

Variable coordinating activity of sulfur in silver(I) complexes with thiophene based N¹-substituted thiosemicarbazones: First case of thiophenyl-thione sulfur bridging in a dinuclear complex

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MS received 20 January 2016; revised 29 April 2016; accepted 1 May 2016

Abstract. Thiophene-2-carbaldehyde/acetaldehyde-N¹-substituted thiosemicarbazones {R¹R²C² = N³-N(H)-C¹(=S)N¹HR; R¹, R², R : C₄H₃S, H, Me, Httsc-NMe; C₄H₃S, H, Et, Httsc-NEt; C₄H₃S, H, Ph, Httsc-NPh; C₄H₃S, Me, Et, Hattsc-NEt} and furan-2-carbaldehyde-N-ethyl thiosemicarbazone (C₄H₃O, H, Et, Hftsc-NEt) were reacted with silver(I) halides/silver(I) acetate in presence of triphenylphosphine in organic solvents. These reactions yielded a series of dinuclear [Ag₂(μ-Br)₂(κ¹-S-Httsc-NEt)₂(PPh₃)₂]·2MeOH **1**, [Ag₂Cl₂(κ¹-S-Httsc-NPh)₂(μ-S,S-Httsc-NPh)₂] **2**, [Ag₂Cl₂(μ-S-Hftsc-NEt)₂(κ¹-S-Hftsc-NEt)₂] **4**, [Ag₂(μ₃-N³,S-ttsc-NMe)₂(Ph₃P)₂]·2(CH₃)₂CO **5**, [Ag₂(μ₃-N³,S-attsc-NEt)₂(Ph₃P)₂]·0.5(CH₃)₂CO **6** and mononuclear [AgBr(κ¹-S-Httsc-NPh)(PPh₃)₂]·MeCN **3** complexes, all of which have been characterized using analytical techniques, IR and NMR spectroscopy, and X-ray crystallography. Thio-ligands bind in neutral form in complexes **1-4** and in anionic form in complexes **5-6**. Further, the sulfur donor atoms have shown variable coordination modes in complexes, namely, κ¹-S in **1** and **3**; κ¹-S, μ-S in **4**; κ¹-S, μ-S,S (thiophenyl-thione) in **2** and μ₃-N³, S in **5** and **6**. Tertiary-phosphine (PPh₃) showed dual function of ligation/de-ligation towards silver(I) chloride during the synthesis of complexes **2** and **4**. The bridge bonding of Httsc-NPh in **2** through thiophenyl ring sulfur and thione sulfur is unprecedented in metal-thiosemicarbazone chemistry.

Keywords. Silver chloride; silver bromide; silver acetate; triphenylphosphine; thiophene-2-carbaldehyde-N¹-substituted thiosemicarbazones; thiosemicarbazones.

1. Introduction

Thiosemicarbazones {R¹R²C²(=N³)N²HC(=S)N¹R³R⁴} represent an important class of thio-ligands whose coordination chemistry has been extensively investigated, especially with respect to structural diversity and biological properties of metal complexes.¹ Unlike copper(I)/copper(II),^{1–9} coordination chemistry of silver(I) with thiosemicarbazone ligands is relatively of recent origin.^{10–17} Dilworth *et al.*, reported first structurally characterized hexanuclear silver(I) complex, [Ag₆(Hstsc)₆] (Hstsc[–] is anion of salicylaldehyde thiosemicarbazone) in which thio-ligand coordinates in μ₃-N², S- triply bridging mode E (chart 1).¹⁶

Recently, several new complexes of thiosemicarbazones (Htsc) with silver(I) salts (e.g., chloride/bromide/nitrate/acetate) have been reported from our laboratory.^{10–15} Silver(I) halides yielded five types of

compounds, namely, halogen-bridged [Ag₂(μ-X)₂(κ¹-S-Htsc)₂(PPh₃)₂],^{10,14} and sulfur-bridged [Ag₂(κ¹-X)₂(μ-S-Htsc)₂(PPh₃)₂],^{10–12} dinuclear complexes, bond isomers displaying both [Ag₂(μ-X)₂(κ¹-S-Htsc)₂(PPh₃)₂] and [Ag₂(κ¹-X)₂(μ-S-Htsc)₂(PPh₃)₂] modes in the same unit cell,¹² mononuclear complexes, [AgX(κ¹-S-Htsc)(PPh₃)₂],^{10,12,15} and [AgX(κ¹-S-Htsc)₂(PPh₃)₂].¹¹ Other silver(I) salts, namely silver(I) nitrate/acetate have also yielded complexes of various types, namely, [Ag₂(μ₃-N³,S-Htsc)₂(PPh₃)₂](NO₃)₂,¹⁰ [Ag₂(κ¹-S-Htsc)₂(μ-S-Htsc)₂(PPh₃)₂](NO₃)₂,¹⁰ [Ag(ONO₂)(κ¹-S-Htsc)(PPh₃)₂],¹¹ [Ag(κ²-N³,S-Htsc)(PPh₃)₂]X (X = NO₃, OAc),¹¹ and [Ag₂(μ-S-Htsc)(μ-PPh₂-CH₂-PPh₂)₂(κ¹-ONO₂)](NO₃).¹³ In these complexes, the thio-ligands bind as neutral Lewis bases in κ¹-S terminal (**A**), μ-S bridging (**B**), μ₃-N³,S chelating- cum -sulfur bridging (**C**) and N³,S-chelating (**D**) modes (chart 1).

In view of our interest in coordination chemistry of silver(I) with thiosemicarbazones owing to their

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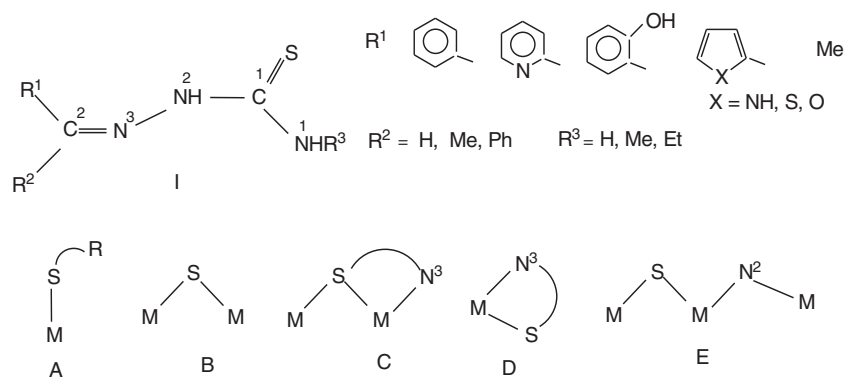


Chart 1. Bonding modes of thiosemicarbazones in complexes.

versatility in forming metal complexes with different stoichiometries and variable bonding properties, this paper reports the interaction of a series of new thiosemicarbazones (chart 2) with silver(I) halides/acetate in presence of triphenyl phosphine as co-ligand. The resulting complexes have been characterized using analytical, spectroscopic and structural techniques. Thiophene moiety at C² atom has shown coordination to silver(I) through its sulfur for the first time in one complex.

