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Heterocyclic-2-thione derivatives of silver(I): Synthesis, spectroscopy and structures of mono- and di-nuclear silver(I) halide complexes

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The scarcely known chemistry of silver(I) halides with a series of heterocyclic thiones in acetonitrile (or methanol–acetonitrile) is described. Silver(I) chloride with a series of imidazolidine-2-thiones [$C_3H_5NS(N{-}R)$] in the presence of one equivalent of PPh_3 with respect to the thione ligand has yielded chloro-bridged dinuclear complexes, [$Ag_2(\mu\text{-}Cl)_2(\kappa^1\text{-}S\text{-}C_3H_5NS(N{-}R))_2(PPh_3)_2$] (**1**, R = H; **2**, R = Me; **3**, R = Et), and in the presence of two equivalents of PPh_3, it has yielded mononuclear complexes, [$Ag(\kappa^1\text{-}Cl)(\kappa^1\text{-}S\text{-}C_3H_5NS(N{-}R))(PPh_3)_2$] (**4**, R = Me; **5**, R = Et). The *n*-propyl-imidazolidine-2-thione with silver(I) chloride formed only a mononuclear complex, [$Ag(\kappa^1\text{-}Cl)(\kappa^1\text{-}S\text{-}C_3H_5NS(N{-}Pr^n))(PPh_3)_2$] (**6**), in the presence of one or two equivalents of PPh_3. In contrast, silver(I) bromide with $C_3H_5NS(N{-}R)$ in the presence of one or two equivalents of PPh_3 with respect to the thione ligand has yielded bromide-bridged dinuclear complexes, [$Ag_2(\mu\text{-}Br)_2(\kappa^1\text{-}S\text{-}C_3H_5NS(N{-}R))_2(PPh_3)_2$] (**7**, R = Me; **8**, R = Et; **9**, R = Pr^n). The related thio-ligands, namely, 1-methyl-imidazoline-2-thione and thiazolidine-2-thione with silver(I) bromide in the presence of one or two equivalents of PPh_3 have formed bromide bridged dimeric [$Ag_2(\mu\text{-}Br)_2(\kappa^1\text{-}S\text{-}C_3H_3NS(N{-}Me))_2(PPh_3)_2$] (**10**) or mononuclear $Ag(\kappa^1\text{-}Br)(\kappa^1\text{-}S\text{-}C_3H_5NS_2)(PPh_3)_2$] (**11**) complexes respectively. The 2,4-dithiouracil ($C_4H_4N_2S_2$) with silver(I) chloride/bromide and PPh_3 has yielded hetero-bridged dinuclear complexes, [$Ag_2(\mu\text{-}S,S\text{-}C_4H_3N_2S_2)(\mu\text{-}X)(PPh_3)_4$] (X = Cl, **12**; Br, **13**) involving rupture of Ag–X bonds directly with a thio-ligand, a rare case of such rupture in metal-heterocyclic thione chemistry.

1. Introduction

Coordination chemistry of heterocyclic thiones, bearing the chemically active groups, $-N(H){-}C({=}S)- \leftrightarrow -N{=}C({-}SH)-$ or $-N(H){-}C({=}S){-}N(H)- \leftrightarrow -N{=}C({-}SH){-}N(H)-$, has been intensively explored [1–8]. Silver(I) complexes with sulfur-containing ligands have shown a wide range of applications in medicine, in analytical chemistry, and in polymer industry [9,10]. The biomedical applications and uses of silver(I) complexes are related to their antibacterial action [11]. Silver(I) complexes with heterocyclic thiones were found to be cytotoxic against murine leukemia (*L1210*), and human T-lymphocyte (*Molt4/C8* and *CEM*) cells, and antiviral activity against a wide variety of viruses [12,13]. The molecular design and structural characterization of silver(I) complexes is therefore an intriguing aspect of metal-based drugs [14,15].

Coordination chemistry of copper(I) halides with several heterocyclic thioamides has been intensively explored unlike that of silver(I) halides [1–6]. As regards silver(I) halides, the complexes reported with PPh_3 as co-ligand are enumerated as follows: mononuclear [$AgCl(\kappa^1\text{-}S\text{-}L)(PPh_3)_2$] {L = pyridine-2-thione, C_5H_5NS [16], $C_3H_5NS(N{-}H)$, R = H, structure I; $C_3H_3NS(N{-}Me)$, structure II, and $C_3H_5NS_2$, structure III [17]} halogen-bridged dimer [$Ag_2(\mu\text{-}Br)_2(\kappa^1\text{-}S\text{-}L)_2(PPh_3)_2$] (L = pyrimidine-2-thione) [18] and sulfur-bridged dimers [$Ag_2(\kappa^1\text{-}X)_2(\mu\text{-}S\text{-}L)_2(PPh_3)_2$] {L = C_5H_5NS, Cl, Br} [19]. Without a co-ligand, a mononuclear [$Ag(\kappa^1\text{-}S\text{-}C_3H_5NS(N{-}H))_3Cl$] [20], [$Ag_2(\kappa^1\text{-}S\text{-}C_3H_5NS(N{-}H))_6](SO_4)$ [20], a few dinuclear [$Ag_2(\mu\text{-}S\text{-}C_3H_5NS(N{-}H))_2(\kappa^1\text{-}S\text{-}C_3H_5NS(N{-}H))_4](NO_3)_2$ [20], $Ag_2(\kappa^1\text{-}S\text{-}C_3H_5NS(N{-}H))_4(\mu\text{-}Br)_2$] [20,21], and a few polynuclear [$Ag(\kappa^1$-S-

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$C_3H_5NS(N{-}H))(\mu\text{-}S\text{-}C_3H_5NS(N{-}H))Cl]_n$ [22a], $[Ag_2(\mu\text{-}S\text{-}C_3H_3NS(N{-}Me))(\mu_3\text{-}I)_2]_n$ [22b] and $\{Ag(C_5H_5NS)Cl\}_n$ complexes have been reported. Further, coordination chemistry of 2,4-dithiouracil ($C_4H_4N_2S_2$, structure IV) is limited and there are only a few structurally characterized complexes of Co^{III}, Ti^{III}, Ru^{II} and Cu^{I} [17,23,24].

In view of our interest in the development of coordination chemistry of silver(I) halides, we have reported complexes with a few heterocyclic thioamides [17,19] and related N, S-donor ligands, namely, thiosemicarbazones [25]. In this paper, reactions of silver(I) halides (X = Cl, Br) with a series of heterocyclic-2-thiones as shown in Chart 1 [structures I (R = H, Me, Et, Pr^n), II, III and IV] have been carried out in the presence of PPh_3 as co-ligand and the resulting complexes characterized using analytical data, IR and multinuclear NMR spectroscopy (^1H and ^{31}P) and single crystal X-ray crystallography (**1**–**4**, **6**–**13**).

2. Experimental section

2.1. Materials and techniques

Silver(I) halides were freshly prepared from $AgNO_3$ and potassium halides (X = Cl, Br) in methanol and dried *in vacuo*. Imidazolidine-2-thione, thiazolidine-2-thione, 1-methyl-imidazoline-2-thione and 2,4-dithiouracil were procured from Aldrich Chemicals Ltd. and used as such. The *N*-alkyl-imidazolidine-2-thiones (1-methyl-imidazolidine-2-thione, 1-ethyl-imidazolidine-2-thione, *n*-propyl-imidazolidine-2-thione and *n*-butyl-imidazolidine-2-thione) were prepared as per the literature methods [26]. The C, H and N analyses were obtained with Thermoelectron FLASHEA 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 $CDCl_3$ with TMS as the internal reference. The ^{31}P NMR spectra were recorded on BRUKER AVANCE II 400 spectrometer operating at a frequency of 161.9 MHz using *o*-phosphoric acid as the external reference set at zero position.

2.2. Synthesis of complexes

2.2.1. $[Ag_2(\mu\text{-}Cl)_2(\kappa^1\text{-}S\text{-}C_3H_5NS(N{-}H))_2(PPh_3)_2]$ **1**

To silver(I) chloride (0.025 g, 0.17 mmol) suspended in acetonitrile was added solid PPh_3 (0.045 g, 0.17 mmol) and the contents were stirred for 24 h. The white solid formed was filtered and dried *in vacuo*. To this solid suspended in chloroform was added solid imdazolidine-2-thione (0.018 g, 0.17 mmol) and the contents were stirred until a clear solution was obtained, which was allowed to evaporate at room temperature. The solid obtained was dissolved in dichloromethane and acetonitrile mixture. A slow evaporation of the solution resulted in colorless crystals of complex **1** (Yield 70%, mp. 163–165 °C). Found: C, 49.54; H, 4.16; N, 6.07. Calc. for $C_{21}H_{21}AgClN_2PS$: C, 49.70; H, 4.14; N, 5.52%. IR absorptions (ν/cm^{-1}): 3150(m), ν(N–H); 3040–2865(w), ν(C–H); 1509(s), 1439(sh), ν(C–N) + δ(C–H); 1186(s), ν(C=S); 1108(w), 986(m), 915(m), $\nu(P{-}C_{Ph})$. ^1H NMR data ($CDCl_3$, δ ppm): 7.79 (s, 1H, NH), 7.26–7.44 (m, 16H, PPh_3 + $CHCl_3$). 3.73 (s, 4H, $C^{4,5}H$).

