# Divalent Copper Complexes with $N_2S_2$ Dono Atom Ligands Derived from Heterocyclic Thiadiazole Diesters

Ashour H. Dawood[*1]; Adnan I. Mohammed[1] and Hiba Mushtaq[2]

1- Department of Chemistry / Science College / Kerbala University

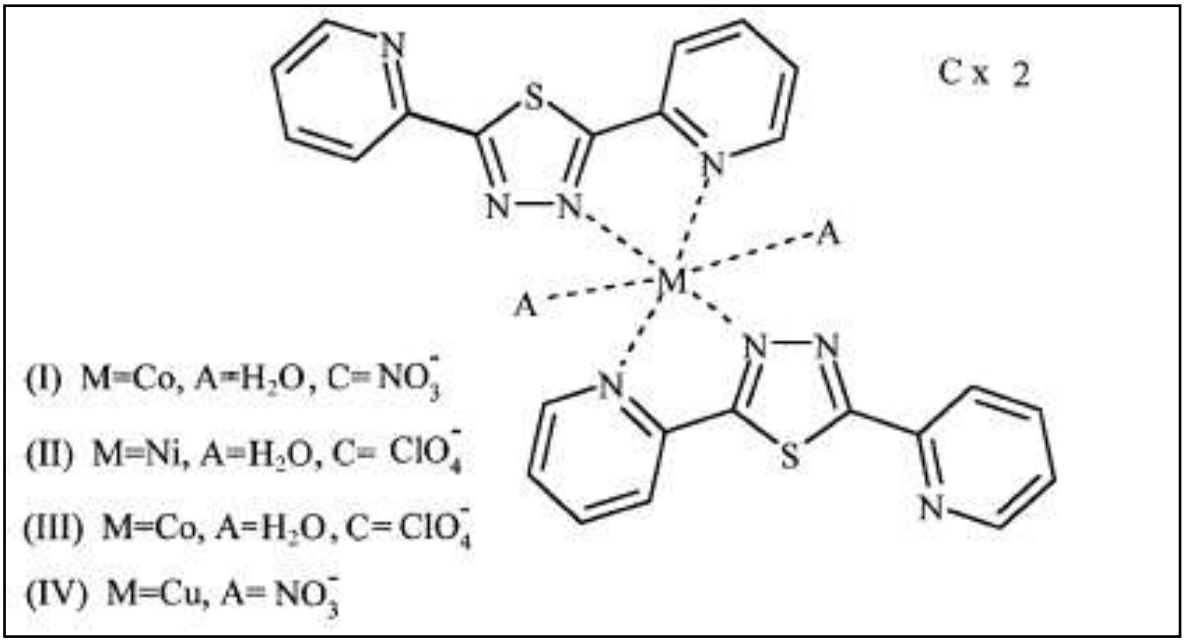
2- Department of Pharmacy / Al-Yarmuk University College

## Abstract

The new thiodiazole heterocyclic ligands have been synthesized from the condensation reaction of terephthaloyl chloride, sebacoyl chloride,and adipoylchloride. with two equivalent of p-hydroxybenzaldehde to form the dialdehyde diesters compounds form. The resulted compound was reacted with an amine ( prepared by adding the thiosemicarbazide to p-hydroxybenzaldehyde and treated with HCl to adjusted the solution to acidic media) the thiodiazole diesters was obtained, thiodiazole compounds as $N_2S_2$ donor atoms. The prepared compounds was characterized by FTIR and UV-Vis spectroscopy, the magnetic susceptibility of copper(II) complexes was measured as well as the melting points. The suggests geometry of complexes are square planar.

