

Synthesis and Spectroscopic Characterization of Iron Complexes with Bidentate Schiff's Base Ligands Derived from 2-Benzoylpyridine, 2-Benzoylthiophene and Thiosemicarbazone, Semicarbazone, and their Biological Activity

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ABSTRACT

Objective: The objective of this study is to synthesize and characterize Schiff's base ligands and their iron complexes and to study their antimicrobial activity.

Materials and Method: The Schiff's base ligands and their complexes were prepared by reflux method for 7–8 h. In each case, pH was adjusted as per the requirement. Ethyl alcohol was used as solvent. Ligand 1 was highly soluble in water, and its complexes were prepared in water. Round bottom flask (100 mL), condenser, and heating mantle were used as apparatus.

Result: The complexes of Fe(III) and Fe(II) having the general composition FeL^2X^3 (where L = 2-benzoylpyridine thiosemicarbazone (L¹), 2-benzoylpyridine semicarbazone (L²), and 2-benzoylthiophene semicarbazone (L³) and X = Cl⁻, NO₃⁻, ½SO₄²⁻) have been synthesized and were characterized by infrared, elemental analysis, magnetic susceptibility, ultraviolet-visible, conductivity, mass spectrometry, and electron paramagnetic resonance spectral studies. On the basis of molar conductance value which was determined using dimethyl sulfoxide as a solvent it can be concluded that all the complexes were 1:1 electrolytic in nature. The value of magnetic moment indicates that all the complexes are of high spin type. On the basis of spectral studies, an octahedral geometry has been proposed for Fe(II) and Fe(III) complexes. The complexes under study were investigated for antifungal (i.e., *Candida krusei* and *Candida persopolis*) and antibacterial (i.e., *Escherichia coli* and *Staphylococcus*) activity.

Conclusion: The synthesized ligands were bidentate, and complexes were found more active toward antimicrobial activity than ligands.

Key words: Electron paramagnetic resonance, infrared, mass, nuclear magnetic resonance, semicarbazone, thiosemicarbazone

INTRODUCTION

Metal complexes with thiosemicarbazone and semicarbazone ligands draw the attention of scientists for their wide range of biological activities^[1,2] including antibacterial,^[3] antiulcer activity,^[4] anti-inflammatory agent,^[5] biological oxygen carrying system,^[6] and their application in analytical field^[7]. Sulfur and nitrogen donor atoms present in Schiff's base ligands act as chelating agent for the transition and non-transition metal ions.^[8] Coordination of these compounds with metal ions such as iron enhances their activities^[9] as observed in case of pathogenic fungi.^[10] In the light of above applications, the present work depicts the result of our investigations on the synthesis, characterization, and antimicrobial studies of iron complexes of Schiff's base ligands.

Experimental Section

All reagents were commercially available and used without purification purchased from Sigma Aldrich, and metal salts were purchased from E. Merck. Solvents were spectroscopic pure or purified by conventional method.

Preparation of Ligand (L¹)

Thiosemicarbazide (0.091 g, 0.01 mol) was dissolved in minimum quantity of ethanol. To this solution, hot ethanolic solution of 2-benzoylpyridine (0.18 g, 0.01 mol) was added very slowly with constant stirring. The resulting solution was refluxed at 78–80°C for 8 h, and the pH was adjusted to approximately 4–5 using acetic acid (according to Scheme 1). On cooling, bright yellow-colored crystals were separated out. These crystals were washed out several times with cold ethanol. The ligand is highly soluble in water.

Preparation of Ligand (L²)

Semicarbazide (0.11 g, 0.01 mol) and sodium acetate (0.11 g, 0.01 mol) were dissolved in a little amount of

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distilled water and added to an alcoholic solution of 2-benzoylpyridine (0.36 g, 0.02 mol) with constant stirring and refluxed for 7–8 h at 78–80°C according to Scheme 2. The resultant solution was cooled for 24 h. On cooling, white shiny crystals were separated out which were washed with ethanol and ether several times to remove excessive reactant and dried over P_4O_{10} .

