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Tetraphenylphosphonium bis(2-thioxo-1,3-dithiole-4,5-dithiolato)aurate(III) acetone solvate and ethyltriphenylphosphonium bis(2-thioxo-1,3-dithiole-4,5-dithiolato)aurate(III)

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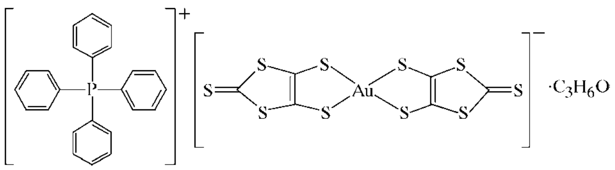
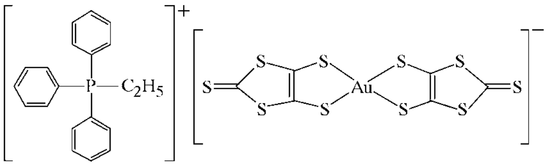
In the two title complexes, $(C_{24}H_{20}P)[Au(C_3S_5)_2]\cdot C_3H_6O$, (I), and $(C_{20}H_{20}P)[Au(C_3S_5)_2]$, (II), the Au^{III} atoms exhibit square-planar coordinations involving four S atoms from two 2-thioxo-1,3-dithiole-4,5-dithiolate (dmit) ligands. The Au—S bond lengths, ranging from 2.3057 (8) to 2.3233 (7) Å in (I) and from 2.3119 (8) to 2.3291 (10) Å in (II), are slightly smaller than the sum of the single-bond covalent radii. In (I), there are two halves of independent Ph_4P^+ cations, in which the two P atoms lie on twofold rotation axis sites. The Ph_4P^+ cations and $[Au(C_3S_5)_2]^-$ anions are interspersed as columns in the packing. Layers composed of Ph_4P^+ and $[Au(C_3S_5)_2]^-$ are separated by layers of acetone molecules. In (II), the $[Au(C_3S_5)_2]^-$ anions and $EtPh_3P^+$ counter-cations form a layered arrangement, and the $[Au(C_3S_5)_2]^-$ anions form discrete pairs with a long intermolecular Au$\cdots$S interaction for each Au atom in the crystal structure.

Comment

The third-order nonlinear optical (TONLO) response is very important in all-optical switching, signal processing and ultrafast optical communications (Sutherland, 1996). For the realisation of all-optical switching devices, the material requirements which have to be met are $W >> 1$ and $T << 1$. These two figures of merit are defined as $W = n_2I/(\alpha\lambda)$ and $T = \beta\lambda/n_2$, where n_2 is the nonlinear refractive index, α is the linear absorption coefficient, β is the nonlinear absorption coefficient, λ is the wavelength and I is the light irradiance. Furthermore, ultrafast response times are required for the nonlinear processes involved. Therefore, to be practically useful for all-optical switching, materials should have a large n_2 at the operating wavelength, small α and β and an ultrafast response time, together with good physicochemical properties, such as environmental stability and processability (Kuang *et al.*, 2003).



(I)



(II)

For nearly three decades, the synthesis and characterization of 2-thioxo-1,3-dithiole-4,5-dithiolate (dmit) complexes and related analogues have been paid great attention (Steimeck & Kirmse, 1979). As special π-electron conjugated systems, dmit and related ligands have been used as building units for electrical conductors and superconductors (Svenstrup & Becher, 1995; Cassoux, 1999; Pullen & Olk, 1999; Robertson & Cronin, 2002). The π-electron delocalization in conjugated systems can also contribute to an ultrafast optical response capability and large TONLO effects (Coe, 2004). Recently, many dmit complexes have been reported as possessing good TONLO properties (Wang *et al.*, 1999; Liu *et al.*, 2002). In our previous studies, the TONLO properties of a series of such complexes were reported. The results showed that they possess large TONLO properties with sub-picosecond response times (Yang *et al.*, 2005; Sun *et al.*, 2006). Along with this research, Au–dmit complexes (Li *et al.*, 2005, 2006) have been found to possess large n_2 and nearly zero absorption with

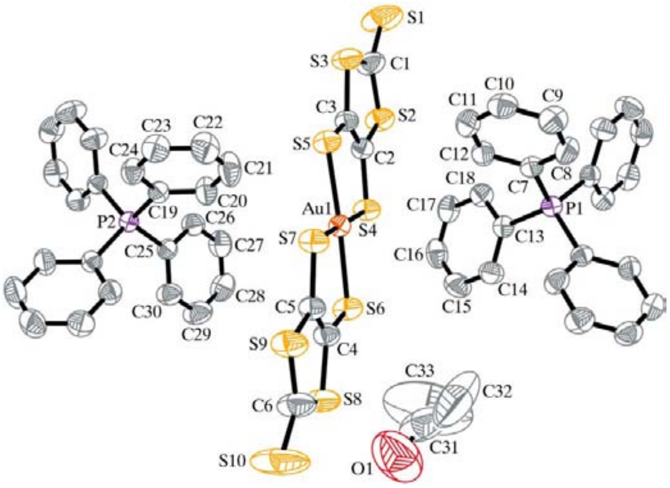


Figure 1
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity. There are two halves of independent tetraphenylphosphonium cations where the two P atoms lie on twofold rotation axis sites.

