Synthesis and characterization of Fe(II),Co(II),Ni(II),Cu(II) and Zn(II) complexes with Hexaaza macromolecule Ligands Derived from Semicarbazide

Saad .K.Dawood Falah.M.Fakhree

Department of Chemistry
College of Science
Mosul University
falahl11111@yahoo.com

ABSTRACT
A new ligands( 3,4,6,14,15,17,23,24-Octaazaatrzyclclo [17.3.1.18,12] tetracosa-1(23),8(24),9,11,19,21- hexaene - 2,5,7,13,16,18 – hexaone), (L1) and 2-(5-hydroxypentanoyl) hydrazinecarboxamide,(L2)was prepared from the reaction of pyridine-2,6-dicarboxylic acid and glutaric acid with semicarbazide by microwave irradiation in solid state ,then was reacted with some transition metal(II) ions to form complexes of the type.

Adducts of the type \([\text{M(}L^1\text{)(PPh}_3\text{)}\text{Cl}_2]\), \([\text{M(}L^2\text{)}\text{Cl}_2]\) and \([\text{M(}L^2\text{)}\text{Cl}_2]\) were prepared by the reaction of the above complexes with triphenylphosphine in a 2:1 and 1:1 molar ratio. The prepared complexes and adducts were characterized by (C,H,N) analysis, metal content analysis, molar conductance, magnetic moment measurements, electronic and IR spectroscopy, the ligand was characterized by \(^1\text{H},^{13}\text{C} -\text{NMR}\). The electronic spectra and magnetic measurements indicated that the complexes have octahedral environment around the metal ions.

**Keywords** Microwave - assisted synthesis .macrocyclic molecules

**INTRODUCTION**

Metal-template synthetic for the preparation of poly-aza macrocyclic compounds are known since the early 2010\(^{(1)}\).Owing to their metal coordinating properties, metal ions are able in several favorable cases, to organize reacting molecular fragments according to specific geometry and to drive the reaction toward the formation of cyclic compound. Transition metal macrocyclic compound have an active part of metalloenzymes as bionomic model compounds due to their resemblance with natural proteins like hemerythrin and enzymes\(^{(2)}\).

Poly aza macrocyclic modified with tetraamide and hexaamide function a cyclic tetra peptide moieties in capsulate bind metal ions without under going any deprotonating process of the amide group and are capable to stabilize even the low oxidation states of the metal ions\(^{(3)}\).On other hand not only the above macro molecules ligands form complexes with transition metals but also they were mixed with the phosphine. Macrocyclic phosphine hold promise as incredibly stable ligands for applications requiring robust complexes such as radio active transition metal complexes for use as radiopharmaceuticals because of this possibility, these ligand and their complexes have been synthetic targets since soon after the macrocyclic effect was discovered.

Microwave techniques for preparation of organic substances have received a great deal of attention due to it's various advantages such as selectivity, rapid and direct controllable internal reactions….etc\(^{(4)}\). This technique has been used to prepare an eighteen member ring ligand and it's reaction with transition metal ion's to form a new complexes of different geometries\(^{(5)}\).

In view of these interesting results and as continuation of our studies on transition metal complexes with macrocyclic ligand\(^{(6,7,8,9)}\),we have prepared new types of complexes containing different donor atoms using microwave technique.
GENERAL

All chemicals used were either analytical grade or chemically pure. IR spectra were recorded on a Fourier-Transform (FT-IR) Spectrophotometer Tensor 27 Co.Bruker in the range (4000-400 cm⁻¹) using KBr discs. The CHN analysis carried out by (Euro Vactor Model EA 3000 in AL-Albeit University (Jordan)). The metal content analyses were carried out by (PYE UNICAM SP9-atomic absorption Spectrophotometer). Conductivity measurements were carried out on 10⁻³ M solution of all complexes in DMSO using (Conductivity Meter Model PCM3-JENWAY), at ambient temperature. The electronic spectra were recorded on Shimadzu-UV-Visible recording ,UV-1650PC-spectrophotometer, using 10⁻³ M of the complexes in DMSO. The magnetic measurement was measured at 25°C on the solids by Farady's method using Bruker BM6 instrument. ¹H-NMR & ¹³C-NMR carried out by (BRUKER 300 MHz Switzerland) and shimadzu QP 5050 A(JAPAN) at Al–Albeit University – Jordan. The ligand prepared in solid state using microwave oven type morph Richards EM 820 CPT.

