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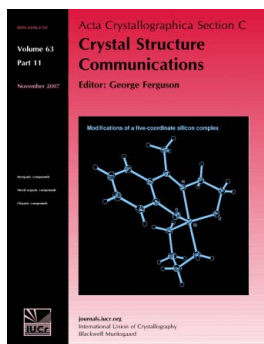
A triclinic polymorph of *cyclo*-tetra- μ -thiosaccharinato- κ^8 S:S-tetrakis[(triphenylphosphane- κ P)silver(I)]

Mariana Dennehy, Eleonora Freire and Ricardo Baggio*Acta Cryst.* (2012). **C68**, m17–m20

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A triclinic polymorph of *cyclo*-tetra- μ -thiosaccharinato- κ^8 S:S-tetrakis-[(triphenylphosphane- κ P)silver(I)]

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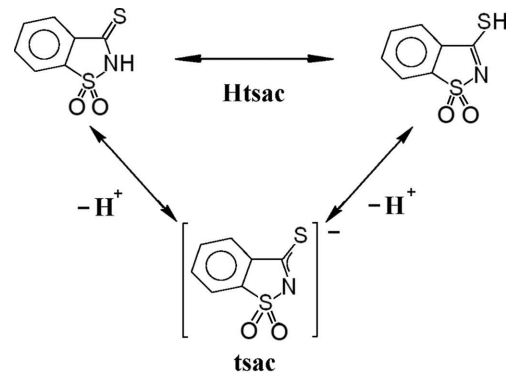
Online 23 December 2011

The triclinic structure of the title compound, *cyclo*-tetrakis(μ -1,1-dioxo-1 λ^6 ,2-benzothiazole-3-thiolato- κ^2 S:S)tetrakis[(triphenylphosphane- κ P)silver(I)], [Ag₄(C₇H₄NO₂S₂)₄(C₁₈H₁₅P)₄], is a polymorph of the previously reported monoclinic structure [Dennehy, Mandolesi, Quinzani & Jennings (2007). *Z. Anorg. Allg. Chem.* **633**, 2746–2752]. In both polymorphs, the complex lies on a crystallographic inversion centre and the bond distances are closely comparable. Some differences can be found in the interatomic angles and torsion angles involving the inner Ag₄S₄ skeleton. The polymorphs contain essentially identical two-dimensional layers, but with different layer stacking arrangements. In the triclinic form, all layers are related by lattice translation, while in the monoclinic form they are arranged around glide planes so that adjacent layers are mirrored with respect to each other.

Comment

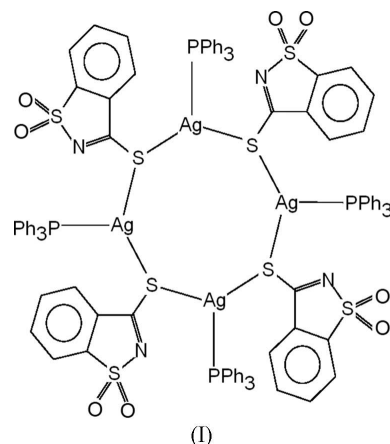
Heterocyclic thiones are versatile *S,N*-chelating ligands and a considerable amount of work has centred around their coordination chemistry. They are capable of binding to metals in a variety of coordination modes and a large number of mononuclear, binuclear and complex polynuclear coordination compounds have been reported after the pioneering work by Raper (1996, 1997). We have developed a sustained interest in the coordination behaviour of heterocyclic thiones in general, and thiosaccharin [the thione form of saccharin, C₆H₄SO₂NHCS, hereinafter tsac; systematic name: 1,1-dioxo-1 λ^6 ,2-benzothiazole-3(2*H*)-thione] in particular. As is well known for other heterocyclic thiones, tsac has a tautomeric equilibrium in solution (see Scheme 1) and in its thiol form it can act as a good coordinating agent for soft metals, building inter-

esting mono- and polynuclear structures with or without the presence of additional ligands. In particular, we have worked on the silver–tsac system, aiming to control its stereochemistry



