

# COPPER(II) AND ZINC(II) COMPLEXES OF REDUCED SCHIFF BASES AND THEIR CATALYTIC ACTIVITIES

## A DISSERTATION

*Submitted in partial fulfillment of the requirements for the award of the degree*

*of*

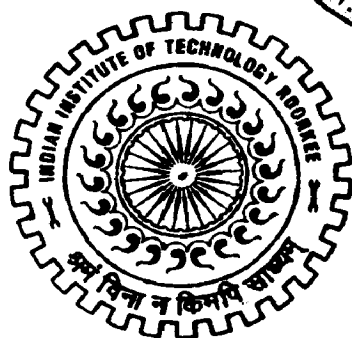
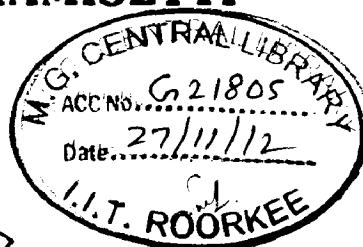
MASTER OF TECHNOLOGY

*in*

ADVANCED CHEMICAL ANALYSIS

*By*

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## CANDIDATE'S DECLARATION

I hereby certify that the work presented in report entitled, "**Copper(II) and Zinc(II) complexes of reduced Schiff bases and their catalytic activities**" has been carried out by me during the period from July 2011 to 15<sup>th</sup> June 2012 under the supervision of Prof. M. R. Maurya.

Date: 15/6/2012

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## CERTIFICATE

This is to certify that declaration made by the candidate is correct to the best of my knowledge and belief.

Date: 15 June, 2012

Place: IIT Roorkee

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*K. Pullaiah Naidu*  
(PULLAIH NAIDU KAMISSETTI)

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## ABSTRACT

The present dissertation describes the synthesis of copper and zinc metal complexes with reduced Schiff base ligands and their characterization by various physicochemical techniques. Styrene catalytic oxidation reaction has been carried out using these complexes as catalyst and suitable reaction conditions have been obtained for the maximum oxidation of styrene. The reaction products have been analyzed by gas chromatograph (GC).

For convenience the work presented in this dissertation has been divided in the following chapters.

First Chapter is the introduction and literature survey, About various copper and zinc complexes with Schiff base and reduced Schiff base ligands and their catalytic activity which are related to present work have been reported.

Second Chapter describes the synthesis of reduced Schiff base ligands viz, H<sub>2</sub>SGly (N(2-hydroxybenzyl)-Glycine) (**A**), H<sub>2</sub>SLue (N-(2-hydroxybenzyl)-Luesine) (**B**), H<sub>2</sub>SPhe (N-(2-hydroxybenzyl)-phenylalanine) (**C**) and Third Chapter is devoted on the synthesis of copper(II) complexes viz, [Cu<sub>2</sub>(Sgly)<sub>2</sub>].H<sub>2</sub>O (**D**), [Cu<sub>2</sub>(Slue)<sub>2</sub>].H<sub>2</sub>O (**E**) and [Cu<sub>2</sub>(Sphe)<sub>2</sub>].H<sub>2</sub>O (**F**). Characterization of these ligands and complexes are achieved by various physicochemical techniques, IR, UV, TGA and VSM. The copper complexes (D, E, F) are found to be active catalysts for the oxidation of styrene using H<sub>2</sub>O<sub>2</sub> as an oxidant. Under optimized reaction conditions we have found that the order of percentage conversion of styrene oxidation with various (D, E, F) catalysts is F (95%) > D (82%) > E (79%).

Chapter four deals with zinc complexes with above mentioned reduced Schiff base ligands (A, B, C). This chapter describes synthesis and characterizations of zinc complexes viz, Zn<sub>2</sub>(Sgly)<sub>2</sub>].H<sub>2</sub>O (**G**), Zn<sub>2</sub>(Slue)<sub>2</sub>].H<sub>2</sub>O (**H**), Zn<sub>2</sub>(Sphe)<sub>2</sub>].H<sub>2</sub>O (**I**). We have also studied the catalytic activity of zinc complexes on styrene oxidation under same

optimized conditions which were used for copper complexes (**D, E, F**). It was found that zinc complexes (**G, H, I**) are not show good catalytic active compared to copper complexes (**D, E, F**).

Finally, it is concluded that copper complexes (**D, E, F**) are good catalyst than zinc complexes (**G, H, I**) for styrene oxidation.



# CHAPTER 1

## INTRODUCTION AND LITERATURE SURVEY

### 1.1 General introduction

Catalysis is the change in rate of a chemical reaction due to the participation of a substance called a catalyst. Berzelius introduced the term catalyst in 1835. Catalysts activate the molecules to bind with it at milder conditions where they react and finally products separate out leaving the catalyst for the next cycle.

The catalytic reactions occur at the specific sites called active sites and rate of the reaction can be significantly improved by enhancing the surface area of the catalyst which in turn enhances the availability of the active sites. Normally, the speed of the catalytic reaction is presented in terms of a "Turn-over Rate"(TOF), which is defined as number of moles of substrate converted on an active site or on a unit catalytic surface area per second at a given condition.

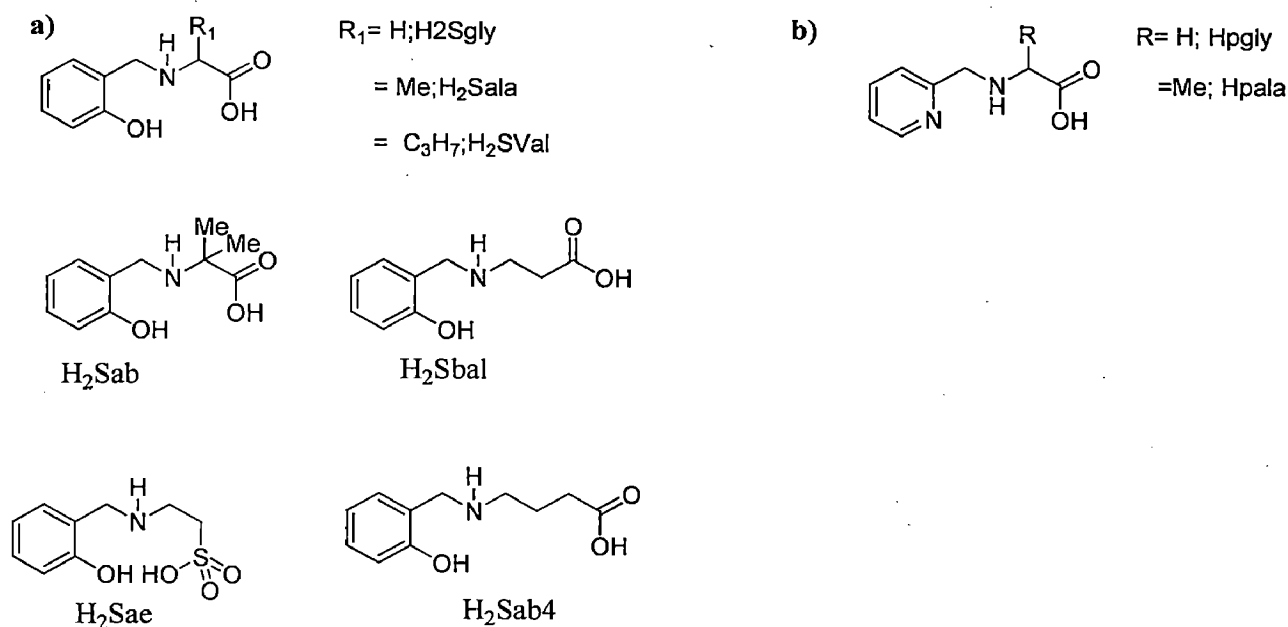
Catalysts can be either heterogeneous or homogeneous, depending on whether a catalyst exists in the same phase as the substrate. Biocatalysts (enzymes) are often seen as a separate group. Homogeneous catalysis is a sequence of reactions that involve a catalyst in the same phase as the reactants. Most commonly, a homogeneous catalyst is co-dissolved in a solvent with the reactants. Heterogeneous catalysis refers to the form of catalysis where the phase of the catalyst differs from that of the reactants. Phase here refers not only to solid, liquid, gas, but also immiscible liquids, e.g. oil and water. The great majority of practical heterogeneous catalysts are solids and the great majority of reactants are gases or liquids. Catalysis plays a major role in improving our atmosphere and reducing pollution. Catalytic oxidation is an effective way to control air pollution. In recent years, the use of catalytic oxidation has been investigated for a variety of applications, such as the control or removal of CO, NO, volatile organic compounds (VOCs), automobile exhaust emissions, by-products from chemical production, and toxic organics in wastewater. While thermal oxidation requires temperatures in excess of 1023

Another transition metal of considerable interest is zinc. For example, carboxypeptidase A and thermolysin are Zn(II)-metalloenzymes that catalyze the hydrolysis of peptides and O-acyl derivatives of  $\alpha$ -hydroxycarboxylic acids. The zinc cation in the active site adopts a tetrahedral coordination geometry attached to the protein backbone by three amino acid residues, two histidine imidazoles and aspartate or glutamate carboxylate, with the fourth coordination site occupied by a water molecule. The ubiquity of zinc in metalloenzymes chemistry has been related to its flexible coordination chemistry, substitutional lability, Lewis acidity, intermediate polarizability and lack of redox activity [4]. Due to high Lewis acidity, nucleophile generation, and leaving group stabilization, zinc(II) is the most common metal ion in the active site of hydrolytic metalloenzymes. Thus, zinc(II) complexes are very useful tools for studying the mode of catalysis of the phosphate diester cleavage in hydrolytic processes, including DNA cleavage [5].

## 1.2. Literature survey

### 1.2.1 Schiff base and reduced Schiff base ligands

Metal coordination compounds derived from several closely related yet different multidentate reduced Schiff base ligands (obtained by reducing the C=N bond in the Schiff bases formed by the condensation of aldehydes and various natural/unnatural amino acids). These multidentate ligands have flexible backbone with hydrogen bond donors and acceptors, and readily form metal complexes and coordination polymers with metal ions such as Cu(II), Zn(II), and Ni(II). In the past decades, significant progress has been achieved in understanding the chemistry of transition metal complexes with Schiff base ligands composed of salicylaldehyde or analogues and  $\alpha$ -amino acids [6]. Schiff base ligands mainly act as tridentate moiety, coordinating through the phenolato oxygen, imine nitrogen, and carboxylate oxygen. The metal complexes containing Schiff bases are the most fundamental chelating systems in coordination chemistry [7]. Casella and Gullotti have shown that Schiff bases formed by amino acids with non-polar side chains



**Figure 1.** Reduced Schiff base ligands a) *N*-(2-hydroxybenzyl)-amino acids and b) *N*-(2-pyridylmethyl)-amino acids.

Apart from the reduced Schiff base ligands with carboxylate donor group, their sulfonic acid analogues are expected not only to improve the solubility in aqueous media but also form interesting supramolecular architectures by modifying the connectivity at the metal centers as well as the hydrogen bonding pattern. In this context, dinuclear copper (II) complexes of *N*-(2-hydroxybenzyl)-amino methane/ethane sulfonic acids in the form of both Schiff base and reduced Schiff base ligands have been employed. A striking difference observed is that the Schiff bases  $\text{H}_2\text{Sams}$  and  $\text{H}_2\text{Saes}$  furnished eight membered dicopper (II) centers with the sulfonate group as bridging moiety where as the reduced Schiff bases  $\text{H}_2\text{Sam}$  and  $\text{H}_2\text{Sae}$  formed the phenoxo bridged  $\text{Cu}_2\text{O}_2$  cores. Herein, different structural features between Schiff base and reduced Schiff base dicopper (II) complexes have been highlighted.

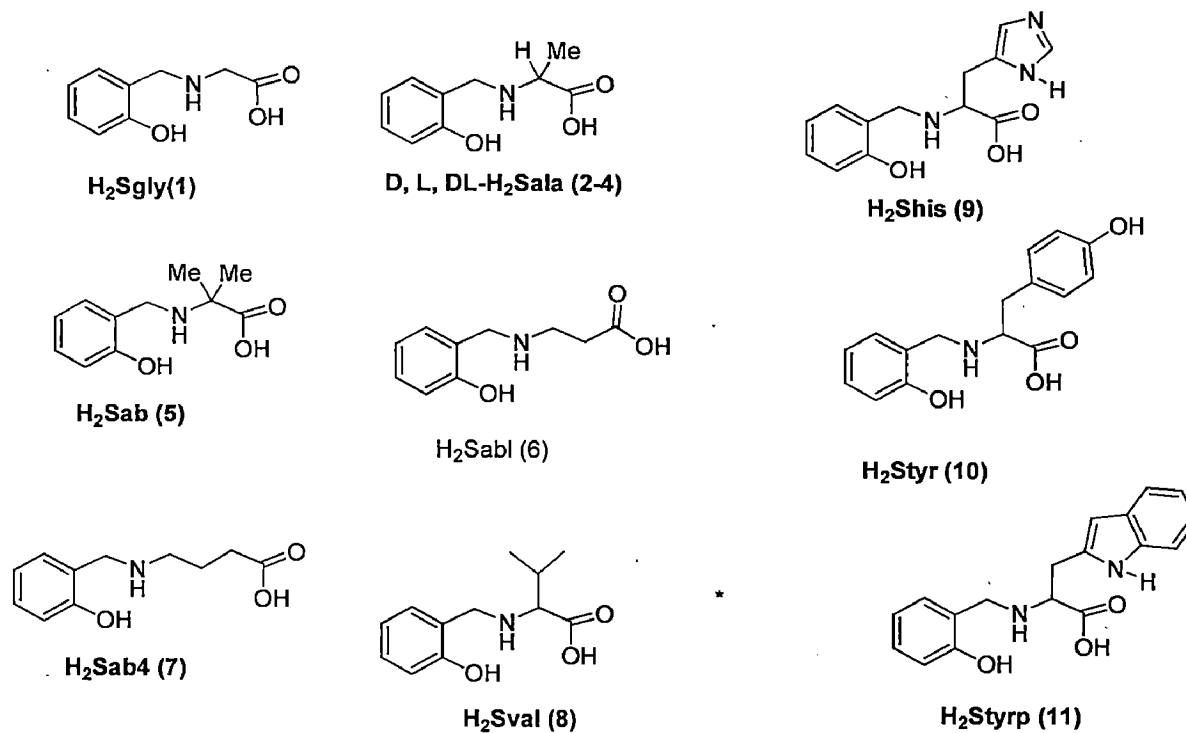
The change in complexation behavior that may occur by the reduction of C=N bond in Schiff base species is illustrated by the two Cu(II) complexes,  $[\text{Cu}_2(\text{Saes})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$  and  $[\text{Cu}_2(\text{Sae})_2] \cdot 2\text{H}_2\text{O}$  containing the Schiff base,  $\text{Saes}^{2-}$  and the corresponding reduced Schiff base, respectively (as shown in Figure 2a) [10].

tridentate ligand binding mode of these ligands [12-13]. Transition metal complexes of N-(2-hydroxysalicylidene)-amino acid ligands have been shown to behave analogously to those of pyridoxal-amino acid Schiff bases [14]. In addition, several Cu(II), Zn(II), Ni(II) and Co(II) complexes of Schiff base ligands formed between pyridoxal or analogues and amino acids have been shown to exhibit analgesic, anti-inflammatory, anti-biotic, antimicrobial and in particular, anti-cancer activities [15].

In view of the significant role as key intermediates in many metabolic reactions of amino acids, considerable efforts have been made to study the coordination chemistry of various transition metal ions derived from salicylaldehyde-amino acid Schiff base ligands [16]. N-(2-hydroxysalicylidene)-amino acid-metal ion mixtures were found to form a series of complexes with different compositions in solution which are qualitatively similar to those found for pyruvate and glyoxalate [17]. Quantitatively, the N-(2-hydroxysalicylidene)-amino acids have a considerably higher affinity for metal ions than do the aliphatic Schiff bases owing to the higher affinity of salicylaldehyde anion itself over pyruvate and glyoxalate for metal ions, and also due to the less steric interference offered by the planar aromatic rings.

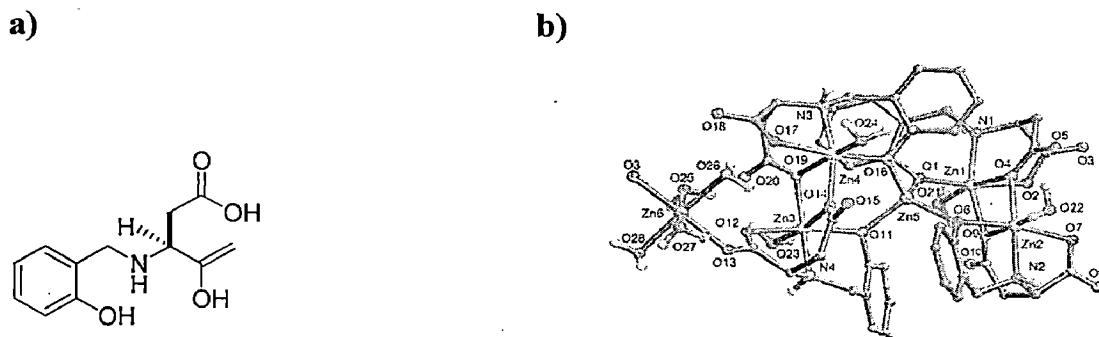
There has also been considerable interest in the study of Cu(II) Schiff base complexes as model compounds of galactose oxidase which is a stereospecific non-blue copper containing metalloenzyme that catalyzes the oxidation of D-galactose and primary alcohols to the corresponding aldehyde [17]. Butcher *et al.* reported the structures of Schiff base Cu(II) complexes derived from L-phenylalanine as models for galactose oxidase [18].

