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Synthesis, potentiometric and antimicrobial studies on metal complexes of isoxazole Schiff bases

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Abstract

The metal complexes of Cu(II), Ni(II) and Co(II) with Schiff bases of 3-(2-hydroxy-3-ethoxybenzylideneamino)-5-methyl isoxazole [HEBMI] and 3-(2-hydroxy-5-nitrobenzylidene amino)-5-methyl isoxazole [HNBMI] which were obtained by the condensation of 3-amino-5-methyl isoxazole with substituted salicylaldehydes have been synthesized. Schiff bases and their complexes have been characterized on the basis of elemental analysis, magnetic moments, molar conductivity, thermal analysis and spectral (IR, UV, NMR and Mass) studies. The spectral data show that these ligands act in a monovalent bidentate fashion, co-ordinating through phenolic oxygen and azomethine nitrogen atoms. Chelates of Co(II), Ni(II) appear to be octahedral and Cu(II) appears to be distorted octahedral. To investigate the relationship between formation constants of binary complexes and antimicrobial activity, the dissociation constants of Schiff bases and stability constants of their binary metal complexes have been determined potentiometrically in aqueous solution at $30 \pm 1\,^{\circ}\mathrm{C}$ and at 0.1 M KNO_3 ionic strength and discussed. Antimicrobial activities of the Schiff bases and their complexes were screened. The structure–activity correlation in Schiff bases and their metal(II) complexes are discussed, based on the effect of their stability constants. It is observed that the activity enhances upon complexation and the order of activity is in accordance with stability order of metal ions.

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Keywords: Isoxazole Schiff bases; Metal chelates; Formation constants; Biological activity

1. Introduction

A wide range of biological activities of isoxazole derivatives include pharmacological properties such as hypoglycemic, analgesic, anti-inflammatory, anti-bacterial, anti-cancer, anti-HIV activity and also agrochemical properties like herbicidal and soil fungicidal activity and have applications as pesticides and insecticides [1]. Studies of a new kind of chemotherapeutic Schiff bases are now attracting the attention of biochemists [2]. Schiff bases derived from an amine and any aldehyde are a class of compounds which co-ordinate to metal ions via the azomethine nitrogen [3]. Metal complexes of Schiff bases derived from substituted salicylaldehydes and various amines have been widely investigated because of their wide applicability [4–7]. Chelating ligands containing O and N donor atoms show broad biological activity and are of special interest because of the variety of ways in which they are bonded to metal ions [8]. It is well known that several Schiff base complexes have anti-inflammatory, antipyretic, analgesic, anti-diabetic, anti-bacterial, anti-cancer and anti-HIV activity [9,10]. The antimicrobial activity of 3-amino-5-methyl isoxazole Schiff bases with methoxy salicylaldehyde, naphthaldehyde and their metal complexes was reported earlier and it was found that these compounds show increased activity when administered as metal complexes rather than as organic compounds [11]. In the present investigation we report here the synthesis, characterization, formation constants and antimicrobial studies of Schiff bases HEBMI, HNBMI and their metal complexes.

2. Experimental

2.1. Synthesis of Schiff bases

Methanolic solution of substituted salicylaldehydes (0.01 mol) was added dropwise to a solution of 3-amino-5-methyl isoxazole (0.01 mol) dissolved in methanol. The mixture was refluxed on water bath for 2 h then cooled to room temperature and filtered. The reaction was monitored by TLC.

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The resulting solution was evaporated under reduced pressure and recrystallized from methanol to get yellow crystals. Yield was about 80–85%.

2.2. Synthesis of complexes: general method

Hot methanolic solution of ligand (0.01 mol) and hot methanolic solution of corresponding metal salts (0.005 mol) were mixed together with constant stirring. The mixture was refluxed for 2–3 h at 70–80 °C on water bath. On cooling, colored solid metal complex was precipitated out. The product was filtered, washed with cold methanol and dried under vacuum over P_4O_{10}. Purity of the complex was checked by TLC and melting points.

2.3. Potentiometric reagents and solutions

All the chemicals and solvents used were of Analar grade. Distilled water was further purified by re-distillation process by using distillation plant. The double distilled water obtained was cooled and used for the preparation of the solutions. All metal ion solutions were prepared from their analytical grade nitrates and were standardized by reported procedures. A standard 0.1 M KOH and 0.04 M HNO_3 solutions (Merck) were prepared and standardized by known procedures. Alkali solutions were stored under a nitrogen atmosphere.

