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A quadrupole–quadrupole stacking synthon in (2,3,5,6-tetrafluorobenzenethiolato-*κS*)(triphenylphosphine-*κP*)gold(I)

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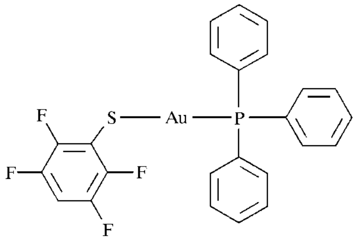
The title compound, [Au(C_6HF_4S)($C_{18}H_{15}P$)], with both aromatic and fluorinated aromatic rings in its molecular system, shows dimerization through a quadrupole–quadrupole stacking synthon. The dimer further aggregates through intermolecular π–π stacking and C—H$\cdots\pi$ interactions, giving a supramolecular three-dimensional network.

Comment

Many approaches to the construction and control of supramolecular systems based on Au^I complexes have been reported (Hao *et al.*, 1999; Hunks *et al.*, 2000; Tzeng *et al.*, 1999). Non-covalent interactions, such as Au$\cdots$Au contacts, hydrogen bonding and the π–π stacking synthon, play important roles in the molecular design of these systems and the architecture of their extended structures. The quadrupole–quadrupole stacking synthon is induced by co-operation between electron-deficient fluorinated aromatic and electron-rich aromatic rings, and contributes significantly to the assembly of molecules (Coates *et al.*, 1997; Williams, 1993). The gold(I) phosphine thiolate complex [Au(PPh_3)(SC_6F_5)], (II), which has three phenyl and one perfluorinated phenyl rings, was the first example of an Au^I complex tightly aggregated through electrostatic quadrupole interactions and π–π stacking in the crystal (Watase *et al.*, 2003). Such an aggregate is disassembled in solution, but a dimeric form still exists even in solution. These results suggest that the quadrupole interaction in such a molecular system is more effective than other intermolecular interactions, leading to a new class of supramolecular aggregation. In order to investigate whether the quadrupole interaction is a general phenomenon in this type of Au^I complex, we have synthesized the title novel gold(I) phosphine complex, [Au(PPh_3)(SC_6H-2,3,5,6-F_4)], (I), incorporating the tetrafluorobenzenethiolate ligand, SC_6H-2,3,5,6-F_4. In this communication, we report the observation in (I) of a dimeric association through distorted dual quadrupole synthons, owing to the H atom at the *para* position of the thiolate ligand, and the supramolecular three-dimensional network observed in the compound.



(I)

The Au centre of (I) has linear two-coordinate geometry to the phosphine and thiolate ligands (Fig. 1 and Table 1). The P1—Au1—S1 axis deviates slightly from linearity [174.46 (8)°], and the Au—S and Au—P bond distances [2.306 (2) and 2.257 (2) Å, respectively] are normal for this type of gold(I) phosphine thiolate complex [literature values for P—Au—S angles are in the range 171.01–176.53°, for Au—S 2.285–2.303 Å and for Au—P 2.253–2.269 Å (Ahmed *et al.*, 1999; de Vos *et al.*, 1999; Forward *et al.*, 1995; Kuz'mina *et al.*, 1993; Nakamoto *et al.*, 1993; Watase *et al.*, 2003)]. The S1—C1 bond distance [1.758 (9) Å] and Au1—S1—C1 angle [108.0 (3)°] correspond to those of analogous compounds (S—C distances in the range 1.739–1.801 Å and Au—S—C angles in the range 96.35–110.82°) and show single-bond character for the thiolate.

