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Chemistry of thiocarboxylates: Synthesis and structures of neutral silver(I) thiocarboxylates with triphenylphosphine †

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The reaction of AgCl, $Na^+R\{O\}CS^-$ (R = Me or Ph) and PPh_3 in the ratio 1 : 1 : 2 gave the corresponding bis-phosphine adducts, $[Ag(SC\{O\}R)(PPh_3)_2]$ (R = Me **1** or Ph **2**). The structure of **2** was shown to be a monomer by X-ray crystallography. The reactions of $Na^+R\{O\}CS^-$ (R = Me or Ph) with mixtures of AgCl and PPh_3 in the ratio 1 : 1 : 1 yielded tetrameric compounds having general formula $[Ag_4(SC\{O\}R)_4(PPh_3)_4]$. The solid state structure of the tetrameric triphenylphosphine silver thiocarboxylates depends on the solvents used for preparation or recrystallization. The neutral compounds $[(AgPPh_3)_4(\mu\text{-}SC\{O\}R)_4]$ (R = Me **3** or Ph **5**) have eight-membered Ag_4S_4 rings in the solid state when crystallized from CH_2Cl_2 solvent. In toluene **3** forms another conformational isomer, **4**, with an Ag ··· Ag interaction of 3.1461(5) Å, whereas **5** gave compound **6** with a stepladder-like arrangement having three fused four-membered rings. The formation of conformational isomers **3** and **4** may be attributed to packing effects. The ability of the sulfur atom in $PhC\{O\}S^-$ ligand forming μ-S and μ_3-S bridging, and that of Ag^I to display variable coordination geometries have aided the formation of two deformational isomers **5** and **6**. The variable temperature ^{31}P NMR of compound **1** may be interpreted in terms of a mixture of monomer and dimer in CH_2Cl_2 solution. The low temperature ^{31}P NMR spectra of the other compounds were not well resolved and indicated the presence of various species present in solution due to dissociation. The structures of **3**–**6** have been determined by single crystal X-ray diffraction methods.

Introduction

Configurational isomers are possible for neutral compounds with the skeletal formula $M_4X_4L_4$. Of these cubane- and chair-like structures are common among coinage metals (where M = Cu or Ag; X = Cl, Br or I; L = monophosphine or arsine, ER_3).[1,2] A large number of silver(I) compounds have cubane-like structure with the exception of $[Ag_4I_4(PPh_3)_4]$ which has both cubane and chair configurations in the solid state depending upon the solvent used for crystallization.[3] For the corresponding copper(I) compounds, on the other hand, a chair-like configuration was observed[4,5] for X = Br or I and a cubane-like structure[6] for X = Cl. A detailed structural analysis by Teo and Calabrese showed that steric repulsions of the types M ··· M, X ··· X, R ··· R and R ··· X are responsible for the formation of chair-like configurations *versus* cubane-like structures.[3] The structural preferences can further be complicated when X has substituents like RS^- and $R\{O\}CS^-$ ions with additional influences due to R groups. In the tetrameric aggregates reported for silver(I) and copper(I) compounds, eight-membered rings[7–14] and three fused four-membered rings[15,16] are frequently encountered structures. However, these two structures have not been observed for the same compound. Recently, we have observed that copper(I) thiobenzoate reacts with PPh_3 to form a highly distorted cubane-like structure whereas the corresponding thioacetate compound has a chair-like configuration.[16] Since cubane-like structures are ubiquitous in $Ag_4X_4(ER_3)_4$ compounds,[2] it is of interest to investigate the structure and stereochemistry of the triphenylphosphine silver(I) thiocarboxylate compounds.

Distortional or deformational isomerism has been an area of recent interest in which the bond stretching is accompanied by significant additional changes within a molecule.[17] The distortional isomerism mainly occurs in transition metal compounds involving metal–metal bond forming or breaking coupled with ligand as well as ring deformation.[18–21] Herein we report a new example of deformational isomerism in the system $[(AgPPh_3)_4(SC\{O\}Ph)_4]$, which involves Ag–S bonds utilizing the μ and μ_3 bridging abilities of sulfur atoms in the thiobenzoate ligands as well as the nature of Ag^I to form two- and three-coordinate geometries. In the corresponding thioacetate compounds a conformational isomerism has been observed and the details are discussed in this paper. Variable temperature ^{31}P NMR studies show the presence of various dissociated species in solution.

Experimental

All materials were obtained commercially and used as received. The solvents were dried by allowing them to stand over 3 Å molecular sieves overnight. The preparations were carried out under a nitrogen atmosphere and the yields are reported with respect to the metal salts. The compound $[Ag_2Cl_2(PPh_3)_4]$ was prepared according to the method reported.[22] The $^{13}C\text{-}\{^1H\}$, ^1H and ^{31}P NMR spectra were recorded on a Bruker ACF300 FT-NMR machine using TMS as internal reference at 25 °C in CD_2Cl_2 or $CDCl_3$, IR spectra (KBr pellet) using a Bio-Rad FTIR spectrophotometer. The elemental analyses were performed in the microanalytical laboratory in the Chemistry Department, National University of Singapore. Thermogravimetric analyses were carried out using a SDT 2980 TGA Thermal Analyzer with a heating rate of 10 °C min^{-1} in a N_2 atmosphere using a sample size of 5–10 mg per run. X-Ray powder patterns were obtained using a D5005 Siemens X-ray diffractometer.

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† Electronic supplementary information (ESI) available: variable temperature ^{31}P NMR spectra and X-ray powder diffraction patterns for the complexes. See http://www.rsc.org/suppdata/dt/b0/b007122f/

