

# Chemistry of thiocarboxylates: syntheses and characterization of silver and copper thiocarboxylate complexes, and the structures of $[\text{Ph}_4\text{P}][\text{M}(\text{SC}(\text{O})\text{Me})_2]$ ( $\text{M} = \text{Cu}$ or $\text{Ag}$ ) and $[\text{Et}_3\text{NH}][\text{Ag}(\text{SC}(\text{O})\text{Ph})_2]$

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Received 14th June 1999, Accepted 21st July 1999

The bis(thiocarboxylate) complexes of silver(I) and copper(I) namely,  $[\text{Ph}_4\text{P}][\text{M}(\text{SC}(\text{O})\text{Me})_2]$ , ( $\text{M} = \text{Cu}$  **1** or  $\text{Ag}$  **2**) and  $[\text{Et}_3\text{NH}][\text{M}(\text{SC}(\text{O})\text{Ph})_2]$  ( $\text{M} = \text{Cu}$  **3** or  $\text{Ag}$  **4**) were prepared from the appropriate metal salt,  $\text{RC}(\text{O})\text{S}^-$  anions and the counter ion in the ratio 1:2:1. The structures of **1**, **2** and **4** were determined by X-ray crystallography. The compounds **1** and **2** are isomorphous and isostructural. In both structures, the metal is bonded to sulfur atoms of two thioacetate ligands to give a near-linear geometry. A crystallographically imposed 2-fold rotational symmetry is present in the anions and the cations. The  $[\text{Ag}(\text{SC}(\text{O})\text{Ph})_2]^-$  anion in **4** also has an approximately-linear  $\text{S}(\text{O})\text{S}$  skeleton. One of the S atom interacts weakly with a second silver(I) ion to form a dimer. The N–H hydrogen atom of the  $\text{Et}_3\text{NH}^+$  cation is involved in N–H $\cdots$ O hydrogen bonding to a carbonyl oxygen atom of the anion. There is a crystallographic center of symmetry present in this ‘ion-pair dimer’, having a rectangular arrangement of  $\text{Ag}_2\text{S}_2$  with a T-shaped coordination geometry around the silver atoms. All the compounds decompose under a nitrogen atmosphere to the corresponding metal sulfides according to weight loss observed in TG.

## Introduction

Thiocarboxylates are an interesting class of ligands with a soft sulfur donor site and a hard oxygen donor site. These ligands are expected to exhibit a variety of interesting bonding modes,<sup>1</sup> as found for the related monothiocarbamates and xanthates. However, the chemistry of metal–thiocarboxylates has not been studied in detail.<sup>2</sup> We have been interested in the chemistry of the thiobenzoate anion.<sup>3–12</sup> In most  $[\text{M}(\text{SC}(\text{O})\text{Ph})_3]^-$  anions of the Group 12 elements, the metal atoms are surrounded by three sulfur atoms in a trigonal planar fashion.<sup>3</sup> This unusual geometry is otherwise exhibited only in complexes of bulky thiolate ligands.<sup>13</sup> In the structure of the  $[\text{Na}\{\text{Cd}(\text{SC}(\text{O})\text{Ph})_3\}_2]^-$  anion, the  $\text{PhC}(\text{O})\text{S}^-$  ligand binds to the soft Cd *via* S, to give a  $\text{CdS}_3$  kernel of trigonal planar geometry.<sup>4</sup> (The hard Na binds to the ligands *via* O to give an  $\text{NaO}_6$  kernel.) Recently, we have reported<sup>10</sup> homoleptic anionic transition metal complexes of the type  $[\text{Ph}_4\text{P}][\text{M}(\text{SC}(\text{O})\text{Ph})_3]$  ( $\text{M} = \text{Mn}, \text{Co}$  or  $\text{Ni}$ ) where both oxygen and sulfur atoms are bonded to the central metal atom in a bidentate fashion. Although structural data for several other thiobenzoate complexes of main-group and transition elements are available in the literature,<sup>14–21</sup> there has been no systematic study. To our knowledge no homoleptic thiocarboxylate complexes of coinage metals have been reported. However, structural data have been given<sup>22</sup> for a dinuclear Cu(I) thiobenzoate triphenylphosphine complex and the simple neutral metal–thiobenzoates of Ag and Cu are known.<sup>23</sup>

