RJC

RASĀYAN *J. Chem.*
Vol. 12 | No. 2 |511 - 518| April - June | 2019
ISSN: 0974-1496 | e-ISSN: 0976-0083 | CODEN: RJCABP
http://www.rasayanjournal.com
http://www.rasayanjournal.co.in

SYNTHESIS OF 3-HYDROXY-2-(2'-THIENYL)-4-OXO-4H-1-BENZOPYRAN (HTC) REAGENT AND SPECTRAL CHARACTERIZATION OF TIN(II)-3-HYDROXY-2-(2'-THIENYL)-4-OXO-4H-1-BENZOPYRAN (HTC) COMPLEX

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ABSTRACT

By reaction between *o*-hydroxyacetophenone and 2-thiophenecarbaldehyde, we synthesized 3-hydroxy-2-(2'-thienyl)-4-oxo-4H-1-benzopyran (HTC) reagent. Tin(II)-HTC complex was synthesized as stoichiometry in 1:2 (stoichiometry ratio is determined by the job's method of continuous variation and mole ratio method) in dry methanol. The complex was characterized by IR, NMR spectra. Further, properties of the complex were studied by UV-Visible spectroscopy, fluorescence spectra and thermal gravimetric analysis (TGA). Complex shows maximum absorbance at 432 nm over negligible absorption of HTC reagent at 432 nm. It is more fluorescent as compared to HTC reagent.

Keywords: *o*-Hydroxyacetophenone, 2-Thiophenecarbaldehyde, Anhydrous Stannous Chloride, Dry Methanol.

INTRODUCTION

The organotin compounds have active chemically, biological, industrials and have significant attention of researcher's worldwide[1-5]in these types of compounds synthesis. Schiff bases and their complexes have interesting biological and pharmacological activities like anticancer[6-9], antimalarial[10], anti-inflammatory[11], anti-HIV, antifertility[12] anticonvulsant[13]antimicrobial activities[14-17]etc.They can play a role as a plant growth regulating agents. Organotin complexes show unusual at synthetic and structural stages and their application can be modified as a result of ligands attached to the central tin metal[18-19].Fundamental features of organotin(IV) complexes, such as thermodynamic and kinetic characteristics, coordination number variations, geometries, and intrinsic properties of the metal ion, have motivated research interest into finding use fore the varied approaches in diverse fields including agricultural, industrialized, and biomedical fields such as in wood preservatives, surface disinfectants, insecticides, antifouling agents[20-22].Therefore, we synthesized new organotin complexes in the surge of more potent and bio-specific antimicrobial and pharmaco-active drugs with better curing effects, which are less toxic to the environment and host.

EXPERIMENTAL

Requirements

All solvents and reagents used are HPLC grade and did not require any further purification during synthesis of reagent and metal reagent complex. Thin-layer chromatography (TLC) was performed using silica-aluminum plates and the plates were visualized using ultraviolet light both long range and short range.

Instruments

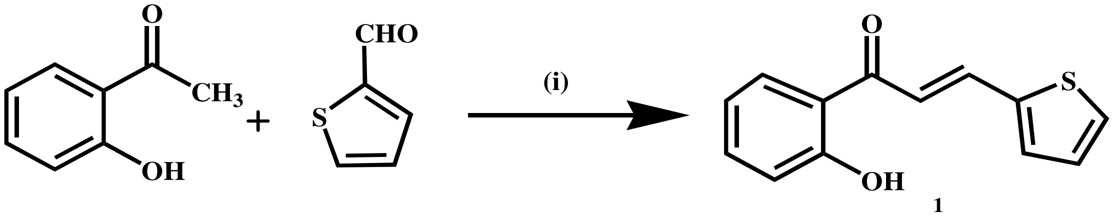
All glassware was dried in an oven before use. Melting point apparatus was used to determine the melting point (beyond the range of apparatus). Infrared spectrum (IR spectrum) was recorded on ABB MB 3000 IR Spectrophotometer. Nuclear magnetic resonance (NMR) data were recorded on a Bruker AV(III)-400

Rasayan J. Chem., 12(2), 511-518(2019)
http://dx.doi.org/10.31788/RJC.2019.1224027