1. Preparation of the Ligands:

3,4,6,14,15,17,23,24-octaaazatricyclo[17.3.1.1₈,1₂]tetracosa-1(23),8(24),9,11,19,21-hexaene - 2,5,7,13,16,18 – hexaone (L₁) has been synthesized according to the following procedure⁵,¹⁰,¹¹. A solid state pyridine-2,6-dicarboxylic acid (0.33 g, 0.002 mol) was mixed with solid semicarbazide (0.15 g, 0.002 mol) and (0.005 g, 0.0001 mol) of cerium ammonium nitrate (CAN) as a catalyst, the solid mixture was irradiated using a microwave 800 W for 10 minutes. A gray solid was formed cooled at room temperature, then ethyl acetate (20 ml) was added and the mixture stirred for about 1 hr to dissolve the CAN which was separated from the mixture by filtration, then a gray precipitate was washed with n-hexane, ethanol and dried under vacuum for several hours. L₂ ligand was prepared by the similar procedure except using (0.30 gm, 0.001 mol) glutaric acid and semicarbazide (0.75 gm, 0.001 mol) to get yellow precipitate.

2. Preparation of [M(L)Cl₂], [M (L₁)Cl₂] and [M(L₁)Cl]Cl:

M= Fe(II), Co(II), Ni(II), Cu(II), and Zn(II)
L= L₁ and 2L₂.

The solution of the ligand (L₁) (0.42 g, 0.001 mole) in (10 ml) DMF and ethanolic solution of the hydrated metal chloride salts (0.001 mole) were mixed together with stirring. The mixture was refluxed for 2
hr, on cooling a colored precipitate were obtained, the product was filtered off, washed with cold ethanol and dried under vacuum. The same procedure was carried out to prepare other complexes.

3. Preparation of the adducts [M(L)(PPh₃)Cl]Cl and [M(L)(PPh₃)]Cl₂: M= Fe(II), Co(II), Ni(II), Cu(II), and Zn(II)

The metal complexes [Fe(L₁)Cl]Cl (0.54 g, 0.001 mol) was dissolved in (10 ml) DMF and added to a solution of triphenylphosphine (0.26 gm, 0.001 mol) in (10 ml) ethanol, the mixture was refluxed for 1 h then a pale brown precipitate formed, filtered off, washed with diethylether and dried. The same procedure was carried out to prepare the other adducts L=L₁, 2L₂.

RESULTS AND DISCUSSION

Microwave irradiation of a mixture of the semicarbazide, dicarboxylic acid and CAN catalyst afforded the ligands (L₁ & L₂) in 90% and 85% Yield respectively, which is stable in air, non-hydroscopic at room temperature.

The ligand(L₁) characterized by ¹H NMR and the chemical shift's data are listed in Table (1) the band at δ(8.6 ppm) attributed to 6 H (H-pyr ring) assisted by the integration. The band at δ(7.2 ppm) attributed to 2H for the NH-NH-CO-pyr group, the band at (δ 8.1 ppm) attributed to 2H for the (NH-NH-CO-pyr) group, and δ(11.2 ppm) attributed to 2H for the (N-H) group. Table (2) contains ¹³C–NMR chemical shift's data, the bands at (160 ppm) for (N-CO-N), (165 ppm) for (-CO-pyr), (140 ppm) for (C-pyr meta), (148.9 ppm) for (C-pyr ortho) and (128 ppm) for (C-pyr Para). The band for the solvent (DMSO) appear at (40 ppm) figure (1), all these data assist the expecting structure for L₁ ligand.

