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Microwave synthesis, spectroscopic, thermal and biological significance of some transition metal complexes containing heterocyclic ligands

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ABSTRACT

*Some new Schiff base complexes of Cr(III), Co(II), Ni(II) and Cu(II) derived from 5-bromosalicylaldehyde with 2-amino-5-nitrothiazole (L^1H) and 4-dimethylaminobenzaldehyde with 2-amino-3-hydroxypyridine (L^2H) have been synthesized by conventional as well as microwave methods. These compounds have been characterized by elemental analysis, FT-IR, FAB-mass, molar conductance, electronic spectra, 1H -NMR, ESR, magnetic susceptibility, thermal, electrical conductivity and XRD analysis. The complexes exhibit coordination number 4 or 6. The complexes are coloured and stable in air. Analytical data revealed that all the complexes exhibited 1:2 (metal: ligand) ratio. The 1H -NMR spectral data indicates that the phenolic protons have been displaced during complexation. FAB-mass and thermal data show degradation pattern of the complexes. The thermal behaviour of metal complexes shows that the hydrated complexes loses water molecules of hydration in the first step; followed by decomposition of ligand molecules in the subsequent step. The Schiff base and metal complexes show a good activity against the Gram-positive bacteria; *Staphylococcus aureus* and Gram-negative bacteria; *Escherichia coli* and fungi *Aspergillus niger* and *Candida albicans*. The antimicrobial results also indicate that the metal complexes are better antimicrobial agents as compared to the Schiff bases.*

Keywords: Microwave method; Heterocyclic ligand; O, N Donor; Thermal study; Biological activity.

INTRODUCTION

Schiff base ligands have been widely studied in the field of coordination chemistry mainly due to their facile syntheses, easily availability, electronic properties and good solubility in common solvents. Transition metal complexes containing the Schiff base ligands have been of interest for many years because the transition metal complexes play a central role in the conduction of

molecular materials, which display unusual conducting, magnetic, thermal properties and find applicability in material chemistry and biochemistry [1-3]. A large number of Schiff bases and their metal complexes have been found to possess important biological and catalytic activity. Due to their great flexibility and diverse structural aspects, a wide range of Schiff bases have been synthesized and their complexation behavior was studied. Heterocyclic compounds are very widely distributed in nature and are essential to many fields of material science and biological systems. Metal complexes with these ligands are becoming increasingly important as biochemical, analytical and antimicrobial reagents in the design of molecular magnets, material chemistry and so on. Various heterocycles, especially thiazole and pyridine, occupy an important place owing to their versatile activities due to the presence of multifunctional groups. Thiazoles and its derivatives play significant part in industry and biology. Benzothiazole are used for production of dyes with photosensitizing properties^{4,7}. Pyridine derivatives play important role in many biochemical reactions. The molecular systems having chelating molecular designing and incorporating pyridine ring have been examined in the field of mycology for the development of metal based drugs. In several decades, efforts have been made to design and development of these drugs with pyridine based molecular devices [4-8].

Microwave irradiated reactions under solvent free or less solvent conditions are attractive offering reduced pollution, low cost and offer high yields together with simplicity in processing and handling. The salient features of microwave approach are shorter reaction times, simple reaction conditions and enhancements in yields [9-13]. Reports on the synthesis of metal complexes by microwave methods have been comparatively less.

In this paper, we have described the synthesis, physicochemical characterization and biological activities of Cr(III), Co(II), Ni(II) and Cu(II) complexes with ligands derived from 5-bromosalicylaldehyde with 2-amino-5-nitrothiazole (L^1H) and 4-dimethylaminobenzaldehyde with 2-amino-3-hydroxypyridine (L^2H). The reaction was carried out by both conventional and microwave methods. This ligand system coordinates with the metal ions in a bidentate manner through the oxygen and azomethine nitrogen. The metal complexes formed with these two new ligands may be used as precursors for the synthesis of new compounds. Some of which they may exhibit interesting physical and chemical properties and potentially useful biological activities.

EXPERIMENTAL SECTION

All the used chemicals and solvents were of Anal R grade. All the reagents used for the preparation of the Schiff bases were obtained from Sigma Aldrich. Metal salts were obtained from Loba Chemie. Elemental analyses were performed on an Elementar Vario EL III Carlo Erba 1108 analyzer. FAB-mass spectra were recorded on a JEOL SX 102/DA 6000 Mass Spectrometer using argon/xenon (6 kV, 10 mA) as the FAB gas. The accelerating voltage was 10 kV and the spectra were recorded at room temperature. Electronic spectra (in DMSO) were recorded on Perkin Elmer Lambda-2B-spectrophotometer. Molar conductance measurements were conducted using 10^{-3} M solution of the complexes in DMSO on Elico-CM 82 Conductivity Bridge at room temperature. Magnetic susceptibility measurements were carried out on a Gouy balance at room temperature using mercuric tetrathiocyanato cobaltate(II) as the calibrant. Diamagnetic corrections were applied in compliance with Pascal's constant. FT-IR spectra were recorded in KBr medium on a Perkin Elmer RX1 spectrophotometer in wave number region $4000-400\text{ cm}^{-1}$. 1H NMR spectra were recorded on a JEOL AL300 FTNMR spectrometer employing TMS as internal reference and DMSO- d_6 as solvent. X-band EPR spectra were recorded on a Varian E-112 spectrometer at room temperature operating at the X-band region with 100 kHz modulation frequency, 5 mw microwave power and 1 G modulation amplitude