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Preparations

$[Ag(SC\{O\}Me)(PPh_3)_2]$ 1. Solid PPh_3 (1.83 g, 7.0 mmol) was dissolved in 15 mL of CH_2Cl_2 and 0.54 g of AgCl (3.5 mmol) was added. The mixture was stirred for *ca.* 15 min to get a clear solution. To this was added $[Et_3NH][MeC\{O\}S]$, prepared *in situ* by addition of 0.5 mL of Et_3N (3.5 mmol) and 0.25 mL of thioacetic acid (3.5 mmol) in 10 mL of CH_2Cl_2, and the reaction mixture turned pale yellow. Stirring was continued for *ca.* 30 min and the solvents were removed. The colorless residue was washed many times with MeOH and Et_2O and dried under vacuum. Yield 1.79 g (72%). Calc. for $C_{35}H_{33}AgOP_2S$: C, 62.60; H, 4.18. Found: C, 60.5; H, 4.18%. ^{1}H NMR ($CDCl_3$): δ 2.25 (3H, CH_3) and 7.23–7.40 (30H, $(C_6H_5)_3P$). ^{13}C NMR ($CDCl_3$): δ (for the thioacetate ligand) 36.4 ($\mathit{C}H_3COS$), 207.9 ($CH_3\mathit{C}OS$); (for the PPh_3) 128.7 (C^3, $^{3}J(P–C) = 9.8$), 130.0 (C^4), 132.4 (C^1, $^{1}J(P–C) = 23.9$) and 133.8 (C^2, $^{2}J(P–C) = 16.3$ Hz). ^{31}P NMR: δ 7.66 (s). IR data (cm^{-1}): 3050.2m, 1630.2, 1589.7, 1475.9s, 1435.4s, 1300.3m, 1105.5s, 1032.2m, 951.1m, 850.8w, 748.6s, 688.8s, 642.5s and 493.9s. Attempts to crystallize this compound from CH_2Cl_2 and Et_2O or hexane gave compound **3**.

$[Ag(SC\{O\}Ph)(PPh_3)_2]$ 2. Thiobenzoic acid (0.13 mL, 1.12 mmol) was deprotonated by Et_3N (0.16 mL, 1.12 mmol) in 5 mL of $CHCl_3$ solvent and added to 0.75 g of $[Ag_2Cl_2(PPh_3)_4]$ (0.56 mmol) in 15 mL of $CHCl_3$. The mixture was stirred for 30 min and the solvent evaporated under vacuum to get a creamy yellow product, which was washed several times with MeOH and Et_2O and dried under vacuum. Yield: 0.86 g (87%). Calc. for $C_{43}H_{35}AgOSP_2$: C, 67.11; H, 4.58. Found: C, 66.95; H, 4.55%. ^{13}C NMR data ($CDCl_3$): δ (for thiobenzoate ligand) 127.6 ($C^{2/6}$ or $C^{3/5}$), 128.8 ($C^{2/6}$ or $C^{3/5}$), 130.9 (C^4), 142.8 (C^1) and 204.2 ($Ph\mathit{C}OS$); (for PPh_3) 129.0 (C^3, $^{3}J(P–C) = 9.8$), 130.1 (C^4), 133.8 (C^1, $^{1}J(P–C) = 18.5$) and 134.2 (C^2, $^{2}J(P–C) = 17.4$ Hz). ^{31}P NMR: δ 5.53. IR data (cm^{-1}): 3056.0m, 1583.9m, 1549.2m, 1475.9s, 1429.6s, 1294.6m, 1207.7s, 1159.5m, 1092.0s, 1032.2m, 931.8s, 748.6s, 696.5s, 513.2s and 493.9s. Single crystals for X-ray diffraction were obtained by slow evaporation of the compound from a solvent mixture of MeCN and toluene.

$[(AgPPh_3)_4(\mu\text{-}SC\{O\}Me\text{-}\mathit{S})_4]$ 3. Solid AgCl (1.00 g, 7.0 mmol) was stirred in a solution of PPh_3 (1.83 g, 7.0 mmol) in 20 mL of CH_2Cl_2. To this suspension was added $NaSC\{O\}Me$ prepared *in situ* by addition of $MeC\{O\}SH$ (0.5 mL, 7.0 mmol) to a solution of NaOH (0.28 g, 7.0 mmol) in 10 mL of water. The reaction mixture was allowed to stir until the aqueous layer became colorless. The CH_2Cl_2 layer was separated and layered with Et_2O to get a colorless compound. Yield 2.5 g (80%). Calc. for $C_{80}H_{72}Ag_4O_4P_4S_4\cdot CH_2Cl_2$: C, 52.14; H, 4.00. Found: C, 51.57; H, 4.06%. ^{1}H NMR ($CDCl_3$): δ 2.2 (12H, CH_3), 5.3 (2H, CH_2Cl_2 solvate) and 7.3–7.47 (60H, $(C_6H_5)_3P$). ^{13}C NMR ($CDCl_3$): δ (for the thioacetate ligand) 36.14 ($\mathit{C}H_3COS$), 206.36 ($CH_3\mathit{C}OS$); (for PPh_3) 128.8 (C^3, $^{3}J(P–C) = 9.8$), 130.2 (C^4), 131.8 (C^1, $^{1}J(P–C) = 27.3$) and 133.9 (C^2, $^{2}J(P–C) = 16.3$ Hz); (for cocrystallized CH_2Cl_2) 53.31. ^{31}P NMR: δ 9.5s. IR data (cm^{-1}): 3063.7m, 1624.5s, 1483.6s, 1435.4s, 1340.9m, 1099.7s, 756.3s, 696.5s, 634.7s and 513.2s. Single crystals suitable for X-ray diffraction experiments were obtained at 5 °C by slow diffusion of Et_2O into the compound dissolved in CH_2Cl_2. TG weight loss for **3**$\cdot CH_2Cl_2$: Calc. 4.6%, found 4.5%.

$[(AgPPh_3)_4(\mu\text{-}SC\{O\}Me\text{-}\mathit{S})_4]$ 4. About 50 mg of compound **3** were dissolved in toluene and set aside for slow evaporation. The following day colorless crystals of **4** were obtained. Calc. for $C_{80}H_{72}Ag_4O_4P_4S_4\cdot C_6H_5CH_3$: C, 55.78; H, 4.30. Found: C, 56.21; H, 4.38%. ^{1}H NMR ($CDCl_3$): δ 2.2 (12H, CH_3COS), 2.4 (3H, $C\mathit{H}_3C_6H_5$) and 7.3–7.47 (65H, $(C_6H_5)_3P$ and $C_6\mathit{H}_5CH_3$). IR data (cm^{-1}): 3063.7m, 2988.5m, 1630.2s, 1483.6m, 1435.4s, 1348.6w, 1140.2m, 1086.2s, 951.1m, 850.8w, 748.6s, 696.5s, 629.0m and 513.2s. TG weight loss for **4**·toluene: calc. 4.9%, found 5.0%.

