



Microwave Assisted Synthesis and Characterization of Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II) Cd(II) and Hg(II) Complexes With 5-Methoxy-2-(5-Methoxy-4, 6 Dimethylpyridin-2-Yl Methanesulfinyl)-1H-Benzimidazole

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ABSTRACT: A series of coordination compounds of 5-Methoxy-2-(5-Methoxy-4, 6 Dimethylpyridin-2-ylmethanesulfinyl)-1H-Benzimidazole with Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II) Cd(II) and Hg(II) were synthesized with the aim of developing potential antibacterial and antifungal agents. They were characterized by FT-IR, ¹H NMR, molar conductance, Magnetic properties, Electronic and elemental analysis. In addition, the in vitro antibacterial and antifungal properties were tested against some human pathogenic microorganisms by agar cup-plate method. All title compounds showed activity against the entire strain of microorganisms. The relationship between the functional group variation and the biological activity of the evaluated compounds were well discussed. Based on the results obtained, compound [Zn(C₁₇H₁₉N₃O₃S)₂]Cl₂ was found to be very active compared to the rest of the compounds which were subjected to antimicrobial assay.

Keywords: Methoxy, Drug, Benzimidazole, Complex, Microwave

I. INTRODUCTION

Developments in pharmaceutical research in recent years have led to more sophisticated and efficient synthesized drugs. However, another less studied but equally significant challenge is to influence the ways the drugs are distributed in the body by tailoring the drug transport agents for targeted delivery and controlled release. While recent research has led to biocompatible polymeric materials that can be used for drug delivery binding these materials to metal centers generates properties not found in polymers by themselves and makes them reactive to their surroundings [1].

Many drugs possess modified pharmacological and toxicological properties when administered in the form of metallic complexes. Probably the most widely studied cation in this respect is Cu²⁺, since a host of low molecular-weight copper complexes have been proven beneficial against several diseases such as tuberculosis, gastric ulcers and cancers [2].

The Omeprazole drug is a proton pump inhibitor with actions. It is used in the treatment of peptic ulcer diseases and in other conditions where inhibition of gastric acid secretion may be beneficial. Omeprazole is

given by mouth as capsules or suspension containing enteric coated granules. The present work deals with the synthesis, characterization and biological activities of various metal complexes with the Omeprazole drug [3].

II. MATERIALS AND METHODS

5 - Methoxy - 2 - [(5-Methoxy - 4, 6 - Dimethyl pyridine - 2-yl methane sulfinyl)-1H-Benzimidazole] (L¹) was purchased from an authorized dealer. The metal chlorides and the solvents viz., DMSO, DMF, methanol, ethanol used were of analytical grade and used as such.

Preparation of Complexes:

A mixture of Metal (II) Chlorides (0.01mole) and ligand (0.02mole) solutions in alcohol was subjected to microwave irradiation for about 20 minutes at a power density of 600 W. Then to the reaction mixture, 1 gram of sodium acetate was added and continued the microwave irradiation for another 10 minutes. The reaction mixture was added to distilled water (100 ml) with constant stirring. The metal (II) complex separated was filtered and washed with distilled water containing small quantity of ethanol and dried in vacuum over fused calcium chloride [4, 5].

III. RESULT AND DISCUSSION

All the complexes are brown to yellow in color. All the complexes are insoluble in common organic solvents, however they are soluble in coordinating solvents like DMF and DMSO. Because of their insolubility in nitrobenzene, the molecular weights could not be determined. The elemental analysis reveals that all the complexes have 1:2 stoichiometry with the general formula $[M(L')_2]Cl_2$.

Molar Conductance. The molar conductance of the complexes were determined in DMF at the concentration of 10^{-3} M and are set out in the Table 1. The observed molar conductance values lie in the range of 70-95 $\text{Ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$. These values are well within the range of electrolytic behavior of the complexes. Hence these complexes are regarded as electrolytic in nature.

Magnetic Property. The magnetic moment obtained at room temperature for the complexes are listed in Table 2.

Manganese (II) Complex: The Manganese (II) complexes exhibit magnetic moment of 5.55 B.M. suggesting the formation of spin free complexes. This clearly agrees with the expected values of 5.90 B.M. for manganese (II) complexes [6, 7].

