

# Synthesis, Characterization, and Crystal Structures of a Thiosemicarbazone Ligand and Its Silver(I) Complex

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**ABSTRACT:** Thiosemicarbazone ligand 4Hbatsc = 4-hydroxybenzaldehyde-thiosemicarbazone and its silver(I) complex  $[Ag(PPh_3)_3(4Hbatsc)]NO_3$  were synthesized and characterized by elemental analysis (CHN), FT-IR spectroscopy, and single-crystal X-ray diffraction. The triclinic unit cell of 4H-ba-tsc (space group *P*-1) contains two independent molecules. Each of the two independent molecules is almost planar, with the sulfur atom (S1/S2) and the hydrazine nitrogen atom (N6/N4) in the *E* position concerning the C3-N5/C4-N4. The title complex is a triclinic *P*-1 mononuclear complex with the silver(I) ion coordinated in a distorted tetrahedral geometry by one S atom of 4H-ba-tsc and three P atoms of three PPh<sub>3</sub>. The complex involves the 4H-ba-tsc thiosemicarbazone ligand in an *S* monodentate binding mode. Besides, the thermal behavior of the complex was studied using thermogravimetry in order to evaluate its thermal stability and thermal decomposition pathway. Finally, nanoparticles of the complex were prepared in an ultrasonic bath.

**KEYWORDS:** Thiosemicarbazone; Silver(I) complex; Single crystal; Triclinic structure; Tetrahedral coordination.

## INTRODUCTION

Thiosemicarbazones and their transition metal complexes have attracted great attention during recent years not only from their versatile structures [1,2], but also for their various interesting properties [3,4]. One of the best reasons for considerable interest is variable bonding modes of thiosemicarbazones [5]. They can bind to metal in the *E* form via S donor atom (Scheme 1, A) [5]

as well as in the *Z* form via N,S-chelating mode after deprotonation at hydrazinic NH hydrogen (Scheme 1, B) [6]. Also, the coordination chemistry of transition metals with thiosemicarbazones is broadly investigated [1,5,6], but within this realm only a few compounds of silver(I) thiosemicarbazone complexes have been reported [7-10]. In continuation of our research of thiosemicarbazone

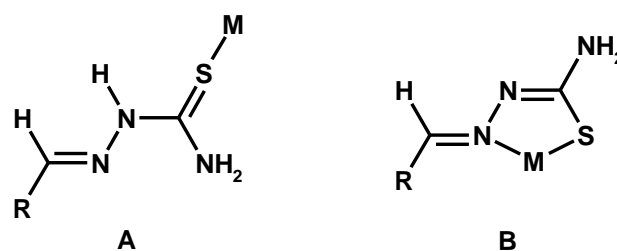
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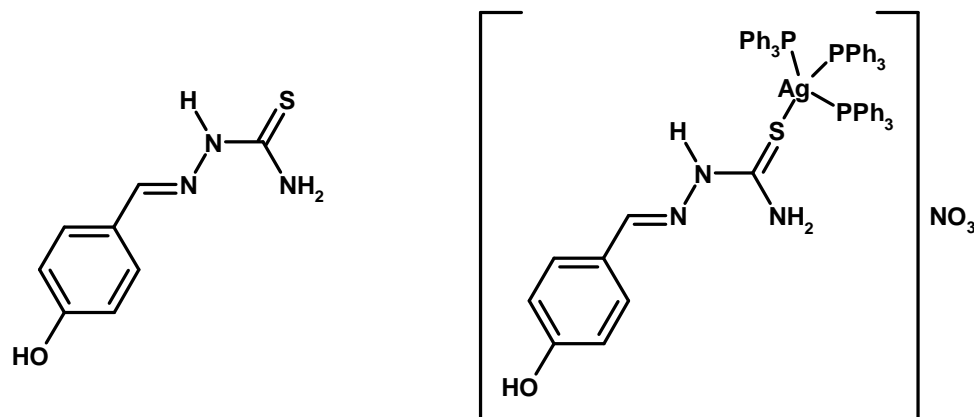
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Scheme 1: E and Z form of thiosemicarbazone coordinated to metal center.



