

Poly[( $\mu_3$ -1,1-dioxo-1,2-benzoisothiazole-3-thiolato- $\kappa^3$ N:S<sup>3</sup>:S<sup>3</sup>)silver(I)]Mariana Dennehy,<sup>a</sup> Oscar V. Quinzani<sup>a\*</sup> and Robert A. Burrow<sup>b</sup><sup>a</sup>Departamento de Química, Universidad Nacional del Sur, Avenida Alem 1253, B8000CPB Bahía Blanca, Argentina, and <sup>b</sup>Laboratório de Materiais Inorgânicos, Departamento de Química, Universidade Federal de Santa Maria, 97105-900 Santa Maria, RS, Brazil

Correspondence e-mail: quinzani@criba.edu.ar

Received 19 July 2007

Accepted 20 July 2007

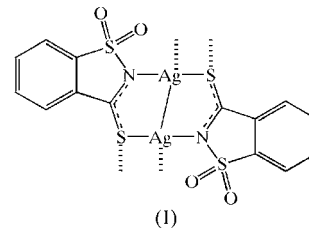
Online 9 August 2007

The centrosymmetric title compound, [Ag(C<sub>7</sub>H<sub>4</sub>NO<sub>2</sub>S<sub>2</sub>)<sub>n</sub>], consists of dinuclear units in which two thiosaccharinate anions each bridge two Ag atoms *via* an endocyclic N atom and an exocyclic S atom across a crystallographic centre of inversion midway between the Ag atoms. The dimeric units are connected *via* Ag—S<sub>exo</sub> interactions to create two-dimensional networks.

## Comment

Thionates, anions produced by the deprotonation of thiones, can coordinate to metals, producing anywhere from mononuclear to polynuclear species. Like other thioamides, thiosaccharine [1,2-benzoisothiazol-3-(2*H*)-thione 1,1-dioxide] is a versatile ligand, with the ability to coordinate to metal centres in many different ways (Dennehy, Quinzani & Jennings, 2007). Ag<sup>I</sup> atoms coordinated to N or S ligands are of particular interest because of their known antibacterial effects (Nomiya *et al.*, 1997, 2000). We have been working with binary and ternary silver thiosaccharinates, first synthesizing the Ag(tsac) complex (where tsac is the thiosaccharinate anion), which crystallized as the hexanuclear cluster [Ag<sub>6</sub>(tsac)<sub>6</sub>] from acetonitrile (MeCN) solution (Dennehy, Tellería *et al.*, 2007). The cluster is insoluble in many organic solvents, but is very soluble in dimethyl sulfoxide (DMSO). The <sup>1</sup>H and <sup>13</sup>C NMR spectra show only one species in the DMSO solution. However, it was not clear if its structure remained hexanuclear or if a smaller unit was present in solution. We recrystallized [Ag<sub>6</sub>(tsac)<sub>6</sub>] from DMSO in order to identify the species probably present in solution, giving the title compound, (I). The fact that the new recrystallization leads to a dimeric unit indicates that the hexanuclear cluster is not present in the DMSO solution. It is not possible, however, to conclude whether there are simple mononuclear units or dimeric units in solution.

In complex (I), the thiosaccharinate anions bridge two Ag atoms by their exocyclic S and endocyclic N atoms across a crystallographic centre of inversion to form a centrosymmetric dimeric unit. The basic dimeric units are linked by Ag—S<sub>exo</sub> interactions into a two-dimensional network parallel to the crystallographic *bc* plane.



In the title complex, the Ag—N distance is 2.199 (2) Å, much shorter than the Ag—N bond in [Ag<sub>6</sub>(tsac)<sub>6</sub>] [2.285 (2) Å; Dennehy, Tellería *et al.*, 2007] or [Ag<sub>4</sub>(tsac)<sub>4</sub>(PPh<sub>3</sub>)<sub>3</sub>] [2.270 (8)–2.331 (8) Å; Dennehy, Quinzani & Jennings, 2007], but close to the average Ag—N<sub>sp<sup>2</sup></sub> distance found in the Cambridge Structural Database (CSD, Version 5.28, update of January 2007; Allen, 2002) of 2.19 (8) Å for 104 observations. The fact that the endocyclic thiosaccharinate N atom is more strongly coordinated to the Ag<sup>I</sup> atom in (I) than are those in [Ag<sub>6</sub>(tsac)<sub>6</sub>] is also reflected by the lengthening of the intra-ligand C—N bond [1.320 (3) Å in (I) *versus* 1.297 (4) Å in the latter].

