

Synthesis, Antimicrobial and Antioxidant Activity of Heterocyclic Schiff Bases and Their Metal Complexes

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Abstract- Schiff bases Transition metal complexes have remained an important and popular area of research due to their versatility, simple synthesis. The current article focus on the synthesis, characterization and biological evaluation of synthesized transition metal complexes from heterocyclic Schiff base ligand. All newly synthesized Transition metals complexes of Fe (III), Co (III), Cu (II), and Ni (II) were screening for their elemental analysis, FT-IR, ESR, and Magnetic Susceptibility. Thermal behavior of the complexes were examined for their kinetic parameters are Energy of activation (Ea), Free energy change (ΔG), Entropy change (ΔS), Order of reaction (n) these are analyzed by Freeman Carroll method. The X- Band of ESR spectra indicates square planer geometry of Cu(II) and Ni(II) complexes and Fe(III) and Co(III) represents octahedral geometry. The screening results of antibacterial and antioxidant activity complex exhibits good antimicrobial and excellent antioxidant activity.

Keywords- Schiff base, Metal complexes, FT-IR, Thermal analysis, ESR, Antimicrobial, Antioxidant, Magnetic susceptibility.

I. INTRODUCTION

Schiff base resulted from amine and any aldehyde are important class of compound which co-ordinate to metal ion via the imine group (CH=N) nitrogen [1]. Schiff base ligand and their transition metal complexes play a significant role in the co-ordination chemistry of transition metal ion [2]. There is interest in chemistry of transition metal complexes of ligand containing Oxygen, Nitrogen, Sulfur donor atom benefactor atom right and proper to Carcinogenic, antitumor, antiviral, antifungal, and antibacterial activity and industrial uses [3-4]. Schiff base ligand and their transition metal complexes capable of cleaving DNA and RNA under hydrolytic mechanism are important binding studies of transition metal complexes have become a very important field in the development of DNA molecule probes and chemotherapeutics in recent year [5-6]. Schiff base not single played determining character in the development of advanced Co-ordination chemistry but moreover played crucial position inorganic and biochemistry, catalysis and optical material [7]. Schiff base behaves as a flexi-dentate ligand and generally co-ordinates through the oxygen atom of the deprotonated phenolic cluster [8]. The Schiff base azomethine nitrogen and other donor atoms like oxygen play a crucial role in co-ordination chemistry. Moreover antibacterial and analgesic activity of reduced Schiff base metal complexes is also evaluated and compared with standard [9]. Aromatic aldehydes especially with an effective conjugation system

form a stable Schiff base, compared to that of aliphatic aldehyde are unstable and easily polymerize [10]. A broad range of Schiff base compound and their behavior studies because these compounds have very flexible and diverse structure [11]. Schiff base generally bi, tri, tetra and penta dentate and Schiff base ligand and form very stable complexes with metal ions. The transition metal complexes of Schiff base ligand also use effectively as a catalyst for oxidation reduction, and hydrolysis reaction [12-16]. Currently, heterocyclic coordination chemistry has received great attention as they use as a versatile ligand in the formation of transition metal complexes [17-19].

In present research paper heterocyclic Schiff base metal complexes were synthesized by condensing substituted aromatic aldehyde and methyl substituted pyridine in anhydrous ethanol along with catalytic amount of Glacial acetic acid. Finally yellow colored precipitate of Schiff base ligand obtained. The methanolic solution of obtained ligand mixed and reflux with solution of different metallic salt with constant stirring. The solvent was degassed by rotary evaporator, after cooling colored solid of Schiff base metal complexes were precipitate out. The yellow and orange colored precipitate of different metal complexes washing by petroleum ether and dried under desiccators by using calcium chloride.

II. RELATED WORK

Design, synthesis and biological evaluation of novel class of heterocyclic Schiff bases. Mahale et.al. In this research article synthesis and investigation of Novel heterocyclic Schiff bases were screened for their antibacterial activity. The Schiff's bases synthesized from the condensation of ortho substituted aldehyde and heterocyclic primary amine exhibited potent antifungal activity against *A.Niger* and *C.Albicans* and show moderate activity against bacteria *S.Aureus*. The newly synthesized azo heterocyclic Schiff's bases can be employed for the synthesis of co-ordination chelating complexes of transition metal such as Ni, Cu, Fe, Co, [2].

III. METHODOLOGY

Material and Method:

Chemical used in present work were purchased from loba chemical and Sigma Aldrich. All the laboratory grade solvent were distilled before use. The reaction was monitored by thin layer chromatography by using pre-coated silica gel aluminum plates and ratio of n-hexane and ethyl acetate 7:3 proportion was used as mobile phase and spot is visualizing in U.V chamber.

Physical measurements:-

A kind of physico-chemicals procedure have been used to characterized the structure of organic Schiff base ligand and their transition metal complexes a detailed information of these methods is given below.

The melting points were taken in to open capillaries and are uncorrected. The FT-IR Characterization was recorded on model no Shimadzu FT-IR 8400 S. using KBr disc method. And ^1H NMR spectra were obtained in CDCl_3 a solvent and Mass spectrum was done by using Bruker Compass Data analysis 4.2 having scanning capacity 600 m/z in SAIF, IIT Chandigarh, India. The X-band of ESR spectra of copper complexes were recorded in the solid state at liquid nitrogen temperature 77 K in DMF as solvents using DPPH as standard on ESR- JEOL.ESR Spectrometer with X band at SAIF, IIT Bombay India. The measurement of magnetic susceptibility of metal complexes was done by Sant Gadge Baba University Amravati at chemical Science Department. The synthesized heterocyclic Schiff bases and their transition metal complexes were screened for antimicrobial activity and antioxidant activity. TGA analysis of all metal complexes were carried out from Ambient temperature to 500°C in nitrogen atmosphere having heating rate 10°C per min using Shimadzu TGA-50, Japan at Department of Chemistry in S.S.V.P.S College Dhule in Maharashtra. The compound name was given as per chem. draw software.

