B.M)
LIGAND [L]	Yellow	201	-	-
$(C_{15}H_{14}NOCI)$				
$[Cu(L)_2(H_2O)_2]$	Green	>350	3.52	1.86
$[Co(L)_2(H_2O)_2]$	Dark brown	>350	4.12	4.94
$[Ni(L)_2(H_2O)_2]$	Brick red	>350	5.16	3.23
$[Ru(L)_2(H_2O)_2]$	Black	>350	6.12	0

Magnetic moment and electronic absorption spectra: The electronic spectra of binary ligand complexes of Cu(II), Co(II), Ni(II) and Ru(II) performed in DMSO solution. The electronic spectra of Cu(II) complex shows one broad band at 410 nm (24390.24 cm⁻¹) due to transition between ${}^{2}E_{g} \longrightarrow {}^{2}T_{2g}$, which implies octahedral geometry[19]. Even the magnetic momentum value of Cu(II) complex is 1.86 BM falls within in the range observed for distorted octahedral geometry. Likewise Co(II), Ni(II) complexes were also observed bands at 407 nm (24570 cm⁻¹) 427 nm which are due to d-d transitions occur between ligand to metal and for Ru(II) complex bands observed at 395 nm which are due to charge transfer bands. The magnetic momentum values for these complexes are 4.94 BM, 3.23 BM and 0 BM confirms the octahedral geometry of the complexes [20, 21 and 22].



UV-Vis. Spectrum of ligand and Co(II) Ni(II) Complexes

ESR spectra

The ESR spectra of powdered Cu(II) complex was recorded at room temperature at a frequency of 9.1GHz under the magnetic field strength of 3000 G (Figure 1). The experimental value of ESR spectral parameters for the $[Cu(L)_2(H_2O)_2]$ complex are g|| = 2.253, $g \perp = 2.136$ and G = 1.875. Here the observed g|| value is less than 2.3, which is in agreement with the covalent character of the metal-ligand bond[23]. The g values of the complex are g|| (2.253) $> g \perp$ (2.136) > 2.0023, indicating that the unpaired electron in the ground state of Cu(II) is predominantly in dx²-y² orbital of Cu(II) ion and the spectral features are characteristic of axial symmetry; tetragonal elongated structure may be assumed for the Cu(II) complex. The exchange interaction term G value caliculated by using the equation

 $G = g \parallel -2.0023/g \perp -2.0023$

If the G value is less than 4.0, the ligand forming the copper(II) complex is considered as strong field ligand while the value of G greater than 4.0 indicates weak field ligand. In the present Cu (II) complex the G value is 1.875 which is less than 4.0 indicates that the ligand (L) is a strong field ligand and the metal-ligand bonding in complex is covalent in nature.



Thermogravimetric analysis: The presence of coordinated and lattice water molecules in the metal complexes were determined by using the TG analysis, on the basis of weight loss with increasing temperature [24]. In the present work, Cu(II) and Ni(II) complexes lose their weight in the temperature range ~200-250 and ~180-200 which indicates the two coordinated molecules present in the complex and corresponding endothermic peak also observed in the DTA curve. After the loss of water molecule, at this temperature an endothermic peak is observed at temperature range ~450-600⁰ C, which indicates the decomposition of organic moiety occurs and the observed resedue corresponds to the respective metal oxide. All these things strengthen the observation of coordinated water molecule peaks of complexes in IR spectrum[25,26].



Figure 2: TGA and DTA curve of the Cu(II) complex

 H^1 NMR: The ligand structure is conformed through the proton nmr values ¹H NMR (400 MHz, CDCl₃): 7.98 (s, 1H, N=CH), 7.61–7.30 (m, 8H, Ph–H).

Infrared spectra

The IR spectral values of ligand and its metal complexes were given in the **Table-3**. In the spectrum, strong absorption bands observed at frequencies 3410 cm^{-1} and 1631 cm^{-1} , which is attributed to the characteristic band of the phenolic –OH and azomethine (-CH=N) linkage of the Schiff base ligand respectively. The disappearance of

phenolic –OH group frequency in the spectrum of the metal complexes indicating probably ligand to metal coordination occurred through the phenolic oxygen moiety. The azomethine frequencies were shifted to lower wave number by 10-30 cm⁻¹ in the metal complexes, suggesting the participation of the azomethine group in the complex formation [27,28]. The azomethine frequencies of all the four metal complexes were shown at range 1606-1620 cm⁻¹. The IR spectra of the metal complexes show a broad diffused bands in the region at around 3142-3307 cm⁻¹, strong bands at 1521-1531 cm⁻¹ and weak intensity bands at 820-838 cm⁻¹ due to the coordinated water molecules [29,30]. The appearance of bands at frequencies 507-549 cm⁻¹ and 408-478 cm⁻¹ are due to ν (M-N) and ν (M-O) frequencies respectively. These are evidences for the coordination azomethine nitrogen and phenolic oxygen to the metal atom.