Apart from exhibiting interesting bonding modes, thiocarboxylates are also used to synthesize ‘single-source’ precursors for metal sulfide materials. Hampden-Smith and co-workers<sup>24,25</sup> have successfully used a variety of metal thiocarboxylates as precursors to prepare metal sulfides that include ZnS and CdS.

In this paper we report the synthesis and characterization of bis(thiocarboxylate) complexes of silver(I) and copper(I) namely  $[\text{Ph}_4\text{P}][\text{M}(\text{SC}(\text{O})\text{Me})_2]$ , ( $\text{M} = \text{Cu}$  **1** or  $\text{Ag}$  **2**) and  $[\text{Et}_3\text{NH}][\text{M}(\text{SC}(\text{O})\text{Ph})_2]$  ( $\text{M} = \text{Cu}$  **3** or  $\text{Ag}$  **4**), and the structures of **1**, **2** and **4** as determined by single crystal X-ray diffraction techniques. The thermal decomposition of these compounds under a nitrogen atmosphere followed by TG is described.

## Experimental

All the materials used in the syntheses were obtained commercially and used as received. Thioacetic acid (97%), thiobenzoic acid (95%) and triethylamine were purchased from Fluka. The solvents were dried over 3 Å molecular sieves and degassed with  $\text{N}_2$  prior to use. All the preparations were carried out under a  $\text{N}_2$  atmosphere. The microanalytical laboratory at NUS performed the microanalysis. For the NMR spectra, recorded on a AC 300 MHz spectrometer, solutions were prepared in  $\text{CDCl}_3$  and external  $\text{SiMe}_4$  was used as the reference. Thermogravimetric analyses under  $\text{N}_2(\text{g})$  were carried out using an SDT 2980 TGA thermal analyser with a heating rate of  $20^\circ\text{C min}^{-1}$  and a sample size of about 5–10 mg per run. Solution IR spectra were obtained using a Bio-Rad FTIR spectrometer using a cell of path length 0.1 mm, with KBr windows.

## Syntheses

**$[\text{Ph}_4\text{P}][\text{Cu}(\text{SC}(\text{O})\text{Me})_2]$  **1**.**  $\text{Et}_3\text{NH}^+\text{MeC}(\text{O})\text{S}^-$  was obtained *in situ* as a pale yellow solution from thioacetic acid (0.5 mL, 7.0 mmol) and an aqueous solution (15 mL) containing triethylamine (1.0 mL, 7.2 mmol). To this, a solution of  $\text{CuCl}$  (0.32 g, 3.2 mmol) in  $\text{CH}_3\text{CN}$  (15 mL) was added slowly with stirring, causing a color change to yellowish red. A solution of  $\text{Ph}_4\text{PCl}$  (1.32 g, 3.5 mmol) in  $\text{H}_2\text{O}$  (10 mL) was added and the

<sup>†</sup> Planar and pyramidal  $\text{CdS}_3$  kernels are found in rhombohedral  $[\text{Ph}_4\text{P}][\text{Cd}(\text{SC}(\text{O})\text{Ph})_3]$ .<sup>11</sup>

