

## Synthesis, biological evaluation of substituted indol-2,3-dione and 2,2-dimethylpropane-1,3-diamine Cu(II), Ni(II) and Fe(II) metal complexes

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**Abstract:** A series 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 5-methylindoline-2,3-dione and 2,2-dimethylpropane-1,3-diamine 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. Thio-carbohydrazide and 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 as 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 or 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 5-methylindoline-2,3-dione and 2,2-dimethylpropane-1,3-diamine and its metal complexes to gain more information about related structural and spectral properties as well as their antimicrobial activities.

**Chemistry***Reagents*

The entire chemicals used were of the analytical reagent grade 5-methylindoline-2,3-dione and 2,2-dimethylpropane-1,3-diamine 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 5-methylindoline-2,3-dione with 2,2-dimethylpropane-1,3-diamine (1:1). 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 (Scheme 1).

#### *Synthesis of the metal complexes*

The metal complexes of the ligand (Z)-3-(3-amino-2,2-dimethylpropylimino)-5-substituted indolin-2-one 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 (Scheme 2).

### **Experimental Protocols**

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 4000-200cm<sup>-1</sup> using Nujol Mull. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra (at room temperature) (in DMSO-d<sub>6</sub>) were recorded on a Bruker AVANCE II 300 DRX or average 400 DRX spectrometer with reference to Me<sub>4</sub>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*

5-methylindoline-2,3-dione (2.0 mmol) in ethanol (10 ml) was added to a hot solution (75 °C) of 2,2-dimethylpropane-1,3-diamine (2.0 mmol) in ethanol (25 mL), The reaction mixture was refluxed for 7 h (58% yield). UV/vis (Nujol mul (nm)): λ = 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,  $\nu(\text{C}=\text{N})$  1678 s,  $\nu(\text{N}-\text{N})$  1115 s  $\text{cm}^{-1}$ . Elemental analysis for  $\text{C}_{14}\text{H}_{19}\text{N}_3\text{O}$  (245.32): calcd. C 68.54, H 7.81, N 17.13; found C 68.52, H 7.78, N 17.11.

#### *Synthesis of the metal complex (1)*

Synthesis of  $[\text{Cu}(\text{C}_{28}\text{H}_{38}\text{N}_6\text{O}_2)\text{Cl}_2]$  complex (1). A solution of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  (1.0 mmol) in methanol (8 mL) was added to a hot solution (75 °C) of ligand (2.0 mmol) in ethanol (20 mL), and the reaction mixture was refluxed for 8 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),  $\nu(\text{C}=\text{N})$  1644 (m),  $\nu(\text{N}-\text{N})$  1122  $\text{cm}^{-1}$  (w). Elemental analysis for  $[\text{Cu}(\text{C}_{28}\text{H}_{38}\text{N}_6\text{O}_2)\text{Cl}_2]$  (625.09): calcd. C 53.80, H 6.13, N 13.44, Cu 10.17; found C 53.78, H 6.10, N 13.45, Cu 10.15.

#### *Synthesis of the metal complex (2)*

Synthesis of  $[\text{Cu}(\text{C}_{28}\text{H}_{38}\text{N}_6\text{O}_2)(\text{NO}_3)_2]$  complex (1). A solution of  $\text{Cu}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  (1.0 mmol) in methanol (8 mL) was added to a hot solution (75 °C) of ligand (2.0 mmol) in ethanol (20 mL), and the reaction mixture was refluxed for 8 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),  $\nu(\text{C}=\text{N})$  1644 (m),  $\nu(\text{N}-\text{N})$  1122  $\text{cm}^{-1}$  (w). Elemental analysis for  $[\text{Cu}(\text{C}_{28}\text{H}_{38}\text{N}_6\text{O}_2)(\text{NO}_3)_2]$  (620.23): calcd. C 54.22, H 6.18, N 13.55, Ni 9.46; found C 54.21, H 6.16, N 13.53, Ni 9.44

