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3d-TRANSITION METAL CHELATES OF SCHIFF BASE LIGAND: SYNTHESIS, CATALYSIS AND ANTIBACTERIAL STUDY

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ABSTRACT: Three metal chelates were synthesized by using metal perchlorates of divalent nickel, cobalt and copper with schiff base (HL). The schiff base ligand (HL) furnished O and N donor atoms for ligation. It has been prepared from anthranilic acid and ortho hydroxybenzaldehyde in ethanol. Techniques like elemental analysis, FT-IR, UV-Visible and mass spectrometry, thermal analysis, molar conductance and magnetic susceptibility were carried out to identify the chelate compounds. General formula of [M(HL)OH] type in all cases was proposed by the spectral and elemental analysis. The ratio of ligand to metal has been found as 1:1 for all metal chelates. Infrared spectral data implied the inclusion of oxygen (of COOH and phenolic OH) and azomethine nitrogen in tridentate coordination mode with central metal ion. The study of conductivity measurement indicated the nonelectrolytic nature of chelates. Catalysis by these chelates was studied. The activation energy for the synthesized metal chelates were evaluated by the broido method. Antibacterial property was examined for all metal chelates and its parent ligand against gram positive (*B. subtilis, B. cereus*) and gram negative (*E. coli, P. aeruginosa*) bacterial species.

KEYWORDS: Schiff base, Metal chelates, Catalysis and Antibacterial activity

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1. INTRODUCTION

Schiff bases are considered as great chelating agents due to their straightforwardness of formation, particular property of azomethine group as well as flexibility of synthesis. Schiff bases, due to azomethine (R-HC=N-R') group are extremely important for chemical and pharmaceutical industries. The presence of a lone pair of sp² hybridized orbital in azomethine nitrogen atom found

Prajapati et al RJLBPCS 2019 www.rjlbpcs.com Life Science Informatics Publications to have an excellent chemical and biological importance. The complexation of metals with various schiff base compounds found to increase the pharmacological properties of schiff base as well as metal also. It has been reported that the metal chelates derived from schiff bases exhibit versatile medicinal properties like antibacterial, anticancer, anti-inflammatory, antifungal, antiviral, analgesic etc. [1-5]. Transition metal complexes with anthranilic acid and vanillin derived schiff base were found as good antibacterial agents [6]. Ruthenium complexes with schiff bases of anthranilic acid attained the attention due to their congenial antifungal and catalytic activity [7]. Complexes of transition metals with schiff base of anthranilic acid reported as good antibacterial agents against some bacterial species [8]. Transition metal complexes with novel schiff base ligand condensed from anthranilic acid and 4-aminoantipyrine attracted the attention because of their exclusive antibiotic property, it was found that they could be used in the treatment of infections caused by several grampositive and gram-negative bacterial species [9]. The good anti-inflammatory property was reported for schiff base compound of anthranilic acid and salicylaldehyde [10]. The Schiff base from anthranilic acid and acetoacetanilide and its copper complex was found to possess insecticidal property [11]. In the present work, synthesis of the metal chelates of Ni(II), Co(II) and Cu(II) with synthesized schiff base ligand have been reported. All compounds are characterized by physical and analytical techniques. The catalytic activity of these metal chelates have also been explored. The schiff base ligand and its metal chelates are also tested for the antibacterial property against such gram-positive and gram-negative bacterial species.

2. MATERIALS AND METHODS

All A.R. grade materials and spectroscopic grade solvents were used for experimental work. For synthesis of chelates, the perchlorates of copper, nickel and cobalt metal prepared by using metal carbonates in standardized 0.2 N perchloric acid solution. Using CHN analyzer of Thermo Finnigan, Flash EA 112 series (Italy), Ligand and its chelates were analyzed for C, H and N elements. Infrared spectra (4000 cm⁻¹ - 400 cm⁻¹) of samples using KBr disks were recorded on Shimadzu, IR Affinity, 1 S Infrared Spectrophotometer. UV-Vis.-Reflectance spectra were carried out from 200nm –800nm on Varian Cary 500, Shimadzu UV-3600, UV-Vis.-Reflectance spectrophotometer for all samples. Chelates were examined for thermal analysis on Perkin Elmer, USAA, Diamond TG/DTA with heating range of Room temp.-1000 °C. The measurement of magnetic susceptibility was carried out by using Gouy's method at room temperature for powder samples of chelates with using Hg[Co(NCS)₄] as a calibrant. In chelates, metal content was find out by the experimental methods according to literature. Catalytic activity for redox reactions and benzopinacol formation reaction had been studied. The zone of inhibition method was used to evaluate biological activity of the synthesized compounds.