Scheme 2: Chemical structures of 4Hbatsc (left) and  $[Ag(PPh_3)_3(4Hbatsc)]NO_3$  (right).

complexes [11,12], in this paper we report on the syntheses and crystal structures of a new thiosemicarbazone ligand and its silver(I) complex (Scheme 2).

## EXPERIMENTAL SECTION

### Materials and measurements

All compounds were purchased from Merck and used as received. The thiosemicarbazone ligand 4H-ba-tsc was prepared following a literature procedure [11]. Elemental analyses were carried out using a Heraeus CHN-O-Rapid analyzer. The TGA was performed on a Perkin Elmer TG/DTA lab system 1 (Technology by SII) in an air atmosphere with a heating rate of 20 °C/min in the temperature span of 30–700 °C. The Scanning Electron Microscopy (SEM) images of the complex were obtained from a Philips XL-30ESEM.

### Synthesis of 4Hbatsc

The ethanolic solution of thiosemicarbazid (2 mmol) was added to an ethanolic solution of 4-hydroxybenzaldehyde (2 mmol) and refluxed for 1.5 h

until the colorless clear solution was obtained. The solution was left at room temperature for several days. Suitable crystals were filtered and washed twice with ethanol, and dried at room temperature. *Anal.* calcd. for  $C_{16}H_{18}N_6O_2S_2$ : C, 49.16; H, 4.91; N, 21.51%. Found: C, 49.22; H, 4.96; N, 21.55%.

### Synthesis of complex $[Ag(PPh_3)_3(4Hbatsc)]NO_3$

The methanolic solution of 4Hbatsc (1 mmol) was added to an acetonitrilic solution of 1 mmol  $AgNO_3$  and 3 mmol of  $PPh_3$  and stirred for 20 min until the colorless clear solution was obtained. The solution was left in refrigerator for several days. The suitable crystals were filtered and washed twice with ethanol and dried at room temperature. *Anal.* calcd. for  $C_{62}H_{54}AgN_3OP_3S \cdot NO_3$ : C, 64.58; H, 4.68; N, 4.86%. Found: C, 64.53; H, 4.72; N, 4.90%.

### X-ray crystallography

Crystallographic measurements were done at 120 K with four circle CCD diffractometer Gemini of Oxford

diffraction, Ltd., with mirrors-collimated Cu-K $\alpha$  radiation. Crystal structures were solved by charge flipping with program SUPERFLIP [13] and refined with the Jana2006 program package [14] by full-matrix least-squares technique on  $F^2$ . The molecular structure plots were prepared by Diamond 4.0 [15]. Structure analysis of **4Hbatsc** was quite standard while for the complex the work was complicated by a disorder of several phenyl groups of PPh<sub>3</sub>. The disorder was described using the rigid body method, where one phenyl was selected as a model molecule and placed to the final positions in the unit cell using refinable rotations and a translation vector. The disorder was then conveniently described by placing such a model molecule in two close positions with reduced occupancy. All hydrogen atoms were mostly discernible in difference Fourier maps (except the disordered molecules) and could be refined to reasonable geometry. According to common practice, H atoms bonded to C were kept in ideal positions with C–H = 0.96 Å,  $U_{iso}(H)$  was set to  $1.2U_{eq}(C)$ . For H atoms bonded to nitrogen, their positions were refined and their  $U_{iso}(H)$  constrained in the same way as for C–H. All non-hydrogen atoms were refined using harmonic refinement. For disordered lattice water molecules, hydrogen atoms could not be determined. Crystallographic data, details of the data collection, structure solution and refinements are listed in Table 1.

