

Crystal structures of copper(I) and silver(I) chloride complexes containing 4-phenylthiosemicarbazide and triphenylphosphine ligands

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ABSTRACT: Copper(I) and silver(I) chloride complexes containing triphenylphosphine (PPh_3) and 4-phenylthiosemicarbazide (4-PTSC) ligands were prepared and structurally analyzed, namely $[\text{CuCl}(\text{4-PTSC})(\text{PPh}_3)_2]$ (1) and $[\text{AgCl}(\text{4-PTSC})(\text{PPh}_3)_2]\text{CH}_3\text{CN}$ (2). Both compounds (1) and (2) exhibit a distorted tetrahedral metal coordination environment with two P atoms from two PPh_3 ligands, one terminal S atom from the 4-PTSC ligand and a chloride ion. Intramolecular $\text{N}-\text{H}\cdots\text{Cl}$ and $\text{N}-\text{H}\cdots\text{N}$ hydrogen bonds are observed (graph set motifs S(6) and S(5), respectively). In the crystals of both complexes, molecules are linked to form dimers via bifurcated $\text{N}-\text{H}\cdots\text{Cl}$ hydrogen bonds involving the amine and chloride units. For compound (2), a solvate acetonitrile molecule acts as a hydrogen bond donor and acceptor via $\text{C}-\text{H}(\text{CH}_3\text{CN})\cdots\text{Cl}$ and $\text{C}-\text{H}\cdots\text{N}(\text{CH}_3\text{CN})$ interactions, leading to the formation of 1D chains along [010].

KEYWORDS: silver(I) chloride, copper(I) chloride, 4-phenylthiosemicarbazide, crystal structure, intra- and intermolecular hydrogen bonding

INTRODUCTION

Thiosemicarbazide and thiosemicarbazide derivatives have for several decades attracted attention due to a range of biological activities that they possess such as anticancer, antimicrobial, antifungal [1, 2], anticonvulsant, antimalarial, analgesic, and antiinflammatory properties [3–6]. Therefore, many scientists have prepared members of these compounds as target structures to estimate and evaluate their biological activities. Thiosemicarbazides may also act as ligands in metal complexes, featuring both soft sulfur and hard nitrogen donor atoms as potential sites for coordination that give them an affinity for chelation to divalent metal ions such as Fe^{2+} , Zn^{2+} , Cu^{2+} , and Mn^{2+} [7, 8]. Many of the thiosemicarbazide's biological and pharmaceutical activities are generally assumed to originate from these metal-complexing properties and their capacity to act as *in vivo* reducing agents. Thiosemicarbazide and their metal complexes have thus been extensively investigated, e.g. for their antiviral properties [9], or for their anticancer activities [10, 11]. Most notable here is 3-aminopyridine-2-carboxaldehyde (3-AP or Triapine®), which is currently tested in a randomized

phase III trial as an addition to the usual chemotherapy treatment (Cisplatin) during radiation therapy for advanced-stage cervical and vaginal cancers [12, 13]. Several copper(I) and silver(I) complexes of thiosemicarbazide derivatives have been prepared and characterized, and an unusual enhancement in antitubercular activity has been observed for some of these complexes [14]. We recently reported a series of metal thiourea complexes prepared by reacting copper(I) or silver(I) halide with triphenylphosphane and 1-(4-nitrophenyl)thiourea, NPTU [15–17]; we report herein the synthesis and crystal structures of copper(I) and silver(I) chloride complexes containing triphenylphosphine (PPh_3) and 4-phenylthiosemicarbazide (4-PTSC) ligands (Fig. 1).

