

## Synthesis of novel metal complexes of 5-(4-isopropoxyphenyl)-N-phenyl-1,3,4-thiadiazol-2-amine

Ahmed AbdulAmier Hussain Al-Amiery\* ,Maysoon Yousif \*  
& Muna A. Shakir\*

Recived on:2/3/2008

Accepted on:6/11/2008

### Abstract

New 5-(4-isopropoxyphenyl)-N-phenyl-1,3,4-thiadiazol-2-amine have been synthesized in good yield by the reaction of N-phenylhydrazinecarbothioamide with a 4-isopropoxybenzoic acid in phosphorus oxychloride. Cr(III), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) complexes of 5-(4-isopropoxyphenyl)-N-phenyl-1,3,4-thiadiazol-2-amine have been prepared, and characterized by elemental analysis, FT-IR, and UV/visible spectra moreover determination of molar ratio M:L, determination of metal content M% by flame atomic absorption spectroscopy, molar conductance in DMF. solution and magnetic moments ( $\mu_{eff}$ ).

**Keywords:** N-phenylhydrazinecarbothioamide, DMF, isopropoxyphenyl, thiadiazol, complexes.

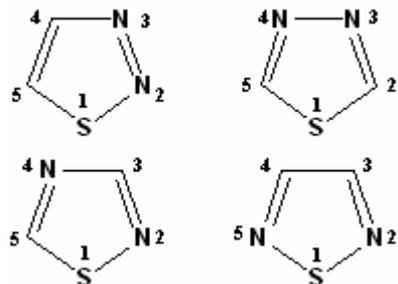
تحضير معقدات جديدة لليكاند 5-(4-ايذوبروبوكسي فنييل)-نتروجين-فنييل-1,3,4-ثياديازول-2-أمين لبعض ايونات العناصر الانتقالية ثنائية التكافؤ

الخلاصة

تم تحضير معقدات جديدة للمشتق (4-ايذوبروبوكسي فنييل)-نتروجين-فنييل-1,3,4-ثياديازول-2-أمين مع الفلزات: الكروم الثلاثي, المنغنيز, الكوبالت, النيكل, النحاس, الزنك, والكاديوم الثنائية. وشخصت بالطرق الطيفية المتوفرة (طيف الأشعة تحت الحمراء, وطيف الأشعة فوق البنفسجية والمرئية). إضافة إلى تحديد النسبة المولية إلى ليكاند: فلز, ثم قياس نسبة الفلز في المعقدات بواسطة طيف الامتصاص الذري أللهبي F.A.A.S, فضلا عن قياس الموصلية المولارية لمحاليل المعقدات في مذيب N,N-ثنائي مثيل فورم اميد وقياس العزم المغناطيسي المؤثر للمعقدات الصلبة.

### Introduction

Thiadiazole contains the five-membered diunsaturated ring structure composed of two nitrogen atoms and one sulfur atom. There are four isomeric types: 1,2,3-thiadiazole (I); 1,3,4-thiadiazole (II); 1,2,4-thiadiazole (III) and 1,2,5-thiadiazole (IV)<sup>1</sup>.



A glance at the standard references show that more studies have been carried out on the 1,3,4-thiadiazoles. Members of this ring system have found their way into such diverse applications as pharmaceuticals, oxidation Inhibitors, cyanine dyes and metal complexing agents. The growing patent literature from the sixties demonstrates that the 1,3,4-thiadiazoles are becoming of great interest, this is primarily due to the large number of uses of 1,3,4-thiadiazoles in the most diverse areas, for example in drug synthesis, scintillation material, dyestuffs