Iron (II) Complex: The octahedral high spin iron (III) complexes are expected 19-20 to possess magnetic moment very close to spin only value of 5.92 B.M. the magnetic moment obtained for this complex is 5.89 B.M. **Cobalt (II) Complex:** The cobalt (II) complexes shows magnetic moment of 5.22 B.M. the spin free octahedral complexes of cobalt (II) is reported to exhibit magnetic moment in the range of 4.46–5.33 B. M.

Hence observed magnetic moment for the cobalt (II) complex under study indicates that, it has an octahedral configuration [8].

Nickel (II) Complex: Nickel (II) is a d^8 ion, having two unpaired electrons can form paramagnetic complexes having six coordinated octahedral geometry. The magnetic moments reported for octahedral Ni (II) Complexes range from 2.82-3.4 B.M. depending on the magnitude of the orbital contribution. In the present study, the observed room temperature magnetic moments for the Ni (II) complexes is 3.12 B.M. this observation suggest that Ni(II) has an octahedral configuration in the complexes [9, 10]

Copper (II) Complex: The Copper (II) complex exhibit magnetic moment of 1.91 B.M. agreeable spin only value. It is reported that the distinct octahedral geometry of copper (II) complex devoid of spin interaction exhibit magnetic moment in the range of 1.80-1.93 B.M. Hence it may be concluded that copper (II) complexes has major spin interaction [11].

Electronic Spectra. The electronic spectral band maxima with their assignments for the complexes are shown in the Table 2. The ligand field parameter such as Dq, B', β and LFSE values are tabulated in Table 3. The electronic spectra of Mn(II), Fe(III), Co(II), Ni(II), and Cu(II) complexes with that of Omeprazole drug have been studied to obtain more information on stereochemistry of the complexes and to produce more support, for the conclusion deduced with the help of magnetic data [12, 13].

Manganese (II) and Iron (III) complexes: The electronic spectra of Manganese (II) omeprazole complex shown high intensity band maximum around 32258.06 cm^{-1} region and this has been assigned to the ligand metal charge transfer band. The remaining d-d bands are observed in the region 24390.24 and 18181.81 cm^{-1} . Like Manganese (II), Iron (III) also has 6s ground state and hence it gives rise to very weak crystal field. The Iron (III) complexes have a tendency to possess high intensity charge transfer bands which makes the identification of d-d bands rather difficult. Iron (II) complexes exhibit a very high intensity band around 23201.85 cm^{-1} due to ligand metal charge transfer, this intends the other d-d transition in visible region. It has been observed in the diffusion reflectance spectra that Iron (III) complex exhibit two bands in the 12500-10640 cm^{-1} and 20000-16670 cm^{-1} region attributable to ${}^6A_{1g} \rightarrow {}^4T_{1g}$ and ${}^6A_{1g} \rightarrow {}^4A_{1g}$ transitions respectively. In this complex a weak and broad maxima in the region 18518.31 and 14306.15 to the ${}^6A_{1g} \rightarrow {}^4T_{1g}$ and ${}^6A_{1g} \rightarrow {}^4A_{1g}$ were observed [14-15].

Cobalt (II) complex: The high spin Co(II) complex has the ground term ${}^4T_{1g}$ arising from the configuration ${}^5T_{2g}$, ${}^5E_{2g}$ and one can expect three spin allowed d-d transitions from the ${}^4T_{1g}$ ground state to the various states viz, ${}^4T_{2g}$, ${}^4A_{1g}$ and ${}^4T_{1g}$ (P) states. These three spin allowed d-d transitions in the order of increasing energy are given below ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ (v_1), ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ (v_2), and ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ (v_3)

The previous reports predict a wide range from 450-1600 nm for the various transition. Electronic spectra of present Co(II) complexes show three bands at 9090.90 cm^{-1} , 16666.66 cm^{-1} and 19607.84 cm^{-1} which may be assigned to the transitions respectively. These transitions indicate octahedral structure for the present Co(II) complex [16]. In the present investigation, the ligand field parameter such as Dq, B', β and LFSE are calculated using the equations derived by Underhill and Billing [17] as given below;

$${}^3D^2 - 18(v_2 + v_3)Dq + v_2 \cdot v_3 = 0$$

$${}^{10}D^4 = v_2 - v_1$$

$$B' = \frac{v_2 - v_1 - 30Dq}{15}$$

Table 1: Elemental Analysis, Melting Point, Color and Conductance Data for Ligand Metal Complexes.

