

Synthesis , Characterization And Powder X-Ray Diffraction Studies Of Cobalt(III) And Vanadium(IV) Complexes With N-(4-Nitrobenzylidene)-N,N'-Dimethyl-4-Amino Antipyrine

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Abstract: The Schiff base ligand N-(4-nitrobenzylidene)-N,N'-Dimethyl-4-aminoantipyrine was prepared by the condensation between 4-nitrobenzaldehyde and 4-aminoantipyrine.. The Co and V 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 cobalt and vanadium complexes were also conducted. From the CHN analysis and IR spectral data the structure of Co complex and V complex are found to be octahedral.

Key Words: Schiff base, aldehyde, amine, XRD.

1. INTRODUCTION:

The field of coordination chemistry is one of the most scholarly and experimentally demanding frontier in modern chemical science. Coordination chemistry is the advancing branch ranging from purely academic synthesis to large scale industrial products. Transition metals have this special property of forming complexes due to high charge to mass ratio and availability of d-orbitals. 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. 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. Coordination compound play a vital role in the field of stereochemistry, isomerism, magnetism, structure and kinetics of reactions⁽¹⁾.

Schiff bases have a melting point from 160-240°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.

2. REVIEW OF LITERATURE:

Sumita Rao *et al*^[2] (1997) have described the subnormal magnetic moments of oxovanadium(IV) Schiff base complexes derived from aroylhydrazones. The results revealed that the tridentate ligand which on reaction with VO²⁺ form stable binuclear oxovanadium(IV) complexes bridging through enolic oxygen and leading to the spin-spin exchange interaction leading to subnormal magnetic moments. The ESR and magnetic susceptibility data of the complexes suggest square-pyramidal geometry around the central metal ion.

Umesh *et al.*^[3] Synthesized and characterized the cationic mononuclear oxovanadium(IV) complexes with tetradentate Schiff base derived from 2,4-dihydroxy-5-acetyl acetophenone and substituted diamines. The electronic spectral data reveals the C_{4v} symmetry to the complex. Cyclic voltammetry assigns quasi-reversibility to the electron transfer step. The FAB mass spectral results suggest the monomeric nature of the complex.

M.R Maurya *et al.* (2003)^[4] reported a comprehensive review of synthesis, reactivity and structural aspects of vanadium through bis(acetylacetonato)oxovanadium (IV). The antimicrobial and cytotoxic properties of oxovanadium(IV) complexes of triazole - derived schiff base were studied and in-vitro antimicrobial evaluation shown that the schiff bases are weaker than their oxovanadium(IV) complexes.

Ramadoss Gomathi et al (2013) ^[5] synthesized two series of Cu(II), Co(II), and Ni(II) complexes with N-benzyl isatin and isonicotinohydrazide schiff base ligand by using modern analytical techniques. All the complexes are soluble in DMF and DMSO. All the complexes adopt octahedral geometry around metal ions. The chemotherapeutic activities of isatin compounds can be achieved by chelation of transition metal ions with these bases and expanding in N-region of these compounds.

N.Raman et al (2007) ^[6] synthesized a new series of transition metal complexes of Cu(II), Ni(II), Co(II), Mn(II), Zn (II), VO(IV), Hg(II) and Cd(II) from the schiff base derived from 4-aminoantipyrine, 3-hydroxy-4-nitrobenzaldehyde and o-phenylenediamine.

K.S. Patel et al (1981) ^[7] synthesized a new series of oxovanadium complexes was synthesized and their $\nu(\text{V}=\text{O})$ stretching frequencies fall in the range 861–994 cm^{-1} and the effective magnetic moments at room temperature of the complexes are found between 1.64 and 1.81 BM. The complexes were green, and their spectroscopic and magnetic properties suggest that they have tetragonal pyramidal structures.

Dr.A.Xavier et al (2014) ^[8] synthesized new schiff base from various aldehydes and amines under magnetic stirrer method. The synthesized Schiff base were characterized by spectral techniques (UV and IR spectra) and the schiff base are yellow colour solid and having sharp melting point and insoluble in organic solvent.

Two reduced schiff base ligands viz, 4-(2-(pyridine-2-yl-methyl)-amino)-ethylimino)-pental-2-one and 4-(2-((pyridine-2-yl-ethyl)amino)-ethylimino)-pental-2-one by the reduction of the corresponding tetradentate unsymmetrical schiff base derived from 1:1:1 condensation of 1, 2-diamino ethane, acetyl acetone and pyridine -2-carboxaldehyde /2-acetyl pyridine have prepared. Four mononuclear complexes of Cu(II), Ni(II) with these two reduced schiff base ligands have been synthesized and structurally characterised by X-ray crystallography (**Biswas et al 2010**) ^[9] and the synthesis of schiff base esters, by two synthetic routes using variably substituted hydroxyl benzaldehydes with para amino phenol in appreciable yields have been reported by **Noureen et al.**

M.Radhakrishna Reddy et al. ^[10] have reported cobalt(II) complexes of Schiffbase ligands derived from benzyl and various diamines.

Z.H. Chohan et al (2010) ^[11] studied antimicrobial and cytotoxic properties of oxovanadium(IV) complexes of triazole-derived Schiff bases were studied and *in-vitro* antimicrobial evaluation shown that the Schiff bases are weaker than their oxovanadium(IV) complexes.

Muhasin Alias. et al (2014) ^[12], derived metal (II) complexes of Cu, Ni and Co with schiff base from potassium 2-N(4-N, N-dimethylamino benzylidene)-4-trithio carbonate 1, 3, 4-thiadiazole(L) were synthesized and characterized by standard physico-chemical procedures. On the basis of these studies 6 coordinated octahedral geometry for all these complexes have been proposed.