industry, photography, and corrosion inhibitors. Numerous 1,3,4-thiadiazoles have been synthesized and reported to be biologically versatile compounds having bactericidal, fungicidal, muscle relaxant properties ...etc. Some 1,3,4-thiadiazole derivatives possess central nervous system (CNS) depressant activity<sup>2-8</sup>. 2,5-Dimercapto-1,3,4-thiadiazole has been used for many years in flame-retardant products<sup>9</sup>. It is utilized in a variety of other applications including synthesizing polymers, in cross linking halogenated polymers; as an additive in lubricating oils and greases; in electrode compositions; as an intermediate or starting material for pharmaceuticals and dyes; as a chelating agent in the analysis of metals; in purifying and treating waste; and as a biocide. It was reported that 1,3,4-thiadiazoles exhibit various biological activities possibly due to the presence of the =N-C-S moiety<sup>10</sup>. In particular, the 1,3,4-thiadiazole derivatives showed these activities<sup>11-15</sup>. Furthermore, a great number of variously substituted 1,3,4-thiadiazoles have been synthesized and tested for their difference activities<sup>16,17</sup>. Substituted thiadiazoles have been reported to display diverse applications as oxidation inhibitor, cyanic dyes and metal complexing agents<sup>18-22</sup>. Metal complexes of 1,3,4-thiadiazole moiety applications. The wide range of application of the ligand and its metal complexes aroused our interest to prepare a new series of some of those metal complexes.

### Experimental

All chemical used were of reagent grade (supplied by Either Merck or Fluka) and used as supplied. The FTIR spectra in the range (4000 – 200)  $\text{cm}^{-1}$  were recorded as cesium iodide disc on FTIR 8300 Shimadzu

Spectrophotometer. The UV-Visible spectra were measured in ethanol using Shimadzu UV-Vis. 160 A spectrophotometer in the range (200-1000) nm. Magnetic susceptibility measurement for complexes were obtained at room temperature using (Magnetic susceptibility Balance), Jhonson Matthey catalytic systems division. Gallencamp M.F.B.600.010 F melting point apparatus were used to measure the melting point of all the prepared compounds. Elemental microanalysis was carried out using CHNOS elemental analyzer model 5500 Carlo-Erba instruments (Italy made).

### Synthesis of the ligand:

#### 5-(4-isopropoxyphenyl)-N-phenyl-1,3,4-thiadiazol-2-amine (L)

To a solution of N-phenylhydrazine carbothioamide (0.01mole) in 50ml of absolute ethanol, 4-isopropoxybenzoic acid 0.01 mole in 50ml of absolute ethanol added with stirring. 5ml of  $\text{POCl}_3$  was added gradually to the mixture, then heated under reflux for 2hr. after cooling a yellow precipitate of (L) was afforded, washed with chloroform and petroleum ether. Recrystallization from ethanol afforded 2.475gm, 8% yield.

### Synthesis of Complexes

Addition of ethanol solution of the hydrated metal chloride Cr(III), Co(II), Ni(II) and Cu(II) to an ethanolic solution of (L) in 2:1 (ligand : metal) molar ratios. After stirring for 2hr., colored precipitates formed at room temperature, the rustling solids were filtered off, washed with distilled water dried and recrystallized from ethanol and dried at 90°C. Preparation of Zn(II) and Cd(II) complexes were prepared in a similar procedure except the molar ratio 1:1 which afforded white and yellow colored complexes in 60 & 70% yield.

### I. UV/visible spectra

Most of the transition metal complexes are colored<sup>23</sup> and their colors are different from the transition metal salts and the ligand, then this is an important indication to the occurrence of coordination<sup>24-25</sup>. Therefore the colored complexes show different characteristic absorption bands in their position, intensity or both when compared with the bands of the ligand and this was another indication for occurrence of coordination<sup>26-27</sup>.

The peak observed in the electronic spectra are reported in table (2). The origin of band observed at about 700nm in the electronic spectra of complexes has been identified in d-d transition. In these complexes the bands observed at 300-400nm could be assigned to nitrogen-metal charge transfer absorption.

Table (2) shows the decomposition point, color and electronic absorption peaks for ligand and complexes. The peaks are classified in to two distinct groups: those that belong to ligand transitions appeared in the UV region while d-d transitions appeared in the visible region. These transitions are assigned in relevance to the structures of complexes and also shown in table (2).

**II. I-R spectra** In the solid state I-R spectra of free ligand showed peak in  $3377.1\text{cm}^{-1}$  due to  $\nu\text{NH}$ . The frequencies of the  $\nu(\text{N-H})_{\text{asm}}$  and  $\nu(\text{N-H})_{\text{sym}}$  in the complex have suffered from a shift to higher values due to the formation of metal-nitrogen bond, (figures 1,2).

