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Synthesis, Characterization and Thermogravimetric Studies Of Zinc (II) and Zirconium (IV) Complexes with N-(4-Nitrobenzylidene)-N, N'-Dimethyl-4-Amino Antipyrine

Charles Finny S. L[1], Shyamapriya M. J[2], Aswathy Sudhakar. S[3]
[1, 2]*PG Student, Department Of Chemistry, Christian College, Kattakada, Kerala, India – 695572*

Abstract: ***The Schiff base ligand N-(4-nitrobenzylidiene)-N,N'-Dimethyl-4-aminoantipyrine was prepared by the condensation between 4-nitrobenzaldehyde and 4-aminoantipyrine.. The Zn and Zr complexes of the corresponding ligand were prepared and was characterized by different methods like IR, UV spectra, magnetic studies and CHN analysis . The X ray diffraction studies of zinc and zirconium complexes were also conducted. From the CHN analysis and IR spectral data the structure of zinc complex is square planar and V complex is octahedral.***
Keywords: Schiff base, aldehyde, amine, XRD

I. INTRODUCTION

The advances in coordination chemistry has provided various complex compound that are used in different industries such as mining, metallurgy and medical science have been of great importance. The term coordination is mainly used to describe the interaction between metals or metal ions with other molecules and ions. Coordination chemistry is the study of compounds that have a central metal surrounded by molecules or ions, known as ligands. The ligands are attached to the central metal atom by dative bonds which is also known as coordinate bonds. The electrons in the bond are supplied by the same atom on the ligand. Coordination compounds of transition metals was discovered in the beginning of 19th century. Schiff bases have a melting point from 160-240^{o}c, above this, it undergo decomposition. They are generally obtained as pale-yellow or orange needles. They are nearly insoluble in water but soluble in aqueous alkaline solution and fairly soluble in benzene, dioxane and chloroform. They are more soluble in hot methanol and ethanol. Hence these solvents are used for recrystallization.C=N stretching frequency of schiff bases in IR spectra occur in between 1562- 1650 cm^{-1}. The shift of this band towards a lower frequency in the spectra of metal complexes shows the coordination of metal with nitrogen of schiff base.

II. MATERIALS AND METHODS

A. Materials

All reagents used for the synthesis of ligand and complexes are of commercial grade and they are directly used without further purification. 4-nitrobenzaldehyde is used as aldehyde and N,N'-Dimethyl-4-aminoantipyrine is used as the amine and the solvent used is methanol.

B. Instruments

Instruments used in this investigation are given below:

1) Schimadzu IR prestige-20 spectrometer
2) Schimadzu Corp- 80282 Spectrometer
3) Systronies conductivity meter 304
4) Gouy type magnetic balance
5) Vario-III CHN elemental analyser
6) Powder X-ray diffractometer

The purity of the compounds were checked by Thin Layer Chromatography (0.5 mm thickness) using silica gel-G and spots were visualized by exposing the dry plates to iodine vapours.

C. Methods

1) *Synthesis Of N-(4-Nitrobenzylidene)-N,N'-Dimethyl-4- Aminoantipyrine:* 4-nitrobenzaldehyde (0.151g, 0.001M) dissolved in 20 ml methanol andN,N'-Dimethyl- 4-aminoantipyrine in 20 ml methanol was mixed well. The resulting mixture was refluxed for about four hours. On cooling, yellow crystals were separated from the solution. These crystals were filtered and dried.

2) *Synthesis of Metal Complexes*

a) *Synthesis of Zinc Complex:* Zinc nitrate has been used as a synthetic intermediate for the preparation of Zn(II) complex. The methanolic solution of the ligand (0.001M) was just heated to dissolve the ligand and to this, methanolic solution of the metal (0.0005M) was added so that the ratio will be 1:2 and the mixture is refluxed for four hours. The pH is maintained between 6-7. Then the volume was reduced to half its initial volume. After concentration, the solution was cooled and the yellow complex formed is separated out. It is filtered, washed with methanol and dried in vacuum.

b) *Synthesis of Zirconium Complex:* Zirconium oxychloride has been used as a synthetic intermediate for the preparation of Zr(IV) complex. The methanolic solution of the ligand (0.001M) was just heated to dissolve the ligand and to this, methanolic solution of the metal (0.0005M) was added so that the ratio will be 1:2 and the mixture is refluxed for four hours. The pH is maintained between 6-7. Then the volume was reduced to half its initial volume. After concentration, the solution was cooled and the yellow complex formed is separated out. It is filtered, washed with methanol and dried in vacuum.

Table 3.3 : physical properties of ligand and complexes.

Compound	Colour	Solubility	Yield(%)
Ligand	Yellow	Chloroform	85%
Zn complex	Yellow	Chloroform	81%
Zr Complex	Yellow	Chloroform	77%

D. Infrared Spectra

IR spectroscopy is a spectroscopic technique used to identify chemical compounds and to investigate sample composition. A comparison of IR stretching frequency of the ligand and its metal complexes gives an idea about the mode of binding in complexes. On complexation with metal ions, the characteristic IR frequencies of the coordinating groups were influenced by the force constant of the metal ligand bond resulting in shifting of the group frequencies. The shift were useful in identifying the coordination sites. The IR spectra of the solid samples were recorded in Schimadzu IR prestige -20 spectrometer in the range of 4000-400 cm^{-1}. Potassium bromide disc method was employed for sample preparation.

E. Electronic Absorption Spectroscopy

Electronic absorption spectroscopy is used to study the stereochemistry of the complexes. By using d-d transitions of the metal ions and their absorption spectra, it is possible to determine the ligand field splitting of the d orbitals of the metal ions. Metal-ligand interaction can be studied from the UV-Visible spectra of free ligand and its metal complexes.

