



Synthesis, spectroscopy and structures of halogen and sulfur-bridged dinuclear silver(I) complexes with N¹-substituted thiophene-2-carbaldehyde thiosemicarbazone

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ABSTRACT

The reactions of silver(I) halides (Cl or Br) with thiophene-2-carbaldehyde N¹-methyl thiosemicarbazone (HttscMe) in the presence of Ph₃P (1:1:1 molar ratio) yield halogen-bridged dimers, [Ag₂(μ-X)₂(η¹-S-HttscMe)₂(PPh₃)₂] (X = Cl, **1**; Br, **2**). The use of 2,2'-bipyridine in lieu of Ph₃P in the reaction of silver(I) chloride with HttscMe yields the sulfur-bridged dimer, [Ag₂(μ-S-HttscMe)₂(η¹-HttscMe)₂] · 2CHCl₃ **3**. The substituents have altered the nature of bridge between the two silver atoms. The Ag...Ag separation (3.4867(5) Å) in complex **3** is less than that in the halogen-bridged dimers (3.734(4) Å **1**; 3.746(5) Å **2**). Unlike PPh₃ the co-ligand 2,2'-bipyridine did not coordinate to the silver center, but was necessary for crystallization in the reaction with the thio-ligand. NMR spectroscopy revealed that the complexes remained unchanged in the solution state (CDCl₃).

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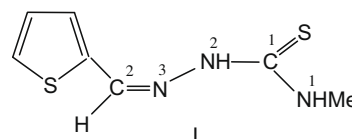
1. Introduction

Among coinage metals (Cu, Ag and Au), the chemistry of copper(I) and copper(II) with N,S-donor ligands based on thiosemicarbazones {R¹R²C=N–N(H)–C(=S)–NR³R⁴} has received considerable attention in recent years [1–14]. However, thiosemicarbazone chemistry of silver/gold salts is limited [7,15–23]. It is pointed out here that the chemistry of silver(I) halides with other N,S-donors is also poorly described in the literature [24–35,40], and most of the complexes reported are with ionic silver(I) salts [36]. There is interest in silver(I) chemistry due to its structural diversity, supramolecular chemistry luminescent/conducting properties, biological and pharmacological activities, such as antimicrobial, anti-fungal properties and metal based drugs [37–39,41].

Recently, from this laboratory, it was reported that silver(I) halides with thiosemicarbazones having R¹, R² substituents such as, Ph, H; Ph, Me or Me, Me formed only halogen-bridged dimers, while heterocyclic ring substituents such as: pyrrole, H; thiophene, H and pyridine, Ph, yielded only sulfur-bridged dimers (Chart 1) [15,16].

In continuation of our interest in silver(I) halide-thiosemicarbazone chemistry, we report in this paper the results of the reaction of silver(I) halides with thiophene-2-carbaldehyde N¹-methyl thiosemicarbazone (Structure I) in the presence of Ph₃P or 2,2'-bipyri-

dine ligands, with the objective of observing the effect of the methyl substituent at N¹ on the nature of the products. These complexes were characterized by elemental analysis, IR, NMR spectroscopy (¹H and ³¹P) and X-ray crystallography.



2. Experimental

2.1. Materials and techniques

Sodium chloride, sodium bromide, thiophene-2-carbaldehyde, 3-methyl thiosemicarbazide and triphenylphosphine were procured from Aldrich Chemicals Ltd. and were used as received. The silver(I) halides (X = Cl, Br) were freshly prepared by reacting silver(I) nitrate with sodium chloride or bromide in methanol. Thiophene-2-carbaldehyde N¹-methyl thiosemicarbazone was prepared by refluxing thiophene-2-carbaldehyde and 3-methylthiosemicarbazide in methanol for 8–10 h. C, H and N analyses were obtained with a Thermoelectron FLASHEA1112 CHNS analyzer. Infrared spectra were recorded from KBr pellets in the range

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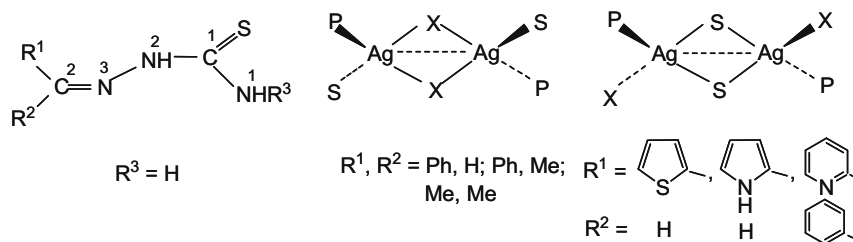


Chart 1.

4000–200 cm^{-1} on a Pye-Unicam SP-3-300 spectrophotometer. Melting points were determined with an electrically heated Galenkamp apparatus. ^1H NMR were recorded on a JEOL AL-300 FT spectrometer operating at a frequency of 300 MHz using CDCl_3 as the solvent with TMS as an internal standard. ^{31}P NMR spectra were recorded on a Bruker ACP-300 spectrometer operating at a frequency of 121.5 MHz with H_3PO_4 as an external standard with $\delta = 0$.

