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## SYNTHESIS AND SPECTROSCOPIC CHARACTERIZATION OF CO (II) COMPLEX DERIVED FROM SCHIFF BASE 2-METHOXY-6-(8- IMINOQUINOLINYL METHYL) PHENOL

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### ABSTRACT—

A Schiff base ligand was synthesized by condensation of o-vanillin with 8-aminoquinoline in 1:1 molar ratio. The Schiff base metal complex of Co (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  $M=Co(II)$  and  $L=$ deprotonated Schiff base ligand.

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

### INTRODUCTION

Vanillin has both phenolic and aldehyde groups while 8-aminoquinoline is an heterocyclic aromatic compound. These compounds have been found to possess biological activity. Schiff bases 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. 5-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 Co(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 80 FTIR system range  $400-4000\text{ cm}^{-1}$  (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.

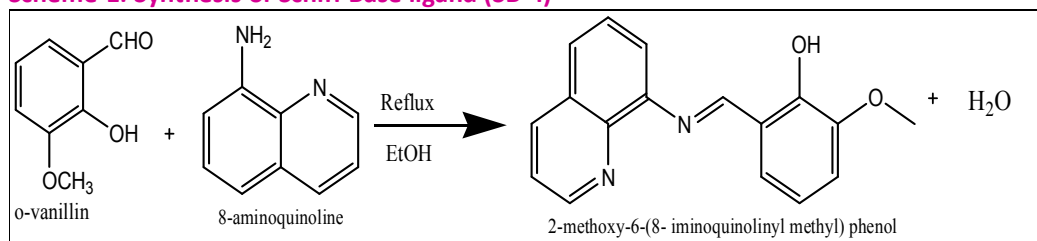
### 2.2 Reagents:

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

### 2.3 Synthesis of Schiff base ligand (SB-4)

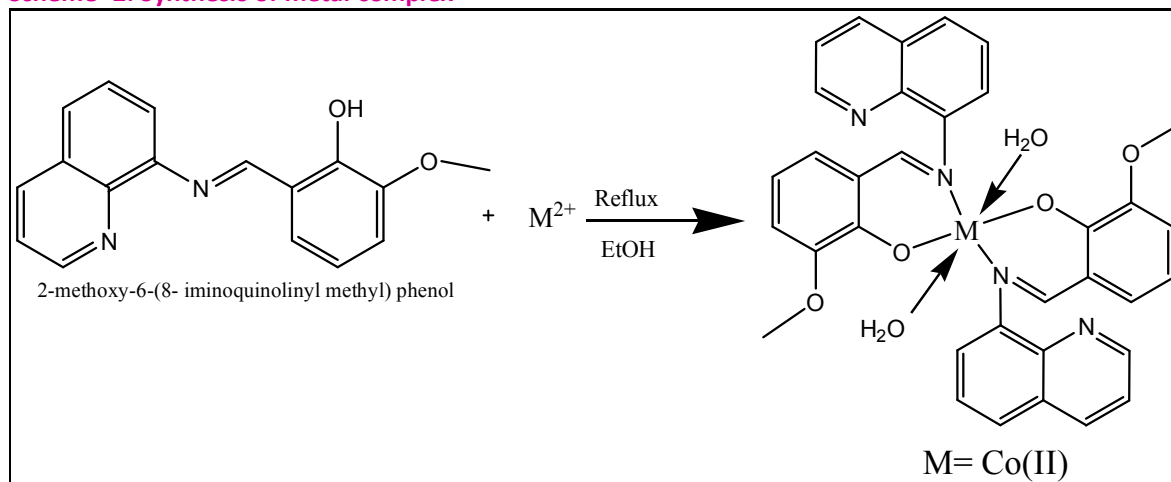
20 mmol (3.04g) of o-vanillin is dissolved in absolute ethanol. Then it was added dropwise into 20 mmol (2.88g) of ethanolic solution of 8-aminoquinoline. The mixture was refluxed for 2 hours then cooled and filtered [10-15]. Intense red colored crystals of Schiff base SB-4 were formed (yield 89%, 5.0 g). The crystals were washed with cold ethanol and anhydrous diethyl ether and dried over anhydrous  $\text{CaCl}_2$ . 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  $\text{CaCl}_2$ . The Co(II) metal complex of Schiff base (SB-4) was prepared by above general method using salt  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ . The preparation of metal complex is shown in Scheme -2.