using TCNE as the internal standard. Thermogravimetric analysis was carried out under atmospheric condition with a heating rate $10\text{ }^{\circ}\text{C min}^{-1}$ on TGA Q500 universal V4.5A TA instrument. Powder X-ray diffraction (XRD) patterns were recorded on a RINT2000 wide angle goniometer. X-ray diffractometer, operated at 40kV and 30 mA generator using the $\text{CuK}\alpha$ line at 1.54056 \AA as the radiation sources. Sample was scanned between 5° to 70° (2θ) at $25\text{ }^{\circ}\text{C}$. The solid state electrical conductivity has been measured by impedance spectroscopic method using HIOKI 3532-50 LCR Hitester at fixed frequency 1 KHz in the temperature range of 298-413 K. Microwave assisted synthesis were carried out in open glass vessel on a modified microwave oven model 2001 ETB with rotating tray and a power source 230 V, microwave energy output 800 W and microwave frequency 2450 MHz. A thermocouple used to monitor the temperature inside the vessel of the microwave. The microwave reactions were performed using on/off cycling to control the temperature.

Conventional Synthesis of Schiff bases

The Schiff bases have been synthesized by the condensation of equimolar ratio of 5-bromosalicylaldehyde (0.201 g, 10 mmol) with 2-amino-5-nitrothiazole (0.145 g, 10 mmol) and 4-dimethylaminobenzaldehyde (0.149 g, 10 mmol) with 2-amino-3-hydroxypyridine (0.110 g, 10 mmol) dissolved in ethanol. The resulting reaction mixture was stirred well, refluxed for 3-4 h and then allowed to cool overnight. The coloured solid precipitate of Schiff base obtained was filtered, washed with cold ethanol several times and dried under reduced pressure in a desiccator. The purity of synthesized compounds was checked by TLC using silica gel G (yield: 70-72.1%).

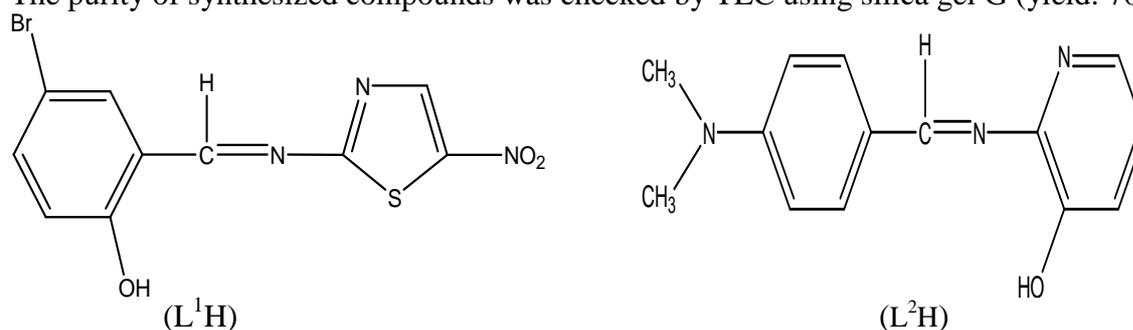


Figure1. Structure of Schiff base ligands

Microwave method for the Synthesis of Schiff bases

The equimolar (1:1) ratio of 5-bromosalicylaldehyde with 2-amino-5-nitrothiazole and 4-dimethylaminobenzaldehyde (L¹H) with 2-amino-3-hydroxypyridine were mixed thoroughly in a grinder. The reaction mixture was then irradiated by the microwave oven by taking 3-4 ml solvent. The reaction was completed in a short time (4-5 min) with higher yields. The resulting product was then recrystallized with ethanol and finally dried under reduced pressure over anhydrous CaCl_2 in a desiccator. The progress of the reaction and purity of the product was monitored by TLC using silica gel G (yield: 86.6-88.1%).

Conventional Synthesis of metal complexes

The metal complexes have been prepared by the mixing of (50 ml) ethanolic solution of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ / $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ / $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ / $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ with the (50 ml) ethanolic solution of Schiff bases (L¹H/L²H) in 1:2 (metal:ligand) ratio. The resulting mixture was refluxed on water bath for 6-10 h. A coloured product appeared on standing and cooling the above solution. The precipitated complex was, filtered washed with ether and recrystallized with ethanol several times and dried under the reduced pressure over anhydrous CaCl_2 in a desiccator. It was further dried in electric oven at $50\text{--}70\text{ }^{\circ}\text{C}$ (yield: 60.5-70.5%).

