*Research Journal of Chemical Sciences*
Vol. **10(3)**, 25-29, October **(2020)**

ISSN 2231-606X
*Res. J. Chem. Sci.*

# Synthesis and characterization of some conjugated β-ketoesters and their Cu(II) complexes

**Saifunneesa Thelakkadan[1] and Muhammed Basheer Ummathur[2*]**

[1]Post Graduate and Research Department of Chemistry, MES Keveeyam College, Valanchery, Kerala-676552, India
[2]Post Graduate Department of Chemistry, KAHM Unity Women's College, Manjeri, Kerala-676122, India
mbummathur@gmail.com

**Available online at: www.isca.in, www.isca.me**
Received 17th May 2020, revised 30th August 2020, accepted 19th September 2020

## Abstract

*Five conjugated β-ketoesters ($HL^1$ to $HL^5$) with the keto group connected to carbon-carbon double bond have been prepared through the condensation of methyl acetoacetate with aromatic aldehydes (4-nitrobenzaldehyde; 4-methoxybenzaldehyde; 3,4-dihydroxybenzaldehyde; 3,4-dimethoxybenzaldehyde and indole-3-carbaldehyde). Structural characterization by physicochemical techniques indicated the occurrence of $HL^1$ in the keto form and $HL^2$ to $HL^5$ in the intra-molecularly hydrogen bonded enol form. Details on the formation and nature of bonding in the $[Cu(HL)(OAc)_2]$ complex of $HL^1$ and $[CuL_2]$ complexes of $HL^2$ to $HL^5$ are confirmed by analytical and spectral techniques.*

**Keywords:** Conjugated β-ketoesters, metal complexes, keto form, enol form, spectral data.

## Introduction

As a part of our investigation on conjugated carbonyl ligands and their metal chelates, this paper includes the preparation and structural identification of five conjugated β-ketoesters and their Cu(II) complexes[1-6]. Such synthetic carbonyl compounds with the carbonyl group attached to olefinic linkages have received much attention recently because many naturally occurring biologically active compounds like curcumin (in turmeric), piperine (black pepper), Cassumunin (ginger), etc contain these type of structural units which are responsible for their biological and medicinal properties[7-10]. Metal complexes of these structural types have gained a prominent place in modern coordination chemistry because in most of the cases metal chelation considerably enhances their medicinal properties[4,8,11].

## Materials and methods

**Instruments and methods:** Elemental analysis was carried out by microanalyses (HERAEUS CHNO rapid analyzer). Metal percentage of Cu(II) chelates was determined by AAS (PERKIN ELMER 2380) after decomposing with concentrated sulphuric acid and nitric acid mixture.

The UV-VISIBLE spectra of the compounds were measured using a JASCO V-550 UV-VISIBLE spectrophotometer in methanol ($10^{-6}$mol/L) solvent, IR spectra (KBr discs) using a JASCO FT/IR 4100 spectrophotometer, $^1$HNMR spectra ($CDCl_3$ or DMSO-$d_6$) using a JEOL 400 NMR spectrometer and mass spectra using a JEOL JMS 600H mass spectrometer (FAB using argon and *meta*-nitrobenzyl alcohol as the matrix). DMF was used for determining the molar conductance of the complexes ($\sim 10^{-3}$mol/L) at 28±1$^0$C. A Guoy type magnetic balance at room temperature was used to determine the magnetic susceptibilities of the Cu(II) complexes.

**Synthesis of conjugated β-ketoesters, ($HL^1$-$HL^5$) and their Cu(II) complexes:** The conjugated β-ketoesters were prepared by reacting methyl acetoacetate with aromatic aldehydes as reported in our previous work[6]. Use of boric oxide and tri (*sec*-butyl) borate block the condensation of aldehydes at the active methylene group of ester. The condensing agent used was *n*-butylamine[6]. The aldehydes used for the synthesis were: 4-nitrobenzaldehyde; 4-methoxybenzaldehyde; 3,4-dihydroxybenzaldehyde; 3,4-dimethoxybenzaldehyde and indole-3-carbaldehyde. The Cu(II) complexes were also synthesized by the reported method[6].

## Results and discussion

All the ligands are stable with finite melting points. The CHN analysis of the ligands (Table-1) confirms the 1:1 stoichiometric reaction between methyl acetoacetate and aromatic aldehydes. The specific conductance of $10^{-3}$M solution of Cu(II) complexes in DMF was found as $<10\ \Omega^{-1}cm^{-1}$. This, along with elemental and metal percentages, indicate the $[CuL_2]$ stoichiometry for all the complexes except that of $HL^1$ which agree with $[Cu(HL)(OAc)_2]$ composition (Table-1).

The results obtained from various spectral data were in agreement with the Figures-1 and 2 of the conjugated β-ketoesters and Figures-3 and 4 of their Cu(II) complexes.