



# Synthesis, Spectral Characterization and Antimicrobial Evaluation of Schiff Base Cu(II), Ni(II) and Co(II) Novel Macrocyclic Complexes

GAJENDRA KUMAR, AMIT KUMAR,  
NUPUR SHISHODIA, Y.P. GARG and B.P. YADAV\*

Department of Chemistry  
Meerut College Meerut 250001, Uttar Pradesh, India  
*gaj.chem@gmail.com*

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**Abstract:** A series of Schiff base macrocyclic complexes of the type [HLMX<sub>2</sub>] where M = Cu(II), Ni(II), Co(II) and X = Cl, OAc have been synthesized by condensation of acetylacetone and thiocarbohydrazide (2:2) in the presence of divalent metal salt in methanolic medium. The complexes have been characterized with the help of elemental analysis, conductance measurements, magnetic measurements and their structural configuration have been determined by various spectroscopic (Electronic, IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR, GCMS) techniques. Electronic and magnetic moments of the complexes indicate that the geometries of the metal centers are octahedral. These metal complexes were also tested for their antimicrobial activities to assess their inhibiting potential.

**Keywords:** Metal complexes, Antimicrobial activity, Spectroscopic study, Thiocarbohydrazide, Acetylacetone

## Introduction

Synthesis and characterization of well-arranged metal-containing macrocycles is an interesting field of coordination chemistry. Schiff base compound containing an imino group (–RC = N–) are usually formed by the condensation of a primary amine with an active carbonyl. The chemistry of metal complexes with multidentate ligand and delocalized  $\pi$ -orbitals such a Schiff base<sup>1</sup> or porphyrin has gained much interest because of their use as models in biological system. The cross linking agents can also be derived from metal complexes with O–N– or –S ligands for example, the intra-coordination salt such as salicylates, anthraanilates and the aliphatic or aromatic amines can form strong five of six membered chelates rings which are able to produce the metal containing crosslinking agents with required properties<sup>2</sup>. There are a number of important molecules shows biological activities

including antibacterial, antifungal<sup>3-6</sup>, antidiabetic<sup>7</sup>, antitumor<sup>8</sup>, antiproliferative<sup>9-10</sup>, anticancer<sup>11-12</sup>, herbicidal<sup>13</sup>, anticorrosion and anti-inflammatory activities<sup>3</sup> Schiff bases represent an important class of compounds because they are utilized as starting materials in the synthesis of industrial products. Moreover, Schiff bases are regarded as privileged ligands<sup>14</sup>. Due to their capability to form complexes with different transition metals can act as catalysts for many different reactions<sup>15-16</sup>. On the other hand, Schiff bases derived from coumarin and its metal complexes have been found to exhibit biological activities and plant regulating activities<sup>17</sup>. The variety of possible Schiff bases metal complexes with wide choice of ligands and coordination environments has prompted us to undertake research in this area<sup>18</sup>. In the present article, we report the synthesis and characterization of Schiff base derived from acetylacetone and thiocarbohydrazone and its metal complexes to gain more information about related structural and spectral properties as well as their antimicrobial activities.

## Experimental

### Reagents

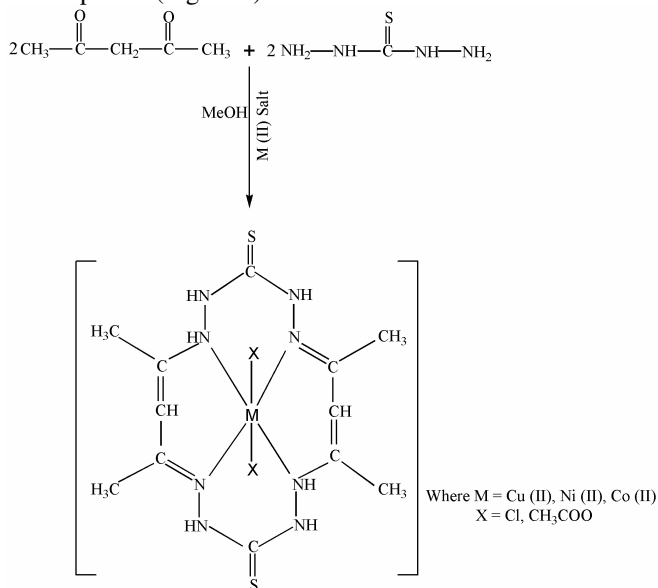
The entire chemicals used were of the analytical reagent grade, acetylacetone and thiocarbohydrazone procured from Acros and S.D.-Fine, respectively. Metal salts were purchased from Merck.

