

Synthesis , Characterization and Thermogravimetric Analysis of Cobalt (III) and Zirconium(IV) Complexes With N-(3-Nitrobenzylidene)-N,N'-Dimethyl-4-Aminoantipyrine

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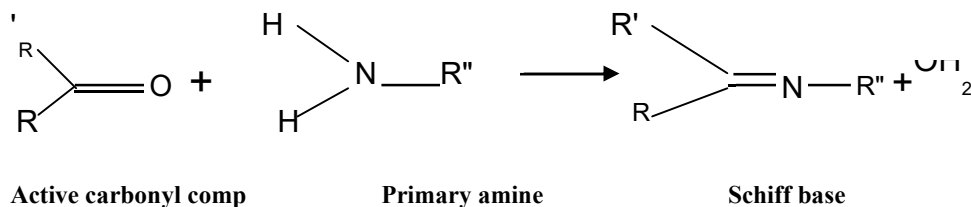
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Abstract : The Schiff base ligand (3-nitrobenzylidene)-N,N'-dimethyl-4-amino antipyrine was prepared by the condensation between 3-nitrobenzaldehyde and N,N'-dimethyl-4-amino antipyrine. The Co and Zr complexes of the corresponding ligand were prepared and was characterized by different methods like CHN analysis, IR and UV spectra. From CHN analysis and IR spectral data the structures of Co complex and Zr complex are found to be octahedral structure. The complexes were analysed for its thermal stability.

Key Words : 3-nitrobenzaldehyde, N, N'-dimethyl-4-aminoantipyrine, Thermogravimetry, Schiff base

I. INTRODUCTION

Coordination Chemistry is a branch of inorganic chemistry which encompasses a great diversity of structures. The term coordination is used to describe the nature of metal ligand bond. Coordination compounds of transition metals was discovered in 1798 by Tassart. The increased development in the field of spectroscopic analysis like IR, UV, Raman, NMR, EPR, Mass spectroscopy etc facilitate the progress of research in the field of coordination compounds.



(R, R' and R'' may be acyclic, alicyclic, aromatic and heterocyclic etc.)

Schiff bases have active imine >(C=N) linkage which provide binding site for the metal ions through nonbonding electrons of nitrogen .

A number of Schiff bases exhibit the ability of capturing proton, good mechanical properties and excellent thermal stability. Schiff base compounds had been shown to exhibit a

According to Werners theory ligand donate electron pair to metal ion or atom to form co-ordinate linkage. This approach was first applied to co-ordination compounds by Linus Pauling and Slater (1931) [1].

Crystal field theory developed by Bethe^[2] and Van Vleck^[3] is another approach to study the complexes .According to this theory, the bond between metal and ligand is neither due to sharing of electron nor due to interaction of atomic orbitals. Crystal field theory involves electrostatic approach to the bonding in complexes.

Schiff bases are condensation products of amines with active carbonyl compounds. They were discovered by a German chemist, Nobel prize winner ,Hugo Schiff in 1864^[4]. The Schiff bases are also called imines, anils and azomethines^[5] They contain azomethine (>C=N) group and hence can act as effective ligand. The chemistry of the carbon–nitrogen double bond plays a vital role in the progress of chemical science. Solvent based synthesis of Schiff bases through classical condensation of aldehyde and amines require P^H control, however, the yield of product, in high and in low P^H range (3-4) depending upon the basicity of amines.

variety of applications including electronic applications, pH and ion sensors, molecular wires, organic lightemitting diodes (OLED), non-linear optical devices and organic photovoltaics^[6].

Application Of Schiff Bases In Various Fields:

Application of Schiff base compounds in various fascinating area is current research interest to the inorganic chemist all over the world. The importance of Schiff base complexes for, bioinorganic chemistry, biomedical application, supramolecular chemistry, catalysis, medical sciences, separation encapsulation processes and formation of compounds with unusual properties and structures has been well recognized and reviewed. Among the several classes of ligands, a new tetradentate Schiff base ligands derived from orthophenylenediamine, salicylaldehyde and isatin /acetyl acetone/2-hydroxy naphthaldehyde containing oxygen and nitrogen donor sites have been recognized and synthesized. The different types of Schiff base ligands and their applications have importance in generating new areas of fundamental chemistry and many opportunities of applied chemistry. The majority of Schiff base ligands represent creative and focused efforts to design molecules which will have particular uses.

