Polymeric (*O*-ethyl dithiocarbonato)-silver(I)

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The title compound, $[Ag(C_3H_5OS_2)]_n$, is polymeric in the solid state and adopts a layered structure in which each Ag atom is five-coordinated in a distorted trigonal-bipyramidal geometry defined by four S atoms belonging to four different xanthate groups and by a neigbouring Ag atom [Ag$\cdots$Ag = 3.0540 (8) Å]. Each S atom is three-coordinated to one C and two Ag atoms. The structure can be envisaged as being formed by $Ag_2(S_2COEt)_2$ units in which every S atom is bonded to another Ag atom from a different unit and the Ag atoms are also bonded to two different S atoms of two other units. The result is a two-dimensional network of condensed metallacycles of six or eight atoms.

Comment

Silver thiolates have been known for some time, and their low solubility suggests they are polymeric in nature. This fact has been confirmed, in the case of silver(I) complexes of dithio-carbamates, by the determination of the crystal structures of $[Ag(S_2CNR_2)]$ (R = Et and *n*-Pr). The α forms of [Ag-$(S_2CNEt_2)]$ (Yamaguchi *et al.*, 1976) and $[Ag(S_2CNPr_2)]$ (Hesse & Nilson, 1969) contain discrete hexameric molecules in which the Ag atoms form a distorted octahedron with six comparatively short and six longer edges. The short edges correspond to metal–metal distances comparable to those in the metallic phase of silver. All Ag atoms are connected to five atoms, *viz.* two Ag and three S atoms, while the S atoms are bonded to one or two Ag atoms. In these hexameric units, the terminal Ag atom in one molecule is bridged by an S atom to that in the adjacent hexamer (Ag—S = 2.99 Å), thus forming a chain structure. The β modification of $[Ag(S_2CNEt_2)]$ (Anacker-Eickhoff *et al.*, 1982) is a true high polymer, in which the Ag atom and the ligands are linked into chains. All the Ag

atoms are coordinated to four S atoms, with distances ranging from 2.51 to 2.74 Å. In addition, there are two short metal–metal distances per six Ag atoms. By contrast, the crystal structures of the silver(I) xanthates, $[Ag(S_2COR)]$ (Kowala & Swan, 1966), have not been determined to date because of the difficulty in obtaining suitable crystals. Silver xantates can react easily, in spite of their low solubility, and when different ligands are added to suspensions of polymeric silver xanthates, monomeric soluble adducts, whose structures are well known, can be obtained. An example of one of these adducts is $[Ag(S_2COEt)(PPh_3)_2]$, of which two polymorphic modifications have been described (Tiekink, 1988; Ara *et al.*, 2003).

We obtained crystals of $[Ag(S_2COEt)]$, (I), from the reaction of $[Zn(S_2COEt)_2]$ and $O_3ClOAgPPh_3$, in which the $[Ag(PPh_3)_4](ClO_4)$ complex (Cotton & Goodgame, 1960; Engelhardt *et al.*, 1985) is the main product, and we studied the structure of (I) in order to determine the nature of the Ag-atom geometry and the mode of coordination of the xanthate ligand.