#### *Synthesis of the metal complex (3)*

Synthesis of  $[\text{Cu}(\text{C}_{28}\text{H}_{38}\text{N}_6\text{O}_2)(\text{CH}_3\text{COO})_2]$  complex (3). A solution of  $\text{Cu}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  (1.0 mmol) in methanol (6 mL) was added to a hot solution (75 °C) of ligand (2.0 mmol) in ethanol (23 mL), and the reaction mixture was refluxed for 8 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),  $\nu(\text{C}=\text{N})$  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  $[\text{Cu}(\text{C}_{28}\text{H}_{38}\text{N}_6\text{O}_2)(\text{CH}_3\text{COO})_2]$  (620.47): calcd. C 54.20, H 6.17, N 13.54, Co 9.50; found C 54.18, H 6.15, N 13.52, Co 9.48

#### *Synthesis of the metal complex (4)*

Synthesis of  $[\text{Ni}(\text{C}_{28}\text{H}_{38}\text{N}_6\text{O}_2)\text{Cl}_2]$  complex (4). A solution of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (1.0 mmol) in methanol (15mL) was added to a hot solution (75 °C) of ligand (1.0 mmol) in ethanol (16mL), the reaction mixture was refluxed for 7 h. The precipitate was filtered off, washed with methanol and dried under vacuum over anhydrous  $\text{CaCl}_2$  (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),  $\nu(\text{C}=\text{N})$  1650 (s),  $\nu(\text{N}-\text{N})$  1146 $\text{cm}^{-1}$  (s). Elemental analysis for  $[\text{Ni}(\text{C}_{28}\text{H}_{38}\text{N}_6\text{O}_2)\text{Cl}_2]$  (678.19): calcd. C 49.59, H 5.65, N 16.52, Cu 9.37; found C 49.57, H 5.64, N 16.51, Cu 9.35

#### *Synthesis of the metal complex (5)*

Synthesis of  $[\text{Ni}(\text{C}_{28}\text{H}_{38}\text{N}_6\text{O}_2)(\text{NO}_3)_2]$  complex (5). A solution of  $\text{Ni}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  (1.0 mmol) in methanol (8 mL) was added to a hot solution (75 °C) of ligand (2.0 mmol) in ethanol (20 mL), and the reaction mixture was refluxed for 8 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),  $\nu(\text{C}=\text{N})$  1644 (m),  $\nu(\text{N}-\text{N})$  1122 $\text{cm}^{-1}$  (w). Elemental analysis for  $[\text{Ni}(\text{C}_{28}\text{H}_{38}\text{N}_6\text{O}_2)(\text{NO}_3)_2]$  (673.34): calcd. C 49.94, H 5.69, N 16.64, Ni 8.72; found C 49.96, H 5.66, N 16.61, Ni 8.70

#### *Synthesis of the metal complex (6)*

Synthesis of  $[\text{Ni}(\text{C}_{28}\text{H}_{38}\text{N}_6\text{O}_2)(\text{CH}_3\text{COO})_2]$  complex (6). A solution of  $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  (1.0 mmol) in methanol (10 mL) was added to a hot solution (75°C) of ligand (2.0 mmol) in ethanol (20 mL), and the reaction mixture was refluxed for 8 h. The precipitate was filtered off, washed with methanol and dried under vacuum over anhydrous  $\text{CaCl}_2$  (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),  $\nu(\text{C}=\text{N})$   $1657$  (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  $[\text{Ni}(\text{C}_{28}\text{H}_{38}\text{N}_6\text{O}_2)(\text{CH}_3\text{COO})_2]$  (673.58): calcd. C 49.93, H 5.69, N 16.64, Co 8.75; found C 49.92, H 5.70, N 16.63, Co 8.77

