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The influence of substituents at the C^2 carbon of thiosemicarbazones on bonding and nuclearity of silver(I) complexes

Tarlok S. Lobana [a,*], Sonia Khanna [a], Geeta Hundal [a], Ben-Jie Liaw [b], Chen W. Liu [b]

[a] Department of Chemistry, Guru Nanak Dev University, Amritsar 143 005, India
[b] Department of Chemistry, National Dong Hwa University, Hualien 974, Taiwan

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ABSTRACT

Several thiosemicarbazones of the type ($R^1R^2C^2{=}N^3{-}N^2H{-}C(=S)N^1H_2$) were reacted with silver salts, yielding a variety of complexes with different ligand coordination modes, nuclearities and stoichiometries. Reaction of silver(I) chloride with 2-benzoylpyridine thiosemicarbazone, HL^1, has formed a sulfur-bridged dimer, $[Ag_2Cl_2(\mu\text{-}S\text{–}HL^1)_2(PPh_3)_2]$ **2**, while a similar reaction with 2-acetylpyridine thiosemicarbazone, HL^2, has formed a mononuclear complex $\{AgCl(\eta^1\text{-}S\text{–}HL^2)_2(PPh_3)\}$ **1**, with an unusual Ag:ligand:PPh_3 stoichiometry of 1:2:1. Reaction of silver(I) nitrate/acetate with benzophenone thiosemicarbazone, HL^3, and acetone thiosemicarbazone, HL^4, have yielded mononuclear complexes, $[Ag(ONO_2)(\eta^1\text{-}S\text{–}HL^3)(PPh_3)_2]$ **3**, and $[Ag(N^3,S\text{–}HL^4)(PPh_3)_2]X$ (X=NO_3 **4**, CH_3COO **5**). In complexes **1** and **3** and in dimeric complex **2**, the ligands exhibit the usual η^1-S-bonding and μ-S-bridging coordination commonly observed for thiosemicarbazone ligands with tetrahedral coinage metal ions. In complexes **4** and **5**, however, weak binding properties of nitrate or acetate anions to silver favored N^3,S-chelation with the methyl substituents at the C^2 carbon of the thiosemicarbazones.

1. Introduction

Thiosemicarbazones, an important class of N–S donor ligands, have displayed variable bonding properties in their complexes and have shown use in a variety of different applications [1–7]. Among coinage metals, copper in its divalent state has been intensively investigated [8,9c], while reports on the chemistry of Cu^I, Ag^I, Au^I are limited [9]. Recently, from our lab, several Cu^I halide complexes of thiosemicarbazones with triphenylphosphine coligands have been reported [10]. In a recent study of Ag^I–thiosemicarbazone complexes, it was observed that thiosemicarbazone ligands with alkyl or aryl rings at the C^2 carbon have formed halogen bridged dimers, $[Ag_2(\mu\text{-}X)_2(Htsc)_2(PPh_3)_2]$ {R^1 = Ph, R^2 = H, X = Br; R^1 = R^2 = Me, X = Br; R^1 = Ph, R^2 = Me, X = Cl, Br, see Chart 1 for substitution patterns of the thiosemicarbazones}, but with five membered rings such as pyrrole or thiophene, only sulfur-bridged dimers $[Ag_2X_2(\mu\text{-}S\text{–}Htsc)_2(PPh_3)_2]$ {R^1 = pyrrole, R^2 = H, X = Br; R^1 = thiophene, R^2 = H, X = Cl} were isolated [11]. For R^1 = pyridine, R^2 = H, only monomer complexes $[AgX(\eta^1\text{-}S\text{–}Htsc)(PPh_3)_2]$ (X = Cl, Br, I) were isolated [11].

The interest into the chemistry of thiosemicarbazone also pertains to their utility in the biosciences as anticancer, antibacterial and antifungal agents and in the analytical field as ion sensors [5–7]. For example, thiosemicarbazone derivatives of copper(II) – especially with pyridyl substituents at the C^2 carbon have proved to be more effective as anticancer or antimicrobial agents than the ligand by itself, probably due to the increased lipophilicity of the complexes as compared to the free ligand alone [8], and the complexes have also shown promising results in vivo. In view of the still limited investigations into the chemistry of silver(I) thiosemicarbazones as described above, we thus intended to investigate the coordination chemistry of particularly pyridyl based thiosemicarbazones with silver(I). In the present paper, we investigate the influence of different combinations of pyridyl, phenyl and methyl substituents at the C^2 carbon of thiosemicarbazones on the bonding patterns and the nuclearity of complexes with silver(I) halides and psuedohalides (Chart 1).

2. Experimental

2.1. Materials and techniques

Silver(I) nitrate, silver(I) acetate, sodium chloride, sodium bromide and triphenylphosphine were procured from Aldrich Chemicals Ltd. and used as received. Silver(I) halides (X = Cl, Br) were freshly prepared by reacting silver(I) nitrate with sodium chloride or bromide in methanol. 2-Benzoylpyridine thiosemicarbazone (HL^1), 2-acetylpyridine thiosemicarbazone (HL^2), benzophenone thiosemicarbazone (HL^3) and acetone thiosemicarbazone (HL^4)

* Corresponding author. Tel.: +91 183 22 57604; fax: +91 183 22 58820.
E-mail address: tarlokslobana@yahoo.co.in (T.S. Lobana).

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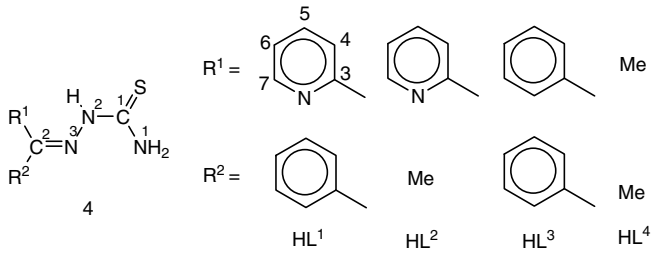


HL[1] = 2-benzoylpyridine thiosemicarbazone
HL[2] = 2-acetylpyridine thiosemicarbazone
HL[3] = benzophenone thiosemicarbazone
HL[4] = acetone thiosemicarbazone

Chart 1.

were prepared using the literature methods [10a,12]. C, H and N analyses were obtained with a Thermoelectron FLASHEA1112 CHNS analyzer. Infrared spectra were recorded from KBr pellets in the range 4000–200 cm^{-1} on a Pye–Unicam SP-3-300 spectrophotometer. Melting points were determined with a electrically heated Gallenkamp 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 the 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 the external standard with $\delta = 0$.

