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Microwave synthesis, spectral, thermal and antimicrobial studies of some Ni(II) and Cu(II) Schiff base complexes

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Resumen

Se sintetizaron bases de Schiff bidentadas y tridentadas (NO), (ONO) a través de la reacción de condensación entre la metil-isobutilcetona y el 2-amino-4clorofonol y 2-hidroxiacetofenona con la hidracina del ácido isonicotínico. Los complejos metálicos 1:1 o 1:2 han sido preparados mediante la interacción de estas bases de Schiff y los iones Ni(II) y Cu(II). La síntesis fue realizada empleando el método convencional y el de microondas, y los productos fueron caracterizados por análisis elemental, FT-IR, UV-Vis, RES, conductancia molar, análisis térmico y difracción de rayos X. Los complejos son coloreados y estables al aire y temperatura ambiente. El comportamiento térmico de los complejos metálicos hidratados muestran una primera etapa de pérdida de agua de hidratación, seguidos de la descomposición de las moléculas de ligando en etapas subsecuentes. El análisis de los cristales del complejo $[Ni(HINH)(H_2O)]Cl.3H_2O$ ***a*** = ***b*** = 13,9338Å, ***c*** = 34,7975Å, V= 6755, 96Å^3, Z = 12, D_{obs} = 1,2421g/cm^3, D_{cal} 1,2847g/cm^3, refleja una estructura cristalina en un sistema ortorómbico. La conductividad eléctrica de estado sólido de los complejos metálicos indica que éstos poseen una naturaleza semiconductora. Las bases de Shiff y los complejos metálicos muestran buena actividad contra bacterias Gram-positivas del tipo *Staphylococcus aureus*, bacterias Gram-negativas del tipo *Escherichia coli* y hongos del tipo *Aspergillus niger* y *Candida albicans*. Los complejos metálicos son mejores agentes antimicrobiales que las bases de Schiff.

Palabras clave: síntesis por microondas; hidracina del ácido isonicotínico; análisis térmico; actividad biológica

Abstract

Bidentate and tridentate (NO), (ONO) Schiff bases have been synthesized by condensing methyl isobutyl ketone with 2-amino-4-chlorophenol and 2-hydroxy acetophenone with isonicotinic acid hydrazide. The 1:1 or 1:2 metal complexes have been prepared by interacting these Schiff bases with metal ions *viz.* Ni(II), Cu(II). These compounds have been synthesized by conventional as well as microwave methods and characterized by elemental analysis, FT-IR, UV-Vis, ESR, molar conductance, thermal analysis and X-ray diffraction. The complexes are colored and stable in air at room temperature. The thermal behavior 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 steps. Crystal data of $[Ni(HINH)(H_2O)]Cl.3H_2O$ complex ***a*** = ***b*** =13.9338Å, ***c*** = 34.7975Å, V = 6755.96Å^3, Z = 12, D_{obs} = 1.2421g/cm^3, D_{cal} 1.2847g/cm^3, reflect that this complex has crystallized in orthorhombic system. The solid state electrical conductivity of the metal complexes has also been measured. Solid state electrical conductivity studies reflect semiconducting nature of the complexes. The Schiff bases and metal complexes show 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 synthesis; isonicotinic acid hydrazide; thermal study; biological activity.

Introduction

Schiff bases and their bio-active complexes have been studied extensively over the past decade. Schiff bases provide potential sites for bio-chemically active compounds. Various transition and inner-transition metal complexes with bi, tri- and tetradenate Schiff bases containing nitrogen and oxygen donor atoms play an important role in biological systems. Interest in the studies of hydrazides and corresponding hydrazones arises from the fact that hydrazides of organic acids and their hydrazones can function as antituberculous. The antituberculous activity was ascribed to their ability to form more or less stable chelates with the transition metal ions[1-3]. Hydrazones possessing an azometine -NHN=CH- proton, constitute an important class of compounds for new drug development. Coordination compounds derived from aroyl hydrazones have been reported to act as enzyme inhibitor and are useful due to their pharmacological applications. Many drugs inhibit modified toxicological and pharmacological properties when they are in the form of metal complexes. The most widely studied metal in this respect is copper (II) which has proved to be beneficial in diseases such as tuberculosis, gastric ulcers, rheumatoid arthritis and cancers. Metal chelation therapy can emerge to answer the problems of multidrug resistance (MDR) as against various viruses, bacteria, fungi and other pathogens[4-7].

Microwave-assisted synthesis is a branch of green chemistry. The application of microwave-assisted synthesis in organic, organometallic and coordination chemistry continues to develop at an astonishing pace. 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[8-12]. Reports on the synthesis of metal complexes by microwave methods have been comparatively less.

The present investigation aims at the conventional and microwave synthesis, physico-chemical characterization and bio-inorganic studies of Schiff bases involving methyl isobutyl ketone with 2-amino-4-chlorophenol and 2-hydroxy acetophenone with isonicotinic acid hydrazide and their metal chelates with Ni(II) and Cu(II).

