# Synthesis and Characterization of Zinc (II) Salicylaldehyde N (4) Arylthiosemicarbazones

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**Abstract:** ***Zinc(II) Salicylaldehyde N (4) phenyl thiosemicarbazone of general formula for the complexes Zn $(HSTC\text{-}Ar)_2$ when R = Phenyl, Salicylaldehyde N(4) Phenyl thiosemicarbazone ($H_2STC$-Ph), p-Methylphenyl, Salicylaldehyde N(4)-p-Methylphenylthiosemicarbazone, ($H_2STC$-p-MePh), p-Methoxyphenyl, Salicylaldehyde N(4)-p-Methoxy phenyl thiosemicarbazone ($H_2$ STC-p-OMePh) and p-Chloro phenyl, Salicylaldehyde N(4)-p- Chlorophenyl thiosemicarbazone ($H_2STC$-p-ClPh) have been synthesized and characterized by elemental analysis and various physico-chemical technique. Molar conductance measurements show the non ionic behavior of the complexes. The TGA and DTA curves of Zn$(HSTC\text{-}p\text{-}MeOPh)_2$ under normal atmospheric conditions show complete decomposition of the compound at $300^0$C. Infrared spectra suggest mono-anionic bidentate mode of bonding of the ligands.***

**Keywords:** Metal complex, Phenylthiosemicarbazone, Ligands

## 1. Introduction

Among several ligands, thiosemicarbazones (TSCs), are a very attractive class of metal-chelating ligands, able to coordinate many transition metals through the sulfur as well as the azomethinic nitrogen atoms [1]. They can act as N, S-multidentate ligands, and moreover, it is possible to modulate the binding properties/stoichiometries through the insertion of other hetero atoms into the backbone structure (i.e., phenolic or pyridyl moieties). They have a great variety of biological properties, both as free ligands and as metal complexes, and several studies have been published reporting on thiosemicarbazone-based complexes with medicinal value [2]-[4]. Thiosemicarbazones are biologically active versatile compounds. Their antitumor, anti-malarial, anti-amoebic, antiviral and antibacterial activities are widely accepted [5]-[11]. The domain of thiosemicarbazones is not limited to biological field only; these have found applications in analytical chemistry as a reagent for the analysis of metals [12]-[14]. In industry these have been used for optical computing, optical storage and optical information processing [15]-[18] and antiwear additives in lubricanting oil [19]-[21] with reduced or zero sulphur and phosphorus content is ecofriendly.

## 2. Synthesis of Ligands

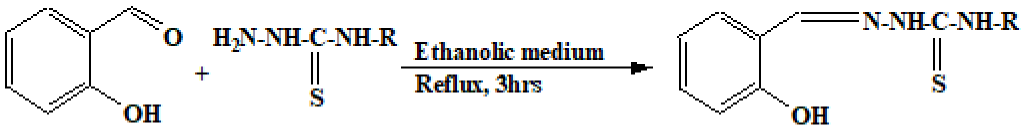
**Synthesis of SalicylaldehydeN(4)-phenyl thiosemicarbazone and its -*p*- substituted derivatives-**
At first N –Arylthiosemicarbazides [22]-[24] were prepared by the condensation of hydrazine hydrate with appropriate aryl isothiocyanate in cold ethanol.

Where R =phenyl-, *p*-methylphenyl-, *p*-methoxyhenyl and *p*-chloro phenyl- groups.

To an ice cold solution of 95% hydrazine hydrate (10ml; 0.2 mole) in ethanol (40ml), a solution of phenylisothiocyanate (12 m; 0.1 mole) in ethanol (20ml) was added with stirring.

The reaction was exothermic and N-phenylthiosemicarbazide formed was crystallized from ethanol.

Salicylaldehyde N(4)substituted phenyl thiosemicarbazones were prepared by the condensation of equimolar quantities of a N- Arylthiosemicarbazides (6.68g; 0.4 mole) in methanol (50ml) and salicylaldehyde (4.88g; 0.4 mole) in methanol (30 ml). The mixture was heated on a steam bath for 1-3 hr. The reaction mixture was cooled and the salicylaldehyde N (4) phenyl thiosemicarbazone which separated from solution was collected and recrystallized



