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TEMPLATE SYNTHESIS AND SPECTRAL STUDIES OF BIOLOGICALLY ACTIVE Ni(II), AND Cu(II) TRANSITION METAL COMPLEXES OF TETRADENTATE AZA-OXO (N₂O₂) MACROCYCLIC LIGAND

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ABSTRACT: A novel series of transition metal complexes of [M(C₁₉H₁₈N₂O₂S)₂], where M = Ni(II), Cu(II), X = Cl⁻, NO₃⁻, ½ SO₄²⁻ and (C₁₉H₁₈N₂O₂S) moiety corresponds to the tetradentate aza-oxo macrocyclic species, were synthesized by template condensation reaction of 1,4-bis(2-formylphenoxy)butane and thiourea in the presence of divalent metal salts in 1:1:1 ratio. The metal complexes were characterized and analyzed by elemental analyses, molar conductance, magnetic measurements, and spectral techniques like IR, mass, UV-VIS, electron paramagnetic resonance spectroscopy, and thermal studies. The low values of the molar conductance values indicate the non-electrolytic nature of synthesized complexes except nitrate complex of Ni (II) which is 1:2 electrolytic in nature. Based on aforesaid spectral studies, [Cu(C₁₉H₁₈N₂O₂S)(SO₄)] complex may possess trigonal bipyramidal geometry, [Ni(C₁₉H₁₈N₂O₂S)](NO₃)₂ complex tetrahedral geometry and rest of the complexes six coordinated octahedral/tetragonal geometry. To explore the complexes in the biological field, synthesized transition metal complexes were examined against the pathogens *A. niger*, *S. rolfsii*, *F. oxysporum*, and *A. brassicae*. All metal complexes displayed good antifungal activity.

INTRODUCTION: Synthetic macrocyclic are a growing class of compounds with varying chemistry with a wide range of different molecular topologies and sets of donor atoms¹. The chemistry of macrocyclic complexes has received much attention in recent years².

Macrocyclic metal complexes were studied extensively because of their attractive chemical and physical properties and their wide range of applications in numerous scientific areas^{3,4,5,6}.

In the biological field, transition metal macrocyclic complexes have received great attention because of their antitumor, antibacterial, antiviral, antifungal and anticarcinogenic activities^{7,8,9}. Such biological activities are due to their ability to form a tetradentate chelate with essential heavy metal ions, bonding through nitrogen, sulfur, and oxygen¹⁰. The complexes of metal ions in combination to macrocyclic ligands are significant, as these

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resemble with natural systems like porphyrin and cobalamine^{11, 12}. We made our efforts to design and develop aza-oxo containing (N₂O₂-donor) macrocyclic metal complexes of 3d transition metal series. The present report deals with the synthesis, spectral studies, thermal study, and biological evaluation of Ni(II), and Cu(II) complexes, which were derived from 1,4-bis(2-formylphenoxy)butane and thiourea.

MATERIALS AND METHODS: All used chemicals were commercial products and used as supplied. Salicylaldehyde, 1, 4-dibromobutane and thiourea were of AR grade and procured from Sigma Aldrich, Bangalore, India. Metal salts were purchased from E. Merck, India and were used as received. All used solvents were of spectroscopic grade.

Synthesis of 1, 4-bis (2-formylphenoxy) butane:

To a stirred solution of salicylaldehyde (24.4 g, 0.2 mol) and K₂CO₃ (13.8 g, 0.1 mol) in DMF (25 mL), 1, 4-dibromobutane (21.6 g, 0.1 mol) was added dropwise. The reaction was refluxed for 10 h in 150-155 °C and then for 5 h at room temperature. The reaction solution was put in a refrigerator. One hour later, the precipitate was formed; it was filtered off, and washed with distilled water, recrystallized from ethanol and dried in vacuum **Fig. 1**.

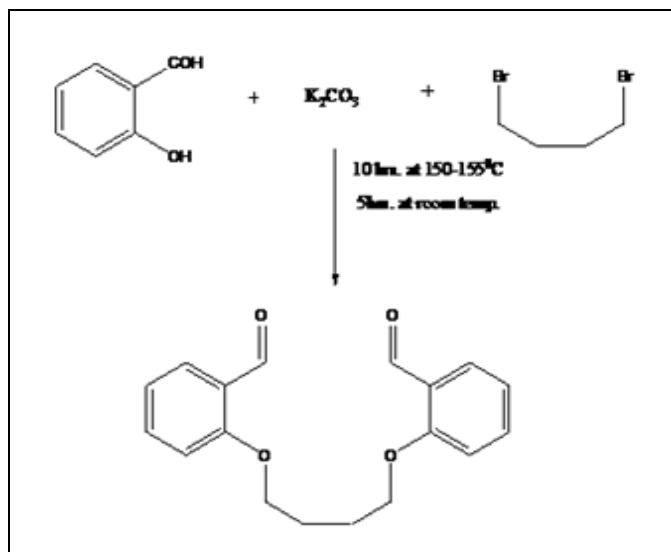


FIG. 1: SYNTHESIS OF 1, 4-BIS (2-FORMYLPHENOXY) BUTANE

Synthesis of Macrocyclic Metal Complexes: All the complexes were synthesized by the template method, *i.e.*, by condensation of 1, 4-bis (2-