Experimental

General experimental procedures:

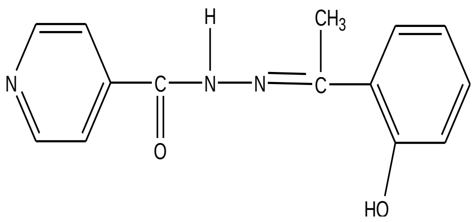
All the used chemicals and metal salts were of A.R. grade. Methyl isobutyl ketone and 2-hydroxy acetophenone were obtained from CDH and isonicotinic acid hydrazide has been purchased from Sigma-Aldrich. Metal salts were purchased from Loba Chemie. Elemental analyses were performed on an Elemental Vario EL III Carlo Erba 1108 analyzer. Electronic spectra (in DMSO) were recorded on Perkin Elmer Lambda-2B-spectrophotometer. Molar conductance measurements were conducted using 10^{-3} M solutions 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 $Hg[Co(SCN)_4]$ as the calibrant. FT-IR spectra were recorded in KBr pellets on a Perkin Elmer RX1 spectrophotometer in wave number region 4000-400cm^{-1}. X-band EPR spectra were recorded on a Varian E-112 spectrometer at room temperature operating at the X-band region with 100kHz modulation frequency, 5mw microwave power and 1 G modulation amplitude using TCNE as the internal standard. Thermogravimetric (TG) analysis was done at NIPER, Chandigarh under N_2 atmosphere with a heating rate of 20°Cmin^{-1}. Powder X-ray diffraction (XRD) patterns were recorded on a RINT2000 wide angle goniometer. X-ray diffractometer, operated at 40kV and 30mA generator using the CuKα line at 1.54056Å as the radiation sources. Sample was scanned between 5° to 60° (2θ) at 25°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 298-377K. 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 230V, microwave energy output 800W and microwave frequency 2450MHz. A thermocouple device was used to monitor the temperature inside the vessel of the microwave. The microwave reactions were performed using on/off cycling to control the temperature.

Biological activity:

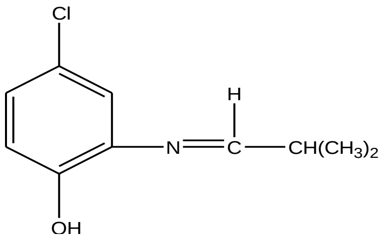
The *in-vitro* biological activity of the Schiff bases and their complexes was tested against the bacteria *Escherichia coli* and *Staphylococcus aureus* by disc diffusion method using nutrient agar as medium and streptomycin as control. The antifungal activities of the compounds were also tested by the Well diffusion method against the fungi *Aspergillus niger* and *Candida albicans*, on potato dextrose agar as the medium and miconazole as control. Each of the compounds was dissolved in DMSO and solutions of the concentrations (25, 50 and 100ppm) were prepared separately. 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 24h for bacteria at 37°C and 72h 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.

Conventional method for the synthesis of Schiff bases:

HINH and MAP Schiff bases (Fig. 1) were synthesized by the condensation of equimolar ratio of methyl isobutyl ketone with 2-amino-4-chlorophenol and 2-hydroxy acetophenone with isonicotinic acid hydrazide dissolved in ethanol. The resulting reaction mixture was stirred well, refluxed for 3-4h and then allowed to cool overnight. The coloured solid precipitate of Schiff base obtained was filtered, washed with cold ethanol several times and dried in air at room temperature and finally stored under reduced pressure in a $CaCl_2$ desiccator. The purity of synthesized compounds was checked by TLC using silica gel G (yield: 75-78%).



(HINH)



(MAP)

Fig. 1: Structure of Schiff base Ligands

Microwave method for the synthesis of Schiff bases:

The equimolar (1:1) ratio of methyl isobutyl ketone with 2-amino-4-chlorophenol and 2-hydroxy acetophenone with isonicotinic acid hydrazide were mixed thoroughly in a grinder. The reaction mixture was then irradiated by the microwave oven by taking 3-4mL of dry ethanol as a solvent. The reaction was completed in a short time (4-5min) with higher yields. The resulting product was then recrystallized with ethanol, finally dried under reduced pressure over anhydrous $CaCl_2$ in a desiccator. The progress of the reaction, purity of the product was monitored by TLC using silica gel G (yield: 87-88%).

Conventional method for the synthesis of metal complexes:

The metal complexes (Figs. 2 and 3) were prepared by the mixing of (50mL) ethanolic solution of $NiCl_2.6H_2O/CuCl_2.2H_2O$ with the (50mL) ethanolic solution of Schiff bases (HINH/MAP) in 1:1 or 1:2 (metal:ligand) ratio. The resulting mixture was refluxed on water bath for 6-8h. 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 50-70°C (yield: 65-70%).

