



DESIGN, SYNTHESIS AND BIOLOGICAL PROPERTIES OF TRANSITION METAL COMPLEXES OF SCHIFF BASE LIGAND DERIVED FROM PYRIDINE DERIVATIVES

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ABSTRACT

Novel classes of heterocyclic Schiff base ligand were prepared from the condensation of 2-methoxy benzaldehyde and 2-amino 4-methyl pyridine in absolute ethanol in presence of catalytic amount of dilute HCl. The resulted novel class of heterocyclic ligand was treated with metal salt or acetate results in the formation of Fe (III), Co (III), Ni (II) & Cu (II) complexes. All newly synthesized resulted ligand its metal complexes were characterized by elemental analysis and FT-IR, Magnetic susceptibility, Antimicrobial, Antioxidant, ESR spectrum for Copper complex in DMF solvent recorded at room temperature. The Electronic spectra and magnetic susceptibility measurements indicates that square planer and octahedral geometry of these complexes also suggest their structure in which (N, O) group acts as bidentate ligand. The thermal stability, decomposition behavior has been investigated by using thermo gravimetric analysis at heating rate 10°C per minute with nitrogen atmosphere and their kinetic parameter was also calculated by using Freeman Carroll method. Screening results of antimicrobial, antioxidant activity of transition metal complexes shows good antibacterial and antifungal activity and excellent antioxidant activity.

Keywords: Heterocyclic Schiff base, Metal complexes, Bidentate ligand, Magnetic moment, Antimicrobial, Antioxidant activity.

1. INTRODUCTION

Schiff bases are most widely used as chelating ligands in coordination chemistry [1]. They are also useful in catalysis and in medicinal as antibiotics, antiallergic and antitumor agents [2]. The metal complexes of Schiff bases derived from heterocyclic compound have been the centre of attraction for many workers in recent years [3-7]. Tetra dentate Schiff bases are well known for their coordination with various metals ions, from the stable compound [8]. Many symmetrical bis tetradentate Schiff base of 1,2diamines with o-hydroxy aldehyde/ketones have been prepared and studied intensively. However, much less attention has been focused on unsymmetrical tetra dentate Schiff base derived from 1, 2-diamines and different aldehydes/ketones. In particular those derived from aromatic 1, 2-diamines have been under investigated [9]. Schiff base and their transition metal complexes play an important role in the development of coordination chemistry [10]. There is an increasing much more efforts to analyze the designing and preparation of

material and to study their chemical functionality, coordination pattern, catenation catalysis and separation [11]. The survey of literature clearly shows that study of this diverse ligand system is linked with many of the key advanced made in inorganic chemistry [12-13]. Non-covalent interaction such as dispersion forces [14], hydrogen bonding [15], Coordination bond [16], and aromatic interaction [17] routinely drive self-assembly processes on surface. The research area of macromolecular metal complexes is due to the astonishing chemical and electronic properties of these materials like conductance, sensors, luminescence, and catalysis of reaction.

2. EXPERIMENTAL

2.1. Material and Method

All the reagents used for the synthesis heterocyclic Schiff bases and their transition metal complexes such as 2-methoxy benzaldehyde, 2-amino 4-methyl pyridine. (Heterocyclic primary amine), Cobalt acetate

tetrahydrate, Nickel Chloride hexahydrate, Cupric acetate monohydrate, Ferric chloride, hexane, methanol, ethyl acetate, glacial acetic acid, petroleum ether, were purchased from Loba Chemie and Sigma Aldrich A.R grade and solvent like anhydrous ethanol were purified by standard distillation method and of good purity. 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 was visualized in UV chamber.

2.2. Physical Measurement

Kinds of physico-chemicals procedure have been used to characterize the structure of organic Schiff base ligand and their transition metal complexes. Detailed information of these methods is given below.

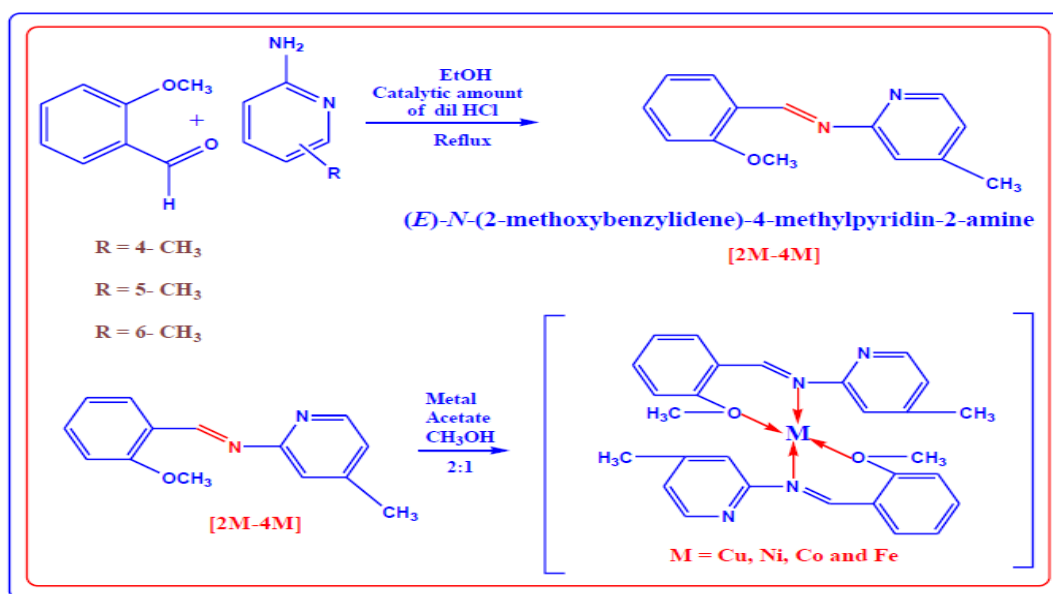
The melting points were taken in to open capillaries and are uncorrected. The FTIR characterization was recorded on model no Shimadzu FTIR 8400 S. using KBr disc method and ^1H NMR spectra were obtained in CDCl_3 and Mass spectrum was done by using Bruker Compass Data analysis 4.2 having scanning capacity 600 m/z in SAIF, IIT Chandigarh, India. The X-band of ESR spectra of copper complexes was recorded in the solid state at room temperature in DMF as solvents using DPPH as standard on ESR- JEOL. ESR Spectrometer was used 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 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.

2.3. General Procedure for Synthesis of Heterocyclic Schiff Bases ligand [2M-4M]. (E)-N-(2-methoxybenzylidene)-4-methylpyridin-2-amine

Schiff base was prepared according to our previously reported method [18] taking a equimolar quantity of 2-methoxy benzaldehyde (0.01 M) and 2-amino 4-methyl pyridine (0.01M) in anhydrous ethanol solvent in presence of catalytic amount dilute HCl. The reaction mixture was heated at reflux with stirring for 4-5 hours and then poured the reaction mixture in ice cold water then colored solid was collected by filtration and recrystallized from ethyl alcohol shown in scheme-1.

Practical Yield (70%); M.P $100-102^\circ\text{C}$; $\lambda_{\text{max}} = 274, 332$ nm IR (KBr, cm^{-1}) (OCH_3), 1285-1240 ($\text{C}=\text{C}$), 1566 ($\text{CH}=\text{N}$) 1612, ^1H NMR (CDCl_3 , 500 MHz); δ : 6.33-8.35 (m, 7H, Ar-H), 1.22 (s, 3H, CH_3), 9.24 (s, 1H, CH). Elem Analysis for $\text{C}_{14}\text{H}_{14}\text{N}_2\text{O}$; C= 74.31, H= 6.24, N=12.38, O= 7.07%. Found C= 74.33, H= 6.23, N= 12.40, O= 7.03%. LCMS (m/z): Calculated 226 Obs 227.22 color: Orange Solid.



Scheme 1: Synthesis of heterocyclic Schiff base ligand & its metal complexes

2.4. Preparation of the Fe (III) Complex [2M-4M] Fe (III)

The drop wise 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 (1:3) was done. The reflux condition was maintained for 4 to 5 hours after completion of reaction, the reaction mixture was filtered and concentrated product was filtered with cold methanol.