formylphenoxy) butane and thiourea in the presence of divalent metal salts in 1:1:1 ratio. In the hot methanolic solution of 1, 4-bis (2-formylphenoxy) butane (1.0 mmol) methanolic solution of the divalent metal salt of Ni(II), and Cu(II) (1 mmol) was added. The resulting solution was refluxed for 5 h, after which thiourea (1.0 mmol) was added to the above solution and then refluxed continue for 8-12 h. On overnight cooling, a coloured precipitate was formed which was filtered, washed with methanol, and dried in vacuum. The obtained yield was \approx 55-65%.

The template condensation of 1,4-bis(2-formylphenoxy)butane and thiourea in the presence of bivalent metal salts, in the molar ratio 1:1:1 is represented in **Fig. 2**.

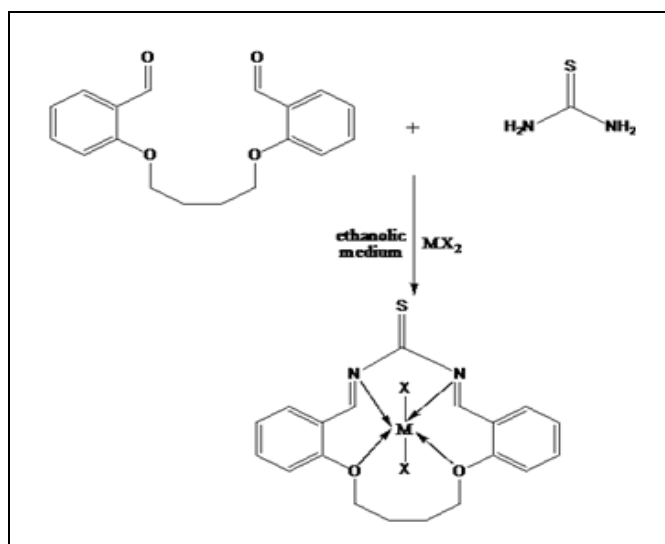


FIG. 2: TEMPLATE SYNTHESIS OF TRANSITION METAL COMPLEXES. (M = Ni (II), Cu (II) and X = Cl⁻, NO₃⁻, ½ SO₄²⁻)

Physical Measurements: Elemental study (CHN) was analyzed on Carlo-Erba 1106 elemental analyzer. Molar conductance was measured on the ELICO (CM82T) conductivity bridge. Magnetic susceptibility was measured at room temperature on a Gouy balance using CuSO₄.5H₂O as calibrant. IR spectra were recorded on FT-IR spectrum BX-II spectrophotometer in KBr pellet. The electronic spectra were recorded in DMSO on Shimadzu UV-visible mini-1240 spectrophotometer. Electronic impact mass spectrum was recorded on JEOL, JMS-DX-303 Mass Spectrometer. EPR spectra of all complexes were recorded at room temperature (RT) on E₄-EPR spectrometer using the DDPH as the g-marker at SAIF, IIT Bombay.

Antifungal Activity: The Poison food Technique¹³ was applied to examine fungicidal investigations of synthesized metal complexes against *A. niger*, *S. rolfisii*, *F. oxysporum*, and *A. brassicae*. DMSO and Captan were employed as control and standard fungicide, respectively. The inhibition of growth of fungi was expressed in percentage and determined by using the following relation, which is given below:

