Preparation and Characterization of Co(II), Ni(II) and Cu(II) ions Binuclear Complexes with Macrocyclic Schiff Base Derived from Acidhydrazide and α-Hydroxy Ketone

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Abstract:

The homogenous binuclear complexes of macrocyclic Schiff base ligand obtained from [2+2] condensation reaction between benzon and α - aminobenzoylhydrazide in presence of the metal salt , in neutral and alkaline media . The complexes were characterized by quantitative determination of the metal and chloride content , molar conductance , spectral and magnetic susceptibility measurement . The different studies revealed that the prepared complexes possess the following formulae [LH₄M₂X₂] and K₂[LM₂X₂]in neutral and alkaline medium respectively (where LH₄ = macrocyclic Schiff base ligand , M⁺²=Co,Ni ,Cu ; X⁻=NO₃ ,Cl⁻). The complexes of neutral medium are non-electrolytes , six coordinat , while alkaline medium complexes are electrolytes of 2:1 ratio and four coordinate

Keywords : Co(II), Ni(II) and Cu(II) , Binuclear Complexes ,Macrocyclic Schiff Base , Acidhydrazide ,α-Hydroxy Ketone

Introduction:

The chemistry of macrocyclic ligands and their complexes has recived extensive attraction towards inorganic and bioinorganic chemists .Since the cyclic arrangement of large number of donor atoms and the flexibility of these ligands make them good host for ions[1] . Consequently they could be used in supramolecular chemistry to mimic some biological molecules like metalloenzymes[2] . In addion to their antifungual ,antibacterial,antioxidant and antimicrobial activities[3-6] .Some macrocycles show high selectivity towards certain cations like Ag (I) , Cu(II) and Cr(III)[7,8] so they could be used as extracting agents in analytical chemistry .The macrocyclic Schiff base complexes usually synthesized by template condensation reaction between the ligand constituents in the presence of metal salt as templating agent [9] ,otherwise the ligand is polymerized or decomposed[10] .Therefore certain techniques must be preformed in order to obtaine metal free macrocyclic Schiff base[11,12] . Binuclear macrocycles had been investigated as early as Robson type macrocycles (1) ,which containing two bridging phenol groups[10] .Such ligands have been widely used to synthesize homo-and hetero-binuclear complexes[13] . So they become of high interest as mimic model for the active sites of metalloenzymes and playing significant role in industrial catalyst design. In another point of view Gao et al have been developed Robson type macrocycles by using different diamines to obtain mononuclear , binuclear and trinuclear complexes , depending on metal:lignand ratio ,type of templating metal and type of condensation , and metal free macrocycles also obtained[14] . Another type of binuclear complexes(2) have been synthesized through template condensation between benziel and o-phenylenediamine in the presence of 3,3 – diaminobenzidine and respective metal salt [6]. Binuclear macrocycle containing metal-metal bond(3) was achived by Ilhan[15].

In the present work we try to synthesize homobinuclear macrocycles by (2+2) condensation between benzione and o-aminobenzoylhydrazided in the presence of Co(II) ,Ni(II ) and Cu(II) salts ,both in neutral and basic medium.
Experimental

Materials and Methods:

All chemical used were reagent grade from B.D.H or Fluka chemical companies, used as supplied. Melting points were determined by using Electrothermal 9300 apparatus. Molar conductance was carried out for 10^{-3} M solutions in DMF at room temperature using an electric conductivity measuring device consort c832. Magnetic susceptibility measurements were preformed on Burkner BM6 instrument at room temperature by Farady method. The infrared spectra were recorded in the range 4000-400 cm^{-1} on Tensor 27 Brucker FT-IR spectrophotometer. The electronic spectra were recorded on Shimadzu UV-1650 CP- spectrophotometer for 10^{-3} M solution of the complexes in DMF at room temperature using 1cm cell. Metal content of the complexes were determined spectrophotometrically by Shimadzu AA670 atomic absorption spectrophotometer, after decomposition with concentrated nitric acid. The chloride contents were determined by Volhard method after decomposition with concentrated sulfuric acid to avoid oxidation of the chloride to chlorine gas.
Preparation of anthranoyl acid hydrazide:
This was prepared by the reaction of methylanthanolate with hydrazine in absolute ethanol by the general procedure reported in literature for the preparation of acid hyrazides \[16\].

