Synthesis and Spectral Study of new Tetradeutate Azo-Azomethine ligand as a drevitave of 4,5-diphenyl Imidazole and it's Complexes with some of metal Ions

Israa Noor Witwit, Hussien Abd-mohamad

University of Babylon, College of Science, Department of Chemistry

Abstract:
A new azo ligand N^1Z, N^2Z) N^1,N^2-Bis ((E-4,5-Di phenyl-1H – imidazole-2-yl)diazenyl) 1,5-di methyl-2-phenyl -1H-pyrazole-3-(2H)-ylidene) ethan-1,2-diamine (BDIDE) prepared by coupling reaction between 4,5-diphenylimidazole and 1,2- Bis (4’-Amino-2',3'-Di methyl-1’-Phenyl- pyrazolyl)-Diimino Ethan , The structure of ligand , mode of bonding, and overall geometry of it's complexes with Co(II),Ni(II) ,Cu(II), Zn(II), Cd(II), and Hg(II) were determined through IR,UV-Vis., ^1H-NMR , and Mass spectral studies, magnetic momentum, elemental analysis, and Molar conductance , also the stability constants of the complexes were calculated geometry for all complexes in which a ligand was a bidentate and coordinated with metal ions through N(3) imidazole and one of nitrogen atoms of azo group spectrophotometrically. These studies revealed octahedral .

Key Wards:
Spectral study, Transition metal complexes, Azo-Shiff base, imidazole,azo.

Introduction:
Azo dyes are versatile compounds take large part of attention in research areas in both of fundamental and application, such as textile, leather, plastics, biological staining, lasers, cosmetics, and drugs(1).

Stability of Azo days, ease of synthesis, and ability to form a colored complexes with a various metal ions in solutions as well their interesting electronic and geometrical features give these compounds an important role in coordination field(2). Azoidazole compounds were found to be a available to determinate many of metal ions, the heterocyclic nitrogen atom in imidazole ring is a vital part science it improved the chelation properties (3), by containing azoimine system (-
Synthesis and Spectral Study of new Tetradeutate Azo-Azomethine ligand as a derivative of 4,5-diphenyl Imidazole and it's Complexes with some of metal Ions.......Israa Noor Witwit , Hussien Abd-mohamad

N=N-C=N-) thence they have the ability to coordinate with metal ions in their different oxidation states \(^4\). 

Azo-Shiffe base ligands which are contain azo (-N=N-) and azomethine (-C=N-) groups considered as \(\pi\) acceptor ligands where have a capability to stabilize metal ions in their low oxidation states \(^5\). The coordination of these compounds can be acquired from one of these groups\(^6\), or by one of them\(^7\).

In this work we are synthesis of new azo-shiffe base ligand as a derivative of 4,5- diphenyl imidazole and six new chelat complexes with Co, Ni, Cu, Zn, Cd, and Hg divalent ions, and characterization the ligand and It’s complexes by using different techniques.

**Materials and Methods:**

All chemicals were from Fluka , Meck , and B.D.H with high purity. Stuart melting point /SMP30 used to measure melting point of ligand and it’s complexes, Element analysis of ligand carried out by CHN element analyzer 1108 and Element analysis of complexes measured by C.H.N.S. mth EA 99 Atomic H-NMR of ligand recoded by using Burker Ultra Sheild (300MHz) by using TMS as a internal standard for calibrating chemical shift of HNMR spectrum.

Electronic spectra in ethanol were recorded by Shimdzu 1800 double beam Spectrophotometer, FTIR spectra recorded 8400,s Shimadzu double beam with KBr disk, MSB –MKI magnetic balance determine used in magntic susceptibility measurements, while mass spectrum of ligand carried out by Shimadzu GCMS-QP2010 Ultra while mass spectra of Complexes measured by, Conductivity measurements carried out by using WTW Cond 730-Laboratory Conductivity meter -1( 20-010), and pH measurements done by using WTW pH meter terminal 740.

**Synthesis of Azo-azomethine ligand**

**Synthesis of 4,5-di phenylimidazole:**

Mixture of ( 2.1gm, 0.01 mol) of benzile , (0.26 gm, 0.01 mol) hexamethylenetetramine, and ( 6 gm, 0.035 mol) of ammonium acetate were dissolved in ( 50) ml of glacial acitic acid, The mixture was refluxed for (1) hour, then the solution was cooled and ( 200) ml of water was added, The imidazole derivative and recrystallized using Ethanol 50%, The purity of this compound was evaluated by TLC, The percentage of yield (80%) and m.p is (219-231) \(^0\)C. Scheme(1).

