

Synthesis, Characterization and Antimicrobial Studies of Copper(II) and Vanadium(IV) Complexes with N-(3-Nitrobenzylidene)-1-Naphthylamine

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Abstract: The ligand was synthesized using 3-nitrobenzaldehyde and 1-naphthyl amine in 1:1 ratio. The Cu(II) and V(IV) Schiff base metal complexes were prepared using the synthesized Schiff base ligand in 1:1 ratio. The complexes were characterized using the basic techniques like IR, UV, CHN, molar conductivity and magnetic measurements. The complexes were tested for antibacterial activity against E Coli, Staphylococcus aureus, KleibSELLA pneumoniae and Streptococcus mutans and antifungal activity against Aspergillus niger and Candida albicans. The results show that the complexes are potent against some bacteria and fungi at some concentrations.

Key Words: Schiff base, aldehyde, antibacterial, antifungal

I. INTRODUCTION

The recorded beginning of the coordination chemistry is the discovery of hexamine cobalt (III) by Tassart in 1798. With the development of theory of chemical bonding by Pauling, a tremendous change was witnessed in 1940. It enables successful correlation of properties with constitution of co-ordination compounds. Schiff base was formed by the condensation product of a primary amine with a carbonyl compound. Azomethines are reported to have antitumour and cytotoxic activities. Schiff base complexes can be used as catalysts which can catalyse different reactions like decomposition, oxidation, polymerization etc. Schiff base complexes have greater conducting property, resistance towards heat, light and oxidation. The formation of metal complexes were studied by Nunez and Eichhorn.

II. MATERIALS, INSTRUMENTS 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 1-naphthyl amine is used as the amine and the solvent used is methanol.

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

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

3-nitrobenzaldehyde (0.151g, 0.001M) dissolved in 20 ml methanol and 1-naphthyl amine (.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: 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 brown complex formed is separated out. It is filtered, washed with methanol and dried in vacuum.

(b) 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 (0.001M) 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	DMSO	80%
Cu Complex	Brown	DMSO	82.3%
V Complex	Dark brown	DMSO	88.5%

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. 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.

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 $1 \times 10^{-3} \text{ M}$.

CHN analysis was done in Vario-III CHN elemental analyser at the Central Laboratory for Instrumentation and Facilitation (CLIF), Kaaryavattom.

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,

$$X_g = (\alpha + \beta F) / W$$

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

2.4 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 oxidises 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_2 . The titration is completed when a pink end point stable atleast for one minute.

2.5 Estimation of Copper

The copper can be estimated gravimetrically. The complex is digested with sulphuric acid mixture and it is made upto 100 ml and 20 ml is pipetted out into a 250 ml beaker. About 5 ml of dil. H_2SO_4 is added followed by 25-30 ml freshly prepared sulphuric acid solution. The solution is diluted to 150 ml and heated to boiling. About 10 ml of freshly prepared 10% ammonium thiocyanate is added slowly 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 severam hours

preferably overnight. The solution is filtered through a previously weighed sintered glass crucible (IG_4) and the residue is washed 10-15 times with a cold solution prepared by adding to every 100 ml of water 1ml of 10% NH_4CNS and 5-6 drops of saturated sulphuric 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 Cu CNS . Heating, cooling and weighing are repeated till constant weight is obtained.

2.6 Antibacterial Activity

Agar- Well Diffusion Method

Materials Required

Muller Hinton Agar Medium is used for bacterial culture.

Streptomycin (standard antibacterial agent, concentration: 10mg / ml)

Culture of test organisms; growth of culture adjusted according to McFards Standard, 0.5%

1. *E.coli*
2. *Staphylococcus aureus*
3. *Kleibsella pneumoniae*
4. *Streptococcus mutans*

Procedure

Petriplates containing 20ml Muller Hinton Agar Medium were seeded with bacterial culture of *E.coli*, *Kleibsella pneumoniae*, *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 $250\mu\text{g/mL}$, $500\mu\text{g/mL}$ and $1000\mu\text{g/mL}$ 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.

2.7 Antifungal Activity

Agar- Well Diffusion Method

Materials Required

Potato Dextrose Agar Medium is used as fungal medium.

2. Clotrimazole (standard antifungal agent, concentration: 10mg / ml)

3. Culture of test organisms; growth of culture adjusted according to McFarland Standard, 0.5%

- *Aspergillus niger* (ATCC 16404)
- *Candida albicans*(ATCC 10231)

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).

III. RESULT AND DISCUSSION

Schiff base derived from 3- nitrobenzaldehyde and 1-Naphthyl amine is used for the synthesis of ligand.

3.1: General Properties

Both V(IV) and Cu(II) complexes are dark brown in colour and are stable in air. Both complexes are sensitive to light. The two complexes are insoluble in water and are soluble in hot methanol, DMSO, Chloroform etc.