$[(AgPPh_3)_4(\mu\text{-}SC\{O\}Ph\text{-}\mathit{S})_4]$ 5. Compound **5** was synthesized using a procedure similar to that for **3** but with $PhC\{O\}SH$. Yield: 84%. Calc. for $C_{100}H_{80}Ag_4O_4S_4P_4\cdot 2CH_2Cl_2$: C, 55.71; H, 3.85. Found: C, 55.26; H, 3.95%. Calc. for unsolvated compound $C_{100}H_{80}Ag_4O_4S_4P_4$: C, 59.19; H, 3.97. Found: C, 60.39; H, 3.70%. ^{13}C NMR data ($CDCl_3$): δ (for thiobenzoate) 127.5 ($C^{2/6}$ or $C^{3/5}$), 128.6 ($C^{2/6}$ or $C^{3/5}$), 130.3 (C^4), 143.9(C^1) and 205.0 ($C_6H_5\mathit{C}OS$); (for PPh_3) 128.9 (C^3, $^{3}J(P–C) = 8.7$), 129.6 (C^4), 134.2 (C^1, $^{1}J(P–C) = 17.4$) and 135.4 (C^2, $^{2}J(P–C) = 6.5$ Hz). ^{31}P NMR: δ 10.48. IR data (cm^{-1}): 3056.0m, 1616.7 s, 1562.7s, 1470.1s, 1435.4s, 1308.1w, 1194.2s, 1099.7s, 1024.5m, 999.4m, 904.8s, 756.3s, 688.8s, 642.5m and 499.7s. Single crystals for X-ray diffraction were obtained at room temperature by slow diffusion of Et_2O into a CH_2Cl_2 solution of the compound. TG weight loss for **5**$\cdot 2CH_2Cl_2$: calc. 7.7%, found 6.4%. The number of CH_2Cl_2 in the crystals was also confirmed from integration of the ^{1}H NMR spectrum. ^{1}H NMR ($CDCl_3$): δ 5.3 (4H, CH_2Cl_2) and 7.52–8.01 (80H, $(C_6H_5)_3P$ and $C_6H_5C\{O\}S$).

$[(AgPPh_3)_4(\mu_3\text{-}SC\{O\}Ph\text{-}\mathit{S})_2(\mu\text{-}SCOPh\text{-}\mathit{S})_2]$ 6. Crystals of compound **6** were obtained by slow evaporation of a solution of 50 mg of **5** in 6–7 mL of toluene. Calc. for $C_{100}H_{80}Ag_4O_4S_4P_4\cdot C_6H_5CH_3$: C, 60.58; H, 4.18. Found: C, 60.59; H, 3.70%. ^{1}H NMR ($CDCl_3$): δ 2.31 (3H, $C\mathit{H}_3C_6H_5$) and 7.14–7.95 (85H, $(C_6H_5)_3P$, C_6H_5COS and $C_6\mathit{H}_5CH_3$). IR data (cm^{-1}): 3050.2m, 1616.7s, 1562.7m, 1483.6m, 1435.4s, 1308.1w, 1194.2s, 1159.5m, 1092.0m, 1024.5w, 904.8s, 748.6s, 696.5s and 507.4m. TG weight loss for **6**·toluene: Calc. 4.3%, found 4.7%.

Reactions of Ph_3P, AgCl and $NaSC\{O\}R$ in the ratios 3 : 4 : 4 and 3 : 2 : 2 in CH_2Cl_2 or toluene led to the isolation of compounds with composition 1 : 1 : 1 and mixtures of 1 : 1 : 1 and 2 : 1 : 1 respectively in quantitative yields as monitored by physical examination of the crystals, elemental analysis, X-ray powder diffraction patterns or ^{1}H NMR spectroscopy.

X-Ray crystallography

The X-ray diffraction experiments were carried out on a Bruker SMART CCD diffractometer with a Mo-Kα sealed tube at 23 °C. The program SMART[23] was used for collecting frames of data, indexing reflections and determination of lattice parameters, SAINT[23] for integration of the intensity of reflections and scaling, SADABS[24] for absorption correction and SHELXTL[25] for space group and structure determination and least-squares refinements on F^2. The relevant crystallographic data and refinement details are shown in Table 1.

The carbonyl oxygen O2 in compound **3** was disordered with occupancies 0.7 and 0.3. The solvents present in **3**–**6** were disordered. The chloride of CH_2Cl_2 was disordered in **3** and the occupancies were fixed at 0.4, 0.4 and 0.2. A common isotropic thermal parameter was refined for all the non-hydrogen atoms of the solvate. One toluene molecule present in the asymmetric unit of **4** is disordered. Two disordered models were resolved with occupancies 0.6 and 0.4. Common isotropic thermal parameters were refined for each model. In **5** two models with occupancies 0.7 and 0.3 were resolved for CH_2Cl_2 solvate. Anisotropic thermal parameters were refined for the major component of the model and common isotropic thermal parameters for the minor disorder model. Soft constraints were applied for the C–Cl and Cl···Cl distances using SADI.[25] A toluene solvate in **6** was present at the crystallographic center of inversion and hence disordered. The disorder was approximated to a simple center of inversion at the benzene ring.

CCDC reference number 186/2290.

See http://www.rsc.org/suppdata/dt/b0/b007122f/ for crystallographic files in .cif format.

Table 1 Crystallographic data for compounds **2**, **3**·CH_2Cl_2 (**3a**), **4**·$C_6H_5CH_3$ (**4a**), **5**·2CH_2Cl_2 (**5a**) and **6**·$C_6H_5CH_3$ (**6a**)

	2	**3a**	**4a**	**5a**	**6a**
Chemical formula	$C_{43}H_{35}AgOP_2S$	$C_{80}H_{72}Ag_4O_4P_4S_4\cdot CH_2Cl_2$	$C_{80}H_{72}Ag_4O_4P_4S_4\cdot C_6H_5CH_3$	$C_{100}H_{80}Ag_4O_4P_4S_4\cdot 2CH_2Cl_2$	$C_{100}H_{80}Ag_4O_4P_4S_4\cdot C_6H_5CH_3$
Formula weight	769.58	1864.89	1873.11	2199.09	2121.51
T/°C	20	20	20	20	20
λ/Å	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Triclinic	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	10.2945(3)	15.5692(2)	11.9826(2)	13.0019(4)	12.8097(3)
b/Å	13.3036(4)	16.8766(2)	12.7489(1)	13.1172(4)	14.5568(1)
c/Å	14.3270(3)	17.7730(2)	14.9433(2)	14.8424(4)	16.0524(3)
α/°	89.246(1)		99.585(1)	104.381(1)	63.426(1)
β/°	76.311(1)	115.656(1)	91.867(1)	100.511(1)	68.868(1)
γ/°	77.161(1)		95.328(1)	100.170(1)	64.198(1)
V/Å^3	1857.13(9)	4207.54(9)	2238.53(5)	2344.52(12)	2358.51(7)
Z	2	2	1	1	1
μ/mm^{-1}	0.717	1.201	1.072	1.146	2.0
$R1$ ($F_o \geq 4\sigma(F_o)$)	0.0664	0.0561	0.0333	0.0403	0.0679
$wR2$ ($F_o \geq 4\sigma(F_o)$)	0.1254	0.1650	0.1043	0.0915	0.1206

