

## КРАТКИЕ СООБЩЕНИЯ

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CRYSTAL STRUCTURE OF COPPER(I) THIOSEMICARBAZONE COMPLEX [CuI(PPh<sub>3</sub>)(catsc)]E. Shahsavani<sup>1</sup>, N. Feizi<sup>1</sup>, V. Eigner<sup>3</sup>, M. Dusek<sup>3</sup>, A.D. Khalaji<sup>4</sup><sup>1</sup>Department of Chemistry, Payame Noor University, Mashhad, Iran<sup>2</sup>Department of Solid State Chemistry, Institute of Chemical Technology, Prague, Czech Republic<sup>3</sup>Institute of Physics of the ASCR, Prague 8, Czech Republic<sup>4</sup>Department of Chemistry, Faculty of Science, Golestan University, Gorgan, Iran

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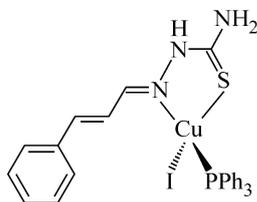
In this paper, we report the preparation of a four-coordinated copper(I) thiosemicarbazone complex [CuI(PPh<sub>3</sub>)(catsc)] from the reaction of PPh<sub>3</sub> and catsc (3-phenylpropenal thiosemicarbazone) with CuI. The synthesized complex is characterized by elemental analyses (CHNS) and FT-IR spectroscopy. The crystal structure of [CuI(PPh<sub>3</sub>)(catsc)] is investigated by single crystal X-ray diffraction. The catsc coordinates to the copper(I) ion as a bidentate ligand *via* the N and S atoms. The complex has a distorted tetrahedral coordination geometry.

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**Keywords:** copper(I), thiosemicarbazone, crystal structure, single crystal.

Thiosemicarbazones, an important class of N,S-donor ligands, react with a range of transition metals [ 1, 2 ]. In recent years, there was interest in thiosemicarbazones due to their structural diversity [ 3, 4 ] and anticancer, antibacterial, antifungal [ 5 ], and ion-sensing abilities [ 6 ]. Comparing with other complexes, the coordination chemistry of copper(I) thiosemicarbazones is less investigated [ 7—12 ]. The main reason for limited information on copper(I) thiosemicarbazones is their insolubility in common organic solvents, such as methanol, chloroform, ethanol etc. In the neutral form, thiosemicarbazone binds to a metal ion as a monodentate ligand *via* an S donor atom or as a bidentate ligand *via* S and N donor atoms.

Herein, we report the synthesis and crystal structure of a new copper(I) thiosemicarbazone complex [CuI(PPh<sub>3</sub>)(catsc)] (Scheme 1).

Scheme 1. The chemical structure of [CuI(PPh<sub>3</sub>)(catsc)]

**Experimental. Material and methods.** All reagents and solvents for the synthesis and analysis were commercially available and used as received without further purifications. Infrared spectra were recorded using KBr disks on a FT-IR Perkin—Elmer spectrophotometer. Elemental analyses were

carried out using a Heraeus CHN-O-Rapid analyzer. The thiosemicarbazone ligand catsc was prepared in a high yield following the literature procedure [ 13 ].

**Synthesis of [CuI(PPh<sub>3</sub>)(catsc)].** To a solution of 190 mg (1 mmol) CuI in 5 ml·l acetonitrile a solution of 262 mg (1 mmol) of PPh<sub>3</sub> in 5 ml·l acetonitrile was added dropwise under the air atmosphere at room temperature. The mixture was stirred for 30 min and then 205 mg (1 mmol) catsc in 5 ml acetonitrile were added and stirred for additional 30 min. An orange-yellow microcrystalline powder was immediately obtained. Single crystals of [CuI(PPh<sub>3</sub>)(catsc)] were obtained by recrystallization from the acetonitrile solution after a few days. The crystals were collected by filtration and dried. *Anal.* Calcd. For C<sub>28</sub>H<sub>26</sub>CuIN<sub>3</sub>PS. Calcd. (%) C 51.11, H 3.98, N 6.39, S 4.87. Found (%): C 51.15, H 4.02, N 6.45, S 4.83. FT-IR (KBr, cm<sup>-1</sup>): 3407, 3274 (NH<sub>2</sub>), 31.73 (NH), 3042, 2928 (CH aromatic and aliphatic), 2851 (—CH=N), 1621 (C=N), 1604 (NH<sub>2</sub>), 1578, 1555, 1478 (C=C).