II. MATERIALS AND METHODS

2.1: Materials

The chemicals used for the synthesis in the present investigation are of commercial grade and they are directly used without further purification. 3-nitrobenzaldehyde is used as aldehyde and N,N' – dimethyl aminoantipyrine is used as the amine and the solvent used is methanol.

2.2: Instruments

Instruments used in this investigation are given below:

1. Shimadzu IR prestige-20 spectrometer
2. Shimadzu UV-2450 A Spectrometer
3. Systronics conductivity meter 304
4. Gouy type magnetic balance
5. Vario-III CHN elemental analyser

2.3: Methods

2.3.1: Synthesis Of N-(3-Nitrobenzylidene)-N,N'-Dimethyl-4-Aminoantipyrine

3-nitrobenzaldehyde (0.151g, 0.001M) dissolved in 20 ml methanol and N,N'-Dimethyl-4-Aminoantipyrine (.231g, 0.0001 M) 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.

2.3.2: Synthesis Of Metal Complexes

(a) Synthesis of Cobalt complex

Cobaltous chloride has been used as a synthetic intermediate for the preparation of V(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 Dark red 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 (0.001M) was added so that the ratio will be 1:1 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 complex formed is separated out. It is filtered, washed with methanol and dried in vacuum.

Table 2.3 : physical properties of ligand and complexes.

Compound	Colour	Solubility	Yield(%)
Ligand	Yellow	Chloroform	76.3%
Zr Complex	Yellow	Chloroform	79%
Co Complex	Dark red	Chloroform	75%

2.4: Infrared Spectra

The IR spectra of the solid samples were recorded in Shimadzu IR prestige -20 spectrometer in the range of 4000-400 cm⁻¹. Potassium bromide disc method was employed for sample preparation.

2.5: Electronic Absorption Spectroscopy

Electronic absorption spectroscopy is used to study the stereochemistry and the geometry of the complexes.

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

2.6: 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)

2.7: CHN Analysis

CHN analysis was done in Vario-III CHN elemental analyser at the Saif, Cochin University of Science and Technology, Kochi.

2.8: 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, $\mu_{\text{eff}} = 2.84\sqrt{X_m T}$

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

2.9. Thermogravimetry

Thermogravimetry is the technique in which a sample is continuously weighed as it is heated at a predetermined and preferably at a linear rate. The resulting weight change vs temperature curve so obtained provides information regarding the thermal stability and composition of the original material, the composition and thermal stability of the intermediate compounds and the composition of residue.

The instrument used is a thermobalance. Both manual and automatic balance are used, but latter type is preferred.

III. RESULT AND DISCUSSION

Schiff base derived from 3-nitrobenzaldehyde and N,N'-dimethyl-4-aminoantipyrine and their cobalt and zirconium complexes are synthesised.

3.1: General Properties

Zr(IV) is dark yellow in coloured and Co(III) complex is dark red in coloured and are stable in air. Both the complexes are sensitive to light and decomposes when exposed to light. The two complexes are insoluble in water and readily soluble in chloroform and DMSO.



ligand

3.2: Molar Conductance

Molar conductance of 10^{-3} M solutions of the metal complexes at 25°C were measured in DMF and N,N'-dimethyl formamide. The molar conductance values of Co(III) and Zr(IV) complexes under investigation are found to be $143 \Omega^{-1}\text{cm}^2\text{mol}^{-1}$ and $138 \Omega^{-1}\text{cm}^2\text{mol}^{-1}$ respectively. The molar conductance value shows that the Co(III) 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.

