



## Microwave synthesis and spectral, thermal and antimicrobial activities of some novel transition metal complexes with tridentate Schiff base ligands

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**Abstract:** Some novel Schiff base metal complexes of Cr(III), Co(II), Ni(II) and Cu(II) derived from 2-[(5-bromo-2-hydroxybenzylidene)amino]pyridin-3-ol (BSAP) and {5-chloro-2-[(2-hydroxy-1-naphthyl)methylene]amino}phenyl}-phenylmethanone (HNAC) were synthesized by conventional as well as microwave methods. These compounds were characterized by elemental analysis, FT-IR, FAB-mass, electronic and ESR spectroscopy, molar conductance, magnetic susceptibility, thermal, cyclic voltammetric and electrical conductivity measurements and XRD analyses. Analytical data revealed that all the complexes exhibited 1:1 (metal:ligand) ratio with a coordination number of 4 or 6. The IR data showed that the ligand coordinates with the metal ions in a tridentate manner. FAB-mass and thermal data showed the degradation pattern of the complexes. The thermal behaviour of the metal complexes showed that the hydrated complexes lose water molecules of hydration in the first step; with decomposition of the ligand molecules in the subsequent steps. The crystal system, lattice parameters, unit cell volume and number of molecules in a unit cell in the lattice of the complexes were determined by XRD analysis. XRD patterns indicated a crystalline nature for the complexes. The solid state electrical conductivity of the metal complexes was also measured. Solid state electrical conductivity studies reflected a semi-conducting nature of the complexes. The Schiff base and metal complexes displayed good activity against the Gram-positive bacteria *Staphylococcus aureus*, the Gram-negative bacteria *Escherichia coli* and the fungi *Aspergillus niger* and *Candida albicans*. The antimicrobial results also indicated that the metal complexes displayed better antimicrobial activity as compared to the Schiff bases.

**Keywords:** microwave method; tridentate ligands; thermal analyses; biological activities.

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## INTRODUCTION

Metal complexes have received considerable attention in the last many years, due to their interesting characteristics in the field of material science and biological systems. Optoelectronic, electrical and magnetic properties of metals and metalloids can be tailored by their reaction with different ligands. A large number of Schiff bases and their complexes may exhibit properties such as reversible binding of oxygen, transfer of an amino group, thermal, varied complexing/redox abilities, and as nanoprecursors. The Schiff bases have high affinity for transition metal ions; hence exhibit potential applications in various areas. Metal complexes are also suitable as molecular materials, because of the electronic properties associated with the metal centres.<sup>1-4</sup>

Transition metal complexes with tridentate Schiff base ligands have been widely investigated since such ligands can bind metal centres at more than one site and thus allow the successful synthesis of metal complexes with interesting stereochemistry and model redox enzyme/biological systems. The Schiff bases of salicylaldehyde with aminopyridines have created a well-known class of predominantly thermochromic compounds and metallobiomolecules.<sup>5-8</sup>

Similarly, a heterocyclic nucleus, namely pyridine based ligands, have also been reported in many biochemical reactions to design and develop molecular systems of biological and medical importance. Such ligating species on coordination with metal ions may emerge as metal-mediated drugs. A 2-hydroxy-1-naphthaldehyde-derived Schiff base has been used as a good chelating agent with 3d-metal ions. 2-Aminobenzophenone derivatives are important compounds in organic chemistry because of their application in heterocyclic synthesis and medicinal compounds.<sup>9-12</sup>

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 offer reduced pollution, low cost and better yield, and simplicity in processing and handling. The main features of the microwave approach are shorter reaction times, simple reaction conditions and enhancement of yields. There are a few reports on the synthesis of metal complexes by microwave methods.<sup>13-18</sup>

In the present paper, the coordination behaviour of Schiff bases (Fig. 1) derived from the condensation of 5-bromosalicylaldehyde with 2-amino-3-hydroxypyridine (BSAP) and 2-hydroxy-1-naphthaldehyde with 2-amino-5-chlorobenzophenone (HNAC) towards some transition elements is described, which may help in more understanding of the mode of chelation of ligands towards metals. For this purpose, the complexes of Cr(III), Co(II), Ni(II) and Cu(II) ions with BSAP and HNAC were synthesized by both conventional and microwave methods and characterized by various physico-chemical and spectral techniques.

The metal complexes prepared with these two new ligands may be used as precursors for the synthesis of new compounds. Some of them may also exhibit interesting physical and chemical properties and useful biological activities.

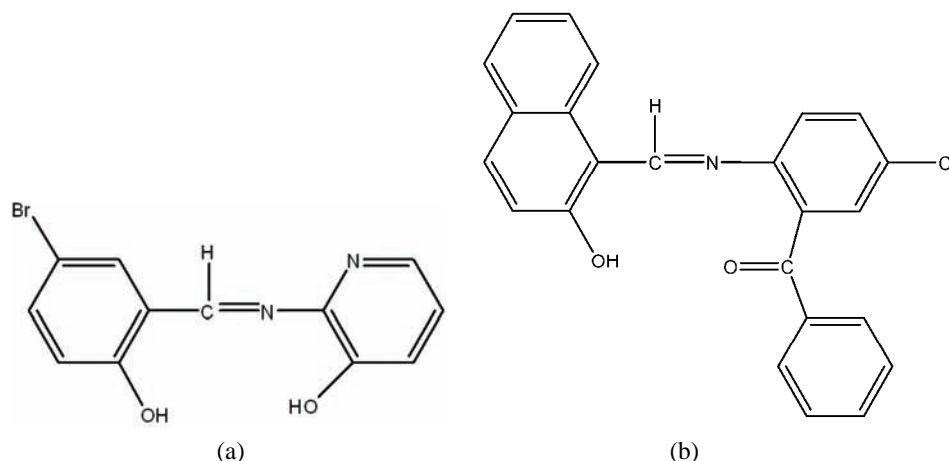


Fig.1. Structure of Schiff base ligands, a) 2-[(5-bromo-2-hydroxybenzylidene)amino]pyridin-3-ol (BSAP) and b) {5-chloro-2-[(2-hydroxy-1-naphthyl)methylene]amino}phenyl}phenylmethanone (HNAC).