Practical Yield: - 75%, Colour: Dark Brown, Solid. λ_{\max} = 343, 414 nm FT-IR (KBr, pellet cm^{-1}) ν_{\max} : 1565 (C=N), 1245 (C-O), 1465 (C=C), 525 (M-O), 450 (M-N). Elemental Analysis calculated for $\text{C}_{28}\text{H}_{28}\text{FeN}_4\text{O}_2$ (%): C= 66.15, H= 5.55, N= 11.02, Fe= 10.98, O= 6.09. Found: C= 66.13, H= 5.52, N= 10.95 and Fe= 10.92, O= 6.04. The magnetic susceptibility μ_{eff} : 1.78 B.M.

2.5. Preparation of the Co (III) Complex [2M-4M] Co (III)

The transition metal complexes were prepared by mixing a stoichiometric ratio (2:1) by dissolving in methanol. The ligand (0.02mol) and Cobalt acetate (0.01mol) 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 is reduced to half, and then colored solid metal complex is formed. Thus obtained solid metal complexes were purified by petroleum ether.

Practical Yield: - 73% Colour: Reddish Brown Solid. λ_{\max} = 628,411nm. FT-IR (KBr, pellet cm^{-1}) ν_{\max} : 1579 (C=N), 1232 (C-O), 1465 (C=C), 510 (M-O), 415 (M-N). Elemental Analysis calculated for $\text{C}_{28}\text{H}_{28}\text{CoN}_4\text{O}_2$ (%): C= 65.75, H= 5.52, N= 10.95, Co= 11.52, O= 6.20. Found: C= 65.71, H= 5.35, N= 10.92, Co= 11.45, O= 6.14. The magnetic susceptibility μ_{eff} : 4.87 B.M.

2.6. Preparation of the Complex. [2M-4M] Ni (II) & Cu (II)

The transition metal complexes were prepared by mixing a stoichiometric ratio (2:1) by dissolving in methanol. The ligand (0.02mol) and metal acetate (0.01mol) 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 is reduced to half, and then colored solid metal complex is formed. Thus obtained solid metal complexes were purified by petroleum ether.

2.6.1. Analytical and spectral data of [2M-4M] Ni (II)

Practical Yield= 70% Colour: light Green, Solid. λ_{\max} = 417,552 nm FT-IR (KBr, pellet cm^{-1}) ν_{\max} : 1562 (C=N), 1293 (C-O), 1554 (C=C), 485 (M-O), 422 (M-N). Elemental Analysis for $\text{C}_{28}\text{H}_{28}\text{NiN}_4\text{O}_2$ (%): C= 60.85, H= 4.32, N= 10.92, Ni= 11.44, O= 12.47. Found: C= 65.78, H= 5.52, N= 10.96, Ni= 11.48, O= 6.26. The magnetic Susceptibility μ_{eff} : 0.00 B.M.

2.6.2. Analytical and spectral data of [2M-4M] Cu (II)

Practical Yield: - 75%, Colour: Dark Brown, Solid. λ_{\max} = 373, 594 nm FT-IR (KBr, pellet cm^{-1}) ν_{\max} : 1560 (C=N), 1235 (C-O), 1464 (C=C), 522 (M-O), 416 (M-N). Elemental Analysis calculated for $\text{C}_{28}\text{H}_{28}\text{CuN}_4\text{O}_2$ (%): C= 65.16, H= 5.47, N= 10.86, Cu= 12.31, O= 6.20. Found: C= 65.14, H= 5.42, N= 10.82, Cu= 12.28, O= 6.18. The magnetic susceptibility μ_{eff} : 1.80 B.M.

3. RESULTS AND DISCUSSION

All newly synthesized metal complexes are colored solid and physical and analytical data of ligand and their metal complexes are in better agreement with the expected values. The heterocyclic ligands prepared in this way are formed nearly high purity and percentage yield of metal complexes relatively lower than that of ligand due to steric hindrance around the coordination center. All synthesized metal complexes are stable at room temperature and soluble in common organic solvents such as methanol, ethanol chloroform. The spectroscopic data of ESR and magnetic measurement indicate square planer and octahedral geometry of complexes.

3.1. Electronic Spectra

The electronics spectra of heterocyclic Schiff base ligand and their transition metals complexes were recorded in DMSO solution between 200-800 nm at ambient temperature. In free ligand, two bands were observed at 274 and 332 nm which can be assigned to $\pi\text{-}\pi^*$ transition of the aromatic ring and for imines groups respectively [19-20]. These bands were also observed at similar position in the UV spectra of complexes. The spectrum of [2M-4M] Cu (II) shows an absorption band having 373 nm due to the ligand to metal charge transfer and 594 nm band showing square planer

geometry. [2M-4M] Ni (II) complex show 417 nm band assign ligand to metal ion charge transfer and d-d transition and 552 nm indicating square planer geometry [21-23]. A band at 628 nm in the spectrum of [2M-4M] Co (III) complex possesses octahedral geometry. The electronic spectra [2M-4M] Fe (III) shows an absorption band 343,414 nm assign for n- π^* Transition and showing octahedral geometry respectively.

3.2. FT-IR spectra

The FT-IR spectrum gives the valuable information about binding modes of ligand toward metal ion, functional group form in ligand and connectivity about ligand to the metal ion in transition metal complexes. The characteristic band of carbonyl and primary amine was disappeared which proved formation of azomethine or imines group (CH=N) at 1598 cm^{-1} , which is shifted to the lower frequency in metal complexes. This decrease in IR frequency indicates that azomethine nitrogen coordinates to metal ion due to decrease in electron density during coordination. In the metal complexes, the band of aryl alkyl ether no longer observed, because non bonding electron pair

coordinates to the metal ions. The characteristic absorption band for C=C in metal complexes was observed at frequency 1461 cm^{-1} & 1466 cm^{-1} respectively suggesting a significant shifting to the lower frequency due to their electronic delocalization. There was a significant change in the position of these bands in case of metal complexes which is absent in the ligand. The absorption band in the region $412\text{--}454\text{ cm}^{-1}$ and $514\text{--}534\text{ cm}^{-1}$ can be assigned to the (M-N) and (M-O) respectively stretching vibration of complexes [24-25]. The mass spectral data confirmed the structure of the heterocyclic ligand indicated by the peak to their molecular mass.

3.3. $^1\text{H-NMR}$

$^1\text{H NMR}$ spectral data of the ligand assigns the valuable information about structure and shows following signals $^1\text{H NMR}$ (CDCl_3 , 500 MHz); the aromatic proton of the compound appear as multiplet in the region δ 7.30 (m, 7H, Ar-H), and methyl proton which attach to ring appear in the region give the singlet δ 2.22-3.91 (s, 3H, CH_3), and main signal in the region of δ 8.24-9.53 (s, 1H, CH).