### Synthesis of the ligand

The ligand was prepared by the condensation of acetylacetone with thiocarbohydrazone (2:2). A mixture of ethanol/1, 2-dichloroethane (1:3) was used as a solvent in the presence of anhydrous magnesium sulphate as a dehydrating agent.

### Synthesis of the metal complexes

The metal complexes of the ligand HL (1) were prepared by mixing a hot methanolic solution of the metal salts with required amount of a hot ethanolic solution of the ligand to form metal/ligand complexes (Figure 1).



**Figure 1.** Scheme for synthesis of novel macrocycles metal complexes

The microanalysis of C, H and N were estimated by elemental analyzer (Perkin Elmer 2400 and the metal contents of Cu(II), Ni(II) and Co(II) were determined by atomic absorption spectrophotometer (Perkin Elmer 5000). IR spectra were recorded on a FT-IR spectrophotometer (Perkin Elmer) in the range 4000-200  $\text{cm}^{-1}$  using Nujol Mull.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra (at room temperature) (in DMSO- $d_6$ ) were recorded on a Bruker AVANCE II 300 DRX or average 400 DRX spectrometer with reference to  $\text{Me}_4\text{Si}$  (0.0 ppm). The FAB mass spectra (at room temperature) were recorded on JEUL JMS-AX-500 mass spectrometer, GC-MS analysis was performed on a Shimadzu GCMS- QP5050A instrument, Indian Institute of Petroleum Dehradun, India. Magnetic susceptibility measurements were carried out at SAIF, IIT Roorkee, on vibrating sample magnetometer (Model PAR 155). Electronic spectra in DMSO were recorded on a Hitachi 330 spectrophotometer (1300-200 nm) at room temperature. The conductivity was measured on digital conductivity meter (HPG system, G-3001).

#### *Synthesis of the Schiff base ligand HL*

Thio-carbohydrazide (206.0 mg, 2.2 mmol) in ethanol (10 mL) was added to a hot solution (75 °C) of acetylacetone (450.0 mg, 4.5 mmol) in ethanol (25 mL), the solid thiocarbohydrazide was dissolved gradually to yield a clear solution. The solution was stirred at 75 °C for 2h. Then anhydrous magnesium sulphate (250.0 mg, 2.5 mmol) was added to the mixture. The reaction mixture was refluxed for 40 h. The solid was filtered. (0.7145 g, 58% yield). UV/Vis (Nujol mul (nm)):  $\lambda = 280, 330, 340$ . UV/VIS ( $1 \times 10^{-4}$  mol, DMSO):  $\lambda = 270, 290, 345$ . IR (KBr):  $\nu(\text{N}^2\text{H})$  3245 m,  $\nu(\text{C}=\text{S})$  861 s,  $\nu(\text{C}=\text{N})$  1678 s,  $\nu(\text{N}-\text{N})$  1115  $\text{s cm}^{-1}$ . Elemental analysis for  $\text{C}_{12}\text{H}_{20}\text{N}_8\text{S}_2$  (340.48): calcd. C 42.33, H 5.92, N 32.91; found C 42.95, H 5.42, N 32.83.

