

Microwave synthesis, spectral, thermal, and antimicrobial activities of some transition metal complexes involving 5-bromosalicylaldehyde moiety

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ABSTRACT

The coordination complexes of Co(II), Ni(II) and Cu(II) derived from 5-bromosalicylidene-3,4-dimethylaniline (BSMA) and 5-bromosalicylidene-3,4-dichloroaniline (BSCA) have been synthesized by conventional as well as microwave methods. These compounds have been characterized by elemental analysis, FT-IR, molar conductance, electronic spectra, ¹H-NMR, FAB-mass, ESR, magnetic susceptibility, electrical conductivity and thermal analysis. The complexes are coloured and stable in air. Analytical data revealed that all the complexes exhibited 1:2 (metal: ligand) ratio with coordination number 4 or 6. IR data shows that the ligand coordinates with the metal ions in a bidentate manner through the phenolic oxygen and azomethine nitrogen. FAB-mass and thermal data show degradation pattern of the complexes. Solid state electrical conductivity studies reflect semiconducting nature of the complexes. 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*.

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1. 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. Optoelectronic, electrical and magnetic properties of the metals and metalloids can be tailored by reacting them with different ligands. A large number of Schiff bases and their complexes may exhibit the properties like to reversibly bind oxygen, transfer of an amino group, as nanoprecursors and varied complexing/redox ability. The Schiff bases have high affinity to chelate with the transition metal ions, hence are attracting attention due to potential applications in areas viz. biology, catalysis,

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thermal, electrical, optical, magnetic etc. Metal complexes are suitable to molecular materials, on the basis of electronic properties associated with the metal center¹⁻³.

Schiff base ligands containing O and N donor atoms play an important role in coordination chemistry related to catalysis and enzymatic reaction, magnetism and molecular architecture. Metal complexes with Schiff base ligands containing salicylaldehyde and its derivatives; have been extensively studied. Metal complexes with such ligands are quite common and also reflect their facile synthesis, accessibility of diverse structural modifications and wide applications in different fields, such as catalysis, biological systems and material chemistry^{4,5}.

Microwave reactions under solvent free and 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 yields⁶⁻¹¹.

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 5-bromosalicylaldehyde with 3,4-dimethylaniline (BSMA) and 3,4-dichloroaniline (BSCA) (Fig. 1). The reaction was carried out by both conventional and microwave methods. 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.

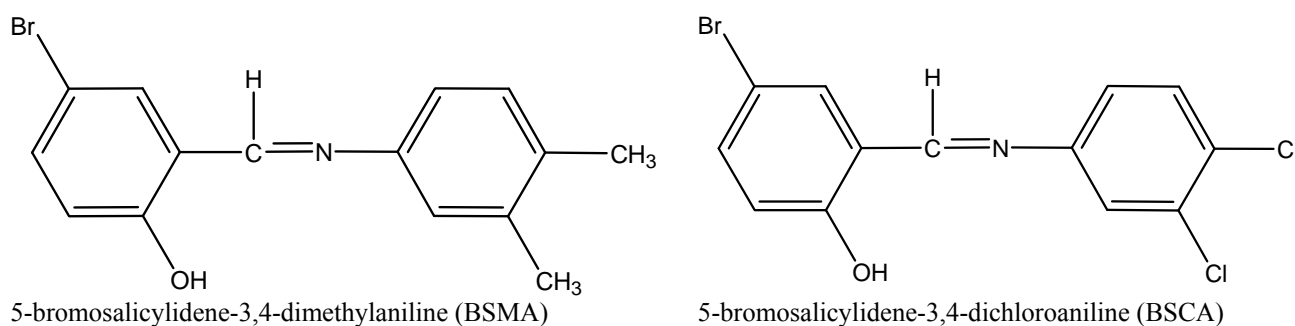


Fig. 1. Structure of Schiff base ligands

2. 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.