Sl. No.	Ligand/Complexes	Elemental Analysis (%) Found (Calculated)						M.P.(°C) Color	Molar Conductance $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$
		C	H	N	S	Cl	M		
1.	$\text{C}_{17}\text{H}_{19}\text{N}_3\text{O}_3\text{S}$	59.11 (59.10)	5.54 (5.45)	12.16 (12.20)	9.28 (9.32)	--	--	180 colorless	--
2.	$[\text{Mn}(\text{C}_{17}\text{H}_{19}\text{N}_3\text{O}_3\text{S})_2]\text{Cl}_2$	50.10 (50.00)	5.83 (5.69)	10.30 (10.29)	7.83 (7.85)	8.55 (8.68)	6.83 (6.72)	>300 Brown	72.33
3.	$[\text{Fe}(\text{C}_{17}\text{H}_{19}\text{N}_3\text{O}_3\text{S})_2]\text{Cl}_2$	50.00 (49.94)	4.58 (4.68)	10.23 (10.28)	7.82 (7.84)	8.77 (8.67)	6.90 (6.83)	>300 Brown	75.00
4.	$[\text{Co}(\text{C}_{17}\text{H}_{19}\text{N}_3\text{O}_3\text{S})_2]\text{Cl}_2$	49.96 (49.76)	4.76 (4.66)	10.34 (10.24)	7.79 (7.81)	8.53 (8.64)	7.58 (7.18)	210 Black	70.00
5.	$[\text{Ni}(\text{C}_{17}\text{H}_{19}\text{N}_3\text{O}_3\text{S})_2]\text{Cl}_2$	49.92 (49.77)	4.53 (4.67)	10.12 (10.24)	7.83 (7.89)	8.68 (8.64)	7.25 (7.14)	280 Brown	80.35
6.	$[\text{Cu}(\text{C}_{17}\text{H}_{19}\text{N}_3\text{O}_3\text{S})_2]\text{Cl}_2$	50.00 (49.48)	4.54 (4.45)	10.22 (10.18)	7.93 (7.77)	8.57 (8.59)	7.72 (7.70)	>300 Green	85.96
7.	$[\text{Zn}(\text{C}_{17}\text{H}_{19}\text{N}_3\text{O}_3\text{S})_2]\text{Cl}_2$	49.63 (49.37)	4.82 (4.63)	10.23 (10.16)	7.69 (7.75)	8.96 (8.57)	7.88 (7.90)	>300 Yellow	90.40
8.	$[\text{Cd}(\text{C}_{17}\text{H}_{19}\text{N}_3\text{O}_3\text{S})_2]\text{Cl}_2$	46.83 (46.71)	4.29 (4.38)	9.82 (9.61)	7.41 (7.33)	8.10 (8.11)	12.76 (12.86)	>300 Yellow	92.67
9.	$[\text{Hg}(\text{C}_{17}\text{H}_{19}\text{N}_3\text{O}_3\text{S})_2]\text{Cl}_2$	42.66 (42.44)	4.00 (3.98)	8.68 (8.73)	6.69 (6.66)	7.48 (7.36)	20.55 (20.84)	>300 Black	95.00

*The values shown in the parenthesis are calculated ones.

Table 2: Electronic Spectral and Magnetic Susceptibility Measurement Data.