## EXPERIMENTAL

### Materials

All the chemicals and solvents used were of Anal R grade. All the reagents employed 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. The 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. The electronic spectra (in DMSO) were recorded on Perkin Elmer Lambda-2B-spectrophotometer. The molar conductance measurements were realised using  $10^{-3}$  M solution of the complexes in DMSO on an Elico-CM 82 conductivity bridge at room temperature. Magnetic susceptibility measurements were performed on a Gouy balance at room temperature using  $\text{Hg}[\text{Co}(\text{SCN})_4]$  as the calibrant. Diamagnetic corrections were applied in compliance with the Pascal constant. FT-IR spectra were recorded in KBr discs on a Perkin Elmer RX1 spectrophotometer in wave number range  $4000\text{--}400\text{ cm}^{-1}$ . The  $^1\text{H-NMR}$  spectra were recorded on a JEOL AL300 FTNMR spectrometer employing TMS as an internal reference and  $\text{DMSO-}d_6$  as the solvent. Cyclic voltammetry was performed with a BAS-100 Epsilon electrochemical analyzer using a three-electrode electrochemical cell. Ag/AgCl was used as a reference electrode, glassy carbon as the working electrode and a platinum wire as the auxiliary electrode. 0.1 M  $\text{NaClO}_4$  was used as the supporting electrolyte and DMSO as the solvent. All measurements were performed at room temperature under a nitrogen atmosphere. The X-band EPR spectra were recorded at room tem-

perature on a Varian E-112 spectrometer operating in the X-band region with 100 kHz modulation frequency, 5 mW microwave power and 1 G modulation amplitude using tetracyanoethylene (TCNE) as the internal standard. Thermogravimetric analysis was realised under atmospheric conditions with a heating rate  $10\text{ }^{\circ}\text{C min}^{-1}$  on TGA Q500 universal V4.5A TA instrument. Powder X-ray diffraction (XRD) patterns were recorded on a RINT2000 wide angle goniometer. X-ray diffractometer was operated at 40 kV and 30 mA generator using the  $\text{CuK}_{\alpha}$  line of  $1.54056\text{ \AA}$  as the radiation sources. The samples were scanned between  $5$  and  $70^{\circ}$  ( $2\theta$ ) at  $25\text{ }^{\circ}\text{C}$ . The solid state electrical conductivity was measured by impedance spectroscopic method using a HIOKI 3532-50 LCR Hitester at a fixed frequency of 1 KHz in the temperature range of 298–413 K. Microwave-assisted syntheses were performed in an open glass vessel using a modified microwave oven model 2001 ETB with a rotating tray and a 230 V power source. The microwave energy output was 800 W and the 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.

#### *Conventional method for the synthesis of Schiff bases*

The 2-[(5-bromo-2-hydroxybenzylidene)amino]pyridin-3-ol Schiff base was synthesized by the condensation of an equimolar ratio of 5-bromosalicylaldehyde (0.201 g, 10 mM) with 2-amino-3-hydroxypyridine (0.110 g, 10 mM) dissolved in ethanol. The resulting reaction mixture was refluxed on a water bath for 4.1 h and then allowed to cool overnight. The coloured solid precipitate of the obtained Schiff base was filtered, washed with cold ethanol several times and dried in air at room temperature and finally preserved under reduced pressure in a desiccator. The purity of the synthesized compounds was checked by TLC using silica gel G. Yield: 78.0 %; m.p.  $179\text{ }^{\circ}\text{C}$ ; Anal. Calcd. for  $\text{C}_{12}\text{H}_9\text{N}_2\text{O}_2\text{Br}$ : C, 49.17; H, 3.07; N, 9.56 %. Found: C, 49.02; H, 3.09; N, 9.50 %. IR (KBr,  $\text{cm}^{-1}$ ): 1625 (C=N, azomethine), 1268 (C–O), 1496 (C=N, pyridine).  $^1\text{H-NMR}$  (300 MHz,  $\text{DMSO-}d_6$ ,  $\delta$  / ppm), 9.29 (1H, s, –CH=N), 13.80 (1H, s, –OH, salicylaldehyde moiety), 10.28 (1H, s, –OH pyridine moiety). FAB-mass ( $m/z$ ), Calcd.: 292; Found: 294.

The {5-chloro-2-[(2-hydroxy-1-naphthyl)methylene]amino}phenyl}phenylmethanone Schiff base was synthesized by the condensation of an equimolar ratio of 2-hydroxy-1-naphthaldehyde (0.172 g, 10 mM) with 2-amino-5-chlorobenzophenone (0.232 g, 10 mM) dissolved in ethanol. The resulting reaction mixture was refluxed on a water bath for 3.8 h and then allowed to cool overnight. The obtained coloured precipitate of the Schiff base 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 the synthesized compounds was checked by TLC using silica gel G. Yield: 74.9 %; m.p.  $160\text{ }^{\circ}\text{C}$ ; Anal. Calcd. for  $\text{C}_{24}\text{H}_{16}\text{NO}_2\text{Cl}$ : C, 74.41; H, 4.18; N, 3.63 %. Found: C, 74.35; H, 4.11; N, 3.58 %. IR (KBr,  $\text{cm}^{-1}$ ): 1613 (C=N, azomethine), 1236 (C–O), 1675 (C=O).  $^1\text{H-NMR}$  (300 MHz,  $\text{DMSO-}d_6$ ,  $\delta$  / ppm), 8.65 (1H, s, –CH=N), 12.67 (1H, s, –OH phenolic). FAB-mass ( $m/z$ ), Calcd.: 386, Found: 388.

#### *Microwave method for the synthesis of the Schiff bases*

An equimolar ratio of 5-bromosalicylaldehyde (0.201 g) with 2-amino-3-hydroxypyridine (0.110 g) and 2-hydroxy-1-naphthaldehyde (0.172 g) with 2-amino-5-chlorobenzophenone (0.232 g) was mixed thoroughly in a grinder. The reaction mixture was then irradiated in 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 better yields than were obtained in the conventional

procedure. The resulting product was then recrystallized from ethanol and finally dried under reduced pressure over anhydrous  $\text{CaCl}_2$  in a desiccator. The progress of the reaction and purity of the product was monitored by TLC using silica gel G (yield: 87.1–87.4 %).