Omar B.Ibrahim. et al (2014) ^[13], have been prepared metal chelates $(\text{M}(\text{HL})_2(\text{H}_2\text{O})_2)\text{X}_2$ (where $\text{M}=\text{Mn}(\text{II}), \text{Co}(\text{II}), \text{Cu}(\text{II}), \text{Ni}(\text{II}),$ or $\text{Zn}(\text{II})$) by elemental analysis. Magnetic and spectroscopic measurements (IR, X-ray powder diffraction and scanning electron microscopy). Infrared spectra of the complexes agree with the coordination to the central metal atom through the N of the 2-chlorophenyl hydrazine (-ph-NH-) group and the S atom of the thiophene ring. The electronic spectra suggest a distorted octahedral geometry for all schiff base complexes.

Karema Masoude Abuamer et al (2014) ^[14] derived schiff base from various aldehydes and amine under magnetic stirrer method. The synthesized schiff base were characterized by spectral techniques (UV and IR spectra) and the schiff base are yellow colour and having sharp melting point and insoluble in organic solvents.

Lawrence.C.Nathan et al. ^[15] have reported the X-ray structures of N,N'-polymethylene-bis(salicyldiminato)copper(II). Schiff base complexes with polymethylene backbones ranging from two to eight carbons. The complexes were found to have square planar and distorted tetrahedral structure. In present work, Cu(II) and Ni(II) Schiff base complexes derived from polymethylene hydroxyacetophenone.

Iqbal et al., (2009) ^[16] had chief focus on neutral complexes of Cu(II), Ni(II) and Co(II) with a Schiff base resulting from sulphonamide and benzaldehyde have been prepared and characterized on the basis of UV-Visible, FTIR, atomic absorption spectroscopic data and molar conductance. Against two bacterial species E.coli these metal complexes were screened for their antibacterial activity.

Lashanizadegan et al (2010) ^[17] have synthesized unsymmetrical Schiff base ligands from o-hydroxyacetophenone, o-phenylenediamine and 2-hydroxy-1-naphthaldehyde and their Zn(II), Co(II) and Cu(II) metal complexes.

Naz et al., (2009) ^[18] had discussed on Ni(II), Co(II) and Fe(II) metal complexes of innovative bases resulting from amoxicillin with sugars (D-Glucose and D-Mannose) have been prepared and characterized by electronic absorption, elemental analysis, FTIR and aromatic absorption spectroscopy. Every complexes have superior biological activities than pure amoxicillin.

B.K.Rai et al., (2014) ^[19] synthesized the complexes of Co(II), Ni(II) and Cu(II) with Schiff bases 2-butyl thioquinazoline-4-3H-thiosemicarbazone. The general formula of the complexes are of the type $\{\text{M}(\text{L})_2\text{X}_2\}$, L=2-butyl

thioquinazoline-4-3H-thiosemicarbazone, X=Cl⁻, Br⁻, I⁻ and NO₃⁻.

G.B.Petheet et al(2015)^[20] have been synthesized complexes of Co(II), Ni(II), Zn(II), Cd(II), Zr(IV) and UO₂(VI) with an unsymmetrical tetradentate Schiff base ligand 1-(5-chloro-2-hydroxy phenyl)ethylidene-1-(2-hydroxy-5-methyl phenyl)-ethylidene-carbohydrazide derived from 2-hydroxy-4-methylacetophenone, 2-hydroxy-4-chloroacetophenone and carbohydrazide. All the complexes have been characterized by elemental analysis, UV-Vis and IR spectroscopy, magnetic measurements and thermal analysis. The complexes were found to be quite stable and decomposition of the complexes ended with respective metal oxides as an end product.

C.Karakaya et al(2016)^[21] synthesized the bidentate schiff base ligand 4-chloro-2-(1-(4-phenylphenyl)ethylideneamino) phenol and its mononuclear Co(II), Ni(II), Cu(II) and Zn (II) complexes. Ligand and metal complexes were characterised by elemental analysis, magnetic susceptibility, molar conductivity, ¹H and ¹³C NMR, FT-IR, UV-Vis, inductively coupled plasma optical emission spectroscopy and thermogravimetric studies. The results suggests that the mononuclear complexes have a metal to ligand ratio 1:2 and the metals (II) ions are coordinated with the phenolic oxygen and imine nitrogen atom. Octahedral structures are proposed for the complexes of schiff base ligand.

A total of five new metal complex derivatives of 2N-salicylidene-5-(p-nitrophenyl)-1,3,4-thiadiazole, HL with the metal ions Vo(II), Co(II), Rh(III), Pd(II) and Au(III) have been successfully prepared in alcoholic medium. The complexes obtained are characterized quantitatively and qualitatively by using micro elemental analysis. FTIR Spectroscopy, ¹H and ¹³C NMR, magnetic susceptibility and conductivity measurements, were reported by **Emad Yousif et al.**,(2012)^[22].

Rosu et al.,^[23] synthesized Cu(II) complexes derived from 4-aminoantipyrine and salicylaldehyde which were characterised by NMR, UV-Visible, IR and ESR Spectroscopy. Antimicrobial activity of ligand and complexes were carried out against some bacteria.

Nair and Thomas et al.,^[24] reported oxovanadium complexes derived from 4-aminoantipyrine and p-chlorophenol by diazotisation and coupling which were characterized by spectral techniques. All the complexes were monomeric and neutral with square pyramidal geometry.

The synthesis of oxovanadium(IV) complexes of „ONO“ donor hydrazones derived from 2-imidazolyl mercaptoaceto hydrazide and 2-hydroxy aryl ketones was reported by **Mallur et al.**^[25]. On comparing the biological activity of the ligands, the oxovanadium complexes found to be more active than standard bactericide and fungicide.

