Synthesis of Binuclear Complexes of Cu (II), Ni (II) and Cr (III) Metal Ions Derived from Di-Imine Compound as Biterminal Binding Site Ligand

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Abstract

The research is concerning synthesis of two di-imine ligands derived from thiazole heterocyclic compounds. 1, 3, 4-thiadiazole-2, 5-dihydrazinoc is considered as ligand (L₁) and starting essential compound that used as precursor to synthesize the new ligand (2, 2′-(((1,3,4-thiadiazole-2,5-diyl)bis (hydrazin-2yl1ylidene))bis (methaneylylide)) dipheno1 (L₂). Six new complexes were derived from the ligands using some transition metal ions like Cu(II), Ni(III), and Cr(III). The synthesized compounds characterized by infrared, ultra-violet-visible and gas chromatography-mass spectroscopy, conductivity, and thermal analysis. The coordination modes were suggested to be N₂ from two terminals to form binuclear complexes.

The mentioned characterization methods showed that the prepared complexes may have chelation pattern (bidentate or tridentate) depending on the suggested geometry (square planer or octahedral) and the type of ligand.

1. Introduction

Imines are compounds of carbon-nitrogen double bond R₁R₂C=N–R₃, where R = hydrogen, aliphatic, aromatic group. Hugo Schiff was the first one to synthesize this compound in 1864 from simple condensation between aldehydes or ketones with primary amines [1]. Schiff's bases have several applications, including: electrochemistry, bio-inorganic chemistry, separation processes, photo degradation, pharmacy, anti-microbial and dyes [2,3]. Schiff's bases have the ability to form stable complexes, due to the nitrogen atom that gives the electron pair the ability to synthesize so many complexes with metal ions [4-8]. Schiff base ligands containing more than one donor sites are extensively used for the preparation of metal complexes with interesting properties due to the chelating effect [9]. 1,3,4-Thiadiazole was one of the most popular isomer in the industrial and the pharmaceuticals fields compared to other species. It’s considered a strong aromatic and high stability circular system and with lack of toxicity or harmful risks for humans [10]. The thiazole and substitutes have different biological activities, such as: Anti-fungal, [11] Anti-pyretic [12], Anti-convulsive [13], Anti-viral [14] and Anti-inflammatory [15]. The aim of this work is to study the behavior of the ligands toward metal ions according to the available donor atoms and to suggest the ability of extracting metal ions from factory's by product to determine the amount photometrical.

2. Experimental

General methods and instruments

All the prepared ligands and complexes characterized by infrared spectra were recorded by using FTIR 8300 Shimadzu Spectrophotometer frequency range of 4000-200 cm⁻¹, ultraviolet-visible (UV-Vis) spectra were recorded by using a Shimadzu U.V-Vis. 160 A-Ultra-violet Spectrophotometer in the range of 200-1100 nm, conductivity measurements were carried out by using a WTW conductivity meter, The Atomic Absorption Spectrophotometer (A.A.S) type: Double-beam, model: AA400 and thermal analysis and GC-Mass spectroscopy. The melting points were recorded by "Digital melting-point apparatus by placing it in the capillary tube.

Synthesis methods of (L₁, L₂), (A₁•A₂) and (B₁•B₂) compounds

Ligands and complexes were synthesized according to general methods mentioned in literatures. Scheme 1 showed the synthesis reaction of L₁ and L₂.
Synthesis of 1, 3, 4-thiadiazole-2, 5-dihydrazine (L₃)
A solution of 1, 3, 4-thiadiazole-2, 5-dithiol (0.01 mole) dissolved in 200 ml of absolute ethanol was mixed with anhydrous hydrazine (0.02 mole) with stirring and when addition completed (drop wisely) the mixture will reflux with constant stirring for 5 hours. After reaction completed (monitored by litmus paper) the solvent is then removed by rotary evaporator where the output separated, which is a desired precipitate. The crystallization occurred by washing the products with ether then dried [16].