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

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 V(IV) and Cu(II) complexes under investigation are found to be $77 \Omega^{-1}\text{cm}^2\text{mol}^{-1}$ and $155.3 \Omega^{-1}\text{cm}^2\text{mol}^{-1}$ respectively.

The molar conductance value shows that the V(IV) and Cu(II) complex was electrolytic in nature. Because there is no charged species in the complex to neutralize the charge of the central metal ion.

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 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 V(IV) and Cu(II) complexes are paramagnetic in nature.

The magnetic moment values of V(IV) and Cu(II) complexes are found to be 1.91 BM and 1.97 BM. From this, it is clear that the V(IV) complex has trigonal bipyramidal and Cu(II) complex has octahedral structure.

Table 3.4(a)

Complex	Colour	Yield(%)	Molecular weight	Magnetic moment(BM)	Molar conductance ($\Omega^{-1}\text{cm}^2\text{mol}^{-1}$)
V(IV) complex	Dark brown	88.5%	397.2515	1.91	77
Cu(II) Complex	Brown	82.3%	688.1662	1.97	155.3

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.

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 V complex is found to be trigonal bipyramidal and that of copper complex is octahedral.

Table 3.5(a)

Complex	C%		H%		N%	
	Experimental	calculated	Experimental	Calculated	Experimental	Calculated
V complex	51	51.39	4.57	4.56	7.70	7.05
Cu complex	47.05	49.68	5.12	4.69	8.03	8.14

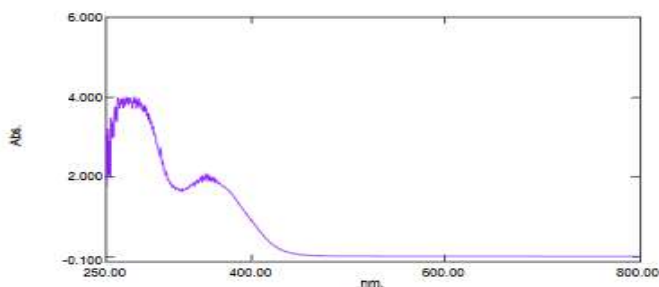
3.6: Electronic Spectra

The electronic spectra are often helpful in the evaluation of result furnished by other methods of analysis. The electronic

spectral bands of the ligand and complexes was recorded over the range 200-800nm in DMSO

3.6a. Electronic Spectrum of Ligand

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



No.	P/V	Wavelength	Abs.	Description
1	⊕	352.50	2.056	
2	⊕	272.50	4.000	
3	⊕	211.00	1.604	
4	⊖	328.50	1.657	
5	⊖	228.00	-4.000	

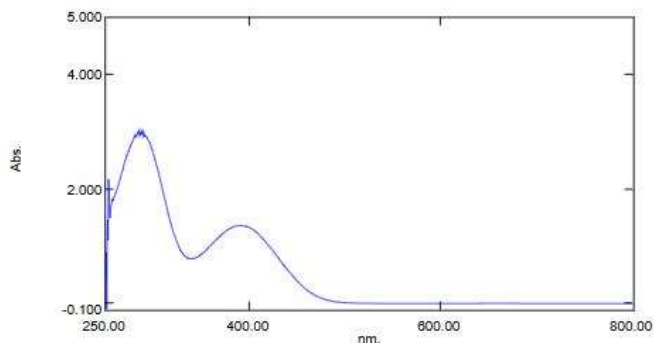
Ultraviolet spectra of the ligands recorded in DMSO showed strong bands around 272.5 nm and at 352.5 nm region which confirms the presence of benzenoid and azomethine linkages,

which are characteristic of $\Pi \rightarrow \Pi^*$ and $n \rightarrow \Pi^*$ transition respectively.

3.6b. Vanadium Complex

Electronic Spectra of Complexes

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



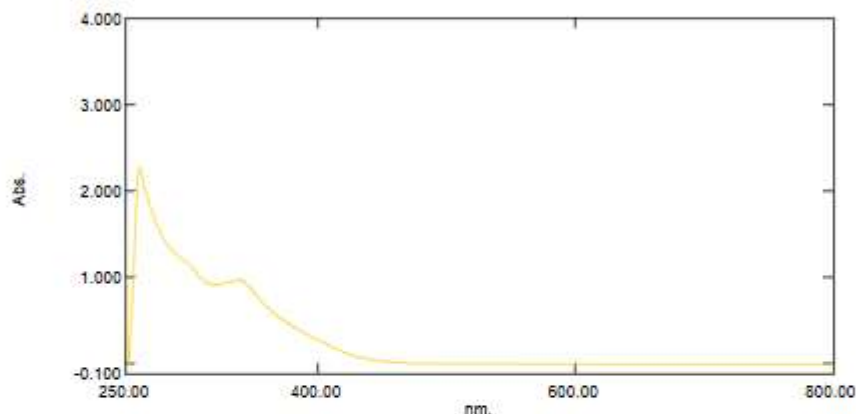
No.	P/V	Wavelength	Abs.	Description
1	⊕	391.50	1.362	
2	⊕	285.50	3.032	
3	⊕	217.50	3.168	
4	⊖	340.50	0.782	
5	⊖	251.50	-0.263	

Ultraviolet spectra of the Nickel complex recorded in DMSO showed strong bands around 285.5 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.

