

Synthesis and Characterisation of a Conjugated Polycarbonyl Ligand and its Cu(II) Complex

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Abstract— A new polycarbonyl compound (H_2L) with the carbonyl groups bonded to a conjugated system has been prepared by the Claisen-Schmidt condensation between terephthalaldehyde and methyl acetoacetate under specified conditions. Analytical, IR, ¹H NMR and mass spectral data clearly support the existence of the compound predominantly in the keto form with a very small percentage of enol content. Dibasic tetradentate coordination of the compound in its Cu(II) complex has been established on the basis of analytical and spectral data.

Keywords— Terephthalaldehyde; Methyl acetoacetate; Conjugated polycarbonyl compound; Metal complex; Spectral data.

I. INTRODUCTION

In continuation of our studies on unsaturated polycarbonyl compounds and their metal complexes [1]-[5], we report herewith the synthesis and characterisation of a new conjugated polycarbonyl compound obtained by the condensation between terephthalaldehyde and methyl acetoacetate. Cu(II) complex of this ligand was also synthesised and characterised.

II. EXPERIMENTAL

A. Materials and Methods

Carbon and hydrogen contents were determined by microanalyses (Heraeus Elemental analyzer) and metal content of the complex by AAS (Perkin Elmer 2380). The UV spectra of the compounds in methanol (10^{-6} M) were recorded on a JASCO V-550 UV-Visible spectrophotometer, IR spectra (KBr discs) on a JASCO FT/IR 4100 instrument, ¹H NMR spectrum ($CDCl_3$ or $DMSO-d_6$) on a JEOL JMS 60011 NMR spectrometer and mass spectra on a JEOL-JMS 600H, FAB mass spectrometer. Molar conductance of the Cu(II) complex was determined in DMF ($\sim 10^{-3}$ mol/L) at $28 \pm 1^\circ C$. Magnetic susceptibility was determined on a Guoy type magnetic balance at room temperature ($28 \pm 1^\circ C$) using $Hg[Co(NCS)_4]$ as the standard. All the chemicals and solvents used were of reagent grade (Merck, Fluka and Sigma-Aldrich).

B. Synthesis of Conjugated Polycarbonyl Compound (H_2L)

Methyl acetoacetate (0.01 mol) and boric oxide (0.01 mol) were mixed thoroughly to get a pasty mass and stirred for ~ 1 h at room temperature on a magnetic stirrer. To this mixture a solution of terephthalaldehyde (0.005 mol) and tri(*sec*-butyl) borate (0.04 mol) dissolved in dry ethyl acetate were added and stirred for ~ 6 h with slow addition of *n*-butylamine (0.2 mL). After keeping the mixture overnight, 10 mL HCl (0.01 M) was added and again stirred for ~ 1 h. The resulting solution was extracted with ethyl acetate and dried over a water bath. The pasty mass obtained was stirred with 15 mL methanol for ~ 2 h and then kept in an ice bath with constant stirring for ~ 3 h. The precipitated product was filtered and recrystallised from hot benzene. The purity of the product was checked by TLC (silica gel) and revealed the presence more than one compound. Hence it was purified by column chromatography.

The product was dissolved in minimum amount of acetone and a pinch of silica gel. It was then placed over a column (2×50 cm) densely packed with silica gel (mesh 60-120) and eluted with 1:5 v/v toluene:chloroform mixture at a uniform flow rate of about 2 mL/minute. As the elution proceeds two bands were developed in the column; a yellow lower band and an orange upper band. The lower yellow band was collected, checked for purity and discarded because of its impure nature. The upper orange band was eluted using 5:1 chloroform-acetone mixture (v/v). The eluates were collected in aliquots of 10 mL in separate test tubes and checked by TLC. The combined extracts were distilled to recover the solvent and then evaporated to dryness. The orange coloured product obtained was washed thoroughly with ethanol

