Synthesis and Characterization of New Thio-allyl-Triazole Ligand
And Complexes with Selected transition Metals

Ahmed S. Majed
Department of Chemistry, College of Science, Al- Nahran University

Abstract
The ligand, 3-(2-Propynyl) thio-4-allyl-5-phenyl-4H,1,2,4-triazole (L) was prepared and characterized by micro elemental analysis (C,H,N) and Infra-Red spectroscopy. Selected metals, which were Cu(II), Zn(II), Cu(II), and Fe(III), where reacted with (L) to produce new complexes. These complexes were identified through micro elemental analysis, Infra red and ultra-violet-visible spectroscopy and other techniques. Depending on the data obtained, chemical formulae and geometry of complexes were suggested. Biological activity of the complexes against selected types of microorganisms was also examined.

Introduction
Metal complexes are suggested as a possible measure of drugs, since the action of many drugs is based on the ability of complex compound of metal ions to traverse biomembranes, whereas individual aquations and ligands almost or completely lack this ability.

A case in point is antibiotics whose activity increases drastically in the presence of metal ions.

Metal chelates differ in their mode of action and activity in biological systems in accord with their structural considerations, e.g., inert, highly stable metal chelates have a considerable activity against microorganisms, fungi and viruses and are used in controlling the spread of neoplastic tissue.

An important and versatile class of well established biologically active compounds are those with the -N=C=S moiety. This group is found in many basic structures of drugs either to be part of an open chain, e.g., thiosemicarbazones, isothiocyanates and thiosemicarbazides, or involved in hetereocyclic ring, e.g.,

Mercapto derivatives of triazoles, oxadiazoles, and thiazole derivatives.

The presence of the "soft" sulfur atom besides the "hard" nitrogen atom in this thiazolidine group, keeping aside the effects of the remainder of the molecule containing it, renders these molecules to be potent ligands with a wide diversity and versatility toward the transition elements. This property is the key for biological importance of these ligands in addition to other uses and applications.

A large number of 1,2,4-triazole derivatives have been synthesized in recent years.

Many of these derivatives are reported to exhibit broad spectrum of biological effects.

Among the interesting ones are the tuberolalthentic,, fungicidal,, anti-inflammatory, and antibacterial agents.

Biological activities triazole and its derivatives are well documented in the literature. The bimutilities of these compounds together with similar heterocyclic have been correlated with their complexation ability with metal ions.

A great number of 1,2,4-triazole derivatives substituted with thiol, ethylenethio, aryl, substituted aryl, allyl, ahyd and 2-thienyl, or one or more of the 3,4-and 5-positions of the 1,2,4-triazole ring were prepared and screened for their antibacterial activity.

In 1986, N.M. Hamadi and co-workers studied the interaction of amino-triazole with glutathione under physiological conditions and found that these derivatives were substrates for the enzyme.

In this work, we report the preparation of the ligand "3-(2-Propynyl) thio-4-allyl-5-phenyl-4H-1,2,4-triazole" (L), and some metal complexes. These compounds were prepared with the intention of finding new potentially biologically active compounds.

Experimental Chemistry
Elemental microanalysis was carried out using (C,H,N) elemental analyzer model 5500 Carlo Erba instruments (Italy).

The metal on test of the complexes was measured using atomic absorption technique by Pye Unicam of Philips Scientific Instrument which employed the Hollow Cathode Lamp of the Pye Unicam Ltd. Cambridge.

The IR spectra of the prepared compounds were recorded using Perkin-Elmer 1130 infra red
The ligand (L) was prepared according to the following procedure:

\[ \text{The Ligand (L)} \]

The compound 3-mercaptop-4-allyl-5-phenyl-411-1,2,4-triazole was prepared and used as a precursor for the ligand L.