2.2. Synthesis of the complexes

2.2.1. [AgCl(η^1-S–HL^2)$_2$(PPh$_3$)] (**1**)

To AgCl (0.025 g, 0.17 mmol) suspended in acetonitrile (15 mL) was added ligand HL^2 (0.034 g, 0.17 mmol), and stirring was continued for 24 h. To the white solid formed was added solid PPh_3 (0.046 g, 0.17 mmol), which partially cleared the solution. Addition of another mole of PPh_3(0.046 g, 0.17 mmol) resulted in the formation of a clear solution, which was filtered and kept for crystallization. Slow evaporation yielded crystals of [AgCl(HL^2)$_2$(PPh$_3$)] (**1**) along with that of the known [AgCl(PPh$_3$)]$_4$ cubane (50%) which were manually separated (**1** white, 37 %, m.p. 190–192 °C). *Anal.* Calc. for $C_{34}H_{35}AgClN_8PS$: C, 51.38; H, 4.41; N, 14.10. Found: C, 51.66; H, 4.89; N, 14.25%. Main IR peaks (KBr, cm^{-1}): ν(N–H) 3542s, 3427s, 3412m, 3280b (–NH_2–), 3153m (–NH–); ν(C=N) + δNH_2 + ν(C=C) 1585s, 1550s, 1521s; ν(C=S) 770s, 836s; ν(C–N) 1050s; ν(P–C_{Ph}) 1095s. The complex is soluble in $CHCl_3$ and partially in CH_3CN.

2.2.2. [Ag$_2$Cl$_2$(μ-S–HL^1)$_2$(PPh$_3$)$_2$] (**2**)

Compound **2** was prepared in a similar fashion as compound **1**. (Yellow, 57 %, m.p. 183–185 °C). *Anal.* Calc. for $C_{62}H_{54}Ag_2Cl_2N_8P_2S_2$: C, 56.20; H, 4.08; N, 8.46. Found: C, 56.60; H, 4.29; N, 8.93%. Main IR peaks (KBr, cm^{-1}): ν(N–H) 3417s, 3217s (–NH_2–); ν(N–H) 3170 cm^{-1}; ν(C=N) + δNH_2 + ν(C=C) 1604s, 1602s, 1477s; ν(C=S) 816s, 895s; ν(C–N) 995s; ν(P–C_{Ph}) 1096s. The complex is soluble in $CHCl_3$ and partially in CH_3CN.

2.2.3. [Ag(ONO$_2$)(η^1-S–HL^3)(PPh$_3$)$_2$] (**3**)

To $AgNO_3$ (0.025 g, 15 mmol) in CH_3CN (15 mL) was added PPh_3 (0.076 g, 30 mmol) and stirring was continued at a temperature of 50–60 °C for 2 h. The solid ligand HL^3 was added (0.037 g, 15 mmol) to the clear hot solution, and stirring was continued for another 30 min after switching off heating. The resulting clear solution was filtered and kept for crystallization to form light yellow colored crystals. The complex is highly soluble in $CHCl_3$. (Yellow, 69%, m.p. 185–187 °C). *Anal.* Calc. for $C_{50}H_{43}AgN_4O_3P_2S$: C, 63.17; H, 4.53; N, 5.90. Found: C, 63.03; H, 4.64; N, 6.23%. Main IR peaks (KBr, cm^{-1}): ν(N–H) 3458s, 3321s (–NH_2–), 3141m (–NH–); ν(NO) 1434s, 1471s, 1369b; ν(C=N) + δNH_2 + ν(C=C) 1608s, 1565s, 1500s; ν(C=S) 823s (thioamide moiety); ν(C–N) 1184m, 1064s; ν(P–C_{Ph}) 1094s. The complex is soluble in $CHCl_3$ and partially in CH_3CN.

2.2.4. [Ag(N^3,S–HL^4)(PPh$_3$)$_2$](NO$_3$) (**4**)

To $AgNO_3$ (0.025 g, 0.15 mmol) in CH_3CN (15 mL) was added HL^4 (0.020 g, 15 mmol) and stirring was continued for 2 h. To the white solid formed was added PPh_3 (0.039 g, 0.15 mmol), which partially cleared the solution. Addition of another mole of PPh_3 (0.039 g, 0.15 mmol) resulted in the formation of a clear solution, which was filtered and kept for crystallization. The complex is soluble in $CHCl_3$. (White, 65%, m.p. 154–156 °C). *Anal.* Calc. for $C_{40}H_{39}AgN_4O_3P_2S$: C, 58.14; H, 4.72; N, 6.78. Found: C, 58.42; H, 3.98; N, 6.81% Main IR peaks (KBr, cm^{-1}): ν(N–H) 3375s, 3325m (–NH_2–), 3186m (–NH–); ν(NO) 1359s, 1301b; ν(C=N) + δNH_2 + ν(C=C) 1645b, 1562s; ν(C=S) 823s (thioamide moiety); ν(C–N) 1041s, 1068s; ν(P–C_{Ph}) 1095s. The complex is soluble in $CHCl_3$ and partially in CH_3CN.