When R = Phenyl , Salicylaldehyde N(4) Phenyl thiosemicarbazone ($H_2STC$-Ph)
*p*-Methylphenyl , Salicylaldehyde N(4)-*p*-Methylphenyl thiosemicarbazone($H_2STC$-*p*-MePh)
*p*- Methoxyphenyl, Salicylaldehyde N(4)-*p*-Methoxy phenyl thiosemicarbazone ($H_2STC$-*p*-OMePh)
*p*- Chlorophenyl, Salicylaldehyde N(4)-*p*- Chlorophenyl thiosemicarbazone ($H_2STC$-*p*-ClPh)

**Synthesis and characterization of Zinc(II) complexes of salicylaldehyde N (4) aryllthiosemicarbazones**

The structure of salicylaldehydeN (4) arylthiosemicarbazones used for the preparation of the complexes are given below-

When
R = Phenyl, Salicyaldehyde N(4) Phenyl thiosemicarbazone ($H_2$STC-Ph)
= *p*-Methylphenyl, Salicylaldehyde N(4)-*p*-Methylphenyl thiosemicarbazone ($H_2$STC-*p*-MePh)
= *p*-Methoxyphenyl, Salicylaldehyde N(4)-*p*-Methoxy phenyl thiosemicarbazone ($H_2$ STC-*p*-OMePh)
= *p*-Chloro phenyl, Salicylaldehyde N(4)-*p*-Chlorophenyl thiosemicarbazone ($H_2$STC-*p*-ClPh**)**

The Zn (II) thiosemicarbazones were prepared according to the following reaction-

$$(CH_3COO)_2Zn.2H_2O \longrightarrow +2H_2STC\text{-}R$$

Zn(HSTC-Ar)$_2$ + 2$CH_3COOH$ + 2$H_2O$

## 3. Preparation of the Complexes

For preparation of Zn (II) Salicylaldehyde N (4) phenylthiosemicarbazone [23,24] a solution of Zn(OAc)$_{2}$.2$H_2O$ 0.01mol, 2.71g in ethanol and a solution of salicylaldehyde N (4)phenylthiosemicarbazone 0.02mol, 5.42g in hot ethanol were mixed and refluxed for 3-4 hours. On cooling, solid yellow precipitate was appeared. The precipitate filtered, washed with ethanol and ether and dried *in vacuo* over $CaCl_2$, m.pt >280 d$^0$C.

## 4. Analysis of the Complexes

Zinc was estimated as gravimetrically zinc oxinate in the laboratory. About 0.2 g of compound was treated with 5 ml 3:1 ($HCl+HNO_3$) mixture in porcelain dish and strongly heated to dryness and then 0.5 ml conc. $H_2SO_4$ was added to destroy the organic matter. The residual solid was extracted with dilute HCl and NH4OH was added to maintain the pH should around 5.5. The solution was treated with 8-hydroxyquinoline and yellow precipitate was obtained. The precipitate was digested at 60 - 80$^0$C for 15 minutes, allowed to stand for 10-20 minutes, and filtered through a sintered glass crucible. It was dried at 130 - 140$^0$Cto constant weight.

Carbon, hydrogen and nitrogen were determined micro analytically. The analytical data are collected in table 1. The molar conductance values of all the complexes lie in the range 12-15 ohm$^{-1}$ mol$^{-1}$cm$^2$, indicating their non-ionic behavior. The complexes are insoluble in common organic solvents. On the basis of analytical data the general formula for the complexes Zn(HSTC-Ar)$_2$ [where R = Phenyl, Salicylaldehyde N(4) Phenyl thiosemicarbazone ($H_2$STC-Ph), *p*-Methylphenyl, Salicylaldehyde N(4)-*p*-Methylphenyl-thiosemicarbazone, ($H_2$STC-*p*-MePh), *p*-Methoxyphenyl, Salicylaldehyde N(4)-*p*-Methoxy phenyl thiosemicarbazone ($H_2$ STC-*p*-OMePh) and *p*-Chloro phenyl, Salicylaldehyde N(4)-*p*- Chlorophenyl thiosemicarbazone ($H_2$STC-*p*-ClPh**).** The TGA and DTA curves of Zn(HSTC-*p*-MeOPh)$_2$ under normal atmospheric conditions show complete decomposition of the compound at 300$^0$C.