MHz. All samples were analyzed in $CDCl_3$/ DMSO-d_6. The reference (residual solvent)used for NMR show their chemical shift at $\delta = 7.656$ ($CDCl_3$), $\delta = 2.601$ (DMSO-d_6) for proton-NMR (^{1}H-NMR) and $\delta = 77.1$ ($CDCl_3$), $\delta = 40$ (DMSO-d_6) for ^{13}C-NMR. The abbreviations: s = singlet, d = doublet, m = multiplets were used for multiplicities of coupled signals given in Hertz. The electronic spectrum was recorded on T 90 UV-Visible spectrometer in the region 200–600 nm and emission spectra were recorded on Shimadzu-5301pc spectrofluorophotometer. Thermal Gravity Analysis (TGA) was observed at Perkin Elmer TGA 4000 by heating at a rate of 5°C per minute.

Synthesis and Schemes for the Synthesis of HTC Reagent

Compound **1** i.e. (E)-1-(2-hydroxyphenyl)-3-(thiophene-2-yl)prop-2-en-1-one was synthesized by modification in the reported process[23]. Prepare a solution of NaOH (4 g in 8 mL of 50% ethanol). Then add solutions of *o*-hydroxy-acetophenone(4.08 g in 30 mL ethanol) dropwise and were stirred for 2 hrs, below 60^0C as in scheme-i. Then add thiophene-2-aldehyde (3.36 g) was added dropwise in the above solution. The orange-red mass (I, m.p.100^0C) thus obtained was neutralized with dilute 0.2 M HCl (prepared from conc. HCl) and recrystallized from ethanol.

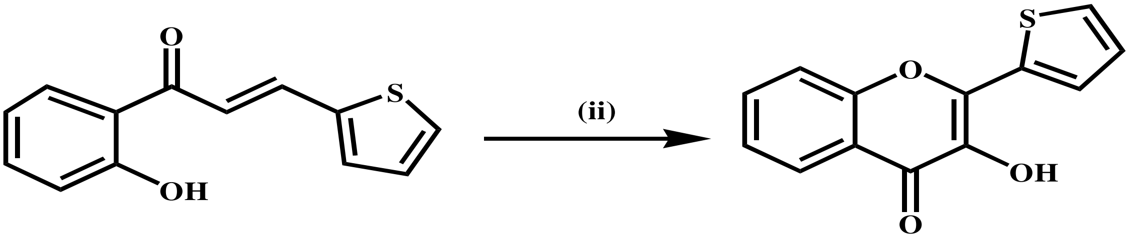


Scheme (i). NaOH/EtOH, stirred 2hr,T<60 °C

Scheme-1

Synthesis of 3-hydroxy-2-(2'-thienyl)-4-oxo-4H-1-benzopyran (HTC)

Solutions of NaOH (8 mL of 20 % in methanol),then add compound 1 (2 g in 20 mL methanol) and Hydrogen peroxide (4 mL, 30 %) were mixed, stirred for 2 hr, below 10^0C, as in Scheme-2 and neutralized with dilute acetic acid. The yellow compound so obtained after crystallization from ethanol and water is HTC, melting point 199^0C (Literature melting point 200^0C) as shown in scheme (ii). 0.1% (w/v) [0.1 g of HTC reagent in 100 mL of distilled ethanol] solution of HTC in ethanol was prepared.



Scheme (ii). H_2O_2/NaOH, stirred 2hr, T<10 °C

Scheme-2

Characterization of HTC Reagent

HTC reagent was characterized and studied by Infrared (IR) and nuclear magnetic resonance (NMR) spectroscopy.

IR Spectrum of HTC Reagent

The IR spectrum of reagent HTC [FiG.-1] was observed and discussed. IR spectra of HTC reagent displayed a strong, broad peak near 3178 cm^{-1} due to -OH stretching. The peak near 2924, 2862 cm^{-1} was observed due to –CH stretching. The intense peak near 1605, 1558, 1474, 1427 cm^{-1} due to -C=O, –C=C and -C=S stretching respectively.

