



MICROWAVE SYNTHESIS, SPECTRAL, THERMAL AND ANTIMICROBIAL ACTIVITIES OF Co(II), Ni(II) AND Cu(II) SCHIFF BASE METAL COMPLEXES

Rajendra Jain*, A.P. Mishra, A. Tiwari and S.K. Gupta

Synthetic Inorganic & Coordination Chemistry Laboratories, Dept of Chemistry, Dr. H.S. Gour Central University, Sagar (M.P), India.

*Corresponding author's E-mail: jainrajchem@gmail.com

Accepted on: 17-11-2011; Finalized on: 20-01-2012.

ABSTRACT

New some Schiff bases and their Co(II), Ni(II) and Cu(II) complexes formed by the condensation of salicylaldehyde with 2-amino-4-hydroxy-6-methylpyrimidine (SAP) and 2-chloroacetophenone with 2-chloro-4-nitroaniline (CCA) 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, ESR, magnetic susceptibility, thermal and XRD analysis. The complexes are coloured and stable in air. Analytical data revealed that all the complexes exhibited 1:2 (metal:ligand) ratio with the coordination 4 or 6. FAB-mass and thermal data show degradation pattern of the complexes. XRD patterns indicate crystalline nature for the complexes. The Schiff base and metal complexes show a good activity against the bacteria; *E. coli*, *S. aureus*, *S. fecalis* and fungi *A.niger*, *T. polysporum*, *C. albicans*. The antimicrobial results also indicate that the metal complexes are better antimicrobial agents as compared to the Schiff bases.

Keywords: Microwave synthesis, 2-amino-4-hydroxy-6-methylpyrimidine, Thermal analyses, Biological activity.

INTRODUCTION

Metal complexes have been receiving considerable attention for many years, due to their interesting characteristics in the field of material science and biological systems. A large number of Schiff bases and their complexes have possess important properties e.g. their ability to reversibly bind oxygen, transfer of an amino group and complexing ability towards some toxic metals. The high affinity for the chelation of the Schiff bases towards the transition metal ions is utilized in preparing their solid complexes. Metal complexes of Schiff bases derived from substituted salicylaldehyde and heterocyclic compounds which usually contain nitrogen, sulphur and/or oxygen as ligand atoms are becoming increasingly important as biochemical, analytical homogenous and heterogenous catalysis, magnetism and antimicrobial agents, in the design of molecular modeling and industrial fields. 2-amino-4-hydroxy-6-methyl pyrimidine is able to inhibit the synthesis of t-R.N.A. Thus, they may acts as valuable substrates in the synthesis of antitumor chemotherapeutic agents.¹⁻⁴

Microwave-assisted synthesis is a branch of green chemistry. Microwave irradiated reactions are offering reduced pollution, low cost and offer high yield together with simplicity in processing and handling. The basis of this technique of synthesis is much faster with high yields compared to conventional methods. The salient features of microwave approach are shorter reaction times, simple reaction conditions and enhancements in yields.⁵⁻¹⁰ Reports on the synthesis of metal complexes by microwave methods have been comparatively less.

In this study we report the synthesis, physicochemical characterization and biological significances of Co(II), Ni(II) and Cu(II) complexes with ligands derived from

salicylaldehyde with 2-amino-4-hydroxy-6-methyl pyrimidine (SAP) and 2-chloroacetophenone with 2-chloro-4-nitroaniline (CCA) (Fig. 1). The metal complexes formed with these two new ligands may be used as precursors for the synthesis of new compounds. Some of them may exhibit interesting physical chemical and biological properties.

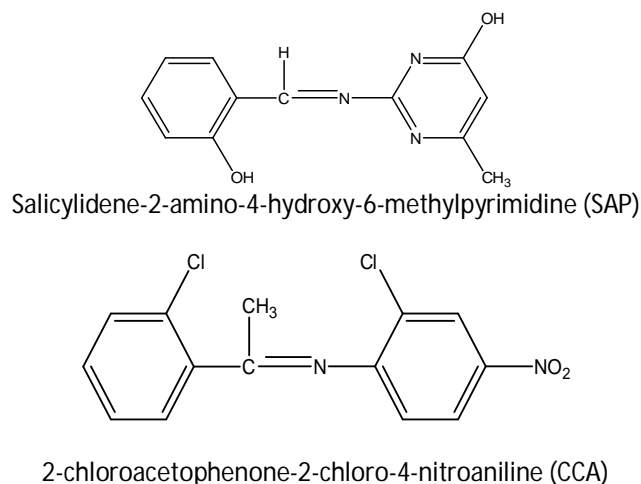


Figure 1: Structure of Schiff base ligands.

