17

## Ian Dance,\* Lyn Fitzpatrick, Marcia Scudder, and Don Craig

School of Chemistry, University of New South Wales, Kensington, NSW 2033, Australia

 $(Ph_3P)_4(AgSBut)_{14}$ , virtual symmetry  $C_{2h}$ , contains a 28-membered cycle of alternating sulphur and silver atoms with phosphine ligands at Ag-(1),-(6),-(8),-(13), folded without contracycle connections into an orthorhombic molecular box, while  $(Ph_3P)_2(AgSCMeEt_2)_8$  contains weakly connected Ag<sub>4</sub>(SR)<sub>4</sub> and  $(Ph_3P)_2Ag_4(SR)_4$  cycles.

We report two new molecular structure types for silver thiolates, in the derivatives  $(Ph_3P)_4(AgSR)_{14}$  and  $(Ph_3P)_2(AgSR)_8$  with small proportions of phosphine. Prior to this work the two known  $(AgSR)_n$  structure types in crystals were the cyclic molecule  $(AgSC_6H_{11})_{12}$ , (1), stabilised by a small number of intra- and inter-molecular secondary Ag--S interactions,<sup>1</sup> and the non-molecular structure of the tertiary thiolate  $AgSCMeEt_2$ , (2), containing a chain of two intertwined but totally unconnected  $\{-Ag-(\mu-SR)-\}_{\infty}$  strands.<sup>2</sup> The significant structural feature of (2) is the zig-zag arrangement of linear S-Ag-S segments in two parallel planes, with each strand crossing from one plane to the other such that the chain repeat unit is octameric  $[(2)]_8$ . On this basis a structural mechanism was proposed<sup>2</sup> for interconversion of the known octameric<sup>3</sup> molecule  $[(2)]_8$  in solution and the non-molecular structure of the crystal.



Solutions of AgSBu<sup>t</sup> and Ph<sub>3</sub>P in chloroform yield colourless block-like crystals<sup>†</sup> of (Ph<sub>3</sub>P)<sub>4</sub>(AgSBu<sup>t</sup>)<sub>14</sub>, (3). The molecule (shown in Figure 1) is a 28-membered centrosymmetric cycle of alternating silver and sulphur atoms, with ten linear S-Ag-S segments and four bent segments in which phosphine ligands are attached to trigonal planar silver atoms. A pseudo-twofold axis along the length Ag(7) - -Ag(7') of this unique molecule relates all atoms except the Ph<sub>3</sub>P phenyl rings. There are no secondary Ag--S interactions: the opposing directions of S-Ag-S segments related by the pseudo-twofold axis allow the closest approach of strands



Figure 2. Diagrammatic representation of the sections of (3): (a), zig-zag; (b), crossover; (c), bending; (d), end-connecting.



**Figure 1.** Centrosymmetric  $(Ph_3P)_4(AgSBu^t)_{14}$ . (a) View showing zig-zag, crossover, and end segments, and the box-like molecular shape. Phenyl rings are omitted. (b) View rotated from (a) by 70° about the pseudo-twofold axis Ag(7)– -Ag(7'), including only thiolate  $C_{\alpha}$  atoms. Ag(3)– -Ag(4') 3.12(1), Ag(2)– -Ag(5') 3.09(1), Ag(2)– -Ag(7') 3.14(1), Ag(5)– -Ag(7) 3.14(1) Å.

Figure 3.  $(Ph_3P)_2(AgSCMeEt_2)_8$ , excluding all except thiolate  $C_{\alpha}$  carbon atoms. The weak secondary interactions are drawn as broken lines: Ag(1) - S(57) 2.97, Ag(2) - S(58) 2.90, Ag(7) - S(13) 2.87, Ag(8) - S(23) 2.86 Å. S(13) - Ag(3) - S(23) 172.8, S(14) - Ag(4) - S(24) 170.9, S(57) - Ag(5) - S(58) 173.8, S(67) - Ag(6) - S(68) 173.2,  $S(57) - Ag(7) - S(57) - Ag(8) - S(68) 165.8^{\circ}$ .

Published on 01 January 1984. Downloaded by University of California - Riverside on 25/10/2014 05:25:14.

across the axis to be between silver atoms, at non-bonding distances of ca. 3.1 Å.