Complex	colour	Yield(%)	Molecular Weight	Magnetic moment (BM)	Molar conductance ($\Omega^{-1}\text{cm}^2\text{mol}^{-1}$)
Co(III) complex	Dark red	75%	823.773	6.02	143
Zr(IV) complex	yellow	79%	856.064	diamagnetic	138
Table 3.2(a)					

3.3: 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 Co(III) are paramagnetic in nature and and Zr(IV) complex is diamagnetic ratio.

The magnetic moment values of Co(III) is found to be 6.02 BM From this, it is clear that the Co(III) complex has octahedral structure and Zr(IV) is diamagnetic and hence it has an octahedral structure.

3.4 : CHN Analysis

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.

Table 3.4 (a)

COMPLEX	C%		H%		N%	
	experimental	calculated	experimental	calculated	experimental	Calculated
Co complex	51.8%	52.44%	5.29%	4.37%	12.35%	13.59%
Zr complex	49%	50.46%	4.53%	4.20%	6.98%	6.54%

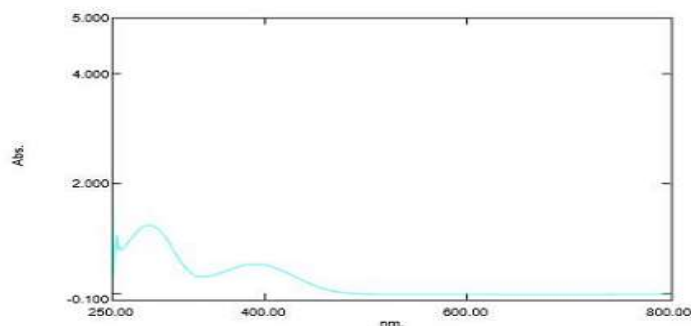
Here, the CHN analysis values are in good agreement with the calculated percentage of carbon, hydrogen and nitrogen in the complex. The ligand is bidentate. The structures of the complexes can also be confirmed from CHN analysis. The structure of Zirconium complex Vanadium complexes are octahedral .

3.6: 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 DMSO .

3.6 A : Electronic Spectrum of Ligand

DST FIST UV Vis spectrophotometer Department of Chemistry



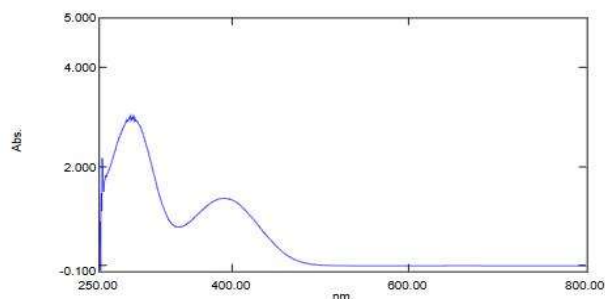
No.	P/V	Wavelength	Abs.	Description
1	●	390.00	0.542	
2	●	286.50	1.247	
3	●	226.50	1.204	
4	●	213.50	1.712	
5	●	204.50	2.988	
6	●	339.50	0.313	
7	●	237.00	0.137	
8	●	224.00	-4.000	
9	●	211.50	-0.142	

Ultraviolet spectra of the ligands recorded in DMSO showed strong bands around 286.5 nm and at 339.5 nm region which confirms the presence of benzenoid and azomethine linkages, which are characteristic of $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transition respectively.

Electronic Spectra Of Complexes.

3.6 b : Cobalt Complex

DST FIST UV Vis spectrophotometer Department of Chemistry
Sample: nickel
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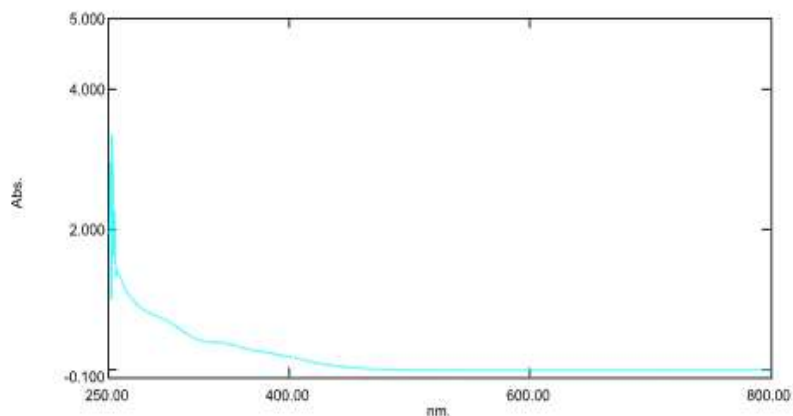


