



SYNTHESIS AND SPECTRAL CHARACTERIZATION OF TRANSITION METAL CU(II) COMPLEX WITH 5-(4-METHOXYBENZYLIDENE)THIAZOLIDINE-2,4-DIONE

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ABSTRACT:

Complex of Cu(II) with 5-(4-methoxybenzylidene)Thiazolidine-2,4-dione ligand has been synthesized under microwave irradiation and characterized by NMR and FT-IR spectral studies. Composition and non-electrolytic nature (1:0 type) of the complex was confirmed by the micro analytical, metal estimation and molar conductance values. NMR and FT-IR spectra of the complex confirm the 5-(4-methoxybenzylidene) Thiazolidine - 2,4-dione coordination through nitrogen atom.

KEY WORDS: 4-methoxybenzaldehyde, Thiazolidine-2,4-dione, Cu (II) complex, Microwave.

INTRODUCTION

Thiazolidine-2,4-dione belongs to a pharmacologically important class of heterocyclic compounds used for the treatment of type-2 diabetes.1-2 TZD derivatives lower the plasma glucose levels by acting as ligands for γ -peroxyzone proliferators-activated receptors.3- 4 In addition, this class of heterocyclic compounds possesses various other biological activities such as antihyperglycemic, antimicrobial, anti-inflammatory, anticonvulsant and insecticidal, etc., 5-7 TZDs are also known for lowering the blood pressure and thereby reducing chances of heart failure and microalbuminuria in patients

with type-2 diabetes.8-9 A survey of literature reveals that metal complexes of many drugs have been found to be more effective than the drug alone.10-11 Therefore much attention is given to the use of TZD due to its high complexing nature with essential metals. On the other hand, microwave irradiation now a day is an accepted tool for accelerating the organic and inorganic reactions it leads to high reaction selectivity and utilization of minimum amount of solvents: It is an eco-friendly technique.12-13 This paper deals with the microwave assisted preparation and spectral characterization of Cu (II) using 5-(4-methoxybenzylidene) Thiazolidine - 2,4-dione as ligand

EXPERIMENTAL:

1) Materials

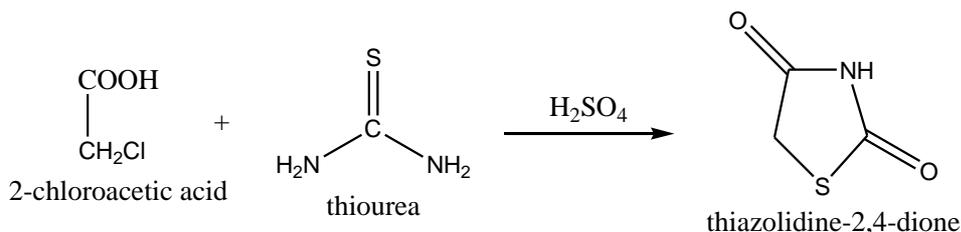
2,4-thiazolidinedione (Merck), 4-methoxybenzaldehyde, Copper Nitrate DMSO, DMF, methanol, ethanol were of AR grade, and used as such without further purification.

2) Method

General synthesis procedure

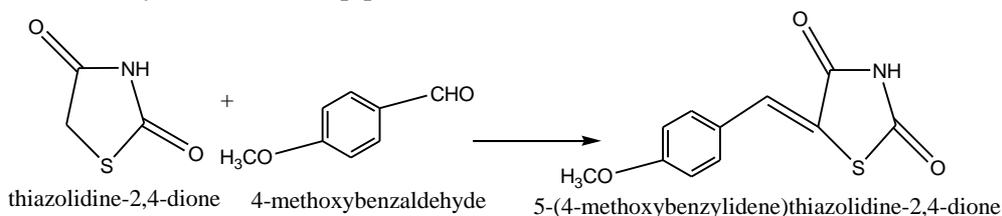
A] synthesis of Thiazolidine - 2,4-dione

In a 250 ml three-necked round-bottomed flask, was placed, solution containing (56.7 g, 0.6 mol) of chloroacetic acid in 60 ml of water and (45.6 g, 0.6 mol) of thiourea dissolved in 65 ml of water. The mixture was stirred



B] synthesis of 5-(4-methoxybenzylidene) Thiazolidine - 2,4-dione

In a 250 ml three-necked round-bottomed flask provided with a Dean-Stark apparatus, 4-methoxybenzaldehyde (24.21 g, 0.178 mol) and 2,4-thiazolidinedione (18.70g, 0.178 mol) were together suspended in ethanol. To this a catalytic amount of piperidine (1



for 30 min. to form a white precipitate, accompanied by considerable cooling. To the contents of the flask was then added slowly 60 ml of concentrated HCl from a dropping funnel, the flask was then connected with a reflux condenser and gentle heat applied to effect complete solution, after which the reaction mixture was stirred and refluxed for 8-10 hr upto 110 °C. On cooling the contents of the flask solidified to a cluster of white needles. The product was filtered and washed with water to remove traces of hydrochloric acid and dried. It was purified by recrystallization from ethyl alcohol. Yield: 79%; m.p.: 123-126 °C.