**Synthesis of 1,2- Bis –(4’-Amino-2’,3’-Di methyl-1’-Phenyl-pyrazolinyl)-Diimino Ethan** \(^8\):
Synthesis and Spectral Study of new Tetradeptate Azo-Azomethine ligand as a drevivatie of 4,5-diphenyl Imidazole and it's Complexes with some of metal Ions………Isaa Noor Witwit , Hussien Abd-mohamad

The Shiff base was synthesized by condensation of 4- amino antipyrene (4.066 gm , 20 mmol) in (80) ml of ethanol and (0.5 gm , 10 mmol) of ethylene diamine , The mixture was refluxed for 2 hours , The yello solid precipitate of Shiff base was filtered , washed with distilled water , dried , and recrystallized from ethanol and finally preserved in desiccators , yield 75% , ( m.p.195-197 °C). The preparation was shown in Scheme(2)

Synthesis of (N^1Z, N^2Z) N^1,N^2-Bis ((E-4,5-Di phenyl-1H-imidazole-2-yl)diazynyl) 1,5-di methyl-2-phenyl -1H-pyrazole-3-(2H)-ylidene) ethan-1,2-diimine (BDIDE)

The Solution of Diazonuim salt was prepared as fellow: (4.305 gm ,0.01 mol) of 1,2- Bis -(4'-Amino-2',3'-Di methyl-1'-Phenyl- pyrazoliny1)-Diimino ethane was dissolve in mixture of (2) ml HCl Conc. and (28) ml distilled water and stirred for ( 15) min. in ice bath then ice cold solution of NaNO₂ (10%) (25) ml was add drop wise on a period of (30) min , the solution become yellowish orange and left for another (30) min, then add drop wise to another ice cooled solution of 4,5- diphenylimidazole (4.420 gm , 0.02 mol) in ( 25) ml of alkaline ethanol , The temperature mentioned below (5) °C during all processes and the solution color change to deep orange , add ( 200) distilled water and allowed to stand overnight ,the precipitate was flittered washed with distilled water , dried in air and recrystallization from ethanol, yield (75%) , m.p. ( 223- 225) °C, Scheme (3)

Synthesis of complexes:

All complexes were prepared by adding ( 0.456 gm , 0.001 mol) of ethanolic solution of the ligand to the ( 0.0005 mol) of metal ion chloride salts in their proprate buffer solutions , The mixtures were stirred for 30 minutes , The precipitations of the complexes were flittered washed with distilled water , dried over CaCl₂ , and recrystallized from absolute ethanol , Table(1) show the physical properties of ligand and it's metal complexes.
Synthesis and Spectral Study of new Tetradeionate Azo-Azomethine ligand as a drevitave of 4,5-diphenyl Imidazole and it’s Complexes with some of metal Ions........Israa Noor Witwit, Hussien Abd-mohamad

Scheme (3): Synthesis of ligand (BDIDE)

Results and Discussion:
Electronic spectra of ligand show two absorption bands in Uv. region (220) nm due to π-π* transitions of aromatic rings thise band appeared also approximately in the same potions in complexes spectra, the second one appeared in (435) nm due to C.T transitions in Vis. region which is shifted to high wave lengths in complexes spectra as a result of (MLCT) as showed in Figuer (1) and Table (2).

Fig(1) : UV-Vis. Spectra of ligand (BDIDE) and one of it’s Complexes with Cu(II)
Synthesis and Spectral Study of new Tetridentate Azo-Azomethine ligand as a drevitave of 4,5-diphenyl Imidazole and it's Complexes with some of metal Ions........Israa Noor Witwit , Hussien Abd-mohamad

