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# Crystal structure of [(Z)-O-isopropyl N-(4-nitrophenyl)thiocarbamato- $\kappa$ S]-(triphenylphosphine- $\kappa$ P)-gold(I), $C_{28}H_{26}AuN_2O_3PS$

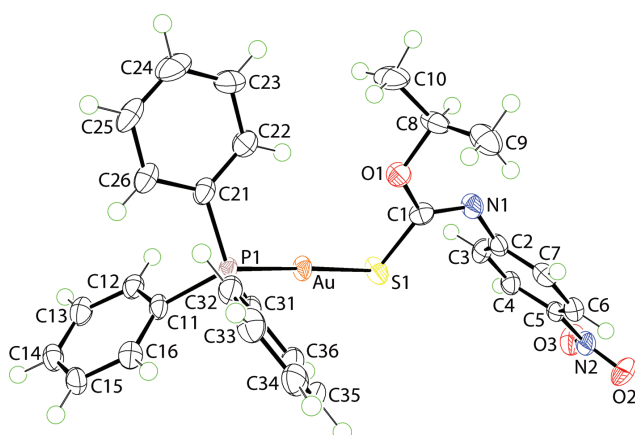


Table 1: Data collection and handling.

Crystal:	Yellow slab
Size:	0.30 × 0.27 × 0.16 mm
Wavelength:	Mo K $\alpha$ radiation (0.71073 Å)
$\mu$ :	5.74 mm <sup>-1</sup>
Diffractometer, scan mode:	SuperNova, $\omega$
$\theta_{\max}$ , completeness:	27.5°, >99%
$N(hkl)_{\text{measured}}$ , $N(hkl)_{\text{unique}}$ , $R_{\text{int}}$ :	30503, 6068, 0.067
Criterion for $I_{\text{obs}}$ , $N(hkl)_{\text{gt}}$ :	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$ , 5608
$N(\text{param})_{\text{refined}}$ :	327
Programs:	CrysAlis <sup>PRO</sup> [1], SHELX [2, 3], WinGX/ORTEP [4]

<https://doi.org/10.1515/ncrs-2020-0306>

Received June 22, 2020; accepted July 8, 2020; available online July 14, 2020

## Abstract

$C_{28}H_{26}AuN_2O_3PS$ , triclinic,  $P\bar{1}$  (no. 2),  $a = 8.6339(3)$  Å,  $b = 11.0503(3)$  Å,  $c = 14.5091(5)$  Å,  $\alpha = 95.615(2)^\circ$ ,  $\beta = 105.606(3)^\circ$ ,  $\gamma = 94.009(2)^\circ$ ,  $V = 1320.14(8)$  Å<sup>3</sup>,  $Z = 2$ ,  $R_{\text{gt}}(F) = 0.0332$ ,  $wR_{\text{ref}}(F^2) = 0.0886$ ,  $T = 100$  K.

CCDC no.: 2014870

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

## Source of material

NaOH (Merck; 0.020 g, 0.50 mmol) in water (5 mL) was added to a suspension of  $Ph_3PAuCl$  (0.247 g, 0.50 mmol) in acetonitrile (20 mL), followed by addition of