To a stirred solution of 3-mercaptop-4-allyl-5-phenyl-411-1,2,4-triazole (0.1 mol, 21.7 g) in acetic acid (500 ml), a solution of potassium hydroxide in ethanol (0.1 mol, 5.6 g) was added followed by drop wise addition of (0.1 mol, 13.1 g) of propargyl bromide, the mixture was refluxed for one hour. After cooling to room temperature, filtered and the filtrate was poured into cold distilled water 1 liter. The precipitate was filtered and recrystallized from ethanol-water.

Metal complexes of (L) were prepared as follows:

(C) Cl, Zn, Cd, Co and Fe complexes

Ethanol solution of (1 mol) of the metal salts (chlorides of Cu(II), Zn(II), Cd(II), Co (II)) and nitrate of Fe(III) was added to (2 mol) of L dissolved in ethanol. The mixture was stirred at room temperature for 1 hour. Fine precipitate was formed, washed with acetone and dried under vacuum at about 50°C.

**Bacteriology**

Biological activity of (L) and complexes were evaluated against representative gram-positive and gram-negative bacteria by agar plate method. All the compounds were prepared freshly by dissolving them in dimethylformamide (DMF) to obtain a final concentration of 1000 mg/ml and cultivated in nutrient agar. The results are found in table (1).

**Discussion**

The identification of the ligand (L) was carried out through elemental analysis: C, 65.47% (calc. 65.88%); H, 5.13% (calc. 5.10%); N, 16.52% (calc. 16.47%)

The olefinic group in the ligand responded positively to both Br2/CCl4 and KMnO4 tests. The acetylenic group in the ligand responded positively to both K2Cr2O7 and Tollens tests. The ligand has a white color and was found to be soluble in ethanol, carbon tetrachloride, diethyl ether, and DMF. It is found to be insoluble in the acetone and n-hexane.

Identification of the complexes was done using different available techniques. Among these techniques are the determinations of metal percentage by atomic absorption, Infrared spectroscopy, magnetic susceptibility and conductivity measurements.
Identification

The absorption bands for (L) and its complexes are shown in Table (2), the absorption bands of the acetylidic group were of great help in the identification of complexes formed especially with respect to the type of bonding with metal. The (C=C) stretching vibration appears at 2111 cm⁻¹ which does not involve absorption due to other groups of the studied ligand. When the spectra of the complexes are compared with that of the ligand one of the following shift may take place, in the case of π-bonding the ν(C=C) shifts to a lower frequency by 90cm⁻¹ and in still lower frequency by 57cm⁻¹ in the case of strong σ-bonding and by 225cm⁻¹ for weak π-bonding, but when both σ and π are involved in bonding with the metal at the same time a red shift of 100cm⁻¹ is observed.

A- Copper (II) complex, C₁

The IR spectrum of (C₁) are shown in Table (2). The ν(C=C) absorption band shift to a lower frequency by 57cm⁻¹ and the band due to ν(C=H) undergo a reduction in its intensity.

These observations led to the conclusion that Copper (II) coordinate to the ligand through acetylidic group by σ-bonding mode.

Conductivity measurements show the complex is non-ionic, Table (3), therefore the following structure can be suggested:

B- Zinc (II), Cadmium (II) and Cobalt

The IR spectra of these complexes shows similar behavior with no much difference compared to that of the ligand.

It gives shift of ν(C=C) absorption band to a lower frequency and the band due to ν(C=H) undergoes a reduction in its intensity.

Also the band at 1550 cm⁻¹ which correspond to ν(C=N) shift to a lower frequency by 10cm⁻¹. These observations indicate the participation of both acetylidic group and nitrogen. A broad band which appeared at 3600cm⁻¹ indicates the presence of water molecules in the structure of the complex.

Tetrahedral geometry can be suggested for the three complexes:

Where: M = Zn, Cd and Co
Conductivity measurements show the complexes are non-conductive, Table (3).

C- Fe (III) complex, C₅:

The IR spectrum of the complex was characterized by a broad band in the region (3000-2500) cm⁻¹ which could be attributed to the ν(OH) of water molecule bonded to the Fe(III) ion. This expected in Iron (III) complex due to its high affinity for water. The ligand can not displace all the water molecules found in the coordination sphere of the metal ion. The broadening of the bond was also noticed in the region (1600-1700) cm⁻¹ which is attributed to the bending vibration of water molecule. This broadening affects the shape of the spectrum and makes the interpretation more difficult. Also it shows shift of ν(C=C) absorption band to a lower frequency and the band due to ν(C=H) undergo a reduction in its intensity.