The Au1—S1—C1—C2 torsion angle of 22.7 (9)° in (I) is relatively small for this type of gold(I) compound, bringing the tetrafluorinated phenyl ring nearly parallel to the P—Au—S axis, similar to what is observed in the pentafluorobenzenethiolate analogue, *viz.* (II). This orientation brings an *ortho*-substituted F atom close to the Au centre, and the resulting Au1$\cdots$F1 distance [2.899 (6) Å] is much shorter than the sum of the van der Waals radii (3.13 Å) of Au and F (1.66 and 1.47 Å, respectively; Bondi, 1964), indicating an intramolecular close contact. In addition, one of the phenyl rings (containing atom C7) of the phosphine ligand is almost parallel to the fluorinated phenyl ring (that containing atom C1), but these rings are not coplanar. This characteristic conformation induces another intramolecular close contact, with an F1$\cdots$H2 distance of 2.58 Å, which is shorter than the sum of the van der Waals radii (2.67 Å) of H (1.20 Å) and F; the C2—F1$\cdots$H2 angle is 154.8°.

A remarkable structural feature of (I) is the dual intermolecular quadrupole interaction between the fluorinated phenyl ring of the thiolate ligand and a phenyl ring of the phosphine ligand of a neighbouring molecule, giving a pseudo-cyclic dimer structure (Fig. 2). The crystal structure of (I) has an identical space group and similar molecular packing to the pentafluorobenzenethiolate analogue (II). In (II), the two

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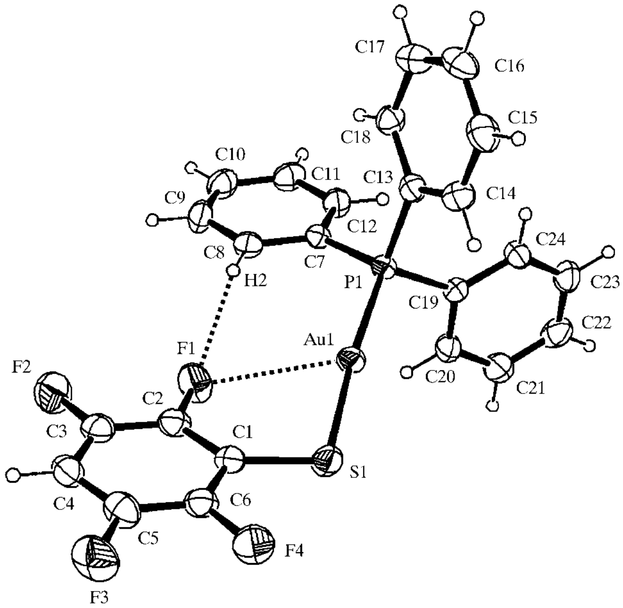

Figure 1
A view of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Dotted lines show intramolecular close contacts.

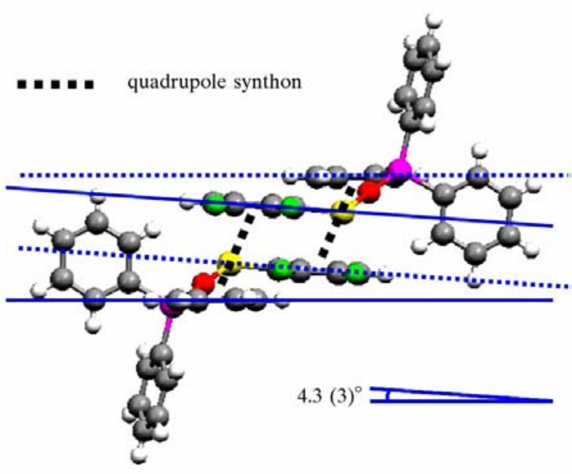

Figure 3
The wedge-shaped configuration of the quadrupole–quadrupole stacking synthon in (I).