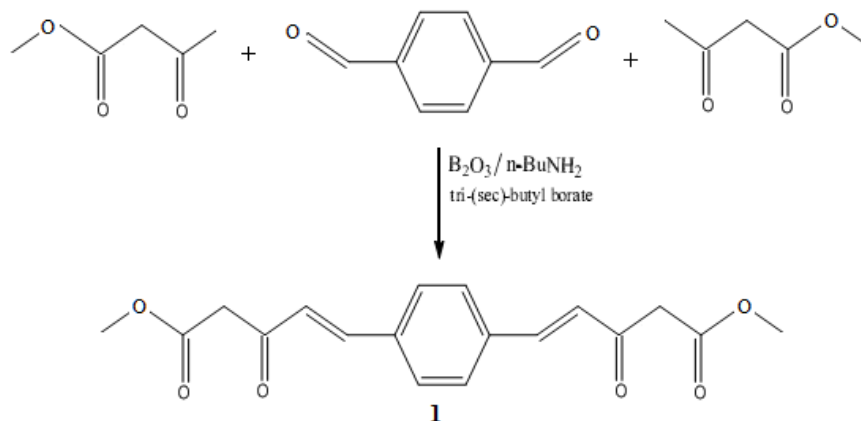
and dried in vacuum. *Yield:* 67%; *M.P.:* 110°C; *Elemental analysis (found/calcd.):* C (65.28/65.45), H (5.42/5.45).

C. Synthesis of Cu(II) Complex of H₂L

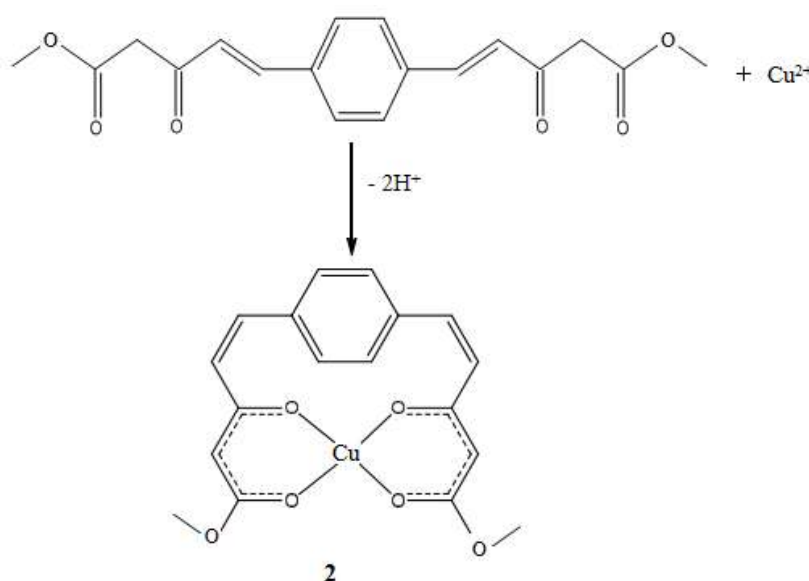
A solution of H₂L (0.005 mol) in 30 mL ethyl acetate-methanol (1:1 v/v) mixture was refluxed on a boiling water bath for half an hour. To this copper(II) acetate (0.005 mol) in 20 mL methanol was added drop by drop and again refluxed for ~6 h. The resulting solution was then concentrated to half the volume and cooled to room temperature. The precipitated complex was filtered, washed several times with ethyl acetate, then with methanol and finally with water. The complex was recrystallised from hot ethanol to make it chromatographically pure. *Yield:* 69%; *M.P.:* 264°C; *Elemental analysis (found/calcd.):* C (55.36/55.24), H (4.06/4.09), Cu (16.18/16.25).

III. RESULTS AND DISCUSSION

The observed elemental analytical data of H₂L clearly suggest the Claisen-Schmidt condensation of both aldehydic groups of terephthalaldehyde with methyl acetoacetate as in Scheme 1. The observed IR, ¹H NMR and mass spectral data also support the proposed structure **1**. The compound formed stable complex with Cu(II) ion. The analytical data together with non-electrolytic nature in DMF (specific conductance <10 Ω⁻¹ cm⁻¹; 10⁻³ M solution) suggest [CuL] stoichiometry for the complex as in Scheme 2. The complex showed normal paramagnetic moment. The observed spectral data of the complex is fully consistent with the proposed structure **2**.