In the free ligand, the band at  $1629\text{cm}^{-1}$  is assigned to the stretching of C = N group showed splitted into two bands related to the two isomethane groups in the thiadiazole ring. One of these bands is shifted to a

### Results and Discussions

lower frequency region which indicates the coordination through the nitrogen in position 3 of thiadiazole ring which is probably due to the lowering of bond order of the carbon – nitrogen bond resulted from complexation. The second C=N band in the ring is shifted to a higher frequency region due to the changing in the electronic environments of the bond. Stretching of metal-nitrogen bonds of the complexes appeared in low frequency region  $497\text{-}472\text{ cm}^{-1}$ . The molar ratio method was followed to detect the ratio of metal ion to ligand in complexes. Ethanol was used as solvent. The [M]/[L] ratio was found to be 1:2 in Cr(III), Co(II), Ni(II), and Cu(II), while it was 1:1 in Zn(II) & Cd(II) complexes. The values of magnetic moment in table (3) supported the suggested structure.

### III. Electronic spectral

The U.V.-Visible of the ligand (L) and its metal complexes recorded in table(4). The solution of the ligand (L) in  $10^{-3}\text{M}$  ethanol exhibited two peaks at 213 & 306 nm, which are attributed to  $\pi \rightarrow \pi^*$  or  $n \rightarrow \pi^*$ .

The red shift in solution of complexes were investigated depending upon  $\pi \rightarrow \pi^*$  or  $n \rightarrow \pi^*$  for all the complexes. The chromium complex showed mixed electronic transition due to low intensity of  $A_{2g} \rightarrow T_{2g}$ , the 480nm which is referred to  $A_{2g} \rightarrow T_{2g}$ . The square planar geometry of Cu(II) complex in the solid state disappeared due to filling the empty orbital of d -  $\text{Cu}^{+2}$  by D.M.F molecule therefore give the peaks at 680nm due to  $E_g \rightarrow T_{2g}$ .

However Ni(II) complex showed charge transfer at 385nm due to  $A_{2g} \rightarrow T_{1g}$ . The complexes of Zn(II) or Cd(II) showed only charge transfer of  $M \rightarrow L$  in the range 307-305nm respectively.

**IV. Magnetic Measurements** The magnetic measurements were used to study and identify some paramagnetic transition metal complexes like (Co<sup>2+</sup>, Ni<sup>2+</sup>, and Cu<sup>2+</sup>) and give us some information about:

1: Oxidation state for transition metal ions to determine the unpaired

electrons in metal ion illustrated the complexes state as low spin or

high spin.

2: Geometry

3: Bond type

The magnetic susceptibility for synthesized complexes at room temperature were measured then the (effective magnetic moment) correlation were measured from this relationship:

$$\mu_{eff} = 2.828 \sqrt{XA. T}$$

*T* = Absolute temperature

*XA* = Atomic susceptibility corrected from diamagnetic

The cause of the experimental  $\mu_{eff}$  values which are lower than the theoretical values attributed to (magnetically dilute) while the cause of the experimental  $\mu_{eff}$  values which are higher than theoretical values attributed to (orbital contribution) in some cases.

The observed magnetic moment value for the Co(III) complex is 3.60 B.M. which is within the predicted high-spin value for an Tetrahedral Co(III) complex with a considerable orbital contribution to the overall magnetic moment.<sup>27</sup>

On the basis of spectral bands, an octahedral geometry is therefore proposed for the Ni(II) ion. The values of ligand field parameters reflect that the M-L bond is quite strong, which in turn suggests sufficient overlapping of the metal orbitals with those of the ligand orbitals.

The compounds are paramagnetic with a room temperature magnetic

moment of 4.25B.M. which is consistent with an S = 1 ground state in an Square planner field.

**V. Molar conductivity measurements:**

The conductivity measurements have been used in coordination chemistry to identify the ionic compound formula in solution or solid state<sup>28</sup>. From (table 4), it is show that all the complexes are non conducting in solution.

**VI. According to the results obtained by:** C.H.N.M. elemental analysis, electronic spectra and I.R spectra, we proposed the following stereo chemistry of the complexes.