MATERIALS AND METHODS

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 purchased from Loba Chemie. Elemental analyses were performed on an Elemental 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 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 $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ 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 $4000 - 400 \text{ cm}^{-1}$. 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 $10^\circ\text{C min}^{-1}$ 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 40 kV 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°C . 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 800W and microwave frequency 2450 MHz. 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.

Antimicrobial Activity

The *in-vitro* biological screening effects of the investigated compounds were tested against *Escherichia coli*, *Staphylococcus aureus* and *Streptococcus fecalis* by the Well diffusion method using agar nutrient as the medium and Gentamycin as the control. The *in vitro* antifungal assay was performed by the disc diffusion method. The complexes and ligand were tested against the fungi *Aspergillus niger*, *Trichoderma polysporum* and *Candida albicans*, cultured on potato dextrose agar as medium. In a typical procedure, a well was created on the agar medium and nystatin as the control was inoculated with the fungi. The well was filled with the test solution, it diffuses and the growth of the inoculated fungi was affected. The inhibition zone developed on the plate was measured. The MIC of the complexes was determined by the serial dilution technique.

Conventional synthesis of the Ligands

SAP Schiff base was synthesized by the condensation of 1:1 ratio of salicylaldehyde with 2-amino-4-hydroxy-6-methylpyrimidine dissolved in ethanol. The resulting reaction mixture was refluxed for 3 h and then allowed to cool overnight. The coloured solid precipitate of Schiff base obtained was filtered, washed with cold ethanol and finally recrystallized from ethanol and ether and dried in air at room temperature and preserved in a CaCl_2 desiccator. The purity of synthesized compounds was

checked by TLC using silica gel G (yield: 78%).

CCA Schiff base was synthesized by the condensation of equimolar ratio of 2-chloroacetophenone with 2-chloro-4-nitroaniline dissolved in ethanol. The resulting reaction mixture was stirred well, refluxed for 3.5 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 in air at room temperature and finally stored under reduced pressure in a desiccator. The purity of synthesized compounds was checked by TLC using silica gel G (yield: 75%).

Microwave method for the Synthesis of Schiff bases

The equimolar (1:1) ratio of salicylaldehyde with 2-amino-4-hydroxy-6-methylpyrimidine (SAP) and 2-chloroacetophenone with 2-chloro-4-nitroaniline (CCA) were mixed thoroughly in a grinder. The reaction mixture was then irradiated by the microwave oven using 3-4 mL solvent. The reaction was completed in a short time (4-5 min). 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 and purity of the product was monitored by TLC using silica gel G (yield: 88-90%).

Conventional synthesis of the metal complexes

The metal complexes have been prepared by mixing the methanolic solution of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ to the methanolic solution of Schiff bases (SAP and CCA) in 1:2 molar ratios. The resulting mixture was then refluxed on water bath for about 6-8 hours. A coloured product appeared on standing and cooling the above solution. The complex was filtered, washed with ether and dried under reduced pressure over anhydrous CaCl_2 in a desiccator. It was further dried in an electric oven at $50-70^\circ\text{C}$ (yield: 64-72%).

Microwave method for the Synthesis of metal complexes

The ligand and the metal salt were mixed in 1:2 (metal:ligand) ratio in a grinder. The reaction mixture was then irradiated in the microwave oven using 3-4 mL solvent. The reaction was completed in a short time (6-8 min). 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: 79-84%).

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 and more or less soluble in common organic solvents. Comparative study results obtained by microwave assisted synthesis; versus conventional heating method is that some reactions which required 6-8 h. by conventional method, was completed within 6-8 min. by the microwave irradiation technique and yields have been improved from 64-78% to 79-90%. The comparison study data of

microwave and conventional methods, with analytical and physical data of the compounds are given in the Table 1. Analytical data show that metal complex have 1:2 (metal:ligand) stoichiometry. The molar conductance in DMSO suggests the complexes of SAP in non-electrolytic nature while all the three complexes of CCA in electrolytic in nature.