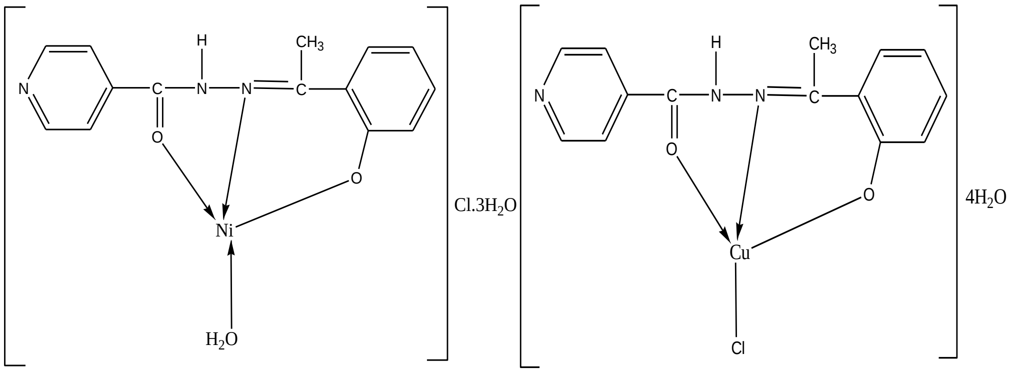


Fig. 2: proposed structure of metal complexes of HINH ligand.

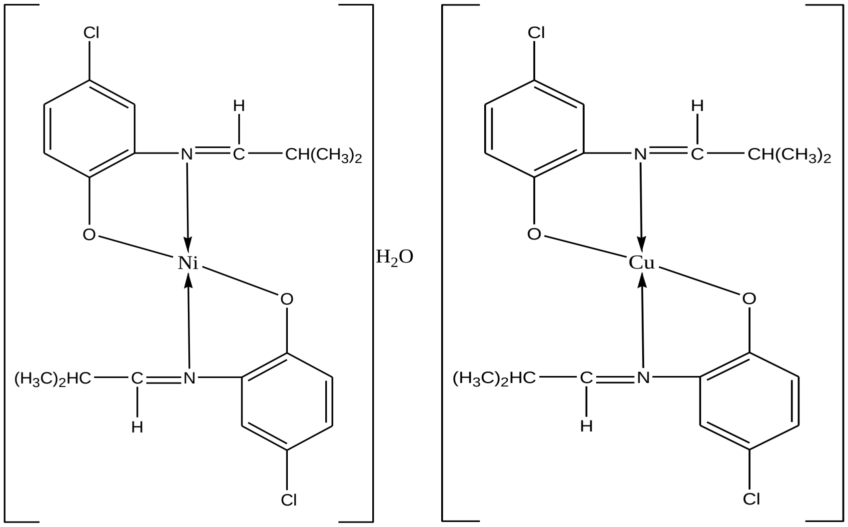


Fig. 3: proposed structure of metal complexes of MAP ligand

Microwave method for the synthesis of metal complexes:

The ligand and the metal salts were mixed in 1:1 or 1:2 (metal:ligand) ratio in a grinder. The reaction mixture was then irradiated by the microwave oven by taking 3-4mL of dry ethanol as a solvent. The reaction was completed in a short time (6-9min) 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: 80-84%).

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.

All the metal complexes are coloured, solid and stable towards air and moisture at room temperature. They decompose on heating at high temperature, more or less soluble in common organic solvents. The comparison study data of microwave and conventional methods, with analytical and physical data of the compounds are given in the Table 1. Analytical date show that metal chelates have 1:1 or 1:2 (metal:ligand) stoichiometry. The observed molar conductance of the complexes in DMSO at room temperature is consistent with non-electrolytic nature of all the complexes except Ni(II) complex of HINH.

IR Spectra:

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 1: The comparative results of conventional and microwave methods, analytical, physical data and magnetic moment values of the compounds

Compounds molecular weight/Colour	Reaction period		Yield (%)		Elemental analysis, found (calcd.) %			$^{*}\Lambda_m$	$^{\#}\mu_{eff}$
	CM (h.)	MM (min.)	CM	MM	C	H	N		
HINH 255.0/Cream	3.6	4.3	78	88	65.72 (65.88)	5.03 (5.09)	16.45 (16.47)	-	-
$[Ni(HINH)(H_2O)]Cl.3H_2O$ 421.2/Yellow	8.0	8.4	67	82	39.89 (39.88)	4.91 (4.98)	9.64 (9.97)	112.5	Diam.
$[Cu(HINH)(Cl)]4H_2O$ 426.0/Light Brown	7.6	7.9	70	84	39.40 (39.43)	4.95 (4.92)	9.64 (9.85)	52.3	1.91
MAP 211.0/Light Coffee	3.5	4.5	75	87	62.32 (62.41)	6.55 (6.61)	6.21 (6.61)	-	-
$[Ni(MAP)_2]H_2O$ 499.7/Blackish Brown	7.5	8.2	65	80	52.75 (52.83)	6.10 (6.00)	6.07 (5.60)	20.5	Diam.
$[Cu(MAP)_2]$ 486.5/Brown	6.5	6.8	67	83	54.30 (54.26)	5.82 (5.75)	6.07 (5.75)	15.7	1.87

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

$^{*}\Lambda_m = (\Omega^{-1}cm^2mol^{-1})$; $^{\#}\mu_{eff}$ = B.M.