No.	P/V	Wavelength	Abs.	Description
1	●	391.50	1.362	
2	●	285.50	3.032	
3	●	217.50	3.168	
4	●	340.50	0.782	
5	●	251.50	-0.263	

Ultraviolet spectra of the Nickel complex recorded in DMSO showed strong bands around 251 nm and at 391.5 nm region which confirms the presence of benzenoid and azomethine linkages, which are characteristic of $\Pi \rightarrow \Pi^*$ and $n \rightarrow \Pi^*$ transition respectively.

3.6 c : Zirconium complex

CHRISTIAN COLLEGE, KATTAKADA, Shimadzu Corp - 80282
 UV - Visible Spectrophotometer
 UV Spectrum



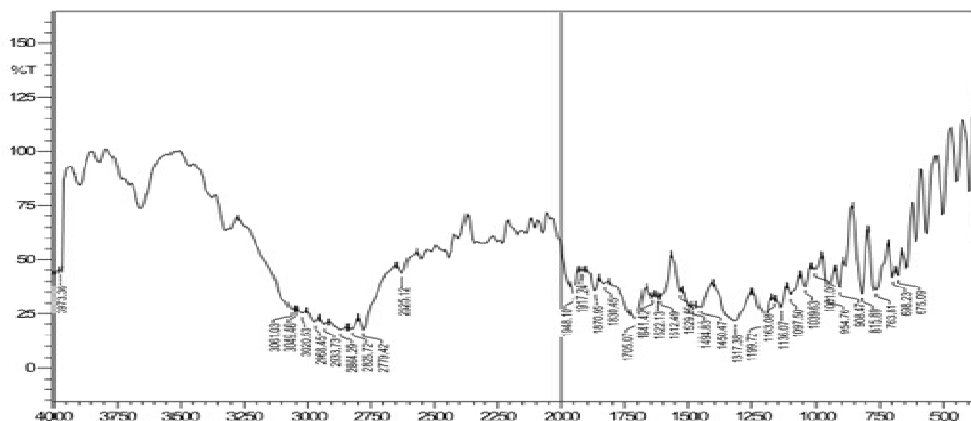
No.	P/V	Wavelength	Abs.	Description
1	●	340.50	0.390	
2	●	221.00	3.440	
3	●	338.50	0.385	

Ultraviolet spectra of the Vanadium complex recorded in DMSO showed strong bands around 221 nm and at 340.5 nm region which confirms the presence of benzenoid and azomethine linkages, which are characteristic of $\Pi \rightarrow \Pi^*$ and $n \rightarrow \Pi^*$ transition respectively.

The IR spectral data of the Schiff base ligand and its metal complexes are presented in table 5.6(a) and 5.6(b). The spectra of the complexes were compared with the spectrum of the ligand