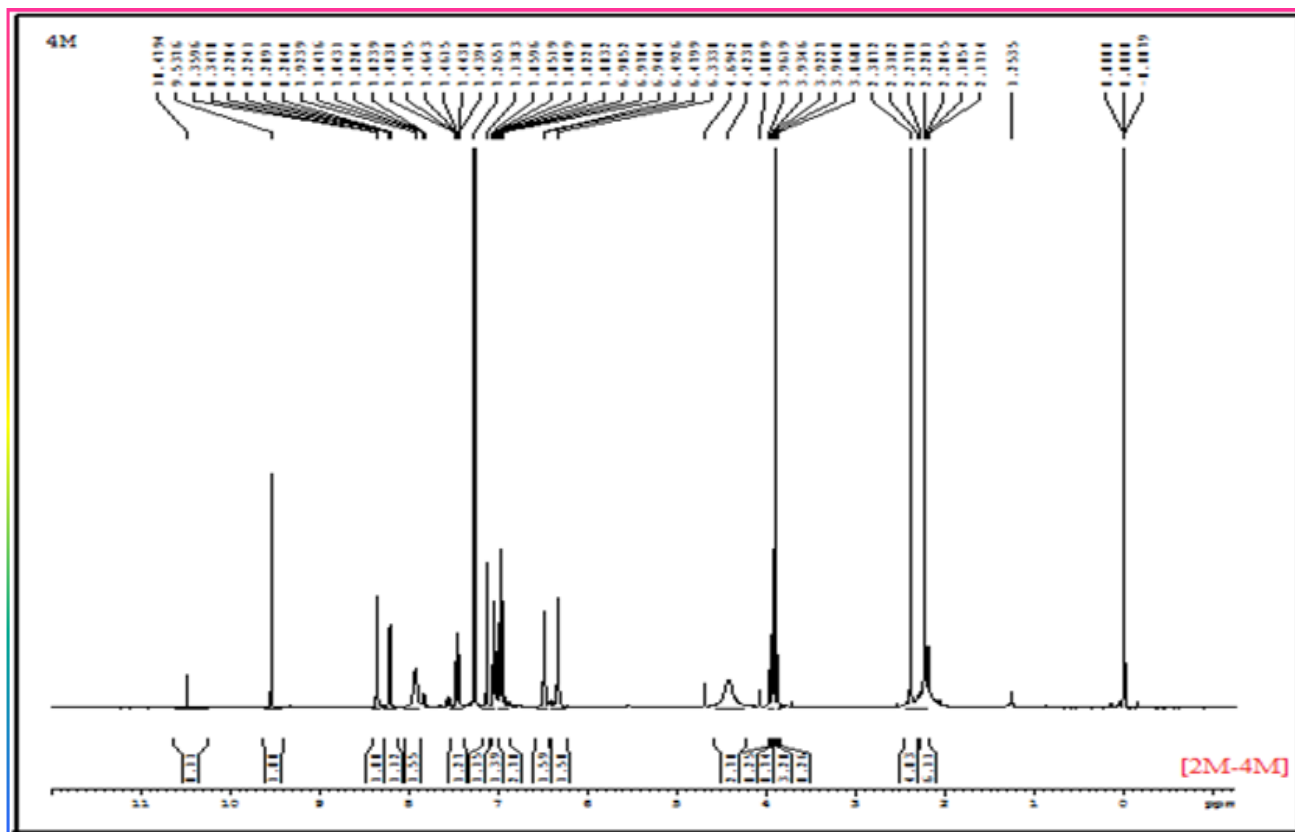


Fig. 1: Spectrum of (E)-N-(2-methoxybenzylidene)-4-methylpyridin-2-amine or [2M-4M]

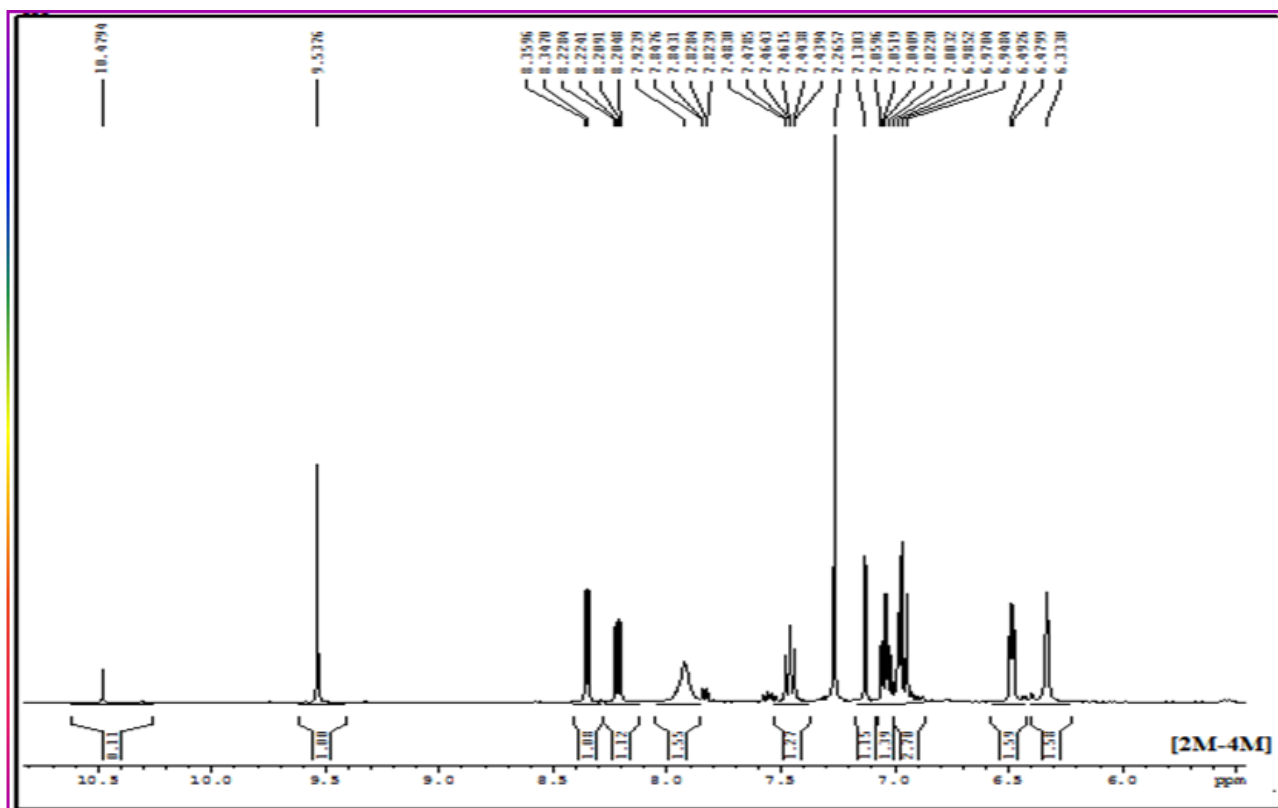


Fig. 2: Spectrum of (E)-N-(2-methoxybenzylidene)-4-methylpyridin-2-amine or [2M-4M]