Scheme 1

and nuclearity, and we have been able to develop new products, for example, by changing the stoichiometry of the soft bulky triphenylphosphane (PPh₃) co-ligand. Surprisingly, the Ag–PPh₃ stoichiometries in the resulting complexes do not always follow the molar ratios in the reaction mixture. For example, a stable tetracoordinated complex [Ag(tsac)(PPh₃)₃] was obtained from reaction mixtures with Ag–PPh₃ molar ratios greater than 1:2, but a different Ag₆(tsac)₆ complex resulted for molar ratios of 1:1 or less (Dennehy, Quinzani & Jennings, 2007). In our search for the appropriate conditions to prepare silver(I) thiosaccharinates with less than three phosphane ligands on the metal nuclei, we recently produced the monoclinic tetranuclear complex [Ag₄(tsac)₄(PPh₃)₄] (Dennehy, Mandolesi *et al.*, 2007). Through a slight variation in the synthesis conditions, we have now obtained a triclinic polymorph of the same compound, which we report herein. The triclinic and monoclinic polymorphs are referred to as (I) and (II), respectively.



Some comparative crystal data for polymorphs (I) and (II) are given in Table 1. In order to highlight the similarities and differences between the structures, triclinic form (I) is described using a nonconventional nonreduced unit cell. The corresponding reduced cell is $a = 13.8914$ (7), $b = 14.0768$ (6), $c = 14.1309$ (7) Å, $\alpha = 77.771$ (4), $\beta = 73.572$ (4) and $\gamma = 66.603$ (4)°.

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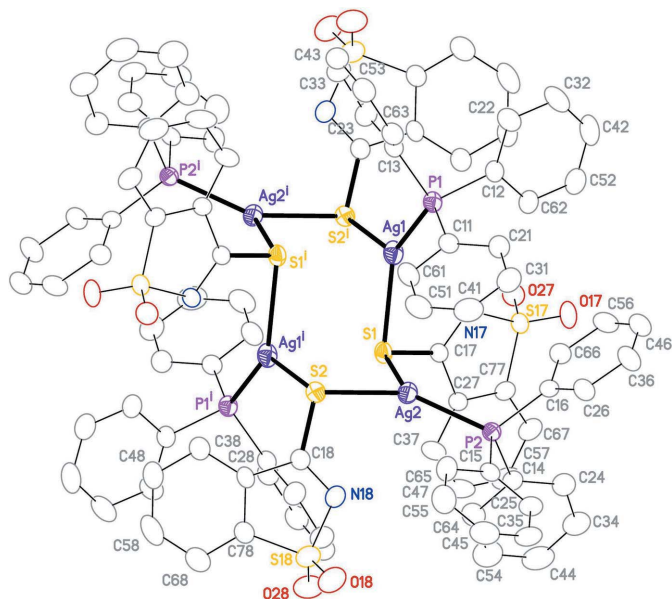


Figure 1
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted. The eight-membered Ag_4S_4 skeleton is highlighted. [Symmetry code: (i) $-x, -y, -z$.]

The tetranuclear unit in (I) (Fig. 1) is very similar to its counterpart in (II). The molecule is composed of four fused $\text{Ag}(\text{tsac})(\text{PPh}_3)$ units, two of them independent and the remaining two generated by an inversion centre. The main characteristic is the centrosymmetric eight-membered skeleton, composed of four thione exocyclic S atoms and four Ag atoms in a regular chair conformation. Each Ag atom is triply coordinated by two S atoms and one PPh_3 group in a slightly distorted planar arrangement; the deviations of the Ag atoms from the ligand coordination plane are 0.0192 (3) Å for Ag1 and 0.1392 (3) Å for Ag2, compared with the corresponding values of 0.0062 (14) and 0.0650 (16) Å for polymorph (II). The coordination distances in both complexes are extremely similar (Table 2), and the bond distances and angles in the bridging tsac ligands are typical of those observed in other related polynuclear silver thiosaccharinates (Dennehy, Mandolesi *et al.*, 2007). A least-squares overlay of the complexes in (I) and (II) gives an r.m.s. deviation of 0.4 Å for 128 non-H atoms (Macrae *et al.*, 2008). A least-squares overlay of the central core of the complex (Fig. 2) shows that (I)

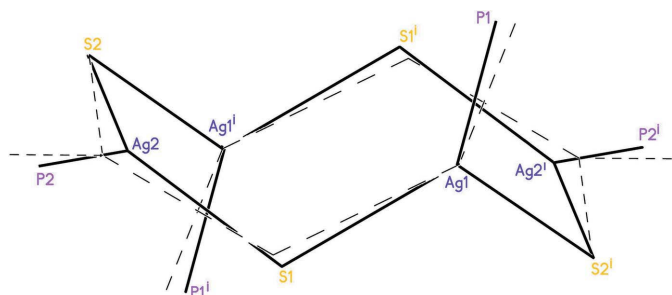


Figure 2
A least-squares overlay of the eight-membered rings in (I) (full lines) and (II) (dashed lines). [Symmetry code: (i) $-x, -y, -z$.]