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

Compound Mol. Wt. (Colour)	Reaction period		Yield (%)		Elemental Analysis; Found (Calcd.) (%)				* Λ_m
	CM (h.)	MM (min.)	CM	MM	C	H	N	M	
C ₁₂ H ₁₀ N ₃ O ₂ [SAP] 229.00 (Pinkish Cream)	3.0	4.2	78	89	62.88 (62.85)	4.34 (4.36)	18.26 (18.34)	-	-
[Co(SAP) ₂].3H ₂ O 569.00 (Dark Blue)	7.3	8.0	66	82	50.34 (50.61)	3.84 (3.86)	14.76 (14.81)	10.30 (10.35)	15.4
[Ni(SAP) ₂].3H ₂ O 569.00 (Yellow)	6.3	6.9	68	80	50.61 (50.08)	3.86 (3.88)	14.66 (14.72)	10.32 (10.28)	18.3
[Cu(SAP) ₂].3H ₂ O 573.00 (Dark Green)	5.9	7.1	74	84	50.08 (50.26)	3.82 (3.83)	14.76 (14.69)	11.05 (11.08)	11.2
C ₁₄ H ₁₀ N ₂ O ₂ Cl ₂ [CCA] 309 (Yellow)	3.5	4.5	75	89	54.36 (54.39)	3.23 (3.28)	9.06 (9.10)	-	-
[Co(CCA) ₂ (H ₂ O) ₂].Cl ₂ 785 (Green)	8.0	7.8	64	79	42.80 (42.85)	3.05 (3.06)	7.13 (7.14)	7.50 (7.51)	142.3
[Ni(CCA) ₂ (H ₂ O) ₂].Cl ₂ .2H ₂ O 821 (Yellow)	7.2	7.0	70	82	42.80 (42.42)	3.41 (3.41)	6.82 (6.83)	7.12 (7.14)	129.4
[Cu(CCA) ₂ (H ₂ O) ₂].Cl ₂ 789 (Yellowish brown)	7.5	6.9	68	81	42.58 (42.63)	3.04 (3.04)	7.09 (7.10)	8.05 (8.06)	139.4

*Conductance (Λ_m) = S cm² mol⁻¹

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

Compound	$\nu(\text{C=N})$	$\nu(\text{C-O})$	$\nu(\text{C=N pyrimidine ring})$	$\nu(\text{H}_2\text{O})$	$\nu(\text{M-O})$	$\nu(\text{M-N})$
[SAP]	1628	1239	1402	-	-	-
[Co(SAP) ₂].3H ₂ O	1602	1276	1403	3451	547	480
[Ni(SAP) ₂].3H ₂ O	1607	1290	1402	3380	549	484
[Cu(SAP) ₂].3H ₂ O	1598	1286	1405	3420	540	490
[CCA]	1626	-	-	-	-	-
[Co(CCA) ₂ (H ₂ O) ₂].Cl ₂	1610	-	-	3397,790	-	484
[Ni(CCA) ₂ (H ₂ O) ₂].Cl ₂ .2H ₂ O	1608	-	-	3387,795	-	480
[Cu(CCA) ₂ (H ₂ O) ₂].Cl ₂	1598	-	-	3368,793	-	476

Table 3: Electronic spectral and magnetic moment values of complexes

Complex	Transitions	Bands (cm ⁻¹)	μ_{eff} (B.M.)	Geometry
[Co(SAP) ₂].3H ₂ O	⁴ A ₂ → ⁴ T ₁ (F) (v ₁)	-	4.42	Tetrahedral
	⁴ A ₂ → ⁴ T ₁ (F) (v ₂)	12315		
	⁴ A ₂ → ⁴ T ₁ (P) (v ₃)	20040		
[Ni(SAP) ₂].3H ₂ O	¹ A _{1g} → ² E _g (v ₁)	12300	Dia.	Square planar
	¹ A _{1g} → ¹ B _{2g} (v ₂)	23255		
	¹ A _{1g} → ¹ B _{1g} (v ₃)	-		
[Cu(SAP) ₂].3H ₂ O	² E _g → ² T _{2g}	15267	1.83	Octahedral
[Co(CCA) ₂ (H ₂ O) ₂].Cl ₂	⁴ A ₂ → ⁴ T ₁ (F) (v ₁)	-	4.15	Tetrahedral
	⁴ A ₂ → ⁴ T ₁ (F) (v ₂)	16321		
	⁴ A ₂ → ⁴ T ₁ (P) (v ₃)	20085		
[Ni(CCA) ₂ (H ₂ O) ₂].Cl ₂ .2H ₂ O	¹ A _{1g} → ² E _g (v ₁)	12545	Dia.	Square planar
	¹ A _{1g} → ¹ B _{2g} (v ₂)	20085		
	¹ A _{1g} → ¹ B _{1g} (v ₃)	-		
[Cu(CCA) ₂ (H ₂ O) ₂].Cl ₂	² B _{1g} → ² B _{2g}	15267	1.94	Square planar
	¹ A _{1g} → ² E _g	19360		