Sl. No.	Ligand/Complexes	Bands		Assignments	$\mu_{\text{eff}}(\text{B. M.})$
		nm	cm ⁻¹		
1.	$[\text{Mn}(\text{C}_{17}\text{H}_{19}\text{N}_3\text{O}_3\text{S})_2]\text{Cl}_2$	550 ν_1	18181.81	${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g} (4\text{G})$ ${}^6\text{A}_{1g} \rightarrow {}^4\text{E}_g$ ${}^6\text{A}_{1g} \rightarrow {}^4\text{A}_{1g} (4\text{D})$	5.55
		410 ν_2	24390.24		
		310 ν_3	32258.06		
2.	$[\text{Fe}(\text{C}_{17}\text{H}_{19}\text{N}_3\text{O}_3\text{S})_2]\text{Cl}_2$	699 ν_1	14306.15	${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g}$ ${}^6\text{A}_{1g} \rightarrow {}^4\text{A}_{1g}$	5.89
		540 ν_2	18518.51		
		430 ν_3	23201.85		
3.	$[\text{Co}(\text{C}_{17}\text{H}_{19}\text{N}_3\text{O}_3\text{S})_2]\text{Cl}_2$	1100 ν_1	9090.90	${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$ ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}(\text{F})$ ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$	5.22
		600 ν_2	16666.66		
		510 ν_3	19607.84		
4.	$[\text{Ni}(\text{C}_{17}\text{H}_{19}\text{N}_3\text{O}_3\text{S})_2]\text{Cl}_2$	980 ν_1	10204.08	${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{F})$ ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{F})$ ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{P})$	3.12
		780 ν_2	12820.51		
		440 ν_3	22727.27		
5.	$[\text{Cu}(\text{C}_{17}\text{H}_{19}\text{N}_3\text{O}_3\text{S})_2]\text{Cl}_2$	680 ν_1	14705.88	${}^2\text{B}_{1g} \rightarrow {}^2\text{A}_{1g}$ ${}^2\text{B}_{1g} \rightarrow {}^2\text{B}_{2g}$ ${}^2\text{B}_{1g} \rightarrow {}^2\text{E}_g$	1.91
		550 ν_2	18181.81		
		310 ν_3	32258.06		

Table 3: Ligand field parameters of representative Co (II) and Ni (II) Complexes.

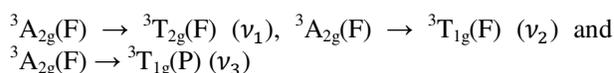
Sl. No.	Complexes	Dq cm^{-1}	B' cm^{-1}	β	ν_2/ν_1	LFSE Kcal mol^{-1}
1.	$[\text{Cu}(\text{C}_{17}\text{H}_{19}\text{N}_3\text{O}_3\text{S})_2]\text{Cl}_2$	757.58	903.14	0.93	1.83	21.64
2.	$[\text{Ni}(\text{C}_{17}\text{H}_{19}\text{N}_3\text{O}_3\text{S})_2]\text{Cl}_2$	261.64	1846.57	1.76	1.25	7.47

From this value, the covalency factor β can be calculated as

$$\beta = \frac{B' \text{ of the complex}}{B \text{ of the free ion}}$$

These data are present in Table 3.

Nickel (II) complex: Nickel (II) complex is octahedral on the basis of magnetic data. The electronic spectra of octahedral Ni (II) complexes exhibit three spins allowed d-d transitions and are designated as:



The prepared paramagnetic Ni(II) complex exhibit three bands as 10204.08 cm^{-1} , 12820.51 cm^{-1} and 22727.27 cm^{-1} are assigned to ν_1 , ν_2 and ν_3 transitions respectively, which indicate the octahedral geometry around Ni(II) ion. The ligand field parameters such as D_q , B' , β , ν_2/ν_1 and LFSE have been calculated using the procedure given by R. S. Drago and the values are tabulated in the Table 3. From the spectral data it is suggested that the Ni(II) complex is ionic in nature and the ratio of ν_2 and ν_1 lies well within the range for octahedral geometry of complex [18].

Copper (II) complex: The band maxima with their assignments of Cu (II) complex are tabulated in **Table 2**. The Cu (II) is a d^8 ion and provides a good example for John Teller effect. In the investigation, three bands are observed at 14705.88 cm^{-1} , 18181.81 cm^{-1} and 32258.06 cm^{-1} which may be assigned to the transitions ${}^2B_{1g} \rightarrow {}^2A_{1g}$, ${}^2B_{1g} \rightarrow {}^2B_{2g}$ and ${}^2B_{1g} \rightarrow {}^2E_g$ respectively. These transitions indicate that the Cu (II) complex may probably have six coordinated octahedral configuration.

Infrared Spectra. The important IR bands and their assignments of 5-methoxy-2-(5-methoxy-4, 6 dimethylpyridin-2-ylmethanesulfinyl)-1H-Benzimidazole complexes are summarized in Table 4.

