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## Physico-chemical and biological studies of Cu(II), Co(II) and Ni(II) complexes of an N<sub>4</sub> coordinating ligand derived from the Schiff base of diacetyl with ethylenediamine and benzoic acid

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**Abstract:** Mononuclear metal complexes of the type [ML<sub>1</sub>]Cl<sub>2</sub> (where, M = Cu(II), Co(II) or Ni(II) and L<sub>1</sub> = ligand) were synthesized by the reaction of a new N<sub>4</sub> coordinating ligand, *N,N'*-{(1,2-dimethylethanediyliidene)bis[nitrilo(2,1-ethanediy1)]}bis[benzamide] derived from the Schiff base of diacetyl with ethylenediamine and benzoic acid, and the corresponding hydrated metal chloride salts. The metal complexes were characterized by elemental analysis, melting point determination, molar conductance and magnetic moment measurements, IR, UV–Vis, <sup>1</sup>H- and <sup>13</sup>C-NMR, and ESR spectroscopy. The ligand and all the metal complexes were stable in the solid state at room temperature. From the analytical and spectroscopic investigations, the stoichiometry of the complexes was found to be 1:1 (metal:ligand). Based on the electronic spectra and magnetic moment data, the metal complexes had a square planar geometry. The molar conductance values show the 1:2 electrolytic nature of the metal complexes. A cyclic voltammetric study of the Cu(II) metal complex has also performed, which showed one electron quasi-reversible reduction around –0.92 to –1.10 V. *In vitro* biological activities of the ligand and metal complexes was checked against two bacteria *Bacillus subtilis* and *Escherichia coli* and two fungi *Aspergillus niger* and *A. flavus* which showed the antibacterial and antifungal properties of the ligand and its metal complexes.

**Keywords:** mononuclear Cu(II), Co(II) and Ni(II) complexes; square planar geometry; antibacterial and antifungal properties.

### INTRODUCTION

Metallo-drugs became an interesting research area after the discovery of cis-platin.<sup>1</sup> Since then, many complexes have been synthesized and tested on a number of biological systems. New areas of research, which mainly focused on the specific synthesis of highly functional metal-based drug complexes have drawn considerable attention. Some transition metals are essential for the normal func-

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tion of living organisms. Schiff bases and their complexes have a variety of applications in biological, clinical, analytical and pharmacological areas.<sup>2,3</sup> When ligands coordinate to transition metals, it is believed that the selectivity towards certain biological systems is improved.<sup>4-7</sup> The enormous interest in the field of coordination chemistry of transition metal ions with Schiff bases is due to use of these compounds as biological models, as oxygen carriers and as drugs.<sup>8,9</sup> Recently synthesized Cu(II), Ni(II), Co(II), Zn(II) and Fe(III) complexes show the current interest of researchers in the field of coordination chemistry of these metal ions.<sup>10,11</sup> *N*-Coordinating ligands and their transition metal complexes have been found to possess important catalytic as well as biological activity.<sup>12-14</sup> Some other transition metal complexes have also been synthesized recently which show good biological activities *viz.* antibacterial, antifungal, toxicity, DNA interaction and antitumour.<sup>15-21</sup> In view of the importance of metal complexes, herein the preparation and characterization of Cu(II), Ni(II) and Co(II) metal complexes of a new N<sub>4</sub> coordinating ligand derived from the Schiff base of diacetyl with ethylenediamine and benzoic acid are reported. The synthesized compounds were characterized by various analytical and spectral studies, such as elemental analysis, magnetic moment and molar conductance measurements, and IR, UV-Vis, NMR and ESR spectroscopy. *In vitro* antibacterial and antifungal activities of the synthesized compounds against some specific bacteria (*viz.* *Bacillus subtilis* and *Escherichia coli*) and fungi (*viz.* *Aspirtgillus niger* and *A. flavus*) were also studied.