Preparation of Ligand (L³)

Thiosemicarbazide (0.91 g, 0.01 mol) was dissolved in minimum quantity of ethanol. To this solution, hot ethanolic solution of 2-benzoylthiophene (0.01 mol) was added very slowly with constant stirring. The resulting solution was refluxed at 78–80°C for 6 h, and the pH was adjusted to 4–5 using acetic acid (according to Scheme 3). On cooling, bright light yellow-colored crystals were separate out. These crystals were washed out several times with cold ethanol and dry ether several times to remove excessive reactant and dried over P_4O_{10} .

Preparation of Transition Metal Complexes with Ligand (L¹)

Hot aqueous solution (20 mL) of corresponding metal salts (0.01 mol) was mixed with hot aqueous solution of the ligand (0.02 mol) with constant stirring and refluxed for 7–8 h at 65–70°C. On cooling the contents, the colored precipitates were separated out in each case. It was filtered and washed with ethanol and ether. The resultant mixture was dried over P_4O_{10} .

Preparation of Transition Metal Complexes With Ligand (L² and L³)

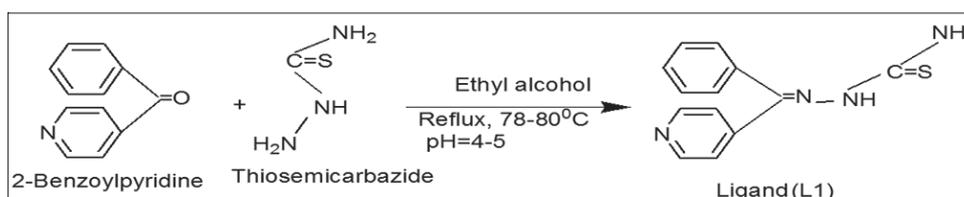
Hot ethanolic solution (20 mL) of corresponding metal salts (0.01 mol) was mixed with hot ethanolic solution of the ligand (0.02 mol) with constant stirring and refluxed for 7–8 h at 78–80°C. On cooling the contents, the colored precipitates were separated out in each case. It was filtered and washed with ethanol and ether. The resultant mixture was dried over P_4O_{10} .

Analytical and Physical Measurement

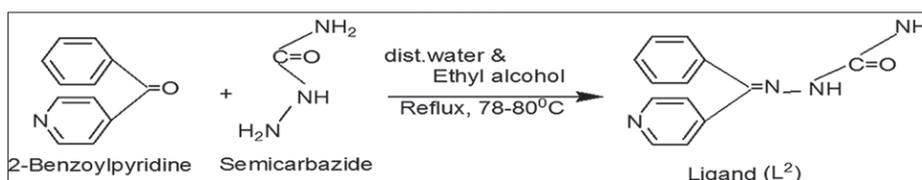
Elemental (CHN) analysis was carried out on a Perkin-Elmer series-II-2400. Infrared (IR) was recorded using a Thermo Scientific Nicolet 6700 Fourier-transform IR (FT-IR) on KBr disc in the wave number ranged 4000–400 cm^{-1} . Mass spectrum was recorded using Bruker microtof-QII. ¹H nuclear magnetic resonance (NMR) spectra were recorded on Bruker advanced DPX-300 spectrometer using dimethyl sulfoxide (DMSO)-d₆ as a solvent and tetramethylsilane as an internal solvent. Electronic spectral studies were conducted on a Perkin-Elmer-lambda 25, ultraviolet (UV) spectrophotometer.

RESULTS AND DISCUSSION

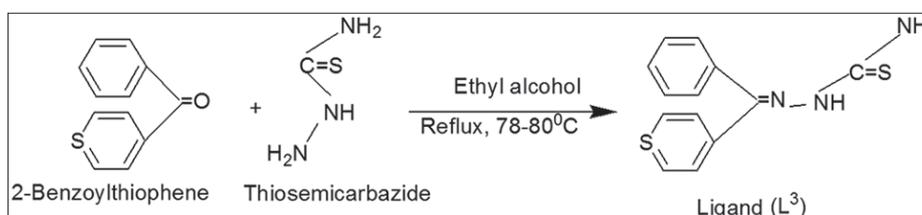
All the iron (III) and iron (II) complexes were synthesized by condensation reaction between ligands and corresponding metal salts. All complexes were synthesized at 6–7pH range. The synthesized complexes were colored and stable at room temperature and were found to be soluble