FAB Mass spectra

The FAB-mass spectra suggested that all the complexes have a monomeric nature. These complexes show molecular ion peaks in good agreement with the empirical formula suggested by elemental analyses.

The FAB mass spectrum of $[\text{Ni}(\text{SAP})_2] \cdot 3\text{H}_2\text{O}$ shows a molecular ion peak (M^+) at m/z 567 suggesting the complex to be monomeric. The spectrum of complex also shows a series of peak at m/z 549, 515, 486, 449, 374, 296 and 95 corresponding to various fragments. Their intensity gives an idea about the abundance and stability of the fragments.

The FAB mass spectrum of $[\text{Ni}(\text{CCA})_2(\text{H}_2\text{O})_2] \cdot \text{Cl}_2 \cdot 2\text{H}_2\text{O}$ shows a molecular ion peak (M^+) at m/z 823 amu which suggests the monomeric nature of the complex. The spectrum of complex also shows series of peaks 777, 713, 665, 600, 540, 447, 369, 293, 190, 89 corresponding to various fragments. The value of 89 corresponds to Ni with N chelated ligand moiety.^{11, 12}

Infrared 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.

The SAP ligand (Schiff base) exhibited a strong band at 1628 cm^{-1} due to azomethine $\nu(\text{C}=\text{N})$ group. This has shifted towards lower frequency. It shifts down by 21-30 cm^{-1} in the metal complexes. This suggests the coordination through the azomethine nitrogen. Strong bands observed at 1402 and 1032 cm^{-1} have been tentatively assigned to pyrimidine ring vibrations. These bands remain unchanged in the spectrum of complexes indicating the non involvement of pyrimidine nitrogen in co-ordination. Another important ligand band, which occurs at about 1361 cm^{-1} due to phenolic $-\text{OH}$, has been found absent in complexes. This indicates that phenolic $-\text{OH}$ is deprotonated on co-ordination with metal. A band at 1239 cm^{-1} due to phenolic C-O in ligand spectra shift to higher side by 1276 ± 10 . The bands $547 \pm 2 \text{ cm}^{-1}$ and $484 \pm 6 \text{ cm}^{-1}$ in the complexes have tentatively been assigned to $\nu(\text{M}-\text{O})$ and $\nu(\text{M}-\text{N})$ bonding respectively. The IR spectrum of complexes exhibited broad band at about 3451 cm^{-1} , 3380 cm^{-1} and 3420 cm^{-1} (stretching) assignable to the associated water molecule.¹³⁻¹⁷

The IR spectrum of CCA ligand exhibited a strong band at 1628 cm^{-1} due to $\nu(\text{C}=\text{N})$ azomethine group. This band shift lower energy region by 20-30 cm^{-1} in the complexes. It suggests the coordination through azomethine nitrogen. This is further supported by the new band at $480 \pm 4 \text{ cm}^{-1}$. The appearance of broad band at $3355 \pm 7 \text{ cm}^{-1}$ in the spectrum of complexes has been assigned to associated water molecules. A medium intensity band at

$790-795 \text{ cm}^{-1}$ suggests the presence of coordinated water in Co(II), Ni(II) and Cu(II) complexes.¹³⁻¹⁷

Magnetic moments and electronic spectra

The electronic spectral data of the metal complexes in DMSO solution are given in Table 3. The nature of the ligand field around the metal ion has been deduced from the electronic spectra.