#### EXPERIMENTAL

All chemicals were of A.R. grade. MeOH, EtOH, *n*-BuOH, diethyl ether and the metal salts were purchased from Qualigens. Diacetyl was purchased from Aldrich. Ethylenediamine and benzoic acid were purchased from CDH. All chemicals were used as obtained without further purification. Elemental analysis (C, H, N) was performed using a Carlo Erba 1106 elemental analyzer. Metals and chlorides were determined volumetrically<sup>22</sup> and gravimetrically,<sup>23</sup> respectively. The IR spectra were recorded using KBr discs (4000–400 cm<sup>-1</sup>) on a Shimadzu 8300 IR spectrophotometer. The electronic absorption spectra in the 200–900 nm range were obtained in dimethylformamide (DMF) (1.0×10<sup>-4</sup> M) on a Systronic UV-Vis spectrophotometer. The molar conductance measurements were performed in dimethyl sulphoxide (DMSO) (≈10<sup>-3</sup> M) at room temperature using a Jenway Model 4070 conductivity meter. The magnetic moment measurements were realized by the Gouy method using Hg[Co(SCN)<sub>4</sub>] as the calibrant. The <sup>1</sup>H- and <sup>13</sup>C-NMR spectra were recorded at room temperature in DMSO-*d*<sub>6</sub> (≈1.0×10<sup>-3</sup> M) on a Bruker AC 700L NMR spectrometer with reference to TMS (tetramethylsilane). Chemical shifts are reported on the  $\delta$  scale. The electrochemical behaviour of the Cu(II) complex was investigated in acetonitrile solution on a CH620A electrochemical analyzer using a platinum electrode. Tetraethylammonium perchlorate (0.4 M) was used as the supporting electrolyte and the potentials are referenced to the saturated calomel electrode (SCE) without junction correction. The cyclic voltammogram was recorded at a scan rate of 50 mV s<sup>-1</sup> with *iR* compensation. The ESR spectrum of the Cu(II) complex was recorded in

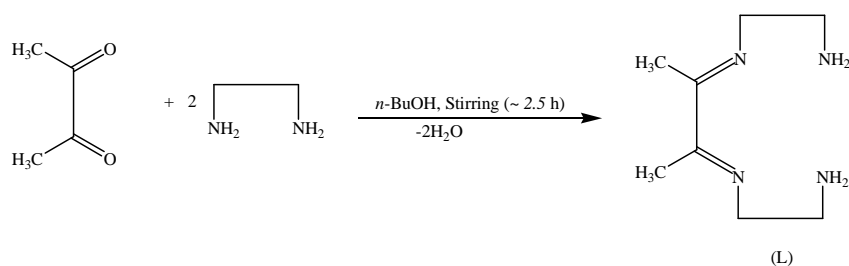
acetonitrile solution at room temperature on an E-112 ESR spectrophotometer employing 2,2-diphenyl-1-picrylhydrazyl (DPPH) as the *g*-marker.

#### Synthesis of the ligand ( $L_1$ )

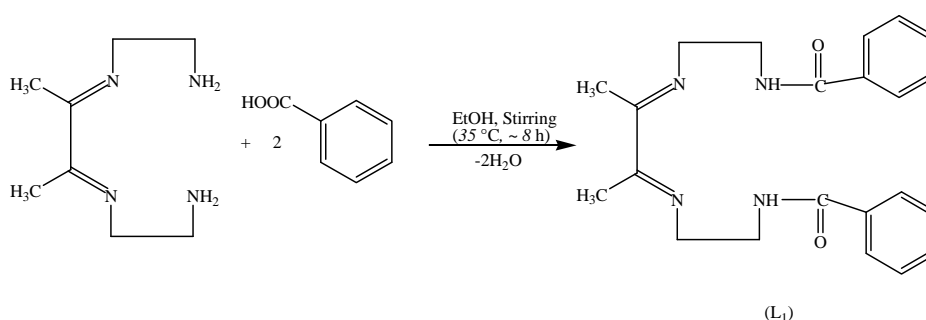
A diacetyl (0.44 ml, 5 mmol) solution in 20 ml of *n*-BuOH was added to ethylenediamine (0.67 ml, 10 mmol) and stirred for  $\approx 2.5$  h. The formed white solid ( $N,N'$ -(1,2-dimethylethanediylidene)bis[1,2-ethanediamine] ( $L$ )) was filtered off, washed with water and diethyl ether and dried in a vacuum desiccator. A solution of  $L$  (0.85 g, 5 mmol) in 30 ml of EtOH was added to a benzoic acid (1.22 g, 10 mmol) solution in 20 ml of EtOH and stirred at 35 °C for  $\approx 8$  h and cooled to room temperature. The precipitated ligand  $N,N'$ -{(1,2-dimethylethanediylidene)bis[nitrilo(2,1-ethanediyl)]}bis[benzamide] ( $L_1$ ) was filtered, washed with diethyl ether and dried in a vacuum desiccator over anhydrous calcium chloride (Scheme 1).

Yield: 76 %; m.p. 104 °C; colour: yellow. Anal. Calcd. for  $C_{22}H_{26}N_4O_2$  (FW: 378.45): C, 69.85; H, 6.92; N, 14.80 %. Found: C, 69.80; H, 6.94; N, 14.85 %.