2. Experimental

2.1 Materials

Silver(I) halides were freshly prepared from AgNO₃ and potassium halides (X = Cl, Br) in methanol and dried in vacuo. Silver(I) acetate was procured from Aldrich Chemicals Ltd. and used as such. N-methylthiosemicarbazide, N-ethylthiosemicarbazide, N-phenylthiosemicarbazide, triphenylphosphine, thiophene-2-carbaldehyde {C₄H₃S-C(=O)H}, thiophene-2-acetaldehyde {C₄H₃S-C(=O)Me} and furan-2-carbaldehyde {C₄H₃O-C(=O)H} were procured from Aldrich Sigma Ltd. The thio-ligands were prepared by the condensation of thiophene-2-carbaldehyde/ thiophene-2-acetaldehyde/ furan-2-carbaldehyde with the respective thiosemicarbazide by adopting the methods used for thiophene-2-carbaldehyde thiosemicarbazone^{18,19} and other details as

reported in literature.²⁰ The C, H and N analyses were obtained with Thermoelectron FLASH EA 1112 CHNS analyzer. The IR spectra were recorded using KBr pellets in the range 4000-400 cm⁻¹ on Varian 660-IR Fourier transform infrared spectrophotometer. The melting points were determined with a Gallenkamp electrically heated apparatus. The ¹H NMR spectra were recorded on a JEOL AL300 FT spectrometer at 300 MHz in CDCl₃ with TMS as the internal reference.

2.2 Synthesis of [Ag₂(μ-Br)₂(κ¹-S-Httsc-NEt)₂(PPh₃)₂].2MeOH (I)

Silver(I) bromide (0.025 g, 0.133 mmol) was suspended in acetonitrile (10 mL) and to it was added solid triphenylphosphine (0.035 g, 0.134 mmol) followed by stirring for 24 h. The white precipitate was separated and then suspended in chloroform-methanol mixture (1:1, v/v, 10 mL) followed by the addition of Httsc-NEt thio-ligand (0.027 g, 0.134 mmol). The mixture was stirred until a clear yellow solution emerged which was allowed to crystallize at room temperature. It gave brown crystals of [Ag₂(μ-Br)₂(κ¹-S-Httsc-NEt)₂(PPh₃)₂].2MeOH **1**. Yield 76%. M.p. 198-200°C. Anal. Found: C, 47.01; H, 3.79; N, 6.37%. Calcd. for C₅₄H₆₀Ag₂Br₂N₆O₂P₂S₄: C, 46.60; H, 4.31; N, 6.04%. IR data (KBr, cm⁻¹): 3364 (s, N¹-H); 3146 (s, N²-H), 3069 (w), 3045 (w), 2984 (m), 2932 (w) (C-H); 1595-1505

X	R ²	R	Abbrev.
S	H	Me	Httsc-NMe
S	H	Et	Httsc-NEt
S	H	Ph	Httsc-NPh
S	Me	Et	Hattsc-NEt
O	H	Et	Hftsc-NEt

Chart 2. The thio-ligands under purview.

(s, C-C, C-N + δ N-H); 1478-1402 (m, δ C-H); 1384(w), 1360(w), 1313(m), 1255(s), 1228(s), 1156(w); 1094(s, P-C_{Ph}), 1046(m); 1027(w); 998(w), 933(m); 856(m, C-S), 833(m), 808(m), 749(s), 704(s), 695(s), 601(m), 559(w), 512(s), 500(s). ¹H NMR (CDCl₃, δ ppm): 12.42s (-N²H), 8.12s (C²H), 7.31-7.65m (C⁶H + PPh₃), 6.64d (C⁴H), 6.55dd (C⁵H), 3.42m (-CH₃), 1.33t (-CH₂-).

The procedure for complexes **2-4** is similar.

2.3 Synthesis of [Ag₂Cl₂(κ^1 -S-Httsc-NPh)₂(μ -S,S-Httsc-NPh)₂](**2**)

Quantities taken: silver(I) chloride (0.020 g, 0.139 mmol), triphenylphosphine (0.037 g, 0.141 mmol), Httsc-NPh thio-ligand (0.035 g, 0.134 mmol). Brown crystals of [Ag₂Cl₂(κ^1 -S-Httsc-NPh)₂(μ -S,S-Httsc-NPh)₂] **2** were formed. Yield 55%. M.p. 194-197°C. Anal. Found: C, 43.79; H, 3.45; N, 12.98%. Calcd. for C₄₈H₄₄Ag₂Cl₂N₁₂S₈: C, 43.23; H, 3.30; N, 12.61%. IR data (KBr, cm⁻¹): 3296 (m, N¹-H); 3106 (m, N²-H), 3056(w), 2924(m), 2854(w) (C-H); 1591-1521 (s, C-C, C-N + δ N-H); 1479-1434 (s, δ C-H); 1386(m), 1314(w), 1273(s), 1205(m), 1069(m), 1043(w), 1026(m); 997(w), 936(m); 856(m, C-S), 831(w), 788(w), 746(s), 725(w), 704(s), 694(s), 651(w), 638(w), 511(s).

2.4 Synthesis of [AgBr(κ^1 -S-Httsc-NPh)(PPh₃)₂].MeCN (**3**)

Quantities taken: silver(I) bromide (0.015 g, 0.080 mmol), Httsc-NPh thio-ligand (0.021 g, 0.080 mmol), triphenylphosphine (0.021g, 0.080 mmol), (in lieu of chloroform-methanol mixture, only chloroform was used). Brown crystals of [AgBr(κ^1 -S-Httsc-NPh)(PPh₃)₂].MeCN **3** were formed. Yield 48%. M.p. 162-167°C. Anal. Found: C, 58.91; H, 4.65; N, 5.87%. Calcd. for C₅₀H₄₄AgBrN₄P₂S₂: C, 59.12; H, 4.34; N, 5.52%. IR data (KBr, cm⁻¹): 3426 (br,s, N¹-H); 3296 (s, N²-H), 3105(w), 3054(m), 2980(w) (C-H); 1539-1520(s, C-C, C-N + δ N-H); 1496-1434 (m, δ C-H); 1394(s), 1314(s), 1268(s), 1197(s); 1094(s, P-C_{Ph}), 1042 (m); 1027(w); 997(w), 856(m, C-S), 831(w), 745(s), 693(s), 571(m), 503(m).

2.5 Synthesis of [Ag₂Cl₂(μ -S-Hftsc-NEt)₂(κ^1 -S-Hftsc-NEt)₂](**4**)

Quantities taken: silver(I) chloride (0.025 g, 0.17 mmol), triphenylphosphine (0.046 g, 0.17 mmol), Hftsc-NEt thio-ligand (0.034 g, 0.17 mmol) (in lieu of chloroform-methanol mixture, only chloroform was used). Brown crystals of [Ag₂Cl₂(μ -S-Hftsc-NEt)₂(κ^1 -S-Hftsc-NEt)₂] **4** were formed. Yield: 64%. M.p.

185-187°C. Anal. Found: C, 35.63; H, 4.02; N, 15.6%. Calcd. for C₃₂H₄₄Ag₂Cl₂N₁₂O₄S₄: C, 35.69; H, 4.09; N, 15.6%. IR data (KBr, cm⁻¹): 3342(s, N¹-H); 3165(m, N²-H); 2954(m), 2737(w) (C-H); 1569-1531 (s, C-C, C-N + δ N-H), 1035(s); 853(s, C-S). ¹H NMR (CDCl₃, δ ppm): 11.41s (-N²H), 8.66s (C²H), 7.32-7.42m (C^{4,6}H), 7.02dd (C⁵H), 3.26d (-CH₃), 1.30t (-CH₂-).