*Conventional method for the synthesis of metal complexes*

The metal complexes were prepared by mixing 50 mL of a 10 mM ethanolic solution of  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ / $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ / $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ / $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  with 50 mL of a 10 mM ethanolic solution of the Schiff bases (BSAP/HNAC) in a 1:1 (metal:ligand) ratio (Figs. 2 and 3). The resulting mixture was refluxed on a water bath for 6–9 h. A coloured product appeared on standing and cooling the solution. The precipitated complexes were filtered, washed with ether and recrystallized several times from ethanol and dried under reduced pressure over anhydrous  $\text{CaCl}_2$  in a desiccator. They were further dried in an electric oven at 50–70 °C (yield: 59.6–69.0 %).

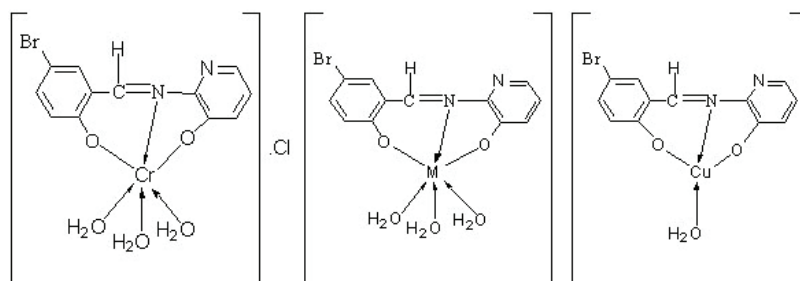


Fig. 2. The proposed structures of the Schiff base complexes of BSAP.

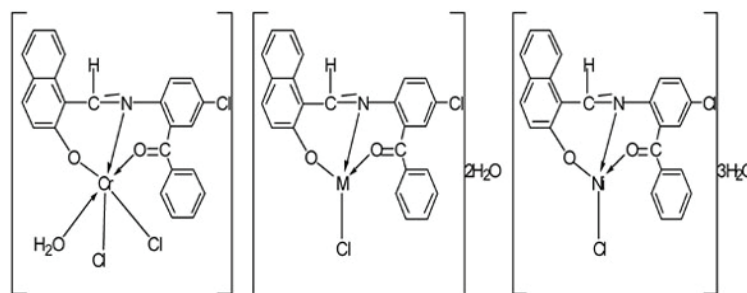


Fig. 3. The proposed structures of the Schiff base complexes of HNAC.

*Microwave method for the synthesis of metal complexes*

The ligands and the metal salts were mixed in a 1:1 (metal:ligand) ratio in a grinder. The reaction mixture was then irradiated in the microwave oven taking 3–5 mL of dry ethanol as the solvent. The reactions were completed in a short time (6–10 min) with better yields than were obtained in the conventional procedure. The resulting product was then recrystallized from ethanol and washed with diethyl ether and finally dried under reduced pressure over anhydrous  $\text{CaCl}_2$  in a desiccator. The progress of the reaction and purity of the product was monitored by TLC using silica gel G (yield: 78.0–85.0 %).

### Biological activity

The *in vitro* biological activity of the investigated Schiff bases and their metal complexes were tested against the bacteria *Escherichia coli* and *Staphylococcus aureus* by the disc diffusion method using nutrient agar as the medium and streptomycin as the 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 the control. Each of the compounds was dissolved in DMSO and the solutions of concentrations 25, 50 and 100 ppm were prepared separately. In a typical procedure, a well was made on the agar medium inoculated with micro-organism. The well was filled with the test solution using a micropipette and the plate was incubated 24 h at 37 °C for the bacteria or 72 h at 30 °C for the fungi. After incubation, the diameter of the clear zone of inhibition surrounding the sample was taken as a measure of the inhibitory power of the sample against the particular test organism.

### RESULTS AND DISCUSSION

As a result of the microwave-assisted synthesis, it was observed that the reaction time decreased from hours to minutes and better yields of the products were obtained compared to those attained by the conventional synthesis method. In the microwave method, homogeneity of the reaction mixture was increased by the rotation of reaction platform tray. The confirmation of the results was also checked by repeating of the synthesis process.

All the metal complexes were coloured, solid and stable towards air and moisture at room temperature. They decomposed on heating at high temperatures and were more or less soluble in common organic solvents. The results of a comparison of the two synthesis methods showed that reactions which required 3.8–8.2 h by the conventional method were completed within 4.0–7.9 min by the microwave irradiation technique and the yields were improved from 59.6–78.0 % to 78.0–87.6 %. The reaction times and yields for all the synthesised compounds are given in Table I.

All the metal chelates had 1:1 (metal:ligand) stoichiometry. The observed molar conductance of the complexes in DMSO at room temperature, given in Table S-I of the Supplementary Material to this paper, were consistent with the non-electrolytic nature of the complexes except for the Cr(III) complex of the BSAP Schiff base ligand, which was electrolytic in nature.

### FAB-mass spectra

The FAB-mass spectra suggested that all the complexes have a monomeric nature. These complexes showed molecular ion peaks in good agreement with the empirical formula suggested by elemental analyses, the results of which are given in Table S-I of the Supplementary Material to this paper.