X. Wang *et al.* reported copper(II) complexes containing the reduced schiff base ligands, namely, N-(2-hydroxybenzyl)-glycinamide (Hsglym) and N-(2-hydroxybenzyl)-L-alaninamide (Hsalam) and characterized. The crystal structures of  $[\text{Cu}_2(\text{sglym})_2\text{Cl}_2]$ ,  $[\text{Cu}_2(\text{sa-lam})_2(\text{NO}_3)_2]\cdot\text{H}_2\text{O}$ ,  $[\text{Cu}_2(\text{salam})_2(\text{NO}_3)(\text{H}_2\text{O})](\text{NO}_3)\cdot 1.5\text{H}_2\text{O}$ ,  $[\text{Cu}_2(\text{salam})_2](\text{ClO}_4)_2\cdot 2\text{H}_2\text{O}$  show that the Cu(II) atoms are bridged by two phenolato oxygen atoms

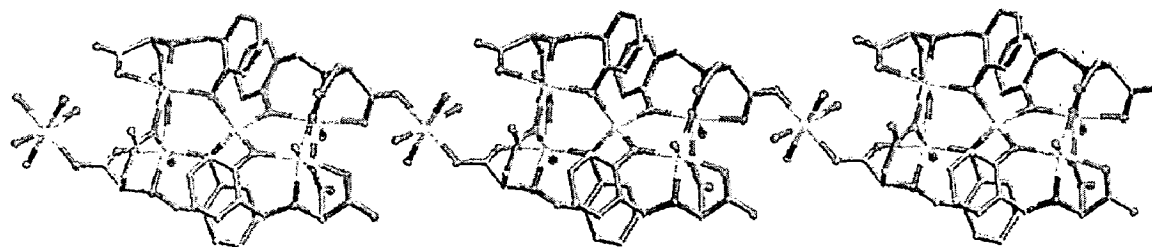


**Scheme 1.2.** Reduced Schiff base ligands. The numbers of the corresponding Cu(II) complexes  $[\text{Cu}_2\text{L}_2(\text{H}_2\text{O})_x] \cdot y\text{H}_2\text{O}$  of these ligands.

K. K. Raja *et al.* have reported the catalytic activity of the complexes,  $\text{M}(\text{X-DPMP})_2$ ,  $\text{DPMP} = 2-[(2,6\text{-diisopropylphenylimino)methyl}]$  phenol,  $\text{X} = \text{Br}, \text{Cl}, \text{I}, \text{BrCl}$  and  $\text{M} = \text{Cu(II)}, \text{Ni(II)}$  or  $\text{Co(II)}$ . The Schiff bases behave as monobasic bidentate ligand in their complexes as shown in Figure 3. Out of these Cu(II), Ni(II) and Co(II) complexes,  $\text{Cu}(\text{Br-DPMP})_2$  was found to be an efficient catalyst for cyanosilylation of aldehydes under mild conditions [20].



**Figure 4.** a) Structural diagram of the H<sub>3</sub>Sas ligand. b) Perspective view of the repeating unit of the coordination polymer [Zn<sub>6</sub>(Sas)<sub>4</sub>(H<sub>2</sub>O)<sub>8</sub>].5H<sub>2</sub>O is shown and all the C–H hydrogen atoms are omitted for clarity.

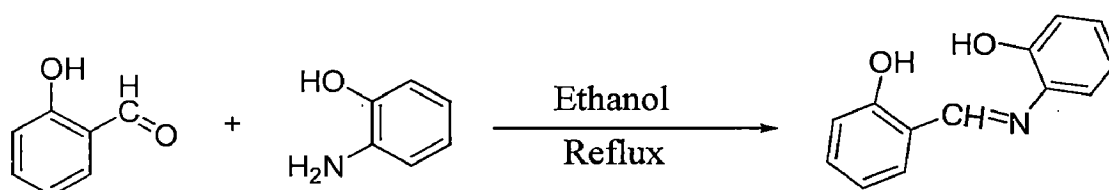


**Figure 5.** A portion of the 1D polymeric chain of [Zn<sub>6</sub>(Sas)<sub>4</sub>(H<sub>2</sub>O)<sub>8</sub>].5H<sub>2</sub>O.

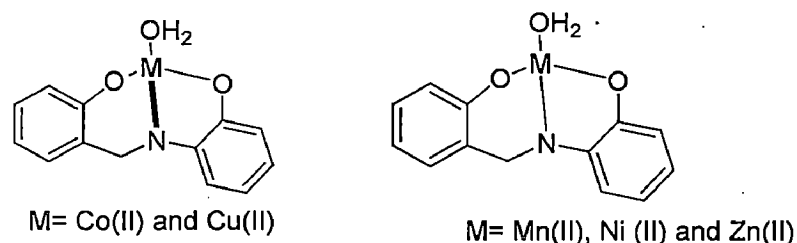
John D. Ranford *et al.* reported crystal structure of [ $\{Zn(sala)(H_2O)_2\}_2\} \cdot 2H_2O$ . [ $\{Zn(sala)(H_2O)_2\}_2\} \cdot 2H_2O$  (Figure 6) was prepared by the reaction of  $Zn(ClO_4)_2 \cdot 6H_2O$  with  $Li_2(sala)$  in aqueous solution, here  $(H_2(sala))$  is N-(2-hydroxybenzyl)-L-alanine [22].

European system Mn(II) has the greatest reduction potential ( $E_0 = 1.18$  V), which explained the highest catalytic activity of its complex and 2) with respect to other metals, the trend in catalytic activity may be explained on the possibility of fact that Mn has variable oxidation states, which enhanced electron transfer through oxidation reactions and this fact was supported by negligible activity of Zn complex, where Zn(II) is limited to oxidation state (+2) [23].

a)

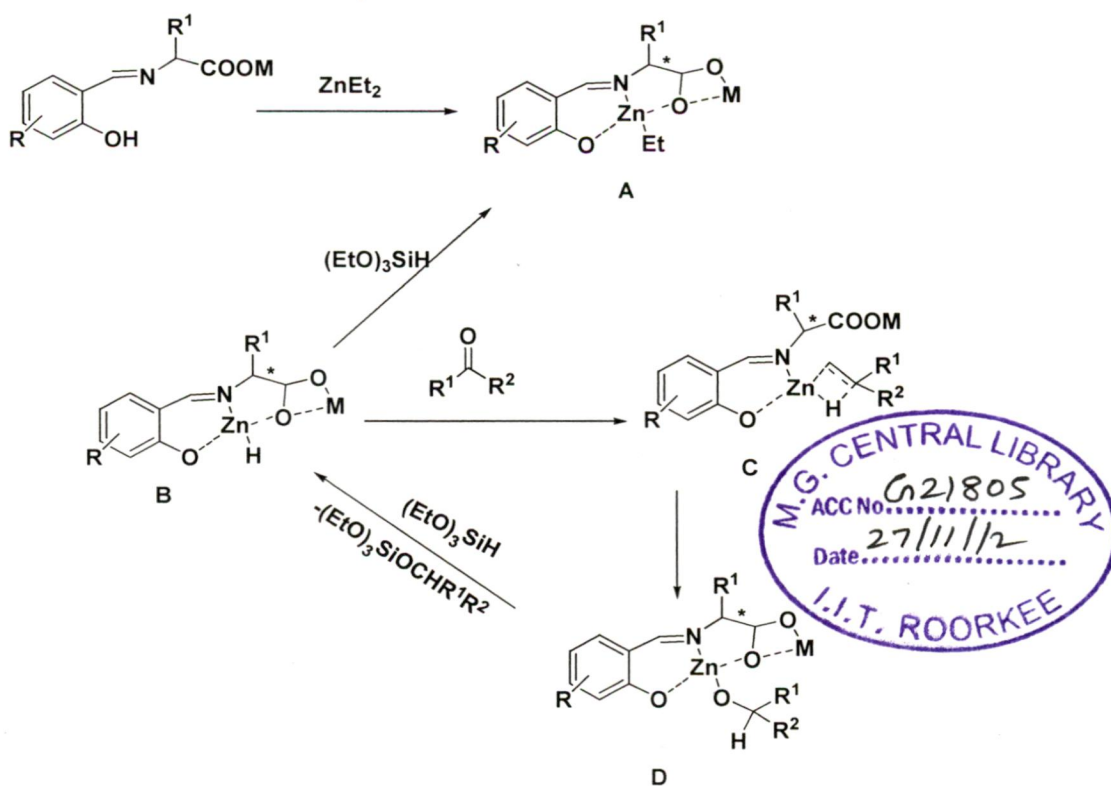


b)



**Scheme 1.3.** a) Synthetic route of N-salicylidene-o-aminophenol (saphH<sub>2</sub>) and b) The proposed structure of salicylidene N-salicylidene-o-aminophenol complexes.

Chiral secondary alcohols are important chiral building blocks in synthetic organic chemistry, especially in the preparations of pharmaceuticals, flavor and fragrance. Recently S. Liu *et al.* reported that enantioselective reduction of ketones by HSi(OEt)<sub>3</sub> was catalyzed with diethylzinc coordinated with Schiff bases ligands derived from substituted salicylaldehydes and inexpensive chiral  $\alpha$ -amino acids **1-9** (figure 7). They have concluded that ligand plays an important role on the catalytic activity and the enantioselectivity. The substituents attached on aromatic ring of substituted salicylaldehyde have a great impact on ees. The -COOK group derived from chiral  $\alpha$ -amino acids plays crucial role on the catalytic properties, as-COONa and -COOLi



**Scheme 1.4.** Proposal mechanism of hydrosilylation of ketones catalyzed with  $\text{ZnEt}_2$ /Schiff base.

Biodiesel (a mixture of Fatty Acid Methyl Esters, FAME) is the second most common biofuel produced in the world. Biodiesel is produced by the transesterification of triglycerides of refined/edible type oils using methanol and an alkaline homogeneous catalyst ( $\text{NaOH}$ ,  $\text{NaOMe}$ ): the reaction is normally performed at  $60\text{--}80^\circ\text{C}$ , but homogeneous alkaline catalysts cannot be used directly with waste oils due to the presence of large amounts of free fatty acids (FFA).

Several methods have been proposed to solve this problem; one of these solutions is to use either a homogeneous or heterogeneous acid catalyst which can catalyze the esterification of FFA and trans esterification of glycerides. Recently M. Di Serio *et al.* have prepared zinc (II) compounds containing functionalized Schiff bases (see Scheme 1.5) and reported that these complexes catalyze the transesterification of soybean oil in mild conditions, and their activity can be modulated by a fine selection of the anions



### 1.3 Scope of the present investigation

In the present investigation, it is proposed to prepare three reduced Schiff base ligands and to synthesize their coordination chemistry with the transition metals especially Cu and Zn.

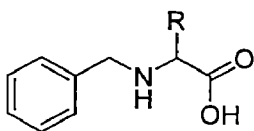
The reduced Schiff base chosen for this project has the following advantages:

1. They are easy to prepare from the commercially available cheap starting materials.
2. The Schiff base formed between salicylaldehyde and amino acids have rigid structure while reduced Schiff base ligands are very flexible.
3. Further this multidentate ligand has been shown to form the expected neutral dimer and make the axial position of the metal centers available for further binding.

Of these, Cu (II) and Zn (II) have attracted our attention for the following reasons:

1. They are divalent ions and hence form expected 1:1 neutral compounds with reduced Schiff base ligands.
2. They are suitable to form complexes with ligands having O and N donors.
3. They can adopt variable coordination number (from 4 to 6) and geometry which are suitable for accommodating aqua ligands.

We have synthesized reduced Schiff base ligands of salicylaldehyde with glycine ( $H_2SGly$ ,  $R=H$ ), leucine ( $H_2SLeu$ ,  $R=CH_2CH(CH_3)_2$ ), phenylalanine ( $H_2SPhe$ ,  $R=CH_2C_6H_5$ ).



$R=H$  ( $H_2SGly$ ),  $R=CH_2CH(CH_3)_2$  ( $H_2SLeu$ ),  $R=CH_2C_6H_5$  ( $H_2SPhe$ )

## CHAPTER 2

### SYNTHESES OF REDUCED SCHIFF BASE LIGANDS

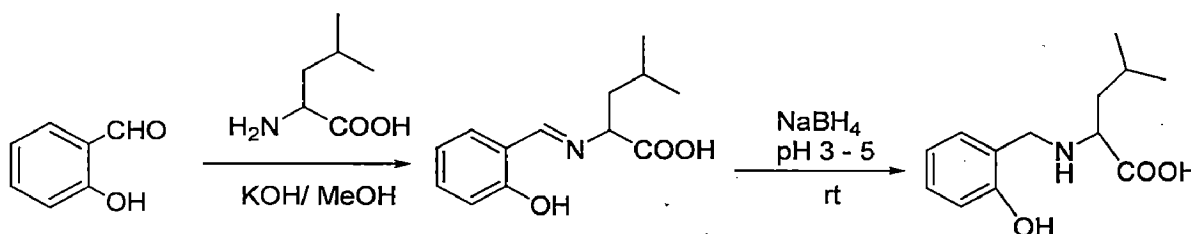
#### 2.1 Experimental

##### 2.1.1 Materials

SERIAL NO.	CHEMICALS	GRADES	COMPANY
1	METHANOL	AG	SRL
2	ETHANOL	AG	C.Y.CHEMICALS, CHINA
3	ACETONITRILE	HPLC	RANKEM
4	30% H <sub>2</sub> O <sub>2</sub>	Extra pure AR	RANKEM
5	NaOH		SRL
6	DMF	L.R	RANKEM
7	DMSO	L.R	RANKEM
8	SALICYLALDEHYDE	Extra pure AR	SRL
9	GLYCINE	Extra pure CHR	SRL
10	L-LUECINE	Extra pure AR	LOBA-CHEMIE
11	L-PHENYL ALANINE	PURE	HIMEDIA
12	Zn(CH <sub>3</sub> COO) <sub>2</sub>	PURE	MERCK
13	Cu(CH <sub>3</sub> COO) <sub>2</sub>	PURE	MERCK
14	KOH	LR	SRL
15	HCl	LR	RANKEM
16	NaBH <sub>4</sub>	LR	HIMEDIA
17	STYRENE	A.R.	HIMEDIA
18	BaSO <sub>4</sub>	PURE	MERCK

### (B) N-(2-hydroxybenzyl)-Luesine, H<sub>2</sub>SLue

Salicylaldehyde (1.20 g, 10 mmol) in ethanol (10 ml) was added to a solution of luesine (1.312g, 10 mmol) and KOH (0.56 g, 10 mmol) in water (10 ml). The obtained yellow solution was heated on a water bath for 30 min and then cooled in ice bath. The NaBH<sub>4</sub> (0.46 g, 12 mmol) was added to the yellow solution. After 10 min the yellow colour slowly discharged, and the solution was acidified with concentrated HCl to pH 3.5-5.0 and left for one hour. The resulting solid was filtered off, washed with distilled water, ethanol followed by diethyl ether, and dried in vacuo. Yield: 57%.



**Scheme 2.2** Reaction scheme for preparation of N-(2-hydroxybenzyl)-Luesine (H<sub>2</sub>SLue)

### (C) N-(2-hydroxybenzyl)-phenyl alanine, H<sub>2</sub>SPhe

Salicylaldehyde (1.20 g, 10 mmol) in ethanol (10 ml) was added to a solution of phenyl alanine (1.692g, 10mmol) and KOH (0.56 g, 10 mmol) in water (10 ml). The obtained yellow solution was heated on a water bath for 30 min and then cooled in ice bath. The NaBH<sub>4</sub> (0.46 g, 12 mmol) was added to the yellow solution. After 10 min the yellow colour slowly discharged, and the solution was acidified with concentrated HCl to pH 3.5-5.0 and left for one hour. The resulting solid was filtered off, washed with distilled water, ethanol followed by diethyl ether, and dried in vacuo. Yield: 86%.

symmetric stretching vibration of the carboxylate group [ $\nu_s(\text{COO}^-)$ ]. The band around the 1259–1285  $\text{cm}^{-1}$  can be assigned to  $\nu(\text{C}-\text{O})$  of phenolic group in ligands (see Figure 11-13).

**Table 2.3** IR spectral data of reduced Schiff base ligands.

Compound	$\nu(\text{OH})$	$\nu(\text{NH})$	$\nu_{\text{as}}(\text{COO}^-)$	$\nu_s(\text{COO}^-)$	$\nu(\text{CO})$ (Phenolic)
H <sub>2</sub> SGly (A)	3435	2963	1573	1365	1279
H <sub>2</sub> Slue (B)	3415	2958	1599	1385	1260
H <sub>2</sub> SPhe (C)	3425	2957	1622	1391	1268

### 2.3.2 Electronic spectral studies of reduced Schiff base ligands

Due to poor solubility of ligands, the diffused reflectance spectra could only be recorded. These reflectance spectra (see Table 3.3 and Figure 20-22) provide very useful information for the ligands. All ligands show two bands at ca. 355 and at ca. 240 nm due to  $n \rightarrow \pi^*$  and  $\pi \rightarrow \pi^*$  transitions, respectively.

**Table 3.3** Electronic spectral data

Ligand	Wave length (nm)	
	Band 1	Band 2
H <sub>2</sub> SGly(A)	357	232
H <sub>2</sub> Slue (B)	354	243
H <sub>2</sub> SPhe (C)	357	245

## CHAPTER 3

### COPPER(II) COMPLEXES WITH REDUCED SCHIFF BASE LIGANDS

#### 3.1 Experimental

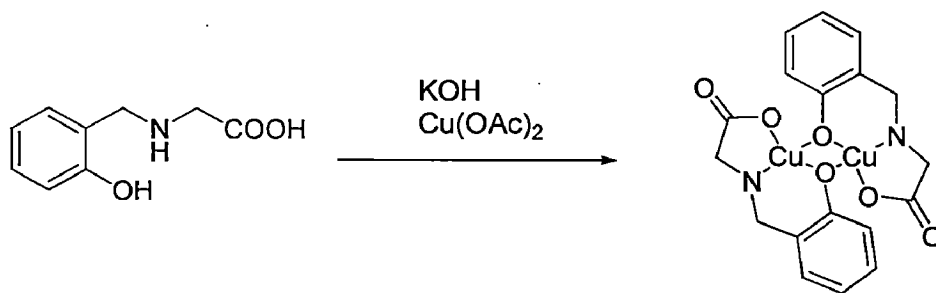
##### 3.1.1 Materials and methods

Material and methods are already mentioned in Chapter 2 (see 2.1.1).