# Introduction

The synthesis and characterization of copper(II) complexes of Thiosemicarbazones have been a subject of interest due to their variable applications in industry and analytical chemistry. Some derivatives of thiosemicarbazones have shown antiparasitic, antimicrobial, antineoplastic, and biological activity. In many cases, the biological activities of thiosemicarbazones are related to their chelating properties to metal ions *in vivo* [1- 5]. sulfur–nitrogen chelating agents, especially those formed from thiosemicarbazide and diazo thiosemicarbazides [6-10] have been stimulated by their interesting physicochemical properties and potentially useful pharmacological properties [11, 12]. N(4)-substituted thiosemicarbazones of 2-acetyl-, 2-formyland 2-benzoylpyridine have been studied extensively because of their promising biological activity [13-15]. However, there have been only a few reports on di-2-pyridyl ketone thiosemicarbazones [16,17]. Recently, we reported a structural and spectral study of di-2-pyridyl ketone N(4)-methyl- and N(4)-dimethylthiosemicarbazones, HDPy4Mand HDPy4DM, respectively [18]. the crystal structures of HDPy4M and [Ni(DPy4DM)Cl], as well as the spectral studies of a selection of cobalt(II), nickel(II) and copper(II) complexes. F. Bentiss [19] and Co-workers have been reported the synthesis and study the properties of the 1-thia-3,4-diazole species with ortho pyridine rings substituted at the 2 and 5 positions [2,5-bis(2-pyridyl)-1,3,4-thiadiazole (bptd)] as a molecular architect with transition metals. We report here the single crystal structures of several complexes formed by bptd with divalent Co (structures I and III), Ni (structure II) andCu (structure IV).



## Experimental section

Reagents were purchased from Fluka and BDH Chemical company. IR spectra were recorded as KBr discs using a Shimadzu 8300 FTIR spectrophotometer in range (4000-400) $cm^{-1}$. Electronic spectra of the prepared compounds were measured in the region (200-800) nm for $10^{-3}$ M solution in DMF at 25 °C using Shimadzu 160 spectrophotometer, with 1.000 ± 0.001 cm matched quartz cell. Electrical conductivity measurements of the complexes were recorded at 25°C for $10^{-3}$ M solution of the sample in DMF using a PW9526 digital conductivity meter.

## 1- Preparation precursors

## A-Preparation of tetrephthalate bis[4-({[5-(4-methoxyphenyl)-1,3,4-thiadiazol-2- yl]imino}methyl)phenyl] compound 1

In 50 ml of dichloromethane (DCM) dissolved 0.224 g (2 mmol) from parahydroxybenzaldehyde with stirring in ice bath after 10 min. the 0.5 mL of pyridine was added then 0.203 g (1 mmol.) from terephthaloyl chloride added to the mixture let the solution stirring for half hour. The neck of flask was sailed by stopper, the ice bath was released and the stirring of mixture contentious for six hours, the solutions transferred to 250 mL size contains 75 mL deionized water mixed for 15 min. putted in separation funnel and added 50 mL of dichloromethane (DCM), two layers was formed taked the organic layer, washed with 75 mL of 5% HCl, the washed with 75 mL sodium bicarbonate $NaHCO_3$, last washed with 100 mL distilled water, after that let the organic layer to dry.

## B-Preparation of bis[4-({[5-(4-methoxyphenyl)-1,3,4-thiadiazol-2-yl]imino}methyl)phenyl]sebacate compound 2

The compound was prepared in the same method which that discussed in the compound tetrephthalate bis[4-({[5-(4-methoxyphenyl)-1,3,4-thiadiazol-2- yl]imino}methyl)phenyl], but the terephthaloyl chloride was instead by 0.239 g of sebacoyl chloride.

## C. Preparation of bis[4-({[5-(4-methoxyphenyl)-1,3,4-thiadiazol-2 yl]imino}methyl)phenyl] hexanedioate compound 3

The compound was prepared in the same method which that discussed in the compound tetrephthalate bis[4-({[5-(4-methoxyphenyl)-1,3,4-thiadiazol-2- yl]imino}methyl)phenyl], but the terephthaloyl chloride was instead by 0.183 g of adipoylchloride.

## 2- Preparation of the amine precursor compound 4

In the round bottomed flask 250 mL in size putted 273 g (3 mmol.) from thiosemicarbazide (TSC) dissolved in 25 mL of 10% sodiumhydroxide the solution filtered, to the filtrate was added 1.5 mL from pyridine let the solution to stirring 15 min. then added the 0.436 g (2.5 mmol.) from 4-methoxy benzoyl chloride as dropwise the resulted mixture was filtered, taked the filtrate and adjusted to acidic solution by hydrochloric acid observed the precipitate was obtained, collected, filtered, washed by diethylether, and dried. For this precipitate the concentrated sulfuric acid $H_2SO_4$ (98%) was added the mixture putted in desiccator at room temperature for two hours, the resultant transmitted to beaker size 500 mL contained the ice, the solution filtered and dried to form the amine compound

## 3- Synthesis of the diesters

The diesters compounds 5, 6 and 7 **[$L^1$], [$L^2$] and [$L^3$]** are synthesized in the same method through the reaction of (1 mmol.) from dialdehyde compounds 1, 2 and 3 with amine compound (2 mmol.) compound 4 to form diketone compound 5, 6 and 7 respectively the reaction carried out via refluxed the mixture for two to three hours in 50 mL absolute ethanol as solvent.