2.2.5. [Ag(N^3,S–HL^4)(PPh$_3$)$_2$](CH$_3$COO) (**5**)

To $Ag(OOCCH_3)$ (0.025 g, 0.15 mmol) in acetone (15 mL) was added HL^4 (0.020 g, 0.15 mmol) and stirring was continued for 2 h. To the white solid formed, was added PPh_3 (0.039 g, 0.15 mmol), which partially cleared the solution. Addition of another mole of PPh_3 (0.039 g, 0.15 mmol) resulted in the formation of a clear solution, which was filtered and kept for crystallization. The complex is soluble in $CHCl_3$. Crystals were grown from an acetone solution at room temperature. (White, 69%, m.p. 150–152 °C). *Anal.* Calc. for $C_{42}H_{42}AgN_3O_2P_2S$: C, 61.26; H, 5.11; N, 5.43. Found: C, 61.62; H, 5.55; N, 5.43%. Main IR bands (KBr, cm^{-1}): ν(N–H) 3285b (–NH_2–), 3130m (–NH–); $\nu(C–O)_{as}$ 1670b, 1585s; $\nu(C–O)_{sym}$ 1404b; ν(C=N) + δNH_2 + ν(C=C) 1564s, 1477m; ν(C=S) 837s (thioamide moiety); ν(C–N) 1152s, 997s; ν(P–C_{Ph}) 1093s. The complex is soluble in $CHCl_3$ and CH_3CN.

3. X-ray crystallography

A suitable crystal of complex **1** was mounted on Bruker AXS SMART APEX CCD diffractometer and likewise crystals of **4** and **5** were mounted on a Bruker APEX II diffractometer with graphite monochromatised Mo Kα radiation (λ = 0.71073 Å). The unit cell dimensions and intensity data were measured at 100(2) K for **1** and at 273(2) K for **4** and **5**. Data were reduced and corrected for absorption using SMART and SAINT (**1**) [13a] or XCAD-49 (**4** and **5**). 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 times (all others) that of the adjacent carbon or oxygen atom.

Suitable light yellow crystals of complexes **2** and **3** were mounted on a Siemens P4 diffractometer and data were collected using a scanning mode with graphite monochromatised Mo Kα radiation (λ = 0.71069 Å). Unit cell dimensions and data were collected at 295(2) K. Cell parameters were refined using 25 reflections in the θ range of 1.70–29.96° using XSCANS [13b]. The data were corrected for Lorentz and polarization effects and a psi-scan absorption correction was also applied. The structures were solved

Table 1
Crystallographic data for complexes **1**–**5**

	1	2	3	4	5
Empirical formula	$C_{34}H_{35}AgClN_8PS$	$C_{62}H_{54}Ag_2Cl_2N_8P_2S_2$	$C_{50}H_{43}AgN_4O_3P_2S$	$C_{40}H_{39}AgN_4O_3P_2S$	$C_{42}H_{42}AgN_3O_2P_2S$
M.wt.	794.11	1323.83	949.75	825.62	822.66
Crystal color	colorless	yellow	pale yellow	colorless	colorless
Crystal system	triclinic	triclinic	triclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P2_1/c$
a (Å)	8.0367(5)	11.804(2)	9.658(5)	12.9850(7)	13.078(2)
b (Å)	10.7546(7)	12.208(2)	9.938(5)	11.2547(6)	11.407(2)
c (Å)	21.1659(14)	12.969(2)	24.028(5)	26.6850(14)	26.611(5)
V (Å^3)	1780.3(2)	1494.6(4)	2250.4(17)	3870.5(4)	3948.5(12)
α (°)	78.391(1)	116.91(1)	89.430(5)	90	90
β (°)	83.457(1)	92.23(1)	87.890(5)	97.025(2)	95.965(3)
γ (°)	88.772(1)	112.04(1)	77.540(5)	90	90
Z	2	1	2	4	4
D_{calc} (Mg m^{-3})	1.481	1.471	1.402	1.417	1.384
μ(Mo Kα) (mm^{-1})	0.840	0.914	0.612	0.700	0.683
Reflections collected	18428	5451	9454	59092	51544
Unique reflections (R_{int})	8804 (0.0355)	5183 (0.0230)	8491 (0.0460)	9659 (0.0957)	9456 (0.0204)
Final R indices					
[$I \geqslant 2\sigma I$], R_1 and wR_2	0.0427, 0.1013	0.0319, 0.0852	0.0364, 0.0949	0.0450, 0.1057	0.0341, 0.0913

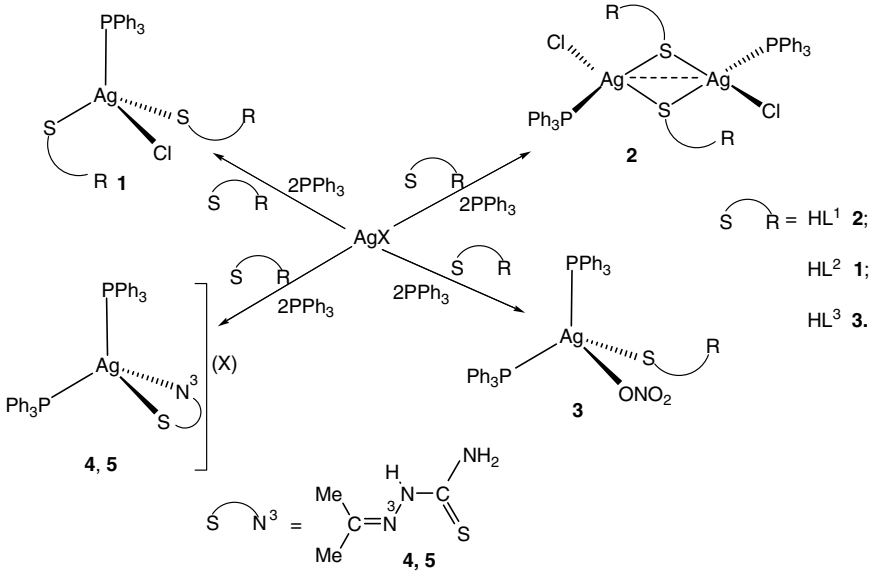
by direct methods and refined by Full-matrix least-squares refinement techniques on F^2 using SIR-92 and SHELXL-97 [13c]. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were attached geometrically riding on their respective carrier atoms with Uiso being 1.5, 1.2 and 1.2 times the Uiso of their carrier methyl, methylene and aromatic carbon atoms, respectively. Scattering factors from the International Tables for X-ray crystallography were used [13d]. Data reduction, structure solution, refinement and drawing of molecular graphics were performed using SHELXTL-PC [13e] and WINGX [13f]. Table 1 gives crystal data for complexes.

