

Synthesis of Mn(II), Co(II), Ni(II) and Cu(II) Complexes of Schiff's Base Ligand: Spectral Studies, Molecular Modelling and Fungicidal Screening

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Mn(II), Co(II), Ni(II) and Cu(II) complexes with Schiff's base ligand, 3-(benzo[*b*]thiophen-2-yliminomethyl)-benzene-1,2-diol have been synthesized. All the complexes were characterized by elemental analysis, molar conductance measurements, NMR, mass, IR, EPR and electronic spectral studies. The geometry of complexes has been optimized by using Gaussian 09 W. The complexes were found to be non electrolytes. These complexes have general composition $[M(L)_2X_2]$ [where L = Schiff's base ligand, M = Mn(II), Co(II), Ni(II) and Cu(II) and X = Cl⁻, CH₃COO⁻]. Spectral data indicates octahedral geometry for Mn(II), Co(II), Ni(II), but Cu(II) complexes were found to have tetragonal geometry. The fungal activity of ligand and complexes has been examined against fungi *Aspergillus niger* and *Candida tropicalis* by means of food poison method. The results suggest that the metal complexes show better antifungal activity in the comparison of ligand.

Keywords: Schiff's base, Spectral studies, Molecular modelling, Antifungal screening.

INTRODUCTION

Condensation reaction between an aldehyde or ketone with amine group leads to the formation of Schiff's base [1]. Schiff's base ligands can be easily synthesized and also have the capability to bind with metal ions and to form stable metal complexes [2]. The studies of Schiff's bases and their coordination compounds have drawn the attention due to their various applications from last two decades [3-9]. The transition metal complexes of Schiff's base ligands are a matter of keen interest due to the presence of nitrogen, sulphur and oxygen as these atoms have lone pair of electron. Their complexes show various interesting chemical, physical, biological properties [10,11] and pharmaceutical activities like antibacterial, anti-proliferative, antiviral, antimicrobial, antifungal, anti-inflammatory, anticonvulsant, anti-tubercular, anti-oxidative effects and inhibition of tumor growth [12].

Transition metal complexes of Schiff's base have significant contribution in catalysis [13], material science [14]. Schiff's base ligands are known to be used as chelating agent [15] and -OH group adjacent to azomethine group enhance the chelation tendency [16]. In the formation of metal ion complexes, hydroxyl group nearby azomethine linkage play a signifi-

cant role [17-21]. More donor atoms present on ligands enhance the tendency to synthesize the complexes [22]. Both amino-benzothiazole [23] and 2,3-dihydroxybenzaldehyde [24] have been selected for synthesis of Schiff's base metal complexes as they have N, O and S atom which play significant role in the coordination of metals and responsible for biological [25] and pharmaceutical activities [26]. In the present work, we have synthesised novel Schiff's base ligand, 3-(benzo[*b*]thiophen-2-yliminomethyl)-benzene-1,2-diol carried out by the condensation reaction between 2,3-dihydroxy benzaldehyde and aminobenzothiazole in ethanol. Here, we report the synthesis and characterisation of complexes of chlorides and acetates of Mn(II), Co(II), Ni(II) and Cu(II) with Schiff's base 3-(benzo[*b*]thiophen-2-yliminomethyl)-benzene-1,2-diol. The so formed metal complexes of Schiff's base ligand have been characterized by various spectroscopic techniques including IR, ¹H NMR, UV-visible spectrophotometry, mass spectrometry, elemental analysis and conductance measurements. The synthesized ligand and complexes are screened for their fungicidal activity. Food poison method is evaluated for screening antifungal activity [27] checked out by screening ligand and their metal complexes of chlorides and acetates of metal Mn(II), Co(II), Ni(II) and Cu(II). Results show that

ligand and its metal complexes are active towards the fungus *A. niger* and *C. tropicalis*. However metal complexes are more active in the comparison of ligand.

