

# **SYNTHESIS, CHARACTERISATION AND ANTIMICROBIAL STUDIES OF VANADIUM (IV) AND COPPER (II) COMPLEXES WITH N- (3-NITROBENZYLIDENE)-p- PHENYLENEDIAMINE**

**<sup>1</sup> Muhsina Rasheed, <sup>2</sup> V.S.Vimal Nayan, <sup>3</sup> Aswathy Sudhakar.S**

<sup>1</sup> PG Student, <sup>2</sup> Guest Lecturer, <sup>3</sup> PG Student

Department of Chemistry Christian College, Kattakada, Kerala, India – 695572

Received: February 21, 2019

Accepted: March 28, 2019

**ABSTRACT:** : The Schiff base ligand (3-nitrobenzylidene)-p-phenylenediamine was prepared by the condensation between 3-nitrobenzaldehyde and p-phenylenediamine dihydrochloride. The Copper and Vanadium complexes of the corresponding ligand were prepared and was characterized by different methods like IR and UV spectra. The biological activity of the complexes were studied by conducting antibacterial and antifungal studies. The Copper and Vanadium complexes shows antibacterial and antifungal activities at different concentrations. Magnatic study and IR spectral data confirms that the structure of both Copper and Vanadium complex is octahedral in nature.

**Key Words:** Schiff base, 3-nitrobenzaldehyde, p-phenylenediamine, antibacterial antifungal.

## INTRODUCTION

Coordination compounds are of great practical importance. Coordination chemistry is one of the most rapidly advancing branches holds great promise for future by embracing areas ranging from purely academic synthesis to large scale industrial products. Many of the biological compounds are coordination complexes.

Most widely accepted version of the theory today was published by Alfred Werner. Werner was able to discover the spatial arrangements of the ligands that were involved in the formation of the complex hexacoordinate cobalt. His theory allows one to understand the difference between a coordinated ligand and a charge balancing ion in a compound, for example the chloride ion in the cobaltamine chlorides and to explain many of the previously inexplicable isomers.

Transition metal complexes often have spectacular colours caused by electronic transitions by the absorption of light. For this reason, they are often applied as pigments. Most transitions that are related to coloured metal complexes are either d-d transitions or charge transfer bands. Most of the coordination compounds originally studied were purely inorganic in nature. Schiff bases forms an interesting class of compounds which found interesting application in medicinal, pharmaceutical, dye and plastic industries as well as liquid crystal technology and mechanistic investigation. Metal complexes with Schiff based as ligands have been amongst the most widely studies coordination compounds. Schiff bases are first reported by Hugo Schiff, various studies have shown that the presence of a lone pair of electron on trigonally hybridized nitrogen atom of C=N group is of fundamental chemical and biological importance.

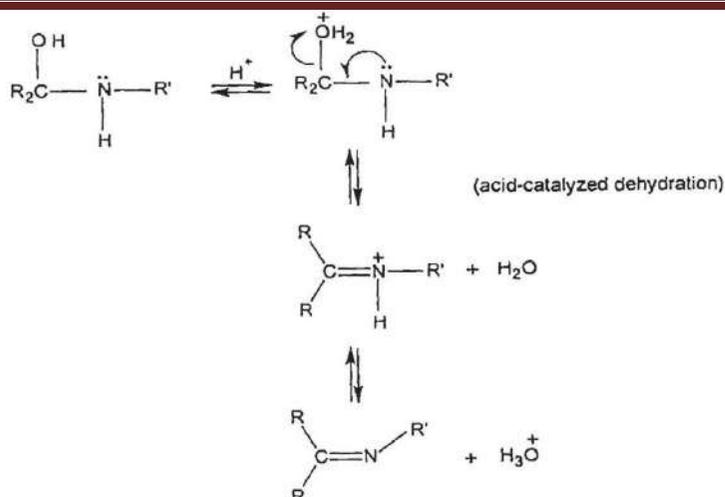
### 1.1 CHEMISTRY OF SCHIFFS BASES

Schiff base are condensation products of primary amines with carbonyl compounds, and they were first reported by Hugo Schiff in 1864. These compounds are named after him and contain a carbon nitrogen double bond with nitrogen atom connected to an aryl or alkyl group. These compounds are variously referred to as imines, azomethines, or anils. Schiff bases of aromatic aldehydes, having an effective conjugation system, are more stable while aliphatic aldehydes are relatively unstable and are readily polymerize.

Formation of Schiff base from aldehyde and ketone is,



$R_1R_2C=NR_3$  is called a Schiff base, where  $R_1$  is an aryl group,  $R_2$  is a hydrogen atom and  $R_3$  is either an alkyl or aryl group. However, usually compounds where  $R_3$  is an alkyl or aromatic group are also regarded as Schiff bases. Schiff bases that contain aryl substituents readily synthesized.



## 1.2 GENERAL INFORMATION ABOUT SCHIFF BASES

Schiff bases were the first to condensed carbonyl compounds with amines and these condensed products were referred to as Schiff bases. IR spectra of Schiff's bases normally shows  $>C=N$  stretching frequency between  $1562 - 1650 \text{ cm}^{-1}$  and shift of this band towards a lower frequency in all Schiff base metal complexes suggest that, the coordination through nitrogen of azomethane group might have taken place.

## 1.3 COORDINATION CHEMISTRY OF 3d METAL IONS

Transition metal ions form many stable complexes because they have vacant 'd' orbitals, which can accommodate the electron pairs of ligands. The spectral and magnetic properties of the complexes are useful to study the stereochemistry of these compounds.