3.6c. Copper complex

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



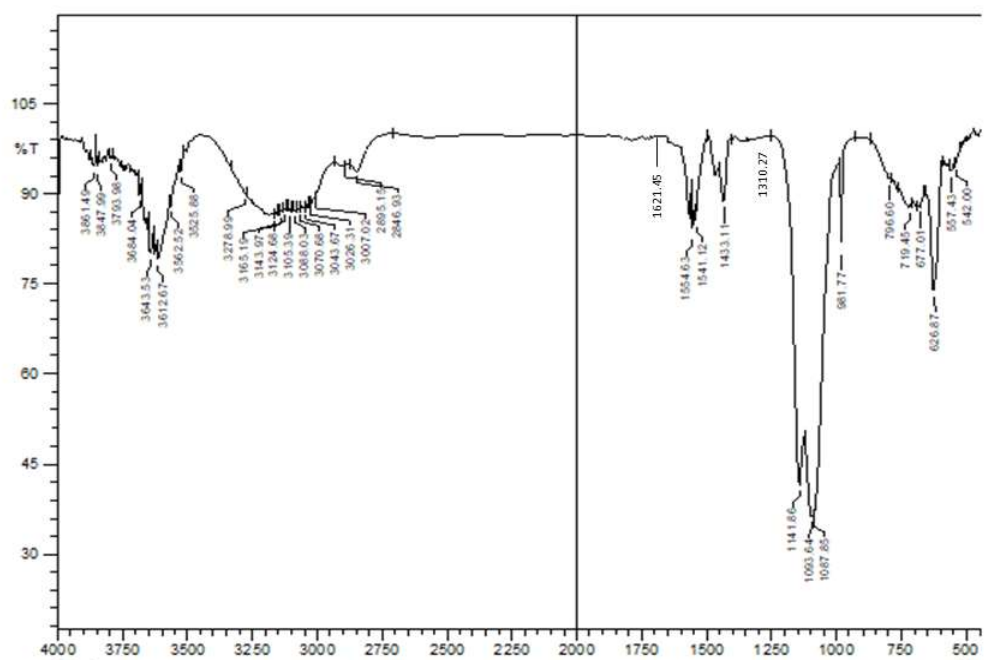
No.	P/V	Wavelength	Abs.	Description
1	●	340.50	0.976	
2	●	261.00	2.272	
3	●	229.00	3.470	
4	●	219.00	2.859	
5	●	319.00	0.912	
6	●	252.50	-0.015	
7	●	223.00	-4.000	

Ultraviolet spectra of the Cobalt complex recorded in DMSO showed strong bands around 261 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.