2.2. Synthesis of the complexes

2.2.1. $[\text{Ag}_2(\mu\text{-Cl})_2(\eta^1\text{-S-HttsMe})_2(\text{PPh}_3)_2]$ (**1**)

To AgCl (0.025 g, 0.17 mmol) suspended in acetonitrile (15 mL) was added solid Ph_3P (0.046 g, 0.17 mmol), and the reaction mixture was stirred for 2 h. The white precipitates that formed were filtered to remove acetonitrile, and to the white solid suspended in chloroform was added the solid HttsMe ligand (0.035 g, 0.17 mmol). The contents stirred for a further period of 10 min and the yellow colored clear solution thus formed was allowed to crystallize. Slow evaporation at room temperature yielded crystals of $[\text{Ag}_2(\mu\text{-Cl})_2(\eta^1\text{-S-HttsMe})_2(\text{PPh}_3)_2]$ (**1**) (1 yellow, 72%, m.p. 175–177 $^\circ\text{C}$). *Anal.* Calc. for $\text{C}_{50}\text{H}_{48}\text{Ag}_2\text{Cl}_2\text{N}_6\text{P}_2\text{S}_4$: C, 49.26; H, 4.35; N, 6.92. Found: C, 49.67; H, 4.0; N, 6.95%. IR data (KBr, cm^{-1}): $\nu(\text{N-H})$ 3340(s); $\nu(-\text{NH}-)$ 3160(m); $\nu(\text{C-H})_{\text{ph}}$ 2951(m); $\nu(\text{C-H})_{\text{Me}}$ 2733(w); $\nu(\text{C=N}) + \nu(\text{C=C})$ 1620(m), 1565(m), 1530(m); $\nu(\text{P-C}_{\text{Ph}})$ 1093(s); $\nu(\text{C-N})$ 1031(s); $\nu(\text{C=S})$ 854(s). ^1H NMR (CDCl_3 , δ ppm): 12.42s ($-\text{N}^2\text{H}$), 8.66s (C^2H), 7.32–7.52m ($\text{C}^{4,6}\text{H} + 15\text{H}$, $\text{PPh}_3 + \text{N}^1\text{H}$), 7.05dd (C^5H), 3.23d ($-\text{CH}_3$). ^{31}P NMR (CDCl_3 , δ ppm): 10.5, $\Delta\delta$ (δ complex – δ ligand) 14.7.

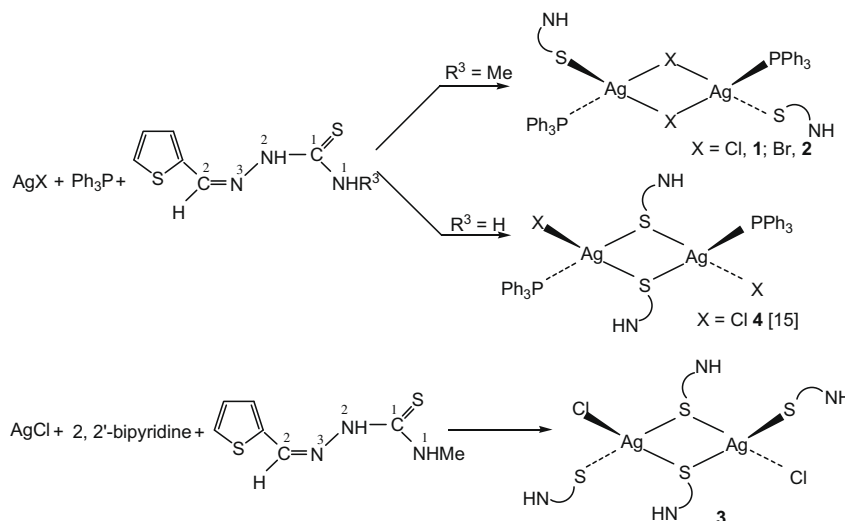
2.2.2. $[\text{Ag}_2(\mu\text{-Br})_2(\eta^1\text{-S-HttsMe})_2(\text{PPh}_3)_2]$ (**2**)

To AgBr (0.025 g, 0.13 mmol) suspended in acetonitrile (15 mL) was added solid Ph_3P (0.035 g, 0.13 mmol), and the reaction mixture

was stirred for 2 h. The white precipitates that formed were filtered to remove acetonitrile, and to the white solid suspended in chloroform was added the solid HttsMe ligand (0.027 g, 0.13 mmol). The contents were stirred for a further period of 10 min and the yellow colored clear solution thus formed was allowed to crystallize. Slow evaporation at room temperature yielded crystals of $[\text{Ag}_2(\mu\text{-Br})_2(\eta^1\text{-S-HttsMe})_2(\text{PPh}_3)_2]$ (**2**) (2 yellow, 69%, m.p. 195–198 $^\circ\text{C}$). *Anal.* Calc. for $\text{C}_{50}\text{H}_{48}\text{Ag}_2\text{Br}_2\text{N}_6\text{P}_2\text{S}_4$: C, 46.47; H, 3.92; N, 6.92. Found: C, 46.28; H, 3.70; N, 6.47%. IR data (KBr, cm^{-1}): $\nu(\text{N-H})$ 3345(s); $\nu(-\text{NH}-)$ 3150(m); $\nu(\text{C-H})_{\text{ph}}$ 2975(m); $\nu(\text{C-H})_{\text{Me}}$ 2753(w); $\nu(\text{C=N}) + \nu(\text{C=C})$ 1632(m), 1555(m), 1532(m); $\nu(\text{P-C}_{\text{Ph}})$ 1094(s); $\nu(\text{C-N})$ 1029(s); $\nu(\text{C=S})$ 853(s). ^1H NMR (CDCl_3 , δ ppm): 11.59s ($-\text{N}^2\text{H}$), 8.61s (C^2H), 7.32–7.52m ($\text{C}^{4,6}\text{H} + 15\text{H}$, $\text{PPh}_3 + \text{N}^1\text{H}$), 7.06dd (C^5H), 3.23d ($-\text{CH}_3$). ^{31}P NMR (CDCl_3 , δ ppm): 6.2, $\Delta\delta$ (δ complex – δ ligand) 10.9.