All the synthesized heterocyclic Schiff bases were tested for their microbiological activity and activity done by using (Disc diffusion method Disc size 6 mm).

Method used and Concentration of compound Agar diffusion assay [Disc diffusion method, Disc size 6mm] stock solution [1000 microgram per ml] of each compound was prepared in distilled water. Assay carried out by taking concentration 100 microgram per disk. Hi-media antibiotics disc: chloramphenicol (10 microgram/disc), moistened with water are used as standard selected microorganism for Antimicrobial activity such as Gram positive bacteria *Staphylococcus Aureus* [NCIM 2079], Gram negative bacteria *Escherichia Coli* [NCIM 2109]. The fungi used for Antifungal activity such as *Aspergillus Niger* [NCIM 545], *Candida Albicans* [NCIM 3471] and *Fusarium Monoliforme* [NFCCI 2953].

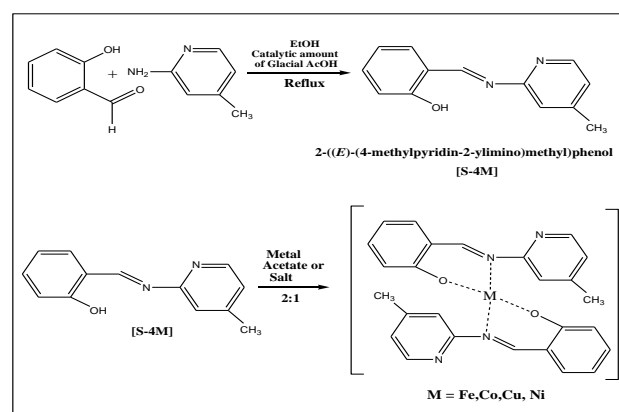
Preparation of Schiff bases from Salicylaldehyde and Heterocyclic amine. [S-4M]

2-((E)-(4-methylpyridin-2-ylimino)methyl)phenol

Schiff base was prepared according to our previously reported method [20] such as taking a equimolar quantity of Ortho hydroxy benzaldehyde (0.01 M) and 2-amino 4-methyl pyridine (0.01M) in anhydrous ethanol in presence of catalytic amount of glacial acetic acid the reaction mixture was heated at reflux with stirring for 3-4 hours after reaction mixture was dried by evaporation of solvent and crude product was extracted with petroleum ether. The residue was kept in freezer and recrystallized from ethyl alcohol. (Scheme-1)

Analytical Spectral data of [S-4M].

Practical Yield = (75%); M.P $94-96^\circ\text{C}$; IR (KBr, cm^{-1}) (OH), 3440-3526 (C=C), 1559 (CH=N) 1610. ^1H NMR (CDCl_3 , 500 MHz); δ 6.5-8.14 (m, 7H, Ar-H), 2.33 (s, 3H, CH_3), 13.2 (s, 1H, OH), 9.1 (s, 1H, CH). Elem Analysis for $\text{C}_{13}\text{H}_{12}\text{N}_2\text{O}$; C=73.56, H=5.70, N=13.20, O=7.54, %. Found C=73.46, H=5.50, N=13.15, O=7.52%. LCMS (m/z): Calculated 213, Observe 213.20; color: Yellow Solid.



Scheme 1:- Synthesis of Schiff base ligand and their metal complexes.

Preparation of the Fe (III) Complex. [S-4M] Fe (III).

The gradual addition of (0.01 mol) hot methanolic solution of ferric chloride to (0.03 mol) of methanolic solution of ligand solution with constant stirring having stoichiometric ratio (3:1) The reflux condition was maintained for 4 to 5

hours after completion of reaction the reaction mixture was filtered and concentrated product was filtered.

Analytical Spectral data of [S-4M] Fe (III).

Practical Yield = 71% Color: Reddish Brown Solid. FT-IR (KBr, pellet cm^{-1}) ν_{max} : 1560 (C=N), 1273 (C-O), 1550 (C=C), 540 (M-O), 450 (M-N). Elemental Analysis for $\text{C}_{26}\text{H}_{22}\text{FeN}_4\text{O}_2$ (%): C= 65.29, H= 4.64, N= 11.71, Fe= 11.68, O= 6.69. Found: C= 65.19, H= 4.58, N= 11.56, Fe=11.50, O= 6.55. The magnetic moment μ_{eff} : 1.80 B.M.

Preparation of the Co (III) Complex. [S-4M] Co (III).

The transition metal complexes were prepared by mixing a stoichiometric ratio (3:1) by dissolving in methanol. The ligand (0.02 mol) and metal acetate (0.01 mol) were mixed in hot condition with continuous stirring. The mixture was heated at reflux for about 4 to 5 hours on cooling the volume of reaction mixture was reduced to half, and then colored solid metal complex was formed. Thus obtained solid metal complexes were purified by petroleum ether.

Analytical Spectral data of [S-4M] Co (III).