3.7: Infrared Spectra

(a) IR Spectrum Of Ligand



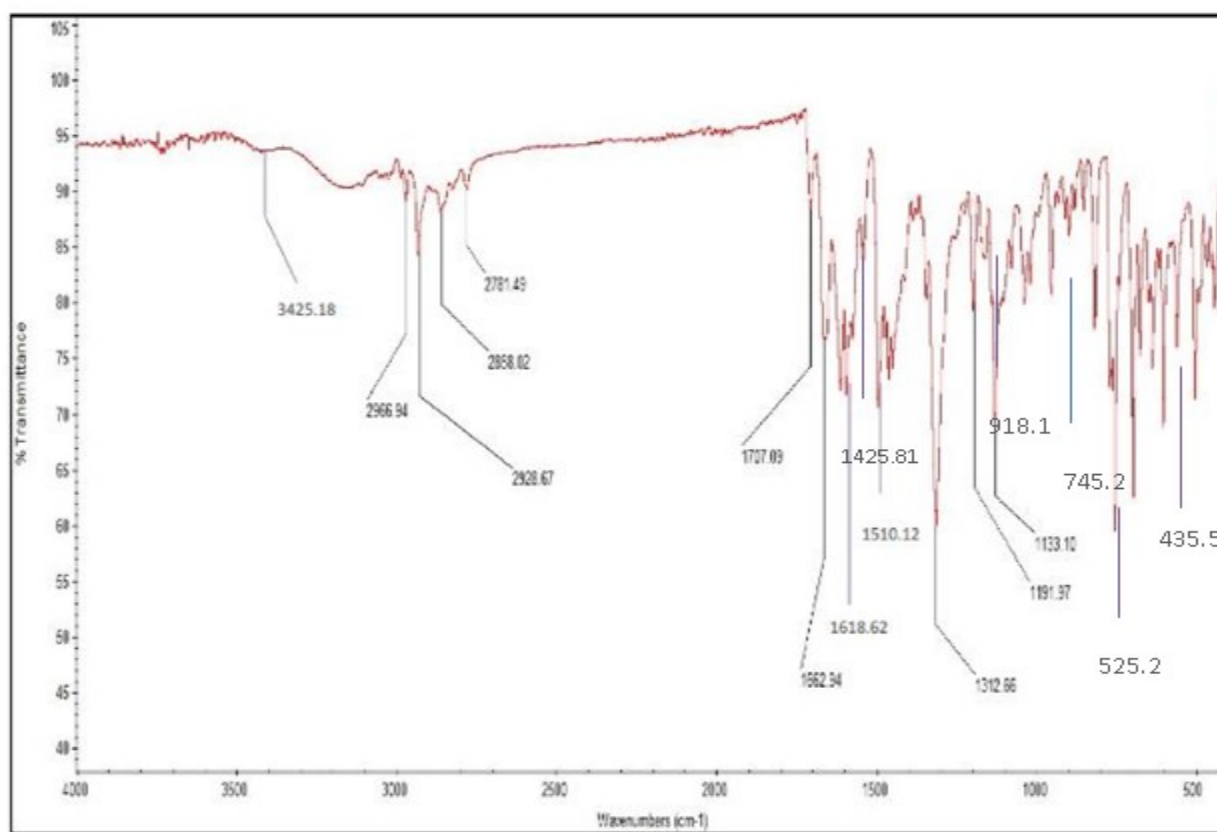
(b) IR Spectrum Of Cobalt Complex

Ligand	Co Complex	Assignment
-	3293.54	Coordinated water molecule
3020.53	3015	=CH
1622.13	1617.50	C=N
1529.55	1492.51	C=C
1450.47	1389.04	N=O (Sym. Bending)
1317.38	1285.71	N=O (asym. Bending)
698.23	726.74	Monosubstituted
-	458.18	Co-N
	528.25	
		Co-O

Table 3.7(b)

In the IR spectrum of the ligand, a medium strength band is observed at 3020.53 cm^{-1} which corresponds to =CH group. In the complex, it is shifted to a lower frequency of 3015 cm^{-1} . The intense band near 1622.13 cm^{-1} can be attributed to ν (C=N) of the ligand. It is shifted to a lower frequency of 1617.50 cm^{-1} which indicates the presence of coordination. Two peaks at 1448.15 cm^{-1} and 1380.21 cm^{-1} corresponds to

the symmetric and asymmetric bending of NO_2 group. In Ni complex, a strong band is obtained in 3293.54 cm^{-1} which indicates the presence of coordinated water molecule. The peak at 458.18 cm^{-1} can be attributed to Co-N bond which is absent in the free ligand. This peak at 458.18 cm^{-1} confirms the coordination in Co complex.