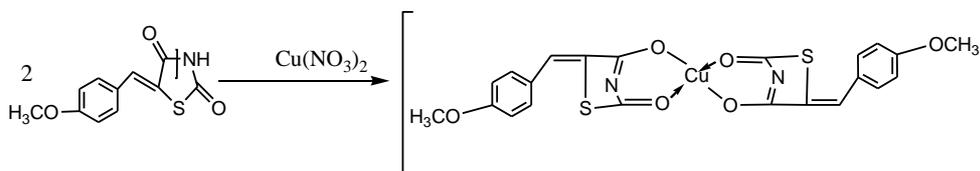
ml) was added. The mixture was stirred and refluxed.

After the complete removal of water and when the temperature reached above 110 °C the reaction mixture was stirred for a further 2 hr. On cooling, the product precipitated out from ethanol. The compound was filtered and washed with cold dry toluene and dry ethanol. Yield: 80%; m.p.: 238-240 °C.

a) Preparation of Cu (II) complex

Copper Nitrate(0.60g 0.0025mol) dissolved in methanol, 5-(4-methoxybenzylidene) Thiazolidine - 2,4-dione (2.35 g 0.005mol) in methanol was

added in drops with constant stirring; The mixture was irradiated in a microwave oven for about 15 seconds. The precipitated coloured complex was filtered, washed with ethanol and dried.



b) Instrumental techniques

The elemental analysis of the complexes was carried out by using (Thermo Finnegan make, Flash EA1112 Series Instrument) CHNS (O) analyzer. The electrical conductivity measurements were conducted using 10⁻³ M solutions of the metal complexes in acetonitrile with Systronic Conductivity Bridge 304 at 30°C. The UV-Visible spectra of Cu (II) complex was recorded on Varian, Cary 5000 model UV Spectrophotometer. The IR spectra of the ligand and complex were recorded on a Perkin Elmer, Spectrum RX-I, FT IR spectrometer in 4000-400 cm⁻¹ range with KBr pellet technique. The Far-IR Spectrum of the complex was recorded by Bruker 3000, FT IR Spectrometer.

RESULTS AND DISCUSSION

Analytical data

The prepared complex was coloured with the yield of about 65%. The elemental analytical data were in good agreement with the calculated values. From the results of elemental analysis and metal estimation, the formula of the complex was given as [Cu(MBD)₂(TZD)₂]. The

molar conductance value (93.2 ohm⁻¹cm²mol⁻¹) indicates the non electrolytic (1:0 type) nature of the complex.

Magnetic moment and UV-Visible spectra:

The magnetic moment value of Cu (II) complex 3.35 BM, which confirm its octahedral geometry. The complex exhibits three λ_{max} values at 587nm (ν₁), 422 nm (ν₂) and 274 nm (ν₃) which corresponds to 4T_{1g} ← 4A_{2g}, 4T_{1g} (F) ← 4A_{2g} and 4T_{1g} (P) ← 4A_{2g}. These transitions also confirm the distorted octahedral geometry of the complex.

FT-IR spectra-

The IR spectra give the information about the functional groups present in the ligand which are entering into the coordination sphere. The IR spectrum of free TZD showed ν(C=O) at 3435cm⁻¹, ν(N-H) at 3450cm⁻¹ and ν(C-N) at 1282 cm⁻¹. The ν(N-H) stretching frequency gets broadened in the complex at 3429cm⁻¹. The 4-methoxybenzaldehyde ion shows the asymmetric and symmetric stretching vibrations of aldehyde group in the region 1248-1345cm⁻¹ which get broadened in the complex. These

observations indicate that the ligands which have entered into the coordination sphere of the Cu(II) complex. In FT-IR spectrum, the M-N coordination of TZD at 507 cm^{-1} confirm the ligating atoms of the ligands.

NMR of Cu (II) complex-

Assignment of 5-(4-methoxybenzylidene) Thiazolidine-2,4-dione with Cu(II) complex, Mol. Formula $[(C_{11}H_{10}NO_3SCH_3)_2 Cu]^+ NO_3^-$

CONCLUSION

Cu(II) complex with 5-(4-methoxybenzylidene) Thiazolidine - 2,4-dione was prepared under microwave irradiation and characterized by various physico-chemical and spectral methods. The molecular formula of the complex is $[Cu(MBD)_2(TZD)_2]$. The probable geometry of the complex is distorted octahedral.

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