2.6 Synthesis of [Ag₂(μ_3 -N,S-ttsc-NMe)₂(Ph₃P)₂](**5**)

Silver(I) acetate (0.025 g, 0.149 mmol) was suspended in acetone (15 mL) and to it was added solid Httsc-NMe ligand (0.029 g, 0.149 mmol) and the reaction mixture was stirred for 4 h. To the yellow precipitate formed was added solid Ph₃P ligand (0.039 g, 0.149 mmol). The contents were stirred for a further period of 10 min and slow evaporation of the yellow solution at room temperature yielded light brown yellow crystals of [Ag₂(μ_3 -N,S-ttsc-NMe)₂(Ph₃P)₂] **5**. Yield 77%. M.p. 206-208°C. Anal. Found: C, 52.76; H, 4.01; N, 7.36%. Calcd. for C₅₀H₄₆Ag₂N₆P₂S₄: C, 52.81; H, 4.05; N, 7.39%. IR data (KBr, cm⁻¹): ν (N-H), 3390m, 3321m, (-NHMe); ν (C-H), 3044m, 2872m; ν (C=N) + ν (C-C), 1572s, 1536s; ν (C-N), 1061s, 1029s; ν (C=S), 762s; ν (P-C_{Ph}), 1094(s). ¹H NMR (CDCl₃, δ ppm): 8.06s (C²H), 7.64-7.33m (C⁶H + PPh₃), 6.61d (C⁴H), 6.56dd (C⁵H), 3.72d (-CH₃).

2.7 Synthesis of [Ag₂(μ_3 -N,S-attsc-NEt)₂(Ph₃P)₂](**6**)

Complex **6** was similarly prepared as **5**. Quantities taken: silver(I) acetate (0.025 g, 0.149 mmol), Hattsc-NEt thio-ligand (0.034 g, 0.149 mmol), triphenylphosphine (0.039 g, 0.149 mmol), Light brown crystals of [Ag₂(μ_3 -N,S-attscEt)₂(Ph₃P)₂] **6** were obtained. Yield: 74%, M.p. 212-214°C. Anal. Found: C, 54.32; H, 4.54; N, 7.06%. Calcd. for C₅₄H₅₄Ag₂N₆P₂S₄: C, 54.36; H, 4.53; N, 7.04%. IR data (KBr, cm⁻¹): ν (N-H), 3420m, 3325m, (-NHet); ν (C-H), 3082m, 3024m, 2892m; ν (C=N) + ν (C-C), 1562s, 1541s; ν (C-N), 1065s, 1030s; ν (C=S), 764s; ν (P-C_{Ph}), 1095(s). ¹H NMR (CDCl₃, δ ppm): 8.02s (C²H), 7.69-7.31m (C⁶H + PPh₃), 6.60d (C⁴H), 6.52dd (C⁵H), 3.92m (-CH₃), 2.92s (-CH₃ of acetyl), 1.17t (-CH₂-).

2.8 X-ray crystallography

A single crystal was mounted on a glass fiber and used for data collection with a Bruker Apex (II) CCD diffractometer (**1**, **2**; 296(2) K), Agilent Eos(Gemini) CCD 'four-circle diffractometer (**3**, 173(2) K), CrysAlis CCD (Oxford) Diffractometer (**4**, 200(2)K, **5,6**, 123(2)K)

equipped with graphite monochromated Cu-K α (**3**: $\lambda = 1.54184 \text{ \AA}$) and Mo-K α (**1**, **2**, **4**, **5**, **6**: $\lambda = 0.71073 \text{ \AA}$). The data recorded for compounds were processed with Bruker APEX II CCD (**1**, **2**) or CrysAlisPro (**3-6**) (data collection) and Bruker SAINT RED (**1**, **2**) or CrysAlisPro RED (**3-6**) (cell refinement, data reduction).²¹ The structure was solved by direct methods using the program SIR-92²² (compound **1**), SHELXS-97 (compounds **2,4-6**),²³ or Superflip (compound **3**), refined by full-matrix least-squares techniques against F^2 using SHELXL-97 (compounds **1-6**) and molecular graphics from SHELXTL (**1,2, 4-6**)²³ or OLEX2(**3**).²⁴ The data were corrected for absorption using SADABS (**1**, **2**) or spherical harmonics implemented in SCALE3 ABSPACK scaling algorithm (**3-6**). Atomic scattering factors were taken from International Tables for Crystallography.

3. Results and Discussion

3.1 Synthesis - comments

Chart 3 gives a pictorial view of complexes synthesized. Reaction of silver(I) bromide with PPh₃ in

acetonitrile gave white precipitate which on further reaction with Httsc-NEt thio-ligand (equimolar reaction) in chloroform–methanol gave a dinuclear complex, [Ag₂(μ -Br)₂(κ^1 -S-Httsc-NEt)₂(PPh₃)₂].2MeOH **1**. Similarly, silver(I) chloride, PPh₃ and Httsc-NPh thio-ligand yielded the dinuclear complex, [Ag₂Cl₂(κ^1 -S-Httsc-NPh)₂(μ -S,S-Httsc-NPh)₂] **2**. In this complex, thiophenyl sulfur coordinates to one Ag center and thione sulfur binds to the second metal center (μ -S,S mode). This coordination by thiophenyl ring and binding behavior of Httsc-NPh is unprecedented.^{1,10,14} Equimolar reaction of silver(I) bromide with PPh₃ and Httsc-NPh did not form a complex similar to dimer **1** or **2**. In this case, silver(I) bromide reacted first with Httsc-NPh thio-ligand in acetonitrile followed by reaction with PPh₃ in chloroform (Cu:thio-ligand:PPh₃ = 1:1:2) which yielded a mononuclear complex, [AgBr(κ^1 -S-Httsc-NPh)-(PPh₃)₂].MeCN **3**. Following the procedure used for dimer **1**, reaction of silver(I) chloride with Ph₃P and Hftsc-NEt yielded a dinuclear complex, [Ag₂Cl₂(μ -S-Hftsc-NEt)₂(κ^1 -S-Hftsc-NEt)₂] **4**, with stoichiometry different from dimer **1**. Here, PPh₃, which initially binds to Ag(I), is de-ligated by the thio-ligand, and the resulting complex **4** has only thio-ligands bonded in both κ^1 -S and μ -S modes.

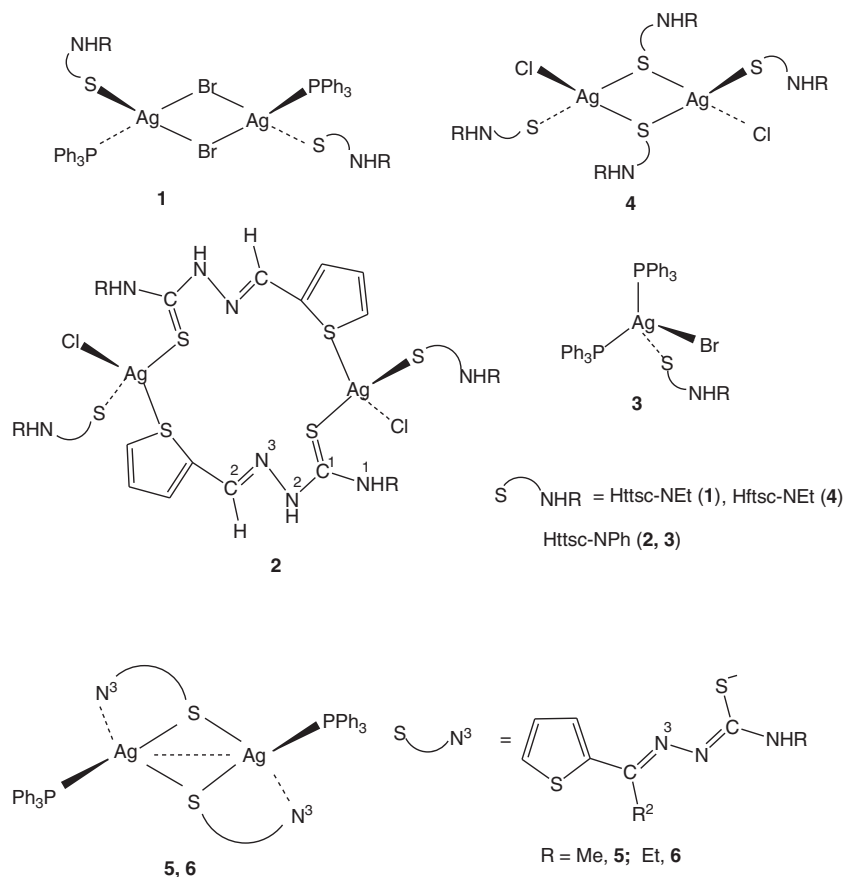


Chart 3. A simplified structural view of metal complexes **1-6**.