#### Step I:



#### Step II:

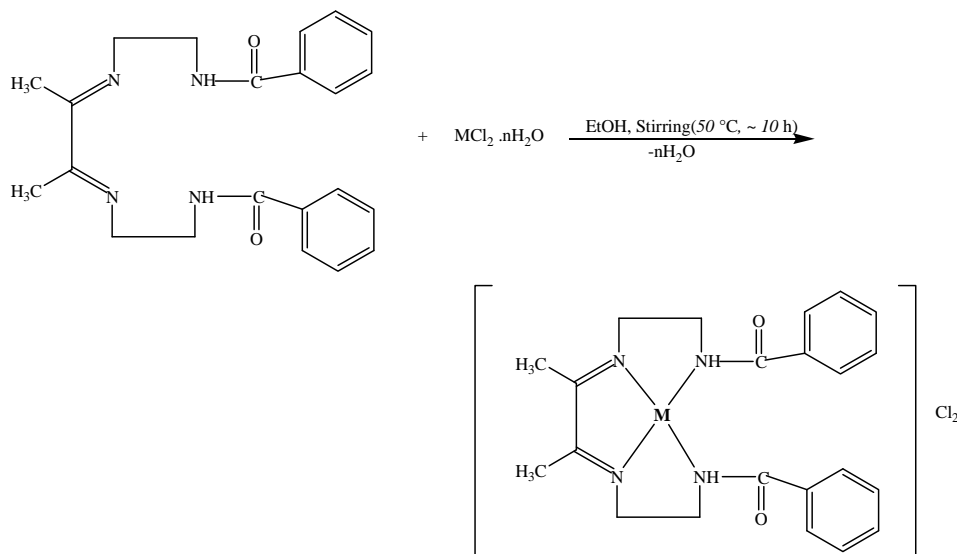


Scheme 1. Synthesis of the ligand  $L_1$ .

#### Synthesis of the metal complexes

A solution of 1.0 mmol of hydrated metal chloride salt ( $CuCl_2 \cdot 2H_2O$  (0.17 g),  $NiCl_2 \cdot 6H_2O$  (0.23 g) and  $CoCl_2 \cdot 6H_2O$  (0.23 g)) in 15 ml EtOH was added to an ethanolic

solution of  $L_1$  (0.38 g, 1.0 mmol) and stirred at 50 °C for  $\approx 10$  h and cooled in refrigerator overnight. Coloured products of the metal complexes were obtained which were filtered off, washed with methanol, ethanol and diethyl ether and dried in a vacuum desiccator over anhydrous calcium chloride (Scheme 2).



Scheme 2. Synthesis of the metal complexes  $[\text{ML}_1]\text{Cl}_2$ .

#### *In vitro* antibacterial and antifungal studies

The antibacterial and antifungal study of the newly synthesized ligand ( $L_1$ ) and all the metal complexes were realised *in vitro* by reported methods.<sup>24</sup> A stock solution ( $1 \text{ mg ml}^{-1}$ ) of the test chemical was prepared by dissolving 10 mg of the test chemical in 10 ml of DMSO. The stock solution was suitably diluted with sterilized distilled water to obtain 500 and  $100 \mu\text{g ml}^{-1}$  solutions. A control for each dilution was prepared by diluting 10 ml of solvent instead of stock solution with sterilized distilled water. All compounds were evaluated for their *in vitro* antibacterial activity against *Bacillus subtilis* and *Escherichia coli* and antifungal activity against *Aspigoillus niger* and *A. flavus* by the agar-well diffusion method. The bacteria were inoculated into Nutrient Broth (Difco) and incubated for 30 h and the studied fungi were incubated in Malt Extract Broth (Difco) for 54 h. In the agar-well diffusion method, Müller Hinton Agar (Oxoid) for the bacteria and Malt Extract Broth (Difco) for the fungi, sterilized in a flask and cooled to  $\approx 48$  °C, were distributed (20 ml) in sterilized petri dishes after injecting 0.01 ml of a culture of a bacterium or fungus, prepared as mentioned above, and allowed to solidify. The dilution plate method was used to enumerate the microorganism ( $10^5$  bacteria per ml and fungi  $10^3$ – $10^4$  per ml) for 24 h. Wells were dug in the culture plates using a sterilized cork borer (7 mm diameter). The compounds dissolved in DMSO were added (0.2  $\mu\text{l}$ ) to these wells. The Petri dishes were left at 4 °C for 2 h and then the plates were incubated at 30 °C for the bacteria (24–28 h) or at 25 °C for the fungi (78 h). Subsequently, the diameters of the inhibition zones formed on the medium were evaluated in millimetres. The bio-

logical activity data of all the compounds are expressed as the % inhibition over the control. The percent inhibition was calculated using the formula:

$$\text{Inhibition level} = 100(C - T) / C$$

where  $C$  is the diameter of the microbial colony in the control plate and  $T$  is the diameter of the microbial colony in the tested plate after same incubation period.