##### 3.1.2 Syntheses of copper(II) complexes

###### (D) $[\text{Cu}_2(\text{Sgly})_2]\cdot\text{H}_2\text{O}$

$\text{H}_2\text{SGly}$  (0.181 g, 1.0 mmol) and KOH (0.056 g, 1.0 mmol) were stirred in methanol (10 ml) for 30 min, and then the reaction mixture was filtered. The filtrate was added to a solution of  $\text{Cu}(\text{CH}_3\text{COO})_2\cdot\text{H}_2\text{O}$  (0.200 g, 1.0 mmol) in methanol (10 ml) and stirred for 2 h which gave a light green product. This was filtered off and washed with water, ethanol, and diethyl ether before drying in Vacuo. Yield: 42 %.



**Scheme 3.1** Reaction scheme for preparation of  $[\text{Cu}_2(\text{Sgly})_2]\cdot\text{H}_2\text{O}$

###### (E) $[\text{Cu}_2(\text{Slue})_2]\cdot\text{H}_2\text{O}$

$\text{H}_2\text{SLue}$  (0.237 g, 1.0 mmol) and KOH (0.056 g, 1.0 mmol) were stirred in methanol (10 ml) for 30 min, and then the reaction mixture was filtered. The filtrate was added to a solution of  $\text{Cu}(\text{CH}_3\text{COO})_2\cdot\text{H}_2\text{O}$  (0.200 g, 1.0 mmol) in methanol (10 ml) and

### 3.1.3 Catalytic reactions of copper(II) complexes

The catalytic reaction was carried out in a 50 ml two necked round bottomed flask equipped with an oil bath and reflux condenser. Styrene (1.04 g, 10 mmol) was dissolved in 7 ml of acetonitrile followed by the addition of 30 % hydrogen peroxide (3.405 g, 30 mmol) as an oxidant and catalyst  $[\text{Cu}_2(\text{Sgly})_2] \cdot \text{H}_2\text{O}$ . The reaction was carried out in an oil bath with continuous stirring while maintaining the reaction temperature at 80 °C. The process of the reaction was monitored by withdrawing the samples at definite time intervals (1h) and analyzing quantitatively through Shimadzu 2010 gas chromatograph equipped with Rtx-1 column (30 m × 0.25 mm × 0.25 μm) and FID detector. Selectivity of different products were made on the basis of the relative peak area of the respective product and the identity of the products was confirmed using a GC-MS model Perkin-Elmer, Clarus 500 and comparing the fragments of each product with the library available.

$$\text{Conversion of reactants into products (\%)} = \frac{\text{Area of all products} \times 100}{\text{Area of reactants} + \text{Area of products}}$$

$$\text{Selectivity of a particular product} = \frac{\text{Area of a particular products} \times 100}{\text{Total Area of products}}$$

### 3.2 Elemental analysis of copper(II) complexes

Elemental analyses of complexes are presented in Table 3.1. The found analyses of different elements are in agreement with the respective calculated value. These data confirm the formulation of complexes.

**Table 3.2.** IR spectral data of copper complexes

Compound	$\nu(\text{OH})$	$\nu(\text{NH})$	$\nu_{\text{as}}(\text{COO}^-)$	$\nu_{\text{s}}(\text{COO}^-)$	$\nu(\text{CO})$ (Phenolic)
$[\text{Cu}_2(\text{Sgly})_2] \cdot \text{H}_2\text{O}$ (D)	3450	2953	1604	1381	1271
$[\text{Cu}_2(\text{Slue})_2] \cdot \text{H}_2\text{O}$ (E)	3442	2951	1629	1384	1274
$[\text{Cu}_2(\text{Sphe})_2] \cdot \text{H}_2\text{O}$ (F)	3430	2926	1618	1382	1263

### 3.3.2 Electronic spectral studies of Copper(II) complexes

Due to poor solubility of complexes, the diffused reflectance spectra could only be recorded for these copper complexes. However, these reflectance spectra provide very useful for the complexes particularly in the 350 - 900 nm regions. Thus, copper(II) complexes display a sharp band in the range 530-510 nm originating due to d - d transition for square planar geometry. In addition they show a medium intensity band in the region 360 - 350 nm due to ligand to metal charge transfer transition and the band in the region 240-225 nm due to  $\pi$  to  $\pi^*$  (see Table 3.3 and Figure 23-25) transition [26, 27, 28].

**Table 3.3.** Electronic spectral data of copper complexes

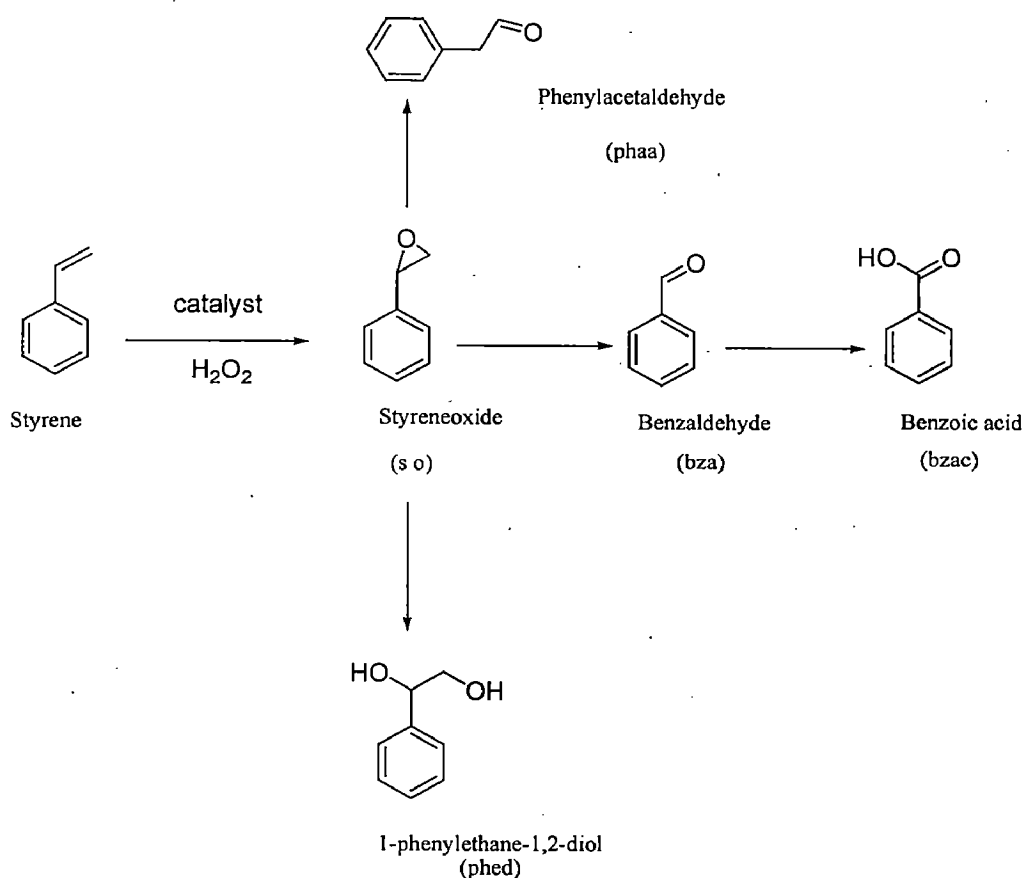
Copper complexes	Wave length (nm)		
	Band 1	Band 2	Band 3
$[\text{Cu}_2(\text{Sgly})_2] \cdot \text{H}_2\text{O}$	529	351	231
$[\text{Cu}_2(\text{Slue})_2] \cdot \text{H}_2\text{O}$	507	354	231
$[\text{Cu}_2(\text{Sphe})_2] \cdot \text{H}_2\text{O}$	507	352	229

### 3.3.3 Thermo gravimetric studies of Copper(II) complexes

Thermo gravimetric analysis of copper complexes was carried out under nitrogen atmosphere in the temperature range of room temperature to 900 °C (see Figure 29-31).

### 3.3.5 Catalytic activity studies of Copper(II) complexes

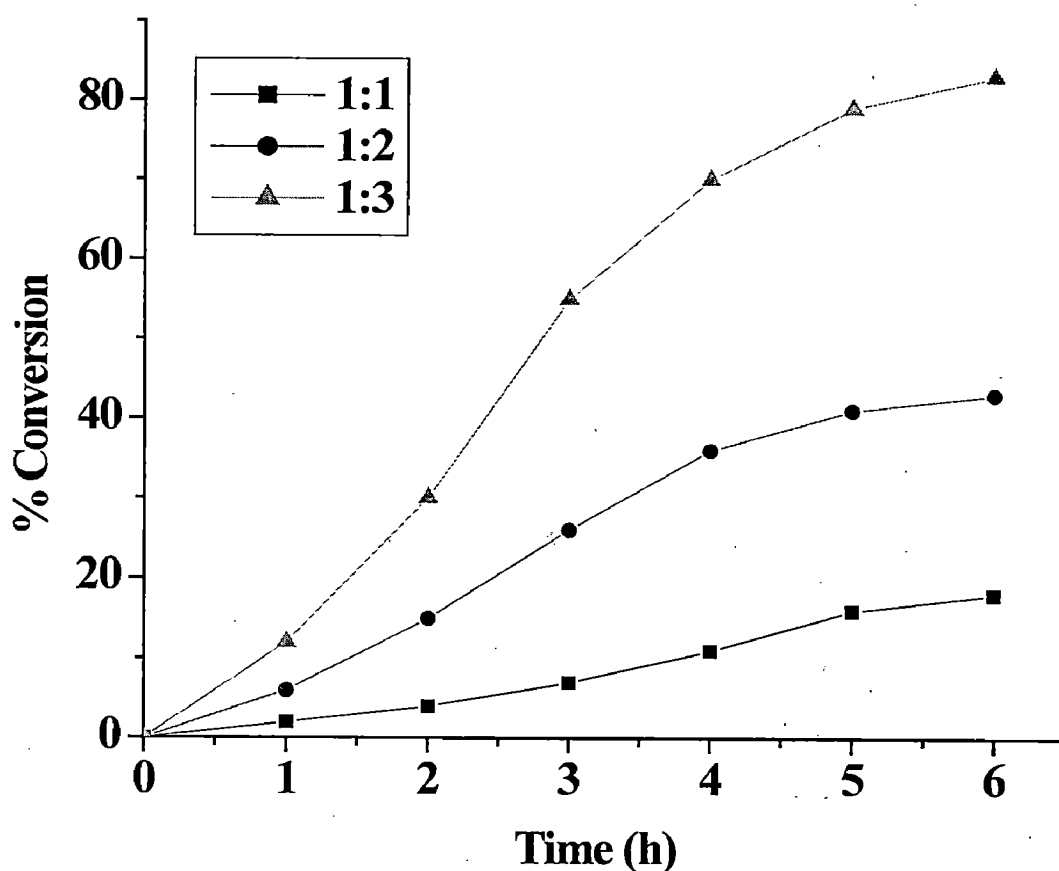
Copper(II) complexes of reduced Schiff base ligands have been used for the oxidation of styrene in presence of  $H_2O_2$  and gave styrene oxide, benzaldehyde, benzoic acid, 1-phenylethane-1,2-diol and phenylacetaldehyde along with a small amount of unidentified product (see Scheme 3.4). These oxidation products have been obtained by others as well [29, 30]. The reaction conditions were optimized considering  $[Cu_2(Sgly)_2].H_2O$  as catalyst for the maximum oxidation of styrene by studying four different parameters, viz., the effect of amount of oxidant (moles of  $H_2O_2$  per mole of styrene), catalyst (amount of catalyst per mole of styrene), temperature and solvent volume of the reaction mixture in detail.



**Scheme 3.4.** Various oxidation products of styrene.



The effect of oxidant was studied considering styrene to aqueous 30% H<sub>2</sub>O<sub>2</sub> ratios of 1:1, 1:2 and 1:3 where the mixture of styrene (1.04 g, 10 mmol), catalyst (0.010 g) and oxidant were taken in 5 ml CH<sub>3</sub>CN and the reaction was carried out at 80 °C. As illustrated in Figure 3.2, the percent conversion of styrene increases from 18% to 83% on increasing the H<sub>2</sub>O<sub>2</sub>. Therefore, it suggesting that 1:3 (styrene : 30% H<sub>2</sub>O<sub>2</sub>) ratio is sufficient enough to perform the reaction with good conversion. (see Entry no. 3 – 5 of Table 3.4) analyze the percent conversion of styrene after 6 h of reaction time under above reaction conditions.



**Figure 9.** Effect of oxidant concentration on styrene oxidation. Reaction conditions: styrene (1.04 g, 10 mmol), catalyst (0.010 g), temperature 80 °C and acetonitrile (5 ml).

**Table 3.4.** Details of conditions applied for the oxidation of 10 mmol (1.04 g)styrene using  $[\text{Cu}_2(\text{Sgly})_2]\cdot\text{H}_2\text{O}$  as catalyst to complete the reaction in 6 h.

Entry No.	Amount of catalyst (g)	Oxidant (g, mmol)	$\text{CH}_3\text{CN}$ (ml)	Temp. ( $^\circ\text{C}$ )	Conversion %
1	0.005	2.27, 20	5	80	30
2	0.010	2.27, 20	5	80	43
3	0.015	2.27, 20	5	80	35
4	0.010	1.14, 10	5	80	18
5	0.010	3.41, 30	5	80	83
6	0.010	3.41, 30	7	80	82
7	0.010	3.41, 30	15	80	40

Thus under optimized reaction conditions, the maximum oxidation of 10 mmol (1.04 g) of styrene requires 0.010 g of catalyst, 30 mmol ((3.405 g) of aqueous 30%  $\text{H}_2\text{O}_2$ , 5 ml of acetonitrile and 80  $^\circ\text{C}$  temperature. Under this reaction condition,  $[\text{Cu}_2(\text{Sgly})_2]\cdot\text{H}_2\text{O}$  gave 83 % conversion of styrene where the selectivity of obtained reaction products follows the order: benzaldehyde (72%) > phenylacetaldehyde (14%) > benzoic acid (7%), 1-phenylethane-1,2-diol (3%) > styrene oxide (2%). Under similar conditions, other complexes i.e. complexes  $[\text{Cu}_2(\text{Slue})_2]\cdot\text{H}_2\text{O}$  and  $[\text{Cu}_2(\text{Sphe})_2]\cdot\text{H}_2\text{O}$  show 78% and 95% conversion, respectively. Selectivity of the reaction products follow the same order as shown by  $[\text{Cu}_2(\text{Sgly})_2]\cdot\text{H}_2\text{O}$  (see Figure 35-37). Table 3.5 summaries the conversion and selectivity data.

of the catalyst could be attributed to the facile formation of this  $\text{Cu}^{\text{III}}$ -peroxide intermediate species.

An alternative mechanism may be mentioned. The binding mode in complexes resembles that of e.g. Galactose oxidase, and may also support other mechanisms for peroxide acting as a hydroxylating agent [32]. Therefore, parallel alternative mechanism may operate, and this may possibly explain the high yield of benzaldehyde obtained in the oxidation of styrene by  $\text{H}_2\text{O}_2$ .

## CHAPTER 4

### ZINC(II) COMPLEXES WITH REDUCED SCHIFF BASE LIGANDS

#### 4.1 Experimental

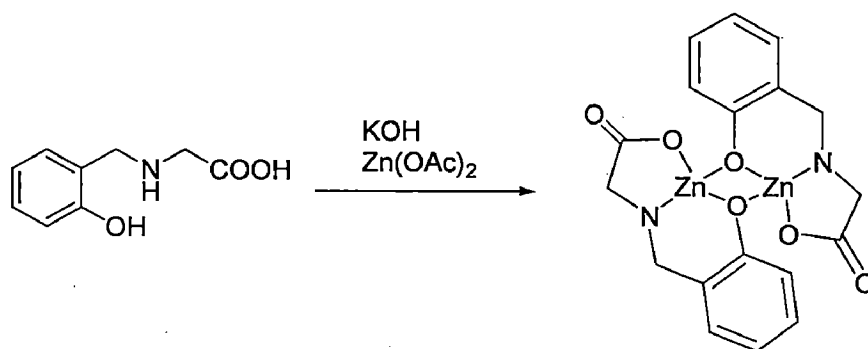
##### 4.1.1 Materials and methods

Material and methods were already mentioned in chapter 1 (see 2.1.1)

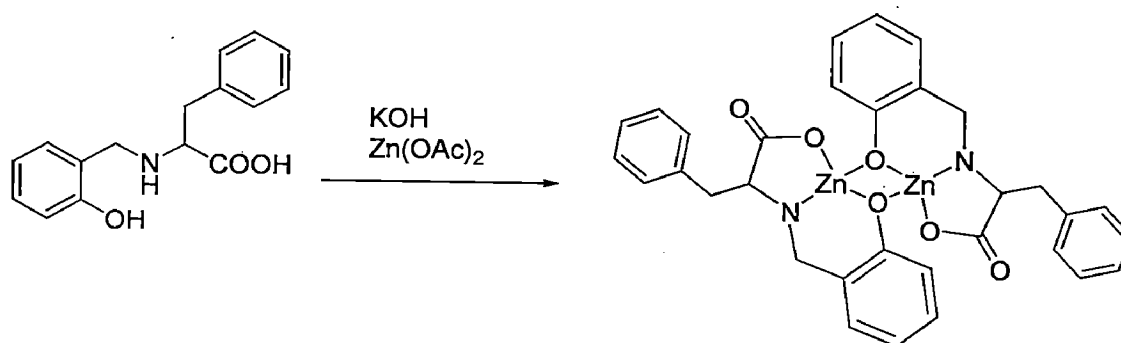
##### 4.1.2 Syntheses of Zinc(II) complexes

###### (G) $[\text{Zn}_2(\text{Sgly})_2] \cdot \text{H}_2\text{O}$

$\text{H}_2\text{Sgly}$  (0.181 g, 1.0 mmol) and  $\text{KOH}$  (0.056 g, 1.0 mmol) were stirred in methanol (10 ml) for 30 min, and then the reaction mixture was filtered. The filtrate was added to a solution of  $\text{Zn}(\text{CH}_3\text{COO})_2$  (0.220 g, 1.0 mmol) in methanol (10 ml) with stirring. After 1 h of stirring the precipitated white product was filtered, washed with water, ethanol, and finally with diethyl ether and dried in Vacuo. Yield: 41 %.