IR spectrum of HINH ligand shows the band at 3116cm^{-1} due to N-H (stretching) frequency. A strong band at about 1682cm^{-1} in the ligand ν(C=O) group has shifted to lower frequency 1651 ± 10cm^{-1} in the complexes. This indicates the involvement of C=O group in coordination. Medium intensity band at about 1607cm^{-1} in the ligand due to ν(C=N) group shifts down by 10-15cm^{-1} in the complexes suggesting coordination through azomethine nitrogen, this can be explained by the donation of electrons from nitrogen to the empty d-orbital of the metal atom. A band in the ligand spectrum at 1373cm^{-1} due to phenolic group (OH-deformation) was found absent in complexes. This suggests deprotonation of phenolic OH, on chelation with metal ion. A band at 1281cm^{-1} due to phenolic ν(C-O) in ligand spectrum shifts to higher side 1338 ± 8cm^{-1} in the metal complexes indicating its involvement in chelation. Practically, no shift in the characteristic bands position of pyridine nitrogen (-N=) has been observed indicating the non-involvement of this donor group in coordination. The appearance of a broad band around 3420 ± 10cm^{-1} in the spectra of complexes has tentatively been assigned to ν_{stre} water molecules. A band of medium intensity at 708 ± 5cm^{-1} (-OH rocking), suggest the presence of coordinated water in Ni(II) complex. This band is absent in the Cu(II) complex. The new bands of weak intensity observed at 556 ± 5 and 481 ± 5cm^{-1} in the spectra of metal complexes, are assignable to ν(M-O) and ν(M-N) mode, respectively[13-16]. The MAP ligand band at 1604cm^{-1} due to ν(C=N) azomethine group shifts down at 1590 ± 10cm^{-1}, suggesting participation of this group in chelation. The ligand spectrum shows band at 3080 and 1386cm^{-1} due to the stretching vibration and phenolic -OH deformation respectively. These remain absent in spectra of complexes. An intense ligand band observed at about 1209cm^{-1} (phenolic C-O) shift to higher frequency (1275 ± 10cm^{-1}) in the spectra of complexes. This suggests deprotonation of the phenolic OH group on its chelation with metal ion. The broad band around 3440 ± 10cm^{-1} in the spectra of Ni(II) complex has been assigned to ν(OH) water molecule. This band is absent in Cu(II) complexes. The new bands at 548 ± 5 and 475 ± 5cm^{-1} in the complexes have tentatively been assigned to ν(M-O) and ν(M-N) mode, respectively[13-16].

Electronic spectra:

The electronic spectral measurements were used for assigning the stereochemistry of metal ions in the complexes, which is based on the position, shape, intensity and number of d-d transition bands.

The electronic spectrum of Ni(II) complex of HINH exhibits two bands at 12465 and 24324cm^{-1}, which are assignable to $^1A_{1g}\rightarrow{}^1E_g$ and $^1A_{1g}\rightarrow{}^1B_{1g}$ transitions, respectively. It is a diamagnetic complex; therefore square planar geometry has been suggested. Two absorption bands at 12553 and 20509cm^{-1} in the spectrum of Cu(II) complex of HINH have tentatively been assigned to $^2B_{1g}\rightarrow{}^2B_{2g}$ and $^2B_{1g}\rightarrow{}^2E_g$ transitions. It magnetic moment is 1.91B.M. This favors the square planar stereo arrangements[17-21].

The electronic spectrum of Ni(II) complex of MAP exhibits two bands at 14823 and 22351cm^{-1} which are assignable to $^1A_{1g}\rightarrow{}^1E_g$ and $^1A_{1g}\rightarrow{}^1B_{1g}$ transitions, respectively. Since the complex is diamagnetic, so square planar geometry has been suggested. Two absorption bands at 14841cm^{-1} and 20148cm^{-1} in the Cu(II) complex have tentatively been assigned to $^2B_{1g}\rightarrow{}^2B_{2g}$ and $^2B_{1g}\rightarrow{}^2E_g$ transitions. The magnetic moment value for this complex is 1.87B.M. On the basis of findings the square planar geometry has been suggested for this complex[17-21].

ESR Spectra

The ESR spectra of Cu(II) provide information about the extent of the delocalization of unpaired electron. The X-band ESR spectrum of Cu(II) complexes (Fig. 4) was recorded in the solid state at room temperature, their $g_{\parallel}$, $g_{\perp}$, Δg, g_{av}, G have been calculated.