EXPERIMENTAL

The chemicals have been used as supplied and are of AR grade. All the chemicals ordered from Sigma-Aldrich, Bangalore, India and Alfa Aesar, Heshyham, England. The solvents used as were of the spectroscopic grade. Metal salts were purchased from E. Merck, India and used as received. Carbon, hydrogen and nitrogen was analyzed on Carlo-Erba EA1106 elemental analyzer at USIC (University of Delhi), Delhi, India. The ELICO (type CM82T) conductivity bridge was used for evaluating molar conductances. IR spectra were recorded in range of 4000-400 cm^{-1} on the instrument FT-IR spectrum BX-II spectrophotometer in KBr pellet. Shimadzu UV-visible mini-1240 spectrophotometer was used for recording electronic spectra in DMSO as solvent. ^1H NMR was recorded on Bruker Advanced DPX-300 spectrometer by using $\text{DMSO-}d_6$ as solvent. LC-ESI-MS based analysis was done for calculating electronic impact mass spectrum. For recording EPR spectrum of metal complexes as polycrystalline samples was recorded by using DPPH as g marker. Molecular modelling of ligand was done on Gaussian 09 W.

Synthesis of Schiff's base ligand: Hot ethanolic solution of 2,3-dihydroxybenzaldehyde (0.001mol, 0.138 g) has been refluxed with the ethanolic solution of aminobenzothiazole (0.001mol, 0.150 g) for about 6-7 h at 70-75 °C. It was allowed to cool and kept in refrigerator overnight. After cooling, the mustard colour solid product was precipitated out. It was then

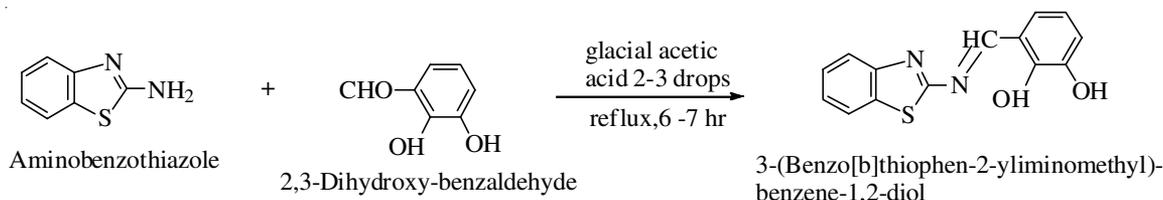
filtered, washed with ethanol and dried in vacuum over P_4O_{10} . (**Scheme-I**).

Synthesis of metal complexes: The hot methanolic solution of Schiff's base ligand (0.001 mol, 0.27 g) was added to the hot methanolic solution of corresponding metal salts (acetate and chloride) (L:M, 2:1) by continuous stirring and then refluxed this mixture for about 14-16 h at 70-75 °C. Few drops of aqueous ammonia was added to adjust the pH 6-7. On cooling, coloured complexes were precipitate out and filtrated. It was washed thoroughly with diethyl ether and dried in vacuum over P_4O_{10} . The analytical data of the complexes is given in Table-1.

Test microorganisms: Fungal species *i.e.* *Aspergillus niger* and *Candida tropicalis* have been used for evaluation of antifungal activities of synthesized ligand and complexes.

Medium: Subaround dextrose agar (SDA) has been used for antifungal assay.

Antifungal screening: Food poison method was used for fungicidal screening [28,29]. Compounds have been dissolved in DMSO for preparation of solutions. Subaround dextrose agar was dissolved in distilled water. By adding proper amount of compound (solution in DMSO) to SDA, 500 ppm, 750 ppm and 1000 ppm concentrations of the compound obtained. Under favourable condition medium was poured into petri-plates in laminar flow hood. After solidification of medium, mycelia discs of 0.5 cm in the diameter from fungus culture was cut down with the help of sterile cork borer and then transferred in the centre of petriplates. Now these petriplates have been put in incubator (25-26 °C) for checking growth. In each petri-plate growth of fungi (mm) has been measured diametrically. The growth inhibition (I) was calculated by formula:



Scheme-I: Synthesis of Schiff's base ligand, 3-(benzo[b]thiophen-2-yliminomethyl)-benzene-1,2-diol