**Scheme 4.1** Reaction scheme for preparation of  $[\text{Zn}_2(\text{Sgly})_2] \cdot \text{H}_2\text{O}$ .



**Scheme 4.3** Reaction scheme for preparation of  $[\text{Zn}_2(\text{Sphe})_2] \cdot \text{H}_2\text{O}$ .

#### 4.1.3 Catalytic reactions of Zinc(II) complexes

The catalytic reaction was carried out in a 50 ml two necked round bottomed flask equipped with an oil bath and reflux condenser. Styrene (1.04 g, 10 mmol) was dissolved in 7 ml of acetonitrile and to this an amount of 0.010 g catalyst and 30 % hydrogen peroxide (3.405 g, 30 mmol) was added. The reaction was carried out in an oil bath with continuous stirring while maintaining the reaction temperature at 80 °C. The process of the reaction was monitored by withdrawing the samples at definite time intervals (1 h) and analyzing quantitatively through gas chromatograph Shimadzu 2010 equipped with Rtx-1 column (30 m × 0.25 mm × 0.25 μm) and FID detector. Selectivity of different products were made on the basis of the relative peak area of the respective product and the identity of the products was confirmed using a GC-MS model Perkin-Elmer, Clarus 500 and comparing the fragments of each product with the library available.

$$\text{Conversion of reactants into products (\%)} = \frac{\text{Area of all products} \times 100}{\text{Area of reactants} + \text{Area of products}}$$

$$\text{Selectivity of a particular product} = \frac{\text{Area of a particular products} \times 100}{\text{Total Area of products}}$$

the region 2895–2976  $\text{cm}^{-1}$  may be assigned to  $\nu(\text{NH})$ . The band in the region 1572–1615  $\text{cm}^{-1}$  is assigned to the asymmetric vibration of coordinated carboxylate group [ $\nu_{\text{as}}(\text{COO}^-)$ ] and the band in the region 1325–1397  $\text{cm}^{-1}$  is attributed to the symmetric stretching vibration of carboxylate group [ $\nu_{\text{s}}(\text{COO}^-)$ ]. The large difference between [ $\nu_{\text{as}}(\text{COO}^-)$ ] and [ $\nu_{\text{s}}(\text{COO}^-)$ ] in frequencies ( $\Delta\nu > 200 \text{ cm}^{-1}$ ) in all complexes is indicative of a monodentate coordination of carboxylate groups.

**Table 4.2** IR spectral data of zinc complexes

Compound	$\nu(\text{OH})$	$\nu(\text{NH})$	$\nu_{\text{as}}(\text{COO}^-)$	$\nu_{\text{s}}(\text{COO}^-)$	$\nu(\text{CO})$ (Phenolic)
$[\text{Zn}_2(\text{Sgly})_2] \cdot \text{H}_2\text{O}$	3424	2930	1624	1362	1273
$[\text{Zn}_2(\text{Slue})_2] \cdot \text{H}_2\text{O}$	3440	2957	1597	1383	1274
$[\text{Zn}_2(\text{Sphe})_2] \cdot \text{H}_2\text{O}$	3477	2925	1580	1356	1276

### 4.3.2 Electronic spectral studies of Zinc(II) complexes

The diffused reflectance spectral data of the zinc complexes are presented in Table 4.3 (see Figure 26 - 28). All zinc complexes display a medium intensity band in the region 350-370 nm which assigned to ligand to metal charge transfer band. In addition a ligand band is observed in the region 230-240 nm in all zinc complexes which is possibly due to  $\pi$  to  $\pi^*$  transition. As expected no d – d transition was observed in these complexes due to  $3d^{10}$  electronic configuration of zinc in these complexes.

**Table 4.3** Electronic spectral data of zinc complexes

Zinc complexes	Wave length (nm)	
	Band 1	Band 2
$[\text{Zn}_2(\text{Sgly})_2] \cdot \text{H}_2\text{O}$	358	234
$[\text{Zn}_2(\text{Slue})_2] \cdot \text{H}_2\text{O}$	365	237
$[\text{Zn}_2(\text{Sphe})_2] \cdot \text{H}_2\text{O}$	366	235

## Conclusions

We have synthesized copper and zinc metal complexes with reduced Schiff base ligands and characterized by various physicochemical techniques e.g. elemental analyses, IR, DRS and TGA. All the complexes are insoluble in common solvents showing their binuclear nature in the solid state. All copper (II) complexes (D, E and F) show significantly high catalytic activity on the oxidation of styrene. Under optimized reaction conditions the order of percentage conversion of styrene oxidation with various copper (D, E and F) catalysts is: F (95%) > D (82%) > E (79%) and selectivity of the styrene oxidation products followed the order: benzaldehyde (72%) > phenylacetaldehyde (14%) > benzoic acid (7%), 1-phenylethane-1,2-diol (3%) > styrene oxide (2%). We have also studied the catalytic activity of zinc complexes (G, H and I) on styrene oxidation under same optimized conditions which are carried out for copper complexes (D, E and F) catalytic activity on styrene oxidation, but zinc complexes (G, H and I) do not show good catalytic activity compare to copper complexes (D, E and F). It may happened because of two reasons i) Cu(II) has the greatest reduction potential, which explained the highest catalytic activity of its complex and ii) copper has variable oxidation states (+1,+2), which enhanced electron transfer through oxidation reactions and this fact was supported by negligible activity of Zn complex, where Zn(II) is limited to oxidation state (+2) and low reduction potential compare to Cu(II) [21].

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# SPECTRA

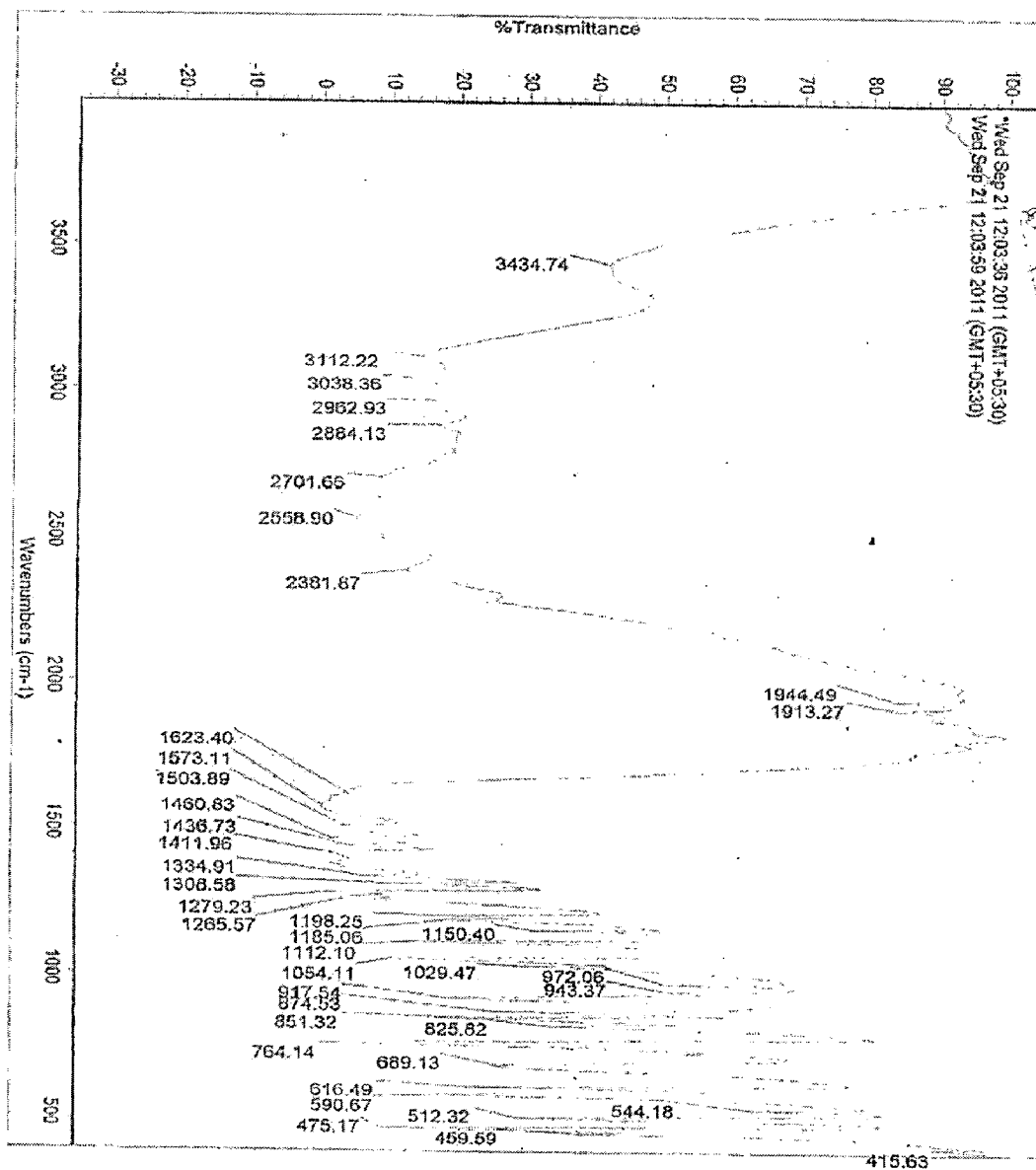


Figure 11. IR spectrum of H<sub>2</sub>SGly

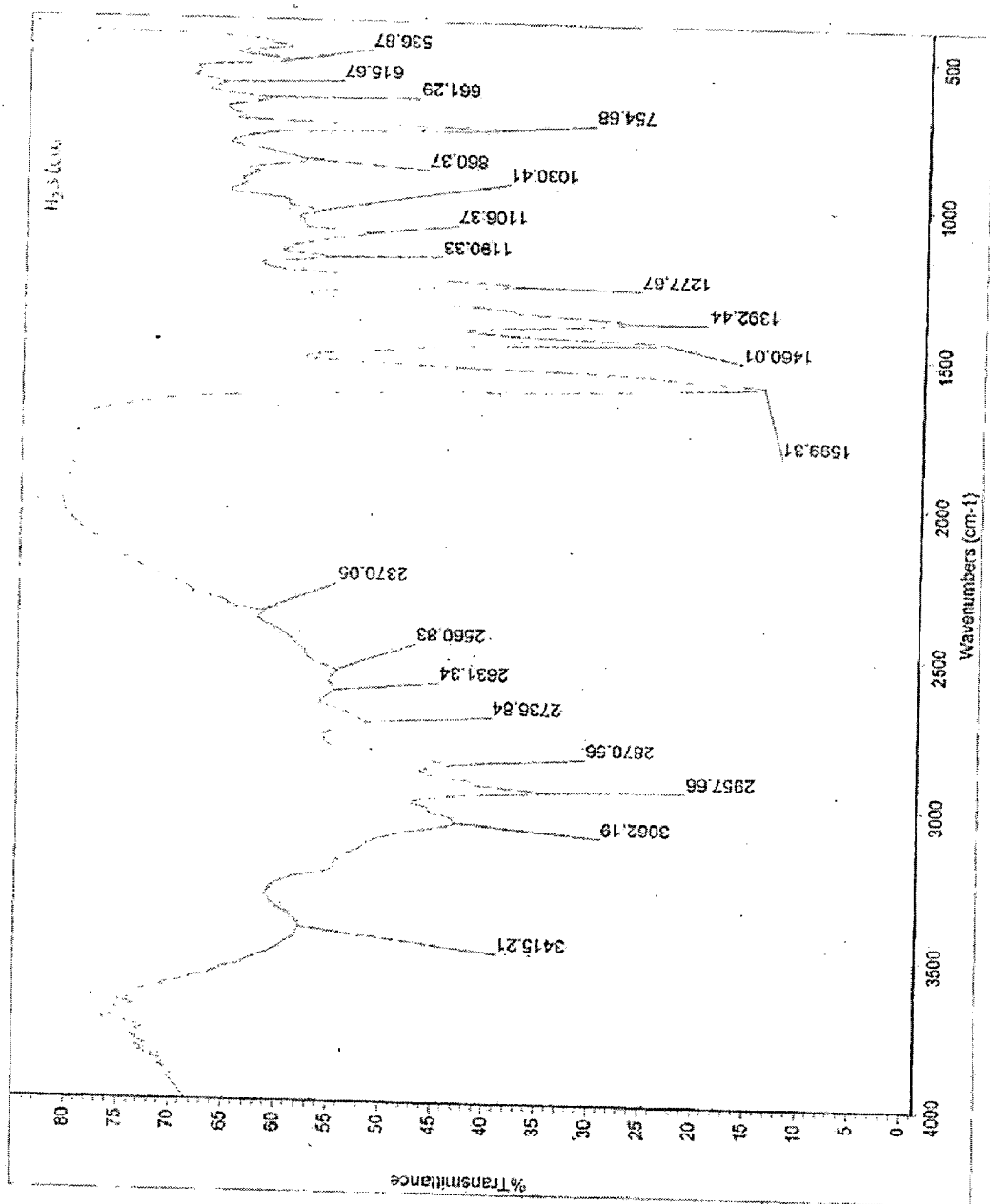


Figure 12. IR spectrum of H<sub>2</sub>SLue

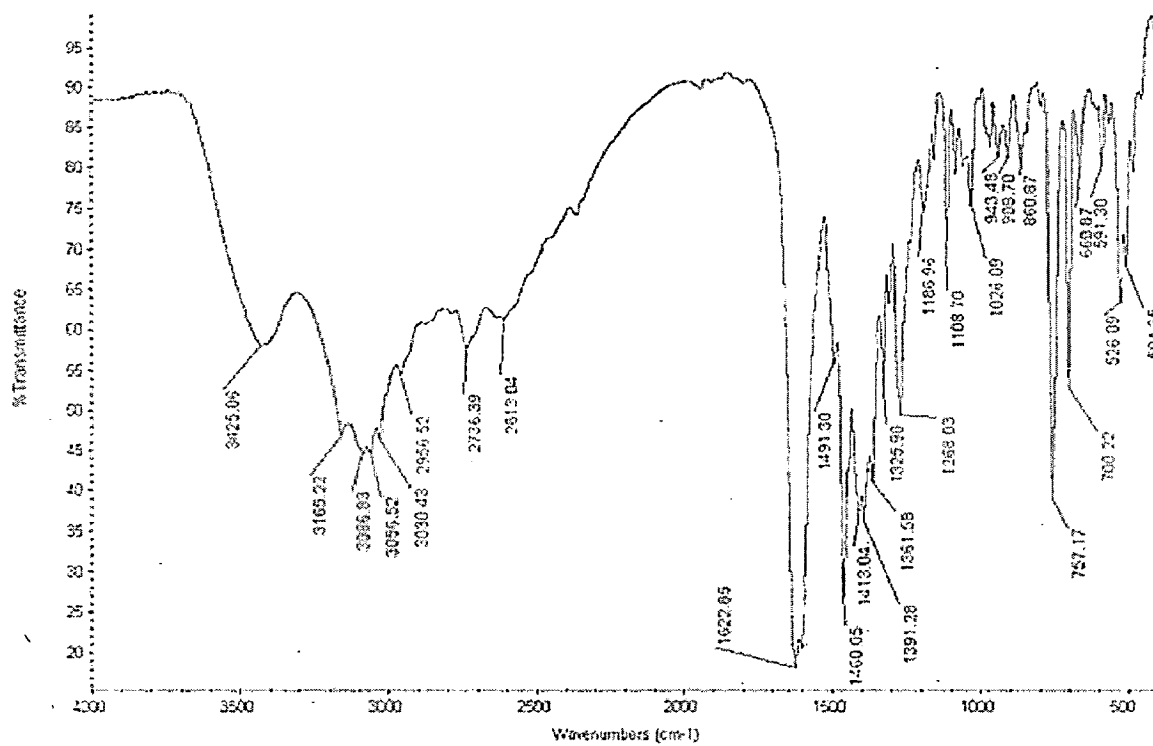


Figure 13. IR spectrum of H<sub>2</sub>SPhe (C)

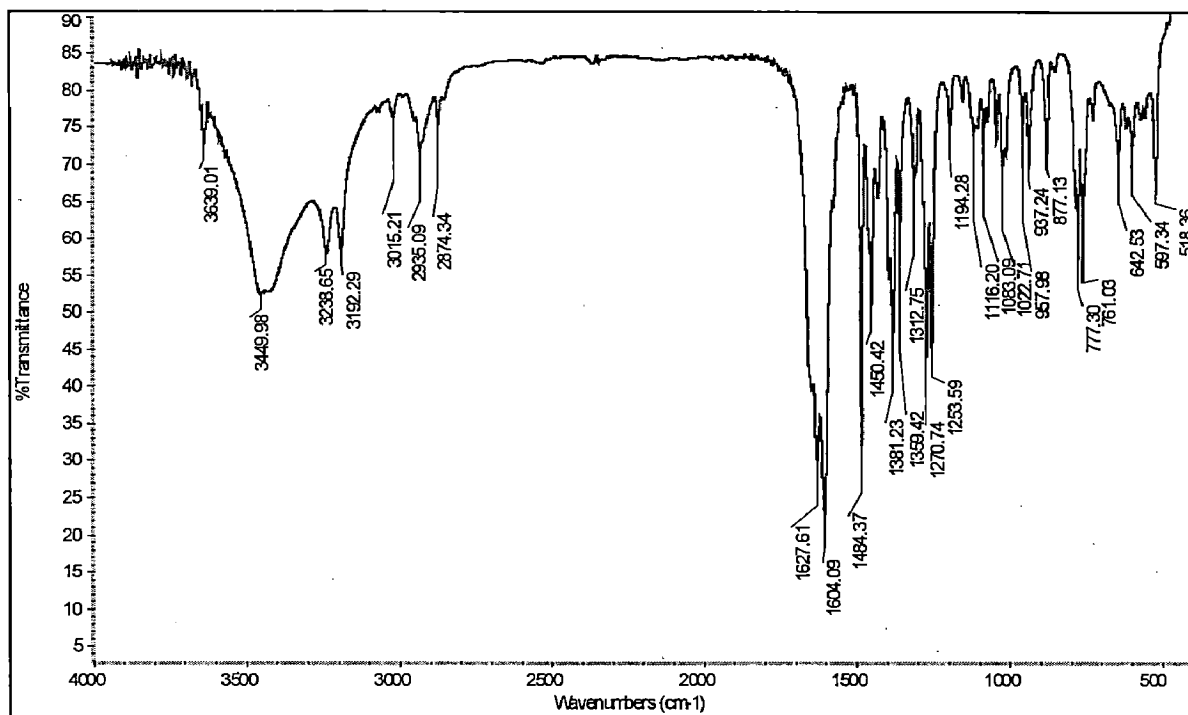


Figure 14. IR spectrum of  $[\text{Cu}_2(\text{Sgly})_2] \cdot \text{H}_2\text{O}$