2.4. Biological screening

2.4.1. Anti-bacterial screening

The bacterial sub-cultures *Pseudomonas aeurogenosa* and *Escherichia coli* were obtained form Botany department, O.U. The anti-bacterial action of the ligand HEBMI, HNBMI and their complexes of Co(II), Ni(II) and Cu(II) was checked by paper disc method [12]. The compounds were dissolved in acetone ($1.0\,mg\,ml^{-1}$) and the discs of Whattmann filter paper No.41 having the diameter 4 mm were prepared and soaked in it. These soaked discs were placed on nutrient agar plates inoculated with bacteria. These plates were incubated for 36 h at 30 °C. The inhibition zone was observed after 36 h. Acetone was used as a control and gentamycin as a standard drug.

2.5. Anti-fungal screening

Aspergillus niger and *Rhizoptonia solani* were used for fungal test. The anti-fungal activity of the ligands and their complexes was studied by paper disc method [12]. The fungal strains were directly mixed with the PDA medium (potato dextrose agar) and dispersed into the Petri plates. Filter paper discs of 4 mm diameter were prepared prior to the experiment. These discs were soaked in acetone in which the test compound was dissolved and the acetone was used as a control. The filter paper discs were placed on nutrient medium mixed with fungal strains. These Petri dishes were incubated at 35 °C for 48 h. The growth of the fungus was measured by recording the diameter of fungal mycelia.

2.6. Physical measurements

^1H NMR spectra of the ligands were recorded at 200 and 300 MHz on Varian Gemini Unity Spectrometer using TMS as internal standard. The EI mass spectra were recorded on a VG micro mass 7070–H Instrument, ESIMS spectra were recorded on VG AUTOSPEC mass spectrometer. IR spectra of the ligand and complexes were recorded using KBr pellets in the range ($4000–400\,cm^{-1}$) on Perkin-Elmer Infrared model 337. The conductivity measurements were measured in DMSO solutions (0.001 M) using Digisun Electronic Digital conductivity meter of model: DI-909 having a dip-type cell calibrated with KCl solution. Electronic spectra of metal complexes in DMSO were recorded on Schimadzu UV-VIS 1601 spectrophotometer. TGA of complexes were carried on Mettler Toledo Star system in the temperature range of 0–1000 °C. Melting points of the ligands and decomposition temperature of complexes were determined on Polmon instrument (model No. MP-96). Magnetic susceptibilities of the complexes were determined on Gouy balance model 7550 using $Hg[Co(NCS)_4]$ as standard. The diamagnetic corrections of the complexes were computed using Pascal's constants. The percentage composition of C, H, N for the complexes and necessary ligands was determined by using microanalytical techniques on Perkin-Elmer 240C (USA) elemental analyzer. The percent compositions of metal ions in solid metal complexes were determined by EDTA titration procedure [13].

2.7. Potentiometric measurements

The potentiometric measurements were carried out using a digital Digisun Electronic model DI-707 pH meter equipped with a combined glass and calomel electrode. The system was calibrated to read the hydrogen ion concentration by titration of HCl solution at 30 ± 1 °C and 0.1 M KNO_3 ionic strength and KOH solution according to Gran's method. The solutions were titrated in the 2.0–11.0 pH range for the ligands and the complexes. There was no precipitation within the pH range at which the titrations performed. The metal ion and ligand ratio was maintained at 1:5, respectively. The pK_a values of Schiff bases and stability constants of their binary complexes were determined by Irwing–Rossotti pH metric technique using computer program. The $\bar{n}A$, $\bar{n}$ and PL values were calculated by using standard equation [14].

3. Results and discussion

On the basis of elemental analysis, the complexes were assigned to possess the composition shown in Table 1. The molar conductance measurements of the complexes in DMSO correspond to non-electrolytes. Thus, the complexes may be formulated as $[M(L)_2(H_2O)_2]$. Where M = Cu(II), Co(II), Ni(II).