$$I (\%) = (CT) / C \times 100$$

TABLE 1: PHYSICAL PROPERTIES AND ANALYTICAL DATA OF NI (II) AND CU (II) COMPLEXES

Compound	Colour	M.P (°C)	M. Wt	Molar conductance	Yield (%)	Elemental Analysis found (calculated)			
						C	H	N	M
1,4-bis (2-formylphenoxy)butane (C ₁₉ H ₁₈ N ₂ O ₄)	Light brown	85	298	-	68	73.01 (72.46)	5.14 (5.04)	-	-
[Ni(C ₁₉ H ₁₈ N ₂ O ₂ S)Cl ₂]	Dark green	>200	467.7	24	58	47.10 (45.86)	5.29 (3.82)	5.88 (5.94)	12.35 (12.46)
[Ni(C ₁₉ H ₁₈ N ₂ O ₂ S)](NO ₃) ₂	Dark brown crystal	>120	520.7	231	54	42.88 (41.16)	4.19 (3.43)	11.62 (10.67)	11.00 (11.18)
[Cu(C ₁₉ H ₁₈ N ₂ O ₂ S)Cl ₂]	Dark green	>360	472.5	25	61	42.93 (45.37)	3.74 (3.78)	5.49 (5.88)	13.38 (13.23)
[Cu(C ₁₉ H ₁₈ N ₂ O ₂ S)(NO ₃) ₂]	green	>340	525.5	27	55	40.98 (40.83)	3.10 (3.40)	11.38 (10.58)	11.77 (11.90)
[Cu(C ₁₉ H ₁₈ N ₂ O ₂ S)(SO ₄)]	Dark green	>250	497.5	22	52	37.01 (36.18)	2.71 (3.01)	4.38 (4.69)	10.50 (10.55)

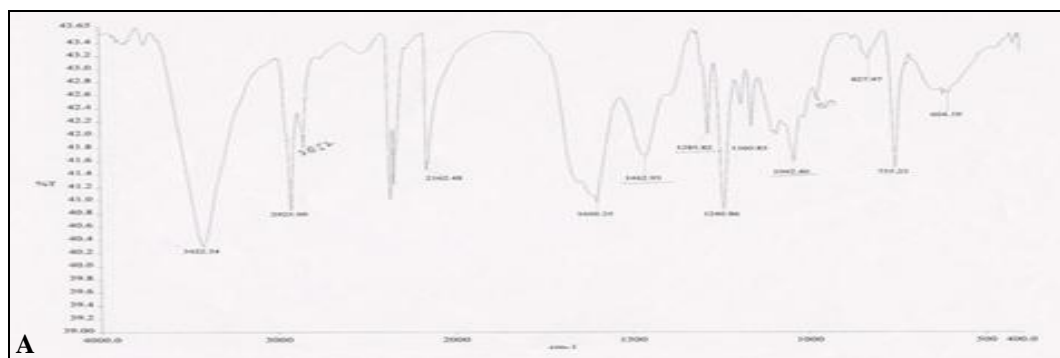
IR Spectra: In IR spectrum of metal complexes bands in the region 2850-2880 cm⁻¹, 1590-1630 cm⁻¹, and 750-780 cm⁻¹, corresponding to the presence of the aromatic stretching, azomethine group (C=N), stretching vibration of C=S group. This binding of donor atoms to a metal ion is also supported by the appearance of new IR bands at 438-480 and 590-610 cm⁻¹ due to ν (M-N) and ν (M-O) vibrations, respectively^{14, 15, 16}. This discussion reveals that the nitrogen atom of the azomethine group and an oxygen atom (present in the macrocyclic ring) coordinates to metal ions as tetradentate chelate to form complexes. However, a strong absorption band in the range of 750-780 cm⁻¹

Where: I = % Inhibition, C = Radial diameters of the colony in control, T = Radial diameter of the colony in the test compound.

RESULTS AND DISCUSSION: Based on elemental analysis data **Table 1**, all the complexes have the general composition [M (C₁₉H₁₈N₂O₂S) X₂], where M = Ni(II), and Cu(II) The complexes were obtained in powder form. These were found to be soluble in DMF and DMSO for spectral measurements.

¹ remain as such in IR spectra of all metal complexes, indicates that C=S don't coordinate to the metal ion.

Bands Due to Anions: In IR spectra of chloride complexes, bands corresponding to (M-Cl) were observed at 345-325 cm⁻¹. The IR spectrum of the nitrate complex of Ni (II) shows a strong band at 1384 cm⁻¹ corresponds to uncoordinated behavior of the nitrate ion. IR spectrum of nitrate complex of Cu (II) displays three (N-O) stretching bands, at 1462 (ν_5), 1285 (ν_1) and 1042 cm⁻¹ (ν_2). The separation of the two highest frequency bands (ν_5 - ν_1) is 177 cm⁻¹ **Fig. 3(a)**.



It is suggesting that both nitrate groups are coordinated to the central metal ion in a unidentate manner. The spectrum of sulfate complex of Cu(II)

shows that band ν_3 split at 1121 cm^{-1} and 1054 cm^{-1} , corresponds to unidentate behaviour of sulfate ion¹⁷ **Fig. 3(b)**.

