



SYNTHESIS AND SPECTRAL STUDIES OF VANILLIN SCHIFF BASE WITH CU (II) COMPLEX

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ABSTRACT

Mixed ligand was synthesized by condensation of o-vanillin with 8-aminoquinoline in 1:1 molar ratio. The metal complex of Cu (II) was prepared using the metal salt and ligand in 1:2 ratio. The ligand was characterized by elemental analysis, UV-Visible, IR, NMR and mass spectra. The metal complex was characterized by using elemental analysis, magnetic susceptibility, UV-Visible, IR spectra and XRD studies. It was also characterized by thermo-gravimetric analysis. The composition of the Schiff base ligand and the metal complex was established by elemental analysis which indicated a metal: ligand ratio of 1:2. Magnetic, thermal and spectral studies indicated that ligand behaved as bidentate coordinating through phenolic oxygen and azomethine nitrogen and formed octahedral metal complex. The metal complex revealed its general formula as $[ML_2(H_2O)_2]$ where $M=Cu(II)$ and $L=$ deprotonated Schiff base ligand.

KEYWORDS: Synthesis, Schiff base ligand, transition metal complexes, spectral characterization, thermal and XRD studies.

1. INTRODUCTION

Schiff bases reported by scientist Hugo Schiff play an important role in co-ordination chemistry. These compounds contain an azomethine group ($-HC=N-$). These are also known as imines. They are prepared by the condensation of primary amines with aldehydes or ketones, resulting into the formation of a new C=N bond. Schiff bases derived from aromatic aldehydes and amines have a wide variety of applications in various fields like biological, inorganic and analytical chemistry. Schiff bases can be synthesized by relatively simple procedures enabling us to design compounds which are structurally similar to some substances of biological origin [1-5].

It is well known that N and O atoms play a key role in the co-ordination of metals at the active sites of many metallic-biomolecules [4]. Schiff bases form stable metal complexes with many transition metals. They have been widely studied because they have various properties like antibacterial, antifungal, anticancer, herbicidal, analytical etc. They find wide applications as catalysts in many synthetic and biological reactions. Besides, they can undergo bonding with metal ions in a variety of ways and the resulting compounds show varied activities. 8-aminoquinoline and o-vanillin are especially known for their antibacterial and antifungal activities and are thus used as synthetic precursors in pharmaceuticals. In continuation of earlier work, a Schiff base derived from 8-aminoquinoline and o-vanillin was used to synthesize its Cu(II) complex. Considering the distinct biological activities of these compounds herein put forth an account of the synthesis and characterization of ligand and its complexes [6-9].

2. EXPERIMENTAL:

2.1 Apparatus:

An UV-VIS-NIR-3600 recording spectrophotometer (Shimadzu, Japan) was used for the UV spectrum scanning and determination experiments. Bruker, Germany Model 3000 Hyperion Microscope with Vertex

80FTIR system range $400\text{-}4000\text{ cm}^{-1}$ (KBr discs) at SAIF, IIT, Bombay was used for IR spectral characterization of the Schiff base ligand and metal complexes. The thermogravimetric analysis of ligand and metal complexes was performed on Perkin-Elmer Diamond TG at SAIF, IIT, and Bombay. X-Ray powder diffraction of metal complexes was scanned on X-Ray Diffractometer Ultima IV of Rigaku Corporation Japan, at Instrumentation centre of PAH Solapur University, Solapur.

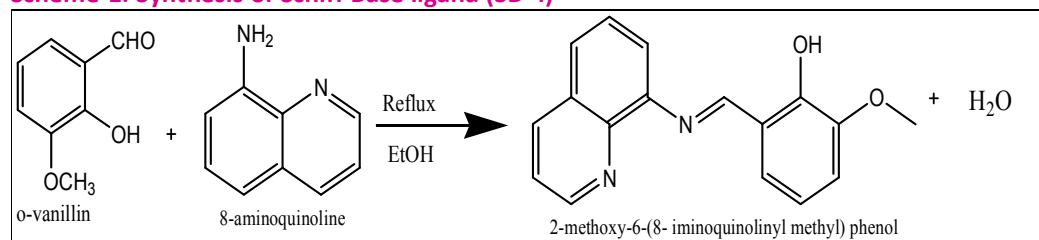
2.2 Reagents:

Sigma- Aldrich o-vanillin, 8-aminoquinoline, and Standard Qualigens (SQ) hydrated Copper (II) chloride was used for synthesis. The solvents ethanol, DMSO etc. was used.