3.7. Infrared Spectrum

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

a) IR Spectrum of Ligand



b) IR Spectrum of Vanadium Complex

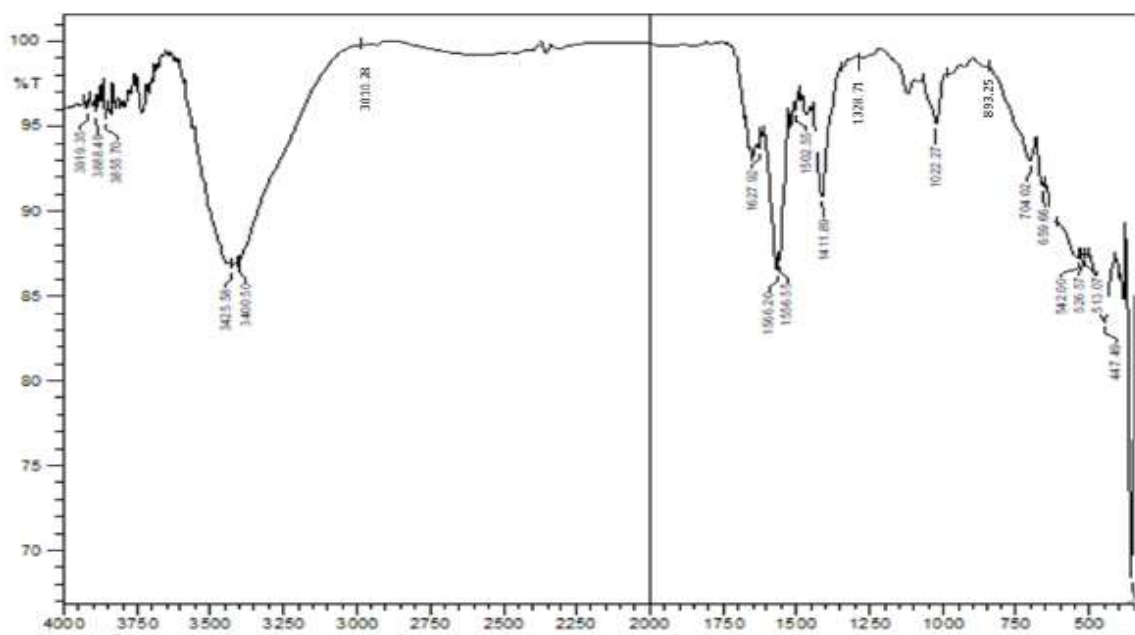


Table 3.7b

Ligand	V complex	Assignment
-	3400.50	Coordinated water molecule
3026.31	3010.28	=CH
1621.45	1627.92	C=N
1433.11	1411.89	C=C
1541.12	1502.55	N=O(Sym.Bending)
1310	1328.71	N=O(Asym.Bending)
719.45	704.02	Monosubstituted
-	893.25	V=O
-	447.49	V-N

In the IR spectrum of the ligand, a medium strength band is observed at 3026.31 cm^{-1} which corresponds to =CH group. In the complex, it is shifted to a lower frequency of 3010.28 cm^{-1} . The intense band near 1621.45 cm^{-1} can be attributed to ν (C=N) of the ligand. It is shifted to a higher frequency of 1627.92 cm^{-1} which indicates the presence of coordination. Two peaks at 1502.55 cm^{-1} and 1328.71 cm^{-1} corresponds to

the symmetric and asymmetric bending of NO_2 group. In V complex, a strong band is obtained in 3400.50 cm^{-1} which indicates the presence of coordinated water molecule. The peaks at 447.49 cm^{-1} and 893.25 cm^{-1} can be attributed to V=O bond which is absent in the free ligand. These peaks confirms the coordination in Ni complex.

