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## Synthesis, Catalysis And Biological Study of Transition Metal(II) Chelates With ONO-Tridentate Schiff Base Ligand

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### ABSTRACT

A new series of chelates was synthesized from metal perchlorates of bivalent cobalt, nickel and copper with tridentate schiff base ligand (5-BSA). The schiff base having ONO donor site obtained from anthranilic acid and 5-bromosalicylaldehyde in methanol. UV Visible, FT-IR and mass spectroscopy, elemental analysis, magnetic susceptibility, molar conductance and thermal analysis techniques were used to investigate the structural features of chelates and ligand. The thermal analysis was carried out for synthesized metal chelates and the values of activation energy for metal chelates were also measured by using the broido method which present the thermal behavior of chelates. The study for electrolytic nature of Co(II), Ni(II) and Cu(II) chelates were carried out at room temperature and the catalytic characteristics of chelates were also studied. The uncomplexed ligand and its metal (II) chelates were evaluated for antibacterial property against gram positive and gram negative bacterial species.

**KEYWORDS:** Metal chelates; schiff base ligand; catalysis; biological activity

### INTRODUCTION

Mostly the schiff bases have been found to be useful as chelating ligand in coordination chemistry. A huge number of schiff bases and their chelates have been studied interestingly due to their emergent properties. Recently schiff bases are attracting the attention of chemists on their selves because of their high affinity toward transition metals for the chelation. They are also having the great ability of complexing toward the toxic metals [1][2]. Metal chelates, those derived from schiff bases contain the versatile properties in medical science and in industries. Schiff base

supported chelates are found to exhibit a massive range of biological properties e.g. antimalarial, antifungal, antiviral, antipyretic, antibacterial, anti-inflammatory etc. Lots of schiff base chelates are having outstanding catalytic activity in various kinds of reactions [3-5]. The complexes of the schiff base derived from 5-bromosalicylaldehyde and 2-aminobenzimidazole found to act as potent antifungal activity versus aspergillus niger and candida albicans [6].

Bivalent copper, cobalt and nickel metal's complexes with 5-bromosalicylaldehyde and *o*-phenylenediamine derived schiff base ligand were studied as excellent antimicrobial agent compared to their free schiff base ligand [7]. A copper metal was found to show good medicinal property on complexation with schiff base ligand prepared from 5-bromosalicylaldehyde and tolylamine [8]. Coordination of several compounds with such transition metal ions, often enhance their biological activity [9]. Such number of complexes have been studied for their medicinal properties, such as complexes of transition metals examined as antiproliferative agent [10], anti-infective agent, antidiabetic and anticancer agent [11,12]. A large number of transition metal complexes attracted vast attentions because of their important catalytic property [13-16].

## EXPERIMENTAL

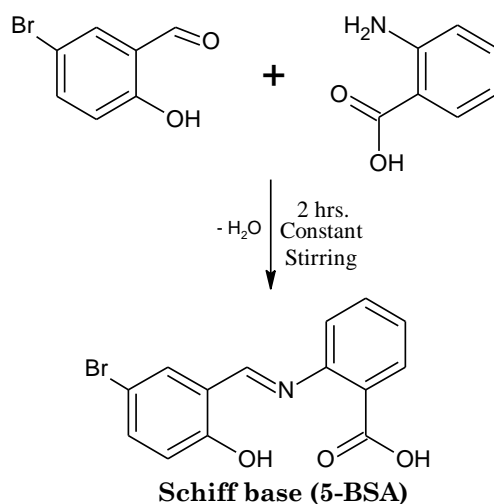
### Materials and instruments

Whole experimental work was carried out using A.R. grade materials and spectroscopic grade solvents. Metal perchlorates of copper, cobalt and nickel were prepared to synthesize the metal chelates by using the metal carbonates in the standardized 0.2 N solution of perchloric acid. The thermal analysis was carried out for chelates in the temperature range of room temp.-1000 °C on Perkin Elmer, USAA, Diamond TG/DTA. Metal chelates and schiff base were analyzed for elemental analysis on Thermo Finnigan, Flash EA 112 series (Italy) CHN analyzer. UV-Visible

spectral analysis was performed on Perkin Elmer lambda 950 UV-VIS-NIR in the range of 200 nm - 2500 nm. The infrared spectra (4000-400  $\text{cm}^{-1}$ ) with Infrared Spectrophotometer of Shimadzu, IR Affinity, 1 S using KBr disks. For powdered samples, the magnetic susceptibility was measured at room temperature based on Gouy's method using  $\text{Hg}[\text{Co}(\text{NCS})_4]$  as a calibrant. Molar conductance of chelates in DMSO solvent was examined at room temperature. On the basis of literature method metal content in synthesized metal(II) chelates was measured experimentally. Catalytic study for such selected redox reactions as well as for reductive coupling reaction were carried out and antibacterial activity for synthesized compounds was examined by zone of inhibition method.

### Tridentate schiff base ligand (5-BSA) formation

Added the 20 ml methanolic solution of anthranilic acid (1.37 gm, 0.01 mole) dropwise to the 20 ml methanolic solution of 5-bromosalicylaldehyde (2.01 gm, 0.01 mole) with constant stirring. In the reaction mixture, after the continuous 2 hours mechanical stirring the dark orange schiff base product was obtained and the solid product was filtered off and purified by recrystallization in cold methanol. The recrystallized product was dried in oven at 40-45 °C temp. and the final yield was obtained with 91 % yield. The melting point of the schiff base was 158 °C (Scheme 1).



**Scheme 1: Synthesis of the schiff base ligand**

### Synthesis of metal(II) chelates

70 ml, 0.1 M solution of schiff base ligand (5-BSA) mixed with 70 ml, 0.1 M solution of metal perchlorate (1:1 molar ratio). This reaction mixture was refluxed at 110-120 °C temperature on heating mantle for 4 to 5 hrs. and then it was cooled to room temperature for 2-3 hrs. and the pH of the reaction mixture was adjusted up to 5-6 pH using 0.1 N alkali solution to acquire nearly neutral condition for the precipitation of product. The isolated chelate product was filtered and washed with hot methanol and deionized water. The product was dried at 45-50 °C temperature in

oven. All metal chelates were synthesized through the same process.