Microwave method for the Synthesis of metal complexes

The ligand and the metal salts were mixed in 1:2 (metal:ligand) ratio in a grinder. The reaction mixture was then irradiated by the microwave oven by taking 3-5 ml solvent. The reaction was completed in a short time (7-10 min) with higher yields. The resulting product was then recrystallized with ethanol and ether and finally dried under reduced pressure over anhydrous CaCl_2 in a desiccator. The progress of the reaction and purity of the product was monitored by TLC using silica gel G (yield: 76.8-83.8%).

Biological Activity

The *in vitro* biological activity of the investigated Schiff base and its metal complexes was tested against the bacteria *Escherichia coli* and *Staphylococcus aureus* by disc diffusion method using nutrient agar as medium and streptomycin as control. The antifungal activities of the compounds were also tested by the Well diffusion method against the fungi *Aspergillus niger* and *Candida albicans*, on potato dextrose agar as the medium and miconazole as control. The stock solution was prepared by dissolving the compounds in DMSO. In a typical procedure, a well was made on agar medium inoculated with microorganism. The well was filled with the test solution using a micropipette and the plate was incubated 24 h for bacteria at 37 °C and 72 h for fungi at 30 °C. During this period, the test solution diffused and the growth of the inoculated microorganism was affected. The inhibition zone was developed, at which the concentration was noted.

Table 1. The comparative results of conventional and microwave methods, analytical and physical data of the compounds

Compounds (Colour)	Reaction time	Yield (%)	Elemental analysis, found(calculated) %					$*\Lambda_m$
	CM (MM)	CM (MM)	C	H	N	S	M	
L^1H (Light brown)	3.8 (4.9)	70.0 (86.6)	36.56 (36.60)	1.83 (1.84)	12.78 (12.81)	9.71 (9.77)	-	-
$[\text{Cr}(\text{L}^1)_2(\text{H}_2\text{O})_2]\text{Cl}$ (Dark brown)	9.2 (9.4)	60.5 (76.8)	30.82 (30.89)	1.78 (1.81)	10.77 (10.81)	8.20 (5.25)	6.60 (6.69)	77.2
$[\text{Co}(\text{L}^1)_2(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ (Brownish yellow)	8.1 (7.6)	69.2 (82.2)	31.25 (31.31)	2.04 (2.10)	10.87 (10.95)	8.27 (8.36)	7.67 (7.68)	9.6
$[\text{Ni}(\text{L}^1)_2] \cdot 3\text{H}_2\text{O}$ (Coffee brown)	6.9 (7.1)	68.8 (80.6)	31.26 (31.32)	2.08 (2.10)	10.92 (10.96)	8.30 (8.36)	7.62 (7.65)	14.5
$[\text{Cu}(\text{L}^1)_2] \cdot 2\text{H}_2\text{O}$ (Yellowish green)	7.8 (7.8)	64.0 (83.5)	31.80 (31.87)	1.80 (1.87)	11.10 (11.15)	8.44 (8.51)	8.40 (8.43)	18.6
L^2H (Orange)	3.2 (4.1)	72.1 (88.1)	69.65 (69.69)	6.25 (6.27)	17.36 (17.41)	9.71 (9.77)	-	-
$[\text{Cr}(\text{L}^2)_2(\text{H}_2\text{O})_2]\text{Cl}$ $\cdot 2\text{H}_2\text{O}$ (Brown)	8.6 (7.9)	64.4 (78.6)	52.48 (52.54)	5.65 (5.67)	13.11 (13.13)	8.20 (5.25)	8.10 (8.12)	71.5
$[\text{Co}(\text{L}^2)_2(\text{H}_2\text{O})_2]$ (Brownish orange)	7.8 (8.1)	66.2 (81.2)	58.39 (58.43)	5.56 (5.60)	14.57 (14.60)	8.27 (8.36)	10.20 (10.24)	16.6
$[\text{Ni}(\text{L}^2)_2] \cdot 2\text{H}_2\text{O}$ (Coffee brown)	7.5 (7.2)	70.5 (83.8)	58.43 (58.46)	5.58 (5.61)	14.54 (14.61)	8.30 (8.36)	10.19 (10.20)	12.6
$[\text{Cu}(\text{L}^2)_2(\text{H}_2\text{O})_2]$ (Yellowish brown)	7.5 (7.0)	68.0 (81.6)	57.91 (57.97)	5.52 (5.56)	14.40 (14.49)	8.44 (8.51)	10.91 (10.95)	11.7

CM = Conventional method, time in hours; MM = Microwave method, time in minutes

$$*\Lambda_m = (\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1})$$

RESULTS AND DISCUSSION

As a result of microwave assisted synthesis, it was observed that the reaction was completed in a short time with higher yields compared to the conventional method. In the microwave method

homogeneity of reaction mixture was increased by the rotating of reaction platform tray. The confirming of the results was also checked by the repeating of the synthesis process. Comparative study results obtained by microwave assisted synthesis; versus conventional heating method is that some reactions which required 3.2-9.2 h. by conventional method, was completed within 4.1-9.4 min. by the microwave irradiation technique, yields have been improved from 60.5-72.1% to 76.8-88.1%.