Sinha et al.,⁽²⁶⁾ synthesized Pd(II) and Ag (II) complexes derived from 4-aminoantipyrine and imidazole. These complexes were characterized by UV-Visible, IR and NMR spectral studies.

V.K Revankar et al.,^[27] reported Co(II), Ni(II), Cu(II) and Zn (II) complexes derived from 2-hydroxy-3-formylquinoline and isatin with 4-aminoantipyrine and characterized by spectral techniques. All the complexes were found to be monomeric and neutral with octahedral geometry.

Prakash et al ^[28] reported Cr(III), Mn(II), Co(III), Ni(II), Cu(II), Zn(II) and Cd(II) chelates of Schiff's base derived from vanillin and 4-aminoantipyrine. All the complexes are shown to be monomeric and octahedral geometry.

Agarwal et al^[29] synthesized lanthanide(III) complexes derived from 4-aminoantipyrine, 4-methoxybenzaldehyde and thiosemicarbazone. These were characterized by magnetic, spectral and thermal techniques. Agarwal et al⁴⁸ synthesized copper(II) complexes of thiosemicarbazones of Schiff bases derived from 4-aminoantipyrine and some aromatic aldehydes, which were characterized through elemental analysis and molecular weight.

3. MATERIALS AND METHODS:

3.1 : 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.

3.2: INSTRUMENTS

Instruments used in this investigation are given below:

- Shimadzu IR prestige-20 spectrometer
- Shimadzu Corp- 80282 Spectrometer
- Systronics conductivity meter 304
- Gouy type magnetic balance
- Vario-III CHN elemental analyser
- 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.

3.3: METHODS

3.3.1: SYNTHESIS OF N-(4-NITROBENZYLIDENE)-N,N'-DIMETHYL-4- AMINOANTIPYRINE

4-nitrobenzaldehyde (0.151g, 0.001M) dissolved in 20 ml methanol and N,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.

3.3.2: SYNTHESIS OF METAL COMPLEXES

(a) Synthesis of Vanadium complex

Ammonium metavanadate 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 Green complex formed is separated out. It is filtered, washed with methanol and dried in vacuum.

(b) Synthesis of Cobalt complex

Cobalt nitrate has been used as a synthetic intermediate for the preparation of Co(III) 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.

Table 3.3 : physical properties of ligand and complexes.

Compound	Colour	Solubility	Yield(%)
Ligand	Yellow	Chloroform	88%
V complex	Dark Green	Chloroform	83%
Co Complex	Dark Red	Chloroform	75%

3.4: 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 Shimadzu IR prestige -20 spectrometer in the range of 4000-400 cm^{-1} . Potassium bromide disc method was employed for sample preparation.

3.5 : 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 Shimadzu UV-2450 A spectrometer in the range of 200-800 nm.

3.6 : 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 1×10^{-3} M. The molar conductance is measured by the equation,
 $M = 1000 \text{ k/c}$ Where c = concentration of the solution in mol/L
k = conductivity (specific conductance)

3.7 : CHN ANALYSIS

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

3.8 : 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,

$$X_g = (\alpha + \beta F) / W \text{ Where } \alpha = \text{Air Displacement Constant} \\ \beta = \text{Tube Constant}$$

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

3.9 :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. Bragg's law states that,

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

Scherrer 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 Scherrer. It is used in the determination of size of particles of crystals in the form of powder.

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

The Scherrer equation can be written as,

Γ - mean size

K - dimensionless shape factor λ - X-ray wavelength

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

3.10 : ESTIMATION OF VANADIUM

By volumetric process vanadium can be estimated. The Vanadium is first obtained in acid solution as vanadate, reduced to the tetravalent state by one of several reducing agents which are available. The solution is then titrated in the presence of sulphuric acid with potassium permanganate solution, which quantitatively oxidises the lower Vanadium salt to Vanadate. Diphenylamine sulfonic acid is used as indicator. Using sulphur dioxide to effect the reduction, the following reaction takes place.

By boiling the reduced solution in an atmosphere of CO₂ excess of sulphur dioxide can be removed before the titration. The titration is completed when a pink end point stable at least for one minute.

3.11 : ESTIMATION OF COBALT

Cobalt(II) was estimated by gravimetric method after the decomposition of the of the complex with concentrated nitric acid. The resulting solution was made up to 100mL. 20mL of the solution was pipetted out into a beaker. Added with constant stirring 4.8mL of mercury (II) chloride solution followed by 5.2mL of ammonium thiocyanate reagent. Scratching the sides of the beakers with stirring rod was avoided. A dark blue precipitate formed after stirring for 1-3minutes, stirring was continued for further 2-3minutes and allowed to stand for 2 hours at room temperature collected the precipitate in a weighed sintered glass or porcelain filtering crucible, used the filtrate to arrest the transfer of any residual precipitate in the beaker. Washed the precipitate with 2-3mL of a dilute solution of the precipitating agent and finally with 5 mL of ice cold water. Dried at 100 °C and weighed as Co(Hg(SCN)₄).

4. RESULT AND DISCUSSION:

Schiff base derived from 4-nitrobenzaldehyde and N,N'-dimethyl-4-aminoantipyrene has been examined as ligand for Cobalt in +3 oxidation state and vanadium in +4 oxidation state.

4.1 : GENERAL PROPERTIES

N-(4-nitrobenzylidene)-N,N'-dimethyl-4-aminoantipyrene ligand is a yellow coloured compound. The V(IV) and Co(III) complexes are dark green and dark red 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



Vanadium complex



Cobalt complex

4.2: 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. The gravimetric analysis of cobalt complex and volumetric analysis of

Vanadium complex are found to be successful and from these, the metal content in the complexes are determined.