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 are that some reactions which required 3.4-7.9 h by conventional method, was completed within 4-8 min by the microwave irradiation technique and yields have been improved from 66-78% to 81-88%. The comparative results of microwave and conventional methods, with analytical and physical data of the compounds are given in the Table 1. All the metal chelates have 1:2 (metal:ligand) stoichiometry. The observed molar conductance of the complexes in DMSO at room temperature is consistent with the non-electrolytic nature of the complexes.

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

Compounds (colour)	Empirical Formula (Formula Weight)	Reaction period		Yield (%)		Elemental analysis, Found (Calcd.) %				A_m ($\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$)
		CM (h)	MM(min)	CM	MM	C	H	N	M	
BSMA (Brown)	$\text{C}_{15}\text{H}_{14}\text{NOBr}$ (304.18)	3.4	4	78	88	59.16 (59.23)	4.59 (4.64)	4.52 (4.60)	-	-
[Co(BSMA) ₂ (H ₂ O) ₂] (Yellowish Brown)	$\text{C}_{30}\text{H}_{30}\text{N}_2\text{O}_4\text{Br}_2\text{Co}$ (701.31)	7.2	8	71	84	51.30 (51.38)	4.22 (4.31)	3.82 (3.99)	8.31 (8.40)	15.2
[Ni(BSMA) ₂]2H ₂ O (Dark Brown)	$\text{C}_{30}\text{H}_{30}\text{N}_2\text{O}_4\text{Br}_2\text{Ni}$ (701.07)	7.0	7	66	83	51.36 (51.40)	4.26 (4.31)	3.98 (4.00)	8.32 (8.37)	12.5
[Cu(BSMA) ₂]2H ₂ O (Yellowish Green)	$\text{C}_{30}\text{H}_{30}\text{N}_2\text{O}_4\text{Br}_2\text{Cu}$ (705.92)	6.5	7	70	85	51.00 (51.04)	4.21 (4.28)	3.92 (3.97)	8.89 (9.00)	9.6
BSCA (Yellow)	$\text{C}_{13}\text{H}_8\text{NOCl}_2\text{Br}$ (345.02)	3.9	4	75	87	45.20 (45.26)	2.29 (2.34)	4.01 (4.06)	-	-
[Co(BSCA) ₂ (H ₂ O) ₂] (Reddish Brown)	$\text{C}_{26}\text{H}_{18}\text{N}_2\text{O}_4\text{Cl}_4\text{Br}_2\text{Co}$ (782.99)	7.9	8	68	82	39.81 (39.88)	2.30 (2.32)	3.54 (3.58)	7.49 (7.53)	11.2
[Ni(BSCA) ₂]2H ₂ O (Brownish Yellow)	$\text{C}_{26}\text{H}_{18}\text{N}_2\text{O}_4\text{Cl}_4\text{Br}_2\text{Ni}$ (782.75)	7.0	8	70	83	39.86 (39.90)	2.25 (2.32)	3.50 (3.58)	7.42 (7.50)	7.9
[Cu(BSCA) ₂] (Yellowish Brown)	$\text{C}_{26}\text{H}_{14}\text{N}_2\text{O}_2\text{Cl}_4\text{Br}_2\text{Cu}$ (751.57)	7.5	7	69	81	41.50 (41.55)	1.80 (1.88)	3.70 (3.73)	8.42 (8.46)	10.3

CM = Conventional Method; MM = Microwave Method

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 of the [Co(BSCA)₂(H₂O)₂] complex exhibited the molecular ion (M^+) peak at $m/z = 702$ suggesting the monomeric nature of the complex. The other important peaks of appreciable intensity have been observed at m/z values, obs.(calcd.) – 663(665), 606(605), 444(445), 298(295) and 116(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 702 corresponds to the nearest composition [Co(BSCA)₂(H₂O)₂] and 116 to Co metal with chelated N and O ligand moiety. The FAB-mass spectrum of the [Ni(BSCA)₂]2H₂O complex showed a characteristic molecular ion (M^+) peak at $m/z = 784$, 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.(calcd.) – 784(783), 745(747), 587(587), 446(445), 296(295) and 118(119) suggesting the fragmentation pattern. The m/z value 784 corresponds to the nearest composition of the [Ni(BSCA)₂]2H₂O and 118 corresponds to Ni metal with chelated O and N ligand moiety^{12, 13}.