MATERIALS AND METHODS

Materials

The reagents and solvents used in the synthesis were obtained from commercial suppliers and used directly without further purification. Copper(I) chloride, silver(I) chloride, triphenylphosphine, and 4-phenylthiosemicarbazide were purchased from Sigma Aldrich (USA). Infrared spectra were mea-

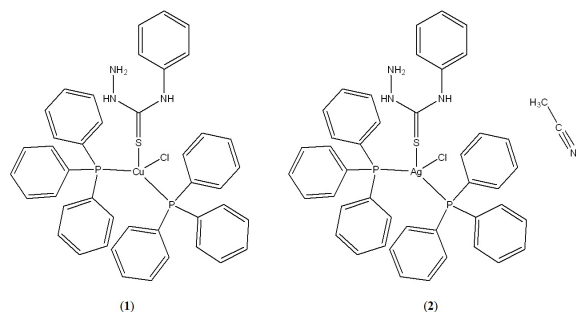


Fig. 1 Chemical structures of $[\text{CuCl}(4\text{-PTSC})(\text{PPh}_3)_2]$ (1) and $[\text{AgCl}(4\text{-PTSC})(\text{PPh}_3)_2]\text{CH}_3\text{CN}$ (2).

sured in the region of $4000\text{--}400\text{ cm}^{-1}$ on a Perkin-Elmer Infrared Spectrophotometer (Spectrum BX, England) using potassium bromide pellets.

Synthesis of $[\text{CuCl}(4\text{-PTSC})(\text{PPh}_3)_2]$ (1)

Triphenylphosphane, PPh_3 (0.16 g, 0.61 mmol), was dissolved in 30 ml of acetonitrile at 339.15 K, and copper(I) chloride, CuCl (0.03 g, 0.30 mmol), was added. The mixture was stirred for 3 h, and then 4-phenylthiosemicarbazide, 4-PTSC (0.05 g, 0.30 mmol), was added. The resulting reaction mixture was heated under reflux for 7 h during which the precipitate gradually disappeared. The resulting clear solution was filtered and left to evaporate for several days at room temperature, leaving a crystalline complex, which was filtered off and dried in vacuo (0.10 g, 42% yield). M.p. 171–172 K. IR bands (KBr , cm^{-1}): 3168.07(w), 1964.93(w), 1888.21(w), 1820.27(w), 1629.43(w), 1594.52(w), 1503.44(w), 1289.86(m), 1090.41(w), 1024.65(w), 897.53(m), 851.50(w), 700.95(s), 509.56(s).

Synthesis of $[\text{AgCl}(4\text{-PTSC})(\text{PPh}_3)_2]\text{CH}_3\text{CN}$ (2)

Triphenylphosphine, PPh_3 (0.16 g, 0.61 mmol), was dissolved in 30 ml of acetonitrile at 340 K, and silver(I) chloride, AgCl (0.04 g, 0.299 mmol), was added. The mixture was stirred for 4 h, and then 4-phenylthiosemicarbazide, 4-PTSC (0.05 g, 0.299 mmol), was added. The resulting reaction mixture was heated under reflux for 7 h during which the precipitate gradually disappeared. The resulting clear solution was filtered and left to evaporate at room temperature. The crystalline complex, which was deposited upon standing for a couple of days, was filtered off and dried in vacuo (0.16 g, 66% yield). M.p. 450–452 K. IR bands (KBr , cm^{-1}): 3311(w), 3263(w), 3148(w),

1961(w), 1625(w), 1599(w), 1544(w), 1432(w), 1282(w), 1209(w), 1094(w), 1026(w), 996(w), 968(w), 907(w), 852(w), 741(m), 686(w), 489(s), 450(w), 437(w).