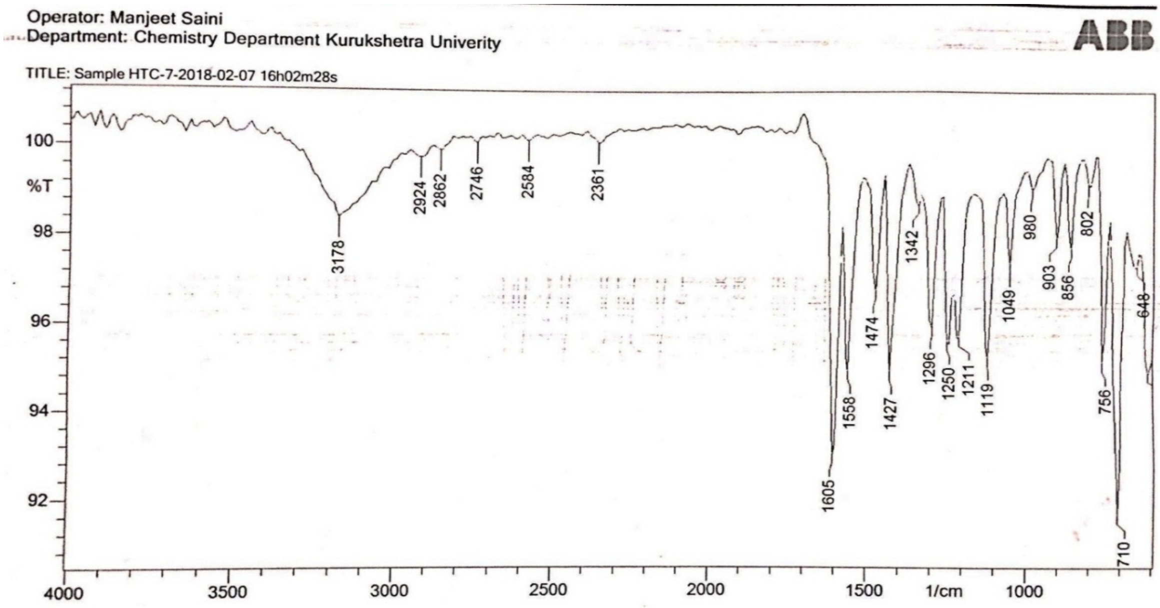


Fig.-1: The IR Spectrum of HTC Reagent

NMR Spectroscopy of HTC Reagent

Yellow solid, m.pt.198-200°C. Yield: 64%; Anal. Calc. $C_{13}H_8O_3S$; ^1H NMR ($CDCl_3$, 400 MHz, δH): 8.275-8.256 (d, 1H, ArH), 8.053-8.045 (d, 1H, thio-H), 7.741-7.702 (t, 1H, thio-H), 7.652-7.640 (d, 1H, thio-H), 7.611-7.590 (d, 1H, ArH), 7.456-7.420 (t,1H, ArH), 7.278-7.250 (t, 1H, ArH),7.037 (broad, 1H, OH) including $CDCl_3$ proton as shown in Fig.-2.