**Table 1:** Analytical data of the Zinc (II) complexes

| Complexes | Colour | M.Pt ($^0$C) | C% Found (Calc.) | H% Found (Calc.) | N% Found (Calc.) | Zn% Found (Calc.) |
|---|---|---|---|---|---|---|
| Zn(HSTCPh)$_2$ | Yellow | >280 d | 55.35<br>(55.53) | 3.94<br>(3.96) | 13.77<br>(13.88) | 10.75<br>(10.74) |
| Zn(HSTC-*p*-MePh)$_2$ | Yellow | >280 d | 56.75<br>(56.87) | 4.40<br>(4.42) | 13.25<br>(13.27) | 10.30<br>(10.26) |
| Zn(HSTC-*p*-MeOPh)$_2$ | Yellow | >280 d | 54.45<br>(54.13) | 4.10<br>(4.21) | 12.42<br>(12.63) | 9.78<br>(9.77) |
| Zn(HSTC-*p*-ClPh)$_2$ | Yellow | >280 d | 49.77<br>(49.85) | 3.27<br>(3.26) | 12.68<br>(12.63) | 9.62<br>(9.64) |

**Infrared spectra**

The tentative assignments of the characteristic IR bands of the ligands and their zinc (II) complexes in the region 4000-400 cm$^{-1}$ are presented in table 2.

The spectra of the free ligands exhibit a band of medium intensity at 3148-3140 cm$^{-}$1which is assigned to ν (N-H) vibration. These bands disappear in the spectra of their complexes providing evidence in favor of coordination of ligands in their deprotonated forms around Zinc (II) ion. The ν (C=N) band appearing around 1600 cm$^{-1}$ in the ligands shows a negative shift of 10-15cm$^{-1}$ in the spectra of all derivatives of Zn (II) complexes. Coordination of azomethine nitrogen is confirmed by the appearance of new bands in the range 415- 435 cm$^{-1}$ assignable to ν (Zn-N) for these complexes. The ν(N-N) bands of the thiosemicarbazones are found at 1158 ± 10 cm$^{-1}$ in free ligands. After complex formation positive shift of about 10-15 cm$^{-1}$ occurs in this band due to increase in its bond strength. This again confirms the coordination via the azomethine nitrogen. The decrease in the stretching frequency of ν(C=S) bands from 870-890 cm$^{-1}$ in the thiosemicarbazone by around 20 cm$^{-1}$ upon complexation indicates coordination via thiolato sulphur. In the complexes a strong new band appears in the region 1515-1550 cm$^{-1}$ due to ν(N=C). Thus it is evident that coordination takes place via thiolato sulphur.