¹H-NMR spectra

The proton NMR spectra of the Schiff base ligands were recorded in DMSO-d₆ solution using TMS as internal standard. The ¹H-NMR spectra of the BSMA and BSCA ligands showed multiplet at δ 7.127-7.652 and 7.232-7.874 ppm due to aromatic protons while the azomethine proton resonates as singlet at δ 8.461 and 8.941 ppm. The phenolic OH groups have signals at δ 12.243 and 12.854 ppm which are disappeared on deuteration^{14, 15}.

IR spectra

The data of the IR spectra of Schiff base ligand and their 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 ligands and complexes were considered and compared.

IR spectra of the BSMA and BSCA Schiff base ligands exhibited the most characteristic bands at 3312-3335 cm^{-1} $\nu(\text{O-H})$, 1620-1628 cm^{-1} $\nu(\text{C=N, azomethine})$ and 1248-1255 cm^{-1} $\nu(\text{C-O})$. The

ligand spectra showed bands at 3316-3304 and 1340-1348 cm^{-1} due to the stretching and deformation of the phenolic OH¹⁶. These are absent in the spectra of the complexes indicates the deprotonation of the hydroxyl group and co-ordination through oxygen. The band 1620-1628 cm^{-1} due to the azomethine group of the Schiff bases have shifted to lower frequency (1595-1605 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 ion. The phenolic $\nu(\text{C-O})$ stretching vibration that appeared at 1248-1255 cm^{-1} in Schiff bases shift towards higher frequencies (25-30 cm^{-1}) in the complexes. This shift confirms the participation of oxygen in the C-O-M bond. The appearance of broad bands around at (3388-3420 cm^{-1}) in the spectra of complexes may be due to water molecules. But this band is not presented in the Cu(II)-BSCA, indicating that the absence of water molecules in Cu(II) complexes. In the low frequency region, a band at 812 and 800 cm^{-1} in Co(II)-BSMA and Co(II)-BSCA (OH rocking), respectively, in the complexes, suggest the presence of coordinated water molecules in these complexes. Two new bands appearing in the low frequency range 538-556 cm^{-1} and 488-496 cm^{-1} are assigned to $\nu(\text{M-O})$ and $\nu(\text{M-N})$, respectively¹⁷⁻¹⁹.

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

Table 2. Selected IR bands (cm^{-1}) of Schiff base ligands and their complexes

Compound	$\nu(\text{C=N})$	$\nu(\text{O-H})$	$\nu(\text{C-O})$	H ₂ O	$\nu(\text{M-O})$	$\nu(\text{M-N})$
BSMA	1620	3312	1248	-	-	-
[Co(BSMA) ₂ (H ₂ O) ₂]	1600	-	1275	3388, 812	538	488
[Ni(BSMA) ₂].2H ₂ O	1598	-	1279	3420	540	489
[Cu(BSMA) ₂].2H ₂ O	1595	-	1278	3390	545	495
BSCA	1628	3335	1255	-	-	-
[Co(BSCA) ₂ (H ₂ O) ₂]	1605	-	1285	3375, 800	556	492
[Ni(BSCA) ₂].2H ₂ O	1599	-	1282	3400	552	496
[Cu(BSCA) ₂]	1604	-	1280	-	554	490

Electronic spectra and magnetic moment

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 spectra of [Co(BSMA)₂(H₂O)₂] and [Co(BSCA)₂(H₂O)₂] exhibited three bands in the region of 9425-9750 cm^{-1} , 15257-15748 cm^{-1} and 19612-19607 cm^{-1} which have tentatively been assigned to ${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{2g}(\text{F})$ (ν_1), ${}^4\text{T}_{1g} \rightarrow {}^4\text{A}_{2g}(\text{F})$ (ν_2) and ${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{1g}(\text{P})$ (ν_3) transitions, respectively. The values of magnetic moment for these complexes are 5.08 and 5.12 B.M., respectively. Thus the octahedral geometry has been suggested for these complexes.