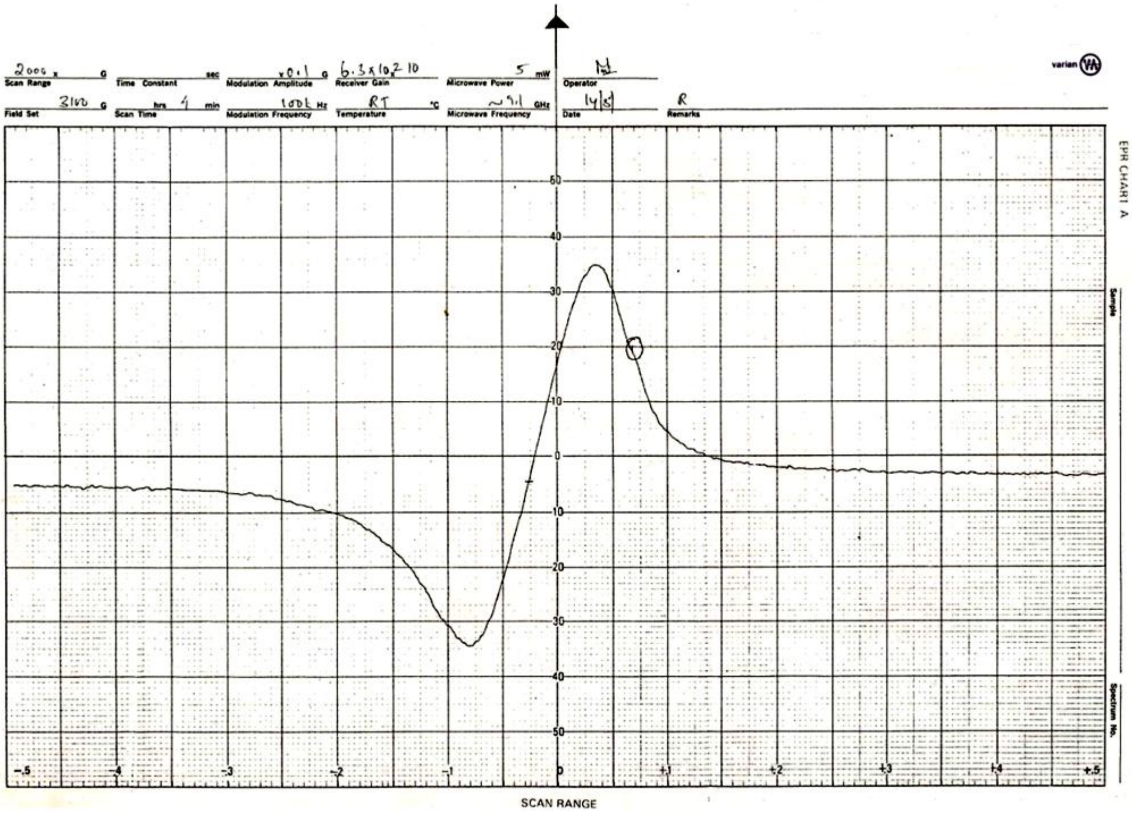


Fig. 4: ESR spectrum of Cu(II) complex of HINH ligand

The values of ESR parameters $g_{\parallel}$, $g_{\perp}$, g_{av}, Δg, G for Cu(II) complex of HINH are 2.2513, 2.0793, 2.1366, 0.1720, 3.2250, 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), 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 these 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 ($G < 4.0$) a considerable exchange coupling is present in solid complex. The G values for these Cu(II) complexes are less than four indicate, considerable exchange interaction in the complexes[22, 23].

Thermal studies:

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.

Thermogram of Ni(II) complex of HINH shows weight loss between 60º-150ºC. This corresponds to three lattice water molecules. The complex does not show any loss in weight between 150-230ºC. Elimination of one coordinated water molecule has been observed between the temperatures 240-260ºC (remaining wt% obs/cal 82/82.91). Above this temperature, a weight loss has been observed in general up to 360ºC, indicating the loss of major part of the ligand in this step (temaining wt% obs/cal 49/42.5). The decomposition of remaining intermediate moiety occurs between 360-500ºC. After 500ºC, a horizontal curve has been obtained; this suggests the formation of an ultimate pyrolysis product i.e metal oxide (remaining wt% obs/cal 21/19.9)[24,25].

