INTRODUCTION

Transition metal ions play an important role in the development of new molecular materials which show magnetic properties and find applications in various fields. During the past few decades, the synthesis of macrocyclic complexes has been a fascinating area of research growing at a fast pace, owing to their resemblance to naturally occurring macrocycles and analytical, industrial and medicinal applications\textsuperscript{1-4}. Synthetic macrocyclic complexes may mimic some naturally occurring macrocycles because of their resemblance with many natural macrocycles like metalloproteins, porphyrins and cobalamines. Transition metal macrocyclic complexes have received a great attention because of their biological activities, including antiviral, anticarcinogenic, antifertile, antibacterial and antifungal. Macrocyclic metal complexes of lanthanide e.g., Gd\textsuperscript{3+} are used as magnetic resonance imaging (MRI) contrast agents\textsuperscript{5-9}. A number of nitrogen donor macrocyclic derivatives have long been used in analytical, industrial and medical applications\textsuperscript{10}. In the present paper, the synthesis and characterization of macrocyclic ligand prepared by isatin and 2,6-diamino-4-chloropyrimidine and its complexes with divalent nickel, copper, zinc salts and trivalent chromium, iron salts have been discussed.

EXPERIMENTAL

2,6-Diamino-4-chloropyrimidine and isatin was purchased from Koch-Light, England. All other chemicals used were of AnalR grade.

Isolation of ligand: Ligand was prepared by refluxing isatin and 2,6-diamino-4-chloropyrimidine in methanolic medium solution was refluxed for 8 h. On overnight cooling dark coloured ppt. formed which was filtered, washed with methanol, acetone, diethyl ether and dried \emph{in vacuo} (Yield 45%). The ligand was found soluble in DMF and DMSO, but insoluble in common organic solvents and water. The syntheses of the ligand may be represented by the following Scheme-I:

Isolation of the metal complexes: All the transition metal complexes were obtained by template synthesis. To a stirring methanolic solution (ca. 50 cm\textsuperscript{3}) of 2,6-diamino-4-chloropyrimidine (10 mmol) was added divalent nickel, copper, zinc and trivalent chromium and iron salt (5 mmol) dissolved in minimum quantity of methanol (20 cm\textsuperscript{3}). The resulting solution was refluxed for 0.5 h. After that isatin (10 mmol) dissolved in ca. 20 cm\textsuperscript{3} methanol added in the refluxing mixture and again refluxed for 8-10 h. On overnight cooling dark coloured precipitate. formed which was filtered, washed with methanol, acetone, diethyl ether and dried \emph{in vacuo} (yield 45%). All the complexes were found soluble in DMF and DMSO, but were
insoluble in common organic solvents and water. They were thermally stable up to ca. 250 °C and then decomposed.

The template syntheses of the complexes may be represented by the following scheme:

\[ C_8H_3O_2N + C_4H_3N_2Cl + MX_2 \xrightarrow{\text{Reflux in methanol}} \]

\[ [M(C_{24}H_{12}N_8Cl_2)X_2] + 4H_2O \]

where \( M = \text{Co(II), Ni(II), Cu(II) and Zn(II)} \). \( X = \text{Cl}^-, \text{NO}_3^-, \text{CH}_3\text{COO}^- \).

\[ C_8H_3O_2N + C_4H_3N_2Cl + MX_2 \xrightarrow{\text{Reflux in methanol}} \]

\[ [M(C_{24}H_{12}N_8Cl_2)X]X_2 + 4H_2O \]

where \( M = \text{Cr(III)} \) and \( \text{Fe(III)} \). \( X = \text{Cl}^-, \text{NO}_3^-, \text{CH}_3\text{COO}^- \).

**Analytical and physical measurements:** The microanalyses of C, H and N were carried out at Sophisticated Analytical Instrument Facility, CDRI, Lucknow. The metal contents were determined by standard EDTA methods. Electronic spectra (DMF) were recorded on Cary 14 spectrophotometer. The magnetic susceptibility measurements were carried at IIT Roorkee. The IR spectra were recorded on Infrared spectrophotometer in the range 4000-200 cm\(^{-1}\) using KBr pellets. The NMR spectra were recorded on Bruker NMR spectrometer (300 MHz). The conductivity was measured on digital conductivity meter (HPG System, G-3001).