The UV-Visible spectra of the samples in Chloroform solution were recorded in Schimadzu UV-2450 A spectrometer in the range of 200-800 nm.

F. Molar Conductance

Molar conductance of transition metal complexes were determined in DMF and N,N"- dimethyl formamide at room temperature using a systolic conductivity Meter 304. The cell constant of the conductivity cell was 1 cm^{-1}. The concentration of the solution was around 1x 10^{-3} M. The molar conductance is measured by the equation,

M = 1000 k/c Where c = concentration of the solution in mol/L

k = conductivity (specific conductance)

G. CHN Analysis

CHN analysis was done in Vario-III CHN elemental analyser at CLIF, Karyavattom campus.

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H. Magnetic Susceptibility

Magnetic susceptibility measurements of the metal complexes were studied at room temperature (3000K) by using Magway MSB Mk1 magnetic susceptibility balance. Diamagnetic corrections were computed using Pascal's constant by adding the diamagnetic contribution of various atoms and structural units. Gram susceptibility was calculated using the formula,

$X_g = (\alpha + \beta F) / W$ Where α = Air Displacement Constant

β = Tube Constant

F = change in weight in milligram W = weight of sample in gram

The effective magnetic moment μ_{eff} was calculated using the formula, $\mu_{eff} = 2.84\sqrt{X_m T}$

where X_m = molar susceptibility corrected for diamagnetism and T = Temperature, 293 K

I. X-RAY Diffraction Studies

Powder X-ray diffraction studies was done in CLIF, Karyavattom campus.

The d spacing of the complexes were determined using Bragg's equation and Scherrer equation.

Braggs law states that,

$$n\lambda = 2d \sin\Theta$$

Sherrer equation in X ray diffraction and crystallography is a formula that relates the size of sub micrometre particles or crystallites in a solid to the broadening of a peak in a diffraction pattern. It is named after Paul sherrer. It is used in the determination of size of particles of crystals in the form of powder.

The sherrer equation can be written as,

$$\tau = \frac{K\lambda}{\beta \cos\theta}$$

Γ - mean size

K - dimensionaless shape factor λ - X-ray wavelength

β - line broadening at half the maximum intensity θ - Bragg's angle

III. RESULT AND DISCUSSION

Schiff base derived from 4-nitrobenzaldehyde and N,N'-dimethyl-4-aminoantipyrine has been examined as ligand for Zinc in +2 oxidation state and zirconium in +4 oxidation state.

A. General Properties

N-(4-nitrobenzylidene)-N,N'-dimethyl- 4-aminoantipyrine ligand is a yellow coloured compound. The Zr(IV) and Zn(II) complexes are yellow coloured and are stable in air. Both the complexes have crystalline nature. Both the complexes are sensitive to light and decomposes when exposed to light. The two complexes are insoluble in water and readily soluble in methanol, ethanol, Chloroform.

Ligand

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B. Analysis

Metal content in the complexes were determined by standard method after decomposing the complexes with hydrochloric acid-sulphuric acid mixture. The metal complexes of Schiff base ligand were prepared by the stoichiometric reaction of the corresponding metal and ligand in 1:2 ratio.

C. Molar Conductance

Molar conductance of 10-3 M solutions of the metal complexes at 25^0C were measured in DMF and N,N‟-dimethyl formamide. The molar conductance values of Zr(IV) and Zn(III) complexes under investigation are found to be 145 Ω-1cm^2mol^{-1} and 169 $\Omega^{-1}cm^2mol^{-1}$ respectively. The molar conductance value shows that the Zn(II) and Zr(IV) complex was electrolytic in nature. Because there is no charged species in the complex to neutralize the charge of the central metal ion.

D. Magnetic Measurements

Magnetic susceptibility of the complexes were determined using Magway MSB Mk1 magnetic susceptibility balance. The measurements were made at room temperature. Table 3.3 (a) shows the effective magnetic moments calculated from the magnetic susceptibility which is corrected for diamagnetic corrections. Some indications about the structure, geometry and coordination of the complexes can be obtained from magnetic moment values.

The Zn(II) and Zr(IV) complexes are diamagnetic in nature.

Zn(II) complex has square planar structure and Zr(IV) complex has octahedral structure.

Complex	colour	Yield(%)	Molecular Weight	Magnetic moment (BM)	Molar conductance ($\Omega^{-1}cm^2mol^{-1}$)
Zn(II) complex	yellow	81%	794.22	diamagnetic	169
Zr(II) complex	Yellow	77%	856.064	diamagnetic	145

E. CHN Analysis

The percentage values of carbon, hydrogen and nitrogen in the two complexes were similar in the theoretical and experimental values found out by CHN analysis. So from the CHN analysis the denticity and thereby the structure of the ligand and complex can be confirmed.

COMPLEX	C%		H%		N%	
	experimental	calculated	experimental	calculated	experimental	Calculated
Zn complex	54%	54.39%	4.2%	4.03%	13.35%	14.10%
Zr complex	51%	50.46%	4.34%	4.20%	12.98%	13.08%

Here, the CHN analysis values are in good agreement with the calculated percentage of carbon, hydrogen and nitrogen in the complex. So by using CHN analysis, it is easy to confirm that the ligand is bidentate. The structures of the complexes can also be confirmed from CHN analysis value. The structure of Zn complex is found to be square planar and that of Zirconium complex is octahedral.