Practical Yield = 64% Color: Brown Solid. FT-IR (KBr, pellet cm^{-1}) ν_{max} : 1560 (C=N), 1230 (C-O), 1450 (C=C), 540 (M-O), 410 (M-N). Elemental Analysis for $\text{C}_{26}\text{H}_{22}\text{CoN}_4\text{O}_2$ (%): C= 64.87, H= 4.61, N= 11.64, and Co= 12.24, O= 6.65. Found: C= 64.78, H= 4.55, N= 11.55, Co=12.22, O= 6.55. The magnetic moment μ_{eff} : 4.85 B.M.

Preparation of the Ni (II) Complex [S-4M] Ni (II) & Cu (II)

The transition metal complexes were prepared by mixing a stoichiometric ratio (2:1) by dissolving in methanol. The ligand (0.02 mol) and metal acetate (0.01 mol) were mixed in hot condition with continuous stirring. The mixture was heated at reflux for about 4 to 5 hours on cooling the volume of reaction mixture was reduced to half, and then colored solid metal complex was formed. The solid metal complexes were purified by petroleum ether.

Analytical Spectral data of [S-4M] Ni (II).

Practical Yield 70% Color: light Green, Solid. FT-IR (KBr, pellet cm^{-1}) ν_{max} : 1590 (C=N), 1292 (C-O), 1558 (C=C), 483 (M-O), 430 (M-N). Elemental Analysis for $\text{C}_{26}\text{H}_{22}\text{NiN}_4\text{O}_2$ (%): C= 64.90, H= 4.61, N= 11.64, and Ni= 12.20, O= 6.65. Found: C= 64.59, H= 4.56, N= 11.55, Ni= 12.08, O= 6.50. The magnetic moment μ_{eff} : 2.55 B.M.

Analytical Spectral data of [S-4M] Cu (II).

Practical Yield = 70% Color: Shining Green, Solid. FT-IR (KBr, pellet cm^{-1}) ν_{max} : 1562 (C=N), 1245 (C-O), 1408 (C=C), 522 (M-O), 412 (M-N). Elemental Analysis for $\text{C}_{26}\text{H}_{22}\text{CuN}_4\text{O}_2$ (%): C= 64.90, H= 4.61, N= 11.64, Ni= 12.20, O= 6.65. Found: C= 64.52, H= 4.55, N= 11.55, Ni= 12.03, O= 6.40. The magnetic moment μ_{eff} : 1.79 B.M.

IV.RESULTS AND DISCUSSION

FT-IR

FT-IR Spectrum of provide the information about functional group and linkage of the ligand to the metal complexes. The Schiff base ligand shows a peak of azomethine group (CH=N) 1590-1610 cm^{-1} which is shifted to lower frequency in both complexes such as Cu (II) & Co(III) complexes at 1562 cm^{-1} & 1579 cm^{-1} , respectively indicate that azomethine nitrogen coordinate to metal ion. The Characteristic absorption band for C=C in Cu & Co was observed at frequency 1460 & 1461 cm^{-1} respectively suggesting a significant shifting to the lower frequency due to their electronic delocalization and phenolic OH band shifting to lower frequency was also a supporting evidences coordinate to the metal ion. The mass spectral data confirmed the structure of the heterocyclic ligand indicated by the peak to their molecular mass

^1H NMR:

2-((E)-(4-methylpyridin-2-ylimino)methyl)phenol

The ^1H NMR spectrum assigns the valuable information about structure give the shows following signals ^1H NMR (CDCl_3 , 500 MHz); the aromatic proton of the compound appear as multiplet in the region δ 7.40-7.42 (m, 7H, Ar-H), and methyl proton which attach to ring appear in the region give the singlet δ 2.32-2.39 (s, 3H, CH_3), and main signal in the region of δ 8.50 9.2 (s, 1H, CH).

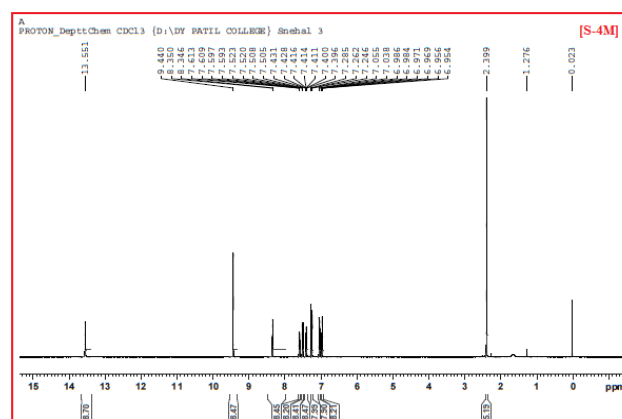


Figure.1: NMR Spectrum of Schiff base ligand [S-4M].

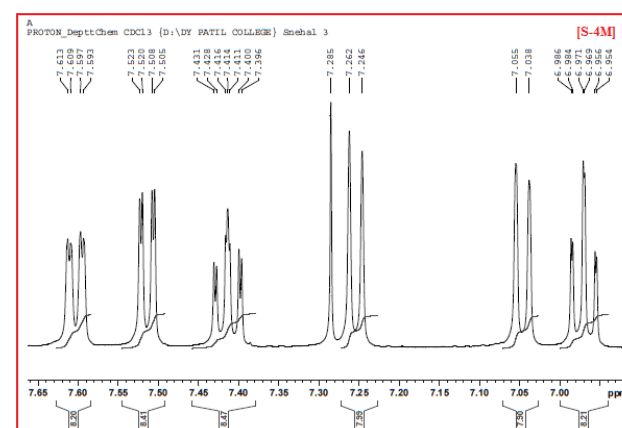


Figure. 2: NMR Spectrum of Schiff base ligand [S-4M].