The bonding pattern of **4** is analogous to that of dimer, $[\text{Ag}_2\text{Cl}_2(\mu\text{-S-Httsc-NMe})_2(\kappa^1\text{-S-Httsc-NMe})_2]\cdot 2\text{CHCl}_3$, as reported in literature.¹⁴ Further, bonding pattern of complex **1** is similar to that reported in dinuclear complexes, $[\text{Ag}_2(\mu\text{-X})_2(\kappa^1\text{-S-Httsc-NMe})_2(\text{PPh}_3)_2]$ ($\text{X} = \text{Cl}, \text{Br}$).¹⁴ Interestingly, Httsc-NH₂ thio-ligand with AgCl and PPh₃ formed dinuclear complex, $[\text{Ag}_2\text{Cl}_2(\mu\text{-S-Httsc-NH}_2)_2(\text{PPh}_3)_2]$,¹⁰ similar to **1**, but is involved in $\mu\text{-S}$ bridging instead of $\mu\text{-X}$ ($\text{X} = \text{Cl}, \text{Br}$) bridging.¹⁴ Silver(I) acetate reacted with Httsc-NMe (or Hattsc-NEt) and Ph₃P in acetone and gave dinuclear complexes, $[\text{Ag}_2(\mu_3\text{-N,S-ttsc-NMe})_2(\text{Ph}_3\text{P})_2]$ **5** and $[\text{Ag}_2(\mu_3\text{-N,S-attsc-NEt})_2(\text{Ph}_3\text{P})_2]$ **6**. In these complexes, thio-ligands bind as anions in $\mu_3\text{-N,S}$ mode. A similar mode was also shown by analogous neutral Httsc-NH₂ thio-ligand in $[\text{Ag}_2(\mu_3\text{-N,S-Httsc-NH}_2)_2(\text{Ph}_3\text{P})_2](\text{NO}_3)_2$, as reported in literature.¹⁰ In brief, the thio-ligands bind through thione sulfur in $\kappa^1\text{-S}$ mode in **1** and **3**; $\kappa^1\text{-S}, \mu\text{-S}$ modes in **4**; $\kappa^1\text{-S}, \mu\text{-S,S}$ (thiophenyl-thione) modes in **2** and as anions in $\mu_3\text{-N}^3\text{,S}$ modes in **5** and **6**.

3.2 Spectroscopy

The infrared spectral bands of the complexes are given in experimental section and some key observations are delineated here. The diagnostic $\nu(\text{N}^2\text{-H})$ bands are shown by complexes **1-4** in the region, 3296-3106 cm^{-1} which suggest that the thio-ligands bind to the metal centers as neutral ligands. The absence of $\nu(\text{N}^2\text{-H})$ bands in complexes **5** and **6** revealed that the thio-ligands bind to the metal centers as anions. The $\nu(\text{N}^1\text{-H})$ bands of $-\text{N}^1\text{HR}$ group are observed in the region, 3296-3426 cm^{-1} , while the $\nu(\text{C-H})$ bands appear as weak to medium bands in the region, 2737 to 3105 cm^{-1} . Finally, the bands due to $\nu(\text{C-C}), \nu(\text{C-N}), \delta(\text{N-H})$ and $\delta(\text{C-H})$ fall in the range, 1595-1402 cm^{-1} . The $\nu(\text{C-S})$ and $\nu(\text{P-C}_{\text{Ph}})$ bands are observed in the regions, 762-856 cm^{-1} and 1094-1095 cm^{-1} , respectively. The ¹H NMR spectra of compounds **1** and **4** have shown imino hydrogen signals of $-\text{N}^2\text{H}$ groups at $\delta = 12.42$ and 11.41 ppm, respectively, and it reveals that the thio-ligands are coordinating as neutral ligands. The NMR signals due to C²H, ethyl protons, C₄H₃S (C₄H₃O) ring and P-Ph ring protons are assigned in the region, 8.66 to 1.30 ppm (see Experimental section). Complexes **5** and **6** did not show NMR signals expected for $-\text{N}^2\text{H}$ protons which revealed deprotonation of imino protons and that the thio-ligands are coordinating as anions. Other signals due to protons of C²H, $-\text{C}^2\text{-CH}_3$, N¹-Me/Et, C₄H₃S and P-Ph moieties were observed in the region, 8.06-3.72 ppm. Poor solubility of complexes **2** and **3** precluded recording of their NMR spectra.

3.3 Molecular structures of complexes

Each of the complexes **1**, **5** and **6** crystallized in the triclinic crystal system in P-1 space group (table 1). Similarly, complexes **2-4** crystallized in monoclinic crystal system in space groups P2₁/n, P2₁/c and P2₁/c, respectively. A brief description of the molecular structures is given below. Molecular structure of the dinuclear complex, $[\text{Ag}_2(\mu\text{-Br})_2(\kappa^1\text{-S-Httsc-NEt})_2(\text{PPh}_3)_2]\cdot 2\text{MeOH}$ **1**, is shown in figure 1. Two metal centers are bridged by two bromine atoms at Ag-Br distances of 2.7322(11) and 2.8528(12) Å which reveal that Ag₂Br₂ core forms a parallelogram. Other important bond distances, Ag-S, 2.5259(17), Ag-P, 2.4556(14) and Ag-Ag, 3.3264(13) Å are similar to those found in $[\text{Ag}_2(\mu\text{-Br})_2(\kappa^1\text{-S-Httsc-NMe})_2(\text{Ph}_3\text{P})_2]$.¹⁴ Interestingly, the Ag-Ag distance is shorter in complex **1** {3.3264(13) versus distance 3.746(5) Å in Httsc-NMe complex}.¹⁴ Thus, the presence of ethyl group at N¹ atom decreases the Ag-Ag distance in **1**. The angles around each silver metal center vary in the range, 101.15 to 118.70°. The Ag₂Br₂ core angles {Ag-Br-Ag, 73.07(2) and Br-Ag-Br, 106.93(2)°} are different from those {86.284(15) and 93.717(15)°} found in $[\text{Ag}_2(\mu\text{-Br})_2(\kappa^1\text{-S-Httsc-NMe})_2(\text{Ph}_3\text{P})_2]$.¹⁴