The absorption spectra of the [Ni(BSMA)₂].2H₂O and [Ni(BSCA)₂].2H₂O exhibited bands at 12112-12689 cm^{-1} and 21648-22152 cm^{-1} , which have tentatively been assigned to the transitions ${}^1\text{A}_{1g} \rightarrow {}^1\text{E}_g$ (ν_1) and ${}^1\text{A}_{1g} \rightarrow {}^1\text{B}_{2g}$ (ν_2), respectively, these are diamagnetic complex, therefore square planar geometry has been suggested. The electronic spectra of the [Cu(BSMA)₂].2H₂O and [Cu(BSCA)₂] showed two bands at 12879-13698 cm^{-1} and 18542-18210 cm^{-1} assignable to ${}^2\text{B}_{1g} \rightarrow {}^2\text{B}_{2g}$ and ${}^2\text{B}_{1g} \rightarrow {}^2\text{E}_g$ transitions, respectively, Since the value of magnetic moment for these complexes found 1.92 and 1.97 B.M.; therefore square planar geometry has been suggested for these Cu(II) complex²⁰⁻²².

Table 3. Magnetic moment values and electronic spectral data of complexes

Complex	μ_{eff} (B.M.)	λ_{max} (cm ⁻¹)	Band assignments
[Co(BSMA) ₂ (H ₂ O) ₂]	5.08	9425	⁴ T _{1g} → ⁴ T _{2g} (F)
		15257	⁴ T _{1g} → ⁴ A _{2g} (F)
		19612	⁴ T _{1g} → ⁴ T _{1g} (P)
[Ni(BSMA) ₂] ₂ H ₂ O	Dia.	12112	¹ A _{1g} → ¹ E _g
		21648	¹ A _{1g} → ¹ B _{2g}
		-	¹ A _{1g} → ¹ B _{1g}
[Cu(BSMA) ₂] ₂ H ₂ O	1.92	12879	² B _{1g} → ² B _{2g}
		18542	² B _{1g} → ² E _g
[Co(BSCA) ₂ (H ₂ O) ₂]	5.12	9750	⁴ T _{1g} → ⁴ T _{2g} (F)
		15748	⁴ T _{1g} → ⁴ A _{2g} (F)
		19607	⁴ T _{1g} → ⁴ T _{1g} (P)
[Ni(BSCA) ₂] ₂ H ₂ O	Dia.	12689	¹ A _{1g} → ¹ E _g
		22152	¹ A _{1g} → ¹ B _{2g}
		-	¹ A _{1g} → ¹ B _{1g}
[Cu(BSCA) ₂]	1.97	13698	² B _{1g} → ² B _{2g}
		18210	² B _{1g} → ² E _g

ESR spectra

The ESR spectra of Cu(II) provide information about the extent of the delocalization of unpaired electron. The X-band ESR spectra of Cu(II) complexes were recorded in the solid state at room temperature 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 BSMA are 2.2225, 2.1132, 2.1496, 0.1093 and 1.9856 respectively. Similarly, the corresponding values for Cu(II) complex of BSCA are 2.2125, 2.1332, 2.1596, 0.0793 and 1.6058 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 (2.2225-2.2125) 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 the Cu(II) complexes (1.9856-1.6058) are less than four indicating, considerable exchange interaction in the complexes^{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 results show good agreement with the suggested formulae from the analytical data (Table 1).