### ❖ COPPER

The most common and stable oxidation state of copper is Cu (II). The cupric ion  $\text{Cu}^{2+}$  has the electronic configuration  $d^9$  and has an unpaired electron thus being paramagnetic in nature. Its complexes are typically coloured due to d-d spectra. Copper (II) is a typical transition metal ion in forming coordination complexes but less typical in its reluctance to take up a regular tetrahedral or octahedral geometry.

The catalytic role of the copper site can sometimes be effectively studied in vitro. For example, copper amino acid complexes can behave as superoxide dismutase's. In medicine, ligands specifically designed to complex and remove copper in Wilson's disease, a condition involving the accumulation of excess copper, have been synthesized and the discovery that copper aspirinate is a more effective and less ulcerogenic anti-inflammatory agent has led to the reinvestigation and extension of the chemistry of complexes of this type.

### ❖ OXOVANADIUM

Vanadium can exist in eight oxidation states ranging from  $-3$  to  $+5$ , but with the exception of  $-2$ . Only the three highest oxidation states,  $+3$ ,  $+4$  and  $+5$  are important in biological systems. Under ordinary conditions, the  $+4$  and  $+5$  oxidation states are the most stable ones. The majority of vanadium (IV) compounds contain the  $\text{VO}^{2+}$  unit (vanadyl ion). These complexes typically have square planar pyramidal or bipyramidal geometries with an axial oxo ligand.

## 1.4 USES OF SCHIFF BASES

Schiff bases are tremendously used in different fields such as agriculture, industries, pharmaceuticals, medicine and so on. Schiff bases are extremely useful in analytical methods, such as condensation reaction of amines and aldehyde or ketones compounds in which the azomethine linkage is formed. Used in complex formation reactions or development in the change of its spectroscopic purpose of changes in pH of the solution or solvent (pH of solvent polarity indicators). However, mainly of Schiff base compounds are chemically unbalanced and shows a tendency to take part in different chemical equilibrium, like 'tautomeric' inter conversions, hydrolysis or formation of ionized class. Consequently, victorious relevance's of Schiff bases requires a vigilant study of its characteristics properties. Fluorescent indicators have different types of functions and are generally employed in all cases, where colorimetric indicators have difficult to examine or required sensitivity.

Metals play a key role in the biological and biological medicinal practices. It is clearly indicating

that, the number of organic molecules were used in medicine, but they do not have in the form of organic approach of accomplishment with some are activated or bio-transformed by metal ions metabolism.

### 1.5 APPLICATION OF SCHIFF'S BASES

Schiff base complexes of various transition metals have been investigated due to their coordinating capability and their applications in various fields. Schiff base complexes have proven effective in constructing supramolecular architectures such as coordination polymers and helical assemblies. They have been found to be associated with biological activities such as antibacterial, antiviral, and antimalarial action. The Schiff base complexes also exhibit catalytic activity and act as homogeneous and heterogeneous catalysts in various reactions. The Schiff base complexes can also serve as efficient models for the metal containing sites in metalloproteins and enzymes. There are Schiff base complexes, which show interesting photochromic properties and magnetic properties.

- 1.8.1 Catalytic Activity
- 1.8.2 Anti Oxidant Action
- 1.8.3 Antimicrobial Activities
- 1.8.4 Anti-Fungal And Anti- Viral Activity
- 1.8.5 Polymers And Dyes
- 1.8.6 Anti- Fertility And Enzymatic Action
- 1.8.7 Applications In Modern Technologies
- 1.8.8 Application In Synthesis And Chemical Analysis

## 2. MATERIALS AND METHODS

### 2.1: MATERIALS

All reagents used for the synthesis of ligand and complexes are of commercial grade and they are directly used without further purification. 3-nitrobenzaldehyde is used as aldehyde and phenylenediamine dihydrochloride 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

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.

### 2.3: METHODS

#### 2.3.1: SYNTHESIS OF (3-NITROBENZYLIDENE)-PHENYLENEDIAMINE

3-nitrobenzaldehyde (0.151g, 0.001M) dissolved in 20 ml methanol and p-phenylenediamine dihydrochloride in 20 ml methanol was mixed well. The resulting mixture was refluxed for about four hours. On cooling, brown crystals were separated from the solution. These crystals were filtered and dried.

#### 2.3.2: SYNTHESIS OF METAL COMPLEXES

##### (a) Synthesis of Copper complex

Copper Chloride has been used as a synthetic intermediate for the preparation of Cu(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 complex formed is separated out. It is filtered, washed with methanol and dried in vacuum.

##### (b) 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 (0.0001M) 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 dark brown complex formed is separated out. It is filtered, washed with methanol and dried in vacuum.

Compound	Colour	Solubility	Yield (%)
Ligand	Brown	DMSO	80.2%

<b>Complex 1</b>	<b>Dark Brown</b>	<b>DMSO</b>	<b>72%</b>
<b>Complex 2</b>	<b>Dark Brown</b>	<b>DMSO</b>	<b>78%</b>

Table 2.3 : physical properties of ligand and complexes.

## 2.4: 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  $\text{cm}^{-1}$ . Potassium bromide disc method was employed for sample preparation.

## 2.5: ELECTRONIC ABSORPTION SPECTROSCOPY

Electronic absorption spectroscopy is used to study the stereochemistry 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 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  $\text{cm}^{-1}$ . The concentration of the solution was around  $1 \times 10^{-3}$  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: 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  $\alpha$  = Air Displacement Constant

$\beta$  = Tube Constant

F = change in weight in milligram

W = weight of sample in gram

The effective magnetic moment  $\mu_{\text{eff}}$  was calculated using the formula,

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

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

## 2.8: ESTIMATION OF COPPER

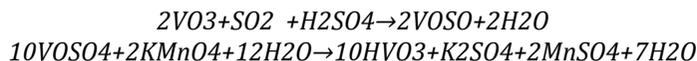
$\text{Cu}^{2+}$  is reduced to  $\text{Cu}^+$  by sulphurous acid which combines with SCN to give a white precipitate of CuCNS.