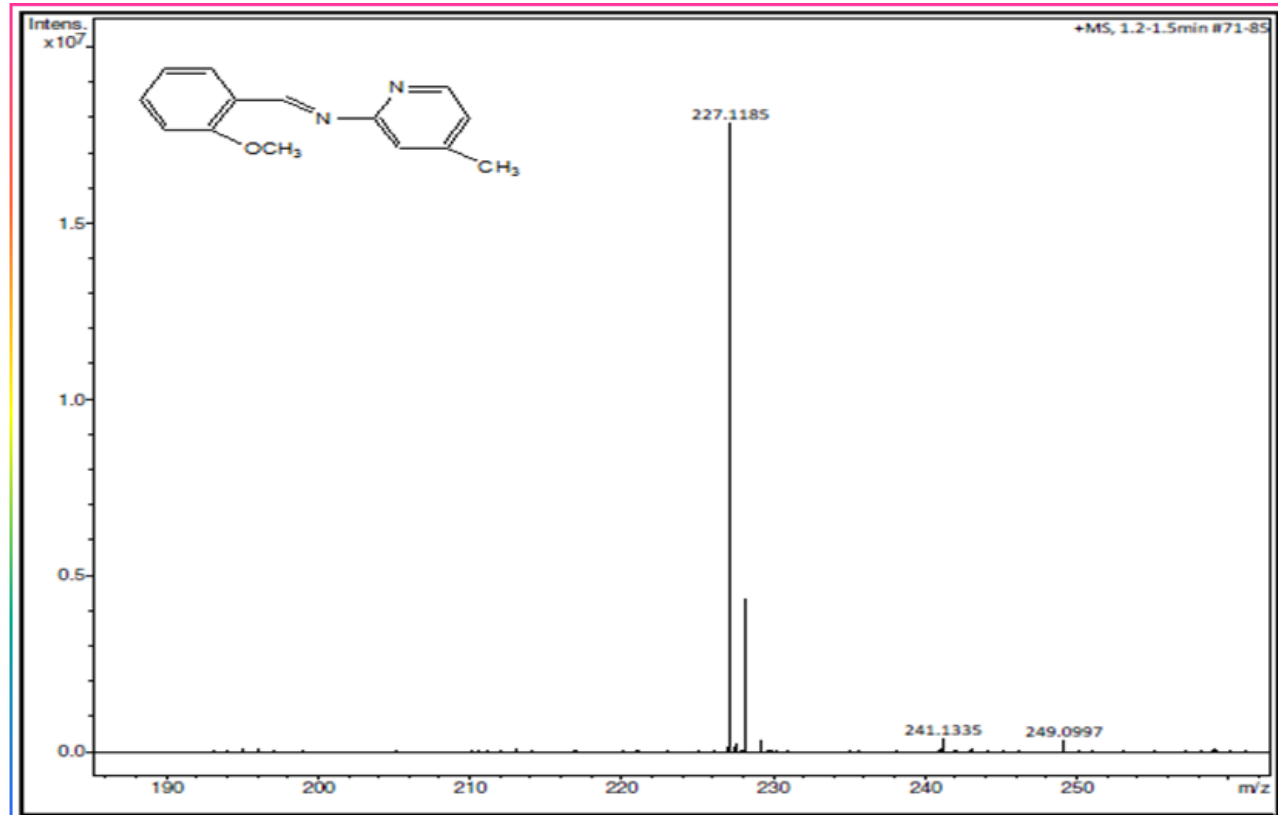


Fig. 3: Mass Spectrum of (E)-N-(2-methoxybenzylidene)-4-methylpyridin-2-amine or [2M-4M]

3.4. Magnetic measurements and ESR Spectra

The data of magnetic moment value of transition metal complexes of Fe (III) and Co (III) suggested that [2M-4M] Fe (III) complexes shows magnetic moment 1.78 B.M which correspond d^5 system having one unpaired electron represent octahedral geometry. The [2M-4M] Co (III) d^6 configuration having four unpaired electron and represent octahedral geometry of the complex. The while the metal ion contain more than d^5 electron favors to form high spin complexes. Similarly, metal ion having less than d^5 electron favors to form low spins complexes. The value of magnetic susceptibility of [2M-4M] Ni (II) & Cu (II) was seen at 0.00, 1.80 B.M. Corresponding to zero and one unpaired electron respectively represent shows square planner geometry [26-27]. Copper is one of the most extensively studied transition metal ion in terms of complex formation. Since d^9 is the whole equivalent of d^1 , one might expect the spectra of copper (II) complexes to the analogous to those of Ti (III), but with the energy level inverted, certainly a simple spectrum would be expected. Unfortunately copper (II) complexes are subject to considerable distortion which renders their absorption spectra quite complex.

ESR study of [2M-4M] Cu (II) complex give the information about hyperfine and super hyperfine. This fact is important in the study of metal ion in

coordination in the complex also give the information about distribution of unpaired electron nature of bonding between chelates and metal ion. The ESR of [2M-4M] Cu (II) recorded in DMF solvent at room temperature represent in fig. 4. The sequence and ESR parameter value shows that $g_{||} > g > g_{\perp}$, the trend indicating the square planner geometry and also supporting that the unpaired electron lies in dx^2-y^2 orbital of Cu (II) ion having $^2B_{1g}$ as ground state [28-31]. The observed value $g_{||} = 2.29$, $g_{\perp} = 2.02$, $g_e (2.0023)$ signify that the unpaired electron occupies the dx^2-y^2 orbital with $^2B_{1g}$ as ground state. The obtained result shows that $g_{||}$ is 2.29 which are confirmedly showing that presence of mixed copper-nitrogen and copper-oxygen bonds in these chelates. If $G > 4.0$, the local tetragonal axes are aligned parallel or If $G < 4.0$, significant exchange coupling is present. The calculated value for the exchange interaction parameter for the copper complex ($G = 5.43$) suggest that the local tetragonal axes are aligned parallel or slightly misaligned and unpaired electron present in dx^2-y^2 . This result also indicates that the exchange coupling effects are not operative in the present complex [32].

According to the Hathway value $G > 4$ exchange interaction is negligible while a value of $G < 4$ suggest a considerable exchange interaction in the complex.

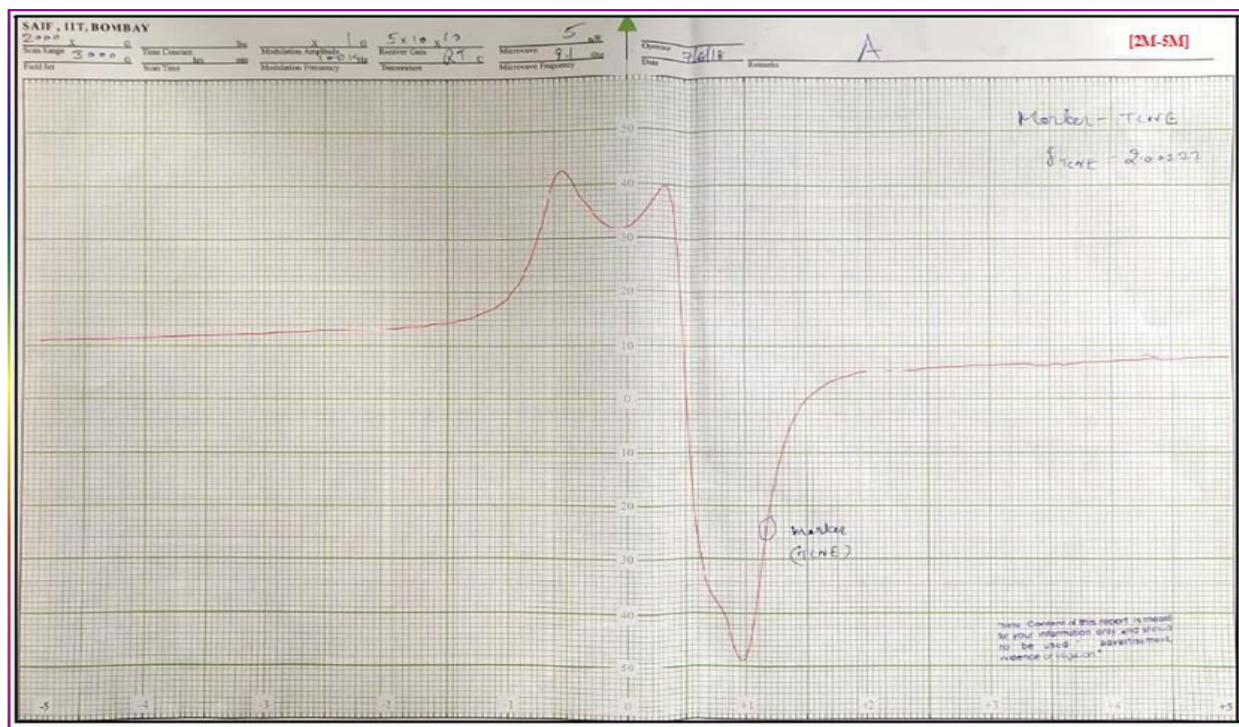


Fig. 4: X-Band of ESR Spectrum [2M-5M] Cu (II).

3.5. Antimicrobial activity

The synthesized transition metal complexes were screened for their antimicrobial activity particularly antibacterial and antifungal activity and were done with the help of disc diffusion method. Microorganisms like gram positive bacteria *Staphylococcus aureus*, Gram negative bacteria *Escherichia coli* and fungi used for these activities were *Candida albicans*, *Aspergillus niger* and *Fusarium moniliforme*.

Agar diffusion assay (disc diffusion method, Disc size 6mm) was used. The stock solution was prepared of 1000 microgram per ml of each compound. The assay was carried out by taking 100 microgram per disk. Chloramphenicol (10 microgram/disc, Amphotericin-B (100 units/disc) moistened with water are used as standard.