## RESULTS AND DISCUSSION

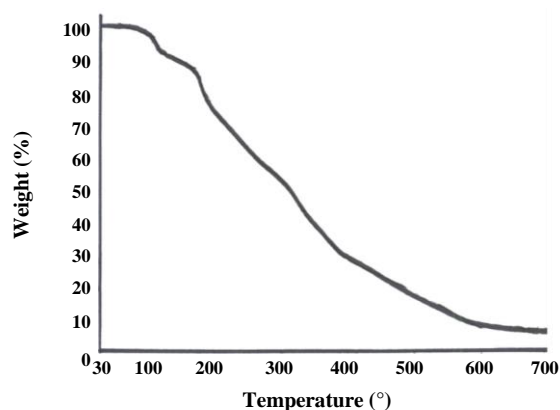
The elemental analyses of the ligand and its silver(I) complex confirmed the expected molecular formula. At room temperature and as a solid, both compounds are quite stable.

The FT-IR spectra have shown a sharp peak at about 1600 cm<sup>-1</sup>, which confirmed the presence of C=N imine group. The existence of NH, NH<sub>2</sub> groups was confirmed by the peaks at 3200–3400 cm<sup>-1</sup>. The medium intensity band at about 1000 cm<sup>-1</sup> was assigned to the C=S stretching vibration [12,16].

Thermal stability of [Ag(PPh<sub>3</sub>)<sub>3</sub>(4Hbatsc)]NO<sub>3</sub> was examined under an air atmosphere. The TG curve (Fig. 1) shows there is no detectable change up to 80 °C, while during further heating the title compound undergoes thermal decomposition in three stages, losing 9.85% of its weight between 80 and 139 °C due to the elimination of NH<sub>2</sub> + OH + NO<sub>3</sub> = 8.23%, losing 25.74% of its weight between 138 and 255 °C due to the elimination of 4 C<sub>6</sub>H<sub>5</sub> = 26.73%, and losing 55.20% of its weight

**Table 1: Crystallographic data and structural refinement details.**

	4Hbatsc	[Ag(PPh <sub>3</sub> ) <sub>3</sub> (4Hbatsc)]NO <sub>3</sub>
Chemical formula	C <sub>16</sub> H <sub>18</sub> N <sub>6</sub> O <sub>2</sub> S <sub>2</sub>	C <sub>62</sub> H <sub>54</sub> AgN <sub>3</sub> OP <sub>3</sub> S·NO <sub>3</sub>
Formula weight	390.5	1152
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
$a$ , Å	3.9464 (2)	13.2508 (4)
$b$ , Å	10.7164 (8)	14.5202 (3)
$c$ , Å	21.0792 (14)	15.4836 (4)
$\alpha$ , deg	87.499 (6)	88.990 (2)
$\beta$ , deg	89.029 (5)	65.425 (3)
$\gamma$ , deg	80.921 (5)	86.244 (2)
$V$ , Å <sup>3</sup>	879.41 (10)	2703.28 (14)
$\mu$ , mm <sup>-1</sup>	2.97	4.63
$Z$	2	2
$S$	1.17	1.88
$R_{int}$	0.039	0.045
Measured reflections	4625	42310
Measured independent	2993	9552
Reflections with $I > 3\sigma(I)$	2381	8311
Parameters	2993	572
$R(F^2 > 3\sigma(F^2))$	0.036	0.049
$wR(F^2)$	0.054	0.127
$\Delta\rho_{max}$	0.21	1.27
$\Delta\rho_{min}$	-0.22	-0.83



**Fig. 1: TG curve of [Ag(PPh<sub>3</sub>)<sub>3</sub>(4Hbatsc)]NO<sub>3</sub>.**

Table 2: Selected bond distances and angles of 4Hbatsc.