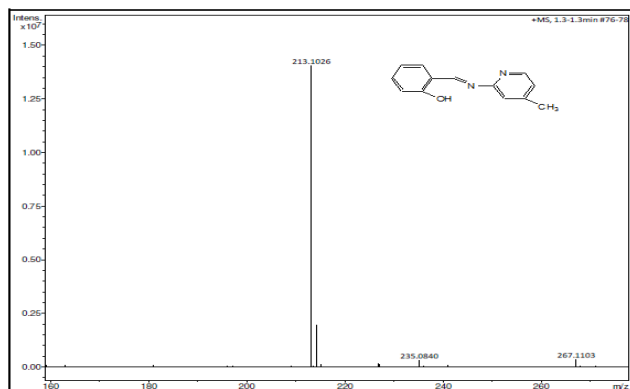


Figure. 3: Mass Spectrum of Schiff base ligand [S-4M].

Magnetic measurements and ESR Spectra:

The result data of magnetic susceptibility value of transition metal complexes of [S-4M] Fe (III) & Co (III) shows magnetic moment 1.80 & 4.85 B.M which correspond to one and four unpaired respectively represents octahedral geometry. While that of magnetic moment of [DH-4M] Cu (II) & Ni (II) shows 1.79 & 2.55 B.M respectively correspond to one or d^9 configuration and two unpaired electron correspond to d^8 Configuration respectively consistent with the square planer geometry.

The ESR spectrum of transition metal Cu(II) chelate offer sequence about hyperfine and superhyperfine arrange which are of great consequence in studying the metal ion environment in the metal complexes. Such as nature of the ligand, geometry, degree of covalency of the metal-ligand bonds. The electron Spin resonance of the Cu (II) complexes at 77 K was recorded in DMF solvent at liquid nitrogen temp. The 'g' tensor values of Cu (II) complexes can be used to derive the ground state [21-22] The ESR spectrum of Cu (II) complex the g value and other factor $g_{||} = 2.31$, $g_{\perp} = 2.065$, $G = 5.66$, $g_{avg} = 2.1$, $f = 133.01$ were derived. The sequence of these value show that $g_{||} > g_{\perp} > g_{avg}$ with f value are reported to be in the range of 105-135 cm^{-1} for square planer complexes and 135-250 cm^{-1} for tetragonal distorted complex This sequence of this pattern indicate that square planer geometry of the complexes [23] and this pattern indicate that the unpaired electron lies along the axis i.e. dx^2-y^2 orbital, [24-27] giving $^2B_{1g}$ as the ground state [28] this observations consistent with the square planer geometry In addition $g_{||}$ at 2.34 is within the range of 2.3-2.4 suggesting the presence of composite of copper-nitrogen and copper-oxygen bonds in the complex [29].

This is supported by the fact that the unpaired electron lies predominantly in the dx^2-y^2 orbital as evident from the expression and this G term has been elaborated by the Hathway expression $G = (g_{||} - 2.303) / (g_{\perp} - 2.303)$. The significance of $\alpha^2 = 0.5$ indicate complete covalent bonding while that of value of $\alpha^2 = 1.0$ suggest perfectly ionic bonding and magnetic moment also supported by the geometry of the complexes. If $G > 4.0$, the local tetragonal axis aligned parallel or only slightly misligand. If $G < 4.0$ significant exchange is present and the misalignment is

appreciable [30]. This data also prove that unpaired electron is present in the dx^2-y^2 [31]. While that of molecular orbital coefficient α^2 (covalent in plane Sigma bonding) β^2 (covalent in plane π bonding) were calculated using the following equation. The value of in plane sigma bonding parameter α^2 was expected from following expression

$$\alpha^2 = - (A_{||}/0.036) + (g_{||} - 2.303) + 3/7 (g_{\perp} - 2.303) + 0.04.$$

$$\beta^2 = (g_{||} - 2.303) E / -8\lambda \alpha^2$$

Where $\lambda = 828 \text{ cm}^{-1}$ for free ion. It is clear that in plane sigma bonding (0.82) is more covalent than in plane π bonding (1.42).

The value of $\alpha^2 = 0.5$ shows that complete covalent bonding, while the value of $\alpha^2 = 1.0$ indicating that complete ionic bonding. The observed value of α^2 is less than 1, which shows that the complex has some covalent character in the ligand environment [32].

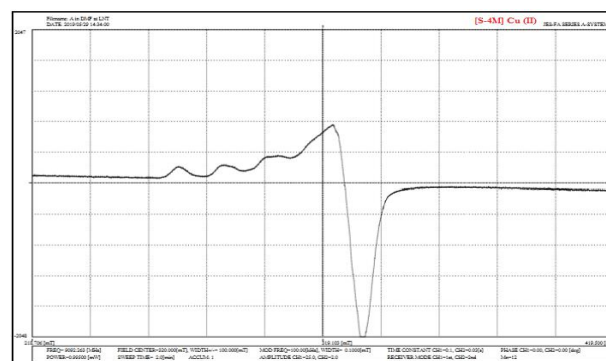


Figure. 4: X-Band ESR Spectrum of [S-4M] Cu (II) complex.

ANTIMICROBIAL ACTIVITIES

The Synthesized transition metal complexes were screened for their antimicrobial activity in vitro particularly Antibacterial and Antifungal activity and this is done with the help of disc diffusion method. Microorganisms like gram positive bacteria Staphylococcus Aureus. Gram negative bacteria Escherichia. The microorganism fungi used for these activities are Candida Albicans, Aspergillus Niger and Fusarium Moniliforme.