**Scheme -2: Synthesis of metal complex**

Schiff base (SB-4) and its Co (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 was 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%
<b>SB-4</b>	C <sub>17</sub> H <sub>14</sub> O <sub>2</sub> N <sub>2</sub>	103	278	Red	72.91 (73.38)	4.87 (5.03)	9.98 (10.07)	-
<b>SB-4-Co</b>	C <sub>34</sub> H <sub>26</sub> O <sub>4</sub> N <sub>4</sub> Co.(H <sub>2</sub> O) <sub>2</sub>	>350	648.93	Dark Pink	62.16 (62.87)	4.77 (4.62)	8.47 (8.62)	8.88 (9.08)

**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 complexes, 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 spectra of Co(II) complex showed two absorptions bands associated with d-d transitions at 639 nm and 531 nm due to  ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$  ( $\nu_2$ ) and  ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(P)$  ( $\nu_3$ ) transitions respectively. These observed d-d transitions for metal complex are consistent with octahedral geometry of Co(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.

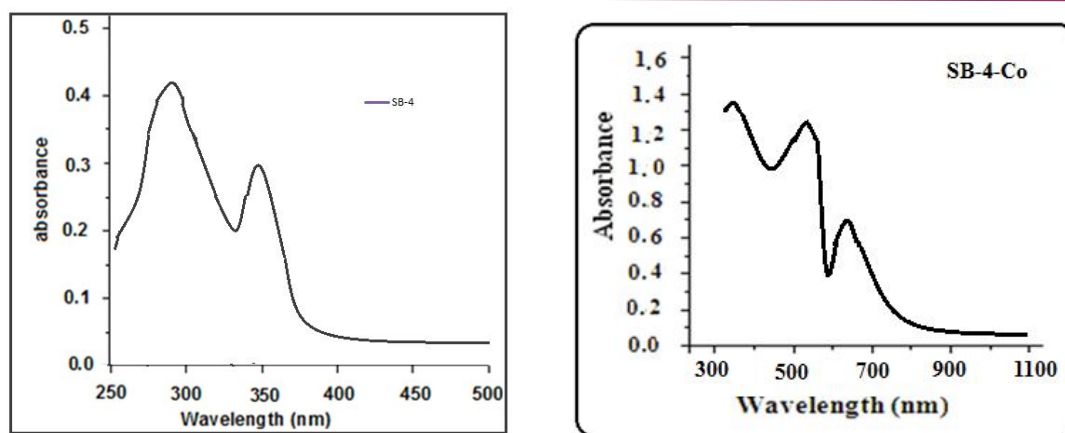


Figure-1: The UV spectra Schiff base and metal complex

### 3.3 Magnetic Susceptibility and molar conductance studies of complex:

The magnetic moments obtained at room temperature for the metal complex indicated Paramagnetism. The Co(II) complex showed the magnetic moment of 4.90 BM. The spin free octahedral complex of Co(II) is reported to exhibit magnetic moment in the range of 4.70 to 5.20 BM. Hence the observed moment of Co (II) complex under study indicates that, it has an octahedral configuration. [22-25].

The solution conductivity of the Co (II) metal complex was determined by measuring their molar conductance values in DMSO as solvent at the concentration of  $1 \times 10^{-3}$  M. The observed solution conductivity  $34.41 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$  revealed its non-electrolytic nature.

### 3.4 FTIR Spectral Analysis:

The IR spectrum of complex was compared with that 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) metal complex was presented in Table-2 and FTIR spectra of these compounds are represented in Figure-2.

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

Assignments	SB-4	SB-4-Co
$\nu$ (Hydrogen bonded O-H)	3428	-
$\nu$ (Coordinated water)	-	3335
$\nu$ (C=N)	1618	1605
$\nu$ (Ar-O)	1244	1265
$\nu$ (C-N)	1348	1372
$\nu$ (O-CH <sub>3</sub> )	3001	3003
$\nu$ (H <sub>2</sub> O rocking)	-	831
$\nu$ (M-O)	-	556
$\nu$ (M-N)	-	436