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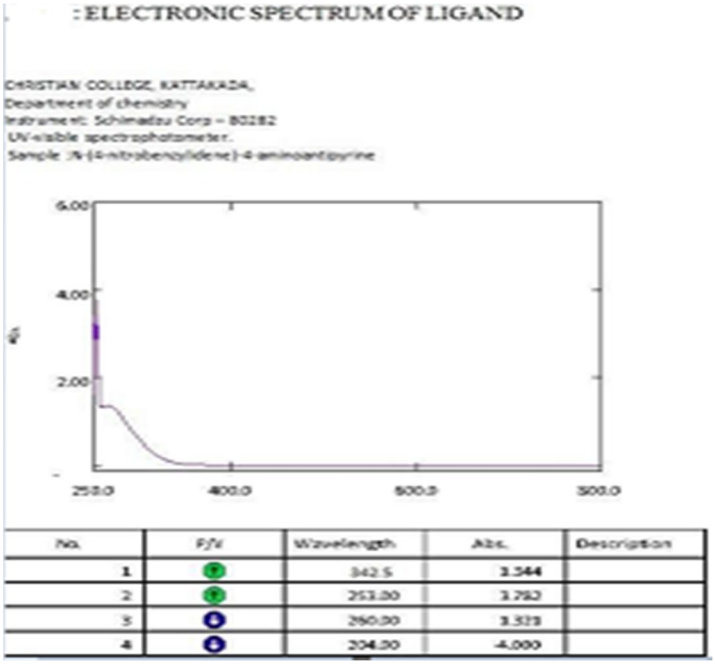
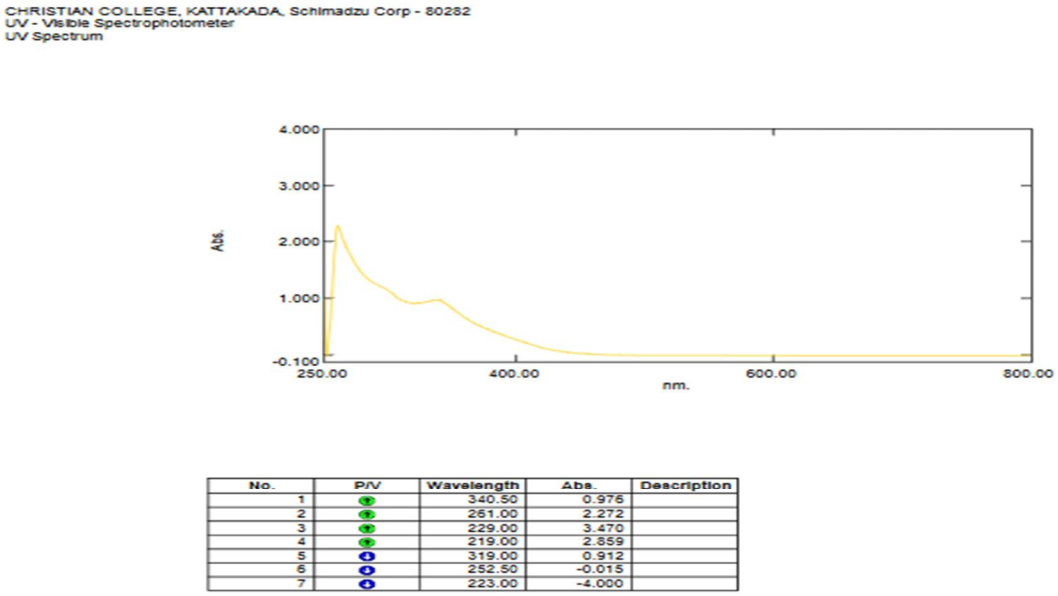
F. Electronic Spectra

The electronic spectra are often helpful in the evaluation of results furnished by other methods of analysis. The electronic spectral bands of the ligand and complexes was recorded over the range of 200-800 nm in chloroform.

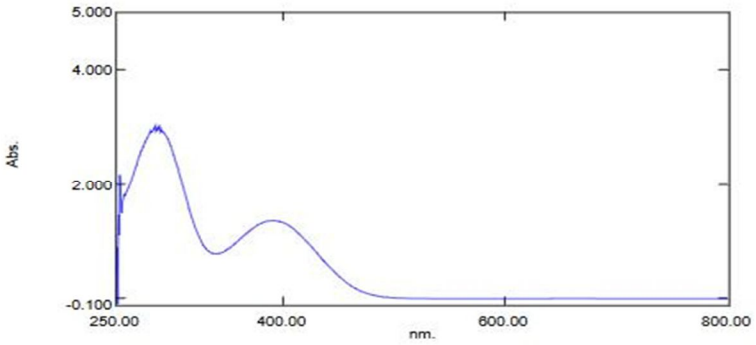


Ultraviolet spectra of the ligand recorded in chloroform showed strong bands around 260 nm and at 342.5 nm region which confirms the presence of benzenoid and azomethine linkages, which are characteristic of Π—›Π* and n—›Π* respectively.



ultraviolet spectra of the zinc complex recorded in chloroform showed strong bands around 261 nm and at 340.5 nm region which confirms the presence of benzenoid and azomethine linkages, which are characteristic of Π—›Π* and n—›Π* respectively.