2.3 Synthesis of Schiff base ligand (SB-4)

20 mmol (3.04g) of o-vanillin is dissolved in absolute ethanol. Then it was added dropwise into 20mmol (2.88g) of ethanolic solution of 8-aminoquinoline. The mixture was refluxed for 2 hours then cooled and filtered [10-15]. Intense red colored crystals of Schiff base SB-4 were formed (yield 90%, 5.0 g). The crystals were washed with cold ethanol and anhydrous diethyl ether and dried over anhydrous CaCl_2 . The synthesis of Schiff base ligand (SB-4) is shown in Scheme-1

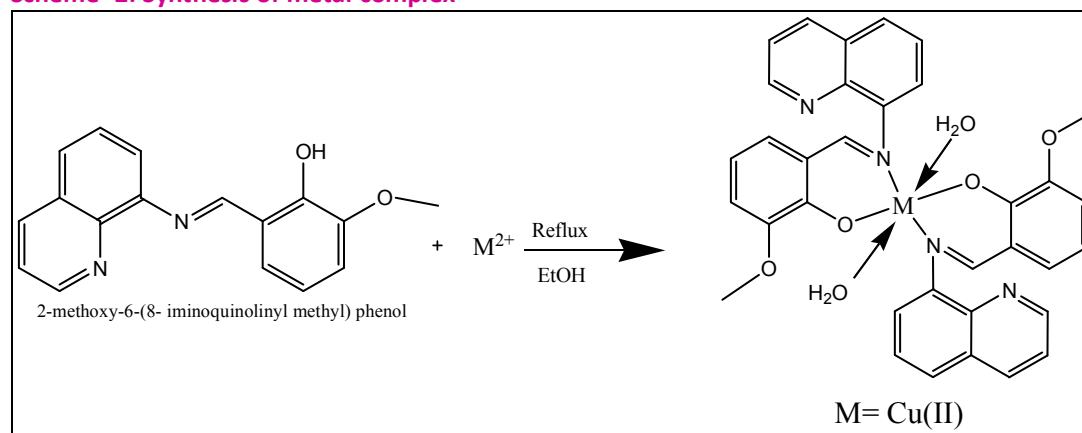
Scheme-1: Synthesis of Schiff Base ligand (SB-4)



2.4 Synthesis of Schiff base transition metal complexes:

20 mmol of Schiff base (SB-4) was dissolved in ethanol (30ml) and added to 10 mmol ethanolic solution (20ml) of metal (II) chloride salt. The metal-ligand molar ratio taken was 1:2. The mixture was refluxed for 3 hours. On cooling, a crystalline metal complex was obtained. It was filtered, recrystallized from ethanol and dried in desiccator over anhydrous CaCl_2 . The Cu(II) metal complex of Schiff base (SB-4) were prepared by above general method using salts $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$. The preparation of metal complex is shown in Scheme -2.

Scheme -2: Synthesis of metal complex



Schiff base (SB-4) and its Cu (II) complex synthesized were stable at room temperature and soluble in common solvents like DMSO, methanol etc.[16-21] The synthesized ligand and the metal complex were characterized by elemental analysis. The geometry of the synthesized compounds has been elucidated on the basis of their elemental and spectral studies.

3. RESULTS AND DISCUSSION:

3.1 Analytical and Physicochemical data:

The stoichiometry of ligand and its metal complex was confirmed by the elemental analysis. The analytical and physicochemical data of Schiff base (SB-4) and its metal complex was found in good agreement with the proposed structure of ligand and the metal complex. The data being listed in Table-1.

Table-1: Analytical and Physicochemical data of Schiff base (SB-4) and its metal complexes

Comp.	Molecular formula	M. p. (°C)	Mol. Weight	Color	% Observed (Theoretical)			
					C%	H%	N%	M%
SB-4	C ₁₇ H ₁₄ O ₂ N ₂	103	278	Red	72.91 (73.38)	4.87 (5.03)	9.98 (10.07)	-
SB-4-Cu	C ₃₄ H ₂₆ O ₄ N ₄ Cu.(H ₂ O) ₂	>350	653.55	Grey	62.25 (62.42)	4.81 (4.59)	8.40 (8.65)	9.52 (9.72)

3.2 UV Spectral Analysis:

The UV spectrum of Schiff base ligand SB-4 is exhibiting two intense bands at 241 nm and 346 nm which can be assigned respectively to $\pi \rightarrow \pi^*$ transition within aromatic moiety and $n \rightarrow \pi^*$ transition of azomethine group of ligand. In the spectra of complex, the bands due to azomethine group are shifted to higher frequency indicating that azomethine nitrogen atom is involved in coordination to the metal ion.