X-Ray Studies

X-Ray powder diffractograms of Complex and were recorded using CuKα (1.54056Å) as source in the range 5º-60 ºC (2θ). X-ray crystal system has been worked out by trial and error method, for finding the best fit between observed and calculated $\sin^2\theta$ values. The crystal system, lattice parameters units cell have been determined with the help of diffraction data. Crystal data for Ni(II) complex of HINH are as a = b = 13.9338Å, c = 34.7975Å, V = 6755. 96Å^3, Z = 12, D_{obs} = 1.2421g/cm^3, D_{cal} 1.2847g/cm^3, reflect that this complex has crystallized in orthorhombic system. Crystal data for Ni(II) complex (Fig. 5) of MAP are as: a = b = 20.5097Å. c = 34.4477Å, V = 14490.34Å^3, Z = 26, D_{obs} = 1.488g/cm^3, Dcal = 1.5176g/cm^3, this reflects that this complex has crystallized in tetragonal system. The calculated values show good agreement and are within experimental error limits[26, 27].

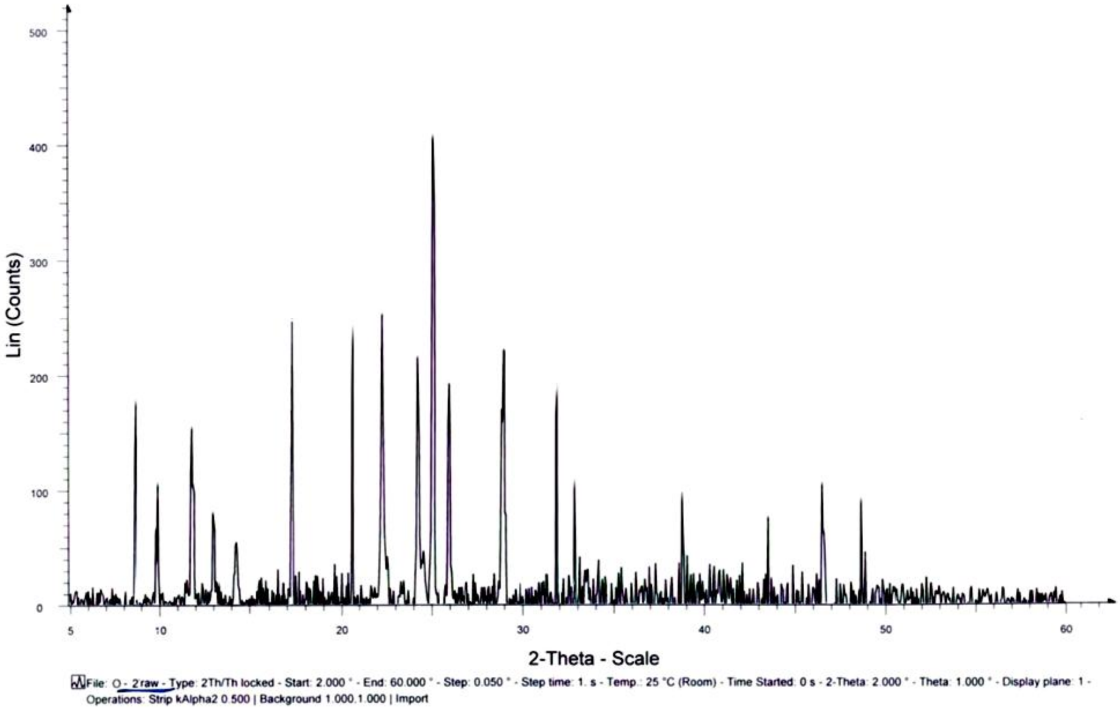


Fig. 5: XRD diffractogram of Ni(II) complex of MAP ligand

Electrical conductivity

The temperature dependence of the solid state conductivity (σ) of the compounds in their compressed pellet form have been measured at fixed frequency 1KHz in the temperature range 297-377K. the values of the solid state electrical conductivity of the Schiff base and its complexes increases with increasing temperature and decreases upon cooling over the studies temperature range indicating their semiconducting behavior. The general behavior of electrical conductivity follows the Arrhenius equation:

$$\sigma = \sigma_o \exp(-Ea/KT)$$

where Ea is the thermal activation energy of conduction, σ_o is the conductivity constant and K is the Boltzman constant.

The lots of σ vs 1000/T for all the compounds are found to be linear over a studies temperature range. The room temperature electrical conductivity of all the compounds lies in the range 6.45×10^{-6}-2.15×10^{-7}ohm^{-1}cm^{-1}. These values show their semi-conducting nature. The electrical conductivity at room temperature for the complexes of HINH are Cu > Ni and for the metal complexes of MAP are Cu > Ni. The activation energy of the compound lies in the range 0.229-0.768eV[28]. The confirming of the temperature dependence conductivity of the compounds was also checked by the repeating of the conductivity measurements.

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.

