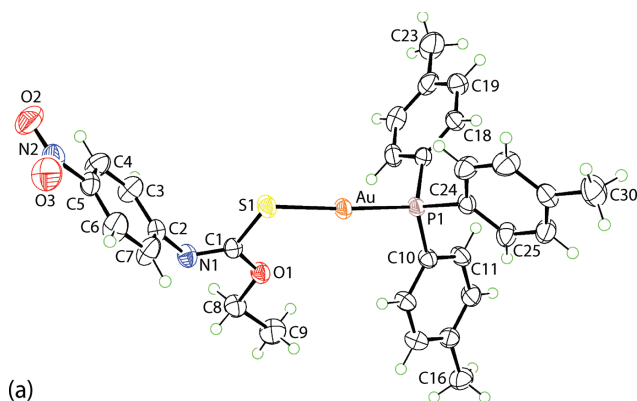
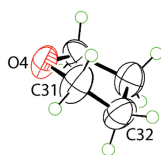


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# Crystal structure of [O-ethyl N-(4-nitrophenyl)thiocarbamato-κS] (tri-4-tolylphosphine-κP)gold(I) tetrahydrofuran solvate, C<sub>30</sub>H<sub>30</sub>AuN<sub>2</sub>O<sub>3</sub>PS, C<sub>4</sub>H<sub>8</sub>O



(a)



(b)

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## Abstract

C<sub>34</sub>H<sub>38</sub>AuN<sub>2</sub>O<sub>4</sub>PS, triclinic,  $P\bar{1}$  (no. 2),  $a = 10.2034(8)$  Å,  $b = 11.5755(9)$  Å,  $c = 15.7533(12)$  Å,  $\alpha = 69.948(2)^\circ$ ,  $\beta = 86.496(2)^\circ$ ,  $\gamma = 71.370(2)^\circ$ ,  $V = 1653.8(2)$  Å<sup>3</sup>,  $Z = 2$ ,  $R_{\text{gt}}(F) = 0.0355$ ,  $wR_{\text{ref}}(F^2) = 0.0858$ ,  $T = 223(2)$  K.

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The molecular structures are shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

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Table 1: Data collection and handling.

Crystal:	Yellow prism
Size:	0.16 × 0.15 × 0.11 mm
Wavelength:	Mo K $\alpha$ radiation (0.71073 Å)
$\mu$ :	4.60 mm <sup>-1</sup>
Diffractometer, scan mode:	Bruker AXS SMART, $\varphi$ and $\omega$
$\theta_{\text{max}}$ , completeness:	30.0°, >99%
$N(hkl)_{\text{measured}}$ , $N(hkl)_{\text{unique}}$ , $R_{\text{int}}$ :	13916, 9419, 0.029
Criterion for $I_{\text{obs}}$ , $N(hkl)_{\text{gt}}$ :	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$ , 8135
$N(\text{param})_{\text{refined}}$ :	391
Programs:	Bruker [1], SHELX [2, 3], WinGX/ORTEP [4]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å<sup>2</sup>).

Atom	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Au	0.22383(2)	0.23082(2)	0.17550(2)	0.03083(5)
S1	0.33883(11)	0.29783(9)	0.04602(6)	0.0376(2)
P1	0.11606(10)	0.15422(8)	0.30186(6)	0.02898(18)
O1	0.1504(3)	0.5087(2)	0.05143(17)	0.0343(5)
O2	0.6365(4)	0.3526(4)	-0.3702(2)	0.0636(9)
O3	0.7886(3)	0.3784(4)	-0.2961(2)	0.0611(9)
O4	0.7170(4)	0.1044(4)	0.8253(2)	0.0624(9)
N1	0.2635(3)	0.5386(3)	-0.0790(2)	0.0351(7)
N2	0.6709(4)	0.3801(3)	-0.3083(2)	0.0455(8)
C1	0.2468(4)	0.4627(3)	-0.0018(2)	0.0292(7)
C2	0.3665(4)	0.4936(3)	-0.1346(2)	0.0316(7)
C3	0.3343(4)	0.4576(4)	-0.2032(3)	0.0440(9)
H3	0.243304	0.458986	-0.211507	0.053*
C4	0.4339(4)	0.4196(4)	-0.2599(3)	0.0443(9)
H4	0.411683	0.393732	-0.306130	0.053*
C5	0.5665(4)	0.4198(4)	-0.2481(2)	0.0344(8)
C6	0.5998(4)	0.4587(5)	-0.1818(3)	0.0491(10)
H6	0.690401	0.459071	-0.174584	0.059*
C7	0.4992(4)	0.4972(5)	-0.1258(3)	0.0474(10)
H7	0.520864	0.526150	-0.081129	0.057*
C8	0.0699(4)	0.6446(3)	0.0152(3)	0.0381(8)
H8A	0.010465	0.661132	-0.037059	0.046*
H8B	0.131022	0.698145	-0.004020	0.046*
C9	-0.0166(5)	0.6752(4)	0.0905(3)	0.0509(11)
H9A	-0.072927	0.765849	0.069454	0.076*
H9B	-0.076311	0.621274	0.108818	0.076*
H9C	0.043616	0.658094	0.141684	0.076*
C10	0.0102(4)	0.2788(3)	0.3442(2)	0.0302(7)
C11	-0.0943(4)	0.2576(3)	0.4019(3)	0.0371(8)