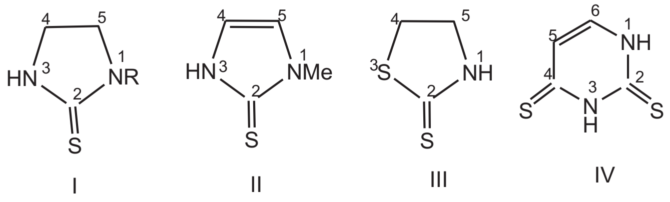


Chart 1. Various thio-ligands used.

2.2.2. $[Ag_2(\mu\text{-}Cl)_2(\kappa^1\text{-}S\text{-}C_3H_5NS(N{-}Me))_2(PPh_3)_2]$ **2**

It was prepared by the method used for complex **1** (Yield 67%, mp. 161–164 °C). Found: C, 51.18; H, 4.52; N, 5.38. Calc. for $C_{45}H_{48}Ag_2Cl_2N_4P_2S_2$: C, 51.06; H, 4.54; N, 5.29%. IR absorptions (ν/cm^{-1}): 3178(m), ν(N–H); 3065–2880(w), ν(C–H); 1513(s), 1478(sh), ν(C–N) + δ(C–H); 1192(m), ν(C=S); 1093(s), $\nu(P{-}C_{Ph})$; 958(w), $\delta(N{-}CH_3)$. ^1H NMR data ($CDCl_3$, δ ppm): 9.14 (s, 1H, NH), 7.50–7.33 (m, 15H, PPh_3), 3.70 (d, 4H, $C^{4,5}H$), 3.10 (s, 3H, CH_3).

2.2.3. $[Ag_2(\mu\text{-}Cl)_2(\kappa^1\text{-}S\text{-}C_3H_5NS(N{-}Et))_2(PPh_3)_2]$ **3**

It was prepared by a method used for complex **1** (Yield 66%, mp. 165–167 °C). Found: C, 51.35; H, 4.61; N, 5.14. Calc. for $C_{46}H_{50}Ag_2Cl_2N_4P_2S_2$: C, 51.51; H, 4.66; N, 5.22%. IR absorptions (ν/cm^{-1}): 3202(m), ν(N–H); 3051–2885(w), ν(C–H); 1516(s), 1478(sh), ν(C–N) + δ(C–H); 1187(m), ν(C=S); 1094(s), $\nu(P{-}C_{Ph})$. ^1H NMR data ($CDCl_3$, δ ppm): 7.50–7.39 (m, 15H, PPh_3), 3.63 (m, 6H, $C^{4,5}H$, $N{-}CH_2$), 1.20 (t, 3H, CH_3).

2.2.4. $[AgCl(\kappa^1\text{-}S\text{-}C_3H_5NS(N{-}Me))(PPh_3)_2]$ **4**

To silver(I) chloride (0.025 g, 0.17 mmol) suspended in acetonitrile was added solid PPh_3 (0.091 g, 0.34 mmol), and the contents were stirred for 24 h. The white solid formed was filtered and dried *in vacuo*. To this solid suspended in chloroform was added solid 1-methyl-imdazolidine-2-thione (0.020 g, 0.17 mmol) and the contents were stirred until a clear solution was obtained, which was allowed to evaporate at room temperature. The solid obtained was dissolved in dichloromethane and acetonitrile mixture. Slow evaporation of the solution resulted in colorless crystals of **4** (Yield 68%, mp. 165–167 °C). Found: C, 61.40; H, 4.95; N, 3.62. Calc. for $C_{40}H_{38}AgClN_2P_2S$: C, 61.26; H, 4.85; N, 3.57%. IR absorptions (ν/cm^{-1}): 3212m (br), ν(N–H); 3066–2799(m), ν(C–H); 1515(s), 1479(s), ν(C–N) + δ(C–H); 1180(m), ν(C=S); 1093(m), $\nu(P{-}C_{Ph})$; 996(w), $\delta(N{-}CH_3)$. ^1H NMR data ($CDCl_3$, δ ppm): 8.64 (s, 1H, NH), 7.42–7.26 (m, 16H, PPh_3 + $CHCl_3$), 3.61 (m, 4H, $C^{4,5}H$), 3.08 (m, 3H, CH_3).

2.2.5. $[AgCl(\kappa^1\text{-}S\text{-}C_3H_5NS(N{-}Et)(PPh_3)_2)]$ **5**

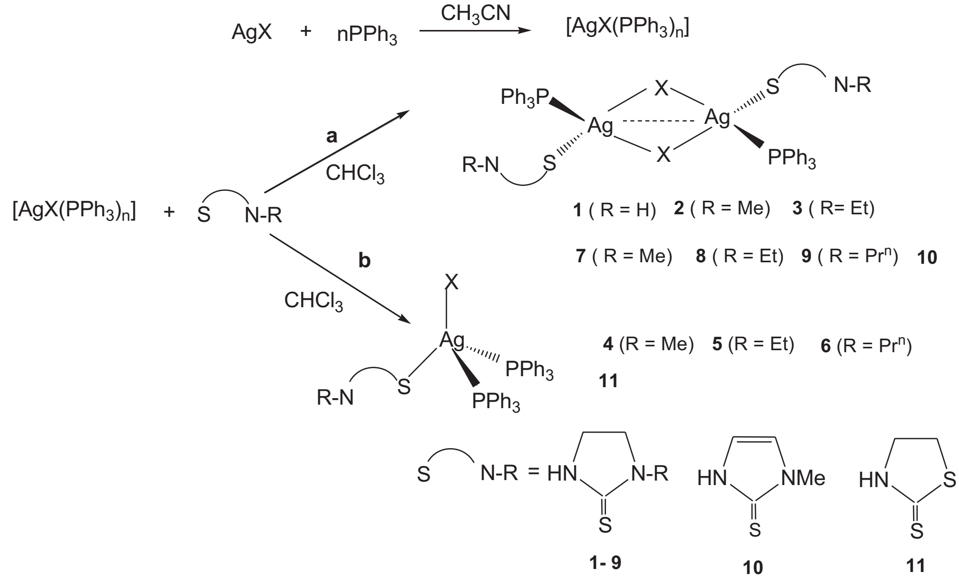
It was prepared by a method used for complex **4** (Yield 66%, mp. 151–154 °C). Found: C, 61.55; H, 4.95; N, 3.62. Calc. for $C_{41}H_{40}AgClN_2P_2S$: C, 61.71; H, 5.01; N, 3.51%. IR absorptions (ν/cm^{-1}): 3202(m), ν(N–H); 3050–2885(m), ν(C–H); 1517(s), 1478(m), ν(C–N) + δ(C–H); 1193(m), ν(C=S); 1094(m), $\nu(P{-}C_{Ph})$. ^1H NMR data ($CDCl_3$, δ ppm): 8.60 (s, 1H, NH), 7.70–7.26 (m, 16H, PPh_3 + $CHCl_3$). 3.58 (m, 6H, $C^{4,5}H$, $N{-}CH_2$), 1.17 (m, 3H, CH_3).

2.2.6. $[AgCl(\kappa^1\text{-}S\text{-}C_3H_5NS(N{-}Pr^n)(PPh_3)_2)]$ **6**

It was prepared by a method used for complex **1** (Yield 67%, mp. 150–153 °C). Found: C, 61.95; H, 5.10; N, 3.48. Calc. for $C_{42}H_{42}AgClN_2P_2S$: C, 62.11; H, 5.17; N, 3.45%. IR absorptions (ν/cm^{-1}): 3092(w), ν(N–H); 3051–2871(m), ν(C–H); 1511(s), 1479(sh), ν(C–N) + δ(C–H); 1186(m), ν(C=S); 1094(m), $\nu(P{-}C_{Ph})$. ^1H NMR data ($CDCl_3$, δ ppm): 7.43–7.26 (m, 16H, PPh_3, $CHCl_3$). 3.61 (m, 4H, C^4H, $N{-}CH_2$), 3.49 (t, 2H, C^5H), 1.55 (m, 2H, $-CH_2$), 0.87 (t, 3H, CH_3).

2.2.7. $[Ag_2(\mu\text{-}Br)_2(\kappa^1\text{-}S\text{-}C_3H_5NS(N{-}Me))_2(PPh_3)_2]$ **7**

To silver(I) bromide (0.025 g, 0.13 mmol) suspended in acetonitrile was added solid PPh_3 (0.070 g, 0.26 mmol) and the contents were stirred for 24 h. The white solid formed was filtered and dried *in vacuo*. To this solid suspended in chloroform was added solid 1-methyl-imdazolidine-2-thione (0.016 g, 0.13 mmol) and the



Scheme 1. Formation of complexes **1**–**11**.

