

A new polymorph of (O-ethyl dithiocarbonato- κ^2S,S')bis(triphenylphosphine- κP)silver(I)

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A new triclinic polymorphic modification of the title compound, $[\text{Ag}(\text{C}_3\text{H}_5\text{OS}_2)(\text{C}_{18}\text{H}_{15}\text{P})_2]$, has been found and compared with the previously known orthorhombic modification [Tiekink (1988). *Coord. Chem.* **17**, 239–243]. The two polymorphs have the same molecular shape, *viz.* a distorted tetrahedral geometry, with a chelating dithiocarbonate (xanthate) and two PPh_3 ligands bonded to the Ag atom. However, in this new polymorph, the xanthate ligand is bonded asymmetrically to the Ag atom, with Ag–S distances of 2.5489 (6) and 2.8055 (7) Å, while for the orthorhombic polymorph these distances are 2.686 (4) and 2.601 (4) Å. The Ag–P distances are similar in both structures.

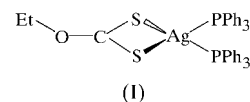
Comment

In recent years, there has been a growing interest in the preparation and study of polymorphs, not only because they are intrinsically interesting phenomena that involve diverse scientific branches (for example, mineralogy, materials science, supramolecular chemistry and thermodynamics), but also because polymorphism has become a major issue in the pharmaceutical, optoelectronic, and dyes and pigments industries.

The addition of various ligands to suspensions of polymeric metal xanthates (dithiocarbonates) often results in the formation of monomeric adducts of different stoichiometries and structures. For instance, $[\text{Cu}(\text{S}_2\text{COEt})(\text{PPh}_3)_2]$ is four-coordinated with a chelating xanthate ligand (Bianchini *et al.*, 1985), $[\text{Hg}(\text{S}_2\text{COEt})_2(\text{PPh}_3)]$ is five-coordinated (Watanabe, 1981), and the linear system $[\text{Au}(\text{S}_2\text{COMe})(\text{PPh}_3)]$ features a monodentate xanthate ligand (Tiekink, 1985). $[\text{Ag}(\text{S}_2\text{COEt})(\text{PPh}_3)_2]$ was first prepared by the addition of PPh_3 to a suspension of $\text{Ag}(\text{S}_2\text{COEt})$ (Kowala & Swan, 1966), although

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the crystal structure was determined later (Tiekink, 1988). The complex crystallizes in the orthorhombic system, with the Ag atom in a distorted tetrahedral environment formed by two S atoms of the chelating S_2COEt ligand and by two PPh_3 groups; this geometry is similar to that of $[\text{Cu}(\text{S}_2\text{COEt})(\text{PPh}_3)_2]$ (Bianchini *et al.*, 1985). The Ag–P distances [2.4193 (6) and 2.4614 (6) Å] are very similar and lie in the range expected for Ag– PPh_3 bonds (2.363–2.529 Å). The Ag–S distances are also similar [2.686 (4) and 2.601 (4) Å], although they are a little longer than the distances found in other comparable Ag coordination compounds (Müller *et al.*, 1979). The S1–Ag1–S2 and P1–Ag1–P2 planes are almost perpendicular (89.81°).



We report here a new polymorph of $[\text{Ag}(\text{S}_2\text{COEt})(\text{PPh}_3)_2]$, (I), that crystallizes in the triclinic system. The triclinic polymorph has the same general molecular shape (Fig. 1) as the orthorhombic polymorph, *i.e.* the Ag atom has a distorted tetrahedral environment, the distortion being due in part to the restricted bite angle of the chelating xanthate ligand [67.345 (19)°]. The Ag–P distances (Table 1) are comparable in both cases. The main difference between the two polymorphs is that (I) features an asymmetrically chelating xanthate ligand. The Ag1–S1 distance is longer than most Ag–S bonds, although similar values have been found in other complexes (Drew *et al.*, 1987). This difference cannot be attributed to packing forces. The bite distance of the xanthate

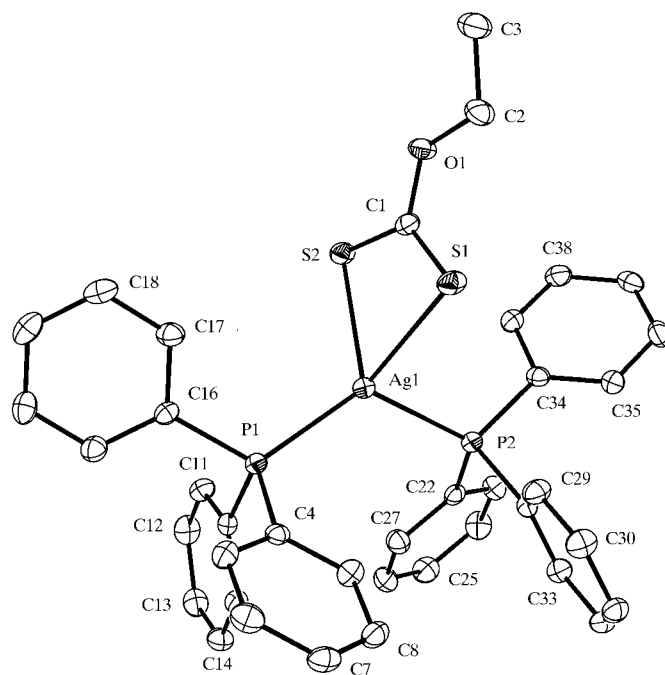


Figure 1

The structure of (I), showing displacement ellipsoids at the 50% probability level and the atom-numbering scheme. H atoms have been omitted for clarity.