**Table 1** Crystal data and experimental details for **1**, **2** and **4**

	<b>1</b>	<b>2</b>	<b>4</b>
Chemical formula	C <sub>28</sub> H <sub>26</sub> CuO <sub>2</sub> PS <sub>2</sub>	C <sub>28</sub> H <sub>26</sub> AgO <sub>2</sub> PS <sub>2</sub>	C <sub>20</sub> H <sub>26</sub> AgNO <sub>2</sub> S <sub>2</sub>
Formula weight	553.12	597.45	484.41
<i>T/K</i>	293(2)	293(2)	295(2)
Crystal system	Tetragonal	Tetragonal	Monoclinic
Space group	<i>P</i> 4 <sub>2</sub> <i>c</i> (no. 114)	<i>P</i> 4 <sub>2</sub> <i>c</i> (no. 114)	<i>P</i> 2 <sub>1</sub> <i>c</i>
<i>a/Å</i>	11.5184(6)	11.7596(1)	11.1129(2)
<i>b/Å</i>	11.5184(6)	11.7596(1)	19.9831(4)
<i>c/Å</i>	19.767(2)	19.1859(3)	10.7747(1)
$\beta/^\circ$			114.225(1)
<i>V/Å</i> <sup>3</sup>	2622.5(3)	2653.18(5)	2182.04(6)
<i>Z</i>	4	4	4
<i>D</i> <sub>c</sub> /g cm <sup>-3</sup>	1.401	1.496	1.475
Reflections measured	11975	16269	13365
Independent reflections	2321 ( <i>R</i> <sub>int</sub> = 0.1320)	3420 ( <i>R</i> <sub>int</sub> = 0.0224)	5326 ( <i>R</i> <sub>int</sub> = 0.0308)
$\mu/\text{mm}^{-1}$	1.076	1.001	1.128
Data/restraints/parameters	1389/0/155	2780/0/156	3320/9/236
Goof on $ F ^2$	1.195	1.061	1.023
Final <i>R</i> indices	<i>R</i> 1 = 0.1072, <i>wR</i> 2 = 0.1439	<i>R</i> 1 = 0.0332, <i>wR</i> 2 = 0.0799	<i>R</i> 1 = 0.0466, <i>wR</i> 2 = 0.0922
<i>R</i> indices (all data)	<i>R</i> 1 = 0.1796, <i>wR</i> 2 = 0.1654	<i>R</i> 1 = 0.0455, <i>wR</i> 2 = 0.0851	<i>R</i> 1 = 0.0910, <i>wR</i> 2 = 0.1190

solvents were removed from the reaction mixture under reduced pressure to give a reddish oily product. This was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (10 mL), H<sub>2</sub>O (15 mL) was added and the mixture was stirred for 5 min. The CH<sub>2</sub>Cl<sub>2</sub> layer was separated and concentrated to ca. 5 mL. Hexane (5 mL) and Et<sub>2</sub>O (30 mL) were added, and the mixture was left undisturbed at 0 °C to obtain a reddish yellow precipitate along with red crystals. The crystals were separated, washed with Et<sub>2</sub>O, and dried in a desiccator under vacuum. Yield: 1.18 g (66%). Calc. for C<sub>28</sub>H<sub>26</sub>CuO<sub>2</sub>PS<sub>2</sub>: C, 60.80; H, 4.70. Found: C, 60.20; H, 5.34%.  $\nu(\text{C=O})$  1616 cm<sup>-1</sup>. NMR data:  $\delta(^1\text{H})$  2.49 (s, 6H, CH<sub>3</sub>), 7.5–7.8 (m, 20 H, Ph);  $\delta(^{13}\text{C})$  39.52 (CH<sub>3</sub>), 117.22 (C<sup>1</sup> of Ph, <sup>1</sup>*J*(P–C) = 89 Hz), 131.39 (C<sup>3,5</sup> of Ph, <sup>3</sup>*J*(P–C) = 13 Hz), 134.98 (C<sup>2,6</sup> of Ph, <sup>2</sup>*J*(P–C) = 10 Hz), 136.42 (C<sup>4</sup> of Ph, <sup>4</sup>*J*(P–C) = 3 Hz), 209.54 (CO).