3. EXPERIMENTAL

3.1 Synthesis of tridentate schiff base ligand (HL)

50ml ethanolic solution of 5.24ml (0.05mol) ortho hydroxybenzaldehyde added dropwise into the 50ml ethanolic solution of 6.86gm (0.05 mol) anthranilic acid with continuous stirring and mechanically stirred for 2 hours. The obtained orange product was filtered off and recrystallized using ethanol. Kept it over night at room temperature to dryness. The pure orange product was formed in 89 % yield and the melting point is 169 °C (Scheme-I).



Synthesis of Schiff base (HL)

(Scheme-1)

3.2 Synthesis of Metal Chelates

70 ml (0.1 M) solution of the schiff base ligand and 70 ml (0.1 M) solution of metal perchlorate were taken in the molar ratio of 1:1. The reaction mixture was refluxed on heating mantle for 4 to 5 hours at 110 °C to 120 °C temperature range. Then the refluxed reaction mixture was cooled to room temperature (2-3 hours) and pH of the reaction mixture was raised up to 5.5 to 6.0 using 0.1 N sodium hydroxide solution to achieve nearly neutral condition for precipitation of the product and the isolated metal chelate was filtered, washed and dried at 40 °C to 45 °C in oven. All chelates were synthesized by the same process.

3.3 Metal content determination of chelates

Accurately weighed 50 mg portion of metal chelates was placed in porcelain evaporating dish. Into the powdered metal chelates, a measured volume of HNO₃, H₂SO₄ and perchloric acid (60%) was added and the mixture was heated gradually to complete digestion. This homogeneous solution was diluted up to exact 50ml and determination of metal content was carried out by EDTA complexometric titration using appropriate indicator.

4. RESULTS AND DISCUSSION

Compound	Formula		Melting	Molar
[Mol. Formula]	weight	Color	Point	conductance
	(gm/mol)		(° C)	(S cm ² mol ⁻¹)
HL	241.24	orange	169	0.933
$[C_{14}H_{11}O_3N]$				
[Co(HL)OH]	316.17	ecru	> 300	1.378
$[C_{14}H_{11}NO_4Co]$				
[Ni(HL)OH]	315.93	light	> 300	1.053
[C ₁₄ H ₁₁ NO ₄ Ni]		green		
[Cu(HL)OH]	320.79	dark	289	1.873
$[C_{14}H_{11}NO_4Cu]$		green		

Table:1 Analytical and Physical data of ligand and its metal chelates

4.1 Characterization of ligand (HL) and its metal chelates

The tridentate schiff base and its metal chelates were prepared as narrated in the experimental section. The schiff base was crystallized, dried and metal chelates were subjected to elemental analysis, UV, FTIR and Mass spectral analysis.

4.2 Elemental analysis of the ligand and metal chelates

The results of elemental analysis of ligand and its metal chelates obtained are in good agreement with those calculated for the suggested formulae (Table:2).

	%	C	% Н		% N		% Metal	
Compound	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Pract.
HL	69.70	68.07	4.60	4.76	5.81	5.80	-	-
[Co(HL)OH]	53.22	50.99	3.51	3.84	4.43	7.72	18.64	17.94
[Ni(HL)OH]	53.18	50.49	3.50	4.01	4.43	8.10	18.58	17.60
[Cu(HL)OH]	52.41	53.13	3.45	3.26	4.36	4.35	19.80	19.06

Table:2 Results of elemental analysis

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

4.3 Mass spectrum of ligand (HL) and its metal chelates

The molecular formula C₁₄H₁₁NO₃ for the HL ligand is as suggested by the analytical data. This corresponds to the formula mass of 241.242 amu which is congruent with the molecular ion peak at m/z = 241.8(M) and at m/z = 242.8(M+1) as proposed in the mass spectrum of HL ligand (Fig.-1). In mass spectrum of the ligand (HL), the sequence of peaks in the range, i.e. 135.8, 195.9 amu ascribable to various fragments of the HL ligand.