Table 2: Antibacterial screening data for the ligands and their complexes

Comp.	***E. coli***						***S. aureus***					
	Diameter of inhibition zone (mm)			% Activity index*			Diameter of inhibition zone (mm)			% Activity index*		
	25	**50**	**100**	**25**	**50**	**100**	**25**	**50**	**100**	**25**	**50**	**100**
HINH	11	14	17	50	58	61	13	16	18	72	73	75
Ni(II)	14	16	20	64	67	71	13	17	19	72	77	79
Cu(II)	16	19	23	73	79	82	14	18	20	78	82	83
MAP	12	14	16	55	58	57	12	15	18	67	68	75
Ni(II)	15	17	21	68	71	75	12	16	18	67	73	75
Cu(II)	17	20	24	77	83	86	14	18	20	78	82	83
Streptomycin (Standard)	22	24	28	100	100	100	18	22	24	100	100	100

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

Table 3: Antifungal screening data for the ligands and their complexes

Compound	Diameter of inhibition zone (mm); Concentration in ppm					
	A. niger			***C. albicans***		
	25	**50**	**100**	**25**	**50**	**100**
HINH	12	16	20	13	16	20
Ni(II)	15	19	23	17	19	24
Cu(II)	14	18	22	14	17	22
MAP	13	17	21	14	16	20
Ni(II)	15	20	24	15	17	22
Cu(II)	15	21	25	18	20	25
Miconazole (Standard)	20	24	30	22	24	29

On comparing the biological activity of the Schiff base and its metal complexes with the standard bactericide and fungicide, it is show that the 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 increases the activity are solubility, conductivity and bond length between the metal and ligand[29-33].The bactericidal and fungicidal investigation data of the compounds are summarized in Tables 2 and 3. The results of the investigations account for the antipathogenic behavior of the compounds and this efficacy is positively modified on complexation.

Conclusion

In the present research studies, our successful efforts are synthesis of some newly compounds from the conventional as well as microwave methods. These synthesized compounds have been 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. Thermal data shows degradation pattern of the complexes. The XRD patterns indicate crystalline nature of the complexes. Electrical conductivity data suggest that all the complexes fall in the semiconducting range. The antimicrobial data show that the metal complexes to be more biological active compared to those parent Schiff base ligand against all phathogenic species. The compounds also inhibit the growth of fungi and bacteria to a greater extent as the concentration is increased. The Schiff base ligands were found to be biologically active and their metal complexes displayed enhanced antimicrobial activity against one or two strains. Chelation tends to make the ligand act as more powerful and potent bactericidal agent. Further chelation can help in MDR problems.

Acknowledegments

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References

1. S Malik, S Ghosh, L Mitu. Complexes of some 3d-metals with a Schiff base derived from 5-acetamido-1,3,4-thiadiazole-2-sulphonamide and their biological activity. **J. Serb. Chem. Soc., 76(10),** 1387–1394 (2011).
2. N Raman, S Raja, J Joseph, J Raja. Synthesis, spectral characterization and DNA cleavage study of heterocyclic Schiff base metal complexes. **J. Chilean Chem. Soc., 52,** 1138-1144 (2007).
3. Z Chohan. Ni(II), Cu(II) and Zn(II) metal chelates with some thiazole derived Schiff-bases: their synthesis, characterization and bactericidal properties. **Metal Based Drugs, 6,** 75-79 (1999).
4. G Bagihalli, S Patil, P Badami. Synthesis, physicochemical investigation and biological studies of Zn(II) complexes with 1,2,4-triazole Schiff bases. **J. Iran Chem. Soc., 6,** 259-267 (2009).
5. J Parekh, P Inamdhar, R Nair, S Baluja, S Chanda. Synthesis and antibacterial activity of some Schiff bases derived from 4-aminobenzoic acid. **J. Serb. Chem. Soc., 70(10),** 1155–1161 (2005).
6. R Coombs, M Ringer, J Blacquiere, J Smith, J Neilsen, U Yoon-Seo, J Gilbert, L Leger, H Zhang, A Irving, S Wheaton, C Vogles, S Westcott, A Decken, F Baerlocher. Palladium(II) Schiff base complexes derived from sulfanilamides and aminobenzothiazoles. **Transition Metal Chem., 30(4),** 411-418 (2005).
7. R Garg, M Saini, N Fahmi, R Singh. Spectroscopic and biochemical studies of some manganese(II), oxovanadium(V) and dioxovanadium(VI) complexes S/O and N donor agents synthesized under microwave conditions. **Transition Metal Chem., 31(3),** 362-371 (2006).
8. K Mahajan, M Swami, R Singh. Microwave synthesis, spectral studies, antimicrobial approach and coordination behavior of antimony(III) and bismuth(III) compounds with benzo-thiazoline. **Russian J. Coord. Chem., 35(3),** 179-185 (2009).
9. K Mahajan, N Fahmi, R Singh. Synthesis, characterization and antimicrobial studies of Sb(III) complexes of substituted thioimines. **Indian J. Chem., A46(8),** 1221-1225 (2007).
10. K Sharma, R Singh, N Fahmi, R Singh. Microwave assisted synthesis, characterization and biological evaluation of palladium and platinum complexes with azomethines. **Spectrochim. Acta, A75(1),** 422-427 (2010).
11. K Mohanan, B Kumari, G Rijulal. Microwave assisted synthesis, spectroscopic, thermal and antifungal studies of some lanthanide(III) complexes with a heterocyclic bishydrazone. **J. Rare Earths, 26,** 16-21 (2008).
12. B Garg, D Kumar. Spectral studies of complexes of nickel(II) with tetradentate Schiff bases having N_2O_2 donor groups. **Spectrochim. Acta, A59(2),** 229-234 (2003).
13. R Dubey, U Dubey, C Mishra. Synthesis and physicochemical characterization of some Schiff base complexes of chromium(III). **Indian J. Chem., A47(8),** 1208-1212 (2008).
14. K Nakamoto. Infrared and Raman Spectra of Inorganic and Coordination Compounds, 5th ed Part A and B, New York; John Wiley & Sons (1998).
15. M Neelakantan, S Marriappan, J Dharmaraja, T Jeyakumar, K Muthukumaran. Spectral, XRD, SEM and biological activities of transition metal complexes of polydentate ligands containing thiazole moiety. **Spectrochim. Acta, A71(2),** 628-635 (2008).
16. G Mohamed, M Omar, A Hindy. Metal complexes of Schiff bases: preparation, characterization and biological activity. **Turk J. Chem., 30,** 361-382 (2006).
17. ABP Lever. Inorganic Electronic Spectroscopy, 2nd Ed. New York; Elsevier (1984).