DST FIST UV Vis
spectrophotometer Department of
Chemistry
Sample. nickel
5.10.2018



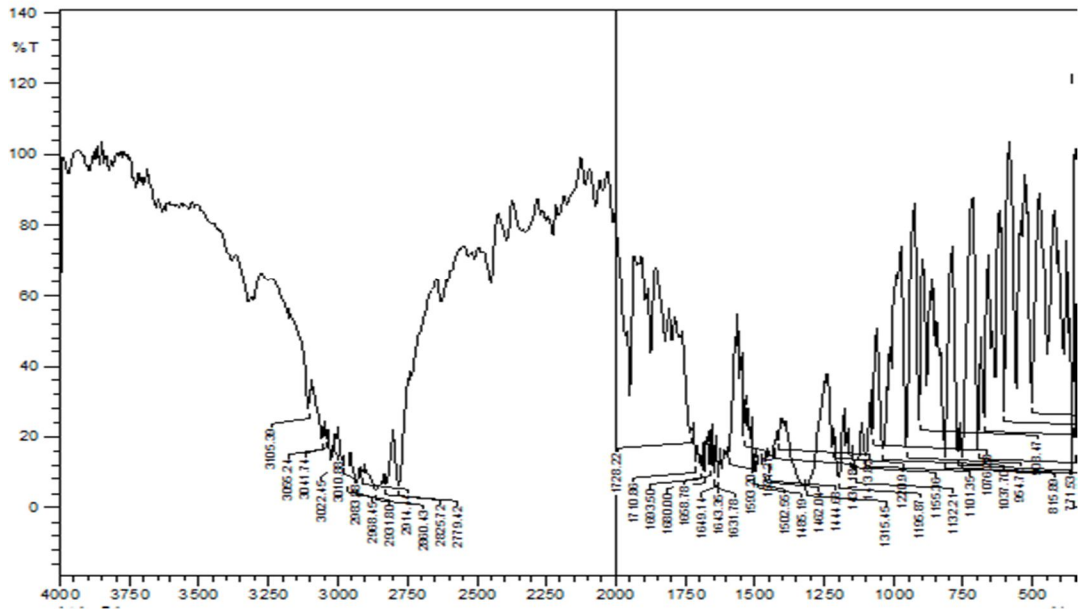
No.	P/V	Wavelength	Abs.	Description
1	↑	391.50	1.362	
2	↑	285.50	3.032	
3	↑	217.50	3.168	
4	↓	340.50	0.782	
5	↓	251.50	-0.263	

Ultraviolet spectra of the Vanadium complex recorded in chloroform showed strong bands around 285 nm and at 391 nm region which confirms the presence of benzenoid and azomethine linkages, which are characteristics of Π—›Π* and n—›Π* transition respectively.

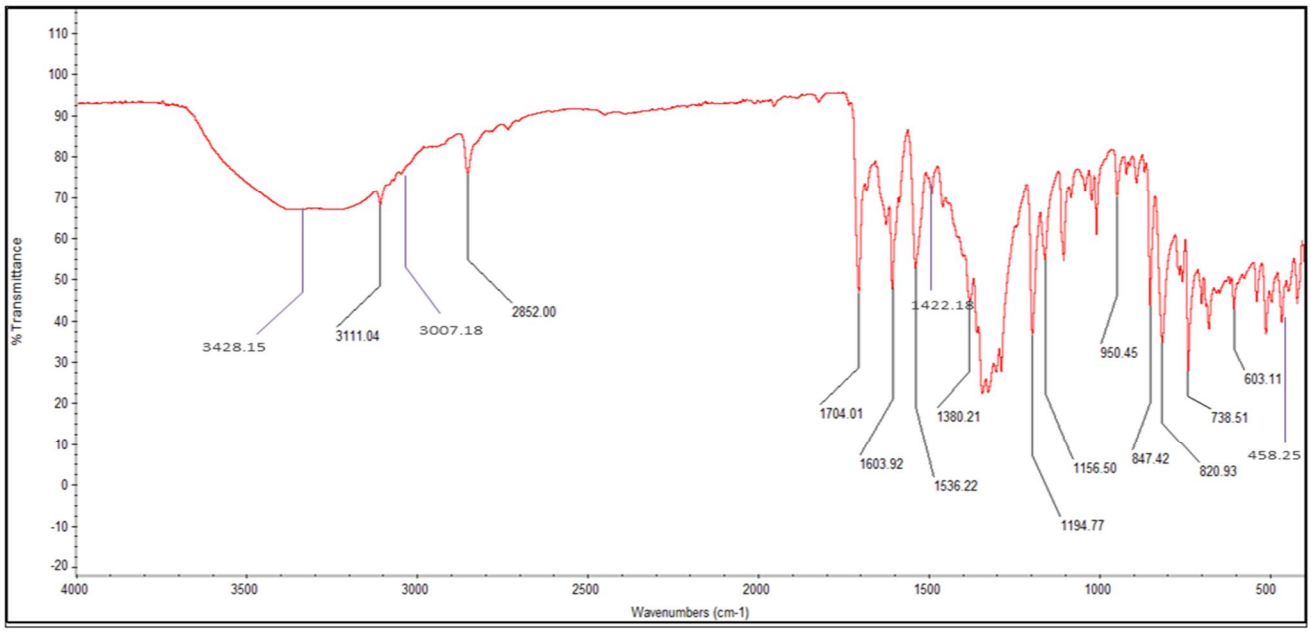
G. Infrared Spectra

The IR spectral data of the Schiff base ligand and its metal complexes are presented in table 3.7 (a) and 3.7(b). The spectra of the complexes were compared with that of the free ligand to determine the coordination sites which involve in chelation