## RESULTS AND DISCUSSION

The newly synthesized ligand and its metal complexes are stable at room temperature in the solid state. The ligand is soluble in common organic solvents whereas the metal complexes are soluble in DMF and DMSO.

Condensation of  $N,N'$ -(1,2-dimethylethanediyldene)bis[1,2-ethanediamine] and benzoic acid readily gives the corresponding ligand  $L_1$ , which is easily identified by its IR,  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  spectra. The metal complexes of general formula  $[\text{ML}_1]\text{Cl}_2$  of Cu(II), Co(II) and Ni(II) were prepared by stirring a mixture of corresponding hydrated metal chloride with the title ligand at a ratio of 1:1. Square planar geometry is proposed for all complexes.

### Analytical data for the complexes

$[\text{CuL}_1]\text{Cl}_2$  (1). Yield: 64 %; m.p. 222 °C. Colour: brown. Anal. Calcd. for  $\text{C}_{22}\text{H}_{26}\text{Cl}_2\text{CuN}_4\text{O}_2$  (FW 512.90): C, 50.51; H, 5.11; N, 10.92; Cu, 12.39; Cl, 13.82 %. Found: C, 51.48; H, 5.07; N, 10.90; Cu, 12.37; Cl, 13.80 %.

$[\text{CoL}_1]\text{Cl}_2$  (2). Yield: 61 %; m.p. 212 °C. Colour: light brown. Anal. Calcd. for  $\text{C}_{22}\text{H}_{26}\text{Cl}_2\text{CoN}_4\text{O}_2$  (FW 508.30): C, 51.98; H, 5.15; N, 11.02; Co, 11.60; Cl, 13.95 %. Found: C, 51.96; H, 5.12; N, 11.08; Co, 11.58; Cl, 13.92 %.

$[\text{NiL}_1]\text{Cl}_2$  (3). Yield: 67 %; m.p. 198 °C. Colour: reddish brown. Anal. Calcd. for  $\text{C}_{22}\text{H}_{26}\text{Cl}_2\text{N}_4\text{NiO}_2$  (FW 508.07): C, 51.00; H, 5.16; N, 11.03; Cu, 11.56; Cl, 13.94 %. Found: C, 51.05; H, 5.12; N, 11.08; Cu, 11.54; Cl, 13.91 %.

The analytical data are in good agreement with the proposed stoichiometry of the complexes.

### IR spectra

The IR spectral data of ligand and metal complexes are given in Table I. The IR spectrum of the ligand shows a sharp band at  $1576\text{ cm}^{-1}$ , which shows the presence of  $\nu(\text{C}=\text{N})$  vibrations.<sup>23</sup> There is no peak of free  $-\text{NH}_2$  groups in the IR spectrum of ligand, which indicates the formation of the proposed ligand. In the IR spectra of metal complexes, the  $\nu(\text{C}=\text{N})$  band is shifted to  $1598\text{--}1626\text{ cm}^{-1}$ , which shows the coordination of  $(\text{C}=\text{N})$ .<sup>25-29</sup> The new band which appeared in the range  $460\text{--}466\text{ cm}^{-1}$  may be assigned  $\nu(\text{M}-\text{N})$  vibrations.<sup>30</sup> A band in the range of  $1762\text{ cm}^{-1}$  in the spectra of the ligand and all the metal complexes show that the  $\text{C}=\text{O}$  group did not participate in the coordination. In the IR spectra of  $L_1$ , the sharp medium band at  $3300\text{ cm}^{-1}$  is assigned to  $\nu(\text{N}-\text{H})$  stretching vibrations. This band is shifted to lower wave numbers in the spectra of Cu(II),

Co(II) and Ni(II), *i.e.*, to 3208, 3200 and 3196  $\text{cm}^{-1}$ , respectively, which indicates the coordination of the ( $-\text{N}-\text{H}$ ) nitrogen.<sup>31,32</sup>

TABLE I. IR spectral data ( $\nu / \text{cm}^{-1}$ ) of the ligand and its metal complexes. All spectra were recorded using KBr discs in the range 4000–400  $\text{cm}^{-1}$

Compound	$\nu(-\text{N}-\text{H})$	$\nu(\text{C}=\text{O})$	$\nu(\text{C}=\text{N})$	$\nu(\text{M}-\text{N})$
$\text{L}_1$	3300	1762	1576	–
$[\text{CuL}_1]\text{Cl}_2$	3208	1765	1598	460
$[\text{CoL}_1]\text{Cl}_2$	3200	1763	1626	462
$[\text{NiL}_1]\text{Cl}_2$	3196	1765	1610	466

