

catena-Poly[[[μ -1,3-bis(diphenylphosphanyl)propane- $\kappa^2 P:P'$][O-ethyl(4-methoxyphenyl)phosphonodithioato- $\kappa^2 S,S'$]silver(I)] chloroform monosolvate]

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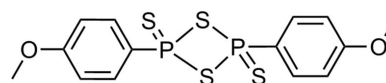
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Reaction of a mixture of AgOAc, Lawesson's reagent [2,4-bis(4-methoxyphenyl)-1,3-dithiadiphosphetane-2,4-disulfide] and 1,3-bis(diphenylphosphanyl)propane (dppp) under ultrasonic treatment gave the title compound, $\{[\text{Ag}(\text{C}_9\text{H}_{12}\text{O}_2\text{PS}_2)(\text{C}_{27}\text{H}_{26}\text{P}_2)]\cdot\text{CHCl}_3\}_n$, a novel one-dimensional chain based on the *in situ*-generated bipodal ligand $[\text{ArP}(\text{OEt})\text{S}_2]^-$ (Ar = 4-methoxyphenyl). The compound consists of bidentate bridging 1,3-bis(diphenylphosphanyl)propane (dppp) and *in situ*-generated bidentate chelating $[\text{ArP}(\text{OEt})\text{S}_2]^-$ ligands. The dppp ligand links the $[\text{Ag}\{\text{ArP}(\text{OEt})\text{S}_2\}]$ subunit to form an achiral one-dimensional infinite chain. These achiral chains are packed into chiral crystals by virtue of van der Waals interactions. No π - π interactions are observed in the crystal structure.

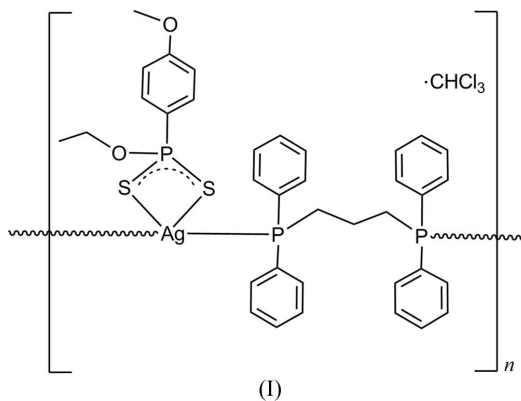
Comment

The design and construction of coordination structures is one of the most attractive areas of crystal engineering, due to their intriguing structural motifs and functional properties (Chen *et al.*, 2010; Blake, Brooks *et al.*, 1999; Blake, Champness *et al.*, 1999; Evans & Lin, 2002; Kitagawa *et al.*, 2004; Yaghi *et al.*, 2003; Sun *et al.*, 2011). Organophosphorus sulfide reagents like P_4S_{10} , Lawesson's reagent [2,4-bis(4-methoxyphenyl)-1,3-dithiadiphosphetane-2,4-disulfide, LR], and modified LRs such as Davy's reagent, Japanese reagent and Belleau's reagent, have been successfully employed as thionation agents for organic substrates to give thiolactones and thiocarbonyls (Scheibye *et al.*, 1981; Jesberger *et al.*, 2003; Foreman & Woollins, 2000; Ozturk *et al.*, 2007). The LR containing a four-membered P_2S_2 ring with alternating P and S atoms can be in equilibrium with a highly reactive dithiophosphine ylide

$[\text{ArPS}_2]^-$ (Ar = 4-methoxyphenyl), which reacts with carbonyl-containing compounds to form P/S-containing anionic ligands. Subsequent assembly of anionic ligands into large Cu^{I} or Ag^{I} aggregates has been reported as an efficient synthetic route to a broader variety of coordination polymers or clusters (Shi, Ahlrichs *et al.*, 2005). Recently, we used this versatile precursor to construct an Ag_{20} cluster based on *in situ*-generated bipodal $[\text{ArP}(\text{OEt})\text{S}_2]^-$ and tripodal $[\text{ArPOS}_2]^{2-}$ ligands incorporating the auxiliary Ph_3P (triphenylphosphane) ligand (Sun *et al.*, 2010). As an extension of our work, we replaced the auxiliary Ph_3P ligand by the 1,3-bis(diphenylphosphanyl)propane (dppp) ligand and intended to exploit the influence of an auxiliary P-donor on the structures of the AgOAc-LR system. The title compound, (I), was obtained as an infinite chain.