The given solution is made up to 10 ml and 5 ml of the made up solution pipetted out into 100 ml beaker. About 1 ml of dil.  $\text{H}_2\text{SO}_4$  added followed by 3-5 freshly prepared sulphurous acid solution. The solution is diluted to 50 ml and heated to boiling. About 5 ml of freshly prepared 10% ammonium thiocyanate is added slowly and with constant stirring. The precipitate of CuCNS should be white and the mother liquor should be colourless and must smell strongly of sulphur dioxide. The precipitate is allowed to stand for several hours, preferably overnight. The solution is filtered through a previously weighed sintered glass crucible by adding to every 100 ml of water 1ml of 10%  $\text{NH}_4\text{CNS}$  and 5-6 drops of saturated sulphurous acid solution. The residue is finally washed with 20% alcohol to remove ammonium thiocyanate. The precipitate is then dried at  $110^\circ - 120^\circ\text{C}$  for 1 hour and weighed as CuCNS. Heating, cooling and weighing are repeated till constant weight is obtained. A duplicate experiment is conducted.

**2.9: ESTIMATION OF VANADIUM**

The most convenient method for the estimation of Vanadium is a volumetric process. 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 oxidizes the lower Vanadium salt to Vanadate. Diphenylamine sulfonic acid is used as indicator. Using sulfur dioxide to effect the reduction, the following reaction take place.



Excess of sulphur dioxide is removed before the titration by boiling the reduced solution in an atmosphere of CO<sub>2</sub>. The titration is completed when a pink end point stable at least for one minute.

**2.10: ANTIBACTERIAL ACTIVITY****AGAR- WELL DIFFUSION METHOD****PRINCIPLE**

The antimicrobials present in the samples are allowed to diffuse out into the medium and interact in a plate freshly seeded with the test organisms. The resulting zones of inhibition will be uniformly circular as there will be a confluent lawn of growth. The diameter of zone of inhibition can be measured in **millimeters**.

**PROCEDURE**

Petriplates containing 20ml Muller Hinton Agar Medium were seeded with bacterial culture of *E.coli*, *Pseudomonas aeruginosa*, *Streptococcus mutans* and *Staphylococcus aureus* (growth of culture adjusted according to McFards Standard, 0.5%). Wells of approximately 10mm was bored using a well cutter and different concentrations of sample such as 250µg/mL, 500µg/mL and 1000µg/mL were added. The plates were then incubated at 37°C for 24 hours. The antibacterial activity was assayed by measuring the diameter of the inhibition zone formed around the well (NCCLS, 1993). Streptomycin was used as a positive control.

**Reference: National Committee for Clinical Laboratory Standards. (1993a). Performance Standards for Antimicrobial Disk Susceptibility Tests—Fifth Edition: Approved Standard M2-A5. NCCLS, Villanova, PA.**

**2.11: ANTIFUNGAL ACTIVITY****AGAR- WELL DIFFUSION METHOD****PRINCIPLE**

In order to access the biological significance and ability of the sample, the antifungal activity was determined by Agar well diffusion method. The antifungals present in the samples are allowed to diffuse out into the medium and interact in a plate freshly seeded with the test organisms. The resulting zones of inhibition will be uniformly circular as there will be a confluent lawn of growth. The diameter of zone of inhibition can be measured in **millimeters**.

**PROCEDURE**

Potato Dextrose agar plates were prepared and overnight grown species of fungus, *Aspergillus niger* and *Candida albicans* were swabbed. Wells of approximately 10mm was bored using a well cutter and samples of different concentrations such as 250µg/mL, 500µg/mL and 1000µg/mL were added. The zone of inhibition was measured after overnight incubation at room temperature and compared with that of standard antimycotic (Clotrimazole). (NCCLS, 1993).

**3. RESULT AND DISCUSSION**

Schiffbase derived from 3-nitrobenzaldehyde and phenylenediamine has been examined as ligand for Copper in +2 oxidation state and Vanadium in +4 oxidation state.

**3.1: GENERAL PROPERTIES**

Both V(IV) and Cu(II) complexes are dark brown 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 methanol, ethanol, Dimethyl Sulphoxide.



Ligand



Copper complex



Vanadium complex

### 3.2: 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 Copper complex and volumetric analysis of Vanadium complex are found to be successful and from these, the metal content in the complexes are determined. Micro analysis of carbon, hydrogen and nitrogen could not be done due to lack of facilities.

### 3.3: 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 Cu(II) and V(IV) under investigation are found to be  $623 \Omega^{-1}\text{cm}^2\text{mol}^{-1}$  and  $141 \Omega^{-1}\text{cm}^2\text{mol}^{-1}$  respectively. The molar conductance value shows that both Cu(II) and V(IV) complex are electrolytic in nature.

Complex	Colour	Yield (%)	Molecular weight	Magnetic moment (BM)	Molar conductance ( $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ )
Cu(II) complex	Dark brown	72%	798.9262	1.8	623
V(IV) complex	Dark brown	78%	453.1315	1.7533	141

Table 3.3(a)

**3.4: MAGNETIC MEASUREMENTS**

Magnetic susceptibility of the complexes were determined using Magway MSB Mk1 magnetic susceptibility balance. The measurements were made at room temperature. Table 5.3(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 Cu(II) and V(IV) complexes are paramagnetic in nature.