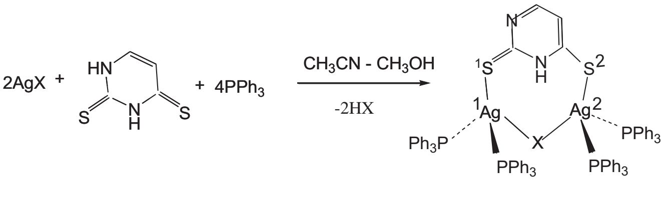
contents were stirred until a clear solution was obtained, which was allowed to evaporate at room temperature. The solid obtained was dissolved in dichloromethane and acetonitrile mixture. A slow evaporation of the solution resulted in colorless crystals of **7** (Yield 69%, mp. 170–173 °C). Found: C, 46.77; H, 3.94; N, 5.10. Calc. for $C_{21}H_{21}AgBrN_2PS$: C, 46.64; H, 4.06; N, 4.95%. IR absorptions (ν/cm^{-1}): 3243(m), ν(N–H); 3051–2883(m), ν(C–H); 1514(s), 1479(sh), ν(C–N) + δ(C–H); 1186(m), ν(C=S); 1114(s), ν(P–C_{Ph}); 945(w), δ(N–CH_3). ^{1}H NMR data ($CDCl_3$, δ ppm): 8.16 (s, 1H, NH), 7.49–7.32 (m, 15H, PPh_3), 3.69 (m, 4H, $C^{4,5}$H), 3.10 (s, 3H, CH_3).

2.2.8. *[$Ag_2(\mu\text{-}Br)_2(\kappa^1\text{-}S\text{-}C_3H_5NS(N\text{–}Et))_2(PPh_3)_2$]* **8**

It was prepared by a method used for complex **7** (Yield 71%, mp. 158–160 °C). Found: C, 47.54; H, 4.41; N, 4.82. Calc. for $C_{46}H_{52}Ag_2Br_2N_4P_2S_2$: C, 47.48; H, 4.47; N, 4.82%. IR absorptions (ν/cm^{-1}): 3237(m), ν(N–H); 3050–2883(w), ν(C–H); 1514(s), 1477(sh), ν(C–N) + δ(C–H); 1187(m), ν(C=S); 1093(m), ν(PvC$_{Ph}$). ^{1}H NMR data ($CDCl_3$, δ ppm): 8.45 (s, 1H, NH), 7.50–7.24 (m, 16H, PPh_3 + $CHCl_3$), 3.61 (m, 6H, $C^{4,5}$H, N–CH_2), 1.19 (m, 3H, CH_3).

2.2.9. *[$Ag_2(\mu\text{-}Br)_2(\kappa^1\text{-}S\text{-}C_3H_5NS(N\text{–}Pr^n))_2(PPh_3)_2$]* **9**

It was prepared by a method used for **7** (Yield 69%, mp. 140–142 °C). Found: C, 48.53; H, 4.50; N, 4.62. Calc. for $C_{48}H_{54}Ag_2Br_2N_4P_2S_2$: C, 48.46; H, 4.54; N, 4.71%. IR absorptions (ν/cm^{-1}): 3235(m), ν(N–H); 3053–2882(w), ν(C–H); 1513(s), 1477(sh), ν(C–N) + δ(C–H); 1184(m), ν(C=S); 1093(m), ν(P–C_{Ph}). ^{1}H NMR data ($CDCl_3$, δ ppm): 8.50 bs (1H, NH), 7.51–7.29 (m, 15H, PPh_3), 3.67 (m, 4H, C^4H, N–CH_2), 3.47 (t, 2H, C^5H), 1.60 (m, 2H, CH_2), 0.92 (t, 3H, CH_3).



Scheme 2. Dithiouracilates of silver(I), X = Cl, **12**; Br, **13**.

2.2.10. *[$Ag_2(\mu\text{-}Br)_2(\kappa^1\text{-}S\text{-}C_3H_3NS(N\text{–}Me))_2(PPh_3)_2$]* **10**

It was prepared by a method used for **7** (Yield 67%, mp. 163–165 °C). Found: C, 47.65; H, 3.81; N, 5.14. Calc. for $C_{39}H_{35}AgClNP_2S_2$: C, 46.80; H, 3.72; N, 4.96%. IR absorptions (ν/cm^{-1}): 3243(s), ν(N–H); 3052–2883(w), ν(C–H); 1514(s), 1479(s), ν(C–N) + δ(C–H); 920(m), ν(C=S); 1093(w), ν(P–C_{Ph}); 748(s), δ(N–CH_3). ^{1}H NMR data (δ, ppm; $CDCl_3$): 7.52–7.39 (m, 15H, PPh_3). 6.75 (t, 1H, C^4H), 6.64 (t, 1H, C^5H), 3.54 (s, 3H, N–CH_3).

2.2.11. *[$Ag(\kappa^1\text{-}Br)(\kappa^1\text{-}S\text{-}C_3H_5NS_2)(PPh_3)_2$]* **11**

It was prepared by a method used for **4** (Yield 72%, mp. 170–173 °C). Found: C, 56.54; H, 4.05; N, 1.62. Calc. for $C_{39}H_{35}AgBrNP_2S_2$: C, 56.31; H, 4.21; N, 1.68%. IR absorptions (ν/cm^{-1}): 3052(m), 3008–2811(m), ν(N–H); ν(C–H); 1527(s), 1479(s), ν(C–N) + δ(C–H); 1093(m), ν(P–C_{Ph}); 996(m), ν(C=S). ^{1}H NMR data ($CDCl_3$, δ ppm): 9.72 bs (1H, NH), 7.43–7.26 (m, 16H, PPh_3 + $CHCl_3$), 3.47 (t, 2H, C^4H), 3.94 (t, 2H, C^5H).

2.2.12. *[$Ag_2(\mu\text{-}S,S\text{-}C_4H_3N_2S_2)(\mu\text{-}Cl)(PPh_3)_4$]* **12**

To silver(I) chloride (0.025 g, 0.17 mmol) suspended in acetonitrile was added solution of 2,4-dithiouracil in methanol (0.025 g, 0.17 mmol) and the contents were stirred for 48 h. To the yellow precipitates formed was added solid PPh_3 (0.091 g, 0.17 mmol) and

Table 1
^{31}P NMR data ($CDCl_3$, δ in ppm) of complexes.

Complex	δ_P	$\Delta\delta = \delta_C - \delta_L$	$\Delta\delta = \delta_C - \delta_L$ (second species)	Remarks
1	13.62	19.10	–	Single species
2	4.64, 29.30	34.75	10.09	Two species
3	3.40, 29.63	35.08	8.85	Two species
4	3.78	9.25	–	Single species
5	10.22	15.69	–	Single species
6	4.54	10.00	–	Single species
7	6.40, 28.59	34.00	11.87	Two species
9	7.13	12.60	–	Single species
10	10.58	15.28	–	Single species
11	2.42	7.10	–	Single species
12	2.62, 29.20	8.12	34.70	Two species
13	2.70, 29.33	8.20	34.80	Two species

Table 2
Crystallographic data for complexes **1**–**4**, **6**–**13**.

	1	**2**	**3**	**4**
Empirical formula	$C_{42}H_{42}Ag_2Cl_2N_4P_2S_2$	$C_{44}H_{46}Ag_2Cl_2N_4P_2S_2$	$C_{46}H_{50}Ag_2Cl_2N_4P_2S_2$	$C_{40}H_{38}AgClN_2P_2S$
Formula weight	1015.50	1043.55	1071.60	784.04
T(K)	295(2)	173(2)	170(2)	123(2)
Crystal system	Monoclinic	Triclinic	Triclinic	Monoclinic
Space group	$P2_1/n$	P-1	P-1	$P2_1/c$
a(Å)	8.855(1)	9.226(1)	9.176(1)	14.3440(2)
b(Å)	15.748(1)	10.180(1)	10.3026(1)	10.236(2)
c(Å)	15.452(1)	13.253(1)	13.473(1)	24.799(1)
α(°)	90	78.590(4)	80.514(7)	90
β(°)	97.853(6)	76.163(4)	75.593(8)	92.018(1)
γ(°)	90	69.983(5)	69.996(10)	90
V (Å^3)	2134.4(2)	1126.44(1)	1154.8(2)	3638.77(9)
Z	2	1	1	4
D_{calcd} (g cm^{-3})	1.580	1.538	1.541	1.431
μ (mm^{-1})	1.251	1.187	1.160	0.804
Total reflections	17,962	10,234	11,764	39,833
Unique reflections, R_{int}	8112, 0.0456	5788, 0.0125	6479, 0.0295	18,259, 0.0284
R (reflections)				
$R1$	0.0518 (5267)	0.0277 (5078)	0.0372 (5234)	0.0368 (14,826)
$wR2$	0.0980 (8112)	0.0783 (5788)	0.0950 (6479)	0.0780 (18,259)

