



Synthesis Characterization and Bioactivity of Novel Pramipexole Schiff base Metal Complexes.

T.Noorjahan Begum, R.MallikarjunaRao, A.Jayaraju and J.Sreeramulu

Department of Chemistry, Sri Krishnsdevaraya University, Anantapur-515003,India

ABSTRACT

The synthesis and investigation of new Schiff base and its solid metal complexes derived from Pramipexole (4,5,6,7-Tetrahydro-N6-propyl,2,6-benzothiazole diamine) and 2,4-dihydroxy acetophenone (2,4 DHAP) by using modified SandMayer's method. The derived colored complexes are Cu (II) and Ru (II) with 2,4DHAPP. The structures of the titled new Schiff base were elucidated. Elemental analysis, IR, NMR, UV-Vis Spectrometry, ESR, TG-DTA and Conduct metric measurements. 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 Salmonella typhi, Enterococcus faecails and Escherichia coli.

Keywords: Synthesis, Characterization, Schiff base (2,4DHAPP), parmipexole, Biological activity

1. INTRODUCTION

The Schiff bases are the most versatile and thoroughly studied ligand in coordination chemistry. Metal complexes of schiff bases have been reported as tuberculosis antitumor antibacterial and antifungal agents. Transitional metal complexes with schiffs base ligands have been prepared in view of their potential applications as antibacterial and antifungal drugs .the importance of schiffs base ligands and their complexes with transitional metal have been enhanced especially due to their biological applications. Schiff bases are very good complexing agents. A perusal of literature survey reveals that the field of Schiff base metal complexes is vast and fast developing on account of numerous applications in various important fields and the wide variety of structures possible for the ligands depend in group on the aldehydes, ketones and amines. Metal complexes of Schiff bases and their applications have been widely investigated during the past years^{1,2}. Schiff base complexes have been used as pesticides^[3], as antiviral and antibacterial agents^{4,5} and as catalysts⁶⁻⁸. The thermal behavior of transition metal complexes of Schiff bases has been widely investigated⁹⁻¹¹.Theapplications of such complexes depend to a large extent on their molecular structure. The author in the present study provides a new series of metal complexes of Cu (II) and Ru(II)with Schiff base ligand derived from Pramipexole and 2,4 Di Hydroxy-acetophenone(2,4 DHAPP). These complexes were characterized by elemental analysis,IR,NMR, UV- Vis Spectrometer, ESR,TGA-DTA and Conductometric measurements to determine the mode of bonding and geometry, biological activities of the ligands and metal complexes were also carried out.

2. 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 resonanance spectra were recorded using the ACF200 Broker Germany Spectrometer. Ultraviolet Spectra were recorded using Prekin-Elmer lab India UV-Vis Spectrometer. The Electron spin reazonce 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 and ethyl alcohol were used as solvent. All chemicals used in the present investigation were pure Aldrich chemicals.

Preparation of the ligand and its metal complexes

(Preparation of Pramipexole and 2, 4-dihydroxy acetophenone Schiff base (2,4 DHAPP))

Pramipexole 4.22g (0.02mole) and 2,4 Di Hydroxy-acetophenone 3.04g (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, light brown 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 (II) metal chloride salts were used. Dissolve 3.2947g (0.01 Mole)of newly synthesized ligand in adequate of methanol. To this solution, aqueous solution of 1.3434 g(0.01Mole) and1.718g (0.01Mole) metal chlorides, and 1 ml of Sodium acetate. The mixturewadrefluxedfor6hoursinawater 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 recrystalised from ether and

dried in vacuum desiccator over CaCl_2 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		
			2,4 DHAPP	$\text{Cu}(2,4\text{DHAPP})_2\text{X}_2$	$\text{Ru}(2,4\text{DHAPP})_2\text{X}_2$
Molecular weight			329.479	789.488	828.01
Co lour			Lightbrown	Dark green	Dark brown
Yield			76	74	72
M.P			210-212	230-232	250-252
Elemental Analysis	C %	Calculated	65.52	54.71	52.17
		Found	62.00	54.05	52.00
	H%	Calculated	6.65	6.33	6.03
		Found	6.05	6.22	6.00
	N %	Calculated	12.15	10.63	10.14
		Found	12.01	10.34	10.01
	O%	Calculated	9.26	12.15	11.59
		Found	9.20	12.00	11.52
	M%	Calculated	-	8.04	11.20
		Found	-	7.99	10.98