<table>
<thead>
<tr>
<th>compound</th>
<th>NH-NH-CO-pyr</th>
<th>NH-NH-CO-pyr</th>
<th>N-H</th>
<th>H-pyr</th>
</tr>
</thead>
<tbody>
<tr>
<td>L₁</td>
<td>7.2</td>
<td>8.1</td>
<td>11.2</td>
<td>8.6</td>
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</table>

<table>
<thead>
<tr>
<th>compound</th>
<th>N-CO-N</th>
<th>-CO-pyr</th>
<th>C-pyr meta</th>
<th>C-pyr ortho</th>
<th>C-pyr Para</th>
</tr>
</thead>
<tbody>
<tr>
<td>L₁</td>
<td>160</td>
<td>165</td>
<td>140</td>
<td>148.9</td>
<td>128</td>
</tr>
</tbody>
</table>
Synthesis and characterization of Fe(II), Co(II), Ni(II), Cu(II) …

(A) Structure of the ligand \( L_1 \)

(B): \(^1\)H NMR for \( L_1 \) ligand

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ligand data are 1

(\( \text{HO-CH} \))

CH-CH=

attributed (7.7 ppm)

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tal shift's

to 3H

to (CH-

1.2 ppm)

(N-H2),

ains \(^{13}\)C–
NMR chemical shift's the band at(35-20 ppm) attributed to (C-C-C-) , (58 ppm) for (HO-C-R) , ( 175 ppm) for (R-CO-N-N) , (156.3 ppm) for (C=O)-NH) and the solvent (DMSO) shows a band at(40 ppm) , figure (1) .All these bands assist the expecting ligand L₂ structure.

Table(3) Chemical shift for L₂ ¹H-NMR

<table>
<thead>
<tr>
<th>compound</th>
<th>HO-CH₂-δ</th>
<th>CH-CH=Oδ</th>
<th>CH-CH=Oδ</th>
<th>N-H₂δ</th>
<th>C-NH-Nδ</th>
</tr>
</thead>
<tbody>
<tr>
<td>L₂</td>
<td>3.4-3.6</td>
<td>2.3</td>
<td>1.2</td>
<td>6.5</td>
<td>7.7</td>
</tr>
<tr>
<td></td>
<td>3H</td>
<td>2H</td>
<td>4H</td>
<td>3H</td>
<td>1H</td>
</tr>
</tbody>
</table>

Table(4) Chemical shift for L₂ ¹³C –NMR

<table>
<thead>
<tr>
<th>compound</th>
<th>C-C-C-</th>
<th>HO-C-R</th>
<th>R-CO-N-N</th>
<th>C(=O)-NH</th>
</tr>
</thead>
<tbody>
<tr>
<td>L₂</td>
<td>35-20</td>
<td>58</td>
<td>175</td>
<td>156.3</td>
</tr>
</tbody>
</table>

(A) structure of the ligand L₂

(B): ¹H NMR for L₂ ligand

(C): ¹³C NMR for L₂ ligand

Fig(2): A,B,C
Synthesis and characterization of Fe(II),Co(II),Ni(II),Cu(II)…..