The thio-ligand Httsc-NPh with silver(I) bromide has yielded a mononuclear complex, $[\text{AgBr}(\kappa^1\text{-S-Httsc-NPh})(\text{PPh}_3)_2]\cdot \text{MeCN}$ **3** unlike the bromo bridged dinuclear complexes formed by Httsc-NMe/Httsc-NEt, namely, $[\text{Ag}_2(\mu\text{-Br})_2(\kappa^1\text{-S-Httsc-NMe})_2(\text{Ph}_3\text{P})_2]$ ¹⁴ and $[\text{Ag}_2(\mu\text{-Br})_2(\kappa^1\text{-S-Httsc-NEt})_2(\text{PPh}_3)_2]\cdot 2\text{MeOH}$ **1**. In **3**, one bromide, one thio-ligand and two PPh₃ ligands coordinate to the silver metal center (figure 2). The Ag-S bond distance of 2.6172(6) Å is longer than that found in **1**, but is comparable {2.6008 to 2.6405 Å} to similar tetrahedral complexes, $[\text{AgBr}(\kappa^1\text{-S-L})(\text{PPh}_3)_2]$ (L = pyridine-2-carbaldehyde thiosemicarbazone,¹⁰ N¹-substituted salicylaldehyde thiosemicarbazones^{12,15}). Further, the Ag-Br bond distance of 2.7286(4) Å and the Ag-P bond distances of 2.4414 to 2.4807 Å are comparable to those (Ag-Br, 2.7206 to 2.8094; Ag-P, 2.4599 to 2.4926 Å) reported in literature.^{10,12,15} Finally, the angles around silver metal center fall in the range, 97.24 to 125.23°, which reveal a distorted tetrahedral geometry, and this range is similar to that (98.686 to 123.93°) reported in literature.^{10,12,15}

It is interesting to note that the thio-ligand Httsc-NPh with silver(I) chloride in presence of PPh₃ has yielded a dinuclear complex, $[\text{Ag}_2\text{Cl}_2(\kappa^1\text{-S-Httsc-NPh})_2(\mu\text{-S}, \text{S-Httsc-NPh})_2]$ **2**, unlike mononuclear complex **3** reported with silver(I) bromide. In **2**, PPh₃ initially coordinates but is de-ligated later when reacted with

Table 1. Crystal data for compounds **1-6**.

T(K)	1 296(2) K	2 296(2) K	3 173(2) K
Empirical formula	C ₅₄ H ₆₀ Ag ₂ Br ₂ N ₆ O ₂ P ₂ S ₄	C ₄₈ H ₄₄ Ag ₂ Cl ₂ N ₁₂ S ₈	C ₅₀ H ₄₄ AgBrN ₄ P ₂ S ₂
<i>M</i>	1390.84	1332.13	1014.73
λ(Å)	0.71073	0.71073	1.54184
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	P-1	P2 ₁ /n	P2 ₁ /c
Unit cell dimensions			
<i>a</i> (Å)	9.808(3)	7.7013(15)	18.5554(2)
<i>b</i> (Å)	13.034(5)	14.221(3)	11.420(1)
<i>c</i> (Å)	13.512(5)	23.858(5)	22.1774(3)
α(°)	64.985(13)	90	90
β(°)	76.185(14)	94.914(7)	97.3454(11)
γ(°)	76.005(13)	90	90
<i>V</i> (Å ³)	1500.4(9)	2603.4(9)	4660.52(10)
<i>Z</i>	1	2	4
<i>D</i> _{calcd} (g cm ⁻³)	1.539	1.699	1.446
μ(mm ⁻¹)	2.220	1.225	6.258
<i>F</i> (000)	700	1344	2064
Reflections collected	22633	21679	20377
Unique reflections	5202(<i>R</i> _{int} = 0.0317)	5863(<i>R</i> _{int} = 0.0409)	8888(<i>R</i> _{int} = 0.0411)
Data/restraints/ parameters	5202/3/332	5863/4/337	8888/0/542
Reflns. with [<i>I</i> > 2σ(<i>I</i>)]	3886	5246	8065
R Indices			
<i>R</i> ₁	0.0451	0.0262	0.0372
<i>wR</i> ₂	0.1444	0.0700	0.0929
<i>R</i> indices (all data)			
<i>R</i> ₁	0.0624	0.0307	0.0415
<i>wR</i> ₂	0.1547	0.0732	0.0974
Largest diff.	1.633,	0.509,	0.877,
Peak and hole	−0.596 e. Å ⁻³	−0.446 e. Å ⁻³	−0.951 e. Å ⁻³
T(K)	4 200(2) K	5 123(2) K	6 123(2)
Empirical formula	C ₃₂ H ₄₄ Ag ₂ Cl ₂ N ₁₂ O ₄ S ₄	C ₅₃ H ₅₂ Ag ₂ N ₆ OP ₂ S ₄	2(C ₅₄ H ₅₄ Ag ₂ N ₆ P ₂ S ₄). C ₃ H ₆ O
<i>M</i>	1075.67	1194.92	2443.98
λ(Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	P2 ₁ /c	P-1	P-1
Unit cell dimensions			
<i>a</i> (Å)	11.3782(5)	8.9210(4)	8.8804(3)
<i>b</i> (Å)	19.1207(4)	13.5335(8)	12.4215(4)
<i>c</i> (Å)	10.3175(3)	13.7932(8)	25.7892(7)
α(°)	90	115.031(6)	96.136(2)
β(°)	106.282(4)	90.142(4)	92.641(2)
γ(°)	90	105.075(4)	107.740(3)
<i>V</i> (Å ³)	2154.64(12)	1444.85(15)	2684.65(14)
<i>Z</i>	2	1	1
<i>D</i> _{calcd} (g cm ⁻³)	1.658	1.373	1.512
μ(mm ⁻¹)	1.278	0.918	0.989
<i>F</i> (000)	1088	608	1248
Reflections collected	22989	14798	41167
Unique reflections	7177 (<i>R</i> _{int} = 0.0367)	14798 (<i>R</i> _{int} = 0.0362)	17860(0.0396)
Data/restraints/ parameters	7177/0/266	14798 / 27 / 327	17860/0/653
Reflns. with [<i>I</i> > 2σ(<i>I</i>)]	3118	10453	11618
R Indices			
<i>R</i> ₁	0.0333	0.0513,	0.0367
<i>wR</i> ₂	0.0708	0.1226	0.0595
Largest diff.	0.726,	1.485,	0.922,
Peak and hole	−0.603 e. Å ⁻³	−0.713 e. Å ⁻³	−0.588 e. Å ⁻³