The physical data of the prepared compounds are shown in Table 1.

Synthesis of 1, 3, 4-thiadiazole-2, 5-bis-N-α-hydroxy phenyl imine (L₂)
0.01 mole of L₁ reacted with 0.02 mole of salicyldehyde in 20 ml absolute ethanol in the presence of some drops of glacial acetic acid. The reaction mixtures were refluxed with stirring for 4 hours, a precipitate will be formed indeed. The product filtered and washed with ether then dried. The physical data of the prepared compounds are shown in Table 1.


color=red

Table 1. The physical properties of the prepared compounds.

| Symbol | Formula | M.p.°C | Color             | Yield % |
|--------|---------|--------|-------------------|---------|
| L₁     | C₆H₁₂N₆S | 226-228 | Pale-yellow       | 85.71   |
| A₁     | [Cu₂L₁(Cl)(H₂O)₂]Cl₂·2H₂O | 253-255 | Pale-brown        | 46.53   |
| A₂     | [Ni₂L₁(Cl)(H₂O)₂]Cl₂ | 290 d  | Dark-brown        | 76.19   |
| A₃     | [Cr₂L₁(Cl)(H₂O)₂]Cl₂ | 237-240 | Olive             | 57.84   |
| L₂     | C₁₀H₁₂N₆O₅S | 223-225 | Yellow            | 83.69   |
| B₁     | [Cu₂L₂(Cl)(H₂O)₂]Cl₂ | 285-287 | Brown-orange (Rusty) | 85.50   |
| B₂     | [Ni₂L₂(Cl)(H₂O)₂]Cl₂ | 268-270 | Brown             | 72.96   |
| B₃     | [Cr₂L₂(Cl)(H₂O)₂]Cl₂·2H₂O | 235-237 | Yellowish-green   | 63.22   |

3. Results and Discussion

A- Infra-red spectra of (L₁, L₂, A₁-A₃) and (B₁-B₃) complexes
The absorption bands of infra-red (IR) spectra of the ligands and complexes are shown in Table 2, were L₁ and L₂ showed strong bands at 1620 cm⁻¹ and 1624 cm⁻¹ respectively, which could be attributed to azomethine group (imine) [18,19].

IR spectra of the prepared complexes were measured to determine the coordination mode of each ligand with metal ions. This can be achieved through the shifting in frequencies of the involved groups in coordination clearly at the spectrum; imine group of L₁ and L₂ was shifted to low frequency by (19-23) cm⁻¹ and (21-23) cm⁻¹ respectively for Cu (II), Ni (II) and Cr (III) complexes. Figure 1 shows the infrared spectra of L₂ and its complexes.
The absorption spectrum of the ligands consisted variable peaks in the range 200 nm to 350 nm due to the presence of different atoms possess n $\rightarrow$ π* and π $\rightarrow$ π* transitions. The electronic spectra of the Cu (II) complexes appeared electronic transitions in the visible region as broad peak belong to d-d transition [20]. The electronic spectra of the Cr (III) complexes showed different bands at visible region which may be attributed to (4A₂g $\rightarrow$ 4T₂g), (4A₂g $\rightarrow$ 4T₁g) and (4A₂g $\rightarrow$ 4T₃g (P)). The Ni (II) complexes showed two broad bands appeared in the range and (15,000-27,000) cm⁻¹, which suggested geometry to these complexes as square planer. Table 3 shows the absorption band and assignments of these complexes. Figure 2 included U.V-Vis. spectra of L₂ and its complexes.