The broad peak observed at  $3428 \text{ cm}^{-1}$  in the IR spectra of Schiff base ligand assigned to  $\nu$ (O-H), was found to be disappeared in all the complexes, thereby indicating deprotonation and formation of metal-oxygen bond. This is further supported by the shifting of phenolic  $\nu$ (Ar-O) towards higher frequency, indicating the coordination of phenolate oxygen to metal ion. The  $\nu$ (C=N) vibration of the Schiff base ligand (SB-4) occurs at  $1618 \text{ cm}^{-1}$ , 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  $\nu$ (C-N) on complexation may be attributed to increase in double bond character of aryl azomethine C-N bond. It is due

to  $\pi$  electron delocalization from the metal ion to the nitrogen atom and resonance interaction with the benzene ring. However the stretching frequencies of Methoxy O-CH<sub>3</sub> bonds for ligand and complexes are almost same, indicating the nonparticipation of methoxy oxygen in coordination. The new bands in IR spectra of complexes at 56 cm<sup>-1</sup> and 436 cm<sup>-1</sup> are ascribed to  $\nu$ (M-O) and  $\nu$ (M-N) vibrations respectively. In the IR spectrum of complex, appearance of a new broad band at 3335 cm<sup>-1</sup> corresponding to the stretching frequency of  $\nu$ (O-H) of H<sub>2</sub>O indicated the presence of coordinated water. It is further confirmed by the appearance of non-ligand band in complexes in the region 831 cm<sup>-1</sup> 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].

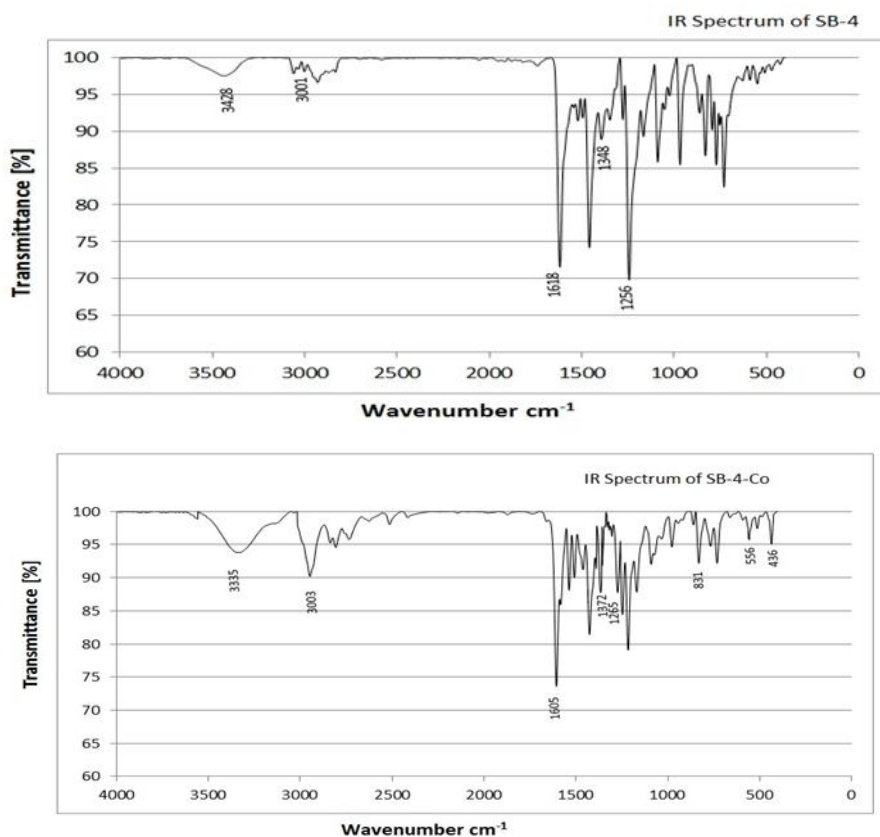


Figure-2: FTIR spectra of Schiff base-4 and its metal complex

### 3.5 Thermal decomposition studies of metal complexes:

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

Table-3 : Thermal data of metal complexes

Complex	Temperature	Loss of molecule	Percentage weight loss
---------	-------------	------------------	------------------------

	(°C)		Calculated	Observed
SB-4 Co	170°C-560°C	2H <sub>2</sub> O	5.54	5.71
	250°C-530°C	Org. moiety	85.37	81.65
	>530°C	CoO	11.54	11.42

In case of Co(II) complex observed weight loss of 5.71% between temperature range 170°C-250°C indicated the presence of two molecules of coordinated water (calculated 5.54%). The anhydrous compound further decomposed rapidly between 250°C-530°C with 81.65% weight loss corresponding to decomposition of organic moiety of the complex (calculated 85.37%) leading to the formation of 11.42% stable residue of cobalt oxide (calculated 11.54%) above 530°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 oxidative decomposition of organic part of the ligand leading to the formation of stable residue of metal oxide. Thermal studies supported the octahedral structure of the metal complex indicating presence of two coordinated water molecules [15-25].