### RESULT AND DISCUSSION

As described in the experimental section, the tridentate ligand and its metal chelates were synthesized and those were analyzed by such analytical techniques like elemental analysis, FTIR, electronic spectra, thermal analysis (TGA) etc. Metal content was determined by E.D.T.A. complexometric titration using the suitable indicator [17]. Such physical measurements for synthesized compounds are listed in Table 1.

**Table 1: Physical data of ligand and metal chelates**

Compound [Mol. Formula]	Formula weight (gm/mol)	Color	Melting Point (° C)	Molar conductance (S cm <sup>2</sup> mol <sup>-1</sup> )
5-BSA [C <sub>14</sub> H <sub>10</sub> NO <sub>3</sub> Br]	320.14	Dark orange	158	-
Co-5-BSA [C <sub>14</sub> H <sub>11</sub> NO <sub>4</sub> BrCo] H <sub>2</sub> O	413.08	Buff color	>300	2.683
Ni-(5-BSA) <sub>2</sub> [C <sub>28</sub> H <sub>18</sub> N <sub>2</sub> O <sub>6</sub> Br <sub>2</sub> Ni]	696.95	Light green	>300	0.592
Cu-5-BSA [C <sub>14</sub> H <sub>10</sub> NO <sub>4</sub> BrCu]	399.68	Dark brown	>300	0.518

### Elemental Analysis

The obtained values of elemental analysis for the schiff base ligand and its metal chelates are consistent with the calculated values (Table 2).

**Table 2: Results of Elemental analysis**

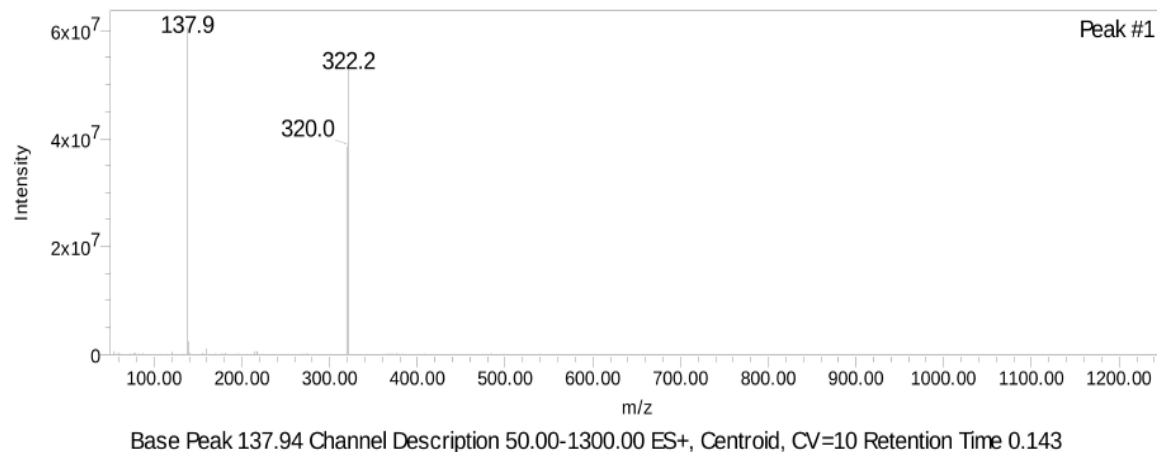
Compound	% C		% H		% N		% Metal	
	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Pract.
5-BSA	52.52	51.59	3.15	3.05	4.37	4.26	-	-
Co-5-BSA	40.71	44.8	2.93	3.58	3.39	5.27	14.27	13.88
Ni-(5-BSA) <sub>2</sub>	48.25	49.81	2.60	3.69	4.02	7.48	8.42	11.73
Cu-5-BSA	42.07	43.90	2.52	2.23	3.50	3.55	15.90	19.06

**Calc.**= Theoretically calculated value, **Found**= Values recorded by the instrument, **Pract.**= % of metal content obtained by EDTA complexometric titration.

### Mass spectrum of the schiff base ligand

Mass spectrum of the synthesized schiff base ligand (5-BSA) (Fig. 1) supports the proposed formula by detecting the following peaks. The peak observed at m/z 137.9 (base peak) is due to C<sub>7</sub>H<sub>6</sub>NO<sub>2</sub> fragment. In the following mass

spectrum, the molecular peak M of ligand is observed at m/z 320 which is consistent with a formula weight of the ligand and the peak observed at m/z value of 322.2 is attributed to the isotopic peak [M+2] conforming presence of Br in the molecule.



**Fig. 1: Mass spectrum of the schiff base ligand (5-BSA)**

### Infrared spectra

Infrared spectroscopy is a suitable and important technique to identify the bonding nature of ligand to metal ion in metal chelates and in other compounds. For the synthesized schiff base ligand (5-BSA) and its metal chelates, IR spectra were recorded in the range of  $4000\text{ cm}^{-1}$  to  $400\text{ cm}^{-1}$

using KBr disks. The infrared spectra of metal chelates compared with the parent ligand in order to assign the coordination sites that may be involved in metal chelates. The IR data of schiff base ligand (5-BSA) and its metal chelates are listed in Table 3.