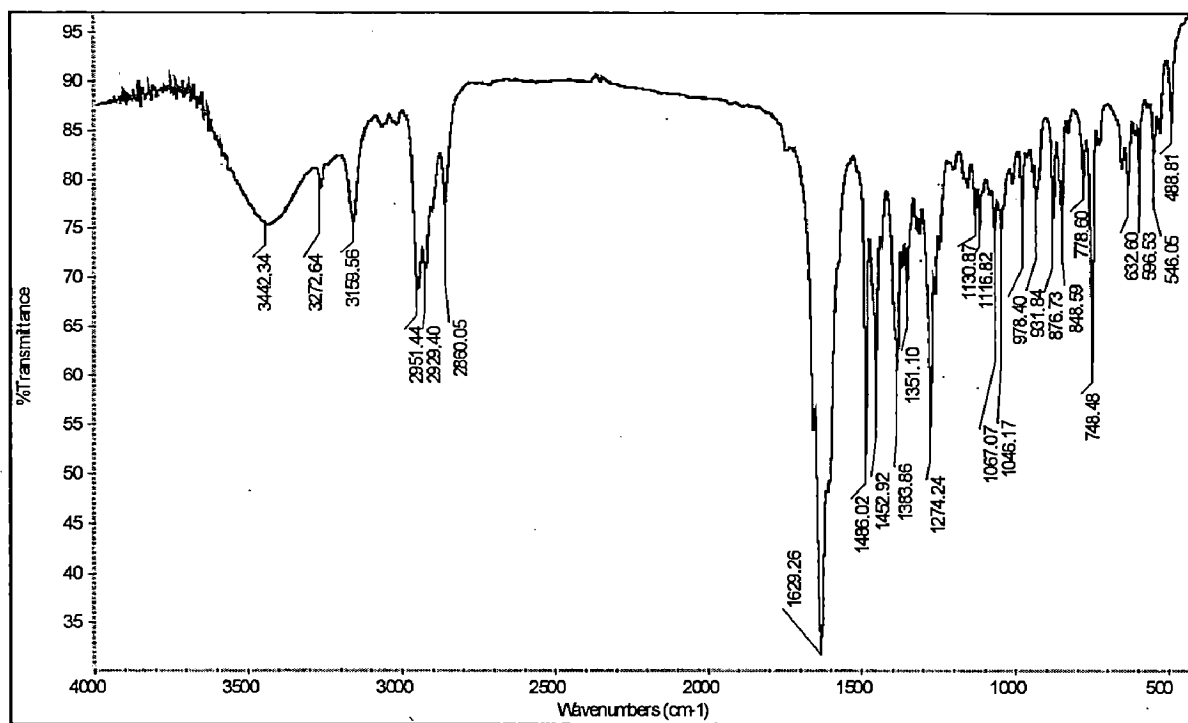


Figure 15. IR spectrum of  $[\text{Cu}_2(\text{Slue})_2] \cdot \text{H}_2\text{O}$

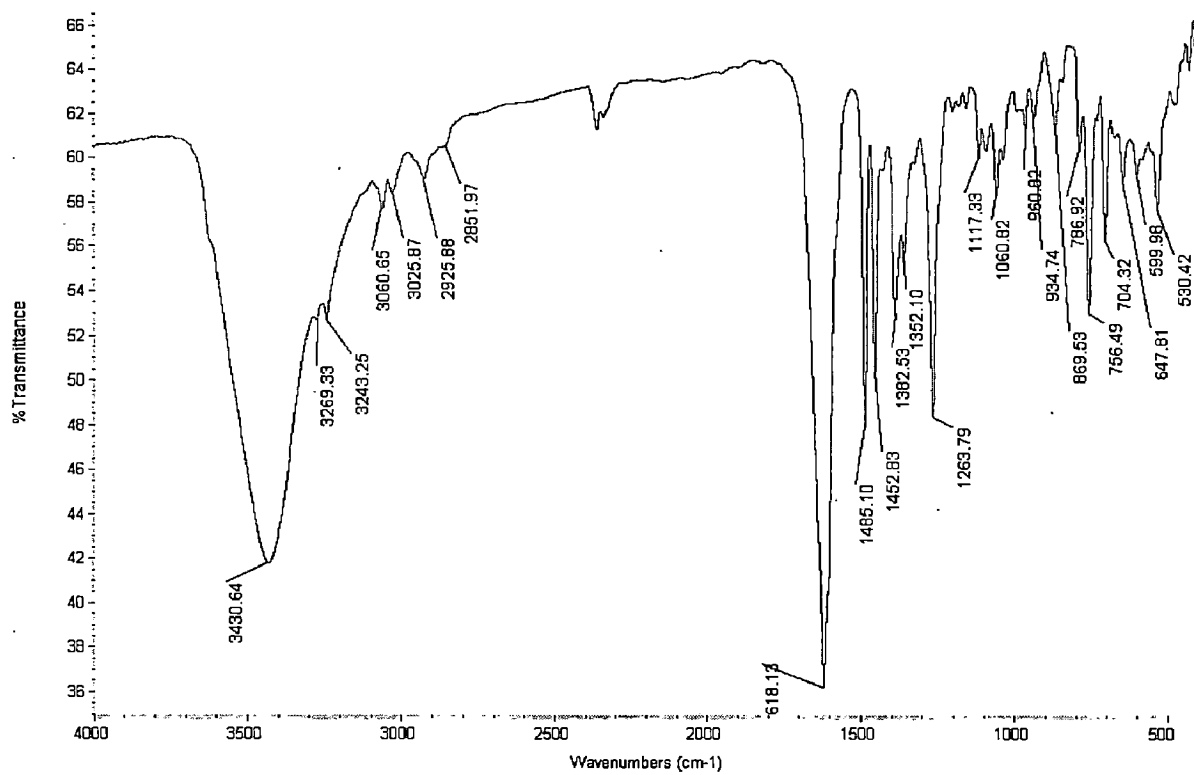


Figure 16. IR spectrum of [Cu<sub>2</sub>(Sphe)<sub>2</sub>].H<sub>2</sub>O



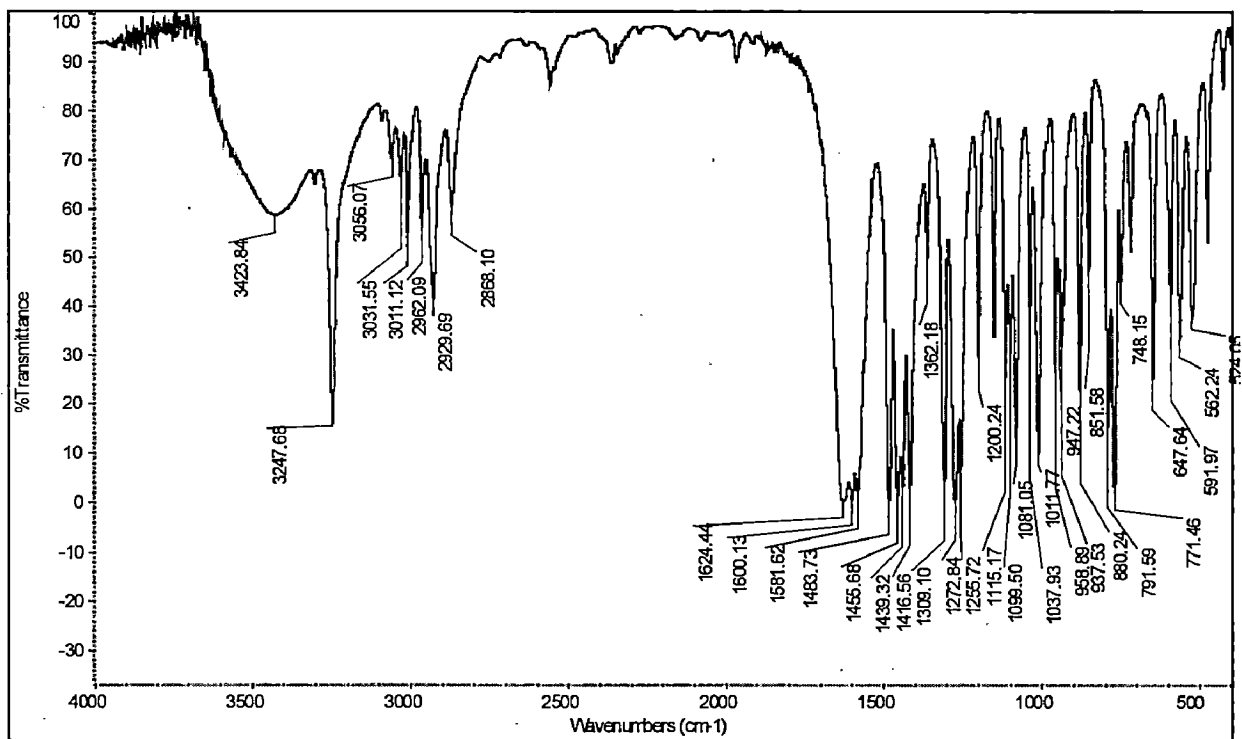
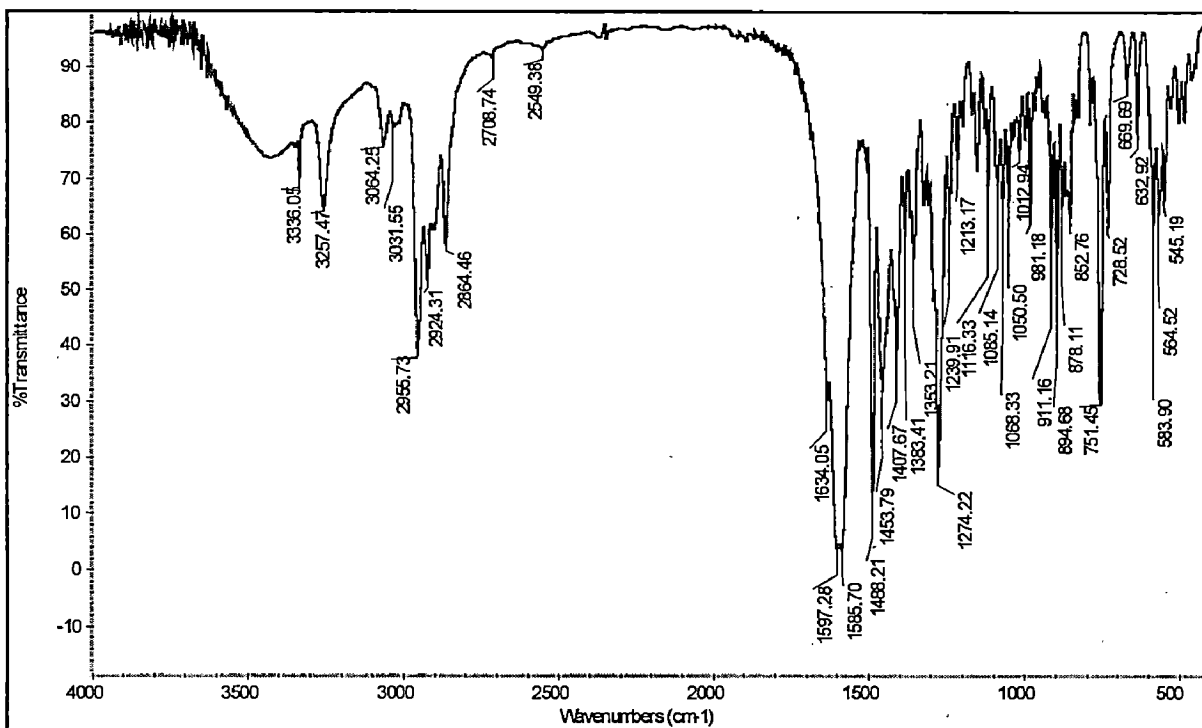


Figure 17. IR spectrum of  $[\text{Zn}_2(\text{Sgly})_2] \cdot \text{H}_2\text{O}$



**Figure 18.** IR spectrum of  $[\text{Zn}_2(\text{Slue})_2]\cdot\text{H}_2\text{O}$

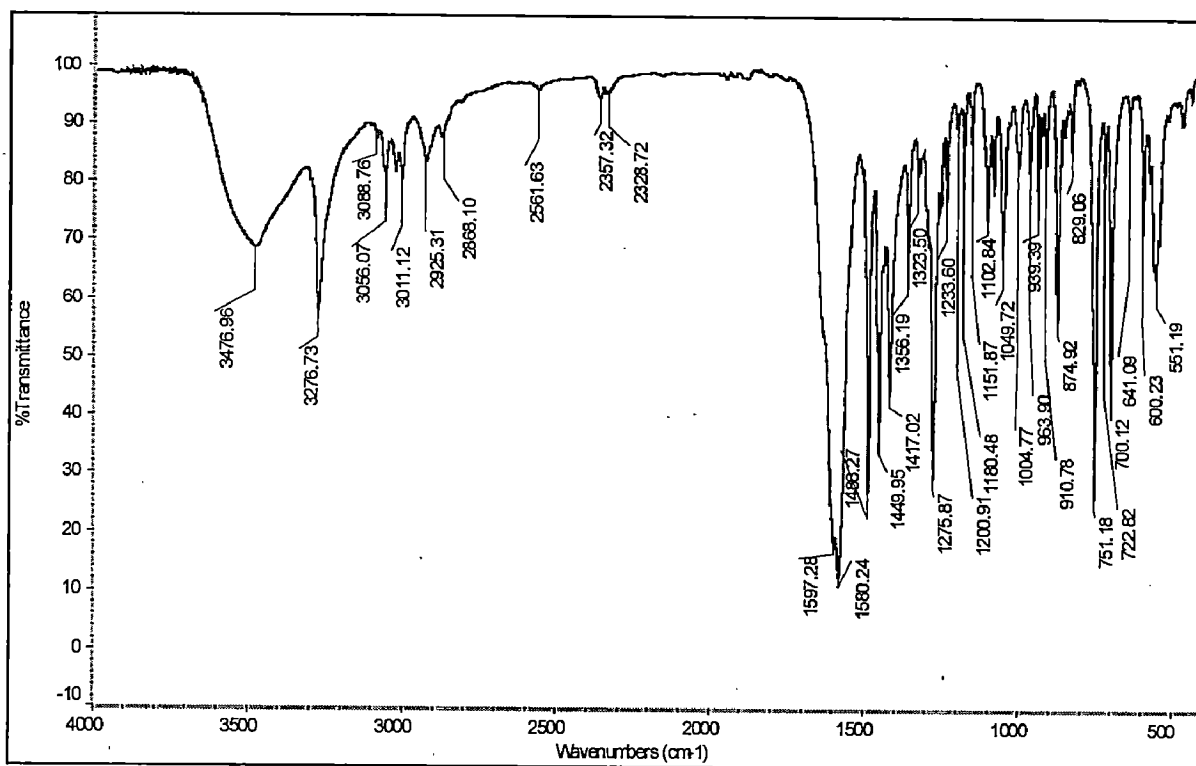


Figure 19. IR spectrum of  $[\text{Zn}_2(\text{Sphe})_2] \cdot \text{H}_2\text{O}$

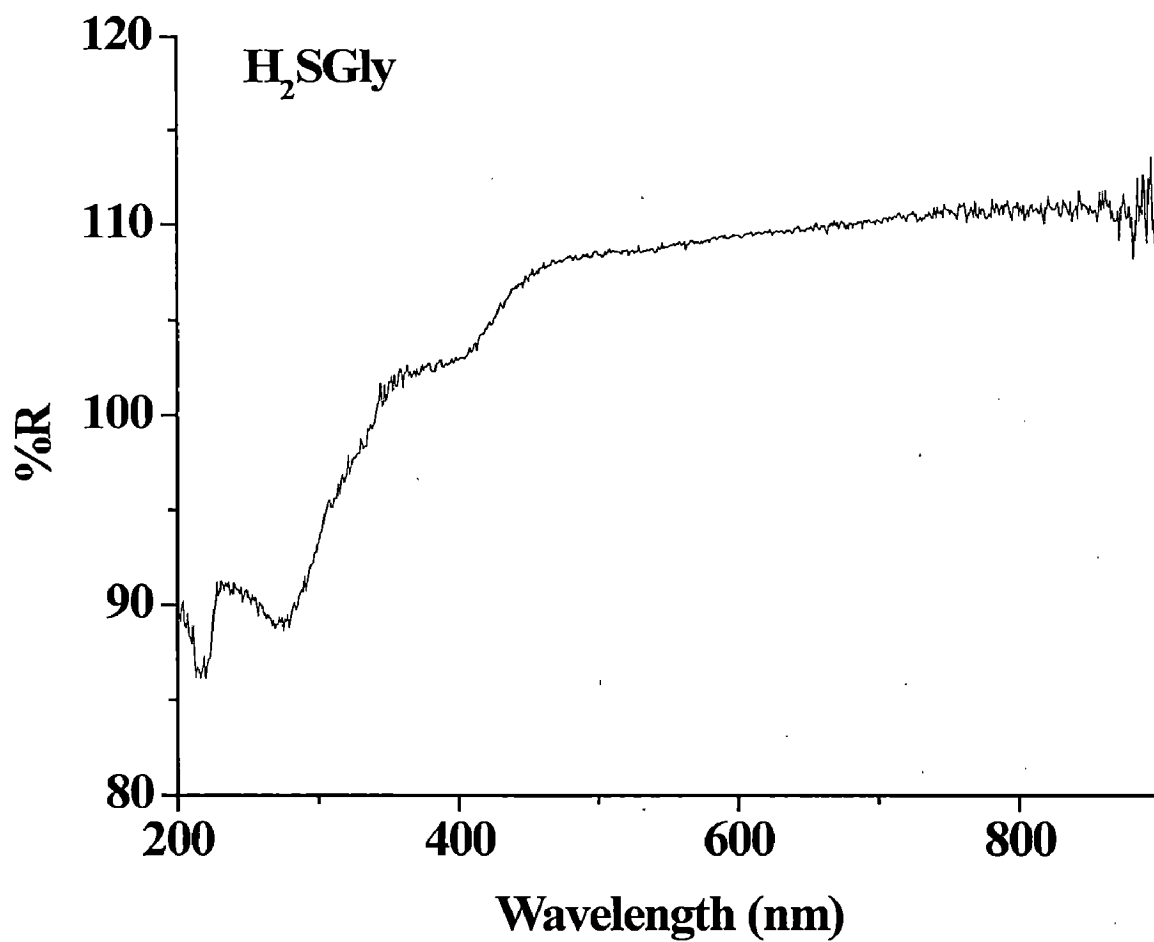


Figure 20. Diffused reflectance spectrum of H<sub>2</sub>SGly (A)