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**Table (1)The elemental analysis of the ligand**

|                   | <b>C%</b>    | <b>H%</b>   | <b>N%</b>    |
|-------------------|--------------|-------------|--------------|
| <b>Calculated</b> | <b>65.60</b> | <b>5.46</b> | <b>13.50</b> |
| <b>Found</b>      | <b>64.80</b> | <b>5.00</b> | <b>12.11</b> |

**Table (2) Electronic spectra for ligand and complexes in ethanol solvent.**

| No. | Symbol | Mp. °C           | Color          | Absorption Bands (nm) | Assigned transition                       |
|-----|--------|------------------|----------------|-----------------------|---|
| 1.  | L      | 160-162          | white - yellow | 220                   | $\pi \rightarrow \pi^*$                   |
|     |        |                  |                | 320                   | $n \rightarrow \pi^*$                     |
| 2.  | CoL    | 190-192          | pink           | 240                   | $\pi \rightarrow \pi^*$                   |
|     |        |                  |                | 590                   | ${}^3A_{2g} \rightarrow {}^3T_{2g}$       |
|     |        |                  |                | 670                   | ${}^3A_g \rightarrow {}^3T_{2g}$          |
| 3.  | CrL    | 218-220          | dark green     | 215                   | $\pi \rightarrow \pi^*$                   |
|     |        |                  |                | 330                   | $n \rightarrow \pi^*$                     |
|     |        |                  |                | 475                   | ${}^4A_{2g} \rightarrow {}^4t_{1g}$       |
| 4.  | NiL    | 240 <sup>d</sup> | dark brown     | 220                   | $\pi \rightarrow \pi^*$                   |
|     |        |                  |                | 350                   | $n \rightarrow \pi^*$                     |
|     |        |                  |                | 390                   | ${}^3A_{2g} \rightarrow {}^3t_{1g}^{(p)}$ |
| 5.  | CuL    | 245-247          | green          | 215                   | $\pi \rightarrow \pi^*$                   |
|     |        |                  |                | 320                   | $\pi \rightarrow \pi^*$                   |
|     |        |                  |                | 705                   | ${}^2E_g \rightarrow {}^2T_{2g}$          |
| 6.  | ZnL    | 214 <sup>d</sup> | white          | 213                   | $\pi \rightarrow \pi^*$                   |
|     |        |                  |                | 320                   | $n \rightarrow \pi^*$                     |
| 7.  | CdL    | 260 <sup>d</sup> | yellow         | 220                   | $\pi \rightarrow \pi^*$                   |
|     |        |                  |                | 315                   | $n \rightarrow \pi^*$                     |

Where: d = decomposed , L= C<sub>17</sub>H<sub>17</sub>N<sub>3</sub>SO

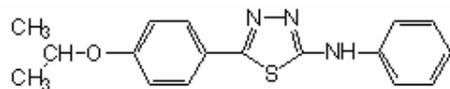
**Table (3) Absorption bands in infrared for ligand and complexes.**

| No. | Symbol | V(C=N) | $\nu(N-H)_{asy.}$ | $\nu(M-N)$ | M% Calc.(found) |
|-----|--------|--------|-------------------|------------|-----------------|
| 1.  | L      | 1629   | 3377.1            | -          | -               |
| 2.  | CrL    | 1606   | 3190(br)          | 497(w)     | 6.9(7.5)        |
| 3.  | NiL    | 1590   | 3100              | 493(w)     | 7.05(8.1)       |
| 4.  | CuL    | 1590   | 3250              | 472(w)     | 9.81(10.5)      |
| 5.  | ZnL    | 1580   | 3391              | 495(w)     | 11.5(12.4)      |
| 6.  | CdL    | 1590   | 3190              | 493(w)     | 11.40(12.30)    |

Where: s= strong , m = medium , w = weak , br = broad . L= C<sub>17</sub>H<sub>17</sub>N<sub>3</sub>SO

