Synthesis, Spectral Characterization and Antimicrobial Studies of Transition Metal Complexes of Benzothiazole Based Schiff Bases

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A series of transition metal complexes of the type $[ML_2] \cdot nH_2O$, where L = 2-(benzothiazolyl-2'-amino)iminoethanone (HBAE), 2-(benzothiazolyl-2'-amino)imino-1,2-dimethylethanone (HBME), 2-(benzothiazolyl-2'-amino)imino-1,2-diphenylethanone (HBPE), M = Cu(II), Co(II), Ni(II) and Zn(II), have been synthesized and characterized on the basis of spectral studies and thermal analyses. The spectroscopic data confirmed octahedral geometrical structures for all the complexes. All these Schiff bases and their metal complexes have been screened for their antibacterial activity against some pathogenic bacteria species (*Bacillus subtilis*, *Bacillus stearothermophilus*, *Escherichia coli* and *Salmonella typhi*) and antifungal activity against some pathogenic fungi strains (*Aspergillus niger* and *Aspergillus flavus*).

Keywords: 2-Hydrazinobenzothiazole, Glyoxal, Diacetyl, Benzil and Transition metal complexes.

INTRODUCTION

Recent years have witnessed a surge in the research interest in the synthesis and characterization of transition metal complexes having metal atoms coordinated to sulphur in the ligand framework. The heavier donor atoms including sulphur [1], due to their availability of vacant 'd' orbitals, act as potent 'd' electron acceptors from the metal ions through d π -d π bond formation. In view of their immense importance in biological systems, they are used as synthetic models for many metallo enzyme reactions [2]. During past several years, the mixed ligand complexes with sulphur donor atoms have drawn considerable interest for synthetic chemists owing to their novel structural features and unusual magnetic properties [3,4]. The role of coordination compounds containing 'NOS' donors as potential drugs, fungicidal and antibacterial [5] agents, cannot be overemphasized. Mixed-ligand complexes of transition metals containing ligands with 'N, S' and 'N, O, S' donors are also known to exhibit interesting antimicrobial [6], anticancer [7], stereochemical, electrochemical and electronic properties [8,9].

Benzothiazole is a bicyclic ring system with multiple applications. During recent years much attention has been devoted to the synthesis of new benzothiazole derivatives due to their diverse chemical reactivity and broad spectrum of biological activity such as antitumor agents [10], antimicrobial [11], analgesics [12], anthelmintic [13], anticancer [14,15], antibacterial [16-18], antifungal [19] and anti HIV [20] activity. The derivatives of 2-aminobenzothiazole have been used for the treatment of diabetes, viral infections and as central muscle relaxants [21]. The activity of some drugs is enhanced when administered as metal complexes than the free ligands. It was reported that several benzothiazole derivatives and their metal complexes showed antifungal and antibacterial activity.

Following all these observations and as a continuation of our research on the coordination chemistry of multidentate ligands [22-27], we report here the synthesis and structural studies on the complexes of Cu(II), Co(II), Ni(II) and Zn(II) with some hydrazone derivatives containing benzothiazole moiety such as 2-(benzothiazolyl-2'-amino)imino ethanone (HBAE), 2-(benzothiazolyl-2'-amino)imino-1,2-dimethylethanone (HBME) and 2-(benzothiazolyl-2'-amino)imino-1,2-diphenyl ethanone (HBPE).

EXPERIMENTAL

All the chemicals used are of AR grade. The solvents were purified before use by standard procedures.

Synthesis of 2-hydrazinobenzothiazole: To a warm solution of 2-mercapto benzothiazole (1.67 g, 0.01 mol) in absolute alcohol (10 mL), hydrazine hydrate (2 mL) was added and the mixture was refluxed on a water bath for 4 h or until H_2S gas ceased to evolve. Then it was concentrated and cooled, during which white needle like crystals separated out (**Scheme-I**). It was filtered and recrystallized from ethanol.