#### Electronic absorption spectra

The electronic absorption data of the metal complexes were obtained in DMF. The absorption region and band assignments of the complexes are given in Table II. The UV–Vis spectra of the Cu(II) complex showed an absorption band at 487 nm, which was assigned to the  ${}^2\text{B}_{1g} \rightarrow {}^2\text{A}_{1g}$  transition characteristic of square planar Cu(II) complexes. The Co(II) complex exhibited an absorption band at 510 nm, which was assigned to the  ${}^1\text{A}_{1g} \rightarrow {}^1\text{B}_{1g}$  transition characteristic of square planar Co(II) complexes. The Ni(II) complex showed absorption bands at 512 nm and 633 nm, which were assigned to  ${}^1\text{A}_{1g} \rightarrow {}^1\text{A}_{2g}$  and  ${}^1\text{A}_{1g} \rightarrow {}^1\text{B}_{1g}$  transitions, respectively, characteristics of square planar Ni(II) complexes. These obtained spectral values are comparable with those of many similar reported metal complexes.<sup>33–36</sup>

TABLE II. Electronic spectral data and magnetic moment values of the metal complexes. All electronic absorption spectra were measured in DMF ( $\approx 1.0 \times 10^{-4}$  M) and magnetic moment values were measured at room temperature using  $\text{Hg}[\text{Co}(\text{SCN})_4]$  as the calibrant

Compound	$\lambda_{\text{max}} / \text{nm}$	Assignments	$\mu_{\text{eff}} / \mu_{\text{B}}$
$[\text{CuL}_1]\text{Cl}_2$	240	INCT	1.76
	380	INCT	
	487	${}^2\text{B}_{1g} \rightarrow {}^2\text{A}_{1g}$	
$[\text{CoL}_1]\text{Cl}_2$	242	INCT	3.62
	378	INCT	
	510	${}^1\text{A}_{1g} \rightarrow {}^1\text{B}_{1g}$	
$[\text{NiL}_1]\text{Cl}_2$	238	INCT	Diamagnetic
	370	INCT	
	512	${}^1\text{A}_{1g} \rightarrow {}^1\text{A}_{2g}$	
	633	${}^1\text{A}_{1g} \rightarrow {}^1\text{B}_{1g}$	

#### ${}^1\text{H}$ - and ${}^{13}\text{C}$ -NMR spectra

The  ${}^1\text{H}$ - and  ${}^{13}\text{C}$ -NMR spectral data of the ligand and the Ni(II) complex were obtained in  $\text{DMSO}-d_6$  and the results are given in Table III. In the  ${}^1\text{H}$ -NMR spectrum of ligand, no signal corresponding to primary amine proton was observed, which suggests the formation of the ligand. In the  ${}^1\text{H}$ -NMR spectrum of

Ni(II) complex, the signal of the signal of ( $\text{H}_3\text{C}-\text{C}=\text{N}$ ) protons and ( $-\text{N}-\text{H}$ ) proton shifted compared to the free ligand, suggesting coordination through azomethine and ( $-\text{N}-\text{H}$ ) nitrogen atoms.<sup>31</sup>

TABLE III.  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectral data of the ligand and its Ni(II) complex. All spectra were measured in  $\text{DMSO}-d_6$  ( $\approx 1.0 \times 10^{-3}$  M) at room temperature with reference to TMS (tetramethylsilane)

Compound	$^1\text{H}$ -NMR ( $\delta$ /ppm)	$^{13}\text{C}$ -NMR ( $\delta$ /ppm)
$\text{L}_1$	1.62 (6H, s, 2 =C-CH <sub>3</sub> ), 3.58 (4H, t, 2 =N-CH <sub>2</sub> ), 3.84 (4H, m, 2 -N-CH <sub>2</sub> ), 7.16–7.35 (10H, m, Ar), 9.68 (2H, s, br, 2 -NH)	10.13 (C-9, C-11), 46.20 (C-6, C-13), 97.13 (C-7, C-12), 116.42 (C-4, C-15), 117.63 (C-(2, 2'), C-(17, 17')), 119.82 (C-(3, 3'), C-(16, 16')), 122.07 (C-1, C-18), 160.40 (C-8, C-10), 165.28 (C-5, C-14)
$[\text{NiL}_1]\text{Cl}_2$	1.11 (6H, s, 2 =C-CH <sub>3</sub> ), 3.46 (4H, t, 2 =N-CH <sub>2</sub> ), 3.83 (4H, m, 2 -N-CH <sub>2</sub> ), 7.06–7.25 (10H, m, Ar), 9.01 (2H, s, br, 2 -NH)	10.06 (C-9, C-11), 44.60 (C-6, C-13), 96.94 (C-7, C-12), 116.41 (C-4, C-15), 117.61 (C-(2, 2'), C-(17, 17')), 119.81 [C-(3, 3'), C-(16, 16')], 122.11 [C-1, C-18), 157.80 (C-8, C-10), 165.26 (C-5, C-14)