4.3 : MOLAR CONDUCTANCE

Molar conductance of 10⁻³ M solutions of the metal complexes at 25^oC were measured in DMF and N,N'-dimethyl formamide. The molar conductance values of V(IV) and Co(III) complexes under investigation are found to be 145 Ω⁻¹cm²mol⁻¹ and 169 Ω⁻¹cm²mol⁻¹ respectively. The molar conductance value shows that the Co(III) and V(IV) complex was electrolytic in nature. Because there is no charged species in the complex to neutralize the charge of the central metal ion.

4.4 : 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) and V(IV) complexes are paramagnetic in nature.

The magnetic moment values of Co(III) and V(IV) complexes are found to be 5.98 BM and

2.04 BM. From this, it is clear that both Co(III) complex and V(IV) complex has octahedral structure

Complex	Colour	Yield(%)	Molecular Weight	Magnetic Moment	Molar conductance (Ω ⁻¹ cm ² mol ⁻¹)
V complex	Dark green	83%	813.7815	2.04	5.36
Co complex	Dark red	75%	823.773	5.98	74

Table 4.4(a)

4.5 : 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 density and thereby the structure of the ligand and complex can be confirmed.

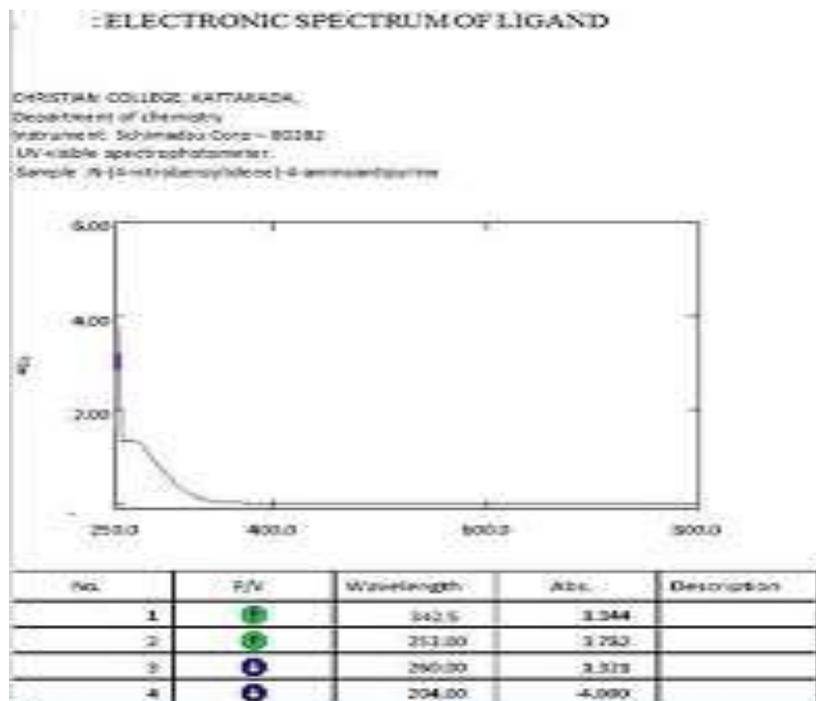
COMPLEX	C%		H%		N%	
	experimental	calculated	experimental	calculated	experimental	calculated
Co complex	53.64%	52.44%	3.75%	4.37%	10.30%	13.59%
V complex	54.63%	52.82%	6.68%	4.17%	15.92%	13.76%

Table : 4.5 (a)

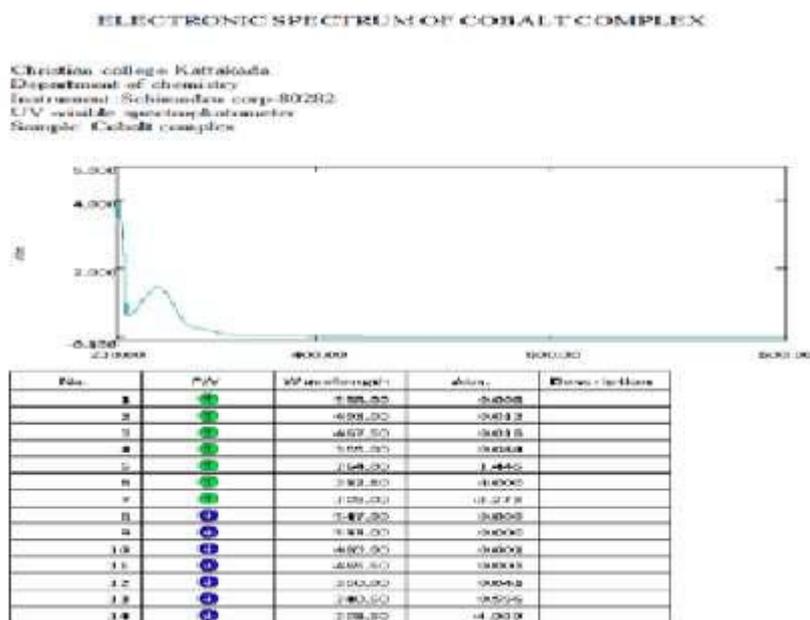
Here, the CHN analysis values are in good agreement with the calculated percentage of carbon, hydrogen and nitrogen in the complex. So by using CHN analysis, it is easy to confirm that the ligand is bidentate. The structures of the complexes can also be confirmed from CHN analysis value. The structure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

4.6 : 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 chloroform.