**[Ph<sub>4</sub>P][Ag(SC{O}Me)] 2.** Thioacetic acid (1.0 mL, 14.0 mmol) was added slowly to an aqueous solution (25 mL) containing triethylamine (2.0 mL, 14.4 mmol) to obtain a pale yellow solution of Et<sub>3</sub>NH<sup>+</sup>CH<sub>3</sub>C{O}S<sup>-</sup>. To this, a solution of AgNO<sub>3</sub> (1.16 g, 6.8 mmol) in H<sub>2</sub>O (15 mL) was added with continuous stirring, to give a cream colored solution. A solution of Ph<sub>4</sub>PCl (2.55 g, 6.8 mmol) in H<sub>2</sub>O (10 mL) was added to this reaction mixture with stirring to give a cream colored precipitate. Dichloromethane (10 mL) was added to the reaction mixture and the whole stirred for 5 min, at which point the CH<sub>2</sub>Cl<sub>2</sub> layer was yellow. The organic layer was separated and concentrated to a volume of ca. 5 mL, then Et<sub>2</sub>O was layered on the concentrate and the mixture was left undisturbed at 0 °C to obtain cream crystals. The crystals were decanted off, washed with Et<sub>2</sub>O and dried under vacuum. Yield: 2.2 g (54%). Calc. for C<sub>28</sub>H<sub>26</sub>AgO<sub>2</sub>PS<sub>2</sub>: C, 56.29; H, 4.35. Found: C, 56.63; H, 4.27%.  $\nu(\text{C=O})$  1610 cm<sup>-1</sup>. NMR data:  $\delta(^1\text{H})$  2.39 (s, 6H, CH<sub>3</sub>), 7.74–7.92 (m, 20H, Ph);  $\delta(^{13}\text{C})$  38.36 (CH<sub>3</sub>), 118.12 (C<sup>1</sup> of Ph, <sup>1</sup>*J*(P–C) = 89 Hz), 131.42 (C<sup>3,5</sup> of Ph, <sup>3</sup>*J*(P–C) = 13 Hz), 135.07 (C<sup>2,6</sup> of Ph, <sup>2</sup>*J*(P–C) = 10 Hz), 136.46 (C<sup>4</sup> of Ph, <sup>4</sup>*J*(P–C) = 3 Hz), 209.97 (CO).

**[Et<sub>3</sub>NH][Cu(SC{O}Ph)] 3.** Thiobenzoic acid (1 mL, 8.5 mmol) was added dropwise with stirring to a solution of triethylamine (1.2 mL, 8.6 mmol) in CHCl<sub>3</sub> (5 mL). The resultant solution of Et<sub>3</sub>NH<sup>+</sup>PhC{O}S<sup>-</sup> was added to CuCl (0.42 g, 4.2 mmol) in CH<sub>3</sub>CN (15 mL) to get a reddish yellow mixture. The mixture was stirred for 15 min., then the solvent was removed under reduced pressure to leave a red viscous oil. The oil was dissolved in CHCl<sub>3</sub> (5 mL) and washed with H<sub>2</sub>O (ca. 30 mL) to remove Et<sub>3</sub>NHCl. The organic layer was separated, layered with hexane (5–8 mL) and Et<sub>2</sub>O (30–40 mL) until it became turbid,

and the mixture was left undisturbed at 0 °C. A reddish yellow solid was obtained in a day. This was separated by decantation, washed with Et<sub>2</sub>O and dried under vacuum. Yield: 1.84 g (77%). Satisfactory elemental analysis could not be obtained. However, the <sup>1</sup>H and <sup>13</sup>C NMR spectra and TG are consistent with the proposed formula, C<sub>20</sub>H<sub>26</sub>CuO<sub>2</sub>NS<sub>2</sub>.  $\nu(\text{C=O})$  1636, 1603 cm<sup>-1</sup>. NMR data:  $\delta(^1\text{H})$  1.37 (t, 9H, CH<sub>3</sub>), 3.29 (q, 6H, CH<sub>2</sub>), 7.34–7.43 (dt, 6H, *m*- and *p*-H of Ph), 8.16 (d, 4H, *o*-H of Ph).  $\delta(^{13}\text{C})$  9.49 (CH<sub>3</sub>), 46.93 (CH<sub>2</sub>), 128.43 (C<sup>2(or 3)</sup> of Ph), 129.17 (C<sup>3(or 2)</sup> of Ph), 132.32 (C<sup>4</sup> of Ph), 141.61 (C<sup>1</sup> of Ph), 208.24 (CO).