3.1. Spectral analysis

3.1.1. Mass spectrum of HEBMI (L_1)

The mass spectrum of isoxazole 3-ethoxy salicylaldehyde (Fig. 1) Schiff base showed molecular ion (M+) peak at *m/z*

Table 1
Analytical and physical properties

Complex	Emperical formula	Molecular weight	Melting point (°C)	C	H	N
HEBMI	$C_{13}H_{14}N_2O_2$	246	147	63.41	5.69	11.38
$[Cu(HEBMI)_2(H_2O)_2]$	$[CuC_{26}H_{30}N_4O_6]$	589.5	190	52.92	5.08	9.49
$[Ni(HEBMI)_2(H_2O)_2]$	$[NiC_{26}H_{30}N_4O_6]$	584.7	250	53.36	5.13	9.57
$[Co(HEBMI)_2(H_2O)_2]$	$[CoC_{26}H_{30}N_4O_6]$	584.9	210	53.34	5.12	9.57
HNBMI	$C_{11}H_9N_3O_4$	247	245	53.44	3.64	17.00
$[Cu(HNBMI)_2(H_2O)_2$	$[CuC_{22}H_{20}N_6O_{10}]$	591.5	210	44.63	3.38	14.20
$[Ni(HNBMI)_2(H_2O)_2]$	$[NiC_{22}H_{20}N_6O_{10}]$	586.7	250	44.99	3.40	14.31
$[Co(HNBMI)_2(H_2O)_2)$	$[CoC_{22}H_{20}N_6O_{10}]$	586.9	250	44.98	3.40	14.31

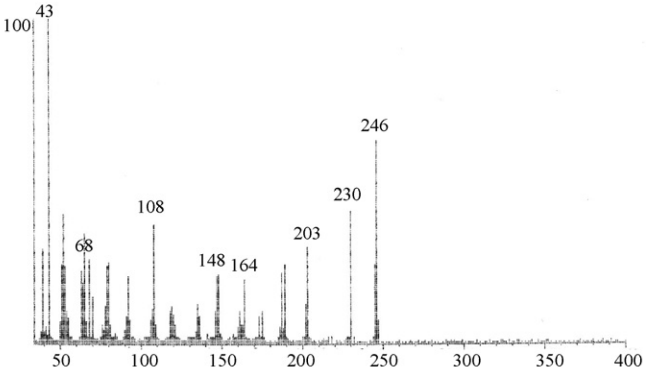


Fig. 1. Mass spectra of L_1.

246. The other fragments were observed at *m/z* 230, 203, 164, 148, 108 and 68.

3.1.2. Mass spectrum of HNBMI (L_2)

The mass spectrum of isoxazole 5-nitro salicylaldehyde Schiff base also exhibits a stable molecular ion (M+) peak at *m/z* 247. Other fragments were observed at *m/z* 230, 202, 156, 141, 119, 68 and 43.

3.1.3. ^{1}H NMR of HEBMI (L_1)

In the ^{1}H NMR ($CDCl_3$) Fig. 2, the imine proton appeared as a singlet at δ 8.93. The isoxazole H-4 appeared at δ 6.07 as a singlet and 5-CH_3 appeared at δ 2.48 as a singlet. Phenyl protons H-4′, 5′, 6′ appeared as a multiplet at δ 6.81–7.07. 2′-OH appeared at δ 12.58, OCH_2 of 3′-OEt appeared at δ 4.15 as quartet ($J = 6.7$ Hz) and CH_3 of 3′-OEt appeared as triplet at δ 1.51 ($J = 6.7$ Hz) base.

3.1.4. ^{1}H NMR of HNBMI (L_2)

The ^{1}H NMR, the imine proton appeared as a singlet at δ 9.10. Isoxazole H-4 appeared at δ 6.12 as a singlet and 5-CH_3 appeared at δ 2.51 as a singlet. Phenyl protons H-3′, 4′, 6′ appeared as multiple δ 7.10–7.19 and 2′-OH appeared as a singlet at δ 13.20.

3.1.5. ^{13}C spectrum of HEBMI (L_1)

^{13}C spectrum of HEBMI (Fig. 3) has167.5 (CH=N), 171.1 (C-3), 96.8 (C-4), 167.1 (C-5), 12.6 (C-5-CH_3), 118.5 (C-1′), 118.5 (C-2′), 147.6 (C-3′), 124.5 (C-4′), 117.5 (C-5′), 118.8 (C-6′), 64.7 (–OCH_2CH_3), 14.7 (–OCH_2CH_3).