Table 2 (continued)

Atom	x	y	z	$U_{iso}^*/U_{eq}$
H11	-0.115169	0.179866	0.415846	0.044*
C12	-0.1682(4)	0.3497(4)	0.4393(3)	0.0392(8)
H12	-0.238909	0.334086	0.478256	0.047*
C13	-0.1385(4)	0.4658(3)	0.4196(3)	0.0358(8)
C14	-0.0348(4)	0.4858(4)	0.3617(3)	0.0392(8)
H14	-0.014121	0.563700	0.347176	0.047*
C15	0.0392(4)	0.3939(3)	0.3245(3)	0.0338(7)
H15	0.109958	0.409557	0.285540	0.041*
C16	-0.2192(5)	0.5649(4)	0.4613(3)	0.0481(10)
H16A	-0.169048	0.552662	0.515748	0.072*
H16B	-0.309216	0.554287	0.476587	0.072*
H16C	-0.231273	0.651376	0.418544	0.072*
C17	0.0001(4)	0.0726(3)	0.2862(2)	0.0299(7)
C18	0.0208(4)	-0.0584(3)	0.3287(2)	0.0340(7)
H18	0.098098	-0.109332	0.369254	0.041*
C19	-0.0709(4)	-0.1160(4)	0.3125(3)	0.0412(9)
H19	-0.055585	-0.205089	0.342632	0.049*
C20	-0.1840(5)	-0.0437(4)	0.2525(3)	0.0431(9)
C21	-0.2054(4)	0.0883(4)	0.2086(3)	0.0447(9)
H21	-0.282106	0.138489	0.167528	0.054*
C22	-0.1144(4)	0.1464(4)	0.2250(2)	0.0385(8)
H22	-0.129796	0.235558	0.194961	0.046*
C23	-0.2851(6)	-0.1067(6)	0.2361(3)	0.0649(14)
H23A	-0.363716	-0.040522	0.197950	0.097*
H23B	-0.317002	-0.151269	0.293463	0.097*
H23C	-0.239294	-0.168499	0.206265	0.097*
C24	0.2371(4)	0.0392(3)	0.3950(2)	0.0302(7)
C25	0.2307(4)	0.0479(4)	0.4803(2)	0.0395(8)
H25	0.161253	0.116228	0.491694	0.047*
C26	0.3244(4)	-0.0419(4)	0.5490(3)	0.0416(9)
H26	0.317719	-0.033485	0.606480	0.050*
C27	0.4281(4)	-0.1442(3)	0.5358(3)	0.0380(8)
C28	0.4340(5)	-0.1525(4)	0.4498(3)	0.0482(10)
H28	0.503223	-0.221310	0.438794	0.058*
C29	0.3413(4)	-0.0628(4)	0.3801(3)	0.0414(9)
H29	0.348340	-0.070513	0.322408	0.050*
C30	0.5273(5)	-0.2437(5)	0.6131(3)	0.0588(12)
H30A	0.560104	-0.199961	0.645794	0.088*
H30B	0.605456	-0.295221	0.589547	0.088*
H30C	0.480186	-0.299889	0.653779	0.088*
C31	0.8373(5)	0.0655(7)	0.8817(4)	0.0722(16)
H31A	0.895320	0.120362	0.854553	0.087*
H31B	0.891532	-0.024861	0.890491	0.087*
C32	0.7898(6)	0.0796(6)	0.9680(4)	0.0689(15)
H32A	0.770141	0.169137	0.965985	0.083*
H32B	0.858474	0.021338	1.017603	0.083*
C33	0.6602(6)	0.0426(6)	0.9781(4)	0.0663(14)
H33A	0.592392	0.090299	1.011000	0.080*
H33B	0.680318	-0.050684	1.010126	0.080*
C34	0.6079(5)	0.0801(5)	0.8818(3)	0.0557(12)
H34A	0.582008	0.009750	0.873825	0.067*
H34B	0.526249	0.158057	0.866460	0.067*

### Source of material

The compound was prepared as per the literature [5] and crystals were harvested from a tetrahydrofuran solution of the compound.