4. Results and discussion

4.1. Synthesis

Several thiosemicarbazones of the type ($R^1R^2C^2$=N–NH–C(=S)N^1H_2) were reacted with a selection of silver salts (see Chart 1 for the substitution patterns of the ligands). Addition of triphenylphosphine to the reaction mixtures yielded a variety of complexes with different ligand coordination modes, nuclearities and stoichiometries. An overview of reaction conditions and products formed is given in Scheme 1.

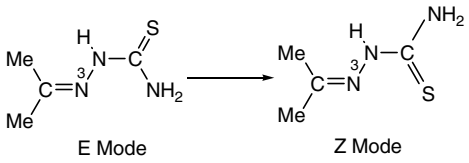
Silver(I) chloride suspended in acetonitrile slowly reacted with HL^2 (R^1 = py and R^2 = Me) over a period of 24 h and formed white insoluble solid and the addition of two moles of triphenylphosphine completely dissolved the solid. The clear solution on slow evaporation at room temperature yielded crystals of tetrahedral complex [AgCl(HL^2)$_2$(PPh_3)] **1**, with an unusual stoichiometry (Ag:Htsc:PPh_3: 1:2:1) along with crystals of the known cubane complex, [AgCl(PPh_3)]$_4$ [14]. Complex **1** differs from the known tetrahedral monomers such as [AgCl(η^1-S–Hpytsc)(PPh_3)$_2$] **6** (Hpytsc = pyridine-2-carbaldehyde thiosemicarbazone) [11]. Reaction of silver(I) chloride with HL^1ligand (R^1 = py and R^2 = Ph) did not form the similar complex, rather a sulfur-bridged dimer, [Ag_2Cl_2(μ-S–HL^1)$_2$(PPh_3)$_2$] **2** along with the known cubane complex [AgCl(PPh_3)]$_4$ were formed. Thus the formation of **2** is analogous to the more general trend of formation of the sulphur-bridged dimers, [Ag_2X_2(μ-S–Htsc)$_2$(PPh_3)$_2$], {R^1 = pyrrole, R^2 = H, X = Br; R^1 = thiophene, R^2 = H, X = Cl}, reported in the literature [11]. It is pointed



Scheme 1.

out here that only 1:1:2 (Ag:Htsc:PPh_3) molar ratio yielded the crystalline products **1** and **2**, and stoichiometry of these complexes is controlled by the nature of the substituents at C^2 carbon. Thus the substitution of the hydrogen atom at the C^2 carbon by a methyl group (sp3 carbon) was able to prevent the binding of a second PPh_3 ligand to the Ag^I center in case of **1.** Introduction of a similarly bulky phenyl substituent at C^2 also did prevent the addition of two phosphine ligands and no tetrahedral monomeric complex either similar to **1** or **6** was formed, and instead yielded a sulfur-bridged dimer, $[Ag_2Cl_2(\mu\text{-}S\text{–}HL^1)_2(PPh_3)_2]$ **2.** Reaction of HL^1 or HL^2 with silver(I) nitrate/acetate led to decomposition and no product could be identified.

Reaction of silver(I) nitrate or acetate with HL^4 ($R^1 = R^2 = Me$) yielded insoluble solids which were reacted with two moles of phosphine ligands and clear solutions formed on slow evaporation at room temperature yielded $[Ag(N^3,S\text{–}HL^4)(PPh_3)_2](NO_3)$ **4** and $[Ag(N^3,S\text{–}HL^4)(PPh_3)_2](CH_3COO)$ **5**, with an N^3, S-chelation mode (Scheme 1). Similar bonding was also observed in one mononuclear tetrahedral complex, $[Cu(HL^4)_2](Cl)$ [9a]. Thus with the methyl substituents at C^2 carbon and with the weak binding to silver by the nitrate or acetate anions vis-à-vis halide ions, HL^4ligand changes conformation from E-mode to Z-mode for chelation to the metal center.



This behaviour of HL^4 is different from that with silver(I) bromide which yielded bromo-bridged dimer $[Ag_2(\mu\text{-}Br)_2(HL^4)_2(PPh_3)_2]$ [11]. Silver(I) nitrate did not react with the ligand HL^3($R^1 = R^2 = Ph$). Thus silver(I) nitrate was first reacted with triphenylphosphine and to the clear solution was added the HL^3 ligand. Slow evaporation of the solution yielded crystals of $[Ag(ONO_2)(\eta^1\text{-}S\text{–}HL^3)(PPh_3)_2]$ **3**. Formation of **3** is analogous to the reaction of copper(I) halides with HL^3, wherein analogous tetrahedral $[CuX(\eta^1\text{-}S\text{–}HL^3)(PPh_3)_2]$ (X = Cl, Br) complexes were obtained [10a]. HL^3 did not react with silver(I) chloride neither directly or nor via reaction of $[AgCl(PPh_3)]_4$ with HL^3. Thus the behaviour of HL^3 and HL^4 is clearly different, and the nature of the substituents (Ph, Ph, **3** versus Me, Me, **4**, **5**) appears to control the final products.

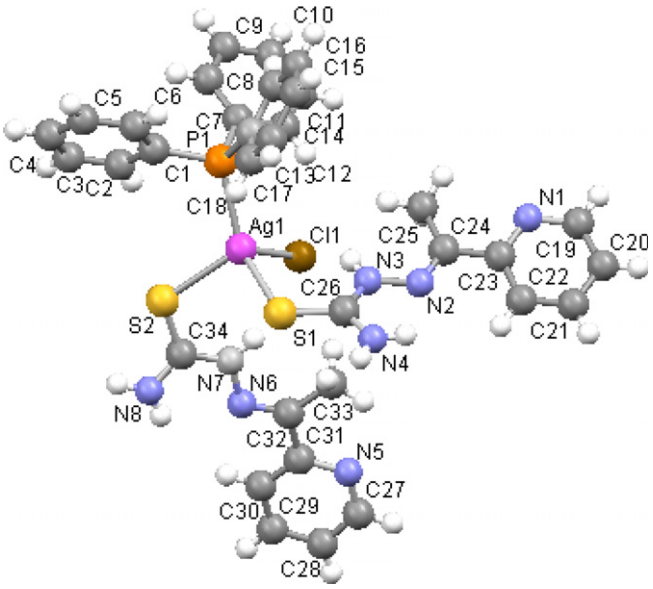


Fig. 1. Molecular structure of complex **1**.