The magnetic moment values of Cu(II) and V(IV) complexes are found to be 1.8 BM and 1.7533 BM. From this, it is clear that both Cu(II) and V(IV) complex have octahedral structure.

**3.5 : 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.

COMPLEX	C%		H%		N%	
	experimental	calculated	experimental	calculated	experimental	calculated
Cu complex	38.76%	39.08%	4.53%	3.28%	10.35%	10.51%
V complex	36.68%	34.45%	3.69%	4.23%	7.5%	9.27%

Table 5.5 (a)

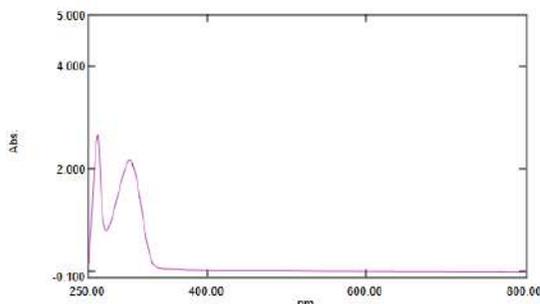
Here, the CHN analysis values are in good agreement with the calculated percentage of carbon, hydrogen and nitrogen in the complex. So by using CHN analysis, it is easy to confirm that the ligand is monodentate. The structures of the complexes can also be confirmed from CHN analysis value. The structure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

**3.5: 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 and methanol.

**ELECTRONIC SPECTRUM OF LIGAND**

DST FIST UV-Vis spectrophotometer Department of Chemistry  
 Sample: 3 nitro ligand  
 5.10.2018



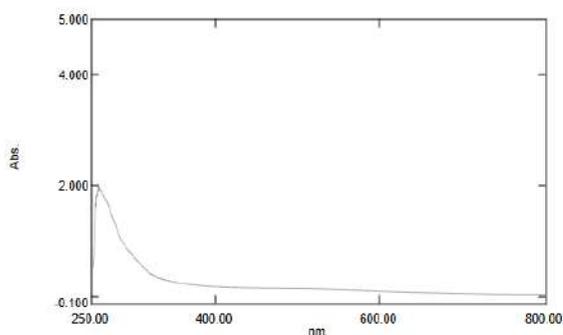
No.	P/V	Wavelength	Abs.	Description
1	●	302.50	2.768	
2	●	262.50	2.648	
3	●	273.00	0.802	
4	●	224.00	-4.000	

Ultraviolet spectra of the ligands recorded in DMSO showed strong bands around 262nm and at 302 nm region, which can be assigned to  $\Pi \rightarrow \Pi^*$  and  $n \rightarrow \Pi^*$  transition respectively.

## ELECTRONIC SPECTRUM OF COMPLEXES

### 3.5 (a) ELECTRONIC SPECTRUM OF COPPER COMPLEX

DST FIST UV/Vis  
spectrophotometer Department of  
Chemistry  
Sample: copper  
5.10.2018

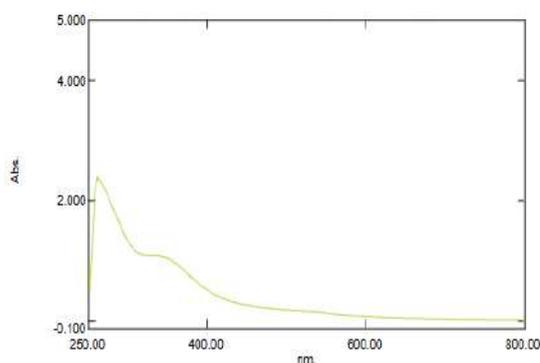


No.	P/V	Wavelength	Abs.	Description
1	①	258.00	2.006	
2	②	217.00	3.091	
3	③	237.00	0.271	
4	④	207.00	-0.311	

Ultraviolet spectra of the Copper complex recorded in DMSO showed strong bands around 237 nm and at 258 nm region which confirms the presence of benzenoid and azomethine linkages, which are characteristic of  $\Pi \rightarrow \Pi^*$  and  $n \rightarrow \Pi^*$  transition respectively.

### 3.5 (b) ELECTRONIC SPECTRUM OF VANADIUM COMPLEX

DST FIST UV/Vis  
spectrophotometer Department of  
Chemistry  
Sample: 3 nitro vanadium  
5.10.2018



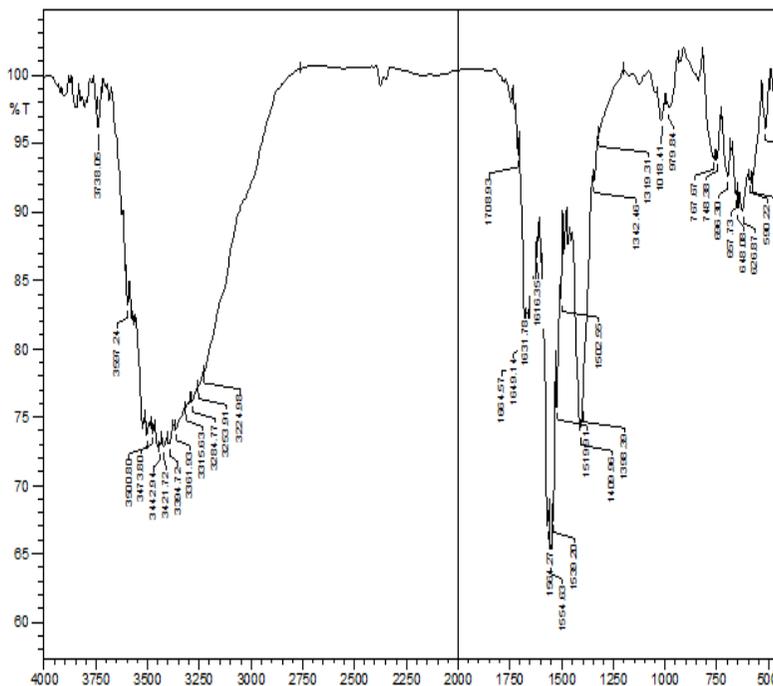
No.	P/V	Wavelength	Abs.	Descriptive
1	①	338.00	1.068	
2	②	281.50	2.362	
3	③	225.50	1.291	
4	④	330.00	1.063	
5	⑤	229.00	-0.707	
6	⑥	224.00	-4.000	