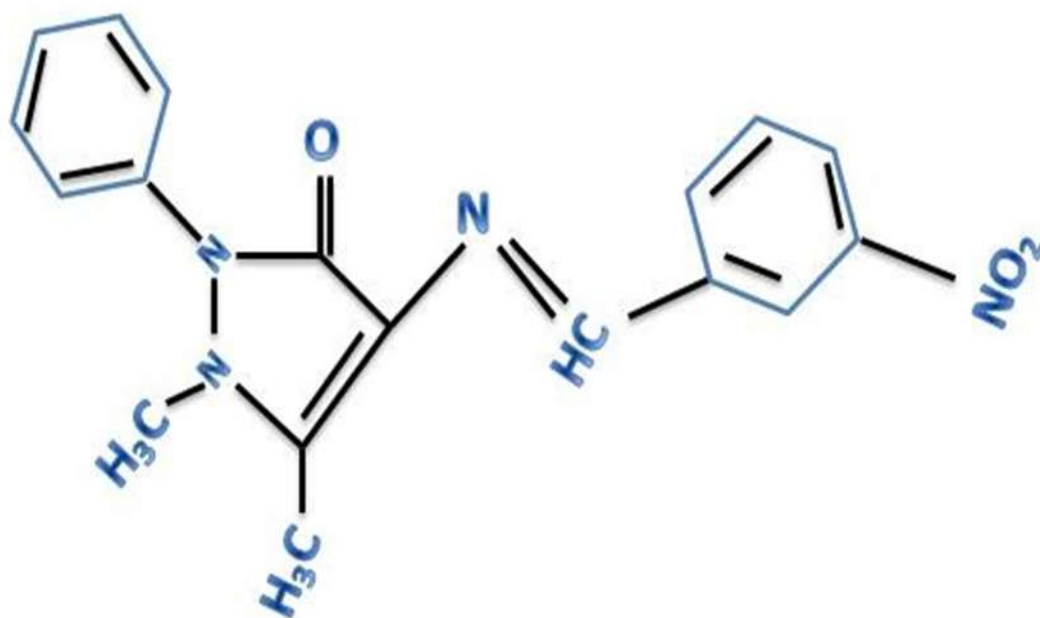
(c) IR Spectrum Of Zirconium Complex

Ligand	Zr Complex	Assignment
-	3425.18	Coordinated water molecule
3020.53	2966.94	=CH
1622.13	1618.62	C=N
1529.55	1510.12	C=C
1317.38	1312.66	N=O (asym.bending)
698.23	745.28	Monosubstituted
-	435.51	Zr-N
-	525.22	Zr-O

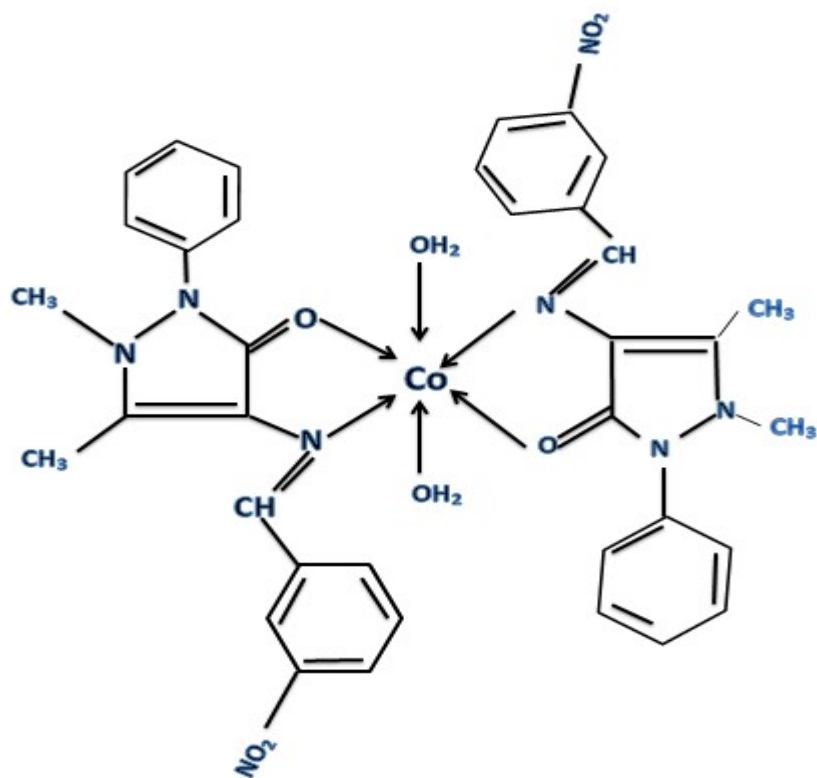
Table 3.7(c)