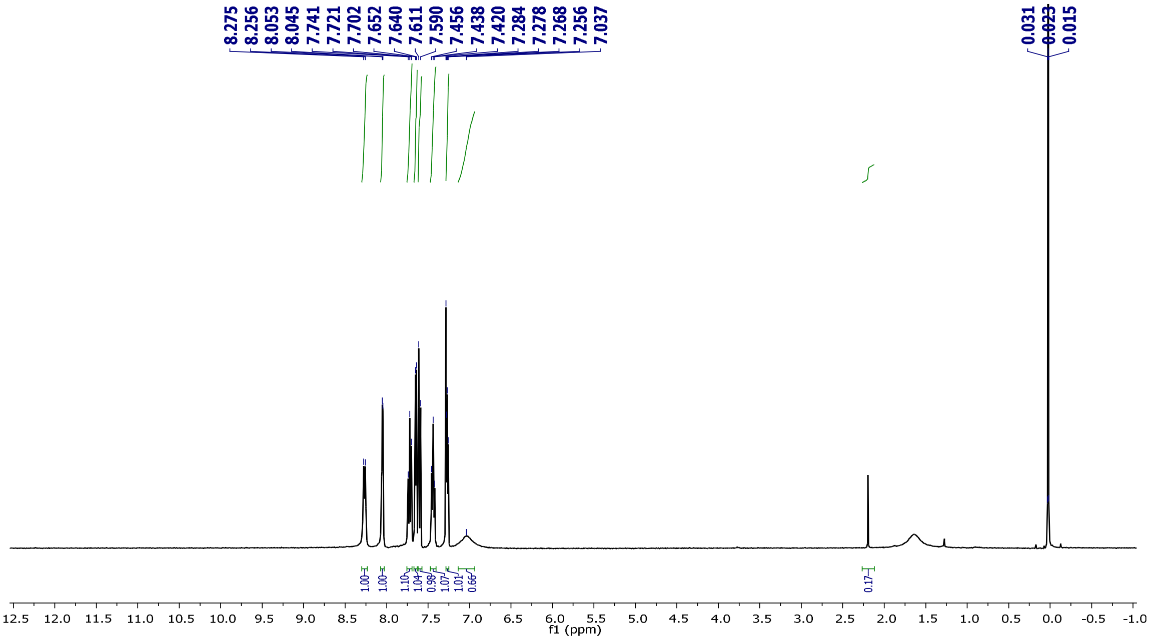


Fig.-2: ^1H Spectrum of HTC Reagent

^{13}C NMR ($CDCl_3$, 100 MHz, δC): 195.741, 155.09 (C=O), 136.316, 135.548, 132.900, 129.890, 129.491, 128.123, 125.450, 124.597, 118.168 ppm as shown in Fig.-3.

Stoichiometry of Complex

By using the spectrophotometric determination of tin(II) with 3-hydroxy-2-(2'-thienyl)-4-oxo-4H-1-benzopyran (HTC) complex into dichloromethane (DCM), we noted that the stoichiometry ratio of the complex established is 1:2 (tin:HTC reagent) by using two methods, first is the job's method of continuous variation[24] and second is mole ratio method.