Ultraviolet spectra of the Vanadium complex recorded in DMSO showed strong bands around 261.50 nm and at 330 nm region which confirms the presence of benzenoid and azomethine linkages, which are characteristic of  $\Pi \rightarrow \Pi^*$  and  $n \rightarrow \Pi^*$  transition respectively.

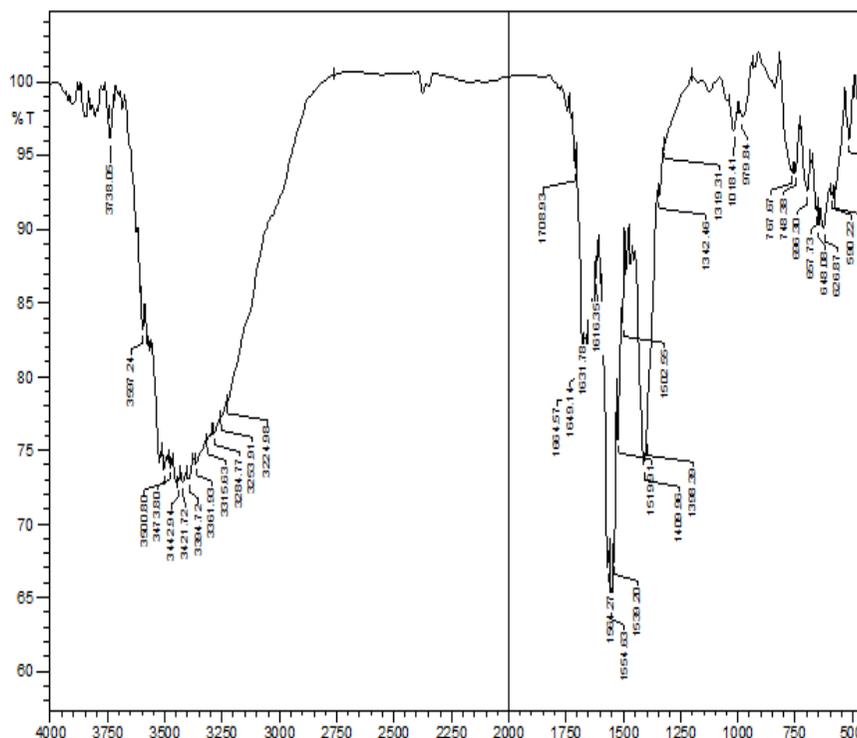
### 3.6: INFRARED SPECTRA

The IR spectral data of the Schiff base ligand and its metal complexes are presented in table.5.6(a)The spectra of the complexes were compared with that of the free ligands to determine the coordination sites which involve in chelation.