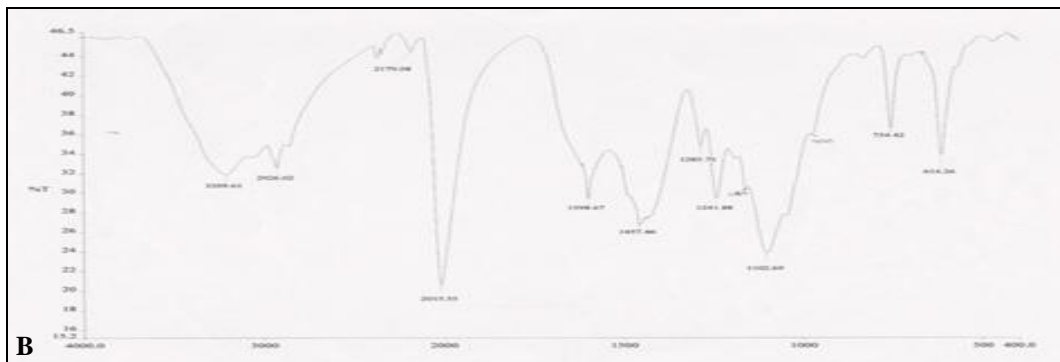


FIG. 3: IR SPECTRUM OF 3(a) $[\text{Cu}(\text{C}_{19}\text{H}_{18}\text{N}_2\text{O}_2\text{S})(\text{NO}_3)_2]$, 3(b) $[\text{Cu}(\text{C}_{19}\text{H}_{18}\text{N}_2\text{O}_2\text{S})(\text{SO}_4)]$

Magnetic Moment: The magnetic moments of Ni (II) complexes lies in the range 2.96-2.98 B.M. These values indicate the presence of two unpaired electrons. At room temperature Cu(II) complexes show the magnetic moment in the range 1.88-1.97 BM corresponding to one unpaired electron **Table 2**.

Electronic Spectra of Nickel (II) Complexes: The electronic spectra of the $[\text{Ni}(\text{C}_{19}\text{H}_{18}\text{N}_2\text{O}_2\text{S})\text{Cl}_2]$ complex shows bands in the range 9661-10834, 11223-18621, and 21739-32573 cm^{-1} and may be assigned to the ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{F})$, ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{F})$ and ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{P})$ transitions, respectively, characteristic to an octahedral geometry¹⁸. The electronic spectra of the $[\text{Ni}(\text{C}_{19}\text{H}_{18}\text{N}_2\text{O}_2\text{S})](\text{NO}_3)_2$ complex show three bands in the range of 9000-10000, 10000-15000,

and 15000-25000 cm^{-1} these transitions correspond to tetrahedral geometry **Fig. 4(a)**.

Copper (II) Complexes: In the electronic spectrum of chloro, and nitrate complexes of Cu(II), bands appear in the range of 9569-12515 cm^{-1} , and 18245-20,450 cm^{-1} may be assigned to the transitions, ${}^2\text{B}_{1g} \rightarrow {}^2\text{A}_{1g}(\nu_1)$, ${}^2\text{B}_{1g} \rightarrow {}^2\text{B}_{2g}(\nu_2)$ respectively. The third band at 30769-37174 cm^{-1} may be due to charge transfer. Therefore, the complexes may be considered to possess a tetragonal geometry¹⁹. The electronic spectrum of the sulfate complex showed bands at 11,709 cm^{-1} , 18,621 cm^{-1} and third band at 36,101 cm^{-1} due to charge transfer **Fig. 4(b)**. This complex may possess either square-pyramidal or trigonal bipyramidal geometry.

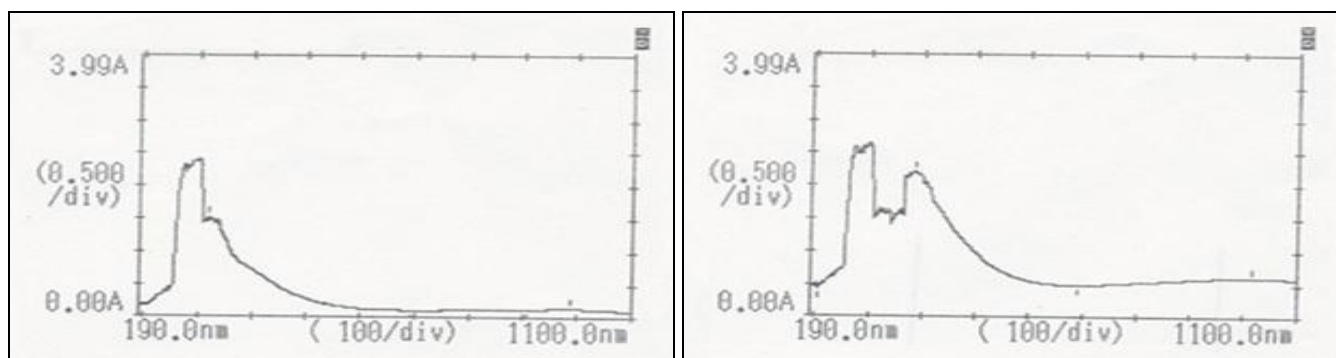


FIG. 4: UV SPECTRUM OF 4(a) $[\text{Ni}(\text{C}_{19}\text{H}_{18}\text{N}_2\text{O}_2\text{S})\text{Cl}_2]$ 4(b) $[\text{Cu}(\text{C}_{19}\text{H}_{18}\text{N}_2\text{O}_2\text{S})(\text{SO}_4)]$