Scheme 1: Synthesis of ligand 1



Scheme 2: Synthesis of ligand 2



Scheme 3: Synthesis of ligand 3

in DMSO and DMF. The molar conductivity value lies in the range from 70 to 80 ($\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$) which indicates 1:1 electrolytic nature. On the basis of elemental analysis, the complexes were found to have general composition FeL_2X_3 , where $\text{L} = \text{L}^1, \text{L}^2, \text{and } \text{L}^3$ and $\text{X} = \text{Cl}^-$ and NO_3^- . All complexes and ligands were found to be biologically active toward test fungi and bacteria. Complexes were found to be more biologically active than ligands. Copper complexes showed maximum antifungal and antibacterial activity in comparison to all other metals. The results obtained from antimicrobial susceptibility testing are depicted in Table 1.

^1H NMR of Ligand ($\text{L}^1, \text{L}^2, \text{and } \text{L}^3$)

^1H NMR of ligands ($\text{L}^1, \text{L}^2, \text{and } \text{L}^3$) was done in DMSO on 44–300 MHz NMR. In ^1H NMR of ligands (L^1 and L^3) [Figure 1], the aromatic proton appears as a set of singlet,

doublet, and multiplet in the range 7.40–8.78 ppm. The singlet for NH proton appears at 9.32 ppm, while two NH_2 protons resonate as a multiplet at 7.34–7.38 ppm. The NH_2 and NH protons are confirmed by their D_2O spectra. All the protons are found in their expected region.

Mass Spectra of Ligand ($\text{L}^1, \text{L}^2, \text{and } \text{L}^3$)

Mass spectra of the ligands [Figure 2] give the important information regarding the proposed formula of the synthesized compounds. Mass spectra of ligands $\text{L}^1, \text{L}^2, \text{and } \text{L}^3$ show a molecular ion peak at $m/z = 255, 239, \text{and } 259$ amu corresponding to species $[\text{C}_{13}\text{H}_{11}\text{N}_4\text{S}]^+, [\text{C}_{13}\text{H}_{11}\text{N}_4\text{O}]^+$ and $[\text{C}_{13}\text{H}_{12}\text{N}_3\text{SO}]^+$, respectively. The peak at $m/z = 255, 239, \text{and } 259$ amu indicates M+1, M+1, and M-1 peaks. These values favor the proposed formulae of the ligands under study.

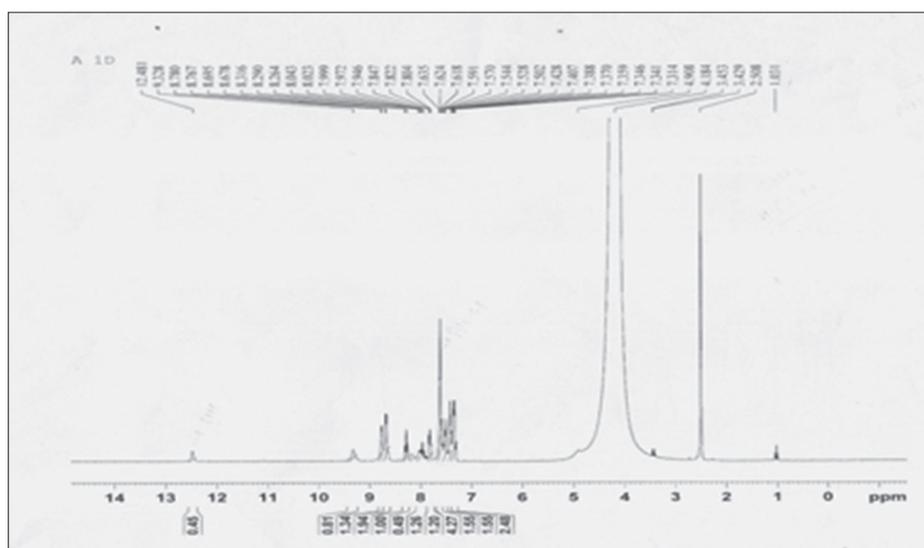


Figure 1: ^1H nuclear magnetic resonance spectrum of ligand (L^1)