In the IR spectrum of the ligand, a medium strength band is observed at 3020.53cm^{-1} which corresponds to =CH group. In the complex, it is shifted to a lower frequency of 2966.94cm^{-1} . The intense band near 1622.13cm^{-1} corresponds to ν (C=N) of the ligand. It is shifted to a lower frequency of 1618.62cm^{-1} which indicates the presence of coordination. The peak at

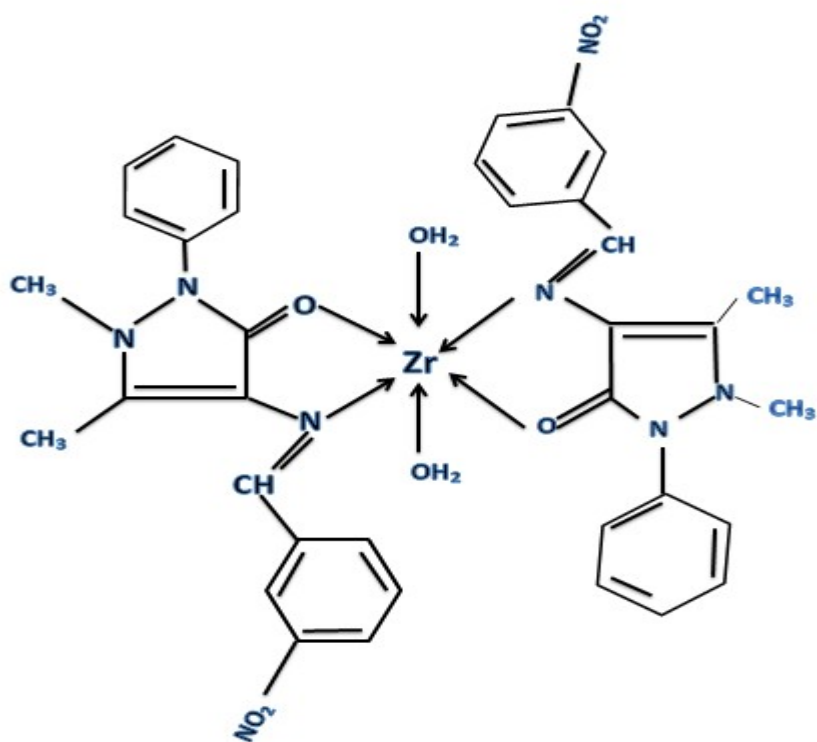
1312.66cm^{-1} indicates the asymmetric bending of NO_2 group. The peak at 3425.18cm^{-1} confirms the presence of coordinated water molecule. The strong bands at 435.51cm^{-1} and 525.55cm^{-1} attribute to Zr-N and Zr - O bonds which are absent in the free ligand. These peaks confirms the formation of metal complexes.



STRUCTURE OF LIGAND



STRUCTURE OF COBALT COMPLEX

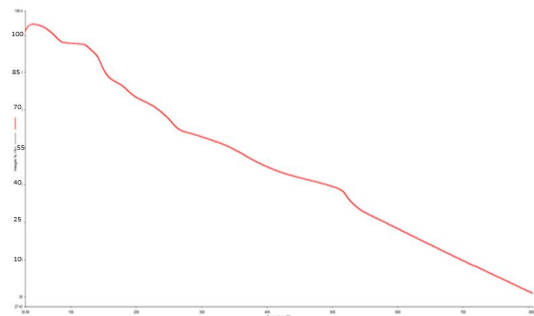


STRUCTURE OF ZIRCONIUM COMPLEX

3.8. Thermogravimetric Analysis

Thermogravimetric analysis of complexes was conducted. TG curve of the complexes are shown below