3.1.6. ^{13}C spectrum of HNBMI (L_2)

^{13}C spectrum of HNBMI has 165.5 (CH=N), 159.8 (C-3), 94.6 (C-4), 167.3 (C-5), 12.0 (C-5-CH_3), 119.6 (C-1′), 167.8 (C-2′), 117.8 (C-3′), 128.4 (C-4′), 141.0 (C-5′), 126.5 (C-6′).

3.1.7. IR data

In order to study the binding mode of the Schiff base to the metal in complexes, the IR spectrum of the free ligand was compared with the spectra of the complexes. The IR spectra

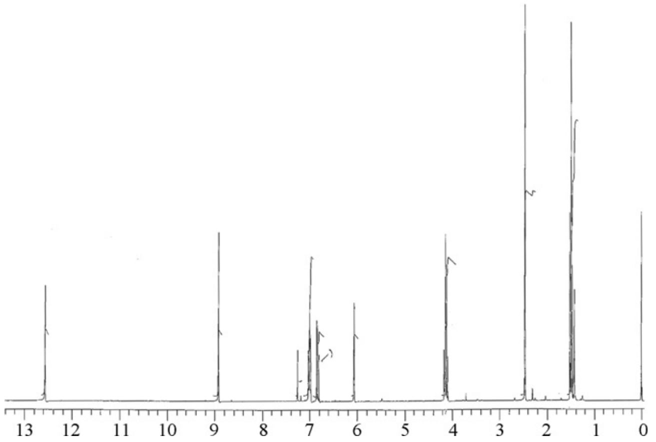


Fig. 2. ^{1}H NMR of L_1.

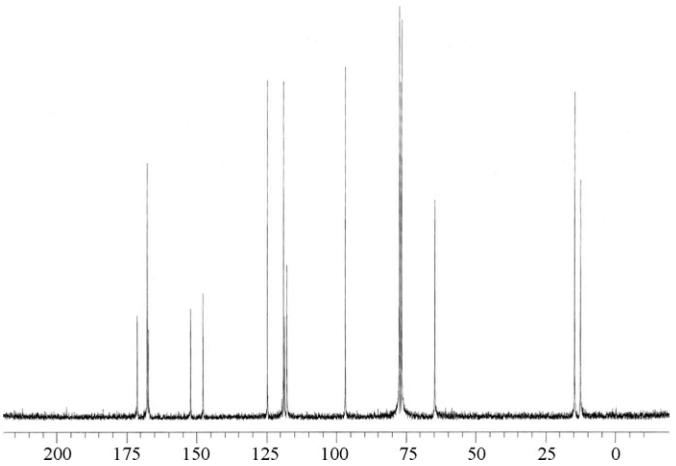


Fig. 3. ^{13}C spectrum of L_1.

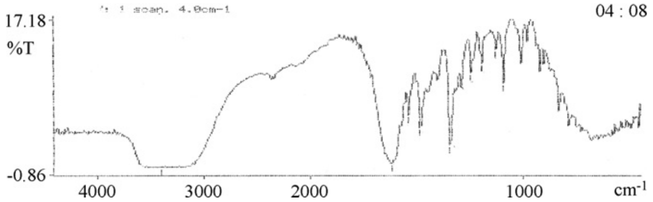


Fig. 4. IR spectra of Ni(II) complex of HEBMI.

of the ligands show a strong band in the 3200–3400 regions assigned to the OH group. The disappearance of this band in the spectra of the complexes [15] indicates the deprotonation of the hydroxyl group and co-ordination through oxygen. The band observed at 1636–1620 cm^{-1} in the ligand is assigned to azomethine group. The shift of this band in the complexes towards lower region to the extent of 10–20 cm^{-1}, indicates co-ordination through the azomethine nitrogen [16,17]. In the free ligands, bands at 1249 cm^{-1} due to C–O (phenolic) shift to higher frequency by 30–50 cm^{-1} in the complexes, indicating co-ordination of the phenolic oxygen atom to the metal ion [18]. These facts suggest that the shifts are due to co-ordination of ligand to the metal atom by the azomethine nitrogen and phenolic oxygen [19]. All the complexes of HEBMI and HNBMI show a broad diffuse band at 3200–3400 cm^{-1}, and appearance of a band at 795–825 cm^{-1} at lower frequency region indicates the presence of water molecules in the co-ordination sphere. This fact is also supported by the results of elemental analyses, and TGA of complexes. Two new bands appearing in the low frequency ranges 515–581 cm^{-1} and 420–481 cm^{-1} are assigned to (M–O) and (M–N), respectively [20] (Fig. 4) (Table 2).