Preparation of \([LH_4M_2X_2]\) Metal complexes:
The complexes were prepared using template method by condensing benzoin with anthranoyl acid hydrazide in the presence of metal salts as following:
To hot stirring methanolic solution (20 ml) of benzoin (0.002 mole, 0.424 g), an ethanolic solution of metal salts (0.002 mole) of \(0.474 \text{ g, CoCl}_2 \cdot 6\text{H}_2\text{O}; 0.474 \text{ g, NiCl}_2 \cdot 6\text{H}_2\text{O}; 0.582 \text{ g, Cu(NO}_3)_2 \cdot 6\text{H}_2\text{O}; 0.582 \text{ g, Ni(NO}_3)_2 \cdot 6\text{H}_2\text{O and} 0.484 \text{ g, Cu(NO}_3)_2 \cdot 3\text{H}_2\text{O}\) which dissolved in a minimum quantity of ethanol (~ 20 ml) were added.

The resulting mixture was refluxed for several minutes. Then methanolic solution (20 ml) of (0.002 mole, 0.32 g) of anthranoyl acid hydrazid was added. The mixture was refluxed for 2 – 3 hours, after that it was cooled down. The precipitated complexes were filtered off, washed with cold ethanol (5 ml) then with ether (5 ml) and dried at 40 – 50°C.

Preparation of \(K_2[M_2L_2X_2]\) Metal complexes:
The same procedure mentioned above performed by using only metal chlorides salt solution and (0.004 mole, 0.224 g) of KOH was added to a hot ethanolic solution of benzoin. Then the addition of other constituents were completed. The reaction mixture allowed to reflux for 15 minutes. Then cooled. The precipitated complexes were filtered off washed with cold ethanol (5 ml) then with ether (5 ml) and dried at 40 – 50°C.

Results and Discussion
Metal free macrocyclic Schiff base ligand cannot be obtained by direct reaction between benzoin and the diamine this leads to the decomposition of the product. So the reaction proceeds between ligand constituents in the presence of metal salt using 1:1:1 molar ratio of benzoin, diamine and metal salt respectively. Template condensation of the type [2+2] is expected to occur. Binuclear complexes of 16-membered polydentatemacrocyclic ligand \([2,3,10,11\text{-tetraphenyl-1,4,5,9,12,13-hexadecane 6,1-dione} ]\) were obtained in neutral and basic medium (Scheme 1). The formulation of the complexes were confirmed by analytical data (Table1).

The molar conductance of \(10^{-3} \text{ M}, \text{in DMF for neutral medium complexes (1-6)}\) show small values in the range \(\text{ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}\), indicating that the complexes are non-electrolytes.

On the other hand basic medium produce complexes of the type \(K_2 [ML] \text{ indicating the deprotonation of the tetrabasic ligand due enolisation (Schem 1,b)}, \) since acid hydrazides undergo keto-enol tautomerism \[17\].

All the prepared complexes are stable to air and moisture have good storage properties. They are soluble in DMF alcohol and insoluble in ether.
Infrared spectra:
The most important vibrational bands of the complexes are given in Table 2. The spectra of all complexes exhibit vibrational modes at 1606-1628, 933-976 and 1540-1568 cm\(^{-1}\) due to \(v(C=N)\), \(v(N-N)\) and \(v(C=C)\) stretches.\(^{17-19}\)

Neutral medium complexes (1-6) show strong bands at 1660-1674 cm\(^{-1}\) and medium bands at 3211-3240 cm\(^{-1}\) which are ascribed to \(v(C=O)\) and \(v(N-H)\) groups respectively\(^{19}\), while such bands are missing in the spectra of basic medium complexes (7-9).

These complexes (7-9) show new bands between 1034-1045 cm\(^{-1}\) related to \(v(C-O)\) band after deprotonation of enolic group and coordination with the metal\(^{20}\).

The I.R spectra of nitrato complexes (2,4,6) show two types of coordinated nitrate ions. A strong absorption bands at 1491-1493 cm\(^{-1}\) and medium sharp bands at 808-822 cm\(^{-1}\) are related to the bidentate bridging NO\(_3\)- groups. The strong bands at 1392-1458 cm\(^{-1}\) are due to the monodentate coordinated nitrate ions\(^{21}\).

The coordinated chloride ions cannot detected since they occurred out of scale of the instrument used. Silver nitrate test indicate the absence of any uncoordinated CI- ions.

The I.R spectra of all complexes exhibit medium or weak absorptions at 480-519 cm\(^{-1}\) related to coordination of carbonyl or the deprotonated enolic oxygen atoms with the metal\(^{17}\).