(a) IR SPECTRUM OF LIGAND



(b) IR Spectrum Of ZINC Complex

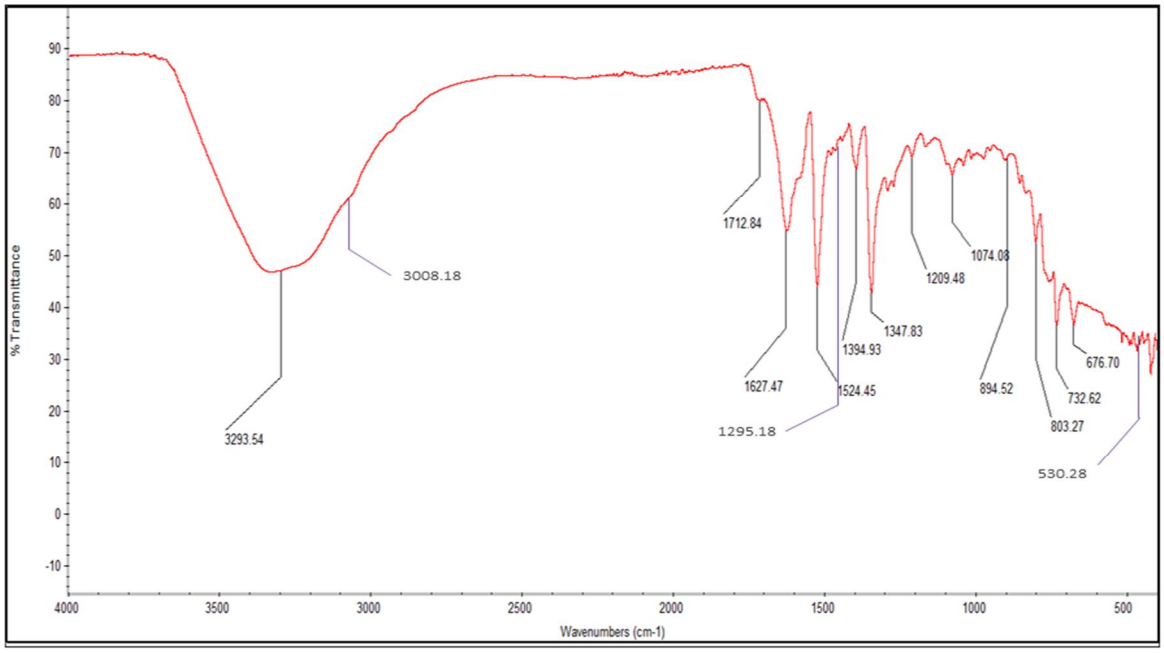


Ligand	Zn Complex	Assignment
-	3428.15	Coordinated water molecule
3022.45	3007.28	=CH
1631.78	1603.92	C=N
1537.27	1536.22	C=C
1431.18 1315.45	1422.18 1380.21	N=O (Sym. Bending) N=O (asym. Bending)
754.17	738.51	Monosubstituted
-	458.25	Zn-N
-	603.11	Zn-O

Table 4.7(a)

In the IR spectrum of the ligand, a band is observed at 3022.45 cm^{-1} which corresponds to =CH group. In the complex, it is shifted to a lower frequency of 3007.28 cm^{-1}. The peak at 1631.78cm^{-1}corresponds to the C=N band of ligand.It is shifted to a lower frequency range 1603.92 cm^{-1} .This peak indicates the presence of coordination.The peak at 3428.15 cm^{-1}in cobalt complex represents the coordinated water molecule. The bands at 1422.18 $cm^{-1}$and 1380.21cm^{-1}corresponds to the symmetric and asymmetric bending of N=O group. In zinc complex there is a strong band at 458.25 cm^{-1}which represents the Zn-N, it confirms the coordination. The presence of Zn-O bond is confirmed by 603.11 cm^{-1} .

(c) IR Spectrum of Zirconium Complex



Ligand	V Complex	Assignment
-	3298.54	Coordinated water molecule
3022.45	3008	=CH
1631.78	1627.47	C=N
1537.27	1524.45	C=C
1431.18 1315.45	1394.93 1295.18	N=O(sym.bending) N=O (asym.bending)
754.17	732.62	monosubstituted
-	676.70	Zr-N
- -	530.28	Zr-O

Table 4.7(b)

In the IR spectrum of the ligand, a medium band is observed at 3022.45 cm^{-1} which corresponds to =CH group. It is shifted to a lower frequency of 3008. cm^{-1} in the complex. The intense band at 1631.78cm^{-1} corresponds to υ (C=N) of the ligand. It is shifted to a lower frequency of 1627.47 cm^{-1} which indicates the presence of coordination. The symmetric and asymmetric bending of N=O groupin complex is represented by 1394.93cm^{-1} and 1295.18 cm^{-1}respectively. The peak at 676.70 cm^{-1} and 530.28 cm^{-1} corresponds to Zr-N and Zr-O bonds respectively.