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good figures of merit, *W* and *T*, for all-optical switching applications at 1064 nm. Therefore, they are potential candidates for all-optical switching device applications. To continue this work, the preparation and structural characterization of the two title compounds, $(C_{24}H_{20}P)[Au(C_3S_5)_2]\cdot C_3H_6O$, (I), and $(C_{20}H_{20}P)[Au(C_3S_5)_2]$, (II), are reported here.

The two structures show similarities with and differences from each other and the previously reported crystal structures of 18 related Au–dmit complexes in the Cambridge Structural Database (CSD; Version 5.38 of May 2007; Allen, 2002). The similarities are that in all these crystal structures, dmit exhibits its typical behaviour as a bidentate ligand and the Au^{3+} ion is coordinated by four S atoms from two dmit molecules in an almost square-planar geometry; the four S atoms are planar, with a slight deviation of the Au atom therefrom, and all of them have a slight T_d distortion. Like the previously reported complexes, the Au—S bond lengths [2.3057 (8)–2.3233 (7) Å for (I) and 2.3119 (8)–2.3291 (10) Å for (II)] are slightly smaller than the sum of the single-bond covalent radii (1.36 Å; Pauling, 1960). The S—Au—S bite angles [87.20 (3)–91.76 (3)° for (I) and 86.97 (3)–91.49 (3)° for (II)] are almost nominal right angles and the *trans* S—Au—S angles [176.97 (3) and 177.20 (3)° for (I), and 178.22 (3) and 178.40 (3)° for (II)] are very close to 180°. The C═S double bond is much longer than the typical C═S bond length (1.599 Å; Allen *et al.*, 1987). The other C—S bonds [1.723 (4)–1.747 (3) Å for (I) and 1.728 (3)–1.751 (3) Å for (II)] are shorter than the typical C—S single bond (1.819 Å; Allen *et al.*, 1987) and are essentially single bonds with some double-bond character. The two C═C bond lengths of the dmit ion [1.345 (4) and 1.340 (4) Å for (I), and 1.336 (5) and 1.340 (5) Å for (II)] are very close to the corresponding double-bond value of 1.341 Å (Allen *et al.*, 1987).

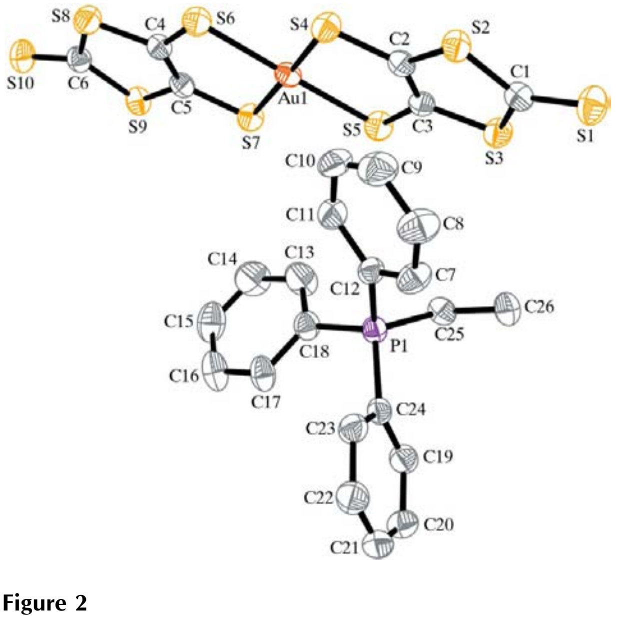

Figure 2
The molecular structure of (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity.