Table 1: Color, melting point, and elemental analyses of Fe (III and II) complexes

Complexes	Color	Molar Conductance	Melting point ($^{\circ}\text{C}$)	Molecular weight found (Calc.)	Found (calculated)%		
					C	H	N
$(\text{Fe}[\text{L}^1]_2\text{SO}_4)$	Green	21	212	745	48.32 (48.56)	4.02 (4.10)	15.03 (15.63)
$\text{FeC}_{26}\text{H}_{24}\text{S}_3\text{N}_8\text{O}_4$							
$(\text{Fe}[\text{L}^1]_2[\text{NO}_3]_2) \text{NO}_3$	Black	86	243	754	41.37 (41.87)	3.18 (3.87)	14.85 (14.98)
$\text{FeC}_{26}\text{H}_{24}\text{S}_2\text{N}_{10}\text{O}_6$							
$(\text{Fe}[\text{L}^1]_2\text{Cl}_2) \text{Cl}$	Black	98	215	675	46.25 (45.90)	3.55 (3.21)	16.06 (16.98)
$\text{FeC}_{26}\text{H}_{24}\text{S}_2\text{N}_8\text{Cl}_2$							
$(\text{Fe}[\text{L}^2]_2\text{Cl}_2) \text{Cl}$	Black	91	204	607	51.4 (51.92)	3.95 (3.97)	18.45 (18.16)
$\text{FeC}_{26}\text{H}_{24}\text{O}_2\text{N}_8\text{Cl}_2$							
$(\text{Fe}[\text{L}^2]_2[\text{NO}_3]_2) \text{NO}_3$	Black	84	210	660	47.27 (47.10)	3.63 (3.95)	21.21 (21.33)
$\text{FeC}_{26}\text{H}_{24}\text{O}_8\text{N}_{10}$							
$(\text{Fe}[\text{L}^2]_2\text{SO}_4)$	Green	11.9	219	632	49.36 (49.01)	3.79 (3.68)	17.72 (17.16)
$\text{FeC}_{26}\text{H}_{24}\text{O}_6\text{SN}_8$							
$(\text{Fe}[\text{L}^3]_2\text{Cl}_2) \text{Cl}$	Yellow brown	76	234	710	43.91 (43.67)	3.37 (3.09)	11.82 (11.43)

Magnetic Moment

Fe(III) d^5 case, under weak field of Oh symmetry, the ground state is ${}^6A_{1g}(t_{2g}^3, e_g^3)$ with $S = 5/2$ (high spin). Such system exhibits magnetic moment close to spin only value, i.e., 5.92 B.M. In the presence of strong field of Oh symmetry, the ground state is ${}^2T_{2g}(t_{2g}^5, e_g^0)$ with $S = 1/2$ (low spin), and in this case, the magnetic moment is close to 2.0 B.M. Greater than the spin, only value of 1.73 B.M. is due to the small contribution of the orbital angular momentum in the t_{2g}^5 configuration. The magnetic moment is intermediate to high or low spin values may arise when the ligand field strength is comparable with the mean electronic pairing energy of the d^5 configuration. In such cases, the two possible ground states ${}^6A_{1g}$ and ${}^2T_{2g}$ are in thermal equilibrium resulting in temperature-dependent variation of magnetic moments between the limiting values of 5.92–2.0 B.M.

IR Spectra

The IR bands of ligands and complexes [Figure 3] were recorded between 4000 and 400 cm^{-1} as listed in Table 2. A band at 1618 cm^{-1} in case of ligand 1 (L^1) and 1577 cm^{-1} in case of ligand 2 (L^2) and another band at 1598 cm^{-1} in case of ligand 3 (L^3) correspond to $\nu(\text{C}=\text{N})$ azomethine group.^[11]