3.1.8. *Mass spectrum of [Ni(HEBMI)$_2$(H$_2$O)$_2$]*

The fast atom bombardment (FAB) spectrum exhibits molecular ion peak (M + 1) at *m*/*z* 585.7, which corresponds to mass of [Ni(HEBMI)$_2$(H$_2$O)$_2$] complex. Wherein, the metal to ligand ratio is 1:2 with two water molecules. Thermal study of the complex supported the presence of co-ordinated water molecules (Fig. 5).

Table 2
IR data of complexes

Compound	(OH)	C=N	C–O	Coordinated water	M–N	M–O
HEBMI	3376	1620	1249	–	–	–
[Cu(HEBMI)$_2$(H$_2$O)$_2$]	–	1613	1295	758	458	551
[Ni(HEBMI)$_2$(H$_2$O)$_2$]	3371	1599	1292	794	–	552.7
[Co(HEBMI)$_2$(H$_2$O)$_2$]	–	1605	1297	766	456	544
HNBMI	3440	1636	1247	–	–	–
[Cu(HNBMI)$_2$(H$_2$O)$_2$]	3429	1613	1290	790	594	440
[Ni(HNBMI)$_2$(H$_2$O)$_2$]	3394	1624	1290	787	–	462
[Co(HNBMI)$_2$(H$_2$O)$_2$]	3394	1624	1290	830	497	–

From this observation, it may be concluded that Schiff bases act as mono negative, bidentate co-ordinating through oxygen of phenolic C–O group and nitrogen of C=N group.

3.1.9. *Mass spectrum of [Ni(HNBMI)$_2$(H$_2$O)$_2$]*

The fast atom bombardment (FAB) spectrum exhibits molecular ion peak (M + Na) at *m*/*z* 609.7, which corresponds to mass of [Ni(HNBMI)$_2$(H$_2$O)$_2$] complex. Wherein, the metal to ligand ratio is 1:2 with two water molecules. Thermal study of the complex supported the presence of co-ordinated water molecules.

4. Magnetic moment and electronic spectral data of the ligands and the complexes

4.1. *Magnetic measurements*

The magnetic moments of the complexes are given in (Table 3). The magnetic moments of the copper(II) complexes

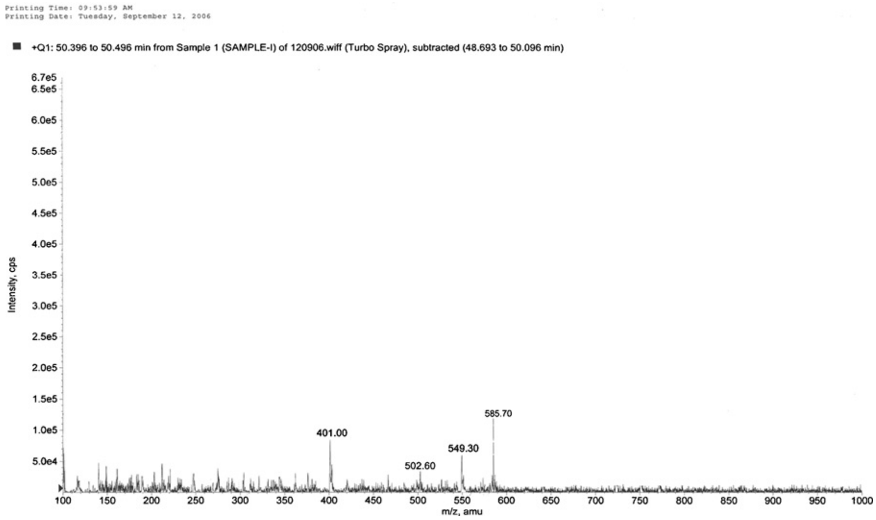
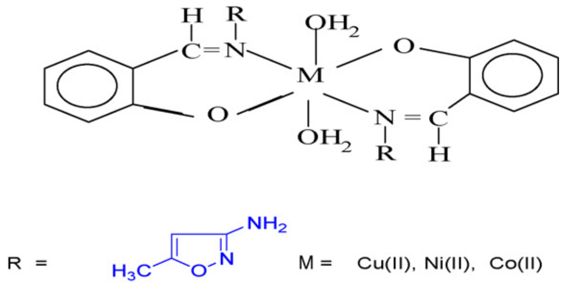


Fig. 5. Mass spectrum of [Ni(HEBMI)$_2$(H$_2$O)$_2$].