Another bands between 418-440 cm\(^{-1}\) due to the coordination of the metal ions with azomethine nitrogen and amino or amido nitrogen atoms\(^{18}\).

Magnetic properties and Electronic Spectra
The effective magnetic moments measured at room temperature(Table 3).
All the prepared complexes show \(\mu_{\text{eff}}\) values that expected for three, two and one unpaired electron for Co(II), Ni(II) and Cu(II) complexes in both neutral and basic medium, which are smaller than spin only value for each metal ion. this was attributed to the binuclear dimeric structure as observed for similar complexes due to antiferromagnetic interaction of the moments on adjacent metal atoms\(^{10,22}\).

The electronic spectra of the complexes were preformed in DMF and the resulting data are given in Table 3. All neutral medium complexes (1-6) show an absorption maxima at 31847-30769 cm\(^{-1}\) due to \(\Pi\rightarrow \Pi^*\) transition of aromatic rings and another absorption between 29761-28571 cm\(^{-1}\) due to \(n\rightarrow \Pi^*\) transitions of \(-C=O\) and \(-C=N\) chromophoric groups.

Also an intense absorptions at the region 26738-22935 cm\(^{-1}\) were observed in the spectra of all of the complexes were assigned to charge transfer transitions.

The electronic spectra of Co(II) complexes (1&2) show absorption bands at 18518 and 18181 cm\(^{-1}\) respectively which are assigned to the \(^4\Pi_1 g(F)\rightarrow^2\Pi_2 g(P)\) \(v_3\) transition, while \(v_2\) and \(v_1\) that related to \(^4\Pi_1 g(F)\rightarrow^2\Pi_3 g(F)\) and \(^4\Pi_1 g(F)\rightarrow^2\Pi_2 g(P)\) transitions respectively are not observed. Because \(v_1\) may be outside the range of the instrument used, while \(v_2\) is too weak since it requires two electronic transitions\(^{23}\).

On the other hand the electronic spectra of Co(II) complex (7) show intense absorption at 15384 cm\(^{-1}\) which is characteristic of the tetrahedral Co(II) complexes\(^{24,25}\) and assigned to \(^4\Pi_1 g(F)\rightarrow^2\Pi_3 g(F)\) respectively, since \(v_1\) and \(v_2\) bands cannot be observed, since their positions are below the limit of our instrument.

This geometry is confirmed by magnetic moments values for Co(II) binuclear complexes\(^{22}\).
Thus the square planar geometry is excluded since it cannot be confirmed by magnetic measurements.
For Ni(II) complexes (3&4), three absorption bands at 10204,15384-16393 and 21276-23809 cm\(^{-1}\) were observed in their electronic spectra. These bands are assigned to \(^3\Pi_2 g(F)\rightarrow^3\Pi_1 g(F)\) \(v_1\), \(^3\Pi_2 g(F)\rightarrow^3\Pi_1 g(F)\) \(v_2\) and \(3\Pi_2 g(F)\rightarrow^1\Pi_1 g(F)\) \(v_1\) transitions respectively and are specific for Ni(II) ion in octahedral environment\(^{22}\), which was also supported by the magnetic moments of the binuclear Ni(II) complexes\(^{22}\).

On the other hand the solution spectra of Ni(II) complex (8) of the basic medium also shows transitions that are characteristic for Ni(II) octahedral coordination, because the solution electronic spectra of Ni(II) complexes in the presence of coordinating solvents always give transitions related to octahedral coordination, such result was obtained by other workers\(^{26,27}\).

The tetrahedral geometry in the solid state is proposed for the later complex which was confirmed by I.R spectra that indicate the deprotonation of the ligand.
In addition to that the electrical conductance value (Table 1) from which we can conclude only one anion is coordinated with each Ni(II) ion in the coordination sphere.

The square planar geometry is excluded according to the magnetic moment value (Table 3).
The electronic spectra of Cu(II) complexes (5&6) show a wide band at 14285-14705 cm\(^{-1}\). These bands are characteristic for Cu(II) ion with tetragonal distorted octahedral geometry and can be assigned to the combination of two or three transitions \(2^1g\rightarrow^2g\), \(2^1g\rightarrow^2\Pi\) and \(2^1g\rightarrow^2\Pi\)\(^{23}\).
The electronic absorption spectra of Cu(II) complex (9) in basic medium contain a broad band between 18867-16949 cm\(^{-1}\) assigned to \(^2\)B,\(g\)→\(^2\)Eg and \(^2\)B,\(g\)→\(^2\)A\(g\) transitions, indicating the squar planar geometry.[25] The formation of the later groups is supported by bonds (double bonds) occurred through formation of two carbon nitrogen single bonds (C-NH\(_2\)).