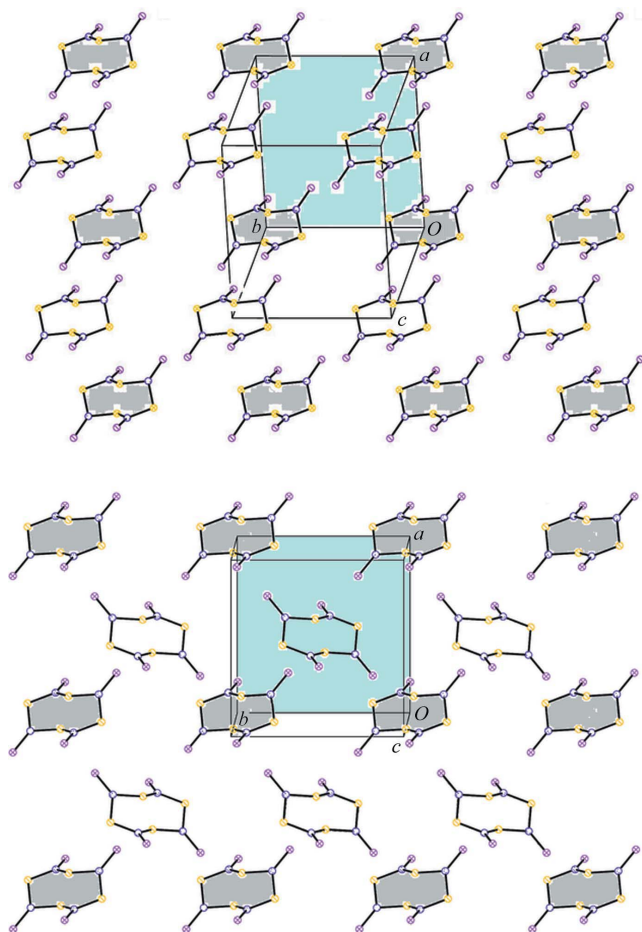


Figure 3
Packing diagrams of (I) (top) and (II) (bottom), projected perpendicular to the (001) plane, showing two consecutive layers in different shading. Only the central ring of each molecule has been drawn, for clarity. Note the very similar a , b and γ cell parameters in the shaded cell faces.

adopts a more regular chair conformation than (II), as reflected by the $\text{Ag1}-\text{S1}-\text{Ag2}-\text{S2}$ torsion angles [89.17 (5)° in (I) *versus* 79.80 (10)° in (II)]. These relatively small differences in the skeleton are magnified towards the outermost parts of the bulky PPh_3 groups on account of the variation in the degree of rotation around the $\text{P}-\text{Ag}$ bonds. However, in both polymorphs the overall globular shape for the molecule is conserved. The changes which arise are reflected in the geometries of the intra- and intermolecular interactions (Tables 3 and 4) to the extent that they cannot readily be correlated between one structure and the other.

The two polymorphs have closely comparable calculated densities (Table 2) but different distributions of the molecules in space. The choice of cell axes for (I) is intended to highlight the similarities in the (001) planes in both structures (see a , b and γ in Table 1, and the shaded ab faces in Fig. 3). Indeed, the structures contain essentially identical layers of molecules parallel to the (001) planes, and they look identical when projected along the b axis. Fig. 3, where for simplicity only the inorganic skeletons are drawn, presents for each structure two consecutive layers (with and without shading) of these (001) planes, projected onto the layer plane. In (I), the layer

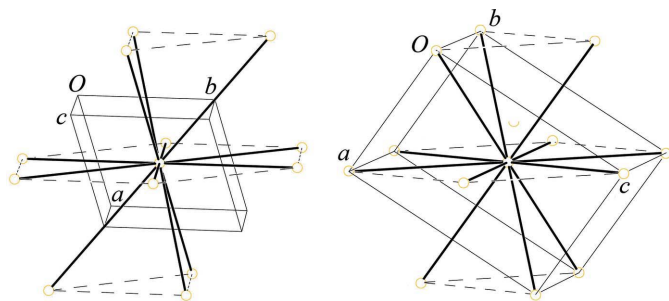


Figure 4
Schematic nearest-neighbours representations of the structures of (I) (left) and (II) (right) (see *Comment* for details).

stacking takes place *via* a consistent $c_{(I)}$ cell shift, so that all layers are related by lattice translation. In (II), the n -glides generate alternating mirror images shifted by one half of the $c_{(II)}$ translation. Taking into account the differences in cell lengths and cell angles, this corresponds to slightly different interplanar spacings: $d_{(001)} = 11.159(2) \text{ \AA}$ for (I) and $d_{(002)} = 10.910(2) \text{ \AA}$ for (II).

