

Chien Ing Yeo and Edward R.T. Tiekink*

Crystal structure of [(*Z*)-*O*-isopropyl *N*-(4-chlorophenyl)thiocarbamato- κ S]-(triphenylphosphine- κ P)-gold(I), $C_{28}H_{26}AuClNOPS$

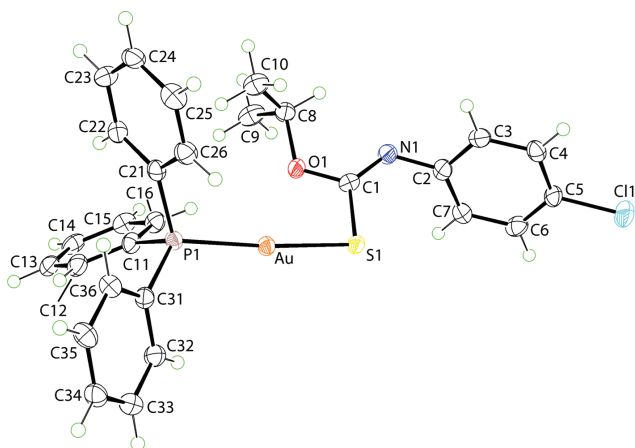


Table 1: Data collection and handling.

Crystal:	Colourless prism
Size:	0.11 × 0.05 × 0.05 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	5.89 mm ⁻¹
Diffractometer, scan mode:	SuperNova, ω
θ_{\max} , completeness:	27.5°, 99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	10945, 5969, 0.031
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 4942
$N(\text{param})_{\text{refined}}$:	309
Programs:	CrysAlis ^{PRO} [1], SHELX [2, 3], WinGX/ORTEP [4]

<https://doi.org/10.1515/ncrs-2020-0307>

Received June 22, 2020; accepted July 8, 2020; available online July 21, 2020

Abstract

$C_{28}H_{26}AuClNOPS$, monoclinic, $P2_1/c$ (no. 14), $a = 9.7445(3)$ Å, $b = 12.4105(4)$ Å, $c = 21.9727(9)$ Å, $\beta = 100.113(1)^\circ$, $V = 2615.96(16)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0292$, $wR_{\text{ref}}(F^2) = 0.0677$, $T = 100$ K.

CCDC no.: 2014871

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 (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 $iPrOC(=S)N(H)C_6H_4Cl$ -4

(0.115 g, 0.50 mmol) in chloroform (20 mL). After stirring for 2 h, the solution was left for slow evaporation at room temperature, yielding colourless crystals after 2 weeks. Yield: 0.313 g (91%). **M. pt** (Biobase automatic melting point apparatus MP450): 436–439 K. **Elemental Analysis** for $C_{28}H_{26}AuClNOPS$ (Leco TruSpec Micro CHN Elemental Analyser): C, 48.88; H, 3.81; N, 2.04%. Found: C, 49.06; H, 3.69; N, 2.06%. **IR** (Bruker Vertex 70v FTIR Spectrophotometer; cm^{-1}): 1436 (s) $\nu(C=N)$, 1138 (s) $\nu(C-O)$, 1094 (s) $\nu(C-S)$. **¹H NMR** (Bruker Ascend 400 MHz NMR spectrometer with chemical shifts relative to tetramethylsilane in $CDCl_3$ solution at 298 K, ppm): δ 7.54–7.42 (m, br, 15H, Ph_3P), 6.97 (dt, 2H, m-aryl-H, $^3J_{HH} = 8.60$ Hz, $^4J_{HH} = 2.46$ Hz), 6.75 (dt, 2H, o-aryl-H, $^3J_{HH} = 8.56$ Hz, $^4J_{HH} = 2.45$ Hz), 5.26 (sept, 1H, OCH, $J_{HH} = 6.20$ Hz), 1.32 (d, 6H, CH_3 , $J_{HH} = 6.20$ Hz). **¹³C{¹H} NMR** (as for ¹H NMR): δ 163.8 (Cq), 150.0 (aryl, C_{ipso}), 134.2 (d, m- Ph_3P , $^3J_{CP} = 13.81$ Hz), 131.7 (d, p- Ph_3P , $^4J_{CP} = 2.34$ Hz), 129.4 (d, i- Ph_3P , $^1J_{CP} = 57.25$ Hz), 129.1 (d, o- Ph_3P , $^2J_{CP} = 11.50$ Hz), 128.8 (aryl, C_{meta}), 127.3 (aryl, C_{para}), 123.4 (aryl, C_{ortho}), 70.6 (OCH), 22.1 (CH_3). **³¹P{¹H} NMR** (as for ¹H NMR but with chemical shift referenced to 85% aqueous H_3PO_4 as the external reference): δ 38.1.