All the metal complexes are coloured, solid and stable towards air and moisture at room temperature. They decompose on heating at high temperature and more or less soluble in common organic solvents. The comparative results of conventional and microwave methods, analytical data of the compounds, together with their physical properties are consistent with proposed molecular formula are given in Table 1. All the metal chelates have 1:2 (metal: ligand) stoichiometry. The observed molar conductance of the complexes in DMSO at room temperature are consistent with the non-electrolytic nature of the complexes except Cr(III) complex of both the Schiff base ligands, which it was electrolytic nature.

FAB-mass spectrum

The FAB-mass of the $[\text{Co}(\text{L}^1)_2(\text{H}_2\text{O})_2]\cdot\text{H}_2\text{O}$ complex exhibited the molecular ion (M^+) peak at $m/z = 768$ suggesting the monomeric nature of the complex. The mass spectrum shows multiple peaks representing successive degradation of the complex molecule by the formation of different fragments. The other important peaks of appreciable intensity have been observed at m/z values, obs.(cal.) – 751(749), 714(713), 557(553), 465(461), 292(295) and 119(119) suggesting the ion species after the successive fragmentation of different groups. The intensities of these peaks give the idea of the stabilities of the fragments. The m/z value 768 corresponds to nearest composition $[\text{Co}(\text{L}^1)_2(\text{H}_2\text{O})_2]\cdot\text{H}_2\text{O}$ and 119 to Co metal with chelated N, O ligand moiety.

The FAB-mass spectrum of the $[\text{Co}(\text{L}^2)_2(\text{H}_2\text{O})_2]$ complex shows a characteristic molecular ion (M^+) peak at $m/z = 577$, which corresponds to the molecular weight of the complex for a monomeric structure. The mass spectrum shows multiple peaks representing successive degradation of the complex molecule by the formation of different fragments. The peaks of appreciable intensity have been observed at m/z values, obs.(cal.) – 577(576), 540(540), 483(480), 451(452), 297(300) and 118(119) suggesting the fragmentation pattern. The m/z value 577 corresponds to nearest composition of the $[\text{Co}(\text{L}^2)_2(\text{H}_2\text{O})_2]$ and 118 corresponds to Co metal with chelated O, N ligand moiety [14-15].

$^1\text{H-NMR}$ spectra

The $^1\text{H-NMR}$ spectra of the L^1H ligand shows the signal at 7.254-7.664 (m) δ for aromatic proton, 6.983 (s) δ for thiazole proton and 9.223 (s) δ for azomethine proton. The peak at 12.275 (s) attributed to the phenolic –OH group, disappeared upon shaken of D_2O . The $^1\text{H-NMR}$ spectra of the L^2H ligand shows the signal at 6.952-7.862 (m) δ for aromatic proton, 3.32 (s, 6H, -N $(\text{CH}_3)_2$) and 8.765 (s) δ for azomethine proton. The peak at 10.191 (s) δ attributed to –OH group present in pyridine moiety, disappeared upon addition of D_2O [16-18].

IR spectra

The data of the IR spectra of Schiff base ligand and its metal complexes are listed in Table 2. The IR spectra of the complexes were compared with those of the free ligand in order to determine the involvement of coordination sites in chelation. Characteristic peaks in the spectra of the ligand and complexes were considered and compared.

Table 2. IR bands of Schiff base ligands and their complexes

Compound	$\nu(\text{C}=\text{N})$	$\nu(\text{O}-\text{H})$	$\nu(\text{C}-\text{O})$	$\nu(\text{C}=\text{N}$ thiazole ring)	$\nu(\text{C}=\text{N}$ pyridine ring)	$\nu(\text{H}_2\text{O})$	$\nu(\text{M}-\text{O})$	$\nu(\text{M}-\text{N})$
L^1H	1635	3326	1256	1563	-	-	-	-
$[\text{Cr}(\text{L}^1)_2(\text{H}_2\text{O})_2]\text{Cl}$	1602	-	1296	1562	-	3374, 816	564	489
$[\text{Co}(\text{L}^1)_2(\text{H}_2\text{O})_2]\cdot\text{H}_2\text{O}$	1612	-	1281	1565	-	3390, 802	550	491
$[\text{Ni}(\text{L}^1)_2]\cdot 3\text{H}_2\text{O}$	1608	-	1287	1564	-	3412	556	496
$[\text{Cu}(\text{L}^1)_2]\cdot 2\text{H}_2\text{O}$	1606	-	1298	1564	-	3419	555	486
L^2H	1622	3279	1232	-	1485	-	-	-
$[\text{Cr}(\text{L}^2)_2(\text{H}_2\text{O})_2]\text{Cl}\cdot 2\text{H}_2\text{O}$	1605	-	1256	-	1486	3342, 789	528	484
$[\text{Co}(\text{L}^2)_2(\text{H}_2\text{O})_2]$	1598	-	1248	-	1485	3361, 812	523	491
$[\text{Ni}(\text{L}^2)_2]\cdot 2\text{H}_2\text{O}$	1604	-	1249	-	1484	3384	528	482
$[\text{Cu}(\text{L}^2)_2(\text{H}_2\text{O})_2]$	1601	-	1246	-	1487	3354, 800	525	485