The band at 781 cm^{-1} and 837 cm^{-1} may be assigned to $\nu(\text{C}=\text{S})$ ^[12] group, and the band at 1660 cm^{-1} corresponds to $\nu(\text{C}=\text{O})$ carbonyl group. In IR of complexes, these values are shifted toward lower side from 10 to 45 cm^{-1} . This indicates that both $\nu(\text{C}=\text{N})$ and $\nu(\text{C}=\text{S})$ in ligand 1 and 3 and $\nu(\text{C}=\text{O})$ group and $\nu(\text{C}=\text{N})$ of ligand 2 are coordinated to central metal ion in complex formation [Figure 3]. The coordination of $\nu(\text{C}=\text{N})$ group is further supported by appearance of new $\nu(\text{M}-\text{N})$ band which appeared in the region from 409 to 553 cm^{-1} ^[13] and $\nu(\text{M}-\text{O})$ band which appeared in the region from 504 to 553 cm^{-1} .^[14] Thus, all the ligands are bidentate and ligand 1 and 3 coordinated through nitrogen and sulfur with central metal ion, whereas ligand 2 (L^2) coordinated through nitrogen and oxygen.

IR Bands Due to Anion

The IR spectra of nitrate complexes iron (III) of ligand 1 and 2 (L^1 and L^2) show three bands at 1412–1425 (ν_5), 1313–1315, and 1203–1215 (ν_1).^[15] The difference in ν_5 and ν_1 is 209 and 210 cm^{-1} ^[16-18] suggesting monodentate behavior of nitrate group in both the complexes of ligand (L^1 and L^2). IR bands of sulfato complexes of iron suggest the bidentate coordination. All the values are listed in Tables 3 and 4.

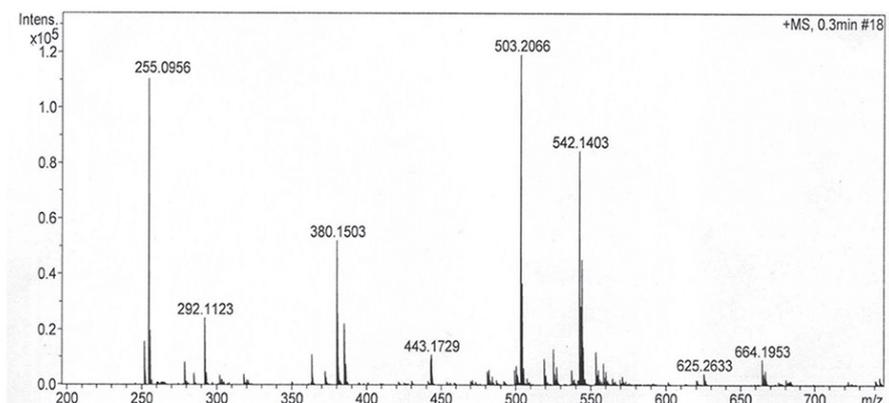


Figure 2: Mass spectrum of ligand (L^1)

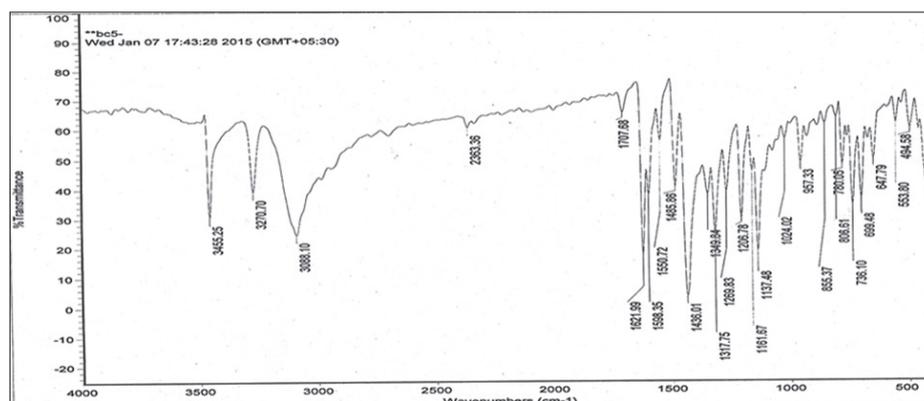


Figure 3: Infrared spectrum of $(\text{Fe}[L^2]_2[\text{NO}_3]_2)\text{NO}_3$

Electronic Spectra

Iron (III) is isoelectronic with Mn(II), but the electronic spectral characterization of iron (III) is less, because of much greater tendency of the trivalent ion to have charge transfer bands in the near UV region with strong low energy wings in the visible that obscure the very weak, spin forbidden d-d bands. The spectra of Fe(III) complexes generally exhibit a small number of fairly broadband rather than the series of narrow bands expected. Electronic spectra of Fe(III) complexes exhibit three bands of varying intensities [Figure 4] in the region of 21150–22350 [ν_1],