The complex [2M-4M] Fe (III) did not affect the growth for the selected microorganism *Staphylococcus aureus* and *Escherichia coli* respectively. Similarly a fungus of microorganism does not show any inhibition except *Candida albicans* show 31% zone of inhibition against its standard Amphotericin-B. From the data of above antimicrobial activity revealed that complex of [2M-4M] Fe (III) show moderate antifungal activity for the fungi of *Candida albicans*. The complex [2M-4M] Co (III) show

less than 70% zone of inhibition to the both bacterium *Staphylococcus aureus* and *Escherichia coli* as well as fungi of *Candida albicans*. The other fungi such as *Aspergillus niger* and *Fusarium moniliforme* which growth does not affected for the synthesized complex Co (III) of its zone of inhibition is none. Above biostatistical data shows that the complex of Co (III) exhibit moderate antibacterial as well as antifungal activity than its standard. The complex of [2M-4M] Ni (II) which growth does not affect on selected microorganism except fungi of *Aspergillus niger* exhibit moderate antifungal activity against its standard. The synthesized metal complex [2M-5M] Cu(II) are the strongest inhibition for the bacterium *Staphylococcus aureus* and about 75% inhibition zone to the bacteria of *Escherichia coli*. Similarly fungi of all microorganism such as *Candida albicans*, *Aspergillus niger* and *Fusarium moniliforme* having zone of inhibition 40%, 67%, and 55% respectively. Copper is strongest compound that inhibit the growth of microorganism the result are more than expected for the bacterium of *Staphylococcus aureus* and it is about 75% for gram negative bacteria *Escherichia coli*. Similarly fungi of all microorganisms give the wonderful response toward synthesized complex [2M-5M] Cu (II).

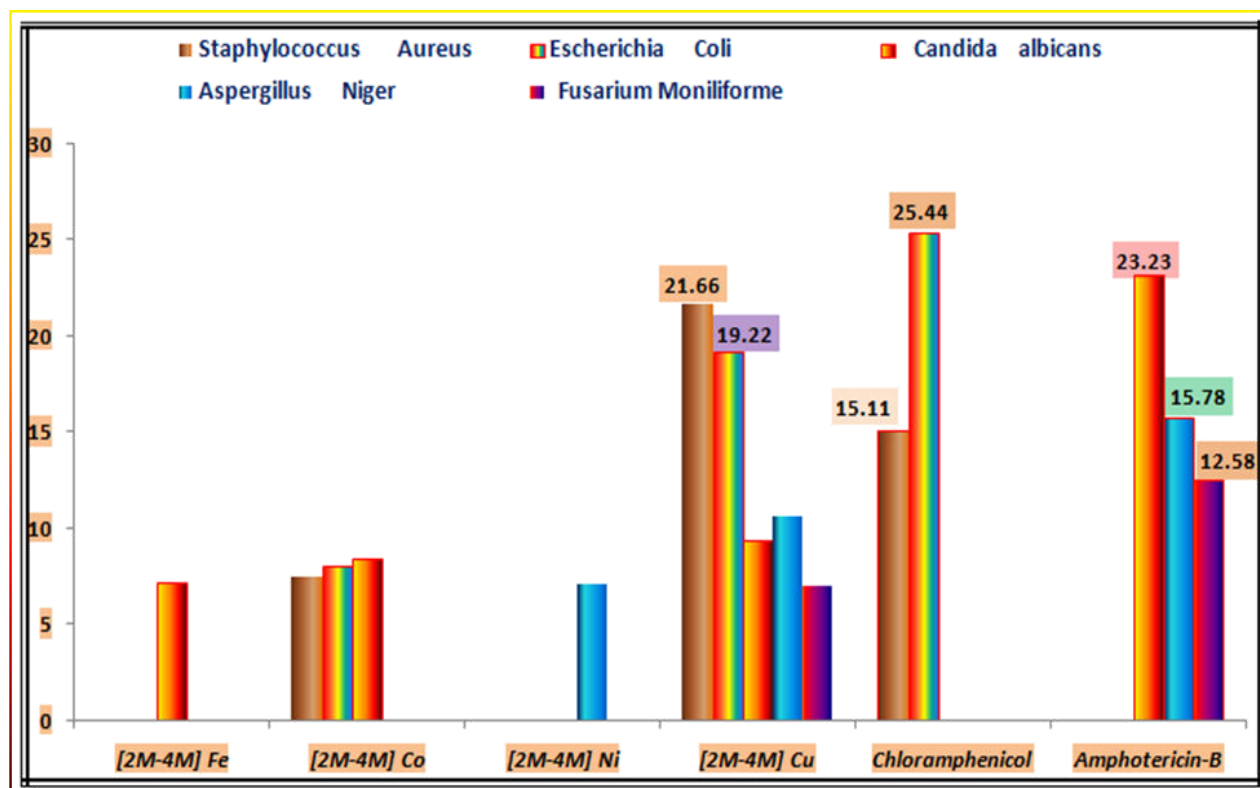


Fig. 5: Graphical representation of Antimicrobial activity

Table 1: Antimicrobial Activity of Metal Complexes

Sr. No	Sample Code	Staphylococcus Aureus	Escherichia Coli	Candida Albicans	Aspergillus Niger	Fusarium Moniliforme
1	[2M-4M] Fe	--	--	7.21	--	--
2	[2M-4M] Co	7.51	8.02	8.44	--	--
3	[2M-4M] Ni	--	--	--	7.13	--
4	[2M-4M] Cu	21.66	19.22	9.43	10.68	7.02
Chloramphenicol		15.11	25.44	NA	NA	NA
Amphotericin-B		NA	NA	23.23	15.78	12.58

'NA' Means not applicable, '--' means no zone of inhibition 100 µgm concentration.

3.6. Antioxidant Activity

The free radical scavenging activity of transition metal complexes were determined using 2, 2 diphenyl-1 picrylhydrazyl radical (DPPH) method. Different concentrations of test compounds 50, 100, 200, 300, 400 mg/ml were used and standard used were Ascorbic acid and Gallic acid. The antioxidant activity of the sample was done by using DPPH radical scavenging method. The assay was carried out in a 96 well microlitre plate to 200µl of DPPH solution, 10µl of each of the test sample or standard solution was added separately in wells of the microlitre plates. The plates were incubated at 37°C for 20 minutes and the observance of each well was at 517 nm, using ELISA reader against corresponding test and standard blanks and the remaining DPPH was calculated. The IC₅₀ (Inhibitory Concentration) is concentration of the sample required to Scavenge 50% DPPH free radicals.

$$\% \text{ Inhibition} = (\text{Control-Sample}/\text{Control}) \times 100$$

The IC₅₀ calculated based on regression equation generated by plotting the graph of Conc. Vs % inhibition.

Regression equation:

$$Y=MX+C$$

Where Y = intercept i.e., 50, C = Concentration

required to inhibit the oxidative radical to 50 %, M and C are the component of regression generated on the graph in MX excel.

Complex [2M-4M] Fe (III) shows less scavenging activity at concentration 400 mg/ml. Similarly maximum scavenging activity at concentration 50 mg/ml having percent inhibition 10.42 with standard deviation 0.28 and show somewhat same activity at concentration 100 and 200 mg/ml. From the conclusion of above data, it shows that complex Fe (III) show good antioxidant activity at concentration 50 mg/ml and exhibit moderate activity at concentration 100 and 200 mg/ml having percent inhibition 17.46 and 17.52 respectively. The antioxidant activity of complex [2M-4M] Co (III) show maximum activity at concentration 50 mg/ml having percent inhibition 13.48 and also show moderate activity at concentration 100 and 200 mg/ml having standard deviation 0 and 0.18 respectively. From the conclusion of above data, it is clear that complex of Co (III) exhibit good antioxidant activity at concentration 50 mg/ml with standard deviation 0.28 and at concentration 100 and 200 mg/ml show moderate activity and its percent inhibition was 15.63 and 16.36 respectively.