phenyl rings of the quadrupole synthon are nearly parallel, with a dihedral angle of 1.8 (3)° (Watase *et al.*, 2003). In (I), the stacking configuration of the equivalent two rings [containing atoms C1 and C7^{i}; symmetry code: (i) $1 - x$, $-y$, $1 - z$] is slightly distorted, with a dihedral angle of 4.3 (3)°, showing a wedge shape from the S atom toward the aromatic H atom at the *para* position of the tetrafluorobenzenethiolate ligand (Fig. 3). As a result of such a wedge-shaped configuration in (I), the distance between the stacked rings [C1-ring$\cdots$C7^{i}-ring = 3.47 (1) Å, calculated by the average shift of the six C atoms of the C7^{i}-ring from the best plane of the C1-ring] is 0.08 Å longer than that in (II). This wedge-shaped configuration is observed only in (I) despite the similarity in crystal packing between compounds (I) and (II), and despite the decrease in steric hindrance in (I) due to the smaller H atom at the *para* position of the thiolate ligand. This fact suggests that the introduction of the H atom into the highly fluorinated-phenyl ring may decrease the electronegativity of the ring and reduce the intermolecular quadrupole interaction, although another indirect effect of the substitution cannot be ruled out.

Although the quadrupole interaction is slightly lessened in (I), the unit cell is slightly smaller compared with (II), particularly the *c* axis, where the reduction is 1.0%. On the other hand, each phenyl and fluorinated-phenyl ring forms other π–π stacking interactions, *i.e.* $C_6H_5\cdots C_6H_5$ [C7-ring$\cdots$C7^{ii}-

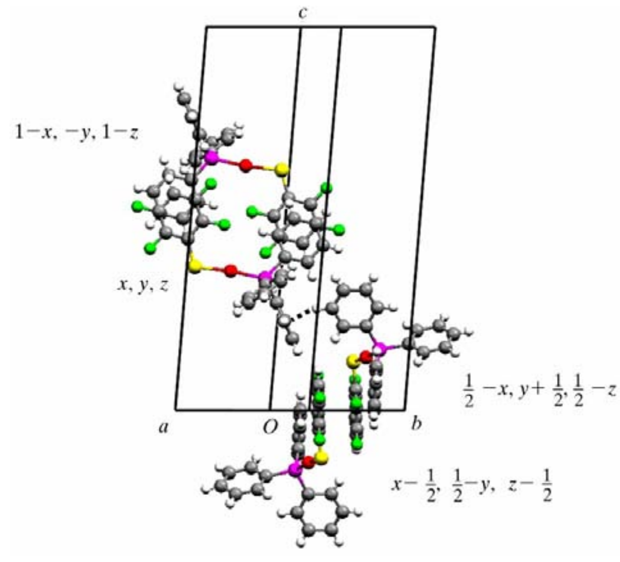

Figure 2
The dimeric association of (I) through the quadrupole–quadrupole stacking synthon.

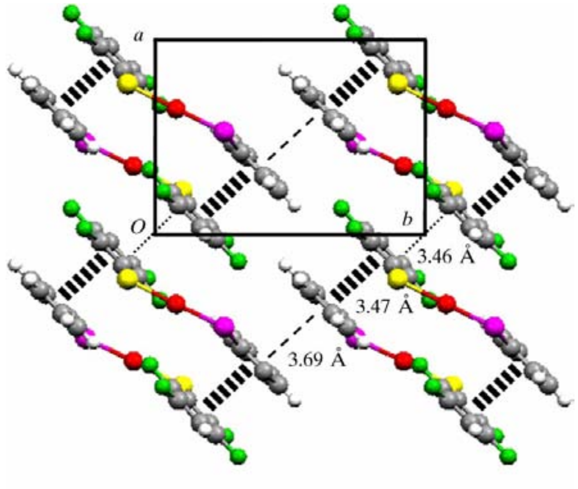

Figure 4
The two-dimensional network showing three types of synthon in (I), *viz.* $C_6HF_4\cdots C_6H_5$ (thick bars), $C_6HF_4\cdots C_6HF_4$ (dotted lines) and $C_6H_5\cdots C_6H_5$ (dashed lines). The C13- and C19-phenyl rings of the phosphine ligands have been omitted for clarity.

ring; symmetry code: (ii) $1-x$, $1-y$, $1-z$] and $C_6HF_4\cdots C_6HF_4$ [C1-ring$\cdots$C1^{iii}-ring; symmetry code: (iii) $2-x$, $-y$, $1-z$], on opposite sides of each ring; the distances of their stacking synthons are 3.46 (1) and 3.69 (2) Å, respectively (Fig. 4). These π–π stacking synthons are responsible for the construction of a two-dimensional supramolecular network, which is built up along the *c* axis. The layers are also linked to each other through a T-shaped C—H$\cdots\pi$ intermolecular interaction between phenyl rings of the phosphine ligand, where the distance of this synthon is 2.855 (8) Å [C13-ring$\cdots$H15^{iv}; symmetry code: (iv) $\frac{1}{2}-x$, $y+\frac{1}{2}$, $\frac{1}{2}-z$].