	IR bands in(cm ⁻¹)						
Schiff base/complex	v _{он} (phenolic)	υ _{ΟΗ} (H ₂ O)	υ _{C=N} (Azomethine)	U _{ОН} (H2O)	ρ _{rOH} (H2O)	U _(M-N)	ს_(M-O)
Ligand [L] (C ₁₅ H ₁₄ NOCl)	3410	-	1631	-	-	-	-
$[Cu(L)_2(H_2O)_2]$	-	3142	1610	1522	820	507	408
$[Co(L)_2(H_2O)_2]$	-	3142	1620	1531	821	540	451
$[Ni(L)_2(H_2O)_2]$	-	3304	1618	1521	835	549	435
$[Ru(L)_2(H_2O)_2]$	-	3307	1606	1527	829	538	478

Table-3. IR	values	of ligand L	and metal	complexes
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Figure-3: IR spectra of Co(II) complex

Mass spectra of the compounds

The mass spectral values of the ligand and metal complexes were given in **Table-4**. All the molecular ion peaks are in good agreement with the expected mass. The mass spectrum of the ligand gives a peak at 260 m/z which is assigned for(L+H). The copper, cobalt and nickel complexes showed molecular ion peaks at 617 m/z, 612 m/z and 612 m/z respectively. All are assigned to [M⁺] peaks. Ru(II) ion complex given peak at 655 m/z, which is assigned to [M+1] peak.

Compound	Caliculated mass (m/z)	Obtained mass (m/z)	Peaks assigned	
Ligand [L] (C ₁₅ H ₁₄ NOCl)	259.5(260)	260	[M+]	
$[Cu(L)_2(H_2O)_2]$	617	617	[M+]	
$[Co(L)_2(H_2O)_2]$	612	612	[M+]	
$[Ni(L)_2(H_2O)_2]$	612	612	[M+]	
$[Ru(L)_2(H_2O)_2]$	654	655	[M+1]	

Table-4: Mass	values	of ligand L	and metal	complexes
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Spectrophotometric studies:

In this technique, the stoichiometric metal to ligand ratio of the complexes were determined by using mole-ratio method.

Mole-ratio Method:

Here a series of solutions were prepared [31] by keeping the molar concentration of the metal being constant and that of the ligand is varied. By adding the buffer, the p^{H} of the solution is maintained at 10.

A graph is plotted between absorbance and mole-ratio of the ligand (Figure 6). Two straight lines were obtained with different slopes. The intersection of the two lines occurs at a point, indicates the composition of Metal-Ligand in the ratio of 1:2, which attributes the combination of the metal and ligand in the complex. It confirms the metal to ligand ratio of the complexes were of 1:2.



Figure-6: Graph between absorbance and mole-ratio of the ligand at 303K for $[Co(L)_2(H_2O)_2]$ (λ_{max} =407 nm)

Antimicrobial Activity: By using disc diffusion method the antimicrobial activity of ligand and its Cu(II), Co(II), Ru(II) and Ni(II) complexes were determined. These compounds were tested against the gram positive strains like *Bacillus subtilis*; *Staphylococcus* aures and gram negative strains like *Pseudomonas putida*; *Escherichia coli* with a standard antibiotic used as control. The zone of inhibition values signifies the metal complexes have shown a greater activity than its free ligand. The enhancement in the antimicrobial activity of a ligand due to its chelation with the metal ions can be explained based on chelation theory [32]. Here the Cu(II), Co(II), Ru(II) complexes exhibited maximum zone of inhibition against Pseudomonas. *E.coli* and *S.aures* and moderate activity against *Bacillus subtilis* and Ni(II) complex have mild to moderate activity against all the strains. Here the control shown highest zone of inhibition than all the compounds and ligand shown the smallest zone of inhibition.

Here in the cultured plates I gave a numbers to the Cu(II), Co(II), Ru(II) and Ni(II) as 1, 5, 7 and 11 respectively. The inhibition zone values given in Table 5 and the images also uploaded.