Ligand Field Parameters: Various ligand field parameters, i.e. Dq , B , and β for the complexes were calculated²⁰. The value of Dq , and B were calculated by using first and third transitions. The calculated parameters were given in **Table 2**. The nephelauxetic parameter β was obtained by using

the relation: $\beta = B(\text{complex})/B(\text{free-ion})$, where B was the Racah inter-electronic repulsion parameter, and the value of B (free ion) for Ni(II) is 1041 cm^{-1} . The values of β are 0.93 and 0.66. These values indicate the covalent character in metal-ligand 'σ' bond.

TABLE 2: ELECTRONIC SPECTRAL BANDS (cm⁻¹) AND LIGAND FIELD PARAMETERS OF THE COMPLEXES

Complexes	$\lambda_{\max}(\text{cm}^{-1})$	$\mu_{\text{eff}}(\text{BM})$	$Dq(\text{cm}^{-1})$	$B(\text{cm}^{-1})$	β	ν_2/ν_1	LFSE (kJmol ⁻¹)
[Ni(C ₁₉ H ₁₈ N ₂ O ₂ S)Cl ₂]	10101, 15432, 29498	2.96	1010	975	0.93	1.52	144
[Ni(C ₁₉ H ₁₈ N ₂ O ₂ S)](NO ₃) ₂	9050, 15000, 22500	2.97	905	690	0.66	1.65	152
[Cu(C ₁₉ H ₁₈ N ₂ O ₂ S)Cl ₂]	9569, 18621, 35335	1.88	-	-	-	-	-
[Cu(C ₁₉ H ₁₈ N ₂ O ₂ S)](NO ₃) ₂	9680, 18621, 36900	1.96	-	-	-	-	-
[Cu(C ₁₉ H ₁₈ N ₂ O ₂ S)](SO ₄)	11709, 18621, 36101	1.92	-	-	-	-	-

Electron Spin Resonance (ESR): ESR studies of copper(II) complexes were carried out on the X-band at 9.1 GHz under the magnetic field strength 3000 G. Polycrystalline samples in DMSO were used to record X-band EPR spectra of the Cu(II)

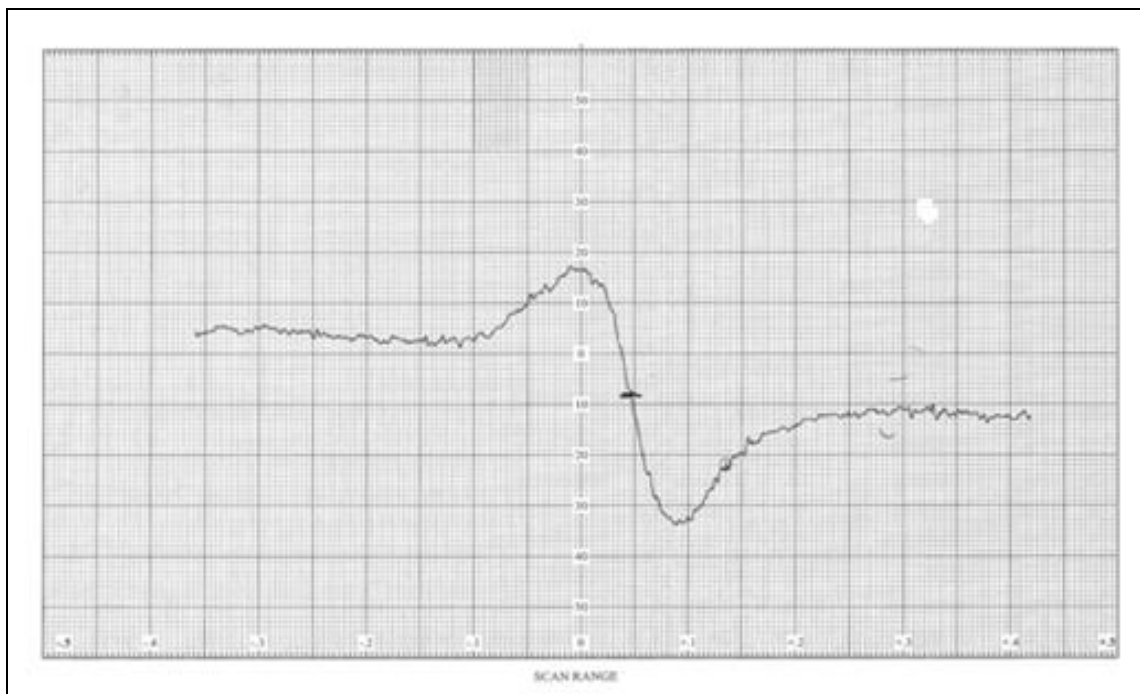
complexes. The trend $g_{\parallel} > g_{\perp} > 2.0024$ indicate that unpaired electron is localized in the $d_{x^2-y^2}$ orbital of the Cu (II) ion and the spectral features are characteristic of tetragonal geometry **Table 3**.