Synthesis of ligands: The ligands used in the present investigation are benzothiazolyl-2-hydrazones of aldehydes and ketones such as glyoxal, diacetyl and benzil which have been synthesized by condensing 2-hydrazinobenzothiazole with respective aldehydes and ketones in the following manner. Ethanolic solution of 2-hydrazinobenzothiazole (0.01 mol in 20 mL) was added to ethanolic solution of glyoxal/diacetyl/benzil (0.01 mol in 20 mL) and the resulting solution was refluxed on a water bath for 6 to 8 h. It was concentrated and allowed to stand overnight when coloured precipitate was separated out. It was filtered, washed and recrystallized from ethanol (**Scheme-II**). The sample was dried *in vacuo* over fused calcium chloride and then analyzed.

Synthesis of metal complexes: The complexes were synthesized by refluxing ethanolic solution of the ligands HBAE/HBME/HBPE (0.02 mol in 20 mL) with a hot ethanolic solution of corresponding hydrated metal(II) chloride (0.01 mol in 20 mL) for about 4 h when coloured complexes precipitated out in each case. The complexes were filtered, washed with ethanol, then by ether and finally dried *in vacuo* over fused CaCl_2 .

Analysis and physical measurements: The metal contents in the complexes were determined gravimetrically following standard procedure [28]. Sulphur was estimated as BaSO_4 . The molar conductance measurements were carried out at room temperature with a Toshniwal Conductivity Bridge (model CL-01-06, cell constant 0.5 cm^{-1}) using $1 \times 10^{-3} \text{ M}$ solution of the complexes in DMSO. Carbon, hydrogen and nitrogen contents of the complexes were determined using a MLW-CHN micro analyzer. The room temperature magnetic moment values of the compounds have been determined by Gouy method with $\text{Hg}[\text{Co}(\text{SCN})_4]$ as calibrant. The FTIR spectra in KBr pellets

were recorded on a Varian FTIR Spectrophotometer, Australia in the range $4000\text{--}400 \text{ cm}^{-1}$. The electronic spectra of the complexes in DMSO were recorded on a Perkin-Elmer Spectrophotometer. The thermo gravimetric analysis was carried out using Netzch-429 thermo analyzer. The $^1\text{H-NMR}$ spectra of the complexes were recorded in $\text{DMSO-}d_6$ medium on JEOL, GSX-400 model equipment using TMS as reference. The electronic spin resonance spectra were recorded as polycrystalline sample on an E-112 EPR Spectrophotometer with field set at 3200G, scan range $2.0 \times 1 \text{ Kg}$, modulation frequency 100 KHz, microwave frequency 9.4 GHz, receiver gain 10×10^2 and modulation amplitude $0.63 \times 10 \text{ G}$.

Microbicides studies: The antimicrobial activities of the synthesized compounds were evaluated at $100 \mu\text{g mL}^{-1}$ concentrations by agar well diffusion assay technique against two Gram-positive bacteria, *i.e.*, *Bacillus subtilis* and *Bacillus stearothermophilus* and two Gram-negative bacteria, *i.e.*, *Escherichia coli* and *Salmonella typhi*. Solutions of the ligands and its metal complexes in DMSO were plated onto the cultured agar medium and incubated for a period of 24 h at 37°C . After the incubation period, the plates were observed for zones of inhibition (cm). The standard drugs ciprofloxacin and gentamycin are also screened under identical conditions. The antifungal activities of the same were determined against two fungal strains, *i.e.*, *Aspergillus niger* and *Aspergillus flavus*. The petri dishes were incubated for 48 h at 28°C . All the determinations were made three times and the average was recorded.

RESULTS AND DISCUSSION

All the hydrazone ligands and their metal complexes are insoluble in water and common organic solvents but moderately soluble in ethanol and readily in dioxane, DMF and DMSO. The complexes formulated from the analytical data and molar conductance data (Table-1) support the suggested formulae. They are highly coloured, non hygroscopic, highly stable under normal conditions and all of them decompose above 250°C . The molar conductance of the synthesized metal complexes in DMSO is in the 7.5 to $13.7 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ range indicating them to be non-electrolyte in nature with no anions outside the coordination sphere. Water molecules present in the metal complexes as lattice water. This view is confirmed by TGA studies.