## 4- Synthesis of the copper (II) complexes

The three copper (II) complexes were prepared through the reaction of copper salt $CuCl_2$. $6H_2O$. in 1:1 mole ratio with ligands **[compound 5], [compound 6] and [compound 7]** to obtained complexes **1, 2** and **3** respectively. With absolute methanol as reaction medium.

## Results and discussion

### A- Synthesis and characterization of precursors

The synthesis of precursors carried out from the reaction of starting material of adipoyl chloride, terphthaloyl chloride, and sebacoyl chloride with parahydroxy benzaldehyde to form dialdehyde compounds **1, 2, 3** respectively while the amine compound was prepared through the reaction of 4-methoxy benzoyl chloride with thiosemicarbazide and treated with hydrochloride acid to form the cyclic thiodiazole amine derivative compound **4**, the general synthetic method of compounds **1, 2, 3, and 4** were summarized in **Scheme (1).** The diesters of thiodiazole derivative compounds were synthesized by the reaction of the dialdehydes compounds **1, 2, 3** with compound **4** to obtained compounds **5, 6, 7 [$L^1$], [$L^2$] and [$L^3$]** respectively. The general method of preparation these compounds were summarized in **Scheme (2).** The prepared compounds were characterised by UV-Vis, and FTIR spectroscopy methods, the solubility of compounds were recorded in different solvents

### B- Synthesis of complexes

The copper(II) complexes was formed from the reaction the prepared ligands **[compound 5], [compound 6] and [compound 7],** with copper (II) salt in methanol to obtain the tera coordinate complexes, This method was summarized in **Scheme (3).** these complexes were characterised by UV-Vis, and FTIR spectroscopy methods, magnetic susceptibility and the solubility of compounds were recorded in different solvents.

## FTIR Spectra

The FTIR spectra of compounds **1,2, and 3 Figs (1, 2, 3)** respectively displays the characteristic two bands at ( 1735, 1685 $cm^{-1}$), (1750, 1695 $cm^{-1}$) and (1684, 1678 $cm^{-1}$) due to the ν( C=O) stretching of carbonyl group as the esteric and aldehydic groups for compounds respectively. The FTIR spectrum for compound **4 Fig (4)** shows the bands at (3238 $cm^{-1}$) attributed to the ν( N-$H_2$) stretching of the amine group, the two isomethine (C=N) groups appears two bands at (1755, 1664 $cm^{-1}$) refer to the ν( C=N) stretching in different environments, the ν( C-S) stretching shows the band at (1139 $cm^{-1}$). While the FTIR spectra for compounds **5,6 and 7, Figs (5,6,7)** respectively show multi bands in the region between (1780 – 1615 $cm^{-1}$) these bands can be attributed to the ν( C=O) , ν( C=N) of heterocyclic ring and ν( C=N) stretching . The FTRIR spectra of the copper (II) complexes with **[compound 5], [compound 6] and [compound 7]**, **Figs (8, 9, 10),** shows the shifting of the ν( C=N) group between 5-20 $cm^{-1}$ to the lower frequency can be attributed to the delocalisation of the electron density of the metal ion in the π-system of the ligand (HOMO → LUMO) [ where HOMO= highest occupied molecular orbital; LUMO = lowest unoccupied molecular orbital], the shifting in the bands of the ν( C=S) stretching group and the new band at (505, 491 $cm^{-1}$), (505, 455 $cm^{-1}$), (505, 455 $cm^{-1}$), in the three complexes attributed to the ν (Cu-N) and ν (Cu-S) stretching respectively. Indicating the coordinate between the copper ion and atoms are occurred [20,21].

## UV-Vis spectra

The electronic spectra of the compounds (**1- 7), Figs. (11 -17))** respectively displays two characteristic peaks refer to the two transitions attributed to the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$, while the electronic spectra of copper ion complexes **Figs. (18-20**) appeared the charge transfer and ligand field as well as the d-d transition since the weak peaks in range between (455 – 550 nm) refer to the d-d transition type $B_{1g} \rightarrow B_{2g}$. indicating the geometry of the copper (II) ion is square planar [22].