The IR spectrum data of \((L_1, L_2)\) Table (6) exhibited absorption frequencies assignable to \(\nu(N-H)\) stretching as a strong band at \((3225 \text{ cm}^{-1})\), \(\delta((\text{N-H})\) appears at \((1236 \text{ cm}^{-1})\), \(\nu(N-N)\) stretching vibration appears at \((1018 \text{ cm}^{-1})\), and the frequency assignable to \(\nu(C=O)\) band at \((1709 \text{ cm}^{-1})\) as medium intensity\(^{(13)}\). The IR spectrum characteristic to \(\nu(N-N), \nu(CO-\text{NH-CO})\) and \(\nu(C=O)\) stretching frequencies confirm the condensation reaction between the carboxylic acid and semicarbazide, to form a 20 membered hexa amide macrocycle \(L_1\&L_2\), as shown in figure \((1)\), on Complexation, the stretching frequencies of \(\nu(N-H), \delta(CO-\text{NH-CO})\) and \(\nu(N-N)\) shifted to lower frequency, which may indicate the coordination of two \((\text{NH})\) from the semicarbazide group figure \((2)\), other support of this coordination comes from the appearance of new bands attributed to \(\nu(M-N)\) stretching at \((418-460 \text{ cm}^{-1})\). However, the position of \(\nu(C=O)\) stretching vibration has been shifted to lower frequencies in complexes number \((7)\), where as the other complexes and adducts number \((1,2,3,4,5,6,8,9)\), the \(\nu(C=O)\) are not shifted\(^{(14,15)}\). A new band attributed to the stretching of \(\nu(M-O)\) group in complexes number \((7)\) at \((509 \text{ cm}^{-1})\) may prove this coordination.

**ELECTRONIC SPECTRA & MAGNETIC MEASUREMENTS**

The spectrum of the \(L_1, L_2\) ligands has a bands in the U.V spectra at \((36760 \text{ and } 45871 \text{ cm}^{-1})\), assigned to \(n \rightarrow \pi^*\) and \(\pi \rightarrow \pi^*\) transition, respectively.

The electronic spectra data and the magnetic moments for all complexes are given in Table \((5)\).

The magnetic moment values for the Fe(II) complexes \((1,3)\) have a magnetic moment values \((4.87 - 5.12 \text{ B.M})\) while the electronic band at \(10224-10526 \text{ cm}^{-1}\) are attributed to \(\text{5}T_2g \rightarrow \text{5}E_g\) transition, indicating octahedral structure\(^{(5)}\).

The cobalt complex number \(4\) has a magnetic moment value \((4.80 \text{ B.M})\) corresponding to three unpaired electrons[Table 5].The U.V-visible spectra show three bands at \(10245 -15625 \text{ cm}^{-1},16889 \text{ cm}^{-1}\) and \(32051 \text{ cm}^{-1}\) due to the transitions \(4T_1g(F) \rightarrow \text{4}T_2g(F)\) \(\nu_1,\)
\(4T_2g(F) \rightarrow \text{4}A_2g(F)\) \(\nu_2\) and \(4T_1g(F) \rightarrow \text{4}T_1g(P)\) \(\nu_3\), respectively. These data may attribute to octahedral structure\(^{(16)}\).