#### *Synthesis of HLCuCl<sub>2</sub> complex (1)*

A solution of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  (286.0 mg, 1.678 mmol) in methanol (8 mL) was added to a hot solution (75 °C) of HL (1) (485.0 mg, 1.421 mmol) in ethanol (20 mL) and the reaction mixture was refluxed for 2 h. The brown solution was concentrated under vacuum. The precipitate was filtered off, washed with methanol and dried under vacuum over anhydrous  $\text{CaCl}_2$  (0.419 g, 68% yield). Conductance  $\Lambda_m$ :  $79 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ . UV/Vis (Nujol mul (nm)):  $\lambda = 260, 280, 300, 500, 715$  and 1155. IR (KBr):  $\nu(\text{N}^2\text{H})$  3277 (br),  $\nu(\text{C}=\text{S})$  847 (m),  $\nu(\text{C}=\text{N})$  1644 (m),  $\nu(\text{N}-\text{N})$  1122  $\text{cm}^{-1}$  (w). Elemental analysis for  $\text{C}_{12}\text{H}_{20}\text{CuCl}_2\text{N}_8\text{S}_2$  (474.93): calcd. C 30.34, H 4.24, N 23.59, Cu 13.38; found C 30.42, H 4.36, N 23.55, Cu 13.08.

#### *Synthesis of HLCu(OC(O)CH<sub>3</sub>)<sub>2</sub> complex (2)*

A solution of  $\text{Cu}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  (388.0 mg, 1.781 mmol) in methanol (6 mL) was added to a hot solution (75 °C) of HL (1) (606.0 mg, 1.781 mmol) in ethanol (23 mL) and the reaction mixture was refluxed for 2 h. The brown solution was concentrated under vacuum. The precipitate was filtered off, washed with methanol and dried under vacuum over anhydrous  $\text{CaCl}_2$  (0.462 g, 61% yield). Conductance  $\Lambda_m$ :  $76 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ . UV/Vis (Nujol mul (nm)):  $\lambda = 255, 271, 320, 515, 724$  and 1145. IR (KBr):  $\nu(\text{N}^2\text{H})$  3272 (br),  $\nu(\text{C}=\text{O})$  1707 (s),  $\nu(\text{C}=\text{S})$  861 (m),  $\nu(\text{C}=\text{N})$  1651 (m),  $\nu(\text{N}-\text{N})$  1146  $\text{cm}^{-1}$  (w).  $\nu_{\text{sym}}(\text{OC}(\text{O})\text{CH}_3)$  1558 (m),  $\nu_{\text{asym}}(\text{OC}(\text{O})\text{CH}_3)$  1369  $\text{cm}^{-1}$  (m), ( $\Delta\nu = 190 \text{ cm}^{-1}$ ). Elemental analysis for  $\text{C}_{16}\text{H}_{26}\text{CuN}_8\text{O}_4\text{S}_2$  (522.12): calcd. C 36.80, H 5.01, N 21.46, Cu 12.17; found C 36.56, H 5.11, N 21.94, Cu 12.42.

### *Synthesis of HLNiCl<sub>2</sub> complex (3)*

A solution of NiCl<sub>2</sub>·6H<sub>2</sub>O (421.0 mg, 1.771 mmol) in methanol (15 mL) was added to a hot solution (75 °C) of HL (1) (602.0 mg, 1.771 mmol) in ethanol (16 mL), the reaction mixture was refluxed for 4 h. The precipitate was filtered off, washed with methanol and dried under vacuum over anhydrous CaCl<sub>2</sub> (0.433 g, 81% yield). Conductance  $\Lambda_m$ : 11  $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ . UV/VIS (Nujol mul (nm)):  $\lambda$ =260, 279, 320, 445, 706, 1145. IR (KBr):  $\nu(\text{N}^2\text{H})$  3265 (br),  $\nu(\text{C}=\text{S})$  845 (m),  $\nu(\text{C}=\text{N})$  1650 (s),  $\nu(\text{N}-\text{N})$  1146  $\text{cm}^{-1}$  (s). Elemental analysis for C<sub>12</sub>H<sub>20</sub>NiCl<sub>2</sub>N<sub>8</sub>S<sub>2</sub> (470.08): calcd. C 30.66, H 4.28, N 23.83, Ni 12.48; found C 30.69, H 4.89, N 23.78, Ni 12.35.