#### *Synthesis of the metal complex (7)*

Synthesis of  $[\text{Co}(\text{C}_{28}\text{H}_{38}\text{N}_6\text{O}_2)\text{Cl}_2]$  complex (7). A solution of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (1.0 mmol) in methanol (15 mL) was added to a hot solution ( $75^\circ\text{C}$ ) of ligand (1.0 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  $\text{CaCl}_2$  (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),  $\nu(\text{C}=\text{N})$   $1632$  (s),  $\nu(\text{N}-\text{N})$   $1145\text{cm}^{-1}$  (s). Elemental analysis for  $[\text{Co}(\text{C}_{28}\text{H}_{38}\text{N}_6\text{O}_2)\text{Cl}_2]$  (672.27): calcd. C 57.17, H 6.60, N 12.50, Cu 9.45; found C 57.15, H 6.59, N 12.51, Cu 9.42

#### *Synthesis of the metal complex (8)*

Synthesis of  $[\text{Co}(\text{C}_{28}\text{H}_{38}\text{N}_6\text{O}_2)(\text{NO}_3)_2]$  complex (8). A solution of  $\text{Co}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  (1.0 mmol) in methanol (8 mL) was added to a hot solution ( $75^\circ\text{C}$ ) of ligand (2.0 mmol) in ethanol (20 mL), and the reaction mixture was refluxed for 8 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),  $\nu(\text{C}=\text{N})$   $1644$  (m),  $\nu(\text{N}-\text{N})$   $1122\text{cm}^{-1}$  (w). Elemental analysis for  $[\text{Co}(\text{C}_{28}\text{H}_{38}\text{N}_6\text{O}_2)(\text{NO}_3)_2]$  (667.42): calcd. C 57.59, H 6.64, N 12.59, Ni 8.79; found C 57.57, H 6.62, N 12.57, Ni 8.77

#### *Synthesis of the metal complex (9)*

Synthesis of  $[\text{Co}(\text{C}_{28}\text{H}_{38}\text{N}_6\text{O}_2)(\text{CH}_3\text{COO})_2]$  complex (9). A solution of  $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  (1.0 mmol) in methanol (12 mL) was added to a hot solution ( $75^\circ\text{C}$ ) of ligand (2.0 mmol) in ethanol (24 mL), the reaction mixture was refluxed for 9 h. The precipitate was filtered off,

washed with methanol and dried under vacuum over anhydrous  $\text{CaCl}_2$  (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),  $\nu(\text{C}=\text{N})$  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  $[\text{Co}(\text{C}_{28}\text{H}_{38}\text{N}_6\text{O}_2)(\text{CH}_3\text{COO})_2]$  (667.66): calcd. C 57.57, H 6.64, N 12.59, Co 8.83; found C 57.55, H 6.66, N 12.57, Co 8.81