In several organic molecules containing $-\text{NH}$ group, $\nu_{\text{N-H}}$ is observed between 3280 cm^{-1} . In the present study the ligand $\nu_{\text{N-H}}$ stretching frequency was observed at 3230 cm^{-1} . In the complexes the $\nu_{\text{N-H}}$ bands occur at the same or slightly higher frequencies, suggesting that the $-\text{NH}$ group does not take part in bonding. The strong absorption in the region 1620 cm^{-1} is assigned as the azomethine group ($\nu_{\text{C=N}}$) present in the Schiff bases. In the complexes the azomethine group is shifted to lower frequency in the region 1600–1580 cm^{-1} . This is further supported by the appearance of a new band around the region 1618-1610 cm^{-1} due to $\nu_{\text{C=N}}$. The $\nu_{\text{C=N}}$ shifts to higher frequency region indicating the involvement of azomethine nitrogen for the coordination in the present complexes. The band due to $\nu_{\text{S-O}}$ is observed at 1415 cm^{-1} in the ligand. In the complexes the band due to $\nu_{\text{S-O}}$ are observed in the region 1483-1432 cm^{-1} indicates that the S-O group is involved in the coordination through Oxygen.

$\nu_{\text{M-N}}$ and $\nu_{\text{M-O}}$

Ligand used in the present study contain nitrogen and cm^{-1} indicates that the S-O group is involved in the coordination through Oxygen oxygen as donor atoms. Study of far infrared spectra is of interest in metal nitrogen and metal oxygen bands.

Metals have heavy mass and M-N and M-O bonds have low bond order and hence the group vibration due to these occurs in the far infrared region. Assignments of bands in the region have been controversial over the years. Yet higher studies are useful, as the direct information about metal ligand coordinate bond have been obtained from spectra.

Nakamura[19] has assigned the band in the region 600 to 700 cm^{-1} for $\nu_{\text{M-N}}$. Some authors have assigned bands in the region 515 – 490 cm^{-1} for $\nu_{\text{M-N}}$. Nakamoto and Kincoind[20] have assigned $\nu_{\text{M-N}}$ in the region 480-450 cm^{-1} $\nu_{\text{M-O}}$ in the region 340 – 280 cm^{-1} on various theoretical background. Chasnet.al. [21] have assigned $\nu_{\text{M-N}}$ in the region 405-370 cm^{-1} and $\nu_{\text{M-O}}$ in the region 300-250 cm^{-1} . Gaonkar *et. al.*, [22] have studied transition metal complexes of Schiff bases and assigned $\nu_{\text{M-N}}$ and $\nu_{\text{M-O}}$ in the region 530-512 cm^{-1} and 480-450 cm^{-1} respectively. Based on the literature data in the present investigation the $\nu_{\text{M-N}}$ and $\nu_{\text{M-O}}$ vibrations have been assigned in the region 460-410 cm^{-1} and 410-400 cm^{-1} respectively.

${}^1\text{H-NMR}$ Spectral Studies. ${}^1\text{H}$ NMR spectra of the ligand (L1) and corresponding complexes were scanned for ${}^1\text{H}$ NMR spectra in DMSO- d_6 solvent in the range of 0-15 $\delta(\text{ppm})$ down field of TMS. The chemical shift values $\delta(\text{ppm})$ with their assignments are given in the Table 5.

${}^1\text{H}$ NMR spectra of ligand (L1) shows two singlets at 2.13 and 2.20 $\delta(\text{ppm})$ and two at 3.61 -3.83 $\delta(\text{ppm})$ are due to methyl protons and methoxy protons respectively. But the ligands also shows a multiplet at 6.90-7.56 $\delta(\text{ppm})$ due to aromatic protons. A signal of imine NH protons which were observed at 10.35 $\delta(\text{ppm})$ as a singlet in ligand. A signal at 4.72 $\delta(\text{ppm})$ is due to the resonating of S-CH2 protons [23].

In the complexes the multiplet observed between 6.66-7.25 $\delta(\text{ppm})$ due to aromatic protons and the signals at 3.62-3.77 $\delta(\text{ppm})$ and 2.20-2.45 $\delta(\text{ppm})$ are due to methoxy protons and methyl protons respectively were shifted to down field due to the complexation through oxygen of S=O group and nitrogen of C=N group. A signal at 10.40-10.51 $\delta(\text{ppm})$ due to resonance acting on imine protons and a signal at 4.76-4.79 $\delta(\text{ppm})$ due to resonating of S-CH2 group protons were shifted to down field due the complex formation through nitrogen of C=N and oxygen of S=O group to the central metal ion respectively [24, 25].