4.4 Mass spectrum study of Cu-chelate



Fig.-2 Mass spectrum of Cu-chelate

The basic types of fragmentations are identified in the mass spectrum of Cu chelate (Fig.-2). The mass spectrum of copper chelate confirms the implied formula by showing a peak at 138.1 (m/z) corresponding to the chelate moiety. The m/z value of each fragment observed by peak agree with the calculated value [12-15]. The possible fragments are shown in Table:3.

Compound	Possible	m/z value		
	Fragments	calculated	found	
	$[C_{14}H_{11}O_3N]$	241.24	241.8	
HL	$[C_{14}H_{11}O_3N]^+$	242.24	242.8	
	$\left[\mathrm{C_7H_7NO_2}\right]^+$	137.05	138.1	
	$[C_{14}H_8NO_2Co]^+$	281.17	279.2	
[Co(HL)OH]	$[C_5H_5OCo]^+$	140.02	138.1	
	$[C_7H_5NO]^+$	119.12	119.8	

Tabla.2	Maga	fragmontation	of motol	abalatas
rapie:5	IVIASS	Iraginentation	of metal	cherates

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		$[C_7H_5O]^+$	105.11	105	
		$[C_{14}H_8NO_2Ni]^+$	280.9	279.2	
	[Ni(HL)OH]	$\left[\mathrm{C}_{11}\mathrm{H_9O}\right]^+$	157.18	157.1	
		$[C_5H_5ONi]^+$	139.7	138	
		$\left[\mathrm{C_{7}H_{5}N}\right]^{+}$	103.1	100.8	
		$[C_{14}H_{11}NO_4Cu]$	320.79	320	
	[Cu(HL)OH]	$\left[C_{14}H_{11}NO_{3}Cu\right]^{+}$	302.77	303.1	
		$[C_{14}H_{11}NO_3]^+$	240.23	242.1	
		$\left[\mathrm{C_7H_7NO_2}\right]^+$	137.13	138.09	

4.5 Infrared spectra of ligand and its metal chelates

Except X-ray crystallography technique, Infrared spectroscopy is also a suitable technique to elucidate the bonding nature in ligand to metal ion and in other compounds. The data of infrared spectra for chelate compounds and HL ligand are presented in Table:4. IR spectra for parent ligand and its chelates were recorded in the range of 4000 cm⁻¹ to 400 cm⁻¹ using KBr disks. Confirmation of the structure of chelates can be proven easily by comparing the infrared spectrum of the free HL ligand with chelates. Such comparisons asserted that the absorption band of azomethine in the ligand appears at 1618 cm⁻¹ which, due to the chelation, shifted to lower wavenumbers by 27 to 37 cm⁻¹ in the spectra of chelates, indicating the coordination through azomethine nitrogen (M-N) and this is confirmed by the bands in the range of 517-556 cm⁻¹ which have been found to absent in the ligand [16, 17]. The stretching vibrations of phenolic OH and C–O in the free ligand are observed at 3670 and 1246 cm⁻¹ respectively, the C–O stretching band shifted to lower or higher values by 4 cm⁻¹ on chelation revealed the participation of phenolic oxygen in coordination with the central metal ion [18]. The bands that appeared at 2954 and 1686 cm⁻¹are assigned to the carboxylic OH and C=O group respectively. On the other hand, the stretching band of 1686 cm⁻¹ shifted up to 72-83 cm⁻¹ lower, indicating the coordination of C=O with metal ion [19, 20] while the bands for OH are observed with lower or higher values by 25-60 cm⁻¹ in chelates and the carboxylic C–O frequency band in the free ligand assigned to have 1318 cm⁻¹ which have been found to be observed at 1326-1331 cm⁻¹ in chelates. Except the ligand the stretching vibrations observed in the range of 3439-3443 cm⁻¹ implied the coordination between free hydroxyl ion and metal [21-23]. While the bands found to have the frequency range of 444-448 cm⁻¹ endorse the presence of M–O coordination in chelates. Thus, from the IR spectra of free ligand (Fig.-3) and its chelates (Fig.-4 & 5 for Cu-chelate), it is concluded that HL acts as tridentate ligand with ONO donor sites and coordinated to the central metal ion via phenolic as well as carboxylate oxygen and azomethine nitrogen and coordinated hydroxyl ion satisfy the other coordination site to fulfil the tetrahedral geometry for cobalt and nickel metal ions while fulfil square planar geometry for copper metal ion.