## Pharmacology

### Antimicrobial activity

Antimicrobial screening of the newly synthesized compound were evaluated using agar well diffusion method<sup>19</sup>. The biological activity of the free ligand, its metal complexes and standard drug (antibacterial Imipenem and antifungal miconazol) were studied against the *Staphylococcus aureus*, *Bacillus subtilis* (as gram positive bacteria) and *Pseudomonas aeruginosa*, *Escherichia coli*, *Salmonella typhi* (as gram negative bacteria) and fungi *Rizoctonia sp.*, *Aspergillus sp.*, *Penicillium sp.* All strains were obtained from Microbial Type Collection and Gene Bank, Institute of Microbial Technology (IMTECH) Chandigarh, India. Wells with 6 mm diameter made, and then solution of test compound was filled to the wells. The plates were incubated at 30°C for 24h. The activity of the compounds was determined by measuring diameter of the inhibition zone (in mm) each test was carried in triplicate<sup>20, 21</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 ( $\text{M}^+$ ) peaks obtained from various complexes are as follows: (1)  $m/e = 245.32$  (Ligand), (2)  $m/e = 625.09$  (complex 1), (3)  $m/e = 620.23$  (complex 2), (4)  $m/e = 620.47$  (complex 3), (5)  $m/e = 678.19$  (complex 4), (6)  $m/e = 673.34$  (complex 5), (7)  $m/e = 673.58$  (complex 6)  $m/e = 672.27$  (complex 7), (6)  $m/e = 667.42$  (complex 8), (7)  $m/e = 667.66$  (complex 9). 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  $\text{cm}^{-1}$  in the complexes may be assigned to N-H stretch<sup>22</sup>. It was noted that a pair of bands corresponding to  $\nu(\text{NH}_2)$  at 3245  $\text{cm}^{-1}$  and 3309  $\text{cm}^{-1}$  are present in the spectra of the thiocarbohydrazide. The value of  $\nu(\text{C}=\text{N})$  stretching vibration is found lower (1520–1560  $\text{cm}^{-1}$ ) than the expected value (1580–1650  $\text{cm}^{-1}$ ). 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>23</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>24</sup>. The C-N stretch in the range 1000-1300  $\text{cm}^{-1}$ . 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>25</sup>. The far infrared spectra show bands in the region 420–450  $\text{cm}^{-1}$  corresponding to  $\nu(\text{M}-\text{N})$  vibrations<sup>26</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>27</sup>. The bands present at 290–310  $\text{cm}^{-1}$  may be assigned due to  $\nu(\text{M}-\text{Cl})$  vibrations<sup>28</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  $\nu_{\text{sym}}(\text{COO}^-)$ <sup>29</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  $^1\text{H}$  NMR spectra of Schiff base ligand (HL) was recorded in  $\text{d}_6$ -dimethylsulfoxide ( $\text{DMF}-d_6$ ) solution using  $\text{Me}_4\text{Si}$  (TMS) as internal standard. The  $^1\text{H}$  NMR spectra of the ligand shows broad signal at 9.4-12.1 ppm due to the  $-\text{NH}^{30,31}$ . The multiplets in the region 1.12-1.56 ppm may be assigned to aliphatic proton.

$^{13}\text{C}$  NMR of the Schiff base ligand, the signal appeared in the region 113-158 are assigned to aromatic carbon. The signal at 182.8-171.2, 165.4-150.7 and 148.1- 15.8 ppm are due to  $\text{C}=\text{N}$ ,  $\text{C}=\text{O}$  and  $\text{CH}_3$  respectively.

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

The electronic spectra of  $\text{Cu(II)}$  complexes 1 and 2 showed absorption band in the region 690-680 nm attributed to  $^2\text{T}_g \leftarrow ^2\text{E}_g$  transition indicative of distorted octahedral geometry<sup>32</sup> The ESR spectrum of copper(II) complexes has been studied and depicted in. 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  $\text{Cu(II)}$  complexes shows reversed axial (compressed octahedral) with  $g_{\parallel} < g_{\perp}$ . The trend  $g_{\parallel} < g_{\perp}$  showed that the electron is delocalised in  $\text{d}_{z^2}$ orbital of the ground state of  $\text{Cu(II)}$ . In this case ( $g_{\parallel} < g_{\perp}$ ) distortion occurs by compression<sup>33</sup>. The parameter  $G$ , determined as  $G = g_{\parallel} - 2.0023/g_{\perp} - 2.0023$ , is found to be much less than 4 suggesting considerable interaction in the solid state (Hathaway et al., 1973). 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:  $^3\text{A}_{2g}(\text{F}) \rightarrow ^3\text{T}_{2g}(\text{F})$ ,  $^3\text{A}_{2g}(\text{F}) \rightarrow ^3\text{T}_{1g}(\text{F})$ ,  $^3\text{A}_{2g}(\text{F}) \rightarrow ^3\text{T}_{1g}(\text{P})$  appearing in the ranges 1145–1054, 706–695 and 461–443 nm, respectively consistent with a typical  $\text{Ni(II)}$  in an octahedral environment<sup>34</sup>. The magnetic moment values for these complexes were found in the range 2.10–2.14 B.M.<sup>34</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  ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$  ( $\nu_1$ ) and  ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(P)$  ( $\nu_3$ ), respectively, suggesting an octahedral geometry around Co(II) ion<sup>35</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*