**RESULTS AND DISCUSSION**

The analytical data of ligand, divalent and trivalent macrocyclic complexes derived from 2,6-diamino-4-chloropyrimidine and isatin and the complexes formulated as: \( C_8H_3N_2Cl \), \( [M(C_{24}H_{12}N_8Cl_2)X] \) and \( [M'(C_{24}H_{12}N_8Cl_2)X]_2 \), respectively where \( M = \text{Ni(II), Cu(II), Zn(II)} \), \( M' = \text{Cr(III), Fe(III)} \) and \( X = \text{Cl}^-, \text{NO}_3^-, \text{CH}_3\text{COO}^- \). Ligand and all the macrocyclic complexes are dark coloured solids and are soluble in dimethyl formamide or dimethyl sulphoxide. Conductivity measurement of divalent metal ion complexes in dimethyl sulphoxide indicated them to be non-electrolyte (10-20 ohm\(^{-1}\) cm\(^2\) mol\(^{-1}\))\(^{11}\). The test for anions is positive only after decomposing the complexes, indicating their presence inside the coordination sphere. The anions test for trivalent metal ion complexes is positive before and after decomposing the complexes, indicating their presence inside as well as outside the coordination sphere. The higher values of molar conductance in dimethylsulphoxide indicate them to be 1:2 electrolytic in nature (140-150 ohm\(^{-1}\) cm\(^2\) mol\(^{-1}\))\(^{12}\). All compounds give satisfactory elemental analyses results as shown in the Table-1. All complexes were decomposed over 250 °C indicating their thermal stability.

**IR Spectra:** It was noted that a pair of bands are present in the spectrum of 2,6-diamino-4-chloropyrimidine at 3400-3200 cm\(^{-1}\) corresponding to \( \nu(NH_2) \) but are absent in the infrared spectra of ligand and all the complexes. Further, no strong absorption band was observed at 1735 cm\(^{-1}\) indicating the absence of \( \nu(C=O) \) group of isatin. This confirms the condensation of carbonyl groups of isatin and amino groups of 2,6-diamino-4-chloropyrimidine. These results provide strong evidence for the formation of macrocyclic frame\(^{13,16}\). A strong absorption band in the region 1615-1595 cm\(^{-1}\) may be due to the C=N group. The unchanged 2,6-diamino-4-chloropyrimidine ring vibrations occurring at 1610-1595, 1585-1565, 1485-1450 and 1430-1410 cm\(^{-1}\) show any change in the 2,6-diamino-4-chloropyrimidine ring vibrations and interestingly enough, it appears that in these complexes 2,6-diamino-4-chloropyrimidine nitrogen does not take part in coordination\(^{21}\). Thus in the presence of metal salts, a quadridentate macrocycle is formed which coordinates through azomethine nitrogen while 2,6-diamino-4-chloropyrimidine nitrogen does not take part in coordination. Moreover, the coordination through 2,6-diamino-4-chloropyrimidine nitrogen does not take place, as it will result in the formation of unstable four membered rings. Infrared spectra of nitrito complexes display three \( \nu(N-O) \) stretching bands at 1455-1410 cm\(^{-1}\) (\( \nu_5 \)), 1315-1305 cm\(^{-1}\) (\( \nu_1 \)) and 1030-1015 cm\(^{-1}\) (\( \nu_2 \)). The separation of two highest frequency bands (\( \nu_5-\nu_1 \)),
suggest that both the nitrate groups are coordinate in unidentate manner. The acetate complexes show two bands at 1640-
1630 cm\(^{-1}\) (\(v_1\)) and 1390-1380 cm\(^{-1}\) (\(v_2\)). These indicate that the acetate group is coordinated and act as unidentate.

**Far IR spectra:** The far IR spectra show bands in the region 450-425 cm\(^{-1}\) corresponding to \(v(M-N)\) vibrations. The presence of bands in all complexes in 450-425 cm\(^{-1}\) region originate from (M-N) azomethine vibrational modes and gives idea about coordination of azomethine nitrogen. The bands present at 315-300 cm\(^{-1}\) may be assigned as being due to \(v(M=Cl)\) vibrations. The bands present at 255-225 cm\(^{-1}\) in all nitrate complexes are assignable to \(v(M-O)\) vibrations. However, the absence of various (P-azomethine) vibrations supports the non-involvement of 2,6-diamino-4-chloropyrimidine nitrogens in coordination.

**\(^1\)H NMR spectra:** The \(^1\)H NMR spectrum of zinc(II) complex show multiplets at 7.2-7.8 ppm which may be assigned due to hydrogens of aromatic rings. A broad singlet at 10.82 ppm may be assigned due to protons of the NH group of isatin.