Table 2: Antioxidant data of Metal complexes

Conc [µg/ml]	[2M-4M] Fe		[2M-4M] Co		[2M-4M] Cu		[2M-4M] Ni	
	% Inhibition	±SD	% Inhibition	±SD	% Inhibition	±SD	% Inhibition	±SD
50	10.42	0.28	13.48	0.28	5.67	0.30	31.95	0.40
100	17.46	0.18	15.63	0.00	5.87	0.68	43.60	0.15
200	17.52	0.28	16.36	0.18	10.38	0.78	56.48	0.26
300	18.69	0.11	26.47	1.84	10.96	0.78	60.79	0.65
400	19.73	0.11	28.92	0.28	14.06	0.59	70.12	0.79
IC ₅₀	1854.95		847.44		1874.18		183.53	

The complex of [2M-4M] Ni (II) for free radical antioxidant activity at different concentrations i.e. 50,

100, 200, 300, 400 having percent inhibition is 31.95, 43.61, 56.46, 60.79, and 70.12 respectively in relation

to their standard deviation. From the upshot of above data it is clear that lower the IC₅₀ value, higher the antioxidant activity hence the complex of Ni (II) show good antioxidant activity at concentration 50 mg/ml compared to the other concentration test solution.

The result of antioxidant activity of complex [2M-4M] Cu (II) is maximum at concentration 50 & 100 mg/ml

having percent inhibition 5.67 & 5.87 respectively. They also show moderate activity at concentration 200 & 300 mg/ml with standard deviation 10.38 & 10.96 respectively. Above biostatistical data indicate that the Cu (II) show good antioxidant activity at concentration 50 & 100 mg/ml and somewhat less scavenging activity at concentration 200 & 300 mg/ml.

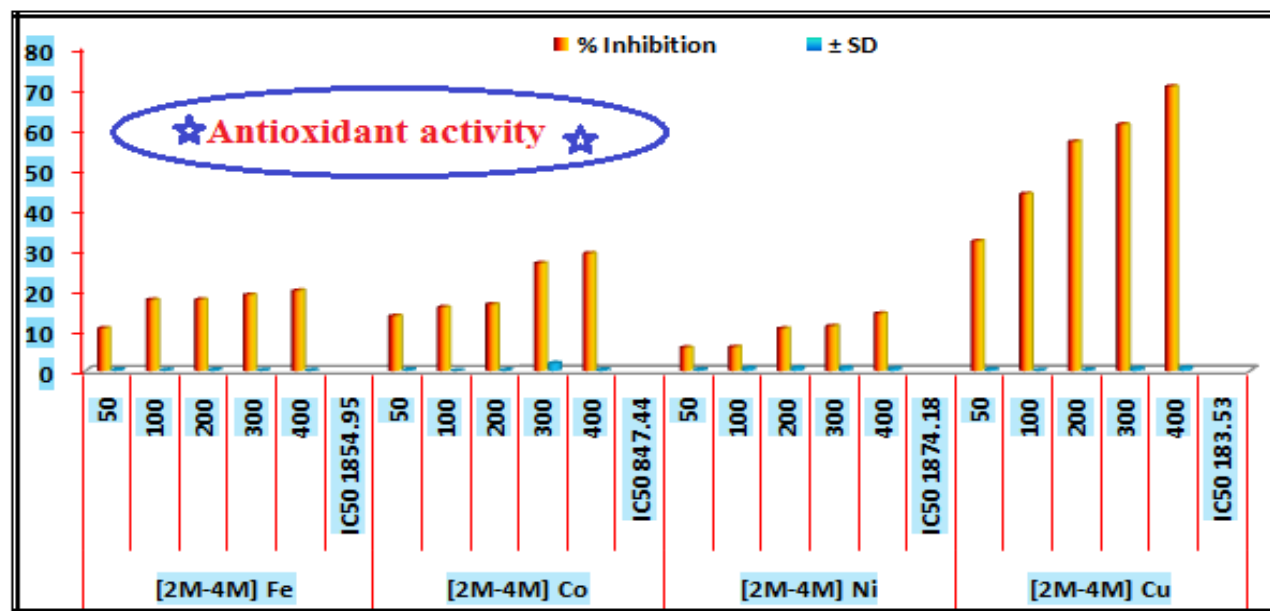


Fig. 6: Graphical representation of Antioxidant activity of Metal complexes

3.7. Thermogravimetric Analysis

Thermal examination was performed to learn out the thermal stability of metal complexes and its degradation arrangement in which the modification in the importance of substance is recorded as serve of temperature. Thermo gravimetric examination was performed in nitrogen atmosphere with heating rate 10°C min⁻¹ and thermogram was recorded in temperature range ambient to 500°C. By via TGA assay quite a lot of kinetics parameters such as Energy of activation (E_a), Free energy (ΔG), Entropy change (ΔS), order of reaction (n) have been analyzed using Freeman Carroll method.

The kinetic parameters of all the transition metal complexes by Freeman and Carroll methods have been determined and computerized software is essential for processing the enormous amount of data involved in this analysis and represented graphically by Microsoft Excel. Procedure adopted was suggested by Nair et al [33].

Freeman and Carroll method:

$$\frac{\Delta \log(dw/dt)}{\Delta \log Wr} = \left(- \frac{E_a}{2.303R} \right) \cdot \frac{\Delta \left(\frac{1}{T} \right)}{\Delta \log Wr} + n$$

Where dw/dt = rate of change of weight with time; Wr = W_c-W, W_c = Weight loss at the completion of reaction, W = Total weight loss up to time t; E_a = Energy of activation, N = order of reaction.

The thermogravimetry of [2M-4M] Fe (III) complex show faster heating rate or due to no intermediaries but in the first phase of decomposition was observed having temperature range 75-145°C with a mass loss 3.11 % (Calculated 3.98%) indicate the loss one crystal lattice water molecule. While in second phase of decomposition having in the temperature range 150-250°C with mass loss 16.75% (Calculated 15.70%) indicate the removal of two chlorine atom. At temperature above 375°C, there was no significant mass loss observed and weight loss remain constant correspond to stable metal oxide shown in Fig. 7.

In the thermal analysis of [2M-4M] Co (III) metal complex, its mass loss pattern was observed due to

faster heating rate or due to no intermediaries. In the first stage of decomposition having temperature range 75-150°C with mass loss 4.45% (calculated 5.12%) indicates the removal two crystal lattice water molecules. In the Second stage of decomposition, no significant mass loss was observed in the temperature range 175-228°C. While at that of temperature above 380°C, there is no significant mass loss was observed over entire range of temperature and weight loss remains constant due to stable metal oxide (Fig. 7).

The thermogram of [2M-4M] Ni (II) complex exhibit single step decomposition but in the first phase of decomposition in the range 80-160°C there is no loss of crystal lattice water molecule and in the second decomposition phase in the range 160-310°C 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 shown. The thermogram of [2M-4M] Cu (II) metal complex exhibit that there is no significant degradation of mass loss. In the first phase of decomposition having temperature range 80-270°C there is no luminous change of mass was observed while that of temperature above 350°C weight loss remain constant there is no significant mass loss observed over the entire range of temperature as shown in Fig. 8.

The kinetic parameters of degradation of the metal complexes were calculated by Freeman-Carroll (FC) method.

Statistical data hints that the value of order of reaction is consistently one. The damaging entropy hints that additional planned activated splendor that may be achievable through chemisorptions of oxygen and other decay product.