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Fig.-4: IR spectrum of [Cu(HL)OH]



Fig.-5: IR Spectrum of [Cu(HL)OH] 600cm⁻¹ to 400cm⁻¹

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	Phe	nolic	Azo-	СООН		*Coord.			
Compound	υ(O-H)	υ(C-O)	methine	υ(C=O)	υ(O-H)	υ(C-O)	free	M-N	М-О
	(cm ⁻¹)	(cm ⁻¹)	υ(HC=N)	(cm ⁻¹)	(cm ⁻¹)	(cm ⁻¹)	υ(O-H)	(cm ⁻¹)	(cm ⁻¹)
			(cm ⁻¹)				(cm ⁻¹)		
HL	3670	1246	1618	1686	2954	1318	-	-	-
[Co(HL)OH]	-	1242	1591	1614	2931	1326	3443	517	444
[Ni(HL)OH]	-	1242	1592	1614	2929	1327	3443	520	448
[Cu(HL)OH]	-	1250	1581	1603	3014	1331	3439	556	447

Table:4 IR data of compounds

*Coordinated free hydroxyl group.

4.6 Molar conductivity measurement

The molar conductance values of 10^{-3} M solution of Ni, Co and Cu chelates in DMSO are listed in Table:1. The conductivity measurement for chelates was carried out at room temperature (at 35°C). The lower molar conductance values 0.12 to 1.87 S·cm² mol⁻¹ for all metal chelates indicating the non-electrolytic nature and they were conceived as non-electrolytes.

4.7 Electronic spectra and Magnetic moment measurements

The spectroscopic data of Ni(II), Co(II) and Cu(II) chelates are presented in Table:5. The electronic spectra of metal chelates (Fig.-7) were recorded from solid samples at room temperature using reflectance technique. The electronic spectrum of the schiff base ligand (HL) (Fig.-6) was recorded using DMSO solvent. In the spectra of ligand, the absorption band at 30075.18 cm⁻¹ represents $n \rightarrow \pi^*$ transition and the absorption bands of 38022.81 cm⁻¹ and 49019.60 cm⁻¹ are associated with $\pi \rightarrow \pi^*$ transitions respectively. In the electronic spectrum of [Ni(HL)OH] chelate, the absorption bands of 13605.44 cm⁻¹and 18348.62 cm⁻¹ assigned to ${}^{3}T_{1} \rightarrow {}^{3}T_{1}(P)$ (υ_{3}) and ${}^{3}T_{1} \rightarrow {}^{1}T_{2}$ transition bands respectively while the band of 25000 cm⁻¹ indicates charge transfer band and 4.093 B.M. value of magnetic moment and the bands at 14005.6 cm⁻¹, 17241.38 cm⁻¹ and 21978.02 cm⁻¹ assigned as ${}^{4}A_{2} \rightarrow {}^{4}T_{1}(P)$ (υ_{3}) transition bands suggest the tetrahedral geometry of [Co(HL)OH] chelate while in the two absorption bands of 17953.32 cm⁻¹ and 30674.85 cm⁻¹ in the spectrum of [Cu(HL)OH] chelate show the ${}^{2}B_{1(g)} \rightarrow {}^{2}A_{1(g)}$ and LMCT transitions respectively and 1.81 B.M. value of magnetic moment indicate the possibility of square planar geometry [24-29].