is 2.9764 (9) Å, and the angle between the S1—Ag1—S2 and P1—Ag1—P2 planes is 75.55 (2)°. Thus, the coordination sphere of the Ag atom in (I) is highly irregular, with a wide variation in bond lengths and angles. There are also some differences in the orientations of the phenyl groups between the two forms. The dihedral angles between the P1—Ag1—P2 plane and the planes of the phenyl rings bonded to P1 and P2 are 86.96 (6), 54.51 (6), 20.76 (8), 53.84 (5), 79.96 (6) and 47.38 (6)°, respectively, in (I). These angles are 69.39, 79.38, 38.47, 31.08, 59.22 and 74.79° for the orthorhombic polymorph.

There is no clear evidence of intermolecular hydrogen bonding; the shortest potential hydrogen-bond interaction involves atoms C8 and S2 (Table 2). This contact could be considered a weak electrostatic interaction, since the separation is 0.3 Å shorter than the sum of the van der Waals radii for H (1.2 Å) and S (1.85 Å) (Whuler *et al.*, 1980). In addition, there is a weak intramolecular interaction (S1···H2A = 2.76 Å) that may be associated with the long Ag1—S1 distance.

Experimental

Compound (I) was obtained from the reaction of [Zn(S₂COEt)₂] (0.200 g, 0.651 mmol) with AgClPPh₃ (0.528 g, 1.302 mmol) in dichloromethane (20 ml) at room temperature. After 30 min, the solid product [a mixture of Ag(S₂COEt) and ZnCl₂] was filtered off and the filtrate evaporated to dryness. The addition of isopropyl alcohol to the residue gave (I) as a white solid (yield = 66%). Analysis, calculated for C₃₉H₃₅AgOP₂S₂: C 62.17, N 4.64, S 8.49%; found: C 61.90, N 4.54, S 8.59%. Single crystals were obtained by slow diffusion of *n*-hexane into a dichloromethane solution of (I) at room temperature.

Crystal data

[Ag(C ₃ H ₅ OS ₂)(C ₁₈ H ₁₅ P) ₂]	Z = 2
<i>M_r</i> = 753.60	<i>D_x</i> = 1.454 Mg m ⁻³
Triclinic, <i>P</i> $\bar{1}$	Mo <i>K</i> α radiation
<i>a</i> = 10.3302 (6) Å	Cell parameters from 4690 reflections
<i>b</i> = 12.8582 (7) Å	θ = 2.3–26.4°
<i>c</i> = 13.8270 (8) Å	μ = 0.83 mm ⁻¹
α = 87.432 (1)°	<i>T</i> = 100 (2) K
β = 74.956 (1)°	Prism, pale yellow
γ = 76.067 (1)°	0.25 × 0.18 × 0.16 mm
<i>V</i> = 1721.17 (17) Å ³	

Data collection

Bruker SMART APEX CCD diffractometer	6873 independent reflections
ω scans	5720 reflections with <i>I</i> > 2σ(<i>I</i>)
Absorption correction: multi-scan (SADABS; Bruker, 1999)	<i>R</i> _{int} = 0.019
<i>T</i> _{min} = 0.819, <i>T</i> _{max} = 0.879	θ _{max} = 26.4°
10 445 measured reflections	<i>h</i> = -12 → 12
	<i>k</i> = -16 → 10
	<i>l</i> = -17 → 17

Refinement

Refinement on <i>F</i> ²	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.032$	$w = 1/[\sigma^2(F_o^2) + (0.0289P)^2]$
$wR(F^2) = 0.067$	where $P = (F_o^2 + 2F_c^2)/3$
<i>S</i> = 0.94	(Δ/σ) _{max} = 0.001
6873 reflections	$\Delta\rho_{max} = 0.79 \text{ e } \text{Å}^{-3}$
406 parameters	$\Delta\rho_{min} = -0.49 \text{ e } \text{Å}^{-3}$

Table 1
Selected geometric parameters (Å, °).

Ag1—P1	2.4196 (7)	S1—C1	1.680 (2)
Ag1—P2	2.4612 (7)	S2—C1	1.693 (3)
Ag1—S2	2.5489 (6)	O1—C1	1.347 (3)
Ag1—S1	2.8055 (7)		
P1—Ag1—P2	123.04 (2)	C1—S1—Ag1	80.29 (9)
P1—Ag1—S2	118.85 (2)	C1—S2—Ag1	88.26 (9)
P2—Ag1—S2	113.08 (2)	O1—C1—S1	122.45 (18)
P1—Ag1—S1	125.71 (2)	O1—C1—S2	113.66 (17)
P2—Ag1—S1	94.25 (2)	S1—C1—S2	123.87 (15)
S2—Ag1—S1	67.345 (19)		

Table 2
Short intermolecular contacts (Å, °).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
C8—H8···S2 ⁱ	0.95	2.76	3.568 (3)	144
C13—H13···S2 ⁱⁱ	0.95	2.79	3.632 (3)	148

Symmetry codes: (i) 1 + *x*, *y*, *z*; (ii) -*x*, 1 - *y*, -*z*.

H atoms were treated as riding, with C—H distances of 0.95 (aromatic), 0.98 (CH₃) and 0.99 Å (CH₂).

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT-Plus* (Bruker, 1999); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2000); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1546). Services for accessing these data are described at the back of the journal.

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