The antifungal activity of newly synthesized compounds, Schiff base ligand and its Cu(II), Ni(II) and Co(II) metal ion complexes exhibited a considerable enhancement against *Aspergillus sp.*, *Rizoctonia sp.* and *Penicillium sp.* at 1, 1.5 and 2 mg/ml concentration. All the compounds show grater activity at the higher concentration (2 mg/ml). The metal complexes show better activity than the ligand. The antifungal activity data of the compounds were compared with the standard (Miconazole). From the table-1 it has been also found that the fungicidal activity depends upon the type of metal ion.  $[Ni(C_{28}H_{38}N_6O_2)(OAc)_2]$  is the only complex to show 82% activity against *Aspergillus sp.*

### *Antibacterial activity*

The results of the bactericidal action of the synthesized compounds are summarized in table-2. The Schiff base ligand, its metal complexes, standard drug Imipenem ( $C_{12}H_{17}N_3O_4S$ ) and DMSO (control) were tested for their antibacterial action against the bacteria *Staphylococcus aureus* and *Bacillus subtilis* (as gram positive bacteria) and *Pseudomonas aeruginosa*, *Escherichia coli* and *Salmonella typhi* (as gram negative bacteria). 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 all organism. Chelation increases the lipophilic nature of the central metal atom, which increases its permeability through the lipid layer of the cell<sup>36</sup>.

### **Conclusion**

The electronic spectral data is in the favor of a five coordinate square pyramidal geometry of the complexes. New synthesized compounds were tested for biological evaluation against some pathogenic strains and compared with standard drug. Antimicrobial study reveals that, metal complexes have more biological activity than free ligand. Complex  $[\text{Ni}(\text{C}_{28}\text{H}_{38}\text{N}_6\text{O}_2)(\text{OAc})_2]$  shows best antimicrobial activity.

### Conflicts of Interest

The authors declare that they have no conflict of interest associated with this work.

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**Table 1.** Fungicidal screening data of the ligand and their corresponding metal complexes.

Compound	% Inhibition of spore germination								
	Aspergillus sp. (mg/ml)			Penicillium sp. (mg/ml)			Rizoctonia sp. (mg/ml)		
	1.0	1.5	2.0	1.0	1.5	2.0	1.0	1.5	2.0
C <sub>14</sub> H <sub>19</sub> N <sub>3</sub> O	31	40	45	13	20	26	34	50	42
[Cu(C <sub>28</sub> H <sub>38</sub> N <sub>6</sub> O <sub>2</sub> )Cl <sub>2</sub> ]	57	62	66	50	51	58	42	47	50
[Cu(C <sub>28</sub> H <sub>38</sub> N <sub>6</sub> O <sub>2</sub> )(NO <sub>3</sub> ) <sub>2</sub> ]	45	51	55	40	42	51	40	42	42
[Cu(C <sub>28</sub> H <sub>38</sub> N <sub>6</sub> O <sub>2</sub> )(OAc) <sub>2</sub> ]	62	65	71	49	52	58	42	41	49
[Ni(C <sub>28</sub> H <sub>38</sub> N <sub>6</sub> O <sub>2</sub> )Cl <sub>2</sub> ]	59	69	71	49	54	66	42	49	50
[Ni(C <sub>28</sub> H <sub>38</sub> N <sub>6</sub> O <sub>2</sub> )(NO <sub>3</sub> ) <sub>2</sub> ]	48	52	63	40	45	58	36	39	46
[Ni(C <sub>28</sub> H <sub>38</sub> N <sub>6</sub> O <sub>2</sub> )(OAc) <sub>2</sub> ]	66	70	77	56	61	70	52	56	62
[Co(C <sub>28</sub> H <sub>38</sub> N <sub>6</sub> O <sub>2</sub> )Cl <sub>2</sub> ]	51	62	68	45	51	59	38	42	55
[Co(C <sub>28</sub> H <sub>38</sub> N <sub>6</sub> O <sub>2</sub> )(NO <sub>3</sub> ) <sub>2</sub> ]	35	45	62	38	42	55	32	35	44
[Co(C <sub>28</sub> H <sub>38</sub> N <sub>6</sub> O <sub>2</sub> )(OAc) <sub>2</sub> ]	64	67	72	52	52	61	42	47	59
Miconazole (standard)	57	69	100	65	78	83	76	82	94

