Investigation of New Tetra Dentate Macrocyclic [N₄] Ligand and it's Complexes with Transition Metal's

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Abstract :  
This paper describes the preparation and study of a number of transition metal Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) with the ligand (2,9-diamin-5,7,12,14-tetraazo-1,4,8,11-tetra-oxo-6,13-dithiacyclotetra-decane)L₁ .  
These complexes also reacted with 4-methyl pyridine (γ-picoline) L₂ to form 1:2 adducts in which the ligand act as a monodentate ligand. All these complexes and the adduct characterized by microanalytical (M%) , molar conductance measurements, magnetic susceptibility measurements, IR, and electronic spectral.

Introduction :  
Thiourea and their complexes have been extensively studied during recent years mainly because of their various biological properties. Thiourea usually act's as chealating ligand with transition metal ions, bonding through the sulfur or nitrogen atoms. Macrocyclic ligands are
known and recognized as examples of organic skeleton containing cyclic structures in which their arrangements of the ligands molecule are sufficiently constrained to influence, often dramatically, the properties of the complex formation with metal\(^{(5,6)}\). Such ligands frequently show selectivity in their complexation properties, coordinating behavior of anions and may modify the redox chemistry of the formed metal complex\(^{(7)}\).

As part of our continuous research work pertaining to the synthesis, characterization of metal complexes from thiourea, we describe here some new transition metal complexes obtained from Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) chlorides.

**Experimental:**

The ligand \(L_1\) has been synthesized according to the following procedure\(^{(8)}\). Aspartic acid (6.6 g, 0.05 mol) was dissolved in hot ethanol (20 ml) and mix with hot ethanolic solution (20 ml) of thiourea (3.8 g, 0.05 mol) with stirring. The mixture then reflux at \(\sim 80^\circ C\) for 7 h in the presence of (2 ml) concentrated hydro- chloric acid, on standing over night, a white precipitate formed which was filtered off washed with cold ethanol and dried under vacuum Scheme (1) some of its physical properties are listed in Table (1).

![Scheme 1](image-url)

Scheme (1) : preparation and structure of the ligand \(L_1\).
A- Preparation of the metal complexes :
The hot solution of the ligand L₁ (0.01 mol, 0.42 g) in 20 ml ethanol and ethanolic solution of the corresponding metal salt (0.01 mol/20 ml) were mixed together with stirring. The mixture was refluxed for 6h at ~80°C, on cooling gives a colored precipitate of the complexes which was filtered off washed with cold EtOH and dried under vacuum.

B- Preparation of the base adducts :
These complexes were prepared by adding excess 4-methyl pyridine dissolved in ethanol and mixed with every complex alone and refluxed at ~80°C for about 3h. On cooling gives coloured precipitate Table (1) which was filtered off washed with cold EtOH and dried under vacuum.

C- Physical measurements :
Metal analysis of all complexes were carried out using standard method. (atomic absorption method). Infrared spectra (4000-400 cm⁻¹) were recorded on Perkin-Elmen 580B spectrophotometer, as KBr discs. Electronic spectra were obtained with Shimadzu UV/Vis, recording UV/160 spectrophotometer at room temperature. The measurements were recorded using in DMSO as a solvent. The magnetic measurements were carried out at 25°C on solid by the Faraday method using Bruker BM6 instrument. Conductivities were measured using conductivity meter mode PCM3-Jenway using 10⁻³M DMSO at 25°C of the complexes.