IR spectrum of the L^1H ligand exhibit the most characteristic bands at 3326 cm^{-1} $\nu(\text{O}-\text{H})$, 1635 cm^{-1} $\nu(\text{C}=\text{N}$, azomethine), 1563 cm^{-1} $\nu(\text{C}=\text{N}$, thiazole), 1256 cm^{-1} $\nu(\text{C}-\text{O})$ and 756 cm^{-1} $\nu(\text{C}-\text{S}-\text{C})$. The formation of Schiff base, 5-bromosalicylidene-2-amino-5-nitrothiazole is noted from the absence of $\text{C}=\text{O}$ and NH_2 peaks in the ligand. All the metal complexes show a broad band at ($3374\text{-}3419\text{ cm}^{-1}$) which may be due to $\nu_{\text{str}}(\text{OH})$. A medium intensity band at 816 and 802 cm^{-1} suggests the presence of coordinated water in Cr(III) and Co(II). The band 1635 cm^{-1} due to the azomethine group of the Schiff base has shifted to lower frequency ($1602\text{-}1612\text{ cm}^{-1}$) after complexation, indicating the bonding of nitrogen of the azomethine group to the metal ion and this can be explained by the donation of electrons from nitrogen to the empty d-orbital of the metal atom [19-21]. The phenolic C-O stretching vibration that appeared at 1256 cm^{-1} in Schiff base shift towards higher frequencies ($25\text{-}42\text{ cm}^{-1}$) in the complexes. This shift confirms the participation of oxygen in the C-O-M bond. The new bands at $550\text{-}564\text{ cm}^{-1}$ and $486\text{-}496\text{ cm}^{-1}$ have been assigned to M-O and M-N modes, respectively. The $\nu(\text{C}=\text{N})$ at 1563 cm^{-1} and $\nu(\text{C}-\text{S}-\text{C})$ at 756 cm^{-1} of the thiazole ring remain unchanged suggested that thiazole group does not coordinate to metal by neither nitrogen nor sulphur atom [22-23]. IR spectrum of the L^2H ligand exhibit the most characteristic bands at 3279 cm^{-1} $\nu(\text{O}-\text{H})$, 1622 cm^{-1} $\nu(\text{C}=\text{N}$, azomethine) and 1485 cm^{-1} $\nu(\text{C}=\text{N}$, pyridine). The formation of Schiff base, 4-dimethylaminobenzylidene-2-amino-3-hydroxypyridine is noted from the absence of $\text{C}=\text{O}$ and NH_2 peaks in the ligand. All the metal complexes show a broad band at ($3342\text{-}3384\text{ cm}^{-1}$) which may be due to $\nu_{\text{str}}(\text{OH})$. A medium intensity band at 789 cm^{-1} , 812 cm^{-1} and 800 cm^{-1} in Cr(III), Co(II) and Cu(II) respectively, suggests the presence of coordinated water in these complexes. But this band is not presented in the Ni(II) complex, indicate that the absence of coordinated water molecules in Ni(II) complex. The band 1622 cm^{-1} due to the azomethine group of the Schiff base has shifted to lower frequency ($1598\text{-}1605\text{ cm}^{-1}$) after complexation. This indicates the involvement of azomethine nitrogen to the metal ion. In the IR spectra of the complexes, the stretching vibration of the free ligand $\nu(\text{O}-\text{H})$ 3279 cm^{-1} is not observed, suggesting deprotonation of the hydroxyl group and formation of M-O bonds. In the low frequency region, the band of weak intensity observed for the complexes in the region $517\text{-}528\text{ cm}^{-1}$ is attributed to (M-O) and in the region $482\text{-}491\text{ cm}^{-1}$ to (M-N). The $\nu(\text{C}=\text{N})$ at 1485 cm^{-1} in ligand, there is no appreciable change in the complexes spectrum which indicates that the pyridine ring nitrogen does not participate in coordination.

The IR data of both the Schiff base and its metal complexes show that the Schiff bases (L^1H and L^2H) behaves as bidentate and is bonded to the metal ion through oxygen and imino nitrogen of azomethine group.