**Table 3: Infrared spectral data of the synthesized compounds**

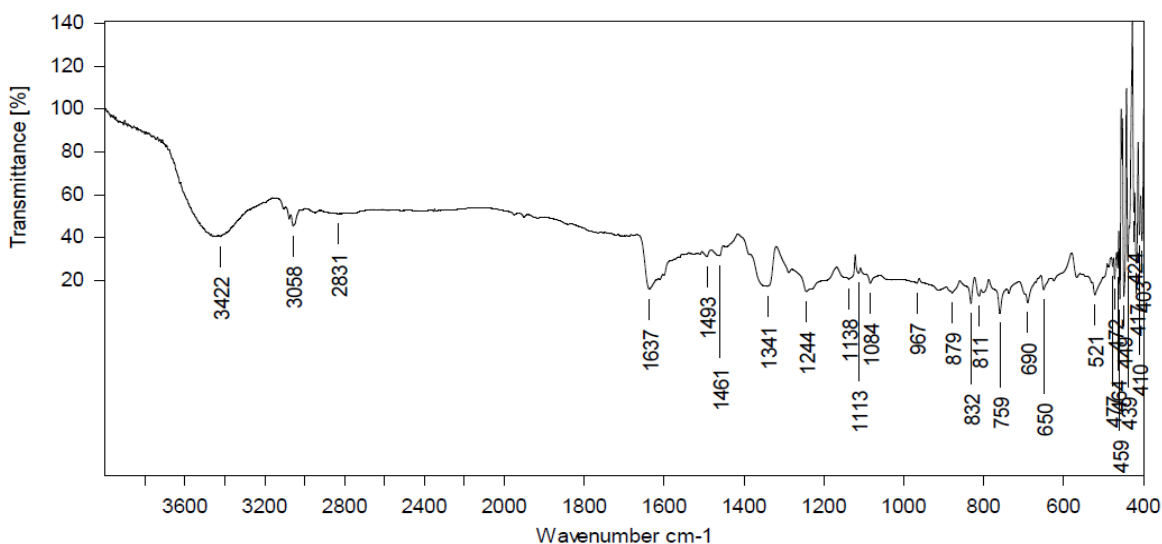
Compound	Phenolic		Azo-methine $\nu(\text{HC}=\text{N})$ ( $\text{cm}^{-1}$ )	COOH			$\nu(\text{H}_2\text{O})$ ( $\text{cm}^{-1}$ )	M-N ( $\text{cm}^{-1}$ )	M-O ( $\text{cm}^{-1}$ )
	$\nu(\text{O-H})$ ( $\text{cm}^{-1}$ )	$\nu(\text{C-O})$ ( $\text{cm}^{-1}$ )		$\nu(\text{C=O})/$ $\nu(\text{COO}^-)^*$ ( $\text{cm}^{-1}$ )	$\nu(\text{O-H}),$ ( $\text{cm}^{-1}$ )	$\nu(\text{C-O})$ ( $\text{cm}^{-1}$ )			
5-BSA	3422	1244	1600	1637 1614	3058	1341	-	-	-
Co-5-BSA	-	1242	1591	*1536 <sub>(asy.)</sub> , *1458 <sub>(sym.)</sub>	-	1326	3452	517	444
Ni-(5-BSA) <sub>2</sub>	-	1241	1592	1614	2930	1327	-	493	450
Cu-5-BSA	-	1242	1597	1635	2924	1320	3450	557	446

These comparisons reveal that the stretching vibrations of phenolic OH and phenolic C-O in the free ligand appear at  $3422$  and  $1244\text{ cm}^{-1}$  respectively and the stretching bands of phenolic C-O have been found at lower values in Co, Ni and Cu chelates indicating the coordination through phenolic oxygen (M-O) which is also confirmed by the bands observed at  $444$ - $450\text{ cm}^{-1}$  those are found to be absent in the free ligand. In the IR spectrum of ligand, the absorption band of  $1600\text{ cm}^{-1}$  appeared due to azomethine which on chelation, is shifted to lower wave numbers by  $3$ - $9\text{ cm}^{-1}$  in metal chelates indicating the

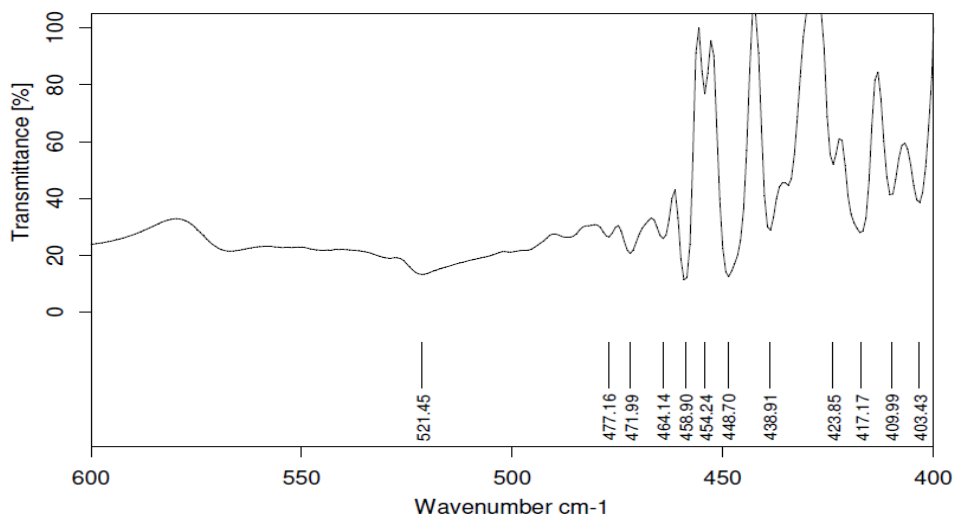
participation of azomethine nitrogen in coordination with central metal ion (M-N) which is also confirmed by the bands observed at  $493$ - $557\text{ cm}^{-1}$  which have been found missing in the free ligand [18-21]. In IR spectrum of the free ligand, the stretching frequency bands of  $1637$  and  $3058\text{ cm}^{-1}$  assigned to carboxylic C=O and O-H respectively which due to the chelation, the frequency band of  $1637\text{ cm}^{-1}$  shifted up to  $23\text{ cm}^{-1}$  lower suggesting the coordination between carboxylic C=O and central metal ion in the chelates of Ni(II) and Cu(II) while the stretching band of O-H (carboxylic) has been found to shift

to higher values by 128-134  $\text{cm}^{-1}$  in Ni(II) and Cu(II) chelate [22-24]. The appearance of two bands at 1536  $\text{cm}^{-1}$  and 1458  $\text{cm}^{-1}$  attributed to  $\nu_{\text{asy.}}(\text{COO}^-)$  and  $\nu_{\text{sym.}}(\text{COO}^-)$  respectively imply the participation of carboxylate oxygen in the coordination with cobalt metal ion in the chelate of Co(II) [25-27]. The stretching band of carboxylic C–O in the ligand is observed at 1341  $\text{cm}^{-1}$  while in metal chelates this frequency band has been found to be observed at 1320-1327  $\text{cm}^{-1}$ . The metal chelate of Co(II) exhibited the broad bands at 3232  $\text{cm}^{-1}$  and 3452  $\text{cm}^{-1}$  assigned to water of coordination and water of crystallization respectively, this is also supported by the TGA analysis of Co(II) chelate. In the chelate of Cu(II),