### *Synthesis of HLNi(OC(O)CH<sub>3</sub>)<sub>2</sub> complex (4)*

A solution of Ni(OAc)<sub>2</sub>·4H<sub>2</sub>O (486.0 mg, 1.953 mmol) in methanol (10 mL) was added to a hot solution (75 °C) of HL (1) (664.0 mg, 1.953 mmol) in ethanol (20 mL) and the reaction mixture was refluxed for 4 h. The precipitate was filtered off, washed with methanol and dried under vacuum over anhydrous CaCl<sub>2</sub> (0.484 g, 78% yield). Conductance  $\Lambda_m$ : 8  $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ . UV/Vis (Nujol mul (nm)):  $\lambda$ = 255, 270, 340, 461, 676 and 1135. IR (KBr):  $\nu(\text{N}^2\text{H})$  3260 (br),  $\nu(\text{C}=\text{O})$  1706 (s),  $\nu(\text{C}=\text{S})$  859 (w),  $\nu(\text{C}=\text{N})$  1657 (s),  $\nu(\text{N}-\text{N})$  1123  $\text{cm}^{-1}$  (m),  $\nu_{\text{sym}}(\text{OC}(\text{O})\text{CH}_3)$  1559 (m),  $\nu_{\text{asym}}(\text{OC}(\text{O})\text{CH}_3)$  1368  $\text{cm}^{-1}$  (m), ( $\Delta\nu=191\text{cm}^{-1}$ ). Elemental analysis for C<sub>16</sub>H<sub>26</sub>NiN<sub>8</sub>O<sub>4</sub>S<sub>2</sub> (517.27): calcd. C 37.15, H 5.06, N 21.66, Ni 11.34; found C 37.22, H 5.08, N 21.54, Ni 11.32.

### *Synthesis of HLCoCl<sub>2</sub> complex (5)*

A solution of CoCl<sub>2</sub>·6H<sub>2</sub>O (410.0 mg, 1.723 mmol) in methanol (15mL) was added to a hot solution (75 °C) of HL (1) (586.0 mg, 1.723 mmol) in ethanol (30 mL), the reaction mixture was refluxed for 6 h. The precipitate was filtered off, washed with methanol and dried under vacuum over anhydrous CaCl<sub>2</sub> (0.547 g, 75% yield). Conductance  $\Lambda_m$ : 19  $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ . UV/Vis (Nujol mul (nm)):  $\lambda$ =260, 279, 320, 417, 652 and 1061. IR (KBr):  $\nu(\text{N}^2\text{H})$  3268 (br),  $\nu(\text{C}=\text{S})$  840 (m),  $\nu(\text{C}=\text{N})$  1632 (s),  $\nu(\text{N}-\text{N})$  1145  $\text{cm}^{-1}$  (s). Elemental analysis for C<sub>12</sub>H<sub>20</sub>CoCl<sub>2</sub>N<sub>8</sub>S<sub>2</sub> (470.32): calcd. C 30.64, H 4.28, N 23.82, Co 12.53; found C 30.54, H 4.92, N 23.51, Ni 12.25.

