

Tetra-*n*-butylammonium tetrakis-(pentafluorobenzenethiolato- κ S)-aurate(III)

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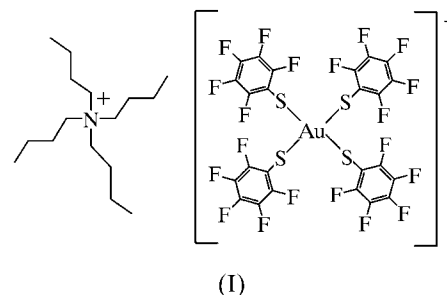
The title compound, (C₁₆H₃₆N)[Au(C₆F₅S)₄], is the first example of a structurally characterized gold(III) complex with monodentate benzenethiolate ligands. The Au atom lies on a fourfold axis and the AuS₄ group has square-planar geometry. The anion shows a two-dimensional linkage through π - π and C-F... π intermolecular interactions.

Comment

The syntheses and structures of gold(III) complexes with monodentate thiolate ligands have been poorly investigated, because reductive elimination reactions of thiolate ligands usually occur to afford a linear two-coordinated gold(I)-thiolate complex and a corresponding disulfide (Beck *et al.*, 1967; Muller *et al.*, 1978). The only example of an isolated gold(III) complex with four monodentate thiolate ligands is [Au(Smetetraz)₄]⁻ (Smetetraz is 1-methyl-1,2,3,4-tetrazole-5-thiolate; Abram *et al.*, 1998; Nöth *et al.*, 1998; Lang *et al.*, 1999), which contains an electron-withdrawing tetrazole unit in the ligand system, as has been confirmed by X-ray diffraction methods. Highly fluorinated thiolate ligands, such as pentafluorobenzenethiolate, are other candidates, and two types of corresponding gold(III) complex have been isolated, *viz.* [Au^{III}(C₆F₅S)₄]⁻ with both tetraethylammonium, Et₄N⁺, and tetraphenylarsonium, Ph₃As⁺ (Muller *et al.*, 1978). However, their crystal structures have not been determined. Recently, we successfully synthesized and crystallized the four-coordinated gold(III) complex with pentafluorobenzenethiolate using the tetra-*n*-butylammonium cation, which is bulkier than tetraethylammonium, as part of our investigation of gold-thiolate complexes (Watase *et al.*, 2000). We report here the crystal structure of this complex, (I).

In the anion of (I), the gold centre is coordinated by four thiolate ligands in a typical square-planar geometry, where the Au atom deviates from the S₄ plane by 0.130 (1) Å and the

S1—Au1—S1ⁱⁱ angle is 89.824 (5)° (Fig. 1 and Table 1). The four thiolate ligands are crystallographically equivalent, since the Au atom is situated on a crystallographic fourfold axis. All thiolate units are aligned almost orthogonally to the S₄ plane and are oriented in the same sense, like a windmill. This anion



also has a structure resembling a four-legged table, since all the S—C bonds deviate from the S₄ plane on the same side, as shown in Fig. 2. The Au1—S1 bond length is slightly shorter than the Au—S bonds in [Au(Smetetraz)₄]⁻ [2.352 (1)–2.358 (1) Å; Abram *et al.*, 1998; Nöth *et al.*, 1998; Lang *et al.*, 1999], but corresponds to those of general gold(III) complexes with dithiolate ligands (2.30–2.35 Å; Nakamoto *et al.*, 1993; Fackler *et al.*, 1999). The S1—C1 bond length is longer than the

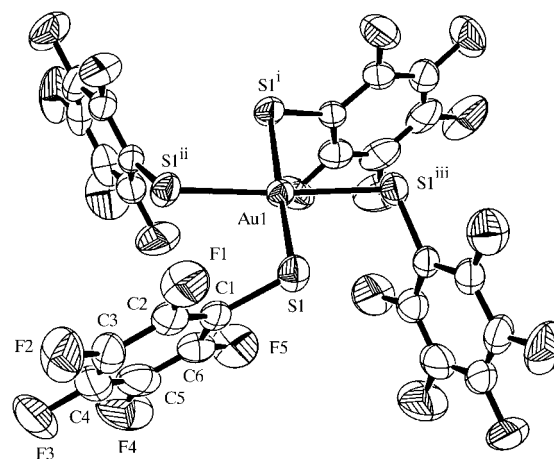


Figure 1

View of the anion of (I). Displacement ellipsoids are drawn at the 30% probability level. [Symmetry codes: (i) $-x, -y, z$; (ii) $-y, x, z$; (iii) $y, -x, z$.]