Results and discussion :
Four new bands appear in the spectrum of free ligand (L₁) assignable to amid I [υ C=O], amid II [υ (C–N) + δ (N–H)], amid III [δ (N–H)] and amid IV [δ C=O] bands respectively. The spectrum also show a splitting band due to υ(–C=S) at 1175, 1122 cm⁻¹. A sharp band's observed at 3250 and 3385 cm⁻¹ which may be assigned to –NH and –NH₂ group respectively, Table (3)

Complexes :
The molar conductance measurements in DMSO show's two types of complexes, a nonelectrolyte nature for Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) while 1:2 electrolyte for the base adduct complexes. Thus these complexes may be formulated as [ML₁X₂] and [ML₁(γ-pic)₂]Cl₂ respectively. On complex formation the shifting to word lower side of υ(NH) bands and also the bands of amide II suggest a coordination through the nitrogen (NH) group [N₄] core, also the band positions due to υ(C=S) did not change and υ(NH₂) indicating un coordinated behavior of C=S and NH₂ groups. A further supported by the
appearance of a medium intensity band in the range of 450-475 cm\(^{-1}\) attributed to \([\nu(M-N)]\).

**Manganese (II) complexes**:

The electronic spectra exhibit bands 30303, 38776 cm\(^{-1}\) may be due to charge transfer \(^{(11,12)}\). The magnetic moment values at room temperature 5.89, 5.99 BM for the manganese (II) complexes were well in accordance with those having octahedral structure with five unpaired electrons \(^{(9,10)}\) Fig (1).

**Iron(II) complexes**:

The electronic spectra of iron (II) complexes at room temperature showed a band at 10162 and 9842 cm\(^{-1}\) which attributed to the \(^{5}T_2\) \(\rightarrow\) \(^{5}E_{g}\) transition and could be assigned to a distorted octahedral structure \(^{(11,12)}\). The values of the Fe(II) complexes magnetic moment at room temperature was 4.56, 4.68 were well in accord with those having distorted octahedral structure \(^{(11)}\).

**Cobalt (II) complexes**:

The two Co(II) complexes exhibit magnetic moment values lie in 4.78 and 4.85 BM corresponding to three unpaired electrons higher value due to orbital contribution Table (2).

The electronic spectra of these complexes showed an absorption in the region(1) 10183, 10708(2) 14810, 15737(3) 18571,25325 and 32258, 33333 cm\(^{-1}\) these bands may be assigned to the transition \(^{4}T_1\) \(\rightarrow\) \(^{4}T_{2g}(F)\) \(\nu_1\), \(^{4}T_1\) \(\rightarrow\) \(^{4}A_{2g}(\nu_2)\) and \(^{4}T_1\) \(\rightarrow\) \(^{4}T_{1g}(P)\) \(\nu_3\) respectively \(^{(11)}\). The fourth band and it may be due to charge transfer. The position of these bands indicates that these complexes have distorted octahedral geometry \(^{(9,10,12)}\) Fig.(1).

**Nickel (II) complexes**:

The magnetic moment values of the two nickel (II) complexes showed 3.04 and 3.17 BM, these values are in turn with high-spin configuration and shows the presence of an octahedral enviroment around Ni(II) ion in complexes \(^{(13)}\). The electronic spectrum of the complexes shows three bands at(1)10162,10893, (2) 15185, 15364 and (3), 25641, 26397 cm\(^{-1}\) correspond to \(^{3}A_{2g}(F)\) \(\rightarrow\) \(^{3}T_{2g}(F)\) \(\nu_1\), \(^{3}A_{2g}(F)\) \(\rightarrow\) \(^{3}T_{2g}(F)\) \(\nu_2\) and \(^{3}A_{2g}(F)\) \(\rightarrow\) \(^{3}T_{2g}(P)\) \(\nu_3\) respectively. These band indicate the complexes has octahedral geometry Fig.(1).

**Copper (II) complexes**:

The magnetic moment values of Cu(II) complexes are 2.05, 1.95 BM which are corresponding of one unpaired electron.
Electronic spectra of the two complexes display one bands which assigned to the $^2E_g \rightarrow ^2T_{2g}$ transition in distorted octahedral structure around the Cu (II) ions.\(^{(7,10,12)}\) Fig. (1).

On the basis of the above discussion we propose the following structure of the metal (II) complexes as in Fig. (1).

![Structure of complexes](image)

Fig(1): Suggested structures of the complexes.

Where:
M= Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II).