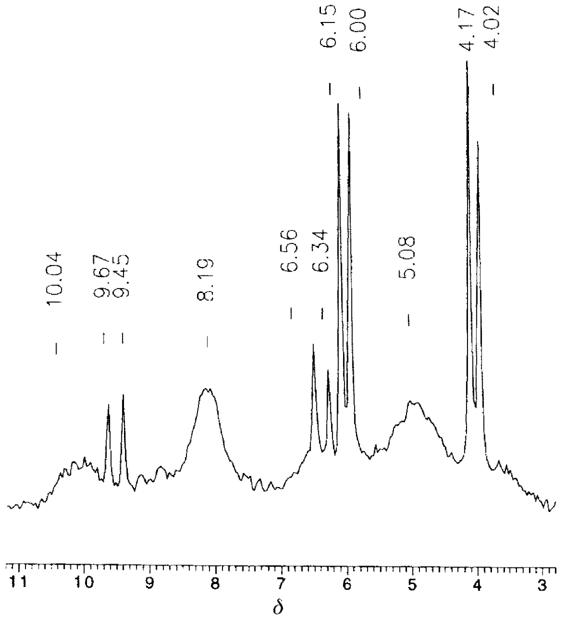


Fig. 1 ^{31}P NMR of compound **1** in CD_2Cl_2 at 200 K.

Results and discussion

The compounds **1**, **2**, **3** and **5** have been synthesized quantitatively (72–87% isolated yield) from AgCl, NaSC{O}R and PPh_3 in CH_2Cl_2 solution in appropriate stoichiometries. Attempts to prepare [$(Ph_3P)_2Ag(\mu$-SC{O}R$)_2Ag(PPh_3)$] and [Ag(μ_3-SC{O}Ph-*S*)(μ_3-SC{O}Ph-*S*,*O*)$(AgPPh_3)_3$] similar to copper analogues[16] led to mixtures of products. All these compounds are soluble in MeCN, Me_2CO, $CHCl_3$, CH_2Cl_2, benzene and toluene. Attempts to crystallize the bis-triphenylphosphine adducts **1** and **2** from CH_2Cl_2 or $CHCl_3$ solutions yielded the corresponding 1 : 1 : 1 compounds. Compound **2** was crystallized by slow evaporation from a mixture of MeCN and toluene. When 1 : 1 : 1 compounds (**3** and **5**) were crystallized from toluene solvent the morphologies of the crystals were different from those of **3** and **5**. However the analytical and spectroscopic data were similar for the desolvated compounds **3** and **4** and **5** and **6**.

Silver has two NMR active nuclei namely ^{107}Ag and ^{109}Ag with a natural abundance of 51.82 and 48.18% respectively. Hence it was thought that the ^{31}P NMR of the compounds in solution could shed some light over the structural preferences. The room temperature ^{31}P NMR spectra of **1** showed only one broad signal at δ 7.66. However, the spectrum at 200 K consisted of two doublet of doublets as shown in Fig. 1. The presence of the broad peak in the center indicated that the exchange process was still occurring. The major peak was centered at δ 5.08 ($^1J(^{109}Ag–P) = 258$, $^1J(^{107}Ag–P) = 220$ Hz) and the minor peak at δ 8.01 ($^1J(^{109}Ag–P) = 403$, $^1J(^{107}Ag–P) = 350$ Hz). The ratios of $^1J(^{109}Ag–P)$ and $^1J(^{107}Ag–P)$ are 1.17 and 1.15 : 1. These values are in agreement with the theoretical ratio of $\gamma(^{109}Ag):\gamma(^{107}Ag) = 1.15:1$.[26,27] The coupling constants may be used as a guide to determine the P–Ag–P angle; the greater the P–Ag–P angle the greater would be the coupling constant.[28–30] Hence the ^{31}P NMR signal centered at δ 8.01 may be assigned to a monomeric species with a trigonally coordinated silver metal atom and that at δ 5.08 to a dimeric compound with the silver atom assuming tetrahedral coordination. Based on the ^{31}P NMR data, it may be concluded that compound **1** is in equilibrium with a dimer in solution according to eqn. (1).

$$2\,[(Ph_3P)_2AgSC\{O\}Me] \rightleftharpoons [((Ph_3P)_2Ag)_2(SC\{O\}Me)_2] \quad (1)$$

The intensity of the two signals immediately suggests that the dimer is the predominant species in solution at lower temperatures. The interpretation based on ^{31}P NMR experiments is tentative, however similar observations have been reported for [AgCl{P(C_6H_4Me-*p*$)_3\}_2$] for which molecular weight determinations using freezing point depression in benzene (at 5 °C) indicated a monomeric structure while the Ag–P coupling constant (378 Hz at −80 °C) suggested a dimeric structure.[26,31] Unfortunately, repeated attempts to get good quality single crystals of compound **1** were unsuccessful. It is not clear whether **1** exists as a monomer or dimer in the solid state. It is interesting that the corresponding copper analog, [{Cu($PPh_3)_2\}_2(\mu$-SC{O}Me-*S*)(μ-SC{O}Me-*S*,*O*)],[16] is a dimer in the solid state. The X-ray powder pattern of **1** indicates that it is not isomorphous with the corresponding copper analog (see ESI supporting information).

The ^{31}P NMR of compounds **2**–**6** gave only broad singlets at room temperature. The absence of any coupling at room temperature could be attributed to some form of dynamic equilibrium process involving the phosphine ligand. This is well documented for phosphine complexes of coinage metals.[26,32] As expected the ^{31}P NMR spectra at low temperatures were more complicated (ESI supporting information). However, it was evident that more than one species could be present in equilibrium.