The thermal degradation behaviour of the Ni(II) complex of BSMA has been studied by thermogravimetric analysis. The TG curve of the complex shows that the complex starts to decompose at 70 °C. Elimination of lattice water molecules has been observed on increasing the temperature up to 115°C (remaining wt.%, obs./calcd., 95.62/94.86). The complex does not show any

loss in weight between 115 and 190 °C. After 190 °C, a loss in weight has been observed in general up to 380 °C corresponding to the loss of partially decomposed ligand part from the complex (remaining wt.%, obs./calcd., 56.50/55.82). Above 420 °C, loss in weight has been occurs up to 580 °C. This indicates the elimination of the remaining thermally degradable part of the complex. After 580 °C a horizontal curve has been observed which corresponds to a mixture of metal oxide as an ultimate pyrolysis product (remaining wt.%, obs./calcd., 22.75/21.50).

The TG curve of the Co(II) complex of BSCA shows (Fig. 2) that the complex is stable upto 120 °C. This indicates the absence of lattice water molecule in the complex. On increasing the temperature decomposition started between the temperature range 120-200 °C, corresponding to elimination of two coordinated water molecules (Remaining Wt.%, Obs./Calcd., 96.42/95.40). After this temperature, a loss in weight has been observed in general up to 400 °C corresponding to the loss of partially decomposed ligand part from the complex (Remaining Wt.%, Obs./Calcd., 52.12/50.50). Above this temperature, a weight loss has been occurred upto 630 °C. This indicates the elimination of the remaining thermally degradable part of the complex. After 630 °C, a plateau has been observed which corresponds to metal oxide as an ultimate pyrolysis product (Remaining Wt.%, Obs./Calcd., 24.84/23.70)^{25, 26}. The thermal analysis evaluates the thermal stability of the metal complexes, this study also helped to characterize the metal complexes.

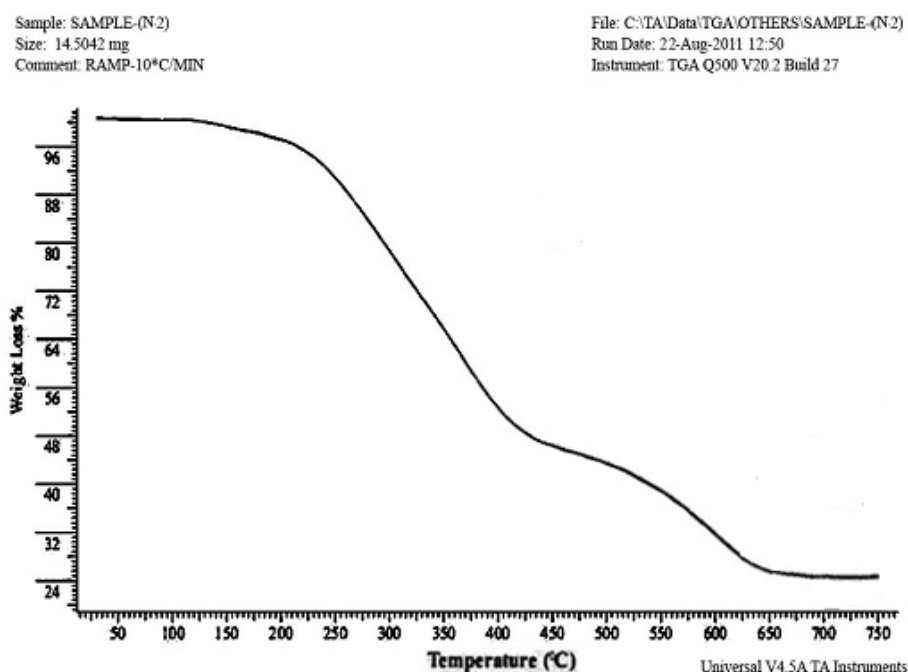


Fig. 2. TG curve of $[\text{Co}(\text{BSCA})_2(\text{H}_2\text{O})_2]$ complex *Electrical conductivity*