Electronic spectra and magnetic moment

The nature of the ligand field around the metal ion has been deduced from the electronic spectra. The electronic spectra of Cr(III) complex of L^1H show bands in the range of 17982 cm^{-1} , 23940 and 35981 cm^{-1} , which may be assigned to ${}^4A_{2g} \rightarrow {}^4T_{2g}(F)$ (ν_1), ${}^4A_{2g} \rightarrow {}^4T_{1g}(F)$ (ν_2) and ${}^4A_{2g} \rightarrow {}^4T_{1g}(P)$ (ν_3) transitions, respectively. The magnetic moment is 3.92 B.M. Thus the octahedral geometry has been suggested for this complex. The value of various ligand field parameters $10Dq$, B , β , $\beta\%$ and LFSE were calculated to be: 17982 cm^{-1} , 566.7 cm^{-1} , 0.55, 44.98 and $257.81\text{ kJ mol}^{-1}$.

The electronic spectrum of Co(II) complex of L^1H exhibit three bands in the region of 9631 cm^{-1} , 14751 cm^{-1} and 20025 cm^{-1} which have tentatively been assigned to ${}^4T_{1g} \rightarrow {}^4T_{2g}(F)$ (ν_1), ${}^4T_{1g} \rightarrow {}^4A_{2g}(F)$ (ν_2) and ${}^4T_{1g} \rightarrow {}^4T_{1g}(P)$ (ν_3) transitions, respectively. The value of magnetic moment is 5.06 B.M.; which indicates the presence of Co(II) complex in octahedral geometry. The value of various ligand field parameters $10Dq$, B , β , $\beta\%$ and LFSE were calculated to be: 10807 cm^{-1} , 771.9 cm^{-1} , 0.69, 31.08 and $103.29\text{ kJ mol}^{-1}$.

The absorption spectrum of Ni(II) complex of L^1H exhibit bands at 13811 cm^{-1} and 19351 cm^{-1} , which have tentatively been assigned to the transitions ${}^1A_{1g} \rightarrow {}^1E_g$ (ν_1) and ${}^1A_{1g} \rightarrow {}^1B_{2g}$ (ν_2) respectively. It is a diamagnetic complex, therefore square planar geometry has been suggested.

The electronic spectrum of the Cu (II) complex of L^1H show two bands at 14212 cm^{-1} and 19518 cm^{-1} assignable to ${}^2B_{1g} \rightarrow {}^2B_{2g}$ and ${}^2B_{1g} \rightarrow {}^2E_g$ transitions, respectively. Since the value of magnetic moment is 1.97 B.M. therefore square planar geometry has been suggested for Cu (II) complex.

The Cr(III) complex of L^2H show electronic spectral bands at 18210 cm^{-1} , 24440 cm^{-1} and 35679 cm^{-1} these are tentatively assigned to ${}^4A_{2g} \rightarrow {}^4T_{2g}(F)$ (ν_1), ${}^4A_{2g} \rightarrow {}^4T_1(F)$ (ν_2) and ${}^4A_{2g} \rightarrow {}^4T_{1g}(P)$ (ν_3) transitions, respectively. The magnetic moment value is 3.88 B.M.; thus the octahedral structure has been suggested for this complex. The value of various ligand field parameters $10Dq$, B , β , $\beta\%$ and LFSE were calculated to be: 18210 cm^{-1} , 596.75 cm^{-1} , 0.58, 42.06 and $261.08\text{ kJ mol}^{-1}$. The electronic spectrum of Co(II) complex of L^2H show three bands at 9281 cm^{-1} , 15540 cm^{-1} and 20480 cm^{-1} , these are tentatively assigned to ${}^4T_{1g} \rightarrow {}^4T_{2g}(F)$ (ν_1), ${}^4T_{1g} \rightarrow {}^4A_{2g}(F)$ (ν_2) and ${}^4T_{1g} \rightarrow {}^4T_{1g}(P)$ (ν_3) transitions, respectively. The magnetic susceptibility value is 4.98 B.M.; which is an indicative of octahedral geometry. The value of various ligand field parameters $10Dq$, B , β , $\beta\%$ and LFSE were calculated to be: 10595 cm^{-1} , 815.0 cm^{-1} , 0.73, 27.23 and $101.27\text{ kJ mol}^{-1}$.

The electronic spectrum of the Ni (II) complex of L^2H show two bands at 13212 cm^{-1} and 18620 cm^{-1} assignable to ${}^1A_{1g} \rightarrow {}^1E_g$ (ν_1) and ${}^1A_{1g} \rightarrow {}^1B_{2g}$ (ν_2) transition, respectively. It is a diamagnetic complex, therefore square planar geometry has been suggested for Ni (II) complex.

The electronic spectrum of the Cu (II) complex of L^2H shows a single broad band at 14480 cm^{-1} corresponding to transition ${}^2E_g \rightarrow {}^2T_{2g}$. The value of magnetic moment for this complex is 1.82 B.M.; thus the octahedral geometry has been suggested for Cu (II) complex. [24-27].