TABLE-1
ANALYTICAL DATA OF LIGAND AND ITS Mn(II), Co(II), Ni(II) AND Cu(II) COMPLEXES

Compd. m.f.	m.w.	Molar conductance ($\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$)	Colour	Yield (%)	m.p. ($^{\circ}\text{C}$)	Elemental analysis (%): Found (calcd.)			
						M	C	H	N
Ligand (L) $\text{C}_{14}\text{H}_{10}\text{N}_2\text{O}_2\text{S}$	270.0	–	Mustard	58	135	–	62.21 (62.19)	3.73 (3.71)	10.36 (10.32)
$[\text{Mn}(\text{L})_2\text{Cl}_2]$	662.9	5	Cream	58	> 280	8.27	50.61 (50.63)	2.73 (2.75)	8.43 (8.45)
$[\text{Mn}(\text{L})_2(\text{CH}_3\text{COO})_2]$	711.0	6	Light pink	56	> 280	7.72	54.01 (53.09)	3.40 (3.41)	7.87 (7.88)
$[\text{Co}(\text{L})_2\text{Cl}_2]$	666.9	5	Brown	65	> 280	8.82	50.31 (50.29)	2.71 (2.73)	8.38 (8.36)
$[\text{Co}(\text{L})_2(\text{CH}_3\text{COO})_2]$	715.0	8	Brown	64	> 280	8.24	53.71 (53.69)	3.38 (3.39)	7.83 (7.81)
$[\text{Ni}(\text{L})_2\text{Cl}_2]$	665.9	6	Mahendi	64	> 280	8.78	50.33 (50.35)	2.72 (2.74)	8.38 (8.37)
$[\text{Ni}(\text{L})_2(\text{CH}_3\text{COO})_2]$	714.0	7	Green	65	> 280	8.20	53.73 (53.71)	3.38 (3.40)	7.83 (7.85)
$[\text{Cu}(\text{L})_2\text{Cl}_2]$	670.9	5	Dark blue	66	> 280	8.82	53.36 (53.35)	3.36 (3.33)	7.78 (7.76)
$[\text{Cu}(\text{L})_2(\text{CH}_3\text{COO})_2]$	719.0	8	Sea green	68	> 280	8.82	53.36 (53.34)	3.36 (3.34)	7.78 (7.76)

$$\text{Inhibition (\%)} = \frac{C-T}{C} \times 100$$

where, C = the growth of the fungus (mm) in control, T = growth of the tested compound.

RESULTS AND DISCUSSION

IR analysis: In IR spectrum of ligand, the band corresponds to carbonyl and free primary amine, was not observed which suggest complete condensation of amino group with keto group. The band observed at 1625 cm^{-1} (Table-2), indicate the formation of azomethine group and assigned the $>\text{C}=\text{N}$ -linkage [30]. The structure of metal complexes can be easily verified by making a comparison in the position of band, in IR spectra of the Schiff's base ligand and that of the respective metal complexes. The band corresponding to -OH group observed in the range of $3450\text{-}3400 \text{ cm}^{-1}$. On complexation, the value observed at 1625 cm^{-1} is shifted to the lower side [31] in the range of $1615\text{-}1591 \text{ cm}^{-1}$. This indicates that coordination takes place through the nitrogen atom of azomethine group.

TABLE-2
IR (ν , cm^{-1}) SPECTRAL BANDS OF THE LIGANDS AND THEIR METAL COMPLEXES

Compound	$>\text{C}=\text{N}$	-OH	M-O	M-N
Ligand (L), $\text{C}_{14}\text{H}_{10}\text{N}_2\text{O}_2\text{S}$	1625	3435	—	—
$\text{MnC}_{28}\text{H}_{18}\text{N}_4\text{O}_4\text{S}_2\text{Cl}_2$	1615	3402	573	415
$\text{MnC}_{32}\text{H}_{24}\text{N}_4\text{O}_8\text{S}_2$	1615	3422	570	455
$\text{CoC}_{28}\text{H}_{18}\text{N}_4\text{O}_4\text{S}_2\text{Cl}_2$	1590	3401	531	420
$\text{CoC}_{32}\text{H}_{24}\text{N}_4\text{O}_8\text{S}_2$	1607	3408	528	408
$\text{NiC}_{28}\text{H}_{18}\text{N}_4\text{O}_4\text{S}_2\text{Cl}_2$	1596	3422	504	405
$\text{NiC}_{32}\text{H}_{24}\text{N}_4\text{O}_8\text{S}_2$	1591	3410	561	428
$\text{CuC}_{28}\text{H}_{18}\text{N}_4\text{O}_4\text{S}_2\text{Cl}_2$	1604	3393	514	458
$\text{CuC}_{32}\text{H}_{24}\text{N}_4\text{O}_8\text{S}_2$	1599	3412	571	467