2.2.3. $[\text{Ag}_2\text{Cl}_2(\mu\text{-S-HttsMe})_2(\eta^1\text{-S-HttsMe})_2] \cdot 2\text{CHCl}_3$ (**3**)

To AgCl (0.025 g, 0.17 mmol) suspended in acetonitrile (15 mL) was added solid 2,2'-bipyridine (0.034 g, 0.17 mmol) and the reaction mixture was stirred for 2 h. The light purple precipitates that formed were filtered to remove acetonitrile, and to the purple precipitates suspended in chloroform was added the solid ligand HttsMe (0.035 g, 0.17 mmol). The contents were stirred for a further period of 10 min and the solution was allowed to crystallize. Slow evaporation at room temperature yielded crystals of $[\text{Ag}_2\text{Cl}_2(\mu\text{-S-HttsMe})_2(\eta^1\text{-S-HttsMe})_2] \cdot 2\text{CHCl}_3$ (**3**) (yellow, 65%, decomposed at 180–185 $^\circ\text{C}$). *Anal.* Calc. for $\text{C}_{28}\text{H}_{36}\text{Ag}_2\text{Cl}_8\text{N}_{12}\text{S}_8$: C, 27.86; H, 3.20; N, 19.0. Found: C, 27.23; H, 2.90; N, 19.4%. IR data (KBr, cm^{-1}): $\nu(\text{N-H})$ 3347(s); $\nu(-\text{NH}-)$ 3142(m); $\nu(\text{C-H})_{\text{ph}}$ 2981(m); $\nu(\text{C-H})_{\text{Me}}$ 2757(w); $\nu(\text{C=N}) + \nu(\text{C=C})$ 1638(m), 1566(m), 1530(m); $\nu(\text{C-N})$ 1029(s); $\nu(\text{C=S})$ 854(s). ^1H NMR (CDCl_3 , δ ppm): 11.68s ($-\text{N}^2\text{H}$), 8.56s (C^2H), 7.86sb (N^1H), 7.32–7.39m ($\text{C}^{4,6}\text{H}$), 7.06dd (C^5H), 3.24d ($-\text{CH}_3$).



Scheme 1.

Table 1
Crystallographic data of complexes **1–3**.

Empirical formula	C ₅₀ H ₄₈ Ag ₂ Cl ₂ N ₆ P ₂ S ₄	C ₅₀ H ₄₈ Ag ₂ Br ₂ N ₆ P ₂ S ₄	C ₂₈ H ₃₆ Ag ₂ Cl ₈ N ₁₂ S ₈
<i>M</i>	1209.80	1298.70	1296.51
<i>T</i> (K)	100(2)	100(2)	200(2)
Crystal system	monoclinic	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>Unit cell dimensions</i>			
<i>a</i> (Å)	10.7279(13)	10.8211(8)	15.6035(10)
<i>b</i> (Å)	16.153(2)	16.3962(13)	9.9952(5)
<i>c</i> (Å)	14.9158(18)	14.8555(11)	17.5911(11)
α (°)	90.00	90.00	90.00
β (°)	102.864(2)	102.868(2)	109.667(7)
γ (°)	90.00	90.00	90.00
<i>V</i> (Å ³)	2519.8(5)	2569.5(3)	2583.5(3)
<i>Z</i>	2	2	2
<i>D</i> _{calc} (g cm ^{−3})	1.594	1.679	1.667
μ (mm ^{−1})	1.155	2.583	1.531
Reflections collected	6680	15505	18520
Unique reflections	6217	6299	8418
<i>R</i> _{int}	0.0399	0.0520	0.0449
Reflections with $[I > 2\sigma(I)]$	5088	4991	6138
Final <i>R</i> indices $[I > 2\sigma(I)]$	<i>R</i> = 0.0506, <i>wR</i> = 0.0977	<i>R</i> = 0.0648, <i>wR</i> = 0.1246	<i>R</i> = 0.0960, <i>wR</i> = 0.1993

3. X-ray crystallography

The data for **1** and **2** were measured on a Bruker AXS SMART APEX CCD diffractometer. Data were reduced and corrected for absorption using SMART and SAINT [42]. The structures were solved by direct methods and refined by full matrix least squares based on *F*² with anisotropic thermal parameters for non-hydrogen atoms using SHELXTL (structure solution, refinement and some molecular graphics). All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions and were refined with an isotropic displacement parameter 1.5 (methyl) or 1.2 (all others) times that of the adjacent carbon or oxygen atom.

A prismatic crystal of complex **3** was mounted on an automatic Enraf–Nonius CAD-4 diffractometer equipped with a graphite monochromator and Mo K α radiation (λ = 0.71073 Å). The unit cell dimensions and intensity data were measured at 200 K. The structure was solved by direct methods and refined by full matrix least squares based on *F*² with anisotropic thermal parameters for non-hydrogen atoms using XCAD-49 (data reduction), and SHELXL (absorption correction, structure solution refinement and molecular graphics) [43]. The thiophene rings of the terminally bonded HttscMe ligand in complex **3** are disordered and the data is 99% complete to a theta value of 25° (2 θ of 50°), which meets the criterion. The reason for the 90% completion figure is that data was collected out to a theta value of 32.51°, but at this angle the data is incomplete due to the shape of the detector (this is normal for area detector data).

4. Results and discussion

4.1. Synthesis

Scheme 1 gives a pictorial representation of formation of the silver(I) halide complexes with thiophene-2-carbaldehyde N¹-methylthiosemicarbazone (HttscMe). To silver(I) chloride suspended in acetonitrile was added triphenylphosphine, and the contents were stirred for 2 h, which formed white precipitates. The ligand HttscMe was added to these precipitates suspended in chloroform and stirred for 10 min. The clear solution was allowed to evaporate at room temperature, which formed crystals of the stoichiometry, [Ag₂(μ -Cl)₂(η^1 -S-HttscMe)₂(PPh₃)₂] **1**. A similar reaction with silver(I) bromide yielded [Ag₂(μ -Br)₂(η^1 -S-HttscMe)₂(PPh₃)₂] **2**. The use of

2,2'-bipyridine in lieu of Ph₃P in the reaction of silver(I) chloride with HttscMe yielded [Ag₂(μ -S-HttscMe)₂(η^1 -HttscMe)₂] · 2CHCl₃ **3**. There was no coordination by 2,2'-bipyridine in this reaction. Reactions of silver(I) halides with thiosemicarbazones in the absence of Ph₃P or 2,2'-bipyridine yield insoluble complexes. Thus the presence of the co-ligand is necessary to get crystalline compounds.