In the present investigation, the electronic spectrum of Cu(II) complex showed one low intensity broad absorption band due to d-d transition at 586 nm assigned to ${}^2E_g \rightarrow {}^2T_{2g}$ (v_2). The observed d-d transition for metal complex is consistent with octahedral geometry of Cu(II) metal complex of Schiff base ligand [12-22]. The UV spectra of Schiff base SB-4 and its metal complex are represented in Figure-1.

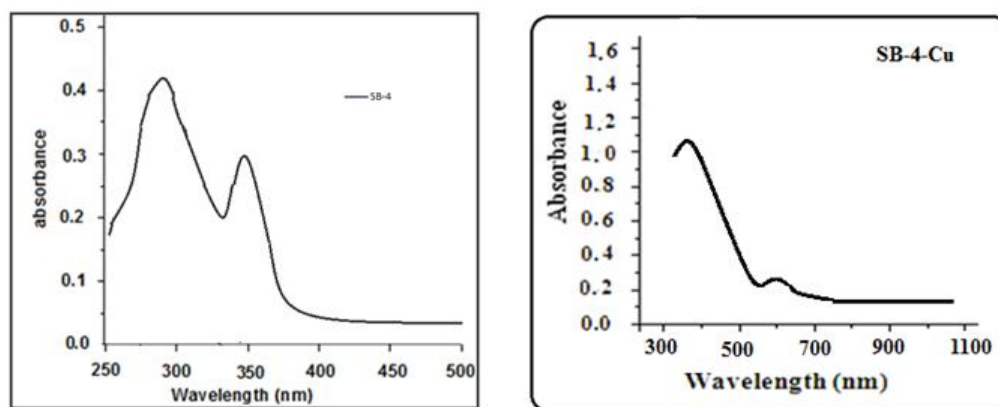


Figure-1: The UV spectra Schiff base and metal complex

3.3 Magnetic Susceptibility and molar conductance studies of complex:

The magnetic moments obtained at room temperature for the metal complex indicate Paramagnetism. For octahedral Cu(II) complexes, the magnetic moment values are expected to be in the range

1.80 to 2.20 BM. The Cu(II) complex under study exhibited magnetic moment of 1.97 BM which indicated its octahedral configuration[22-25].

The solution conductivity of the Cu (II) metal complex was determined by measuring their molar conductance values in DMSO as solvent at the concentration of 1×10^{-3} M. The observed solution conductivity $26.48 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ revealed its non-electrolytic nature.

3.4 FTIR Spectral Analysis:

The IR spectra of complexes are compared with those of ligand in order to determine the coordination sites that may be involved in chelation. The prominent FTIR data with the assignments of bond frequencies of Schiff base ligand (SB-4) and its Co(II), Ni(II) and Cu(II) metal complexes are presented in Table-2 and FTIR spectra of these compounds are represented in Figure-2.

Table-2: FTIR Spectral data (cm^{-1}) of Schiff base ligand and its metal complex

Assignments	SB-4	SB-4-Cu
ν (Hydrogen bonded O-H)	3428	-
ν (Coordinated water)	-	3325
ν (C=N)	1618	1604
ν (Ar-O)	1244	1270
ν (C-N)	1348	1368
ν (O-CH ₃)	3001	3005
ν (H ₂ O rocking)	-	825
ν (M-O)	-	551
ν (M-N)	-	435

The broad peak observed at 3428 cm^{-1} in the IR spectra of Schiff base ligand assigned to ν (O-H), was found to be disappeared in complex, thereby indicating deprotonation and formation of metal-oxygen bond. This is further supported by the shifting of phenolic ν (Ar-O) towards higher frequency, indicating the coordination of phenolate oxygen to metal ion. The ν (C=N) vibration of the Schiff base ligand (SB-4) occurs at 1618 cm^{-1} , which is shifted to a lower frequency of the complex, indicating the involvement of azomethine nitrogen in chelation with the metal ion. The observed increase in magnitude of ν (C-N) on complexation may be attributed to increase in double bond character of aryl azomethine C-N bond. It is due to π electron delocalization from the metal ion to the nitrogen atom and resonance interaction with the benzene ring. However the stretching frequencies of Methoxy O-CH₃ bonds for ligand and complex are almost same, indicating the nonparticipation of methoxy oxygen in coordination. The new bands in IR spectra of complex at 551 cm^{-1} and 435 cm^{-1} are ascribed to ν (M-O) and ν (M-N) vibrations respectively. In the IR spectrum of complex, appearance of a new broad band at 3325 cm^{-1} corresponding to the stretching frequency of ν (O-H) of H₂O indicated the presence of coordinated water. It is further confirmed by the appearance of non-ligand band in complex at 825 cm^{-1} assignable to rocking mode of water. Presence of two molecules of coordinated water in molecules of metal complexes is further confirmed by their thermogravimetric analysis. From the above observations, it can be concluded that the ligand behaves as bidentate coordinating through deprotonated phenolic oxygen and azomethine nitrogen [20-33].