3. RESULTAND DISCUSSION

Infrared Spectral Analysis

Infrared spectra were recorded with a JASCO FT/IR-5300 Spectrometer ($4000-400\text{cm}^{-1}$) using KBr pellets. By utilizing this spectroscopy, the presence of important functional groups in the compound can be identified. Table 2 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 2,4 DHAPP and $\text{Cu}(\text{II})$ and $\text{Ru}(\text{II})$ complexes: The Infrared spectrum of the ligand was compared with the spectra of $\text{Cu}(\text{II})$ and $\text{Ru}(\text{II})$ complexes. The data was summarized in table along their assignment. The typical IR spectra were shown in Fig. 1, 2 and 3. The IR spectrum of the ligand has shows broad band at 1632 cm^{-1} 14, which was assigned to due $\nu\text{C}=\text{N}$ stretching of azomethine group. In complexes this band was shifted to lower regions, 1627 cm^{-1} and 1621 cm^{-1} 15 for $\text{Cu}(\text{II})$ and $\text{Ru}(\text{II})$ complexes

respectively, suggesting the involvement of azomethine group ($>\text{C}=\text{N}$) group in complexation. 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 $\nu(\text{OH})$ bond at 3303 cm^{-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 $\text{Cu}(\text{II})$ and $\text{Ru}(\text{II})$ metal complexes exhibit a broad band around 3309 cm^{-1} and 3331 cm^{-1} respectively, which can be assigned to $\nu(\text{OH})$ of water molecules associated with complex formation. The two weaker bands at 817.50 cm^{-1} and 807.20 cm^{-1} were attributed to OH rocking and wagging vibrations of coordinated water molecules. New bands were observed in the complexes, which were not observed in ligand. The bands at 695 cm^{-1} and 608 cm^{-1} were assigned to stretching frequencies of (M-O), the band at 451 cm^{-1} and 564 cm^{-1} 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)	νOH (Phenolic)	$\nu\text{C}=\text{N}$	$\nu\text{N-H}$	$\nu\text{M-O}$	$\nu\text{M-N}$	$\nu\text{C-H}$
2,4 DHAPP	-	3303	1632	3303	-	-	2964
$\text{Cu}(2,4\text{DHAPP})_2$	3309	-	1627	3309	695	451	2912
$\text{Ru}(2,4\text{DHAPP})_2$	3331	-	1621	3309	608	564	2900

NMR Spectrum of 2,4 DHAPP Ligand and its Metal Complexes

The ^1H NMR spectra of ligand and metal complexes in DMSO-d_6 as solvent were given in fig.4,5 and 6. The chemical shift values of the ligand and metal complexes were shown in Table-3. Ligand shows singlet at 2.71 ppm²¹, which is due to protons bonded to Schiff base group. On complexation this band was shifted to lowfield regions 2.573 ppm and 2.4 ppm for Cu (II) and Ru (II) complexes respectively. This shifting indicates the shielding of azomethine. The aromatic ring protons forms a multiplet at 6.37-6.41 ppm, methylene protons forms a singlet

in the region 1.70 ppm hydroxyl proton²² shows doublet at 5.71-5.72 ppm, which was disappeared in the complexes.

In the ^1H NMR spectra of the Cu (II) and Ru (II) complexes the signal due to azomethine protons were shifted 2.71 ppm to 2.573-2.4 ppm respectively. This shifting indicates the shielding of the azomethine group. The aromatic ring protons that are seen in the 7.2 - 7.3 ppm²² become broad and less intense compared with the corresponding Schiff base. In complexes the aromatic ring protons at 7.2-7.3 ppm become broad and less intense, compared with Schiff base. The following complexation to the metal ion 2.82 ppm in the case of Cu (II) and Ru (II) complexes indicates the complexation of water molecules by coordination with metal ion.