The Ag—S<sub>exo</sub> distance in the dimeric unit of (I) is 2.4111 (7) Å, shorter than the distances observed in the complexes [Ag<sub>6</sub>(tsac)<sub>6</sub>] [2.4861 (7) and 2.5014 (8) Å] and [Ag<sub>4</sub>(tsac)<sub>4</sub>(PPh<sub>3</sub>)<sub>3</sub>] [2.427 (3)–2.660 (3) Å]. The distance in (I) is considerably shorter than the average Ag—S(thiolate) distance found in the CSD of 2.52 (8) Å for 114 observations. The C—S<sub>exo</sub> distance also reflects the change in coordination strength of the S<sub>exo</sub> atom of the ligand to Ag centres in the title compound *versus* [Ag<sub>6</sub>(tsac)<sub>6</sub>]. In the latter, the existence of two strong bonds between the S<sub>exo</sub> atom and two Ag centres produces a longer C—S<sub>exo</sub> distance [1.713 (3) Å] than in complex (I) [1.704 (2) Å], in which the S<sub>exo</sub> atom forms one bond to an Ag atom and only an interaction to another Ag atom.

The Ag<sup>I</sup>···Ag<sup>I</sup> distance [2.9194 (4) Å] in (I) is in the range considered a strong argentophilic interaction, as reported by

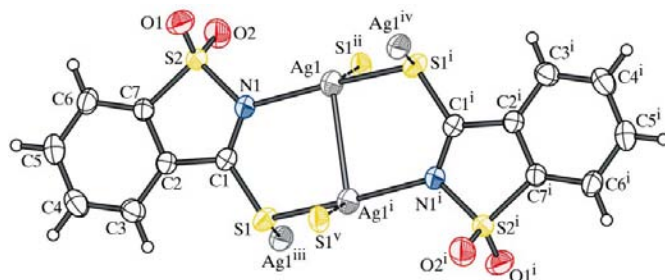
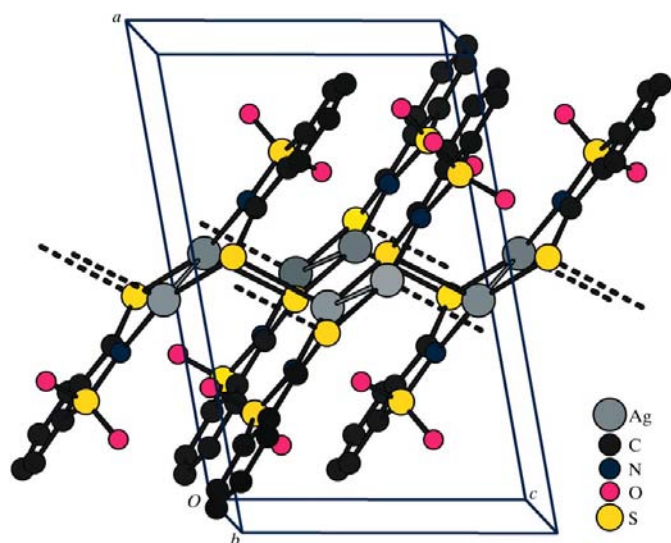


Figure 1

The Ag<sub>2</sub>(tsac)<sub>2</sub> dimer of (I). The Ag<sup>I</sup>···Ag<sup>I</sup> distance is 2.9194 (4) Å. [Symmetry codes: (i) 1 - x, 2 - y, 1 - z; (ii) 1 - x,  $\frac{1}{2}$  + y,  $\frac{3}{2}$  - z; (iii) 1 - x,  $-\frac{1}{2}$  + y,  $\frac{3}{2}$  - z; (iv) x,  $\frac{3}{2}$  - y,  $-\frac{1}{2}$  + z; (v) x,  $\frac{3}{2}$  - y,  $-\frac{1}{2}$  + z.]


**Figure 2**

A packing diagram for (I), showing the two-dimensional network formed by Ag...S interactions between the dimeric units, parallel to the crystallographic *bc* plane.

different authors (Kristiansson, 2001; Chen *et al.*, 2007). Castiñeiras *et al.* (2006) confirmed the Ag–Ag binding in a density functional theory study of a hexanuclear thione–silver(I) cluster. The shortest Ag...Ag distance in Castiñeira's complex [2.9996 (9) Å] is even longer than the Ag...Ag distance in (I).

The existence of silver–thione or silver–thionate coordination polymers is well known (Su *et al.*, 2002). In some, the argentophilic interaction is the major organizing force in the polymeric array. In the title compound, the extended two-dimensional motif is linked by  $\mu_2$ -S:S bridges between Ag<sup>I</sup> atoms of different dimeric units (Fig. 2). The Ag...S interaction of 2.9194 (4) Å is much longer than the sum of the covalent radii of the atoms, considered to be in the range 2.43–2.60 Å (Suresh & Koga, 2001), but much less than the sum of the van der Waals radii (3.52 Å; Bondi, 1964).

The thiosaccharinate ligands of (I) are almost planar (r.m.s. deviation of ring atoms = 0.0378 Å) and stack parallel to each other with an angle of 1.17 (9)° between planes. The distance from the centroid of the benzene ring of the thiosaccharinate ligand to the neighbouring plane is 3.456 Å.