### *Synthesis of HLCo(OC(O)CH<sub>3</sub>)<sub>2</sub> complex (6)*

A solution of Co(OAc)<sub>2</sub>·4H<sub>2</sub>O (460.0 mg, 1.847 mmol) in methanol (12 mL) was added to a hot solution (75 °C) of HL (1) (628.0 mg, 1.847 mmol) in ethanol (24 mL), the reaction mixture was refluxed for 6 h. The precipitate was filtered off, washed with methanol and dried under vacuum over anhydrous CaCl<sub>2</sub> (0.478 g, 71% yield). Conductance  $\Lambda_m$ : 17  $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ . UV/Vis (Nujol mul (nm)):  $\lambda$  = 255, 270, 340, 433, 622, 1051. IR (KBr):  $\nu(\text{H}_2\text{O})$  3344 (br),  $\nu(\text{N}^2\text{H})$  3263 (br),  $\nu(\text{C}=\text{O})$  1705 (s),  $\nu(\text{C}=\text{S})$  854 (w),  $\nu(\text{C}=\text{N})$  1639 (s),  $\nu(\text{N}-\text{N})$  1122 (w),  $\nu_{\text{sym}}(\text{OC}(\text{O})\text{CH}_3)$  1560 (m),  $\nu_{\text{asym}}(\text{OC}(\text{O})\text{CH}_3)$  1367  $\text{cm}^{-1}$  (m) ( $\Delta\nu=193\text{cm}^{-1}$ ). Elemental analysis for C<sub>16</sub>H<sub>26</sub>NiN<sub>8</sub>O<sub>4</sub>S<sub>2</sub> (517.27): calcd. C 37.15, H 5.06, N 21.66, Co 11.34; found C 37.26, H 5.05, N 21.45, Co 11.32.

## **Pharmacology**

### *Antifungal activity*

The free ligand, its metal complexes, fungicide fluconazole and the control DMSO (dimethylsulfoxide) were screened for their antifungal activity against various fungi *viz.* *Rizoctonia* sp., *Aspergillus* sp. and *penicillium* sp. These species were isolated from the infected organs of the host plants on potato dextrose agar (potato 250 g + dextrose 20 g + agar 20 g) medium.

The culture of the fungi was purified by single spore isolation technique. The solution of different concentrations 10 µg/mL of each compound (free ligand, its metal complexes and fungicides fluconazole) in DMSO were prepared for testing against spore germination. A drop of the solution of each concentration was kept separately on glass slides. The conidia, fungal reproducing spores (approx. 200) lifted with the help of an inoculating needle, which was mixed in every drop of each compound separately. Each treatment was replicated thrice and a parallel DMSO solvent control set was also run concurrently on separate glass slide. All the slides were incubated in humid chambers at 25 °C for 24 h. Each slide was observed under the microscope for spore germination and percent germination was finally calculated. The results were compared with a standard fungicide fluconazole at the same concentrations.

#### *Antibacterial activity*

Antibacterial activities were investigated using agar well diffusion method<sup>19</sup>. The activity of the free ligand, its metal complexes and standard drug gentamycin were studied against the *Staphylococcus aureus* and *Bacillus subtilis* (as gram positive bacteria) and *Pseudomonas aeruginosa*, *Escherichia coli* and *Salmonella typhi* (as gram negative bacteria). Strain were obtained from Microbial Type Collection and Gene Bank, Institute of Microbial Technology (IMTECH) Chandigarh, India. The solution of 2 mg/mL of each compound (free ligand, its metal complexes and standard drug gentamycin) in DMSO was prepared for testing against bacteria. Centrifuged pellets of bacteria from a 24 h old culture containing approximately 10<sup>4</sup>-10<sup>6</sup> CFU (colony forming unit) per ml were spread on the surface of Muller Hinton Agar plates. Wells were created in medium with the help of a sterile metallic bores and nutrients agar media (agar 20 g + beef extract 3 g + peptones 5 g) in 1000 mL of distilled water (pH 7.0), autoclaved and cooled down to 45 °C. Then it was seeded with 10 mL of prepared inocula to have 10<sup>6</sup> CFU/mL. Petri plates were prepared by pouring 75 mL of seeded nutrient agar. The activity was determined by measuring the diameter of the inhibition zone (in mm). The growth inhibition was calculated according to reference<sup>19</sup>.

## **Results and Discussion**

#### *Mass spectra*

The FAB mass spectra of Cu(II), Ni(II) and Co(II) Schiff base complexes have been recorded. The molecular ion (M<sup>+</sup>) peaks obtained from various complexes are as follows: (1) m/e = 340.48 (Ligand), (2) m/e = 474.93 (complex 1), (3) m/e = 522.12 (complex 2), (4) m/e = 470.08 (complex 3), (5) m/e = 517.27 (complex 4), (6) m/e = 470.32 (complex 5), (7) m/e = 517.51 (complex 6). This data is in good agreement with the proposed molecular formula for these complexes. In addition to the peaks due to the molecular ion, the spectra exhibit peaks assignable to various fragments arising from the thermal cleavage of the complexes. The peak intensity gives an idea of the stability of the fragments.