	6	**7**	**8**
Empirical formula	$C_{42}H_{42}AgClN_2P_2S$	$C_{44}H_{46}Ag_2Br_2N_4P_2S_2$	$C_{46}H_{52}Ag_2Br_2N_4P_2S_2$
Formula weight	812.10	1132.47	1162.54
T(K)	170(2)	173(2)	295(2)
Crystal system	Triclinic	Triclinic	Triclinic
Space group	P-1	P-1	P-1
a(Å)	10.415(1)	9.358(1)	9.371(1)
b(Å)	13.036(1)	10.259(1)	10.432(1)
c(Å)	15.075(1)	13.313(1)	13.504(1)
α(°)	76.858(6)	77.368(8)	80.323(5)
β(°)	81.323(6)	75.297(9)	75.154(5)
γ(°)	76.605(6)	69.256(10)	69.947(6)
V (Å^3)	1928.4(2)	1144.3(2)	1193.94(12)
Z	2	1	1
D_{calcd} (g cm^{-3})	1.399	1.643	1.617
μ(mm^{-1})	0.761	2.798	2.684
Reflections collected	18,550	10,324	16,844
Unique reflections, R_{int}	9923, 0.0196	5882, 0.0185	9665, 0.0375
R (reflections)			
$R1$	0.0312 (8598)	0.0295 (5012)	0.0654 (5058)
$wR2$	0.0816 (9923)	0.0789 (5882)	0.1965 (9665)

	9	**10**	**11**
Empirical formula	$C_{48}H_{54}Ag_2Br_2N_4P_2S_2$	$C_{44}H_{42}Ag_2Br_2N_4P_2S_2$	$C_{39}H_{35}AgBrNP_2S_2$
Formula weight	1188.57	1128.44	831.52
T(K)	295(2)	295(2)	296(2)
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	P-1	P-1	$P2_1/c$
a(Å)	9.640(1)	9.379(1)	13.987(3)
b(Å)	10.5045(3)	10.273(1)	10.459(2)
c(Å)	13.4030(5)	13.383(1)	24.806(5)
α(°)	80.299(3)	77.297(6)	90
β(°)	75.033(4)	75.270(7)	95.03(3)
γ(°)	70.554(4)	69.366(7)	90
V (Å^3)	1231.27(9)	1154.92(15)	3614.9(13)
Z	1	1	8
D_{calcd} (g cm^{-3})	1.603	1.622	1.528
μ(mm^{-1})	2.604	2.772	7.901
Reflections collected	15,636	21,255	65,346
Unique reflections, R_{int}	8124, 0.0267	11,535, 0.0742	5541, 0.0341
R (reflections)			
$R1$	0.0395 (6102)	0.0576 (3852)	0.0226 (5437)
$wR2$	0.0950 (8124)	0.1463 (11,535)	0.0586 (5541)

	12	**13**
Empirical formula	$C_{76}H_{63}Ag_2ClN_2P_4S_2$	$C_{76}H_{63}Ag_2BrN_2P_4S_2$
Formula weight	1443.47	1487.93
T(K)	100(2)	100(2)
Crystal system	Triclinic	Triclinic
Space group	P-1	P-1
a(Å)	11.976(1)	11.998(1)
b(Å)	14.057(1)	14.106(1)

(*continued on next page*)

Table 2 (*continued*)

	12	**13**
c(Å)	19.928(1)	19.963(1)
α(°)	97.961(5)	98.070(2)
β(°)	91.637(3)	91.384(2)
γ(°)	96.251(5)	96.122(2)
V ($Å^3$)	3299.5(5)	3323.6(3)
Z	2	2
D_{calcd} (g cm^{-3})	1.453	1.487
μ(mm^{-1})	0.840	1.395
Reflections collected	282,780	149,552
Unique reflections, R_{int}	15,097, 0.0522	13,064, 0.0531
R (reflections)		
*R*1	0.0734 (15,063)	0.0698 (8984)
*wR*2	0.1913 (15,097)	0.1136 (13,064)

the contents were stirred until reaction solution becomes clear. The slow evaporation of the solution resulted in yellow prismatic crystals of **12** (Yield 68%, mp. 170–172 °C). Found: C, 63.42; H, 4.22; N, 2.05. Calc. for $C_{76}H_{63}Ag_2ClN_2P_4S_2$: C, 63.18; H, 4.36; N, 1.94%. IR absorptions (ν/cm^{-1}): 3046(m), ν(N–H); 3005–2928(w), ν(C–H); 1542–1478(s), ν(C–N) + δ(C–H); 1125(s), ν(C=S); 1094(m), ν(P–C_{Ph}).

2.2.13. *[Ag_2(μ-S,S-$C_4H_3N_2S_2$)(μ-Br)(PPh_3)$_4$]* **13**

It was prepared by the same method as used for complex **12** (Yield 70%, mp. 155–157 °C). Found: C, 61.37; H, 4.20; N, 1.94. Calc. for $C_{76}H_{63}Ag_2BrN_2P_4S_2$: C, 61.29; H, 4.23; N, 1.88%. IR absorptions (ν/cm^{-1}): 3046(m), ν(N–H); 3010–2926(w), ν(C–H); 1545–1479(s), ν(C–N) + δ(C–H); 1123(s), ν(C=S); 1095(m), ν(P–C_{Ph}).

Ligands. See Supplementary.

2.3. *X-ray crystallography*

The single crystals of compounds **1**–**4**, **6**–**13** were mounted on glass fibers and the data were collected using Xcalibur R (**1**, **4**, **8**–**10**), Xcalibur Eos (**2**, **3**, **6**, **7**) and Bruker APEX-II CCD (**11**), Bruker X8 Kappa APEXII (**12**, **13**) diffractometers, each equipped with a graphite monochromator and Mo-Kα radiation ($\lambda = 0.71073$ Å). The unit cell dimensions and intensity data were measured at 123(2) (**4**), 295(2) (**1**, **8**–**10**), 173(2) (**2**, **7**), 170(2) (**3**, **6**), 296(2) (**11**), 100(2) (**12**, **13**) K. The data were processed (data collection, refinement and reduction) with *CrysAlis Pro* (**1**–**4**, **6**–**10**), and corrected for absorption using spherical harmonics. The data were processed with *APEX2* (data collection) [27] and *SAINT* (cell refinement, data reduction) for complexes **11**–**13** and corrected for absorption using *SADABS* [28]. The structures were solved by the direct methods using the program *SHELXS-97*, and refined by the full matrix least square based on F^2 with anisotropic thermal parameters for the non-hydrogen atoms using *SHELXL-97* and *SHELXTL* (molecular graphics) [29]. The crystallographic data are given in Table 2.

3. Results and discussion

3.1. *Comments on synthetic aspects*

In the preparation of silver(I) halide mixed-ligand complexes **1**–**11**, a silver(I) halide was first reacted with the PPh_3 ligand in acetonitrile followed by removal of the solvent and the resulting solid was reacted with the thio-ligand in chloroform. However, when a thio-ligand, C_3H_5NS(N–H) was reacted with silver(I) chloride in acetonitrile, a white solid was obtained and to this solid the addition of PPh_3 in the same solvent did not yield the mixed ligand complex, rather a known cubane [AgCl(PPh_3)]$_4$ was obtained (the addition of chloroform did not help in the latter procedure). The silver(I) once bonded to PPh_3 and the thio-ligand, as in the former procedure, yielded the stable complexes which were crystallized from CH_2Cl_2–CH_3CN mixture (1:1 v/v). Thus silver(I) chloride with C_3H_5NS(N–R) and PPh_3 has yielded mononuclear complexes for R = H [17], Me (**4**), Et (**5**) and Pr^n (**6**) as well as dinuclear complexes for R = H (**1**), Me (**2**) and Et (**3**). Surprisingly for R = Pr^n, silver(I) chloride has formed only mononuclear complex **6** in the presence of one or two equivalents of PPh_3 with respect to the thione ligand. Interestingly, silver(I) bromide with C_3H_5NS(N–R) and PPh_3 only formed dinuclear complexes for R = Me (**7**), Et (**8**) and Pr^n (**9**) in the presence of one or two equivalents of PPh_3.

Other thio-ligands, namely, C_3H_3NS(N–Me) when reacted with silver(I) chloride in the presence of two equivalents of PPh_3 with respect to the thione ligand gave a mononuclear complex, [AgCl(C_3H_3NS(N–Me))(PPh_3)$_2$] [17]. Similar reaction of silver(I) bromide with C_3H_3NS(N–Me) and one or two equivalents of PPh_3 has formed only dinuclear complex **10**, and this activity is in line with the behavior noted above with C_3H_5NS(N–R) thio-ligands. Thiazolidine-2-thione ($C_3H_5NS_2$) with silver(I) chloride is known to form a tetrahedral complex, [AgCl($C_3H_5NS_2$)(PPh_3)$_2$] [17], and unlike behavior noted for silver(I) bromide above, this thio-lgand has formed a mononuclear complex **11** in the presence of one or two equivalents of PPh_3 with respect to the thione ligand. Scheme 1 shows preparation of complexes and their possible structures (confirmed using X-ray crystallography vide infra).

Due to the lack of solubility of the dithiouracil as well as of silver(I) halides in acetonitrile, the procedure adopted for the preparation of complexes **1**–**11** was not applicable here. Thus complexes **12** and **13** were prepared by the reaction of 2,4-dithiouracil in methanol with a silver(I) halide suspended in acetonitrile followed by stirring of the contents for about 48 h. The resulting light yellow precipitate were reacted with PPh_3 which gave crystalline products (molar ratio was 1:1:1). Here the thio-ligand removed one halogen per two silver(I) halide moieties and bridged two silver(I) ions via *S*,*S*-donor atoms and the remaining halogen formed the second bridge. Scheme 2 shows the formation of complexes **12** and **13**.