NMR and microanalysis established the stoichiometry of compounds **1**–**6**. However we remain interested in finding their

Table 2 Selected bond lengths (Å) and angles (°) for compound **2**

Ag(1)–S(1)	2.505(1)	Ag(1)–P(1)	2.474(1)
Ag(1)–P(2)	2.441(1)	S(1)–C(1)	1.710(6)
O(1)–C(1)	1.232(6)	C(1)–C(2)	1.512(8)
P(1)–Ag(1)–P(2)	124.51(4)	P(1)–Ag(1)–S(1)	114.68(5)
P(2)–Ag(1)–S(1)	120.78(5)	C(1)–S(1)–Ag(1)	89.61(19)
C(2)–C(1)–S(1)	119.4(4)	O(1)–C(1)–S(1)	122.0(5)
O(1)–C(1)–C(2)	118.5(5)		

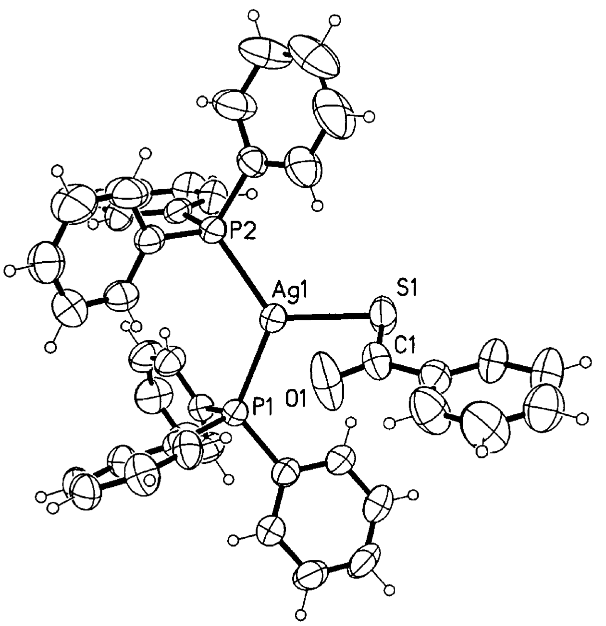


Fig. 2 Drawing of compound **2** with 50% probability ellipsoids (as in all cases shown).

solid state structures as phosphine adducts of silver compounds are known to exhibit structural diversity. Hence X-ray crystallographic determinations were performed for them.

Structural description

Compound **2** is a monomer in the solid state. It is isomorphous and isostructural with the analogous copper compound.[16] The silver metal atom assumes a trigonal planar geometry as it is bonded to two PPh_3 ligands and a Ph{O}CS$^-$ anion. Fig. 2 gives a perspective view of **2** and Table 2 provides relevant bond distances and angles. The thiobenzoate anion is mainly bonded to the silver metal atom through the sulfur donor site. The Ag(1)···O(1) distance, 2.764 Å is, however, less than the sum of the van der Waals radii, 3.2 Å.[33] The sum of the bond angles around Ag(1) 359.97° indicates that the proximity of the O(1) does not distort the trigonal planar coordination geometry. This is also evident from the planarity of the atoms Ag(1), S(1), P(1) and P(2) (rms deviation, 0.0105 Å). The phenyl ring of the thiobenzoate anion makes a dihedral angle of 6.7(4)° with the Ag(1)S(1)O(1)C(1) plane. Similar observations have been noted for the thiobenzoate anion.[16,34–36] The Ag(1)–S(1) distance, 2.505(1) Å, is normal for three-coordinate silver compounds. A CSDS search shows that for silver compounds with a P_2AgS core the Ag–S distances fall within a range of 2.477–2.652 Å.[37]

Table 3 Selected bond lengths (Å) and angles (°) for compound **3**

Ag(1)–S(1)	2.5217(18)	Ag(1)–S(2)	2.5245(15)
Ag(2)–S(2)	2.5417(16)	Ag(2A)^a–S(1)	2.5834(18)
Ag(1)–P(1)	2.4273(17)	Ag(2)–P(2)	2.4317(16)
C(1)–S(1)	1.759(7)	C(3)–S(2)	1.768(7)
C(1)–O(1)	1.203(8)	C(3)–O(2)	1.241(14)
C(1)–C(2)	1.500(10)	C(3)–C(4)	1.511(10)
Ag(1)–S(1)–Ag(2A)^a	119.30(8)	Ag(1)–S(2)–Ag(2)	87.55(5)
S(1)–Ag(1)–S(2)	111.52(6)	S(2)–Ag(2)–S(1A)^a	102.66(5)
P(1)–Ag(1)–S(1)	119.21(6)	P(1)–Ag(1)–S(2)	128.87(6)
P(2)–Ag(2)–S(2)	133.00(6)	P(2)–Ag(2)–S(1A)^a	123.00(6)
C(1)–S(1)–Ag(1)	105.8(2)	C(1)–S(1)–Ag(2A)^a	105.9(2)
C(3)–S(2)–Ag(1)	103.5(3)	C(3)–S(2)–Ag(2)	96.3(2)

^{a} Symmetry transformation used to generate equivalent atoms: $1 - x$, $1 - y$, $-z$.

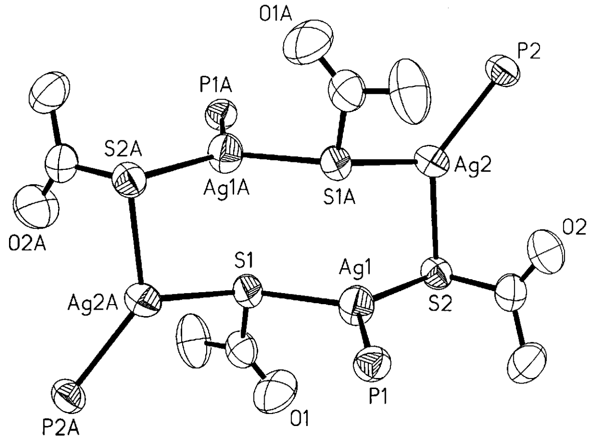


Fig. 3 An ORTEP[38] diagram of compound **3**. The phenyl rings attached to phosphorus atoms and the hydrogen atoms are omitted for clarity.

Compound **3** is tetrameric in the solid state forming an eight-membered ring, Ag_4S_4 with a crystallographic inversion center in the middle. In the crystal structure the rings are located at $0,\frac{1}{2},0$ and $\frac{1}{2},0,\frac{1}{2}$, and the disordered CH_2Cl_2 solvates are located near 0,0,0 and $\frac{1}{2},\frac{1}{2},\frac{1}{2}$. Very weak intermolecular interactions exist between O(2) and H(3F) (2.453 Å), but no close π–π contacts. The Ag_4S_4 ring has the 'chair-like' or 'stepladder' conformation as shown in Fig. 3 and appears to be a rectangle when viewed from the top. The average width of the chair is 3.021 Å obtained from the Ag(1)···S(1A) distance which is also inferred from the angles Ag(1)–S(2)–Ag(2) 87.55(5)° and S(2)–Ag(2)–S(1A) 102.66(5)°. These Ag···S interactions across the chair may be considered absent since these atoms are moved far away from normal Ag–S bond lengths. The reclination angle in this chair is *ca.* 115.4°. The Ag(1)–S(1), Ag(1)–S(2), Ag(2)–S(2) and Ag(2A)–S(1) distances are 2.522(2), 2.525(2), 2.542(2) and 2.583(2) Å respectively (Table 3). These are longer than those found in the anionic complex $[PPh_4][Ag(SC\{O\}Me)_2]$[36] probably due to the effect of the PPh_3 ligand. Similarly the Ag–P distances in **3** are comparable to the range 2.392–2.524 Å observed in compounds with the same core structure.[37]

