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CHAPTER - II

SYNTHESIS AND CHARACTERISATION OF  
5-NITROSALICYLALDEHYDE THIOSEMICARBAZONE

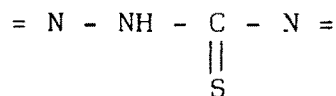
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## CHAPTER - II

SYNTHESIS AND CHARACTERISATION OF  
5-NITROSALICYLALDEHYDE THIOSEMICARBAZONE.

Introduction :

Thiosemicarbazones are a class of compounds obtained by condensing thiosemicarbazide (TSC) with suitable aldehydes or ketones. These compounds are easily crystallisable and possess sharp melting points. Hence, they have long been commonly used for identification of individual aldehydes or ketones. However, the first report on analytical use of this class of compounds was made by Scott et al. as late as 1945.<sup>1</sup> Since then voluminous work on their analytical applications has appeared in the literature. The realisation of the importance of thiosemicarbazones as analytical reagents is reflected in gradual increase in the number of papers dealing with their applications in analytical problems. The review of the work on transition metal complexes of thiosemicarbazides and thiosemicarbazones was written by Campbell.<sup>2</sup> Singh<sup>3</sup> et al. recently gave a critical review on analytical applications of thiosemicarbazones and semicarbazones. Thiosemicarbazones contain active grouping for chelation as shown below



Which involves bonding through sulphur atom with possible further coordination by the hydrazino nitrogen atom to give a five

membered chelate ring. Depending upon the type of aldehyde or ketone used for condensation thiosemicarbazones can act as unidentate, bidentate or multidentate chelating agents for several metal ions producing highly coloured complexes. In case of unidentate ligands, bonding occurs only through the sulphur atom. The coloured complexes are used in selective and sensitive determination of metal ions. Domagk<sup>4</sup> et al. Pioneered Pharmaceutical application of metal thiosemicarbazone for the treatment of tuberculosis. Since then a number of papers have appeared on the pharmacology of these compounds. Moreover, these compounds have been shown to be active against influenza,<sup>5</sup> protozoa,<sup>6</sup> smallpox<sup>7</sup> and certain kinds of tumours and possess very good pesticidal<sup>9</sup> and fungicidal<sup>10</sup> activity. The biological activity of thiosemicarbazones may be attributed to the ability of the reagent to form chelates with traces of metal ions present in biological systems. The antituber activity of p-acetamidobenzaldehyde thiosemicarbazone is found to be enhanced by the presence of a small amounts of copper ions.<sup>11</sup> These findings have led recently to an increased interest in the chemistry of transition metal chelates of thiosemicarbazones.

A large number of thiosemicarbazones are used as spectrophotometric reagents in analytical chemistry. They are used for trace determination of metal ions in various materials. Metal-thiosemicarbazone complexes are formed in conditions ranging from moderately acidic to moderately alkaline. However, there are relatively few reports on spectrometric determination of metal

ions in highly acidic medium.<sup>12-14</sup> Metal complexes are also extractable in various organic solvents resulting in an enhanced sensitivity thereby enabling extraction and simultaneous photometric determination of metal ions.<sup>15-16</sup> It was generally observed that thiosemicarbazones containing hydroxy groups ortho to the aldehyde group gave good colour reactions. Besides the applications in spectrophotometry, thiosemicarbazones have been reported as gravimetric reagents for many metal ions,<sup>17-20</sup> as indicators in the direct titration of metals with EDTA<sup>21-22</sup>, in titration in non-aqueous solvents.<sup>23</sup> Recently reports have appeared on separation of metal ions using thiosemicarbazones by thin layer chromatography on alumina with ethyl acetate as a solvent.<sup>24</sup>

In this chapter, the synthesis and characterisation of 5-nitrosalicylaldehyde thiosemicarbazone is described.

#### Synthesis of 5-Nitrosalicylaldehyde Thiosemicarbazone

(5-NO<sub>2</sub>SAT).

The starting material 5-nitrosalicylaldehyde was first prepared in the laboratory according to ~~method of Duff~~<sup>nitration method</sup><sup>25</sup> and this was used for condensation with thiosemicarbazide to obtain thiosemicarbazone.