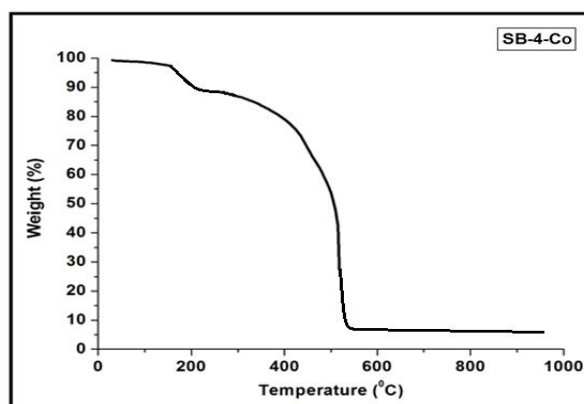


Figure-3: Thermogram of metal complex

### 3.6 H<sup>1</sup> NMR Spectroscopic Studies:

The H<sup>1</sup> NMR Spectrum of the Schiff base (SB-4) Shows D<sub>2</sub>O exchangeable broad singlet at 14.544ppm integrating for one proton is assigned to –OH. The H<sup>1</sup> NMR spectrum of Schiff base shows multiplet in the range 6.856-8.994ppm due to aromatic protons. The -N=CH- proton of Schiff base exhibits singlet at 8.998ppm. The H<sup>1</sup> NMR spectrum of Schiff base is shown in Figure-4.

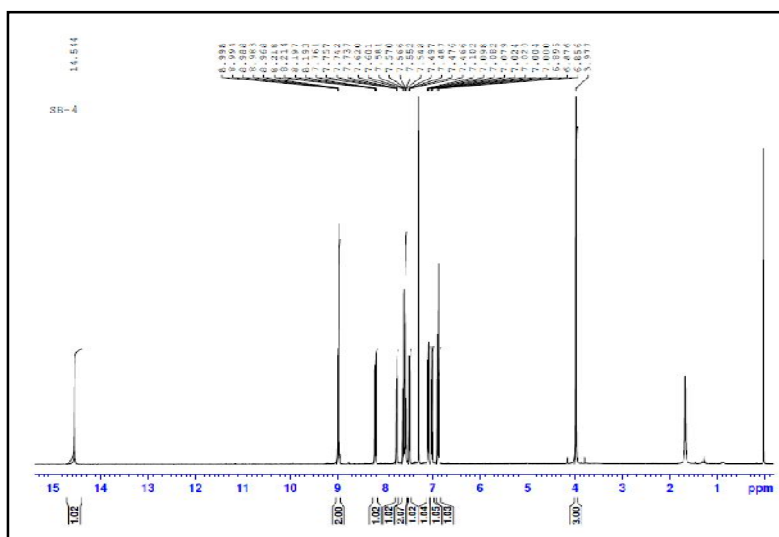


Figure-4 :  $^1\text{H}$  NMR spectra of Schiff Base (SB-4)**3.7 Mass spectroscopic Studies:**

The mass spectrum of Schiff base (SB-4) was recorded. It shows parent peak due to molecular ion ( $\text{M}^+$ ). The proposed molecular formula of Schiff base was confirmed by comparing its molecular formula weight with  $m/z$  value. The molecular ion peak with  $m/z = 279.3$ , corresponds with the proposed molecular formula of Schiff base. In addition, the mass spectrum exhibited peaks assignable to various fragments arising from the thermal cleavage of the compound have been observed[26-33]. The mass spectrum of Schiff base is shown in Figure-5.