(I)
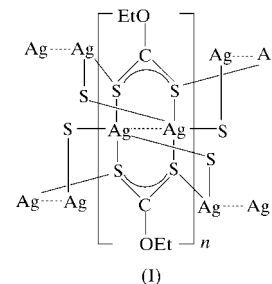
The structure of (I) consists of a two-dimensional polymeric array of molecules (Fig. 1). All Ag atoms in each layer have the same environment, *viz.* a distorted trigonal bipyramid, in
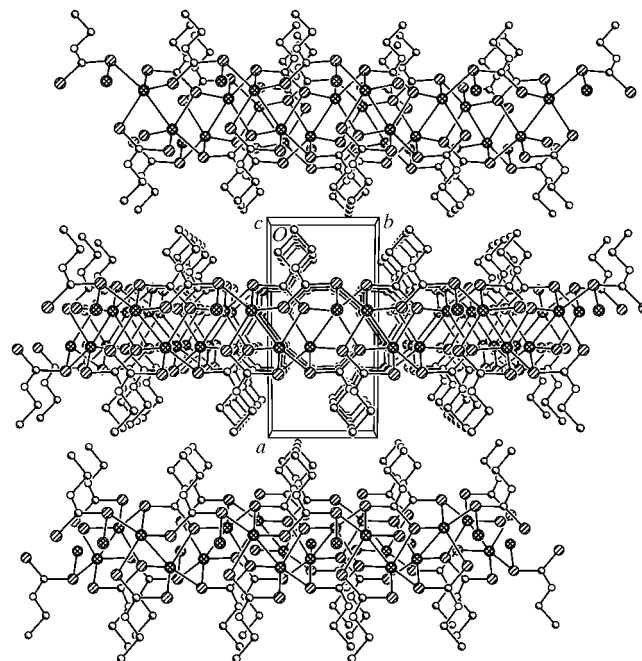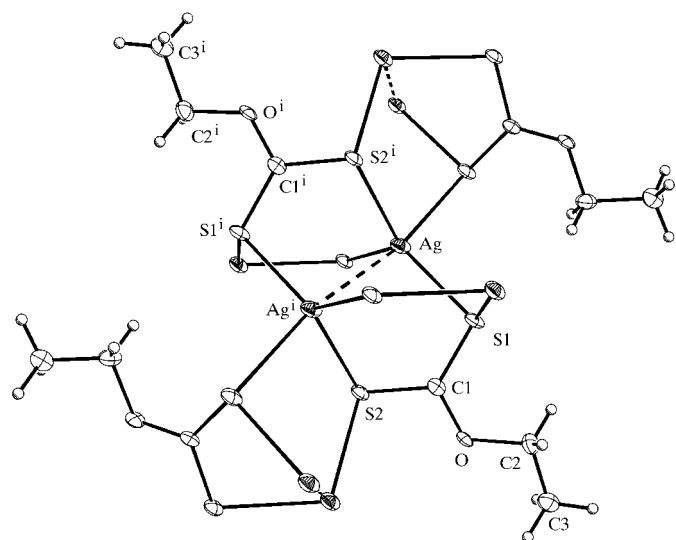

Figure 1
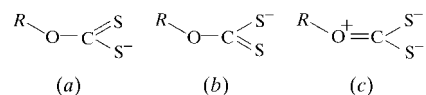Packing diagram of (I), viewed along the *c* axis.

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metal-organic compounds

Figure 2
A view of the structure of the $Ag_2(S_2COEt)_2$ moieties of (I), showing the coordination geometry and the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry code: (i) $1 - x, -y, 1 - z$.]

which the three S atoms are located in equatorial (eq) positions, and the axial (ax) positions are occupied by an S and an Ag atom. The S—Ag—S angles in the trigonal plane range from 109.40 (3) to 124.38 (5)°, the S_{eq}—Ag—Ag angles range from 75.73 (4) to 98.08 (4)°, the S_{eq}—Ag—S_{ax} angles range from 84.41 (4) to 105.36 (5)° and the Ag—Ag—S_{ax} angle is 168.43 (4)°. The Ag—S_{eq} distances are very similar and range from 2.5073 (15) to 2.5578 (14) Å. By contrast, the Ag—S_{ax} distance is significantly longer [2.8379 (14) Å]. The Ag···Ag distance of 3.0540 (8) Å is long enough to postulate only a weak interaction between the two metal atoms (Wang & Mak, 2001). In addition to this weak interaction, both Ag atoms are bonded by a bridging xanthate ligand in which the S1···S2 distance of 3.0201 (19) Å is somewhat longer than the bite distance shown by chelating xanthate ligands (Chan *et al.*, 1982). All the S atoms in the structure are three-coordinated (to two Ag atoms and one C atom), thus forming a distorted non-planar trigonal environment, with the S atoms lying above or below the coordination plane (0.8520 and 0.7701 Å for S1 and S2, respectively). The xanthate ligand can be considered as a tetradentate group, since each S atom is bonded to two different Ag atoms. The bonding mode within the xanthate ligand can be represented by the valence-bond formalism shown in the *Scheme* below (Coucouvanis, 1970). In general, resonance forms (*a*) and (*b*) best describe the structures of xanthate complexes, but in (I), the short C1—O and long S—C1 distances (Table 1) suggest that the contribution of resonance structure (*c*) is not negligible. The structure is best envisaged as being formed by units of two Ag atoms bridged by two xanthate ligands (Fig. 2). If the Ag···Ag interaction is disregarded, these units form cycles of eight atoms (two Ag, four S and two C atoms). Each S atom is also bonded to another Ag atom from a different unit, thus forming a cycle of

six atoms (two Ag, three S and one C atom). Thus, the whole array consists of non-planar fused metallacycles of six and eight atoms, in which all atoms belong to both types of cycle.