The UV – visible spectra of the Ni (II) complexes number\((5,6)\) shows three bands at \((10111,9469 \text{ cm}^{-1}), (15337,14534 \text{ cm}^{-1})\) and \((22676,21233 \text{ cm}^{-1})\) corresponding to three spin allowed transition \(3A_2g(F) \rightarrow \text{3}T_2g(F)(\nu_1),\) \(3A_2g(F) \rightarrow \text{3}T_1g(F) (\nu_2)\), and \(2A_2g(F) \rightarrow \text{3}T_1g(P) (\nu_3)\), respectively. The magnetic moment values \((2.99 , 3.31 \text{ B.M})\) agree with high spin configuration indicating an octahedral environment around the Ni(II)ions\(^{(10)}\).
The magnetic moment of the Cu(II) complexes number(7,8) lie in the range (2.11, 2.03 B.M.), corresponding to one unpaired electron and electronic spectra have a band in the range (20832, 22935 cm\(^{-1}\)) assigned to the \(^2\text{E}_g(F) \rightarrow ^2\text{T}_2\) transition in distorted octahedral environment\(^{(17)}\). The \(\mu_{\text{eff}}\) values of the two Zn(II) complexes were diamagnetic as expected.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Color</th>
<th>M.P.</th>
<th>CHN Analysis</th>
<th>Conductance</th>
<th>(\mu_{\text{eff}})</th>
<th>(\rho) cm(^{-1}) (\text{cm}) (\Omega)</th>
<th>(\gamma) %</th>
<th>(\delta) %</th>
<th>(\epsilon) %</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Cu(II)(PPH)_3]Cl</td>
<td>Brown</td>
<td>204(9)</td>
<td>6.31(6.09)</td>
<td>6.00(6.35)</td>
<td>11.71(13.0)</td>
<td>11.42(11.0)</td>
<td>10.69(10.5)</td>
<td>4.98</td>
<td>4.87</td>
</tr>
<tr>
<td>[Ni(II)(PPH)_3]Cl</td>
<td>Green</td>
<td>17.3(17.30)</td>
<td>17.3(17.30)</td>
<td>17.3(17.30)</td>
<td>17.3(17.30)</td>
<td>17.3(17.30)</td>
<td>17.3(17.30)</td>
<td>17.3(17.30)</td>
<td>17.3(17.30)</td>
</tr>
<tr>
<td>[Co(II)(PPH)_3]Cl</td>
<td>Blue</td>
<td>2.03</td>
<td>2.03</td>
<td>2.03</td>
<td>2.03</td>
<td>2.03</td>
<td>2.03</td>
<td>2.03</td>
<td>2.03</td>
</tr>
<tr>
<td>[Fe(II)(PPH)_3]Cl</td>
<td>Yellow</td>
<td>36</td>
<td>36</td>
<td>36</td>
<td>36</td>
<td>36</td>
<td>36</td>
<td>36</td>
<td>36</td>
</tr>
<tr>
<td>[Fe(II)(Cl)]Cl</td>
<td>Green</td>
<td>150</td>
<td>150</td>
<td>150</td>
<td>150</td>
<td>150</td>
<td>150</td>
<td>150</td>
<td>150</td>
</tr>
</tbody>
</table>

Note: \(\rho\) = \(\text{cm}\cdot\text{cm}\cdot\Omega\)
Synthesis and characterization of Fe(II), Co(II), Ni(II), Cu(II), and Zn(II) complexes and adducts.

Conclusion

On the basis of the above results, we proposed the following structures for the Fe(II), Co(II), Ni(II), Cu(II), and Zn(II) complexes and adducts.

Fig(2): Proposed structures of the complexes and the adducts
Table (6): Selected I.R bands and their assignment in cm$^{-1}$

<table>
<thead>
<tr>
<th>No</th>
<th>Band maxima ($\lambda_{max}$) nm</th>
<th>I.R spectra</th>
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<tbody>
<tr>
<td></td>
<td>N-$\nu$(H)</td>
<td>N-$\delta$(H)</td>
</tr>
<tr>
<td>---</td>
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<td>---</td>
</tr>
<tr>
<td>L1</td>
<td>3250</td>
<td>1306</td>
</tr>
<tr>
<td>L2</td>
<td>3265</td>
<td>1257</td>
</tr>
<tr>
<td>1</td>
<td>10526</td>
<td>3124</td>
</tr>
<tr>
<td>2</td>
<td>30121</td>
<td>3211</td>
</tr>
<tr>
<td>3</td>
<td>10224</td>
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</tr>
<tr>
<td>4</td>
<td>10245,15625,16889,32051</td>
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</tr>
<tr>
<td>5</td>
<td>10111,15337,22676,36496</td>
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</tr>
<tr>
<td>6</td>
<td>9469,14534,21233,36761</td>
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<tr>
<td>7</td>
<td>20833,32679</td>
<td>3232</td>
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<tr>
<td>8</td>
<td>22935,32055</td>
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</tr>
<tr>
<td>9</td>
<td>31278,35421</td>
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REFERENCES

Synthesis and characterization of Fe(II),Co(II),Ni(II),Cu(II).....