The electronic spectrum of Co(II) complex of SAP shows two bands of appreciable intensity at 12315 cm^{-1} and 20040 cm^{-1} . These transitions have tentatively been assigned to ${}^4\text{A}_2 \rightarrow {}^4\text{T}_1$ (ν_2) and ${}^4\text{A}_2 \rightarrow {}^4\text{T}_1$ (P) (ν_3) cm^{-1} respectively. The magnetic moment is 4.42 B.M. Thus, the tetrahedral geometry has been suggested for this complex. The electronic spectrum of Ni(II) complex of SAP exhibited two bands at 12300 cm^{-1} and 23255 cm^{-1} , which are assignable to ${}^1\text{A}_{1g}(\text{F}) \rightarrow {}^2\text{E}_g$ (ν_1) and ${}^1\text{A}_{1g} \rightarrow {}^1\text{B}_{2g}$ (ν_2) transitions, respectively. It is a diamagnetic complex. Therefore, square planar geometry has been suggested for this complex. In the spectrum of Cu(II) complex of SAP, a single broad band at 15267 cm^{-1} has been observed which is attributed to ${}^2\text{E}_g \rightarrow {}^2\text{T}_{2g}$ transition. Its magnetic moment is 1.83 B.M. An octahedral geometry has been suggested for this Cu(II) complex.¹⁸⁻²²

The electronic spectrum of Co(II) complex of CCA shows two bands of appreciable intensity at 16321 cm^{-1} and 20085 cm^{-1} which have tentatively been assigned to ${}^4\text{A}_2 \rightarrow {}^4\text{T}_1$ (F) (ν_2) and ${}^4\text{A}_2 \rightarrow {}^4\text{T}_1$ (P) (ν_3) transitions. The magnetic moment is 4.35 B.M. Thus the tetrahedral geometry has been suggested for this complex. The electronic spectrum of Ni(II) complex of CCA exhibited two bands at 12545 cm^{-1} and 20086 cm^{-1} , which are assignable to ${}^1\text{A}_{1g} \rightarrow {}^2\text{E}_g$ (ν_1) and ${}^1\text{A}_{1g} \rightarrow {}^1\text{B}_{2g}$ (ν_2) transition respectively. It is a diamagnetic complex. Therefore, square planar geometry has been suggested for this complex. The absorption spectrum of Cu(II) complex of CCA showed two bands at 15267 and 19360 cm^{-1} which have been assigned to ${}^2\text{B}_{1g} \rightarrow {}^2\text{B}_{2g}$ and ${}^1\text{A}_{1g} \rightarrow {}^2\text{E}_g$ transition respectively. The magnetic moment is 1.94 B.M. Thus the square planar geometry has been suggested for this complex.¹⁸⁻²²

ESR Spectra

The spectra of Cu(II) complex have been recorded on X-band at frequency 9.5 GHz under the magnetic field strength 3400 Gauss. The values of ESR parameters of Cu(II) complex of SAP viz. g^{11} , g^{\perp} , g_{av} , Δg and G are 2.2495, 2.0599, 2.1018, 0.7285 and 1.6 respectively.

The parameter g_{av} was obtained by equation [$(g_{av}) = 1/3(2g^{\perp} + g^{11})$]. The g -tensor values of Cu(II) complex can be used to derive the ground state. The value of $g^{11} > g^{\perp}$ in the complex, suggest that the unpaired electron is localized in $d_{x^2-y^2}$ orbital. The value of g^{11} for the Cu(II) complex indicates the prevalence of covalent character in the metal-ligand bond. The g values are related to the axial symmetry parameter G by the Hathway expression $G = (g^{11} - 2)/(g^{\perp} - 2)$. According to Hathway if the value of 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 interaction is indicated in the complex.^{23, 24}

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 TG curve of the $[\text{Co}(\text{SAP})_2] \cdot 3\text{H}_2\text{O}$ complex shows a weight loss between 70-140°C; the weight loss indicates the presence of three lattice water molecules (Remaining Wt.%, Obs./Calcd. 91.3/90.5). The complex does not show any loss in weight between 160-280°C. Above 290°C, a general weight loss has been observed up to 450°C. This corresponds to the loss of partially decomposed ligand part from the complex. (Remaining Wt.%, Obs./Calcd. 54.10/52.18). Above 460°C, an inflection occurs in the curve and weight loss goes up to the temperature 650°C.