Lawesson's reagent, LR



(I)

The asymmetric unit of (I) contains one Ag^{I} cation, one dppp ligand, one anionic $[\text{ArP}(\text{OEt})\text{S}_2]^-$ ligand and one chloroform solvent molecule. As shown in Fig. 1, the Ag^{I} cation is in a tetrahedral environment, completed by two P atoms from two dppp ligands and two S atoms from one $[\text{ArP}(\text{OEt})\text{S}_2]^-$ ligand, with average Ag-P and Ag-S bond lengths of 2.4500 (11) and 2.6477 (12) Å, respectively. The distortion of the tetrahedron can be indicated by the calculated value of the τ_4 parameter (Yang *et al.*, 2007) to describe the geometry of a four-coordinate metal system, which is 0.80 for Ag^{I} (for perfect tetrahedral geometry, $\tau_4 = 1$). The Ag-P and Ag-S bond lengths (Table 1) are comparable with reported values (Shi *et al.*, 2007).

In (I), the $[\text{ArP}(\text{OEt})\text{S}_2]^-$ anion is a bidentate chelating ligand which coordinates one Ag^{I} centre to form the $[\text{Ag}\{\text{ArP}(\text{OEt})\text{S}_2\}]$ subunit. The bidentate bridging dppp ligands link the $[\text{Ag}\{\text{ArP}(\text{OEt})\text{S}_2\}]$ subunits to form an achiral one-dimensional infinite chain along the *a* axis (Fig. 2). There are no obvious hydrogen-bonding or π -stacking interactions between adjacent chains. Therefore, these achiral chains are packed into chiral crystals by virtue of van der Waals inter-

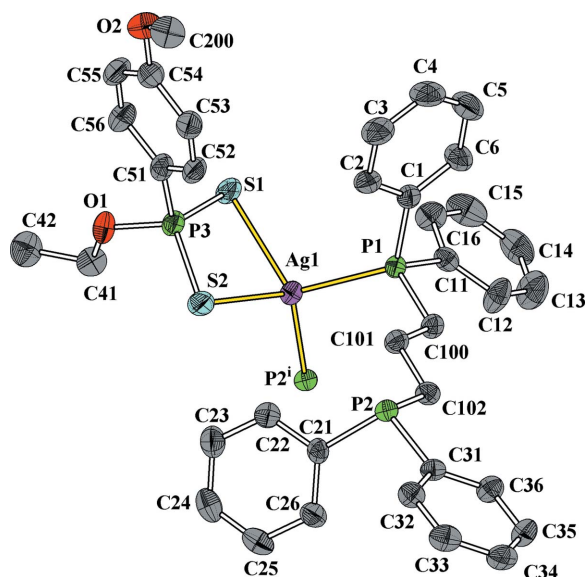


Figure 1
The structure of (I), showing the atom-numbering scheme and the coordination environment around the Ag^I centre. Displacement ellipsoids are drawn at the 50% probability level. H atoms and the chloroform solvent molecule have been omitted for clarity. [Symmetry code: (i) $x + 1, y, z$.]

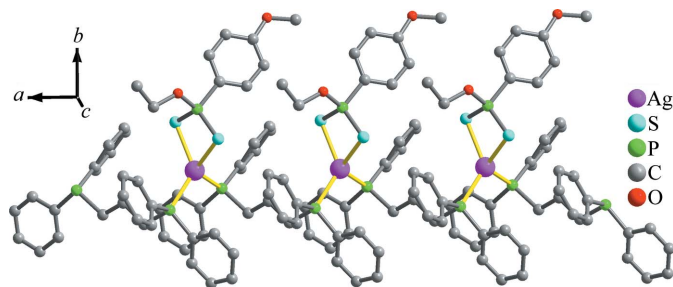


Figure 2
A ball-stick perspective view of the one-dimensional chain in (I). H atoms and chloroform solvent molecules have been omitted for clarity.

actions. The chloroform molecules minimize the voids in the crystal structure.