iPrOC(=S)N(H)C<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>-4 (0.120 g, 0.50 mmol) in chloroform (20 mL). After stirring for 2 h, the solution was left for slow evaporation at room temperature, yielding yellow crystals after 2 weeks. Yield: 0.314 g (90%). **M. pt.** (Biobase automatic melting point apparatus MP450): 439–440 K. Elemental Analysis for  $C_{28}H_{26}AuN_2O_3PS$  (Leco TruSpec Micro CHN Elemental Analyser: C, 48.14; H, 3.75; N, 4.01%. Found: C, 47.78; H, 3.47; N, 3.76%. **IR** (Bruker Vertex 70v FTIR Spectrophotometer; cm<sup>-1</sup>): 1435 (s)  $\nu$ (C=N), 1149 (s)  $\nu$ (C–O), 1097 (s)  $\nu$ (C–S). **<sup>1</sup>H NMR** (Bruker Ascend 400 MHz NMR spectrometer with chemical shifts relative to tetramethylsilane in CDCl<sub>3</sub> solution at 298 K; ppm):  $\delta$  7.93 (dt, 2H, m-aryl-H,  $^3J_{\text{HH}} = 8.92$  Hz,  $^4J_{\text{HH}} = 2.42$  Hz), 7.56–7.39 (m, br, 15H, Ph<sub>3</sub>P), 6.89 (dt, 2H, o-aryl-H,  $^3J_{\text{HH}} = 8.92$  Hz,  $^4J_{\text{HH}} = 2.42$  Hz), 5.25 (sept, 1H, OCH,  $J_{\text{HH}} = 6.20$  Hz), 1.33 (d, 6H, CH<sub>3</sub>,  $J_{\text{HH}} = 6.20$  Hz). **<sup>13</sup>C{<sup>1</sup>H} NMR** (as for <sup>1</sup>H NMR):  $\delta$  164.7 (Cq), 157.6 (aryl, C<sub>ipso</sub>), 142.6 (aryl, C<sub>para</sub>), 134.1 (d, m-Ph<sub>3</sub>P,  $^3J_{\text{CP}} = 13.79$  Hz), 131.9 (d, p-Ph<sub>3</sub>P,  $^4J_{\text{CP}} = 2.36$  Hz), 129.2 (d, o-Ph<sub>3</sub>P,  $^2J_{\text{CP}} = 11.55$  Hz), 129.1 (d, i-Ph<sub>3</sub>P,  $^1J_{\text{CP}} = 57.52$  Hz), 124.9 (aryl, C<sub>meta</sub>), 122.5 (aryl, C<sub>ortho</sub>), 71.5 (OCH), 22.0 (CH<sub>3</sub>). **<sup>31</sup>P{<sup>1</sup>H} NMR** (as for <sup>1</sup>H NMR but with chemical shift referenced to 85% aqueous H<sub>3</sub>PO<sub>4</sub> as the external reference):  $\delta$  37.9.

## Experimental details

The C-bound H atoms were geometrically placed (C–H = 0.95–1.00 Å) and refined as riding with  $U_{\text{iso}}(\text{H}) = 1.2$ – $1.5U_{\text{eq}}(\text{C})$ . The maximum and minimum residual electron density peaks of 3.05 and 2.13 eÅ<sup>-3</sup>, respectively, were each located 0.86 Å from the Au atom.