3.2. *Infrared and NMR spectroscopy*

The IR spectra of complexes **1**–**13** reveal the presence of both the thio-ligands and triphenyl phosphine (see Experimental section). In complexes **1**–**13**, the ν(N–H) peaks appear in the range 3046–3237 cm^{-1} and reveal that the ligands are neutral in complexes **1**–**11** and as uninegative anions in **12** and **13** (X-ray crystallography vide infra). The most significant bands due to ν(C–S) lie in the range 1180–1193 cm^{-1} in complexes **1**–**9**; in the region 920–996 cm^{-1} in **10** and **11** and in the region 1123–1125 cm^{-1} in complexes **12** and **13**. The presence of triphenyl phosphine is

Table 3
Bond lengths (Å) and angles (°) for compounds **1**–**4**, **6**–**13**.

Halogen-bridged dimmers	**1**	**2**	**3**	
Ag–S	2.5105(8)	2.5211(6)	2.515(1)	
Ag–P	2.4520(7)	2.4394(5)	2.427(1)	
Ag–Cl	2.6907(7)	2.6591(6)	2.635(1)	
Ag–Cl*	2.7028(7)	2.7207(6)	2.662(1)	
C–S	1.696(3)	1.692(2)	1.701(2)	
Ag···Ag	697(2)	3.402(2)	3.442(1)	
P–Ag–S	130.07(3)	116.77(2)	116.71(2)	
P–Ag–Cl	105.86(2)	107.01(2)	109.71(2)	
P–Ag–Cl*	109.45(2)	111.14(2)	112.15(2)	
S–Ag–Cl	104.82(3)	109.28(2)	108.31(2)	
S–Ag–Cl*	106.98(2)	109.93(2)	109.50(2)	
Cl–Ag–Cl*	93.401(2)	101.56(2)	98.94(2)	
Ag–Cl–Ag*	86.599(2)	78.44 (1)	81.06(2)	
Ag–S–C	109.06(10)	108.66(8)	108.72(9)	
	7	**8**	**9**	**10**
Ag–S	2.5271(7)	2.5257(13)	2.5270(7)	2.5343(9)
Ag–P	2.4509(6)	2.4433(10)	2.4484(6)	2.4562(8)
Ag–Br	2.7970(5)	2.7247(6),	2.7323(3)	2.7502(5)
Ag–Br*	2.7448(5)	2.7591(6)	2.7704(4)	2.8017(5)
C–S	1.694(2)	1.702(4)	1.691(2)	1.690(4)
Ag···Ag	3.421(1)	3.474(1)	3.3495(4)	3.350(1)
P–Ag–S	115.68(2)	115.86(4)	115.09(2)	115.39(3)
P–Ag–Br	106.718(18)	111.06(3)	110.306(17)	110.35(3)
P–Ag–Br*	110.205(19)	110.91(3)	111.199(17)	107.14(2)
S–Ag–Br	108.27(2)	109.70(3)	110.665(18)	111.37(3)
S–Ag–Br*	111.384(19)	106.84(4)	103.95(2)	108.32(3)
Br–Ag–Br*	103.767(13)	101.398(18)	105.012(10)	103.480(15)
Ag–Br–Ag*	76.233(13)	78.603(18)	74.989(10)	76.520(15)
Ag–S–C	109.13(8)	109.05(17)	109.05(17)–110.19(9)	109.13(13)
Hetero-bridged dimmers	**12**	**13**		
Ag1–S1	2.547(1)	Ag1–S1	2.556(2)	
Ag1–Cl1	2.632(2)	Ag1–Br1	2.742(1)	
Ag1–P1	2.451(1)	Ag1–P1	2.442(2)	
Ag1–P2	2.470(1)	Ag1–P2	2.472(2)	
Ag ··· Ag	5.028(1)	Ag ··· Ag	5.148(1)	
Ag2–S2	2.599(4)	Ag2–S2	2.526(2)	
Ag2–Cl1	2.596(2)	Ag2–Br1	2.736(1)	
Ag2–P3	2.385(2)	Ag2–P3	2.435(2)	
Ag2–P4	2.456(3)	Ag2–P4	2.514(2)	
C–S	1.729(5), 1.744(9)	C–S	1.704(8); 1.789(10)	
P1–Ag1–S1	114.60(4)	P1–Ag1–S1	114.57(6)	
P2–Ag1–S1	107.79(4)	P2–Ag1–S1	107.99(6)	
P1–Ag1–Cl1	103.40(6)	P1–Ag1–Br1	103.39(5)	
P2–Ag1–Cl1	99.57(5)	P2–Ag1–Br1	97.35(4)	
S1–Ag1–Cl1	102.49(5)	S1–Ag1–Br1	104.81(5)	
P1–Ag1–P2	125.15(4)	P1–Ag1–P2	125.09(6)	
Ag2–Cl1–Ag1	148.21(8)	Ag2–Br1–Ag1	140.06(4)	
P3–Ag2–S2	113.93(8)	P3–Ag2–S2	116.34(7)	
P4–Ag2–S2	114.60(9)	P4–Ag2–S2	118.12(7)	
P3–Ag2–Cl1	104.77(6)	P3–Ag2–Br1	103.64(5)	
P4–Ag2–Cl1	95.88(7)	P4–Ag2–Br1	89.71(6)	
S2–Ag2–Cl1	102.61(6)	S2–Ag2–Br1	104.58(5)	
P3–Ag2–P4	120.66(7)	P3–Ag2–P4	117.81(7)	
Ag–S–C	108.9(2); S1 114.2(4) S2	Ag–S–C	110.6(3; S1 118.2(3) S2	
Monomers	**4** (Cl)	**6** (Cl)	**11** (Br)	
Ag–S1	2.637(1)	2.721(1)	2.683(1)	
Ag–X	2.570(1)	2.5751(5)	2.659(1)	
Ag–P1	2.467(1)	2.455(1)	2.469(1)	
Ag–P2	2.477(1)	2.475(1)	2.478(1)	
C–S	1.700(1)	1.702(2)	1.680(3)	
P1–Ag–S1	105.90(1)	105.78(2)	106.24(3)	
P2–Ag–S1	114.15(1)	105.70(2)	108.66(3)	
P1–Ag–X	110.71(1)	109.55(2)	112.50(2)	
P2–Ag–X	98.09(1)	111.05(2)	101.78(2)	
S1–Ag–X	105.43(1)	97.89(2)	104.46(2)	
P2–Ag–P1	121.37(1)	123.51(2)	121.94(3)	
Ag–S–C	108.36(5)	100.48(7)	109.63(9)	

The significance of asterisk shows center of symmetry.

supported by its characteristic ν(P–C_{Ph}) bands in the range, 1093–1114 cm^{-1}.

The proton NMR spectra of complexes (experimental) reveal the presence of characteristic groups, namely, –NH, –NR, CH_2, CH, and PPh_3 and these groups generally appear at positions low field/different positions relative to those of the ligands (see Supplementary). For instance, the –NH groups show a broad signal in the ligands and move to low field in their complexes (range, 7.79–9.72 ppm). Similarly, the $C^{4,5}H$ protons of free C_3H_5NS(N–H) ligand appear as a singlet at δ 3.59 ppm which shifted to the low field at δ 3.79 ppm in its complex **1**. In other complexes, the C^4H and C^5H protons appeared as a set of the multiplets. The proton signals of PPh_3 in complexes appeared as multiplets in the region, 7.26–7.70 ppm.

Table 1 shows the ^{31}P NMR data of complexes. Mononuclear complexes, **4**–**6** and **11**, exist as single species in the solution state in line with the solid state behavior (vide infra) and coordination shifts fall in the range, 7.10–15.69 ppm. Further, the coordination shifts of dinuclear complexes **1**, **9** and **10** lie in the range, 12.60–19.10 ppm and these dimers exist in the solution as single species. Dimers, **2**, **3**, **7**, **12** and **13** showed the presence of more than one species in solution whose nature is not well understood.

3.3. *Crystal and molecular structures*

The crystal data of complexes **1**–**4**, **6**–**13** are given in Table 2, and the bond parameters are given in Table 3. Complexes **1**, **4** and **11** crystallized in the monoclinic crystal system with the space groups $P2_1/n$ (**1**) and $P2_1/c$ (**4**, **11**), while other complexes (**2**, **3**, **6**–**10**, **12**, **13**) crystallized in the triclinic crystal with the space group P-1.