The complex [S-4M] Cu (II) Show more than 71% zone of inhibition for the gram positive bacteria Staphylococcus Aureus and Gram negative bacteria show the 50 % zone of inhibition against Escherichia Coli. The fungi Candida Albicans show the 46% zone of inhibition against its standard Amphotericin-B. While that of Aspergillus Niger and Fusarium Moniliforme which growth does not affected by synthesized transition metal complex Cu (II). The complex [S-4M] Co (III) shows more than 75% zone of inhibition for the bacterium Staphylococcus Aureus and 43% inhibition zone for bacteria of Escherichia Coli. And the fungi of Candida Albicans show 45% zone of inhibition against its standard Amphotericin-B. On the basis of above biographical data shows that the complex [S-4M] Co (III) exhibit moderate to good antibacterial activity as well as antifungal activity for the species of

Staphylococcus Aureus, Escherichia Coli and fungi of Candida Albicans respectively.

Table. 1. Antimicrobial data of metal complexes.

Sr. No	Sample Code	S. Aureus	E. Coli	C. Albicans	A. Niger	F. Moniliforme
1	[S-4M] Fe	--	--	--	--	--
2	[S-4M] Co	11.8	11.12	10.65	--	--
3	[S-4M] Ni	--	--	--	--	--
4	[S-4M] Cu	10.77	12.39	10.69	--	--
Chloramphenicol		15.11	25.44	NA	NA	NA
Amphotericin-B		NA	NA	23.23	15.78	12.58

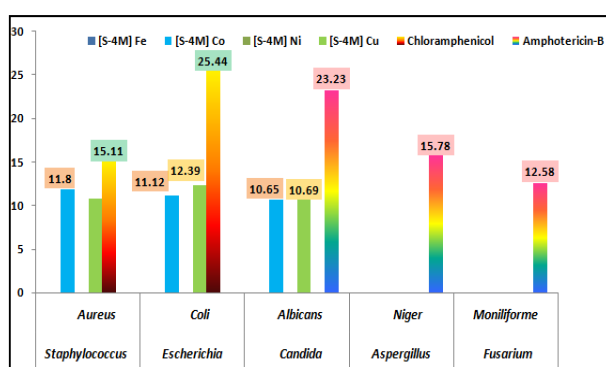


Figure.5. Graphical representation of Biological activity

ANTIOXIDANT ACTIVITY

The free radical scavenging activity of the Schiff bases and their transition metal complexes. Its test sample was determined using 2, 2 diphenyl-1 picrylhydrazyl radical (DPPH) method. Different concentration of test compound 50,100,200,300,400 mg/ml and its standard is Ascorbic acid as well as Gallic acid.

F.Al-Salman et.al.2020 of natural phytocomplex focus on Inorganic Analysis and Antioxidant Activity assay [33] and the biostatistical data of this present research study indicates that lower the inhibition concentration higher is the rate of Antioxidant activity The complex [S-4M] Fe (III) show the 6.83 percent inhibition at concentration 50 mg/ml indicate iron complex exhibit show good antioxidant activity at concentration 50 mg/ml. While that of complex [S-4M] Cu (II) show different percent inhibition at different concentration but at concentration 50 mg/ml its percent inhibition is 2.96 indicate that high antioxidant activity. Similarly at 400 mg/ml concentration its percent inhibition is 14.18 with standard deviation is 0.42 shows low scavenging activity against synthesized metal complex Lower the IC₅₀ values denote high antioxidant activity. The complex [S-4M] Co (III) shows that the concentration 50 mg/ml has percent inhibition is 1.85 with standard deviation is 0.4 indicate that complex has good antioxidant activity as compare to the other concentration. Similarly it also shows low scavenging activity at concentration 400 mg/ml its percent inhibition is

17.47 along with standard deviation is 0.26. The transition metal complex of [S-4M] Ni (II) show lower percent inhibition 2.13 at concentration 100 mg/ml having standard deviation 0.12 means good antioxidant activity. From the above data hints that the complex [S-4M] Fe (III) exhibit excellent antioxidant activity compared to the rest of the complexes.

Table.2. Antioxidant data of transition metal complexes.

Conc [µg/ml]	[S-4M] Fe		[S-4M] Co		[S-4M] Cu		[S-4M] Ni	
	IC ₅₀	±SD	IC ₅₀	±SD	IC ₅₀	±SD	IC ₅₀	±SD
50	6.83	0.18	1.85	0.4	2.96	0.5	2.39	0.13
100	11.12	0.25	5.95	0.44	7.21	0.24	2.35	0.12
200	15.5	0.12	6.53	0.26	9.94	0.73	4.55	0.2
300	15.8	0.26	9.24	0.2	11.62	0.84	6	0.48
400	69.22	0.3	17.74	0.26	14.18	0.42	6	1.05
IC ₅₀	385.02		1282.72		1617.24		3985.42	

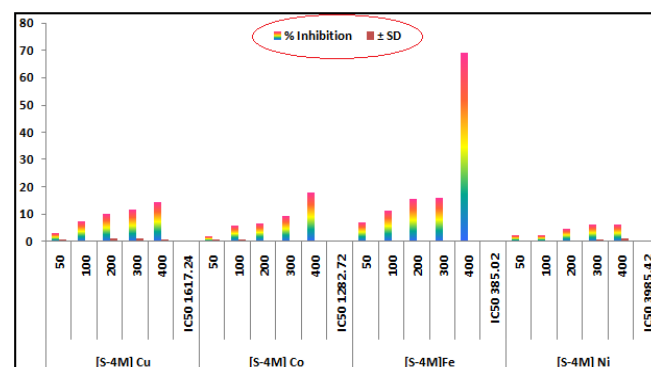


Figure. 6: Graphical representation Antioxidant activity of metal complexes.