**X-ray crystallography.** A [CuI(PPh<sub>3</sub>)(catsc)] single crystal of the dimensions 0.36×0.25×0.08 mm was chosen for the X-ray diffraction study. Crystallographic measurements were carried out at 120 K on a four-circle Gemini CCD diffractometer (Oxford diffraction, Ltd.) with mirrors-collimated CuK<sub>α</sub> radiation ( $\lambda = 1.54184 \text{ \AA}$ ). Although the quality of the single crystals was low (as indicated by the  $R_{\text{int}}$  factor in Table 2 for merging symmetry equivalent reflections) the crystal structure could be nevertheless easily solved by charge flipping using the SUPERFLIP program [ 14 ] and refined using the Jana2006 program package [ 15 ] by the full-matrix least-squares technique on  $F^2$ . The molecular structure plots were prepared by ORTEP III [ 16 ]. Hydrogen atoms were mostly discernible in difference Fourier maps and could be refined to a reasonable geometry. According to the common practice, hydrogen atoms attached to carbon atoms were kept in ideal positions during the refinement. The isotropic atomic displacement parameters of hydrogen atoms were set to 1—1.2 $U_{\text{eq}}$  of their hydrogen atoms. Crystallographic data and details of the data collection and structure solution and refinements are listed in Table 1.

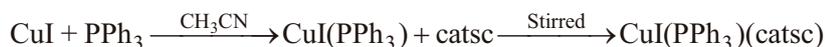
**Results and discussion.** The [CuI(PPh<sub>3</sub>)(catsc)] complex was synthesized by the reaction of CuI, PPh<sub>3</sub>, and catsc in acetonitrile in the 1:1:1 molar ratio (Scheme 2). Orange-yellow crystals of the

Table 1

Crystallographic and refinement data for [CuI(PPh<sub>3</sub>)(catsc)]

Empirical formula	C <sub>28</sub> H <sub>26</sub> Cu <sub>1</sub> I <sub>1</sub> N <sub>3</sub> P <sub>1</sub> S <sub>1</sub>
Formula weight	658
Crystal system, space group	Triclinic, <i>P</i> -1
<i>a</i> , <i>b</i> , <i>c</i> , Å	7.9954(4), 12.9402(7), 13.1156(8)
$\alpha$ , $\beta$ , $\gamma$ , deg.	91.234(5), 92.261(5), 100.516(5)
<i>V</i> , Å <sup>3</sup>	1332.57(13)
<i>Z</i>	2
$\mu$ , mm <sup>-1</sup>	11.78
<i>T</i> , K	120
Crystal size, mm	0.36×0.25×0.08
<i>T</i> <sub>min</sub> , <i>T</i> <sub>max</sub>	0.084, 0.506
Meas. / independent / reflections with $I > 3\sigma(I)$	31600 / 4739 / 4332
$R_{\text{int}}$	0.127
$R[F^2 > 3\sigma(F^2)]$	0.033
$wR(F^2)$	0.087
<i>S</i>	1.52
Reflections / parameters	4739 / 317
$\Delta\rho_{\text{max}}$ , $\Delta\rho_{\text{min}}$ , e/Å <sup>3</sup>	1.10, -0.75

[CuI(PPh<sub>3</sub>)(catsc)] complex were obtained in a good yield (83 %). This complex is stable in the air in the solid state.