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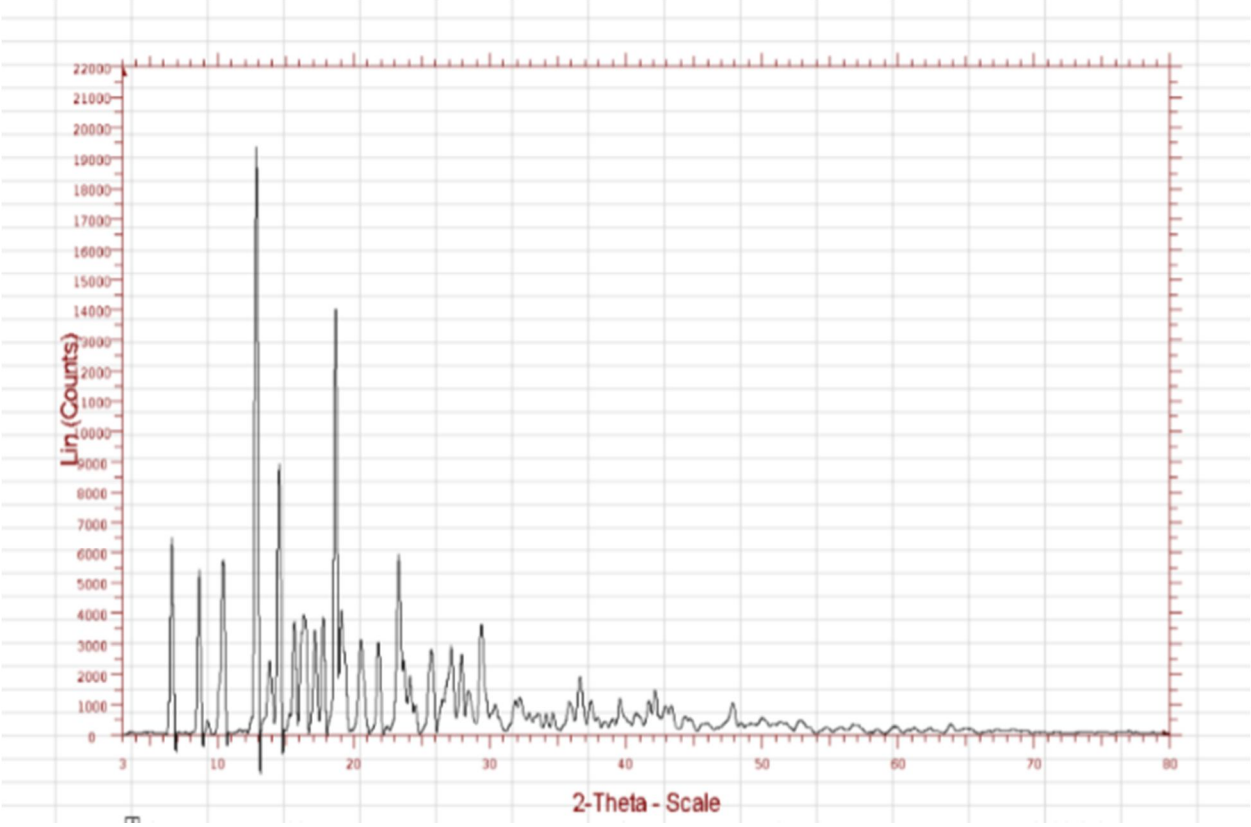
H. Powder X-Ray Diffraction Studies

1) XRD of ZINC Complex



Ø observed	Ø calculated	$d_{observed}$	$d_{calculated}$	$d_{scherrer}$	Plane
16.069	16.1531	5.216	5.1663	5.1232	131
21.235	21.2162	4.363	4.3885	4.57	102
23.531	23.2748	3.830	3.8172	4.04	060
27.133	27.0540	3.253	3.2900	2.29	311
29.055	29.9258	3.20	3.22	3.26	171

The sharp crystalline peaks of the zinc complex are attributed to the monoclinic structure. The XRD peaks at 2θ = , 16.069, 21.235, 23.531, 27.133, 29.055, degrees can be assigned for X-ray scattering from (131), (102), (060), (311) and (171) planes. The obtained value is in good agreement with the data of monoclinic phase . The intense peak at 2θ = 21.235^0 corresponds to the plane (102) which is the characteristic of monoclinic phase.

The average value of crystal lattice parameter a was about 3.544 A^0. The crystallite size ws calculated by Scherrer equation

$$\tau = \frac{K\lambda}{\beta \cos\theta}$$

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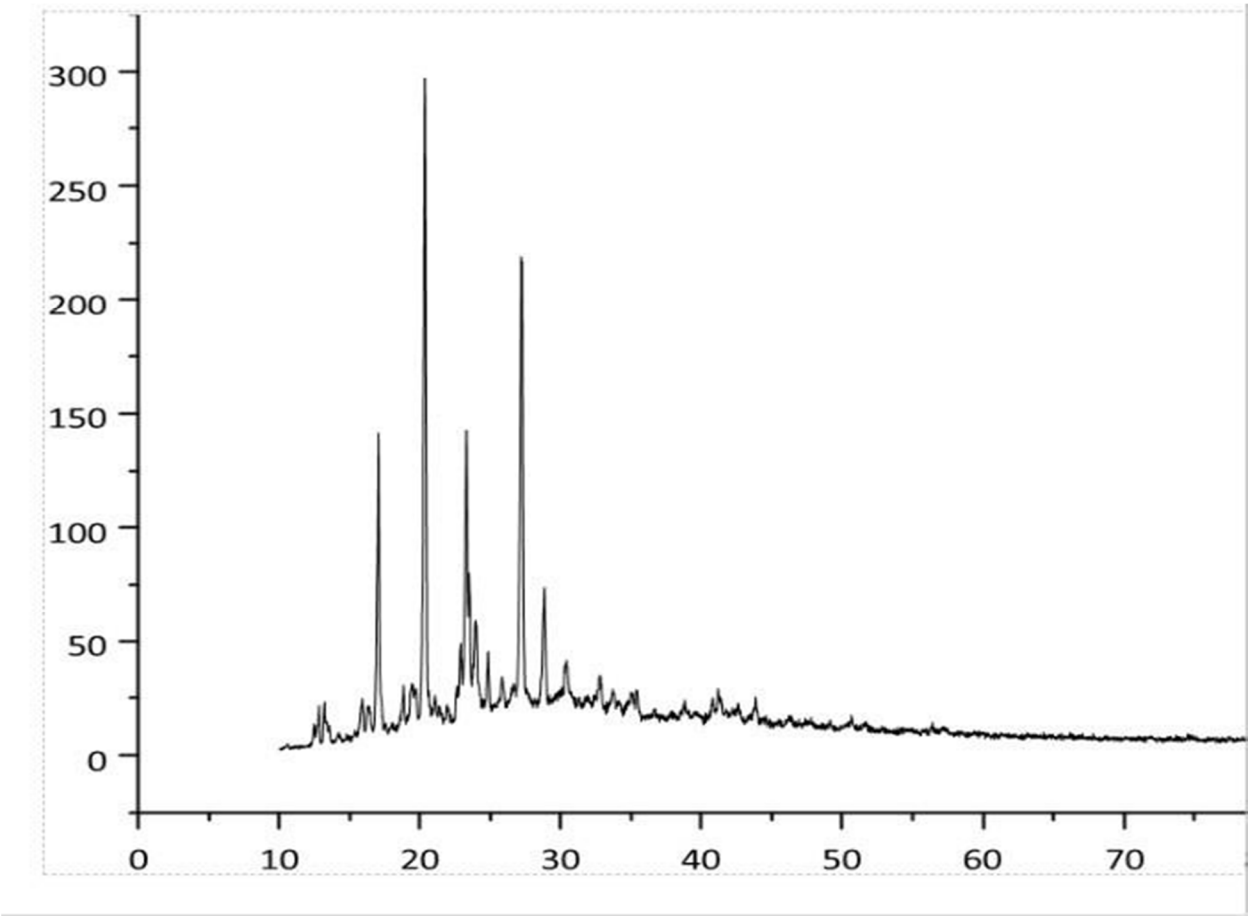
2) XRD OF Zirconium Complex