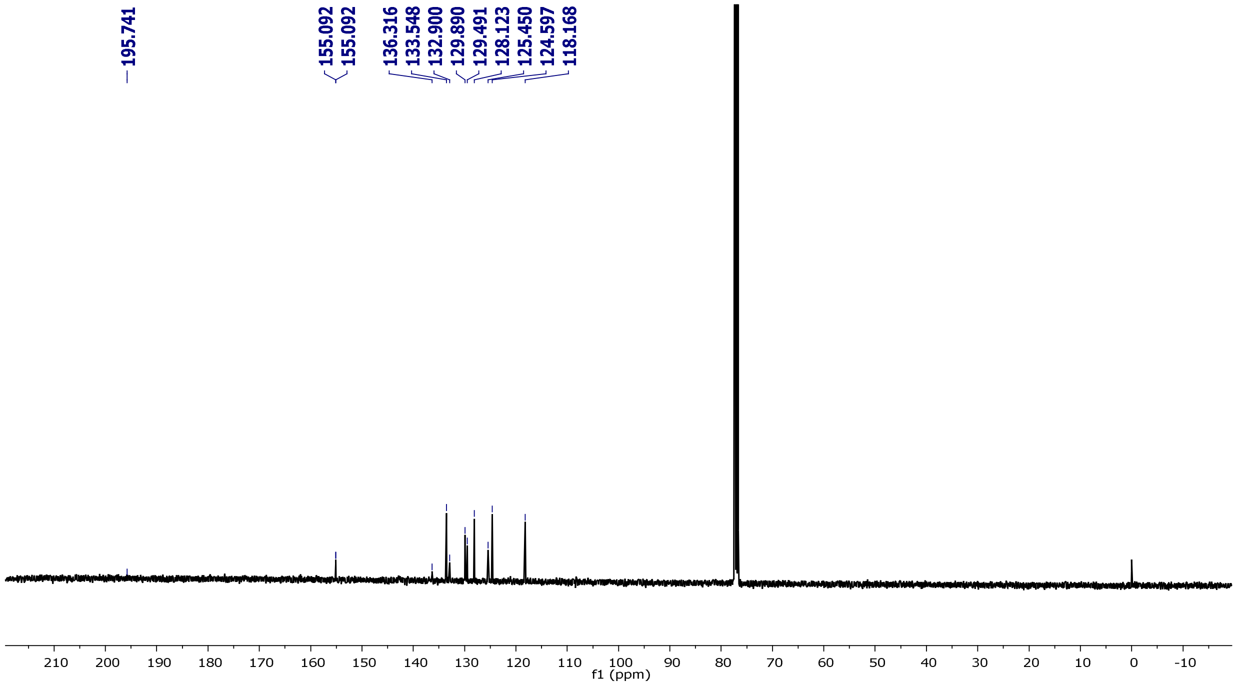


Figure 3- ^{13}C spectra of HTC reagent

Synthesis of Tin(II)-HTC Complex

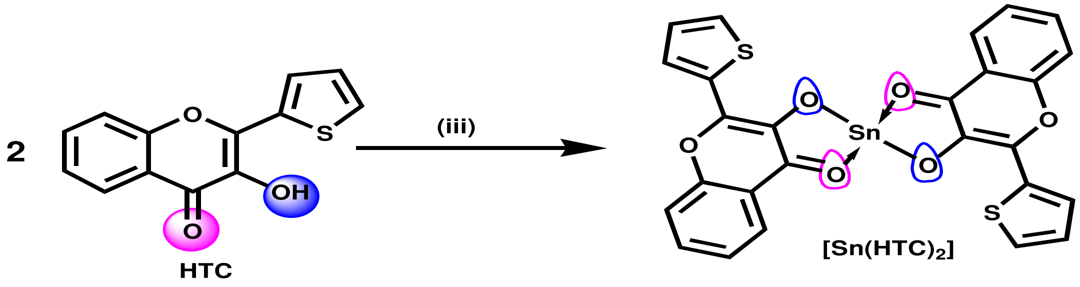
In one round bottom flask, synthesized reagent HTC (0.4885 g, 2 mmol) was dissolved in dry methanol under nitrogen environment. In other RB flask, anhydrous stannous chloride (0.1896 g, 1 mmol) was dissolved in dry methanol under nitrogen environment. Then stannous chloride solution was injected to HTC reagent solution under the same environment, stirred for 6 hr (Scheme-3). The progress of the reaction was monitored regularly by TLC. After the completion of the reaction, the solid product was obtained and then filtered, washed with dry methanol and dried under reduced pressure. Solid was recrystallized by ethanol and characterized by spectral analysis (IR, NMR). The yield obtained 70%. The melting point is above 250ºC beyond the limit of apparatus.

IR Spectrum of [Sn(HTC)$_2$]Complex

Reagent HTC and tin metal binding [Sn(HTC)$_2$]complexwas assigned on the support of displacing in the fundamental frequency and lowering in the intensities of the absorptions in the complexes as compared to the HTC reagent as shown in Fig.-1. In the IR spectrum of the complex as shown in Fig.-4, stretching band near 3178 cm^{-1} (O–H stretching) present in IR spectra of HTC reagent which completely disappeared in the tin HTC complexes; it is strong evidence for the Sn-HTC complex formation. It also indicated that de-protonation of -OH proton with the formation of covalent bond through oxygen site of ligand to Sn. Further, major change observed in a carbonyl frequency band which is a shift in complex toward lower frequency sites. Hence, IR spectroscopy studies of the reagent HTC and complex provide efficient information about complex formation. It also suggests deprotonation of O-H moiety, the formation of -O-Sn[25] and =O-Sn- bond.

NMR Spectra of [Sn(HTC)$_2$] Complex

The binding sites (-C=O, OH) of the HTC reagent were further confirmed by comparing the ^{1}H NMR with their complexes which were in accordance with the IR spectrum. The main characteristic peak in the reagent as shown in Fig.-2 was a singlet due to OH proton observed in the region at δ 7.037 (broad, ^{1}H, OH) found to be missing in ^{1}H NMR spectra of [Sn(HTC)$_2$] complex. A change in chemical shift related to another proton in HTC reagent was observed due to coordination of tin metal with HTC reagent. The result provides strong evidence for the tin complexation with HTC reagent as shown in Fig.-5.