<table>
<thead>
<tr>
<th>Compound</th>
<th>Color</th>
<th>M.P. (°C)</th>
<th>% of prod.</th>
<th>Found (Calc.) %</th>
<th>C%</th>
<th>H%</th>
<th>N%</th>
<th>M%</th>
</tr>
</thead>
<tbody>
<tr>
<td>(BDIDE)</td>
<td>Orange</td>
<td>220-224</td>
<td>78</td>
<td>(72.62)</td>
<td>72.56</td>
<td>5.48</td>
<td>(21.96)</td>
<td>-----</td>
</tr>
<tr>
<td>Co(CDIDE) Cl₂</td>
<td>Red</td>
<td>173-175</td>
<td>65</td>
<td>(63.41)</td>
<td>63.50</td>
<td>4.67</td>
<td>(19.17)</td>
<td>(5.76)</td>
</tr>
<tr>
<td>Ni(CDIDE) Cl₂</td>
<td>Clarate</td>
<td>187-189</td>
<td>71</td>
<td>(63.42)</td>
<td>63.53</td>
<td>4.68</td>
<td>(19.18)</td>
<td>(5.74)</td>
</tr>
<tr>
<td>Cu(CDIDE) Cl₂</td>
<td>Dark red</td>
<td>192-194</td>
<td>75</td>
<td>(63.12)</td>
<td>62.86</td>
<td>4.75</td>
<td>(19.08)</td>
<td>(6.18)</td>
</tr>
<tr>
<td>Zn(CDIDE) Cl₂</td>
<td>Clarate</td>
<td>180-182</td>
<td>68</td>
<td>(63.01)</td>
<td>63.07</td>
<td>4.65</td>
<td>(19.05)</td>
<td>6.35</td>
</tr>
<tr>
<td>Cd(CDIDE) Cl₂</td>
<td>Purpel</td>
<td>168-171</td>
<td>80</td>
<td>(60.26)</td>
<td>60.34</td>
<td>4.52</td>
<td>(18.22)</td>
<td>10.44</td>
</tr>
<tr>
<td>Hg(CDIDE) Cl₂</td>
<td>Clarate</td>
<td>155-157</td>
<td>73</td>
<td>(55.69)</td>
<td>55.54</td>
<td>4.21</td>
<td>(16.84)</td>
<td>16.80</td>
</tr>
</tbody>
</table>

Table (2) : Electronic spectra , conductivity , and magnetic moment of ligand (BDIDE) and it's complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>Type of transition</th>
<th>λ max (nm)</th>
<th>Conductivity S. mol⁻¹.cm⁻¹</th>
<th>μ eff (B.M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(BDIDE)</td>
<td>CT</td>
<td>453</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>Co(BDIDE) Cl₂</td>
<td>MLCT</td>
<td>461</td>
<td>8</td>
<td>4.70</td>
</tr>
<tr>
<td>Ni (BDIDE) Cl₂</td>
<td>MLCT</td>
<td>464</td>
<td>10.5</td>
<td>2.82</td>
</tr>
<tr>
<td>Cu(BDIDE) Cl₂</td>
<td>MLCT</td>
<td>535</td>
<td>18</td>
<td>1.73</td>
</tr>
<tr>
<td>Zn(BDIDE) Cl₂</td>
<td>MLCT</td>
<td>556</td>
<td>12</td>
<td>Dia</td>
</tr>
<tr>
<td>Cd (BDIDE) Cl₂</td>
<td>MLCT</td>
<td>530</td>
<td>10</td>
<td>Dia</td>
</tr>
<tr>
<td>Hg (BDIDE) Cl₂</td>
<td>MLCT</td>
<td>562</td>
<td>7</td>
<td>Dia</td>
</tr>
</tbody>
</table>

Magnetic Susceptibility and Molar Conductance :

The magnetic moment values of Co(II), Ni(II), and Cu(II) suggested the Octahedral geometry of the complexes (9-10), while Zn(II), Cd(II) , and Hg complexes are found to be diamagnetic as expected for d⁰ configuration, while the conductivity of 10⁻³ M of the complexes solutions in DMF at room temperature indicating the non-conductive character of them as shown in Table (2).

Infrared spectra

FTIR spectra of ligand showed absorption band in (3431.4) cm⁻¹ represented the stretching band of ν (N-H) of imidazole ring (11-13) and it does not affected during the complexation, The same thing occur with the absorption band at (1655.20) cm⁻¹ which assigned for ν (C=N) of azomethine group in ligand spectra, there is no signifiant change in
Synthesis and Spectral Study of new Tetradeutate Azo-Azomethine ligand as a drevitave of 4,5-diphenyl Imidazole and it's Complexes with some of metal Ions...Israa Noor Witwit, Hussien Abd-mohamad