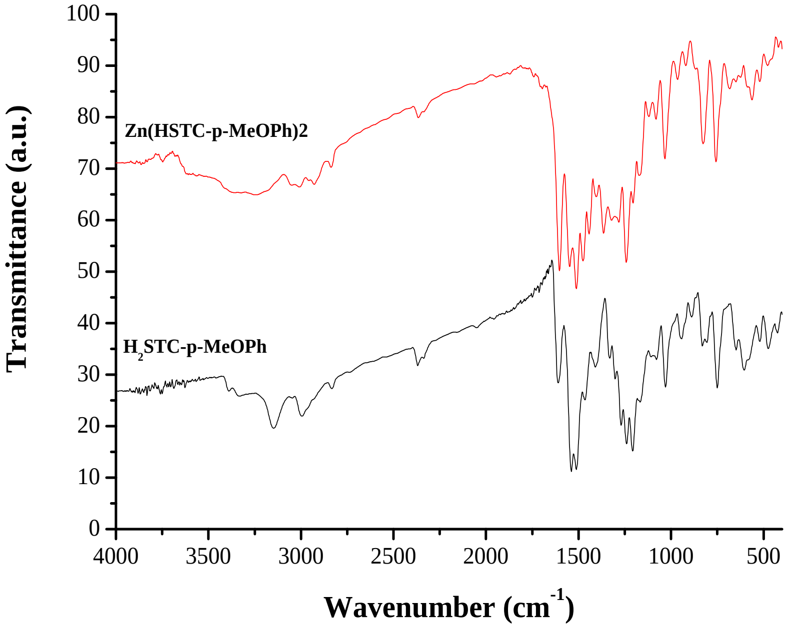


**Figure 1:** Infrared spectra of salicylaldehyde N (4) –*p*-methoxyphenyl thiosemicarbazones and its Zinc (II) complex

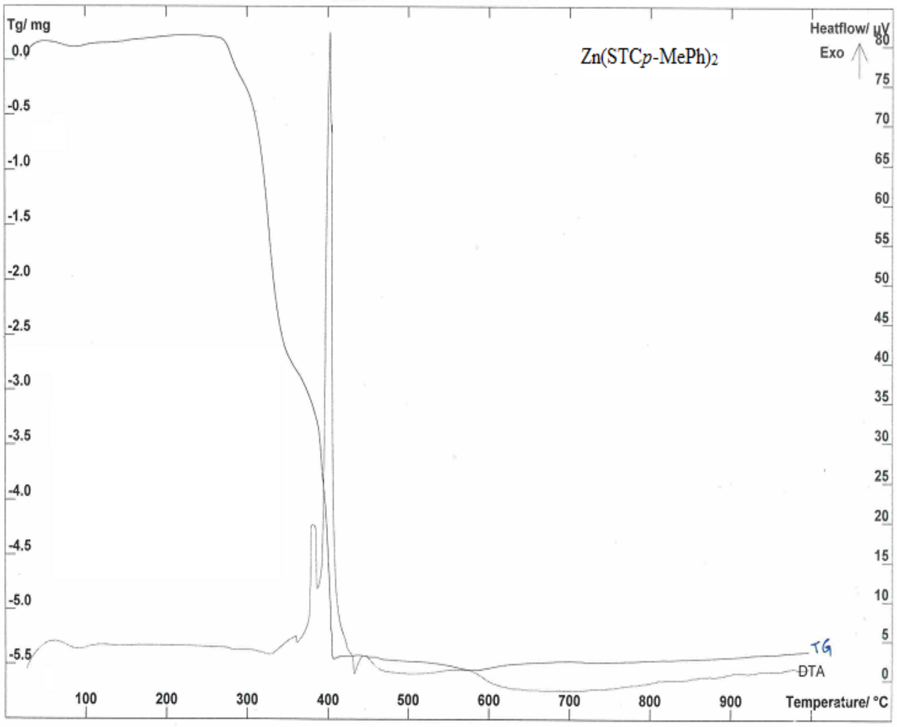


**Figure 2:** TGA and DTA curves salicylaldehyde N (4) –*p*-methoxyphenylthiosemi carbazones and its Zinc (II) complex in oxygen atmosphere

**Table 2:** IR spectral data (cm$^{-1}$) of ligands and their corresponding Zinc (II) complexes

| Complexes | N (C=N) | ν(N=C) | ν (N-N) | ν (C-S) | ν (C-O) | ν (Zn-N) |
|---|---|---|---|---|---|---|
| $H_2$STCPh | 1613 | - | 1149 | 1328, 874 | 1255 | - |
| Zn(HSTCPh)$_2$ | 1596 | 1542 | 1154 | 1327, 864 | 1204 | 421 |
| $H_2$STC-*p*-MePh | 1610 | - | 1155 | 1327, 870 | 1267 | - |
| Zn(HSTC-*p*-MePh)$_2$ | 1600 | 1516 | 1170 | 1311, 850 | 1240 | 415 |
| $H_2$STC-*p*-MeOPh | 1610 | - | 1166 | 1325, 889 | 1265 | - |
| Zn(HSTC-*p*-MeOPh)$_2$ | 1600 | 1545 | 1172 | 1321, 865 | 1242 | 418 |
| $H_2$STC-*p*-ClPh | 1608 | - | 1162 | 1320, 875 | 1265 | |
| Zn(HSTC-*p*-ClPh)$_2$ | 1600 | 1552 | 1170 | 1309, 852 | 1233 | 420 |

On the basis of analytical and IR spectra data, the following structure has been proposed for the complexes.

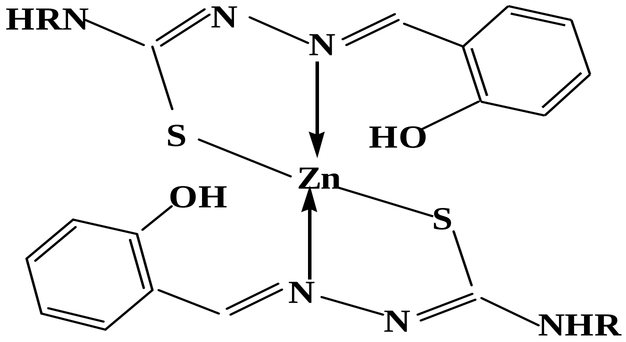


**Figure 3:** Tentative structure for Zinc (II) complexes of salicylaldehyde N (4) aryllthiosemicarbazones

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