Mass analysis: A molecular ion peak has been observed at m/z 271.05, in the electronic mass spectrum (Fig. 1) of Schiff's base ligand which confirm the proposed formula $[\text{C}_{14}\text{H}_{11}\text{N}_2\text{O}_2\text{S}]^+$. The spectrum also shows a series of peaks observed at 129.01, 158.94, 159.95, 212.94, 213.93, 214.93, 230.95 corresponding to various fragments. Intensities of the peaks give an idea of the stabilities of fragments.

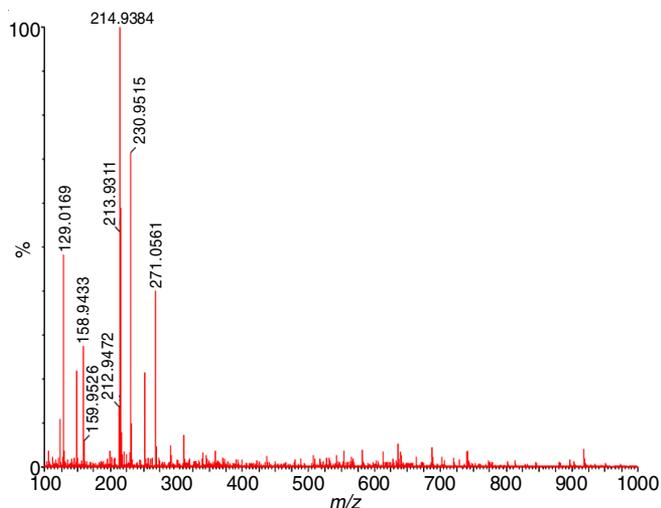


Fig. 1. Mass spectrum of the ligand

$^1\text{H NMR}$ analysis: $^1\text{H NMR}$ spectrum of ligand 3-(benzo[*b*]-thiophen-2-yliminomethyl)-benzene-1,2-diol in $\text{DMSO-}d_6$ shows following signals: 8.1 ppm, (1H, s, $>\text{C}=\text{NH}$), 7.05-8.33 ppm, (4H, m, Ar-H), 6.7-7.3 ppm (3H, m, Ar-H), 10.24 ppm (2H, s, -OH).

Electronic analysis: Electronic spectra of the complexes have been recorded in DMSO as solvent. Electronic spectra of Mn(II) complexes show bands in region of 18315-18527, 22511-22541, 26537-27134 and 33754 cm^{-1} corresponding to ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{2g}({}^4\text{G})$, ${}^6\text{A}_{1g} \rightarrow {}^4\text{E}_g$, ${}^4\text{A}_{1g}({}^4\text{G})$ (10B+5C), ${}^6\text{A}_{1g} \rightarrow {}^4\text{E}_g({}^4\text{D})$ (17B+5C) and ${}^6\text{A}_{1g} \rightarrow {}^4\text{E}_g({}^4\text{D})$ (17B+5C) and ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{2g}({}^4\text{P})$ [32], suggested an octahedral geometry for Mn(II) complexes. Electronic spectra of Co(II) complexes show bands in region of 9699-9745, 12499-12578, 18322-19453 and assigned for three transition ${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{2g}(\text{F})$, $\text{T}_{1g} \rightarrow {}^4\text{A}_{2g}(\text{F})$, $\text{T}_{1g} \rightarrow {}^4\text{T}_{1g}(\text{P})$, respectively. Fourth band appear at $33121\text{-}35768 \text{ cm}^{-1}$ may be due to the charge transfer. Position of bands indicate an octahedral geometry for Co(II) complexes [33,34]. Electronic spectra of Ni(II) complexes show bands in region of 9129-9566, 14676-15223 and $18543\text{-}19576 \text{ cm}^{-1}$. Ground state of Ni(II) in octahedral coordination termed as ${}^3\text{A}_{2g}$. So that three spin allowed transitions are assigned ${}^3\text{A}_{2g} \rightarrow {}^3\text{A}_{2g}(\text{F})$, ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{F})$ and ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{P})$ corresponding to octahedral geometry for Ni(II) complexes [35,36]. Electronic spectra of Cu(II) complexes show bands in region of 12211-14121 cm^{-1} , $16421\text{-}18542$, $27202\text{-}36222 \text{ cm}^{-1}$ assigned to ${}^2\text{B}_{1g} \rightarrow {}^2\text{A}_{1g}$, ${}^2\text{B}_{1g} \rightarrow {}^2\text{B}_{2g}$, ${}^2\text{B}_{1g} \rightarrow {}^2\text{E}_g$ transitions and indicate the tetragonal geometry for Cu(II) complexes [37]. Absorption bands in the region $37594\text{-}37743 \text{ cm}^{-1}$ corresponding to charge transfer band. Electronic spectral data is shown in Table-3.