Table-3: ^1H NMR Spectrum of the ligands and its metal complexes in DMSO-d_6 in ppm

Compound	$\text{CH}_3\text{-C=N}$	Ar-H	OH-H ₂ O	CH ₂	Ar-OH	N-H
2,4DHAPP	2.71	6.37-7.65	-	1.70	5.71	12.69
Cu(2,4DHAPP) 2	2.573	6.64-6.62	4.7	1.73	7.27	12.7
Ru(2,4 DHAPP) 2	2.4	6.41-7.59	4.9	1.81	7.2	8.35

Conductivity Measurements

The molar conductance of complexes in DMF ($\sim 10^{-3}$ M) was determined at 27±20°C using Systronic 303 direct reading conductivity bridge. A known amount of solid complexes is transferred into 25 ml 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 100 ml beaker. The molar conductance's 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-2,4 DHAPP Complexes: Cell constant: 1.00

S.No.	Metal Complex	Conductance Ohm^{-1}	Specific Conductance $\text{Ohm}^{-1} \text{cm}^{-1}$	Molar Conductance $\text{Ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$
1.	Cu(2,4DHAPP)2	0.00017×10^{-3}	0.017×10^{-3}	17
2.	Ru(2,4DHAPP)2	0.00020×10^{-3}	0.020×10^{-3}	20

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 2,4 DHAPP 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 292 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

Complexes	λ_{max} of the complex in nm	λ_{max} of the ligand in nm
Cu(2,4 DHAPP) 2	316	292
Ru(2,4 DHAPP) 2	330	292

Electronic Spin Resonance Spectra

In the present study the X-band (~9.3GHz) ESR spectra of Cu(II) and Ru(II) complexes in DMF were recorded at room temperature and at liquid nitrogen temperature (LNT) on a JES-FA SERIES spectrometer. DPPH radical was used as a field maker.

Analysis of 2,4 DHAPP through ESR spectra of Cu (II) complex:

The ESR spectra of the complex in poly crystalline state exhibit only one broad signal, which is attributed to dipolar broadening and enhanced spin lattice relaxation. Anisotropic spectra obtained for these complexes in DMF at LNT and representative ESR spectra of Cu (II) complexes were presented in Fig. 7. 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 the Cu(II) complex was presented in Table 6. The g_{\parallel} and g_{\perp} are computed from the spectrum using DPPH free radical as g marker. Kvelson & Neiman²³ have reported that g_{\parallel} value is less than 2.3 for covalent character and is greater than 2.3 for 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^[24]. The trend $g_{\parallel} > g_{ave} > g_{\perp} > 2.0023$ observed for the complex suggest that the unpaired electron is localized in $dx^2 - y^2$ and dz^2 orbital of the copper (II) ions for the complex. It is observed that G value for these complexes are greater than four and suggest that there are no interactions between metal-metal 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 (α^2), the dipolar interaction (P)^[25]. The observed $K_{\parallel} < K_{\perp}$ indicates the presence of out of plane Pi-bonding. The α^2 values for the present chelates lie in the range 0.42-0.48 and support the covalent nature of these complexes. Giordano and Bereman suggested the identification of bonding groups from the values of dipolar term P. The reduction of P values from the ion value (0.036cm^{-1}) might be attributable to the strong

covalent bonding. The values of P obtained for the present complexes in between $0.029-0.036\text{cm}^{-1}$ and remain consistent with bonding of metal 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 these complexes²⁶.