Scheme 2. Synthesis of the [CuI(PPh<sub>3</sub>)(catsc)] complex

The complex was purified by recrystallization from acetonitrile and characterized by elemental analyses (CHNS) and FT-IR spectroscopy. Elemental analyses revealed that the ratio of the PPh<sub>3</sub>, Cu, I, and catsc in the [CuI(PPh<sub>3</sub>)(catsc)] complex is 1:1:1:1.

FT-IR spectroscopy of [CuI(PPh<sub>3</sub>)(catsc)] confirmed the presence of catsc and PPh<sub>3</sub> *via* their  $\nu(\text{N—H})$ ,  $\nu(\text{C—N})$ ,  $\nu(\text{C=C})$ ,  $\nu(\text{C=S})$ ,  $\nu(\text{C=N})$ , and  $\nu(\text{C—P})$  bands (Fig. 1). Its FT-IR spectrum showed the presence of the  $\nu(\text{N—H})$  band at 3407 cm<sup>-1</sup> and 3274 cm<sup>-1</sup> (due to —NH<sub>2</sub>) and 3173 cm<sup>-1</sup> (due to —NH—). Also, the  $\nu(\text{C=N})$  and  $\nu(\text{C=S})$  appeared at 1621 cm<sup>-1</sup> and 989 cm<sup>-1</sup>, respectively. A band due to  $\nu(\text{C—P})$  at 1093 cm<sup>-1</sup> indicates the presence of PPh<sub>3</sub> [ 11 ].

An ORTEP view of [CuI(PPh<sub>3</sub>)(catsc)] is shown in Fig. 2 and selected bond lengths and angles are given in Table 2. The [CuI(PPh<sub>3</sub>)(catsc)] complex crystallized in the triclinic system with the space group *P*-1. In this complex, the copper ion is bonded to the bidentate N,S-chelate ligand catsc, the triphenylphosphine P atom, and the I atom, forming a distorted tetrahedral environment coordination geometry. The Cu1—S1, Cu1—N3, Cu1—I1, and Cu1—P1 distances are 2.3237(10) Å, 2.060(3) Å, 2.6356(6) Å, and 2.2095(2) Å respectively, and they are similar to the literature reports. The bond angles around the copper(I) ion in this structure are in the range from 85.42° (S1—Cu1—N3) to 124.94° (P1—Cu1—N3), confirming a distorted tetrahedral geometry around the copper(I) ion.

From the molecular structure of [CuI(PPh<sub>3</sub>)(catsc)] (Fig. 2), it can be seen that two hydrogen atoms of triphenylphosphine are engaged in the intramolecular hydrogen bonding. One hydrogen atom forms an intramolecular hydrogen bond with the iodine atom (C21—H1c21···I1, 3.098 Å) and another hydrogen atom forms an intramolecular hydrogen bond with the catsc sulphur atom (C10—H1c10···S1, 2.878 Å). There is also an intermolecular hydrogen bond (N2—H1N2···I1, 2.7759(2) Å) which connects the molecules of the complex into a chain along *a*.

