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Synthesis and crystal structures of metal(I) bromide complexes containing 4-phenylthiosemicarbazide and triphenylphosphane ligands

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ABSTRACT: Two new mononuclear 4-phenylthiosemicarbazide complexes $[Cu(4\text{-}PTSC)(PPh_3)_2]Br$ (**1**) and $[AgBr(4\text{-}PTSC)(PPh_3)_2]\cdot 0.18H_2O$ (**2**) [where PPh_3 = triphenylphosphane and 4-PTSC = 4-phenylthiosemicarbazide] were synthesized and characterized by infrared spectroscopy and single crystal X-ray diffraction analysis. In the complexes, the 4-PTSC ligand acts in a monodentate fashion through the sulfur donor site to Ag(I) ion (in **2**) or exhibits bidentate chelating coordination via the sulfur and the nitrogen being both bound to the Cu(I) ion (in **1**). The structures exhibit distorted tetrahedral coordination around the metal ions. In the crystal of complex salt **1**, the Br anions are not bonded to the metal and are linked the complex molecules via $N—H\cdots Br$ hydrogen bonds to form salt pair dimers (graph set motifs $R_2^1(6)$ and $D_1^1(2)$ combining to larger $R_4^2(10)$ and $R_4^2(14)$ motifs). In complex **2**, where the bromide ion is bonded to the metal, intramolecular $N—H\cdots Br$ and $N—H\cdots N$ hydrogen bonds are observed (graph set motifs $S_1^1(6)$ and $S_1^1(5)$, respectively). The complex molecules of **2** are linked to form dimers via bifurcated $N—H\cdots Br$ hydrogen bonds involving the amine and bromide groups (graph set motif $R_4^4(14)$).

KEYWORDS: silver(I) bromide, copper(I) bromide, triphenylphosphane, 4-phenylthiosemicarbazide, crystal structure, hydrogen bonding

INTRODUCTION

Thiosemicarbazide and its derivatives are considered an important class of N,S-donor ligands. They can be considered âĂŸborder line’ bases in the hard-soft concept of acids and bases, namely having three nitrogen centers and one sulfur donor center that are capable of binding to both hard as well as soft metal ions [1]. Their rapid coordination tendencies are such that they can bond to metals through the sulfur donor site or they can behave as bidentate ligands and coordinate via both sulfur and the hydrazinic nitrogen in a chelating manner. Thiosemicarbazide derivatives and their metal complexes have received considerable attention because of their biological activities such as antimicrobial [2, 3], antimalarial [4], antitumor [5], anticancer, and antiviral activities [6]. For example, indium (In) complexes showed higher cytotoxicity to cancer cells and less toxicity toward normal cells relative to cisplatin [7], and novel indole-based thiosemicarbazides exhibited notable antiviral activity against the Coxsackie B4 virus [8].

Copper(I) and silver(I) ions are well known for their ability to readily form complexes with phosphane ligands and adopt diversified coordination geometries in mononuclear, polynuclear, and cluster complexes [9–13]. Besides their widespread use as “spaceholder” ligands, e.g. in catalysis [14, 15], phosphane ligands have recently also received attention in their own right as components of biologically active complexes. Copper(I)-phosphane complexes, for example, have recently been investigated as potential antitumor agents, and the studies suggest that these copper(I) complexes interact with DNA in an intercalative way [16]. Meanwhile, silver(I) complexes with phosphane ligand were investigated as highly potent antimalarial and anticancer agents [17].

Keeping in mind the various biomedical applications of these classes of compounds, we recently reported a series of metal thiosemicarbazide complexes prepared by reacting copper or silver(I) chloride with triphenylphosphane and 4-phenylthiosemicarbazide [18]. Herein, we report the synthesis and crystal structures of the analogue bromide compounds $[Cu(4\text{-}PTSC)(PPh_3)_2]Br$ (**1**) and $[AgBr(4\text{-}PTSC)(PPh_3)_2]\cdot 0.18H_2O$ (**2**).