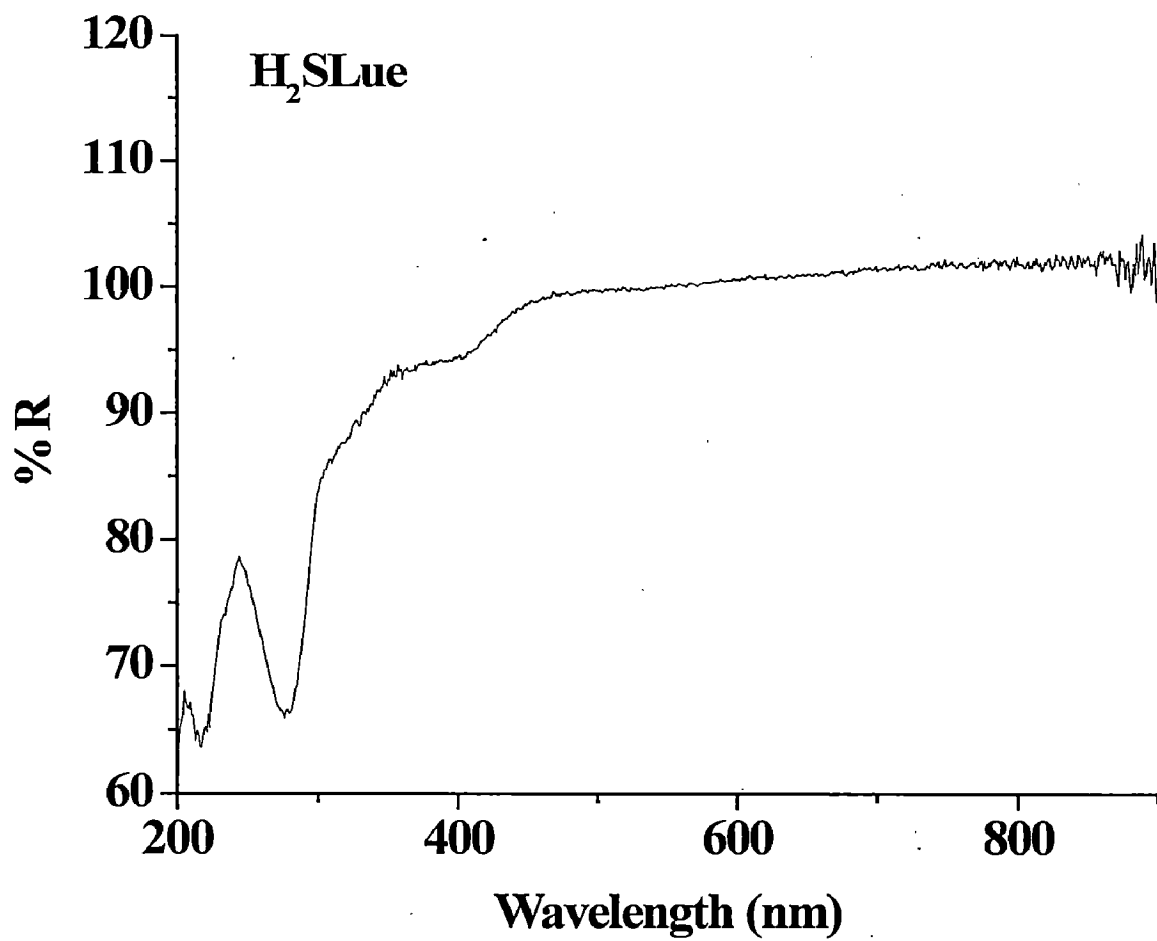


Figure 21. Diffused reflectance spectrum of H<sub>2</sub>Slue (B)

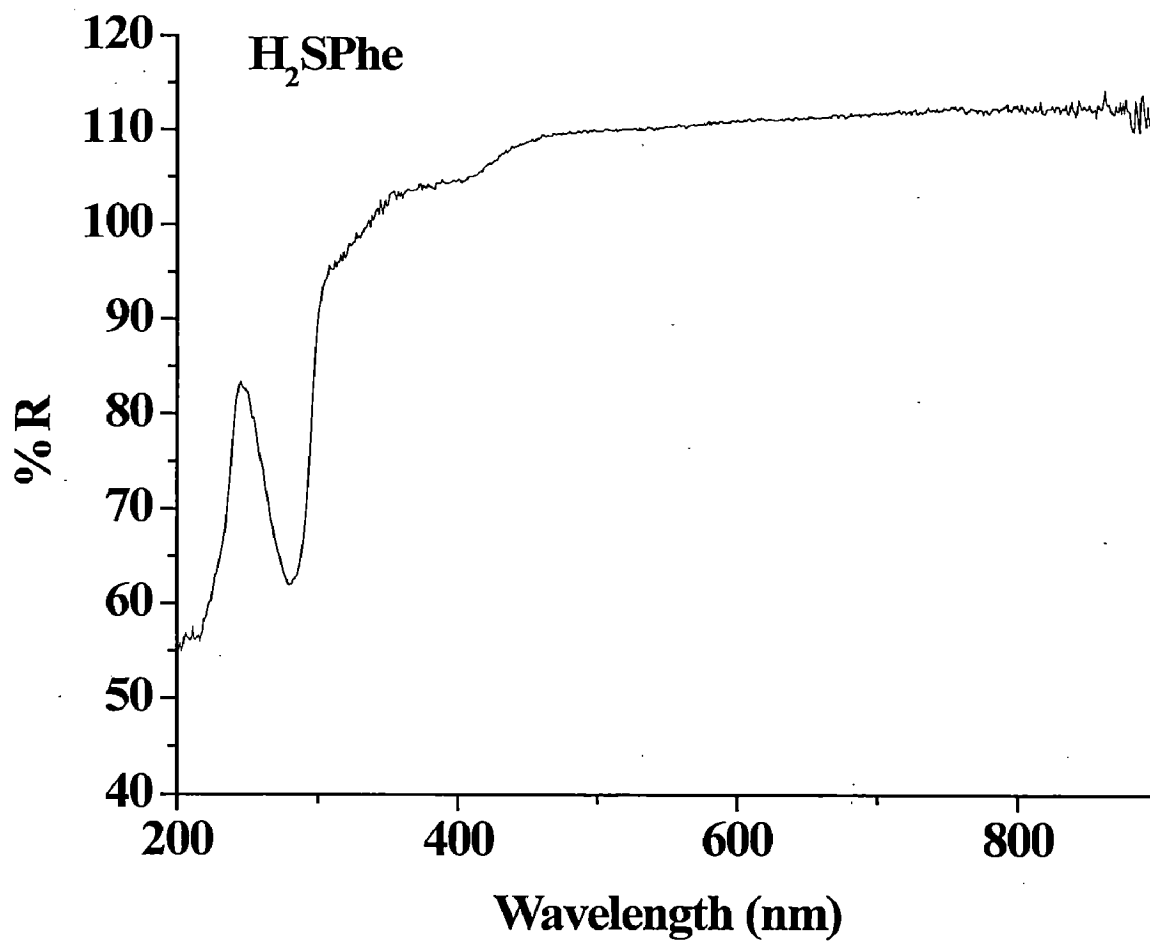
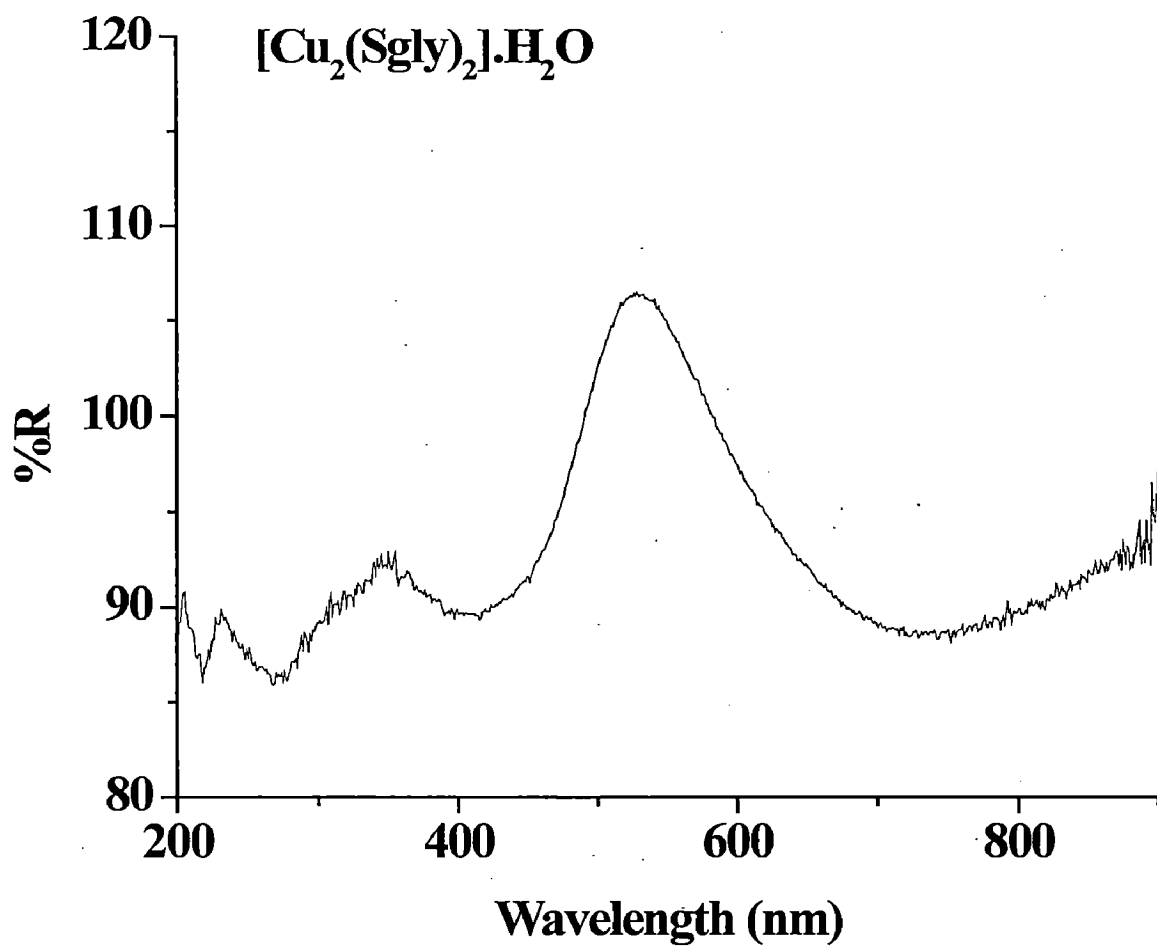


Figure 22. Diffused reflectance spectrum of H<sub>2</sub>SPhe (C)



**Figure 23.** Diffused reflectance spectrum of [Cu<sub>2</sub>(Sgly)<sub>2</sub>].H<sub>2</sub>O

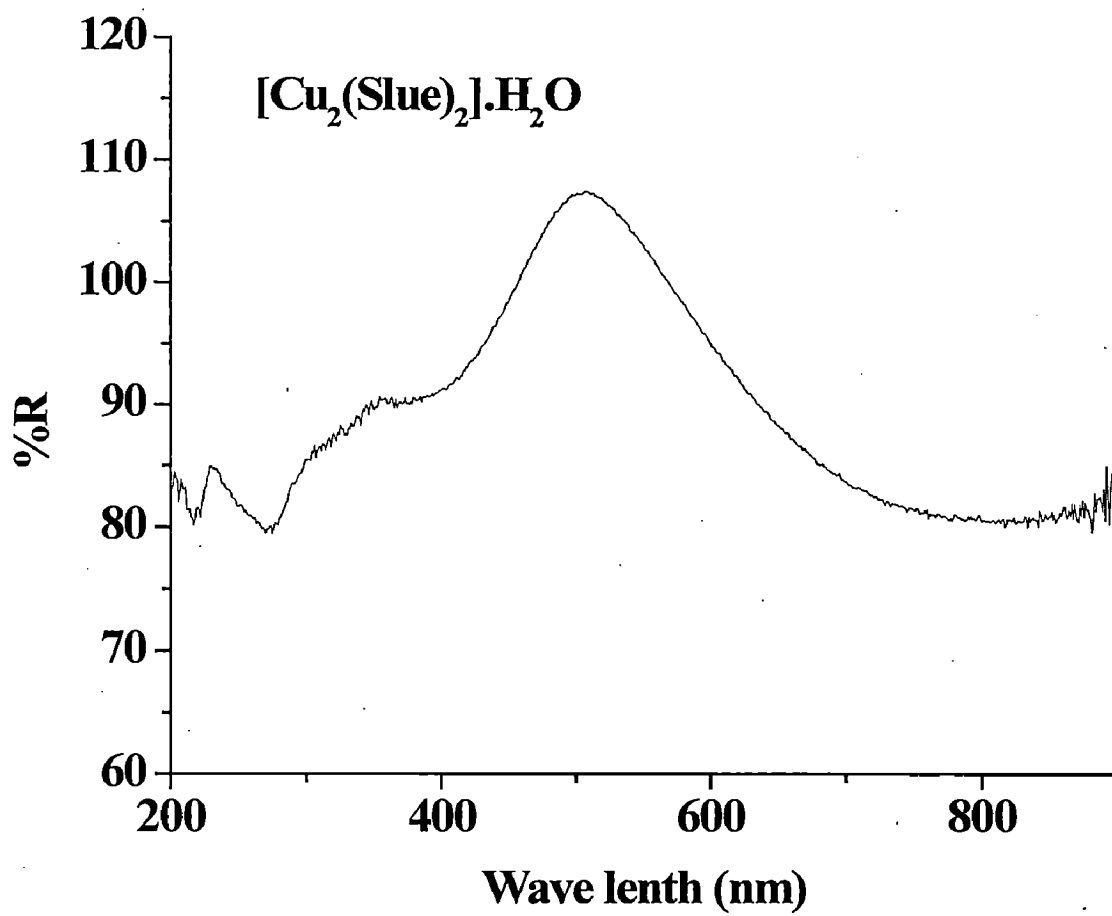


Figure 24. Diffused reflectance spectrum of  $[\text{Cu}_2(\text{Slue})_2] \cdot \text{H}_2\text{O}$



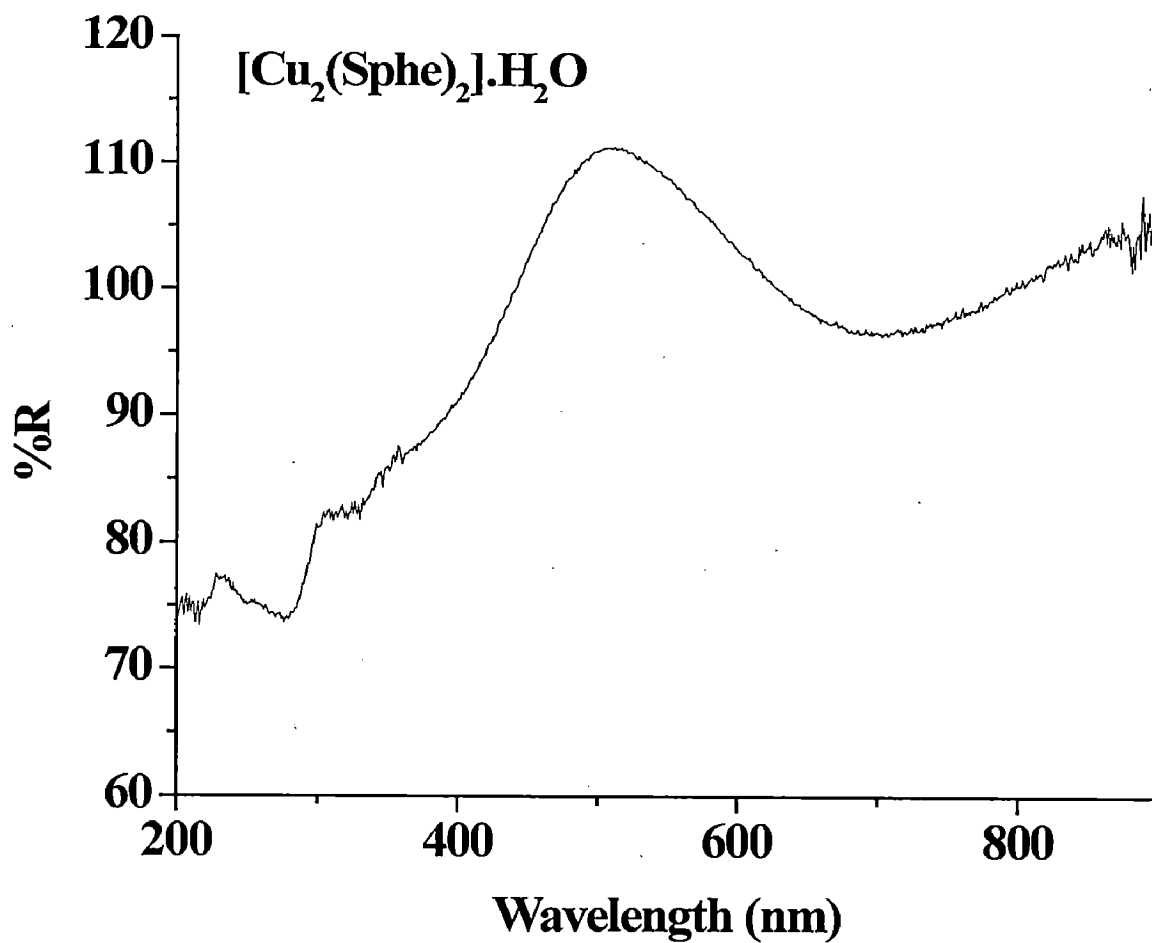


Figure 25. Diffused reflectance spectrum of  $[\text{Cu}_2(\text{Sphe})_2] \cdot \text{H}_2\text{O}$