Scheme (iii). Anhydrous SnCl$_2$, Dry CH$_3$OH, stirred at RT for 6 hr

Scheme-3

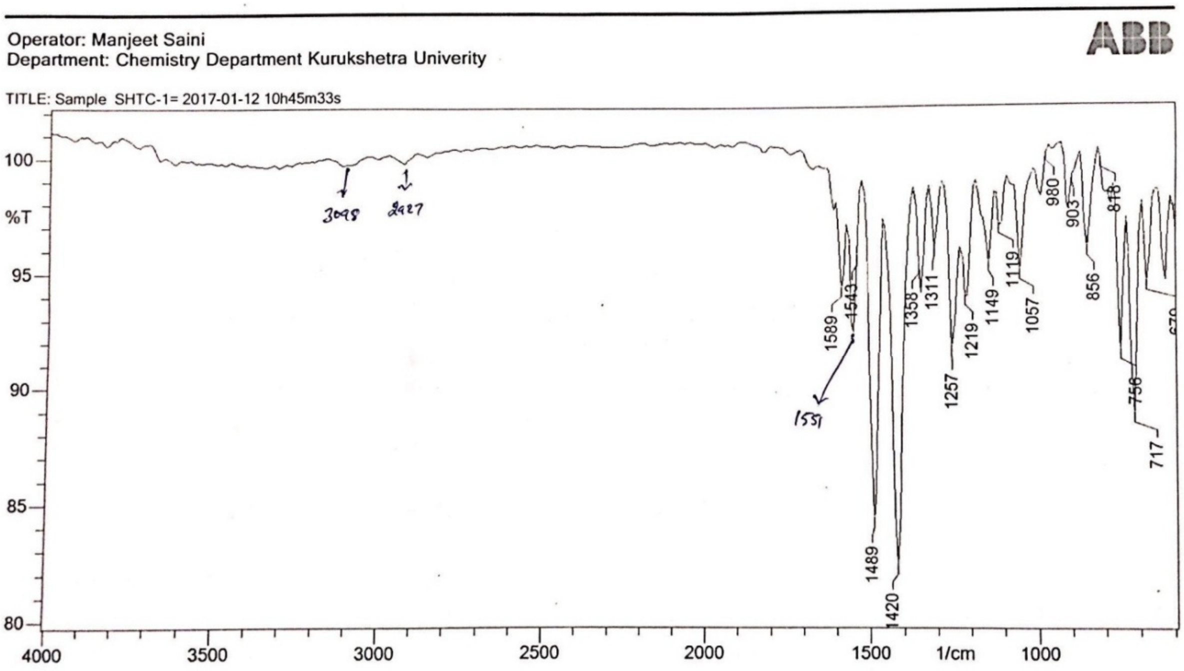


Fig.-4: IR Spectrum of [Sn(HTC)$_2$]Complex

The UV-Visible Spectrum of Tin-HTC Complex

Tin(II) reacts with 3-hydroxy-2-(2'-thienyl)-4-oxo-4H-1-benzopyran (HTC) ligandin an acidic medium (HCl) to form a yellow colored species, which can be quantitatively extracted into the dichloromethane (DCM). The absorption spectrum of the yellow color complex in extraction solvent dichloromethane (DCM) with that of the blank is shown in (Fig.-6, Curve –A).The reagent blank shown strong absorption at 390nm but there was a sharp decrease in absorbance on going towards longer wavelength and becomes negligibly small in the region 432 nm (Fig.-6, Curve-B). Then we checked out the various parameters which affect the formation and absorbance of the complex were studied at 432 nm.

The Fluorescence Spectrum of Tin-HTC Complex

The fluorescence spectrum of HTC reagent, tin-HTC complex was observed. Reagent HTC show weak emission spectra near 475 nm. Complex fluorescence spectra [Fig.-7] show an enhancement in emission intensity near 512 nm (490-531 nm, broad range) in respective of reagent spectra. In HTC reagent, the nonbonding electrons of carbonyl oxygen and –OH oxygen induce to the acceptor part of reagent. As a result, emission occurs due to Photoelectron induced transfer (PET)[26(a)]. In the complex, the electron of the carbonyl group coordinated with the tin metal and deprotonation of the hydroxyl –OH group that forms oxygen tin bond. Due to complexation, PET affects and chelating occur. The increase in fluorescence referred to chelation-enhanced fluorescence (CHEF).[26(b)]