When compound **3** was recrystallized from toluene, **4**·C_6H_5Me was produced. X-Ray crystallography reveals that the molecular structure is different from that of **3**. The tetramer is discrete in the solid state and located at the center of the unit cell ($Z = 1$). The disordered toluene solvates are located at the corners of the unit cell. There appear to be no close π–π contacts in the solid state. The molecule has a crystallographic center of inversion. Selected bond distances and angles are provided in Table 4 and a perspective view of **4** is shown in Fig. 4. The width of the chair, 3.113 Å is comparable to that in **3**. However, the Ag(1)S(2)Ag(2)S(1A) plane is distorted since the silver atoms come closer together (Ag(1)···Ag(2) distance 3.1461(5) Å). This distortion is quite clear from the angles S(1A)–Ag(2)–S(2) 114.20(3)° and Ag(1)–S(2)–Ag(2) 76.42(3)°. The Ag···Ag distance 2.886 Å was not considered as bonding in $[\{Ag(SCMeEt_2)\}_n]$,[39] however in $[(AgPPh_3)_4(SPh)_4]$ reported recently the Ag···Ag distance 3.1300(3) Å was attributed to weak Ag···Ag interaction.[14] The structure of **4** appears similar to that of $[(AgPPh_3)_4(SPh)_4]$ in which the Ag···S bond distance is 3.008(8) Å across the chair and the Ag···Ag distance is 3.130(1) Å.[14] A similar structure involving a weak metal–metal interaction between copper metal atoms has been reported by

Table 4 Selected bond lengths (Å) and angles (°) for compound **4**

Ag(1)–S(1)	2.544(1)	Ag(1)–S(2)	2.519(1)
Ag(2)–S(1A)[a]	2.531(1)	Ag(2)–S(2)	2.567(1)
Ag(1)–P(1)	2.425(1)	Ag(2)–P(2)	2.467(1)
S(1)–C(1)	1.764(4)	S(2)–C(3)	1.771(5)
O(1)–C(1)	1.205(6)	O(2)–C(3)	1.217(6)
C(1)–C(2)	1.509(6)	C(3)–C(4)	1.489(7)
P(1)–Ag(1)–S(2)	131.98(4)	P(2)–Ag(2)–Ag(1)	162.43(3)
P(1)–Ag(1)–S(1)	119.54(4)	S(1A)[a]–Ag(2)–Ag(1)	65.46(3)
S(2)–Ag(1)–S(1)	107.31(4)	S(2)–Ag(2)–Ag(1)	51.11(2)
P(1)–Ag(1)–Ag(2)	121.40(3)	S(2)–Ag(1)–Ag(2)	52.48(3)
C(1)–S(1)–Ag(2A)[a]	103.5(1)	S(1)–Ag(1)–Ag(2)	101.77(3)
C(1)–S(1)–Ag(1)	101.7(2)	P(2)–Ag(2)–S(1A)[a]	125.63(4)
Ag(2A)[a]–S(1)–Ag(1)	123.46(5)	P(2)–Ag(2)–S(2)	120.17(4)
C(3)–S(2)–Ag(1)	108.3(2)	S(1A)[a]–Ag(2)–S(2)	114.20(3)
C(3)–S(2)–Ag(2)	92.7(2)	Ag(1)–S(2)–Ag(2)	76.42(3)

[a] Symmetry transformation used to generate equivalent atoms: $-x + 1$, $-y + 1$, $-z + 1$.

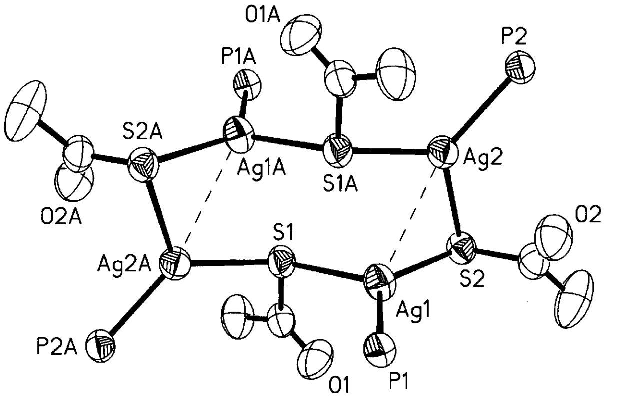
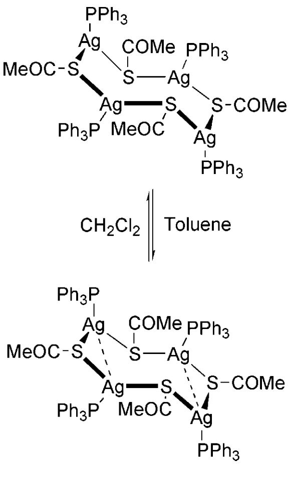


Fig. 4 An ORTEP[38] diagram of compound **4**. Details as in Fig. 3.

Ohlmann *et al.* for the compound $[Cu_4(SR)_4L_2]$ (R = 2,4,6-$i\mathrm{Pr}_3C_6H_2$; L = 2,2′-bipyridyl).[40] While aurophilicity is widely acknowledged, argentophilic interactions remain in their infancy.[41] Recently theoretical, spectroscopic and structural evidence has been accumulated to confirm the existence of weak silver–silver interactions.[41]

When the recrystallization was repeated in the solvents CH_2Cl_2 and toluene, the interconversion between the conformational isomers was found to be reversible (Scheme 1). The



Scheme 1

interconversion of the compounds was followed by X-ray powder diffraction experiments.[42] The crystal packing energies in **3** and **4** are probably of similar magnitude to the distortion energies of the coordination stereochemistry. The conformational differences in these thioacetate compounds may be attributed to different crystal packing caused by the presence of different solvent molecules in the crystal lattice. Compounds **3** and **4** provide a good illustration of this principle.