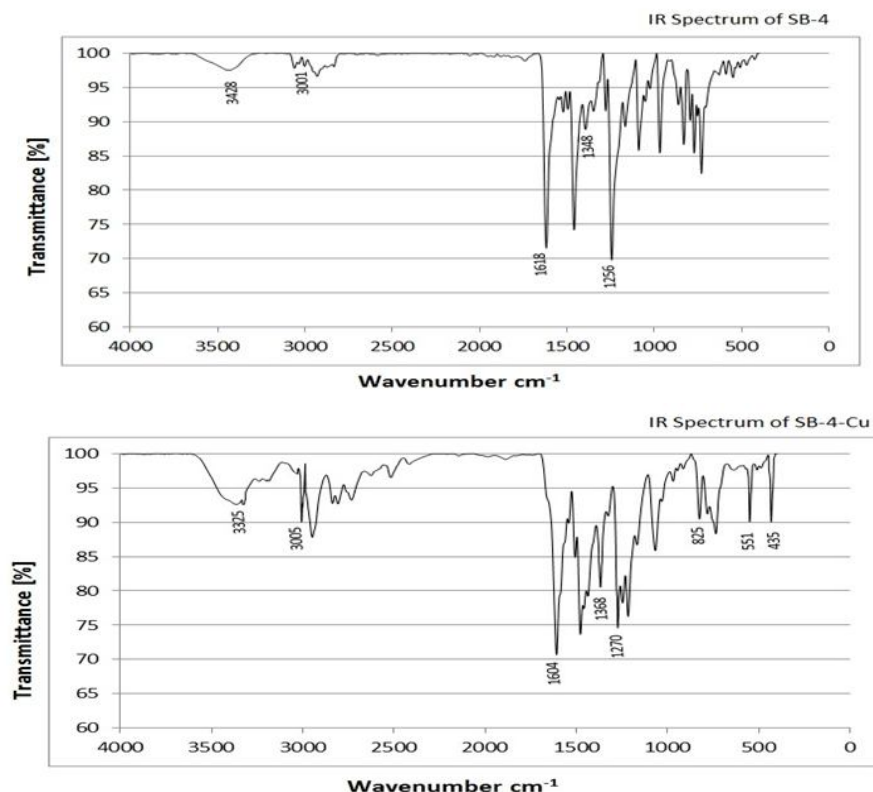


Figure-2: FTIR spectra of Schiff base-4 and its metal complex

3.5 Thermal decomposition studies of metal complex:

Thermal decomposition studies of metal complex have been undertaken to know the presence or absence of coordinated water molecules. Thermal decomposition data of metal complex of Schiff base -4 is reported in Table-3. The thermograms of complex is shown in Figure-3

Table-3 : Thermal data of metal complex

ex	Compl	Temperature (°C)	Loss of molecule	Percentage weight loss	
				Calculated	Observe d
	SB-4Cu	150°C-220°C	2H ₂ O	5.50	5.00
		220°C-550°C	Org. moiety	84.76	85.20
		>550°C	CuO	12.17	11.42

In case of Cu(II) complex observed weight loss of 5.00% between temperature range 150°C-220°C indicated the presence of two molecules of coordinated water (calculated 5.50%). The anhydrous compound further decomposed rapidly between 220°C-550°C with 85.20% weight loss corresponding to decomposition of organic moiety of the complex (calculated 84.76%) leading to the formation of 11.42% stable residue of cobalt oxide (calculated 12.17%) above 550°C. The complex is found to follow two step decomposition pattern. In the first step there is loss of two molecules of coordinated water and in the second step there is

arising from the thermal cleavage of the compound have been observed[26-33].The mass spectrum of Schiff base is shown in Figure-5.