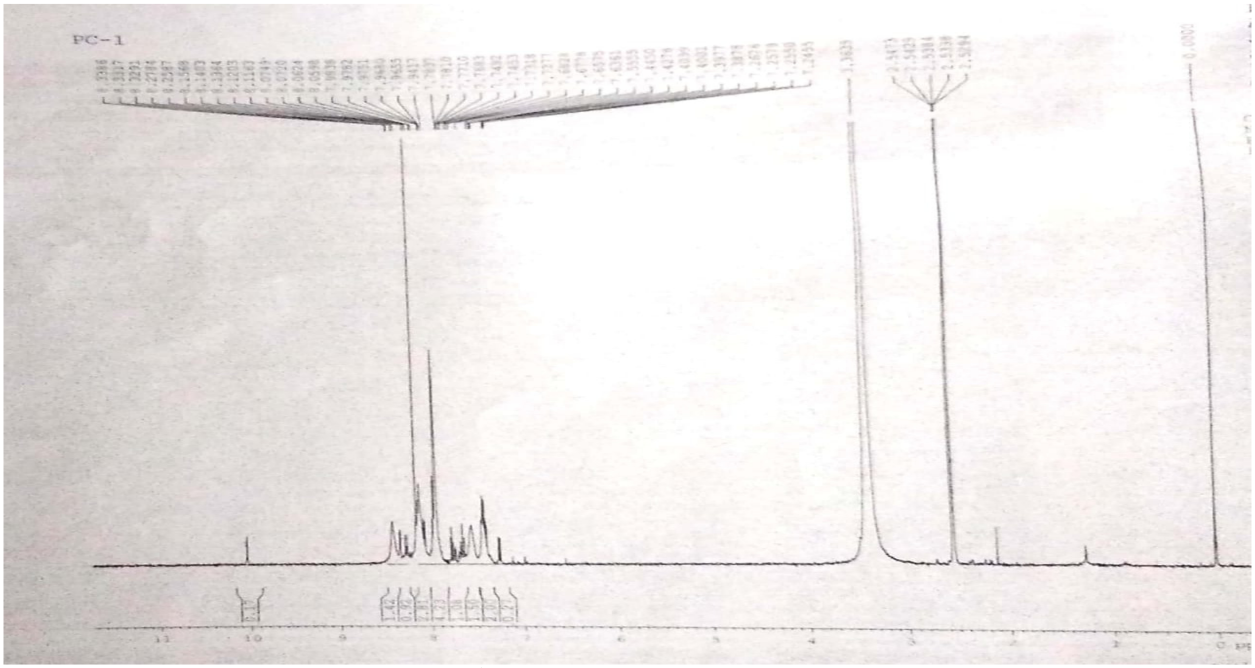


Fig.-5: ^{1}H Spectra of [Sn(HTC)$_2$] Complex

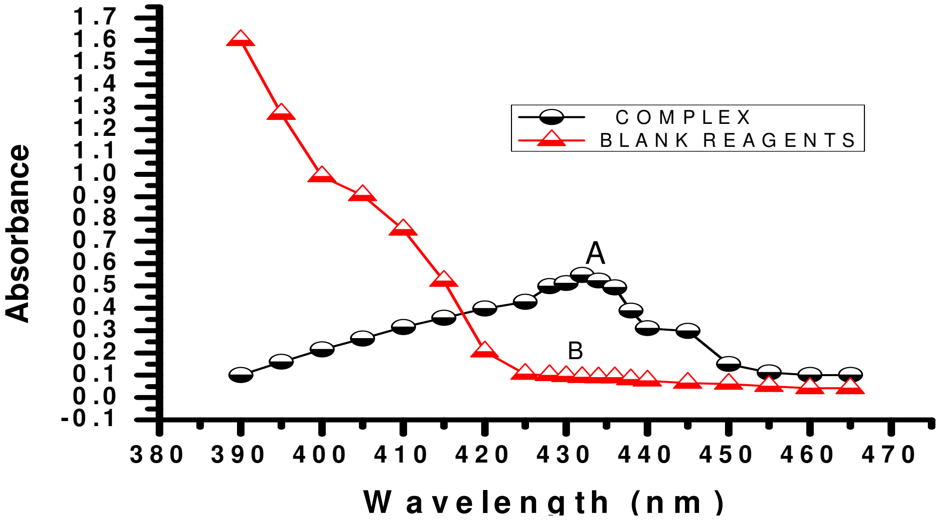


Fig.-6: Absorption Spectra of Sn(II)-HTC Complex

Thermal Studies of [Sn(HTC)$_2$]Complex

Thermal study of [Sn(HTC)$_2$] complex was studied in nitrogen environment[27] (Fig.-8). Thermo gravimetric analysis (TGA) data for the samples were obtained in the standard form of weight % loss as a function of temperature along Y-axis at heating rate 5ºC min^{-1} is shown in Fig.-8. There was negligible weight loss (1.98 %) was observed up to 242ºC due to loss of absorbing moisture. The major weight loss observed was found in two stages. In the first stage, weight loss between temperature range 243-400°C is 17.19% (calc. 24.55 %). This weight loss occurred due to the breakdown of thiophene moiety from[Sn(HTC)$_2$]complex. In