Through these intra- and intermolecular interactions, the title complex forms a tightly packed three-dimensional assembly of dimers in the crystal.

Experimental

Tetrafluorobenzenethiol (0.2 g, 1 mmol) was reacted with [Au(PPh$_3$)Cl] (0.5 g, 1 mmol) in the presence of triethylamine (0.1 g, 1 mmol) in tetrahydrofuran for 3 h at room temperature. The white precipitate of Et$_3$NHCl was filtered off and the tetrahydrofuran was removed under reduced pressure, giving a white residue. Colourless crystals of (I) were obtained by recrystallization from dichloromethane–*n*-hexane.

Crystal data

[Au(C$_6$HF$_4$S)(C$_{18}$H$_{15}$P)]
$M_r = 640.38$
Monoclinic, $P2_1/n$
$a = 8.2743$ (3) Å
$b = 11.3537$ (3) Å
$c = 23.4382$ (8) Å
$\beta = 96.579$ (1)°
$V = 2187.4$ (1) Å^3
$Z = 4$

$D_x = 1.944$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 28 391 reflections
$\theta = 1.8$–30.5°
$\mu = 6.96$ mm^{-1}
$T = 296.2$ K
Prism, colourless
0.20 × 0.14 × 0.09 mm

Data collection

Rigaku R-AXIS RAPID imaging-plate diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min} = 0.297$, $T_{max} = 0.534$
23 270 measured reflections

5018 independent reflections
3410 reflections with $F^2 > 3\sigma(F^2)$
$R_{int} = 0.034$
$\theta_{max} = 27.5°$
$h = -10 \rightarrow 10$
$k = -14 \rightarrow 13$
$l = -28 \rightarrow 30$

Refinement

Refinement on F^2
$R(F) = 0.037$
$wR(F^2) = 0.103$
$S = 1.58$
3410 reflections
280 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + \{0.05[\max(F_o^2,0) + 2F_c^2]/3\}^2]$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.93$ e Å^{-3}
$\Delta\rho_{min} = -0.98$ e Å^{-3}

All H atoms were placed in calculated positions (C—H = 0.95 Å) and treated as riding.

Table 1
Selected geometric parameters (Å, °).

Au1—S1	2.306 (2)	P1—C7	1.801 (8)
Au1—P1	2.257 (2)	P1—C13	1.823 (8)
Au1—F1	2.899 (6)	P1—C19	1.802 (8)
S1—C1	1.758 (9)		
S1—Au1—P1	174.46 (8)	Au1—P1—C13	111.8 (3)
S1—Au1—F1	72.8 (1)	Au1—P1—C19	111.6 (2)
Au1—S1—C1	108.0 (3)	Au1—F1—C2	106.6 (5)
Au1—P1—C7	115.8 (2)		
Au1—S1—C1—C2	22.7 (9)	Au1—P1—C13—C14	42.4 (7)
Au1—S1—C1—C6	−160.3 (6)	Au1—P1—C13—C18	−136.0 (6)
Au1—P1—C7—C8	26.1 (7)	Au1—P1—C19—C20	55.3 (7)
Au1—P1—C7—C12	−157.3 (6)	Au1—P1—C19—C24	−123.3 (7)

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *TEXSAN* (Molecular Structure Corporation, 2000); program(s) used to solve structure: *SIR*92 (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: OB1163). Services for accessing these data are described at the back of the journal.

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