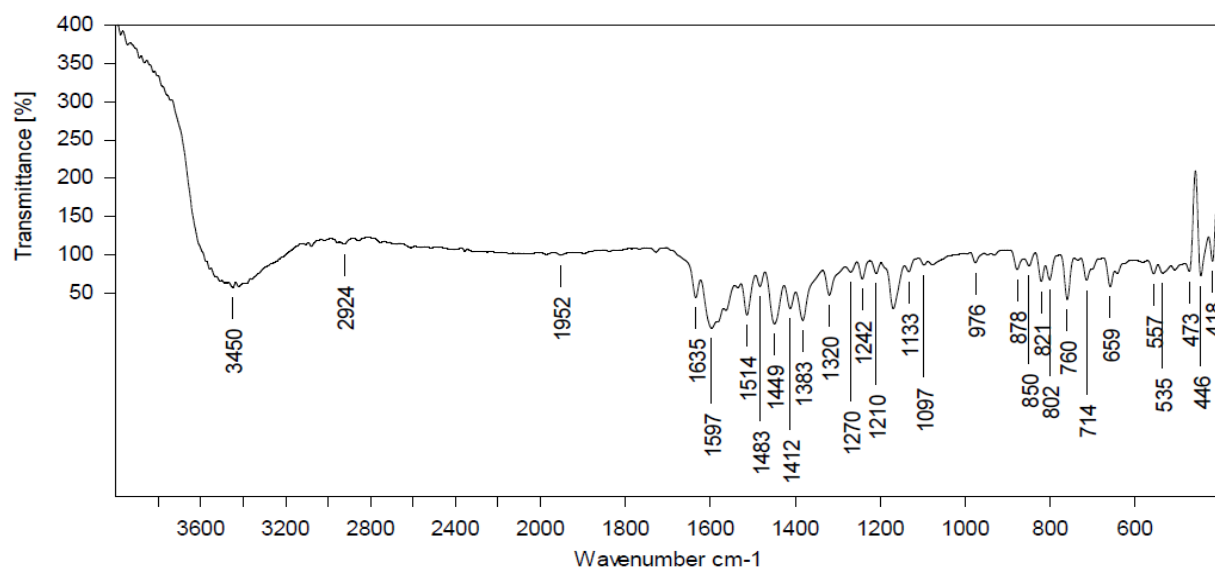
the stretching band at 3450  $\text{cm}^{-1}$  is attributed to free  $\text{OH}^-$  ion which satisfies the fourth coordination site in Cu-chelate [28-31]. Thus, the infrared spectra of schiff base ligand (5-BSA) and its chelates of Co(II), Ni(II) and Cu(II) asserted that the schiff base ligand act as a tridentate ligand with ONO donor sites and coordinated to the central metal ion through phenolic oxygen, azomethine nitrogen as well as carboxylic/carboxylate oxygen while other coordination site in cobalt chelate is satisfied by  $\text{H}_2\text{O}$  and in Cu(II) chelate, coordinated hydroxyl ion satisfy the other coordination site which fulfil the square planar geometry of Cu-chelate.



**Fig. 2: Infrared spectrum of the schiff base ligand (5-BSA)**



**Fig. 2(a): Infrared spectrum of the schiff base ligand (600  $\text{cm}^{-1}$  to 400  $\text{cm}^{-1}$ )**



**Fig. 3: Infrared spectrum of Cu-5-BSA**

#### Molar Conductivity measurement

The molar conductivity of metal chelates was measured using  $10^{-3}$  M solution in DMSO solvent at room temperature ( $35\text{ }^{\circ}\text{C}$ ). The values of molar conductance for Co(II), Ni(II) and Cu(II) chelates are listed in Table 1. The molar conductivity values of 2.68, 0.59 and  $0.52\text{ S cm}^2\text{ mol}^{-1}$  implied the non-electrolytic nature for Co(II), Ni(II) and Cu(II) chelates. Thus, all chelates were non-electrolytes [32].

#### Electronic spectra and Magnetic moment

The electronic spectra of selected compounds are presented in Fig. 4 & 5. The electronic spectra of metal chelates were recorded from solid samples at room temperature using UV-Reflectance technique while the electronic spectrum of schiff base (5-BSA) was recorded using DMSO solvent and magnetic moment of the synthesized metal chelates were also recorded at room temperature. The electronic spectral data and magnetic moment values of Co(II), Ni(II) and Cu(II) chelates are listed in Table 4. In the electronic

spectrum of 5-BSA ligand, three bands are observed at  $38240$ ,  $48899$  and  $29498\text{ cm}^{-1}$  which can be assigned to  $\pi\rightarrow\pi^*$  and  $n\rightarrow\pi^*$  transitions. The electronic spectrum of Co(II) chelate exhibits the absorption bands at  $8658$ ,  $21598$  and  $26315\text{ cm}^{-1}$  in which first two absorption bands are attributed to  ${}^4\text{A}_2\rightarrow{}^4\text{T}_{1g}(\text{F})$  and  ${}^4\text{A}_2\rightarrow{}^4\text{T}_1(\text{P})$  transitions respectively while the third one band implied the charge transfer band and the magnetic moment value of  $4.47\text{ B.M.}$  for Co(II) chelate proposes the possibility of tetrahedral geometry. Three bands of  $9478$ ,  $16863$  and  $26315\text{ cm}^{-1}$  in the electronic spectrum of Ni(II) chelate are associated with  ${}^3\text{A}_{2g}\rightarrow{}^3\text{T}_{2g}$ ,  ${}^3\text{A}_{2g}\rightarrow{}^3\text{T}_{1g}(\text{F})$  and  ${}^3\text{A}_{2g}\rightarrow{}^3\text{T}_{1g}(\text{P})$  transitions respectively and  $3.21\text{ B.M.}$  value of magnetic moment support the possibility of octahedral environment around Ni(II) ion.  $1.89\text{ B.M.}$  value of magnetic moment and two absorption bands at  $13280\text{ cm}^{-1}$  and  $21231\text{ cm}^{-1}$  assigned to  ${}^2\text{B}_{1g}\rightarrow{}^2\text{E}_{1g}$  and  ${}^2\text{B}_{1g}\rightarrow{}^2\text{A}_{1g}$  transitions respectively support the possibility of square planar geometry of Cu(II) chelate [33-36].