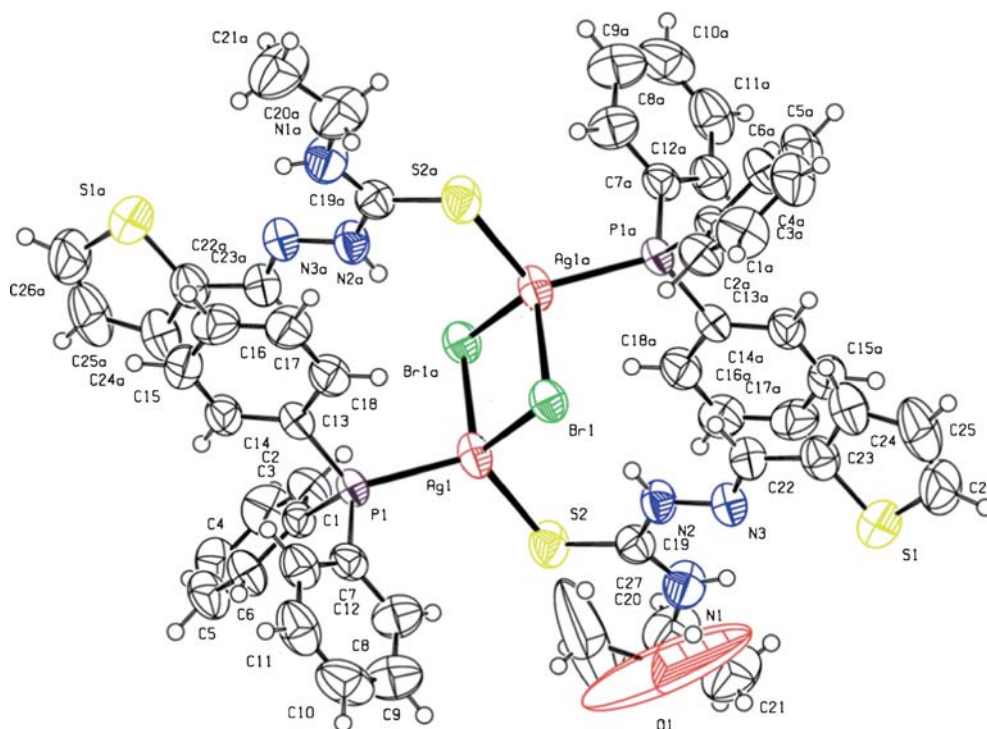


Figure 1. Structure of the complex $[\text{Ag}_2(\mu\text{-Br})_2(\kappa^1\text{-S-Httsc-NEt})_2(\text{PPh}_3)_2]\cdot 2\text{MeOH}$ **1** with atomic numbering scheme. Selected bond lengths/Å and angles/°: Ag1–S2, 2.5259(17); Ag1–Br1, 2.7322(11); Ag1–Br1, 2.8528(12); Ag1–P1, 2.4556(14); Ag1–Ag1, 3.3264(13); S2–C19, 1.686(5); P1–Ag1–S2, 118.70(5); P1–Ag1–Br1, 110.98(4); S2–Ag1–Br1, 111.70(4); P1–Ag1–Br1, 106.09(4); S2–Ag1–Br1, 101.15(5); Ag1–Br1–Ag1, 73.07(2); Br1–Ag1–Br1, 106.93(2).

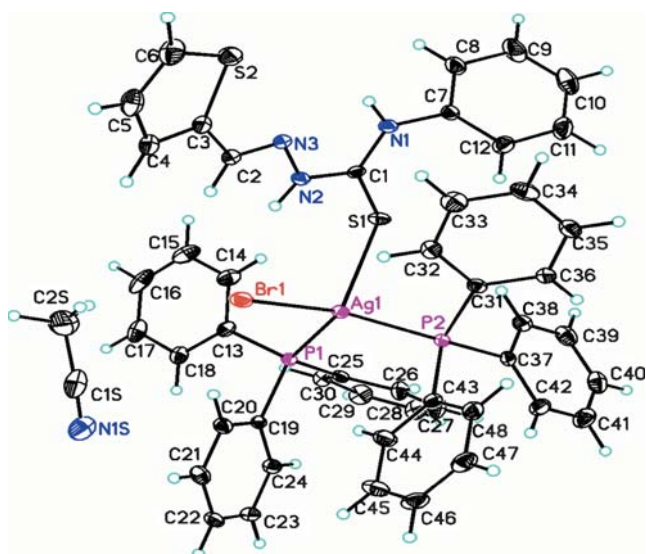


Figure 2. Structure of the complex $[\text{AgBr}(\kappa^1\text{-S-Httsc-NPh})(\text{PPh}_3)_2]\cdot \text{MeCN}$ **3** with atomic numbering scheme. Selected bond lengths/Å and angles/°: Ag1–Br1, 2.7286(4); Ag1–S1, 2.6172(6); Ag1–P1, 2.4414(6); Ag1–P2, 2.4807(7); S1–C1, 1.700(3); S1–Ag1–Br1, 107.741(17); P1–Ag1–Br1, 102.699(18); P1–Ag1–S1, 115.08(2); P1–Ag1–P2, 125.23(2); P2–Ag1–Br1, 108.011(18); P2–Ag1–S1, 97.24(2).

Httsc-NPh thio-ligand thus giving a different product. In this complex, thiophenyl sulfur of one thio-ligand coordinates to one Ag metal center and thione sulfur binds to the second metal center ($\mu\text{-S,S}$ mode), while the second thio-ligand is $\kappa^1\text{-S}$ bonded. In literature, silver(I) chloride with similar thio-ligands and PPh_3 has yielded sulfur bridged $[\text{Ag}_2\text{Cl}_2(\mu\text{-S-L})_2(\text{PPh}_3)_2]$ ($\text{L} = \mu\text{-S-Httsc-NH}_2$,¹⁰ $\text{L} = \text{H}_2\text{stsc-salicylaldehyde thiosemicarbazone}$,¹² 2-benzoylpyridine thiosemicarbazone,¹¹) and halogen-bridged dinuclear complexes, $[\text{Ag}_2(\mu\text{-Cl})_2(\kappa^1\text{-S-L})_2(\text{PPh}_3)_2]$ ($\text{L} = \text{Httsc-NMe}$,¹⁴ $\text{L} = \text{acetophenone thiosemicarbazone}$ ¹⁰). The stoichiometry of **2** is similar to $[\text{Ag}_2\text{Cl}_2(\kappa^1\text{-S-Httsc-NMe})_2(\mu\text{-S-Httsc-NMe})_2]$,¹⁴ though it has differently bonded thio-ligands. Here in this latter complex, 2,2'-bipyridine initially binds to silver but was later de-ligated by the thio-ligands.¹⁴ In dimer **2**, a set of two thione sulfur { Ag–S1, 2.5053(6), Ag–S3, 2.4999(6) Å}, one chloride { Ag–Cl1, 2.6050(7) Å} and one thiophene ring sulfur { Ag–S4, 2.9454(7) Å} donor atoms coordinate to each silver metal center (figure 3). The Ag–S1/S3 bond distances are shorter than those found in dimer **1** or monomer **3**, but Ag–S4 distance is much longer. It is longer than