Electron Spin Resonance Spectral Studies (ESR). ESR spectra of the copper complex were recorded at room temperature. ESR spectra of the polycrystalline Cu(II) complex shown in Fig. 1.

Table 4: Some Important IR Stretching Frequencies of Metal Complexes (in cm^{-1}).

Sl. No.	Abbreviation	Ligand/Complexes	$\nu_{\text{N-H}}$	$\nu_{\text{C=N}}$	$\nu_{\text{S-O}}$	$\nu_{\text{C-N}}$	$\nu_{\text{M-N}}$	$\nu_{\text{M-O}}$
	L^1	$\text{C}_{17}\text{H}_{19}\text{N}_3\text{O}_3\text{S}$	3230 [□]	1590 [□]	1415 [□]	1260 [□]	-	-
1.	$[\text{Mn}(\text{L}^1)_2]\text{Cl}_2$	$[\text{Mn}(\text{C}_{17}\text{H}_{19}\text{N}_3\text{O}_3\text{S})_2]\text{Cl}_2$	3240	1635	1433	1270	457	409
2.	$[\text{Fe}(\text{L}^1)_2]\text{Cl}_2$	$[\text{Fe}(\text{C}_{17}\text{H}_{19}\text{N}_3\text{O}_3\text{S})_2]\text{Cl}_2$	3240	1632	1433	1270	459	407
3.	$[\text{Co}(\text{L}^1)_2]\text{Cl}_2$	$[\text{Co}(\text{C}_{17}\text{H}_{19}\text{N}_3\text{O}_3\text{S})_2]\text{Cl}_2$	3242	1633	1433	1271	417	409
4.	$[\text{Ni}(\text{L}^1)_2]\text{Cl}_2$	$[\text{Ni}(\text{C}_{17}\text{H}_{19}\text{N}_3\text{O}_3\text{S})_2]\text{Cl}_2$	3245	1637	1434	1271	451	410
5.	$[\text{Cu}(\text{L}^1)_2]\text{Cl}_2$	$[\text{Cu}(\text{C}_{17}\text{H}_{19}\text{N}_3\text{O}_3\text{S})_2]\text{Cl}_2$	3240	1634	1432	1270	456	408
6.	$[\text{Zn}(\text{L}^1)_2]\text{Cl}_2$	$[\text{Zn}(\text{C}_{17}\text{H}_{19}\text{N}_3\text{O}_3\text{S})_2]\text{Cl}_2$	3245	1636	1483	1272	455	405
7.	$[\text{Cd}(\text{L}^1)_2]\text{Cl}_2$	$[\text{Cd}(\text{C}_{17}\text{H}_{19}\text{N}_3\text{O}_3\text{S})_2]\text{Cl}_2$	3240	1636	1433	1271	456	405
8.	$[\text{Hg}(\text{L}^1)_2]\text{Cl}_2$	$[\text{Hg}(\text{C}_{17}\text{H}_{19}\text{N}_3\text{O}_3\text{S})_2]\text{Cl}_2$	3241	1633	1432	1271	458	406

*The superscript 'a' indicates ligand data as reported in literature.

Table 5: ^1H NMR Spectral data of Zn(II), Cd(II) and Hg(II) Complexes with ligand (L^1).

Sl. No.	Abbreviation	Ligand/Complexes	Aromatic protons	Methoxy Protons	Imino Protons	CH_3 Protons	S- CH_2 Protons
	L^1	$\text{C}_{17}\text{H}_{19}\text{N}_3\text{O}_3\text{S}$	6.90-7.56	3.61, 3.83	10.35	2.13, 2.20	4.72
1.	$[\text{Zn}(\text{L}^1)_2]\text{Cl}_2$	$[\text{Zn}(\text{C}_{17}\text{H}_{19}\text{N}_3\text{O}_3\text{S})_2]\text{Cl}_2$	6.68-7.20	3.62, 3.70	10.40	2.28, 2.40	4.79
2.	$[\text{Cd}(\text{L}^1)_2]\text{Cl}_2$	$[\text{Cd}(\text{C}_{17}\text{H}_{19}\text{N}_3\text{O}_3\text{S})_2]\text{Cl}_2$	6.66-7.25	3.66, 3.71	10.51	2.20, 2.45	4.78
3.	$[\text{Hg}(\text{L}^1)_2]\text{Cl}_2$	$[\text{Hg}(\text{C}_{17}\text{H}_{19}\text{N}_3\text{O}_3\text{S})_2]\text{Cl}_2$	6.70-7.22	3.64, 3.77	10.48	2.30, 2.42	4.76

Table 6: ESR Spectral Data of $[\text{Cu}(\text{L}^1)_2]\text{Cl}_2$ complex.