4.2. Structures of complexes

The complexes were analyzed using single crystal X-ray diffraction. Complexes **1** and **2** crystallized in triclinic crystal system while complexes **3**–**5** crystallized in monoclinic system. Complex **2** is dinuclear while other complexes (**1**, **3**–**5**) are mononuclear. Table 2 shows important bond parameters and coordination modes of thiosemicarbazone ligands.

Silver(I) is coordinated by two sulfur atoms, one phosphorus and one chlorine atoms in mononuclear complex $[AgCl(\eta^1\text{-}S\text{–}HL^2)_2(PPh_3)]$ **1**(Fig. 1). The uncommon stoichiometry of this complex results in a slight deviation of both bond angles and distances relative to the commonly known tetrahedral Ag(I) complexes, such

Table 2
A comparison of important bond distances (Å) and bond angles (°) for complexes **1**–**5** with other related complexes

Complex no.	X, (mode)	Ag–S	Ag–X (Ag–P)	P–Ag–P	P–Ag–X	S–Ag–X	P–Ag–S
1	Cl (η^1-S)	2.5330(7), 2.6113(7)	2.6509(7) (2.4178(8))		109.63(2)	101.35(2), 101.01(2)	129.88(3), 112.35(2)
3	O (η^1-S)	2.5627(13)	2.557(3) (2.4689(13), 2.4956(10))	122.86(3)	93.80(8), 108.10(7)	97.62(7)	128.37(4), 100.80(3)
4	N^3 (N^3,S)	2.5723(10)	2.484(3) (2.4416(9), 2.4625(10))	129.95(3)	109.06(8), 111.98(7)	73.31(7)	113.43(3), 104.76(4)
5	N^3 (N^3,S)	2.5618(7)	2.4642(18) (2.4625(7), 2.4800(7))	128.155 (19)	110.88(5), 111.25(5)	74.07(4)	105.40(2), 114.13(2)
6 [11]	Cl (η^1-S)	2.6284(7)	2.6448(7) (2.4409(7), 2.4879(7))	120.03(2)	101.98(2), 109.26(2)	102.72(2)	102.97(2), 117.54(2)
		Ag–S	Ag–X (Ag–P)	Ag–S–Ag, S–Ag–S	P–Ag–X (S–Ag–X)	P–Ag–S	Ag···Ag
2	Cl (μ-S)	2.6772(10) 2.6715(10)	2.4839(10) (2.4318(10))	88.98(3), 91.02(3)	127.16(4), 107.21(4) (104.12(3))	102.48(3) 117.08(3)	3.748(4)
7 [11]	Br, (μ-S)	2.6070(9) 2.6851(9)	2.6857(4) (2.4394(9))	82.96(2), 97.04(2)	113.66(2), 111.31(2) (113.66(2))	114.88(3) 112.60(3)	3.5057(0)
8 [11]	Cl, (μ-S)	2.611(2) 2.876(2)	2.520(2) (2.428(18))	68.33(6), 111.67(6)	124.85(6), 106.53(6) (93.97(3))	113.45(6) 104.36(6)	3.0902(15)

$[AgCl(\eta^1\text{-}S\text{–}Hpytsc)(PPh_3)_2]$ (**6**) (Hpytsc = pyridine-2-carbaldehyde thiosemicarbazone), $[Ag_2Br_2(\mu\text{-}S\text{–}Hptsc)_2(PPh_3)_2]$ (**7**) (Hptsc = pyrrole-2-carbaldehyde thiosemicarbazone), $[Ag_2Cl_2(\mu\text{-}S\text{–}Httsc)_2(PPh_3)_2]$ (**8**) (Httsc = thiophene-2-carbaldehyde thiosemicarbazone) [11].

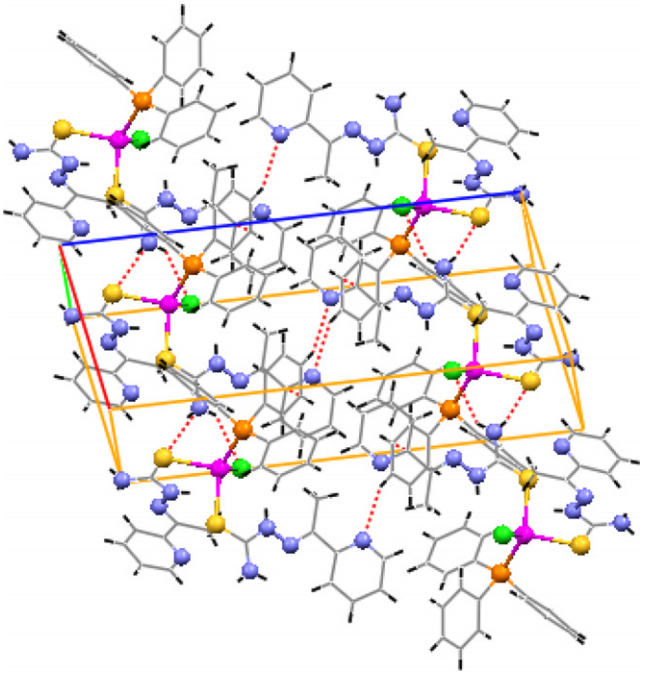


Fig. 2. Packing diagram of complex **1**.