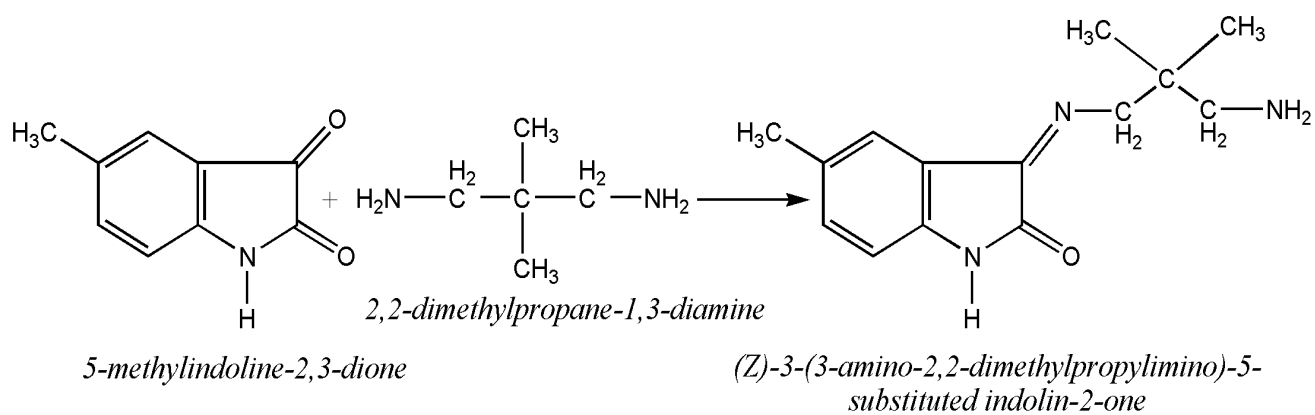
**Table 2.** Bactericidal screening data of the ligand and their corresponding metal complexes.

Microorganism	Ligand	Complexes									Imipenem
		1	2	3	4	5	6	7	8	9	
Gram-positive											
<i>Staphylococcus aureus</i>	22	4	11	31	50	61	82	22	12	51	100
<i>Bacillus subtilis</i>	13	32	17	26	48	57	78	28	17	46	100
Gram-negative											
<i>Escherichia coli</i>	03	02	07	23	05	31	57	30	12	21	100
<i>Salmonella typhi</i>	02	05	17	26	48	27	51	29	17	22	100
<i>Pseudomonas aeruginosa</i>	02	03	11	21	28	15	46	22	12	52	100