It was reported earlier that thiophene-2-carbaldehyde thiosemicarbazone (Httsc, R³ = H) with silver(I) chloride formed a sulfur-bridged complex, [Ag₂Cl₂(μ -S-Httsc)₂(Ph₃P)₂] · 2CH₃CN **4** [15], and the replacement of one hydrogen at the N¹ nitrogen with a methyl group has changed the nature of bonding from sulfur-bridging (**4**) to halogen-bridging (**1** and **2**). Complex **3** shows S-bridging, as in **4**, and probably is dominated by the presence of four

Table 2
Bond lengths (Å) and bond angles (°).

<i>[Ag₂(μ-Cl)₂(η^1-HttscMe)₂(Ph₃P)₂] 1</i>			
Ag(1)–P(1)	2.4258(8)	C(2)–S(1)	1.700(3)
Ag(1)–S(1)	2.5693(8)	C(2)–N(2)	1.348(4)
Ag(1)–Cl(1)	2.6335(8)	C(2)–N(1)	1.322(4)
Ag(1)–Cl(1)	2.6493(8)	N(2)–N(3)	1.379(4)
Ag–Ag ^{#1}	3.734(4)		
P(1)–Ag(1)–S(1)	112.32(3)	S(1)–Ag(1)–Cl(1)	105.84(3)
P(1)–Ag(1)–Cl(1)	114.88(3)	Cl(1)–Ag(1)–Cl(1)	90.15(2)
S(1)–Ag(1)–Cl(1)	109.81(3)	Ag(1)–Cl(1)–Ag(1)	89.85(2)
P(1)–Ag(1)–Cl(1)	121.58(3)	C(2)–S(1)–Ag(1)	109.00(11)
<i>[Ag₂(μ-Br)₂(η^1-HttscMe)₂(Ph₃P)₂] 2</i>			
Ag(1)–P(1)	2.4414(11)	C(2)–S(1)	1.699(5)
Ag(1)–S(1)	2.5625(12)	C(2)–N(2)	1.361(5)
Ag(1)–Br(2)	2.7357(5)	C(2)–N(1)	1.324(6)
Ag(1)–Br(2)	2.7422(5)	N(2)–N(3)	1.374(5)
Ag–Ag ^{#1}	3.746(5)		
P(1)–Ag(1)–S(1)	113.10(4)	S(1)–Ag(1)–Br(2)	112.08(3)
P(1)–Ag(1)–Br(2)	122.13(3)	Br(2)–Ag(1)–Br(2)	93.717(15)
S(1)–Ag(1)–Br(2)	105.60(3)	Ag(1)–Br(2)–Ag(1)	86.284(15)
P(1)–Ag(1)–Br(2)	108.68(3)	C(2)–S(1)–Ag(1)	109.38(15)
<i>[Ag₂(μ-S-HttscMe)₂(η^1-HttscMe)₂] · 2CHCl₃ 3</i>			
Ag–S(1A)	2.5168(7)	Ag–S(1A)	2.6259(8)
Ag–Cl	2.5770(8)	S(1A)–C(2A)	1.721(3)
Ag–S(1A)	2.5969(7)	S(2A)–C(7A)	1.722(3)
Ag–Ag ^{#1}	3.4867(5)	N(1A)–C(2A)	1.327(4)
S(1B)–Ag–Cl	111.31(2)	Cl–Ag–S(1A)	108.46(2)
S(1B)–Ag–S(1A)	109.49(2)	S(1A)–Ag–S(1A)	96.24(2)
Cl–Ag–S(1A)	116.71(2)	C(2A)–S(1A)–Ag	100.25(8)
S(1B)–Ag–S(1A)	113.94(2)	Ag–S(1A)–Ag	83.76(2)

S-donor atoms in this dimer, and this also enhances the argentophilicity with a relatively short Ag...Ag contact.

The presence of two $\nu(\text{N-H})$ bands in the ranges $3340\text{--}3347\text{ cm}^{-1}$ (due to $-\text{N}^1\text{HR}$) and $3142\text{--}3160\text{ cm}^{-1}$ (due to $-\text{N}^2\text{H}$) in complexes