Table 5 Selected bond lengths (Å) and angles (°) for compound **5**

Ag(1)–P(1)	2.4345(8)	Ag(2)–P(2)	2.4249(8)
Ag(1)–S(1)	2.5017(8)	Ag(1)–S(2)	2.5372(9)
Ag(2)–S(1A)[a]	2.5640(9)	Ag(2)–S(2)	2.4598(9)
C(1)–S(1)	1.769(3)	C(2)–S(2)	1.769(4)
C(1)–O(1)	1.223(4)	C(2)–O(2)	1.214(4)
Ag(1)–S(2)–Ag(2)	112.97(4)	Ag(1)–S(1)–Ag(2A)[a]	97.77(3)
S(1)–Ag(1)–S(2)	108.58(3)	S(2)–Ag(2)–S(1A)[a]	114.37(3)
P(1)–Ag(1)–S(1)	121.03(3)	P(1)–Ag(1)–S(2)	123.92
P(2)–Ag(2)–S(2)	131.17(3)	P(2)–Ag(2)–S(1A)[a]	113.83(3)
C(1)–S(1)–Ag(1)	102.42(11)	C(1)–S(1)–Ag(2A)[a]	99.36(10)
C(2)–S(2)–Ag(1)	108.43(12)	C(2)–S(2)–Ag(2)	100.80(12)

[a] Symmetry transformation used to generate equivalent atoms: $1 - x$, $-y + 1$, $-z + 2$.

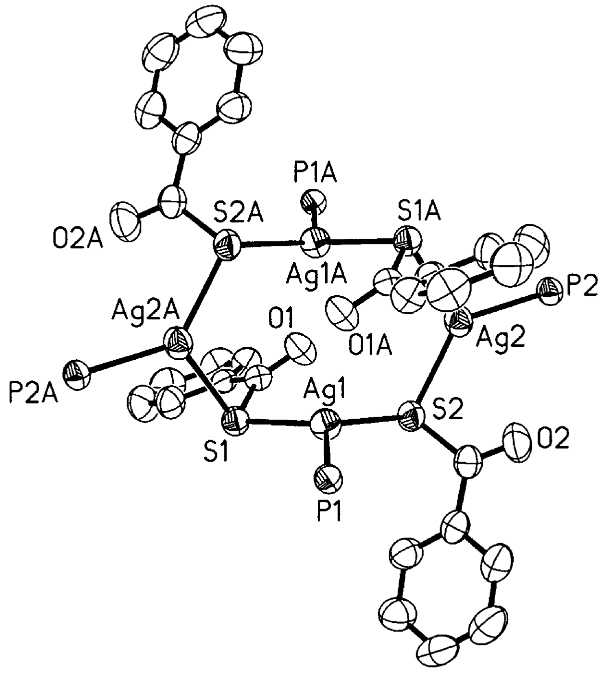


Fig. 5 A perspective view of compound **5**. Details as in Fig. 3.

A view of the tetramer **5** is shown in Fig. 5 and selected bond distances and angles are in Table 5. The Ag_4S_4 ring in **5** is conformationally different from that of the thioacetate analog, **3**, and has a crystallographic inversion center ($Z = 1$). The rings are situated at $0,\frac{1}{2},0$ in the unit cell and the solvates are located near the *a* axis. There are very weak intermolecular interactions (S(2)···H(1SB), 2.781 Å and Cl(1A)···H(3F), 2.836 Å) and π–π interactions between the rings C(1–6)F and C(1–6)CA, 3.67 Å, rings C(11–16) and C(1–6)AA, 3.75–3.93 Å, in the solid state. Viewed down from the top the tetramer ring appears to be a distorted hexagon. The oxygen atoms O(1) and O(1A) of the two thiobenzoate ligands are disposed above and below the ring. The Ag(1)···O(1A) distance is 2.775 Å, less than the sum of the van der Waals radii, 3.2 Å.[33] The reclination angle of the chair is *ca.* 105.3°. It appears that there are no Ag···Ag or Ag···S interactions across the width of the chair as inferred from the distances Ag(1)···Ag(1a) 4.458 Å and Ag(1)···S(1A) 4.519 Å. The Ag–S distances (2.5017(8), 2.5372(9) Å, 2.5640(9) and 2.4598(9) Å) found in **5** are again longer than those in the anionic complex $[Et_3NH][Ag(SC\{O\}Ph)_2]$.[36] The Ag(2)–S(2) bond distance (2.4598(9) Å) is shorter than those observed in similar compounds.

Recrystallization of compound **5** from toluene gave **6**·C_6H_5Me. X-Ray crystallography reveals a tetramer with a

Table 6 Selected bond lengths (Å) and angles (°) for compound **6**

Ag(1)–P(1)	2.452(2)	Ag(2)–P(2)	2.388(2)
Ag(1)–S(1)	2.587(2)	Ag(1)–S(2)	2.735(2)
Ag(1)–S(2A)[a]	2.606(2)	Ag(2)–S(2)	2.733(2)
Ag(2)–S(1)	2.440(2)	C(1)–S(1)	1.745(8)
C(2)–S(2)	1.755(8)	C(1)–O(1)	1.207(9)
C(2)–O(2)	1.213(8)		
Ag(1)–S(1)–Ag(2)	86.97(7)	Ag(1A)[a]–S(2)–Ag(1)	69.12(5)
Ag(1A)[a]–S(2)–Ag(2)	126.45(8)	Ag(2)–S(2)–Ag(1)	78.54(6)
S(1)–Ag(1)–S(2)	88.91(6)	S(1)–Ag(1)–S(2A)[a]	109.97(6)
S(2)–Ag(1)–S(2A)[a]	110.88(5)	S(1)–Ag(2)–S(2)	92.05(6)
S(1)–Ag(1)–Ag(1A)[a]	106.05(5)	S(2)–Ag(1)–Ag(1A)[a]	53.44(4)
S(2A)[a]–Ag(1)–Ag(1A)[a]	57.44(5)	P(1)–Ag(1)–S(1)	123.19(7)
P(1)–Ag(1)–S(2)	116.96(7)	P(1)–Ag(1)–S(2A)[a]	106.(10)
P(2)–Ag(2)–S(1)	145.71(7)	P(2)–Ag(2)–S(2)	118.87(7)
P(1)–Ag(1)–Ag(1A)[a]	130.34(6)	C(1)–S(1)–Ag(1)	108.2(3)
C(1)–S(1)–Ag(2)	109.1(3)	C(2)–S(2)–Ag(1)	98.8(3)
C(2)–S(2)–Ag(1A)[a]	110.6(2)	C(2)–S(2)–Ag(2)	115.8(2)

[a] Symmetry transformation used to generate equivalent atoms: $-x+1$, $-y+1$, $-z+1$.