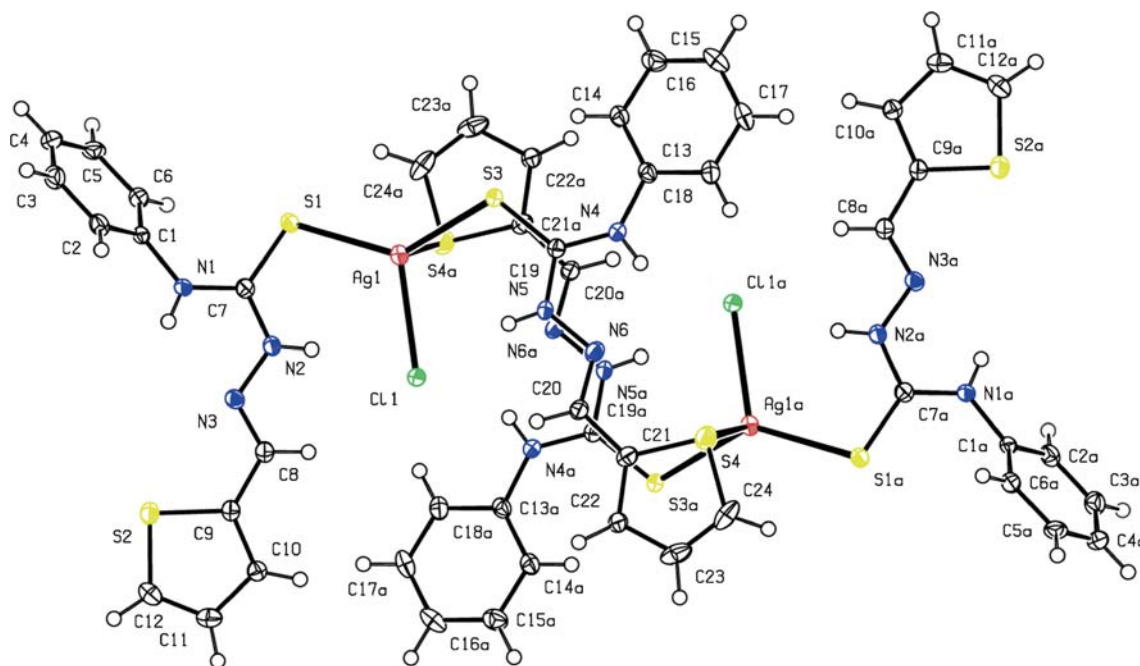


Figure 3. Structure of the complex $[Ag_2Cl_2(\kappa^1\text{-S-Httsc-NPh})_2(\mu\text{-S,S-Httsc-NPh})_2]$ **2** with atomic numbering scheme. Selected bond lengths/Å and angles/ $^\circ$: Ag1–S1, 2.5053(6); Ag1–S3, 2.4999(6); Ag1–S4, 2.9454(7); Ag1–Cl1, 2.6050(7); S1–C7, 1.703(2); S3–Ag1–S1, 134.495(19); S3–Ag1–S4, 91.66(2); S1–Ag1–S4, 91.61(2); S3–Ag1–Cl1, 110.561(18); S1–Ag1–Cl1, 114.279(19); S4–Ag1–Cl1, 95.31(2).

the sum of ionic radii of Ag^+ and S^{2-} ($1.08 + 1.70 = 2.78$ Å), but less than the sum of van der Waals radii of Ag and S atoms ($1.80 + 1.70 = 3.50$ Å).²⁵ The angles around each metal center vary in the range, 91.61 to 134.495°. The sum of the angles in the basal plane comprising S1, Cl1 and S3 is about 355° and with S4–Ag–S3 angle is about 91°. It is inferred that the geometry around each silver atom of dimer **2** is flattened tetrahedron. The flattening occurs along Ag–S4 axis. In literature, thiophene moiety was found to be pendant in silver(I) based dinuclear metallacycles with linear geometry around each metal center.²⁶

Dinuclear complex of furan based thio-ligand, namely, $[Ag_2Cl_2(\mu\text{-S-Hftsc-NEt})_2(\kappa^1\text{-S-Hftsc-NEt})_2]$ **4** is similar in stoichiometry and bonding to $[Ag_2Cl_2(\mu\text{-S-Httsc-NMe})_2(\kappa^1\text{-S-Httsc-NMe})_2]$.¹⁴ Each Ag atom of dimer **4** is bonded to by one chloride, one terminal sulfur and two bridging sulfur atoms at Ag–Cl, Ag–S1A and Ag–S1B bond distances of 2.5810(6), 2.4805(6) (terminal) and 2.5024(6), 2.8211(7) Å (bridging), respectively (figure 4). The Ag_2S_2 core with unequal Ag–S bond distances forms a parallelogram and the angles at S {74.392(18) Å} and Ag {105.608(18) Å} atoms of the core are characteristic of such cores.¹⁰ The Ag...Ag bond distance of 3.2282(4) Å is less than twice the sum of van der Waals radius of silver atoms (3.40 Å).²¹ This separation is less than that (3.487 Å) observed in analogous complex, $[Ag_2Cl_2(\mu\text{-S-Httsc-NMe})_2]$.

$(\kappa^1\text{-S-Httsc-NMe})_2]$.¹⁴ The intramolecular –C–H...Cl and –N–H...Cl interactions appear to favour sulfur-bridging in **4**.

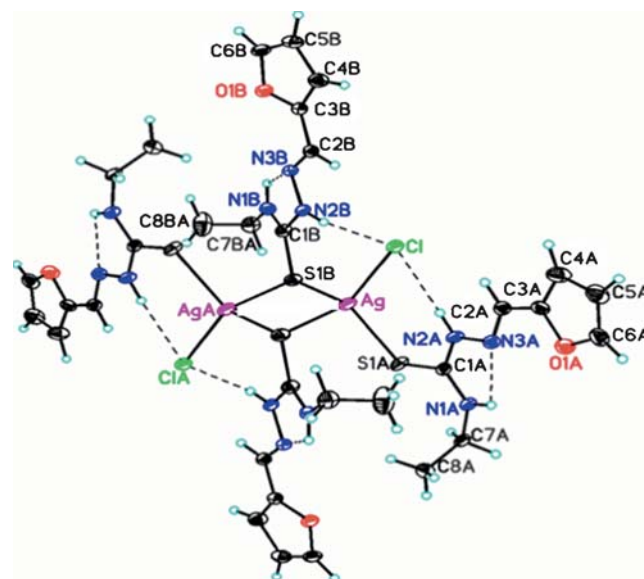


Figure 4. Structure of the complex $[Ag_2Cl_2(\mu\text{-S-Hftsc-NEt})_2(\kappa^1\text{-S-Hftsc-NEt})_2]$ **4** with atomic numbering scheme. Selected bond lengths/Å and angles/ $^\circ$: Ag–S1A, 2.4805(6); Ag–S1B, 2.5024(6); Ag–S1B, 2.8211(7); Ag–Cl, 2.5810(6); S1A–C1A, 1.697(2); Ag–Ag, 3.2282(4); S1A–Ag–S1B, 116.99(2); S1A–Ag–Cl, 113.84(2); S1B–Ag–Cl, 114.94(2); Cl–Ag–S1B*, 101.14(2); S1A–Ag–S1B*, 101.47(2); S1B–Ag–S1B*, 105.608(18); Ag–S1B–Ag, 74.392(18).

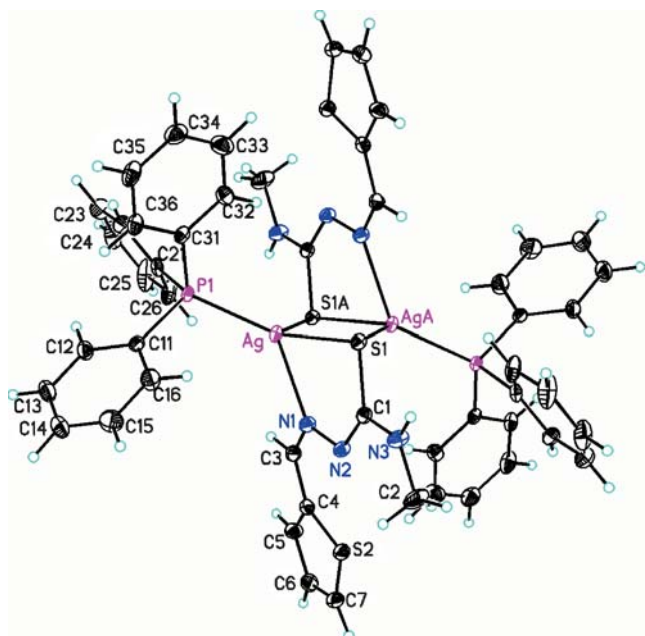


Figure 5. Structure of the complex $[\text{Ag}_2(\mu_3\text{-N,S-ttsc-NMe})_2(\text{Ph}_3\text{P})_2]\cdot(\text{CH}_3)_2\text{CO}$ **5** with atomic numbering scheme. Selected bond lengths/Å and angles/°: Ag – S1, 2.5718(8), 2.7414(8); Ag–N1, 2.367(3); Ag–P, 2.3880(8); S1–C6, 1.752(3); Ag–Ag, 3.0443(5); N1–Ag–P, 133.53(7); N1–Ag–S1, 74.06(7); N1–Ag–S1*, 88.25(7); P–Ag–S1, 129.09(4); P–Ag–S1*, 112.16(3); S1–Ag–S1*, 110.17(2); Ag–S1–Ag, 69.83(2).