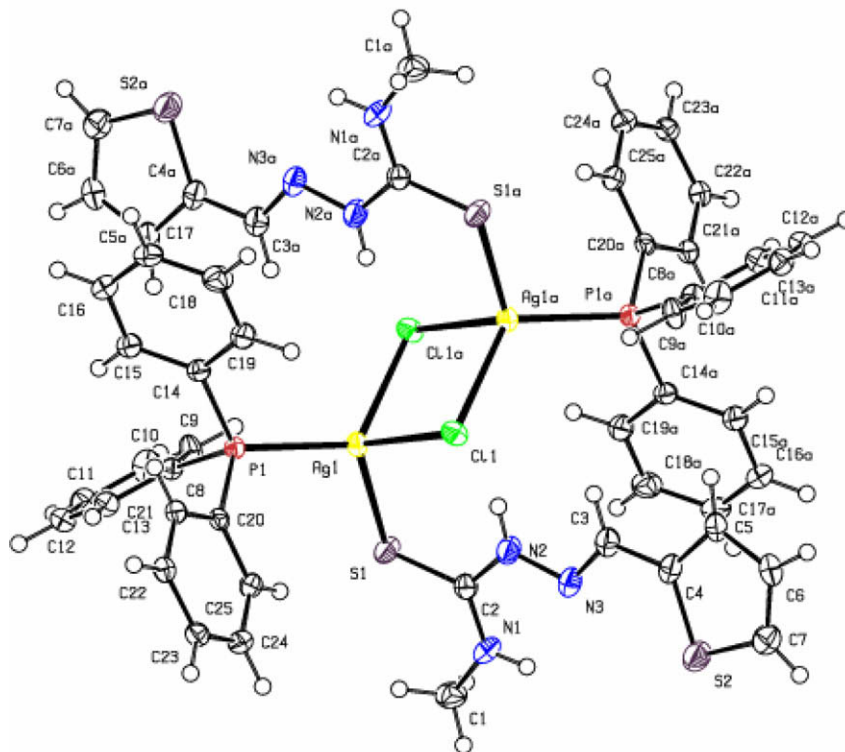


Fig. 1. ORTEP drawing of $[\text{Ag}_2(\mu\text{-Cl})_2(\eta^1\text{-HttsMe})_2(\text{Ph}_3\text{P})_2]$, **1**, showing thermal ellipsoids at the 50% probability level.

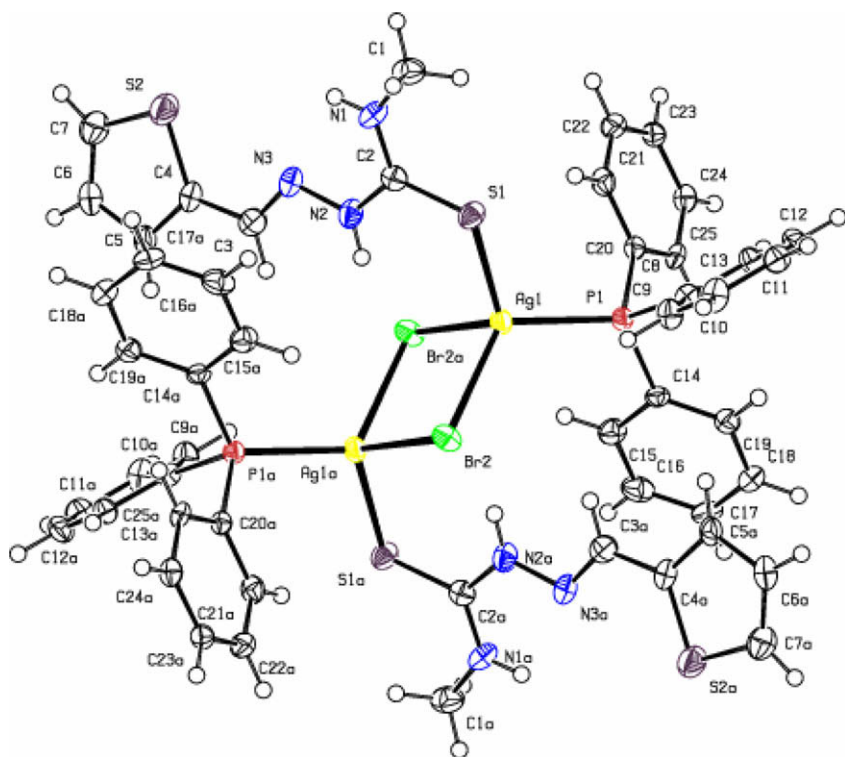







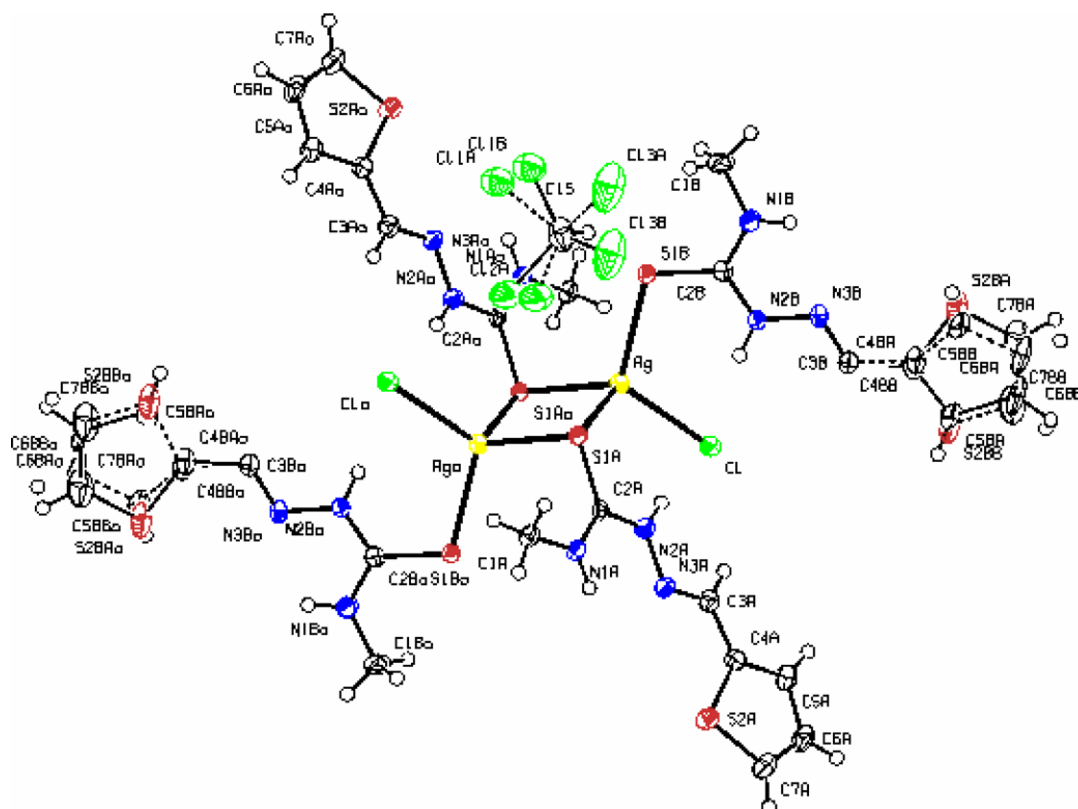


Fig. 2. ORTEP drawing of $[\text{Ag}_2(\mu\text{-Br})_2(\eta^1\text{-HttsMe})_2(\text{Ph}_3\text{P})_2]$, **2**, showing thermal ellipsoids at the 50% probability level.

