# **Journal of Rare Cardiovascular Diseases**

ISSN: 2299-3711 (Print) | e-ISSN: 2300-5505 (Online)



#### **RESEARCH ARTICLE**

# Chemical Synthesis, Spectroscopic Characterization and DNA Binding Studies of 2, 4-Dihydroxy Acetophenone Pramipexole Schiff base Metal complexes

Dr T.Noorjahan Begum<sup>1</sup>, Dr N.Vijaya Lakshmi<sup>2</sup>, Dr P.Uma Maheshwari<sup>3</sup>, Dr A.Kalpana<sup>4</sup>, Dr D.Zarena<sup>5,\*</sup>

- 1, 4 Department of chemistry, JNTUA College of Engineering, JNTUA, Anantapur-515002, A.P, India
- 2 Department of Pharmacy, JNTUA OTPRI, Anantapur-515002, A.P, India
- 3 Department of Chemical Engineering, JNTUA college of Engineering, JNTUA, Anantapur-515002, A.P, India
- 5 Department of Physics, JNTUA College of Engineering, JNTUA, Anantapur-515002, A.P, India

# \*Corresponding Author **DrD.Zarena**

Article History

Received: 12.07.2025 Revised: 13.08.2025 Accepted: 09.09.2025 Published: 25.10.2025 Abstract: The synthesis and investigation of new Schiff base and its solid metal complexes derived from Pramipexole ((S)-4,5,6,7-Tetrahydro-N6-propyl-2,6-benzothiazolediamine) and 2,4-dihydroxy acetophonenone (2,4 DHAP) by using modified Sand Mayer's method. The derived colored complexes are Co (II) and Ni (II) with 2,4DHAPP. The structures of the titled new Schiff base were elucidated Elemental analysis, IR, NMR, UV-Vis Spectrometry, TG-DTA and Conductometric measurements,Powder XRD. In addition the authors have been screened the compounds for DNA binding studies. Additionally, the compounds were examined by the authors for DNA binding studies. It was discovered that these complexes had a strong affinity for DNA binding.

**Keywords:** Synthesis, Characterization, Schiff base (2,4-DHAPP), Parmipexole, DNA Binding studies.

## INTRODUCTION

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 depending upon the aldehydes, ketones and amines. Metal complexes of Schiff bases and their applications have been widely investigated during the past years [1-<sup>2]</sup>.Schiff base complexes have been used as pesticides <sup>[3]</sup>, as antiviral and antibacterial agents [4, 5] and as catalysts [6-8]. The thermal behavior of transition metal complexes of Schiff bases has been widely investigated [9-11]. The applications 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 Co (II) and Ni(II) with Schiff base ligand derived from Pramipexole and 2,4 Di Hydroxy acetophenone (2,4 DHAPP). These complexes were characterized by elementalanalysis, IR, NMR, UV- Vis Spectrometer, TGA-DTA,XRD and Conductometric measurements to determine the mode of bonding and geometry, DNA Binding studies of the ligands and metal complexes were also carried out.

## MATERIALS AND METHODS

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 reasonce 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.

,,

How to Cite this: T.Noorjahan Begum, N.Vijaya Lakshmi, P Uma Maheshwari, A.kalpana, and D.Zarena. Chemical synthesis, Spectroscopic characterization and DNA Binding Studies of 2,4 Dihydroxy Acetophenone Pramipexole Schiff base metal Complexes ,*J Rare Cardiovasc Dis* 2025 3(S1):23-35



2,4-Hydroxy Acetophenone

Pramipexole

(Resacetophenone)

For the Preparation of Co(II) and Ni (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 added. The mixture was refluxed for 6hours in a water bath and then cooled to room temperature dark blue colored, parrot green colored sharp needles were separated out. The coloured metal complexes were washed with water and then methanol,

RAPP

and were recrystalised from ether and dried in vacuum dessicator over CaCl2 anhydrous. The elemental analysis [12,13] was carried out for the newly synthesized ligand metal complexes. The prepared metal complexes were in 1:2 ratios. 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	Co(2,4DHAPP)2X2	Ni(2, 4DHAPP)2X2
M	olecular weigh	nt	329.479	789.488	828.01
	Co lour		Lightbrown	Dark blue	Parrot green
	Yield		76	74	72
	M.P			230-232	250-252
	C %	Calculated	65.52	54.71	52.17
		Found	62.00	54.05	52.00
Elemental	Н%	Calculated	6.65	6.33	6.03
Analysis		Found	6.05	6.22	6.00
	N %	Calculated	12.15	10.63	10.14
		Found	12.01	10.34	10.01
	Ο%	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

## **RESULTS**

#### Infrared spectral analysis:-

Infrared spectra were recorded with a JASCO FT/IR-5300 Spectrometer (4000-400cm1) 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 Co (II) and Ni (II) complexes:

The Infrared spectrum of the ligand was compared with the spectra of Co(II) and Ni(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 vC=N stretching of azomethine group. In complexes this band was shifted to lower regions, 1627 cm  $^{1}$  and 1621 cm  $^{1[15]}$  for Cu(II) and

respectively, complexes suggesting involvement of azomethine group(>C=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 v(OH)<sup>[16]</sup> bond at 3303 cm<sup>-1</sup>. 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 phenolicgroup. The IR spectra of Co(II) and Ni(II) metal complexes exhibit a broad band [17] around3530cm land 3397 cm<sup>-1</sup> respectively, which can be assigned to v(OH) of water molecules associated with complex formation. The two weaker bands at 817.50 cm<sup>-1</sup> and 807.20 cm<sup>-1</sup> were attributed to OH rocking and wagging vibrations of coordinated water molecules. The complexes display asharpbandinthe 946-968 cm<sup>-1</sup> region due to the v(V=O)mode .New bands were observed in the complexes,



which were not observed in ligand. The bands at 644 cm<sup>-1</sup> and 668 cm<sup>-1</sup> were assigned to stretching frequencies of (M-O), the band at 421cm<sup>-1</sup>and 486cm<sup>-1</sup>[<sup>18]</sup> 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)	υOH (Phenolic)	υC=N	υ N-H	υ M-O	υ M-N	υ С-Н
2,4 DHAPP	-	3303	1632	3303	-	-	2964
Co(2,4DHAPP)2	3530	-	1590	3308	644	421	2912
Ni(2,4 DHAPP) <sub>2</sub>	3397	=	1627	3297	668	486	2900

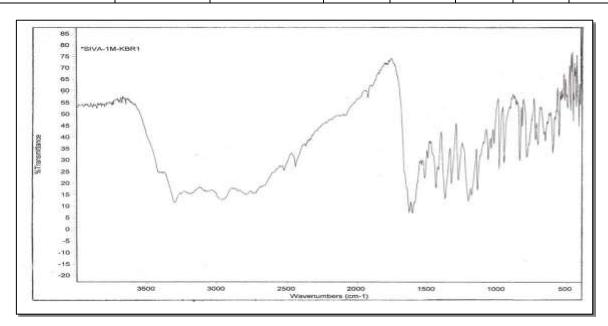


Figure-2: IR Spectrum of Co (2,4 DHAPP)  $_2$  complex.

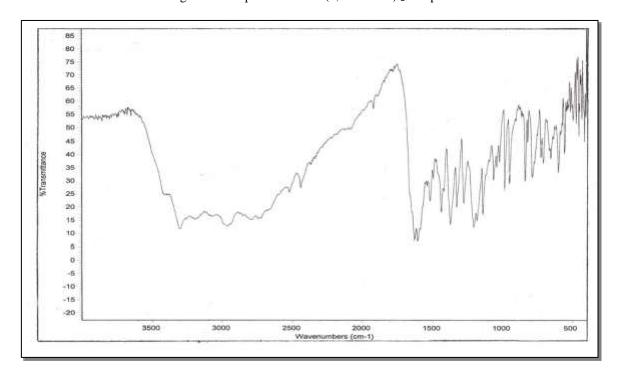
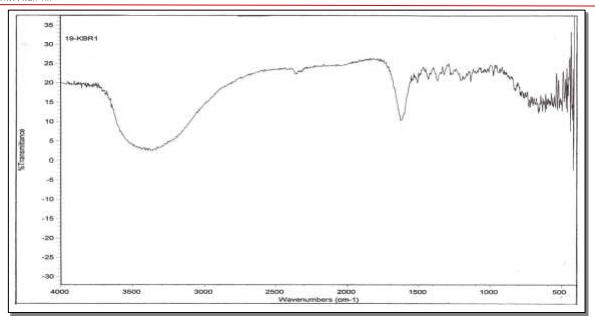


Figure-3: IR spectrum of Ni (2,4DHAPP) 2 Complex.

How to Cite this T.Noorjahan Begum, N.Vijaya Lakshmi, P Uma Maheshwari, A.kalpana, and D.Zarena. Chemical synthesis, Spectroscopic characterization and DNA Binding Studies of 2,4 Dihydroxy Acetophenone Pramipexole Schiff base metal Complexes ,*J Rare Cardiovasc Dis* .2025.3(S1):23-35





#### NMR Spectrum of 2,4 DHAPP Ligand and its Metal complexes:

The <sup>1</sup>H NMR spectra of ligand and metal complexes in DMSO-d6 as solvent were given in fig.4,5 and6. The chemical shift values of the ligand and metal complexes were shown in Table-3. A singlet observed at 2.71 ppm for <sup>1</sup>H NMR spectrum of the RAPP ligand is assigned to the methyl protons attached to azomethine (C=N) group <sup>[17]</sup>. The singlet appeared at 1.70 ppm is attributed to the methelene protons of the cyclohexane ring. Another doublet observed at 5.71-5.72 ppm for <sup>1</sup>H NMR spectrum of the O and P- hydroxyl proton of the phenyl ring. A multiplet is observed in the region 6.37-7.65 <sup>[22]</sup> due to the aromatic C-H protons of phenyl ring. A singlet appeared at 7.2 ppm is attributed to the C-H proton attached to the phenyl ring in the ligand <sup>1</sup> The doublet appeared at 7.63-7.65 ppm due to two C-H proton attached to the phenyl ring The singlet appeared at 12.69 ppm due to N-H proton of ligand.

In the  $^1H$  NMR spectrum of the RAPP - Co complex, a signal appeared due to methyl protons attached to azomethine group has been shifted to 2.7 ppm compared to 2.71 ppm in the case of ligand  $^{[23]}$ . This downfield shift indicates the deshielding of azomethine proton on coordination through nitrogen atom of azomethine group . The signal observed at 1.65 ppm due to the methelene protons of cyclohexane ring for the (Co) complex. A signal is appeared due to para at 7.45 ppm due to OH proton on Para position of phenolic group.