X-ray crystallographic analysis

X-ray diffraction data for (1) and (2) were obtained on a Bruker Quest diffractometer (D8 Quest, Germany) with $\text{Mo-K}\alpha$ radiation ($\lambda = 0.71073\text{ \AA}$) at 150 K. Data were collected, and reflections were indexed and processed using APEX3 [18]. Space groups were assigned, and structures were solved by direct methods using XPREP within the SHELXTL suite of programs [19,20] and refined using Shelxl [21] and Shelxle [22]. Crystallographic data are given in Table 1. Refinements for (1): crystal data, data collection, and structure refinement details are summarized in Table 1. All H atoms attached to carbon atoms were positioned geometrically and constrained to ride on their parent atoms with $\text{C-H} = 0.95\text{ \AA}$. The nitrogen bound H atoms were located in difference-Fourier maps and were refined with an $\text{N-H} = 0.831$ (19)–0.89 (2) \AA . $U_{\text{iso}}(\text{H})$ values were set to $1.2 U_{\text{eq}}(\text{C/N})$. Refinements for (2): crystal data, data collection, and structure refinement details are summarized in Table 1. All H atoms attached to carbon atoms were positioned geometrically and constrained to ride on their parent atoms with $\text{C-H} = 0.95\text{ \AA}$. The nitrogen bound H atoms were located in difference-Fourier maps and were refined with an $\text{N-H} = 0.858$ (19)–0.892 (19) \AA . $U_{\text{iso}}(\text{H})$ values were set to $1.2 U_{\text{eq}}(\text{C/N})$. Reflections $-1\ 1\ 2$, $2\ 1\ 0$, $-2\ 1\ 1$, and $2\ 0\ 4$ were affected by the beam stop and were omitted from the refinement. CCDC 2042521 for (1) and 2042520 for (2) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center (<https://www.ccdc.cam.ac.uk>).

RESULTS AND DISCUSSION

The reaction of copper(I) chloride with 4-phenylthiosemicarbazide (4-PTSC) and triphenylphosphine (PPh_3) ligands in 1:1:2 ratio in acetonitrile yielded the copper complex $[\text{CuCl}(4\text{-PTSC})(\text{PPh}_3)_2]$ (1) in a triclinic setting in space group $P\bar{1}$. The analogous reaction with silver(I) chloride yielded the silver complex $[\text{AgCl}(4\text{-PTSC})(\text{PPh}_3)_2]$, which crystallized as the mono-acetonitrile solvate $[\text{AgCl}(4\text{-PTSC})(\text{PPh}_3)_2]\text{CH}_3\text{CN}$ (2) in space group $P2_1/c$. Soft sulfur donor atom from the thiosemicarbazide

Table 1 Crystal data and structure refinement details for (1) and (2).

	[CuCl(4-PTSC)(PPh ₃) ₂] (1)	[AgCl(4-PTSC)(PPh ₃) ₂]CH ₃ CN (2)
Crystal data		
Chemical formula	C ₄₃ H ₃₉ ClCuN ₃ P ₂ S	C ₄₃ H ₃₉ AgClN ₃ P ₂ S · C ₂ H ₃ N
<i>Mr</i>	790.76	876.14
Crystal system, space group	Triclinic, <i>P</i> $\bar{1}$	Monoclinic, <i>P</i> 2 ₁ / <i>c</i>
Temperature (K)	150	150
<i>a</i> , <i>b</i> , <i>c</i> (Å)	10.1234 (4), 13.2260 (6), 16.4011 (7)	16.5657 (7), 9.4156 (4), 26.5967 (11)
α , β , γ (°)	105.0998 (16), 93.9536 (16), 112.2322 (15)	90, 95.4679 (13), 90
<i>V</i> (Å ³)	1927.76 (14)	4129.6 (3)
<i>Z</i>	2	4
Radiation type	Mo <i>K</i> α	Mo <i>K</i> α
μ (mm ⁻¹)	1.81	0.72
Crystal size (mm)	0.46 × 0.32 × 0.22	0.56 × 0.53 × 0.33
Data collection		
Diffractometer	Bruker AXS D8 Quest CMOS diffractometer	Bruker AXS D8 Quest CMOS diffractometer
Absorption correction	Multi-scan SADABS 2016/2: Krause L, Herbst-Irmer R, Sheldrick GM, Stalke D, <i>J Appl Cryst</i> 48 (2015), 3–10	Multi-scan SADABS 2016/2: Krause, L., Herbst-Irmer R, Sheldrick GM, Stalke D, <i>J Appl Cryst</i> 48 (2015), 3–10
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	93937, 14713, 11031	54737, 15053, 12221
<i>R</i> _{int}	0.041	0.047
(sin θ / λ) _{max} (Å ⁻¹)	0.771	0.770
Refinement		
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.036, 0.086, 1.03	0.028, 0.074, 1.05
No. of reflections	14713	15053
No. of parameters	472	525
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho$ max, $\Delta\rho$ min (e Å ⁻³)	0.60, -0.43	0.63, -0.54

Computer programs: Apex3, SAINT [18], SHELXS9 [19], SHELXL2014/7 [20], SHELXLE Rev714 [21], Mercury [26], SHELXL97, and publCIF [27].