Table-6 : Spin Hamiltonian and orbital reduction parameters of copper and Manganese complexes in DMF solution

Parameters	Cu(2,4DHAPP) ₂
g_{\parallel}	2.04559
g_{\perp}	1.99000
g_{ave}	2.00853
G	3.8201
A_{\parallel}^*	0.0182
A_{\perp}^*	0.0022
A_{ave}^*	0.0081
d-d	13500
K_{\parallel}	0.8891
K_{\perp}	0.9824
P*	0.036
α^2	0.420

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

The effective magnetic moment values for all the complexes are represented in the Table 7. There are considerable orbital contribution and effective magnetic moments for octahedral complex at room temperature. The magnetic moments of the present (2,4 DHAPP)₂ Cu complex is 4.82 B.M. and the value is less than the spin only value, it shows reduced Paramagnetism, which suggest the formation of low-spin complex having octahedral geometry. The magnetic moments of the present (2,4 DHAPP)₂ V complex is 1.79 B.M. and this value is less than the spin-only value, showing reduced paramagnetism, which suggest the formation of low-spin complex having square planar.

Table-7: Magnetic moments of copper and Manganese

S.No.	Metal Complexes	Effect. In B.M.		Number of unpaired electron
		Theoretical	Observed	
1.	Cu(2,4 DHAPP) ₂	4.90	4.82	4
2.	Ru(2,4 DHAPP) ₂	1.68	1.79	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 2,4 DHAPP and its Cu (II) and Ru (II) 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 upto 160°C. The first stage of the decomposition corresponding to endothermic dehydration of the complex and the two lattice water molecules are lost in the temperature range 160-1700C to give anhydrous complex²⁸. The second decomposition stage with two endothermic is known as stable intermediate formed around 180-350 °C²⁹⁻³⁰. Exothermic decomposition express to give the

corresponding metal oxides as final decomposition product at a high temperature i.e. above 360-720°C. The decomposition behavior of the complexes was observed in nitrogen atmosphere. All the experimental mass loss has shown Table.8. The Ru complexes are thermally stable up to 1500C. The first stage of the decomposition corresponding to exothermic dehydration of the complex and the two lattice water molecules are lost in the temperature range 150-170°C to give anhydrous complexes. The second decomposition stage with two exothermic is known as stable intermediate formed between 180-350°C. Exothermic decomposition express to give the corresponding metal oxides as final decomposition product at a high temperature i.e. above 5200C. The decomposition behavior of the complexes was observed in nitrogen atmosphere. 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 (II).

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

Complex X=H ₂ O	Molecular weight in gms	Weight of the complex take in mgs	Temperature Range during weight loss in 0C	% of fraction of weight	Probable assignment
[Cu.L ₂ .X ₂] L= C ₁₈ H ₂₃ N ₃ SO ₂	789.48	8.1910	140-160.46 200-380 500-850	12.95 42.89 7.6	Loss of 2H ₂ O molecule. Loss of two L molecules. Remaining residue Corresponds to CuO.
[Ru.L ₂ .X ₂] L= C ₁₈ H ₂₃ N ₃ SO ₂	828.01	12.1630	150-170 180-350 Above 520	10.56 57.16 10.39	Loss of 2H ₂ O molecule. Loss of two L molecules. Remaining residue Corresponds to RuO.

Biological Activity

The author in this present investigation attempted to find out antibacterial activity of ligand and their metal complexes against Salmonella typhi, Enterococcus faecalis and Escherichia coli 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 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 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 lipophilicity³¹ 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(II) Complexes of Swift, is found to be more .

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

S.No.	Compound	Salmonella Typhi	Enterococcus Faecails	Escherichia coli
1	2,4 DHAPP	12	14	15
2	Cu(2,4 DHAPP) ₂	17	19	18
3	Ru(2,4 DHAPP) ₂	16	18	19

4. CONCLUSION

The above study results reveals that, it can be concluded that Schiff base of O-Vanillin with aminenamelyp-Toulid hydrazide acts as a very good complexing agent towards many transition metalions. By using above spectral studies these behave bidentate during complexation. All the metal complexes carry no charge and are thermally stable. As such no single technique is independent of predicting final structures of the complexes.

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