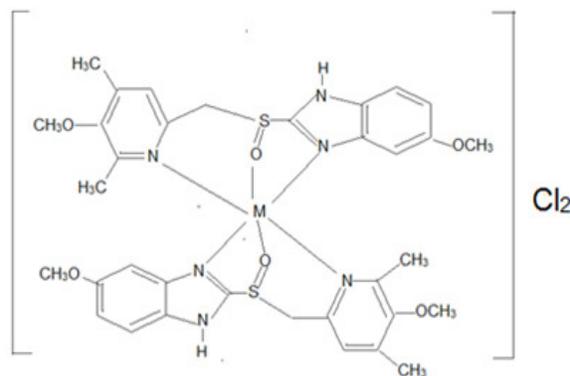
Sl. No.	Complex	g_{\square}	g_{\perp}	G	g_{av}
01	$[\text{Cu}(\text{L}^1)_2]\text{Cl}_2$ $[\text{Cu}(\text{C}_{17}\text{H}_{19}\text{N}_3\text{O}_3\text{S})_2]\text{Cl}_2$	2.47038	2.16656	2.854936	2.272351

The 'g' values obtained from the spectra are represented in Table 6. When the monomeric species change into dimeric species having axial symmetry and identical sites, the 'g' values also change due to the change in symmetry. The width and shapes of the absorption lines offer a means of the substances. From the observed 'g' values $g_{\square} > g_{\perp}$, it is evident that the unpaired electron lies predominantly in the dx^2-y^2 orbital of copper (II) ion [26].

Kivelson and Neiman [27] have reported the 'g' value less than 2.3 for covalent character of the metal-ligand bond and greater than 2.3 for ionic character. In the present study, $[\text{Cu}(\text{L}^1)_2]\text{Cl}_2$ complex has 'g' value 2.47, this indicates the ionic character of the Copper-ligand bond.

In order to obtain additional information about the structure of copper (II) complex, ESR studies of the complex have been made. The magnetic parameters have been evaluated from the spectra and tend $g_{\square} > g_{\perp}$, observed in the 'g' values suggests the presence of an unpaired electron in the dx^2-y^2 orbital [60-61]. Based on these observations copper (II) complex may have octahedral geometry.

On the basis of elemental analysis, magnetic susceptibility, conductivity, electronic, IR, ^1H NMR, ESR spectral data the octahedral geometry with coordination number six is assigned for all the complexes.



Where M = Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Hg(II)

Fig.1. Proposed Structure of the complexes.

Antimicrobial Activity. The antimicrobial activity of all the ligands and their metal complexes were determined by agar cup-plate method. The antibacterial activity against *Klebsiella* and *Pseudomonas* and antifungal activity against *Aspergillus niger* and *C. albicans*, were screened by the ligands and their metal complexes. The medium was prepared as per the instructions of the manufacturer of dry Mueller Hinton agar powder (Hi-

Media). The test ligands and their metal complexes were dissolved in DMSO at a concentration of 1 mg/ml. Gentamicin (100µg/ml) in DMSO was used as a standard for antibacterial and Fluconazole (100µg/ml) in DMSO was used as reference standard for antifungal activity. The solvent control (only DMSO) was also maintained throughout the experiment [24-26]. The zones of inhibition are reported in Table 7 and 8.

Table 7: Antibacterial Activities of ligand and their metal complexes.