the second stage, major weight loss between temperature range 400-452°C is 47.93% (calc. 47.64 %) was occurred at a constant rate due to loss of chromones and chloride part from the complex. Weight % loss from temperature range452-680°C was found to be 4.45 %. The remaining yield of the complex was found 27.564% due to a non-decompose oxide of tin[28].

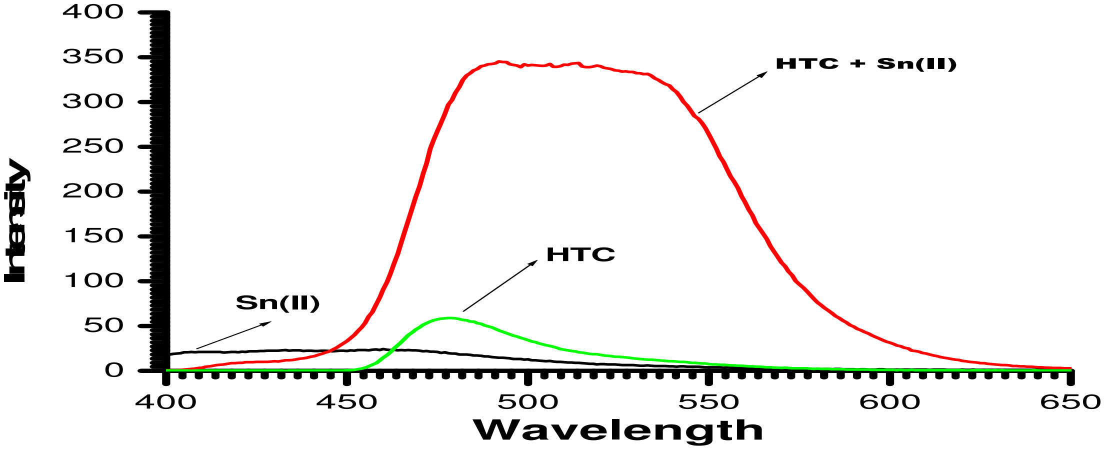


Fig.-7: Fluorescence Spectra of [Sn(HTC)$_2$] Complex

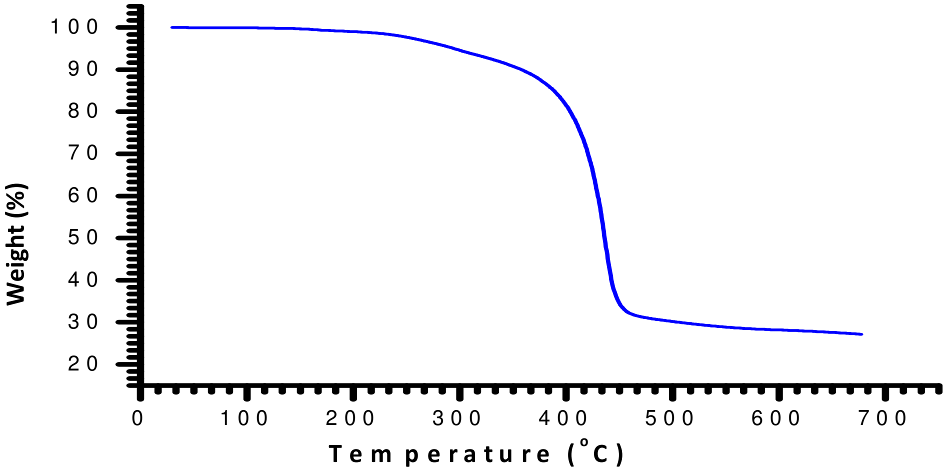


Fig.-8: Thermo Gravimetric Analysis (TGA) Graph for [Sn(HTC)$_2$] Complex

ACKNOWLEDGMENT

The authors are thankful to CSIR for providing senior research fellowship (SRF), Kurukshetra University, Kurukshetra and non-teaching staff for providing the necessary facilities.

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[RJC-4027/2018]