The temperature dependence of the solid state conductivity (σ) of the compounds in their compressed pellet form have been measured at fixed frequency 1 KHz in the temperature range 297–397 K. The values of the solid state electrical conductivity of the Schiff base and its complexes increase with increasing temperature and decrease upon cooling over the studies temperature range indicating its semiconducting behaviour. The general behavior of electrical conductivity follows the Arrhenius equation:

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

where E_a 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 studied temperature range. The room temperature electrical conductivity of all the compounds lies in the range 4.35×10^{-7} – 7.26×10^{-8} ohm⁻¹ cm⁻¹. These values show their semi-conducting nature. The electrical conductivity at room temperature for the complexes of BSMA are $\text{Co} > \text{Cu} > \text{Ni}$ and for the

metal complexes of BSCA are $\text{Co} > \text{Cu} > \text{Ni}$. The activation energy of the compound lies in the range $0.218\text{--}0.787 \text{ eV}^{27,28}$. The confirmation 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. The bactericidal and fungicidal investigation data of the compounds are summarized in Tables 4 and 5. Moreover, all the complexes are moderately active as compared to the standard bactericide and fungicide (Streptomycin and Miconazole). A comparative study of the ligands and their transition metal complexes indicates that the complexes are more active than their respective ligands, the activity increases upon coordination. The increased activity of the metal chelates 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 a 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 the 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 also, which increase the activity *viz.* solubility, lipophilicity/hydrophilicity, conductivity and M-L bond length²⁹⁻³².

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

Compound	<i>E. coli</i>						<i>S. aureus</i>					
	Diameter of inhibition zone (in mm)			% Activity index			Diameter of inhibition zone (in mm)			% Activity index		
	25 ^a	50 ^a	100 ^a	25 ^a	50 ^a	100 ^a	25 ^a	50 ^a	100 ^a	25 ^a	50 ^a	100 ^a
BSMA	15	17	20	68	71	71	13	16	18	72	73	75
[Co(BSMA) ₂ (H ₂ O) ₂]	22	24	27	100	100	96	18	20	22	100	91	92
[Ni(BSMA) ₂]2H ₂ O	16	20	22	73	83	79	14	18	20	78	82	83
[Cu(BSMA) ₂]2H ₂ O	20	22	26	91	92	93	17	20	24	94	91	100
BSCA	14	16	18	64	67	64	12	14	16	67	64	67
[Co(BSCA) ₂ (H ₂ O) ₂]	20	21	23	91	88	82	17	20	21	94	91	88
[Ni(BSCA) ₂]2H ₂ O	16	18	20	73	75	71	13	16	18	72	73	75
[Cu(BSCA) ₂]	20	23	26	91	96	93	15	18	21	83	82	88
Streptomycin (Standard)	22	24	28	100	100	100	18	22	24	100	100	100

^aConcentration in ppm

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

Table 5. Antifungal screening data for the ligands and their complexes

Compound	<i>A. niger</i>			<i>C. albicans</i>		
	Diameter of inhibition zone (in mm)			Diameter of inhibition zone (in mm)		
	25 ^a	50 ^a	100 ^a	25 ^a	50 ^a	100 ^a
BSMA	12	15	20	14	18	20
[Co(BSMA) ₂ (H ₂ O) ₂]	16	20	25	15	18	24
[Ni(BSMA) ₂]2H ₂ O	15	20	24	16	18	23
[Cu(BSMA) ₂]2H ₂ O	18	24	27	17	20	25
BSCA	13	17	22	14	16	20
[Co(BSCA) ₂ (H ₂ O) ₂]	18	22	28	20	22	28
[Ni(BSCA) ₂]2H ₂ O	16	19	24	16	18	22
[Cu(BSCA) ₂]	18	23	28	19	21	26
Miconazole (Standard)	20	25	30	22	24	29