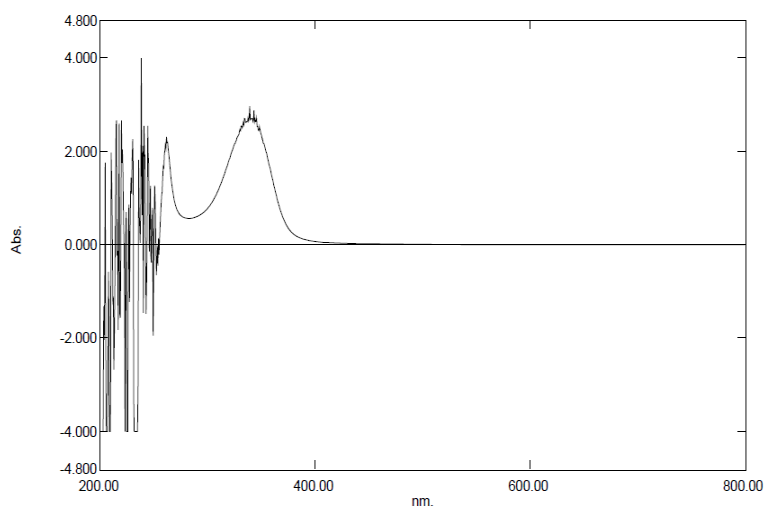


Fig. 4: Electronic spectrum of 5-BSA (ligand)

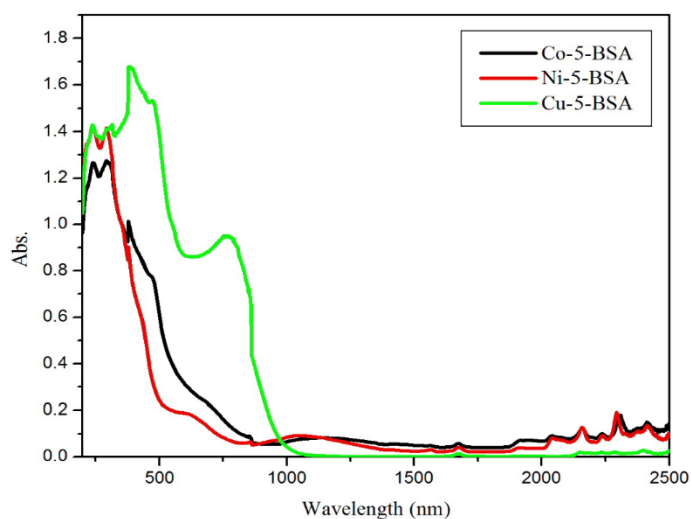


Fig. 5: Electronic spectra of metal chelates

Table 4: Electronic spectral data of compounds

Compound	Absorption $\lambda_{\max}$ (cm <sup>-1</sup> )	Assignment	Magnetic moment $\mu_{\text{eff}}$ (B.M.)	Possible Geometry
5-BSA	29498.52	$n \rightarrow \pi^*$	-	-
	38240.91	$\pi \rightarrow \pi^*$		
	48899.75	$\pi \rightarrow \pi^*$		
[Co(5-BSA)H <sub>2</sub> O]H <sub>2</sub> O	8658.01	$^4A_2 \rightarrow ^4T_{1g}(F)$	4.47	Tetrahedral
	21598.27	$^4A_2 \rightarrow ^4T_1(P)$		
	26315.79	LMCT		
[Ni(5-BSA) <sub>2</sub> ]	9478.67	$^3A_{2g} \rightarrow ^3T_{2g}$	3.21	Octahedral
	16863.4	$^3A_{2g} \rightarrow ^3T_{1g}(F)$		
	26315.8	$^3A_{2g} \rightarrow ^3T_{1g}(P)$		
[Cu(5-BSA)OH]	13280.2	$^2B_{1g} \rightarrow ^2E_{1g}$	1.89	Square Planar
	21231.4	$^2B_{1g} \rightarrow ^2A_{1g}$		

### Thermal analysis (TGA)

The study of thermo gravimetric analysis for Co(II), Ni(II) and Cu(II) chelates was carried out in the inert atmosphere within the temperature range from room temperature (R.T.) to 1000 °C with the heating rate of 10 °C/min. (Fig. 6). Within the congruent temperature range, the weight loss for each metal chelates is calculated. The determined temperature ranges, percentage weight losses and presence of water of crystallization and water of coordination in solid metal chelates are listed in Table 5. Between the temperature range of room temperature to 150 °C, the TG curve of cobalt chelate shows 5.51 % weight loss (22.81 gm/mole) suggests the loss of a

lattice water molecule as well as the cobalt chelate lost a water molecule of coordination with 6.66 % weight loss (27.58 gm/mole) within the temperature range of 150 °C to 250 °C. The % weight loss of 0.56 (3.89 gm/mole) and 0.49 (1.96 gm/mole) indicate the absence of lattice water molecule in chelates of Ni(II) and Cu(II) respectively between the temperature range of room temperature to 150 °C while between the temperature range of 150 °C to 250 °C, the TG data assert no loss of water molecule in Ni(II) and Cu(II) chelates respectively suggest the absence of water molecule of coordination in the chelate of Ni(II) and Cu(II).