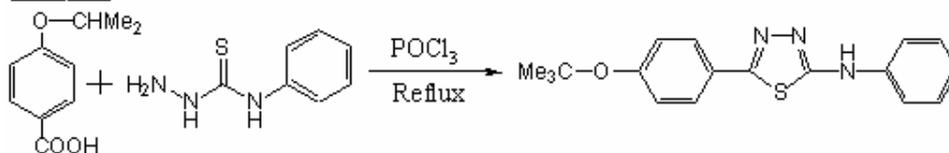
**Table (4) Names and physical data of pou synthesized compounds.**

| No | Symbol | Suggested formula structure  | Name  | Magnetic moment $\mu(B.M)$ | Suggested structure | $\Omega$ ohm <sup>-1</sup> cm <sup>2</sup> mol <sup>-1</sup> |
|----|--------|--|---|----------------------------|---------------------|--|
| 1. | L      | C <sub>17</sub> H <sub>17</sub> N <sub>3</sub> SO  | 5-(4-isopropoxyphenyl)-N-phenyl-1,3,4-thiadiazol-2-amine                            | -                          | -                   | -  |
| 2. | CrL    | Cr[(C <sub>17</sub> H <sub>17</sub> N <sub>3</sub> SO) <sub>2</sub> Cl <sub>2</sub> ]<br>]Cl | Bis(5-(4-isopropoxyphenyl)-N-phenyl-1,3,4- thiadiazol-2-amine)chromium(III)chloride | 5.28                       | Octahedral          | 90   |
| 3. | CoL    | [Co(C <sub>17</sub> H <sub>17</sub> N <sub>3</sub> SO) <sub>2</sub> Cl]<br>2                 | Bis(5-(4-isopropoxyphenyl)-N-phenyl-1,3,4- thiadiazol-2-amine)Cobalt(II) Chloride   | 3.60                       | Tetrahedral         | 198  |
| 4. | CuL    | [Cu(C <sub>17</sub> H <sub>17</sub> N <sub>3</sub> SO) <sub>2</sub> Cl]<br>2                 | Bis(5-(4-isopropoxyphenyl)-N-phenyl-1,3,4- thiadiazol-2-amine)Copper(II)chloride    | 1.17                       | Square planner      | 180  |
| 5. | NiL    | [Ni(C <sub>17</sub> H <sub>17</sub> N <sub>3</sub> SO) <sub>2</sub> ]                        | Bis(5-(4-isopropoxyphenyl)-N-phenyl-1,3,4- thiadiazol-2-amine)Nickel(II)chloride    | 4.25                       | Square planner      | 170  |
| 6. | ZnL    | [Zn(C <sub>17</sub> H <sub>17</sub> N <sub>3</sub> SO)]                                      | Bis(5-(4-isopropoxyphenyl)-N-phenyl-1,3,4- thiadiazol-2-amine) zinc(II).            | 5.41                       | Tetrahedral         | 20   |
| 7. | CdL    | [Cd(C <sub>17</sub> H <sub>17</sub> N <sub>3</sub> SO)]                                      | Bis(5-(4-isopropoxyphenyl)-N-phenyl-1,3,4- thiadiazol-2-amine)Cadmium(II).          | 3.22                       | Tetrahedral         | 18   |

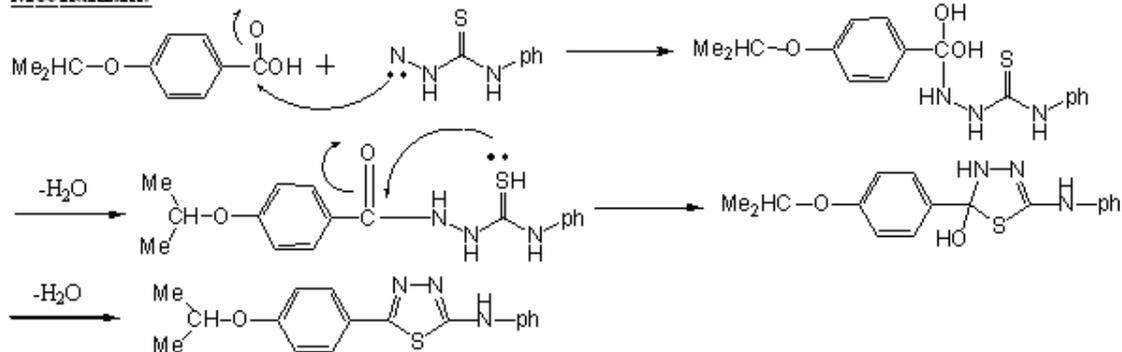


5-(4-isopropoxyphenyl)-N-phenyl-1,3,4-thiadiazol-2-amine (L)

**Reaction**



**Mechanism:**



**Scheme(1) : Preparation of the ligand**