Table (1): Molar conductance and metal analysis of the complex

<table>
<thead>
<tr>
<th>No.</th>
<th>Compound</th>
<th>Colours</th>
<th>M.P °C</th>
<th>Yield %</th>
<th>Molar conductance $\Omega^1$.cm$^2$.Mol$^{-1}$</th>
<th>Salts</th>
<th>Metal analysis (found/calculated) %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>[Mn(L$_1$)Cl$_2$]</td>
<td>White</td>
<td>235</td>
<td>74</td>
<td>21.5</td>
<td>MnCl$_2$</td>
<td>11.21 (11.64)</td>
</tr>
<tr>
<td>2.</td>
<td>[Mn(L$_1$)(γ-pic)$_2$]</td>
<td>Yellow</td>
<td>234</td>
<td>68</td>
<td>81.0</td>
<td>MnCl$_2$</td>
<td>9.25 (9.73)</td>
</tr>
<tr>
<td>3.</td>
<td>[Fe (L$_1$)Cl$_2$]</td>
<td>Brown</td>
<td>217</td>
<td>70</td>
<td>16.8</td>
<td>FeCl$_2$</td>
<td>11.14 (11.90)</td>
</tr>
<tr>
<td>4.</td>
<td>[Fe (L$_1$)(γ-pic)$_2$]</td>
<td>Deep yellow</td>
<td>231</td>
<td>82</td>
<td>83.0</td>
<td>FeCl$_2$</td>
<td>9.12 (9.91)</td>
</tr>
<tr>
<td>5.</td>
<td>[Co (L$_1$)Cl$_2$]</td>
<td>Green</td>
<td>230</td>
<td>64</td>
<td>13.0</td>
<td>CoCl$_2$.6H$_2$O</td>
<td>11.86 (12.40)</td>
</tr>
<tr>
<td>6.</td>
<td>[Co (L$_1$)(γ-pic)$_2$]</td>
<td>Brown</td>
<td>254</td>
<td>63</td>
<td>85.0</td>
<td>CoCl$_2$.6H$_2$O</td>
<td>10.01 (10.37)</td>
</tr>
<tr>
<td>7.</td>
<td>[Ni (L$_1$)Cl$_2$]</td>
<td>Brown</td>
<td>241</td>
<td>58</td>
<td>12.0</td>
<td>NiCl$_2$.6H$_2$O</td>
<td>11.65 (12.36)</td>
</tr>
<tr>
<td>8.</td>
<td>[Ni (L$_1$)(γ-pic)$_2$]</td>
<td>Dark brown</td>
<td>300</td>
<td>86</td>
<td>72.0</td>
<td>NiCl$_2$.6H$_2$O</td>
<td>9.98 (10.33)</td>
</tr>
<tr>
<td>9.</td>
<td>[Cu (L$_1$)Cl$_2$]</td>
<td>Gray</td>
<td>219</td>
<td>81</td>
<td>19.0</td>
<td>CuCl$_2$</td>
<td>12.94 (13.24)</td>
</tr>
<tr>
<td>10.</td>
<td>[Cu (L$_1$)(γ-pic)$_2$]</td>
<td>Gray</td>
<td>239</td>
<td>67</td>
<td>82.9</td>
<td>CuCl$_2$</td>
<td>10.80 (11.09)</td>
</tr>
<tr>
<td>11.</td>
<td>[Zn (L$_1$)Cl$_2$]</td>
<td>Pink</td>
<td>233</td>
<td>83</td>
<td>14.6</td>
<td>ZnCl$_2$</td>
<td>12.82 (13.58)</td>
</tr>
<tr>
<td>12.</td>
<td>[Zn (L$_1$)(γ-pic)$_2$]</td>
<td>Brown</td>
<td>271</td>
<td>80</td>
<td>76.5</td>
<td>ZnCl$_2$</td>
<td>10.87 (11.38)</td>
</tr>
</tbody>
</table>
References:

7) S. Chandra. R. Kumar, J. Ind. Chem. Soc. 82, 693, 2005.