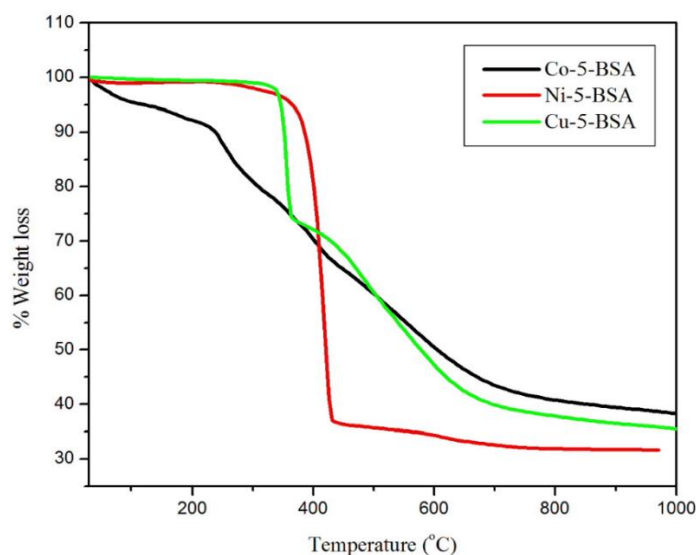


Fig. 6: TGA of metal chelates

Table 5: Water content and weight loss data of metal chelates

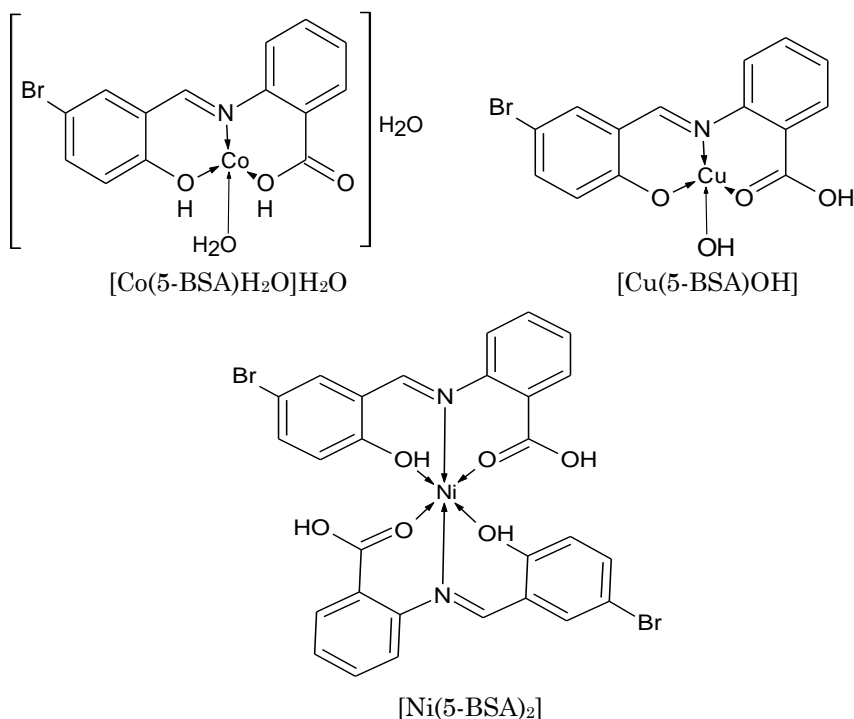
Metal Chelate	R.T. to 150 °C		No. of Water molecule (H <sub>2</sub> O of crystallization) to be present in a metal chelate	150 °C to 250 °C		No. of Water molecule (H <sub>2</sub> O of coordination) to be present in a metal chelate
	Weight loss in %	gm/mole		Weight loss in %	gm/mole	
[Co(5-BSA)H <sub>2</sub> O] H <sub>2</sub> O	5.508	22.752	1	6.661	27.515	1
[Ni(5-BSA) <sub>2</sub> ]	0.558	3.888	0	0.114	0.794	0
[Cu(5-BSA)OH]	0.491	1.962	0	0.224	0.895	0

### The possible geometry of synthesized metal(II) chelates

The possible geometries for the synthesized metal(II) chelates are given in Figure 7. Metal

chelate of cobalt(II) presents the tetrahedral geometry with H<sub>2</sub>O molecule while octahedral and square planar geometries for Ni(II) and Cu(II) chelates have been proposed respectively.

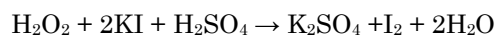
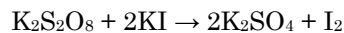




**Fig. 7: Possible geometries of Co(II), Ni(II) and Cu(II) chelates**

#### The catalytic study of redox reactions

Three types of redox reactions were selected for studying the catalytic behavior of synthesized metal chelates and those second order redox



With and without the catalytic amount of 1 mol % of metal chelates, selected redox reactions were performed. The results of catalytic study (Table 6) show that the metal chelates of Co(II), Ni(II) and Cu(II) increase the reaction rate of potassium persulphate and hydrogen peroxide with potassium iodide respectively while the reaction rate was found to reduce of the reaction between potassium bromate with potassium iodide in presence of Co(II), Ni(II) and Cu(II) chelates. In

reactions were potassium persulphate with potassium iodide, potassium bromate with potassium iodide and hydrogen peroxide with potassium iodide [37].

the reactions of potassium persulphate and hydrogen peroxide with potassium iodide respectively, the moderate increment in the reaction rate was found for the cobalt chelate than that of nickel and the highest value of reaction rate with 271 % implies the highly effective catalytic nature of Cu(II) chelate for the redox reaction of potassium persulphate with potassium iodide.

**Table 6: Reaction rate with/without metal chelates**

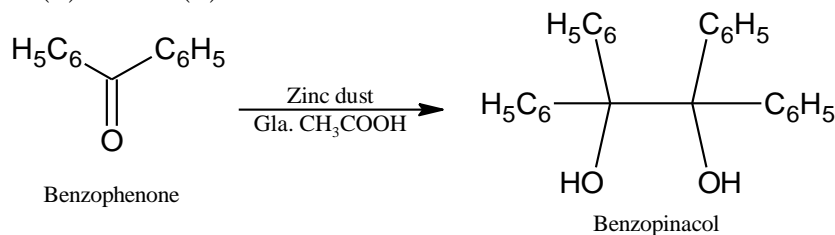
Reactions	$\text{K}_2\text{S}_2\text{O}_8 + \text{KI}$	$\text{KBrO}_3 + \text{KI} + \text{HCl}$	$\text{H}_2\text{O}_2 + \text{KI}$
k without metal chelates	$3.31 \times 10^{-5}$	$7.18 \times 10^{-4}$	$2.34 \times 10^{-4}$
k with [Co(5-BSA)H <sub>2</sub> O]H <sub>2</sub> O	$3.72 \times 10^{-5}$	$6.86 \times 10^{-4}$	$2.51 \times 10^{-4}$
k with [Ni(5-BSA) <sub>2</sub> ]	$3.65 \times 10^{-5}$	$5.41 \times 10^{-4}$	$2.46 \times 10^{-4}$
k with [Cu(5-BSA)OH]	$12.29 \times 10^{-5}$	$6.35 \times 10^{-4}$	$2.83 \times 10^{-4}$

