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 JE02 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 (~10^{-3} mol/L) at 28±1^{0}C. Magnetic susceptibility was determined on a Guoy type magnetic balance at room temperature (28±1^{0}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