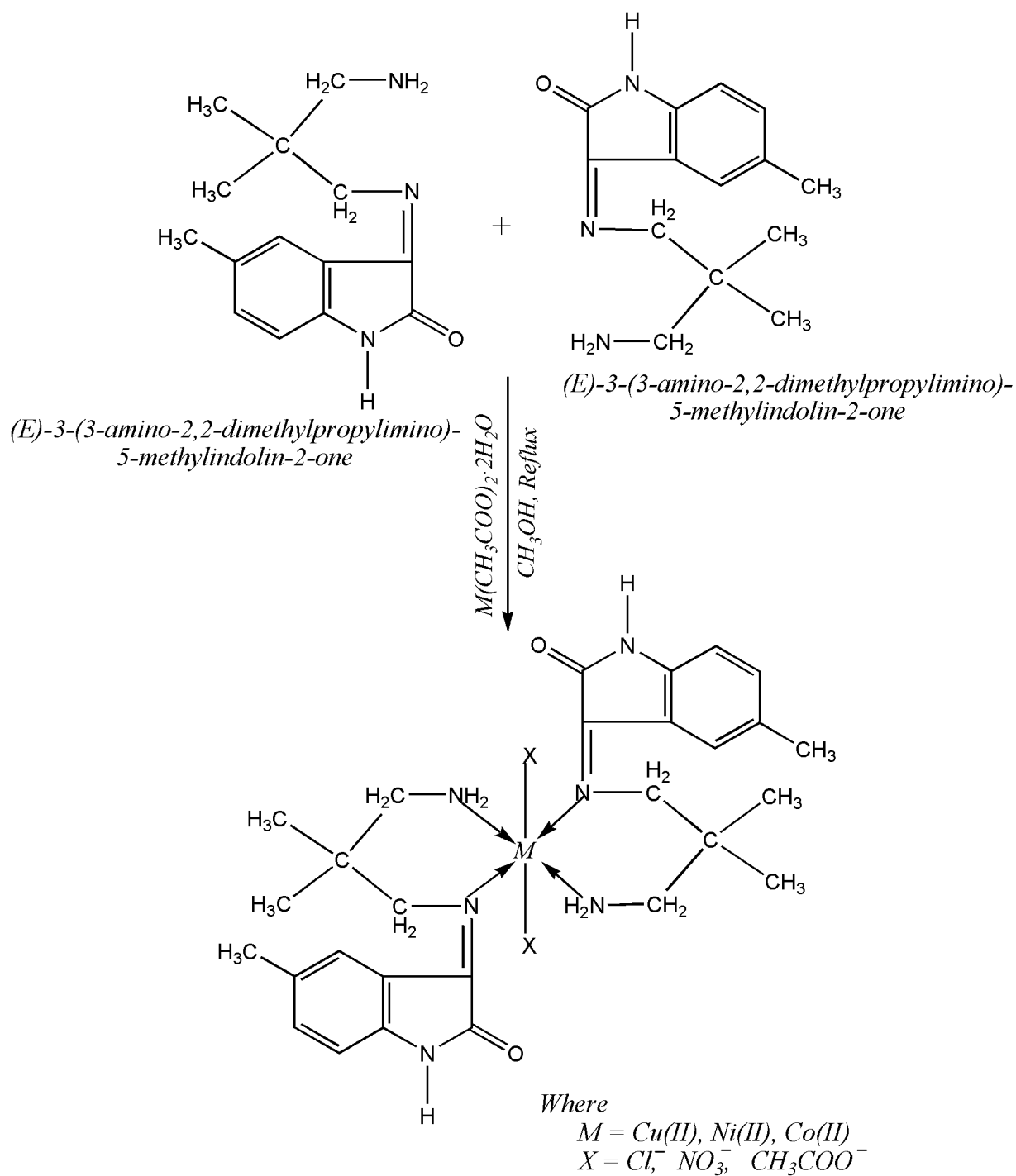
<sup>a</sup> Excellent activity (90-100% inhibition), Good activity (60-70% inhibition), Significant activity (30-50% inhibition), negligible activity (08-20% inhibition),

<sup>b</sup> Complex 1=[Cu(L)Cl<sub>2</sub>], 2=[Cu(L)(NO<sub>3</sub>)<sub>2</sub>], 3=[Cu(L)(OAc)<sub>2</sub>], 4=[Ni(L)Cl<sub>2</sub>]<sub>2</sub>, 5=[Ni(L)(NO<sub>3</sub>)<sub>2</sub>], 6 = [Ni(L)(OAc)<sub>2</sub>] 7 =[Co(L)]Cl<sub>2</sub> 8=[Co(L)(NO<sub>3</sub>)<sub>2</sub>] 9=[Co(L)(OAc)<sub>2</sub>]

<sup>c</sup> Imipenem = Standard drug.

**Scheme- 1:-** Synthesis of Ligands





**Scheme- 2:-** Synthesis of M(II) Transition Metal Complexes