THERMAL ANALYSIS

Thermal study is performed to find out the thermal stability of complexes and its degradation pattern in which the change in the weight of the substance is recorded as function of temperature. By using TGA analysis several kinetics parameter such as energy of activation (E_a), free energy change (ΔG), Entropy change (ΔS), Order of reaction (n) these thermal data have been analyzed using Freeman Carroll method.

In the thermogram of [S-4M] Fe (III) complex show gradual loss of mass over the entire range. In the first phase of decomposition show in the range 50.-150⁰C with a mass loss 2.79% (Calculated 3.09%) indicate loss of one crystal lattice water molecule. In the second phase of decomposition was shown in the range 150-230⁰C with a mass loss 6.89% (Calculated 6.18%) indicate the loss of coordinated water molecule while that of there is no significant weight loss observe from above 250⁰C over the entire range means complex do not decomposed completely.

In case of [S-4M] Co (III) complex exhibit no maximum mass change over entire range of temperature. In the first

phase of decomposition was shown in the range 35-150⁰C with a mass loss 2.21% (Calculated 2.69%) indicate the removal of one crystal lattice water molecule. In the second phase of decomposition in the range 200-500⁰C weight loss remain constant corresponding to stable metal oxide cobalt oxide 11.71% (Calculated 11.17%) and no further significant loss is observe. In the thermogram of [S-4M] Ni (II) complex exhibit single step decomposition was observed but in the first phase of decomposition show in the range 80-160⁰C there is no loss of crystal lattice water molecule and in the second decomposition phase shown in the range 160-310⁰C indicate there is no loss of coordinated water molecule and no significant mass loss was observed over the entire range due to stable metal oxide. In this thermogram of [S-4M] Cu (II) metal complexes their no mass losses up to 150⁰C indicate absence of crystal lattice water. And second step of decomposition observe in the range 200-350⁰C correspond to mass loss due to coordinated part of ligand and non coordinated water molecule 37.54% (Calcd 37.04%). Afterward the weight losses remain constant. The kinetic parameters of degradation of the metal complexes calculated by Freeman-Carroll (FC) method.

Table. 3. Table of kinetic parameters by Freeman Carroll method.

Sample Code	Method	Order of Reaction (n)	Energy of Activation Ea (kJ/mole)	Free energy Change (ΔG)	Entropy Change (ΔS)	μ effective B.M
[S-4M] Fe	FC	1.2	6452.58	80224.34 J	-145.22	1.8
[S-4M] Co	FC	1	13211.53	95763.06 J	-139.21	4.85
[S-4M] Ni	FC	1.1	7084.44	77585 J	-139.71	2.94
[S-4M] Cu	FC	1	11909.52	86442.18 J	-140.099	1.79

Negative (ΔS) value indicates more ordered activated state that may be possible through chemisorptions of oxygen and other decomposition product. The more order nature may be due to the polarization of bond in activated state. While that of the value of order of reaction is consistently one.

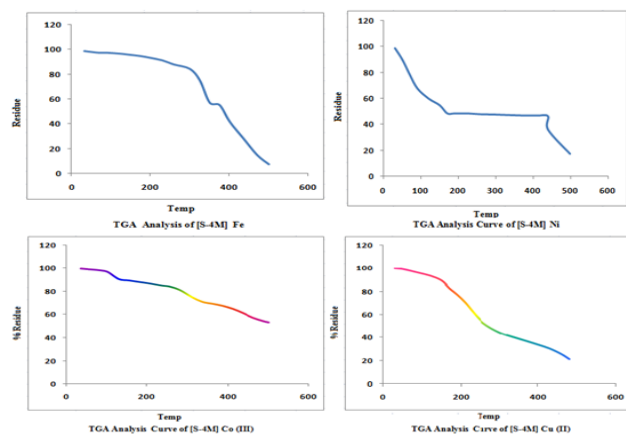


Figure. No. 7: Thermal analysis curve of [S-4M] Fe (III), Ni (II), Co (III), Cu (II).]

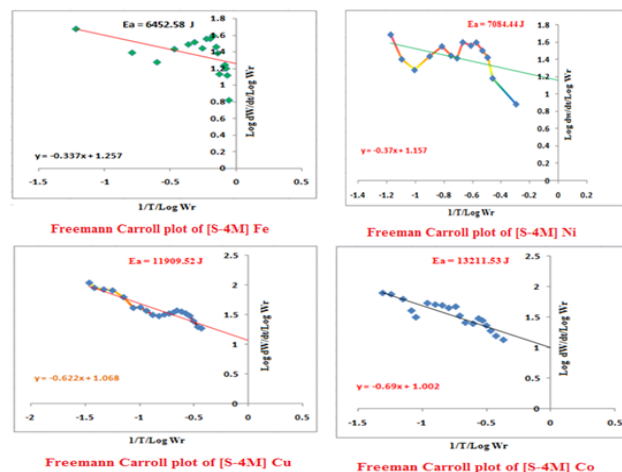


Figure. 8: Plot of Freeman Carroll equation of [S-4M] Fe (III), Co (III), Ni (II), and Cu (II).