MATERIALS AND METHODS

Materials

Reagents and solvents used in the synthesis were obtained from commercial suppliers and used directly without further purification. Copper(I) bromide, silver(I) bromide, triphenylphosphine, and 4-phenylthiosemicarbazide were purchased from Sigma Aldrich (USA). Infrared (IR) spectra were measured in the region 4000–400 cm^{-1} on a Perkin-Elmer Infrared Spectrophotometer (Spectrum BX, England) using potassium bromide pellets.

Synthesis of $[Cu(4\text{-}PTSC)(PPh_3)_2]Br$ (1)

Copper(I) bromide, CuBr (0.08 g, 0.56 mmol), and triphenylphosphane, PPh_3, (0.32 g, 1.12 mmol) were dissolved in 30 ml of acetonitrile at 339.15 K. The mixture was stirred for 3 h and then 4-phenylthiosemicarbazide, 4-PTSC (0.10 g, 0.60 mmol), was added. The reaction mixture was heated under reflux for 7 h during which the precipitate gradually disappeared. The resulting clear solution was filtered and left to partially evaporate for several days at room temperature, leaving a yellow crystalline complex, which was filtered off and dried in vacuo (0.35 g, 70% yield). M.p. 445–447 K. IR bands (KBr, cm^{-1}): 3236(s), 3190(s), 3122(s), 1962(w), 1633(m), 1596(m), 1561(m), 1545(m), 1478(m), 1433(m), 1323(m), 1145(m), 1093(m), 1025(w), 997(w), 857(w), 748(m), 740(m), 705(s), 692(s).

Synthesis of $[AgBr(4\text{-}PTSC)(PPh_3)_2]{\cdot}0.18H_2O$ (2)

Silver(I) bromide, AgBr (0.11 g, 0.59 mmol), and triphenylphosphane, PPh_3, (0.31 g, 1.18 mmol) were dissolved in 30 ml of acetonitrile at 339.15 K. The mixture was stirred for 3 h and then 4-phenylthiosemicarbazide, 4-PTSC (0.10 g, 0.60 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 partially evaporate at room temperature. The crystalline complex, which deposited upon standing for a couple of days, was filtered off and dried in vacuo (0.38 g, 73% yield). M.p. 436–438 K. IR bands (KBr, cm^{-1}): 3308(m), 3860(m), 3164(s), 1939(w), 1852(w), 1628(m), 1595(m), 1545(s), 1500(s), 1467(m), 1447(w), 1391(w), 1339(m), 1298(m), 1280(s), 1208(m), 1077(w), 1036(m), 908(s), 894(m).

X-ray crystallographic analysis

X-ray diffraction data for **1** and **2** were obtained on a Bruker Quest diffractometer with either Cu-K_α ($\lambda = 1.54178$ Å) and Mo-K_α ($\lambda = 0.71073$ Å) radiation, respectively, at 150 K. Data were collected, and reflections were indexed and processed using APEX3 [19]. The space groups were assigned using XPREP within the SHELXTL suite of programs, and the structures were solved by direct methods using ShelXS and refined using Shelxl and Shelxle [20–22] (Table 1).

Refinement 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 C—H = 0.95 Å. The nitrogen bound H atoms were located in difference-Fourier maps and were refined with an N—H = 0.87 (3)–0.89 (3) Å. U_{iso}(H) values were set to 1.2 U_{eq}(C/N).

Refinement 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 C—H = 0.95 Å. Amine NH_2 H atom positions were refined and N—H distances were restrained to 0.88 (2) Å. A water molecule was found to be partially occupied. Water H atom positions were refined, and O—H and H$\cdots$H distances were restrained to 0.84 (2) and 1.36 (2) Å, respectively. The H atom positions were further restrained based on hydrogen bonding considerations toward the amine lone pair of N3 and a carbon atom of a neighboring phenyl ring (C—H$\cdots\pi$ interactions), and the H atom was also restrained to have a minimum distance of 2.60 (2) Å from other nearby H atoms (H3, H18 at $1/2 + x$, $3/2 - y$, $1/2 + z$ and H33 at $-1/2 + x$, $3/2 - y$, $1/2 + z$). Subject to these conditions, the occupancy refined to 0.177 (7). U_{iso}(H) values were set to 1.2 U_{eq}(C/N) and 1.5 U_{eq}(O). CCDC 2119288 (for **1**) and 2119289 (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 compounds, $[Cu(4\text{-}PTSC)(PPh_3)_2]Br$ (**1**) and $[AgBr(4\text{-}PTSC)(PPh_3)_2]{\cdot}0.18H_2O$ (**2**), were prepared by reacting the copper(I) bromide and silver(I) bromide with PPh_3, followed by addition of 4-PTSC in acetonitrile in 1:2:1 molar ratios. The complexes were formed in high yield (70–73%) (Scheme 1).