Table 2 Hydrogen-bond geometry (Å, °) for [CuCl(4-PTSC)(PPh₃)₂] (1) and [AgCl(4-PTSC)(PPh₃)₂]CH₃CN (2).

D—H...A	D—H	H...A	D...A	D—H...A
Compound (1)				
N ₁ —H ₁ ...N ₃	0.832 (19)	2.235 (18)	2.6500 (18)	111.1 (15)
N ₂ —H ₂ ...Cl ₁	0.831 (19)	2.373 (19)	3.1751 (12)	162.5 (17)
N ₃ —H ₃ A...Cl ₁ ⁱ	0.89 (2)	2.62 (2)	3.5046 (14)	173.5 (16)
Compound (2)				
N ₁ —H ₁ ...N ₃ a	0.88	2.12	2.592 (10)	113
N ₁ —H ₁ ...N ₄	0.88	2.45	3.155 (2)	138
N ₂ a—H ₂ a...Cl ₁	0.88 (2)	2.34 (2)	3.200 (11)	164 (4)
N ₂ Bb—H ₂ Bb...Cl ₁	0.89 (2)	2.21 (3)	3.086 (13)	168 (5)
N ₃ Bb—H ₃ Cb...Cl ₁ ⁱⁱ	0.86 (2)	2.72 (5)	3.353 (13)	131 (5)
C33—H33...N ₄ ⁱⁱⁱ	0.95	2.60	3.317 (2)	133
C45—H45A...Cl ₁ ⁱⁱ	0.98	2.57	3.517 (2)	164

Symmetry codes: (i) $-x + 1, -y, -z$; (ii) $-x + 1, -y + 2 - z + 1$; and (iii) $x, -y + 3/2, z + 1/2$.

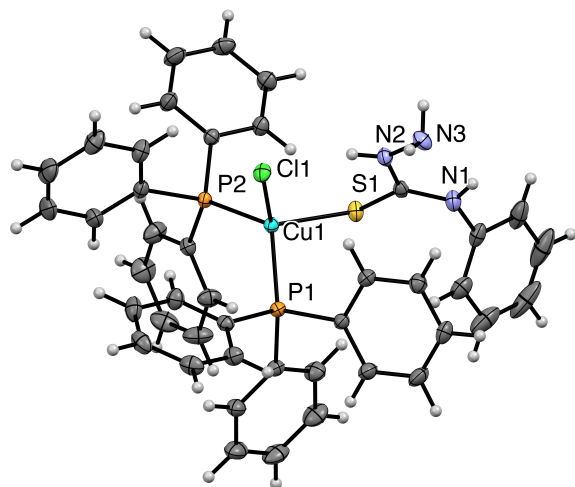


Fig. 2 Molecular structure of $[\text{CuCl}(\text{4-PTSC})(\text{PPh}_3)_2]$ (1) with ellipsoid displacement drawn at the 50% probability level.

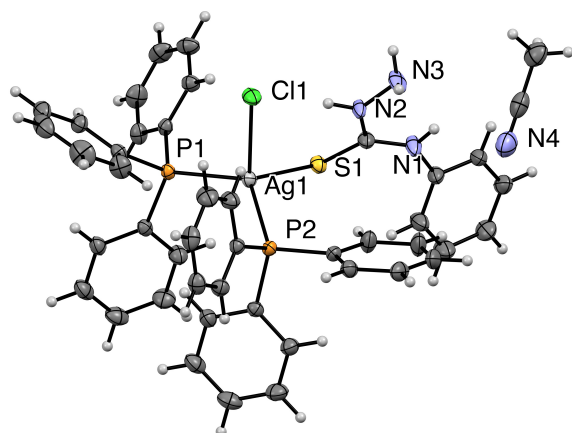


Fig. 3 Molecular structure of $[\text{AgCl}(\text{4-PTSC})(\text{PPh}_3)_2]$ CH_3CN (2) with ellipsoid displacement drawn at the 50% probability level. Disordered atoms were omitted for clarity.