Scheme-I

R = H (Compd. 1), CH_3 (Compd. 2), C_6H_5 (Compd. 3)

Scheme-II: Synthetic route of the ligands

TABLE-1
 ANALYTICAL AND PHYSICAL DATA OF THE COMPOUNDS

Compounds	Yield (%)	Λ_m (Ohm ⁻¹ cm ² mol ⁻¹)	Elemental analysis (%): Found (calcd.)				
			C	H	N	S	M
HBAE	80	—	52.64 (52.68)	3.38 (3.41)	20.43 (20.48)	15.58 (15.61)	—
HBME	72	—	56.60 (56.65)	4.68 (4.72)	17.96 (18.02)	13.70 (13.73)	—
HBPE	75	—	70.53 (70.58)	4.17 (4.20)	11.73 (11.76)	8.92 (8.96)	—
[Co(BAE) ₂].H ₂ O	65	8.2	44.49 (44.53)	2.44 (2.47)	17.30 (17.32)	13.15 (13.19)	12.13 (12.16)
[Ni(BAE) ₂].H ₂ O	62	12.3	44.55 (44.58)	2.44 (2.48)	17.29 (17.34)	13.18 (13.21)	12.02 (12.07)
[Cu(BAE) ₂].2H ₂ O	63	11.5	42.52 (42.56)	3.11 (3.15)	16.52 (16.55)	12.58 (12.61)	12.48 (12.51)
[Zn(BAE) ₂].H ₂ O	67	9.6	43.94 (43.99)	2.40 (2.44)	17.07 (17.10)	13.01 (13.03)	13.20 (13.24)
[Co(BME) ₂].H ₂ O	62	7.5	48.75 (48.79)	3.66 (3.69)	15.48 (15.52)	11.79 (11.82)	10.85 (10.90)
[Ni(BME) ₂].H ₂ O	65	7.8	48.80 (48.84)	3.68 (3.70)	15.50 (15.54)	11.81 (11.84)	10.78 (10.82)
[Cu(BME) ₂].2H ₂ O	59	13.7	46.80 (46.85)	4.22 (4.25)	14.87 (14.90)	11.31 (11.35)	11.23 (11.27)
[Zn(BME) ₂].H ₂ O	62	11.5	48.23 (48.26)	3.61 (3.65)	15.32 (15.35)	11.65 (11.70)	11.85 (11.88)
[Co(BPE) ₂].H ₂ O	63	11.8	63.84 (63.87)	3.49 (3.54)	10.60 (10.64)	8.09 (8.11)	7.43 (7.47)
[Ni(BPE) ₂].H ₂ O	60	7.6	63.87 (63.91)	3.53 (3.55)	10.61 (10.65)	8.08 (8.11)	7.38 (7.42)
[Cu(BPE) ₂].2H ₂ O	61	10.3	62.11 (62.14)	3.90 (3.94)	10.31 (10.35)	7.84 (7.89)	7.80 (7.83)
[Zn(BPE) ₂].H ₂ O	64	12.2	63.35 (63.39)	3.48 (3.52)	10.53 (10.56)	8.03 (8.05)	8.14 (8.17)

IR spectra: In the high frequency region, 2-hydrazino-benzothiazole exhibits a strong band located at about 3230 cm⁻¹ which may be due to symmetric and asymmetric stretching mode of vibration of -NH₂ group [29], being overlapped with ν (N-H) of secondary amino group. A multiple band system of medium intensity is observed at about 1616 ν (C=C), 1506 ν (C=N) cyclic and 1278 ν (C-N) cm⁻¹ which may be due to benzothiazole moiety. The band observed at about 1610 cm⁻¹ may be assigned to N-H bending vibration mode of 1° amino group. The bands occurring at about 1250 and 1030 cm⁻¹ may be due to C-N exo-cyclic stretching and N-N stretching vibrations, respectively. The intense absorption bands around 950-650 cm⁻¹ are due to C-H out of plane deformation vibration [29], characteristics of benzothiazole derivatives. Besides the above bands, a broad band of medium intensity appears at ~ 870 cm⁻¹ in the IR spectra of 2-hydrazino-benzothiazole which is assignable to ν (C-S-C) mode of vibration of thiazole moiety.

Reaction of 2-hydrazinobenzothiazole with glyoxal, diacetyl and benzil brings about significant changes in the IR spectra of the products, which are used as ligands. The most notable features of the spectra are the disappearance of the -NH₂ stretching vibration at about 3230 cm⁻¹ and appearance of two new bands at about 1677 and 1551 cm⁻¹, respectively due to ν (C=O) (carbonyl) and ν (C=N) (azomethine). Appearance of ν (C=O) and ν (C=N) bands confirms the condensation of 2-hydrazinobenzothiazole with glyoxal/diacetyl/benzil in 1:1 proportion with retention of one unreacted carbonyl function of the parent dialdehyde/diketones. The spectra of the ligands as well as their metal complexes are very complex with a profusion of bands in the finger print region. However, there are several characteristics bands, which can be identified and used to explain the structure of the ligands and their complexes.