In the IR spectra of complexes **1** and **2**, bands at 3308 and 3122 cm^{-1} regions are due to the stretching frequency for different types of NH_2 and NH groups. No band due to the SH group was observed between 2600–2800 cm^{-1} indicating the absence of thiolate form of the ligands.

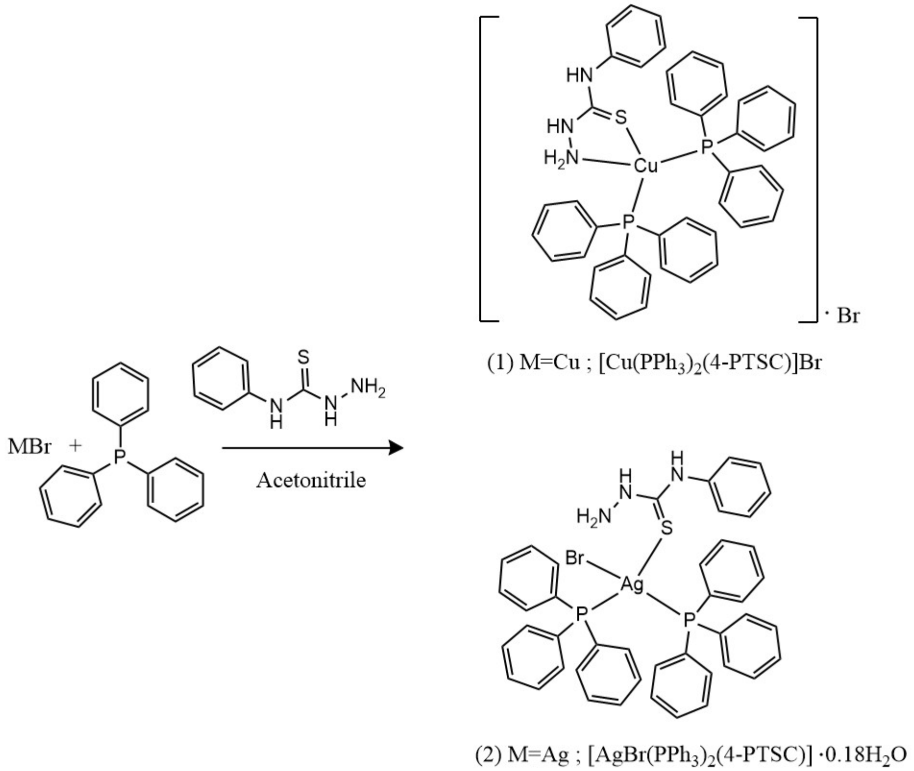
The characteristic peak of ν(C=S) of both complexes appeared at lower frequency as compared to the stretching absorption observed in the free 4-PTSC ligand (896 cm^{-1}), which confirmed the coordination of the thione sulfur to a metal center. The bands in the range 1340–1077 cm^{-1} are characteristics for the skeletal vibrations of $\nu(P\text{-}C_{ph})$ which confirmed the presence of phosphane ligand in both complexes.

The complexes were monometallic and crystallize in the monoclinic crystal system in the space groups $P2_1/c$ for **1** and $P2_1/n$ for **2**, respectively. The copper complex **1** was obtained as a bromide salt with the halogen being not bonded to the metal. The silver complex **2**, on the other hand, formed an uncharged molecular complex with the bromide covalently bonded to the metal. In both compounds, the M(I) ion is coordinated to exactly two P atoms from two PPh_3 ligands. The coordination mode of the thiosemicarbazide differed between the two complexes. In **1**, it was coordinated in a bidentate chelating fashion to the Cu center through both the sulfur and the nitrogen

Table 1 Crystal data and structure refinement details for **1** and **2**.