#### 3.6.1: IR spectrum of ligand



#### 3.6.2: IR spectrum of 3-nitro copper complex

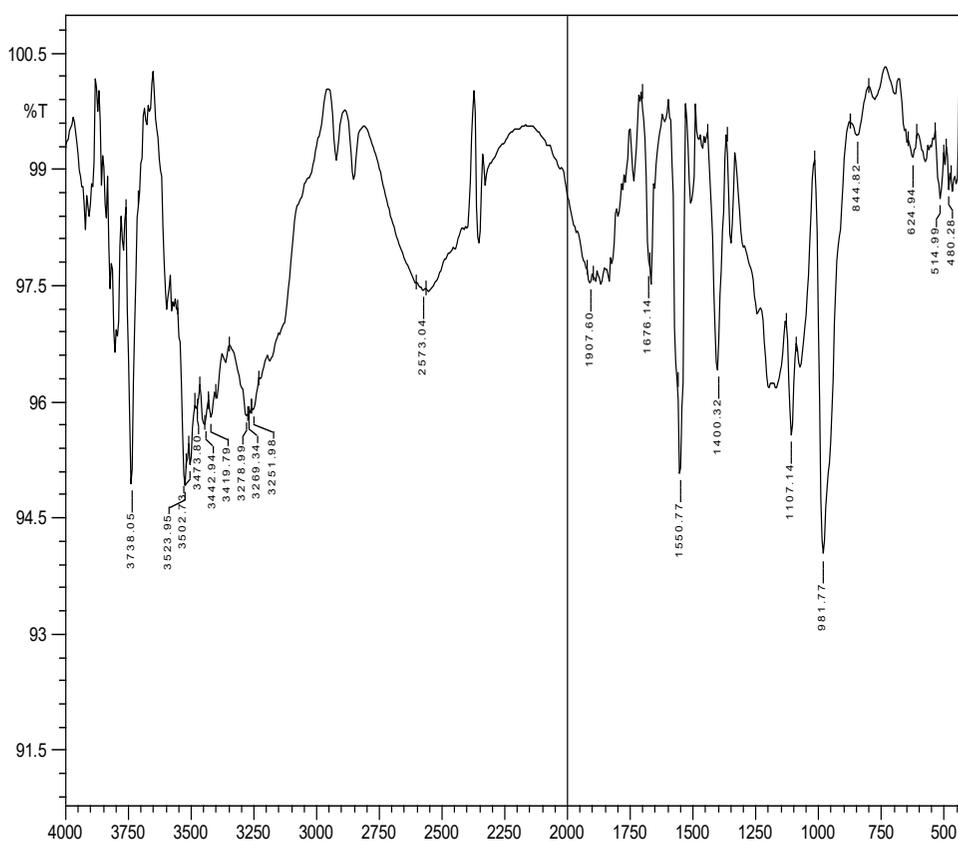


Ligand	Cu Complex	Assignment
-	3421.72	Coordinated H <sub>2</sub> O molecule
1618.28	1616.35	C=N
1479.40	1409.96	C=C
1527.62	1519.91	N=O (sym. bending)
1319.31	1342.46	N=O (asym. bending)
734.88	748.38	monosubstituted
-	626.87	Cu-N
-	450	Cu-Cl

Table 3.6(a)

In the IR spectrum of the ligand, an intense band is observed at 1618.28 cm<sup>-1</sup> which attributed to  $\nu(\text{C}=\text{N})$  of the ligand. It is shifted to a lower frequency of 1616.35cm<sup>-1</sup> which indicates the presence of coordination. Two peaks at 1527.62cm<sup>-1</sup> and 1319.31cm<sup>-1</sup> corresponds to the symmetric and asymmetric bending of NO<sub>2</sub> group. In the Cu(II) complex, a strong band is obtained in 626.87 cm<sup>-1</sup> which is attributed to Cu-N bond which is absent in the free ligand. This peak at 427.87 cm<sup>-1</sup> confirms the coordination in Cu complex. The appearance of bands at 450cm<sup>-1</sup> in the IR spectrum is assigned to Cu-Cl stretching vibration. The band at 3421.72 cm<sup>-1</sup> suggest the presence of coordinated H<sub>2</sub>O in the complex.

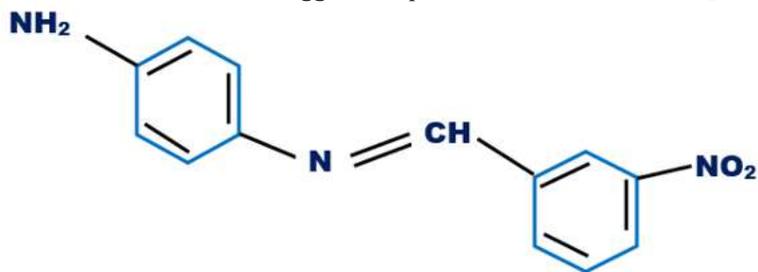
### 3.6.3: IR spectrum of 3-nitro Vanadium complex



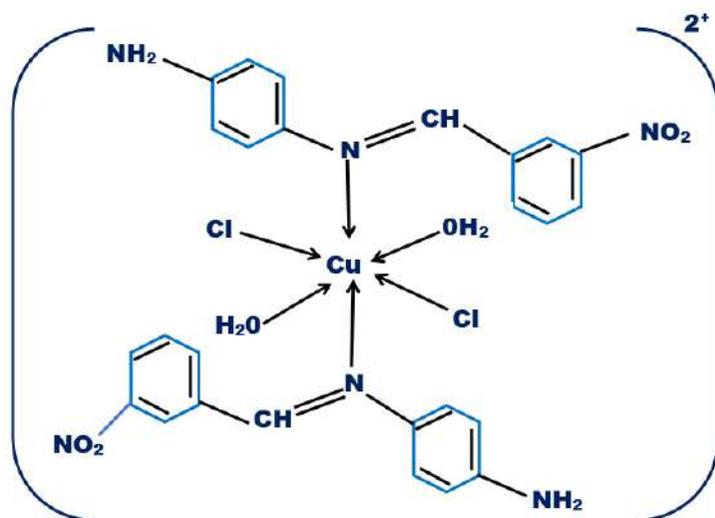
Ligand	V Complex	Assignment
	3419.79	Coordinated H <sub>2</sub> O molecule
1618.28	1676.14	C=N
1479.40	1400.32	C=C
1527.62	1550.77	N=O (asym.bending)
-	480.28	V-N
-	844.82	V=O

Table 3.6(b)

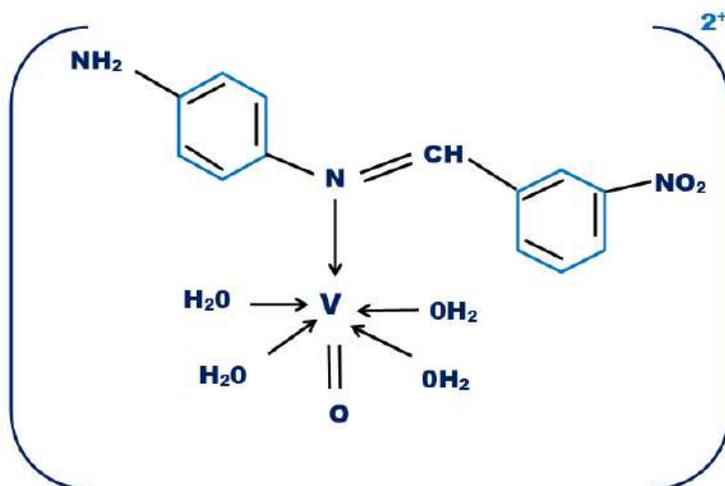
In the IR spectrum of the complex an intense band near  $1618.28\text{ cm}^{-1}$  corresponds to  $\nu(\text{C}=\text{N})$  of the ligand. It is shifted to a higher frequency of  $1676.14\text{ cm}^{-1}$  which indicates the presence of coordination. The peak at  $1527.62\text{ cm}^{-1}$  indicates the asymmetric bending of  $\text{NO}_2$  group. The strong bands at  $480.28\text{ cm}^{-1}$  and  $844.82\text{ cm}^{-1}$  attribute to  $\text{V}-\text{N}$  and  $\text{V}=\text{O}$  bonds which are absent in the free ligand. These peaks confirm the formation of metal complexes. The band at  $3419.79\text{ cm}^{-1}$  suggest the presence of coordinated  $\text{H}_2\text{O}$  in the complex.