position and intensity of this band in complexes spectra, that suggested the complexation does not occur through these group. The absorption band appeared in (1514.17) cm\(^{-1}\) in ligand spectrum refers to \(\nu\) (C=N) of imidazole ring which shifted to a lower frequencies in complexes spectra with a change in intensity, indicate the complexation can be occur through the non-bonding lone pair on nitrogen atom\(^{(14-17)}\). The bands of \(\nu\) (N=N) group appeared in (1496.81) and (1452.45) cm\(^{-1}\) in ligand spectrum shifted to a lower frequencies in complexes spectra that indicated the azo group coordinated with metal ion\(^{(18)}\). The two mono substituted aromatic rings on imidazole ring were indicated by the absorption at (761.91) and (698.25) cm\(^{-1}\). Complexes spectra show new band in (500-400) cm\(^{-1}\) region due to \(\nu\) (M-N)\(^{(20)}\), as show in figures (2,3) of ligand and one of it’s prepared complexes and listed in Table (3).

Fig (2): IR spectra of ligand

Table (3): Selected FTIR absorption band of ligand and it’s complexes in cm\(^{-1}\) units

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\nu) (N-H)</th>
<th>(\nu) (C=N)</th>
<th>(\nu) (C=N) imi.</th>
<th>(\nu) (N=N)</th>
<th>(\nu) (M-N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(BDIDE)</td>
<td>3431.48 wbr</td>
<td>1655.20 w</td>
<td>1514 w</td>
<td>1496.81 m</td>
<td>----</td>
</tr>
<tr>
<td>Co(BDIDE) Cl(_2)</td>
<td>3431.48 wbr</td>
<td>1655.12 w</td>
<td>1510 m</td>
<td>1455 m</td>
<td>422 w</td>
</tr>
<tr>
<td>Ni (BDIDE) Cl(_2)</td>
<td>3422.18 wbr</td>
<td>1656.00w w</td>
<td>1512 m</td>
<td>1458 m</td>
<td>338 w</td>
</tr>
<tr>
<td>Cu(BDIDE) Cl(_2)</td>
<td>3409.83 wbr</td>
<td>1655.20 w</td>
<td>1508 m</td>
<td>1449 m</td>
<td>412 w</td>
</tr>
<tr>
<td>Zn(BDIDE) Cl(_2)</td>
<td>3430.23 wbr</td>
<td>1655.20 w</td>
<td>1510 m</td>
<td>1458 m</td>
<td>357 w</td>
</tr>
<tr>
<td>Cd (BDIDE) Cl(_2)</td>
<td>3425.13 wbr</td>
<td>1655.42 w</td>
<td>1510 m</td>
<td>1567 m</td>
<td>427 w</td>
</tr>
<tr>
<td>Hg (BDIDE) Cl(_2)</td>
<td>3429.24 wbr</td>
<td>1655.20 w</td>
<td>1511 m</td>
<td>1542 m</td>
<td>436 w</td>
</tr>
</tbody>
</table>
Synthesis and Spectral Study of new Tetradequate Azo-Azomethine ligand as a drevitave of 4,5-diphenyl Imidazole and it's Complexes with some of metal Ions........Israa Noor Witwit , Hussien Abd-mohamad

Mass spectra
The mass spectra can be used to confirm the suggested structure of both ligand and it's complexes, the molecular ion of ligand appeared at (e/z = 893) corresponding to the molecular formula (C_{54}H_{48}N_{14}) , while the base peak appeared in (e/z = 220) corresponding to 4,5- diphenylimidazol fragment (C_{15}H_{12}N_{2})^{21} . The molecular peak of Ni(II) complex appeared in (e/z = 1022) with low m/z (less 1%) due to the large Mwt. of ligand corresponding to the [NiC_{54}H_{48}N_{14} - Cl_{2}] fragment and the base peak in (e/z = 220) which is related to [(C_{15}H_{12}N_{2}) ] fragment , The successive fragmentation of ligand and it's complex with Ni (II) ion were show in schemes (4) and (5) , while mass spectra of them shown in the figures (4) and (5)

Fig (4 ) : Mass spectra of ligand
Synthesis and Spectral Study of new Tetradentate Azo-Azomethine ligand as a derivative of 4,5-diphenyl Imidazole and it's Complexes with some of metal Ions........Israa Noor Witwit , Hussien Abd-mohamad

Scheme (4): Mass fragmentation of ligand
Synthesis and Spectral Study of new Tetradentate Azo-Azomethine ligand as a drevitave of 4,5-diphenyl Imidazole and it's Complexes with some of metal Ions........Israa Noor Witwit, Hussien Abd-mohamad

Scheme(5) : Mass fragmentation of Ni (II) complex with ligand

HNMR Spectra
HNMR spectrum of ligand in DMSO showed signals in $\delta$ (12.49) ppm due to (N-H) proton of imidazole ring ($^7$), multiples of aromatic protons in $\delta$ (7.50- 7.19) ppm ($^{20}$), while three signals in $\delta$ (2.80) ppm due to (-C–CH$_2$-C-) protons , while the other two signals at $\delta$ (2.50 ) ppm and $\delta$ (3.37) ppm due to (-C-CH$_3$) and (-N-CH$_3$) of pyrazole ring as shown in figure (6).