The position of bands due to ν (C=N) (cyclic), ν (C=C) of the benzothiazole moiety remain practically unchanged in the present complexes indicating non-participation of ring nitrogen atom in coordination. However, the red shift in the position of ν (C-S-C) band by 10-20 cm⁻¹ in all the complexes is indicative of the participation of ring sulphur atom in coordination to the metal ions [23] and results due to the electron drainage from the thiazole moiety to the metal center *via* resonance. In

the spectra of the complexes the band due to ν (C=O) was found to be absent and two new bands of medium intensities are observed at about 1460 and 1300 cm⁻¹ assigned to ν (C=C) and ν (C-O), respectively, suggesting coordination through enolized 'O' after deprotonation of enolic -OH group. The bands observed due to ν (C=N) and ν (N-N) in the ligand are found to be absent and a new band due to ν (N=N) (azo group) appears at ~ 1585 cm⁻¹ showing there by coordination of one of the nitrogen atoms of the azo group with the metal ion. This fact is further supported by the disappearance of band at about 3230 cm⁻¹ due to ν (N-H) (secondary) vibration. Thus IR spectral investigation provides evidence of coordination of ligand to the metal center through conversion of keto form to enol form.

A pair of sharp bands of moderate intensities are observed in the IR spectra of all the metal complexes, the first band appearing at about 520 cm⁻¹ and the second one at 450 cm⁻¹. These bands are distinctly absent in the spectra of ligands. Considering the sharpness and intensity, higher band is attributed to ν (M-N) and lower band to ν (M-O) vibrations. However, the ν (M-S) band could not be studied due to instrumental limitation, as it occurs in far IR region. The above observations lead us to believe that the enolized oxygen, nitrogen of the azo group and the ring sulphur atom, all three, of the ligand moiety are involved in coordination to the metal ions. The band observed at 3500 cm⁻¹ may be assigned to ν (O-H) of lattice water [30]. The important IR bands of the ligands as well as their metal complexes are recorded in Table-2.

Thermal analysis: Thermal characteristics of the metal complexes obtained from the ligands HBAE, HBME and HBPE are recorded in Table-3. All the complexes follow similar thermal decomposition pattern. The complexes remain unaffected up to 40 °C, after which the depression of thermogram starts and continues up to 120 °C. The loss of weight in this temperature range corresponds to loss of lattice water, for coordinated water molecules require relatively higher temperatures to be removed. This is in conformity with our IR spectra and analytical investigations. In case of Cu(II) complexes the loss in weight corresponds to weight of two water molecules [31], while for other complexes it is due to one water molecule. The anhydrous complexes remain stable up to 300 °C which

TABLE-2
 INFRARED SPECTRAL DATA OF COMPLEXES (cm⁻¹)

HBAE	[Cu(BAE) ₂].2H ₂ O	HBME	[Co(BME) ₂].H ₂ O	HBPE	[Ni(BPE) ₂].H ₂ O	Assignments
–	3500	–	3475	–	3505	v(O-H) (lattice water)
–	–	2880	2875	–	–	v(C-H) (-CH ₃)
1677	–	1667	–	1660	–	v(C=O)
1616	1615	1620	1620	1610,1590	1605	v(C=C) (cyclic)
1600	–	1605	–	1600	–	δ(N-H)
–	1585	–	1580	–	1575	v(N=N)
1551	–	1555	–	1550	–	v(C=N) (azomethine)
1506	1510	1505	1505	1510	1512	v(C=N) (cyclic)
–	1460	–	1460	–	1465	v(C=C)
–	1300	–	1305	–	1300	v(C-O)
1278	1265	1275	1270	1278	1275	v(C-N) (exocyclic)
1030	–	1040	–	1035	–	v(N-N) (exocyclic)
950-650	930-675	955-660	950-655	960-670	955-675	δ(C-H) (out of plane)
870	855	875	860	870	860	v(C-S-C)