The globular shape of the molecules involved and the absence of strong directional intermolecular interactions leads to arrangements compatible with the packing of spheres. A nearest-neighbours calculation for the molecular centroids gives exactly 12 neighbours for each structure, in the narrow range 14.667(2)–15.672(3) \AA for (II) and the slightly broader range 13.8914(12)–17.7086(13) \AA for (I), in both cases followed by a 3 \AA gap to the second nearest-neighbour shell. The distribution of the centroids in both structures can be envisaged as a hexagonal arrangement, parallel to (100) in (I) or (101) in (II), bicapped by two parallel inverted triangles, resembling a $\bar{3}$ distribution (Fig. 4). The distribution in (II) is rather regular, with the line through the triangular centres being almost perpendicular to the equatorial plane [angle = 179.91(14) $^\circ$] and the interplanar distances [corresponding to $d_{(101)}$] being 11.838(2) \AA . The distribution in (I) is more deformed, with corresponding values of 171.78(16) $^\circ$ for the line-to-plane angle and 12.432(2) \AA for $d_{(100)}$.

Experimental

Thiosaccharin (Htsac) was prepared by the reaction of saccharin (3.00 g; Mallinkrodt) with Lawesson's reagent (3.64 g; Fluka) in toluene (25 ml). $\text{Ag}_6(\text{tsac})_6$ was obtained as a yellow solid by reaction of AgNO_3 and thiosaccharin in acetonitrile in a 1:1 molar ratio (Dennehy, Tellería *et al.*, 2007). The title $[\text{Ag}_4(\text{tsac})_4(\text{PPh}_3)_4]$ complex

Table 1

Comparison of the crystal data for (I) (this work) and (II) (Dennehy, Mandolesi *et al.*, 2007).

	(I)	(II)	(I)	(II)
Crystal system	Triclinic	Monoclinic	Space group	$P\bar{1}$
a (\AA)	15.3566(10)	15.024(3)	α ($^\circ$)	77.771(4)
b (\AA)	14.1309(7)	14.681(3)	β ($^\circ$)	123.880(3)
c (\AA)	14.0768(6)	21.914(4)	γ ($^\circ$)	86.465(1)
V (\AA^3)	2416.9(2)	4812.77	Z	1
D_x (Mg m^{-3})	1.562	1.569		2

Table 2

Comparison of selected bond lengths and angles ($\text{\AA}, ^\circ$) in (I) (this work) and (II) (Dennehy, Mandolesi *et al.*, 2007).

	(I)	(II)
Ag1–P1	2.3904(13)	2.398(3)
Ag2–P2	2.3952(15)	2.396(2)
Ag1–S2 ⁱ	2.5440(13)	2.551(2)
Ag2–S2	2.5008(14)	2.505(2)
Ag1–S1	2.5484(13)	2.549(3)
Ag2–S1	2.5852(13)	2.582(3)
P1–Ag1–S2 ⁱ	126.76(5)	122.81(9)
P2–Ag2–S2	135.38(4)	135.79(9)
P1–Ag1–S1	133.92(5)	132.07(9)
P2–Ag2–S1	126.12(4)	131.66(8)
S2 ⁱ –Ag1–S1	99.30(4)	105.13(8)
S2–Ag2–S1	97.49(4)	92.33(8)
S2 ⁱ –Ag1–S1–Ag2	–164.95(5)	–163.22(8)
S1–Ag2–S2–Ag1 ⁱ	1.93(4)	11.17(10)
Ag1–S1–Ag2–S2	89.17(5)	79.80(10)
Ag2–S2–Ag1 ⁱ –S1 ⁱ	–88.11(6)	–95.45(9)

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

was prepared by slow addition of an acetonitrile solution containing 2,5-dimethylpyrazine (10 mg) to another yellow solution of $\text{Ag}_6(\text{tsac})_6$ (0.0120 g, 0.04 mmol of Ag) and PPh_3 (0.0100 g, 0.04 mmol) in acetonitrile (10 ml). The resulting clear yellow solution was kept at room temperature and crystals of (I) had formed after one month.