### Magnetic measurements and electronic spectra

**Chromium complexes:** Magnetic moment of chromium complexes were found in the range of 4.25-4.50 BM at room temperature which is close to the predicted values for three unpaired electrons in the metal ion. The electronic spectra of chromium(III) complexes show bands at 9300-9310, 13045-13335, 17460-18320, 27435-27830 and 34815 cm\(^{-1}\). However, these spectral bands cannot be interpreted in terms of four- or six-coordinated environment around the metal atom. In turn, the spectral bands are consistent with that of five-coordinated chromium(III) complexes, whose structure have been confirmed with the help of X-ray measurements. Thus keeping in view, the analytical data and electrolytic nature of these complexes, a five coordinated square pyramidal geometry may be assigned for these complexes. Thus, assuming the symmetry \(C\overline{4v}\) for these complexes, the various spectral bands may be assigned as: \(B_1 \rightarrow E^*\), \(B_2 \rightarrow B_3\), \(B_3 \rightarrow A_1\) and \(B_1 \rightarrow E\).

**Iron complexes:** The magnetic moment of iron complexes lie in the range 5.85-5.90 BM corresponding to the five unpaired electrons and is close to predicted high spin values for these metal ions. The electronic spectra of iron(III) complexes show various bands at 9835-9960, 15530-15570, 27625-27730 cm\(^{-1}\) and are consistent with the range of spectral bands reported for five coordinate square pyramidal iron(III) complexes. Assuming \(C\overline{4v}\) symmetry for these complexes, the various bands can be assigned as: \(d_{xy} \rightarrow d_{xz}\), \(d_{yz}\) and \(d_{z^2}\). Any attempt to make accurate assignment is difficult due to interactions of the metal-ligand \(\pi\)-bond systems lifting the degeneracy of the \(d_{xy}\) and \(d_{z^2}\) pair.

**Nickel complexes:** The magnetic moment of nickel complexes at room temperature lie in the range 2.94-2.96 BM, in all the complexes. The solution spectra of Ni(II) complexes exhibit a well discernable band with a shoulder on the low energy side. The other two bands generally observed in the region at 16,660-17,050 cm\(^{-1}\) (\(v_1\)) and 27,850-28255 cm\(^{-1}\) (\(v_2\)), may be assigned to \(A_1 \rightarrow T_{1g}\) (\(v_1\)) and \(3A_2 \rightarrow T_{1g}\) (\(v_2\)), respectively. The first two bands result from the splitting of one band, \(v_1\) and are in the range at 9730-10,320 and 11,740-

### Table 1

<table>
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<tr>
<th>S. No</th>
<th>Complexes</th>
<th>M</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>Cl</th>
<th>colour</th>
<th>m.w.</th>
<th>Cond. ((\Omega^2))</th>
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</thead>
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<td>1</td>
<td>(\text{C}_2\text{H}_2\text{N}_2\text{Cl}_2)</td>
<td>59.60</td>
<td>2.49</td>
<td>23.18</td>
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<td>2</td>
<td>[(\text{Ni}(\text{C}_2\text{H}_2\text{N}_2\text{Cl}_2))\text{Cl}]</td>
<td>9.56</td>
<td>47.03</td>
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<td>18.27</td>
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<td>612.69</td>
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<td>14</td>
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<td>3</td>
<td>[(\text{Ni}(\text{C}_2\text{H}_2\text{N}_2\text{Cl}_2))\text{NO}_3]</td>
<td>8.83</td>
<td>43.27</td>
<td>1.82</td>
<td>21.02</td>
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<td>665.69</td>
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<td>4</td>
<td>[(\text{Ni}(\text{C}_2\text{H}_2\text{N}_2\text{Cl}_2))\text{OAc}]</td>
<td>8.93</td>
<td>50.90</td>
<td>2.70</td>
<td>16.96</td>
<td>Dark green</td>
<td>659.69</td>
<td></td>
<td>15</td>
</tr>
<tr>
<td>5</td>
<td>[(\text{Cu}(\text{C}_2\text{H}_2\text{N}_2\text{Cl}_2))\text{Cl}]</td>
<td>10.24</td>
<td>46.63</td>
<td>1.97</td>
<td>18.13</td>
<td>Yellow</td>
<td>617.50</td>
<td></td>
<td>10</td>
</tr>
<tr>
<td>6</td>
<td>[(\text{Cu}(\text{C}_2\text{H}_2\text{N}_2\text{Cl}_2))\text{NO}_3]</td>
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<td>42.99</td>
<td>1.72</td>
<td>20.85</td>
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<tr>
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<td>2.75</td>
<td>16.66</td>
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<tr>
<td>8</td>
<td>[(\text{Cr}(\text{C}_2\text{H}_2\text{N}_2)\text{Cl}_2)</td>
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<td>44.87</td>
<td>1.85</td>
<td>17.47</td>
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<td>641.50</td>
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<td>144</td>
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<tr>
<td>9</td>
<td>[(\text{Cr}(\text{C}_2\text{H}_2\text{N}_2\text{Cl}_2))\text{NO}_3]</td>
<td>7.24</td>
<td>39.96</td>
<td>1.68</td>
<td>21.35</td>
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<td>149</td>
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<tr>
<td>10</td>
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<td>7.33</td>
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<td>11</td>
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<td>8.62</td>
<td>44.66</td>
<td>1.87</td>
<td>17.34</td>
<td>Blackish brown</td>
<td>645.00</td>
<td></td>
<td>140</td>
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<tr>
<td>12</td>
<td>[(\text{Fe}(\text{C}_2\text{H}_2\text{N}_2\text{Cl}_2))\text{NO}_3]</td>
<td>7.68</td>
<td>39.73</td>
<td>1.64</td>
<td>21.28</td>
<td>Dark blue</td>
<td>724.50</td>
<td></td>
<td>147</td>
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<tr>
<td>13</td>
<td>[(\text{Fe}(\text{C}_2\text{H}_2\text{N}_2\text{Cl}_2))\text{OAc}]</td>
<td>7.75</td>
<td>50.34</td>
<td>2.92</td>
<td>15.62</td>
<td>Orange</td>
<td>715.50</td>
<td></td>
<td>145</td>
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<tr>
<td>14</td>
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<td>50.46</td>
<td>2.71</td>
<td>16.80</td>
<td>White</td>
<td>666.34</td>
<td></td>
<td>14</td>
</tr>
</tbody>
</table>