c) Spectrum of Copper Complex

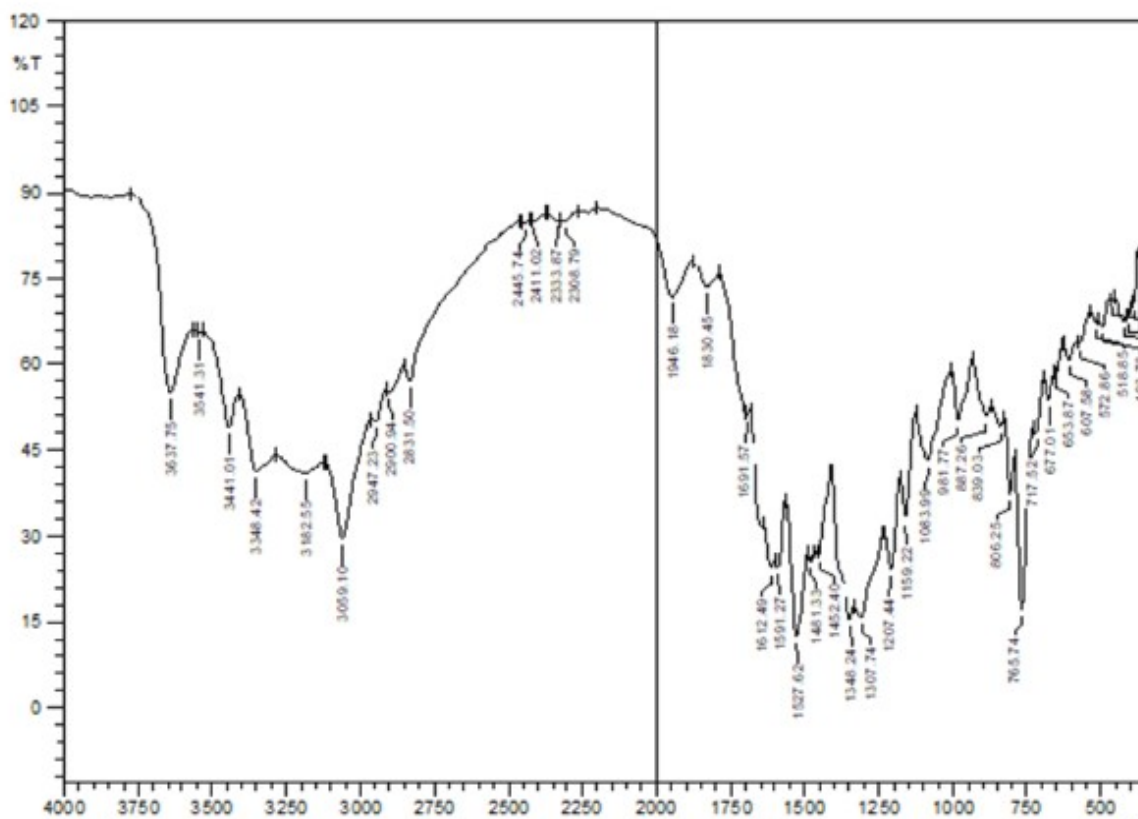


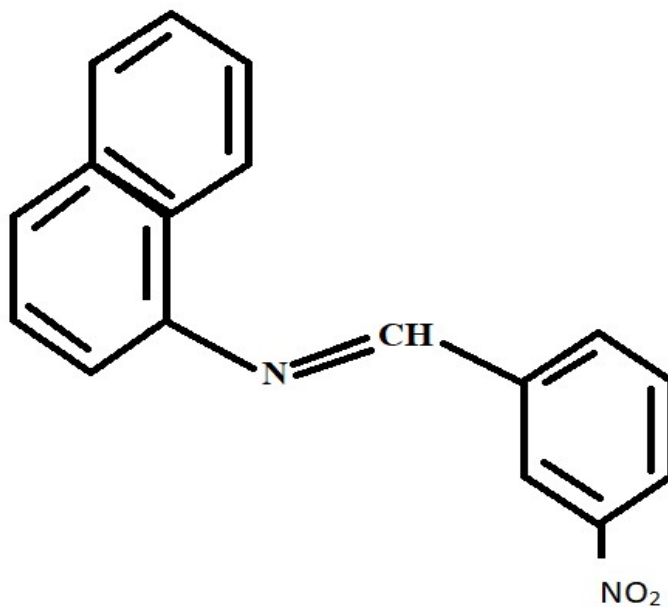
Table 3.7c

Ligand	Co complex	Assignment
-	3442.01	Coordinated water molecule
3026.31	3059.10	=CH
1621.45	1612.49	C=N
1433.11	1452.40	C=C
1541.12 1310	1527.62 1307.74	N=O(Sym.Bending) N=O(Asym.Bending)
719.45	717.52	Monosubstituted
-	518.85	Cu-N

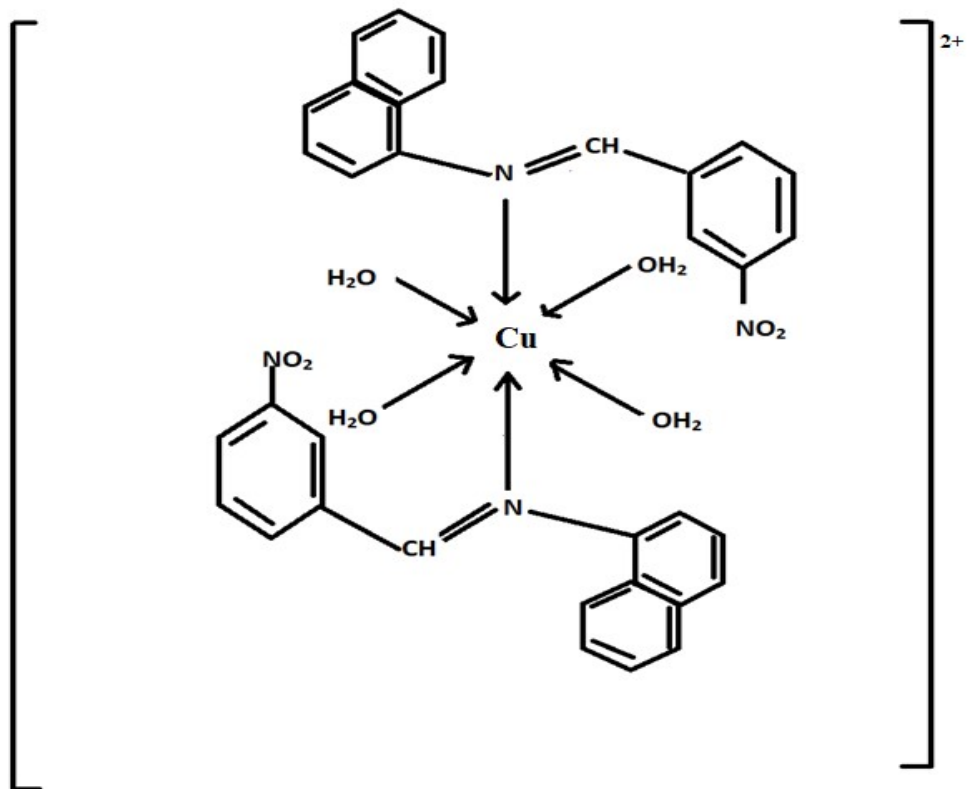
In the IR spectrum of the ligand, a medium strength band is observed at 3026.31 cm^{-1} which corresponds to =CH group. In the complex, it is shifted to a lower frequency of 3059.10 cm^{-1} . The intense band near 1621.45 cm^{-1} can be attributed to ν (C=N) of the ligand. It is shifted to a lower frequency of 1612.49 cm^{-1} which indicates the presence of coordination. Two peaks at 1527.62 cm^{-1} and 1307.74 cm^{-1} corresponds to

the symmetric and asymmetric bending of NO_2 group. In Co complex, a strong band is obtained in 3441.01 cm^{-1} which indicates the presence of coordinated water molecule. The peak at 518.85 cm^{-1} can be attributed to Co-N bond which is absent in the free ligand. This peak at 518.85 cm^{-1} confirms the coordination in Co complex.