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

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>iso</sub> <sup>*</sup> / <i>U</i> <sub>eq</sub>
Au	0.90609(2)	0.14301(2)	0.37306(2)	0.01835(7)
S1	0.86000(13)	0.22266(11)	0.51492(8)	0.0251(2)
P1	0.94848(12)	0.07667(9)	0.23047(8)	0.0154(2)
O1	1.1696(3)	0.2830(3)	0.5424(2)	0.0226(6)
O2	0.5538(4)	0.6587(3)	0.8053(3)	0.0328(8)
O3	0.5482(4)	0.4944(3)	0.8745(2)	0.0321(7)
N1	1.0654(4)	0.3865(3)	0.6516(3)	0.0210(7)
N2	0.5967(4)	0.5576(3)	0.8199(3)	0.0232(7)
C1	1.0436(5)	0.3071(4)	0.5776(3)	0.0186(8)
C2	0.9391(5)	0.4218(4)	0.6885(3)	0.0188(8)
C3	0.8639(5)	0.3472(4)	0.7399(3)	0.0209(8)
H3	0.891098	0.265794	0.745156	0.025*
C4	0.7516(5)	0.3901(4)	0.7829(3)	0.0197(8)
H4	0.702013	0.339650	0.818497	0.024*
C5	0.7117(5)	0.5092(3)	0.7732(3)	0.0178(8)
C6	0.7810(5)	0.5843(4)	0.7209(3)	0.0215(8)
H6	0.750336	0.664460	0.713483	0.026*
C7	0.8964(5)	0.5396(4)	0.6795(3)	0.0210(8)
H7	0.946761	0.590428	0.644560	0.025*
C8	1.3295(5)	0.3504(4)	0.5922(3)	0.0246(9)
H8	1.352834	0.347343	0.663216	0.029*
C9	1.3336(6)	0.4813(4)	0.5720(4)	0.0326(10)
H9A	1.313121	0.484120	0.502524	0.049*
H9B	1.440091	0.524060	0.605803	0.049*
H9C	1.250293	0.520977	0.594645	0.049*
C10	1.4476(5)	0.2804(5)	0.5538(4)	0.0341(11)
H10A	1.435384	0.194746	0.565244	0.051*
H10B	1.558076	0.316160	0.586758	0.051*
H10C	1.425868	0.284783	0.484384	0.051*
C11	0.8160(5)	−0.0541(3)	0.1596(3)	0.0171(8)
C12	0.8076(5)	−0.1605(3)	0.2035(3)	0.0187(8)
H12	0.866172	−0.161492	0.268978	0.022*
C13	0.7135(5)	−0.2646(4)	0.1513(3)	0.0232(9)
H13	0.710985	−0.337880	0.180305	0.028*
C14	0.6235(5)	−0.2618(4)	0.0573(3)	0.0213(8)
H14	0.557566	−0.332852	0.022334	0.026*
C15	0.6286(5)	−0.1565(4)	0.0135(3)	0.0231(9)
H15	0.566404	−0.155499	−0.051230	0.028*
C16	0.7255(5)	−0.0513(4)	0.0646(3)	0.0205(8)
H16	0.729567	0.021217	0.034767	0.025*
C21	1.1512(5)	0.0318(4)	0.2450(3)	0.0192(8)
C22	1.2685(5)	0.0749(4)	0.3304(3)	0.0265(9)
H22	1.240824	0.122430	0.380736	0.032*
C23	1.4286(5)	0.0475(5)	0.3416(4)	0.0338(11)
H23	1.509893	0.078189	0.399222	0.041*
C24	1.4681(5)	−0.0226(4)	0.2703(4)	0.0336(11)
H24	1.576592	−0.040931	0.279064	0.040*
C25	1.3512(5)	−0.0678(4)	0.1848(4)	0.0272(10)
H25	1.379645	−0.116519	0.135351	0.033*
C26	1.1917(5)	−0.0407(4)	0.1723(3)	0.0225(9)
H26	1.110931	−0.071535	0.114472	0.027*
C31	0.9253(5)	0.1958(3)	0.1508(3)	0.0180(8)
C32	1.0193(5)	0.2090(4)	0.0875(3)	0.0222(8)
H32	1.099597	0.155291	0.084839	0.027*
C33	0.9950(5)	0.3019(4)	0.0280(3)	0.0244(9)

**Table 2** (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>iso</sub> <sup>*</sup> / <i>U</i> <sub>eq</sub>
H33	1.057836	0.310981	−0.015989	0.029*
C34	0.8779(5)	0.3813(4)	0.0333(3)	0.0247(9)
H34	0.862374	0.445337	−0.006408	0.030*
C35	0.7843(5)	0.3670(4)	0.0963(3)	0.0233(9)
H35	0.703589	0.420433	0.098899	0.028*
C36	0.8082(5)	0.2753(4)	0.1554(3)	0.0206(8)
H36	0.744904	0.266315	0.199158	0.025*