**[Et<sub>3</sub>NH][Ag(SC{O}Ph)] 4.** Thiobenzoic acid (1.0 mL, 8.5 mmol) was added dropwise to a CHCl<sub>3</sub> solution (5 mL) containing triethylamine (1.2 mL, 8.6 mmol). A solution of AgNO<sub>3</sub> (0.69 g, 4.1 mmol) in H<sub>2</sub>O (15 mL) was added to give a cream colored turbid mixture, which was stirred for 15 min. The yellow CHCl<sub>3</sub> layer was separated, MeOH (2–3 mL) and Et<sub>2</sub>O (15–20 mL) were added, and the mixture was left to crystallize at 0 °C. The creamy white crystals were decanted off, washed with Et<sub>2</sub>O and dried in vacuum. Yield: 1.55 g (79%). Calc. for C<sub>20</sub>H<sub>26</sub>AgO<sub>2</sub>NS<sub>2</sub>: C, 49.59; H, 5.37; N, 2.89. Found: C, 49.50; H, 5.16; N, 2.90%. NMR data:  $\delta(^1\text{H})$  1.38 (t, 9H, CH<sub>3</sub>), 3.30 (q, 6H, CH<sub>2</sub>), 7.32–7.44 (dt, 6H, *m*- and *p*-H of Ph), 8.15 (d, 4H, *o*-H of Ph);  $\delta(^{13}\text{C})$  9.65 (CH<sub>3</sub>), 47.33 (CH<sub>2</sub>), 128.38 (C<sup>2(or 3)</sup> of Ph), 129.09 (C<sup>3(or 2)</sup> of Ph), 132.06 (C<sup>4</sup> of Ph), 142.63 (C<sup>1</sup> of Ph), 208.13 (CO).

#### Crystal structure determinations

The diffraction experiments were carried out on a Bruker AXS SMART CCD 3-circle diffractometer with a Mo-K $\alpha$  sealed tube at 23 °C. The software used was: SMART<sup>26</sup> for collecting frames of data, indexing reflections and determination of lattice parameters; SAINT<sup>26</sup> for integration of intensity of reflections and scaling; SADABS<sup>27</sup> for empirical absorption correction; and SHELXTL<sup>28</sup> for space group determination, structure solution and least-squares refinements on *F*<sup>2</sup>. The single crystals were obtained during the syntheses. The crystals were mounted at the ends of glass fibres and used for diffraction experiments. The crystal data and experimental details are given in Table 1. Poor agreement factors for **1** may be attributed to the weakly diffracting nature of the crystals. The absolute structure parameters were refined to –0.02(7) and 0.02(4) for **1** and **2** respectively.

CCDC reference number 186/1589.

See <http://www.rsc.org/suppdata/dt/1999/3153/> for crystallographic files in .cif format.

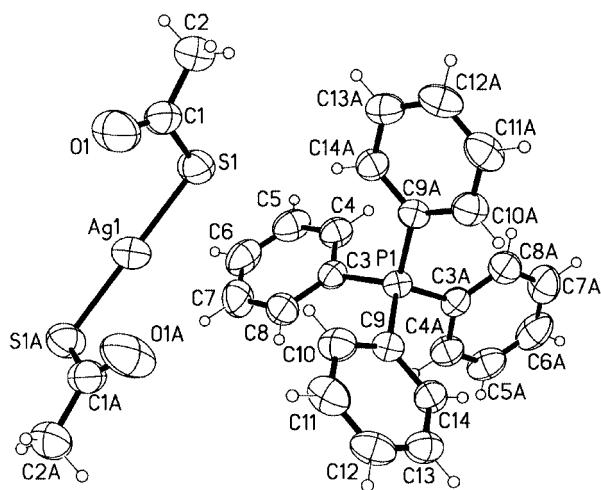
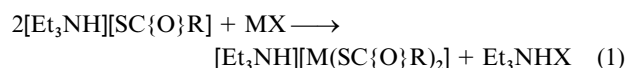