Ø observed	Ø calculated	$d_{observed}$	$d_{calculated}$	$d_{scherrer}$	Plane
16.982	17.1531	5.216	5.1663	5.1232	131
21.377	21.2155	4.363	4.3885	4.57	102
23.205	23.2748	3.830	3.8172	4.04	060
27.3975	27.0540	3.253	3.2900	2.29	311
29.7201	29.9336	3.20	3.22	3.26	171

The sharp crystalline peaks of the Zirconium complex are attributed to the monoclinic structure. The XRD peaks at 2θ = 16.982, 21.377, 23.205, 27.3975 and 29.7201 degrees can be assigned for X-ray scattering from (131), (102), (060), (311) and (171) planes. The obtained value is in good agreement with the data of monoclinic phase. The intense peak at 2θ = 21.377^0 corresponds to the plane (102) which is the characteristic of monoclinic phase.

The average value of crystal lattice parameter a was about 8.678 A^0. The crystallite size ws calculated by Scherrer equation

$$\tau = \frac{K\lambda}{\beta \cos\theta}$$

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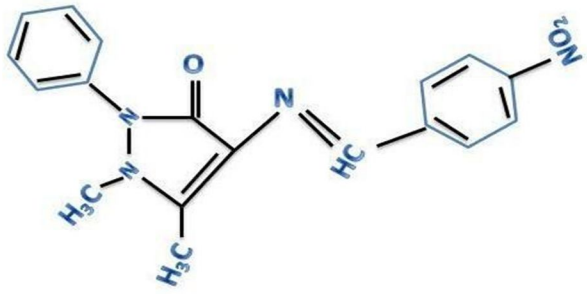
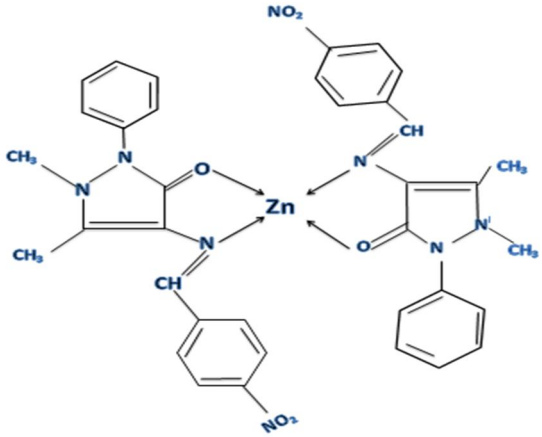
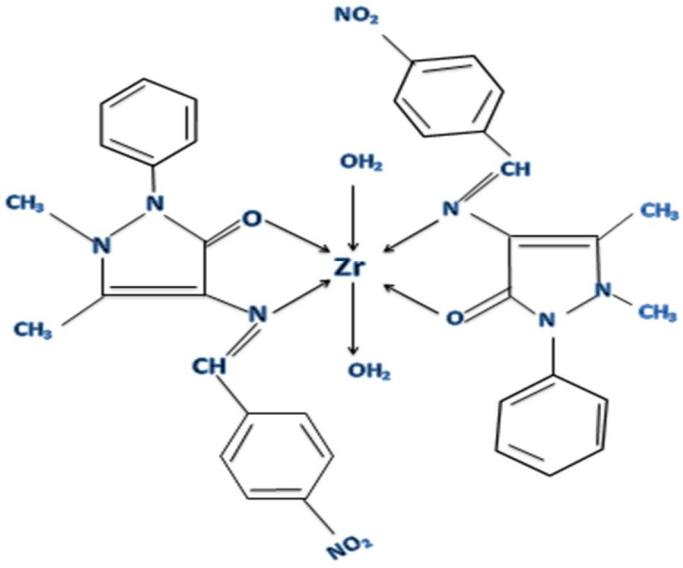


Structure of Ligand



Structure of Zinc Complex



Structure of Zirconium Complex

IV. SUMMARY AND CONCLUSION

The condensation process of 4-nitrobenzaldehyde and N,N'-dimethyl-4- aminoantipyrine gives the Schiff base ligand N-(4-nitrobenzylidene)-N,N'-Dimethyl-4- aminoantipyrine.The ligand has 85% yield and is obtained as yellow coloured form which is soluble in chloroform. The ligand is bidentate, it is confirmed by spectral data.