#### *Infrared spectra*

The IR spectra provide valuable information regarding the nature of functional group attached to the metal atom. The presence of a single medium band in the region 3250-3330 cm<sup>-1</sup> in the complexes may be assigned to N-H stretch<sup>20</sup>. It was noted that a pair of bands corresponding to  $\nu(\text{NH}_2)$  at 3245 cm<sup>-1</sup> and 3309 cm<sup>-1</sup> are present in the spectra of the thiocarbohydrazide. The value of  $\nu(\text{C}=\text{N})$  stretching vibration is found lower (1520-1560 cm<sup>-1</sup>) than the expected value (1580-1650 cm<sup>-1</sup>). This lower value of  $\nu(\text{C}=\text{N})$  stretching may be explained on the basis of a drift of lone pair density of azomethine nitrogen towards the metal atom<sup>21</sup> indicating that coordination takes place through nitrogen of (C=N) groups. The bands present in the range

3020–3040  $\text{cm}^{-1}$  may be assigned due to (C–H) stretching vibrations of benzil and naphthalene ring<sup>22</sup>. The C–N stretch in the range 1000–1300  $\text{cm}^{-1}$ . The band near 780  $\text{cm}^{-1}$  in thiocarbonylhydrazide may be assigned as being due to free  $\nu(\text{C}=\text{S})$ . The band at 3292–3438  $\text{cm}^{-1}$  is due to the presence of OH group in the complexes. This band is also present in the spectra of all the complexes, which indicate that sulphur is not coordinating to the metal atom<sup>23</sup>. The far infrared spectra show bands in the region 420–450  $\text{cm}^{-1}$  corresponding to  $\nu(\text{M}-\text{N})$  vibrations<sup>24</sup>. The presence of bands in all complexes in the region 420–450  $\text{cm}^{-1}$  originates from the (M–N) azomethine vibrational modes and identifies coordination of azomethine nitrogen<sup>25</sup>. The bands present at 290–310  $\text{cm}^{-1}$  may be assigned due to  $\nu(\text{M}-\text{Cl})$  vibrations<sup>26</sup>.

The appearance of two characteristic bands in the ranges 1561–1559  $\text{cm}^{-1}$  and 1370–1367  $\text{cm}^{-1}$  in the case of complexes was attributed to  $\nu_{\text{asym}}(\text{COO}^-)$  and  $\nu_{\text{sym}}(\text{COO}^-)$ , respectively, indicating the participation of the carboxylate oxygen in the complexes formation. The mode of coordination of carboxylate group has often been deduced from the magnitude of the observed separation between the  $\nu_{\text{asym}}(\text{COO}^-)$  and  $\nu_{\text{sym}}(\text{COO}^-)$ . The separation value,  $\Delta\nu(\text{COO}^-)$ , between  $\nu_{\text{asym}}(\text{COO}^-)$  and  $\nu_{\text{sym}}(\text{COO}^-)$ , in these complexes were more than 190  $\text{cm}^{-1}$  (191–193  $\text{cm}^{-1}$ )<sup>27</sup>.

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

A survey of literature reveals that the NMR spectroscopy has been proved useful in establishing the structure and nature of many Schiff base ligand and their complexes. The <sup>1</sup>H NMR spectra of Schiff base ligand (HL) was recorded in *d*<sub>6</sub>-dimethylsulfoxide (DMFO-*d*<sub>6</sub>) solution using Me<sub>4</sub>Si (TMS) as internal standard. The <sup>1</sup>H NMR spectra of the ligand shows broad signal at 9.4–12.1 ppm due to the –NH<sup>29</sup>. The multiplets in the region 1.12–1.56 ppm may be assigned to aliphatic proton.