**Notes:** Computations were carried out on a VEGA 30 computer using the Gaussian 98 program for ground state geometry optimization. Spectra were taken on a Perkin Elmer Fourier transform infrared spectrometer with KBr pellets and Nujol mulls. Magnetic measurements were made on a vibrating sample magnetometer (VSM) and electronic absorption spectra were recorded on a UV-visible spectrophotometer.
12,310 cm\(^{-1}\), which can be assigned to \(^3B_{1g} \rightarrow ^3E_g\) and \(^3B_{1g} \rightarrow ^3B_{2g}\), assuming the effective symmetry to be \(D_{4h}\) (component of \(3T_{1g}\) in \(O_h\) symmetry\(^{15}\)). The intense higher energy band at 34,510 cm\(^{-1}\) may be due to a \(\pi-\pi^*\) transition of the (C=N) group. Various bands do not follow any regular pattern and seem to be anion independent. The spectra are consistent with distorted octahedral nature of these complexes.

**Copper complexes:** The magnetic moments of copper complexes lay in the range 1.75–1.78 BM. The absorption spectra of the copper complexes exhibit bands in the region 17,520–19,625 cm\(^{-1}\) with a shoulder on the low energy side at 14,540–16,000 cm\(^{-1}\) and show that these complexes are distorted octahedral\(^{14}\). Assuming tetragonal distortion in the molecule, the d-orbital energy level sequence for these complexes may be: \(x^2\rightarrow y^2 > z^2 \rightarrow xy > xz > yz\) and the shoulder can be assigned to: \(z^2 \rightarrow x^2\ \gamma^2\) \((^3B_{1g} \rightarrow ^3B_{2g})\) and the broad band contains both the \(xy \rightarrow x^2\ \gamma^2\) \((^3B_{1g} \rightarrow ^3E_g)\) and \(xz, yz \rightarrow x^2\ \gamma^2\) \((^3B_{1g} \rightarrow ^3A_{2g})\) transitions\(^{36}\). The band separation of the spectra of the complexes is of the order 2980 cm\(^{-1}\), which is consistent with proposed geometry of the complexes\(^{36}\). Therefore, it may be concluded that all the complexes of Cu(II) metals of this series are distorted octahedral.

**Conclusion**

Based on various physicochemical studies like elemental analyses, conductivity measurements, magnetic measurements, electronic and IR spectral studies, a distorted octahedral geometry may be proposed for all of divalent metal complexes as shown in Fig. 1 and five coordinate square pyramidal geometry for all trivalent metal complexes as shown in Fig. 2.

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**REFERENCES**