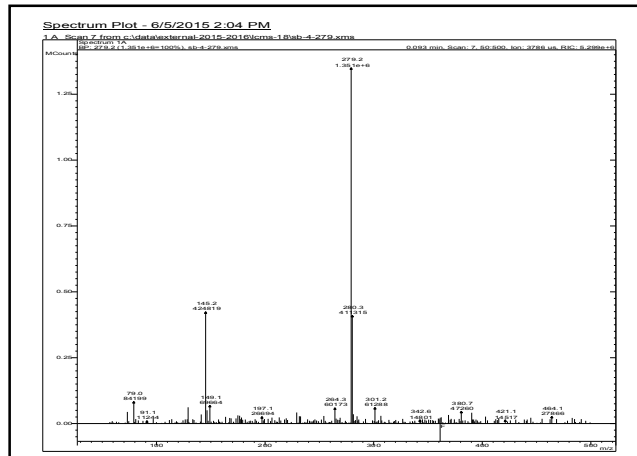


Figure- 5 : Mass spectrum of Schiff base (SB-4)

3.8X-Ray diffraction study of metal complex:

The Cu(II) metal complex of Schiff base ligand SB-4 showed sharp peaks in its diffractogram(Figure-6) indicating sharp crystalline nature of metal complex. The observed interplanar d-spacing values of the metal complex have been found to be in good agreement with their observed values(Table-3). Further, indexed data of the metal complex indicated $a \neq b \neq c$ and $\alpha = \beta = \gamma = 90^\circ$ which clearly support the orthorhombic crystal system with primitive (P) Bravais type for metal complex[30-33].

Table -3: X-Ray Diffraction Data of Metal Complex SB-4-Cu

Sys.ORTH. S.G.P*** Lambda= 1.540510 F19= 3.4(.036,155)

L20/155 M19= 4.1: 1 $\alpha = \beta = \gamma = 90^\circ$

a= 4.9211Å^ob=19.7661Å^o c= 8.9959Å^o V= 875.04 (Å^o)³

Sr No.	d-spacing Å.		Indices			SinSqTheta*E4		2Theta Deg.		
	obs.	calc.	h	k	l	obs.	calc.	obs.	calc.	diff.
1	9.883	9.883	0	2	0	60.7	60.7	8.94	8.94	0
2	4.921	4.921	1	0	0	245	245	18	18.01	0
3	4.386	4.386	0	1	2	308.4	308.4	20.2	20.23	0
4	3.708	3.715	0	3	2	431.6	429.9	24	23.93	0.046
5	3.469	3.487	1	4	0	493.1	488	25.7	25.52	0.137
6	3.291	3.294	0	6	0	547.7	546.7	27.1	27.04	0.027
7	3.14	3.147	1	2	2	601.8	599	28.4	28.33	0.067
8	2.957	2.965	0	1	3	678.6	675	30.2	30.12	0.083
9	2.859	2.869	0	2	3	725.9	720.6	31.3	31.14	0.118
10	2.727	2.729	0	3	3	798.1	796.5	32.8	32.79	0.034
11	2.559	2.561	1	0	3	906.2	904.8	35	35.01	0.029
12	2.46	2.461	2	0	0	980.2	979.9	36.5	36.49	0.005
13	2.273	2.274	1	4	3	1148	1147.8	39.6	39.61	0.004
14	2.193	2.193	0	2	4	1233.9	1233.8	41.1	41.13	0.003
15	2.14	2.139	2	4	1	1296	1296.2	42.2	42.2	-0
16	1.968	1.971	2	6	0	1532.4	1526.6	46.1	46	0.091
17	1.856	1.855	2	7	0	1722.3	1724	49	49.07	-0.03

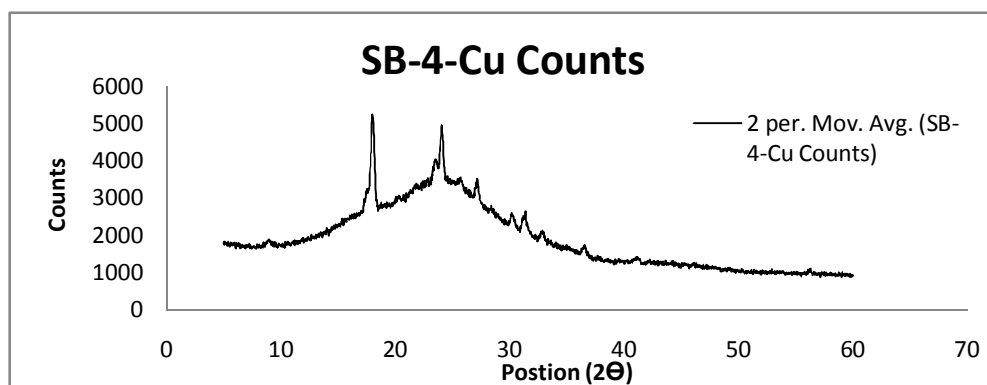


Figure-6:X-Ray Diffractogram of Metal Complex SB-4-Cu

4. ACKNOWLEDGEMENT:

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