## Experimental

Solid thiosaccharin was prepared according to a previously reported procedure (Dennehy, Tellería *et al.*, 2007). The Ag(tsac) complex was synthesized by dropwise addition of a solution of AgNO<sub>3</sub> (24 mg) in MeCN (6 ml) to an MeCN solution (6 ml) containing thiosaccharin (30 mg), with mechanical stirring at room temperature. The resulting yellow solid was filtered off and washed with diethyl ether. By dissolution of the solid (12 mg) in DMSO (2 ml), a yellow solution was obtained. Slow diffusion of CH<sub>2</sub>Cl<sub>2</sub> into this solution yielded yellow plate-shaped crystals of [Ag(tsac)]<sub>n</sub>, (I), suitable for single-crystal X-ray diffraction. IR spectra were obtained in KBr dispersion and in Nujol mulls, showing no differences in the vibrational bands; ( $\nu$ , cm<sup>-1</sup>): 1458 (*m*), 1401 (*m*), 1324 (*m*), 1235 (*m*), 1166 (*s*), 1230 (*w*),

1012 (*m*), 1006 (*m*), 950 (*w*), 802 (*m*), 766 (*m*), 736 (*w*), 628 (*w*), 588 (*m*), 556 (*m*), 537 (*m*), 436 (*m*).

## Crystal data

[Ag(C<sub>7</sub>H<sub>4</sub>NO<sub>2</sub>S<sub>2</sub>)]  
 $M_r = 306.10$   
 Monoclinic,  $P2_1/c$   
 $a = 12.8718$  (6) Å  
 $b = 8.0615$  (3) Å  
 $c = 8.3059$  (3) Å  
 $\beta = 100.695$  (2)°  
 $V = 846.90$  (6) Å<sup>3</sup>  
 $Z = 4$   
 Mo  $K\alpha$  radiation  
 $\mu = 2.83$  mm<sup>-1</sup>  
 $T = 294$  (2) K  
 $0.38 \times 0.35 \times 0.10$  mm

## Data collection

Bruker X8 Kappa-APEXII CCD area-detector diffractometer  
 Absorption correction: Gaussian [XPREP (Bruker, 2006) and SADABS (Bruker, 2006)]  
 $T_{\min} = 0.413$ ,  $T_{\max} = 0.765$   
 14582 measured reflections  
 2787 independent reflections  
 2404 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.026$

## Refinement

$R[F^2 > 2\sigma(F^2)] = 0.030$   
 $wR(F^2) = 0.075$   
 $S = 1.05$   
 2787 reflections  
 118 parameters  
 H-atom parameters constrained  
 $\Delta\rho_{\max} = 1.86$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -1.40$  e Å<sup>-3</sup>

**Table 1**

Selected geometric parameters (Å, °).

Ag1–N1	2.199 (2)	Ag1...Ag1 <sup>i</sup>	2.9194 (4)
Ag1–S1 <sup>i</sup>	2.4111 (7)	C7–S2	1.755 (2)
Ag1–S1 <sup>ii</sup>	2.8031 (7)		
N1–Ag1–S1 <sup>i</sup>	161.93 (6)	S1 <sup>ii</sup> –Ag1...Ag1 <sup>i</sup>	112.273 (19)
N1–Ag1–S1 <sup>ii</sup>	90.60 (6)	N1–C1–S1	125.53 (19)
S1 <sup>i</sup> –Ag1–S1 <sup>ii</sup>	107.45 (2)	C2–C1–S1	120.11 (17)
N1–Ag1...Ag1 <sup>i</sup>	87.89 (6)	C1–N1–S2	111.09 (17)
S1 <sup>i</sup> –Ag1...Ag1 <sup>i</sup>	84.458 (18)	Ag1 <sup>i</sup> –S1–Ag1 <sup>iii</sup>	117.19 (3)

Symmetry codes: (i)  $-x + 1, -y + 2, -z + 1$ ; (ii)  $-x + 1, y + \frac{1}{2}, -z + \frac{3}{2}$ ; (iii)  $-x + 1, y - \frac{1}{2}, -z + \frac{3}{2}$ .

All H atoms were refined using a riding model, with C–H = 0.93 Å and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ .

Data collection: APEX2, BIS and COSMO (Bruker, 2006); cell refinement: SAINT (Bruker, 2006); data reduction: SAINT, SADABS and XPREP (Bruker, 2006); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: DIAMOND (Brandenburg, 2007); software used to prepare material for publication: publCIF (Version 1.5.1c beta; Westrip, 2007).

MD and OVQ thank SGCyT–UNS for the financial support of Project No. M24/Q025. The diffractometer was funded by a CT–INFRA grant from the Financiadora de Estudos e Projetos (FINEP), Brazil.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3125). Services for accessing these data are described at the back of the journal.

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