3.3.1. *Mononuclear [Ag(κ^1-S-HL)(PPh_3)$_2$X] complexes (**4**, **6**, **11**)*

Figs. 1–3 depict molecular geometries of mononuclear complexes **4**, **6** and **11** along with their numbering schemes respectively. In each of these complexes, the silver atom is bonded to two P atoms of Ph_3P ligands, one S atom of a thio-ligand and one halogen atom (**4**, **6**, Cl; **11**, Br). The Ag–S bond distances, 2.637(1) (**4**), 2.721(1) (**6**) and 2.683(1) Å (**11**) are longer than that {2.603(1) Å} observed in analogous complex, [Ag(κ^1-S-C_3H_5NS(N–H))(PPh_3)$_2$Cl] **14** [17], but are smaller than the expected Ag–S single

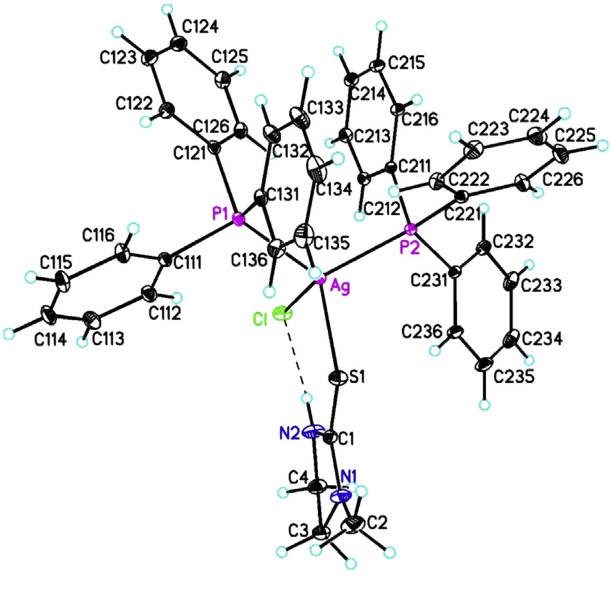


Fig. 1. Molecular structure of [AgCl(κ^1-S-C_3H_5NS(N–Me))(PPh_3)$_2$] **4**.

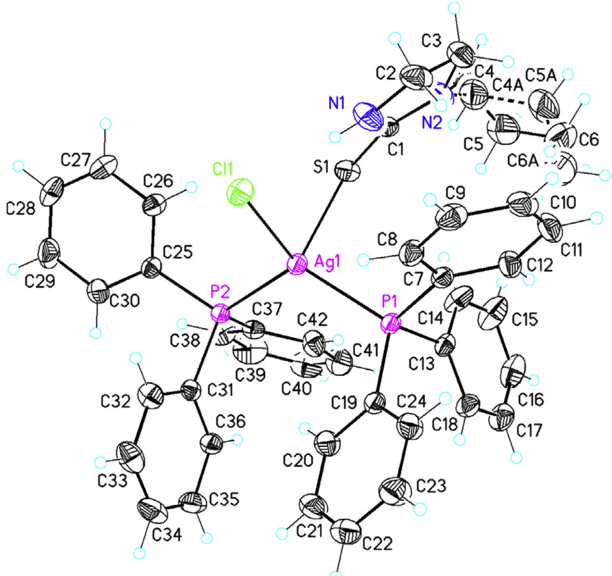


Fig. 2. Molecular structure of $[AgCl(\kappa^1\text{-}S\text{-}C_3H_5NS(N\text{-}Pr^n))(PPh_3)_2]$ **6**.

bond distance of 2.78 Å [30]. It may be noted that the Ag–S bond distances increase with the variation of R at N in the order: **6** (Pr^n) > **4** (Me) > **14** (H). The Ag–S bond distance observed in silver(I) bromide complex **11** is shorter than that found in **6**. The Ag–P bond distances (Table 3) of **4**, **6** and **11** are comparable but somewhat longer than in **14** {2.452(1), 2.445(1) Å} [17]. The Ag–Cl bond distances, 2.570(1) **4** and 2.575(1) Å **6**, are less than the sum of the ionic radii of Ag^+ and Cl^-, 2.75 Å [30]. The Ag–Br bond distance of 2.659(1) Å in complex **11**is less than the sum of the ionic radii of Ag^+ and Br^-, 2.90 Å [30], and longer than that {2.631(1) Å} observed in similarly bonded bromide in the sulfur-bridged dimeric complex, $[Ag_2Br_2(\mu\text{-}S\text{-}C_5H_5NS)_2(PPh_3)_2]$ (C_5H_5NS = pyridine-2-thione) [19]. The bond angles around each silver atom vary in the range, 98.00–123.50° with P–Ag–P being the largest angle in view of the steric effect of Ph_3P ligands. Further, the Ag–S–C angle at sulfur is shortest in **6** and largest in **11**, that is it varies in the order: **11** > **4** > **6**. The geometry around each metal center is distorted tetrahedral.

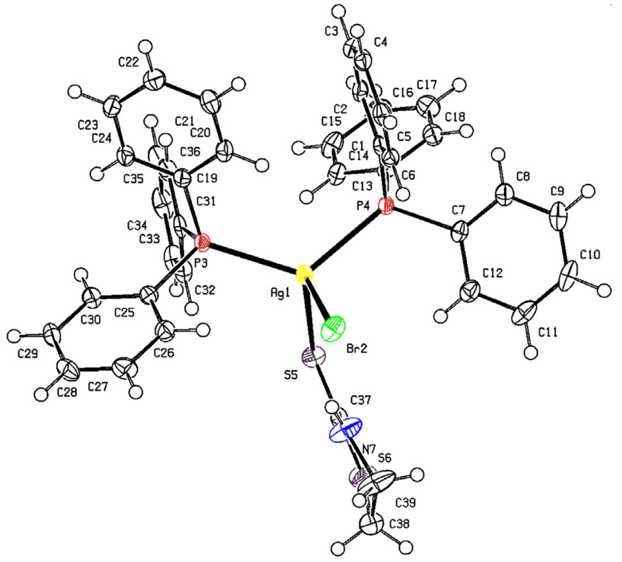


Fig. 3. Molecular structure of $[Ag(\kappa^1\text{-}Br)(\kappa^1\text{-}S\text{-}C_3H_5NS_2)(PPh_3)_2]$ **11**.

3.3.2. *Halogen-bridged dinuclear $[Ag_2(\mu\text{-}X)_2(\kappa^1\text{-}S\text{-}L)_2(PPh_3)_2]$ complexes (**1–3**, **7–10**)*

Figs. 4–6 depict molecular structures of the chloro-bridged dinuclear complexes **1–3**, while Figs. 7–10 depict those of the bromo-bridged dinuclear complexes, **7–10**. In these complexes, each Ag atom is bonded to one S atom of a thio-ligand, one P atom of Ph_3P and two bridging halogens (Cl, **1–3**; Br, **7–10**). In the dinuclear complexes **1–3**, it can be seen from Table 3 that the variation of the substituents at one nitrogen atom of the thio-ligands, $C_3H_5NS(N\text{-}R)$ marginally affected the Ag–S and Ag–P bond distances, however, the Ag–Cl distances of $Ag(\mu\text{-}Cl)_2Ag$ cores were affected to somewhat greater extent. The shorter Ag–Cl bond distances are noted for R = ethyl at N atom in complex **3**. The Ag–S bond distances are shorter while Ag–P distances are similar to those in the mononuclear complexes, **4** and **6**. Owing to the halogen-bridging in **1–3**, the Ag–Cl distances are expectedly much longer than in the mononuclear complexes **4** and **6** with terminal halogens. The angles around each Ag metal center suggest distorted tetrahedral geometry. The Ag–Cl bond distances and the Ag–Cl–Ag and Cl–Ag–Cl angles of the $Ag(\mu\text{-}Cl)_2Ag$ core reveal that the central cores of the dimers **1–3** deviate from a square. The Ag–S–C angles lie in the range, 108.66(8)–109.06(10) and are typical of the κ^1-S bonded heterocyclic thione ligands [1–6].

The bonding pattern of the bromo-bridged dinuclear complexes **7–10** (Figs. 7–10) is similar to that of the chloro-bridged complexes **1–3**. The Ag–S and Ag–P distances in **7–9** are similar to those found in **1–3**, except in complex **10** which has relatively longer Ag–S/Ag–P distances. The variation of the substituents (R) at one nitrogen atom of a thio-ligand, $C_3H_5NS(N\text{-}R)$ marginally affected the Ag–S and Ag–P bond distances. However, the Ag–Br distances of $Ag(\mu\text{-}Br)_2Ag$ cores were affected to a greater extent. Owing to the bromo-bridging in **7–10**, the Ag–Br distances are much longer than in the mononuclear bromide complex **11**. The angles around each Ag metal center suggest a distorted tetrahedral geometry. The Ag–S–C angles lie in the range, 109.05(17)–110.19(9) which are close to those found in complexes **1–3**.