#### I) Synthesis of 5-nitrosalicylaldehyde :

5-nitrosalicylaldehyde was prepared according to the method of Duff.<sup>25</sup> A mixture of 50 gm salicylaldehyde and

200 gm glacialacetic acid were placed in a 500 ml round bottom flask fitted with thermometer and a mechnical stirrer and cooled to odg. To this was added fuming nitric acid (40 gm.d. 1.50) Sloly temperature below 15 degree and finaly the temperature was allowed to rise during one hour to 45 degree.

The mixture was immidiately poured into 1 litre water containing crushed ice and allowed to stand for five hours.

The solid obtained was a mixture of 3 nitro and 5-nitro isomers. This mixture was dissolved in a solution of sodium hydroxide (10 gm in 300 ml water) by warming it and then left overnight.

The nitro isomer which precipitated as the sodium salt of the phenol, gave the 5-nitrosalicylaldehyde on neutralisation.

Melting point  $126^{\circ}\text{C}$ .

Reported melting point  $126^{\circ}\text{C}$

Yield = 60%

## II) Synthesis of 5-nitrosalicylaldehyde thiosemicarbazone :

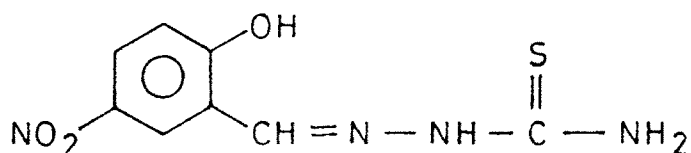
5-nitrosalicylaldehyde (2 or 3 gm, 10 nm) was dissolved in 20 ml ethanol. Thiosemicarbazide (1 gm; 10 nM) was dissolved in 20 ml of hot distilled water. The solutions were mixed, 2-3 drops of glacial acetic acid were added, and the mixture was refluxed for 2 hours. The mixture was then cooled in ice bath, the pale yellow crystals separated out.

The product was filtered through suction pump, dried in air. It was further crystallised twice from 1:1 water-ethanol mixture (V/V) to give yellow crystals. The product has high melting point (above 340<sup>o</sup>C).

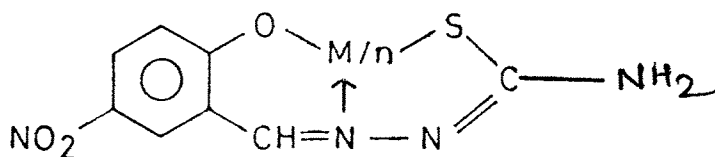
The crystal obtained were yellow in colour and needle shaped which were analysed for carbon, hydrogen, nitrogen, and sulphur.

Molecular weight = 240.

**Structural Formula** :



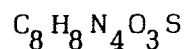
The probable structure of the metal complex is as follows :



Where n = 1 for Mo(V) and n = 2 for Cu (II)

**Elemental analysis** :

	C	N	H	S	O
<u>Found</u>	40.00	23.34	3.33	13.32	20.00
Calculated (%) for	40.00	23.33	3.35	13.33	20.00



**Properties of the Reagent :**

5-nitrosalicylaldehyde thiosemicarbazone ( $C_8H_8N_4O_3S$ ) occurs as yellow needle shaped and light shining crystals with high melting point ( $340^{\circ}C$ ). Before melting it becomes yellowish and then turns black. The compound is sparingly soluble in cold water ( $0.04 \text{ g L}^{-1}$  at room temperature) but soluble in hot ethanol, methanol and oxygenated solvents. It is moderately soluble in dioxane. The organic solvents in which the compound is sparingly soluble are benzene, carbon tetrachloride and chloroform. The solution of the compound in dioxane is stable for more than a week. The compound is stable towards light and can be stored for several months without deterioration.

**Ultraviolet Absorption Spectra :**

The absorption spectra of 5-nitrosalicylaldehyde thiosemicarbazone in dioxane  $.05 \times 10^{-5}$  solution is shown in Fig. 1. The curve exhibits sharp absorption maximum around 310 nm with extinction coefficient  $3.8 \times 10^6 \text{ LM}^{-1} \text{ CM}^{-1}$ .

**Infrared Spectra :**

Infrared absorption spectra in the range 200 to  $4000 \text{ cm}^{-1}$  were run on a Perkin Elmer 221 IR spectrophotometer using KBr Pallet technique. The characteristic absorption bands were observed as follows (as shown in Fig. 2).