Fig.(6) : HNMR Spectra of ligand
Synthesis and Spectral Study of new Tetradeutate Azo-Azomethine ligand as a drevitave of 4,5-diphenyl Imidazole and it's Complexes with some of metal Ions.........Israa Noor Witwit , Hussien Abd-mohamad

Mole Ratio showed that , all complexes are prepared in(1:2) (M:L) . The Stability Constants for prepared complexes were calculated spectrophotometrically and found that the Stability Constants were varied in the arrangement Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+} which agree with Irving – Williams Series , as show in Table (4)

<table>
<thead>
<tr>
<th>Compound</th>
<th>α</th>
<th>K</th>
<th>Log K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co(BDIDE) Cl₂</td>
<td>0.023</td>
<td>3.078 × 10¹⁷</td>
<td>7.488</td>
</tr>
<tr>
<td>Ni (BDIDE) Cl₂</td>
<td>0.013</td>
<td>8.520 × 10¹⁷</td>
<td>7.930</td>
</tr>
<tr>
<td>Cu(BDIDE) Cl₂</td>
<td>0.011</td>
<td>11.620 × 10¹⁷</td>
<td>8.065</td>
</tr>
<tr>
<td>Zn(BDIDE) Cl₂</td>
<td>0.020</td>
<td>4.083 × 10¹⁷</td>
<td>7.611</td>
</tr>
<tr>
<td>Cd (BDIDE) Cl₂</td>
<td>0.027</td>
<td>2.070 × 10¹⁷</td>
<td>7.316</td>
</tr>
<tr>
<td>Hg (BDIDE) Cl₂</td>
<td>0.034</td>
<td>1.341 × 10¹⁷</td>
<td>7.127</td>
</tr>
</tbody>
</table>

M= Co(II), Ni(II) ,Cu(II), Zn(II) , Cd(II) , Hg(II)

Fig. (7) : The proposed structure of the complexes

References :
Synthesis and Spectral Study of new Tetradeionate Azo-Azomethine ligand as a drevitate of 4,5-diphenyl Imidazole and it's Complexes with some of metal Ions........Israa Noor Witwit , Hussien Abd-mohamad

Synthesis and Spectral Study of new Tetradeionate Azo-Azomethine ligand as a drevitate of 4,5-diphenyl Imidazole and it's Complexes with some of metal Ions……..Israa Noor Witwit , Hussien Abd-mohamad


الخلاصة:

تم تحضير الليكائين الجديد (N²,N¹( N²Z, N¹Z) – ثنائي (E)- 5,4- ثنائي فنيل أميدازول – 2- يل- دايازانييل) 5- ثنائي ميثيل – 2- فنيل – بايرازول – 3- (H²) – يل دايبين (BDIDE) بواسطة تفاعل الأزواج بين المركبين 4- ثنائي فنيل أميدازول والمركب 2- ثنائي (‘N’- أمينو- ‘2’- ثنائي ميثيل – 1- بايرازولينيل)– ثنائي Co(II), Ni(II) , Cu(II) بواسطة أطياف الأشعة تحت الحمراء ، فوق البنفسجية – المرئية ظرف الرنين النووي المغناطيسي ، طيف الكتلة ، الحساسية المغناطيسية , التحليل الكمي الدقيق ، إضافة إلى التوصيلية المولارية كما تم حساب ثوابت الأسترثار للمعقدات المحضرة ومن نتائج الدراسة تم إفتراض الشكل الثنائي الموجب لجميع المعقدات المحضرة مع الليكائين والذي يتناسق كليكائين ثنائي المخلب مع الأيونات المدروسة من خلال ذرة نتروجين رقم (3) لحلقة الأميدازول وذرة نتروجين مجموعة الأرو المبهدمة عن الحلقة غير المتجانسة.