An obvious difference between these 20 compounds lies in the type of $[Au(C_3S_5)_2]^-$ anion. There is one type of $[Au(C_3S_5)_2]^-$ anion in some of these complexes, with large counter-cations (Miura *et al.*, 2004; Li *et al.*, 2006), and compounds (I) and (II) belong to this class. In other complexes, there are two kinds of crystallographically independent $[Au(C_3S_5)_2]^-$ anions in another type of $[Au(C_3S_5)_2]^-$ anion (Matsubayashi & Yokozawa, 1990; Li *et al.*, 2005), with small counter-cations. The counter-cations and their orientations with respect to the $[Au(C_3S_5)_2]^-$ anions are different in these crystal structures. In (I), there are two halves of independent $(C_{24}H_{20}P)^+$ cations, in which the two P atoms lie on twofold rotation axis sites. The $(C_{24}H_{20}P)^+$ cations and $[Au(C_3S_5)_2]^-$ anions are interspersed as columns in the packing. Layers composed of $(C_{24}H_{20}P)^+$ and $[Au(C_3S_5)_2]^-$ are separated by layers of acetone. In (II), there are layers of $(C_{21}H_{22}P)^+$ cations and of $[Au(C_3S_5)_2]^-$ anions, and the $[Au(C_3S_5)_2]^-$ anions form discrete pairs with a long intermolecular Au···S interaction for each Au atom in the crystal structure.

All the data show that the two $[Au(C_3S_5)_2]^-$ ring systems in the title compounds have a high degree of electron delocalization. The most striking physical characteristic of these two crystal structures is the extended electronically delocalized core, comprising the central Au^{3+} ion, four S atoms and the adjacent C═C units in the quasi-square plane. It has been shown that when Au^{3+} takes the place of group 12 metal ions (Zn^{2+}, Cd^{2+} and Hg^{2+}), electron delocalization is enhanced (Li *et al.*, 2003). This is due to the unfilled *d* electron shell of Au^{3+}, which allows the possibility of low-energy charge-transfer transitions and is an important contribution to optical nonlinearity. In particular, the 3*p* orbitals of S and 3*d* orbitals of Au^{3+} can overlap to form a highly delocalized system. This delocalization will greatly enhance hyperpolarizability and nonlinear susceptibility and lead to large TONLO properties. The TONLO properties of these two compounds were measured by the *Z*-scan technique (Sheik-Bahae *et al.*, 1989, 1990), in m*M* solutions of both acetone and acetonitrile at 1064 nm. These revealed that their nonlinear refractive indices were superior to that of CS_2.

Experimental

For the preparation of (I), 4,5-bis(furoylsulfanyl)-1,3-dithiole-2-thione (1.211 g) (Wang *et al.*, 2005) was suspended in methanol (15 ml). Under a nitrogen atmosphere, a sodium methoxide solution obtained from Na (0.145 g) in methanol (15 ml) was added to the above-mentioned mixture at room temperature to give a dark-red solution. To this solution, separate solutions of $NaAuCl_4\cdot 2H_2O$ (0.597 g) dissolved in methanol (5 ml) and $C_{24}H_{20}PBr$ (0.659 g) in methanol (5 ml) were added consecutively with stirring at room temperature. The reaction mixture was stirred for about 30 min. The product was collected by filtration and washed with methanol to afford a dark-brown precipitate of $(C_{24}H_{20}P)[Au(C_3S_5)_2]$. An acetone solution of the product was left standing at room temperature, and brown crystals of the solvate, (I), suitable for structure determination were obtained. Electronic absorption (Hitachi model U-3500 recording spectrophotometer, nm): 339 and 347 (π–π* transition of the dmit ligand), 466 (Au←S charge-transfer transition).

For the preparation of (II), 4,5-bis(furoylsulfanyl)-1,3-dithiole-2-thione (1.211 g) was suspended in methanol (15 ml). Under a nitrogen atmosphere, a sodium methoxide solution obtained from Na (0.145 g) in methanol (15 ml) was added to the above-mentioned mixture at room temperature to give a dark-red solution. To this solution, separate solutions of $NaAuCl_4 \cdot 2H_2O$ (0.597 g) dissolved in methanol (5 ml) and $C_{24}H_{20}PBr$ (0.584 g) in methanol (5 ml) were added consecutively with stirring at room temperature. The reaction mixture was stirred for about 30 min. The product was collected by filtration and washed with methanol to afford a dark-brown precipitate of (II). An acetone solution of (II) was left standing at room temperature, and brown crystals of (II) suitable for structure determination were obtained. Electronic absorption (Hitachi model U-3500 recording spectrophotometer, nm): 316 and 367 (π–π* transition of the dmit ligand), 446 (Au←S charge-transfer transition).

Compound (I)

Crystal data

$(C_{24}H_{20}P)[Au(C_3S_5)_2] \cdot C_3H_6O$
$M_r = 987.07$
Monoclinic, $P2/c$
$a = 24.4198$ (7) Å
$b = 7.4511$ (2) Å
$c = 23.1654$ (6) Å
$\beta = 115.7720$ (10)°

$V = 3795.78$ (18) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 4.50$ mm^{-1}
$T = 296$ (2) K
0.24 × 0.23 × 0.15 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*APEX2*; Bruker, 2005)
$T_{min} = 0.379$, $T_{max} = 0.508$

33785 measured reflections
8724 independent reflections
7545 reflections with $I > 2\sigma(I)$
$R_{int} = 0.024$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.023$
$wR(F^2) = 0.054$
$S = 1.03$
8724 reflections
419 parameters

14 restraints
H-atom parameters constrained
$\Delta\rho_{max} = 0.62$ e Å^{-3}
$\Delta\rho_{min} = -0.44$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °) for (I).