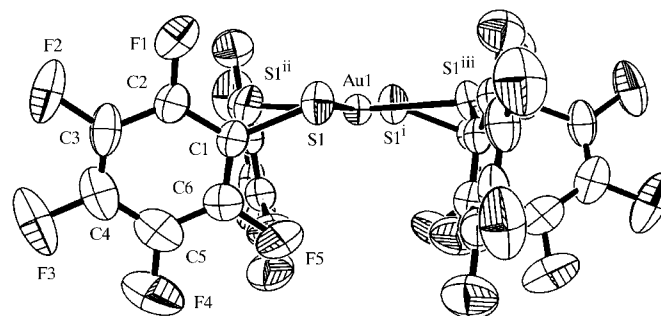


Figure 2

Side view of the anion of (I). The symmetry codes are the same as in Fig. 1.

S—C bonds in $[\text{Au}(\text{Smetetraz})_4]^-$ [1.722 (4)–1.743 (6) Å], but is compatible with those of $(n\text{-Bu}_4\text{N})_2[\text{Pt}_2(\mu\text{-C}_6\text{F}_5\text{S})_2(\text{C}_6\text{F}_5\text{S})_4]$, which is an isoelectronic platinum(II) complex with the same thiolate ligand [1.752 (2)–1.785 (7) Å; Rivera *et al.*, 2001]. The ligands still have a thiolate character, as revealed by the S—C bond lengths, which lie in the normal range for a single (1.82 Å) rather than a double bond (1.56 Å; Cea-Olivares *et al.*, 1995). The Au1—S1—C1 angle is consistent with the values of similar angles in $[\text{Au}(\text{Smetetraz})_4]^-$ [106.2 (1)–107.2 (2)°] and $(n\text{-Bu}_4\text{N})_2[\text{Pt}_2(\mu\text{-C}_6\text{F}_5\text{S})_2(\text{C}_6\text{F}_5\text{S})_4]$ [105.7 (2)–109.5 (2)°].

The packing of (I) is depicted in Fig. 3. The structure is layered, with the $[\text{Au}(\text{C}_6\text{F}_5\text{S})_4]^-$ anions and $n\text{-Bu}_4\text{N}^+$ cations stacked alternately along the *c* axis. There are two independent cations, which show disordered structures, since the N atoms have crystallographically imposed $4/m$ symmetry. The anion layer, viewed along the *c* axis, is shown in Fig. 4. All the ligands of the anions are aligned orthogonally to the AuS₄ plane and are oriented in the same sense, resembling a counterclockwise windmill. The side view of this anion layer (Fig. 3), however, shows that there are two conformational isomers (*i.e.* enantiomers) of the anion, *viz.* a top and a

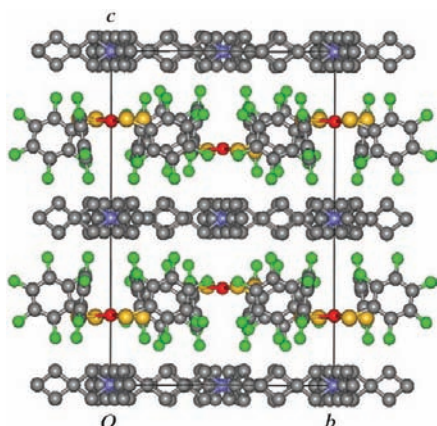


Figure 3
Packing diagram of (I), projected along *a*. The H atoms of the cations have been omitted for clarity.

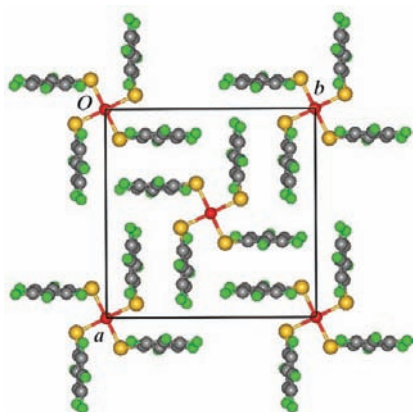


Figure 4
Anion layer of (I), projected along *c*.