## Magnetic susceptibility and molar conductivity

The magnetic properties of the prepared complexes were measured by Faradi method shows the complexes are paramagnetic with (1.87, 1.77, 1.81 BM), and the molar conductivity of the complexes was recorded in DMSO solvent appears the complexes were electrolyte with 1:2 ration

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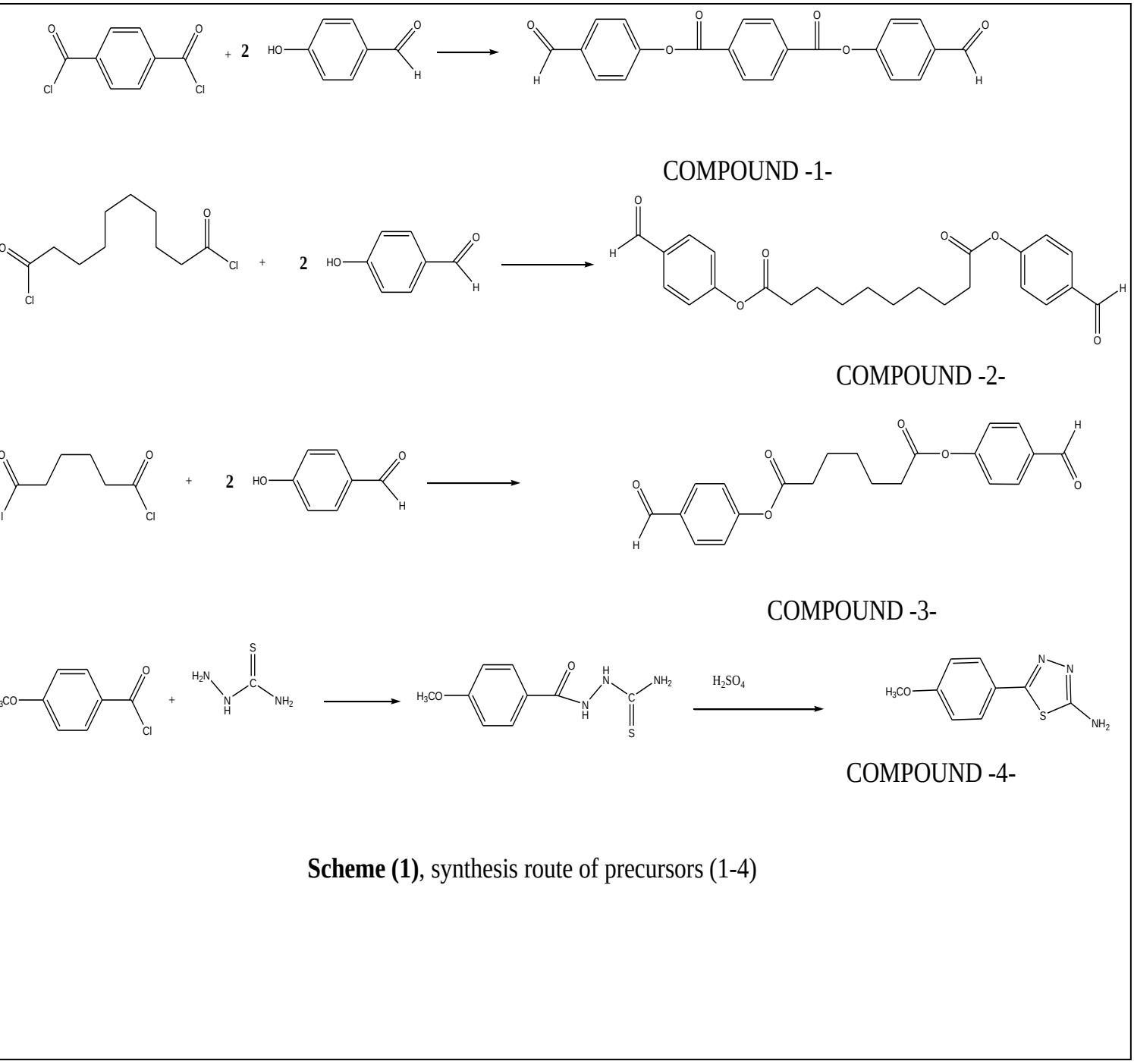
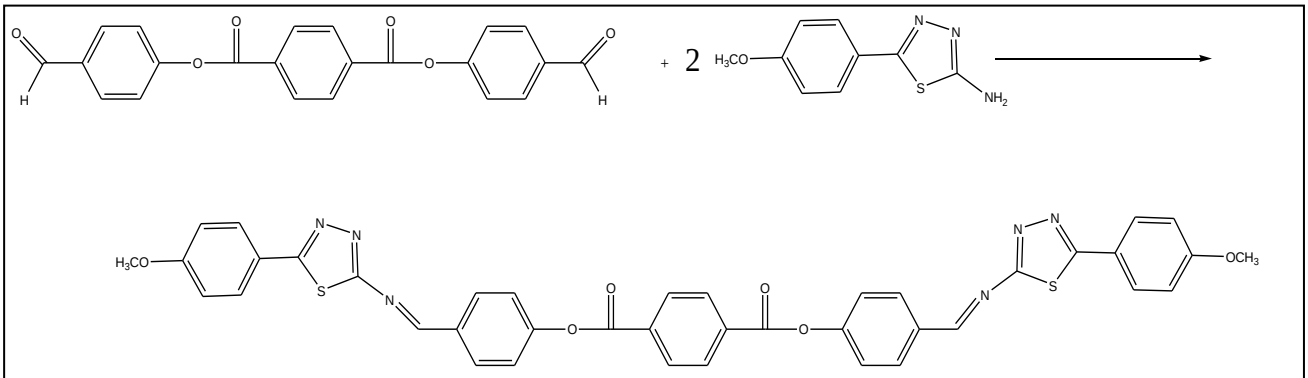
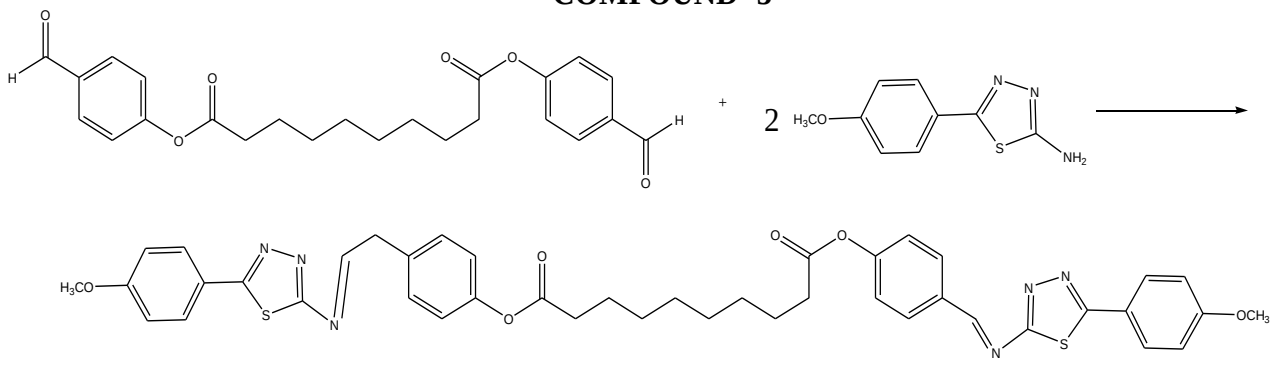