In the  $^{13}\text{C}$  NMR spectrum of Ni(II) complex, change in the chemical shift values compared to the free ligand, show coordination through nitrogen atom of azomethine and ( $-\text{NH}$ ) group. On the other hand, no change in the chemical shift value of carbon of carbonyl group moiety indicates that oxygen atom of this group did not participate in the coordination. Thus,  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectral data support proposed structure (Fig. 1) of ligand and metal complex and as well coordination behaviour of ligand.<sup>31</sup>

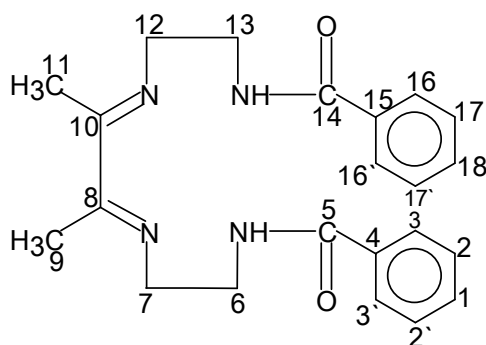


Fig. 1. Numbering of the C-atoms in the ligand ( $\text{L}_1$ ).

#### Molar conductance measurements

The molar conductance ( $\Lambda_M$ ) values of all the metal complexes were measured in DMSO and the obtained values ( $8.4$ ,  $5.2$  and  $9.8 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$  for complexes **1**, **2** and **3**, respectively) show their 1:2 electrolyte nature.<sup>37</sup>

### Magnetic moment measurements

Magnetic moments of metal complexes were measured at room temperature and the effective magnetic ( $\mu_{\text{eff}}$ ) values of the complexes are given in Table II. The magnetic moment of Cu(II) complex is  $1.76 \mu_{\text{B}}$ , which corresponds to a single unpaired electron of the  $d^9$ -system of square planar Cu(II).<sup>38</sup> The magnetic moment of the Co(II) complex is  $3.62 \mu_{\text{B}}$ , which corresponds to square planar geometry of Co(II). The Ni(II) complex is diamagnetic.

### ESR spectrum of the Cu(II) metal complex

The ESR spectrum of the Cu(II) complex shows four lines due to hyperfine splitting with nuclear hyperfine  $3/2$ . For Cu(II) complex, the observed  $g_{\parallel}$  value was 2.31 while the  $g_{\perp}$  value was 2.02. The relation  $g_{\parallel} > g_{\perp}$  is typical for Cu(II) having one unpaired electron in a  $d_{x^2-y^2}$  orbital.<sup>39</sup> The  $g_{\text{av}}$  value, calculated according to the relation  $= 1/3 (g_{\parallel} + 2g_{\perp})$ , was found to be 2.12. A  $\langle g \rangle$  value less than 2.3 indicates a square planer geometry around Cu(II).<sup>40</sup>

### Cyclic voltammetric study of the Cu(II) complex

The electrochemical properties of Cu(II) complex were studied by cyclic voltammetry in acetonitrile solution vs. SCE. The cyclic voltammogram of Cu(II) complex was recorded in the potential range 0 to  $-1.4$  V. The voltammogram shows one quasi-reversible reduction wave at a negative potential in the range  $-0.90$  to  $-1.04$  V, which was assigned to Cu(II) to Cu(I) reduction.

### In vitro antibacterial and antifungal activity

The *in vitro* antimicrobial activities of the newly synthesized ligand and metal complexes were determined against the bacteria *B. subtilis* and *E. coli* and the fungi *A. niger* and *A. flavus* and the results are summarized in Table IV. The values indicate that all complexes have higher antimicrobial activity than the free ligand. Of the tested metal complexes, the Co(II) metal complex shows the highest biological activity against all microbes. Such increased activity of the metal

TABLE IV. *In vitro* antibacterial and antifungal activity data of the ligand and the metal complexes (inhibition level, %). The agar well diffusion technique was used to evaluate the antibacterial and antifungal activity of the synthesized compounds