V. CONCLUSION

The present article includes the synthesis and characterization of novel heterocyclic Schiff base and their transition metal complexes with metal ion Fe, Co, Ni, and Cu. Analytical method include FT-IR, ¹H NMR, TGA, Magnetic Susceptibility, ESR, Antimicrobial, Antioxidant. The data of ESR of Cu and magnetic moment possess the square planner geometry

Coordination of the ligand to metal ion through its oxygen and nitrogen donor sites was confirmed by ESR and FT-IR spectra. Furthermore, the structure of Fe, Co, Ni was confirmed by magnetic moment and I.R spectra. The complex of, Cu (II) and Ni (II) show the square planner geometry. The complex of Fe (III) and Co (III) shows the octahedral geometry. The result of antimicrobial activity indicates that the complex of Cu and Co exhibit moderate to good activity against its standard. While that of antioxidant activity represent that the complex of Co exhibit the excellent antioxidant activity having percent inhibition is 1.85 having standard deviation 0.40 at concentration 50 mg/ml compared to the rest of the complexes.

The thermal data show that some complexes thermally stable and its thermal decomposition, as well as kinetic parameter such as Energy of activation (E_a), order of reaction (n), Free energy change (ΔG), Entropy change (ΔS) was calculated by using Freeman Carroll method. The order of reaction of all complexes is consistently one. Negative (ΔS) value indicates more ordered activated state that may be possible through chemisorptions of oxygen and other decomposition product. The more order nature may be due to the polarization of bond in activated state. While that of the value of order of reaction is consistently one. The observed stoichiometry and geometry of the complexes is evidenced from the data of kinetic parameters.

The synthesized Schiff base ligand (N-substituted Pyridine) is reacting with transition metal salts (FeCl₃, NiOAc, CoOAc, CuOAc) to obtain Schiff base transition metal complexes.

The Schiff bases transition metal complexes having broad range of application in oxidation, reduction and in catalysis field Antioxidant and Antimicrobial activity: The in biological screening effects of the synthesized Schiff base transition metal complexes were examine against the some Gram positive, Gram negative bacteria and fungi by the disc-diffusion method.

The Schiff bases transition metal complexes has centered role in the area of bioinorganic chemistry. The transition metal complexes provide synthetic interesting models for the metal-containing sites in enzymes and metallo-proteins.

To examine quality and purity of Schiff base transition metal complexes by analytical and spectral techniques such as elemental analysis, TGA Analysis, FT-IR, UV-Visible spectroscopy, magnetic EPR and NMR studies.