The signal disappeared at 5.71-5.72 ppm due to phenolic hydroxyl proton is absent in the NMR spectrum of (Co) complex indicating the deprotonation of hydroxyl group and the involvement of that oxygen in coordination .The multiplet observed in the region 6.37-7.65 ppm due to aromatic protons for the ligand showed a shift to 6.45-7.65 ppm for (Co) complex may be due to the drifting of ring of electrons towards the metal ion. A new signal is observed as a singlet at 5.05ppm in the case of Co (II) complex indicating the presence of water molecules coordinated to the metal atom A signal observed at 12.69 ppm in ligand due to N-H proton is shifted to 12.95 ppm for Co complex.

In the <sup>1</sup>H NMR spectrum of the RAPP –Ni complex, a signal appeared due to methyl protons attached to azomethine group has been shifted to 2.579 ppm compared to 2.71 ppm in the case of ligand <sup>[24]</sup>. This down field shift indicates the deshielding of azomethine proton on coordination through nitrogen atom of azomethine group. The signal observed at 1.64 ppm due to the methelene protons of cyclohexane in the Ni complex. The signal dis appeared at 5.71-5.72 ppm due to phenolic hydroxyl proton is absent in the NMR spectrum of Ni complex indicating the deprotonation of hydroxyl group and the involvement of that oxygen in coordination. A new signal is observed as a singlet at 4.5 ppm in the case of Ni (II) complex indicating the presence of water molecules coordinated to the metal atom. The multiplet observed in the region 6.35-7.65 ppm due to aromatic protons for the ligand showed a shift to 6.39-7.66 ppm for Cu complex may be due to the drifting of ring of electrons towards the metal ion. A signal observed at 12.7 ppm due to N-H proton for Ni complex.



Table-3: <sup>1</sup>H NMR Spectrum of the ligands and its metal complexes in DMSO-d6 in ppm

Compound	H <sub>3</sub> C-C=N	Ar-H	CH <sub>2</sub>	Ar-OH	N-H	Н2О-ОН
RAPP	2.71	6.37-7.65	1.70	7.20	12.69	
RAPP-Co	2.7	6.45-7.65	1.65	7.45	12.95	5.05
RAPP-Ni	2.579	6.39-7.66	1.64	7.2	12.7	4.5

Figure-4: NMR Spectrum of 2,4 DHAPP

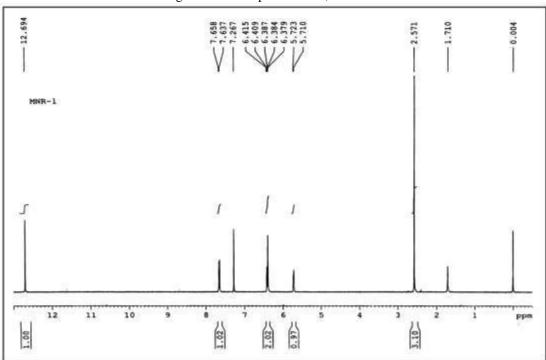
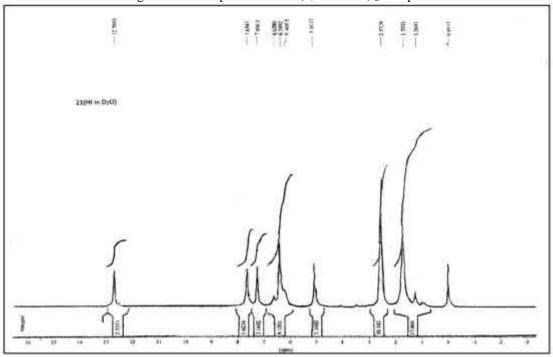
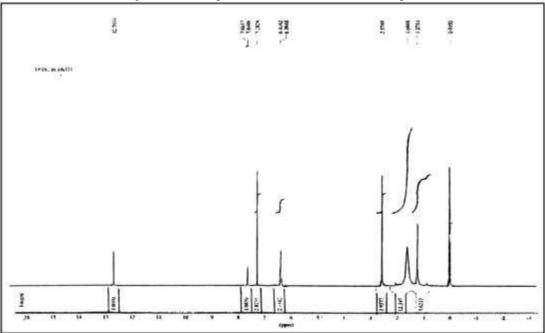


Figure-5: NMR Spectrum of Co (2,4 DHAPP) <sub>2</sub> complex









#### Conductivity measurements:

The molar conductance of complexes in DMF (~10<sup>-3</sup> M) was determined at 27+20C using Systronic 303 direct reading conductivity bridge. A known amount of solid complexes is transferred into 25ml 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 100ml beaker. The molar conductances of the complexes were less than 20 Ohm<sup>-</sup>1 cm<sup>2</sup> mol<sup>-</sup>1 indicating the Non-electrolytic nature [25]. 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- <sup>1</sup>	Specific Conductance Ohm 1 cm <sup>-1</sup>	Molar Conductance Ohm 1 cm2 mol-1
1.	Co(2,4DHAPP)2	0.00019 x 10 <sup>-3</sup>	0.00019 x 10 <sup>-3</sup>	19
2.	Ni(2,4DHAPP)2	0.00016 x 10 <sup>-3</sup>	0.00016 x 10 <sup>-3</sup>	16

#### **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 [26]. New bands were observed in the complexes at corresponding to the charge transfer transitions. In high conception spectra of complexes d-d transitions were observed in visible region

Table-5: Electronic spectral data

	$\mathbf{r}$						
Complexes	λmax of the complex in nm	λmax of the ligand in nm					
Co(2,4 DHAPP) 2	313	292					
Ni(2,4 DHAPP) 2	320	292					

#### Powder X-RD Studies:

The powder X-ray diffraction data obtained for metal complexes with difractograms using DROL-2 powder diffractometer. Radiation filled by metal foil.