24370–25500 [ν_2], and 26789–27767 [ν_3] cm^{-1} , but the assignments of bands are difficult.^[19] It is very unlikely that the spectra of Fe(III) derivatives, which are more covalent than those of manganese(II), can be described in terms of B and C.

Antimicrobial Activity

All the synthesized compounds were tested for their antibacterial and antifungal activity (minimum inhibitory concentration [MIC]) *in vitro* by broth dilution method^[20] with two Gram-positive bacteria *Staphylococcus aureus*, one Gram-negative bacteria *Escherichia coli*, and two fungal strains *Candida parapsilosis* and *Candida krusei*. The MIC values for all the newly synthesized compounds, defined as the lowest concentration of the compound preventing the visible growth, were determined using microdilution broth method. Serial dilutions of the test compounds and biological activities of ligands and their metal complexes were prepared in Mueller-Hinton agar. Drugs (0.005, 0.050, and 0.500 mg) were dissolved in DMSO, 1 mL. 0.5 McFarland solution of *E. coli*, *S. aureus*, and *C. parapsilosis* and *C. krusei* was prepared and applied on Mueller-Hinton agar contained in a Petri plate with the help of sterilized swab. Then, 10 μL solution of concentration (0.005, 0.050, and 0.500 mg) in 1 mL DMSO

Table 2: Important IR spectral bands (cm^{-1}) and their assignments

Complexes	V (C=O)	V (C=N)	V (C=S)	V (M-N)	V (M-O)
Ligand 1	-	1618	781	-	-
(Fe[L ¹] ₂ Cl ₂)	-	1602	749	421	-
(Fe[L ¹] ₂ [SO ₄])	-	1591	748	409	-
(Fe[L ¹] ₂ [NO ₃] ₂)	-	1583	745	446	-
Ligand 2	1577	1660	-	-	-
(Fe[L ²] ₂ Cl ₂)	1560	1630	-	-	556
(Fe[L ²] ₂ [NO ₃] ₂)	1551	1622	-	-	554
(Fe[L ²] ₂ [SO ₄])	1550	1619	-	-	551
Ligand 3		1599	814		
		1578	814		425

Table 3: Important IR spectral bands (cm^{-1}) due to anions

Complexes	V1	V2	V3	V5-V1	Results
Ligand 1	-	-	-	-	-
(Fe[L ¹] ₂ Cl ₂) Cl	-	-	-	-	-
(Fe[L ¹] ₂ [SO ₄])	1131	1042	950		Unidentate sulfate
(Fe[L ¹] ₂ [NO ₃] ₂) NO ₃	1419	1338	1203	216	Unidentate nitrate
Ligand 2					
(Fe[L ²] ₂ Cl ₂)	-	-	-	-	-
(Fe[L ²] ₂ [NO ₃] ₂) NO ₃	1428	1395	1201	218	Unidentate nitrate
(Fe[L ²] ₂ [SO ₄])	1133	954	419		Unidentate sulfate
(Fe[L ³] ₂ Cl ₂) Cl	-	-	-	-	-