### Table 2. The characteristic absorption bands of the ligands and complexes.

| Compound | (O–H) | (N–H) | (C–H) aromatic | (C=O) | (C–H) aromaticity | ortho-Subs. |
|----------|-------|-------|----------------|-------|--------------------|------------|
| L₁       | –     | 3410  | 3248 3143     | –     | 1620               | – –        |
| L₂       | 3520  | 3406  | 3043 1624     | 1573  | 1485               | 752        |
| A₁       | 3401(br) | 3158  | 3052 1601     | –     | –                  | – –        |
| A₂       | 3352(br) | Obscure | 3028 1605  | –     | –                  | – –        |
| A₃       | 3401(br) | 3402  | –             | 1605  | –                  | – –        |
| B₁       | 3568 3631 | 3442  | 3010 1603     | 1542  | 1471               | 759        |
| B₂       | Obscure | Obscure | 3032 1601     | 1531  | 1460               | 752        |
| B₃       | 3571  | 3442  | –             | 1604  | –                  | 763        |

### B- Electronic transitions spectra of metal complexes

The absorption spectrum of the ligands consisted variable peaks in the range 200 nm to 350 nm due to the presence of different atoms possess n $\rightarrow$ π* and π $\rightarrow$ π* transitions. The electronic spectra of the Cu (II) complexes appeared electronic transitions in the visible region as broad peak belong to d-d transition [20].
Figure 2. U.V-Vis. spectra of L₂ and its complexes.

| Compounds | λ nm | cm⁻¹ | Assignments | Suggested structure |
|-----------|------|------|-------------|---------------------|
| A₁        | 647  | 15,455 | ¹B₁g → ¹B₉ | Square planer |
|           | 629  | 15,898 | ²B₂g → ²A₁g  |
|           | 280  | 35,714 | n→π*        |
|           | 266  | 37,593 | π→π*        |
| A₂        | 816  | 12,254 | ¹A₁g → ¹A₂g |
|           | 318  | 31,446 | ¹A₁g → B₁g  |
|           | 284  | 35,211 | n→π*        |
|           | 224  | 44,642 | π→π*        |
| A₃        | 629  | 15,898 | ³A₂g → T₂g  |
|           | 485  | 20,618 | ³A₂g → T₁g  |
|           | 319  | 31,347 | C.T         |
|           | 265  | 37,735 | π→π*        |
| B₁        | 434  | 23,041 | ²B₁g → ²B₉  |
|           | 295  | 33,898 | ²B₁g → ²A₁g |
|           | 288  | 34,722 | n→π*        |
|           | 252  | 39,682 | π→π*        |
| B₂        | 628  | 15,923 | ¹A₁g → A₂g  |
|           | 433  | 23,094 | ¹A₁g → B₁g  |
|           | 415  | 24,096 | C.T         |
|           | 352  | 28,409 | n→π*        |
|           | 291  | 34,364 | π→π*        |
| B₃        | 620  | 16,129 | ⁴A₂g → T₂g  |
|           | 498  | 20,080 | ⁴A₂g → T₁g  |
|           | 393  | 25,445 | n→π*, C.T   |
|           | 265  | 37,735 | π→π*        |

Table 3. The electronic transitions and assignments of (A₁-A₃) and (B₁-B₃) complexes.
GC-Mass spectroscopy

Mass spectrometry is the study of system generating the formation of gaseous ions, with or without fragmentation; which are then characterized by their mass to charge ratios (m/z) and relative abundances.

In measuring of $L_1$, the ligand appeared fragment that represent this structure (CH=NH−O) was lose 43 M.wt from the compound, considering the (HN−N=CH−CH) as intermediate state during this loss [21].

When the electronic bombardment of complexes the hydrogen sulfide molecule has been lost from the heterocyclic compound and the reason for this is due to that is very stable molecule and considered as driving force (H$_2$S). the disruption of the benzene ring which converted to five membered ring (69 M.wt) which considered one of the important peaks. Finally the most important peak is of the charged molecular weight at 352 M.wt after losing two terminal hydrogen atoms. Table 4 included the most important peaks and the suggested fragments of $L_2$ compound depending on GC-Mass spectrum that shown in Figure 3.