Scheme 1. Claisen-Schmidt condensation between terephthalaldehyde and methyl acetoacetate



Scheme 2. Formation of Cu(II) complex of H₂L

The IR spectrum of H₂L in the 1600-1800 cm⁻¹ region is characterised by the presence of three strong bands at 1605, 1654 and 1725 cm⁻¹. Methyl acetoacetate shows the ester carbonyl stretching band at 1750

cm^{-1} and the acetyl carbonyl stretching band at 1720 cm^{-1} [6]. Enolisation and hydrogen bonding decreases these stretching frequencies. Therefore the two strong bands appeared in the spectrum of H_2L at 1725 and 1654 cm^{-1} can safely be assigned to the stretching of the ester carbonyl and the cinnamoyl carbonyl groups respectively as in structure 1 [7]. The band observed at 1605 cm^{-1} can arise due to the stretching of $\text{C}=\text{C}$ vibrations of the highly conjugated molecule. The slightly broad band present in the $2500\text{-}3500 \text{ cm}^{-1}$ region of the spectrum indicates the low percentage of enol tautomer of the compound.

In the IR spectrum of the Cu(II) complex the free ligand bands observed at 1725 and 1654 cm^{-1} due to the ester and cinnamoyl carbonyl functions disappeared and instead, two prominent bands appeared at 1690 and 1627 cm^{-1} assignable to the stretching of the metal bonded ester and cinnamoyl carbonyl functions respectively [8] as in structure 2. The presence of medium intensity bands in the $400\text{-}470 \text{ cm}^{-1}$ region of the spectrum, due to $\nu(\text{M-O})$ vibrations, also confirms the involvement of carbonyl groups in metal chelate formation [8].

The ^1H NMR spectrum of H_2L displayed a signal at $\sim\delta$ 3.9 ppm due to the methoxy protons. Aromatic protons appeared as a complex multiplet in the range δ 7-8 ppm. There is no signal in the low field region above 12 ppm which strongly suggests the existence of the compound predominantly in the keto form [9]. Integrated intensities of various signals agree well with the formulation of the compound as in structure 1.

The FAB mass spectrum of H_2L showed molecular ion peak at m/z 330 in accordance with its formulation as in structure 1. Other prominent peaks are due to the fragmentation of the molecular ion with the elimination of $-\text{CH}_3$, $-\text{OCH}_3$ and other ligand fragments (m/z : 330, 315, 299, 271, 268, 257, 229, 212, 184, 128, 101).

The FAB mass spectrum of the Cu(II) complex showed a moderately intense molecular ion peak at m/z 391 in conformity with the proposed structure 2 of the complex. The base peaks are due to the ligand moiety and its different fragments. The spectrum contains a number of fragments containing copper in the 3:1 natural abundance of ^{63}Cu and ^{65}Cu isotopes [10] (m/z : 393, 391, 378, 376, 363, 361, 330, 299, 271, 212, 184, 128, 101).

Two absorption maxima of the free ligands, observed at 380 and 280 nm due to various $n\rightarrow\pi^*$ and $\pi\rightarrow\pi^*$ transitions, are shifted slightly to longer wavelength in the UV spectrum of the Cu(II) complex indicating the involvement of carbonyl groups in metal complexation [11].

IV. CONCLUSIONS

The carbonyl groups of terephthalaldehyde were subjected to Claisen-Schmidt condensation with the acetyl methyl group of methyl acetoacetate after blocking the Knoevenagel condensation of the more reactive methylene group by protecting as a boron complex. The highly conjugated polycarbonyl compound thus formed exists predominantly in the keto form as revealed from the analytical and various spectral data. During the formation of the Cu(II) complex, the keto-enol equilibrium shifts towards the enol form and the enolic proton is replaced by the Cu(II) ion. $[\text{CuL}]$ stoichiometry of the complex is revealed from analytical and spectral techniques.

ACKNOWLEDGMENT

The authors are thankful to University Grants Commission, New Delhi, India for providing financial assistance. Thanks are due to National Institute for Interdisciplinary Science and Technology, Thiruvananthapuram, India; and Cochin University of Science and Technology, Kochi, India for providing analytical and spectral facilities.

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