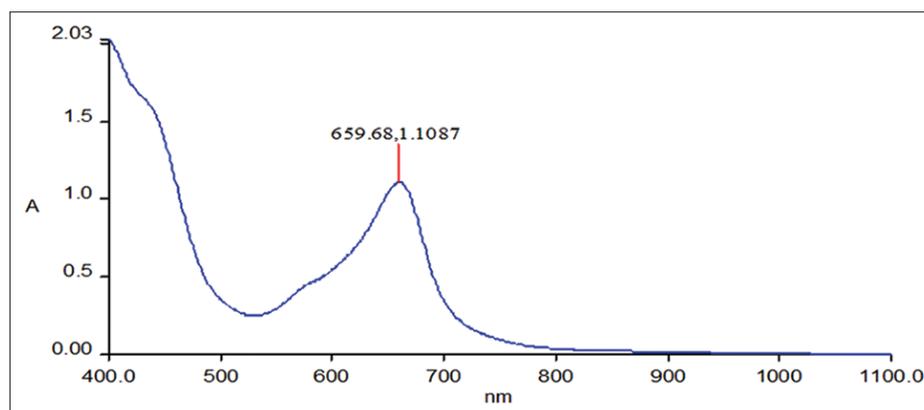


Figure 4: Ultraviolet spectrum of (Fe[L¹]₂[NO₃]₂)NO₃

Table 4: Electronic spectral bands (cm^{-1}) and magnetic moment (B.M.) of Fe (III) complexes

Complexes	Spectral bands in (cm^{-1})	μ_{eff}
(Fe[L ¹] ₂ Cl ₂) Cl	9832, 11086, 10,952, 15, 174, 17, 241, 28, 761	4.96
(Fe[L ¹][SO ₄])	10, 449, 11, 098, 15, 847, 26, 041, 32, 981	4.87
(Fe[L ¹] ₂ [NO ₃] ₂) NO ₃	11, 627, 14, 265, 15, 174, 17, 182, 26, 041	4.56
(Fe[L ²] ₂ Cl ₂) Cl	11, 574, 14, 867, 15, 987, 17, 281, 32, 154	4.67
(Fe[L ²] ₂ [NO ₃] ₂) NO ₃	9, 876, 12, 345, 15, 678, 18654, 33, 452	4.98
(Fe[L ²][SO ₄])	9871, 10, 234, 21, 098, 32, 897	4.75
(Fe[L ³] ₂ [Cl] ₂) Cl	10, 698, 14, 678, 15, 653, 17, 890, 31, 256	4.58

Table 5: Antibacterial screening results of ligand 1 and its complexes

Name	Concentrations (μg)	<i>E. coli</i> diameter (mm)	<i>S. aureus</i> diameter (mm)
Ligand 1	0.005	NA	10
	0.050	10	14
	0.500	14	17
L ₁ FeCl ₃	0.005	NA	NA
	0.050	18	24
	0.500	26	29
L ₁ FeNO ₃	0.005	NA	NA
	0.015	12	14
L ₂	0.005	10	NA
	0.050	14	14
	0.500	18	15
L ₂ FeCl ₃	0.005	NA	NA
	0.050	12	12
	0.500	13	15
L ₂ FeNO ₃	0.005	NA	NA
	0.050	19	21
	0.500	21	23
L ₃	0.005	NA	10
	0.050	10	12
	0.500	13	18
L ₃ FeSO ₄	0.005	R	R
	0.050	23	15