 TABLE-3
 IMPORTANT FEATURES OF THERMO GRAVIMETRIC ANALYSIS (TGA)

Compounds	Temp. range of water loss (°C)	Water loss (%)		Decomposition temperature (°C)	Residue (%)		Composition of the residue
		Found	Calcd.		Found	Calcd.	
[Co(BAE) ₂].H ₂ O	40-100	3.68	3.71	255	15.41	15.46	CoO
[Ni(BAE) ₂].H ₂ O	50-105	3.66	3.71	290	15.34	15.37	NiO
[Cu(BAE) ₂].2H ₂ O	50-119	7.06	7.09	285	15.62	15.66	CuO
[Zn(BAE) ₂].H ₂ O	45-110	3.62	3.66	275	16.43	16.49	ZnO
[Co(BME) ₂].H ₂ O	45-100	3.31	3.33	275	13.83	13.86	CoO
[Ni(BME) ₂].H ₂ O	50-110	3.29	3.33	272	13.74	13.78	NiO
[Cu(BME) ₂].2H ₂ O	55-120	6.34	6.38	295	14.08	14.11	CuO
[Zn(BME) ₂].H ₂ O	50-105	3.26	3.29	310	14.75	14.80	ZnO
[Co(BPE) ₂].H ₂ O	45-110	2.24	2.28	282	9.46	9.50	CoO
[Ni(BPE) ₂].H ₂ O	50-112	2.25	2.28	265	9.42	9.45	NiO
[Cu(BPE) ₂].2H ₂ O	50-115	4.39	4.44	280	9.74	9.80	CuO
[Zn(BPE) ₂].H ₂ O	40-105	2.23	2.26	300	10.15	10.19	ZnO

is indicated by a plateau in the thermogram, following which further weight loss occurs till around 600 °C due to decomposition of organic constituents of the complexes ultimately leading to the formation of their corresponding oxides. The decomposition temperature varies from one complex to other. Thermal stability of these complexes is in the order:

HBAE complexes: Co(II) < Zn(II) < Cu(II) < Ni(II)

HBME complexes: Ni(II) < Co(II) < Cu(II) < Zn(II)

HBPE complexes: Ni(II) < Cu(II) < Co(II) < Zn(II)

Electronic spectra and magnetic moments: In the present ligands, bands due to benzothiazolyl ring, azomethine group, carbonyl group and phenyl group are expected to occur. However, the spectra of the above ligands exhibit two strong bands in the region ~ 210-230 nm and ~ 300-375 nm assignable to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions, respectively indicating extensive conjugation.

The electronic spectral data and μ_{eff} of Co(II) complexes with ligands HBAE, HBME and HBPE are recorded. The magnetic moment values for these complexes at room temperature lie in the range 4.7–4.8 B.M., which are higher than the spin only values calculated for three unpaired electrons in high spin configuration ($t_{2g}^5 e_g^2$). This may be attributed to large orbital contribution, which is reinforced by spin orbit coupling [32]. The possibility of formation of low spin octahedral complexes

having ground state configuration $t_{2g}^6 e_g^1$ with one unpaired electron is ruled out on the basis of the magnetic moment values. Further this would envisage a strong Jahn Teller distortion from regular O_h geometry [33] which is contradicted by our spectral investigation. The electronic spectra of these complexes in DMSO exhibit a band system at around ~ 9,000 cm⁻¹ (1100 nm) and ~ 20,500 cm⁻¹ (488 nm) corresponding to ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ (ν_1) transition and ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ (ν_3) transition, respectively under octahedral symmetry. The ${}^4T_{1g} \rightarrow {}^4A_{2g}$ (ν_2) transition being formally a two electron transition involves high energy and hence remains unobserved.

The magnetic moment (μ_{eff}) values of Ni(II) complexes with the above ligands are in fair agreement with six coordinated octahedral Ni(II) species. The electronic spectra of these complexes in DMSO are found to possess three well resolved bands observed at around ~ 9,800 cm⁻¹ (1020 nm), ~ 16,400 cm⁻¹ (609 nm) and ~ 25,800 cm⁻¹ (387 nm) assignable to ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ (ν_1), ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ (ν_2) and ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ (ν_3) transitions, respectively under octahedral field [33,34].