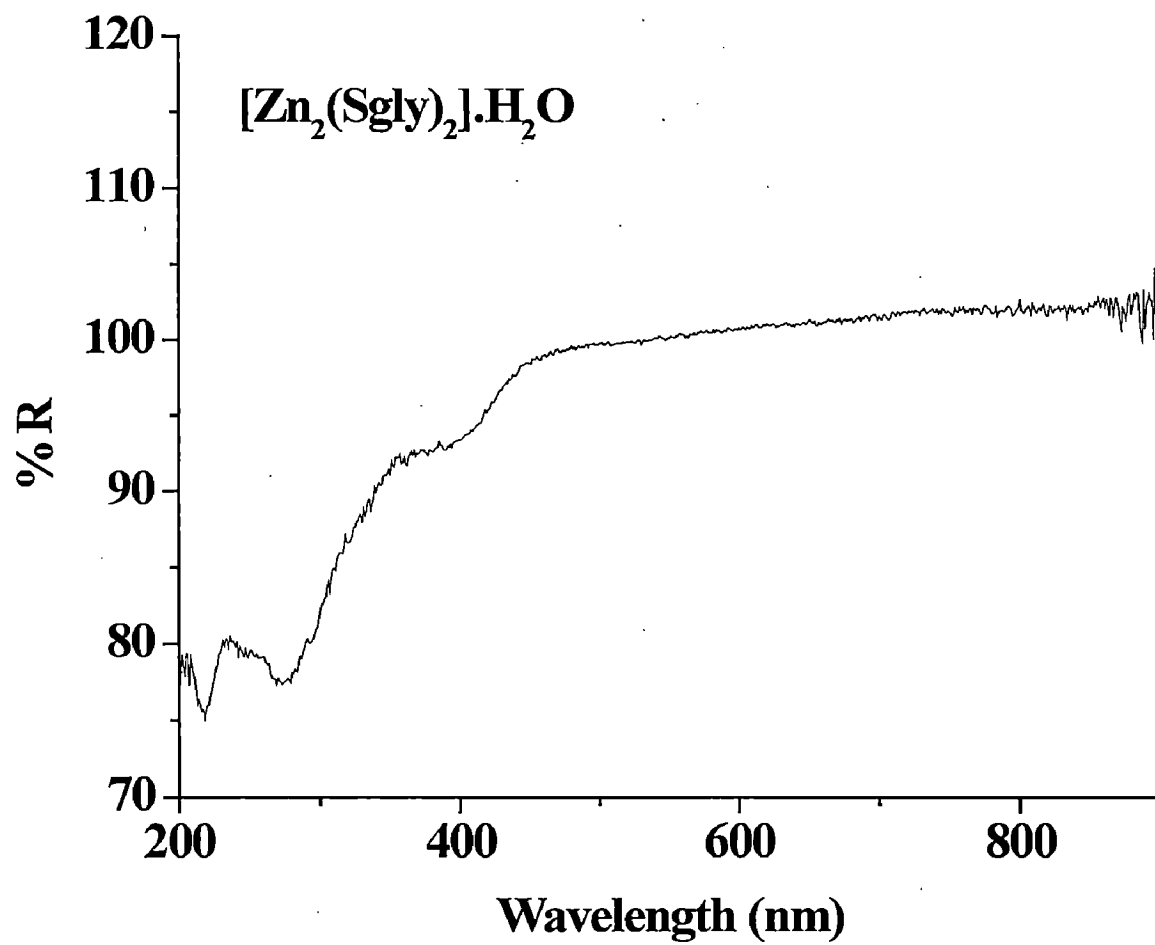


Figure 26. Diffused reflectance spectrum of  $[\text{Zn}_2(\text{Sgly})_2] \cdot \text{H}_2\text{O}$

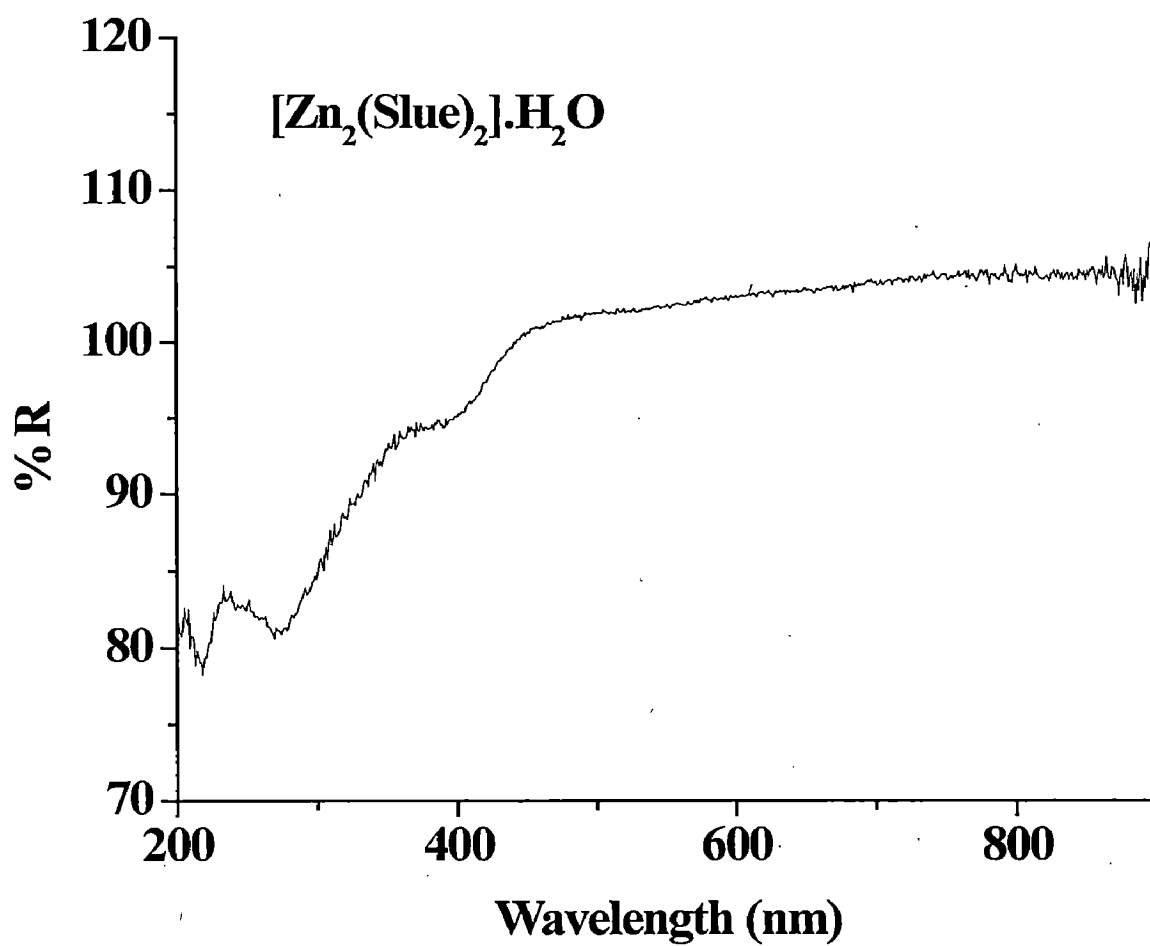


Figure 27. Diffused reflectance spectrum of  $[\text{Zn}_2(\text{Slue})_2] \cdot \text{H}_2\text{O}$

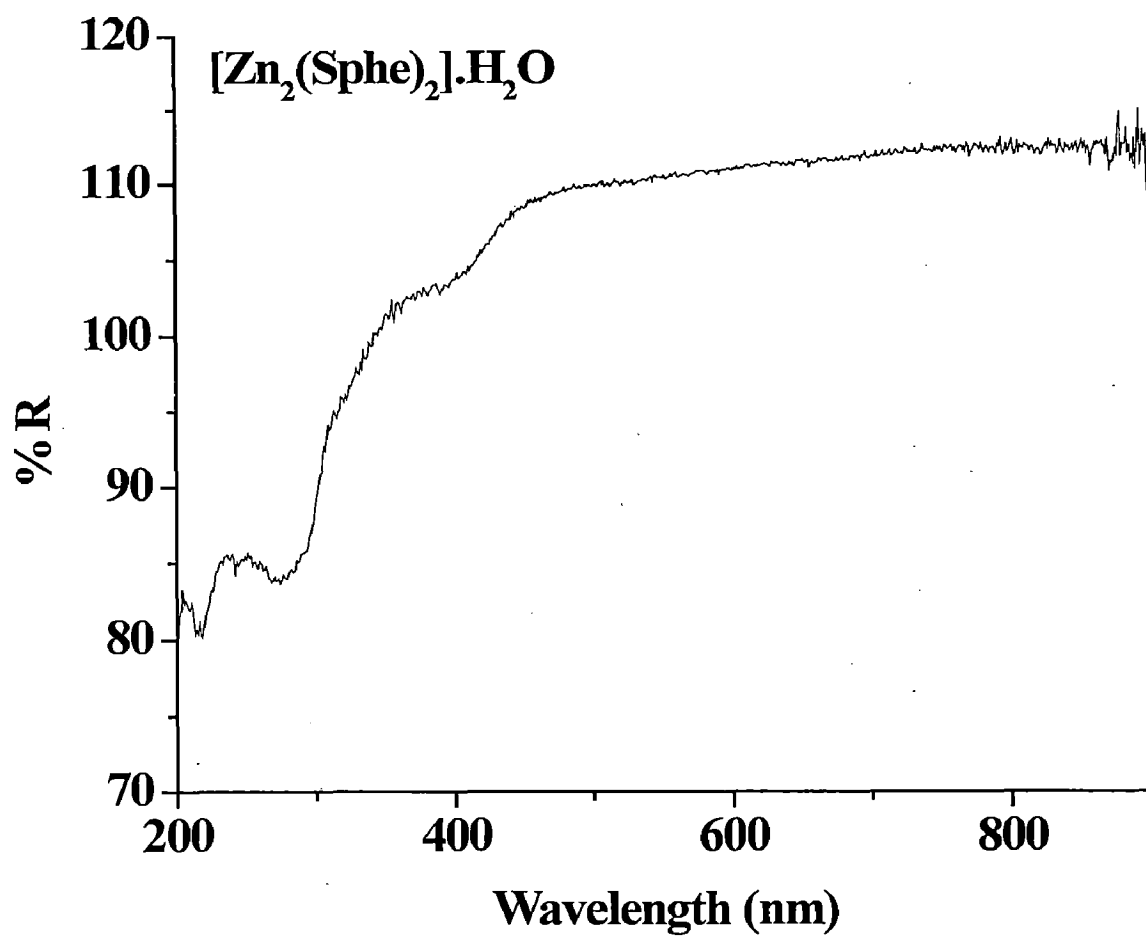


Figure 28. Diffused reflectance spectrum of  $[\text{Zn}_2(\text{Sphe})_2] \cdot \text{H}_2\text{O}$ .

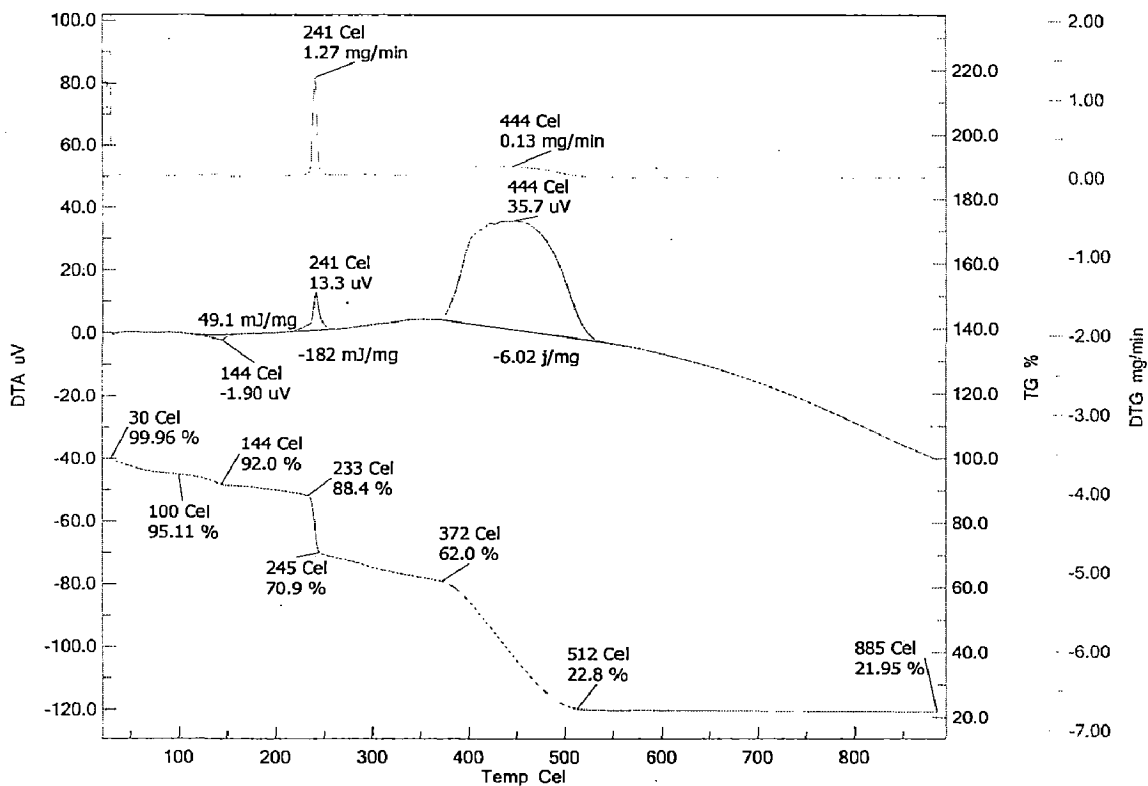


Figure 29. TG and DTG of  $[\text{Cu}_2(\text{Sgly})_2] \cdot \text{H}_2\text{O}$

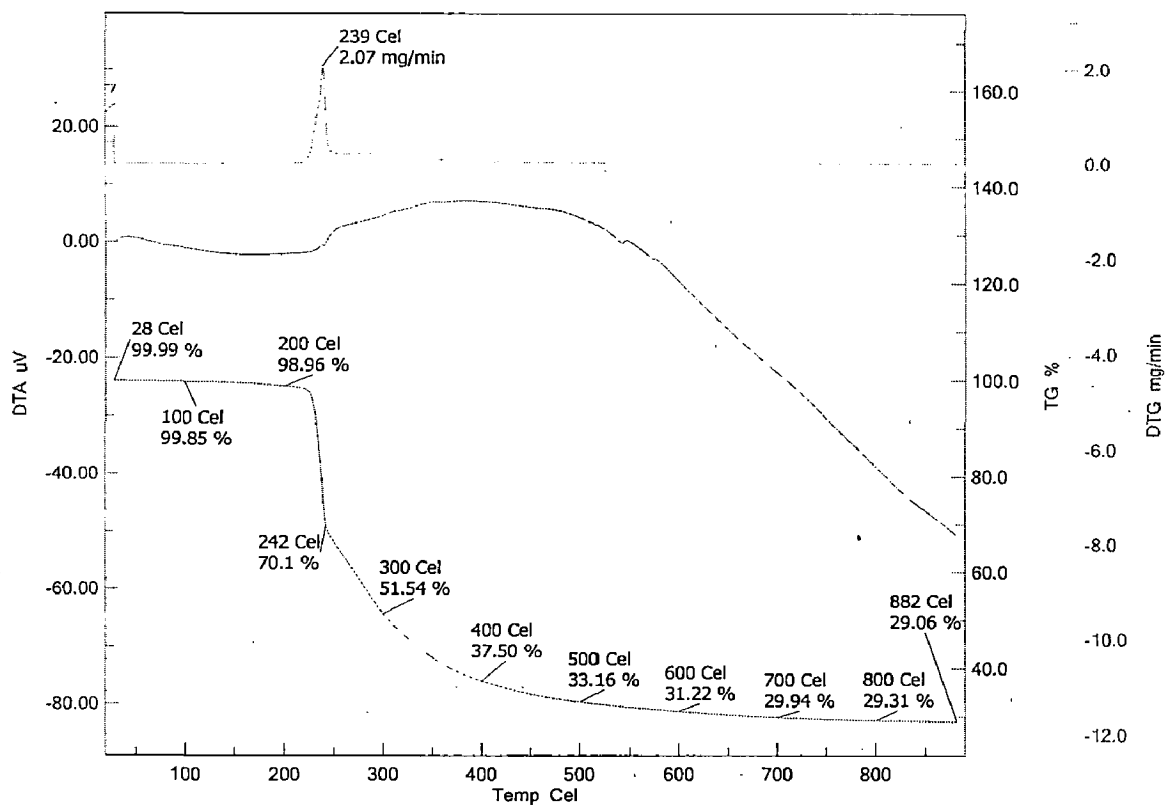
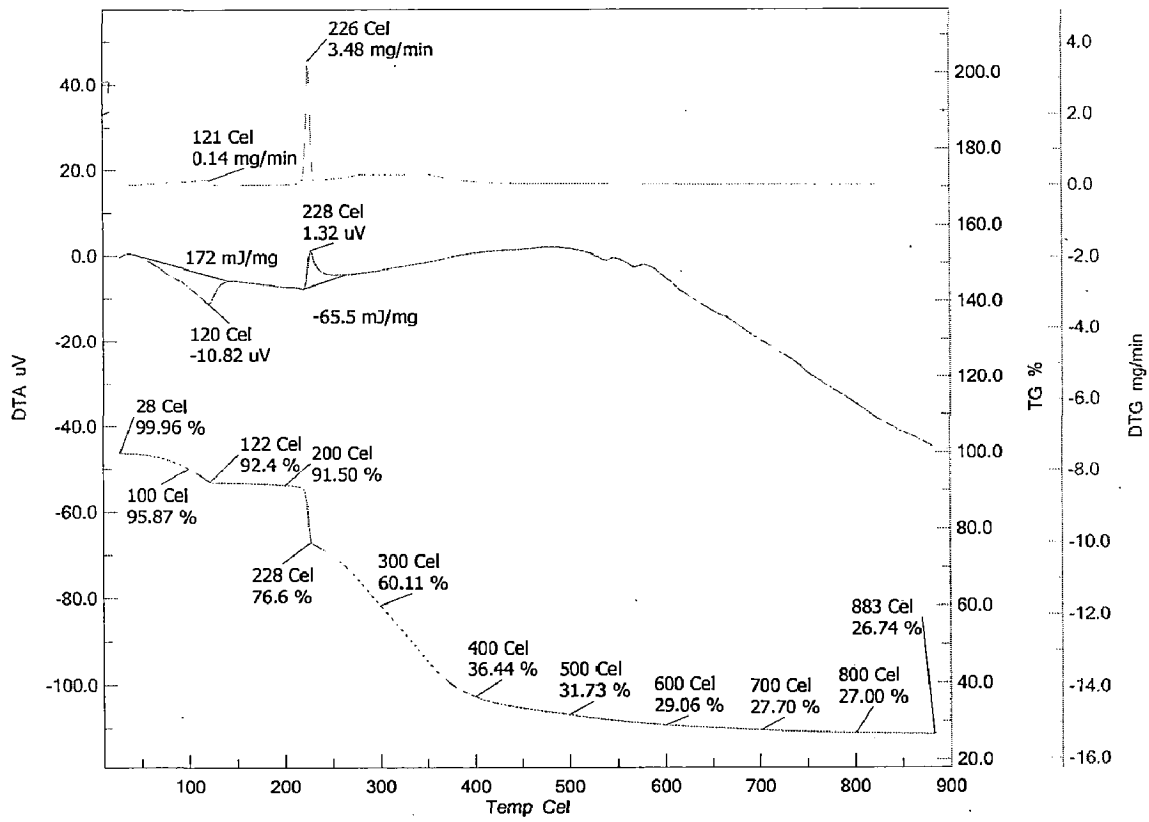