TABLE-3
MAGNETIC MOMENT (μ_{eff}) AND ELECTRONIC SPECTRAL DATA (λ_{max}) OF COMPLEXES

Complexes	μ_{eff} (B.M.)	λ_{max} (cm^{-1})
$[\text{Mn}(\text{L})_2\text{Cl}_2]$	5.91	18315, 22511, 26537
$[\text{Mn}(\text{L})_2(\text{CH}_3\text{COO})_2]$	5.94	18527, 22541, 27134, 33754
$[\text{Co}(\text{L})_2\text{Cl}_2]$	4.97	9699, 12499, 18322
$[\text{Co}(\text{L})_2(\text{CH}_3\text{COO})_2]$	4.96	9745, 12578, 19453
$[\text{Ni}(\text{L})_2\text{Cl}_2]$	2.89	9129, 14676, 18543.
$[\text{Ni}(\text{L})_2(\text{CH}_3\text{COO})_2]$	2.92	9566, 15223, 19576
$[\text{Cu}(\text{L})_2\text{Cl}_2]$	1.94	12211, 16421, 27202
$[\text{Cu}(\text{L})_2(\text{CH}_3\text{COO})_2]$	2.03	14121, 18542, 36222

EPR analysis: EPR spectra of Cu(II) and Mn(II) have been recorded at room temperature and of Co(II) at liquid nitrogen temperature at frequency of 9.1 GHz and magnetic field strength of 3000 G EPR spectra of Co(II) was recorded at liquid nitrogen temperature as rapid spin lattice relaxation for Co(II) broadens lines at the higher temperature [38,39]. The Co(II) complexes at LNT show broad signal. In complexes deviation for g values from free electron value *i.e.* 2.0023 is due to the angular momentum contribution [40]. The values of g are summarized in Table-4. $g_{\parallel} < 2.3$ indicates the covalent character of the metal ligand bond. The value of g_{\parallel} is observed in the range 2.20-2.28 and for g_{\perp} in the range 1.90-2.12. For Mn(II) complexes g_{iso} is observed in the range of 2.097-2.073. Observation of trend $g_{\parallel} > g_{\perp} > 2.0023$, indicates that the unpaired electron localized in $d_{x^2-y^2}$ orbital of Cu(II) ions and a tetragonal geometry confirmed for Cu(II) complexes [41]. Geometric parameter

G was calculated by making a relation in between g_{\parallel} and g_{\perp} and formulated as $G = (g_{\parallel} - 2)/(g_{\perp} - 2)$. G was calculated as 3.7, 3.92 for Cu(II) ions. The exchange interaction between metal centers in the polycrystalline solid was calculated by geometric parameter G. Greater than 4 value for G indicate negligible exchange interaction and lesser than 4 value for G indicate the considerable exchange interaction in solid complexes [42]. Table-4 shows the values of these parameters.