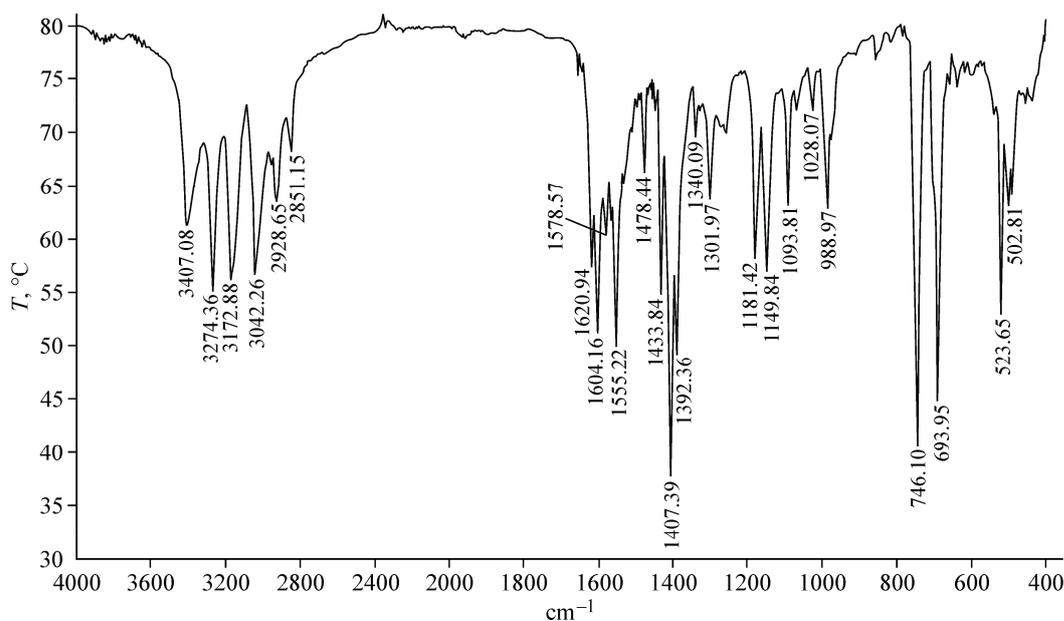


Fig. 1. FT-IR spectrum of [CuI(PPh<sub>3</sub>)(catsc)]

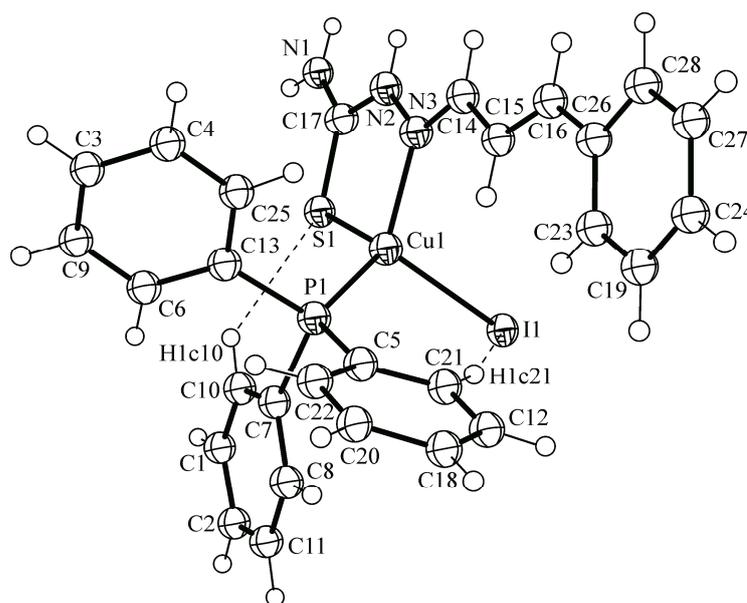
Fig. 2. Molecular structure of [CuI(PPh<sub>3</sub>)(catsc)]

Table 2

Selected bond distances and angles for [CuI(PPh<sub>3</sub>)(catsc)]

I1—Cu1	2.6356(6)	I1—Cu1—P1	110.71(3)	P1—Cu1—S1	115.27(4)
Cu1—P1	2.2095(9)	I1—Cu1—S1	105.69(3)	S1—Cu1—N3	85.42(8)
Cu1—S1	2.3237(10)	P1—Cu1—N3	124.94(9)	Cu1—N3—N2	114.7(2)
Cu1—N3	2.060(3)	Cu1—N3—C14	129.5(2)	N2—N3—C14	115.8(3)
N3—C14	1.290(5)	N3—C14—C15	119.8(3)	S1—C17—N1	122.2(3)
S1—C17	1.689(3)	S1—C17—N2	122.3(2)	N1—C17—N2	115.4(3)
N1—C17	1.330(4)	I1—Cu1—N3	111.17(8)		
N2—N3	1.384(4)				
N2—C17	1.354(4)				

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Crystallographic data (excluding structure factors) for the structure reported in this paper has been deposited with the Cambridge Crystallographic Center, CCDC No. 984807. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, fax: +44 1223 336 033, e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>.

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