Crystal data		
Chemical formula	$C_{43}H_{39}CuN_3P_2S \cdot Br$	$C_{43}H_{39}AgBrN_3P_2S{\cdot}0.18(H_2O)$
Mr	835.22	882.72
Crystal system, space group	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/n$
Temperature (K)	150	150
a, b, c (Å)	14.8871 (6), 9.8740 (4), 26.2939 (11)	15.0649 (9), 16.3463 (10), 16.8942 (10)
β (°)	94.1413 (16)	107.443 (2)
V (Å^3)	3855.0 (3)	3969.0 (4)
Z	4	4
Radiation type	Cu-K_α	Mo-K_α
μ (mm^{-1})	3.57	1.68
Crystal size (mm)	0.28 × 0.17 × 0.11	0.55 × 0.43 × 0.28
Data collection		
Diffractometer	Bruker AXS D8 Quest CMOS diffractometer	Bruker AXS D8 Quest CMOS diffractometer
Absorption correction	Multi-scan, Apex3 v2016.9-0 (Bruker, 2016)	Multi-scan, Apex3 v2016.9-0 (Bruker, 2016)
No. of measured, independent and observed $[I > 2\sigma(I)]$ reflection	53040, 17948, 15843	135622, 15230, 12438
R_{int}	0.033	0.035
$(\sin\theta/\lambda)$ max (Å^{-1})	0.638	0.772
Refinement		
$R[F2 > 2\sigma(F2)]$, $wR(F2)$, S	0.028, 0.069, 1.05	0.034, 0.081, 1.12
No. of reflection	7843	15230
No. of parameter	487	483
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
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å^{-3})	0.37, −0.50	1.52, −0.91

Computer programs: Apex3 [19], *SAINT*, *SHELXS-97*, *SHELXL2018/3*, ShelXle Rev1183 [22], *Mercury* [23], and *publCIF* [24].



(1) M=Cu ; $[Cu(PPh_3)_2(4\text{-PTSC})]Br$

(2) M=Ag ; $[AgBr(PPh_3)_2(4\text{-PTSC})] \cdot 0.18H_2O$

Scheme 1: Synthesis of compounds **1** and **2**.

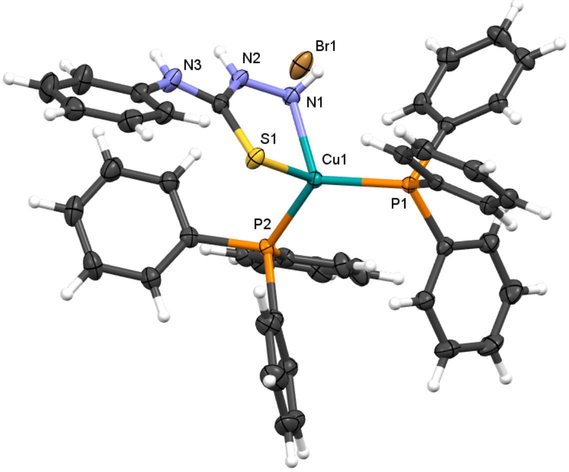


Fig. 1 Molecular structure of [Cu(4-PTSC)$(PPh_3)_2$]Br (**1**) with ellipsoid displacement drawn at the 50% probability level.