ESR spectra

The ESR spectra of Cu(II) provide information about the extent of the delocalization of unpaired electron. ESR spectra of both Cu(II) complexes have been recorded on X-band and their g_{\parallel} , g_{\perp} , Δg , g_{av} and G have been calculated. The values of ESR parameters g_{\parallel} , g_{\perp} , g_{av} , Δg and G for

Cu(II) complex of L¹H are 2.1992, 2.1307, 2.1535, 0.0685 and 1.5322 respectively. Similarly, the corresponding values for Cu(II) complex of L²H are 2.2375, 2.0665, 2.1235, 0.1710 and 3.6512 respectively.

ESR spectra of the complexes revealed two g values (g_{\parallel} and g_{\perp}). Since the g_{\parallel} and g_{\perp} values are closer to 2 and $g_{\parallel} > g_{\perp}$ suggesting a tetragonal distortion around the Cu(II) ion. The trend $g_{\parallel} > g_{\perp} > g_e$ (2.0023) shows that the unpaired electron is localized in $d_{x^2-y^2}$ orbital in the ground state of Cu(II) and spectra are characteristic of axial symmetry. The $g_{\parallel} > 2.3$ is characteristic of an ionic environment and $g_{\parallel} < 2.3$ indicates a covalent environment in metal ligand bonding. The g_{\parallel} values for the complexes are less than 2.3, suggesting the environment is covalent.

The exchange coupling interaction between two Cu(II) ions is explained by Hathaway expression $G = (g_{\parallel} - 2.0023) / (g_{\perp} - 2.0023)$. According to Hathaway, if the value G is greater than four ($G > 4.0$), the exchange interaction is negligible; whereas when the value of G is less than four ($G < 4$) a considerable exchange coupling is present in solid complex. The G values for the Cu(II) complexes are less than four indicate considerable exchange interaction in the complexes[28-30].

Thermal analyses

The thermal behavior of metal complexes shows that the hydrated complexes lose molecules of hydration first; followed by decomposition of ligand molecules in the subsequent steps.

The thermal degradation behavior of the Ni(II) complex of L¹H has been studied by thermogravimetric analysis. The TG curve of the complex shows that the complex starts decomposition at 65 °C. Elimination of lattice water molecules has been observed on increasing the temperature up to 120 °C (remaining wt.%, obs./cal., 93.15/92.96). The complex does not show any loss in weight between 120 -210 °C. After 210 °C, a loss in weight has been observed in general up to 370 °C corresponding to the loss of partially decomposed ligand part from the complex (remaining wt.%, obs./cal., 62.12/59.32). Above 450 °C, an inflection occurs in the curve and loss in weight goes up to 655 °C. This indicates the elimination of the remaining thermally degradable part of the complexes. After 655 °C a horizontal curve has been observed which corresponds to a mixture of metal oxide as an ultimate pyrolysis product (remaining wt.%, obs./cal., 23.42/19.54). The DTG curve of the complex shows peak at 102, 325 and 610 °C.

The thermogram of the Cu(II) complex of L²H indicates that the complex is stable upto 110 °C. Above 110 °C, an elimination of two coordinated water molecules has been observed between the temperature range 110-205 °C (Remaining wt.%, obs./calc., 93.80/93.79). Above this temperature a weight loss has been observed in general up to 410 °C indicating the decomposition of the ligand moiety (Remaining wt.%, obs./calc., 50.25/45.87). The decomposition of remaining ligand moiety occurs between 460-630 °C above 620 °C a horizontal curve has been obtained suggesting the ultimate pyrolysis product as metal oxide (Remaining wt%, obs./calc., 24.70/20.52). DTG curve of the Cu(II) complex shows peak at 179, 378 and 598 °C [31].

Apart from evaluating the thermal stability of the metal complexes, this study also helped to characterize the metal complexes.

X-ray diffraction study

X-ray diffraction was performed of metal complexes. The XRD patterns indicate crystalline nature for the complexes. X-ray powder diffractogram of the complexes were recorded using

CuK α as source in the range 5°-70° (2 θ). X-ray crystal system has been worked out by trial and error methods for finding the best fit between observed and calculated $\sin^2\theta$. The diffractogram of Ni(II) complex of L¹H has recorded 12 reflections with maxima at $2\theta = 7.97465$ with interplanar distance $d = 11.07775$. The complex crystallized in tetragonal system. $\sin^2\theta$ and hkl values for different lattice planes have been calculated. Crystal data for complex, $a = b = 15.67077 \text{ \AA}$, $c = 23.24351 \text{ \AA}$, $V = 5707.98 \text{ \AA}^3$, $Z = 6$, $D_{\text{obs}} = 1.3386 \text{ g/cm}^3$ and $D_{\text{cal}} = 1.2864 \text{ g/cm}^3$. The observed and calculated values of density and $\sin^2\theta$ show good agreement [32].