Conclusion

The macrocycles obtained in the present investigation occurred through formation of two carbon nitrogen double bonds (C=N) and two carbon nitrogen single bonds (C-NH\(_2\)). The formation of the later groups is supported by other workers\(^{28}\), showing that the reaction between aliphatic or aromatic amines with C-OH moiety lead to the formation of carbon nitrogen single bond with the elimination of H\(_2\)O molecule.

This is analogous with the reaction of dihaloethane with amines that lead to the formation of carbon nitrogen bond with elimination of HX molecule\(^{11}\). In addition to that, our investigation reveals that the basic medium binuclear macrocycles could be formed even if 0.5 equivalent of metal salt is used. Hence we can conclude that the nature of macrocycles not only depends on the metal:ligand ratio or the size of the metal ion, but the PH of the reaction medium also has a significant effect on the nature and the coordination properties of the macrocycles.

Table 1: Physical properties and analytical data of metal complexes analysis

<table>
<thead>
<tr>
<th>NO.</th>
<th>Complex</th>
<th>Colour</th>
<th>m.p (C˚)</th>
<th>% Yield</th>
<th>Found(calculated)</th>
<th>(\lambda) (1) MF 10(^{-5}) M ohm(^{-1}) cm(^{-1})</th>
<th>M%</th>
<th>% Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>[Co(_2)L(_2)Cl(_4)]</td>
<td>Pink</td>
<td>230*</td>
<td>76</td>
<td>12.21 (12.91)</td>
<td>15.00 (15.53)</td>
<td>28.7</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>[Co(_2)L(_4)(NO(_3))(_4)]</td>
<td>Dark pink</td>
<td>240</td>
<td>65</td>
<td>11.62 (11.56)</td>
<td>14.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>[Ni(_2)L(_2)Cl(_4)]</td>
<td>Bright green</td>
<td>245*</td>
<td>71</td>
<td>12.45 (12.91)</td>
<td>15.21 (15.53)</td>
<td>15.5</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>[Ni(_3)L(_4)(NO(_3))(_4)]</td>
<td>Gray</td>
<td>235*</td>
<td>68</td>
<td>11.64 (11.56)</td>
<td>13.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>[Cu(_2)L(_2)Cl(_4)]</td>
<td>Dark green</td>
<td>159</td>
<td>75</td>
<td>13.43 (13.75)</td>
<td>15.00 (15.38)</td>
<td>23.1</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>[Cu(_2)L(_4)(NO(_3))(_4)]</td>
<td>Green ish brown</td>
<td>211*</td>
<td>66</td>
<td>12.01 (12.34)</td>
<td>24.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>K(_2)[Co(_2)L(_2)Cl(_4)]</td>
<td>Purple</td>
<td>320</td>
<td>80</td>
<td>12.46 (12.88)</td>
<td>7.32 (7.64)</td>
<td>75.5</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>K(_2)[Ni(_2)L(_2)Cl(_4)]</td>
<td>Pale green</td>
<td>291</td>
<td>79</td>
<td>12.25 (12.88)</td>
<td>7.43 (7.64)</td>
<td>70.9</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>K(_2)[Cu(_2)L(_2)Cl(_4)]</td>
<td>Dark green</td>
<td>293</td>
<td>81</td>
<td>13.25 (13.72)</td>
<td>7.22 (7.56)</td>
<td>100.3</td>
<td></td>
</tr>
</tbody>
</table>

Table 2: Some selected infrared frequencies (cm\(^{-1}\)) of the metal complexes.