#### Powder XRD study of RAPP -Co complex:

The powder X-ray diffraction data obtained for metal complexes with diffractograms using DROL-2 powder diffractometer. Radiation filled by metal foil. The diffractogram (09-diffractions) reflects Fig.7 between 10-35 (2 $\theta$ ) values for RAPP-Co complex values for Co complex. Where  $\theta$  is Bragg's angle all the main peaks are indicted and calculated values of Miller indices (h k l) along with observed d-specified and reveled intensities are specified in the Fig. 7. all the peaks have been indexed 2 $\theta$  values compared in graph. Comparison values revels that there is good agreement between values of 2 $\theta$  and d-values. The powder x-ray diffraction data showed identical features [27] with very poor crystalinity. The patterns are qualitative and dispersive in intensity for Co complex. The XRD patterns are used to explain qualitatively the degree of crystalinity. X-ray Diffraction data of RAPP-Co complex are presented in Table 6.

Table: 6. X-ray Diffraction data of RAPP-Co complex

S.No.	d expt	d Calc	2θ expt	Calc	hkl
1.	5.6534	5.6432	15.66	15.55	642
2.	5.6451	5.6234	15.68	15.66	633
3.	5.6245	5.6123	15.74	15.46	7 4 2
4.	5.6102	5.6102	15.78	15.16	7 3 1
5.	2.8298	2.8119	31.58	31.22	8 4 2
6.	2.8210	2.8205	31.68	31.45	965
7.	2.8194	2.8176	31.70	31.58	965
8.	2.8179	2.8162	31.72	31.68	984
9.	2.8040	2.8012	31.88	31.66	995

#### Powder XRD study of RAPP -Ni complex

The powder X-ray diffraction data obtained for metal complexes with diffractograms using DROL-2 powder diffractometer. Radiation filled by metal foil. The diffractogram (09-diffractions) reflects Fig.8 between 20-35 (2 $\theta$ ) values for RAPP-Ni complex values for Nicomplex. Where  $\theta$  is Bragg's angle all the main peaks are indicted and calculated values of Miller indices (h k l) along with observed d-specified and reveled intensities are specified in the Fig. 8. All the peaks have been indexed 2 $\theta$  values compared in graph. Comparison values revels that there is good agreement between values of 2 $\theta$  and d-values. The powder x-ray diffraction data showed identical features [28] with very poor crystalinity. The patterns are qualitative and dispersive in intensity for Ni complex. The XRD patterns are used to explain qualitatively the degree of crystalinity. X-ray Diffraction data of RAPP-Ni complex are presented in Table.7 .

Table: 7.X-ray Diffraction data of RAPP-Ni complex

Table: 7.X-ray Diffraction data of RAPP-Ni complex							
S. No.	d expt	d Calc	2θ expt	Calc	hkl		
1.	3.6811	3.6809	24.02	24.00	862		
2.	3.6549	3.6533	24.16	24.10	871		
3.	3.6362	3.6344	24.22	24.11	892		
4.	3.6060	3.6035	24.34	24.02	901		
5.	3.5872	3.5856	24.42	24.21	924		
6.	3.5847	3.5834	24.64	24.44	947		
7.	3.5367	3.5355	25.02	25.10	963		
8.	3.5343	3.5323	25.10	25.09	970		
9.	3.4780	3.4769	25.46	25.34	992		



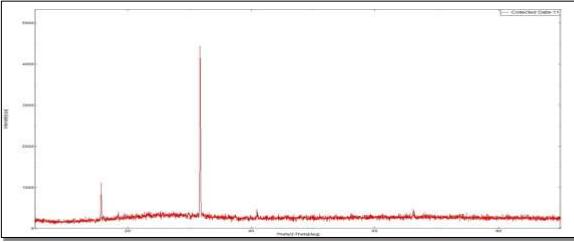


Fig: 7 Powder XRD of Co (RAPP) complex

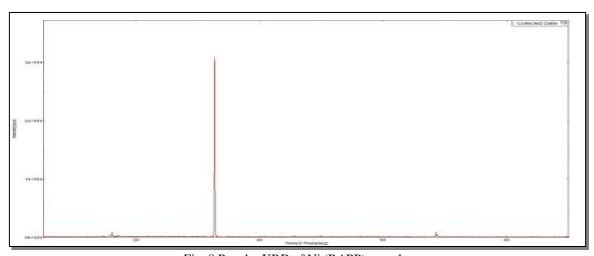


Fig: 8 Powder XRD of Ni (RAPP) complex

#### Magnetic susceptibility measurements of cobalt (II) and Nickel (II) complexes:

The effective magnetic moment values for all the complexes are represented in the Table.8. The magnetic properties Cobalt complex helps to know the geometry of them. The octahedral and tetrahedral complexes differ in their magnetic properties at room temperature 3.42 B.M range is in favour of octahedral geometry. The magnetic moment of the present Cobalt (II) complex value is 3.42 B.M <sup>[29]</sup> suggest a high spin octahedral geometry. The magnetic properties of Nickel complex help to know the geometry of them. The magnetic moment of the present Nickel (II) complex is 4.22 B.M suggest tetrahedral geometry.