TABLE 3: EPR SPECTRAL DATA OF CU(II) COMPLEXES

Complex	g_{\parallel}	g_{\perp}	g_{iso}	G	g_1	g_2	g_3	R
[Cu(C ₁₉ H ₁₈ N ₂ O ₂ S)Cl ₂]	2.34	2.05	2.18	3.5	-	-	-	-
[Cu(C ₁₉ H ₁₈ N ₂ O ₂ S)](NO ₃) ₂	2.36	2.01	2.16	3.1	-	-	-	-
[Cu(C ₁₉ H ₁₈ N ₂ O ₂ S)](SO ₄)	-	-	2.17	-	2.27	2.15	2.10	2.4

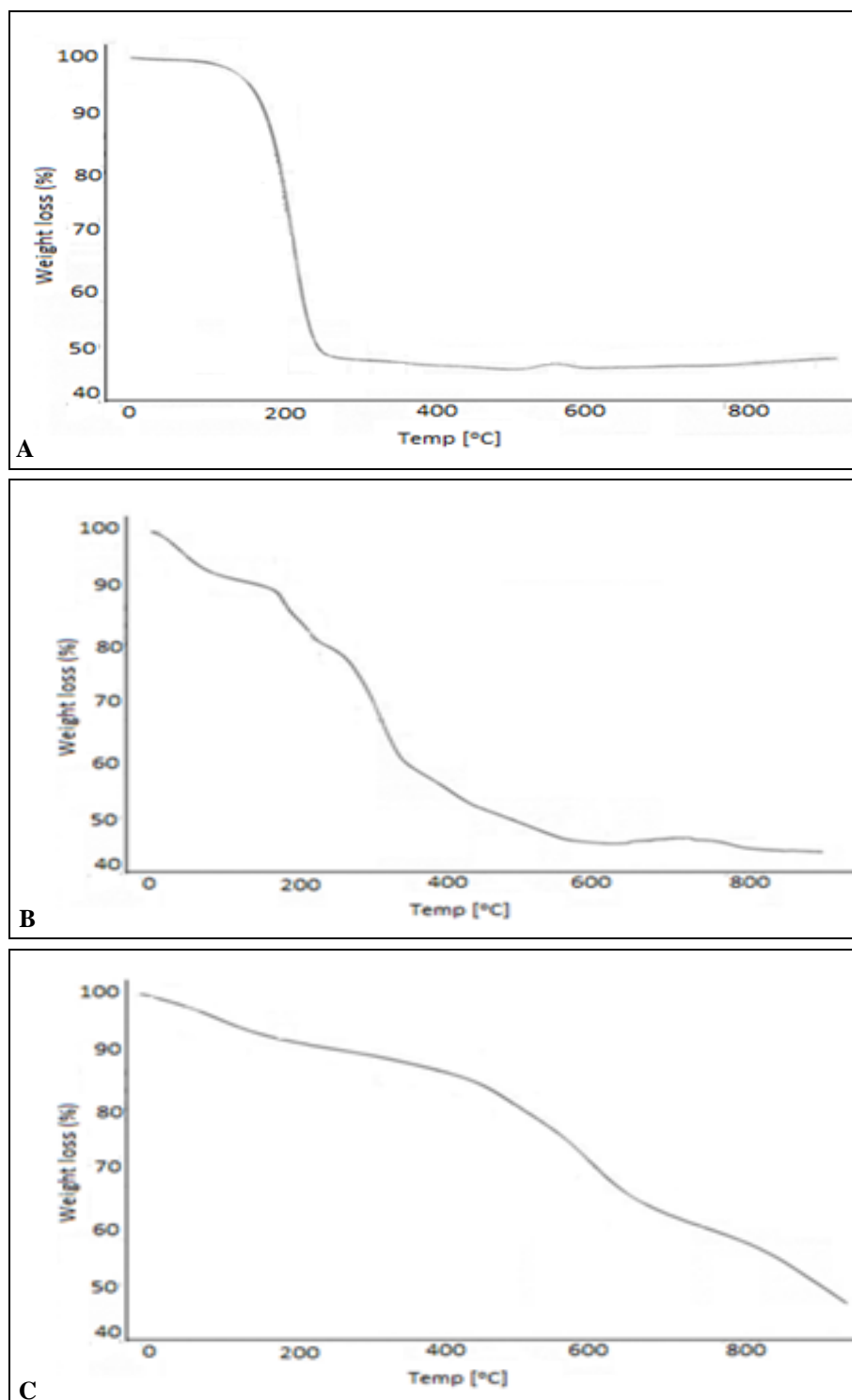
The parameter G, determined as $G = (g_{\parallel} - 2) / (g_{\perp} - 2)$, which measures the exchange interaction between the metal centers in a polycrystalline solid, has been calculated. The Cu (II) complexes show “G” values, which are greater than 4, indicating the exchange interaction is absent in solid complexes^{21, 22}. The IR spectrum of [Cu (C₁₉H₁₈N₂O₂S) (SO₄)] complex suggested five coordinated geometry. Two basic structures were possible for five coordinated geometry, *i.e.* trigonal bipyramidal or square pyramidal, which was characterized by the ground states $d_{x^2-y^2}$ or d_{z^2} , respectively. EPR spectrum of this complex provides an excellent basis for