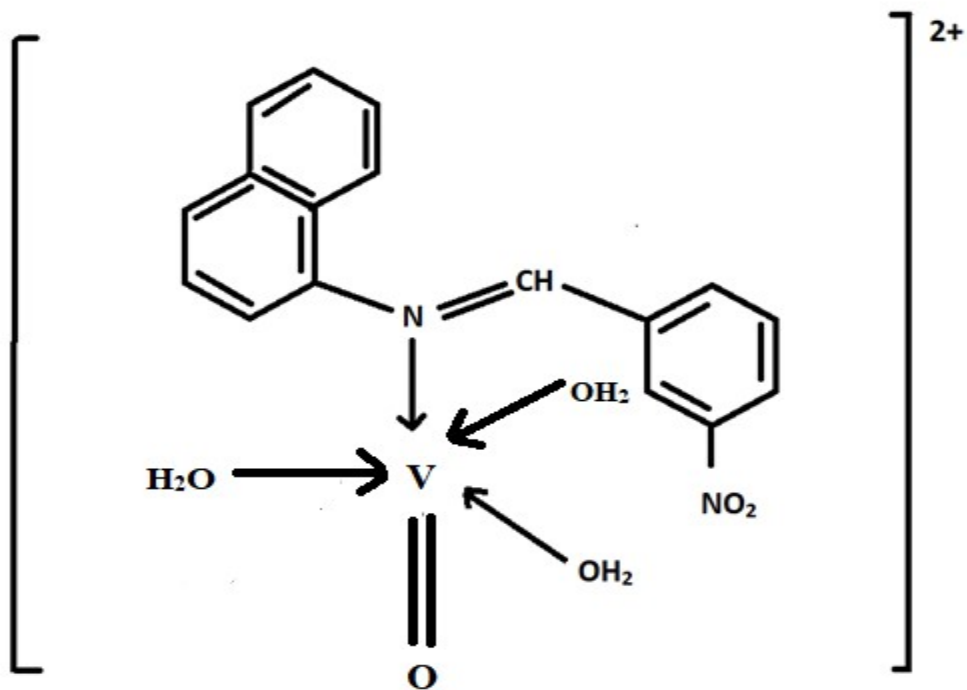
STRUCTURE OF LIGAND



STRUCTURE OF COPPER COMPLEX



STRUCTURE OF VANADIUM COMPLEX

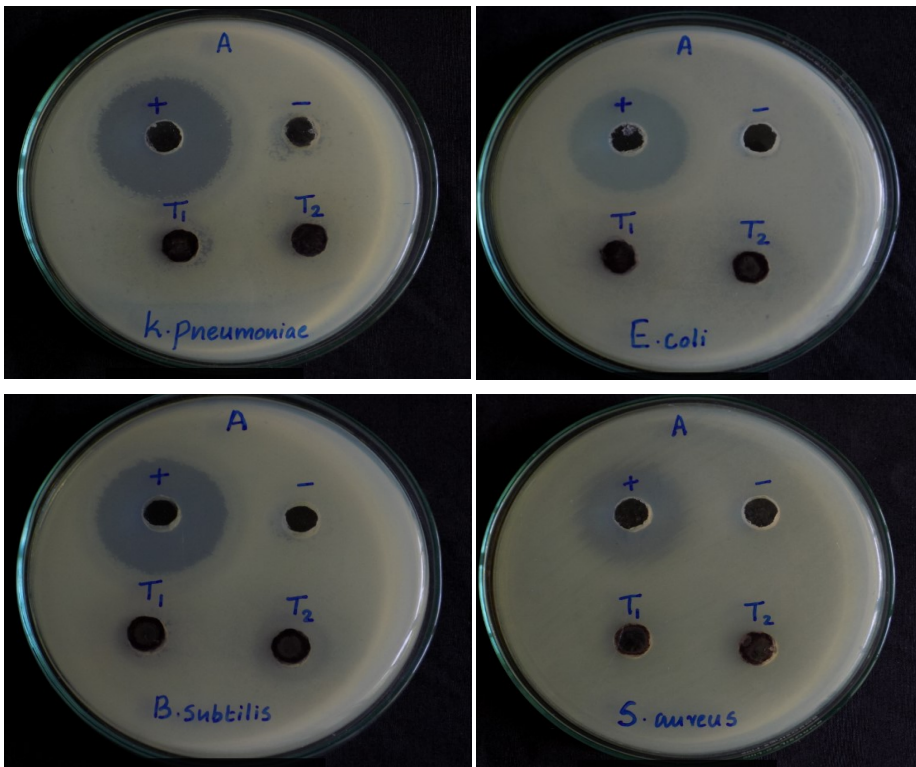


3.8: Antimicrobial Studies

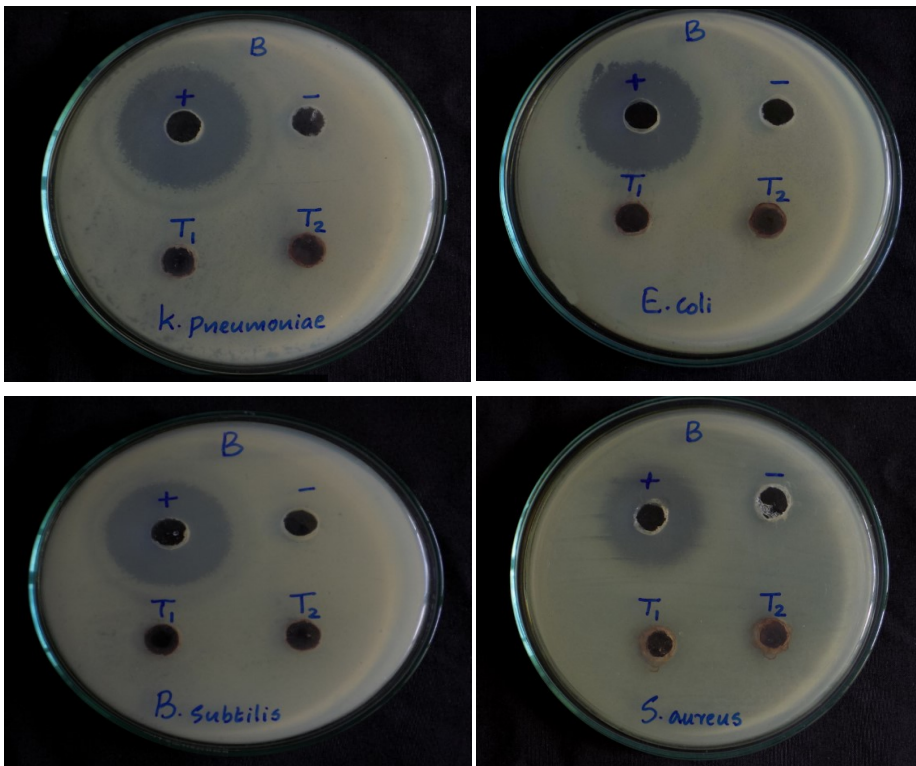
Antibacterial Studies

The antibacterial and antifungal studies were conducted by comparing the zone of inhibition of a standard bacterial agent with the complexes.

3.8(a): Antibacterial Studies of Copper Complexes



3.8(b) Antibacterial Studies Of Vanadium Complexes