Table 3

Comparison of bond parameters of dimers 1–8.

R ¹ , R ² , R ³ (No.)	Ag–S	Ag–X	Ag–X–Ag	X–Ag–X	Ag...Ag	Ref.
<i>Ag(μ-X)₂Ag cores</i>						
 Me (1)	2.5693(8)	2.6335(8); 2.6493(8)	89.85(2) (Cl)	90.15(2)	3.734(4)	this work
 Me (2)	2.5625(12)	2.7357(5); 2.7422(5)	86.284(15) (Br)	93.717(15)	3.746(5)	this work
Me, Me H (5)	2.507(2)	2.6454(7); 2.8378(7)	82.24(2) (Br)	97.75(2)	3.6089(9)	[16]
 H (6)	2.5881(6)	2.7252(3); 2.7914(3)	78.004(8) (Br)	101.997(8)	3.4722(3)	[16]
 H (7)	2.5851(8)	2.6254(8); 2.7056(8)	78.01(2) (Cl)	101.99(2)	3.3558(5)	[16]
 H (8)	2.5927(6)	2.7210(3); 2.8115(3)	73.2.27(8) (Br) Ag–S–Ag	106.721(8) S–Ag–S	3.3023(3)	[15]
<i>Ag(μ-S)₂Ag cores</i>						
 Me (3)	2.5967(11); 2.6259(12)	2.5771(12)	83.77(3) (Cl)	96.23(3)	3.4867(5)	this work
 H (4)	2.611(2); 2.876(2)	2.520(2)	68.33(6) (Cl)	111.67(6)	3.0902(15)	[15]

R¹R²C=NNHC(=S)NHR³.

1–3 supports the coordination of HttscMe as a neutral ligand. The (N–H) band of the $-N^1HR$ group showed a high-energy shift in the complexes vis-à-vis the free ligand (3326 cm^{-1}). The most characteristic thioamide band due to $\nu(C=S)$ lies in the range $852\text{--}854\text{ cm}^{-1}$ in complexes **1–3** and is at a somewhat low energy region (free ligand, 860 cm^{-1}). This indicates the coordination of sulfur to the silver center. The $\nu(P-C_{Ph})$ bands in complexes **1** and **2** at 1093 and 1094 cm^{-1} , respectively, support the presence of coordinated triphenylphosphine in these complexes [15,16].

4.2. Structures of the complexes

The crystallographic data and important bond parameters (bond lengths and bond angles) of complexes **1–3** are given in Tables 1 and 2, respectively. The molecular structures along with the numbering scheme are given in Figs. 1–3, respectively. All the three complexes crystallized in the monoclinic crystal system with space group $P2_1/n$.

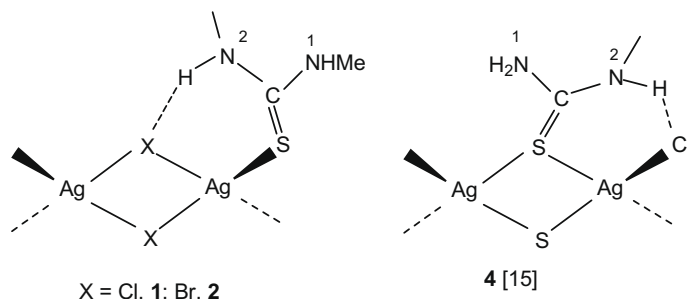
4.3. Structures of the dimers 1–3

Complexes **1** and **2** have similar structures. In each complex, silver(I) is coordinated to two bridging halogen atoms, one terminal S atom and one terminal P atom. The central $Ag(\mu-X)_2Ag$ cores of these dimers are almost square planar as the $X-Ag-X$ and $Ag-X-$

Ag angles are close to 90° ($90.15(12)$, $89.85(2)^\circ$ **1**; $93.717(15)$, $86.284(15)^\circ$ **2**), while similar cores of complexes **5–8** form parallelograms (Table 3). In complex **3**, two bridging sulfurs, one terminal sulfur and one terminal chloride atom are coordinated to the silver(I) centers. The central core $Ag(\mu-S)_2Ag$ is a parallelogram ($S-Ag-S$, $Ag-S-Ag$, 109.49° , 83.76°). The geometries around each silver atom in complexes **1–3** can be treated as distorted tetrahedral. The $Ag-X-Ag$ and $X-Ag-X$ or $Ag-S-Ag$ and $S-Ag-S$ bond angles vary in a complementary fashion, the larger the angle at the bridging halogen/sulfur, the greater is the $Ag\cdots Ag$ contact. The $Ag\cdots Ag$ separation (3.487 \AA) in sulfur-bridged complex **3** is close to twice the sum of the van der Waals radius of silver atoms (3.40 \AA [44]) and this separation is less than that ($3.734(4)\text{ \AA}$ for **1**; $3.746(5)\text{ \AA}$ for **2**) in the halogen-bridged dimers.