% Increase in reaction rate at 306 K temp. [Co(5-BSA)H <sub>2</sub> O]H <sub>2</sub> O	12.38	-4.46	7.23
% Increase in reaction rate at 306 K temp. [Ni(5-BSA) <sub>2</sub> ]	10.23	-24.68	5.33
% Increase in reaction rate at 306 K temp. [Cu(5-BSA)OH]	271.46	-11.49	20.83

### Catalysis of an organic reaction

The catalytic property of synthesized Co(II), Ni(II) and Cu(II) was further evaluated and a

reductive coupling reaction was selected for the catalysis.



### Reaction: Reductive Coupling (Benzopinacol from benzophenone)

Reaction of benzophenone with Zn dust and glacial acetic acid to give benzopinacol is a commonly used reductive coupling reaction [38]. This reaction process was performed for 1 hour with same conditions and parameters with and without synthesized metal chelates. The results are listed in **Table 7**. The results of the catalytic study exhibit that without catalyst, 27.95 % (2.1 gm) product was found with 1 hour of reaction while in presence of the catalyst (metal chelate), the yield was found to increase with same

reaction time. An enhancement in product of the same reaction with 1 hour reaction was found to exhibit 4.14 %, 9.09 % and 11.23 % by Co(II), Ni(II) and Cu(II) chelates respectively which clearly indicates that the catalysis resulted in 4.95 % to 7.09 % increment in presence of synthesized metal chelates in compared with uncatalyzed reaction. Overall, Ni(II) and Cu(II) chelates were found to possess a good catalytic property than Co(II) chelate.

**Table 7: % yield with/without metal chelates with 1 hour of reflection.**

% yield without chelate (1 hour)	% yield with Co-5-BSA (1 hour)	% yield with Ni-5-BSA (1 hour)	% yield with Cu-5-BSA (1 hour)	% Increase of yield in presence of Co-5-BSA	% Increase of yield in presence of Ni-5-BSA	% Increase of yield in presence of Cu-5-BSA
27.95	29.11	30.49	31.09	4.14	9.09	11.23

### The determination of Activation energy (E<sub>a</sub>) by Broido method

To calculate the activation energy, Broido introduced a method in which kinetic parameters can be calculated using the TG curves of the compounds. The following equation was used to calculate the activation energy (E<sub>a</sub>),

$$\ln \ln \left( \frac{1}{y} \right) = - \left( \frac{E_a}{R} \right) \cdot \left( \frac{1}{T} \right) + Constant$$

where,  $y = (w_t - w_\infty) / (w_o - w_\infty)$ ,

$w_t$  indicates the weight of the compound at any time (t),

$w_\infty$  indicates the initial weight of the compound and  $w_o$  indicates the weight of the residue at the end of degradation,

R indicates the gas constant.

Broido method is a graphical method in which the slope of the plot ( $\ln(\ln(1/y))$ ) versus  $1000/K$  is concerned to the activation energy ( $E_a$ ). where,  $y$  indicates the fraction which not yet decomposed [39][40].