Thus, mass spectra of the complexes  $[\text{Ni}(\text{BSAP})(\text{H}_2\text{O})_3]$  (FW 403.84) and  $[\text{Co}(\text{HNAC})\text{Cl}] \cdot 2\text{H}_2\text{O}$  (FW 515.25), as representative complexes, showed the

highest mass peaks at  $m/z$  at 406 and 518, respectively, which agree well with the formula weights of the complexes.<sup>19,20</sup>

TABLE I. Reaction times and yields for the conventional and microwave synthesis methods

Compound (colour)	Empirical formula (FW)	Reaction period		Yield, %	
		CM, h	MM, min	CM	MM
BSAP (brown)	C <sub>12</sub> H <sub>9</sub> N <sub>2</sub> O <sub>2</sub> Br (293.12)	4.1	4.5	78.0	87.6
[Cr(BSAP)(H <sub>2</sub> O) <sub>3</sub> ]Cl (Greenish brown)	C <sub>12</sub> H <sub>7</sub> N <sub>2</sub> O <sub>2</sub> BrClCr (432.60)	8.2	7.9	59.6	79.8
[Co(BSAP)(H <sub>2</sub> O) <sub>3</sub> ] (Dark brown)	C <sub>12</sub> H <sub>13</sub> N <sub>2</sub> O <sub>5</sub> BrCo (404.08)	7.3	7.2	67.5	80.8
[Ni(BSAP)(H <sub>2</sub> O) <sub>3</sub> ] (Coffee brown)	C <sub>12</sub> H <sub>13</sub> N <sub>2</sub> O <sub>5</sub> BrNi (403.84)	7.8	7.5	66.2	83.5
[Cu(BSAP)(H <sub>2</sub> O)] (black)	C <sub>12</sub> H <sub>9</sub> N <sub>2</sub> O <sub>3</sub> BrCu (372.66)	6.9	6.5	62.0	85.0
HNAC (Yellowish brown)	C <sub>24</sub> H <sub>16</sub> NO <sub>2</sub> Cl (385.84)	3.8	4.0	74.9	87.1
[Cr(HNAC)(H <sub>2</sub> O)Cl <sub>2</sub> ] (Dark green)	C <sub>24</sub> H <sub>17</sub> NO <sub>3</sub> Cl <sub>3</sub> Cr (525.75)	7.9	7.8	60.1	78.0
[Co(HNAC)Cl]·2H <sub>2</sub> O (Tobacco green)	C <sub>24</sub> H <sub>19</sub> NO <sub>4</sub> Cl <sub>2</sub> Co (515.25)	7.8	7.0	64.5	78.9
[Ni(HNAC)Cl]·3H <sub>2</sub> O (Yellowish green)	C <sub>24</sub> H <sub>21</sub> NO <sub>5</sub> Cl <sub>2</sub> Ni (533.03)	7.2	7.3	69.0	84.2
[Cu(HNAC)Cl]·2H <sub>2</sub> O (Coffee brown)	C <sub>24</sub> H <sub>19</sub> NO <sub>4</sub> Cl <sub>2</sub> Cu (519.86)	7.0	7.5	66.2	82.7

#### <sup>1</sup>H-NMR spectra

The proton NMR spectra of the Schiff base ligands were recorded in DMSO-*d*<sub>6</sub> solution using TMS as an internal standard. The <sup>1</sup>H-NMR spectra of the BSAP ligand showed signals at  $\delta$  6.94–7.86 (*m*) for the aromatic protons and 9.29 (*s*) for the azomethine proton. The peaks at  $\delta$  13.80 (*s*) and 10.28 (*s*) were attributed to the phenolic –OH group present in the salicylaldehyde moiety and the –OH group present in the pyridine moiety, respectively; the –OH peaks disappeared after D<sub>2</sub>O addition.

The <sup>1</sup>H-NMR spectra of the HNAC ligand showed signals at  $\delta$  7.23–7.69 (*m*) for the aromatic protons and 8.65 (*s*) for the azomethine proton. The peak at 12.67 (*s*) attributed to the phenolic –OH group, disappeared upon addition of D<sub>2</sub>O.<sup>21–25</sup> The IR data support these assignments.

#### IR spectra

The data of the IR spectra of Schiff base ligands and their metal complexes are listed in Table S-II of the Supplementary Material to this paper. The IR spectra of the complexes were compared with those of the free ligands in order to de-



termine the involvement of the coordination sites in the chelation. Characteristic peaks in the spectra of the ligand and complexes were considered and compared.

IR spectrum of the BSAP ligand exhibited the most characteristic bands at  $1625\text{ cm}^{-1}$   $\nu(\text{C}=\text{N}$ , azomethine),  $1268\text{ cm}^{-1}$   $\nu(\text{C}-\text{O})$  and  $1496\text{ cm}^{-1}$   $\nu(\text{C}=\text{N}$ , pyridine). The formation of the Schiff base, 2-[(5-bromo-2-hydroxybenzylidene)amino]pyridin-3-ol (BSAP) was noted from the absence of  $\text{C}=\text{O}$  and  $\text{NH}_2$  peaks in the ligand. The ligand spectrum showed bands at  $3150$  and  $1361\text{ cm}^{-1}$  due to the stretching and deformation of the phenolic OH. These were absent in the spectra of the complexes. The band at  $1625\text{ cm}^{-1}$  due to the azomethine group of the Schiff base was shifted to lower frequencies ( $1596\text{--}1607\text{ cm}^{-1}$ ) after complexation, indicating the bonding of nitrogen of the azomethine group to the metal ions. The phenolic  $\text{C}-\text{O}$  stretching vibration that appeared at  $1268\text{ cm}^{-1}$  in Schiff base shifted towards higher frequencies ( $20\text{--}27\text{ cm}^{-1}$ ) in the complexes. This suggests deprotonation of the phenolic OH group after its chelation with the metal ion. The appearance of broad bands at around  $3343\text{--}3398\text{ cm}^{-1}$  in the spectra of complexes may be due to water molecules. A band of medium intensity at  $807\text{--}822\text{ cm}^{-1}$  (OH rocking) suggests the presence of coordinated water in all four complexes. In the low frequency region, the band of weak intensity observed for the complexes in the region  $522\text{--}540\text{ cm}^{-1}$  is attributed to  $\text{M}-\text{O}$  and in the region  $486\text{--}497\text{ cm}^{-1}$  to  $\text{M}-\text{N}$ . There was no appreciable change in the  $\nu(\text{C}=\text{N})$  at  $1496\text{ cm}^{-1}$  in ligand on complex formation, which indicates that the pyridine ring nitrogen does not participate in the coordination.<sup>26-30</sup>