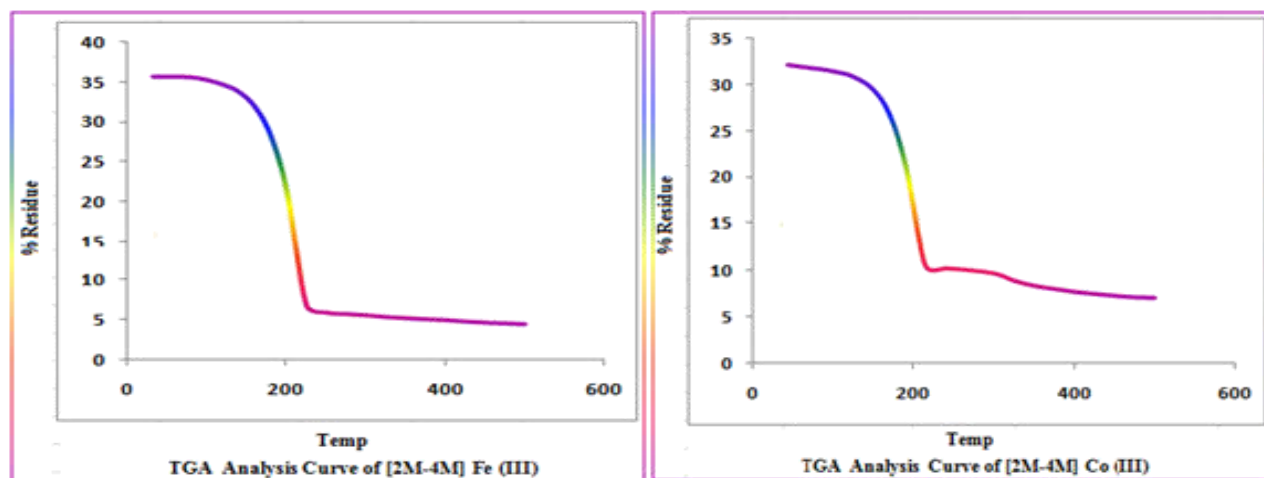


Fig. 7: TGA Analysis curve of [2M-4M] Fe & Co

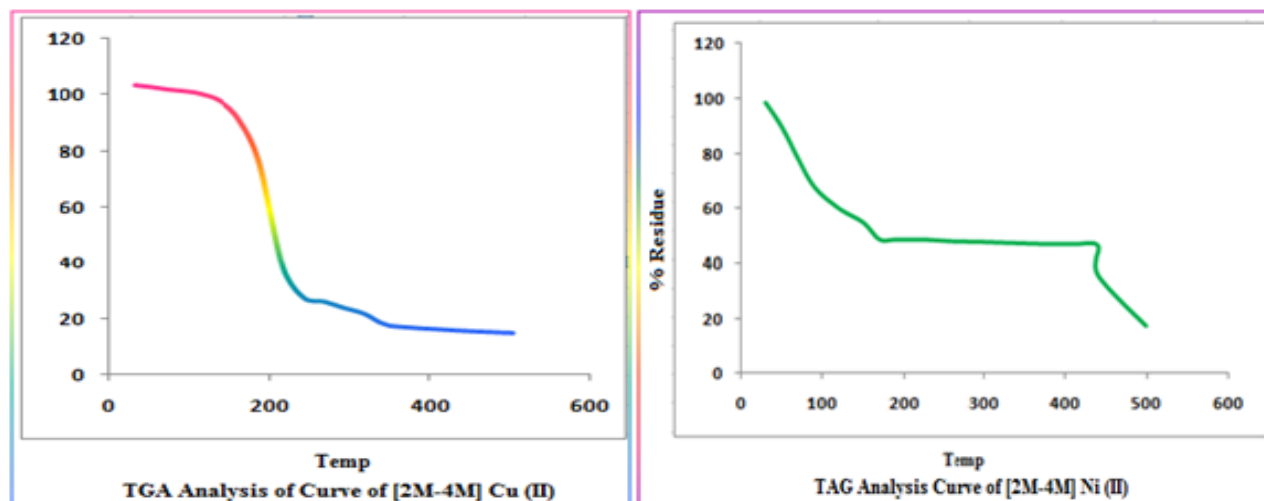


Fig. 8: TGA Analysis curve of [2M-4M] Cu & Ni

Table 3: Table of kinetic parameters by Freeman Carroll method

Sample Code	Method	Order of Reaction (n)	Energy of Activation Ea (kJ/mole)	Entropy Change (ΔS)	Free energy Change (ΔG)	μ effective B.M
[2M-4M] Fe	FC	1.1	7850.03	-201.86	72273.73 J	1.78
[2M-4M] Co	FC	1.02	7275.91	-145.01	75865.73 J	4.87
[2M-4M] Ni	FC	1.07	7084.44	-139.71	77585 J	2.94
[2M-4M] Cu	FC	1.06	8884.27	-143.28	87473.27 J	1.81