Table-8: Magnetic moments of Co and Ni

		Effect. In B.M.		
S.No.	Metal Complexes	Theoretical	Observed	
1.	Co(2,4 DHAPP)2	3.90	3.42	
2.	Ni(2,4 DHAPP)2	4.36	4.22	

#### 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 Co (II) and Ni (II) metal complexes by TGA-DTA spectra:

Thermoanalytical data of metal complexes were given in the Table.9. The repersentative thermograms were shown in the fig.9 and 10. The thermogram of the Cobalt complex shows, First stage of decomposition around 120°C to 160°C, which indicates the presence of coordinated water molecules and this decomposition corresponds to small endothermic dehydration of the complex and gives anhydrous complex [30]. The second decomposition stage with one broad exothermic peak corresponds to the degradation of ligand moiety in the region 270°C to 420°C forming M(RAPPP)<sub>2</sub> intermediate.



This on subsequent stages undergoes exothermic decomposition to give the corresponding CoO as the final decomposition product at a high temperature above 720°C as shown in the Table. 9.

The thermogram of the Nickel complex shows Fig. 10, First stage of decomposition around  $140^{\circ}\text{C}$  to  $160^{\circ}\text{C}$ , which indicates the presence of coordinated water molecules and this decomposition corresponds to small endothermic dehydration of the complex and gives anhydrous complex [28]. The second decomposition stage with one broad exothermic peak corresponds to the degradation of ligand moiety in the region  $200^{\circ}\text{C}$  to  $650.56^{\circ}\text{C}$  forming M (RAPP)<sub>2</sub> intermediate . This on subsequent stages undergoes exothermic decomposition to give the corresponding NiO as the final decomposition product at a high temperature in the region  $490\text{-}730^{\circ}\text{C}$  as shown in the Table.9.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 Co (II)> Ni(II).

Table 9: Thermal analytical data of the Ligand and their metal complexes

Complex X=H <sub>2</sub> O	Temperature range	Probable assignment	Mass loss (%)	Total mass loss
	in °C			(%)
[Co.L2.X2]	120-160	Loss of 2H <sub>2</sub> O	5.13	71.04
$L = C_{18}H_{23}N_3SO 2$	270-420	molecules	56.46	
	Above-720	Decomposition of L	9.45	
		Formation of CoO		
[Ni.L <sub>2.</sub> X <sub>2</sub> ]	140-160	Loss of 2H <sub>2</sub> O	13.1	87.52
$L=C_{28}H_{23}N_3SO_2$	170-460	molecules	68.96	
	490-730	Decomposition of L	5.46	
		Formation of NiO		

Figure-9: TG & DTA Spectrum of 2, 4 DHAPP-Co

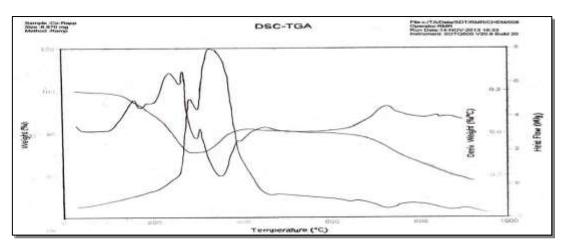
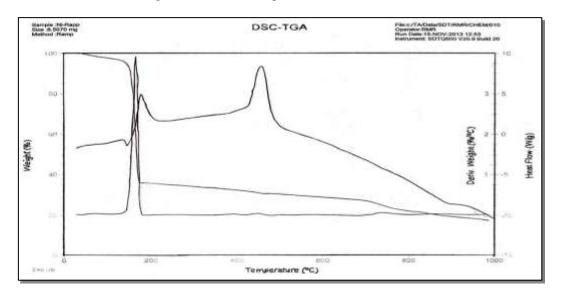


Figure-10: TG & DTA spectrum of 2, 4 DHAPP- Ni





#### DNA binding Experimental studies of metal complexes:

The interactions of all the newly synthesised complexes were monitored by UV–Visible spectral studies. Disodium salt of calf thymus DNA was stored at 5°C. Solution of DNA in the buffer 45 mM NaCl/5 mM Tris HC1 (pH 7.1) in water gave a ratio 1:9 of UV absorbance at 260 and 280 nm, A260/A280, indicating that the DNA was sufficiently free from protein. The concentration of DNA was measured by using its coefficient at 260 nm (6600 Cm<sup>-1</sup>) after 1:100 dilutions.