IR spectrum of the HNAC ligand showed the most characteristic bands at  $1613\text{ cm}^{-1}$   $\nu(\text{C}=\text{N}$ , azomethine),  $1675\text{ cm}^{-1}$   $\nu(\text{C}=\text{O})$  and  $1236\text{ cm}^{-1}$   $\nu(\text{C}-\text{O})$ . The ligand spectrum showed bands at  $3230$  and  $1336\text{ cm}^{-1}$  due to the stretching and deformation of the phenolic OH. These were absent in the spectra of the complexes. The band  $1613\text{ cm}^{-1}$  due to the azomethine group of the Schiff base was shifted to lower frequencies ( $1582\text{--}1594\text{ cm}^{-1}$ ) after complexation, indicating bonding of the azomethine nitrogen to the metal ions. This can be explained by the donation of electrons from nitrogen to the empty d-orbital of the metal atom. The band at  $1675\text{ cm}^{-1}$ , due to the carbonyl group of the Schiff base, was shifted to lower frequencies by  $23\text{--}35\text{ cm}^{-1}$  in the spectra of complexes, indicating involvement of carbonyl oxygen to metal ions in the coordination. The phenolic  $\text{C}-\text{O}$  stretching vibration that appeared at  $1236\text{ cm}^{-1}$  in Schiff base shifted towards higher frequencies ( $19\text{--}27\text{ cm}^{-1}$ ) in the complexes. This shift confirms the participation of oxygen in the  $\text{C}-\text{O}-\text{M}$  bond. The appearance of broad bands around at ( $3365\text{--}3408\text{ cm}^{-1}$ ) in the spectra of the complexes may be due to water molecules. A medium intensity band at  $785\text{ cm}^{-1}$  in the spectrum of the  $\text{Cr(III)}$  complex suggests the presence of coordinated water molecules in this complex. This band was not observed in other complexes, indicating the absence of coordinated water molecules in the  $\text{Co(II)}$ ,  $\text{Ni(II)}$  and  $\text{Cu(II)}$  complexes. In the low



frequency region, the band of weak intensity observed in the spectra of the complexes in the region 519–529  $\text{cm}^{-1}$  is attributed to (M–O) and in the region 485–492  $\text{cm}^{-1}$  to (M–N).<sup>26–30</sup>

The IR data of both the Schiff bases and their metal complexes showed that the Schiff bases (BSAP and HNAC) were coordinated to the metal ion in a tridentate manner.

#### *Electronic spectra and magnetic moment*

The electronic spectral data of the metal complexes in DMSO solution are displayed in Table S-III of the Supplementary Material to this paper. The nature of the ligand field around the metal ion was deduced from the electronic spectra.

The electronic spectra of Cr(III) complex of BSAP showed bands at 16654  $\text{cm}^{-1}$ , 24212 and 35982  $\text{cm}^{-1}$ , which may be assigned to  $^4\text{A}_{2\text{g}} \rightarrow ^4\text{T}_{2\text{g}}(\text{F})$  ( $\nu_1$ ),  $^4\text{A}_{2\text{g}} \rightarrow ^4\text{T}_{1\text{g}}(\text{F})$  ( $\nu_2$ ) and  $^4\text{A}_{2\text{g}} \rightarrow ^4\text{T}_{1\text{g}}(\text{P})$  ( $\nu_3$ ) transitions, respectively. The magnetic moment was 3.88  $\mu_{\text{B}}$ ; thus octahedral geometry is suggested for this complex. The electronic spectrum of Co(II) complex of BSAP exhibited three bands at 9486, 15823 and 20618  $\text{cm}^{-1}$ , which were tentatively assigned to  $^4\text{T}_{1\text{g}} \rightarrow ^4\text{T}_{2\text{g}}(\text{F})$  ( $\nu_1$ ),  $^4\text{T}_{1\text{g}} \rightarrow ^4\text{A}_{2\text{g}}(\text{F})$  ( $\nu_2$ ) and  $^4\text{T}_{1\text{g}} \rightarrow ^4\text{T}_{1\text{g}}(\text{P})$  ( $\nu_3$ ) transitions, respectively. The value of magnetic moment was 5.02  $\mu_{\text{B}}$ , which indicates the presence of Co(II) complex in an octahedral geometry. The electronic spectrum of the Ni(II) complex of BSAP showed three bands at 10691, 20360 and 23838  $\text{cm}^{-1}$ , assignable to  $^3\text{A}_{2\text{g}} \rightarrow ^3\text{T}_{2\text{g}}(\text{F})$  ( $\nu_1$ ),  $^3\text{A}_{2\text{g}} \rightarrow ^3\text{T}_{1\text{g}}(\text{F})$  ( $\nu_2$ ) and  $^3\text{A}_{2\text{g}} \rightarrow ^3\text{T}_{1\text{g}}(\text{P})$  ( $\nu_3$ ) transitions, respectively. The value of magnetic moment was 3.04  $\mu_{\text{B}}$ ; therefore octahedral geometry is suggested for this complex. The electronic spectrum of the Cu(II) complex of BSAP showed two bands at 15150 and 19230  $\text{cm}^{-1}$ , assignable to  $^2\text{B}_{1\text{g}} \rightarrow ^2\text{B}_{2\text{g}}$  and  $^2\text{B}_{1\text{g}} \rightarrow ^2\text{E}_{\text{g}}$  transitions, respectively. Since the value of magnetic moment was found 1.92  $\mu_{\text{B}}$ , square planar geometry is suggested for the Cu(II) complex.<sup>31–34</sup>