Crystal data

$[\text{Ag}_4(\text{C}_7\text{H}_4\text{NO}_2\text{S}_2)_4(\text{C}_{18}\text{H}_{15}\text{P})_4]$	$\gamma = 86.465(1)^\circ$
$M_r = 2273.49$	$V = 2416.9(2) \text{ \AA}^3$
Triclinic, $P\bar{1}$	$Z = 1$
$a = 15.3566(10) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 14.1309(7) \text{ \AA}$	$\mu = 1.10 \text{ mm}^{-1}$
$c = 14.0768(6) \text{ \AA}$	$T = 291 \text{ K}$
$\alpha = 77.771(4)^\circ$	$0.20 \times 0.16 \times 0.12 \text{ mm}$
$\beta = 123.880(3)^\circ$	

Data collection

Oxford Gemini CCD S Ultra diffractometer	20631 measured reflections
Absorption correction: multi-scan (CrysAlis PRO; Oxford Diffraction, 2009)	11017 independent reflections
$T_{\min} = 0.98, T_{\max} = 0.99$	5568 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.060$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.055$	577 parameters
$wR(F^2) = 0.112$	H-atom parameters constrained
$S = 0.94$	$\Delta\rho_{\text{max}} = 0.72 \text{ e \AA}^{-3}$
11017 reflections	$\Delta\rho_{\text{min}} = -0.70 \text{ e \AA}^{-3}$

All H atoms were visible in a difference Fourier map, but they were placed in idealized positions and allowed to ride for subsequent refinement, with C–H = 0.93 \AA and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Attention is drawn to a refinement paradox. When checking the final results with *PLATON checkCIF* (Spek, 2009), the Hirshfeld tests implemented therein generated a significant number of alerts regarding suspiciously large 'Hirshfeld test differences' (HTD) for many of the Ag–S bonds, thus advising careful review of the cation-type assignment. To our surprise, lower R indices and better Hirshfeld indicators were obtained when the structure was refined with Pd atoms in place of Ag; the R , wR and HTD values are 0.0553, 0.0882

Table 3

Hydrogen-bond geometry for (I) (Å, °).

*Cg*1 and *Cg*2 are the centroids of the S18/N18/C18/C28/C78 and C13/C23/C33/C43/C53/C63 rings, respectively.

<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>
C46—H46...O27 ⁱ	0.93	2.44	3.350 (10)	165
C52—H52...O17 ⁱ	0.93	2.56	3.196 (10)	126
C23—H23... <i>Cg</i> 1 ⁱⁱ	0.93	2.99	3.865 (6)	158
C37—H37... <i>Cg</i> 2 ⁱⁱ	0.93	2.93	3.734 (9)	146

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

Table 4

π - π interactions (Å, °) for (I).

*Cg*3 is the centroid of the C27/C37/C47/C57/C67/C77 ring, ccd is the centre-to-centre distance (distance between ring centroids), ipd is the interplanar distance (distance from one plane to the neighbouring centroid) and sa is the slippage angle (angle subtended by the intercentroid vector to the plane normal). For details, see Janiak (2000).

Group 1/group 2	ccd (Å)	ipd (Å)	sa (°)
<i>Cg</i> 3... <i>Cg</i> 3 ⁱⁱ	3.735 (4)	3.441 (2)	22.8 (2)

Symmetry code: (ii) $-1 - x, -y, -1 - z$.

and 17.3, respectively, for Ag, and 0.0543, 0.0830 and 13.2, respectively, for Pd. This contradicts clear synthetic and analytical evidence for the composition of the complex; an EDAX analysis on a Philips 515 microscope (Philips Export BV, Eindhoven, The Netherlands) equipped with an EDAX PV9100 probe (EDAX International Inc., Prairie View, Illinois, USA) showed that Ag was the only metallic element present. Even if surprising, this is not a novel paradox; we have previously found similar refinement 'misbehaviour' with different cation pairs (e.g. Cu^{II} versus Ni^{II}; Perec & Baggio, 2010).

Data collection: *CrysAlis PRO* (Oxford Diffraction, 2009); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2009).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BI3030). Services for accessing these data are described at the back of the journal.

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