The electronic spectral data and room temperature μ_{eff} values of Cu(II) complexes with ligands HBAE, HBME and HBPE are reported. The μ_{eff} value of these complexes lie in the range 1.75-1.83 B.M. which is well within the range expected for distorted octahedral Cu(II) species. The electronic spectra of all these complexes show two main bands at ~ 14,600 cm⁻¹

(684 nm) (ν_2) and $\sim 16,340\text{ cm}^{-1}$ (611 nm) (ν_3) assignable, respectively to ${}^2B_{1g} \rightarrow {}^2B_{2g}$ and ${}^2B_{1g} \rightarrow {}^2E_g$ transitions under D_{4h} symmetry. In this the band due to ${}^2B_{1g} \rightarrow {}^2A_{1g}$ (ν_1) is not observed most probably due to superimposition by ν_2 band owing to its broadness. In this case tetrahedral or pseudo-tetrahedral symmetry is ruled out, as no band is observed below $\sim 10,000\text{ cm}^{-1}$.

The electronic spectral bands along with ligand field and nephelauxetic parameters of the complexes are presented in Table-4. The ligand field strength are found to decrease in the order HBME > HBAE > HBPE for almost all the metal complexes which is evident from their $10D_q$ values. This may be attributed to the +I effect of methyl groups attached to the ligand system in HBME, that tend to pump electron to the donor atoms, thereby facilitating stronger coordination to the metal centers, which acts otherwise incase of HBPE, in which phenyl groups withdraw electron from the donor centers by virtue of -I effect. Further, the decrease in B values in the order $[M(\text{BME})_2] > [M(\text{BAE})_2] > [M(\text{BPE})_2]$ in most of the metal complexes can be justified by the fact that the delocalization of d -electron charge cloud of the metal ions into the ligand orbitals gets substantially reduced in the ligand BME due to +I effect of methyl groups, acting in opposite direction to the flow of electron by delocalization. On the contrary, the $M \rightarrow L$ charge delocalization is accelerated in case of BPE ligands due to electron withdrawing phenyl groups attached to the ligands. Consequently, the inter electronic repulsion is considerably reduced in the corresponding $[M(\text{BPE})_2]$ complexes as compared to their free ion values. This is reflected in the minimum B values of these complexes. This also reveals greater degree of covalency in $[M(\text{BPE})_2]$ complexes than $[M(\text{BME})_2]$, where the extent of delocalization is minimum.

${}^1\text{H}$ NMR spectra: The ${}^1\text{H}$ NMR spectra of the ligands and their Zn(II) complexes are recorded in DMSO- d_6 medium. The ${}^1\text{H}$ NMR spectrum of the ligand HBPE shows a complex broad multiplet at δ 7.2-7.9 ppm corresponding to 14 aromatic protons of the three phenyl groups and a singlet at δ 8.9 ppm due to proton of secondary amino group. On the other hand the ligand HBME shows a complex broad multiplet in the region δ 7.2-7.8 ppm corresponding to 4 aromatic protons and

a singlet at δ 9.1 ppm of secondary amino group and a twin peak at δ 2.8 ppm and δ 2.5 ppm assignable to methyl protons for $-\text{N}=\text{C}-\text{CH}_3$ and $\text{O}=\text{C}-\text{CH}_3$ group, respectively. The proton signal due to secondary amino hydrogen is absent in the ${}^1\text{H}$ NMR spectra of the complexes indicating deprotonation of enolic OH *via* tautomerization after complexation in conformity with the results of IR investigations, while the positions of other peaks of the ligand remain practically unaltered.

ESR spectra: The ESR spectra of copper complexes were recorded in DMSO at 300 K. The nature of the spectra is similar for all the complexes. Hence the representative spectrum of $[\text{Cu}(\text{BME})_2] \cdot 2\text{H}_2\text{O}$ is discussed here. The ESR spectrum of the complex exhibits a well resolved four line spectrum with no features characteristic for a binuclear complex. This is also supported by the magnetic moment of copper complex, which confirms the mononuclear nature of the complex. The spin Hamiltonian parameters for the copper complex were calculated from the spectrum. The observed order ($A_{\parallel} = 118 > A_{\perp} = 38$; $g_{\parallel} = 2.34 > g_{\perp} = 2.06 > 2.0023$) indicates that the complex has distorted octahedral geometry [34] with tetragonal elongation in which the unpaired electron resides in $d_{x^2-y^2}$ orbital [35]. The exchange interaction term G , estimated from the expression: $G = g_{\parallel} - 2.0023/g_{\perp} - 2.0023$ is found to be 5.42 which is greater than 4.0 (*i.e.* $G > 4.0$). This suggests the moderate crystal field strength of the ligands in the complexes. Further the covalency parameter α^2 ($=0.73$) calculated using standard equation [36] indicates certain degree of covalency existing in the complexes.