Molecular modelling: Optimization of the molecule has been carried out in order to obtain the structural information. Geometry optimisation was done by using Gaussian 09 W. Molecular modelling analysis helps in finding the bond angles and bond lengths [43]. Structure of optimized ligand, [Ni(L)₂Cl₂] and [Mn(L)₂Cl₂] complexes are shown in Figs. 2 and 3, respectively. In the ligand structure, bond length for C=N is 1.302 Å, C-S is 1.423 Å and bond angle for C=N-C is 119.3°, C-S-C

is 108°. In [Ni(L)₂Cl₂] and [Mn(L)₂Cl₂] complexes, both axial positions are occupied by Cl atoms.

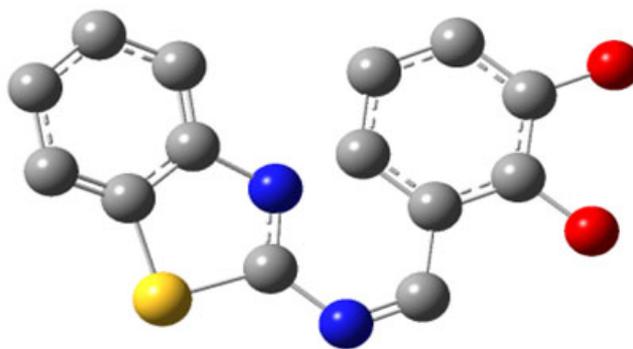


Fig. 2. Geometry optimized structure of ligand (L)

Complexes	At RT				At LNT			
	g_{\parallel}	g_{\perp}	g_{iso}	G	g_{\parallel}	g_{\perp}	g_{iso}	G
[Mn(L) ₂ Cl ₂]	–	–	2.097	–	–	–	–	–
[Mn(L) ₂ (CH ₃ COO) ₂]	–	–	2.073	–	–	–	–	–
[Co(L) ₂ Cl ₂]	–	–	–	–	2.24	1.906	–	–
[Co(L) ₂ (CH ₃ COO) ₂]	–	–	–	–	2.20	2.12	–	–
[Cu(L) ₂ Cl ₂]	2.22	2.061	–	3.7	–	–	–	–
[Cu(L) ₂ (CH ₃ COO) ₂]	2.28	2.073	–	3.92	–	–	–	–