4.4. H-bonded networks

Scheme 2 shows the intra-molecular interactions in complexes **1** and **2**. Complex **4** has S-bridging and the imino group is H-bonded to the terminal chlorine. The presence of the methyl group at the N^1 atom modulates the bonding property of HttscMe, probably by way of higher steric crowding if it was in a sulfur-bridged dimer. This paves way for halogen-bridging and the imino group now H-bonds to this halogen ($N^2H\cdots Cl$, 2.45 \AA **1**; $N^2H\cdots Br$, 2.614 \AA **2**). The two chloro-bridged dimeric units of **1** are interconnected



Scheme 2.

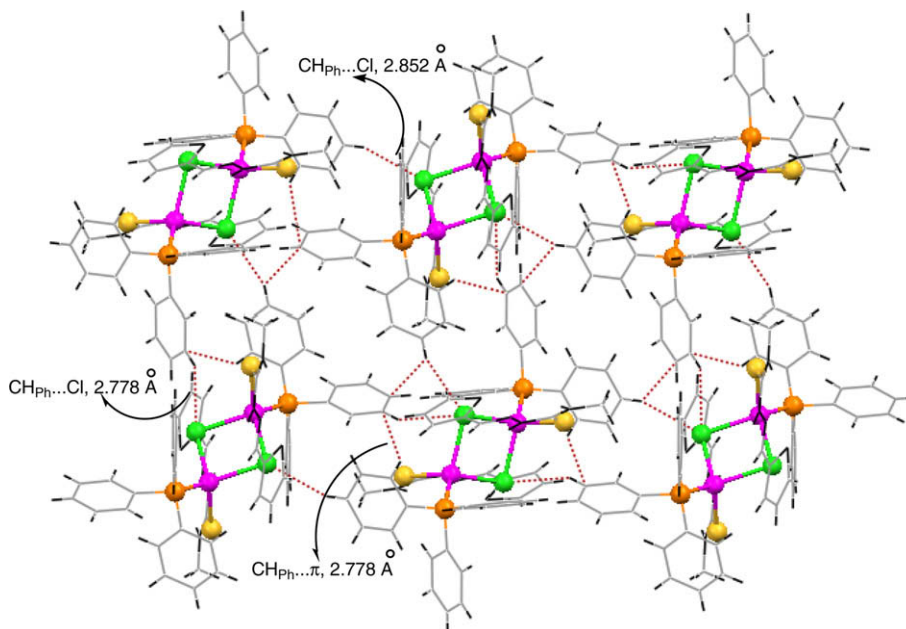


Fig. 4. Packing diagram of $[Ag_2(\mu-Cl)_2(\eta^1\text{-HttscMe})_2(Ph_3P)_2]$ **1**.

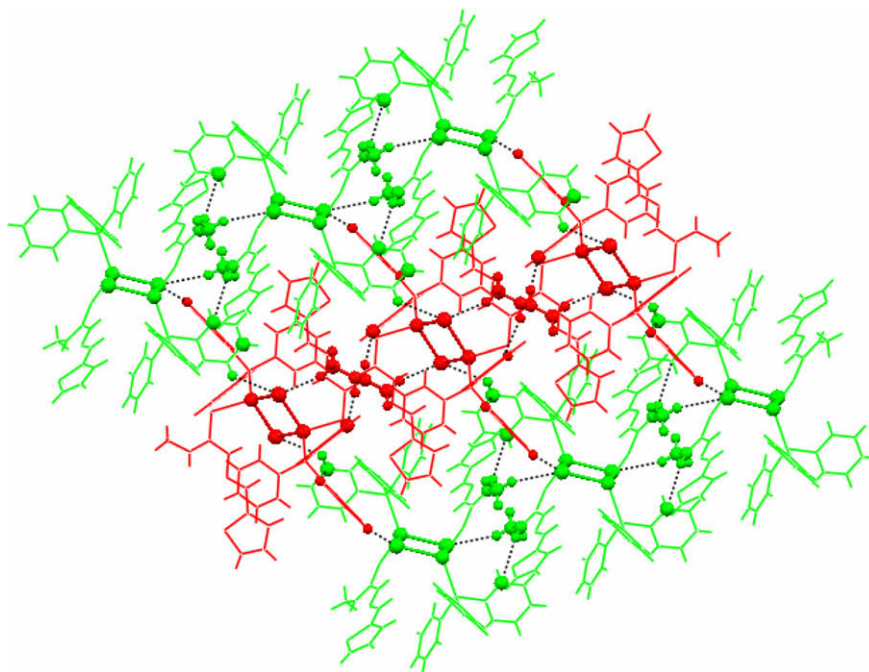


Fig. 5. Packing diagram of $[\text{Ag}_2(\mu\text{-Br})_2(\eta^1\text{-HttsMe})_2(\text{Ph}_3\text{P})_2]$ **2**.