is coordinated to both Cu and Ag, and no interaction of the amine moiety with the metal is observed. Both complexes are monomeric and exhibit a distorted tetrahedral geometry in which the metal ion is coordinated to two P atoms from two PPh_3 ligands, one terminal S atom from the 4-PTSC ligand and a chloride ion (Fig. 2 and Fig. 3). The monomeric structures are stabilized by an intramolecular $\text{N}_2\text{--H}_2\cdots\text{Cl}_1$ hydrogen bond between the NH_2 (4-PTSC) and the Cl atom and $\text{N}_1\text{--H}_1\cdots\text{N}_3$ hydrogen bond between NH_2 and NH of the thiosemicarbazide

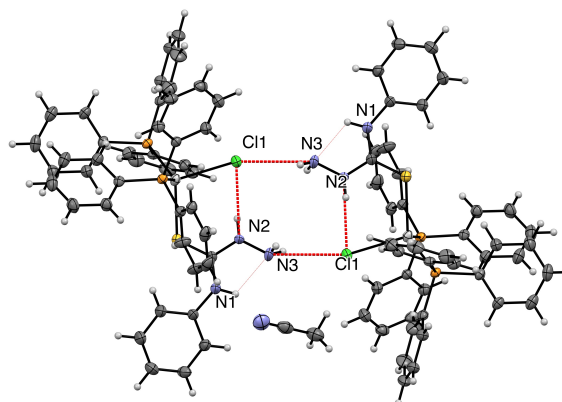


Fig. 4 Part of the crystal structure of $[\text{AgCl}(\text{4-PTSC})(\text{PPh}_3)_2]\text{CH}_3\text{CN}$ (2), showing the dimer formed by intermolecular $\text{N--H}\cdots\text{Cl}$ hydrogen bonds (shown as dashed lines).

moiety (graph set [23] motif S(6) and S(5), respectively) (Table 2). The Cu–S distance in (1) of 2.3389 (4) Å is close to that of another related tetrahedral complex, $[\text{CuCl}(\eta^1\text{-S-H}_2\text{itsc})(\text{Ph}_3\text{P})_2]$ (H_2itsc = isatin-3-thiosemicarbazone) [24], but smaller than 2.3893 (5) Å in $[\text{CuCl}(\eta^1\text{-S-H Intsc})(\text{Ph}_3\text{P})_2]$ [14]. The Cu–P bond lengths of 2.2710 (4)–2.3109 (4) Å are a bit larger than the values of 2.2602 (4)–2.2671 (4) Å observed for $[\text{CuCl}(\text{C}_7\text{H}_7\text{N}_3\text{O}_2\text{S})(\text{C}_{18}\text{H}_{15}\text{P})_2]$ [15]. In compound (2), the Ag–S bond length of 2.6108 (4) Å is similar to the bond length of 2.628 (8) Å found in $[\text{AgCl}(\eta^1\text{-S-H Intsc})(\text{Ph}_3\text{P})_2]$ [14]. The Ag–P bond lengths of 2.4703 (3)–2.4750 (4) Å are close to the values of 2.4409 (7)–2.4879 (7) Å for $[\text{AgCl}(\eta^1\text{-S-H pytsc})(\text{PPh}_3)_2]\cdot\text{CH}_3\text{CN}$ [25]. In the crystals of (1) and (2), the amine NH_2 moieties of 4-PTSC and Cl atom of neighboring molecules are linked through intermolecular $\text{N}_3\text{--H}_3\cdots\text{Cl}_1$ hydrogen bonds, forming dimers (Fig. 4). For compound (2), the acetonitrile molecules are connected to dimers through $\text{C}_{45}\text{--H}_{45}\text{A}(\text{CH}_3\text{CN})\cdots\text{Cl}_1$ and $\text{C}_{33}\text{--H}_{33}\cdots\text{N}_4(\text{CH}_3\text{CN})$ hydrogen bonds, leading to the formation of 1D chains along [010] (Fig. 5, Table 2). The results from IR spectroscopy are corresponding to the X-ray crystallographic data; the characteristic peak of $\nu(\text{C}=\text{S})$ of both complexes appeared at lower energy than that of the stretching presented in the free 4-PTSC ligand (896 cm^{-1}) supporting the coordination of the thione sulfur to a metal center.