3.3.3. *Hetero-bridged dinuclear $[Ag_2(\mu\text{-}X)(\mu\text{-}\kappa^1S,\ \kappa^1S\text{-}C_4H_3N_2S_2)(PPh_3)_4]$ complexes (**12**, **13**)*

In complex $[Ag_2(\mu\text{-}Cl)(\mu\text{-}S,S\text{-}C_4H_4N_2S_2)(PPh_3)_4]$, **12**, each Ag is bonded to two P atoms of two PPh_3 ligands and one μ-Cl atom. During the reaction, the dithiouracil deprotonates one –NH

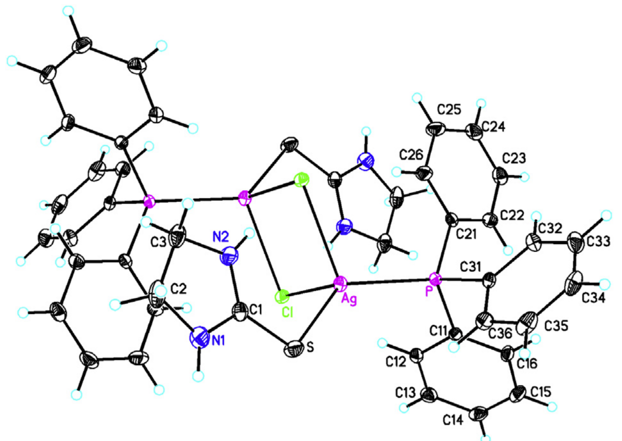


Fig. 4. Molecular structure of $[Ag_2(\mu\text{-}Cl)_2(\kappa^1\text{-}S\text{-}C_3H_5NS(N\text{-}H))_2(PPh_3)_2]$ **1**.

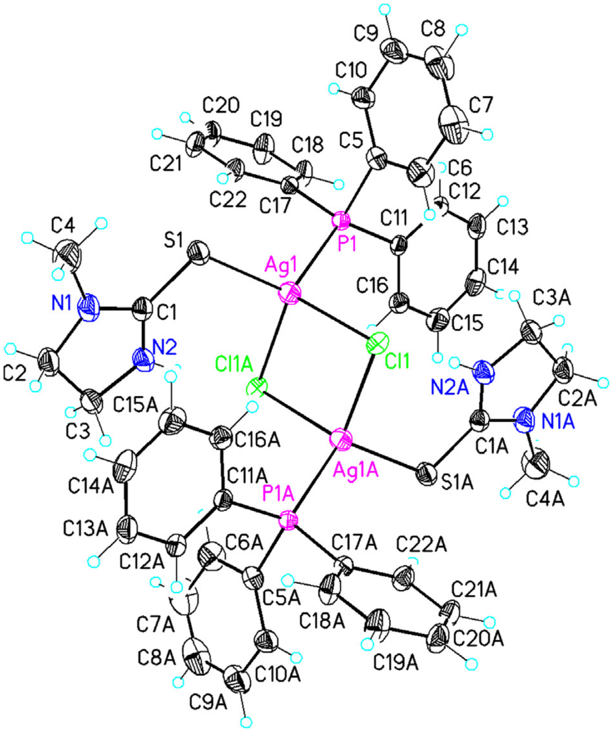


Fig. 5. Molecular structure of [$Ag_2(\mu\text{-}Cl)_2(\kappa^1\text{-}S\text{-}C_3H_5NS(N\text{-}Me))_2(PPh_3)_2$] **2**.

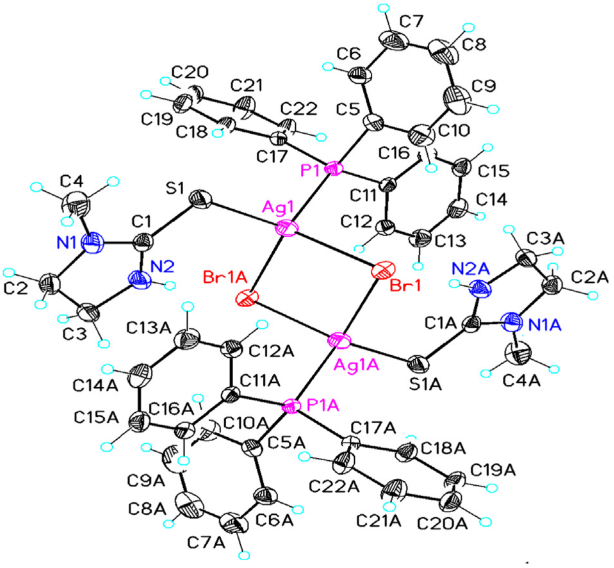


Fig. 7. Molecular structure of [$Ag_2(\mu\text{-}Br)_2(\kappa^1\text{-}S\text{-}C_3H_5NS(N\text{-}Me))_2(PPh_3)_2$] **7**.

hydrogen and as anion it binds to two different Ag atoms through its two S donor atoms, thus completing a central eight membered metallacyclic ring (Fig. 11). The Ag1–S1 bond distance of 2.547(1) Å is somewhat shorter than Ag2–S2 bond distance of 2.599(4) Å, while the Ag1–Cl1 bond distance (2.632(2) Å) is longer than Ag2–Cl1 bond distance (2.596(2) Å). Further, the Ag–P bond distances are longer with Ag1 and shorter with Ag2. The C(11)–S(1) and C(15)–S(2) bond distances of 1.729(5) and 1.744(9) Å suggest that Ag1 is bonded to the thione sulfur and Ag2 is bonded to the thiolate sulfur of the dithiouracilate anion. Further, the angles around Ag1 and Ag2 vary in the range 95–125° with P–Ag–P angles being the largest as usual. In the eight membered ring, the Ag1–Cl–Ag2 angle of 148.21(8)° is largest as compared to the other angles observed. The bonding pattern for complex **13** is same as that of complex **12**. The C(11)–S(1) and C(15)–S(2) bond distances of 1.704(8) and 1.789(10) Å in **13** suggest that there is a significant variation in the C–S bond distances in the two cases.

3.4. The C–S bond distances, nature of bridging in dimers and Ag···Ag contacts

The C–S bond distances of 1.700(10), 1.702(2) and 1.680(3)) Å respectively observed in mononuclear complexes, **4**, **6** and **11** are significantly longer than the C=S double bond distance of 1.62 Å [31], but shorter than a C–S single bond distance of 1.81 Å [31] suggesting partial double bond character in the C–S bond. Similarly in the halogen-bridged dimers **1**–**3** and **7**–**10**, the C–S bond

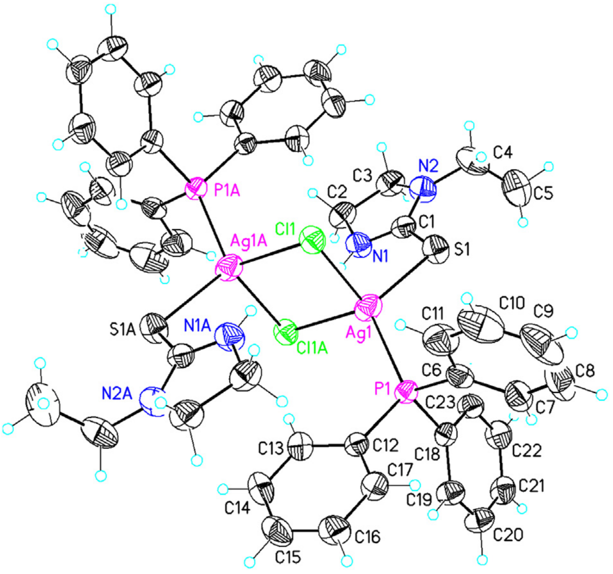


Fig. 6. Molecular structure of [$Ag_2(\mu\text{-}Cl)_2(\kappa^1\text{-}S\text{-}C_3H_5NS(N\text{-}Et))_2(PPh_3)_2$] **3**.

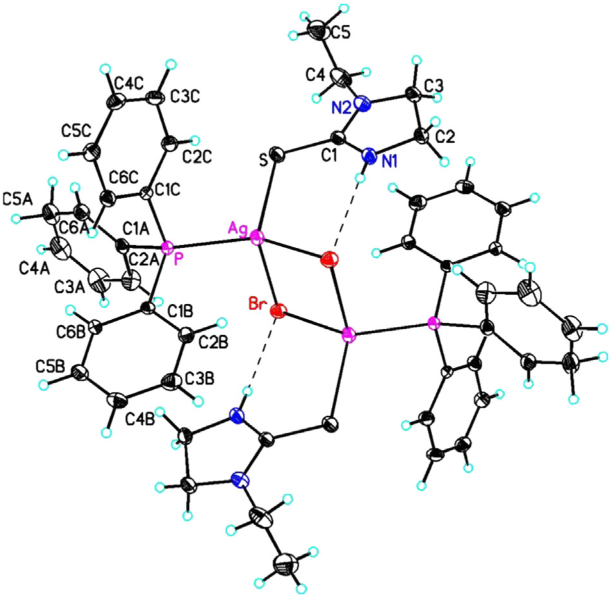


Fig. 8. Molecular structure of [$Ag_2(\mu\text{-}Br)_2(\kappa^1\text{-}S\text{-}C_3H_5NS(N\text{-}Et))_2(PPh_3)_2$] **8**.