Fig. 1 A perspective view of the molecule, **2**. The non-hydrogen atoms are drawn as 50% probability thermal ellipsoids.

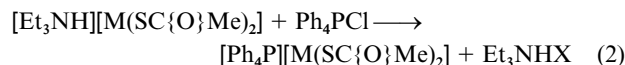
## Results and discussion

### Preparation of $[\text{Ph}_4\text{P}][\text{M}(\text{SC}(\text{O})\text{CH}_3)_2]$ and $[\text{Et}_3\text{NH}][\text{M}(\text{SC}(\text{O})\text{Ph})_2]$ ( $\text{M} = \text{Ag}$ or $\text{Cu}$ )

The complexes **1–4** were prepared by reacting suitable metal salts with two equivalents of the appropriate deprotonated thio-carboxylic acid [eqn. (1)]. For thioacetate complexes, the



triethylamine base served to remove the proton from  $\text{PhC}(\text{O})\text{SH}$  and the resultant  $\text{Et}_3\text{NH}^+$  cation was used as the counter ion to isolate the product in the solid state. The  $\text{Et}_3\text{NH}^+$  salts of the thioacetate complexes were found to be moisture sensitive, very unstable in air and the yellow color changed to dark brown even under nitrogen at 5 °C. However, the  $\text{Ph}_4\text{P}^+$  cation was successfully used to isolate the thioacetate complexes of Cu and Ag as shown in eqn. (2).



The isolated yield of these compounds varies from 54 to 79%. The compounds were characterized by elemental analysis,  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra in solution and IR spectra and are consistent with the empirical formula. The crystal structures of the compounds were determined by single crystal X-ray diffraction techniques.

### Molecular structures

The compounds **1** and **2** are isomorphous and isostructural. The anions and the cations are well separated in the two structures. The structure of the  $\text{Ph}_4\text{P}^+$  cation is unexceptional and will not be discussed further. In the  $[\text{M}(\text{SC}(\text{O})\text{Me})_2]^-$  anion, the central metal atom is coordinated to the sulfur atoms of the thioacetates to give a two-coordinate near-linear geometry. The anion has a crystallographically imposed 2-fold symmetry. A representative view of the anion in **2** is shown in Fig. 1. Selected bond distances and angles for the anions in **1** and **2** are summarized in Table 2. In the anion of **1**, the Cu–S distance and S–Cu–S angle are 2.151(3) Å and 176.6(2)° respectively. A search in the Cambridge Structural Database (CSD) System<sup>29</sup> revealed there are only 9 compounds containing two-coordinate Cu(I) as  $\text{CuS}_2$  fragments.‡ Of those, only two contain discrete monomeric

‡ The anions  $\text{MS}_2^-$  ( $\text{M} = \text{Cu}, \text{Ag}$ ) are known in the gas phase, and are thought to be linear.<sup>30</sup>

Table 2 Selected bond distances (Å) and angles (°) for the anions in **1** and **2**

	<b>1</b>	<b>2</b>
M(1)–S(1)	2.151(3)	2.359(1)
S(1)–C(1)	1.716(12)	1.730(4)
O(1)–C(1)	1.210(12)	1.999(4)
C(1)–C(2)	1.494(14)	1.499(5)
S(1)–M(1)–S(1A)	176.6(2)	178.96(5)
C(1)–S(1)–M(1)	100.2(4)	98.99(12)
O(1)–C(1)–C(2)	122.7(11)	120.9(3)
O(1)–C(1)–S(1)	124.5(9)	124.4(3)
C(2)–C(1)–S(1)	112.8(9)	114.8(3)

Symmetry operator: A  $-x + 1, -y, z$ .