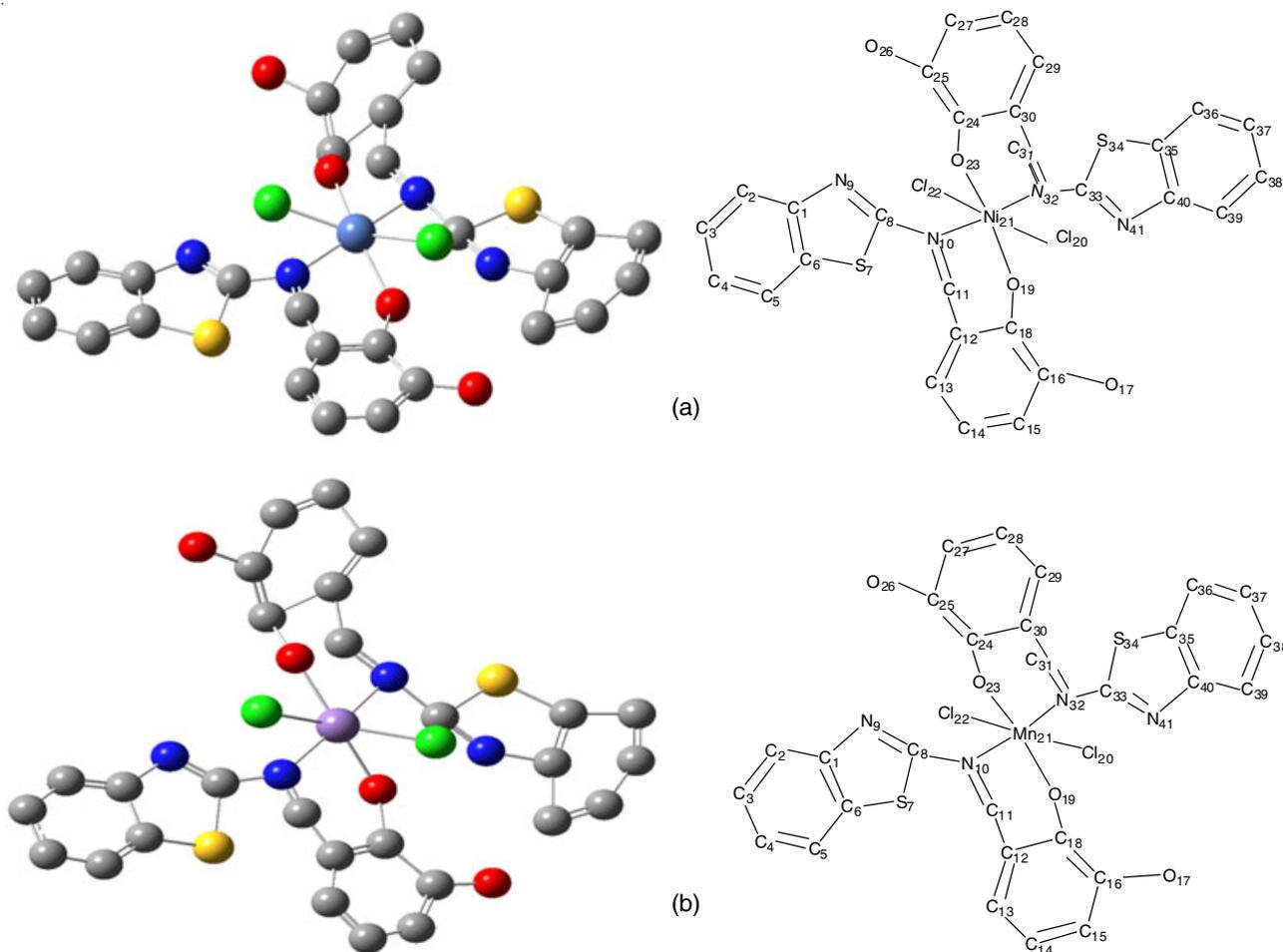


Fig. 3. Geometry optimized structure of metal complexes (a) [Ni(L)₂Cl₂], (b) [Mn(L)₂Cl₂]

[Ni(L)₂Cl₂] and [Mn(L)₂Cl₂] complexes possessed octahedral geometry. In [Ni(L)₂Cl₂] two equatorial Ni-N distances were 2.87 Å, 3.01 Å and two axial Ni-Cl distances were 1.133 Å, 1.242 Å. In [Mn(L)₂Cl₂] two equatorial Mn-N distances were 2.84 Å, 2.35 Å and two axial Mn-Cl distances were 1.824 Å, 1.834 Å. The other important bond lengths and angles are summarized in Tables 5 and 6, respectively.

Antimicrobial activity: Antifungal activity for ligand and its metal complexes has been examined. The study of values of

growth inhibition zone indicates that metal complexes were more active in the comparison of ligand. It may be due to greater lipophilicity of complex as it increase activity of metal complex, can be explained by overtone's concept and theory of Tweedy's chelation [44]. It has also been proposed that concentration plays a vital role in increasing the degree of inhibition, as the concentration increases, the activity increases (Table-7).

The activity order shown as follows:

Aspergillus niger: Cu(II) > Mn(II) > Ni(II) > Co(II) > L

Candida tropicalis: Mn(II) > Co(II) > Cu(II) > Ni(II) > L

Proposed structure of complexes: On the basis of various characterization techniques, we proposed a six coordinated octahedral geometry for the complexes as shown Fig. 4.

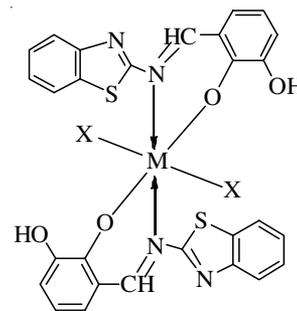


Fig. 4. Proposed chemical structure of the synthesised complexes; [M = Mn(II), Co(II), Ni(II), Cu(II) and X = Cl⁻, CH₃COO⁻]