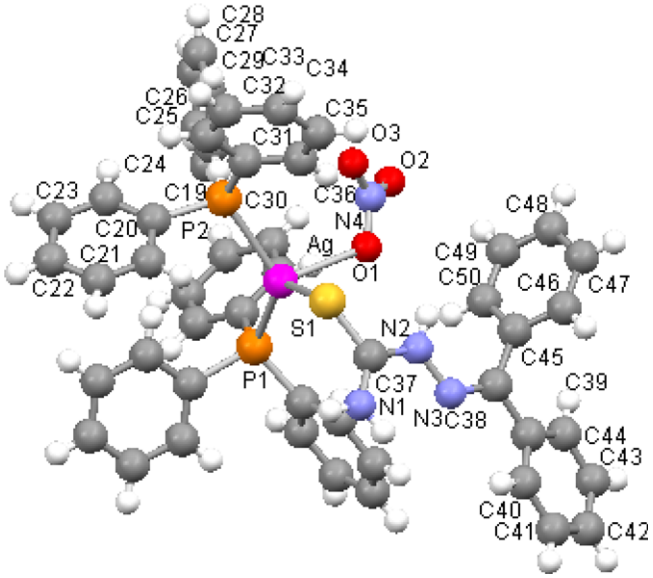


Fig. 3. Molecular structure of complex **3**. (Hydrogen atoms have been omitted for clarity.)

as [AgCl(η^1-S–Hpytsc)(PPh_3)$_2$] **6** (Hpytsc = pyridine-2-carbaldehyde thiosemicarbazone) [11]. The packing of complex **1** shows intermolecular $N^1H\cdots Cl$ and N^1–$H\cdots S$ hydrogen bonds forming 1D polymeric chains, which are further interlinked via intermolecular C–$H_{Ph-P}\cdots N^4_{(py)}$ hydrogen bonds to form a 2D structure (Fig. 2). Molecular structure of complex [Ag(ONO_2)(η^1-S–HL^3)(PPh_3)$_2$] **3** is similar to that of related tetrahedral complex **6**, except for the presence of the O-bonded nitrate group in lieu of the chlorine atom (Fig. 3). The presence of the weakly coordinating nitrate group significantly alter the bond angles and distances of **3** relative to those of **6** [11]. The packing diagram of **3** shows the presence of intermolecular $-HN^1H\cdots O$ type of hydrogen bonds between amino and nitrate groups resulting in a 1D linear chain parallel to the *a* axis. The linear chains are further extended into a 2D network by means of $CH_{Ph}\cdots S$ and $CH_{Ph}\cdots O_{NO3}$ interactions involving phenyl rings of PPh_3 (Figs. 4a and 4b).

The thiosemicarbazone ligand is N^3, S-chelated in complex [Ag(N^3,S–HL^4)(PPh_3)$_2$](NO_3) **4** (Fig. 5). The cation is linked to nitrate via its C–$H_{(methyl)}\cdots O$, N^2-$H\cdots O$ and N^1–$H\cdots O$ hydrogen bonds. Two units of **4** combine via second N^1–$H\cdots O$ hydrogen bonds forming a dimer (Fig. 6). The bonding and packing pattern of [Ag(N^3,S–HL^4)(PPh_3)$_2$](CH_3COO)] **5** is similar to **4**.

Finally the dinuclear complex [Ag_2Cl_2(μ-S–HL^1)$_2$(PPh_3)$_2$] **2** is sulfur bridged and its central $Ag_2(\mu\text{-}S)_2Ag$ core forms a parallelogram. Each silver atom is further coordinated to a terminal chlorine and one P atom of PPh_3 (Fig. 7). The bond parameters and core angles are comparable to other sulfur-bridged dimers reported in the literature (Table 2) [11]. Complex **2** shows the presence of intramolecular $-HN^1H\cdots Cl$ and $N^2H\cdots N^4$ hydrogen bonds and two dimeric molecules are further linked via short $CH\cdots Cl$ contacts involving phenyl rings of PPh_3 resulting in 1D polymeric chain. The chain is extended in 2D via intermolecular $CH\cdots\pi$ interactions (Fig. 8).

5. IR and NMR spectral studies

IR spectroscopy of all complexes confirmed the presence of the individual ligands and counterions via their ν(N–H), ν(C–N), ν(C=C), ν(C=N), and ν(N–O), ν(P–C) vibrational modes. The ν(C=S) thioamide bands are located at 770–837 cm^{-1}, which suggests (in agreement with the X-ray data) a significant weakening of the C=S double bond in all complexes. The ^{1}H NMR spectra of complexes **1**–**4** reveal the presence of -N^2H, -N^1H_2, methyl and ring proton signals generally at low field relative to their corresponding free ligands (Table 3). The ^{31}P NMR spectra of tetrahedral complexes**1**, **3**–**5** showed coordination shifts ($\delta_{complex} - \delta_{ligand}$) comparable to the literature reports on tetrahedral silver(I)–thiosemicarbazone complexes [11]. An additional band at δ 30.81 ppm in **3** reveals the formation of another species, probably a sulfur-bridged dimer in the solution state.

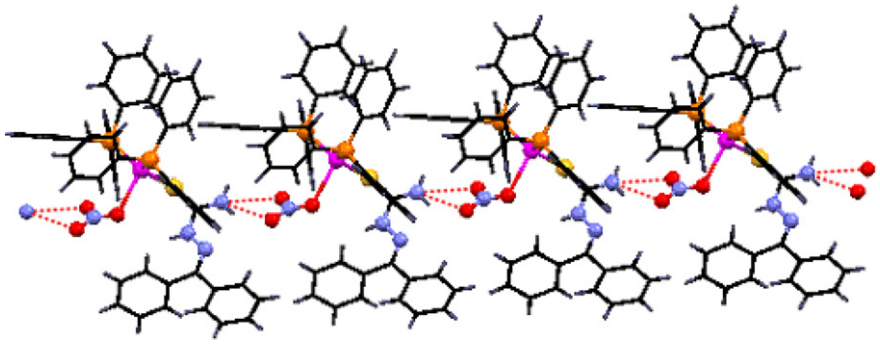


Fig. 4a. Formation of a 1D linear chain due to amine N1 and NO_3^- hydrogen bonding interactions parallel to *a* axis.