Fig.-6: UV Vis. Abs. spectrum of the ligand (HL)





Ligand (HL)	is abbreviated	as AOHB in	such figures
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Compounds	Absorption	Assignment	Magnetic Moment	Possible
	λ_{max} (cm ⁻¹)		µeff (B.M.)	Geometry
	30075.18	$n \rightarrow \pi^*$		
HL	38022.81	$\pi {\rightarrow} \pi^*$	-	-
(Orange)	49019.60	$\pi {\rightarrow} \pi^*$		
	14005.6	${}^{4}A_{2} \rightarrow {}^{4}T_{1}(P)$		

Table:5 UV-Reflectance and Magnetic data

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[Co(HL)OH]	17241.38	${}^{4}A_{2} \rightarrow {}^{4}T_{1}(P)$	4.32	Tetrahedral	
(Ecru color)	21978.02	${}^{4}A_{2} \rightarrow {}^{4}T_{1}(P)$			
	13605.44	${}^{3}T_{1} \rightarrow {}^{3}T_{1}(P)$			
[Ni(HL)OH]	18348.62	${}^{3}T_{1} \rightarrow {}^{1}T_{2}$	4.093	Tetrahedral	
(Light green)	25000	LMCT			
[Cu(HL)OH]	17953.32	${}^{2}B_{1(g)} \rightarrow {}^{2}A_{1(g)}$	1.81	Square	
(Green)	30674.85	LMCT		Planar	

4.8 Thermal Analysis (TGA)

The thermogravimetric analysis of metal chelates were carried out within a temperature range from room temperature to 1000 °C in the inert atmosphere with the heating rate of 5 °C/min. From the TGA data, weight losses for each metal chelate are calculated within the compatible range of temperature. The assessed temperature ranges, percentage weight losses and the presence of lattice and coordinated water molecules in solid chelates are given in Table:6. The curve of TG for the chelate of Ni, Co and Cu between the temperature range from R.T. to 150 °C showed 0.86% (2.73 gm/mole), 0.73% (2.31 gm/mole) and 1.16% (3.71 gm/mole) weight losses respectively showed the absence of water of crystallization in chelates. On the other hand, between the temperature range of 150 °C to 250 °C the data of TG (as shown in Table:6) revealed no loss of water molecule which proved the absence of water of coordination in all metal chelates.



Fig.-8: TGA of Metal Chelates

		R.T. – 1	50 °C	150 °C – 250 °C		
Complex	Weight loss in %	gm/mole	No. of H ₂ O molecule (water of crystallization) to be present in metal chelate	Weight loss in %	gm/mole	No. of H ₂ O molecule (water of coordination) to be present in metal chelate
[Co(HL)OH]	0.733	2.317	0	0.652	2.061	0
[Ni(HL)OH]	0.865	2.732	0	0.472	1.491	0
[Cu(HL)OH]	1.159	3.717	0	0.88	2.822	0

Table:6 Water content and weight loss data of metal chelates

4.9 Possible Structure of Metal Chelates

From the all spectroscopic, physical and analytical data, the possible structure for all synthesized metal chelates is proposed as shown below (Fig.-9),



M = Ni(II), Co(II) and Cu(II)

Fig.-9 The possible structure of Metal Chelates

4.10 Catalytic Study of the Redox Reaction

To the catalytic study of the synthesized complexes, potassium bromate with potassium iodide, potassium persulphate with potassium iodide and hydrogen peroxide with potassium iodide types of three second order redox reactions were selected [30].

$$\begin{split} \text{KBrO}_3 + 6\text{KI} + 6\text{HCl} &\rightarrow \text{KBr} + 6\text{KCl} + 3\text{H}_2\text{O} + 3\text{I}_2\\ \text{K}_2\text{S}_2\text{O}_8 + 2\text{KI} &\rightarrow 2\text{K}_2\text{SO}_4 + \text{I}_2\\ \text{H}_2\text{O}_2 + 2\text{KI} + \text{H}_2\text{SO}_4 &\rightarrow \text{K}_2\text{SO}_4 + \text{I}_2 + 2\text{H}_2\text{O} \end{split}$$

All these second order reactions were performed with and without the catalytic amount (1 mol %) of synthesized metal chelates.