Conclusion

Complexes of chlorides and acetates of Mn(II), Co(II), Ni(II) and Cu(II) with ligand, 3-(benzo[*b*]thiophen-2-ylimino-methyl)-benzene-1,2-diol is synthesized and characterized. The structure is confirmed by analytical, spectral, magnetic, electrochemical and molecular modelling. Schiff's base and complexes show potential activity towards microbial strains. All the complexes have octahedral geometry.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

TABLE-7
ANTIFUNGAL ACTIVITIES DATA OF THE LIGAND (L) AND THEIR COMPLEXES

Compounds	Fungal inhibition (%)					
	<i>Aspergillus niger</i>			<i>Candida tropicalis</i>		
	500 ppm	750 ppm	1000 ppm	500 ppm	750 ppm	1000 ppm
L	–	–	12.23	13.54	26.54	29.54
[Mn(L) ₂ Cl ₂]	29.54	32.64	40.87	35.92	39.81	46.65
[Co(L) ₂ Cl ₂]	18.96	22.36	31.57	29.19	39.13	45.65
[Ni(L) ₂ Cl ₂]	28.48	30.43	37.76	18.84	37.64	41.56
[Cu(L) ₂ Cl ₂]	49.73	52.43	67.87	19.32	38.32	42.42

TABLE-5
OPTIMIZED GEOMETRY OF THE SCHIFF'S BASE
LIGAND AND METAL COMPLEXES (BOND LENGTHS, Å)

Atoms	Ligand	[Ni(L) ₂ Cl ₂]	[Mn(L) ₂ Cl ₂]
C ₁ -N ₉	1.457	1.421	1.412
C ₆ -S ₇	1.423	1.474	1.467
C ₈ -N ₁₀	1.276	1.492	1.490
C ₁₁ -C ₁₂	1.333	1.298	1.291
C ₁₈ -C ₁₆	1.394	1.289	1.280
N ₁₀ -C ₁₁	1.302	1.468	1.461
C ₁₈ -O ₁₉	1.992	1.989	1.982
C ₁₆ -O ₁₇	1.391	1.354	1.351
C ₁₄ -C ₁₅	1.394	1.321	1.311
Cl ₂₂ -Ni ₂₁	–	1.242	–
Cl ₂₀ -Ni ₂₁	–	1.133	–
Cl ₂₂ -Mn ₂₁	–	–	1.834
Cl ₂₀ -Mn ₂₁	–	–	1.824
N ₃₂ -C ₃₁	–	1.212	1.202
C ₂₄ -O ₂₃	–	1.811	1.801
C ₂₅ -O ₂₆	–	1.282	1.280
C ₂₇ -C ₂₈	–	1.232	1.231

TABLE-6
OPTIMIZED GEOMETRY OF THE SCHIFF'S BASE
LIGAND AND METAL COMPLEXES (BOND ANGLES, °)

Atoms	Ligand	[Ni(L) ₂ Cl ₂]	[Mn(L) ₂ Cl ₂]
N ₉ -C ₁ -N ₁₀	123.4	124.5	122.5
C ₆ -S ₇ -C ₈	108.7	107.5	106.5
C ₅ -C ₆ -S ₇	132.5	130.5	129.5
C ₄ -C ₅ -C ₆	121.0	120.5	120.0
C ₁₂ -C ₁₃ -C ₁₄	120.0	119.5	119.0
C ₁₈ -C ₁₆ -O ₁₇	121.0	118.5	118.0
C ₁₄ -C ₁₅ -C ₁₆	119.0	120.5	120.0
C ₁ -N ₉ -C ₈	108.2	107.5	107.0
N ₁₀ -Mn ₂₁ -O ₁₉	–	–	135.6
O ₂₃ -Ni ₂₁ -N ₃₂	–	99.1	–
O ₂₃ -Mn ₂₁ -N ₃₂	–	–	98.1
C ₈ -N ₁₀ -C ₁₁	119.3	118.7	118.0
C ₃₁ -N ₃₂ -C ₃₃	–	164.9	–
Cl ₂₀ -Ni ₂₁ -Cl ₂₂	–	136.4	–
Cl ₂₀ -Mn ₂₁ -Cl ₂₂	–	–	138.5
N ₁₀ -Ni ₂₁ -O ₁₉	–	136.0	–

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