Activation energy ( $E_a$ ) =  $-2.303 \times \text{slope} \times R$

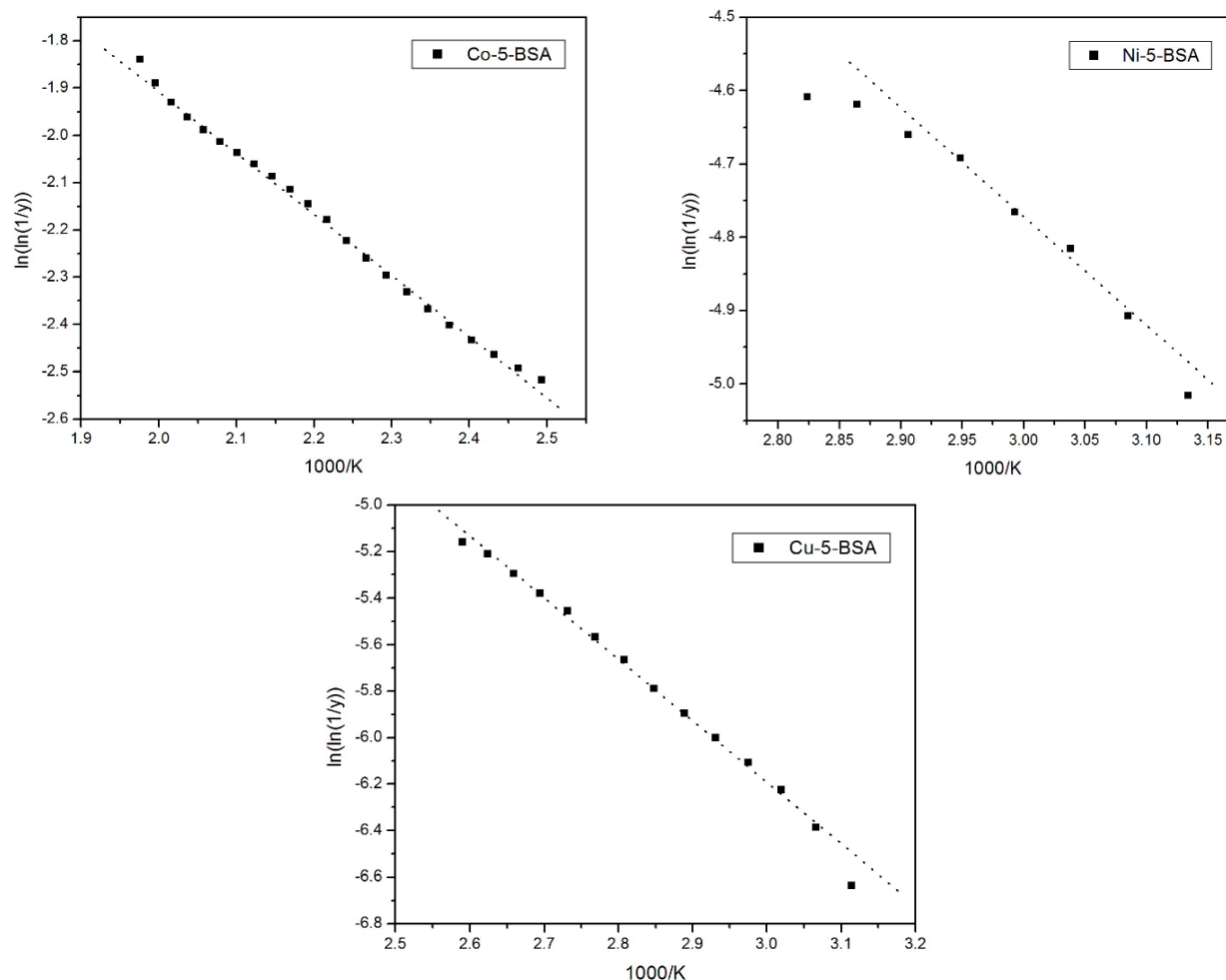


Fig. 8: Plot of  $\ln(\ln(1/y))$  versus  $1000/K$  for Co(II), Ni(II) and Cu(II) chelates

Table 8:  $E_a$  (activation energy) values for metal chelates

Metal chelates	[Co(5-BSA)H <sub>2</sub> O]H <sub>2</sub> O	[Ni(5-BSA) <sub>2</sub> ]	[Cu(5-BSA)OH]
Activation energy ( $E_a$ ) kJ/mol	26.31	30.26	50.26
Temperature range (°C)	128-233	46-81	48-113

The activation energy values for Co(II), Ni(II) and Cu(II) chelates have been calculated by Broido method are listed in Table 8. Within a determined temperature range, the activation energy values of 26.31, 30.26 and 50.26  $\text{kJ} \cdot \text{mol}^{-1}$  were found for Co(II), Ni(II) and Cu(II) chelates respectively.

The activation energy values reveal that the metal chelates are thermally stable.

#### Antibacterial study

The schiff base ligand and its synthesized metal chelates were studied for the antibacterial property against gram positive (*Bacillus subtilis*,

*B. cereus*) and gram negative (*Escherichia Coli*, *Pseudomonas Aeruginosa*) bacterial species. Ciprofloxacin, a broad-spectrum antibacterial drug was used as a standard for antibacterial

study. Agar well diffusion method was used to evaluate the antibacterial property of 5-BSA ligand and its Co(II), Ni(II) and Cu(II) chelates.

**Table 9: Results of antibacterial activity for ligand and its metal chelates**

Bacterial species	Concentration (µg/ml)	Zone of Inhibition (mm)				
		5-BSA	Co(II) chelate	Ni(II) chelate	Cu(II) chelate	Ciprofloxacin
B. subtilis (G+)	100	-	-	-	+	+++
	200	-	+	+	+	+++
	300	+	+	++	++	+++
	400	++	++	++	+++	+++
B. cereus (G+)	100	-	-	-	+	+++
	200	-	-	+	+	+++
	300	+	+	+	++	+++
	400	+	++	++	++	+++
E. coli (G-)	100	-	-	-	+	+++
	200	+	+	+	+	+++
	300	+	++	++	++	+++
	400	++	++	+++	+++	+++
P. aeruginosa (G-)	100	-	-	-	+	+++
	200	-	-	+	+	+++
	300	+	+	++	++	+++
	400	+	++	++	++	+++

*G+* and *G-* indicate gram-positive and gram-negative bacterial species respectively, - indicates inhibition zone less than 6 mm (inactive), + indicates inhibition zone of 6-10 mm (less active), ++ indicates inhibition zone of 10-14 mm (moderately active) and +++ indicates inhibition zone greater than 14 mm (highly active)

The results of antibacterial activity (Table 9) showed that the free ligand possess the moderate antibacterial activity while its synthesized metal(II) chelates exhibit the higher antibacterial activity than that of free ligand [41]. Though the ligand (5-BSA) and its Co(II), Ni(II) and Cu(II) chelates possess antibacterial activity, it could not reach the effectiveness of ciprofloxacin, a standard drug. The antibacterial activity increases with the enhancement in the concentration of metal chelates. The biological study revealed that the chelates of Ni(II) and Cu(II) were found to exhibit good antibacterial activity than that of Co(II) chelate against gram-positive and gram-negative bacterial species. The biological activity order of synthesized metal chelates and their free ligand is as follows: [Cu(5-

BSA)OH] > [Ni(5-BSA)<sub>2</sub>] > [Co(5-BSA)H<sub>2</sub>O]H<sub>2</sub>O > 5-BSA.

## CONCLUSION

Based on spectral techniques and physical measurements, it has been confirmed that the synthesized schiff base ligand acts as a tridentate ligand and coordinates to the central metal ion through azomethine nitrogen as well as phenolic and carboxylic/carboxylate oxygen. The spectral study reveal the [ML·H<sub>2</sub>O]·yH<sub>2</sub>O, [ML<sub>2</sub>] and [ML·OH] type compositions for cobalt, nickel and copper chelates respectively. The possible structures of synthesized metal chelates were proposed based on spectral data, elemental analysis, magnetic moment and thermal gravimetric analysis. Tetrahedral, octahedral and square planar geometries have been assigned

to Co(II), Ni(II) and Cu(II) chelates respectively. The thermal analysis and the values of activation energy revealed that the synthesized Co(II), Ni(II) and Cu(II) chelates are thermally stable. It could be seen from the catalytic study of redox reactions that all metal chelates were found to increase the reaction rate of potassium persulphate and hydrogen peroxide with KI. On the other hand, metal(II) chelates of nickel and copper also exhibited good catalytic activity for benzopinacol formation reaction. It has been concluded from the biological study that synthesized metal(II) chelates display the antibacterial activity better than that of uncomplexed ligand.

#### CONFLICT OF INTEREST STATEMENT

The authors declare no conflict of interest in this research article.

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