$3340 \text{ cm}^{-1}$  OH,       $3450 \text{ cm}^{-1}$  NH and  $\text{NH}_2$   
 $1600 \text{ cm}^{-1}$  (C = N)      and       $1600 \text{ to } 1670 \text{ cm}^{-1}$  ( C = S).

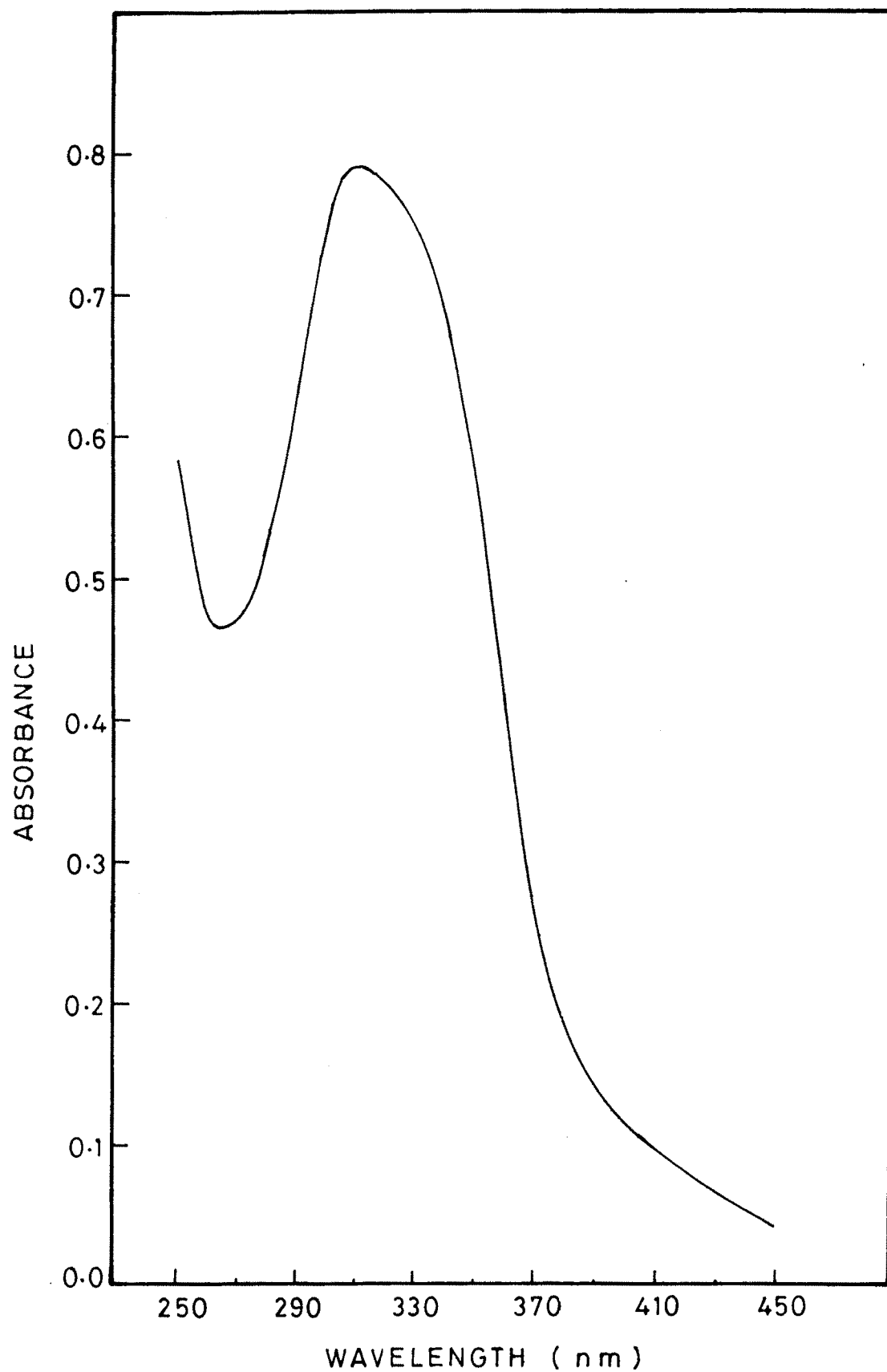


FIG. 1 - ABSORPTION SPECTRUM OF 5-NITRO SAT  
IN DIOXANE .