The structural units of (3) are shown diagrammatically (in bonbon motif) in Figure 2, as the zig-zag, the crossover, the bending, and the end-connecting sections, the first two corresponding to the sections of (2). It can be seen from Figure 1(a) that the 24 silver and sulphur atoms of all the linear segments in the zig-zag, crossover, and end sections of (3) lie in six planes which are the six faces of an orthorhombic molecular box. The bent section evidently is necessary to connect the crossover and end sections without the Ag–S–Ag angles becoming too acute.

The convoluted but highly symmetrical and compact molecule (3) suggests several structural principles. One, which is apparent also from (2), is that  $\{-Ag-(\mu-SR)-\}_n$  strands, although co-ordinately saturated, are unhindered by substituents and come together without connection to maximise crystal density. Another is that recognisable structural functions that (i) extend a chain (zig-zag segments), (ii) entwine double strands (crossover segments), and (iii) terminate a chain (bend and end segments), may be combined in the construction of molecules.

From solutions of (2) and  $Ph_3P$  in acetone we have crystallised  $(Ph_3P)_2(AgSCMeEt_2)_8$ , (4).† A molecular struc-

<sup>+</sup> Crystal data for (3),  $C_{128}H_{186}Ag_{14}S_{14}P_4(CHCl_3)_x$ ,  $P\bar{1}$ , a = 13.523(8), b = 13.852(7), c = 21.808(12) Å,  $\alpha = 79.86(4)$ ,  $\beta = 86.08(4)$ ,  $\gamma = 85.75(4)^\circ$ , Z = 1,  $D_m = 1.69(2)$ ,  $D_c = 1.69$  g cm<sup>-3</sup> (x = 2), 2690 observed (Mo- $K_\alpha$ ) reflections,  $2\theta_{max} = 30^\circ$ ,  $R(R_w) 0.092$  (0.123) based on non-hydrogen atoms, isotropic. For (4),  $C_{84}H_{134}Ag_8S_8P_2$ ,  $P2_1/c$ , a = 14.736(8), b = 27.108(4), c = 24.939(15) Å,  $\beta = 99.85(3)^\circ$ , Z = 4,  $D_m = 1.57(2)$ ,  $D_c = 1.57$  g cm<sup>-3</sup>; 9098 observed (Mo- $K_\alpha$ ) reflections,  $R(R_w) 0.056(0.073)$ , Ag, S, P atoms anisotropic.

The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

$$(AgSC_{6}H_{11})_{12} Ag_{4}(\mu-SR)_{4}$$
(1)
(6)
(Ph\_{3}PAg)\_{2}Ag\_{2}(\mu-SR)\_{4}
(7)

J. CHEM. SOC., CHEM. COMMUN., 1984

ture such as (5), predicted from the foregoing structural principles, does not occur, but instead there are two cycles,  $Ag_4(\mu$ -SR)<sub>4</sub>, (6), and  $(Ph_3PAg)_2Ag_2(\mu$ -SR)<sub>4</sub>, (7), (see Figure 3) which face each other and are connected by four weak secondary Ag– –S interactions.‡ Cycle (6) is analogous to that in (CuOBut)<sub>4</sub>,<sup>4</sup> and contains four linear S–Ag–S segments, while cycle (7) contains two linear S–Ag–S segments linked by two trigonal silver atoms with co-ordinated phosphine. Although the occurrence of the small monocycles in (4) is difficult to rationalise in view of the patterns set by (2) and (3), the structure (4) is consistent with the principle of strand agglomeration, by secondary Ag––S interactions in the absence of strand entwinement.

This research is supported by the Australian Research Grants Scheme.

Received, 9th September 1983; Com. 1210

## References

- 1 I. G. Dance, Inorg. Chim. Acta, 1977, 25, L17.
- 2 I. G. Dance, L. J. Fitzpatrick, A. D. Rae, and M. L. Scudder, *Inorg. Chem.*, 1983, **22**, in the press.
- 3 S. Åkerström, Ark. Kemi, 1965, 24, 505.
- 4 T. Greiser and E. Weiss, Chem. Ber., 1976, 109, 3142.

<sup>‡</sup> The weakness of the secondary interactions is shown by their lengths, all 0.5 Å longer than the mean Ag–S bond length of unconnected linear segments, and by the minor perturbations of digonal or trigonal stereochemistry at the connected silver atoms.