bottom inversion, situated alternately along the layer. Each phenyl ring of the anion is exactly parallel to one of the phenyl rings of an adjacent anion (Fig. 4), as a result of the space-group-imposed symmetry. The least-squares distance between the planes of two neighbouring phenyl rings is about 3.5 Å, and a weak intermolecular π – π interaction can exist, despite the Coulomb repulsion between anions. The phenyl ring and two of the F atoms of a neighbouring anion also show close contacts [$\text{F}2 \cdots \text{C}4^{\text{iv}} = 3.145$ (9) Å and $\text{F}3 \cdots \text{C}3^{\text{iv}} = 3.177$ (10) Å; symmetry code: $(\text{iv}) \frac{1}{2} - y, \frac{1}{2} + x, \frac{1}{2} - z$]. These are comparable to the sum of the van der Waals radii (3.17 Å) of the C (1.70 Å) and F (1.47 Å) atoms (Bondi, 1964). The lengths of the intermolecular π – π -stacking and C–F \cdots π interactions in (I) are slightly shorter than the analogous π – π -stacking (3.6 Å) and C–F \cdots π interactions (3.24 Å) in the reported Ti^{IV} complex with the same thiolate ligand, $(\text{Et}_2\text{NH}_2)_3[\text{Ti}(\text{C}_6\text{F}_5\text{S})_5](\text{C}_6\text{F}_5\text{S})_2$ (Carmalt *et al.*, 2000). As a result of these intermolecular interactions, the anions of (I) are linked together and form a two-dimensional sheet-like structure in the (001) plane. In addition, the tetra-*n*-butylammonium cation has the most flattened conformation. The alkyl chains spread in the same direction as the Au–S bonds of the anion and may contribute to the stabilization of the crystal structure (Fig. 3).

Experimental

To a solution of $(n\text{-Bu}_4\text{N})[\text{AuBr}_4]$ (0.76 g, 1 mmol) in tetrahydrofuran (15 ml), a mixture of pentafluorobenzenethiol (0.8 g, 4 mmol) and triethylamine (0.4 g, 4 mmol) in the same solvent (20 ml) was added dropwise at room temperature with stirring. After 3 h, a white precipitate was filtered off and the tetrahydrofuran was removed under reduced pressure to give a red residue. Red crystals of (I) were obtained by recrystallization from a mixed tetrahydrofuran/methanol solution (isolated yield 41%). Analysis calculated for $\text{C}_{40}\text{H}_{36}\text{-AuF}_{20}\text{NS}_4$: C 38.87, H 2.94, N 1.13%; found: C 38.63, H 2.83, N 1.12%.

Crystal data

$(\text{C}_{16}\text{H}_{36}\text{N})[\text{Au}(\text{C}_6\text{F}_5\text{S})_4]$
 $M_r = 1235.91$
 Tetragonal, $I4/m$
 $a = 14.7427$ (4) Å
 $c = 22.0412$ (6) Å
 $V = 4790.6$ (2) Å³
 $Z = 4$
 $D_x = 1.713$ Mg m⁻³

Mo $K\alpha$ radiation
 Cell parameters from 25 852 reflections
 $\theta = 1.7\text{--}27.5^\circ$
 $\mu = 3.36$ mm⁻¹
 $T = 296.2$ K
 Prism, red
 $0.32 \times 0.15 \times 0.10$ mm

Data collection

Rigaku R-Axis RAPID imaging-plate diffractometer
 ω scans
 Absorption correction: multi-scan (Higashi, 1995)
 $T_{\text{min}} = 0.499$, $T_{\text{max}} = 0.714$
 22 114 measured reflections

2835 independent reflections
 1975 reflections with $F^2 > 2\sigma(F^2)$
 $R_{\text{int}} = 0.039$
 $\theta_{\text{max}} = 27.5^\circ$
 $h = -19 \rightarrow 19$
 $k = -19 \rightarrow 19$
 $l = -28 \rightarrow 28$

Refinement

Refinement on F
 $R = 0.037$
 $wR = 0.043$
 $S = 1.05$
 1975 reflections
 176 parameters

H-atom parameters not refined
 $w = 1/[\sigma^2(F_o) + 0.00063|F_o|^2]$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 2.55$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.96$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Au1—S1	2.340 (1)	S1—C1	1.770 (6)
S1—Au1—S1 ⁱ	173.64 (9)	Au1—S1—C1	107.1 (2)
S1—Au1—S1 ⁱⁱ	89.824 (5)		

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

The two independent tetra-*n*-butylammonium cations show orientational disorder, and atoms N1, N2, C8, C10, C12 and C14 lie on mirror planes perpendicular to *c*. The occupancy factors of atoms C7, C9, C11 and C13 and all the H atoms of the cations are 50%. H atoms were placed in calculated positions (C—H = 0.95 Å) but were not refined.

Data collection: *PROCESS* (Rigaku, 1996); cell refinement: *PROCESS*; data reduction: *TEXSAN* (Molecular Structure Corporation, 2000); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *TEXSAN*; molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *TEXSAN*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB1105). Services for accessing these data are described at the back of the journal.

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