SYNTHESIS, SPECTROSCOPIC CHARACTERIZATION AND BIOLOGICAL EVALUATION OF MACROCYCLIC SCHIFF’S BASE BENZIL BIS(5-AMINO-1,3,4-THIADIAZOLE-2-THIOL) WITH NI(II), AND CO(II) METAL COMPLEXES

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ABSTRACT
Co (II) and Ni (II) complexes of general composition [ML2]X2 (M = Co(II), Ni(II); X = Cl, NO3) were synthesized by the condensation of metal salts with semicarbazone / thiosemicarbazone derived from pdimethylaminobanzaldehyde. The metal complexes were characterized by elemental analysis, molar conductance, magnetic susceptibility measurements, IR and atomic absorption spectral studies. On the basis of electronic and infrared spectral studies, the metal complexes were found to have tetrahedral geometry. The Schiff bases and their metal complexes were tested for their antibacterial and antioxidan.

INTRODUCTION
Schiff bases are regarded as “privileged ligands” due to their capability to form complexes with a wide range of transition metal ions yielding stable and intensely colored metal complexes. Some of them have been shown to exhibit interesting physical and chemical properties and potential biological activities (Chandra et al, 2009). Thiosemicarbazones are very versatile ligands. They can coordinate to metal as neutral molecules or after deprotonation as anionic ligands and can adopt 1: They have better co-ordination tendency.
2: They form more stable complexes.
3: They have better selectivity.
4: They may form macrocyclic ligands.
5: They have the ability to produce some new and unique complexes with enhanced biological and analytical properties. Thiosemicarbazones usually act as chelating ligands with transition metal ion bonding through the sulphur and hydrazine nitrogen atom. Thiosemicarbazones and their complexes have received considerable attention because of their pharmacological activities (Kothari and Sharma, 2011). Thiosemicarbazones and their complexes have received considerable attention because of their antifungal (Prasad and Agarwal, 2007), antitumor (Ainscough et al., 1998) antibacterial (Chandra et al., 2009), antiamoebic, antimalarial, antiviral (Kolocouris et al., 2002) radio protective and anti-inflammatory activities. Certain thiosemicarbazones are relatively specific inhibitors of ribonucleotide reductase, which is an important metabolic target for the development of chemotherapeutic agents against cancer (Sandercock et al, 2007).

RESULTS AND DISCUSSION
The hydrazone based Schiff’s base ligand L was obtained in good yield by reacting benzil and carbohyrazide in 1:2 ratio (Supplementary material). The complexes with Ni(II) and Co(II) metal ions were also obtained in the satisfactory yield on reaction of the ligand with metal salts.

Physical properties
The complexes are insoluble in the nonpolar solvents but soluble in the polar solvents like DMSO. The elemental, molar conductivities studies of the complexes suggest the[M(L)X2 and[Co(L)X2] compositions, where M = Ni(II) and CO(II), and X¼NO andCl. The analytical data of ligand and its complexes with their physical properties are given in Table 1 in supporting information, which indicates 1:1:2 metal:ligand:anion stoichiometry for all the complexes. Measured values of magnetic moments indicate that the nickel (II) complexes are diamagnetic whereas the copper(II) and cobalt(II) complexes are paramagnetic having the magnetic moments 1.86–1.93 and 4.80–4.92 BM respectively.

Electronic spectra
The UV/Visible spectra of complexes were recorded in DMSO solvent. The data of electronic spectra are summarized in Table 1.
3.1. Molar conductance
The molar conductance (\(\Lambda_M\)) values of the complexes (Table 1) have been carried out using DMF as the solvent at the concentration of 10–3 M are in the range of 12–181 cm² mol⁻¹ for all the complexes. The low values indicate the non-electrolytic nature of the complexes. Thus, the complexes may be formulated as [CoL₂X₂].

3.2. Magnetic susceptibility measurements
The complexes show room temperature magnetic moments in the range 4.67–4.92 BM (Table 1) corresponding to three unpaired spins of high spin cobalt(II), but these values are noticeably higher than the spin-only value, i.e. 3.87 BM for d⁷ case. The deviation from the spin-only value is due to mixing of angular momentum from excited states via spin–orbit coupling[10] (Fig. 1).