<table>
<thead>
<tr>
<th>NO.</th>
<th>(\nu) (NH)</th>
<th>Amide I</th>
<th>(\nu) (C-N) azomethine</th>
<th>(\nu) (C=C) phenyl</th>
<th>(\nu) (C=C) enolic</th>
<th>(\nu) (N-N)</th>
<th>(\nu) (NO(_3))</th>
<th>(\nu) (M-O)</th>
<th>(\nu) (M-N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3224(w)</td>
<td>1674(s)</td>
<td>1606(s)</td>
<td>1568(m)</td>
<td>933(m)</td>
<td>1491(s,808(m,sp)</td>
<td>1392 (s)</td>
<td>505(w)</td>
<td>440(m)</td>
</tr>
<tr>
<td>2</td>
<td>3230(m)</td>
<td>1675(s)</td>
<td>1610(s)</td>
<td>1550(m)</td>
<td>962(m)</td>
<td>1491(s,808(m,sp)</td>
<td>1392 (s)</td>
<td>495(w)</td>
<td>420(w)</td>
</tr>
<tr>
<td>3</td>
<td>3225(m)</td>
<td>1668(s)</td>
<td>1618(s)</td>
<td>1566(m)</td>
<td>958(m)</td>
<td>1491(s,808(m,sp)</td>
<td>1458 (s)</td>
<td>498(w)</td>
<td>439(w)</td>
</tr>
<tr>
<td>4</td>
<td>3238(m)</td>
<td>1660(s)</td>
<td>1628(s)</td>
<td>1540(m)</td>
<td>976(m)</td>
<td>1491(s,808(m,sp)</td>
<td>1458 (s)</td>
<td>498(w)</td>
<td>439(w)</td>
</tr>
<tr>
<td>5</td>
<td>3224(w)</td>
<td>1674(s)</td>
<td>1606(s)</td>
<td>1568(m)</td>
<td>933(m)</td>
<td>1493(s,808(m,sp)</td>
<td>1450 (s)</td>
<td>519(w)</td>
<td>424(w)</td>
</tr>
<tr>
<td>6</td>
<td>3211(m)</td>
<td>1665(s)</td>
<td>1620(s)</td>
<td>1552(m)</td>
<td>953(m)</td>
<td>1493(s,808(m,sp)</td>
<td>1450 (s)</td>
<td>519(w)</td>
<td>424(w)</td>
</tr>
</tbody>
</table>

* s=strong  m=moderate  w=weak  sh=sharp
Table 3: Magnetic susceptibility and electronic spectra of the metal complexes.

<table>
<thead>
<tr>
<th>Complex no.</th>
<th>$\chi_{\text{eff}}$/two metalion</th>
<th>Electronic spectra cm$^{-1}$</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>5.56</td>
<td>318471,29761,26737,18518</td>
</tr>
<tr>
<td>2</td>
<td>6.88</td>
<td>31645,29411,24875,181818</td>
</tr>
<tr>
<td>3</td>
<td>4.36</td>
<td>31,446,28571,26595,23809sh,16393,10204</td>
</tr>
<tr>
<td>4</td>
<td>4.85</td>
<td>31645,29411,26738,21276sh,15384,10204</td>
</tr>
<tr>
<td>5</td>
<td>2.68</td>
<td>31847,29411,26041,14285</td>
</tr>
<tr>
<td>6</td>
<td>2.64</td>
<td>31645,28571,22935,14705</td>
</tr>
<tr>
<td>7</td>
<td>6.12</td>
<td>(31250-26595)br,15384</td>
</tr>
<tr>
<td>8</td>
<td>4.22</td>
<td>31250,29411,26595,23255sh,15384,10204</td>
</tr>
<tr>
<td>9</td>
<td>2.8</td>
<td>(30769-23809)br,18867,16949</td>
</tr>
</tbody>
</table>

sh=shoulder    br=broad

References
   * 1st ed. , Pergamom Press U.K.


الخلاصة:

تم في هذا البحث تحضير معقدات ثنائية النوى لأيونات الكوبالت الثنائي والنيكل الثنائي والنحاس الثنائي مع قواعد شيف للحلقة الكبيرة المشتقة من الحامض الهايديزازيني و α – هيدروكسى كيتون

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الخلاصة: تم في هذا البحث تحضير معقدات ثنائية النوى الأيونية لقاعدة شيف الحلقية بواسطة التفاعل الكيميائي [2+2] بين البنزينوين والأروماتيونوزويل هيديزاز ووجود الملح اللفاري في الوسطين المعادل والفاعلي وقد شخصت المعقدات الناتجة من خلال التدبير الكيميائي للجزيئات والتعرفهم المولاري والدراسات الطيفية، فضلاً عن الدراسات المغناطيسية، وقد اتضح من هذه الدراسات امتلاك المعقدة للصين [LH4M2X2]2-3Cl=x: لكي تكون قاعدة شيف الحلقية على (K2[LM2X2]NO-3Cl)=X; ومعدات الوسط المعادل والفاعلي على التنويه (K2[LM2X2]NO-3Cl)=X; ومعدات الوسط المعادل غير الكتاليتيحة سلبيه التناسق في حين كانت معقدات الوسط الفاعلي الكتاليتيحة بنسبة 2:1 رياحية التناسق .