18. S Chandra, D Jain, A Sharma, P Sharma. Coordination modes of a Schiff base pentadentate derivative of 4-aminoantipyrine with cobalt(II), nickel(II) and copper(II) metal ions: synthesis, spectroscopic and antimicrobial studies. **Molecules, 14,** 174-190 (2009).
19. B. Cristovao. Spectral, thermal and magnetic properties of Cu(II) and Ni(II) complexes with Schiff base ligands. **J. Serb. Chem. Soc., 76(12),** 1639–1648 (2011).
20. R Dutta, A Syamal. Elements of Magneto Chemistry, 2nd Ed, New Delhi; Affiliated East West Press (1993).
21. B Hathaway. Comprehensive Coordination Chemistry, Pergamon Press (UK) 5, 534-540, (1987).
22. A Mishra, L Pandey, Synthesis, characterization and solid state structural studies of oxovanadium(IV)-O,N donor Schiff base chelates. **Indian J. Chem., A44(1),** 94-97 (2005).
23. A Al-Shihri, H Abdel-Fattah. Thermogravimetric and spectroscopic characterization of trivalent lanthanide chelates with some Schiff bases, **J. Therm. Anal. Cal., 71,** 643-649 (2003).
24. Y Wang, J Liu, H Xian, G ZhaoL. Synthesis, crystal structure and kinetics of thermal decomposition of the nickel(II) complex of the Schiff base 2-[(4-methylphenylimino)-methyl]-6-methoxyphenol. **Molecules, 14,** 2582-2593 (2009).
25. K Mohanan, C Athira, Y Sindhu, M Sujamol. Synthesis, spectroscopic characterization, electrochemical behavior and thermal decomposition studies of some transition metal complexes with an azo derivative. **Spectrochim. Acta, A75(1),** 106-112 (2010).
26. A Mishra, M Soni. Synthesis, structural and biological studies of some Schiff bases and their metal complexes. **Metal Based Drug,** doi:10.1115/2008/875410(2008).
27. J Makode, A Yaul, S Bhadange, A Aswar, Physicochemical characterization, thermal and electrical conductivity studies of some transition metal complexes of bis-chelating Schiff base. **Russian J. Inorg. Chem., 54,** 1372-1378 (2009).
28. G Mohamed, M Omar, A Ibrahim. Biological activity studies on metal complexes of novel tridentate Schiff base ligand Spectroscopic and thermal characterization. **Eur. J. Med. Chem., 44,** 4801-4812 (2009).
29. Z Chohan, A Munawar, C Supuran. Transition metal ion complexes of Schiff bases synthesis, characterization and antibacterial properties. **Metal Based Drugs, 8,** 137-143 (2001).
30. W Hanna, M Moawad. Synthesis, characterization and antimicrobial activity cobalt(II), nickel(II) and copper(II) complexes with new asymmetrical Schiff base lagands derived from 7-formyanil- substituted diamine-sulphoxine and acetylacetone. **Transition Metal Chem., 26(6),** 644-651 (2001).
31. J Iqbal, S Tirmizi, F Watto, M Imran. Biological Properties of Chloro-Salicylidene Aniline and its Complexes With Co(II) And Cu(II). **Turk J. Biol., 30,** 1-4 (2006).
32. V Singh, A Katiyar. Synthesis, characterization of some transition metal(II) complexes of acetone p-amino acetophenone salicyloyl hydrazone and their antimicrobial activity. **Bio Metals, 21(4),** 491-501 (2008).