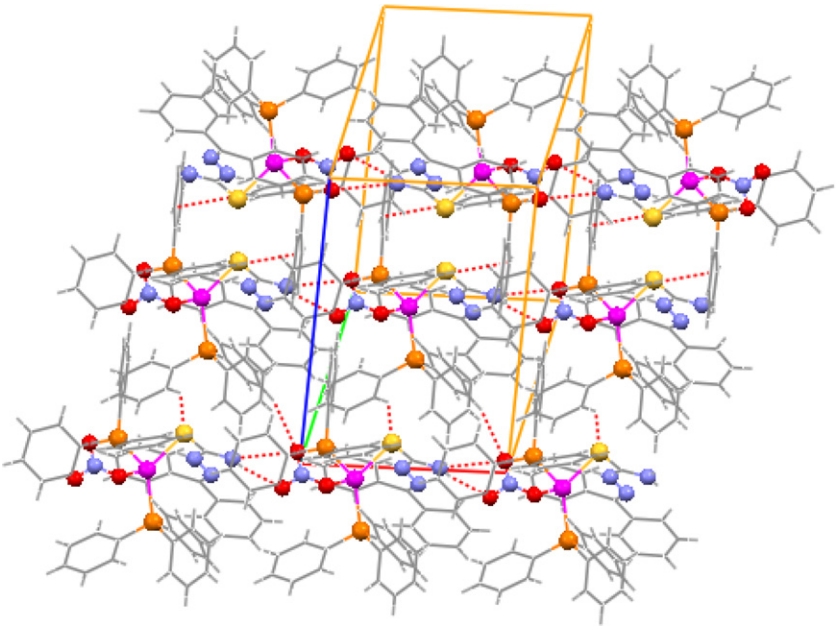


Fig. 4b. Formation of a 2D network in the *ab* plane of complex **3**.

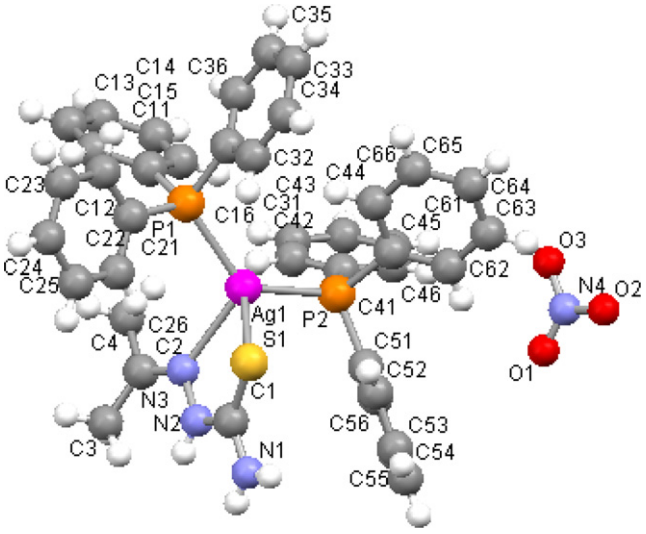


Fig. 5. Molecular structure of complex **4** (complex **5** has a similar structure).

6. Conclusion

The substituents at C^2 carbon appear to control the stoichiometry, nuclearity and dentacy of thiosemicarbazone complexes of silver(I) salts. For R^1 = pyridyl and R^2 = H, only tetrahedral monomers, $[AgCl(\eta^1\text{-S–Hpytsc})(PPh_3)_2]$ (X = Cl **6**) were formed [11]. The substitution of the hydrogen atom at the C^2 carbon by a methyl group (sp^3 carbon) (R^1 = pyridyl and R^2 = Me) was able to prevent the binding of a second PPh_3 ligand to the Ag^Icenter in case of **1** and formed complex $[AgCl(HL^2)_2(PPh_3)]$ **1**, with an unusual stoichiometry (1:2:1: Ag:Htsc:PPh_3). Introduction of a similarily bulky phenyl substituent at C^2 also did prevent the addition of two phosphine ligands, and presumably formed three coordinate species, $\{AgCl(HL^1)(PPh_3)\}$ which dimerised to yield a sulfur-bridged dinuclear complex, $[Ag_2Cl_2(\mu\text{-S–}HL^1)_2(PPh_3)_2]$ **2**, and no tetrahedral monomeric complex either similar to **1** or **6** was formed. The presence of both the methyl groups at C^2 carbon ($R^1 = R^2$ = Me, HL^4) favored N^3, S-chelation in **4** and **5**, and this property of HL^4 is supported by chelation in $[Cu(HL^4)_2]Cl$ reported in the literature [9a]. Also when the anion is more tightly bonded to the metal cen-

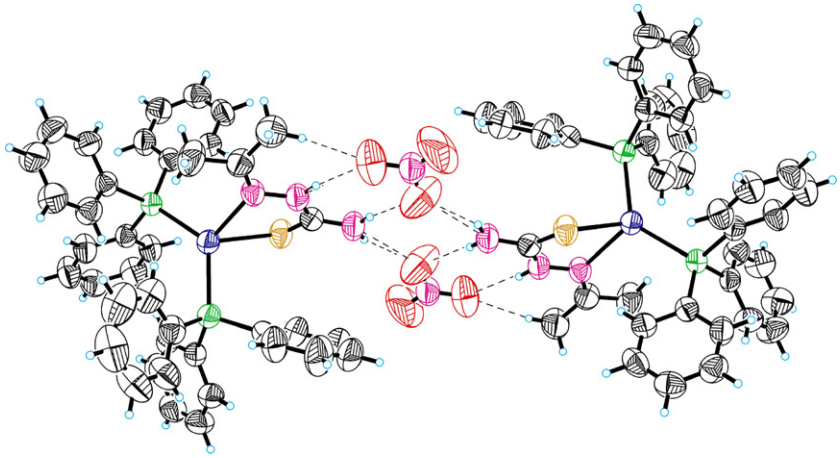


Fig. 6. Packing diagram of complex **4**.