### Experimental details

The H atoms were geometrically placed (C–H = 0.94–0.98 Å) and refined as riding with  $U_{iso}(H) = 1.2\text{--}1.5U_{eq}(C)$ . Owing to poor agreement, a number of reflections, i.e. (0 0 1), (–2 –1 6), (–1 0 6), (0 1 0), (2 8 15), (4 0 4), (–4 6 5), (–2 0 12), (8 0 6) and (–1 0 7), were omitted from the final cycles of refinement. The maximum and minimum residual electron density peaks of 1.36 and 0.84 e Å<sup>–3</sup>, respectively, were located 0.89 and 1.31 Å from the Au and S1 atoms, respectively.

### Comment

Conformational flexibility about the S–C bond in phosphane-gold(I) thioamide molecules of the general formula R<sub>3</sub>PAu[SC(OR')=NR''] means either the alkoxy-O atom is orientated towards the gold(I) centre, forming an intramolecular Au···O contact, or the arene ring is disposed towards the gold(I) centre, enabling the formation of an intramolecular Au···π interaction. DFT calculations suggest the latter is more favourable [6]. Nevertheless, Au···O interactions are generally formed, possibly owing to electronic effects/steric congestion [7, 8]. Although conformational polymorphs featuring Au···O or Au···π interactions are comparatively rare [9, 10], unsolvated forms of the title solvate, (4-tolyl)<sub>3</sub>PAu[SC(OEt)=NC<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>-4]. THF (I), are known to feature Au···O [5] or Au···π [11] interactions. In on-going systematic studies of R<sub>3</sub>PAu[SC(OR')=NR''] molecules, the crystal and molecular structures of (I) are described.

The molecular structures are shown in the figure (50% displacement ellipsoids). The gold(I) atom is in the expected linear geometry [P1–Au–S1 = 176.88(3)°] defined by phosphane-P [Au–P1 = 2.2589(9) Å] and thiolato-S [Au–S1 = 2.3115(9) Å] atoms. The thiolato-C1–S1 [1.746(3) Å] and imine-C1–N1 [1.282(6) Å] bond lengths in (I) have lengthened and shortened, respectively, compared with the equivalent thione [1.672(2) Å] and amine [1.354(3) Å] bonds in the parent acid, i.e. EtOC(=S)N(H)C<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>-4 [12]. The orientation of the thiolato ligand is such as to place the ethoxy-O1 atom in close proximity to the gold(I) atom with the Au···O separation being 3.009(2) Å. The Au–S1 [2.3105(8) Å], Au–P1 [2.2611(8) Å] and Au···O1 [2.915(2) Å] separations in the solvent-free form [5] are very close to those in (I) with the shorter Au···O separation correlating with a greater deviation from 180° for the P1–Au–S1 angle [175.80(3)°], i.e. by approximately 1° compared with that in (I). For the conformational polymorph featuring the intramolecular Au···π interaction [11], Au–S1 [2.303(3) Å] is experimentally equivalent to those above but, the Au–P1 bond length [2.271(3) Å] appears to have lengthened, perhaps owing to steric congestion due to the proximity of the arene ring.

In the crystal of (I), tolyl-C—H···N(imine) interactions [C22—H22···N1<sup>i</sup>: H22···N1<sup>i</sup> = 2.60 Å, C22···N1<sup>i</sup> = 3.469(5) Å with angle at H22 = 153° for symmetry operation (i):  $-x, 1 - y, -z$ ] lead to centrosymmetric dimers. These are connected into a supramolecular chain aligned, approximately, along  $[-1 -2 6]$ , sustained by tolyl-C—H··· $\pi$ (tolyl) interactions [C26—H26···Cg(C17—C22)<sup>ii</sup>: H26···Cg(C17—C22)<sup>ii</sup> = 2.93 Å with angle at H26 = 133° for (ii)  $-x, -y, 1 - z$ ]. The packing of the chains define columns parallel to the a-axis direction in which reside the solvent THF molecules. The closest contact involving the THF molecule is a tolyl-C—H···O(THF) interaction [C29—H29···O4<sup>iii</sup>: H29···O4<sup>iii</sup> = 2.64 Å with angle at H29 = 160° for (iii)  $1 - x, -y, 1 - z$ ]. The lack of directional interactions between the host and guest molecules accounts for the instability of the crystals of (I), which lose solvent upon standing in the atmosphere.

A further investigation of the molecular packing was conducted by calculating the Hirshfeld surfaces and two-dimensional fingerprint plots with the aid of Crystal Explorer 17 [13] following literature procedures [14]. The dominant contacts about the THF molecule are H···H [64.1%] and H···C/C···H [15.2%], with the next most dominant being H···O/O···H at 7.5% and H···S/S···H at 5.6%. The distribution of contacts for the gold-containing molecule follow similar trends with the dominant contacts being H···H [52.2%] and H···C/C···H [21.0%], but reduced and increased, respectively, compared with the THF molecule. Contacts due to H···N/N···H, with a characteristic forceps-like distribution in the two-dimensional fingerprint plot account for only 2.3% of surface contacts with greater contributions from H···O/O···H [14.2%] and H···S/S···H [5.1%] but at separations exceeding the sums of the respective van der Waals radii.

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