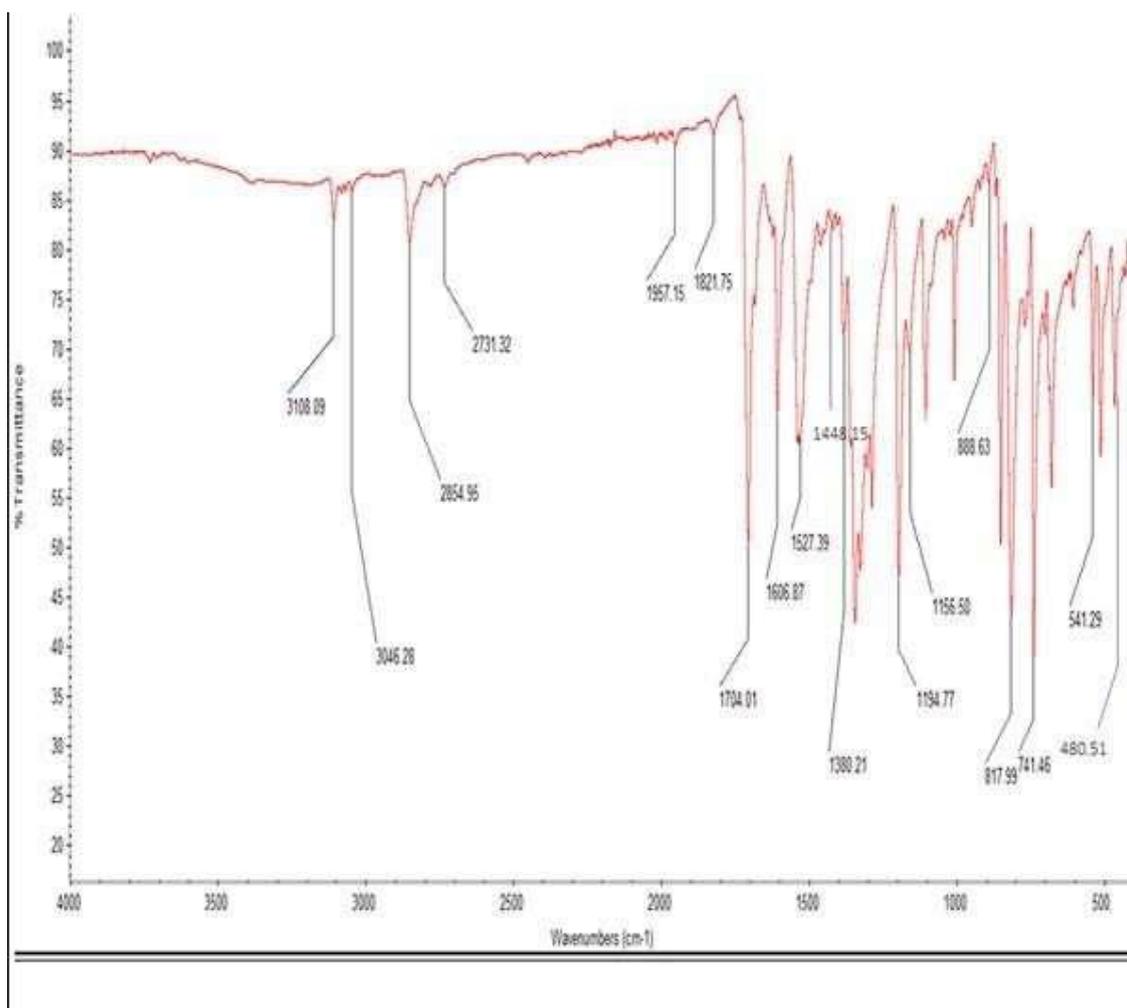


ultraviolet spectra of the ligand recorded in chloroform showed strong bands around 260 nm and at 342.5 nm region which confirms the presence of benzenoid and azomethine linkages, which are characteristic of $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ respectively.



ultraviolet spectra of the cobalt complex recorded in chloroform showed strong bands around 264 nm and at 350 nm region which confirms the presence of benzenoid and azomethine linkages, which are characteristic of $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ respectively.