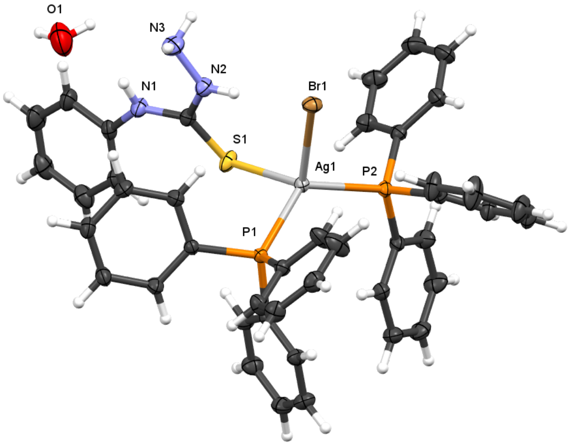


Fig. 2 Molecular structure of [AgBr(4-PTSC)$(PPh_3)_2$]·$0.18H_2O$ (**2**) with ellipsoid displacement drawn at the 50% probability level.

donor. In **2**, the ligand coordinated in a monodentate manner to the Ag via the terminal S atom, and the fourth coordination site was taken up by the bromide atom. This led both **1** and **2** to distorted tetrahedral environments with a CuP_2SN coordination sphere for **1** and $AgBrP_2S$ for **2** (Figs. 1 and 2).

The bond distances and bond angles of complexes **1** and **2** are given in Table 2. The Cu—S bond lengths in **1** agree with those found in the literature [18, 25]. The Cu—P bond lengths of 2.2417 (4)–2.2877 (5) are similar to the values of 2.2181 (9)–2.2276 (9) Å for [Cu(Sulfasalazine)$(PPh_3)_2$] [27]. The angles at the Cu(I) ion vary from 83.94 (4)° to 121.279 (17)°. The bite angle of the five-membered chelate ring N1-Cu1-S1 is 83.94 (4)°. In compound **2**, the Ag1–S1 bond length of 2.5973 (5) is shorter than the mean value of 2.8789 (10) found in [AgBr(Atu)$(PPh_3)_2$] [28]. The Ag1–P1 and Ag1–P2 distances of 2.4819 (4) and 2.4647 (4) Å are close to the values of [AgCl(4-PTSC)$(PPh_3)_2$] · CH_3CN [18].

Table 2 Selected bond lengths and angles for (Å, °) [Cu(4-PTSC)$(PPh_3)_2$]Br (**1**) and [AgBr(4-PTSC)$(PPh_3)_2$]·$0.18H_2O$ (**2**).

Bond length (Å)		Bond angle (°)	
Compound **1**			
Cu1–N1	2.1416 (15)	N1–Cu1–P1	110.53 (4)
Cu1–P1	2.2417 (4)	N1–Cu1–P2	110.58 (5)
Cu1–P2	2.2877 (5)	P1–Cu1–P2	121.279 (17)
Cu1–S1	2.3266 (5)	N1–Cu1–S1	83.94 (4)
		P1–Cu1–S1	119.900 (18)
		P2–Cu1–S1	104.425 (18)
Compound **2**			
Ag1–P2	2.4647 (4)	P2–Ag1–P1	126.010 (15)
Ag1–P1	2.4819 (4)	P2–Ag1–S1	110.930 (16)
Ag1–S1	2.5973 (5)	P1–Ag1–S1	99.906 (16)
Ag1–Br1	2.7504 (3)	P2–Ag1–Br1	105.047 (12)
		P1–Ag1–Br1	106.036 (11)
		S1–Ag1–Br1	107.894 (12)

The two structures are stabilized by intramolecular and intermolecular N—H···Br, N—H···N, and N—H···O hydrogen bonds involving the NH_2 and NH groups of the thiosemicarbazide ligands. In the copper complex **1**, all hydrogen bonds are toward the bromide anion with one H atom of each nitrogen atom forming an H-bond with the halogen. The two N—H groups chelate the bromide anion (at $2-x$, $1-y$, $1-z$; graph set motif $R_2^1(6)$ [29]), while the N1—H1*B*···Br1 bond originating from the NH_2 group is linear (graph set motif $D_1^1(2)$). All three N—H···Br interactions connect two complex cations and two bromide anions into a salt pair dimer with combined graph set motifs for the dimer of $R_4^2(10)$ and $R_4^2(14)$ (Fig. 3). The hydrogen bonding environment of the bromide is completed by a weak C10—H10···Br1 interaction originating from H10 of one of the PPh_3 ligands (at $+x$, $1+y$, $+z$). The second H-atom of the NH_2 group, H1*A*, is not involved in an N1—H1···Br hydrogen bond and instead forms an N—H···π bond toward the phenyl ring of a thiosemicarbazide ligand of a neighboring cation at $2-x$, $-y$, $1-z$ (Table 3, Fig. 4).