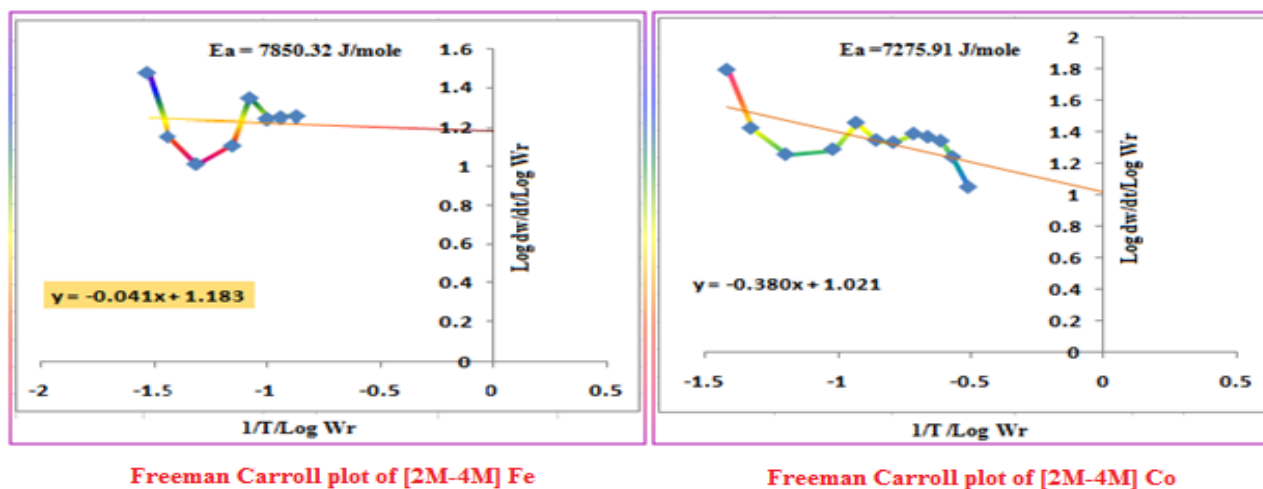


Fig. 9: Plot of Freeman Carroll equation of [2M-4M] Fe & Co

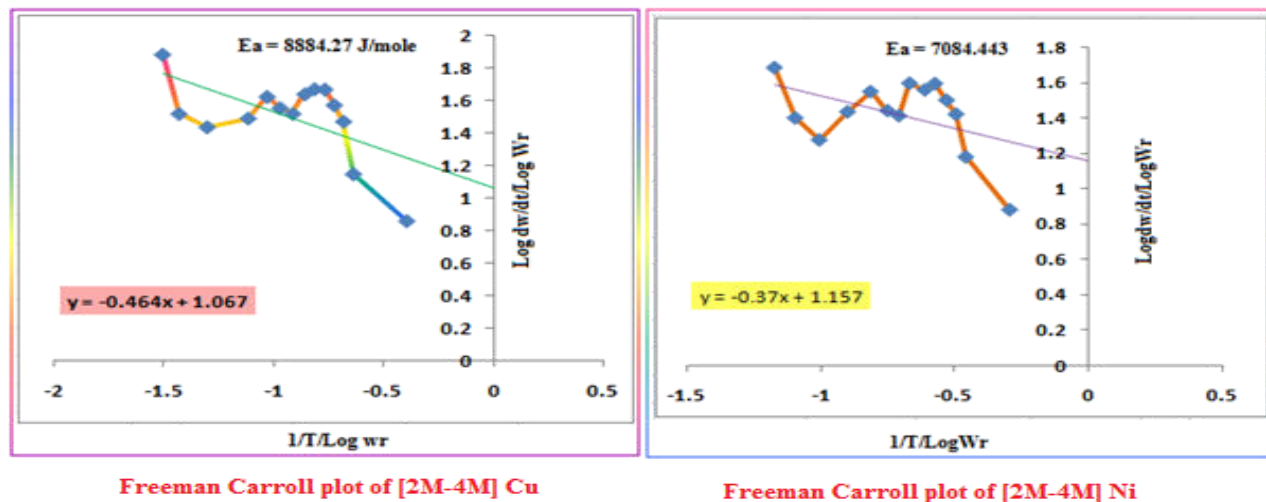


Fig. 10: Plot of Freeman Carroll equation of [2M-4M] Cu & Ni

4. CONCLUSION

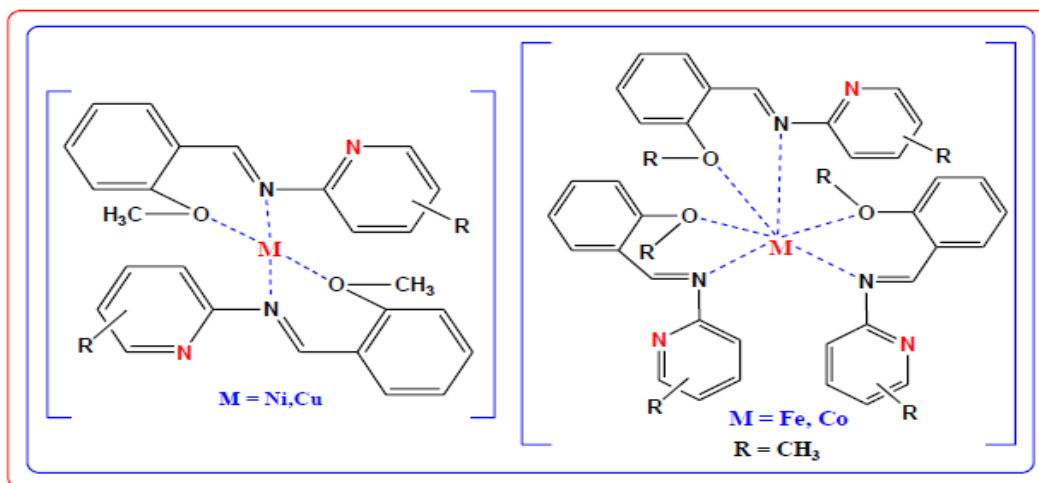
The present investigation includes the synthesis, characterization of novel class Schiff base ligand and their transition metal complexes. The characterization of compounds includes FT-IR, Mass, $^1\text{H-NMR}$, TGA, ESR, antimicrobial, antioxidant activity and magnetic susceptibility studies.

The result indicated that the complex [2M-4M] Cu (II) shows potent antibacterial and good antifungal activity against. The screening results of antioxidant activity assay indicated that the complex [2M-4M] Ni (II) & Co (III) exhibits excellent scavenging activity. The data of ESR Cu (II) recorded at room temperature DMF solvent and magnetic moment provides the information

about geometry of complexes. The sequence of $g_{\parallel} > g_{\perp} > g_{\text{avg}}$ suggesting the complex is square planer geometry and unpaired electron lies in dx^2-y^2 orbital. The additional supporting evidences like magnetic moment and FT-IR helpful for geometry of complex. The complexes of Cu (II), Ni (II), shows square planar geometry and complex of Fe (III), Co (III) show octahedral geometry. The screening of thermal investigation of complex [2M-4M] Fe, Co, Cu, exhibits large single decomposition and slightly different decomposition pattern was observed in Ni (II) complex afterward weight loss remain constant. By using this

thermogram, kinetic parameters such as Energy of activation (E_a), order of reaction (n), free energy change (ΔG), Entropy change (ΔS) were calculated using the Freeman Carroll method. The order of reaction was consistently one and negative value of entropy indicate that more ordered activated state that may be possible through chemisorptions of oxygen and decomposition product and more ordered nature may be due to polarization of bond in activated state.

From the elemental analysis, spectral data and chemical analysis, following proposed structure can be assigned to complexes.



Geometry of Ni (II) and Cu (II) metal complexes exhibit square planer having (Metal ligand ratio 1:2) and Fe (III), Co (III) represent Octahedral shape having (Metal ligand ratio 1:3).

5. ACKNOWLEDGEMENT

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Conflict of Interest

The authors declare no conflict of interest.

6. REFERENCES

- Shibuya Y, Nabari K, Kondo M, Yasue S, Maeda K, et.al. *Chem Lett.*, 2008; **37** (1):78-79.
- Gangani BJ, Parsania PH. *Spectroscopic Lett.*, 2007; **40**(1):97-112.
- Kumari BS, Rijulal G, Mohan K. *Inorg. Met-Org. Nano-Met. Chem.*, 2004; **39**(1):24-30.
- Thanakmony M, Mohanan K. *Indian. J.Chem. A.*, 2007; **46**(2):247-251.
- Raman N, Dhavethu J, Sakthivel A, et.al. *J. Chem. Sci.*, 2007; **119**(4):303-310.
- Wang, D, Yang Y, Yang, Y, Zhao T, Wu X, et.al. *Sci Bulletin*, 2006; **51**:785-780.
- Shivakumar K, Shashidhar Halli MB, et.al. *J. Co-ord. Chem.*, 2006; **59**(16):1847-1856.
- Sadeek, S, Refat M, et.al. *J. Korean. Chem. Soc.*, 2006; **50**(2):107-115.
- Tan SF, Ang KP. *Tran. Met. Chem.*, 1988; **13**(1):64-68.
- Odds F, Brown A, Gow N. *Trend in Microbiology*, 2003; **11**(6):272-279.
- Fidel P, Vazquez J, Sobelm J. *Clinical Microbiology Review*, 1999; **12**(1):80-96.

12. Prasad R, Berlin Springer-Verlag Heidelberg New York., 1991; **267**, 281.
13. Gupta A, Tomas E. *Dermatologic clinics*, 2003; **21**:565-576.
14. Chami N, Chami F, Bennis S, Trouillas J, et.al. *Brazilians. J. Infectious Diseases*, 2004; **8(3)**:217-226.
15. Choi K, Lee H, Park B, Kim H, Kim J, Kim M, et.al. *Polyhedron*, 2001; **20(4)**:2003-2009.
16. Jones R, Summerville D, Basolo F. *Chemical Reviews*, 1979; **79(2)**:139-179.
17. Wang M, Wang L, Li Y, Li Q, Xu Z. *Tran. M. Chem.*, 2001; **26(3)**:307-310.
18. Borase J, Mahale R, Rajput S. *Eur. J. Biomed. Phar. Sci.*, 2017; **4(10)**:842-845.
19. Neelakantan MA, Rusalraj F, Dharmaraja J, Johnsonraja S, et.al. *Spectrochimica Act Part A: Molecular and Biomolecular Spect.*, 2008; **71(4)**:1599-1609.
20. Kandil SS, Ali GY, El-Dissouky A. *Tran. M. Chem.*, 2002; **27(4)**: 398-406.
21. You ZL, Zhu HL, Liu WS, *Allgemeine Chemie.*, 2004; **630(11)**: 1617-1622.
22. You ZL, Zhu H, et.al. *Allgemeine Chemie.*, 2004; **630(15)**: 2754-2760.
23. Benial A, Ramkrishnan V, Murugeson R. *Spectrochim. Acta Part A: Molecular & Bimol. Spectro.*, 2000; **56(14)**:2775-2781.
24. Nair C, Madhusudhanan P. *Thermochimica Acta.*, 1976; **14**:373-382.
25. Alan I, Kriza A, Badea M, Stanica, N, et al. *J. Ther. Ana. Calo.*, 2013; **111(1)**:483-490.
26. Pawar SP, Patil TJ, Bendre RS, *Asian J. Resea. Chem.*, 2018; **11(1)**:8-14.
27. Nair MS, Josephus, RS, et al. *Molecular & Biomolecular Spectroscopy*, 2008; **70(4)**: 749-753.
28. Fu HL, Zheng K, Zhang, MJ, Li, YT, Wu ZY, et al. *J. Photochemistry & Photobiology B: Biology*, 2016; **161**:80-90.
29. Ray RK, George B, et al. *Inorg. Chimica Acta.*, 2004; **173(2)**:207-214.
30. Jeyasubramanian K, Samath SA, Thambidurai S, Murugesan R, et al. *Tran. M. Chem.*, 1995; **20(1)**:76-80.
31. Raj BB, Kurup MP, Suresh E, et al. *Mol. & Biomol. Spectro.*, 2008; **71(4)**:1253- 1260.
32. Raman N, Thangaraja C, Johnsonraja S. *Open Chem.*, 2005; **3(3)**:537-555.
33. Nair CGR, Madhusudanan PM. *Thermochimica Acta.*, 1976; **14(3)**:373-382.