Compound	Pseudomonas Putida(Pp)	Escherichia coli(E.coli)	Staphylococcus aures(Sa)	Bacillus subtilis(Bs)
Ligand(L)	2	3	2	1
$[Cu(L)_2(H_2O)_2]$	20	13	11	10
$[Co(L)_2(H_2O)_2]$	20	12	12	8
$[Ni(L)_2(H_2O)_2]$	20	14	11	9
$[Ru(L)_2(H_2O)_2]$	5	9	3	0
Control	22	16	15	13

Table-5: Zone of inhibition of ligand L and metal complexes in (mm)



Figure-7 Anti bacterial activity against Pseudo monas where 7 is Ru(II) complex

Figure-8 Anti bacterial activity against E.coli where 7 is Ru(II) complex

DNA cleavage activity of metal complexes

The DNA cleavage ability of the metal complexes and ligand were determined through the agarose gelelectrophoresis technique by using pUC18 DNA. Here the cleavage experiment was done in the presence of H_2O_2 as an oxidant. From Fig.9 it is understood that the complete DNA cleavage occurs with Cu(II) Co(II) and Ru(II) complexes. Where as Ni(II) complex have shown partial cleavage and free Ligand have exhibit no significant cleavage activity in the presence of oxidant. The general oxidative mechanism proposed account for DNA cleavage by hydroxyl radicals via abstraction of a hydrogen from sugar units and predict the release of specific residues coming from transformed sugars, depending on the position from which the hydrogen atom is removed. It is due to ability of the metal complexes to activate dioxygen or its reduced form hydrogen peroxide, will tend to the functionalisation of an inert C-H bond of a DNA to a C-O bond. The oxidation of DNA with metal complexes occurs by C-H bond activation at the deoxyriboses[33,34].

 $\label{eq:Figure-9} \begin{array}{l} \textbf{ Bigure-9 DNA cleavage activity of free ligand and its metal complexes} \\ [1] Marker [2] Vector [3] Vector + Ligand + H_2O_2 [4] [Cu(L)_2 (H_2O)_2] + DNA + H_2O_2 \\ [5] [Co(L)_2 (H_2O)_2] + DNA + H_2O_2 [6] [Ru(L)_2 (H_2O)_2] + DNA + H_2O_2 [7] [Ni(L)_2 (H_2O)_2] + DNA + H_2O_2 \\ [6] [Ru(L)_2 (H_2O)_2] + DNA + H_2O_2 [6] [Ru(L)_2 (H_2O)_2] + DNA + H_2O_2 [7] [Ni(L)_2 (H_2O)_2] + DNA + H_2O_2 \\ [6] [Ru(L)_2 (H_2O)_2] + DNA + H_2O_2 [6] [Ru(L)_2 (H_2O)_2] + DNA + H_2O_2 [7] [Ni(L)_2 (H_2O)_2] + DNA + H_2O_2 \\ [7] [Ni(L)_2 (H_2O)_2] + DNA + H_2O_2 [6] [Ru(L)_2 (H_2O)_2] + DNA + H_2O_2 [7] [Ni(L)_2 (H_2O)_2] + DNA + H_2O_2 \\ [8] [Ru(L)_2 (H_2O)_2] + DNA + H_2O_2 [7] [Ni(L)_2 (H_2O)_2] + DNA + H_2O_2 \\ [8] [Ru(L)_2 (H_2O)_2] + DNA + H_2O_2 [7] [Ni(L)_2 (H_2O)_2] + DNA + H_2O_2 \\ [8] [Ru(L)_2 (H_2O)_2] + DNA + H_2O_2 [7] [Ni(L)_2 (H_2O)_2] + DNA + H_2O_2 \\ [8] [Ru(L)_2 (H_2O)_2] + DNA + H_2O_2 [7] [Ni(L)_2 (H_2O)_2] + DNA + H_2O_2 \\ [8] [Ru(L)_2 (H_2O)_2] + DNA + H_2O_2 [7] [Ni(L)_2 (H_2O)_2] + DNA + H_2O_2 \\ [8] [Ru(L)_2 (H_2O)_2] + DNA + H_2O_2$

CONCLUSION

The novel Cu(II), Co(II), Ni(II) and Ru(II) complexes were synthesised by using Schiff base ligand (NPEHS). These complexes were characterised by various physio-chemical methods. All these analyses confirmed the stoichiometry and structure of the compounds. From the spectrophotometric studies it is evident that the metal to ligand ratio is 1:2. The Geometry of the complexes is assigned as octahedral. Here the main focus is on the biological studies of the metal complexes. Anti microbial activity and DNA cleavage experiments revealed that the metal complexes have shown a greater activity than its free ligand.

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Proposed structures of all the four metal complexes

M = Cu(II), Co(II), Ni(II) and Ru(II) ions

3D Images of proposed structure for metal complexes

ligand(NPEHS)

Metal complexes(Cu(II), Co(II),Ni(II) and Ru(II).[M(L)2(H2O)2].

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