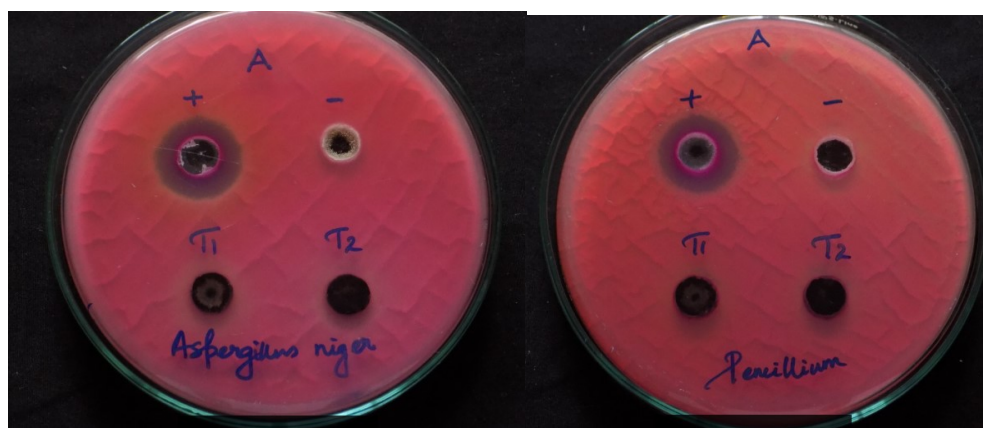


ANTIBACTERIAL ASSAY					
Organisms		<i>Staphylococcus aureus</i> (mm)	<i>Bacillus subtilis</i> (mm)	<i>Escherichia coli</i> (mm)	<i>Klebsiella Pneumonia</i> (mm)
Samples	Concentration of samples	Positive control- Gentamycin 80mcg			
COPPER	Gentamycin	22	29	27	30
	Negative control	-	-	-	-
	T1 (400mcg)	-	-	-	-
	T2 (800mcg)	-	-	-	-
VANADIUM	Gentamycin	24	28	29	31
	Negative control	-	-	-	-
	T1 (400mcg)	-	-	-	-
	T2 (800mcg)	-	-	-	-