**Comment**

Phosphanegold(I) thioamide molecules of the general formula R<sub>3</sub>PAu[SC(OR')=NR''] are known to adopt two distinct molecular conformations. The basic, linear P—Au—S fragment is common to all structures with the difference arising in the relative orientations of the OR' and NR'' groups with respect to the gold atom which lead to an intramolecular Au···O or Au···π interaction, respectively. This variation in structure is nicely exemplified by the series of structures where R'' = 4-nitrophenyl. Thus, when R' = Me, and R = Ph [5], R = *o*-tolyl, as CHCl<sub>3</sub> and H<sub>2</sub>O solvates, and R = *m*-tolyl [6], the conformation featuring the Au···O contact is observed. This conformation is also seen in the crystals of the R' = Et compounds with R = Ph (as the CH<sub>2</sub>Cl<sub>2</sub> solvate) [7] and *p*-tolyl [8]. More recently, for R' = Et and R = *p*-tolyl, the conformation where a Au···π interaction forms instead of a Au···O contact was reported, i.e. a conformational polymorph [9]. Studies suggest the Au···O/Au···π phenomenon correlates with kinetic factors associated with crystallisation as DFT calculations indicate the Au···π interactions are more stable than Au···O contacts [10, 11]. In continuing systematic studies in this area, the title compound, i.e. Ph<sub>3</sub>PAu[SC(O-*i*Pr)=NC<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>-4], (I), was investigated crystallographically.

The molecular structure of (I) is shown in the figure (70% displacement ellipsoids) and features a linear coordination of the gold atom [P1—Au—S1 = 176.31(3)°] defined by phosphane-P [Au—P1 = 2.2582(10) Å] and thiolate-S [Au—S1 = 2.3032(11) Å] atoms. The C1—S1 [1.750(4) Å] and C1—N1 [1.282(6) Å] bond lengths in (I) have lengthened and shortened, respectively, compared with the equivalent bonds in the neutral ligand, i.e. *i*PrOC(=S)N(H)C<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>-4, of 1.678(3) and 1.352(3) Å, respectively [12]. As is usually found in R<sub>3</sub>PAu[SC(OR')=NC<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>-4] structures, an intramolecular Au···O interaction [3.060(3) Å] is observed in (I).

The molecular packing for (I) features phenyl-C—H···O(nitro) interactions [C35—H35···O3<sup>i</sup>: H35···O3<sup>i</sup> = 2.54 Å, C35···O3<sup>i</sup> = 3.451(6) Å with an angle at H35 = 162° for symmetry operation (i) 1 − *x*, 1 − *y*, 1 − *z*] which link molecules into centrosymmetric dimers. The dimers are linked into a supramolecular tube along the *a*-axis

via methyl-C—H $\cdots\pi$ (nitrophenyl) [C10—H10b $\cdots$ Cg(C2—C7)=2.93 Å with angle at H10b=159 Å for (ii) 1 + x, y, z] and  $\pi$ (nitrophenyl) $\cdots\pi$ (P-phenyl) inter-centroid Cg(C2—C7) $\cdots$ Cg(C31—C36) distance=3.753(2) Å with angle of inclination=18.7(2)° for (iii) 2 − x, 1 − y, 1 − z].

As the tubes exhibit no directional interactions between them in the crystal, the supramolecular association was also probed by an analysis of the calculated Hirshfeld surfaces and two-dimensional fingerprint plots using Crystal Explorer 17 [13] and literature procedures [14]. As anticipated, H $\cdots$ H contacts dominate the Hirshfeld surface, contributing 43.3% of all contacts. Distinctive features are noted in the fingerprint plots for the H $\cdots$ C/C $\cdots$ H [24.2%] and H $\cdots$ O/O $\cdots$ H [14.6%] contacts reflecting the specified intermolecular contacts. Similarly, a characteristic arrow distribution is noted for the C $\cdots$ C contacts but, the contribution to the surface is small at 2.9%. Other contacts, such as H $\cdots$ S/S $\cdots$ H [7.2%] and H $\cdots$ N/N $\cdots$ H [3.0%] along with a number of other minor contributions occur at distances beyond the sums of the respective van der Waals radii.

**Acknowledgements:** Sunway University Sdn Bhd is thanked for financial support of this work through Grant No. STR-RCTR-RCCM-001-2019.

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