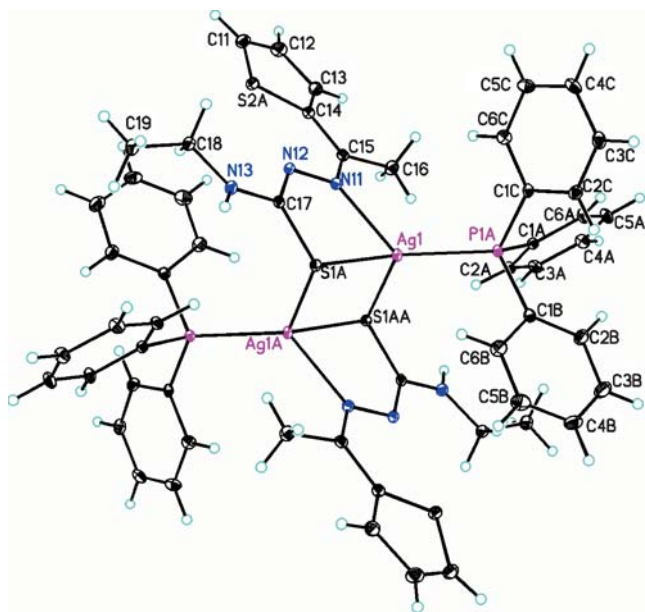


Figure 6. Structure of the complex $[\text{Ag}_2(\mu_3\text{-N,S-attsc-NEt})_2(\text{Ph}_3\text{P})_2]\cdot 0.5(\text{CH}_3)_2\text{CO}$ **6** with atomic numbering scheme. Selected bond lengths/Å and angles/°: Ag1–N11, 2.3386(16); Ag1–P1A, 2.3945(5); Ag1–S1A, 2.5382(5); Ag1–S1A*, 2.7666(6); S1A–C17, 1.7593(19); Ag1–Ag1, 3.2500(3); N11–Ag1–P1A, 127.78(4); N11–Ag1–S1A, 76.49(4); P1A–Ag1–S1A, 133.413(18); N11–Ag1–S1A, 94.86(4); P1A–Ag1–S1A, 110.773(17); S1A–Ag1–S1A, 104.574(14); Ag1–S1A–Ag1, 75.426(14).

Figures 5 and 6 display the molecular structures of complexes, $[\text{Ag}_2(\mu_3\text{-N,S-ttsc-NMe})_2(\text{Ph}_3\text{P})_2]\cdot(\text{CH}_3)_2\text{CO}$ **5** and $[\text{Ag}_2(\mu_3\text{-N,S-attsc-NEt})_2(\text{Ph}_3\text{P})_2]\cdot 0.5(\text{CH}_3)_2\text{CO}$ **6**, respectively. In both the dinuclear complexes, each Ag metal atom is coordinated by one P, two bridging S and one N atoms with Ag–P, Ag–S and Ag–N bond distances of 2.388–2.395, 2.538–2.767 and 2.339–2.367 Å, respectively. The angles around each metal center vary in a wide range, 74–134° which suggest severely distorted tetrahedral geometry. The Ag–S–Ag and S–Ag–S bond angles of Ag_2S_2 core of **5** are 69.83 and 110.17°, respectively, with Ag ··· Ag distance of 3.0443 Å. Similar bond parameters of Ag_2S_2 core of **6** are 75.426 and 104.574°, respectively, with Ag ··· Ag distance of 3.2500 Å. Among complexes **4–6**, Ag ··· Ag distance varies in the order: **5** < **4** < **6**. The Ag ··· Ag bond distances are less than twice the sum of van de Waals radii of silver atoms (3.40 Å).²⁵ The bond pattern of complexes **5** and **6** is similar to that observed in the analogous complex, $[\text{Ag}_2(\mu_3\text{-N,S-Hftsc-NH}_2)_2(\text{Ph}_3\text{P})_2](\text{NO}_3)_2$, reported in literature.¹⁰

4. Conclusions

Thiophene/furan based thiosemicarbazones with silver (I) chloride/bromide in presence of PPh_3 as co-ligand have shown variable bonding properties. The thio-ligand, Httsc-NPh with silver(I) chloride yielded an unprecedented product, $[\text{Ag}_2\text{Cl}_2(\kappa^1\text{-S-Httsc-NPh})_2(\mu\text{-S,S-Httsc-NPh})_2]$ **2** in which two thio-ligands bridge two silver metal centers through thiophene sulfur and thione sulfur, while two other thio-ligands are terminally bonded. It was noted that the thio-ligand Httsc-NH₂ with silver(I) chloride formed sulfur-bridged dinuclear complex, $[\text{Ag}_2\text{Cl}_2(\mu\text{-S-Httsc-NH}_2)_2(\text{PPh}_3)_2]$,¹⁰ and the bridging changed to halogen-bridging with Httsc-NMe in $[\text{Ag}_2(\mu\text{-Cl})_2(\kappa^1\text{-S-Httsc-NMe})_2(\text{PPh}_3)_2]$.¹⁴ Interestingly, Httsc-NMe with silver(I) chloride in presence of bipy as co-ligand, yielded a different product, $[\text{Ag}_2\text{Cl}_2(\kappa^1\text{-S-Httsc-NMe})_2(\mu\text{-S-Httsc-NMe})_2]$.¹⁴ Silver(I) chloride with analogous thio-ligand, Hftsc-NEt has also yielded a similar product, $[\text{Ag}_2\text{Cl}_2(\kappa^1\text{-S-Hftsc-NEt})_2(\mu\text{-S-Hftsc-NEt})_2]$ **4**. Silver(I) bromide with Httsc-NMe/Httsc-NEt has yielded halogen-bridged dinuclear complexes, $[\text{Ag}_2(\mu\text{-Br})_2(\kappa^1\text{-S-Httsc-NMe})_2(\text{PPh}_3)_2]$ ¹⁴ and $[\text{Ag}_2(\mu\text{-Br})_2(\kappa^1\text{-S-Httsc-NEt})_2(\text{PPh}_3)_2]$ **1**. The thio-ligand, Httsc-NPh with silver(I) bromide in presence of PPh_3 formed only a mononuclear complex, $[\text{AgBr}(\kappa^1\text{-S-Httsc-NPh})(\text{PPh}_3)_2]$ **3**. Finally, Httsc-NMe/Httsc-NEt with silver(I) acetate have yielded new $\mu_3\text{-N,S}$ -bridged dinuclear complexes, $[\text{Ag}_2(\mu_3\text{-N,S-ttsc-NMe})_2(\text{PPh}_3)_2]$ **5** and $[\text{Ag}_2(\mu_3\text{-N,S-attsc-NMe})_2(\text{PPh}_3)_2]$ **6**.

Complexes **5** and **6** have thiosemicarbazones coordinating as anions similar to those observed in copper(I) chemistry.²⁰ In brief, both the nature of anion and the presence of substituents at N¹ atom appear to influence the type of silver(I) complexes.

Supplementary Information (SI)

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC 1446847 for **1**, 1446848 for **2**, 1446849 for **3**, 1446850 for **4**, 1446851 for **5** and 1446852 for **6** (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, <http://www.cam.ac.uk>).

Acknowledgements

Financial assistance from the Council of Scientific and Industrial Research, India (Scheme No.: 01(1993)/05/EMRII), Emeritus Scientist Grant [21(0904)/12-EMRII] to T.S. Lobana and grant from the Department of Science and Technology (DST), India for X-ray diffractometer to Department of Chemistry, GNDU, Amritsar are gratefully acknowledged. JPJ acknowledges the NSF-MRI program (Grant No. CHE-1039027) for funds to purchase the X-ray diffractometer.

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