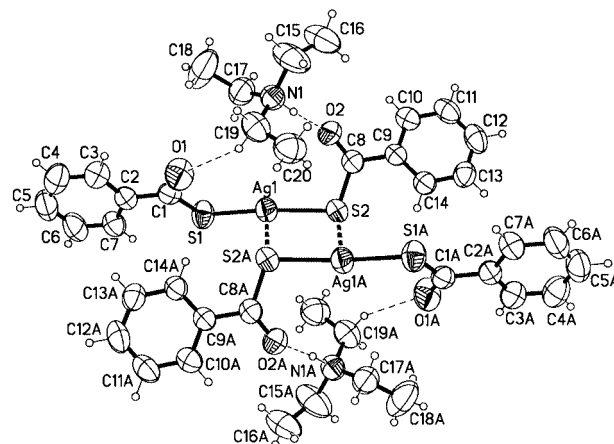


Fig. 2 The structure of the 'ion-pair dimer' **4** in the solid state. The thermal ellipsoids are shown at the 50% probability level.

$[\text{Cu}(\text{SR})_2]^-$  anions. Both of these have bulky R groups: SR = 2,3,5,6-tetramethylbenzenethiolate<sup>31</sup> and adamantylthiolate.<sup>32</sup> (We have noted earlier that  $\text{PhC}(\text{O})\text{S}^-$  mimics bulky thiolates as a ligand.<sup>3</sup>) The Cu–S distances observed in these two thiolate complexes, 2.137 and 2.147 Å, are slightly lower than the value observed in **1**. The  $\text{Cu} \cdots \text{O}$  distance, 2.998 Å, indicates that there is no interaction between the Cu and O atoms (sum of the van der Waals radii,<sup>33</sup> 2.9 Å). The atoms Cu(1), S(1), O(1), C(1) and C(2) are in a plane (deviation, 0.01 Å) and the interplanar angle between the two thioacetates is 76.6(3)°.

The Ag–S distance and S–Ag–S angle in the anion of **2** are 2.359(1) Å and 178.96(5)° respectively. The CSD search revealed no mononuclear two-coordinate silver(I) thiolate complexes. In all the 12 hits, linear  $\text{AgS}_2$  fragments were present in polynuclear silver thiolate anions. Thus, to the best of our knowledge, **2** is the first example of a structurally characterized mononuclear Ag complex having a linear S–Ag–S geometry.‡ The Ag–S distances found in **2** are comparable to those reported in the literature (range, 2.289–2.528 Å). There appears to be no interaction between the Ag and the carbonyl oxygen atoms of the thioacetate ligands ( $\text{Ag}(1) \cdots \text{O}(1)$  and the sum of the van der Waals radii of Ag and O are 3.082 and 2.9 Å respectively). All the non-hydrogen atoms in the thioacetate ligand and Ag(1) are in a plane (deviation, 0.006 Å) and the inter-planar angle between the two such planes, is 71.8(1)°.

The structure of **4** is shown in Fig. 2, and selected bond distances and angles are given in Table 3. In the complex anion, Ag(1) is bonded to two thiobenzoate anions to give an approximately linear S–Ag–S coordination geometry. The Ag–S distances are 2.359(1) and 2.382(1) Å. The S–Ag–S angle, 161.16(4)°, is smaller than S–M–S observed in **1** and **2**. The Ag(1)–S(2) distance is longer than Ag(1)–S(1). The phenyl rings in the two  $\text{PhC}(\text{O})\text{S}^-$  ligands are twisted from the C–C(O)S plane by 12.1(2) and 22.0(1)°. The interplanar angle between