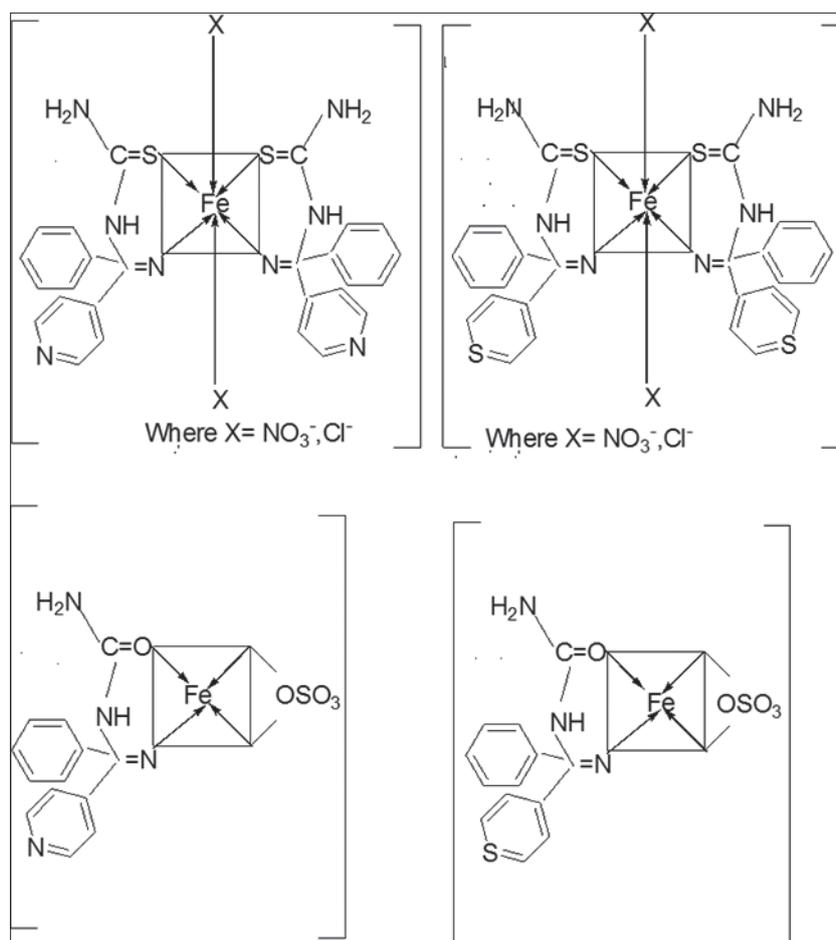
E. coli: Escherichia coli, *S. aureus*: Staphylococcus aureus

was dropped on it with the help of micropipette. This Petri plate was incubated for 24 h at $22 \pm 29^\circ\text{C}$. The growth of fungi and bacteria was measured diametrically. The values are listed in Tables 5 and 6.

To ensure that the solvent had no effect on the bacterial growth, a control was performed with the test medium supplemented with DMSO at the same dilutions as used in the experiments and it was observed that DMSO had no effect on the microorganisms in the concentrations studied [Figure 5].

CONCLUSION

The antimicrobial screening of all investigated compounds provided information about the biological activity of ligands and its complexes which is important in model compounds study. Thus, on the basis of magnetic susceptibility, molar conductance measurement, IR, and electronic spectral studies and the subsequent discussion for the complexes given above, the following structure may be proposed for these complexes.



Scheme 4: Structure of complexes under study

Table 6: Antifungal screening results of ligand 1 and its complexes

Name	Concentrations (μg)	<i>C. krusei</i> diameter (mm)	<i>C. parapsilosis</i> diameter (mm)
Ligand 1	0.005	10	R
	0.050	15	10
	0.500	17	17
L ₁ FeCl ₃	0.005	NA	10
	0.050	22	17
	0.500	24	21
L ₁ FeNO ₃	0.005	NA	NA
	0.015	10	18
	0.050	NA	NA
L ₂	0.005	NA	NA
	0.050	10	10
	0.500	14	12
L ₂ FeCl ₃	0.050	10	11
	0.500	16	13
L ₂ FeNO ₃	0.050	12	11
	0.500	18	16
L ₃	0.005	10	10
	0.050	12	10
	0.500	15	12
L ₃ FeSO ₄	0.005	NA	NA
	0.050	12	10

C. krusei: *Candida krusei*, *C. parapsilosis*: *Candida parapsilosis*

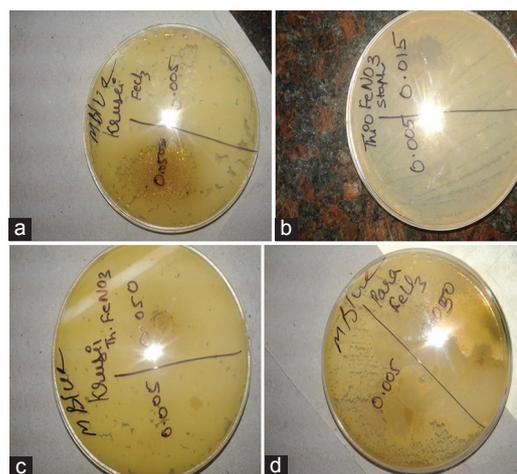


Figure 5: (a-d) Antibacterial and antifungal activity of complexes under study

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