The following tentative structure (Fig. 1) has been proposed for the present complexes on the basis of the foregoing observations.

Antimicrobial activity: The free ligands and their metal complexes have been examined *in vitro* for their antibacterial and antifungal activities at $100\text{ }\mu\text{g mL}^{-1}$ concentrations by using the agar well diffusion technique. The results are presented in Table-5. It is observed that metal complexes exhibit greater activity than the ligands against all organisms. This may be explained on the basis of chelation theory. Moreover, coordination reduces the polarity [37,38] of the metal ion mainly because of the partial involvement of its positive charge with

TABLE-4
ELECTRONIC SPECTRA, MAGNETIC MOMENT, LIGAND FIELD
PARAMETERS AND NEPHELAUXETIC PARAMETERS OF COMPLEXES

Compound	μ_{eff} (BM)	Absorption bands (cm^{-1})			D_q (cm^{-1})	$10D_q$ (cm^{-1})	B (cm^{-1})	β
		ν_1 ${}^4T_{1g} \rightarrow {}^4T_{2g}$	ν_2 ${}^4T_{1g} \rightarrow {}^4A_{2g}$	ν_3 ${}^4T_{1g} \rightarrow {}^4T_{1g}(\text{P})$				
$[\text{Co}(\text{BAE})_2] \cdot \text{H}_2\text{O}$	4.78	8750	—	20100	997	9970	826	0.85
$[\text{Co}(\text{BME})_2] \cdot \text{H}_2\text{O}$	4.72	9300	—	21550	1069	10690	878	0.91
$[\text{Co}(\text{BPE})_2] \cdot \text{H}_2\text{O}$	4.81	8200	—	19600	972	9720	774	0.80
		ν_1 ${}^3A_{2g} \rightarrow {}^3T_{2g}$	ν_2 ${}^3A_{2g} \rightarrow {}^3T_{1g}$	ν_3 ${}^3A_{2g} \rightarrow {}^3T_{1g}(\text{P})$				
$[\text{Ni}(\text{BAE})_2] \cdot \text{H}_2\text{O}$	2.86	9550	15900	25400	955	9550	843	0.82
$[\text{Ni}(\text{BME})_2] \cdot \text{H}_2\text{O}$	2.79	9775	16400	25750	978	9780	855	0.83
$[\text{Ni}(\text{BPE})_2] \cdot \text{H}_2\text{O}$	2.91	9200	15750	24900	920	9200	870	0.845
		ν_2 ${}^2B_{1g} \rightarrow {}^2B_{2g}$	ν_3 ${}^2B_{1g} \rightarrow {}^2E_g$					
$[\text{Cu}(\text{BAE})_2] \cdot 2\text{H}_2\text{O}$	1.81	—	14400	15860	1513	15130	—	—
$[\text{Cu}(\text{BME})_2] \cdot 2\text{H}_2\text{O}$	1.79	—	14950	16420	1569	15685	—	—
$[\text{Cu}(\text{BPE})_2] \cdot 2\text{H}_2\text{O}$	1.84	—	14150	15450	1480	14800	—	—

TABLE-5
ANTIBACTERIAL AND ANTIFUNGAL ACTIVITIES OF THE COMPOUNDS (CONCENTRATION OF 100 µg mL⁻¹)