Also the band at 1555 cm⁻¹ which correspond to ν(C=N) shift to a lower frequency by 50cm⁻¹. These observations indicate the participation of both acetylidic group and nitrogen. Therefore the following structure is suggested for the (C₅) complex:

The above complex is non-ionic due to the conductivity measurement, Table (3).
Table (2) the absorption bands in infra-red spectra for (L) and its complexes, all data are in cm⁻¹.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>w(0-ν)</th>
<th>Thiosemic band (II)</th>
<th>Thiosemic band (IV)</th>
<th>ν(C≡C)</th>
<th>ν(C=O)</th>
<th>ν(C=H)</th>
<th>δ(0-ν)</th>
</tr>
</thead>
<tbody>
<tr>
<td>L</td>
<td>1275(m)</td>
<td>770(m)</td>
<td>1550(m)</td>
<td>2100(w)</td>
<td>3035(m)</td>
<td>620(w)</td>
<td>-</td>
</tr>
<tr>
<td>Cl</td>
<td>1260(m)</td>
<td>750(m)</td>
<td>1540(w)</td>
<td>2020(w)</td>
<td>3035(w)</td>
<td>620(w)</td>
<td>925(w)</td>
</tr>
<tr>
<td>C2</td>
<td>1260(m)</td>
<td>750(m)</td>
<td>1540(w)</td>
<td>2020(w)</td>
<td>3035(w)</td>
<td>620(w)</td>
<td>925(w)</td>
</tr>
<tr>
<td>C3</td>
<td>1260(m)</td>
<td>750(m)</td>
<td>1540(w)</td>
<td>2020(w)</td>
<td>3035(w)</td>
<td>620(w)</td>
<td>925(w)</td>
</tr>
<tr>
<td>C4</td>
<td>1260(m)</td>
<td>750(m)</td>
<td>1540(w)</td>
<td>2020(w)</td>
<td>3035(w)</td>
<td>620(w)</td>
<td>925(w)</td>
</tr>
<tr>
<td>C5</td>
<td>1260(m)</td>
<td>750(m)</td>
<td>1540(w)</td>
<td>2020(w)</td>
<td>3035(w)</td>
<td>620(w)</td>
<td>925(w)</td>
</tr>
</tbody>
</table>

Where: m=medium, w=weak, b=broad.

Electronic spectral analysis and magnetic measurements

The electronic spectra of Zn (II) and Cd (II) complexes in the visible region are of little help as because these ions have a d⁰ configuration and their complexes do not exhibit any d-d transition. All the complexes of these metal ions were found to be diamagnetic.

A- Cu (II) complex, C1

Cu (II) compounds are blue or green because of a single broad absorption band in the region (11,600-15,000) cm⁻¹. The d⁰ ion is characterized by large distortion from octahedral symmetry and the band is unsymmetrical, being the result of a number of transitions, which are by no means easy to assign unambiguously. In the present work, the green (C1) complex shows a broad band at 15,774 cm⁻¹ which can be assigned to the 

\[ B_{1g} ightarrow B_{3g} \]  

transitions.²³

B- Cu (II) complex, C4

C4 complex spectrum in DME shows three bands. The first two bands at 16,611 and 14,860 cm⁻¹ were assigned to the transition:

\[ 4T_{1g}(F) \rightarrow 4T_{2g}(F) (μ_j) \]

since this transition is known to be a triplet in the range (14,000-17,500) cm⁻¹ in the divalent cobalt of tetrahedral geometry. This splitting is due to spin orbit coupling.²⁴ Therefore, ν₆, s having been calculated as the average of these two bands.