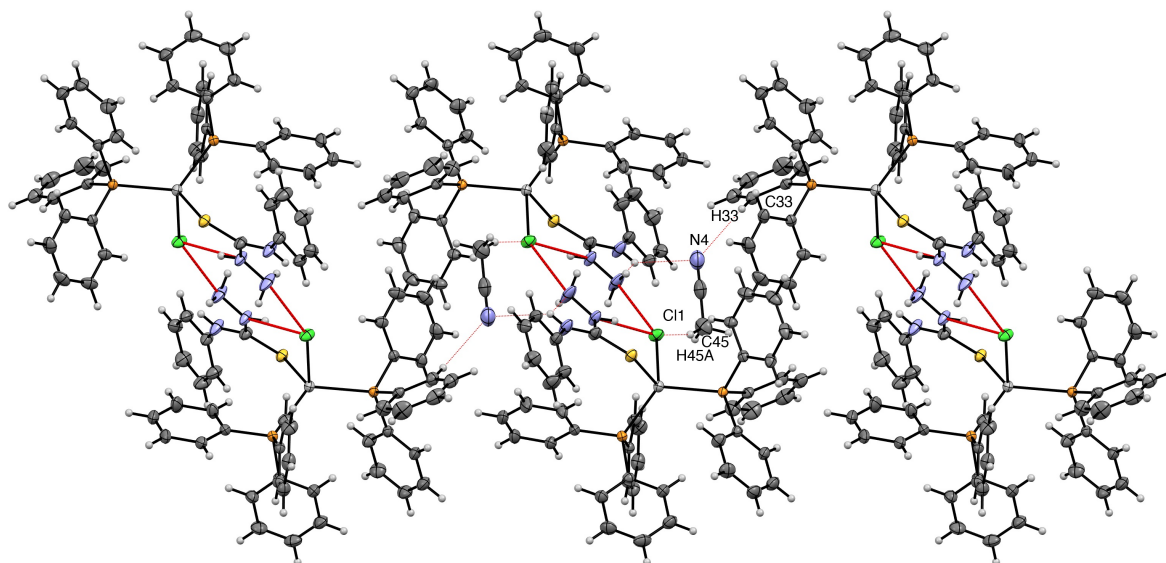


Fig. 5 Part of the crystal structure of $[\text{AgCl}(4\text{-PTSC})(\text{PPh}_3)_2]\text{CH}_3\text{CN}$ (2), showing intermolecular $\text{C-H}\cdots\text{N}$ and $\text{C-H}\cdots\text{Cl}$ hydrogen bonds and forming long chains along b -axis (shown as dashed lines).

CONCLUSION

The complexes $[\text{CuCl}(4\text{-PTSC})(\text{PPh}_3)_2]$ (1) and $[\text{AgCl}(4\text{-PTSC})(\text{PPh}_3)_2]\text{CH}_3\text{CN}$ (2) were prepared from $\text{MCl}:4\text{-PTSC}:\text{PPh}_3$ in 1:1:2 molar ratios in acetonitrile. The structures of the complexes were determined using single crystal X-ray diffraction analysis and further characterized by IR spectroscopy. Both complexes display a distorted tetrahedral coordination with two PPh_3 ligands, one 4-PTSC ligand and a chloride ion. In the crystals, there are intra- and intermolecular hydrogen bonds to connect complexes into dimers. The existence of a solvate acetonitrile in (2) plays an important role in connecting each dimer to form a one-dimensional network.

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