Sl. No.	Abbreviation	Ligand/Complexes	Klebsiella (in mm)	Pseudomonas aeruginosa (in mm)
	L ¹	C ₁₇ H ₁₉ N ₃ O ₃ S	11.32	13.32
1.	[Mn(L ¹) ₂]Cl ₂	[Mn(C ₁₇ H ₁₉ N ₃ O ₃ S) ₂]Cl ₂	12.68	13.38
2.	[Fe(L ¹) ₂]Cl ₂	[Fe(C ₁₇ H ₁₉ N ₃ O ₃ S) ₂]Cl ₂	17.38	15.48
3.	[Co(L ¹) ₂]Cl ₂	[Co(C ₁₇ H ₁₉ N ₃ O ₃ S) ₂]Cl ₂	-	14.43
4.	[Ni(L ¹) ₂]Cl ₂	[Ni(C ₁₇ H ₁₉ N ₃ O ₃ S) ₂]Cl ₂	6.88	--
5.	[Cu(L ¹) ₂]Cl ₂	[Cu(C ₁₇ H ₁₉ N ₃ O ₃ S) ₂]Cl ₂	11.12	14.12
6.	[Zn(L ¹) ₂]Cl ₂	[Zn(C ₁₇ H ₁₉ N ₃ O ₃ S) ₂]Cl ₂	6.00	18.00
7.	[Cd(L ¹) ₂]Cl ₂	[Cd(C ₁₇ H ₁₉ N ₃ O ₃ S) ₂]Cl ₂	15.20	16.33
8.	[Hg(L ¹) ₂]Cl ₂	[Hg(C ₁₇ H ₁₉ N ₃ O ₃ S) ₂]Cl ₂	12.33	11.66
9.		Gentamicin	19.00	17.35

Table 8: Antifungal Activities of ligand and their metal complexes.

Sl. No.	Abbreviation	Ligand/Complexes	A. Niger (in mm)	C. albicans (in mm)
	L ¹	C ₁₇ H ₁₉ N ₃ O ₃ S	10.09	11.02
1.	[Mn(L ¹) ₂]Cl ₂	[Mn(C ₁₇ H ₁₉ N ₃ O ₃ S) ₂]Cl ₂	11.00	7.00
2.	[Fe(L ¹) ₂]Cl ₂	[Fe(C ₁₇ H ₁₉ N ₃ O ₃ S) ₂]Cl ₂	14.44	6.00
3.	[Co(L ¹) ₂]Cl ₂	[Co(C ₁₇ H ₁₉ N ₃ O ₃ S) ₂]Cl ₂	16.23	5.66
4.	[Ni(L ¹) ₂]Cl ₂	[Ni(C ₁₇ H ₁₉ N ₃ O ₃ S) ₂]Cl ₂	10.63	7.92
5.	[Cu(L ¹) ₂]Cl ₂	[Cu(C ₁₇ H ₁₉ N ₃ O ₃ S) ₂]Cl ₂	15.49	10.23
6.	[Zn(L ¹) ₂]Cl ₂	[Zn(C ₁₇ H ₁₉ N ₃ O ₃ S) ₂]Cl ₂	14.66	7.00
7.	[Cd(L ¹) ₂]Cl ₂	[Cd(C ₁₇ H ₁₉ N ₃ O ₃ S) ₂]Cl ₂	12.83	4.89
8.	[Hg(L ¹) ₂]Cl ₂	[Hg(C ₁₇ H ₁₉ N ₃ O ₃ S) ₂]Cl ₂	11.88	9.83
9.		Fluconazole	24.12	23.32

IV. CONCLUSION

A few complexes of omeprazole drug with first row transition metal ions have been reported in this chapter. These complexes analyzed for the stoichiometry of the type (1:2) M(L1)₂. The spectral data indicates that omeprazole drug shows tridentate behavior, coordination takes place through oxygen and nitrogen from the omeprazole drug (L1). The conductivity data shows the electrolytic nature of these complexes. The magnetic susceptibility measurements obtained at room temperature for Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) complexes agrees with the spin only values. The electronic, IR, ¹H NMR, ESR, spectral data suggest that Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) complexes with omeprazole drug (L1) exhibit coordination number six.

Antibacterial activities: It is clear from the Table-7 that the Mn(II), Fe(III), Cd(II) & Hg(II) complexes show moderate activities against *Klebsiella* and Mn(II), Fe(III), Co(II), Cu(II), Zn(II), Cd(II) and Hg(II) complexes show moderate to high activity against *Pseudomonas aeruginosa*.

Antifungal activities: From the Table-8, it is clear that the Fe(III), Co(II), Cu(II) & Zn(II) complexes are moderately active against *A. niger* and Mn(II), Fe(III), Co(II), Cu(II), Zn(II), Cd(II) and Hg(II) complexes show less activity against *C. albicans*.

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