Antimicrobial activities

The *in vitro* Antimicrobial activity of the synthesized Schiff base ligands and their corresponding metal complexes on selected bacteria *E. coli* and *S. aureus* and two fungi *A. niger* and *C. albicans* was carried out. All of the tested compounds showed good biological activity against microorganism. On comparing the biological activity of the Schiff base and its metal complexes with the standard bactericide and fungicide, it is show that some metal complexes have good activity as compared to the standard but all the complexes are more active than their respective ligands. The higher inhibition zone of metal complexes than those of the ligands can be explained on the basis of Overtone's concept and Chelation theory. On chelation, the polarity of the metal ion will be reduced to greater extent due to the overlap of the ligand orbital and partial sharing of the positive charge of the metal ion with donor groups. Further, it increases the delocalization of π -electrons over the whole chelating ring and enhances the penetration of the complexes into lipid membranes and blocking of the metal binding sites in the enzymes of microorganisms. There are other factors which also increase the activity are solubility, conductivity and bond length between the metal and ligand [33-38].

The antibacterial data listed in Table 3. The investigation of antibacterial data revealed that the Co(II) and Cu(II) complex of L¹H exhibited better antibacterial activity against *E. coli* and *S. aureus* compared to the other compounds. The antifungal data of compounds are given in Table 4. The antifungal results show that the Co(II) and Cu(II) complex of L²H displayed highly activity against fungi in comparison to other compounds. All the compounds show bacterial and fungal growth inhibition in follow the order:

Metal complexes>Metal salts>Schiff base ligands

Table 3. Antibacterial screening data for the ligands and their complexes

Compound	Diameter of inhibition zone (mm); Concentration in $\mu\text{g/ml}$											
	<i>E. coli</i>						<i>S. aureus</i>					
				% Activity index*						% Activity index*		
	25	50	100	25	50	100	25	50	100	25	50	100
HL ¹	13	15	18	59	63	64	10	12	15	55	55	63
Cr(III)	10	14	20	45	58	71	11	14	16	61	64	67
Co(II)	22	25	32	100	104	114	13	17	19	72	77	79
Ni(II)	16	18	21	73	75	75	11	14	17	61	64	71
Cu(II)	21	23	29	95	96	103	16	20	24	89	91	100
L ² H	10	12	14	45	50	50	9	11	-	50	50	50
Cr(III)	12	13	16	55	54	57	11	14	19	61	64	79
Co(II)	14	16	19	64	67	68	13	16	20	72	73	83
Ni(II)	15	18	22	68	75	79	13	17	19	72	77	79
Cu(II)	16	18	23	73	75	82	15	18	20	83	82	83
Streptomycin (Standard)	22	24	28	100	100	100	18	22	24	100	100	100

$$*\% \text{ Activity Index} = \frac{\text{Zone of inhibition by test compound (diameter)}}{\text{zone of inhibition by standard (diameter)}} \times 100$$

Table 4. Antifungal screening data for the ligands and their complexes

Compound	Diameter of inhibition zone (mm); Concentration in $\mu\text{g/ml}$					
	<i>A. niger</i>			<i>C. albicans</i>		
	25	50	100	25	50	100
HL ¹	10	13	16	12	14	18
Cr(III)	12	15	18	14	16	20
Co(II)	16	20	25	16	18	22
Ni(II)	14	18	22	15	17	21
Cu(II)	15	19	24	17	19	24
L ² H	11	13	16	11	13	17
Cr(III)	11	14	17	12	13	16
Co(II)	15	19	23	15	18	22
Ni(II)	15	20	24	17	19	24
Cu(II)	16	20	25	16	18	23
Miconazole (Standard)	20	25	30	22	24	29

CONCLUSION

In this report, we are described coordination chemistry of a Schiff base metal complexes obtained from the reaction of 5-bromosalicylaldehyde with 2-amino-5-nitrothiazole (L¹H) and 4-dimethylaminobenzaldehyde with 2-amino-3-hydroxypyridine (L²H) have synthesized and characterized by various physicochemical and spectral analyses. In the result of microwave assisted synthesis, it has been observed that the reaction time decreased from hours to minutes and availability of the product within better yields compared to the classical method. The synthesized Schiff base ligand of L¹H coordinates with the metal ions in a bidentate manner through the phenolic oxygen and azomethine nitrogen, whereas L²H ligand coordinates with the metal ions through the pyridyl-O and azomethine-N. The ¹H-NMR data suggest that both the Schiff base ligand deprotonated after complexation. FAB-mass and thermal data show degradation pattern of the complexes. Thermogravimetric studied of the complexes also helped to characterize the complexes. Antimicrobial data suggests that the metal complexes are better antibacterial and antifungal agents as compared to their ligands. The compounds also inhibit the growth of fungi and bacteria to a greater extent as the concentration is increased.

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