Concentrated stock solutions of the complexes were prepared by dissolving in DMSO and diluting suitably with the corresponding buffer to the required concentrations for all the experiments. The absorption spectra of complexes were compared in the absence and presence of CT–DNA. In the presence of increasing amounts of DNA, the spectra of complexes showed a strong decrease (hypochromicity) in intensity with shift in absorption [31] maxima towards higher (red–shift) wavelengths. The binding of intercalative molecules to DNA has been well characterized by large hypochromism and significant red–shift due to strong stacking interaction between the aromatic chromophore of the ligand and DNA base pairs with the extent of hypochromism and red shift commonly consistent with the strength of intercalative interaction.

To enable quantitative comparison of the DNA binding affinities the intrinsic binding constants  $K_b$  of the complexes for binding with CT DNA were obtained by using the equation.

$$[DNA]/(\epsilon_a - \epsilon_f) = [DNA]/(\epsilon_b - \epsilon_f) + 1 K_b (\epsilon_b - \epsilon_f)$$

Where [DNA] is the concentration of DNA in base–pairs,  $\varepsilon_a$  is the apparent extinction coefficient obtained by calculating  $A_{obs}$  / [complex],  $\varepsilon_f$  corresponds to the extinction coefficient of the complex in its free form and  $\varepsilon_b$  refers to the extinction coefficient of the complex in the bound form. Each set of data, when fitted to the above equation, gave a straight line with a slope of  $1/(\varepsilon_a - \varepsilon_f)$  and a y–intercept of  $1/K_b$  ( $\varepsilon_b - \varepsilon_f$ ) and  $K_b$  was determined from the ratio of the slope to intercept. The intrinsic binding constants  $K_b$ , obtained for the complexes.

Absorption spectra were recorded 240–400 ranges. The ranges were selected where maximum absorption change observed on addition of DNA. Electronic absorption spectral data upon addition of CT–DNA and binding constants were given in Table. 10 it was evident that these complexes bind with DNA with high affinities and the estimated binding constants are in the range of  $10^5$ – $10^6$  M<sup>-1</sup>. This may due to the presence of pi–stacking of the pyridine ring present in the ligand moiety [32].

Table.10. DNA binding constants of metal complexes

S.No	Complex (X= H <sub>2</sub> O)	λmax nm		A2	Н%	$K_b(M^{-1})$	
		Free	Bound	Δλ nm	П%	$\mathbf{K}_b(\mathbf{N}\mathbf{I})$	
1	$[Co(RAPP)_2X_2]$	286	290	4	6.36	$2.50\times10^{5}$	
2	[Ni (RAPP) <sub>2</sub> X <sub>2</sub> ]	315	320	5	6.36	$1.66\times10^{5}$	

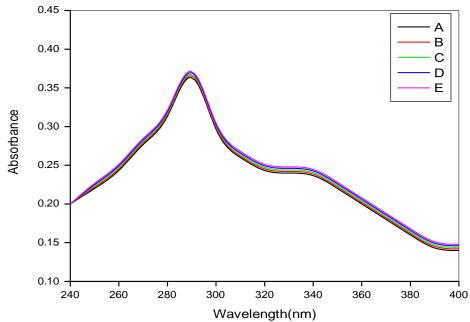


Fig:11 DNA Binding interaction of Co[RAPP]



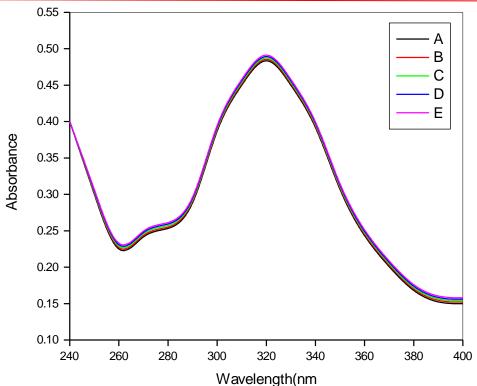


Fig: 12 DNA Binding interaction of Ni [RAPP]

# CONCLUSION

The outcome of the above results confirms the stoichiometryof the complexes to be 1:2 [M: L] as indicated by elementalanalysis and conductometric measurements. IR spectra suggest that the ligand behaves as bidentate and coordinates to the central metal ion through azomethine nitrogen and phenolic -OH group. This has been further confirmed on the basis of NMR spectral studies. Thus, the complexes are discovered to have a better DNA Binding capability as compared to the respective ligand and the parent medication on the basis of the aforementioned physicochemical and spectral tests, which perhaps justifies the goal of the research work. The current work will be expanded upon to include the creation of metal complexes employing additional physiologically active metals and assessment of their DNA binding studies. The metal complexes are all thermally stable and conduct electricity. As a result, no one technique can anticipate the complexes' final architecture independently. All the metal complexes carry on charge and are thermally stable. As such no single technique is independent of predicting final structures of the complexes.

#### **AUTHOR CONTRIBUTION STATEMENT**

T. Noorjahan Begum collected and com plied the data forDNA binding studies . P.Uma Maheshwari and A.Kalpana analysed the data. Dr. D Zarena conceived the idea of the this work and prepared the manuscript.

# **Acknowledgements:**

The facilities for elemental analysis were provided by CDRI, Lucknow, for which the authors are grateful. The

University of Hyderabad's Central Instruments Laboratory Director provided assistance to the authors in getting IR,NMR data, for which they are grateful. They are appreciative of the IR and NMR provided by IIT Madras. They are grateful for the TG& DTA, UV, and DNA Binding Studies provided by Sri Krishnadevaraya University, Anantapur.