STRUCTURE OF LIGAND



STRUCTURE OF COPPER COMPLEX



STRUCTURE OF VANADIUM COMPLEX

**3.7: ANTIBACTERIAL AND ANTIFUNGAL STUDIES.**

**Antibacterial studies**

The antibacterial and antifungal studies were conducted by comparing the zone of inhibition of a standard bacterial agent with the complexes and their extend of antimicrobial activity is measured.

**3-nitro copper complex**

**E COLI**



**PSEUDOMONAS AERGINOSA**



**STREPTOCOCCUS MUTANS**



**STAPHYLOCOCCUS AUREUS**



ORGANISM	ANTIBACTERIAL AGENT	ZONE OF INHIBITION (mm)			
		AGENT	250 (ml)	500 (ml)	1000 (ml)
<i>E Coli</i>	Streptomycin	26	11	12	15
<i>Pseudomonas aeruginosa</i>	Streptomycin	30	11	12	14
<i>Streptococcus mutans</i>	Streptomycin	26	12	13	15
<i>Staphylococcus aureus</i>	Streptomycin	27	10	13	17

3-nitro copper complex have antibacterial activity for gram-negative and gram-positive bacteria. The complex shows moderate activity for gram negative stain such as *E Coli* and *Pseudomonas aeruginosa* at 250, 500, 1000 concentrations. It also shows moderate activity for gram positive stain *Streptococcus mutans* and *Staphylococcus aureus* at 250, 500, 1000 concentrations.

3-nitro vanadium complex

**E COLI**



**PSEUDOMONAS AERGINOSA**



**STREPTOCOCCUS MUTANS**



**STAPHYLOCOCCUS AUREUS**



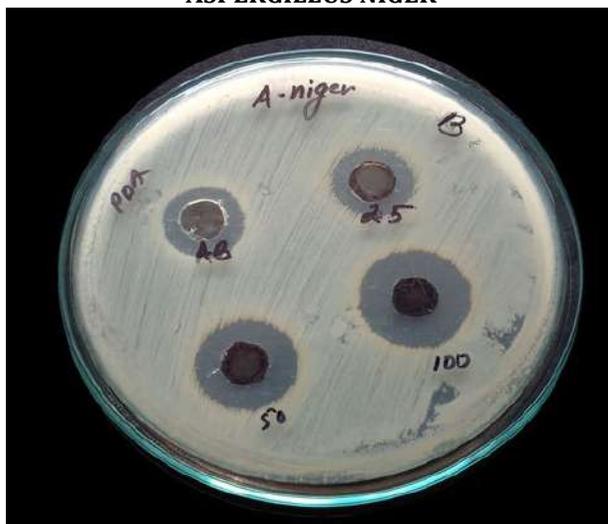
ORGANISM	ANTIBACTERIAL AGENT	ZONE OF INHIBITION (mm)			
		AGENT	250 (ml)	500 (ml)	1000 (ml)
<i>E Coli</i>	Streptomycin	20	10	12	14
<i>Pseudomonas Aerginosa</i>	Streptomycin	30	-	-	10
<i>Streptococcus mutans</i>	Streptomycin	26	12	14	16
<i>Staphylococcus aureus</i>	Streptomycin	27	11	12	15

3-nitro vanadium complex shows moderate antibacterial activity for gram-negative stain *E coli*. It shows 10mm, 12mm, 14 mm values at concentrations of 250, 500 and 1000 ml. The complex is inactive for gram-negative stain *Pseudomonas Aerginosa* at 250 and 500 ml concentration, but it shows slight activity at 1000 ml concentration. 3-nitro vanadium complex shows moderate activity for gram-positive stain *Streptococcus mutans* and *Staphylococcus aureus* at 250, 500, 1000 ml concentrations.

**Antifungal studies**

- **3-nitro copper complex**

**ASPERGILLUS NIGER**



**CANDIDA ALBICANS**



ORGANISM	ANTIFUNGAL AGENT	ZONE OF INHIBITION (mm)			
		AGENT	250 (ml)	500 (ml)	1000 (ml)
<i>Aspergillus niger</i>	Clotrimazole	15	16	20	23
<i>Candida albicans</i>	Clotrimazole	15	-	16	23

3-nitro copper complex shows antifungal activity. The complex is highly active for antifungal stain such as *Aspergillus niger*. Standard value of antifungal agent “Clotrimazole” is 15mm. But increasing the concentration from 250 to 1000 zone inhibition value reaches 23. In the antifungal stain *Candida albicans*, the complex is inactive at 250 ml concentration. At higher concentration of 500 and 1000 ml the complex is highly active.