The most fascinating feature of (I) is the *in situ*-generated anionic [ArP(OEt)S₂][−] ligand. In spite of the disassociation of LR_s into S^{2−}, [ArP(O)S₂]^{2−}, [ArS₂P–O–PS₂Ar]^{2−}, [ArPS₃]^{2−} and [ArP(O)(OAc)S][−] ligands that has been observed (Shi, Shafaei-Fallah *et al.*, 2005), it is noteworthy that the generation of the bipodal [ArP(OEt)S₂][−] ligand in the course of the reaction between AgOAc and LR is rarely observed. The formation of the bipodal [ArP(OEt)S₂][−] anion involves P–S and C–O bond cleavages of LR and acetate, respectively. To the best of our knowledge, the P–O bond is much stronger than the P–S bond, which makes LR_s vulnerable to attack by potential nucleophiles, electrophiles and radicals, as demonstrated by Rauchfuss & Zank (1986), whereby the LR underwent reversible cleavage to give ArPS₂ radicals. This could be concluded to be one of the important thermodynamic driving forces behind the formation of the P/S ligand.

Experimental

All reagents and solvents were obtained commercially and used without further purification. A mixture of Lawesson's reagent (202 mg, 0.50 mmol), AgOAc (334 mg, 2.00 mmol) and dppp (412 mg, 1.00 mmol) was dissolved in chloroform (10 ml). The mixture was treated under ultrasonic conditions (323 K, 160 W, 40 kHz, 20 min), during which time the solution changed from colourless to yellow. The mixture was filtered and diffusion of diethyl ether into the reaction mixture produced colourless crystals of (I) after two weeks (yield *ca* 45%, based on AgOAc). Elemental analysis calculated for C₃₇H₃₉AgCl₃O₂P₃S₂: C 50.10, H 4.43%; found: C 49.88, H 4.59%. Selected IR peaks (ν , cm^{−1}): 3064 (*w*), 2960 (*w*), 2936 (*w*), 1588 (*s*), 1494 (*m*), 1481 (*m*), 1436 (*s*), 1381 (*s*), 1244 (*w*), 1177 (*m*), 1107 (*m*), 1030 (*s*), 933 (*m*), 747 (*m*), 695 (*s*), 625 (*s*), 545 (*m*).

Crystal data

[Ag(C ₉ H ₁₂ O ₂ PS ₂)(C ₂₇ H ₂₆ P ₂)] [−] ·CHCl ₃	$\beta = 92.95 (3)^\circ$
$M_r = 886.93$	$V = 1959.8 (7) \text{ \AA}^3$
Monoclinic, $P2_1$	$Z = 2$
$a = 7.1493 (14) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 16.137 (3) \text{ \AA}$	$\mu = 0.98 \text{ mm}^{-1}$
$c = 17.010 (3) \text{ \AA}$	$T = 173 \text{ K}$
	$0.10 \times 0.08 \times 0.08 \text{ mm}$

Data collection

Oxford Gemini S Ultra diffractometer	26211 measured reflections
Absorption correction: multi-scan (<i>CrysAlis RED</i> ; Oxford Diffraction, 2008)	7381 independent reflections
$T_{\min} = 0.908, T_{\max} = 0.926$	6876 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.053$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.038$	H-atom parameters constrained
$wR(F^2) = 0.074$	$\Delta\rho_{\text{max}} = 0.64 \text{ e \AA}^{-3}$
$S = 1.01$	$\Delta\rho_{\text{min}} = -0.78 \text{ e \AA}^{-3}$
7381 reflections	Absolute structure: Flack (1983), with 3390 Friedel pairs
433 parameters	Flack parameter: $-0.01 (2)$
1 restraint	

Table 1

Selected geometric parameters (\AA , $^\circ$).

Ag1–P ²ⁱ	2.4424 (11)	Ag1–S1	2.6343 (12)
Ag1–P1	2.4575 (12)	Ag1–S2	2.6610 (12)
P ²ⁱ –Ag1–P1	104.67 (4)	P ²ⁱ –Ag1–S2	116.14 (4)
P ²ⁱ –Ag1–S1	128.23 (4)	P1–Ag1–S2	119.67 (4)
P1–Ag1–S1	109.36 (4)	S1–Ag1–S2	78.33 (4)

Symmetry code: (i) $x + 1, y, z$.

All H atoms were generated geometrically and allowed to ride on their parent atoms in the riding-model approximation, with aromatic C–H = 0.95 \AA , methine C–H = 1.00 \AA , methylene C–H = 0.99 \AA and methyl C–H = 0.98 \AA , and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ [$1.5U_{\text{eq}}(\text{C})$ for methyl groups].

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2008); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2008); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg,

2008) and *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97* and *publCIF* (Westrip, 2010).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SF3156). Services for accessing these data are described at the back of the journal.

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