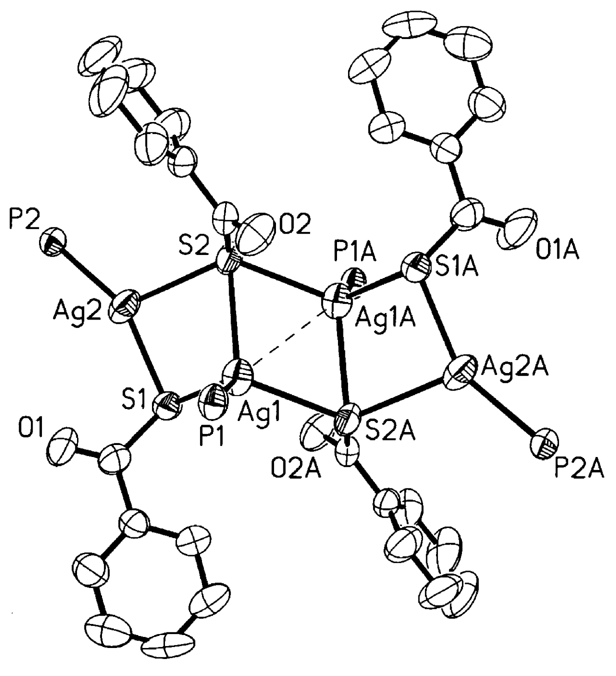
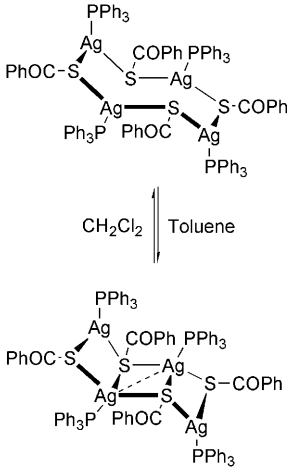


Fig. 6 A perspective view of compound **6**. Details as in Fig. 3.

crystallographic center of symmetry configurationally different from that found in **5**. A perspective view of **6** is shown in Fig. 6, which indicates that the silver and sulfur atoms interact across the eight-membered ring to form three four-membered rings maintaining a chair-like conformation. Now the new Ag(1)–S(2) distance, 2.735 Å **6** (Table 6), is longer than Ag(1)–S(2A) 2.606 Å in **3**. The central four-membered ring is perfectly planar while the other two four-membered rings are highly distorted. The dihedral angle between the Ag(1), S(1), Ag(2) plane and Ag(1), S(2), Ag(2) plane is 37.8°. There are several R_3P–M–X type compounds having stepladder like conformations in **6** (where M = Cu or Ag, X = halide, SPh or SC{O}Me).[3–5,15,16]

Molecules **3**–**6** contain twelve phenyl rings from four PPh_3 ligands and are expected to interact in the solid state. Such phenyl embraces are recognized by Dance and Scudder[43] however the influences of these supramolecular motifs based on intermolecular phenyl–phenyl attractions on the conformational or configurational isomerism and bond parameters are yet to be understood.

From the syntheses and structure determination of compounds **3**–**6** it is clear that both solvent and substitution on thiocarboxylate influence the solid state structures of the eight-membered rings. When the recrystallization was repeated in solvents CH_2Cl_2 and toluene the interconversion between the configurational isomers **5** and **6** was also found to be reversible (Scheme 2) as monitored by X-ray powder diffraction experiments.[42]



Scheme 2

Conclusion

There are a number of salient features concerning the results obtained in this investigation. The isomeric compounds, **5** and **6**, are different from the thioacetate analogs **3** and **4**, which are conformationally different from each other. Compounds **5** and **6** of $[(AgPPh_3)_4(SC\{O\}Ph)_4]$ appear to be new examples of configurational isomerism that involves Ag–S interactions. μ_3-S bridging in thiocarboxylate ligands is rare and has been reported recently in copper compounds.[16] The μ-S $\longleftrightarrow$ μ_3-S interconversion has been achieved utilizing the ability of silver(I) to form two- and three-coordinate geometries with sulfur containing ligands. These isomers can be interconverted by changing the crystallization solvent. A similar solvent dependent system involving C–N bond lengths has been reported by Köhn *et al.*[44]

Although the effect of R on the structures is delineated in the present study, the exact role played by the substituent is not clear. Further, the formation of the two different structures **5** and **6** may not just be attributed to packing effects due to the different solvates in the crystal lattice. The low temperature ^{31}P NMR in CD_2Cl_2 and toluene solvents indicated that ligand exchange and dissociation of the tetramer prevail in solution. It is likely that these neutral tetramers assemble during or prior to nucleation. The size and the coordinating ability of the solvents have a role to play in these systems. The solvent CH_2Cl_2 being smaller in size with more coordinating ability keeps the atoms in the Ag_4S_4 ring away from each other preventing any bonds across the eight-membered rings, whereas the atoms in the Ag_4S_4 tetramer are pushed across the ring to interact with each other due to the poor coordinating ability and relatively larger size of toluene. It is interesting that the existing examples[18–21] of deformational isomerism are also associated with changes in the number of different solvent molecules co-crystallized in the crystal lattice.

The chemistry of the neutral triphenylphosphine adducts of silver thiocarboxylates is quite different from that of their copper analogs. First, the copper compounds did not show any solvent dependent changes in their solid state structure[45] contrary to the silver compounds. Secondly, a distorted cubane-like copper thiobenzoate compound of formula $[Cu(\mu_3\text{-SC}\{O\}Ph\text{-}S)(\mu_3\text{-SC}\{O\}Ph\text{-}S,O)_3(CuPPh_3)_3]$ and yet another unsymmetrical dimer $[Cu_2(\mu\text{-SC}\{O\}Ph)_2(PPh_3)_3]$ have been observed. Silver thiobenzoates did not yield the analogous compounds. Further, the present investigation demonstrates the influence of the substituent R of the thiocarboxylate ligand on their chemistry. In the case of thiobenzoate a deformational isomerism has been observed while thioacetate exhibits conformational isomerism.

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42 The crystals obtained from the given solvent have uniform shape, morphology and color. In order to check whether the single crystals represent the bulk X-ray powder diffraction experiments were done. However, the diffraction patterns of the solvated crystals **3**–**6** did not match with that generated from the single crystal data due to change of the crystal system by desolvation. However, the patterns of desolvated **3**–**6** were used to follow the interconversion (ESI supporting information).

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