(b) IR SPECTRUM OF COBALT COMPLEX

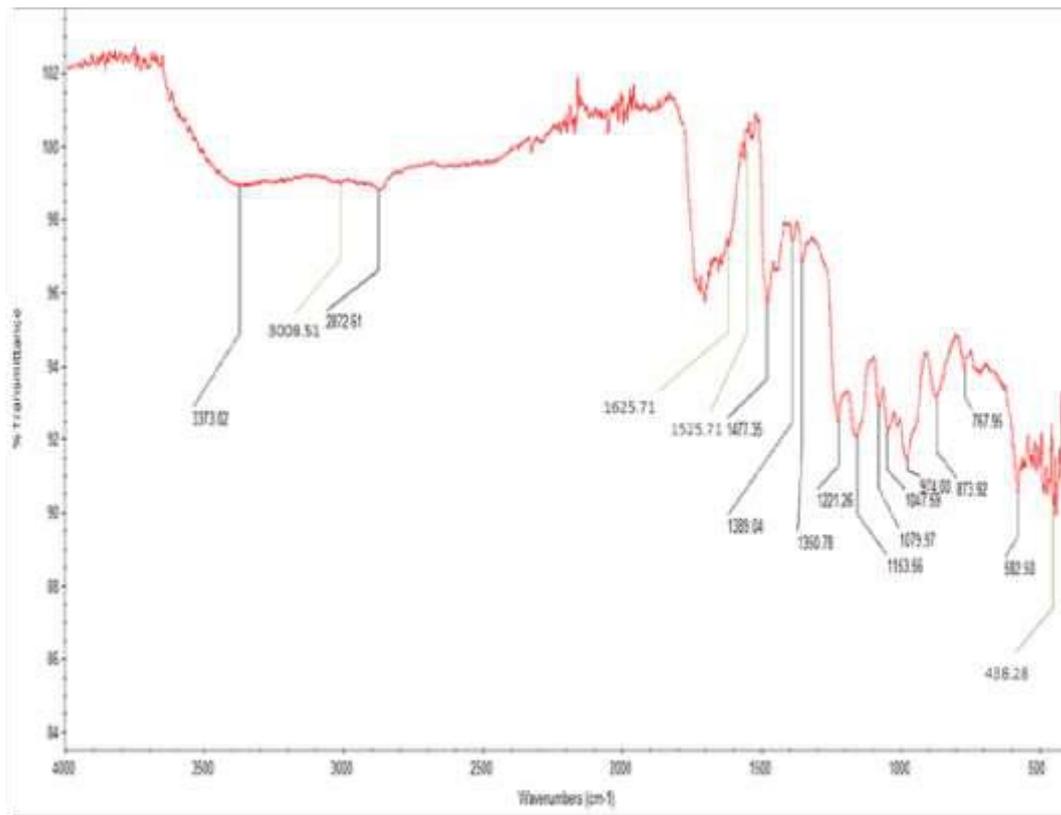


Ligand	Co Complex	Assignment
-	3108.09	Coordinated water molecule
3022.45	3046.28	=CH
1631.78	1606.87	C=N
1537.27	1527.39	C=C
1431.18	1448.15	N=O (Sym. Bending) N=O (asym. Bending)
1315.45	1380.21	
754.17	741.46	Monosubstituted
-	480.51	Co-N
-	541.29	Co-O

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 higher frequency of 3046.28 cm^{-1} . The peak at 1631.78 cm^{-1} corresponds to the C=N band of ligand. It is shifted to a lower frequency range 1606.87 cm^{-1} . This peak indicates the presence of coordination. The peak at 3108.09 cm^{-1} in cobalt complex represents the coordinated water molecule. The bands at 1448.15 cm^{-1} and 1380.21 cm^{-1} corresponds to the symmetric and asymmetric bending of N=O group. In cobalt complex there is a strong band at 480.51 cm^{-1} which represents the Co-N, it confirms the coordination. The presence of Co-O bond is confirmed by 541.29 cm^{-1} .

(c) IR SPECTRUM OF VANADIUM COMPLEX



Ligand	V Complex	Assignment
-	3373.02	Coordinated water molecule
3022.45	3008.51	=CH
1631.78	1625.28	C=N
1537.27	1525.71	C=C
1431.18	1477.35	N=O(sym.bending) N=O
1315.45	1350.78	(asym.bending)
754.17	767.95	monosubstituted
-	438.28	V-N
-	873.92	V=O V-O
-	582.50	

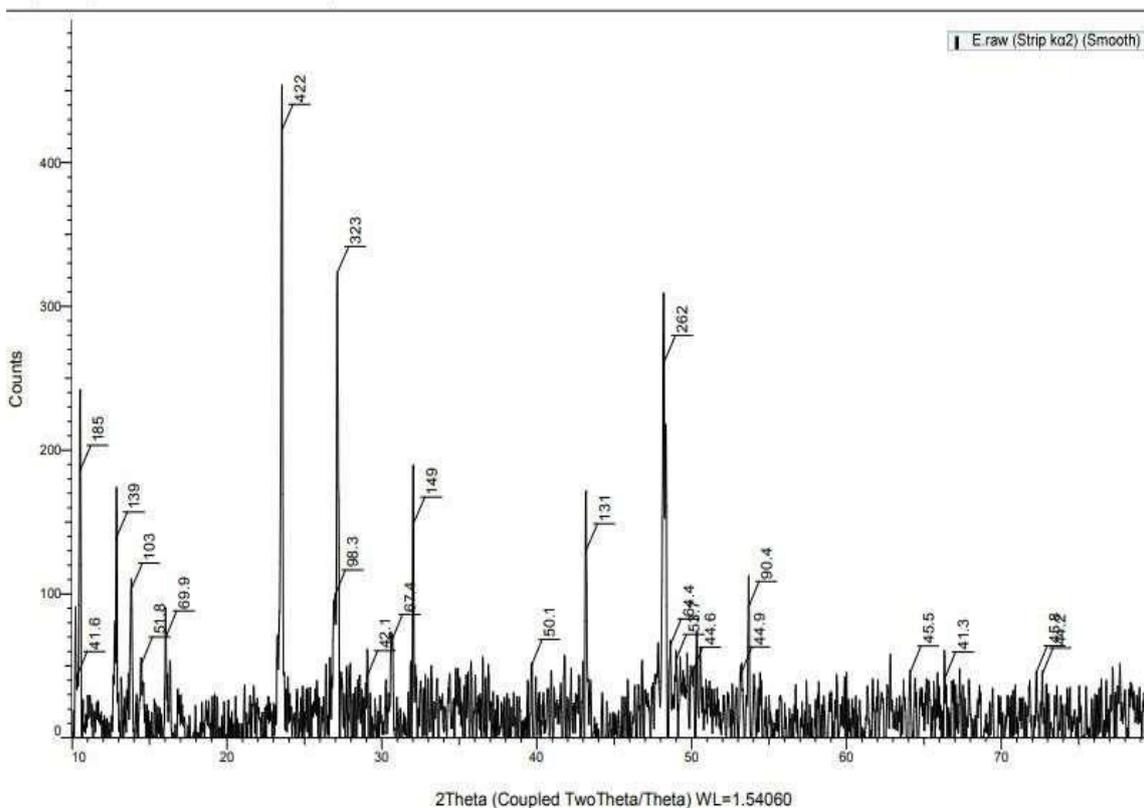
Table 4.7(b)

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 3008.51 cm⁻¹ in the complex. The intense band at 1631.78cm⁻¹ corresponds to ν (C=N) of the ligand. It is shifted to a lower frequency of 1625.28 cm⁻¹ which indicates the presence of coordination. The symmetric and asymmetric bending of N=O group in complex is represented by 1477.35cm⁻¹ and 1350.78cm⁻¹ respectively. V-O and V=O bands are observed at 582.50cm⁻¹ and 873.92cm⁻¹. The coordination of V-N is confirmed by the intense peak at 438.28cm⁻¹.