#### **CONFLICT OF INTEREST**

Conflict of interest declared none

### REFERENCES

- N. Raman, V. Muthuraj, S. Ravichandran, and A. Kulandaisamy, "Synthesis, characterisation and electrochemical behaviour of Cu(II), Co(II), Ni(II) and Zn(II) complexes derived from acetylacetone and p-anisidine and their antimicrobial activity," . J Chem Sci, vol. 115, no. 3, pp. 161–167, 2003. doi: 10.1007/BF02704255
- C. Briickner, S. J. Rettig, and D. Dolphin, "2-Pyrrlythiones asmonoanionicbidentateN, Schelators: synthesis and molecular structure of 2pyrrlythionato complexes of Ni(II), Co(II) andHg(II)," Inorg Chem, vol. 39, pp. 6100–6106, 2000. doi: 10.1021/ic0004636 PMID 11151510
- Y. Prashanthi, K. Kiranmai, Ira. Kumar, S. Chityala, and V. K.Shivraj, "Spectroscopic characterization and biological activity of mixed ligand complexes of Ni(II) with 1,10-phenanthroline and heterocyclic schiff bases," *Bioinorganic Chemistry* and Applications, vol. 2012, Article ID 948534, 8 pages, 2012.



- N. Raman, S. J. Raja, J. Joseph, A. Sakthivel, and J.D.Raja, "Designing, synthesis, spectral characterization of antimicrobial and DNA active tridentate Schiff base ligands and their complexes,". J Chil Chem Soc, vol. 53, no. 3, pp. 1599–1604, 2008.
- E. Malhotra, N.K. Kaushik, and H. S. Malhotra, "Synthesis and studies of ionic chelates of hafnocene with guanine," Indian J Chem, vol. 45, no. 2, pp. 370– 376, 2006.
- 6. V. Muresan, L. S. Sbirna, S. Sbirna, C. I. Lepadatu, and N. Muresan, "Transition metal complexes with a new thioamide of the dibenzofuran series," Acta Chim Slov vol. 48, no. 3, pp.439–443, 2001.
- A. Choudhary, R. Sharma, M. Nagar, and M. Mohsin, "Transition Metal complexes with N, S donor ligands as synthetic antioxidants: synthesis, characterization and antioxidant activity, J Enzyme Inhib Med Chem, vol.26, no. 3,pp. 394–403, 2011.doi: 10.3109/14756366.2010.518966. PMID20939764.
- L. Tatar, D. Ulku, and O. Atakol, "Zinc(II) complexes of bidentateSchiff base ligands containing methoxyphenyl and nitrophenyl groups," Acta Crystallogr C Cryst Struct Commun, vol. 55, part 4, pp.508–510, 1999.doi: 10.1107/S0108270198015406.
- P. Piotr, H. Adam, P. Krystaian, B. Bogemil, and B. Franz, "Biological Properties of Schiff bases and azo derivatives of phenols," Curr Org Chem, vol. 13, no. 2, pp. 124–148, 2009. doi: 10.2174/138527209787193774
- 10. F. Shabani, L. A. Saghatforoush, and S. Ghammamy, "Synthesis, characterization and anti-tumour activity of iron(III) Schiff Base complexes with unsymmetric tetradentate ligands," Bull Chem Soc Eth, vol. 24, no. 2, pp. 193–199, 2010. doi: 10.4314/bcse.v24i2.54741
- C. T. Supuran, "Complexes with biologically active ligands.Part 1. Synthesis of coordination compounds of diazoxide with transition - and main-group cations," Met Based Drugs, vol. 3,no. 1, pp. 25–30, 1996. doi: 10.1155/MBD.1996.25, PMID 18472790
- 12. S. Jain, N. K. Jain, and K. S. Pitre, "Electrochemical analysis of sparfloxacin in pharmaceutical formulation and biochemical screening of its Co(II) complex," J Pharm Biomed Anal, vol. 29, no. 5, pp. 795–801, 2002. doi: 10.1016/s0731-7085(02)00178-4 PMID 12093511
- 13. S. Chandra, D. Shukla, and L. K. Gupta, "Synthesis and spectroscopic studies of Co(II), Ni(II) and Cu(II) complexes with donor(N4) macrocyclic ligand(DSLF)," J Indian Chem Soc, vol. 85, pp. 800–806, 2008.
- 14. S.Malik, S. Ghosh, and L.Mitu, "Complexes of some 3d-metalswith a Schiff base derived from 5-acetamido-1,3,4-thiadiazole-2-sulphonamide and their biological activity," . J Serb Chem Soc. vol. 76, no. 10, pp. 1387–1394, 2011. doi: 10.2298/JSC1101111118M
- 15. S. Ghosh, S. Malik, B. Jain, and M. Gupta, "Synthesis, spectral and pharmacological studies