**Table 3** Selected bond distances (Å) and angles (°) for the anion in **4**

Ag(1)–S(1)	2.359(1)	O(1)–C(1)	1.213(4)
Ag(1)–S(2)	2.382(1)	O(2)–C(8)	1.232(4)
S(1)–C(1)	1.727(4)	C(1)–C(2)	1.512(4)
S(2)–C(8)	1.729(3)	C(8)–C(9)	1.485(4)
S(1)–Ag(1)–S(2)	161.16(4)	C(2)–C(1)–S(1)	116.9(2)
C(1)–S(1)–Ag(1)	106.8(1)	O(2)–C(8)–C(9)	119.8(3)
C(8)–S(2)–Ag(1)	107.2(1)	O(2)–C(8)–S(2)	123.2(3)
O(1)–C(1)–C(2)	119.6(3)	C(9)–C(8)–S(2)	117.0(3)
O(1)–C(1)–S(1)	123.5(3)		

**Table 4** Thermogravimetry for **1**, **2**, **3** and **4**

Compound	Temperature range/°C	Remaining weight (%)	
		Observed	Calculated <sup>a</sup>
<b>1</b>	150–460	16.3	14.4
<b>2</b>	180–460	21.7	20.7
<b>3</b>	100–280	17.7	18.1
<b>4</b>	110–340	25.6	25.6

<sup>a</sup> Calculated for the formation of the corresponding metal sulfide, M<sub>2</sub>S.

the planes containing S(1), O(1), C(1), C(2) (deviation, 0.00 Å) and S(2), O(2), C(8), C(9) (deviation, 0.06 Å) is 57.8(1)°. This value is much smaller than the corresponding ones observed in **1** or **2**. These differences may be explained if we consider the secondary interactions of [Ag(SC{O}Ph)<sub>2</sub>]<sup>−</sup> in the crystal lattice.

The carbonyl oxygen atoms of the PhC{O}S<sup>−</sup> ions are involved in hydrogen bonding. The N–H hydrogen atom is strongly hydrogen bonded to O(2). The relevant parameters are: H(1)⋯O(2), 1.887(4) Å, N(1)⋯O(2), 2.776(4) Å, N–H⋯O, 165.0(1)°. This N–H⋯O=C hydrogen bonding appears to weaken the C(8)–O(2) bond (1.232(4) Å) as compared to C(1)–O(1). Also found is a very weak interaction between H(19) and O(1). The relevant parameters are: H(19)⋯O(1), 2.436(5) Å, C(19)⋯O(1), 3.340(5) Å, C–H⋯O, 155.0(1)°. Evidently the anion and the cation are present as an ion-pair in the solid state. There is also a weak intermolecular interaction between Ag(1) and S(2A) atoms in the solid state. The Ag(1)⋯S(2A) distance, 3.106 Å between adjacent [Ag(SC{O}Ph)<sub>2</sub>]<sup>−</sup> anions is less than the sum of the van der Waals radii,<sup>33</sup> 3.50 Å. If we consider this interaction, then the structure can be described as an 'ion-pair dimer' in the solid-state (Fig. 2) with T-shaped geometry around the silver atoms. The presence of a crystallographic centre of inversion results in this 'ion-pair dimer' having rectangular geometry. Such ion-pairs exist in [Et<sub>3</sub>NH][Cd(SC{O}Ph)<sub>3</sub>]<sup>6</sup> also.

### Thermogravimetric analysis

Thermal decomposition of the compounds was studied by thermogravimetry under an N<sub>2</sub> atmosphere. All the complexes decompose in multi-step processes. A summary of the overall weight losses is displayed in Table 4. The residual weight at the end of the decomposition indicated the formation of the corresponding metal sulfides.

### Acknowledgements

J. J. V. would like to thank the National University of Singapore for a research grant (Grant No. RP970618), and P. A. W. D. thanks the Natural Sciences and Engineering Research Council of Canada for financial support.

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