Table 3
Magnetic moments and electronic spectrum data of the ligands and complexes

Ligand	ν (cm^{-1})	υ_2/υ_1	10 DQ	B	β	B.M.
HEBMI	34,482; 44,247	–	–	–	–	–
Cu(II)	11,483					1.87
Co(II)	12,135; 21,739; 25,641	1.79	9,604	731	0.75	4.98
Ni(II)	9,987; 16,534; 24,096	1.65	9,987	711	0.69	3.21
HNBMI	31,847; 38,775	–	–	–	–	–
Cu(II)	13,280; 29,850					1.96
Co(II)	14,692; 26,041; 29,411	1.77	11,349	758	0.78	5.01
Ni(II)	9,363; 16,309; 26,315	1.74	9,363	969	0.94	3.05

are 1.87 and 1.96 B.M., consistent with distorted octahedral geometry [21]. The magnetic moments of the cobalt(II) complexes are 4.98 and 5.01 B.M., which suggest an octahedral geometry [22]. And magnetic moments of nickel(II) complexes are 3.05 and 3.21 B.M., indicating that these complexes are octahedral [23].



4.2. Electronic spectral data

The electronic spectra of the metal complexes were recorded in DMSO in the range of 200–1100 nm. The electronic spectra of Cu(II) complexes exhibit single broad band at 11,483 and 13,280 cm^{-1} which may be assigned to the transition $^2E_g \rightarrow {}^2T_{2g}$ (D) in distorted octahedral geometry [24]. The cobalt(II) complexes exhibit three bands at 12,135–14,6925; 21,739–26,041; 25,641–29411 cm^{-1} which may be assigned to the transitions $^4T_{1g}$ (F) → $^4T_{2g}$ (F) (υ_1); $^4T_{1g}$ (F) → $^4A_{2g}$ (F) (υ_2); and $^4T_{1g}$(F) → $^4T_{1g}$(P) (υ_3), expected for an octahedral structure [25]. The electronic spectra of Ni(II) complexes exhibit three bands at 9369–10,000; 16,300–17,000; 24,096–26,400 cm^{-1}, which may be due to the transitions $^3A_{2g}$(F) → $^3T_{2g}$(F) (υ_1); $^3A_{2g}$(F) → $^3T_{1g}$(F) (υ_2) and $^3A_{2g}$(F) → $^3T_{1g}$(P) (υ_3), respectively, which suggests an octahedral geometry [26] (Fig. 6).

The values of the ligand field splitting energy (Dq), Racah inter-electronic repulsion parameter (B), nephelauxetic ratio (β) and ratio υ_2/υ_1 for the cobalt(II) and nickel(II) are presented in Table 3. The assignment of an octahedral geometry to the complexes is further supported by their υ_2/υ_1, which lies in the range 1.65–1.79.

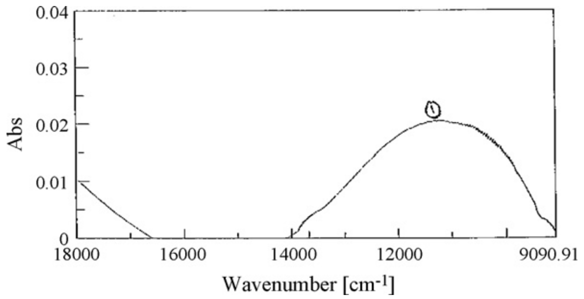


Fig. 6. VISIBLE spectra of Cu(II) of HEBMI.

4.3. Thermal analysis

The TGA curves show that the initial mass loss occurring within 136–150 °C range is interpreted as loss of moisture and hydrated water molecules during the chelate drying process, and the second weight loss within 150–280 °C range is due to coordinated water molecules.