The Cr(III) complex of HNAC showed electronic spectral bands at 16871, 23837 and 34942  $\text{cm}^{-1}$ ; these were tentatively assigned to  $^4\text{A}_{2\text{g}} \rightarrow ^4\text{T}_{2\text{g}}(\text{F})$  ( $\nu_1$ ),  $^4\text{A}_{2\text{g}} \rightarrow ^4\text{T}_{1\text{g}}(\text{F})$  ( $\nu_2$ ) and  $^4\text{A}_{2\text{g}} \rightarrow ^4\text{T}_{1\text{g}}(\text{P})$  ( $\nu_3$ ) transitions, respectively. The magnetic moment value was 3.84  $\mu_{\text{B}}$ ; thus, an octahedral structure is suggested for this complex. The electronic spectrum of the Co(II) complex of HNAC showed bands at 14142 and 19514  $\text{cm}^{-1}$ , these were tentatively assigned to  $^4\text{A}_{2\text{g}} \rightarrow ^4\text{T}_{1\text{g}}(\text{F})$  ( $\nu_2$ ) and  $^4\text{A}_{2\text{g}} \rightarrow ^4\text{T}_{1\text{g}}(\text{P})$  ( $\nu_3$ ) transitions, respectively. The magnetic moment value was 4.32  $\mu_{\text{B}}$ , which is indicative of tetrahedral geometry. The absorption spectrum of the Ni(II) complex of HNAC exhibited bands at 12748 and 20750  $\text{cm}^{-1}$ , which were tentatively assigned to the transitions  $^1\text{A}_{1\text{g}} \rightarrow ^1\text{E}_{\text{g}}$  ( $\nu_1$ ) and  $^1\text{A}_{1\text{g}} \rightarrow ^1\text{B}_{2\text{g}}$  ( $\nu_2$ ), respectively. It is a diamagnetic complex, therefore square planar geometry is proposed. The electronic spectrum of the Cu(II) complex of HNAC showed two bands at 15110 and 19456  $\text{cm}^{-1}$ , assignable to  $^2\text{B}_{1\text{g}} \rightarrow ^2\text{B}_{2\text{g}}$

and  ${}^2B_{1g} \rightarrow {}^2E_g$  transitions, respectively. The value of magnetic moment for this complex was  $1.81 \mu_B$ ; thus, square planar geometry is suggested for the Cu(II) complex.<sup>31–34</sup>

The different parameters such as ligand field stabilization energy ( $10Dq$ ), Racah inter-electronic repulsion parameter ( $B$ ), nephelauxetic ratio ( $\beta$ ), percent of covalent character ( $\beta\%$ ) and ligand field stabilization energy ( $LFSE$ ) were calculated. The values of these parameters are presented in Table S-III of the Supplementary Material to this paper. The complexes showed lower value of  $B$  than those of the free ions, which indicates orbital overlapping and delocalization of the d-orbital. The value of  $\beta$  lied in the range of 0.68–0.78, indicating appreciable covalent character of the metal–ligand bonding.<sup>31–34</sup>

### ESR Spectra

The ESR spectra of Cu(II) provide information about the extent of the delocalization of the unpaired electron. The X-band ESR spectra of the Cu(II) complexes were recorded in the solid state at room temperature and their  $g_{\parallel}$ ,  $g_{\perp}$ ,  $\Delta g$ ,  $g_{av}$  and  $G$  were calculated. The values of ESR parameters  $g_{\parallel}$ ,  $g_{\perp}$ ,  $g_{av}$ ,  $\Delta g$  and  $G$  for Cu(II) complex of BSAP were 2.2530, 2.1205, 2.1647, 0.1325 and 2.1181, respectively. Similarly, the corresponding values for Cu(II) complex of HNAC were 2.2072, 2.1342, 2.1585, 0.0730 and 1.5535, respectively.

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

The exchange coupling interaction between two Cu(II) ions is explained by the Hathaway Expression:

$$G = (g_{\parallel} - 2.0023)/(g_{\perp} - 2.0023)$$

According to Hathaway, if the value  $G$  is greater than 4 ( $G > 4.0$ ), the exchange interaction is negligible; whereas when the value of  $G$  is less than 4 ( $G < 4.0$ ), a considerable exchange coupling is present in a solid complex. The  $G$  values for the complexes were less than four, indicating considerable exchange interaction in the complexes.<sup>35,36</sup>

### Thermal analyses

The thermal behaviour of the metal complexes showed that the hydrated complexes first lost molecules of hydration, followed by decomposition of the ligand molecules in the subsequent steps.

The thermal degradation behaviour of the Co(II) complex of BSAP was studied by thermogravimetric analysis. The TGA curve of the complex showed three stages of decomposition within the temperature range 30–750 °C. The complex did not show any loss in weight up to 110 °C, indicating the absence of lattice water molecules. A weight loss was observed after elimination of three coordinated molecules of water between the temperature range 110–225 °C (remaining mass %, obs./calcd.: 87.50/86.63). Above 225 °C, a weight loss was observed in general up to 380 °C, indicating decomposition of the non-coordinated part of the ligand (remaining mass %, obs./calcd.: 48.20/45.05). The decomposition of remaining ligand moiety occurred between 480–620 °C, above 620 °C a horizontal curve was observed suggesting the ultimate pyrolysis product as metal oxide (remaining mass %, obs./calcd.: 29.64/25.99).

The TGA curve of the Ni(II) complex of HNAC showed a weight loss between 72–116 °C. This corresponds to the loss of three lattice water molecules in the complex (remaining mass %, obs./calcd.: 90.10/89.87). Above 116 °C, the complex did not show any loss in weight up to 200 °C. After 200 °C, weight loss was observed up to 400 °C, which corresponded with the decomposition of thermally degradable part of the ligand (remaining mass %, obs./calcd.: 64.55/62.10). After this temperature, a weight loss was observed, suggesting the elimination of the remaining part of the ligand. Above 590 °C, a constant weight region was observed due to metal oxide, as the final pyrolysis product (remaining mass %, obs./calcd.: 25.72/20.66).<sup>37,38</sup>

The thermal analysis evaluation of the thermal stability of the metal complexes aided in the characterization of the metal complexes.

#### *Kinetic study*

Kinetic evaluations of the thermal decomposition of the complexes were performed. All stages were selected for the study of kinetics of decomposition of the complexes. Based on the thermal decomposition data, the kinetic parameter, *i.e.*, activation energy ( $E^*$ ), pre-exponential factor ( $Z$ ), entropy of activation ( $\Delta S^*$ ), enthalpy of activation ( $\Delta H^*$ ) and free energy of activation ( $\Delta G^*$ ) were calculated using the Piloyan–Novikova<sup>39</sup> and Coats–Redfern<sup>40</sup> Equations. The determined values of the kinetic parameters are summarized in Table S-IV of the Supplementary Material to this paper.