Figure 30. TG and DTG of  $[\text{Cu}_2(\text{Slue})_2] \cdot \text{H}_2\text{O}$



**Figure 31.** TGA and DTG of  $[\text{Cu}_2(\text{Sphe})_2] \cdot \text{H}_2\text{O}$

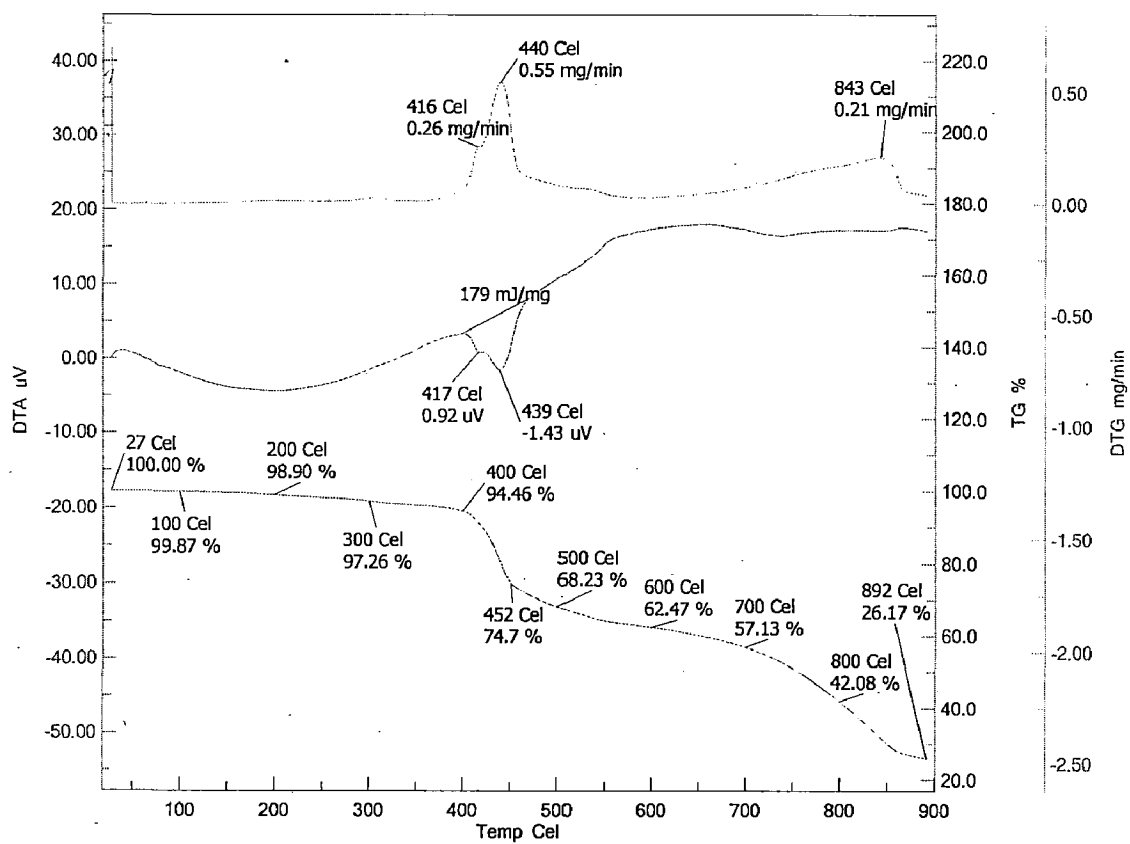


Figure 32. TG and DTG of  $[Zn_2(Sgly)_2] \cdot H_2O$



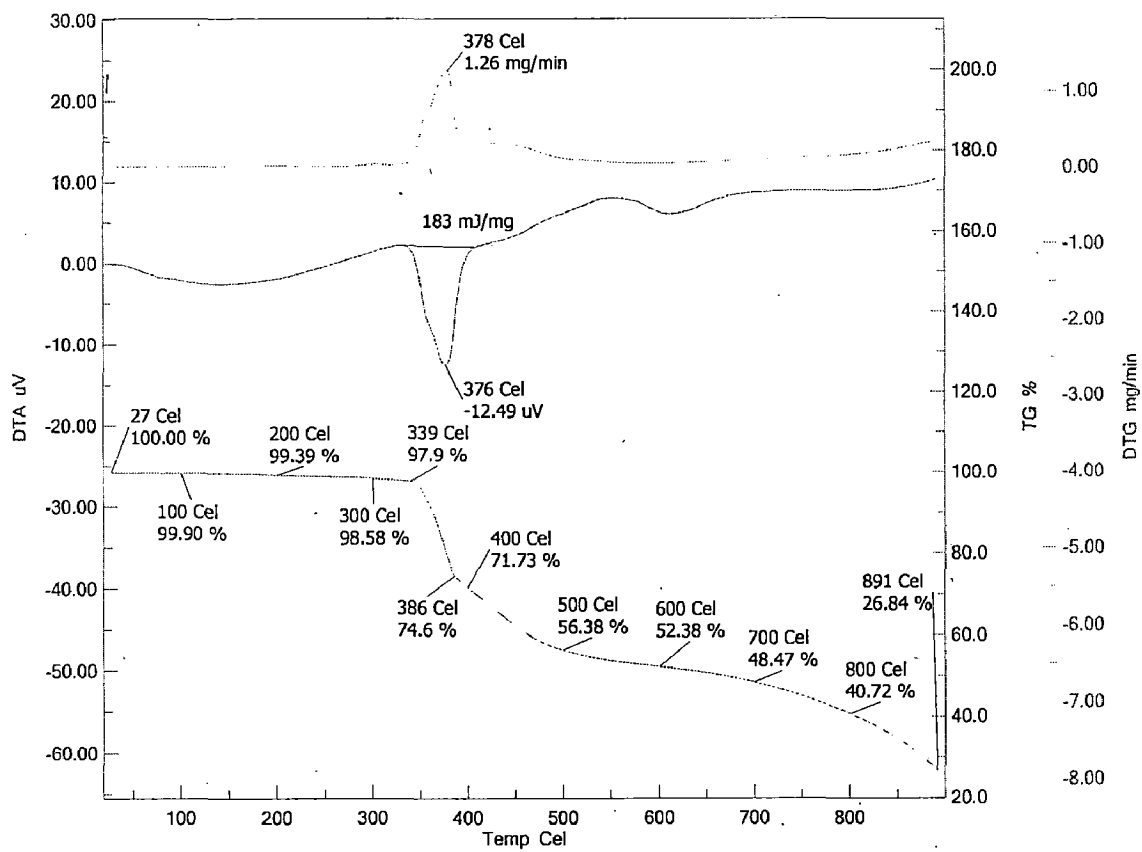
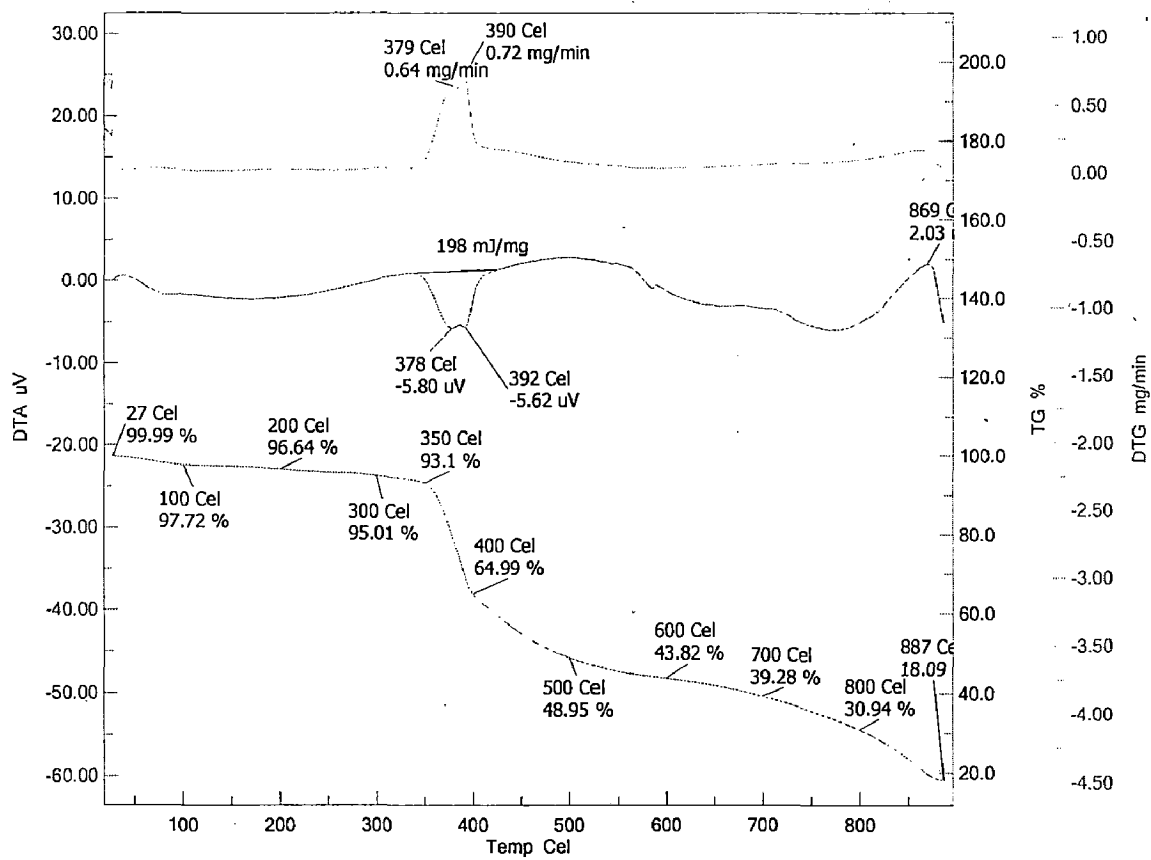


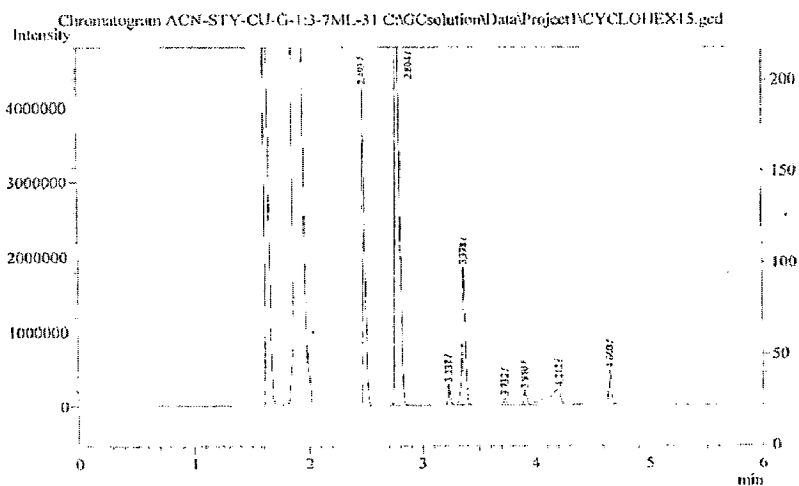
Figure 33. TGA and DTG of  $[Zn_2(Slue)_2] \cdot H_2O$



**Figure 34.** TG and DTG of  $[Zn_2(Sphe)_2] \cdot H_2O$

Sample Information

Analysis Date & Time : 4/11/2012 7:28:06 PM  
 User Name : Admin  
 Vial# : 1  
 Sample Name : ACN-STY-CU-G-1:3-7ML-31  
 Sample ID : CYCLOHEX



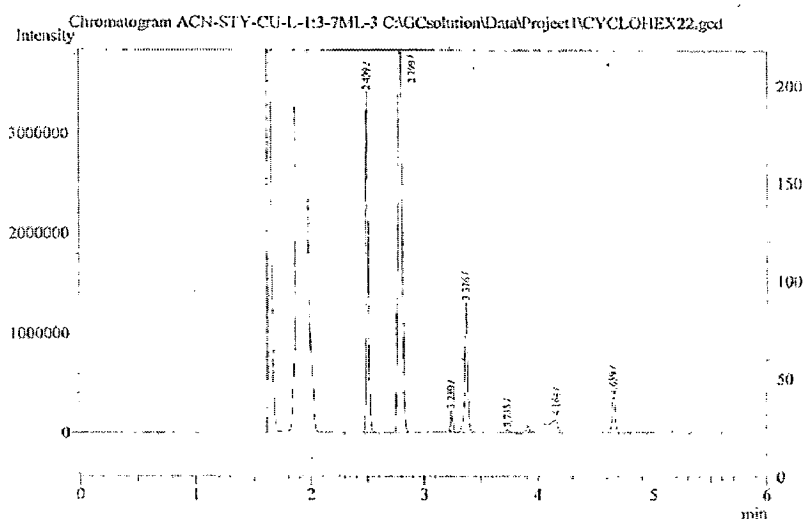
Peak Table - Channel 1

Peak#	Ret. Time	Area	Height	Area%
1	2.493	5723265	4102693	19.3781
2	2.804	17058299	7113386	57.7569
3	3.237	377532	276905	1.2783
4	3.378	3442193	1802540	11.6548
5	3.732	147541	98016	0.4996
6	3.910	289454	190065	0.9800
7	4.212	1666522	217771	5.6426
8	4.660	829852	461695	2.8098
Total		29534658	4263071	100.0000

**Figure 35.** Gas chromatogram of styrene oxidation by  $[\text{Cu}_2(\text{Slue})_2] \cdot \text{H}_2\text{O}$

Analysis Date & Time : 4/12/2012 9:24:40 PM  
 User Name : Admin  
 Vial# : 1  
 Sample Name : ACN-STY-CU-1-1-3-7ML-3  
 Sample ID : CYCLOHEX

Sample Information



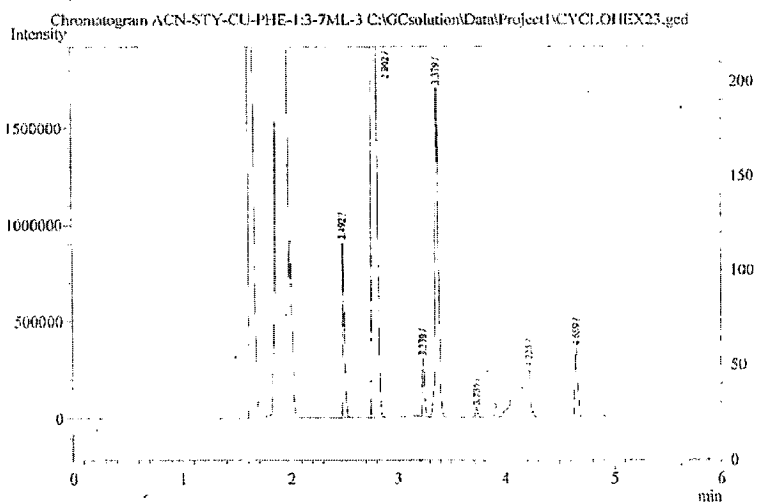
Peak Table - Channel 1

Peak#	Ret. Time	Area	Height	Area%
1	2.499	4501993	3318270	22.0420
2	2.799	11520092	5445854	56.4029
3	3.239	290721	207194	1.4234
4	3.376	2259207	1281781	11.0612
5	3.735	57233	37620	0.2802
6	4.164	1173220	149494	5.7441
7	4.659	622173	352017	3.0462
Total		20424639	10792230	100.0000

Figure 36. Gas chromatogram of styrene oxidation by  $[\text{Cu}_2(\text{Slue})_2] \cdot \text{H}_2\text{O}$

Analysis Date & Time : 4/12/2012 9:37:26 PM  
 User Name : Admin  
 Vial# : 1  
 Sample Name : ACN-STY-CU-PHE-1:3-7ML-3  
 Sample ID : CYCLOHEX

Sample Information



Peak Table - Channel 1

Peak#	Ret. Time	Area	Height	Area%
1	2.492	1146943	871590	5.2859
2	2.802	14416977	6192392	66.4429
3	3.239	404068	283291	1.8622
4	3.379	3078473	1648800	14.1876
5	3.735	70695	46087	0.3258
6	4.225	1979993	241143	9.1251
7	4.659	601148	344898	2.7705
Total		21698297	9628201	100.0000

Figure 37. Gas chromatogram of styrene oxidation by  $[\text{Cu}_2(\text{Sphe})_2] \cdot \text{H}_2\text{O}$ .