4.4. Potentiometric studies

The dissociation constants of HBBMI, HCBMI and stability constants of their Co(II), Ni(II) and Cu(II) have been reported earlier. It is found that the order of stability constants was in accordance with basicity order of ligands [27]. In the present investigation HEBMI is greater than HNBMI. This is attributed to more basic nature of HEBMI compound. The stability constants of binary complexes of HEBMI and HNBMI with bivalent Co(II), Ni(II) and Cu(II). Follow the order w.r.t. ligands M(II) HEBMI > M(II) HNBMI. This order is in accordance with the basicity order of ligands. Order of stability with respect to metal ions is Cu(II) > Ni(II) > Co(II). This is in accordance with the Irwing–Williams natural order.

4.5. Biological activity

The ligands presented here and their transition metal complexes gave better results against the growth of bacteria and fungi. It is found that the activity increases upon co-ordination. The increased activity of the metal chelates can be explained on the basis of chelation theory [28]. The orbital of each metal

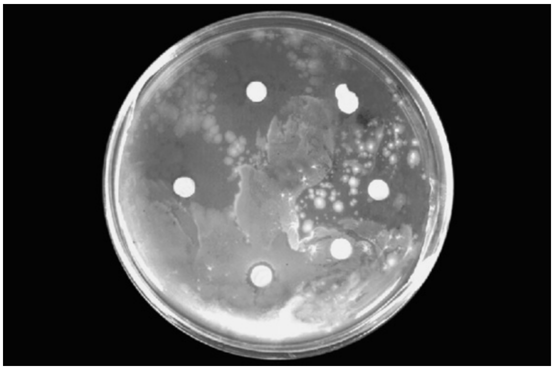


Fig. 7. *E. coli* action on Cu(II) of HEBMI.

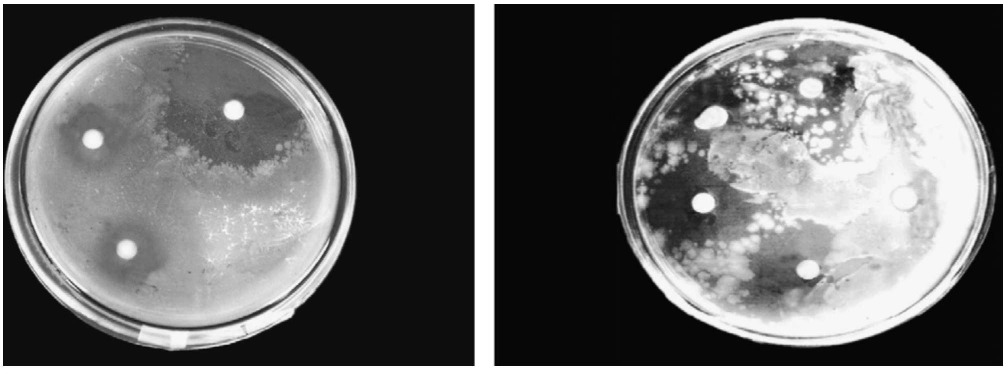


Fig. 8. *R. oryzae* action on Cu(II) of HEBMI and HNBMI.

Table 4
Stability constants and Biological activity of ligands and complexes

Complex	pK_a	$\log k_1$	$\log k_2$	*E. coli*	*P. aeurogenosa*	*R. oryzae*	*A. niger*
HEBMI	8.58	–	–	+	+	+	+
Cu(II)	–	6.45	4.78	+++	+++	++	–
Ni(II)	–	4.75	3.48	++	++	++	++
Co(II)	–	4.27	3.09	++	+	++	++
HNBMI	6.05	–	–	+	+	–	+
Cu(II)	–	6.31	4.75	+++	++	+++	+
Ni(II)	–	5.20	4.50	++	++	++	++
Co(II)	–	4.70	4.23	++	+++	++	+

Note: Maximum zone of inhibition was represented as +++ (20–35 mm). Medium zone of inhibition as ++ (10–20 mm). Minimum zone of inhibition as + (5–10 mm).

ion is made so as to overlap with the ligand orbital. Increased activity enhances the lipophilicity of complexes due to delocalisation of pi-electrons in the chelate ring [29]. In some cases increased lipophilicity leads to breakdown of the permeability barrier of the cell [30,31]. The results of anti-fungal and antibacterial screening, indicate that Cu(II) complexes show more activity than the other complexes. These results may be due to higher stability constant of the Cu(II) complexes than the other complexes (Figs. 7 and 8) (Table 4).

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