S1 C3	1.699(2)	S2 C4	1.697(3)
O1 C15	1.368(3)	O2 C6	1.360(3)
N1 C4	1.331(4)	N2 C3	1.328(3)
N3 N4	1.382(3)	N5 N6	1.382(3)
N3 C4	1.339(3)	N5 C3	1.340(3)
N4 C16	1.283(3)	N6 C13	1.282(3)
N4 N3 C4	120.9(2)	N3 N4 C16	114.3(2)
N6 N5 C3	119.9(2)	N5 N6 C13	115.6(2)
S1 C3 N2	122.6(2)	S1 C3 N5	119.57(17)
N2 C3 N5	117.8(2)	S2 C4 N1	122.7(2)
S2 C4 N3	119.1(2)	N1 C4 N3	118.2(2)
N6 C13 C8	122.0(2)	N4 C16 C5	122.5(2)

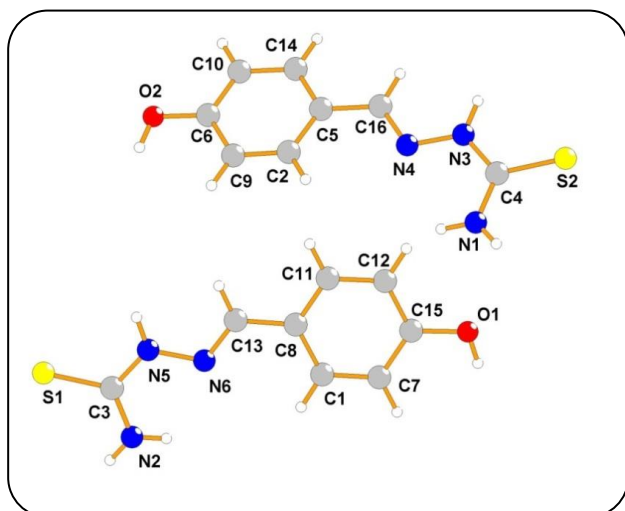
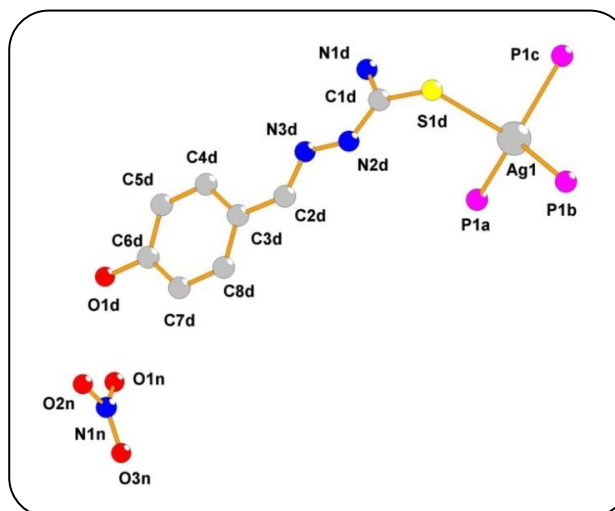


Fig. 2: Crystal structure of 4Hbatsc.

Fig. 3: Crystal structure of  $[Ag(PPh_3)_3(4Hbatsc)]NO_3$ . All atoms H and C atoms of PPh<sub>3</sub> molecules are omitted for clarity.

between 255 and 700 °C due to the elimination of  $5 C_6H_5 + C_8H_5N_3S + 3 P = 56.68\%$ . The final product is Ag (8.36%).