| Table 4. The fragmentation and suggested molecular weights of $L_1$. |
|---------------------------------------------------------------|
| **Lost fragment** | **M.wt.** | **Chemical formula** | **M.wt.** |
| H$_2$ | 2 | C$_{16}$H$_{12}$N$_6$O$_2$S$_1$ | 352 |
| O$_2$ | 32 | C$_{16}$H$_{12}$N$_6$S$_1$ | 320 |
| 2(C$_6$H$_4^+$) | 76 | C$_{16}$H$_{12}$N$_6$S$_1$ | 168 |
| 2(CH=NH−NH) | 43 | C$_{16}$H$_{12}$N$_6$S$_1$ | 236 |
| 2(C$_6$H$_4$N)$^+$ | 92 | C$_{16}$H$_{12}$N$_6$S$_1$ | 137 |
| 2(CH) | 13 | C$_6$N$_3$S$_1$ | 111 |
| N$_2$ | 14 | C$_6$N$_3$S$_1$ | 83 |
| (N) | 14 | C$_6$N$_3$S$_1$ | 69 |
| (CH$_2$) | 14 | C$_6$N$_3$S$_1$ | 55 |

**Figure 3.** GC-Mass spectrum of the synthesized $L_2$ ligand.

Molar Conductance

The complexes are dissolved naturally with DMF, which must be non-reactive toward the measured compound and have reasonably high electrical stability and low viscosity to be electrical compound [22]. The molar conductance of the complexes was measured and all complexes are
electrolytic except complex B₂ was non-electrolytic. Table 5 included the conductivity measurements of the complexes in 10⁻³ M.

### Table 5. The conductivity measurements of complexes in DMF.

| Complexes | Conductivity (MS/cm) | Electrolytic property |
|-----------|----------------------|-----------------------|
| Ligand    |                      |                       |
| A₁        | 141.1 M.s/cm         | Electrolytic          |
| A₂        | 133.8 M.s/cm         | Electrolytic          |
| A₃        | 165.4 M.s/cm         | Electrolytic          |
| B₁        | 137.8 M.s/cm         | Electrolytic          |
| B₂        | 22.5 M.s/cm          | Non-electrolytic      |
| B₃        | 137.0 M.s/cm         | Electrolytic          |

** Atomic Absorption Spectrometry**

The atomic absorption technique is based on the absorption of light by free metal ions to determine the concentration of chemical elements (a specific element) in a sample of the complexes created. It can measure more than 70 elements by absorbing the optical beam (light) of free atoms in the gaseous state [23]. The calculated and found values showed in Table 6 and both values are in good agreements.

### Table 6. The atomic absorption values of the synthesized complexes (A₁-A₃) and (B₁-B₃).

| Complexes | Chemical formula          | M.wt. (g/mol) | Calculated Values | Experimental Values |
|-----------|---------------------------|---------------|-------------------|---------------------|
| A₁        | [Cu₂L₁(Cl)₂(H₂O)₃]Cl₂·2H₂O| 469           | 27.1 %            | 26.89%              |
| A₂        | [Ni₂L₂(Cl)₃(H₂O)₄]Cl₂     | 441           | 26.5 %            | 25.5 %              |
| A₃        | [Cr₂L₂(Cl)₃(H₂O)₄]Cl₂     | 535           | 19.4 %            | 17.3 %              |
| B₁        | [Cu₂L₂₂(Cl)₃(H₂O)₄]Cl₂    | 659           | 19.2 %            | 18.98 %             |
| B₂        | [Ni₂L₂₂(Cl)₃]·3H₂O        | 667           | 17.5 %            | 16.4 %              |
| B₃        | [Cr₂L₂₂(Cl)₃(H₂O)₄]Cl₂₂   | 708           | 14.6 %            | 13.3 %              |

**Thermal Analysis**

This technique is concerned with thermal analysis of inorganic and organic compounds, whether solid, semi-solid or liquid. All thermal analysis techniques simply measure the change of a specific property of a substance as a function of temperature and access to required information related to chemical compounds, including dynamic and thermal equilibrium.