^aConcentration in ppm

3. Conclusions

In the present research studies, our efforts were to synthesize and characterize some new compounds from the conventional as well as microwave methods. Microwave method has been considered a green chemical route. These synthesized compounds were characterized by various physicochemical and spectral analyses. In course of microwave assisted synthesis, it was observed that the reaction time decreased from hours to minutes and availability of the product with better yield as compared to the conventional method. Use of solvent is also minimized. The synthesized Schiff base ligands bind with the metal ions in a bidentate manner, with ON donor sites of deprotonated phenolic-O and azomethine-N. The $^1\text{H-NMR}$ data suggest that both the Schiff base ligand deprotonated after complexation. Such metal complexes may be of stereoselective and stereoactive in nature to be applicable for various catalytic reactions. Thermogravimetric studies reflect their thermal stability. The antimicrobial data showed that the metal complexes to be more biologically active compared to those parent Schiff base ligands against all pathogenic species. Such studies may assist to search some novel chemotherapeutics to answer the emerging problem of drug resistance in health sciences.

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Experimental

Materials

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.

Physical measurements

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. 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 $\text{Hg}[\text{Co}(\text{SCN})_4]$ as the calibrant.

FT-IR spectra were recorded in KBr pellet on a Perkin Elmer RX1 spectrophotometer in wave number region $4000\text{-}400\text{ cm}^{-1}$. ^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 $10^\circ\text{C min}^{-1}$ on TGA Q500 universal V4.5A TA instrument. 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 297–397 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 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 investigated Schiff base and their 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. Each of the compounds was dissolved in DMSO and solutions of different concentrations (25, 50 and 100 ppm) 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 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. All determinations were performed in thrice.

Conventional method for the synthesis of Schiff bases

BSMA and BSCA Schiff bases were synthesized by the condensation of 1:1 ratio of 5-bromosalicylaldehyde with 3,4-dimethylaniline and 3,4-dichloroaniline dissolved in ethanol. The resulting reaction mixture was 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 and finally recrystallized from ethanol and ether and dried in air at room temperature and preserved in a CaCl₂ desiccator. The purity of synthesized compounds was checked by TLC using silica gel G (BSMA - Yield: 78%; BSCA – 75%).

Microwave method for the synthesis of Schiff bases

The equimolar (1:1) ratio of 5-bromosalicylaldehyde with 3,4-dimethylaniline and 3,4-dichloroaniline were mixed thoroughly in a grinder. The reaction mixture was then irradiated by the microwave oven by taking 3-4 mL of dry ethanol as a 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 CaCl₂ in a desiccator. The progress of the reaction and 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 were prepared by the mixing of (50 mL) ethanolic solution of CoCl₂.6H₂O/NiCl₂.6H₂O/CuCl₂.2H₂O with the (50 mL) ethanolic solution of Schiff bases (BSMA/BSCA) (Figs. 3 and 4) in 1:2 (metal:ligand) ratio. The resulting mixture was refluxed on water bath for 6-8 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 CaCl₂ in a desiccator. It was further dried in electric oven at 50-70°C (yield: 67-71%).

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 of dry ethanol as a solvent. The reaction was completed in a short time (6-8 min) with higher yields. The resulting product was then recrystallized with ethanol and ether and finally dried under reduced pressure over anhydrous CaCl₂ in a desiccator. The progress of the reaction and purity of the product was monitored by TLC using silica gel G (yield: 81-84%).