- of some transition metal complexes derived from Schiff base of Acetazolamide drug," J Indian Chem Soc, vol. 89, pp. 471–478, 2012.
- 16. R.Sreenivasulu, J.Sreeramulu, K.SudhakarBabu" Synthesis and spectrochemical characterization of Cu (II) and Co (II) new imine metal complexes -Biological activity" J Electrochem Soc India, 54-64, Vol.11 (2005).
- 17. M.Najamuddin, F.E.Smith, R.C.Hynes; The preparation, characterization, crystal structure and biological activities of some copper(II) complexes of the 2-benzoylpyridine Schiff bases of S-methyl- and S-benzyldithiocarbazate; Inorg chim Acta,249, 207-213 (1996). doi: 10.1016/0020-1693(96)05098-0
- 18. T.J.Mabry, K.R.Markham; "6 Flavones, Flavonols and their Glycosides": Methods Plant Biochem Volume 1, 1989, Pages 197-235 doi: 10.1016/B978-0-12-461011-8.50012-3
- 19. W.Heiber, P.John; "RaumisomereDicarbonyldihalogenoruthenium(II)-Komplexe, Ru(CO)<sub>2</sub>L<sub>2</sub>X<sub>2</sub>, mit ein- und zweizähligen Liganden. Chem Ber., 103, 2161 (1970). doi: 10.1002/cber.19701030722
- Z.Jaworska, C.Jose, J.Urbanski; "Nature of metal complexes of 1-hydroxyanthraquinone" J.Spectrochim. Acta, 30a, 1161 (1974). doi: 10.1016/0584-8539(74)80031-0.
- 21. B.Singh, R.D.Singh; Physicochemical Studies on the Mixed Ligand Complexes of 1-Substituted Tetrazoline-5-thiones & Ethylenethiourea with Chromium (III) Ind.J.Chem., 21, 648 (1982).
- 22. Tarek MA.Ismail "Synthesis, characterization and biological activities of mononuclear and binuclear Fe (III) complexes with some symmetric and unsymmetric Schiff-Base ligands" J Coord Chem., 59(3), p. 255-270 (2006). doi: 10.1080/00958970500095563
- A.H.Maki, B.R.Mcgarvey; Electron spin resonance in transition metal chelates. I. Copper (II) bisacetylacetonate J Chem Phys., 29, 31- 35 (1958). doi: 10.1063/1.1744456
- 24. CA Kilner, M Thornton-Pett, MA Halcrow, "Complexes of 2-hydroxy-5-methyl-1, 4-benzoquinone as models for the 'TPQ-on'form of copper amine oxidases" et al. Commun. J Chem., 2465 (1998).
- 25. M.R.Wagon R, F.A.Walker; "Spectroscopic study of 1: 1 copper (II) complexes with Schiff base ligands derived from salicylaldehyde and L-histidine and its analogs" J.Inorg.Chem., 22, 3021 (1983).
- 26. J.Costa, R.Delgado, M.C.Figuera, R.T.Henriques, M.C.Teixeira; "single synthesis and spectroscopic investigation of cu (ii) and mn (ii) new azomethine metal complexes: biological activity" J.Chem., Soc., Dalton Trans., 65(1997).
- 27. J.M.Bret, P.Castan, G.Collèges, J.P.Laurent, D.Muller; Discrimination between two isomeric platinum mixed-valence complexes by means of 13 C nmr spectroscopy (solution and solid state) J.Chem.Soc., Chem.Commun. 1273(1983).

How to Cite this: T.Noorjahan Begum, N.Vijaya Lakshmi, P Uma Maheshwari, A.kalpana, and D.Zarena. Chemical synthesis, Spectroscopic characterization and DNA Binding Studies of 2,4 Dihydroxy Acetophenone Pramipexole Schiff base metal Complexes ,*J Rare Cardiovasc Dis* 2025 3(S1):23-35



- 28. MauricoCavicchioli, P.P.Corbi, Petr Melnikov, AntonicC.Massabni; Synthesis, Characterization and Thermal Behavior of Complexes of Cu (II), Zn (II) and Cd (II) with S, S'-Methylenebis (Cysteine)J.Coord.Chem., 55(8), pp.951-959 (2002). doi: 10.1080/0095897022000002277
- 29. M.M.Abou-Sekkina, M.G.Abou El-Azm; "Thermal and spectral studies on Co (II), Ni (II) and Cu (II) complexes of sulfamethazine Schiff base"Thermochim.Acta, 79, 47 (1984).
- 30. Gose Ramamohan<sup>1</sup>, A. JayaRaju<sup>2</sup>A. Soma Sekhar<sup>3</sup>, N. Nagaraju<sup>4</sup>, Y.C. Pullanna<sup>5</sup> and J. Sreeramulu<sup>1</sup> Synthesis, Spectro Chemical Investigation of 4-Methyl Benzylamine Schiff Base Metal Complexes and Its Biological Studie Int J Life Sci Pharma Re s.ijlpr 2022.12(3);63-69. doi 10.22376/ijpbs/lpr.2022.12.3P63-69
- 31. T. Noorjahan Begum, A. Jaya Raju, R. Mallikarjuna Rao, K. Ramesh Babu and J. Sreeramulu\*, Synthesis, Spectroscopic Investigation and DNA Binding Studies Of Pramipexole SchiffbaseMetal Complexes J Pharm Re 2014,8(3),366-373.
- 32. T.Noorjahan Begum, A.Jaya Raju, K.Aruna,J.Sreeramulu, Synthesis, Spectroscopic characterization andDNA Binding studies of Ortho hydroxybenzaldehydepramipexole Schiff base MetalComplexes Journal of Emerging Technologies and Innovative research JETIR 2022,9(11),693-706 http://doi.one/10.1729/Journal.32024