This indicates the elimination of remaining thermally degradable part of the complex. After this temperature, a horizontal region in the curve showing no weight change due to the metal oxide as a final pyrolysis product (Remaining Wt.%, Obs./Calcd. 17.21/15.99).²⁵

The TG curve of the $[\text{Co}(\text{CCA})_2(\text{H}_2\text{O})_2] \cdot \text{Cl}_2$ complex shows no loss in weight up to 120°C. This indicates the absence of lattice water molecule in the complex. On increasing the temperature above 120°C, a weight loss has been observed corresponding to two coordinated water molecules (Remaining Wt.%, Obs./Calcd. 96.00/95.41). The decomposition of remaining ligand moiety occurs between 220-370°C. This corresponds to the loss of partially decomposed ligand part from the complex. (Remaining Wt.%, Obs./Calcd. 48.6/45.25). The decomposition of remaining ligand moiety occurs between 400-620°C. A horizontal curve has been obtained above 620°C, suggesting the formation of ultimate pyrolysis product the metal oxide. (Remaining Wt.%, Obs./Calcd. 19.78/18.56).²⁵

Table 4: Antimicrobial data (at MIC) of the investigated compounds

Compound	Antibacterial									Antifungal								
	<i>E. coli</i>			<i>S. aureus</i>			<i>S. fecalis</i>			<i>A. niger</i>			<i>T. polysporum</i>			<i>C. albicans</i>		
	25*	50*	100*	25*	50*	100*	25*	50*	100*	25*	50*	100*	25*	50*	100*	25*	50*	100*
SAP	12	15	18	13	15	18	12	14	16	12	16	19	12	16	19	10	13	15
Co(II)	22	26	30	18	20	23	17	19	22	15	18	20	18	21	23	17	20	25
Ni(II)	16	20	24	15	18	21	16	19	22	14	16	19	17	20	23	15	18	21
Cu(II)	22	25	32	18	21	24	17	20	22	16	19	22	19	22	24	18	20	26
CCA	11	14	15	10	12	14	11	13	15	11	15	18	13	17	20	12	15	18
Co(II)	20	24	28	16	18	20	17	20	23	17	19	22	19	22	24	18	20	25
Ni(II)	18	22	26	12	15	18	13	15	19	16	18	20	18	20	22	16	19	22
Cu(II)	22	25	32	13	15	19	16	18	21	15	18	20	20	23	25	19	21	26
Nystatin	-	-	-	-	-	-	-	-	-	20	22	24	23	25	27	20	23	29
Gentamycin	20	25	29	19	22	24	18	21	23	-	-	-	-	-	-	-	-	-

X-ray diffraction (XRD)

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 $\text{CuK}\alpha$ as source in the range 5°-70° (2θ). X-ray crystal system has been worked out by trial, error methods for finding the best fit between observed and calculated $\sin^2\theta$. The X-ray diffractogram of Ni(II) complex of SAP, shows 20 reflections with maximum of reflection at $2\theta = 4.64$ which corresponds to $d = 17.659 \text{ \AA}$. A comparison of the value reveals that there is a good agreement between calculated and observed value of $\sin 2\theta$. The observed values fit well in the orthorhombic system and gives a unit cell with lattice constant $a = 19.02 \text{ \AA}$, $b = 16.65 \text{ \AA}$, $c = 15.17 \text{ \AA}$, and cell volume $V = 4804.08 \text{ \AA}^3$, $Z = 6$, (number of molecule per unit cell). The observed value of density is 1.2160 g/cm^3 while the calculated value has been found to be 1.262 g/cm^3 .^{26, 27}

The diffraction of Co(II) complex of CCA consist 17 reflections. A comparison of the value reveals that there is a good agreement between calculated and observed value of $\sin^2\theta$. The observed values fit well in the

tetragonal system and gives a unit cell with lattice constant $a = b = 52.16 \text{ \AA}$, $c = 7.92 \text{ \AA}$ and cell volume $V = 21547.67 \text{ \AA}^3$ and $Z = 17$ (number of molecule per unit cell). The cell volume gives the observed value of density 1.0046 g/cm^3 while the calculated value of density has been found to be 1.0050 g/cm^3 . The density of complex has been determined experimentally which show good agreement with the calculated values.^{26, 27}

Antimicrobial activity

The *in vitro* anti-microbial activity of the investigated compounds was, tested against the microorganisms *E. coli*, *S. aureus*, *S. fecalis*, *A. niger*, *T. polysporum*, *C. albicans* by the serial dilution method. The minimum inhibitory concentration (MIC) values of the compounds against the growth of micro-organisms are summarized in Table 4.