The zinc complex of this ligand is obtained as yellow crystal form. It is about 81 % yield and is soluble in chloroform. Molar conductance value of this schiff base complex is found to be 169 $\Omega^{-1}cm^2mol^{-1}$.This indicates its electrolytic nature. The IR spectra shows two bands at 458.25 cm^{-1} and 603.11 cm^{-1} corresponding to Zn-N and Zn-O bonds. Thus in this complex ligand is bidentate. The X-ray diffraction studies of zinc complex showed that it is monoclinic.

The zirconium complex of this ligand is dark green crystals having 77% yield and is soluble in chloroform. Molar conductance is obtained as 145 $\Omega^{-1}cm^2mol^{-1}$. .It is also slightly electrolytic in nature.. IR spectra of complex shows peaks at 676.70 cm^{-1} and 530.28 cm^{-1} corresponding to Zr-N and Zr-O. It also shows the presence of a bidentate ligand. X-ray diffraction studies of zirconium complex shows a monoclinic structure.

The experimental percentage values of carbon, hydrogen and nitrogen in the two complexes found out by CHN analysis were similar to the percentage calculated from the theoretical aspects. So from CHN analysis, the structure and denticity of the ligand and complex can be confirmed.

By magnetic moment and by CHN analysis, zinc complex shows square planar and zirconium has octahedral structure.

The UV spectra of ligand and complexes shows characteristic absorption at the range of 285 nm and at 340 nm region which confirms the presence of benzenoid and azomethine linkages, which are characteristic of Π—›Π* and n—›Π* transition respectively.

V. ACKNOWLEDGEMENT

We acknowledge the Department of Science and Technology (DST) for providing fund under the scheme of "Fund for Improvement of S & T infrastructure in universities and higher education institutions (FIST)" for providing fund to purchase equipment in instrumentation lab and also for computer facilities in Computer and Networking Lab.

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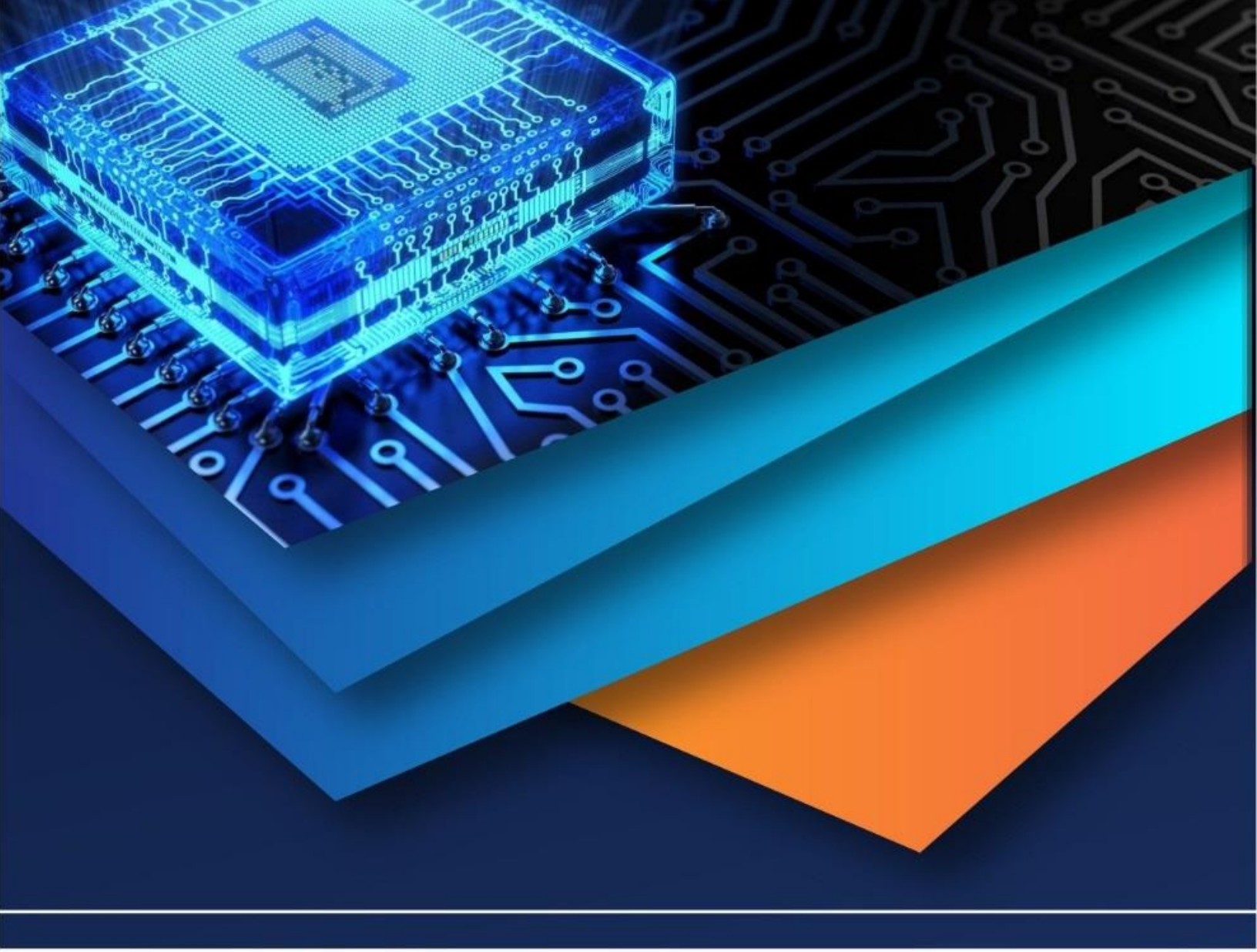

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