The third band which appears as a weak band at 9,345 cm⁻¹ was assigned to the transition ν₅: 

\[ 4T_{1g}(F) \rightarrow 4A_{2g} \]

while ν₂ could not be observed since it is expected to appear in a range out of the instrument scale so it was calculated using Tanabe-Sugano diagram for d⁰ system and found to be 6,256 cm⁻¹ which belong to the transition ∆T₁g(F) → ∆T₂g(F).²⁵

The different ligand field parameter has been calculated using the same diagram. Comparison of the results obtained in this work with the literature data suggests high spin tetrahedral geometry around Cobalt (II) ion. Magnetic measurements show that the complex is paramagnetic (μₒ ≈ 4.35 B.M.) Table (3) which accordance with the high spin tetrahedral.²⁶²⁷ The low ratio of μ₂/μ₁ (1.49) indicates the tetrahedral geometry.²⁸ The molar conductivity measurement in DME show that the complex was non-electrolyte.

C- Fe (III) complex, C5:

The electronic spectrum of C5 shows two bands, the first one at 20,408 cm⁻¹ and the second at 26,453 cm⁻¹, they could be assigned to the transitions:

\[ \text{A}_{1g} \rightarrow \text{T}_{2g} (20,408 \text{cm}^{-1}) \]

\[ \text{A}_{1g} \rightarrow \text{T}_{1g} (26,453 \text{cm}^{-1}) \]

The value of the measured magnetic moment for C5 is (5.15 B.M.), which could be related to high-spin d⁶ ferric ion so that the octahedral geometry is suggested to this complex.²⁹

From Tanabe-Sugano diagram for d⁶ octahedral field, the value of 10B₇ was found to equal to 20.693 cm⁻¹ and the high value of nephelauxetic factor (β) (0.88) indicated the ionic character of the complex.
Table (3) Magnetic moment, conductivity, and suggested structure for complexes of (L)

<table>
<thead>
<tr>
<th>Complex</th>
<th>Magnetic moment, ( \mu_B/2 )</th>
<th>Conductivity, ( \Omega^{-1} \cdot cm^{-1} )</th>
<th>Suggested structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diagonal</td>
<td>1.35</td>
<td>15</td>
<td>Tetrahedral</td>
</tr>
<tr>
<td>Diamagnetic</td>
<td>47</td>
<td></td>
<td>Square planar</td>
</tr>
<tr>
<td>Diamagnetic</td>
<td>33</td>
<td></td>
<td>Tetrahedral</td>
</tr>
<tr>
<td>Diamagnetic</td>
<td>37</td>
<td></td>
<td>Tetrahedral</td>
</tr>
<tr>
<td>C5</td>
<td>5.15</td>
<td>22</td>
<td>Tetrahedral</td>
</tr>
</tbody>
</table>

**Bactericidal activity**

Preliminary screening experiments are intended to detect the in vitro activity of metal complexes. The complexation of (L) with all the metal ions used exhibited no activity except Zn (II) complex (C2) against both Staph. aureus and E-Coli, while Cd (II) and Fe (III) complexes (C3 and C5) have an activity towards E-Coli and Staph. aureus respectively.

**Table (4) Biological activity for ligand and complexes (at concentration of 1 mg/mL).**

<table>
<thead>
<tr>
<th>Symbols</th>
<th>Staphylococcus aureus</th>
<th>Escherichia Coli</th>
</tr>
</thead>
<tbody>
<tr>
<td>L</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C1</td>
<td>++</td>
<td>-</td>
</tr>
<tr>
<td>C2</td>
<td>+</td>
<td>++</td>
</tr>
<tr>
<td>C3</td>
<td>+</td>
<td>++</td>
</tr>
<tr>
<td>C4</td>
<td>+</td>
<td>++</td>
</tr>
<tr>
<td>C5</td>
<td>++</td>
<td>++</td>
</tr>
</tbody>
</table>

Where: (-) no inhibition, (+) inhibition zone(6-8)mm, (+ +) inhibition zone(8-10)mm, (+++) inhibition zone(>10)mm

**References**

الخلاصة