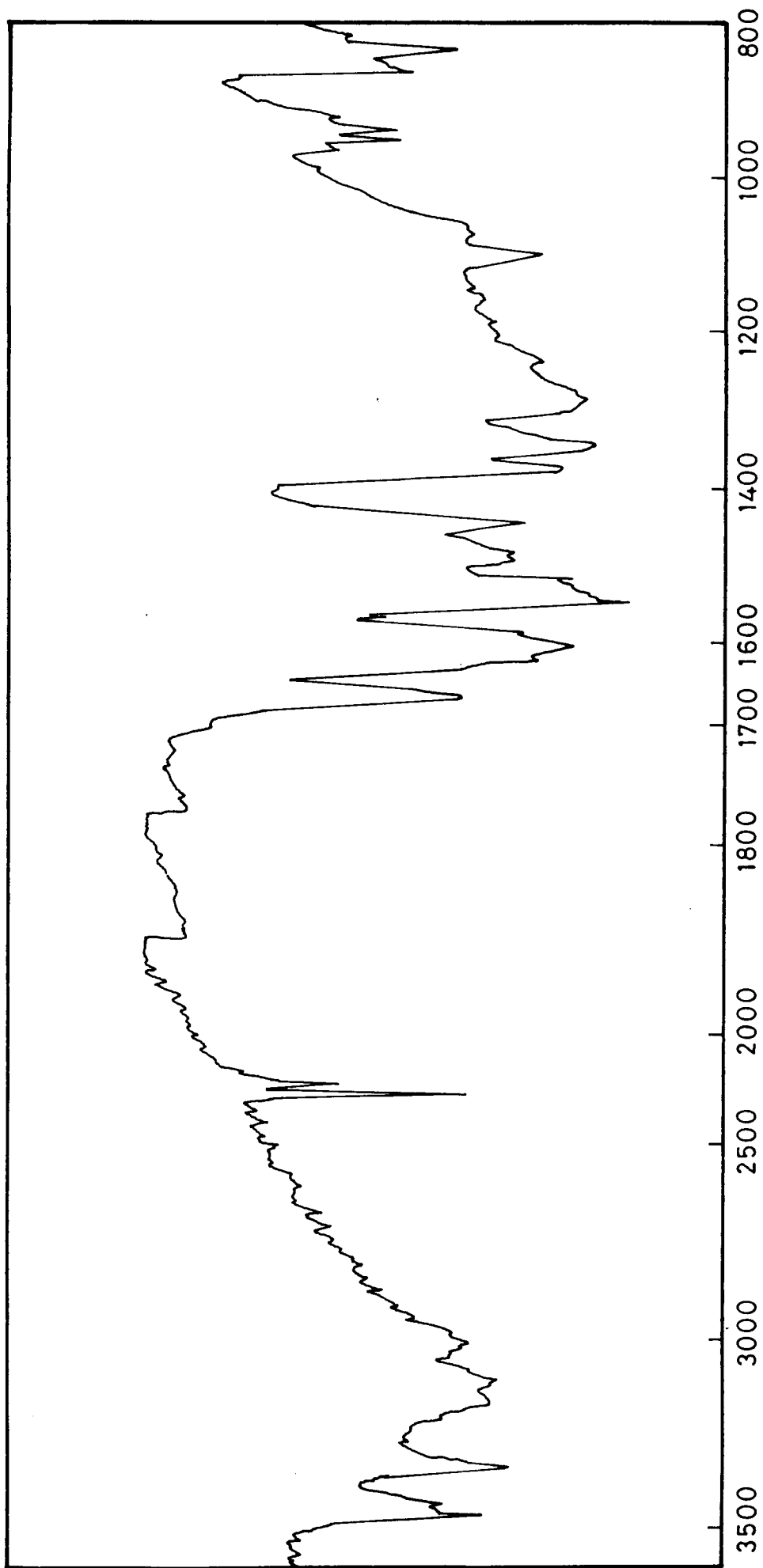


Fig.2 I.R. SPECTRUM OF 5-NITRO SAT.

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