4.8: POWDER X-RAY DIFFRACTION STUDIES

4.8.1 : XRD OF COBALT COMPLEX

E (Coupled TwoTheta/Theta)



2θ observed	2θ calculated	d _{observed}	d _{calculated}	d _{scherrer}	Plane
10.287	10.29	8.59	8.589	8.824	100
12.843	12.99	6.88	6.809	6.10	001
16.069	16.33	5.51	5.42	5.13	110
23.531	23.73	3.77	3.746	3.50	101
27.133	27.09	3.28	3.29	4.02	020
30.646	30.79	2.91	2.90	3.6	120
32.055	32.13	2.78	2.783	2.05	111
43.207	43.2	2.09	2.092	1.71	211
48.234	48.24	1.88	1.88	1.76	031
53.22	53.6	1.71	1.708	1.87	230

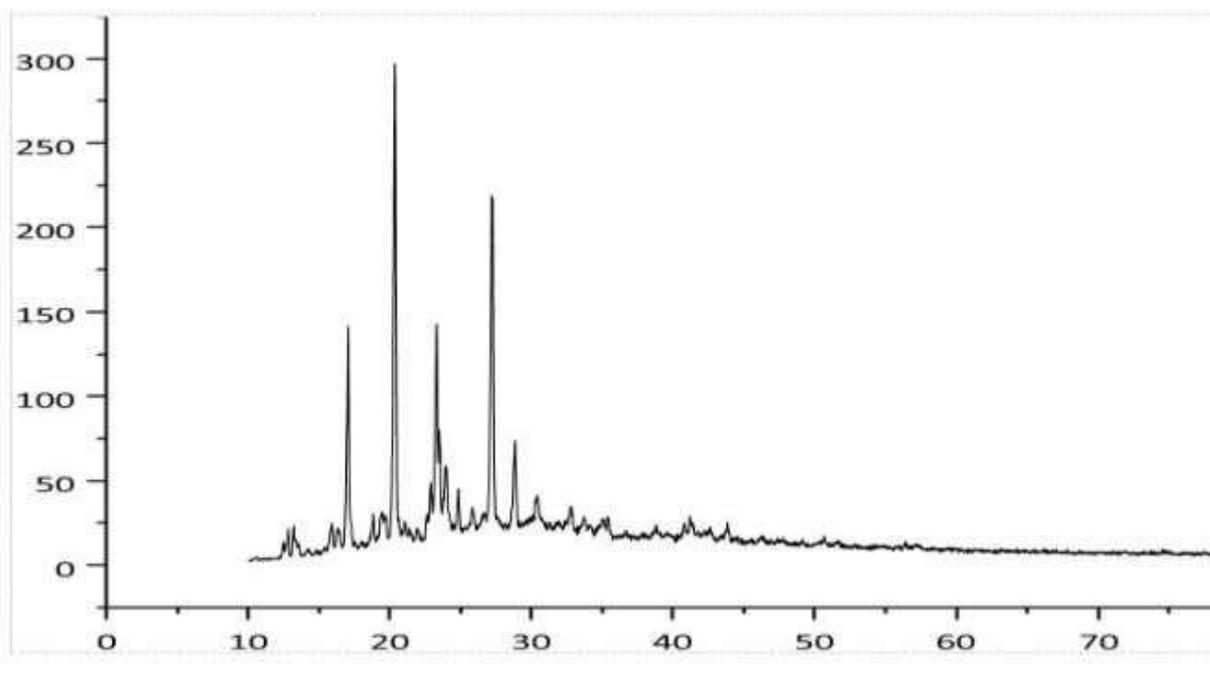
The sharp crystalline peaks of the cobalt complex are attributed to the orthorhombic structure. The XRD peaks at $2\theta = 10.287, 12.843, 16.069, 23.531, 27.133, 30.646, 32.055, 43.207, 48.234$ and 53.22 degrees can be assigned for X-ray scattering from (100), (001), (110), (101), (020), (120), (111), (211), (031) and (230) planes.

The obtained value is in good agreement with the data of orthorhombic cobalt phase (JCPDS No : 09-234). The intense peak at $2\theta = 23.531^\circ$ corresponds to the plane (101) which is the characteristic of orthorhombic phase.

The average value of crystal lattice parameter was about 3.544 \AA . The crystallite size was calculated by Scherrer equation

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

3.8.2 : XRD OF VANADIUM COMPLEX

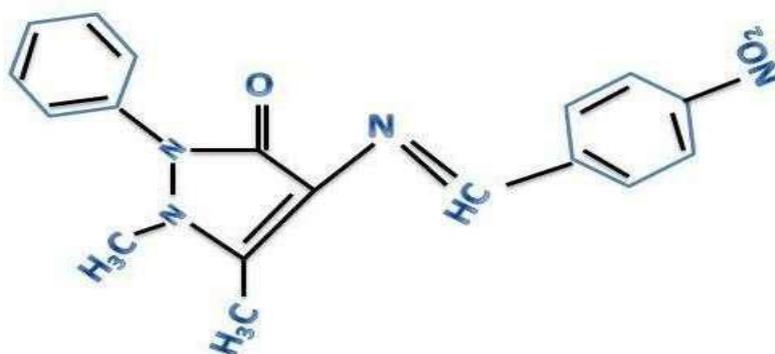


θ observed	θ calculated	d_{observed}	$d_{\text{calculated}}$	d_{scherrer}	Plane
16.959	17.1562	5.223	5.1623	5.1219	131
20.377	20.2155	4.354	4.3875	4.47	102
23.205	23.2748	3.830	3.8172	4.04	060
27.3975	27.0540	3.253	3.2900	2.29	311
28.7201	28.9336	3.10	3.0822	3.26	171