These observations show that the majority of the complexes are more active than their respective Schiff base ligand. 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. The



chelation either enhances or reduces the antimicrobial activity; sometimes it remains neutral. Thus, metal chelation may increase or decrease/ suppress the therapeutic value of organic compounds (drug). It may keep the property intact by further stabilizing the drug and/or reducing the biodegradability/metabolic decay of the organic ligands through chelation.²⁸⁻³²

CONCLUSION

In the present research studies, our efforts are synthesized of some newly compounds from the conventional as well as microwave methods. These synthesized compounds 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. FAB-mass and thermal data show degradation pattern of the complexes. Thermogravimetric studied of the complexes also helped to characterize the complexes. The XRD patterns indicate crystalline nature of the complexes. The findings of the bactericidal and fungicidal investigation of the compounds against the opportunistic pathogens reveal that the synthesized compounds have the antipathogenic activity.

Acknowledgements: We are thankful to I.I.T. Mumbai for ESR analysis. We also acknowledge SAIF, CDRI Lucknow for micro analysis and spectral analysis. Thanks are also due to the Head, Department of Chemistry, Botany and Physics, Dr. Hari Singh Gour University, Sagar (M.P.) for providing Laboratory facilities.

REFERENCES

- Shukla D, Gupta L K and Chandra S, Spectroscopic studies on chromium(III), manganese(II), cobalt(II), nickel(II) and copper(II) complexes with hexadentate nitrogen-sulfur donor [N2S4] macrocyclic ligand. *Spectrochim. Acta*, 71A, 2008, 746-750.
- Soliman A A and Mohamed G G, Study of the ternary complexes of copper with salicylidene-2-aminothiophenol and some amino acids in the solid state. *Thermochim. Acta*, 421, 2004, 151-159.
- Raman N, Raja S J, Joseph J and Raja J D, Synthesis, spectral characterization and DNA cleavage study of heterocyclic Schiff base metal complexes. *J. Chil. Chem. Soc.*, 52, 2007, 1138-1141.
- Mishra A P and Pandey L R, Synthesis, structure and reactivity of oxovanadium(IV) Schiff base complexes. *Indian J. Chem.*, 44A, 2005, 1800-1805.
- Mahajan K, Fahmi N and Singh R V, Synthesis, characterization and antimicrobial studies of Sb(III) complexes of substituted thioimines. *Indian J. Chem.*, 46A, 2007, 1221-1225.
- Mohanan K, Kumari B S and Rijulal G, Microwave assisted synthesis, spectroscopic, thermal and antifungal studies of some lanthanide(III) complexes with a heterocyclic bishydrazone. *J. Rare Earths*. 26, 2008, 16-21.
- Sharma K, Singh R, Fahmi N and Singh R V, Microwave assisted synthesis, characterization and biological evaluation of palladium and platinum complexes with azomethines. *Spectrochim. Acta A*. 75, 2010, 422-427.
- Garg R, Saini M K, Fahmi N and Singh R V, Spectroscopic and biochemical studies of some manganese(II), oxovanadium(V) and dioxovanadium(VI) complexes S/O and N donor agents synthesized under microwave conditions. *Trans. Met. Chem.*, 31, 2006, 362-367.
- Sun Y, Machala M L and Castellano F N, Controlled microwave synthesis of Ru^{II} synthons and chromophores relevant to solar energy conversion. *Inorg. Chim. Acta.*, 363, 2010, 283-287.
- Mahajan K, Swami M and Singh R V, Microwave synthesis, spectral studies, antimicrobial approach and coordination behavior of antimony(III) and bismuth(III) compounds with benzothiazoline. *Russ. J. Coord. Chem.*, 35, 2009, 179-185.
- Dubey R K, Dubey U K and Mishra CM, Synthesis and physicochemical characterization of some Schiff base complexes of chromium(III). *Indian J. Chem.*, 47, 2008, 1208-1212.
- Mishra A P and Soni M, Synthesis, structural and biological studies of some Schiff bases and their metal complexes. *Metal Based Drug*, 2008.
- Mohamed G G, Omar M M and Hindy A M, Metal complexes of Schiff bases: preparation, characterization and biological activity. *Turk J. Chem.*, 30, 2006, 361-379.
- Ourari A, Ouari K, Moumeni W and Sibous L, Unsymmetrical tetradentate Schiff base complexes derived from 2,3-diphenol and salicylaldehyde or 5-bromosalicylaldehyde. *Trans. Met. Chem.*, 31, 2006, 169-175.
- Nakamoto K, Infrared and Raman Spectra of Inorganic and Coordination Compounds, 5th ed. John Wiley and Sons, Part A and B, New York, 1998.
- Abdallah S M, Zyed M A and Mohammed G G, Synthesis and spectroscopic characterization of new tetradentate Schiff base and its coordination compounds of NOON donor atoms and their antibacterial and antifungal activity. *Arabian J. Chem.*, 3, 2010, 103-113.
- Garg B S and Kumar D N, Spectral studies of complexes of nickel(II) with tetradentate Schiff bases having N₂O₂ donor groups. *Spectrochim. Acta A*. 59, 2003, 229-234.
- Mishra A P, Mishra R K and Shrivastava S P, Structural and antimicrobial studies of coordination compounds of Vo(II), Co(II), Ni(II) and Cu(II) with some Schiff bases involving 2-amino-4chlorophenol. *J. Serb. Chem. Soc.*, 74, 2009, 523-535.
- Lever A B P, Inorganic Electronic Spectroscopy, 2nd ed. Elsevier, New York, 1984.
- Chandra S, Jain D, Sharma A K and Sharma P, 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, 2009, 174-190.
- Makode J T, Yaul A R, Bhadange S G and Aswar A S, Physicochemical characterization, thermal and electrical conductivity studies of some transition metal complexes of