Compound	$c / \mu\text{g ml}^{-1}$	<i>B. subtilis</i>	<i>E. coli</i>	<i>A. niger</i>	<i>A. flavus</i>
$L_1$	100	40	51	62	65
	500	48	58	74	78
$[\text{Cu}L_1]\text{Cl}_2$	100	48	54	71	72
	500	53	55	83	85
$[\text{Co}L_1]\text{Cl}_2$	100	52	73	82	80
	500	61	82	89	86
$[\text{Ni}L_1]\text{Cl}_2$	100	46	59	69	70
	500	52	64	77	79



chelates can be explained based on chelation theory. On chelation, the polarity of the metal ion will be reduced largely due to overlap of the ligand orbital and the partial sharing of the positive charge of the metal ion with the donor groups. Furthermore, it increases the delocalization of the  $\pi$ -electrons over the whole chelate ring, which enhances the penetration of the complexes into the lipid membranes and the blocking of the metal binding sites in the enzymes of the microorganisms. These complexes also disturb the respiration process of the cell and thus block the synthesis of proteins, which restricts further growth of microorganisms.<sup>41</sup>

### CONCLUSIONS

The newly synthesized  $N_4$  coordinating ligand was used to prepare Cu(II), Co(II) and Ni(II) complexes. The ligand and all the metal complexes were characterized by various physico-chemical methods. The data obtained from these studies were in good agreement with the proposed structure and composition of the ligand and the metal complexes. Square planar geometry was confirmed for the metal complexes by electronic absorption spectroscopy, ESR spectroscopy [Cu(II)] and the magnetic moment values. Molar conductance values showed the 1:2 electrolyte nature of all the metal complexes. The electrochemical behaviour of the Cu(II) complex was studied and the results showed a one electron quasi-reversible reduction of the Cu(II) to Cu(I). *In vitro* antibacterial and antifungal studies showed that metal complexes were more biologically active than the free ligand. The [CoL<sub>1</sub>]Cl<sub>2</sub> complex showed the highest antibacterial and antifungal activity against all the studied bacterial and fungal strains.

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### ИЗВОД

#### ФИЗИЧКО-ХЕМИЈСКА И БИОЛОШКА ИСПИТИВАЊА Cu(II), Co(II) И Ni(II) КОМПЛЕКСА СА $N_4$ -ТИПОМ ЛИГАНАДА КОЈИ СУ ДОБИЈЕНИ ИЗ ШИФОВЕ БАЗЕ ДИАЦЕТИЛА СА ЕТИЛЕНДИАМИНОМ И БЕНЗОЕВЕ КИСЕЛИНЕ

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Полазећи од новог лиганда  $N_4$ -типа  $N,N'$ -{(1,2-диметилетандиилиден)бис[нитрило(2,1-етандиил)]}бис[бензамида] који је изведен из шифове базе диацетила са етилендиамином у и бензоеве киселине и хидратисане хлоридне соли јона метала синтетизовани су мононуклеарни комплекси опште формуле [ML<sub>1</sub>]Cl<sub>2</sub> (M = Cu(II), Co(II) или Ni(II); L<sub>1</sub> = лиганд). Комплекси су окарактерисани помоћу елементалне микроанализе, одређивања њихових тачки топљења, моларне проводљивости и магнетних момената, као и спектроскопских IR, UV-Vis, <sup>1</sup>H- и <sup>13</sup>C-NMR и ESR мерења. Лиганд и одговарајући комплекси су стабилни на собној температури у чврстом стању. На основу аналитичких и спектроскопских резултата закључено

је да су у комплексима лиганд и јон метала координовани у 1:1 молском односу. На бази електронских спектра и вредности магнетног момента закључено је да испитивани комплекси имају квадратно-планарну геометрију. Вредности за моларну проводљивост показују да су комплекси електролити типа 1:2. Циклично-волтаметријска испитивања за одговарајући Cu(II) комплекс показују једноелектронску квазиреверзибилну редукцију на  $-0,92$  до  $-1,10$  V. Нађено је да лиганд и одговарајући комплекси показују одређену антибактеријску и антифунгалну активност при *in vitro* испитивањима на две врсте бактерија, *Bacillus subtilis* и *Escherichia coli*, и гљива *Aspiggillus niger* и *A. flavus*.