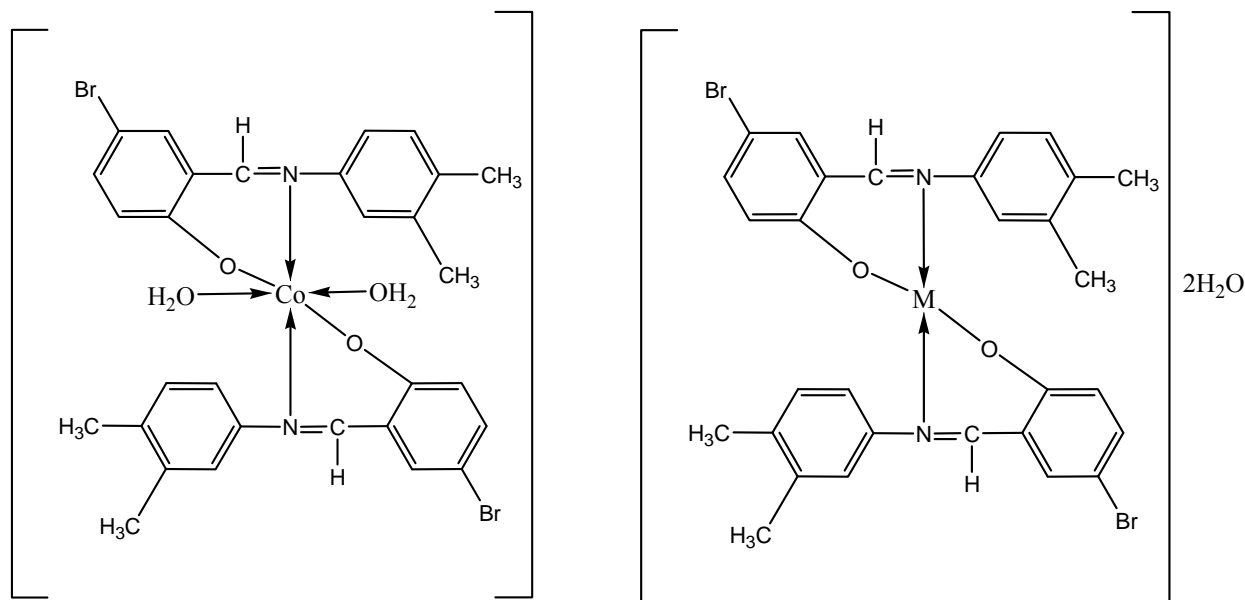


Fig. 3. Proposed structures of metal complexes of BSMA

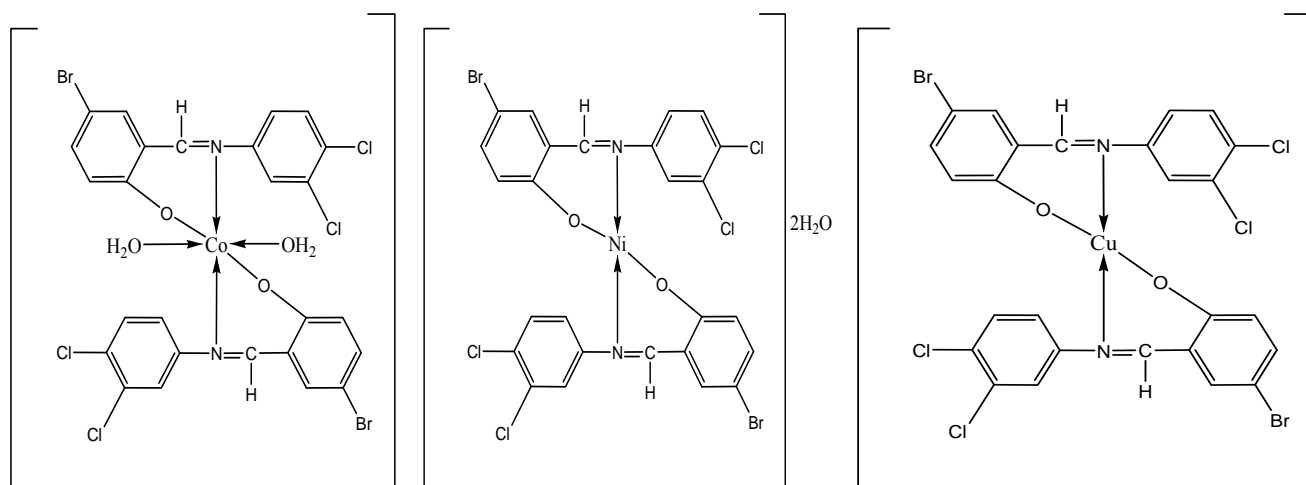


Fig. 4. Proposed structures of metal complexes of BSCA

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