**IR spectra**
The main assignments of IR absorption bands of the ligand and its metal complexes are given in Table 2. The IR spectrum of free ligand shows m(C=N) azomethine band at 1606cm⁻¹[14] and band at 786cm⁻¹ due to m(C=S)[15] (Fig. 1). On complexation, the position of these bands is shifted towards lower frequency.

**EPR speaturm**
EPR studies of Copper(II) complexes were carried out on the X-band at 9.1 GHz under the magnetic field strength 3000 G. polycrystalline samples in DMSO were used to record X-band EPR spectra of the Cu(II) complexes and the spectra were recorded in DMSO at room temperature (Table 4). The trend \(g_l > g_g > 2.0024\) indicated that the copper the unpaired electron is localize xy2 orbital of the Cu(II) ion and the spectral figures are characteristic for the axial symmetry tetragonal geometry. The parameter

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**Table 1** Molar conductance data of complexes with their physical properties.

<table>
<thead>
<tr>
<th>S. no.</th>
<th>Complex</th>
<th>Color</th>
<th>m.p. (°C)</th>
<th>Molar conductance (Ω⁻¹ cm² mol⁻¹)</th>
<th>Yield (%)</th>
<th>Micronanalytical data (%) calcd. (found)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>[Ni(L)₂]</td>
<td>Orange</td>
<td>225</td>
<td>130</td>
<td>68</td>
<td>M 12.66 (12.70) C 18.68 (18.76) H 1.82 (1.84) N 21.88 (21.94)</td>
</tr>
<tr>
<td>4</td>
<td>[Ni(L)₂(H₂O)₂]</td>
<td>Brown</td>
<td>300</td>
<td>142</td>
<td>72</td>
<td>M 10.18 (10.20) C 14.78 (14.80) H 3.32 (3.34) N 25.82 (25.86)</td>
</tr>
<tr>
<td>5</td>
<td>[Cr(L)₂Cl₂]</td>
<td>Brown</td>
<td>190</td>
<td>13</td>
<td>65</td>
<td>M 12.27 (12.31) C 18.52 (18.60) H 3.72 (3.74) N 24.30 (24.34)</td>
</tr>
<tr>
<td>6</td>
<td>[Cr(L)₂(NO₃)₂]</td>
<td>Brown</td>
<td>230</td>
<td>12</td>
<td>67</td>
<td>M 10.82 (10.86) C 16.52 (16.60) H 3.56 (3.60) N 26.52 (26.56)</td>
</tr>
</tbody>
</table>

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**Fig. 1. Structure of the ligand.**

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**Fig. 2.** IR spectrum of macrocyclic Schiff’s base Ligand.
G, determined as $G = (g || 2)/(g \perp 2)$, which measures the exchange interaction between the metal centers in a polycrystalline solid, has been calculated. According to Hathaway [27] if $G > 4$, the exchange interaction is negligible, but $G < 4$ indicates considerable exchange interaction in the solid complexes. The Cu(II) complexes reported in this paper gave the “G” values which are greater than 4 indicating the exchange interaction is absent in solid complexes.

A.

B.

Fig.3: electronic spectra of the complexes (a) Co(L)Cl$_2$ and (b) Ni(L)Cl$_2$.

Table 2: Magnetic movement and electric spectral bands of Ni(II) and Cu(II) complexes with MSB ligands.

<table>
<thead>
<tr>
<th>Complexes</th>
<th>Electronic spectral bands (cm$^{-1}$)</th>
<th>$\mu_{df}$ (B.M.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$v_1$</td>
<td>$v_2$</td>
</tr>
<tr>
<td>[Ni(L)Cl$_2$]</td>
<td>9542</td>
<td>10799</td>
</tr>
<tr>
<td>[Ni(L)(OAc)$_2$]</td>
<td>9479</td>
<td>12642</td>
</tr>
<tr>
<td>[Ni(L)Cl$_2$]</td>
<td>10695</td>
<td>19066</td>
</tr>
<tr>
<td>[Co(L)(OAc)$_2$]</td>
<td>10373</td>
<td>18622</td>
</tr>
</tbody>
</table>

Table 3: Epr data of Ni(II) and Co(II) complexes with MSB ligands.