From the catalytic study, chelate of nickel and copper were able to raise the rate of reaction between potassium persulphate and potassium iodide while the reaction rates of all these three reactions decreased with cobalt chelate. In the reactions of potassium bromate and hydrogen peroxide with potassium iodide respectively, all chelates were found to reduce the reaction rate. The chelate of nickel was found to show moderate increase in reaction rate of potassium persulphate and potassium

Prajapati et al RJLBPCS 2019 www.rjlbpcs.com Life Science Informatics Publications iodide while cobalt chelate showed less increment in reaction rate than nickel and copper chelates and overall in the reaction of potassium persulphate and potassium iodide in the presence of copper chelate, the value of 297 % indicates that the copper chelate is highly effective as a redox catalyst.

Reactions	KBrO ₃ + KI + HCl	$K_2S_2O_8 + KI$	$H_2O_2 + HI$
k without metal chelates	7.1791 × 10 ⁻⁴	3.30786×10^{-5}	2.34078×10^{-4}
k with [Co(HL)OH]	6.00341×10^{-4}	3.57261×10^{-5}	2.28897×10^{-4}
k with [Ni(HL)OH]	5.40149×10^{-4}	3.63687×10^{-5}	2.32342×10^{-4}
k with [Cu(HL)OH]	6.28825×10^{-4}	1.31249×10^{-4}	2.12551 × 10 ⁻⁴
% Increase in reaction rate at	-16.3766	8.0038	-2.2134
306 K temp. [Co(HL)OH]			
% Increase in reaction rate at	-24.7609	9.9465	-0.7418
306 K temp. [Ni(HL)OH]			
% Increase in reaction rate at	-12.4089	296.7781	-9.19651
306 K temp. [Cu(HL)OH]			

Table:7 Rate of reactions with and without metal chelates

where, **k** = Rate of reaction

4.11 Catalysis of an organic reaction

All metal chelates were examined for the catalytic nature and a reductive coupling reaction was selected to investigate the catalytical property of Co(II), Ni(II) and Cu(II) chelate.



Reaction: Benzopinacol from Benzophenone (Reductive Coupling) (Scheme-2)

0.041 mole (7.5 gm) benzophenone and 4 gm zinc dust, 20 ml deionized water and 110 ml glacial acetic acid were mixed and this reaction mixture was refluxed at 110 °C temperature for 2 hours [31]. The refluxed reaction mixture was cooled out at room temperature and separated product was recrystallized by glacial acetic acid and 29.87 % (2.24 gm) yield was found. This reaction with same conditions and parameters was accomplished with and without synthesized Co(II), Ni(II) and Cu(II) chelates for 1 hour. The results are listed in Table:8. The data of catalytic study showed that the product on 1hour reflection was acquired of 27.95 % (2.1 gm) while the results of the same reaction with cobalt, nickel and copper chelates respectively with 1hour reflection display 4.42 %, 7.23 % and 8.95 % extension respectively in comparison to the reaction of 1hour reflection without catalyst. It was found from the catalytic study that the catalysis occurred up to 4.42 % to 8.95 % increment in the presence of metal chelates compared with uncatalyzed reaction. The chelates of Ni(II) and © 2019 Life Science Informatics Publication All rights reserved

Peer review under responsibility of Life Science Informatics Publications 2019 March – April RJLBPCS 5(2) Page No.774 Prajapati et al RJLBPCS 2019 www.rjlbpcs.com Life Science Informatics Publications Cu(II) were showed their good catalytic property than the chelate of cobalt.

% yield	% yield	% yield	% yield	% Increase	% Increase	% Increase
without	with	with	with	of yield in	of yield in	of yield in
chelate	Co-chelate	Ni-chelate	Cu-chelate	presence of	presence of	presence of
(1 hours)	(1 hour)	(1 hour)	(1 hour)	Co-chelate	Ni-chelate	Cu-chelate
27.95	29.19	29.97	30.45	4.42	7.23	8.95

 Table:8 % yield with/without metal chelate with 1-hour reflection.

4.12 The Activation Energy by Broido method

Broido is the method to calculate the activation energy (E_a) was introduced by A. Broido. The broido method was used to appraise the kinetic parameters from the TGA curves of the compounds. The activation energy was calculated using the following equation,

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

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

R= gas constant,

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

 w_{∞} indicates the beginning weight of the material and w_o indicates the weight of the

residue at the end of degradation.