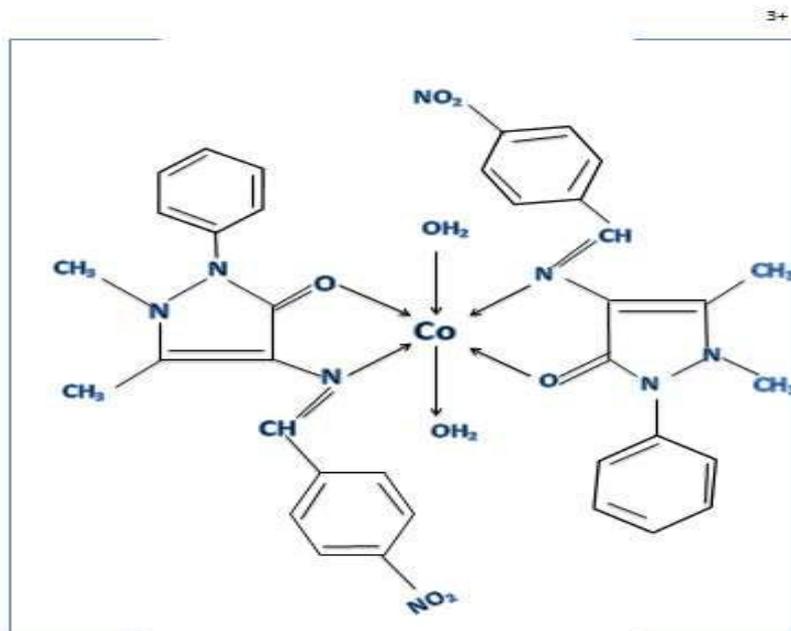
The sharp crystalline peaks of the vanadium complex are attributed to the monoclinic structure. The XRD peaks at $2\theta = 16.959, 20.377, 23.205, 27.3975$ and 28.7201 degrees can be assigned for X-ray scattering from (131), (102), (060), (311) and (171) planes. The obtained value is in good agreement with the data of monoclinic vanadium phase (JCPDS No : 49-2497). The intense peak at $2\theta = 20.377^\circ$ corresponds to the plane (102) which is the characteristic of monoclinic phase.

The average value of crystal lattice parameter a was about 8.739 \AA . The crystallite size was calculated by Scherrer equation

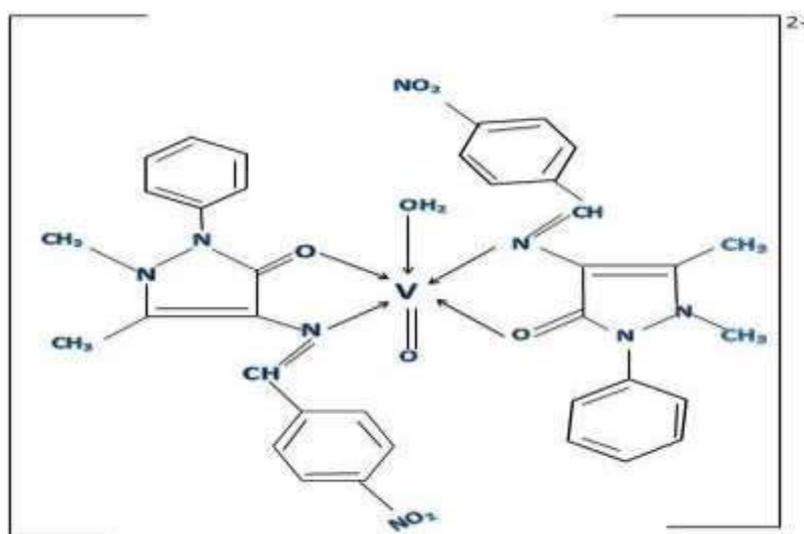
$$\tau = \frac{K\lambda}{\beta \cos \theta}$$



STRUCTURE OF LIGAND



STRUCTURE OF COBALT COMPLEX



STRUCTURE OF VANADIUM COMPLEX

5. 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 88% yield and is obtained as yellow coloured form which is soluble in chloroform. The ligand is bidentate, it is confirmed by spectral data.

The cobalt complex of this ligand is obtained as dark red crystal form. It is about 75% yield and is soluble in chloroform. Molar conductance value of this schiff base complex is found to be $169 \Omega^{-1}\text{cm}^2\text{mol}^{-1}$. This indicates its electrolytic nature. The IR spectra shows two bands at 480.51 cm^{-1} and 541.29 cm^{-1} corresponding to Co-N and Co-O bonds. Thus in this complex ligand is bidentate. Magnetic moment value of complex is 5.98 B.M. The X-ray diffraction studies of cobalt complex showed that it is orthorhombic.

The oxovanadium complex of this ligand is dark green crystals having 83% yield and is soluble in chloroform. Molar conductance is obtained as $145 \Omega^{-1}\text{cm}^2\text{mol}^{-1}$. It is also slightly electrolytic in nature. Magnetic moment is found to be 2.04 B.M. IR spectra of complex shows peaks at 438.28 cm^{-1} and 582.50 cm^{-1} corresponding to V-N and V-O. It also shows the presence of a bidentate ligand. X-ray diffraction studies of vanadium 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, Cobalt and vanadium complexes shows 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 $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transition respectively.

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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