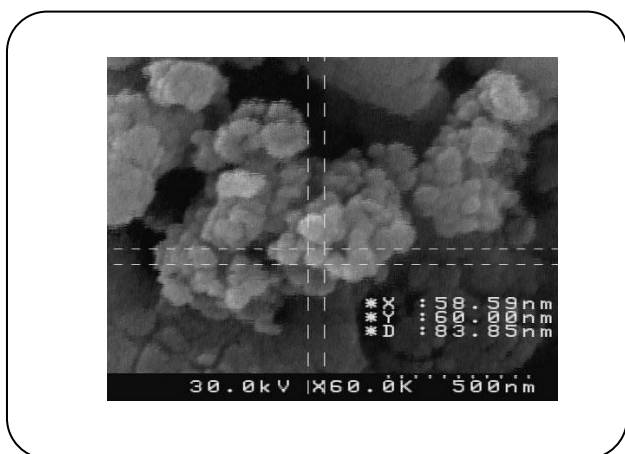
Figs. 2 and 3 show molecular structures of 4Hbatsc and  $[Ag(PPh_3)_3(4Hbatsc)]NO_3$ , respectively. The compounds crystallize in the triclinic system with the space group *Pt*. The selected bond distances and angles are presented in Tables 2 and 3, respectively. The different bond distances N-N, N-C, and C=N of the free 4Hbatsc and its complex correspond to the coordination of 4Hbatsc to silver(I) ion. The silver(I) ion is four coordinated by three phosphorus atoms of three triphenylphosphin molecules and one sulfur atom of thiosemicarbazide ligand 4Hbatsc. The resulting

geometry is distorted tetrahedral, because of the difference between bond distances Ag-P and Ag-S [7-10]. The distortion is also manifested by deviations from  $109.5^\circ$  of the bond angles S-Ag-P and P-Ag-P (Table 2).

To prepare nanoparticles of  $[Ag(PPh_3)_3(4Hbatsc)]NO_3$ , 10 mL of  $AgNO_3$  (0.1 mmol) in acetonitrile was placed in an ultrasonic bath, with a power output of 40 KHz. Into this solution, a 10 mL solution of 4Hbatsc (0.1 mmol) and  $PPh_3$  (0.3 mmol) was added dropwise. The obtained precipitate was filtered off, washed with acetonitrile, and then dried in air. Fig. 4 shows the scanning electron microscopy of  $[Ag(PPh_3)_3(4Hbatsc)]NO_3$ . The SEM image shows the uniform morphology of the aggregated nanoparticles.

Table 3: Selected bond distances and angles of  $[Ag(PPh_3)_3(4Hbatsc)]NO_3$ .

Ag1 P1a	2.5113(9)	Ag1 P1b	2.5261(10)
Ag1 P1c	2.5643(11)	Ag1 S1d	2.684(6)
S1d C1d	1.710(5)	O1d C6d	1.359(7)
O1n N1n	1.265(6)	O2n N1n	1.258(5)
O3n N1n	1.235(5)	N1d C1d	1.303(6)
N2d N3d	1.379(6)	N2d C1d	1.337(7)
P1a Ag1 P1b	115.31(3)	S1d Ag1 P1a	106.66(3)
P1b Ag1 P1c	109.99(4)	S1d Ag1 P1b	106.97(4)
P1a Ag1 P1c	118.17(3)	S1d Ag1 P1c	97.53(4)
N3d N2d C1d	121.1(4)	N2d N3d C2d	114.1(4)
S1d C1d N1d	124.5(4)	S1d C1d N2d	117.2(4)
N1d C1d N2d	118.3(4)	N3d C2d C3d	123.9(5)
C1d S1d Ag1	106.62(5)		

Fig. 4: SEM image of  $[Ag(PPh_3)_3(4Hbatsc)]NO_3$ .

## CONCLUSIONS

In summary, we obtained thiosemicarbazone 4Hbatsc and its complex  $[Ag(PPh_3)_3(4Hbatsc)]NO_3$  and characterized them by spectroscopic, thermogravimetry, and diffraction methods. The silver(I) ion is four coordinated and the geometry around it is distorted tetrahedral. Thermal decomposition of  $[Ag(PPh_3)_3(4Hbatsc)]NO_3$  takes place in three stages, yielding the final product is Ag (8.36%) at 700 °C. The complex can also be prepared in an ultrasonic bath in a form of nanoparticles.

## Supplementary data

Crystallographic data (excluding structure factors) for the structure reported in this paper has been deposited with the Cambridge Crystallographic Center, CCDC Nos. 1536300 (ligand) and 1536278 (complex). Copy of the data can be obtained free of charge on deposit@ccdc.cam.ac.uk.

## Acknowledgments

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