- bis-chelating Schiff base. *Russ. J. Inorg. Chem.*, 54, 2009, 1372-1377.
22. Dutta R L and Syamal A, Elements of Magneto Chemistry, 2nd ed. Affiliated East West Press, New Delhi, 1993.
23. Mishra A P and Pandey L R, Synthesis, characterization and solid state structural studies of oxovanadium(IV)-O,N donor schiff base chelates, *Indian J. Chem.*, 44, 2005, 94-97.
24. Hathaway B J and Billing D E, *Coordination Chemistry Review*, 5, 1970, 143.
25. Wang Y F, Liu J F, Xian H D and Zhao G L, 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, 2009, 2582-2593.
26. Sujamol M S, Athira C J, Sindhu Y and Mohanan K, Synthesis, spectroscopic characterization, electrochemical behavior and thermal decomposition studies of some transition metal complexes with an azo derivative. *Spectrochim. Acta A*, 75, 2010, 106-112.
27. Singh V P, Katiyar A and Singh S, Synthesis, characterization of some transition metal(II) complexes of acetone p-amino acetophenone salicyloyl hydrazone and their antimicrobial activity. *Bio Metals*, 2008.
28. Chohan Z H, Ni(II), Cu(II) and Zn(II) metal chelates with some thiazole derived Schiff-bases: their synthesis, characterization and bactericidal properties. *Metal Based Drug*, 6, 1999, 75-79.
29. Coombs R R, Westcott S A, Decken A and Baerlocher F J, Palladium(II) Schiff base complexes derived from sulfanilamides and aminobenzothiazoles. *Trans. Met. Chem.*, 30, 2005, 411-418.
30. Mohamed G G, Omar M M and Ibrahim A A, Biological activity studies on metal complexes of novel tridentate Schiff base ligand. Spectroscopic and thermal characterization. *Eur. J. Med. Chem.*, 44, 2009, 4801-4812.
31. Neelakantan M A, Marriappan S S, Dharmaraja J, Jeyakumar T and Muthukumaran K, Spectral, XRD, SEM and biological activities of transition metal complexes of polydentate ligands containing thiazole moiety. *Spectrochim. Acta A*, 71, 2008, 628-635.
32. Chohan Z H, Munawar A and Supuran C T, Transition metal ion complexes of Schiff bases synthesis, characterization and antibacterial properties. *Metal Based Drugs*, 8, 2001, 137-143.