<sup>13</sup>C NMR of the Schiff base ligand, the signal appeared in the region 113–158 are assigned to aromatic carbon. The signal at 198.3–185.6, 182.8–171.2, 165.4–150.7 and 148.1–15.8 ppm are due to C=S, C=N, C=O and CH<sub>3</sub> respectively.

### Magnetic, electronic and electron spin resonance spectral studies

The electronic spectra of Cu(II) complexes **1** and **2** showed absorption band in the region 690–680 nm attributed to  ${}^2T_g \leftarrow {}^2E_g$  transition indicative of distorted octahedral geometry<sup>30</sup>. The ESR spectrum of copper(II) complexes has been studied. The  $g_{\parallel}$  and  $g_{\perp}$  values have been found to be 2.04351 and 2.15835, respectively. The  $g_{av}$  was calculated to be 2.12007. Complex (**1** and **2**) exhibits  $g_{\parallel} < 2.3$ , suggesting covalent characters of the copper–ligand bonding in this complex. The Cu(II) complexes shows reversed axial (compressed octahedral) with  $g_{\parallel} < g_{\perp}$ . The trend  $g_{\parallel} < g_{\perp}$  showed that the electron is delocalised in  $d_z^2$  orbital of the ground state of Cu(II). In this case ( $g_{\parallel} < g_{\perp}$ ) distortion occurs by compression<sup>31</sup>. The parameter *G*, determined as  $G = g_{\parallel} - 2.0023/g_{\perp} - 2.0023$ , is found to be much less than complex **4** suggesting considerable interaction in the solid state<sup>31</sup>. The magnetic moment value for this complex was found to be 1.48–1.63 B.M.

The absorption spectral bands of nickel(II) complexes **3,4** showed three spin allowed transitions:  ${}^3A_{2g}(\text{F}) \rightarrow {}^3T_{2g}(\text{F})$ ,  ${}^3A_{2g}(\text{F}) \rightarrow {}^3T_{1g}(\text{F})$  and  ${}^3A_{2g}(\text{F}) \rightarrow {}^3T_{1g}(\text{P})$  appearing in the ranges 1145–1054, 706–695 and 461–443 nm, respectively consistent with a typical Ni(II) in an octahedral environment<sup>32</sup>. The magnetic moment values for these complexes were found in the range 2.10–2.14 B.M.<sup>32</sup> expected for octahedral nickel complexes.

The electronic spectra of the cobalt(II) complexes **5** and **6** gave two bands at 1200–1051 and 489–433 nm, which could be assigned to the transitions  ${}^4T_{1g}(\text{F}) \rightarrow {}^4T_{2g}(\text{F})$  ( $\nu_1$ ) and

${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(P)$  ( $v_3$ ), respectively, suggesting an octahedral geometry around Co(II) ion<sup>33</sup>. The complexes **5** and **6** show magnetic moment values in the range 2.2–2.5 B.M., which is smaller than the calculated value for two Co(II) ions in octahedral geometries and this may be due to antiferromagnetism between the two ion-centers.

#### Antifungal activity

From the experimental data (Table 1), it has been observed that the ligand as well as its complexes shows a significant degree of antifungal activity against *Aspergillus* sp., *Rizoctonia* sp. and *Penicillium* sp. DMSO control has showed a negligible activity as compare to the metal complexes and ligand. However, the metal complexes shows better activity than the ligand<sup>32,34</sup>. The complexes are highly effective against *Aspergillus* sp. HLNi(OAc)<sub>2</sub> is the only complex to show 100% activity against *Aspergillus* sp. the antifungal activity of the complexes varies in the following order of fungal species: *Aspergillus* sp. > *penicillium* sp. > *Rizoctonia* sp.

**Table 1.** Antimicrobial results of Schiff base ligand and its metal complexes at 10  $\mu\text{g mL}^{-1}$  concentration.