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REFERENCES

- [1]. K.Arora, K.P.Sharma, "Studies on high-coordination complex of dioxouranium (VI) with a Schiff base" *Synthesis and reactivity in Inorganic and metal-Organic chemistry*, Vol-32, Issue 5, PP 913-922, 2002.
- [2]. C.Celik, M.Tumer, S.Serin, "Complex of tetradentate Schiff base ligand with divalent transition metal" *Synthesis and reactivity in Inorganic and Metal- Organic chemistry*, Vol-32, Issue 10, PP 1839-1854, 2002.
- [3]. R.Ramesh, M.Sivagamsundri, "Synthesis, Spectral and antifungal activity of Ru (II) Mixed ligand complexes" *Synthesis and reactivity in Inorganic and Metal- Organic chemistry*, Vol-33, Issue 5, PP 899-910, 2003.
- [4]. R.C.Maurya, R.Verma, T.Singh, "Synthesis, magnetic mono and binuclear dioxomolybdenum (VI) complexes with chelating hydrazones and furfural or Thiopene-2-aldehyde" *Synthesis and reactivity in Inorganic and Metal- Organic chemistry*, Vol-33, Issue 2, PP 309-325, 2003.
- [5]. P.J.Dardier, R.E.Homlin, "Synthesis, DNA-binding and cleavage studies of macrocyclic copper (II) complex" *J.K.Barton Science*. Vol-274, 1465, 1997.
- [6]. A.S.Sitalani, E.C.Long, A.M.Pyle, "DNA photocleavage by phenanthrenequinone diimine complexes of rhodium (III)" *Journal of American chemical Society*. Vol-114, Issue 7, PP 2303-2312, 1992.
- [7]. J.Tisato, F.Refosco, F.Bandoli, "Synthesis and characterization of square planer nickel (II) complexes with O, N, O, donor tridentate pendant Schiff base" *Journal of American chemical society*. Rev.135, Vol-325, 1994.
- [8]. D.Worku, M.Negussie, V.J.T.Raju, "Synthesis and study of Schiff base ligand" *Bulletin of the chemical society of Ethiopia*. Vol-17, Issue 30, 2002.
- [9]. M.Fujita, Doguro, M.Miyazawa, H.Oka, K.Yamaguchi and K.Ogura, *Nature*, Vol-378, 469, 1995.
- [10]. P. Paul, "Ruthenium, Osmium and Rhodium complexes of polypyridyl ligand" *Journal of chemical science*. Vol-114, Issue 4, PP 443-449, 2002.
- [11]. L.A.Paquette, W.a.Benjamin, "Study of Schiff base compound and its derivatives" *Principles of Modern Heterocyclic Chemistry*. Vol-318, 1968.
- [12]. N.H. Lee, j.C.Byun, J.S.Baik, "Development of Mn (II) Schiff base complexes for the catalyst of olefin oxygenation to alcohol in the presence of NaBH₄" *Bulletin of Korean chemical science*. Vol-23, Issue 10, PP 1365-1366, 2002.
- [13]. S.A.Patel, S.Sinha, A.N.Mishra, R.N.Ram, "olifine epoxidation catalyzed by Mn (II) Schiff base complex in Heterogeneous-Homogeneous system. *Journal of molecular catalysis A*: Vol-192, Issue 1-2, PP 53-61, 2003.
- [14]. O.Pouralimardan, A.C.Chamayou, C.Janiak, Hosseini Hasasan, "Hydrazones Schiff base-manganese (II) complexes" *Inorganica chimica Acta*, Vol-360, Issue 5, PP 1599-1608, 2007.
- [15]. A.R.Moosavi-Zare, H.Goudarziafshar, Khadijeha Saki, "Synthesis of pyranopyrazoles using nano-Fe-[Phenylsalicylaldiminemethylpyranopyrazole] Cl₂ as a new Schiff base complex and catalyst" *Applied Organometallic chemistry*. Vol-32, Issue 1, PP 3698-;1-8, 2017.
- [16]. Beyazit, D.Cakmak, C.Demetgul, "Synthesis of salen-type of Schiff base metal complexes" *Journal of Tetrahedron*, Vol-73, PP 2774-2779, 2017.
- [17]. A.S.Abu-Surrah, k.A.Abu-safieh, M bearing pyrazole based Schiff base ligand" *European Journal of medicinal chemistry*. Vol-5, Issue 2, PP 471-475, 2010.
- [18]. J.Joseph, M.S.Muneera, "Synthesis, spectroscopic and thermal studies of Fe (III) and V (IV) complexes" *Der Pharma chimica*. Vol-12, Issue 45-60, 2016.
- [19]. K.R.Surati, P.A.Sathe, "Schiff base pyrazolone complex of iron (III)" *Medicinal chemical Research*. Vol-25, Issue 12, PP 2742-2751, 2016.
- [20]. J.N.Borase, R.G.Mahale, S.S.Rajput, "Synthesis characterization of novel class of heterocyclic Schiff base" *European Journal of Biomedicine Pharmaceutical Science*. Vol-4, Issue 10, PP 842-845, 2017.
- [21]. C.J.Ballhausen, "Introduction to ligand field theory" McGraw-Hill, New York, 1962.
- [22]. S. Srinivasan, P. Athapan, G. Rajgopal, "Synthesis, spectral and redox properties of metal complexes of macrocyclic tetraaza chiral Schiff base" *Transition metal chemistry*, Vol-26, PP 588-593, 2001.
- [23]. R.S.Bendre, S.K.Tadvi, M. Patil, "Synthesis, crystal structure and biological activities of transition metal complexes of a salen-type ligand" *Transition metal chemistry*. Vol-43, Issue 1, PP 4863-4879, 2017.
- [24]. R. M. Kadam, M.D. Sastry, M.K Bhide, S.A.Chavan, J.V.Yakhmi, and O. Khan "EPR studied on (NBu₄)₂CO₂[Cu(opbu)] 3-S" *Chemical physics letters*. Vol-357, Issue (5-6), PP 457-463, 1997.
- [25]. M.Base, K. Ohta, Y. Babu and M.D. Sastry "Synthesis, spectral characterization of Schiff base transition metal complexes" *Chemistry of physics letters*, PP 324-330, 2000.
- [26]. R. K Ray and G.B. Kauffman, "EPR spectra and covalency of bis (amidinourea) copper (II)" *Inorganica chimica Acta*. Vol-173, Issue 2, PP 207-214, 1990.
- [27]. K.Jeyasubramanian, S. A. Samath, S. Thambidurai, R.Murugesan and S.K. Ramalingam "Electronic spectra of some

transition metal complexes: Derivatives of Dq and B” Transition metal chemistry. Vol-20, Issue 76, 1996.

- [28]. B.B. Raj, M.P. Kurup, E. Suresh, "Synthesis, spectral characterization and crystal structure of N-2-Hydroxy-4-Methoxy benzaldehyde-N-4-nitro benzoyl hydrazone and its square planer Cu (II) complex" Spectrochimica Acta part A: Molecular Bimolecular spectroscopy, Vol-71, Issue 4, PP 1253-1260, 2008.
- [29]. N.Raman, Y.P.Raja, A. Kulandaisamy, "Synthesis and characterization of Cu (II), Ni(II), Mn(II), Zn(II) and VO(II) Schiff base complexes derived from orthophenylenediamine and acetoactanilide" Journal of Chemical science. Vol-113, PP 183-189, 2001.
- [30]. B. Hathaway, D.E.Billing, "The electronic properties and stereochemistry of mono-nuclear complex of the copper (II)" Coordination chemistry Reviews, Vol-5, PP 143-207, 1970.
- [31]. A. M. F. Benial, V.Ramakrishna and Murugesan, "Synthesis, Spectral characterization of Schiff base transition metal complex" Spectrochimica Acta: part: A. Vol-56, 2775, 2000.
- [32]. N.Raman, S Ravichandran, "Synthesis and characterization of a new Schiff base" Inorganic Metal-organic and Nano metal chemistry. Vol-35, Issue 6, PP 439-444, 2005.
- [33]. F. Al-Salman, A. Ali Redha, Zahraa Al-Zaimoor, "Inorganic Analysis and Antioxidant Activity of Shilajit" International Journal of Scientific Research in Chemical Sciences Vol.7, 3, PP.05-10, 2020.

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