Au1—S7	2.3057 (8)	C3—S5	1.739 (3)
Au1—S4	2.3166 (7)	C3—S3	1.743 (3)
Au1—S5	2.3191 (7)	C4—C5	1.340 (4)
Au1—S6	2.3233 (7)	C4—S8	1.745 (3)
C1—S1	1.645 (3)	C4—S6	1.746 (3)
C1—S2	1.723 (4)	C5—S9	1.736 (3)
C1—S3	1.730 (4)	C5—S7	1.744 (3)
C2—C3	1.345 (4)	C6—S10	1.639 (4)
C2—S4	1.742 (3)	C6—S9	1.725 (4)
C2—S2	1.747 (3)	C6—S8	1.729 (4)
S7—Au1—S4	177.20 (3)	S7—Au1—S6	91.48 (3)
S7—Au1—S5	87.20 (3)	S4—Au1—S6	89.68 (3)
S4—Au1—S5	91.76 (3)	S5—Au1—S6	176.97 (3)

Compound (II)

Crystal data

$(C_{20}H_{20}P)[Au(C_3S_5)_2]$
$M_r = 880.96$
Monoclinic, $P2_1/n$
$a = 17.3058$ (2) Å
$b = 9.93060$ (10) Å
$c = 19.0668$ (2) Å
$\beta = 103.9590$ (10)°

$V = 3179.99$ (6) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 5.35$ mm^{-1}
$T = 296$ (2) K
0.24 × 0.17 × 0.13 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*APEX2*; Bruker, 2005)
$T_{min} = 0.361$, $T_{max} = 0.536$ (expected range = 0.336–0.499)

22548 measured reflections
7292 independent reflections
5381 reflections with $I > 2\sigma(I)$
$R_{int} = 0.027$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.027$
$wR(F^2) = 0.057$
$S = 1.01$
7292 reflections

344 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 0.80$ e Å^{-3}
$\Delta\rho_{min} = -0.27$ e Å^{-3}

Table 2
Selected geometric parameters (Å, °) for (II).

Au1—S4	2.3119 (8)	C3—S3	1.743 (3)
Au1—S6	2.3215 (10)	C3—S5	1.747 (3)
Au1—S7	2.3215 (8)	C4—C5	1.340 (5)
Au1—S5	2.3291 (10)	C4—S6	1.741 (3)
C1—S1	1.637 (3)	C4—S8	1.751 (3)
C1—S3	1.728 (3)	C5—S9	1.743 (3)
C1—S2	1.728 (4)	C5—S7	1.743 (4)
C2—C3	1.336 (5)	C6—S10	1.634 (3)
C2—S2	1.739 (3)	C6—S8	1.731 (4)
C2—S4	1.740 (4)	C6—S9	1.741 (4)
S4—Au1—S6	86.97 (3)	S4—Au1—S5	91.43 (3)
S4—Au1—S7	178.22 (3)	S6—Au1—S5	178.40 (3)
S6—Au1—S7	91.49 (3)	S7—Au1—S5	90.11 (3)

For compound (I), all H atoms were placed in geometrically calculated positions and refined using a riding model, with C—H = 0.93 (for CH groups) or 0.96 Å (for CH_3 groups), and with $U_{iso}(H) = 1.2U_{eq}(C)$ or $1.5U_{eq}$(methyl C). Although atoms S1 and S10 had large anisotropic parameters, no suitable disorder model could be found. Their U^{ij} components were restrained to isotropic behaviour. The three C atoms of the acetone molecule were also disordered and no treatment could be applied. The C32—C33 and C31—C32 distances were restrained to reasonable values. Since the reflections 100 and $\overline{3}02$ were obscured by the beam stop, F_o^2 is much less than F_c^2 in these reflections. They were omitted in the final refinement.

For compound (II), all H atoms were placed in geometrically calculated positions and refined using a riding model, with C—H = 0.93 (for CH groups) or 0.96 Å (for CH_3 groups), and with $U_{iso}(H) = 1.2U_{eq}(C)$ or $1.5U_{eq}$(methyl C).

For both compounds, data collection: *APEX2* (Bruker, 2005); cell refinement: *APEX2*; data reduction: *APEX2*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3168). Services for accessing these data are described at the back of the journal.

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