Experimental

Crystal data

[Ag(C₃H₅OS₂)]	D_x = 2.565 Mg m⁻³
M_r = 229.06	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 1495
a = 12.6929 (12) Å	reflections
b = 6.1566 (6) Å	θ = 3.3–26.3°
c = 7.8385 (7) Å	μ = 3.97 mm⁻¹
β = 104.419 (2)°	T = 100 (2) K
V = 593.25 (10) Å³	Thin plate, yellow
Z = 4	0.36 × 0.18 × 0.02 mm

Data collection

Bruker SMART APEX CCD diffractometer	1211 independent reflections
	1042 reflections with $I > 2\sigma(I)$
ω scans	R_{int} = 0.032
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	θ_{max} = 26.4°
	h = −15 → 11
T_{min} = 0.329, T_{max} = 0.925	k = −7 → 7
3390 measured reflections	l = −9 → 9

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)]$ = 0.039	$w = 1/[\sigma^2(F_o^2) + (0.0546P)^2]$
$wR(F^2)$ = 0.092	where $P = (F_o^2 + 2F_c^2)/3$
S = 1.03	$(\Delta/\sigma)_{max}$ < 0.001
1211 reflections	$\Delta\rho_{max}$ = 2.08 e Å⁻³
64 parameters	$\Delta\rho_{min}$ = −1.25 e Å⁻³

Table 1
Selected geometric parameters (Å, °).

Ag—S1	2.5073 (15)	S1—C1	1.701 (5)
Ag—S2ⁱ	2.5302 (15)	S2—C1	1.710 (5)
Ag—S2ⁱⁱ	2.5578 (14)	O—C1	1.318 (6)
Ag—S1ⁱⁱⁱ	2.8379 (14)	O—C2	1.462 (6)
Ag···Agⁱ	3.0540 (8)	C2—C3	1.504 (8)
S1—Ag—S2ⁱ	124.16 (5)	S2ⁱ—Ag···Agⁱ	75.73 (4)
S1—Ag—S2ⁱⁱ	124.38 (5)	S2ⁱⁱ—Ag···Agⁱ	98.08 (4)
S2ⁱ—Ag—S2ⁱⁱ	109.40 (3)	S1ⁱⁱⁱ—Ag···Agⁱ	168.43 (4)
S1—Ag—S1ⁱⁱⁱ	105.36 (5)	Ag—S1—Agⁱᵛ	105.06 (5)
S2ⁱ—Ag—S1ⁱⁱⁱ	92.76 (4)	Agⁱ—S2—Agᵛ	112.63 (5)
S2ⁱⁱ—Ag—S1ⁱⁱⁱ	84.41 (4)	S1—C1—S2	124.6 (3)
S1—Ag···Agⁱ	82.64 (4)		

Symmetry codes: (i) $1 - x, -y, 1 - z$; (ii) $x, -\frac{1}{2} - y, z - \frac{1}{2}$; (iii) $x, \frac{1}{2} - y, z - \frac{1}{2}$; (iv) $x, \frac{1}{2} - y, \frac{1}{2} + z$; (v) $x, -\frac{1}{2} - y, \frac{1}{2} + z$.

The final electron-density difference map showed four peaks above 1 e Å^{-3}, all of them located less than 1 Å from the Ag atom. These residual densities are probably the result of an insufficient absorption-correction procedure. H atoms were refined as riding, with methyl C—H = 0.98 Å and methylene C—H = 0.99 Å.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT-Plus* (Bruker, 1999); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL* (Bruker, 2000); software used to prepare material for publication: *XCIF* in *SHELXTL*.

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