Compound	<i>B. subtilis</i>	<i>B. stearothermophilus</i>	<i>E. coli</i>	<i>S. typhi</i>	<i>A. niger</i>	<i>A. flavus</i>
HBAE	16.38	13.62	18.43	20.12	7.83	9.27
HBME	17.75	15.39	19.54	21.66	12.54	11.48
HBPE	21.37	24.76	28.41	27.25	27.85	30.72
[Co(BAE) ₂].H ₂ O	20.43	19.35	21.43	25.21	16.25	17.46
[Ni(BAE) ₂].H ₂ O	19.71	21.44	24.65	23.47	21.32	20.61
[Cu(BAE) ₂].2H ₂ O	22.38	25.78	29.40	27.27	21.86	19.73
[Zn(BAE) ₂].H ₂ O	23.24	22.87	28.72	27.56	18.25	20.72
[Co(BME) ₂].H ₂ O	24.85	26.26	28.49	25.32	20.61	19.56
[Ni(BME) ₂].H ₂ O	21.84	23.27	24.43	22.37	20.31	17.58
[Cu(BME) ₂].2H ₂ O	25.83	24.19	28.46	27.34	21.23	20.34
[Zn(BME) ₂].H ₂ O	22.85	24.27	23.48	25.32	20.61	17.38
[Co(BPE) ₂].H ₂ O	31.42	32.46	28.52	29.34	25.47	21.38
[Ni(BPE) ₂].H ₂ O	27.83	24.18	26.44	28.32	21.23	24.35
[Cu(BPE) ₂].2H ₂ O	39.53	36.63	42.62	45.85	36.53	34.35
[Zn(BPE) ₂].H ₂ O	29.83	25.19	27.46	28.32	22.23	26.34
Gentamycin	—	—	—	—	62.3	58.7
Ciprofloxacin	53.5	49.2	55.7	59.4	—	—

Fig. 1. M = Co(II), Ni(II), Cu(II) and Zn(II); R = H (compd. 1), CH₃ (compd. 2), C₆H₅ (compd. 3) and n = 1 or 2

the donor groups and possible π -electron delocalization within the whole chelate ring formed during coordination. This process further increases the lipophilic nature of the central metal atom, which subsequently favours its permeation through the lipid layer of the micro-organism [39,40] more efficiently thus destroying them more aggressively.

In addition to this, many other factors like nature of the ligand, solubility, dipole moment, conductivity and geometry, which are influenced by the metal ion may be responsible for the antimicrobial activities of these metal complexes [41,42].

Conclusions

- All the complexes are neutral in nature, which is evident from their low values of conductivity.
- The enolic nature of coordinated 'O' is established from IR spectra due to tautomerism in the system, which gives a band due to $\nu(\text{C}=\text{O})$. This is also evidenced by the presence of $\nu(\text{C}=\text{C})$, $\nu(\text{C}=\text{N})$, $\nu(\text{N}=\text{N})$ and absence of $\nu(\text{N}-\text{H})$ in the IR spectra of the complexes. It is further supported by ¹H NMR spectra which shows the absence of proton signal due to $-\text{NH}-$ group in the complexes. The 'O' coordination is reaffirmed by the appearance of $\nu(\text{M}-\text{O})$ in the IR spectra of the complexes.
- The absence of bands due to $\nu(\text{C}=\text{N})$ and $\nu(\text{N}-\text{N})$ and appearance of a new band at about 1585 cm⁻¹ due to $\nu(\text{N}=\text{N})$

(azo group) in the complexes suggest, thereby, the coordination of one of the nitrogen atoms of the azo group with the metal ion. It is further supported by the presence of $\nu(\text{M}-\text{N})$ in the IR spectra of the complexes.

- Although direct evidence of coordination of 'S' to the metal ions could not be obtained from the IR spectra of the complexes due to limitation of the instrument, the red shift of $\nu(\text{C}-\text{S}-\text{C})$ band to the extent of 10-20 cm⁻¹ in all complexes indicates coordination of ring sulphur atom to metal ions.

- The calculation of ligand field parameters from the absorption bands in the UV-visible spectra of the complexes reveal that the order of ligand field strength in the complexes is HBME > HBAE > HBPE. The nephelauxetic parameters data indicate certain degree of covalency in the complexes which follow the order $[\text{M}(\text{BME})_2] < [\text{M}(\text{BAE})_2] < [\text{M}(\text{BPE})_2]$. This is corroborated by the ESR spectral data in which the value of covalency parameter, $\alpha^2(0.73)$ lies below 1.0.

- The complexes showed good antimicrobial activity compared to the ligands. This may be explained due to enhanced lipophilic property of the central metal ion as a result of chelation with the ligand moieties.

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CONFLICT OF INTEREST

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

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