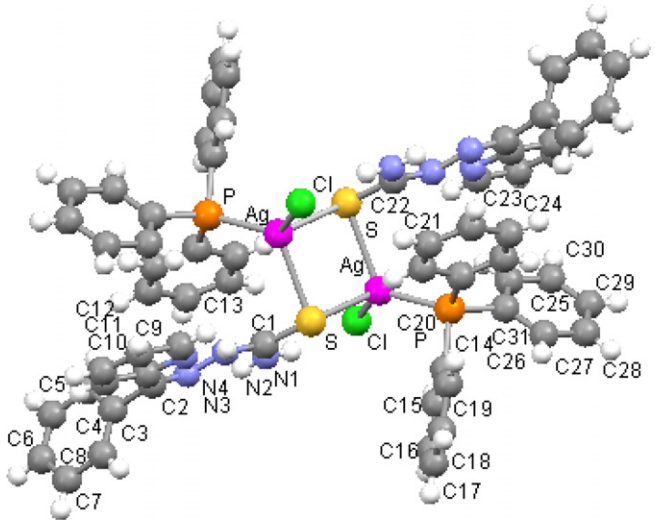


Fig. 7. Molecular structure of complex **2**.

ter as in silver(I) bromide, this ligand yielded a bromo-bridged dimer, $[Ag_2(\mu\text{-}Br)_2(\eta^1\text{-}S\text{–}HL^4)_2(PPh_3)_2]$ [11]. With both phenyl groups at C^2 carbon ($R^1 = R^2 = Ph$, HL^3), only tetrahedral complexes of more common stoichiometry, $[Ag(ONO_2)(\eta^1\text{-}S\text{–}HL^3)(PPh_3)_2]$ **3** or $[CuCl(\eta^1\text{-}S\text{–}HL^3)(PPh_3)_2]$ [10a] are formed.

In short stoichiometry, dentacy and nuclearity of coinage metal complexes with thiosemicarbazones is influenced by the substituents at C^2 carbon, and also by the nature of the anion/metal. The chelation by neutral thiosemicarbazones is limited and apart from three examples discussed in this paper, there are only two more examples of chelation by neutral thiosemicarbazones [11,15].

Acknowledgements

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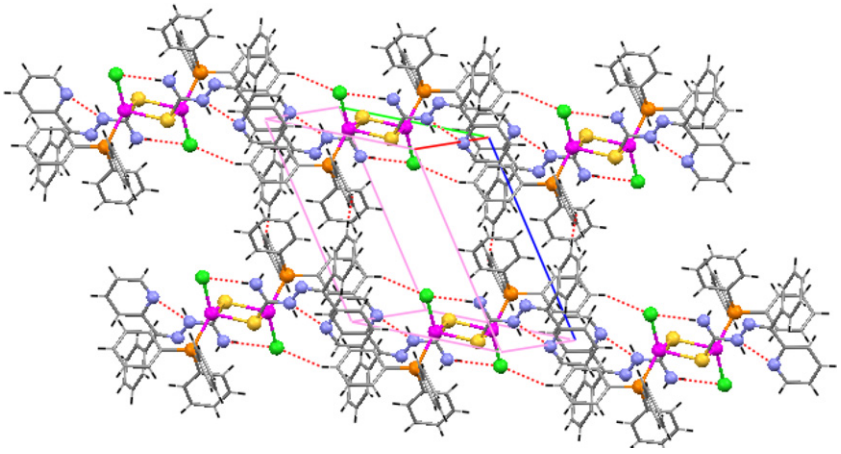

Fig. 8. Packing diagram of complex **2**.

Table 3
NMR data (δ, ppm) for complexes **1**–**5**

Compound	^{1}H NMR				^{31}P ($\Delta\delta$)
	$-N^2H$	$-N^1H_2$	CH_3	Ligand protons	
$[AgCl(\eta^1\text{-}S\text{–}HL^2)_2(PPh_3)]$ **1**	14.79b	9.24b	2.49s, 2.14s	8.76d, 8.61d (C^7H); 7.57d, 7.95d (C^4H); 7.72–7.75m ($C^{5,6}H$); 7.30–7.44m (Ph + N^1H_2)	6.55 (11.2)
$[Ag_2Cl_2(\mu\text{-}S\text{–}HL^1)_2(PPh_3)_2]$ **2**	14.07s	9.52s, 7.67b,		8.83d (C^7H); 7.81td (C^6H); 7.30–7.61m (Ph + $C^{4,5}H$)	11.21 (15.9)
$[Ag(ONO_2)(\eta^1\text{-}S\text{–}HL^3)(PPh_3)_2]$ **3**	9.20s	8.55sb		7.27–7.70m (Ph + N^1H_2)	30.81 (35.51) 2.74 (7.44)
$[Ag(N^3,S\text{–}HL^4)(PPh_3)_2](NO_3)$ **4**	11.64s		1.98s, 1.91s	7.25–7.43m (Ph + N^1H_2)	8.8 (13.5)
$[Ag(N^3,S\text{–}HL^4)(PPh_3)_2](CH_3COO)$ **5**[a]			2.17s, 2.01s	7.27–7.70m (Ph + N^1H_2)	7.3 (12.0)
HL^1	13.86s	8.56s		8.23d (C^7H); 7.77td (C^6H); 7.30–7.56m (N^1H_2 + Ph + C^5H); 7.31d (C^4H)	
HL^2	14.7s	8.86sb	2.44s, 2.40s	8.77d, 8.62d (C^7H); 7.97d, 7.54d (C^4H); 7.55–7.92m (N^1H_2 + $C^{5,6}H$)	
HL^3	8.68s	7.81s, 7.45s		7.27–7.61m (Ph)	
HL^4	8.44s	7.27s, 6.19sb	2.02s, 1.91s		

[a] It did not show this $-N^2H$ signal probably due to its exchange with the acetate anion in solution.

Appendix A. Supplementary data

CCDC 673439, 666768, 658221, 673440 and 673441 contain the supplementary crystallographic data for **1**, **2**, **3** and **4**. 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. See supplementary for bond parameters, X-ray figures and packing diagrams of various complexes. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2008.04.027.

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