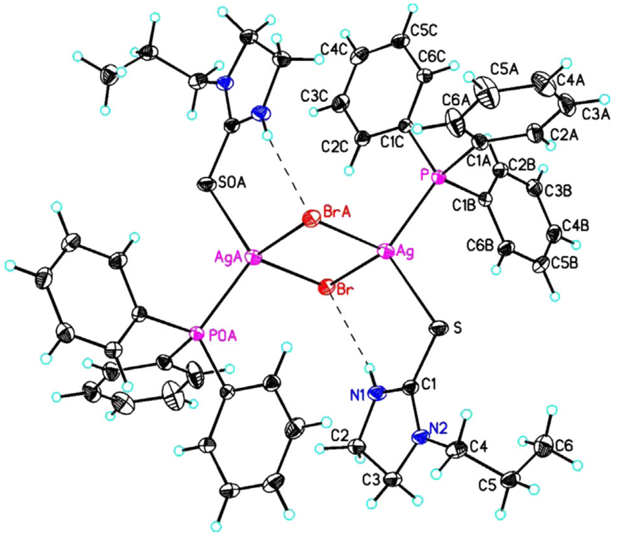


Fig. 9. Molecular structure of $[Ag_2(\mu\text{-}Br)_2(\kappa^1\text{-}S\text{-}C_3H_5NS(N{-}Pr^n))_2(PPh_3)_2]$ **9**.

distances lie in the range 1.690(4)–1.702(4)° (Table 4) and these are similar to the terminally bonded thio-ligands in **4**, **6** and **11**. Interestingly, in bromo-bridged dimer of pyrimidine-2-thione, $[Ag_2(\mu\text{-}Br)_2(\kappa^1\text{-}S\text{-}L)_2(PPh_3)_2]$ **15** (L = pyrimidine-2-thione) [18], the C–S distance was 1.689(4), similar to those values in the above mentioned dimers. The C–S distances observed in sulfur-bridged dinuclear $[Ag_2X_2(\mu\text{-}S\text{-}L)_2(PPh_3)_2]$ complexes (L = C_5H_5NS; X = Cl, **16**, Br, **17**) [19] are longer as anticipated.

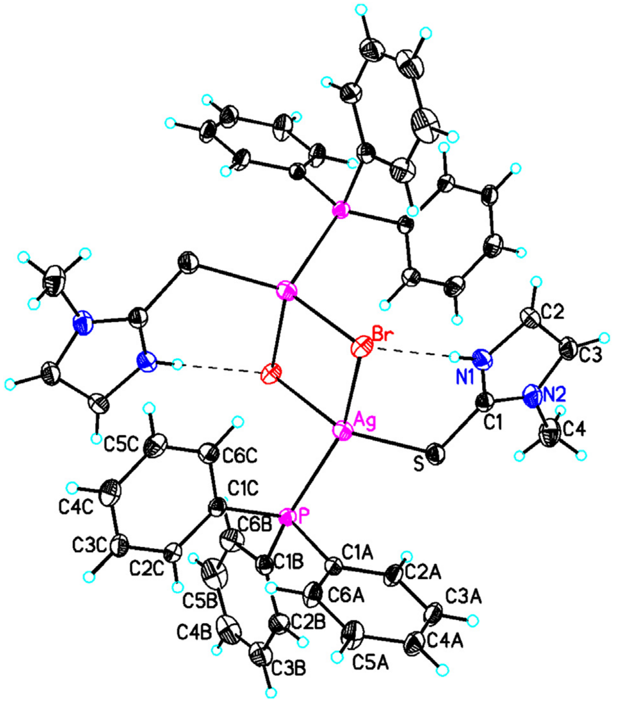


Fig. 10. Molecular structure of $[Ag_2(\mu\text{-}Br)_2(\kappa^1\text{-}S\text{-}C_3H_3NS(N{-}Me))_2(PPh_3)_2]$ **10**.

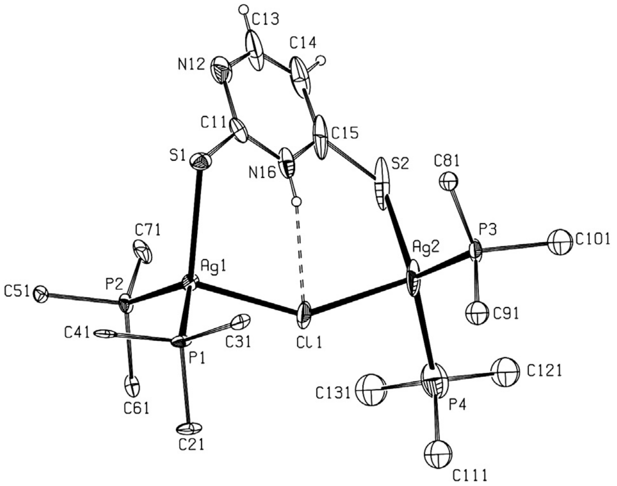


Fig. 11. Molecular structure of $[Ag_2(\mu\text{-}Cl)(\mu\text{-}S,S\text{-}C_4H_4N_2S_2)(PPh_3)_4]$ (**12**)(see Supplementary Fig S1 for**13**).

From Table 4, some interesting observations about the type of a bridge between two Ag metal centers in the mixed ligand complexes under study made are given as follows. It is found that the thio-ligand, namely, pyridine-2-thione (**16**, **17**) with a C:N ratio of 5:1 favored sulfur-bridging, while pyrimidine-2-thione with C:N ratio of 2:1 favored halogen-bridging (**15**). In the dimers **1**–**3**, **7**–**10** with C:N ratio of 3:2 or 3:1, all favored halogen-bridging. As regards 2,4-dithiouracil, each sulfur binds to one Ag metal center in κ^1-S mode only (**12**, **13**) and does not bridge two Ag metals unlike that in pyridine-2-thione complexes **16** and **17**. A plausible explanation for the behavior as highlighted above is attributed to the reduction in Lewis basicity of exo-cyclic sulfur when a ring contains two electronegative nitrogen atoms, i.e. low C:N ratio. This makes sulfur more electronegative by contracting charge around sulfur nucleus. It paves way for bridging by the halogens in various complexes discussed above. Alternatively, it can be argued that the halogen bridges existing in silver(I) halides (polymeric) are not cleaved by thio-ligands when C:N ratio is low. The trend pertains to the mixed ligand complexes with a thione and a PPh_3 ligand as given in Table 4 and the C:N ratio considered is of the ring carbons ands nitrogens only.

The rupture of the silver-halogen bonds as found in the dinuclear **12** and **13** complexes is attributed to the geometric positions of the sulfur atoms which in their bid to bind to two Ag metals centers knock out one halogen while second halogen is retained which acts as a bridge. This leads to an unusual eight membered ring formed by two Ag, one halogen, two sulfur, two carbons and one nitrogen atoms. It is observed that dimers **2**, **3**, **7**–**10** have Ag···Ag distances in the range, 3.350(1)–3.474(1) Å, which are close to twice the sum of van der Waals radius of Ag atom, 3.40 Å [30,31]; dimer **1** has Ag···Ag distance of 3.697(2). All these distances are much shorter than those found in dimers **12**, **13**, **16** and **17** {3.821(10–5.148(1)) Å, Table 4}. The shortest Ag···Ag distances

Table 4
A comparative account of some important distances.

	C–S, Å	Ag···Ag, Å	Type of bridge	[Ref]
1	1.693(3)	3.697(2)	$Ag(\mu\text{-}Cl)_2Ag$	This work
2	1.692(2)	3.402(2)	$Ag(\mu\text{-}Cl)_2Ag$	This work
3	1.701(2)	3.442(1)	$Ag(\mu\text{-}Cl)_2Ag$	This work
7	1.694(2)	3.421(1)	$Ag(\mu\text{-}Br)_2Ag$	This work
8	1.702(4)	3.474(1)	$Ag(\mu\text{-}Br)_2Ag$	This work
9	1.691(2)	3.350(1)	$Ag(\mu\text{-}Br)_2Ag$	This work
10	1.690(4)	3.438(1)	$Ag(\mu\text{-}Br)_2Ag$	This work
12	1.729(5); 1.744(9)	5.028(1)	$Ag(\mu\text{-}Cl)(\kappa^1S, \kappa^1S)_2$ Ag	This work
13	1.704(8); 1.789(10)	5.148(1)	$Ag(\mu\text{-}Br)(\kappa^1S, \kappa^1S)_2$ Ag	This work
15	1.689(4)	–	$Ag(\mu\text{-}Br)_2Ag$	[18]
16	1.722(2)	3.844(1)	$Ag(\mu\text{-}S)_2Ag$	[19]
17	1.717(2)	3.821(1)	$Ag(\mu\text{-}S)_2Ag$	[19]

3.350(1)–3.474(1) are found when the five membered rings have alkyl substituent at one N-atom of the ring.

4. Conclusion

In the synthesis of complexes **1**–**11**, it was found that Ag(I) be first bonded to PPh_3 in acetonitrile and after removal of the solvent, it be bonded to the thione sulfur in chloroform. The C:N ratio of a heterocyclic ring (excluding the substituent at N) appeared to affect the nature of bridging between two metals. The thio-ligand substituents affected silver–silver distances. Finally, the rupture of the silver–halogen bonds by a thio-ligand (dithiouracil in the present case) and the formation of an eight membered metallacyclic ring are rare features encountered in metal–heterocycilic thione chemistry. This study makes a significant contribution to silver(I) halide–heterocyclic thione chemistry by reporting twelve new silver(I) complexes which are structurally characterized.

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Appendix A. Supplementary material

CCDC 911388–911399 for compounds **1**–**4**, **6**–**13** respectively contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Appendix B. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2013.08.020.

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