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#### REFERENCES

1. M. C. Orving, J. Abrams, *Chem. Rev.* **99** (1999) 2201
2. T. Hitoshi, N. Tamao, A. Hideyuki, F. Manabu, M. Takayuki, *Polyhedron* **16** (1997) 3787
3. T. Punniamurthy, S. J. S. Kalra, J. Iqbal, *Tetrahedron Lett.* **36** (1995) 8497
4. A. Tavman, N. M. Agh-Atabay, S. Güner, F. Gücin, B. Dülger, *Transition Met. Chem.* **32** (2007) 172
5. P. G. Ramappa, K. G. Somasekharappa, *J. Inorg. Biochem.* **55** (1994) 13
6. A. Tavman, N. M. Agh-Atabay, A. Neshat, F. Gücin, B. Dülger, D. Hacı, *Transition Met. Chem.* **31** (2006) 194
7. Q. Zhou, P. Yang, *Inorg. Chim. Acta* **359** (2006) 1200
8. R. K. Parashar, R. C. Sharma, A. Kumar, G. Mohan, *Inorg. Chim. Acta* **151** (1988) 201
9. K. S. Suslick, T. J. Reinert, *J. Chem. Educ.* **62** (1985) 974
10. M. D. Revenco, O. V. Palamarcu, P. N. Bourosh, J. Lipkowski, M. Gdaniec, Y. A. Simonov, R. Clerac, *Inorg. Chim. Acta* **368** (2011) 157
11. A. Alagha, L. Parthasrathi, D. Gaynor, H. M. Bunz, Z. A. Starikova, E. Farkas, E. C. O. Brien, M. J. Gil, K. B. Nolan, *Inorg. Chim. Acta* **368** (2011) 58
12. R. K. O. Sigel, H. Sigel, *J. Am. Chem. Soc.* **119** (1997) 744
13. B. Song, R. K. O. Sigel, H. Sigel, *Chem. Eur. J.* **3** (1997) 29
14. H. Sigel, *Chem. Soc. Rev.* **22** (1993) 255
15. S. Tabassum, N. P. Singh, J. Mussarat, *Synth. React. Inorg. Met.-Org. Chem.* **31** (2001) 1803
16. M. Palil, R. Hunoor, K. Gudasi, *Eur. J. Med. Chem.* **45** (2010) 2981
17. K. Singh, D. Pal, *J. Serb. Chem. Soc.* **75** (2010) 917
18. S. Chandra, M. Tyagi, S. Agarwal, *J. Serb. Chem. Soc.* **75** (2010) 935
19. S. Tabassum, G. C. Sharma, F. Arjmand, A. Azam, *Nanotechnology* **21** (2010) 195102
20. N. P. Singh, A. N. Srivastava, *Int. J. Chem. Environ. Pharm. Res.* **1** (2010) 27
21. N. P. Singh, A. N. Srivastava, *E-J. Chem.* **8** (2010) 809
22. C. N. Reilley, R. W. Schmidt, F. A. Sadek, *J. Chem. Educ.* **36** (1959) 619
23. A. I. Vogel, *A Text Book of Quantitative Inorganic Analysis*, Longmans, London, 1961, p. 433
24. A. K. Sadna, Y. Mirza, A. R. Aneja, O. Prakash, *Eur. J. Med. Chem.* **38** (2003) 533
25. M. S. Deshpande, A. S. Kumbhar, *J. Chem. Sci.* **117** (2005) 153
26. R. C. Maurya, J. Chourasia, P. Sharma, *Indian J. Chem., A* **47** (2008) 517
27. M. Sonmez, M. Sekerci, *Pol. J. Chem.* **76** (2002) 907
28. M. Sonmez, A. Levent, M. Sekerci, *Synth. React. Inorg. Met.-Org. Chem.* **33** (2003) 1747
29. M. Sonmez, A. Levent, M. Sekerci, *J. Coord. Chem.* **30** (2004) 655

30. M. Tumer, N. Deligonul, A. Golcu, E. Akgum, M. Dolaz, H. Demirelli, M. Digrak, *Transition Met. Chem.* **31** (2006) 1
31. R. M. Silverstein, C. G. Bassler, T. C. Morrill, *Spectrometric Identification of Organic Compounds*, 3<sup>rd</sup> ed., Wiley, New York, 1974, p. 108
32. J. Pons, A. Chadghan, J. Casabo, A. Alvarez-Larena, J. F. Piniella, J. Ros, *Polyhedron* **20** (2001) 2531
33. L. N. Sharda, M. C. Ganorkar, *Indian J. Chem., Sect A* **27** (1988) 617
34. D. V. Warad, C. D. Satish, V. H. Kulkarni, C. S. Bajgur, *Indian J. Chem., Sect A* **39** (2000) 415
35. R. L. Farmer, F. L. Urbach, *Inorg. Chem.* **13** (1974) 587
36. A. B. P. Lever, *Inorganic Electronic Spectroscopy*, 2<sup>nd</sup> ed., Elsevier, New York 1968
37. W. J. Geray, *Coord. Chem. Rev.* **7** (1971) 81
38. J. D. Crane, D. E. Fenton, J. M. Latour, A. J. Smith, *J. Chem. Soc., Dalton Trans.* (1991) 2279
39. J. C. Duff, *J. Chem. Soc.* (1941) 547
40. E. Billing, R. W. William, I. Bernol, H. B. Grey, *Inorg. Chem.* **3** (1964) 663
41. N. Dharmaraj, P. Viswanathamurthi, K. Natarajan, *Transition Met. Chem.* **26** (2002) 105.