The high values of the activation energies reflect the thermal stability of the complexes. The complexes have negative entropy, which indicates that the decomposition reactions proceed with a lower rate than normal ones. The negative value of entropy also indicates that the activated complexes have a more ordered and more rigid structure than the reactants or intermediates. The negative values of the entropies of activation are compensated by the values of enthalpies of activation, leading to almost the same values for the free energy of activation.<sup>41,42</sup>

### Electrochemical studies

The electrochemical properties of the two complexes of BSAP were studied by cyclic voltammetry (CV) under a nitrogen atmosphere in DMSO solution in the potential range  $-1.0$  to  $1.2$  V vs. an Ag/AgCl reference electrode. The Co(II) complex of BSAP showed a reduction peak at  $E_{pc} = -619$  mV with a corresponding oxidation peak at  $E_{pa} = -428$  mV at a scan rate  $100 \text{ mV s}^{-1}$ . The peak separation  $\Delta E_p$  was  $191$  mV for this couple. Thus, the cyclic voltammetric studies gave evidence to a quasi-reversible Co(II)/Co(I) couple.

The cyclic voltammogram of the Cu(II) complex of BSAP exhibited a one-electron quasi-reversible transfer process with a reduction peak at  $E_{pc} = -725$  mV with an associated oxidation peak at  $E_{pa} = -444$  mV at scan rate  $100 \text{ mV s}^{-1}$  which increased with scan rate. The peak separation of this couple ( $\Delta E_p$ ) was  $281$  mV. The most significant feature of the Cu(II) complex was the Cu(II)/Cu(I) couple. This redox process was consistent with a quasi-reversible process.<sup>43,44</sup>

### X-Ray diffraction study

X-Ray diffraction (XRD) analysis of the Ni(II) complexes was performed. The XRD patterns indicate the crystalline nature of the complex. The X-ray powder diffractogram of the complex were recorded using  $\text{CuK}\alpha$  as the source in the  $2\theta$  range  $5-70^\circ$ . The X-ray crystal system was determined by trial and error methods for finding the best fit between the observed and calculated  $\sin^2\theta$ . The Ni(II) complex of BSAP crystallized in an orthorhombic system. The  $\sin^2\theta$  and  $hkl$  values for different lattice planes were calculated for this complex. The crystal data for this complex were  $a = 12.67352 \text{ \AA}$ ,  $b = 23.79049 \text{ \AA}$ ,  $c = 16.62566 \text{ \AA}$ ,  $V = 5012.79 \text{ \AA}^3$ ,  $Z = 11$ ,  $D_{\text{obs}} = 1.4713 \text{ g cm}^{-3}$  and  $D_{\text{cal}} = 1.4652 \text{ g cm}^{-3}$ . The observed and calculated values of density and  $\sin^2\theta$  show good agreement.<sup>45,46</sup>

### Electrical conductivity

The temperature dependence of the solid state conductivity ( $\sigma$ ) of the compounds in their compressed pellet form was measured at a fixed frequency of  $1 \text{ kHz}$  in the temperature range  $297-413 \text{ K}$ . The values of the solid state electrical conductivity of the Schiff bases and their complexes increased with increasing temperature and decreased upon cooling over the studied temperature range, indicating their semi-conducting behaviour. The general behaviour of electrical conductivity follows the Arrhenius Equation:

$$\sigma = \sigma_0 \exp(-E_a/kT)$$

where  $E_a$  is the thermal activation energy of conduction,  $\sigma_0$  is the conductivity constant and  $k$  is the Boltzman constant. The plots of  $\sigma$  vs.  $1000/T$  for all the compounds were found to be linear over the studied temperature range. The room temperature electrical conductivity of all the compounds lies in the range  $1.241 \times 10^{-7} - 3.525 \times 10^{-12} \text{ }\Omega^{-1} \text{ cm}^{-1}$ . These values showed their semi-conducting

nature. The order of the electrical conductivity at room temperature for the complexes of BSAP and those of HNAC was  $\text{Co} > \text{Cr} > \text{Cu} > \text{Ni}$ . The activation energy of the compounds lie in the range 0.221–0.768 eV.<sup>47–49</sup> Confirmation of the temperature dependence of the conductivity of the compounds was checked by repetition of the conductivity measurements.

#### Antimicrobial activities

The *in vitro* antimicrobial activities of the synthesized Schiff base ligands and their corresponding metal complexes against two selected bacteria *E. coli* and *S. aureus* and two fungi *A. niger* and *C. albicans* were determined. Any chemotherapeutic agent reduces the growth of microbes by microcidal or microstatic mechanisms. All of the tested compounds showed good biological activity against the micro-organism. On comparing the biological activities of the Schiff base ligands and their metal complexes with those of a standard bactericide and fungicide, it was shown that the metal complexes had moderate activity as compared to the standard but all the complexes were more active than their respective ligands. The higher inhibition zone of the metal complexes than those of the ligands can be explained based on the Overtone concept and the chelation theory. Upon chelation, the polarity of the metal ion is reduced to a great extent due to the overlap of the ligand orbital and the partial sharing of the positive charge of the metal ion with donor groups. Furthermore, it increases the delocalization of the  $\pi$ -electrons over the whole chelating ring and enhances the penetration of the complexes into lipid membranes and the blocking of the metal binding sites in the enzymes of micro-organisms. There are other factors that increase the activity, *viz.* solubility, lipophilicity/hydrophilicity, conductivity and M–L bond length.<sup>50–53</sup>

The bactericidal and fungicidal data of the compounds are summarized in Tables II and III, respectively. The results of the investigations account for the antipathogenic behaviour of the compounds and this efficacy is positively modified on complexation.