The hydrogen bonding interactions in compound **2** are more variable. With the bromide ion being covalently bonded, it is not as available as a hydrogen bonding acceptor (due to steric constraints and the lesser charge density at the halogen). In **2**, the by far strongest hydrogen bond is not toward the bromide ion but is an intramolecular N1—H1···N3 bond with the lone pair of the NH_2 group as the acceptor (graph set motif $S_1^1(5)$). This type of hydrogen bond is not present in **1** as the NH_2 group is metal coordinated and not available as a hydrogen bond acceptor. Instead, both N—H groups in **1** are engaged in N—H···Br bonds

Table 3 Hydrogen-bond geometry (Å, °) for [Cu(4-PTSC)(PPh$_3$)$_2$]Br (**1**) and [AgBr(4-PTSC)(PPh$_3$)$_2$]·0.18H$_2$O (**2**).

D–H···A	D–H	H···A	D···A	D–H···A
Compound **1**				
N1–H1B···Br1	0.89 (3)	2.59 (3)	3.4525 (16)	161 (2)
N2–H2···Br1^{i}	0.87 (3)	2.46 (3)	3.2798 (14)	157 (2)
N3–H8···Br1^{i}	0.89 (3)	2.61 (3)	3.4599 (16)	159 (2)
C10–H10···Br1^{ii}	0.95	2.915	3.789 (2)	153
N1–H1A···π(C2-C7)^{iii}	0.87 (3)	2.79	3.500	140
Compound **2**				
N1–H1···N3	0.88	2.14	2.606 (2)	113
N1–H1···O1	0.88	2.40	3.248 (14)	161
N2–H2···Br1	0.88	2.47	3.3427 (16)	172
N3–H3B···Br1^{iv}	0.88 (2)	2.60 (2)	3.4729 (19)	172 (2)
C7–H7···S1	0.95	2.61	3.2061 (19)	121
C9–H9···Br1	0.95	3.11	3.870 (2)	139
C31–H31···Br1	0.95	2.94	3.816 (2)	153
O1–H1B···N3	0.83 (2)	2.24 (2)	2.912 (12)	138 (4)

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

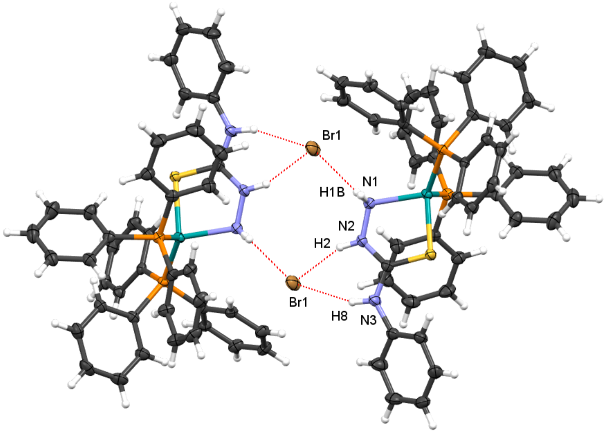


Fig. 3 Part of the crystal structure of [Cu(4-PTSC)(PPh$_3$)$_2$]Br (**1**), showing intermolecular N—H···Br hydrogen bonds (shown as dashed lines).