distinguishing between these two ground states. For this system, parameter R is calculated [$R = (g_2 - g_1) / (g_3 - g_2)$]. If the value of ‘R’ is greater than 1 ($1 < R$), the ground state is predominantly to d_{z^2} . On the other hand, the value of ‘R’ is less than 1 ($1 > R$), the ground state is predominantly to $d_{x^2-y^2}$. EPR spectrum of the [Cu (C₁₉H₁₈N₂O₂S) (SO₄)] complex shows three g values. The values of g_1 , g_2 , g_3 , and R are 2.27, 2.15, 2.10, and 2.4, respectively. As the value of ‘R’ is more than one, the ground state is predominantly d_{z^2} and this is suggested that complex has trigonal bipyramidal geometry²³ **Fig. 5**.

**FIG. 5: EPR SPECTRUM OF [Cu (C₁₉H₁₈N₂O₂S) (SO₄)]**

Thermal Analysis: The thermal stability of macrocyclic complexes was investigated using thermogravimetric analyses (TGA). TGA was carried out at a heating rate of 10 °C/min in a nitrogen atmosphere over a temperature range of 30-800 °C. The thermogram of the complexes of Cu (II) and Ni (II) does not show any peak below

150 °C, which indicates that there was no water molecule inside or outside the coordination sphere. On heating Ni (II) and Cu (II) complexes decompose in three steps. First step was due to the decomposition of coordinated anion at temperature 220 °C. Second and third step indicate decomposition of organic moieties **Fig. 6 (a-c)**.



**FIG. 6: THERMAL SPECTRUM OF 6(a) 1, 4-BIS (2-FORMYLPHENOXY) BUTANE
 6(b) [Cu (C₁₉H₁₈N₂O₂S) Cl₂], 6(c) [Cu (C₁₉H₁₈N₂O₂S) Cl₂]**

Antifungal Activity: The antimicrobial activity of macrocyclic complexes $[\text{Cu}(\text{C}_{19}\text{H}_{18}\text{N}_2\text{O}_2\text{S})(\text{NO}_3)_2]$, $[\text{Cu}(\text{C}_{19}\text{H}_{18}\text{N}_2\text{O}_2\text{S})(\text{SO}_4)]$, and $[\text{Ni}(\text{C}_{19}\text{H}_{18}\text{N}_2\text{O}_2\text{S})](\text{NO}_3)_2$ were examined. A comparative study of the growth inhibition zone values of metal complexes shows that $[\text{Cu}(\text{C}_{19}\text{H}_{18}\text{N}_2\text{O}_2\text{S})(\text{SO}_4)]$ complex exhibit higher activity than other complexes. Higher activity of the metal complex was probably due to the greater lipophilic nature of the complex. It increased the activity of the metal complex and can be explained based on Overtone's concept and Tweedy's chelation theory^{24, 25}.