- **3-nitro vanadium complex**

**ASPERGILLUS NIGER**



**CANDIDA ALBICANS**



ORGANISM	ANTIFUNGAL AGENT	ZONE OF INHIBITION (mm)			
		AGENT	250 (ml)	500 (ml)	1000 (ml)
<i>Aspergillus niger</i>	Clotrimazole	15	-	11	14
<i>Candida albicans</i>	Clotrimazole	15	-	-	-

3-nitro vanadium complex shows antifungal activity. In the antifungal stain such as *Aspergillus niger* the complex is inactive at 250 ml concentration. But increasing the concentration it become active and reaches near to standard value of antifungal agent. In *Candida albicans* the complex does not show any activity at all concentration.

**SUMMARY AND CONCLUSION**

The Schiff base ligand, (3- nitrobenzylidene)- phenylenediamine has been synthesized by the condensation of 3- nitrobenzaldehyde and p-phenylenediamine dihydrochloride. It is brown in colour and having 80.2% yield and soluble in dimethyl sulphoxide. The spectral data of the ligand concluded that the ligand is monodentate.

The Copper complex of this ligand is dark brown in colour and having 72% yield and soluble in DMSO. The molar conductance value of this complex were found to be  $623 \Omega^{-1}\text{cm}^2\text{mol}^{-1}$ . This value indicates that the complex is electrolytic in nature. The magnetic moment value of this complex is 1.8 BM which suggests that the complex has octahedral structure. The appearance of new bands at  $626.87\text{cm}^{-1}$  in the IR spectrum is assigned to Cu-N stretching vibration. The appearance of bands at  $450\text{cm}^{-1}$  in the IR spectrum is assigned to Cu-Cl stretching vibration.

The oxovanadium complex of this ligand is dark brown in colour and having 78% yield and soluble in DMSO. The molar conductance value of this complex were found to be  $141 \Omega^{-1}\text{cm}^2\text{mol}^{-1}$ . This value indicates that the complex is electrolytic in nature. The magnetic moment value of this complex is 1.7533 BM which suggests that the complex has octahedral structure. The appearance of new bands at  $480.28 \text{cm}^{-1}$  and  $844.82 \text{cm}^{-1}$  in the IR spectrum are assigned to V-N and V=O stretching vibrations.

The UV spectra of ligand and complexes shows characteristic absorption at the range of 235 nm and at 350nm region which confirms the presence of benzenoid and azomethine linkages, which are characteristic of  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transition respectively.

The antibacterial and antifungal studies of complexes were conducted by comparing the zone of inhibition of a standard bacterial agent with the complexes and their extend of antimicrobial activity is measured. 3-nitro copper complex is moderately active for gram negative bacteria such as E Coli and *Pseudomonas aeruginosa* at 250, 500, 1000 ml concentrations. The complex is also moderately active for gram positive bacteria such as *Streptococcus mutans* and *Staphylococcus aureus* at all concentration.

3-nitro vanadium complex is moderately active for gram negative bacteria like E Coli, but the complex is inactive for the gram-negative stain like *Pseudomonas Aeruginosa* at 250 and 500 ml concentration. The complex become slightly active at 1000 ml of concentration. The complex shows moderate activity for gram positive bacteria such as *Streptococcus mutans* and *Staphylococcus aureus* at all concentration.

## ACKNOWLEDGEMENT

I 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.

## REFERENCES

1. J. Hine and C.Y. Yeh, *J. Am. Chem. Soc.*, 89 (1967)2669.
2. R.J.Fessenden and J.S.Fessenden, *Organic Chemistry*, Brooks/Cole Publishing Company, USA, 1998.
3. Z. Cimerman, S. Miljanic and N.Galic, *Croatica Chemica Acta*, 73 (2000) 81.
4. A. Elmali, M. Kabak and, Y. Elerman, *J. Mol. Struct.*, 477 (2000)151.
5. A. Earnshaw, N.N Green wood, "Chemistry of the elements", Oxford University Press, 2<sup>nd</sup> Edn.,1998.
6. N. Kataoka and H. Kon, *J. Amer.Chem.Soc.*,90,2978,1968.
7. J.R. Anacona, E. Bastardo and, J. Camus, *Trans. Met. Chem.*, 24 (1999)478.
8. R. H. Holm, *J. Am. Chem. Soc.*, 82 (1960) 5632.
9. E. C. Niederhoffer, J. H. Timmons, J. H. Timmons, A. E. Martell, *Chem.Rev.*, 84 (1984) 137.
10. C. O. Rodriguez de Barbarin, N. A. Bailey, D. E. Fenton, Q.-Y. He, *J. Chem. Soc., Dalton Trans.*, (1997) 161.
11. E. J. Larson, V. L. Pecoraro, *J. Am. Chem. Soc.*, 113 (1991) 3810.
12. H. J. Choi, J. J. Sokol, J. R. Long, *Inorg. Chem.*, 43 (2004) 1606.
13. H.A. John and E.Teller, *Proc.Roy.Soc.*,A161,220,1937.
14. M. Ciampolini and N. Nardi, *Inorg.Chem.*,5,41,1966.
15. H. Schiff, *Ann. Chem.*,131,118,1864.
16. S. Patai, "The chemistry of the Carbon-Nitrogen Double Bond", John Wiley, London, 2<sup>nd</sup> Edn., 64,1963..
17. N. Agarwal, G. Mishra and R. K. Upadhyay *J. Indian. Chem. Soc.*, 72,849,1995.
18. S.Chandra and J.Sangeetika, *J.Ind.Chem.Soc.*,81(2004)203.
19. H. Schiff, *Ann. Chem. Pharm.*, 150 (1869)193.
20. A. R. Silva, K. Wilson, J. H. Clark, C. Freire, *Stud. Surf. Sci. Catal.*, 158 (2005) 1525.