**Scheme (1)**, synthesis route of precursors (1-4)



**COMPOUND -5-**



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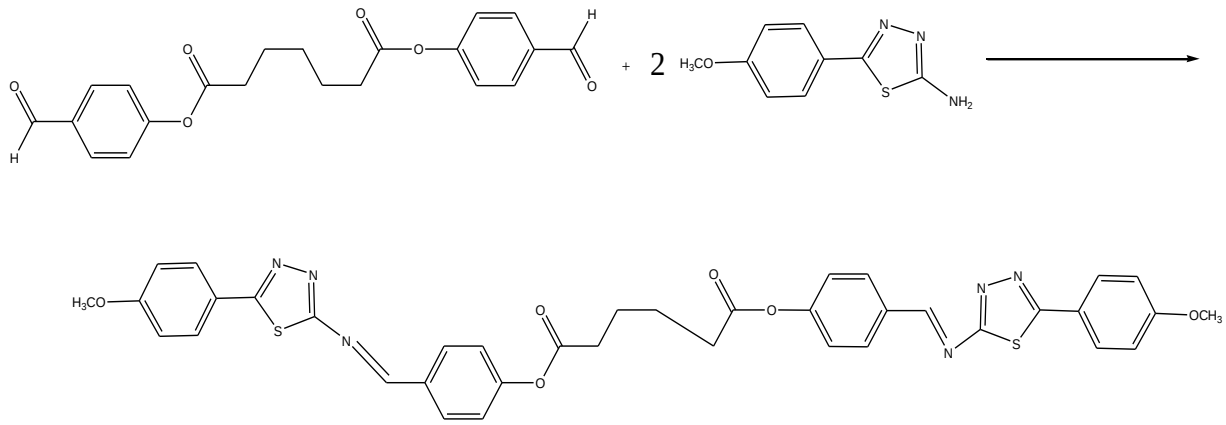
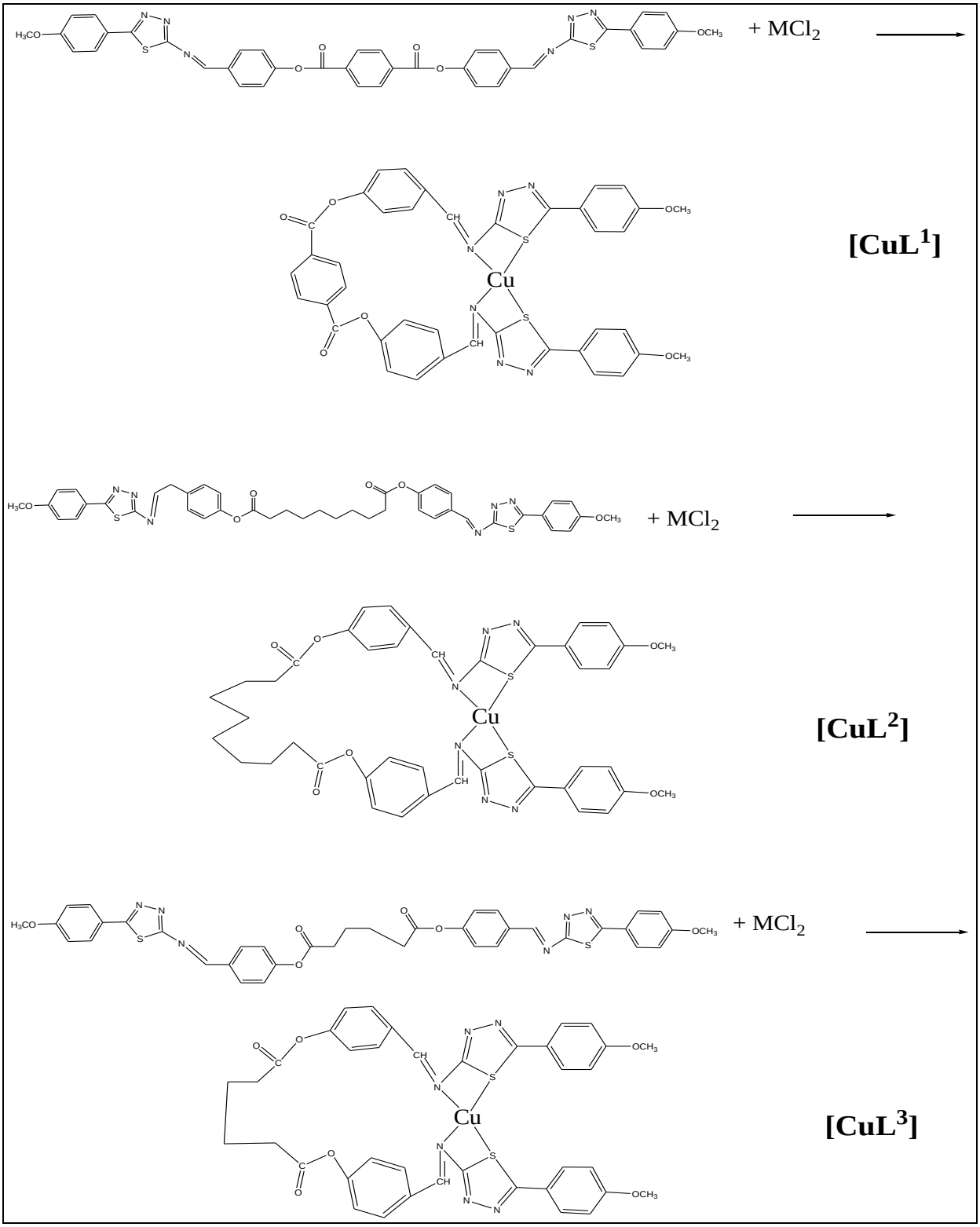


**COMPOUND -7-**

**Scheme (2), Synthesis route of compounds (5-7)**




Scheme (3), Copper (II) complexes