On chelation, the polarity of the metal ion will be reduced to a greater extent due to the overlap of the ligand orbital and partial sharing of the positive charge of the metal ion with donor groups. Further, it increases the delocalization of the π electrons over the whole chelate ring and enhances the lipophilicity of the complex. This increased lipophilicity enhances the penetration of the complexes into the lipid membrane and thus blocks the metal binding sites on enzymes of microorganisms. These metal complexes also disturb the respiration process of the cell and thus

block the synthesis of proteins, which restricts further growth of the organism²⁶. For antifungal activity, macrocyclic complexes were screened *in-vitro* against *A. niger*, *S. rolfisii*, *F. oxysporum*, and *A. brassicae*. The complexes were tested at the concentration 1000, 750, 500, and 250 ppm in DMSO **Table 4**. Result reveals that the $[\text{Cu}(\text{C}_{19}\text{H}_{18}\text{N}_2\text{O}_2\text{S})(\text{SO}_4)]$ complex shows good activity against *S. rolfisii*, and *A. niger*. Order of antifungal activity of complexes was found in the following order:

A. niger: Standard > $[\text{Cu}(\text{C}_{19}\text{H}_{18}\text{N}_2\text{O}_2\text{S})(\text{NO}_3)_2]$ > $[\text{Cu}(\text{C}_{19}\text{H}_{18}\text{N}_2\text{O}_2\text{S})(\text{SO}_4)]$ > $[\text{Ni}(\text{C}_{19}\text{H}_{18}\text{N}_2\text{O}_2\text{S})](\text{NO}_3)_2$

S. rolfisii: Standard > $[\text{Cu}(\text{C}_{19}\text{H}_{18}\text{N}_2\text{O}_2\text{S})(\text{SO}_4)]$ > $[\text{Cu}(\text{C}_{19}\text{H}_{18}\text{N}_2\text{O}_2\text{S})(\text{NO}_3)_2]$ > $[\text{Ni}(\text{C}_{19}\text{H}_{18}\text{N}_2\text{O}_2\text{S})](\text{NO}_3)_2$

F. oxysporum: Standard > $[\text{Cu}(\text{C}_{19}\text{H}_{18}\text{N}_2\text{O}_2\text{S})(\text{SO}_4)]$ > $[\text{Ni}(\text{C}_{19}\text{H}_{18}\text{N}_2\text{O}_2\text{S})](\text{NO}_3)_2$ > $[\text{Cu}(\text{C}_{19}\text{H}_{18}\text{N}_2\text{O}_2\text{S})(\text{NO}_3)_2]$

A. brassicae: Standard > $[\text{Ni}(\text{C}_{19}\text{H}_{18}\text{N}_2\text{O}_2\text{S})](\text{NO}_3)_2$ > $[\text{Cu}(\text{C}_{19}\text{H}_{18}\text{N}_2\text{O}_2\text{S})(\text{SO}_4)]$ > $[\text{Cu}(\text{C}_{19}\text{H}_{18}\text{N}_2\text{O}_2\text{S})(\text{NO}_3)_2]$

TABLE 4: ANTIFUNGAL ACTIVITY RESULT OF THE SCHIFF'S BASE LIGAND AND ITS METAL COMPLEXES

Compounds	Concentration (ppm)	<i>A. niger</i>	<i>R. rolfisii</i>	<i>F. oxysporum</i>	<i>A. brassicae</i>
$[\text{Cu}(\text{C}_{19}\text{H}_{18}\text{N}_2\text{O}_2\text{S})(\text{NO}_3)_2]$	1000	89	86	87	89
	750	73	79	79	74
	500	53	67	66	59
	250	47	43	46	42
$[\text{Cu}(\text{C}_{19}\text{H}_{18}\text{N}_2\text{O}_2\text{S})(\text{SO}_4)]$	1000	93	91	91	86
	750	88	88	86	77
	500	76	72	78	62
	250	69	59	44	57
$[\text{Ni}(\text{C}_{19}\text{H}_{18}\text{N}_2\text{O}_2\text{S})](\text{NO}_3)_2$	1000	87	94	85	85
	750	72	89	79	73
	500	67	69	64	67
	250	53	58	47	53
Standard (Captan)	1000	96	98	97	98
	750	87	91	92	93
	500	81	86	85	87
	250	73	78	78	79

CONCLUSION: The macrocyclic transition metal complexes of Ni (II) and Cu (II) have been synthesized and characterized by using various spectroscopic studied. Ni (II) complexes were found to have octahedral/tetrahedral, whereas the Cu (II) complexes were of tetragonal/trigonal bipyramidal geometry. The macrocyclic moiety

coordinates to metal ions in tetradentate fashion (N_2O_2) to give the stable aza-oxo complexes. Analytical data correspond to the monomeric composition of the complexes. The antifungal examination led to the conclusion that the metal complexes inhibit the growth capacity of tested fungus strains.

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CONFLICT OF INTEREST: Nil

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