TABLE II. Antibacterial screening data for the ligands and their complexes

Compound	<i>E. coli</i>						<i>S. aureus</i>					
	Diameter of			Activity index <sup>a</sup>			Diameter of			Activity index		
	inhibition zone, mm			%			inhibition zone, mm			%		
	Concentration, μg ml <sup>-1</sup>											
	25	50	100	25	50	100	25	50	100	25	50	100
BSAP	11	13	16	50	54	57	11	14	16	61	64	67
Cr(III)	14	16	19	64	67	68	12	15	18	67	68	75
Co(II)	18	20	24	82	83	86	14	18	20	78	82	83
Ni(II)	16	19	25	73	79	89	12	15	18	67	68	75
Cu(II)	17	20	24	77	83	86	15	19	21	83	86	88
HNAC	10	12	15	45	50	54	—	10	12	—	45	50
Cr(III)	11	13	16	50	54	57	11	14	17	61	64	71

TABLE II. Continued

Compound	<i>E. coli</i>						<i>S. aureus</i>					
	Diameter of			Activity index <sup>a</sup>			Diameter of			Activity index		
	inhibition zone, mm			%			inhibition zone, mm			%		
	Concentration, µg ml <sup>-1</sup>											
	25	50	100	25	50	100	25	50	100	25	50	100
Co(II)	15	18	22	68	75	79	14	18	21	78	82	88
Ni(II)	14	16	20	64	67	71	12	16	18	67	73	75
Cu(II)	16	19	23	73	79	82	13	17	19	72	77	79
Streptomycin (standard)	22	24	28	100	100	100	18	22	24	100	100	100

$$^a \text{Activity index} = \frac{\text{Inhibition zone by test compound (diameter)}}{\text{Inhibition zone by standard (diameter)}} \times 100$$

TABLE III. Antifungal screening data for the ligands and their complexes (diameter of inhibition zone, mm)

Compound	<i>A. niger</i>			<i>C. albicans</i>		
	Concentration, $\mu\text{g ml}^{-1}$					
	25	50	100	25	50	100
BSAP	11	14	18	12	13	17
Cr(III)	12	15	19	14	16	20
Co(II)	14	18	22	16	18	23
Ni(II)	12	16	20	15	17	22
Cu(II)	15	20	24	17	19	23
HNAC	12	16	20	11	14	18
Cr(III)	13	15	21	15	18	22
Co(II)	16	21	26	18	20	25
Ni(II)	15	20	25	16	18	23
Cu(II)	14	19	23	19	21	26
Miconazole (standard)	20	25	30	22	24	29

## CONCLUSIONS

In the present research study, the aim was to synthesize and characterize some new compounds prepared by the conventional and the microwave method. The microwave method is considered a green chemical route. The synthesized compounds were characterized by various physico-chemical and spectral analyses. In course of the microwave assisted syntheses, it was observed that the reaction time was decreased from hours to minutes and the products were obtained in better yield as compared to those of the conventional method. The use of solvent was also minimized. The synthesized BSAP Schiff base ligand bound with the metal ions in a tridentate manner, with ONO donor sites of the phenyl-O, azomethine-N and pyridyl-O, whereas the HNAC ligand also coordinated to the metal ions in a tridentate manner, with ONO donor sites of phenolic-O, azomethine-N and carbonyl-O. Such metal complexes may be stereoselective and



stereoactive in nature and thus applicable in various catalytic reactions. Thermo-gravimetric studies reflected their thermal stability. The XRD patterns indicated the crystalline nature of the complexes. The electrical conductivity data suggested that all the complexes fall into the semi-conducting range. The antimicrobial data showed that the metal complexes were more biologically active compared to the parent Schiff base ligands against all the tested pathogenic species. Such studies may assist in the search for some novel chemotherapeutics to answer the emerging problem of drug resistance in health sciences.

#### SUPPLEMENTARY MATERIAL

Analytical, conductivity, spectral, magnetic, kinetic and thermodynamic data of the synthesized complexes are available electronically from <http://www.shd.org.rs/JSCS/>, or from the corresponding author on request.

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#### ИЗВОД

#### СИНТЕЗА ПОМОЋУ МИКРОТАЛАСА И СПЕКТРАЛНА, ТЕРМИЧКА И АНТИМИКРОБНА СВОЈСТВА НЕКИХ НОВИХ КОМПЛЕКСА ПРЕЛАЗНИХ МЕТАЛА СА ТРИДЕНТАТНОКООРДИНОВАНИМ ШИФОВИМ БАЗАМА КАО ЛИГАНДИМА

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Применом конвенционалних метода и микроталаса, синтетизовани су нови комплекси Cr(III), Co(II), Ni(II) и Cu(II) са Шифовим базама 2-[(5-бромо-2-хидроксibenзилиден)амино]пиридин-3-олом (BSAP) и {5-хлоро-2-[[[(2-хидрокси-1-нафтил)метилен)-амино]фенил]фенилметаноном (HNAC)}. За карактеризацију комплекса употребљени су елементална микроанализа, FT-IR и електронска спектроскопија, FАВ-масена спектрометрија, мерења моларне и електричне проводљивости и магнетне суцептибилности, термичке методе, циклична волтаметрија и XRD анализа. На основу аналитичких података нађено је да су одговарајући јон метала и лиганд у овим комплексима координовани у 1:1 молском односу, при чему је координациони број лиганда 4 или 6. На основу IR спектроскопских резултата закључено је да се лиганд координује тридентатно за наведене јоне метала. Начин разлагања ових комплекса је одређен на основу FАВ-масених и термичких података, при чему је нађено да хидратисани комплекси прво губе молекуле хидратационе воде, а затим долази до разлагања лиганда. Применом XRD анализе одређене су кристалне структуре синтетизованих комплекса, као и параметри, запремина и број молекула у јединичној ћелији кристалне решетке. Измерена је електрична проводљивост комплекса у чврстом стању, при чему су ова мерења показала да су синтетизовани комплекси полупроводници. Испитивана је антибактеријска активност синтетизованог лиганда и одговарајућих комплекса на грам-позитивне (*Staphylococcus aureus*) и на грам-негативне (*Escherichia coli*) бактерије, као и антифунгална активност на сојевима *Aspergillus niger* и *Candida albicans*. Добијени резултати ових испитивања су

показали да комплекси наведених јона метала имају већу антибактеријску односно антифунгалну активност у односу на некоординоване Шифове базе.

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