This technique calculates the lost weights of vehicles in several steps, after gradually increasing temperatures from −150 °C up to 2400 °C [24]. As there is an initial loss of water molecules and gases, then partial loss of the compounds occurs by breaking them down by high temperature. Thus, we obtain metal oxides [25] as a final step of the thermal decomposition process for these processed complexes. The Table 7 described assignments of the complexes for thermal gravimetric analysis. Figure 4 shows thermal graphic analysis of the synthesized complexes (A₁-A₃) and (B₂-B₃).
Table 7. The lost parts at temperature ranges of (A<sub>1</sub>-A<sub>3</sub>) and (B<sub>2</sub>, B<sub>3</sub>) complexes.

| Complexes | TGA range °C | Mass lose % | Theoretical | Assignments |
|-----------|--------------|-------------|-------------|-------------|
| A<sub>1</sub> | 0 – 135 | 4.6% | 3.8% | Loss of one (H<sub>2</sub>O) lattice molecule. |
| | 135 - 360 | 50.09% | 52.0% | Loss of 2Cl<sub>2</sub>, 2(H<sub>2</sub>O) and 2(NH<sub>3</sub>NH<sub>2</sub>). |
| | 360 – 530 | 14.77% | 17.9% | Loss of C2N2S. |
| | > 620 | 31.7% | 33.9% | Removal 2(CuO) residue. |
| A<sub>2</sub> | 0 – 320 | 36.8% | 40.3% | Loss 2 H<sub>2</sub>O and 2 Cl<sub>2</sub>. |
| | > 620 | 57.5% | 59.6% | Loss of L<sub>1</sub> and Ni<sub>2</sub> metal. |
| | > 620 | 5.6% | – | Not found residue (99.53) |
| A<sub>3</sub> | 0 – 230 | 9.97 | 13.2% | Loss of Cl<sub>2</sub>. |
| | 230 – 500 | 52.52 | 51.9% | Loss of 2Cl<sub>2</sub>, 4H<sub>2</sub>O coordinate water molecule and 2NH<sub>3</sub>NH<sub>2</sub>. |
| | > 620 | 28.2% | 25.9% | Loss of Cr metal and C<sub>2</sub>N<sub>2</sub>S. |
| | > 620 | 9.3% | 14.2% | Loss of ½ CrO<sub>3</sub>. |
| B<sub>2</sub> | 0 – 325 | 8.3% | 8.0% | Loss of (3H<sub>2</sub>O) lattice molecule. |
| | 325 – 480 | 47.8% | 49.1% | Loss of 2Cl<sub>2</sub>, 2(C<sub>6</sub>H<sub>5</sub>OH) molecule. |
| | 480 – 590 | 31.2% | 33.9% | Loss of C<sub>4</sub>H<sub>8</sub>N<sub>6</sub>S molecule. |
| | > 620 | 12.5% | 11.1% | Removal NiO metal oxide. |
| B<sub>3</sub> | 0 – 190 | 20.4% | 15.1% | Loss of 2H<sub>2</sub>O Lattice water and Cl<sub>2</sub>. |
| | 190 – 350 | 18.2% | 20.1% | Removal Cl<sub>2</sub> and 4H<sub>2</sub>O coordinate. |
| | 350 – 610 | 54.53% | 57.3% | Loss L<sub>2</sub> and Cr metal. |
| | > 610 | 12.2% | 14.1% | Remove CrO<sub>3</sub>. |
4. Conclusion
In complexes of L₁ the coordination pattern is N₂-bidentate chelation forming stable 5-membered ring for the three metal ions, in complexes of L₂ the presence of hydroxyl group assisted to form tridentate coordination pattern of N₂O of facial geometry using 6-membered ring in chromium complex and not the other. Therefore, according to the previous results the suggested structures and chemical formula for all complexes are shown below:
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