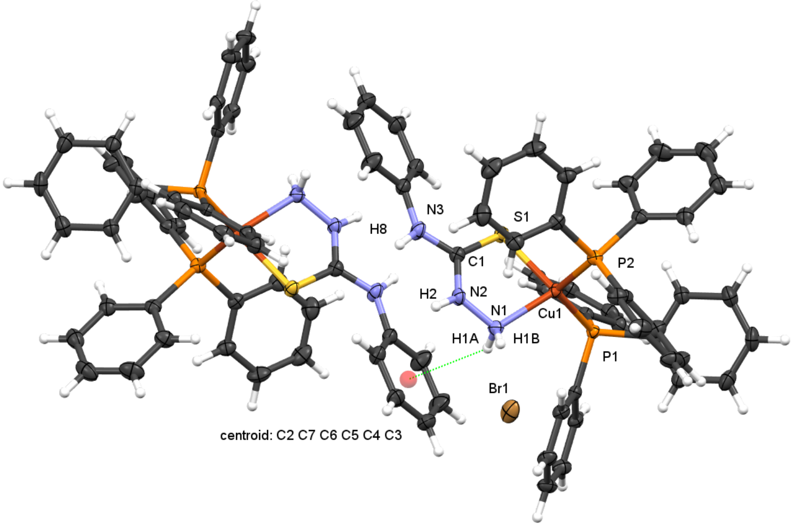


Fig. 4 Part of the crystal structure of [Cu(4-PTSC)(PPh$_3$)$_2$]Br (**1**), showing intermolecular N—H···π bond (shown as dashed lines).

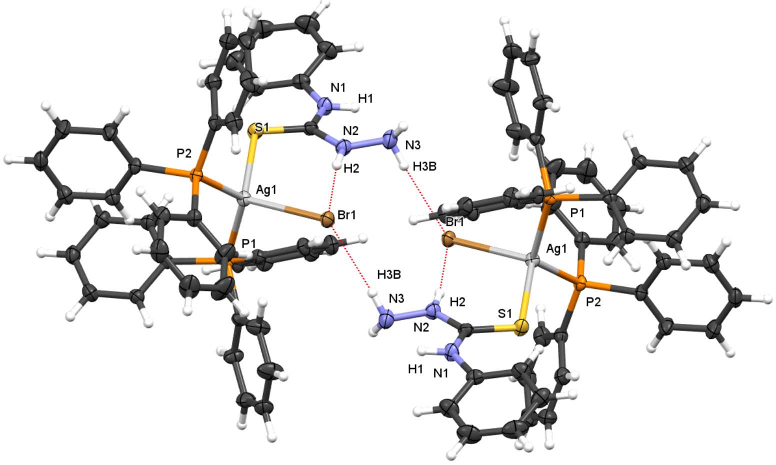


Fig. 5 Part of the crystal structure of $[AgBr(4\text{-}PTSC)(PPh_3)_2]\cdot 0.18H_2O$ (**2**), showing intermolecular N—H···Br hydrogen bonds (shown as dashed lines). The water molecule has been omitted for clarity.

toward the same bromide ion. In **2**, the bromide ion still acts as the acceptor for two N—H···Br hydrogen bonds, originating from the N—H and NH_2 groups of the NH—NH_2 group. The N2—H2···Br1 of the N—H group is intramolecular (graph set motif $S_1^1(6)$), assisted by the complex geometry, and points toward the "belt" of the bromine carrying the largest negative charge, and the H···Br distance is thus about as short as that of the N—H···Br bonds toward the anionic bromine in **1**. The other N3—H3*B*···Br1 bond involves the NH_2 group, is intermolecular, and points partially toward the sigma hole of the bromide ion with > 3.9 Å much longer. It is, however, still the strongest always present intermolecular interaction and leads toward the formation of centrosymmetric dimers (Fig. 5, graph set motif $R_4^4(14)$). The remaining hydrogen bonds in **2** (Table 3) involve the partially occupied water molecule and do not substantially contribute to structure stability or the general arrangement in the solid state.

CONCLUSION

In conclusion, new copper(I) and silver(I) complexes with triphenylphosphane and 4-phenylthiosemicarbazide have been successfully prepared and characterized by IR spectroscopy and X-ray single crystal analysis methods. The complexes display a distorted tetrahedral coordination. The thiosemicarbazide acts in the silver complex as a monodentate ligand through the sulfur donor. In the copper complex, it features bidentate chelating coordination via sulfur and the nitrogen donors. In the crystals, there are intra- and inter-molecular hydrogen bonds leading to the formation of dimers.

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