<table>
<thead>
<tr>
<th>S.no</th>
<th>Complexes</th>
<th>g$\parallel$</th>
<th>g$\perp$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>[Co(L)Cl$_2$]</td>
<td>2.226</td>
<td>2.182</td>
</tr>
<tr>
<td>2</td>
<td>[Co(L)(OAc)$_2$]</td>
<td>2.214</td>
<td>2.524</td>
</tr>
<tr>
<td>3</td>
<td>[Ni(L)Cl$_2$]</td>
<td>2.113</td>
<td>2.017</td>
</tr>
<tr>
<td>4</td>
<td>[Ni(L)(OAc)$_2$]</td>
<td>2.138</td>
<td>2.242</td>
</tr>
</tbody>
</table>
Ligand field parameters
Various ligand field parameters were calculated and listed in Table 3. The values of Dq have been calculated from transition energy ratio diagram[39] Our results are in agreement with the same type of complexes reported earlier.[40] The Nepelhauze.

Table 4: ligands field parameter of Co(II) and Ni(II) complexes with MSB ligands.

<table>
<thead>
<tr>
<th>Complexes</th>
<th>Dq (cm⁻¹)</th>
<th>B (cm⁻¹)</th>
<th>C</th>
<th>β</th>
<th>F₁</th>
<th>F₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ni(L)Cl₂]</td>
<td>959.2</td>
<td>266.86</td>
<td>1618.08</td>
<td>.339</td>
<td>498.01</td>
<td>46.23</td>
</tr>
<tr>
<td>[Ni(L)(OAc)₂]</td>
<td>952.9</td>
<td>730.46</td>
<td>1049.4</td>
<td>.929</td>
<td>880.36</td>
<td>29.98</td>
</tr>
<tr>
<td>[Co(L)Cl₂]</td>
<td>1069.5</td>
<td>926.6</td>
<td>1960.0</td>
<td>.827</td>
<td>1206.0</td>
<td>56.0</td>
</tr>
<tr>
<td>Co(L)(OAc)₂</td>
<td>985.4</td>
<td>454.33</td>
<td>2319.4</td>
<td>.405</td>
<td>785.63</td>
<td>66.26</td>
</tr>
</tbody>
</table>

ACKNOWLEDGEMENTS
Authors are thankful to the Sophisticated Analytical Instrument Facility of IIT Bombay for recording EPR spectra and USIC, University of Delhi, for recording IR, Mass and NMR spectra. We also acknowledge the financial assistance of UGC and DRDO De.

CONCLUSION
The size of cavity and different donor atoms in the macrocyclic ligands affected the stability of complexes, which can be easily explained by comparing between the values of crystal field splitting energy. The redox properties and stability of the complexes towards oxidation wave explored by cyclic voltammetry are related to the electron withdrawing or releasing ability of the substituents of macrocyclic ligands moiety. Proposed structures of the ligands and their nickel (II) complexes have been given. It is found out that the geometry of the complexes is dependent on the number of coordination sites of the ligands and different anion. All the complexes are showing diamagnetic character comparatively other anions in L₁ ad L₂. Magnetic moment data are supported by the infrared information about the diamagnetic nickel (II) complexes which show uncoordinated behaviour of nitrate group. The detailed information about the geometrical arrangements of dimethylaminoazacyclotetradecane sedon the basis of 1H NMR and 13C NMR data. The cyclic voltammetry of the complexes showed that the nickel (II) complexes undergo electron reduction and oxidation to from the corresponding nickel (I) and nickel (III). These kinds of different oxidizing compounds may be found being used as one electron redox reagent since the former is a strong reducing agent and the latter is strong oxidizing agent. All the complexes in present study show kinetic property due to the chemical reaction coupled between two charges transfer processes in which irreversible first order chemical reaction is interposed between two successive one-electron transfers. The EF values of the complexes are strongly anion dependent. Ligands.

REFERENCES


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