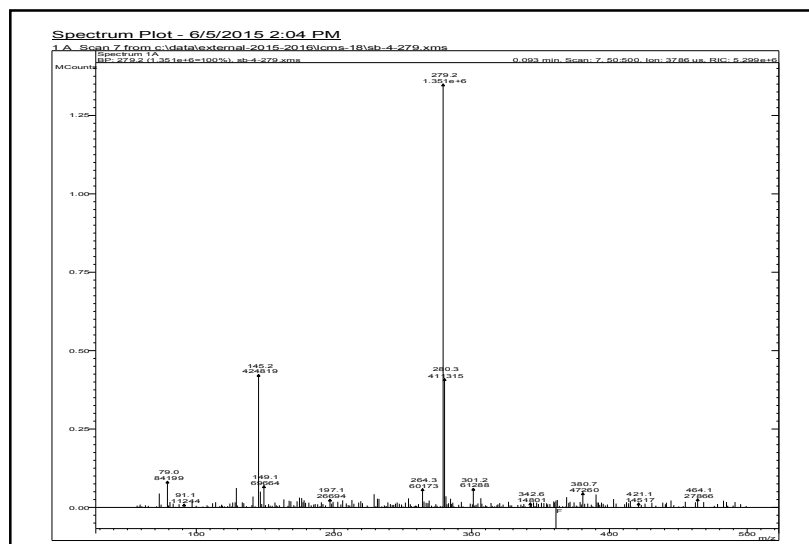


Figure- 5 : Mass spectrum of Schiff base (SB-4)

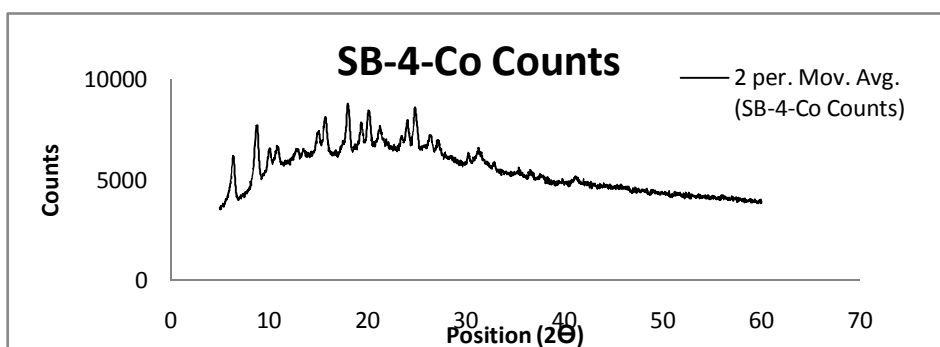
**3.8 X-Ray diffraction study of metal complex:**

The Co(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[30-34].

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

Sys.ORTH. S.G.P\*\*\*      Lambda= 1.540510 F26= 1.7( .054,288)  
 L30/288 M20= 2.4: 2       $\alpha = \beta = \gamma = 90^\circ$   
 a=14.6999A°. b=13.8635A° c= 8.7938A° V= 1792.11 (A°)<sup>3</sup>

Sr No.	d-spacing A.		Indices			SinSqTheta*E4		2Theta Deg.		
	obs.	calc.	h	k	l	obs.	calc.	obs.	calc.	diff.
1	13.86	13.86	0	1	0	30.9	30.9	6.37	6.37	0
2	10.09	10.09	1	1	0	58.3	58.3	8.76	8.76	0
3	8.794	8.794	0	0	1	76.7	76.7	10.1	10.05	0
4	6.878	6.932	0	2	0	125.4	123.5	12.9	12.76	0.1
5	6.51	6.494	2	1	0	140	140.7	13.6	13.62	-0.03
6	5.633	5.64	2	0	1	187	186.5	15.7	15.7	0.02
7	4.918	4.9	3	0	0	245.3	247.1	18	18.09	-0.07
8	4.609	4.62	3	1	0	279.3	278	19.2	19.19	0.045
9	4.407	4.408	1	3	0	305.4	305.3	20.1	20.13	0.005
10	4.178	4.191	0	1	2	340	337.8	21.3	21.18	0.07
11	3.703	3.713	0	2	2	432.6	430.4	24	23.95	0.064
12	3.579	3.574	2	3	1	463.3	464.4	24.9	24.89	-0.03
13	3.377	3.373	1	4	0	520.3	521.4	26.4	26.4	-0.03
14	3.282	3.273	3	0	2	550.9	554	27.2	27.23	-0.08
15	2.948	2.953	2	4	1	682.6	680.5	30.3	30.24	0.048
16	2.86	2.868	0	1	3	725.4	721.4	31.3	31.16	0.09
17	2.725	2.725	1	5	0	799.1	799.2	32.8	32.84	-0
18	2.54	2.534	2	2	3	919.3	923.8	35.3	35.39	-0.09
19	2.458	2.45	6	0	0	982.3	988.4	36.5	36.65	-0.12
20	2.391	2.387	5	3	1	1038	1040.9	37.6	37.64	-0.06
21	2.268	2.261	4	1	3	1153	1160.7	39.7	39.84	-0.14
22	2.193	2.199	0	0	4	1233.3	1227.5	41.1	41.02	0.101

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



**4. ACKNOWLEDGEMENT:**

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