The activation energy (E_a) is related to the slope of the plot $\ln(\ln(1/y)) \rightarrow 1000/K$. where, y denotes the fraction which not yet decomposed [32, 33].

Activation Energy $(E_a) = -2.303 \times slope \times R$





Fig.-10 Plot of $ln(ln(1/y)) \rightarrow 1000/K$ for Co, Ni and Cu chelates

The values of activation energy for synthesized metal chelates were evaluated by using the Broido method are listed in Table:9.

	61			
Metal Chelate	Temperature range	Activation Energy (E _a)		
	(° C)	kJ/mol		
[Co(HL)OH]	60 - 260	31.16		
[Ni(HL)OH]	48 - 133	67.11		
[Cu(HL)OH]	64 - 129	23.51		

Table:9 Activation energy of metal chelates

The values of the activation energy were found to have 31.16, 67.11 and 23.51 kJ/mol for decomposing Co(II), Ni(II) and Cu(II) chelates respectively. The values of the activation energy reflect that synthesized metal chelates are thermally stable.

4.13 Antibacterial activity

Antibacterial activity of the compounds was examined against some gram-positive and gramnegative bacterial species such as *Bacillus subtilis*, *B. cereus*, *Escherichia Coli* and *Pseudomonas Aeruginosa*. A broad-spectrum antibacterial drug, Ciprofloxacin was used as a standard for antibacterial activity. Antibacterial activity was carried out using agar well diffusion method.

 Table:10 Results of the antibacterial activity for all compounds

Zone of Inhibition (mm)						
Bacterial	Concentration	HL	[Co(HL)OH]	[Ni(HL)OH]	[Cu(HL)OH]	Ciprofloxacin
species	(µg/ml)					
B. subtilis (G+)	100	-	-	-	+	+++
	200	-	-	-	+	+++
	300	+	+	+	++	+++
	400	+	++	++	+++	+++

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	100	-	-	-	+	+++
B. cereus	200	+	+	+	++	+++
(G+)	300	+	+	++	++	+++
	400	++	++	++	+++	+++
	100	-	-	-	+	+++
E. coli	200	-	+	+	+	+++
(G-)	300	+	+	+	++	+++
	400	++	++	++	++	+++
	100	-	-	-	+	+++
Р.	200	-	-	+	+	+++
aeruginosa	300	+	+	+	++	+++
(G-)	400	++	+	++	++	+++

G+ and G- indicate gram-positive and gram-negative bacterial species respectively.

- indicates < 6 mm (inactive), + indicates the inhibition zone of 6-10 mm (less active), ++ indicates the inhibition zone of 10-14 mm (moderately active) and +++ indicates the inhibition zone > 14 mm (highly active).

From the Table-10, it is clear that the inhibition zone of the metal chelates is higher than that of the free ligand (HL). The antibacterial activity increases with increase in the concentration of metal chelates and on chelation, the lipophilic nature of the central metal ion increases which cause the good antibacterial activity in metal chelates than that of ligand [34]. The results of the antibacterial study show that the ligand is moderately active and metal chelates are more active than the free ligand. From the biological data it is clearly shown that the copper chelate is highly active against the gram-positive and gram-negative bacterial species compared with other metal chelates. The activity order of the synthesized metal chelates is as follows: [Cu(HL)OH] > [Ni(HL)OH] > [Co(HL)OH] > HL.

5. CONCLUSION

The characterization techniques confirm that the schiff base ligand (HL) is coordinated tridentately to the central metal ion via azomethine nitrogen and two oxygen of phenolic and carboxylic group. Based on spectroscopic and physical data, tetrahedral geometry for cobalt and nickel chelates while the square planar geometry for the copper chelate have been proposed. The thermal study and the values of activation energy asserted that the synthesized metal chelates are thermally stable. All metal chelates exhibited reaction rate increase catalytic activity for the persulphate iodide redox reaction as well as for benzopinacol formation reaction. The antibacterial study shows that the synthesized metal chelates exhibit good antibacterial property than that of parent ligand and it was found that the Cu(II) chelate showed enhanced antibacterial activity compared to the other compounds.

The authors have declared that they have no conflict of interest.

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