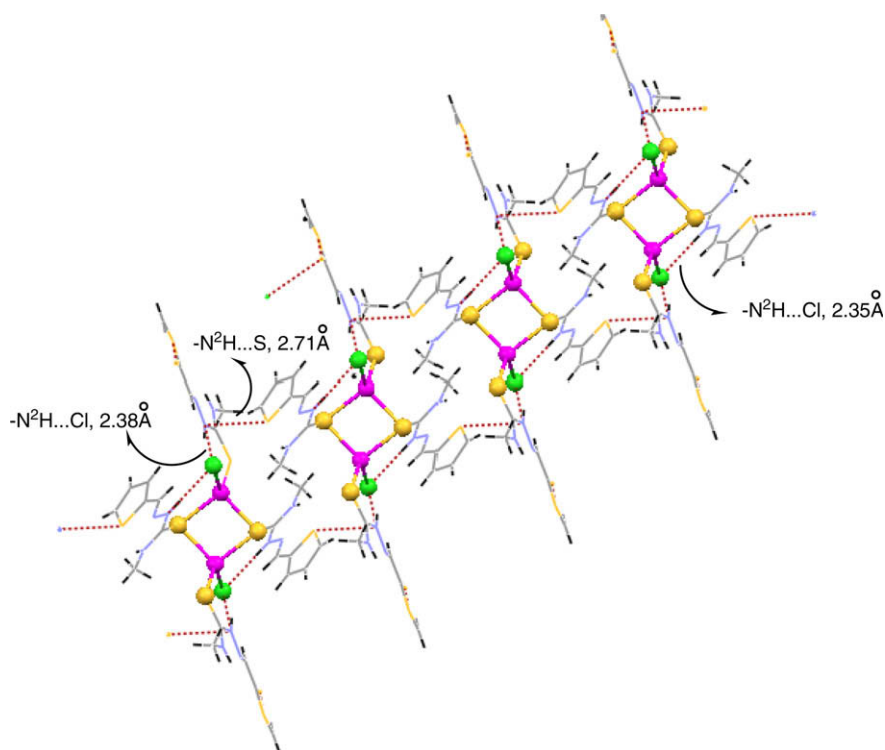


Fig. 6. Packing diagram of $[\text{Ag}_2(\mu\text{-S-HttsMe})_2(\eta^1\text{-HttsMe})_2] \cdot 2\text{CHCl}_3$ **3**.

via phenyl hydrogen–chlorine ($\text{CH}_{\text{Ph}} \cdots \text{Cl}^{\#1}$, 2.852 Å) and phenyl hydrogen– π , ($\text{CH}_{\text{Ph}} \cdots \pi$, 2.626 Å) interactions to form a linear chain along the a -axis (Fig. 4). Two such linear chains are further interconnected by a phenyl hydrogen–chlorine ($\text{CH}_{\text{Ph}} \cdots \text{Cl}^{\#2}$, 2.778 Å) interaction which forms a H-bonded 2D polymer. In the dimer **2**, two units are H-bonded via $\text{MeN}^1\text{H} \cdots \pi$ (2.768 Å) and methyl–bro-

mine, ($\text{H}_2\text{CH} \cdots \text{Br}$, 2.972 Å) interactions, which form a H-bonded linear chain. Two linear chains are connected via phenyl hydrogen–bromine ($\text{CH}_{\text{Ph}} \cdots \text{Br}^{\#1}$, 2.996 Å) interaction and form a H-bonded 2D polymer (Fig. 5).

The imino hydrogen atom of terminal as well as bridging ligands forms a strong intra-molecular H-bond with the chlorine

atom ($-N^2H_{ter}\cdots Cl$, 2.38 Å; $-N^2H_{bri}\cdots Cl$, 2.35 Å) in complex **3**. Two dimeric units are interconnected via the imino hydrogen of a terminal ligand of one unit and the sulfur atom of a bridging ligand of the second unit ($-N^2H_{ter}\cdots S_{bri}$, 2.71 Å), which forms a linear chain polymer (Fig. 6). The lack of Ph_3P , which provides $CH-\pi$ interactions, limits the dimensionality of **3** to 1D.

4.5. Solution phase behaviour

The 1H NMR spectra of complexes **1–3** show shifts in the N^2H proton signal to low field (δ 12.42, 11.60 and 11.68 ppm, respectively) relative to the free ligand (δ 9.15 ppm). The presence of the N^2H proton signals in these complexes ensures that no deprotonation occurred during complexation. The C^2H proton signals also appear shifted to low field: δ 8.66 (**1**), 8.61 (**2**) and 8.56 ppm (**3**) (free ligand, 7.93 ppm). The ring protons of Ph_3P in complexes **1** and **2** appear in the range δ 7.32–7.51 ppm and appear to have obscured the N^1HMe proton signals. The methyl protons of $-N^1HCH_3$ appear as a doublet in the range, δ 3.22–3.25 ppm in **1–3**. The C^5H protons of the thiophene ring appeared as a doublet of doublets in the range, δ 7.07–7.1 ppm in these complexes, while the other ring protons are obscured by proton signals for triphenyl phosphine in complexes **1** and **2** and N^1HMe proton signals (δ 7.34–7.86 ppm) in complex **3**.

Complexes **1** and **2** showed ^{31}P NMR bands at δ 10.05 and 6.2 ppm, respectively. The coordination shifts, ($\Delta\delta = \delta_{complex} - \delta_{ligand}$) are 14.7 (**1**) and 10.9 ppm (**2**). These coordination shifts are similar to those found in halogen-bridged dimers in silver(I)-thiosemicarbazone chemistry [15].

5. Conclusion

For the mixed ligand complexes $[AgX_2(Htsc)_2(Ph_3P)_2]$ it is interesting to note that for $R = H$ at N^1HR of $(C_4H_4S)CH=N-NH-C(=S)-N^1HR$, a sulfur-bridged dimer, **4**, was formed [15], while for $R = Me$ at N^1HR , halogen-bridged dimers **1** and **2** have been obtained. It demonstrates the influence of methyl substituents at the N^1 nitrogen on the bonding properties of thiophene-2-carbaldehyde thiosemicarbazones, which would enhance the steric crowding if the ligand were sulfur-bridged. In the absence of a co-ligand, as in compound **3**, the presence of four sulfur donor atoms prefers S-bridging over chloride-bridging. This also enhances the argentophilicity, with a relatively short $Ag\cdots Ag$ contact induced by the S-bridging. It is the first example of a complex of the stoichiometry $[Ag_2Cl_2(HtscMe)_4]$ among thiosemicarbazone/heterocyclic thioamide chemistry of coinage metals. Compounds **1–3** present the first report of complexes of N^1 -substituted thiosemicarbazones with silver(I).

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Appendix A. Supplementary data

CCDC 705112–705114 contains the supplementary crystallographic data for **1–3**, respectively. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.poly.2009.01.041](https://doi.org/10.1016/j.poly.2009.01.041).

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