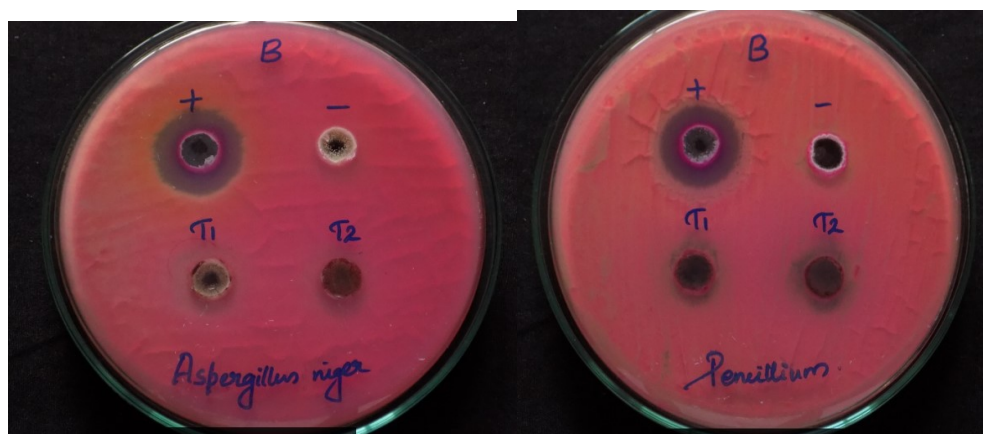
There is no antibacterial activity shown by copper and vanadium complexes against *Staphylococcus aureus* (mm), *Bacillus subtilis*(mm), *Escherichia coli*(mm), *Klebsiella Pneumonia*(mm) upto the concentration of 800mcg.

3.9 : Antifungal Activities

3.9(a) Antifungal activity of copper complexes



3.9(b) : Antibacterial activity of vanadium complexes



ANTIFUNGAL ASSAY			
Organisms		<i>Aspergillus niger(mm)</i>	<i>Penicillium notatum (mm)</i>
Samples	Concentration of samples	Positive control- Clotrimazole 80mcg	
COPPER	Clotrimazole	18	17
	Negative control	-	-
	T1 (400mcg)	-	-
	T2 (800mcg)	-	-
VANADIUM	Clotrimazole	19	17
	Negative control	-	-
	T1 (400mcg)	-	11
	T2 (800mcg)	-	12

Copper complex does not show any antifungal activity against *Aspergillus niger* and *Penicillium notatum*. But vanadium complex show moderate antifungal activity against *Penicillium notatum* at 400 and 800 mcg.

IV. SUMMARY AND CONCLUSION

The Schiff base ligand (3-nitrobenzylidene)-1-naphthyl amine has been synthesized by the condensation of 3-nitrobenzaldehyde and 1-naphthyl amine. It is yellow in colour and having 80% 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 brown in colour and having 82.3% yield and soluble in DMSO. The molar conductance value of this complex was found to be $155.3 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$. This value indicates that the complex is electrolytic in nature. The magnetic moment value of this complex is 1.97 BM which suggests that the complex has octahedral structure. The appearance of new bands at 518.85 cm^{-1} in the IR spectrum is assigned to Cu-N stretching vibration. The spectral data of the ligand concluded that the ligand is monodentate. Copper complexes does not show any antibacterial and antifungal activities.

The V complex of this ligand is dark brown in colour and having 88.5% yield and soluble in DMSO. The molar conductance value of this complex were found to be $77 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$. This value indicates that the complex is electrolytic in nature. The magnetic moment value of this complex is 1.91 BM which suggests that the complex has trigonal bipyramidal structure. The appearance of new bands at 447.49 and 893.25 cm^{-1} in the IR spectrum are assigned to V-N and V=O stretching vibrations. It does not show any antibacterial activity but it is moderately active against the fungi *Penicillium notatum*.

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.

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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REFERENCES

- [1]. D. D. Willett, D. Gatteschi, O. Kahn, *Magneto-Structural Correlations in Exchange Coupled Systems*, Reidel: Dordrecht, The Netherlands, (1985).
- [2]. D. Gatteschi, O. Kahn, J. S. Miller, F. Palacio, *Magnetic Molecular Materials*, NATO ASI Series 198, Kluwer Academic Publishers: Dordrecht, The Netherlands, (1991).
- [3]. O. Kahn, *Molecular Magnetism*; VCH, New York, (1993).
- [4]. B. J. Hathaway, G. Wilkinson, R. D. Gillard, J. A. McCleverty, *In Comprehensive Coordination Chemistry*, Eds. Pergamon Press: Oxford, England, 5 (1987) 533.
- [5]. D. A. Harvey, C. J. L. Lock, *Acta Cryst.*, C42 (1986) 799.
- [6]. W. J. Geary. *Coord. Chem. Rev.*, 7 (1971) 81.
- [7]. M. C. Day, J. Selbin, *Theoretical Inorganic Chemistry*, East-West press, Madras, (1977).
- [8]. P. S. N. Reddy, B. V. Agarwala, *Synth. React. Inorg. Met.-Org. Chem.*, 17 (1987) 585.
- [9]. K. Nakamoto, *Coordination Compounds. In Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th Ed.; John Wiley and Sons, Inc.: New York, (1986).
- [10]. G.A. Kolawole and K.S. Patel, *J. Chem. Soc., (Dalton Trans.)* 1241 (1981)