Compound	Activity against bacteria, mm					Activity against fungi, mm		
	<i>Staphylococcus aureus</i>	<i>Bacillus subtilis</i>	<i>Escherichia coli</i>	<i>Salmonella typhi</i>	<i>Pseudomonas aeruginosa</i>	<i>Aspergillus</i> sp.	<i>Penicillium</i> sp.	<i>Rizoctonia</i> sp.
Ligand	14	14	10	10	08	09	08	10
HLCuCl <sub>2</sub>	11	14	09	11	12	14	13	12
HLCu(OAc) <sub>2</sub>	15	12	14	14	10	20	16	14
HLNiCl <sub>2</sub>	16	16	08	14	12	20	19	14
HLNi(OAc) <sub>2</sub>	22	20	18	18	16	24	22	19
HLCuCl <sub>2</sub>	18	16	18	18	16	18	21	18
HLCu(OAc) <sub>2</sub>	19	18	16	14	16	20	19	16
Fluconazole	-	-	-	-	-	14	16	20
Gentamycin	24	20	22	24	24	-	-	-

22-24 = Excellent activity, 16-22 = Good activity, 12-14 = Significant activity, 10-12 = negligible activity, 08-10 = no activity, Gentamycin = Standard antibacterial drug, fluconazole = Standard antifungal drug

The antifungal experimental results of the compounds were compared with the standard antifungal drugs fluconazole at the same concentration. All the metal complexes exhibited greater antifungal activity against *Aspergillus* sp. as compare to the standard drug fluconazole. However, they show slightly lesser activity against *Rizoctonia* sp. than standard drug fluconazole. The Co(II) and Ni(II) complexes are more effective against *Penicillium* sp. than the standard drug. From the data it has been also observed that the activity depends upon the type of metal ion and varies in the following order of the metal ion: Ni > Co > Cu.

#### Antibacterial activity

The ligand, its metal complexes and standard drug gentamycin were screened separately for their antibacterial activity against the bacteria *Staphylococcus aureus* and *Bacillus subtilis* (as gram positive bacteria) and *Pseudomonas aeruginosa*, *Escherichia coli*

and *Salmonella typhi* (as gram negative bacteria). The diffusion agar technique was used to evaluate the antibacterial activity of the synthesized metal complexes<sup>35</sup>. The results of the bactericidal study of the synthesized compounds are displayed in Table 1. From the bactericidal activity, it is apparent that the complexes were more toxic towards gram positive strains than gram negative strains. The reason is the difference in the structure of the cell walls. The walls of gram negative cells are more complex than those of gram positive cells. The zones of inhibition (ZOI) values obtained indicate that the ligand has moderate activity against *S. typhi* and *E. coli* but no activity against *P. aeruginosa*. Ligand also showed a significant activity towards *B. subtilis* and *S. aureus*. Antibacterial activity of all the complexes towards gram positive and gram negative bacteria is quite significant. Further to it, the ligand showed moderate, and the complexes moderate to high activities as compared to standard drug towards the entire organism.

The variation in the antimicrobial activity of different metal complexes against different microorganisms depends on their impermeability of the cell or the differences in ribosomes in microbial cell<sup>36</sup>. The lipid membrane surrounding the cell favors the passage of any lipid soluble materials and it is known that liposolubility is an important factor controlling antimicrobial activity<sup>37</sup>.

In the present study low activity of the some metal complexes is may be due to their low lipophilicity, because of which penetration of the complex through the lipid membrane was decreased and hence, they could neither block nor inhibit the growth of the microorganism.

## Conclusion

The analytical data show the presence of one metal ion per ligand molecule and suggest a mononuclear structure for the complexes. The electronic spectral data is in the favor of octahedral geometry of the complexes. The ligand and its Cu(II), Ni(II) and Co(II) complexes were tested for antimicrobial activity against some pathogen. Antimicrobial study reveals that, metal complexes have more biological activity than free ligand. Complex (4) [HLNi(OAc)<sub>2</sub>] shows best antimicrobial activity against all microorganism.

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