a) TG Analysis Of Zirconium Complex

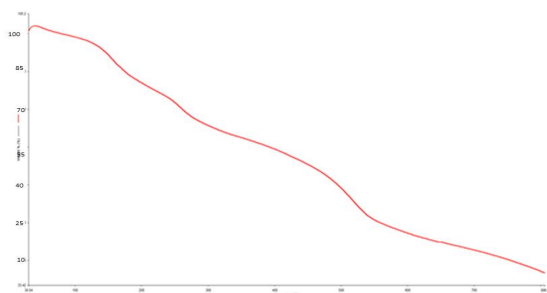


Temperature range °C	Mass Loss In %		Assignment
	Experimental	Calculated	
30-90	4.51	4.20	Removal of two molecules of water
160-240	15.57	16.12	Removal of three molecules of NO ₂
270-670	69.98	70.55	Removal of two molecules of C ₁₈ H ₁₆ N ₅
	9.55	9.13	Leaving of metal residue

Table 3.8.(a)

The thermogravimetric analysis (TG) curve obtained during the decomposition of Zr-complex is shown in the figure. This demonstrate that the decomposition occur at several step. The weight loss(4.51%) curve between a temperature range of 30-90°C represent the elimination of two water molecule. At the temperature range 160-240°C the weight loss is 15.57% represent the removal of three molecules of NO₂. At the temperature range 270-670°C the weight loss is 70.55% represent the removal of two molecules of C₁₈H₁₆N₅.

(b) TG Analysis Of Cobalt Complex



Temperature range °C	Mass loss in %		Assignment
	Experimental	Calculated	
120-180	4.53	4.37	Removal of two molecules of water
200-260	15.98	16.75	Removal of three NO ₂ molecule
280-670	72.98	73.32	Removal of C ₁₈ H ₁₆ N ₅
	5.17	5.56	Leaving of metal residue

The thermogravimetric analysis (TG) curve obtained during the decomposition of Co-complex is shown in the figure. This demonstrate that the decomposition occur at several step. The weight loss(4.37%) curve between a temperature range of 120-180°C represent the elimination of two water molecule. The Weight loss (16.75%) at temperature range 200-260°C represent removal of three molecules of NO₂. At the temperature range 280-670°C the weight loss is 73.32% represent the removal of a molecules of C₁₈H₁₆N₅.

IV. SUMMARY AND CONCLUSION

The Schiff base ligand, N-(3- nitrobenzylidene)-N,N'-dimethyl -4-aminoantipyrine has been synthesized by the condensation of 3-nitrobenzaldehyde and N,N'-dimethyl -4-aminoantipyrine. It is yellow in colour and having 76.3% yield and soluble in chloroform. The spectral data of the ligand concluded that the ligand is bidentate.

The cobalt complex of this ligand is dark red in colour and having 75% yield and soluble in chloroform. The molar conductance value of this complex were found to be 143 Ω⁻¹cm²mol⁻¹. This value indicates that the complex is electrolytic in nature. The magnetic moment value of this complex is 6.02 BM which suggests that the complex has tetrahedral structure. The appearance of new bands at 458.18 cm⁻¹ in the IR spectrum is assigned to Co-N stretching vibration. The spectral data of the ligand concluded that the ligand is bidentate. From TG analysis it is confirmed that two water molecules, three NO₂ and two C₁₈H₁₆N₅ molecules were eliminated at different temperature range.

The zirconium complex of this ligand is yellow in colour and having 79% yield and soluble in chloroform. The molar conductance value of this complex were found to be 138 Ω⁻¹cm²mol⁻¹. the zirconium complex is diamagnetic in nature. The complex has octahedral structure. The appearance of new bands at 458.18 cm⁻¹ in the IR spectrum are assigned to Zr-N and stretching vibrations. From TG analysis it is confirmed that two water molecules, three NO₂ and two C₁₈H₁₆N₅ molecules were eliminated at different temperature range.

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.

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.

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