Experimental details

The C-bound H atoms were geometrically placed ($C-H = 0.95$ – 1.00 Å) and refined as riding with $U_{\text{iso}}(H) = 1.2$ – $1.5U_{\text{eq}}(C)$. The maximum and minimum residual electron density peaks of 2.22 and $1.04 e \text{ Å}^{-3}$, respectively, were located 0.93 and 0.72 Å, respectively, from the Au atom.

*Corresponding author: Edward R.T. Tiekink, Research Centre for Crystalline Materials, School of Science and Technology, Sunway University, 47500 Bandar Sunway, Selangor Darul Ehsan, Malaysia, e-mail: edwardt@sunway.edu.my. <https://orcid.org/0000-0003-1401-1520>

Chien Ing Yeo: Research Centre for Crystalline Materials, School of Science and Technology, Sunway University, 47500 Bandar Sunway, Selangor Darul Ehsan, Malaysia

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
Au	0.23533(2)	0.72519(2)	0.20933(2)	0.02012(6)
Cl1	−0.26566(12)	0.62356(10)	0.50411(5)	0.0395(3)
S1	0.06582(10)	0.71975(8)	0.27116(4)	0.0217(2)
P1	0.38311(10)	0.72033(8)	0.14107(4)	0.0193(2)
O1	−0.0170(3)	0.5995(2)	0.17396(11)	0.0268(6)
N1	−0.1261(3)	0.5574(3)	0.25471(14)	0.0250(7)
C1	−0.0384(4)	0.6150(3)	0.23279(17)	0.0230(8)
C2	−0.1553(4)	0.5758(3)	0.31438(18)	0.0243(9)
C3	−0.1174(4)	0.4996(3)	0.36066(18)	0.0255(9)
H3	−0.068132	0.436895	0.352120	0.031 [*]
C4	−0.1504(4)	0.5135(3)	0.41929(18)	0.0254(9)
H4	−0.122399	0.462050	0.451044	0.031 [*]
C5	−0.2253(4)	0.6045(3)	0.43017(18)	0.0265(9)
C6	−0.2665(4)	0.6798(4)	0.38507(18)	0.0291(9)
H6	−0.318375	0.741156	0.393478	0.035 [*]
C7	−0.2317(4)	0.6657(3)	0.32705(17)	0.0258(9)
H7	−0.260105	0.717720	0.295639	0.031 [*]
C8	−0.0578(4)	0.4957(3)	0.14389(18)	0.0282(9)
H8	−0.114092	0.453296	0.169425	0.034 [*]
C9	−0.1445(5)	0.5196(4)	0.0811(2)	0.0372(11)
H9A	−0.228731	0.558940	0.086505	0.056 [*]
H9B	−0.170845	0.451786	0.059343	0.056 [*]
H9C	−0.089929	0.563506	0.056995	0.056 [*]
C10	0.0772(5)	0.4367(4)	0.1403(2)	0.0344(10)
H10A	0.130961	0.427428	0.182075	0.052 [*]
H10B	0.131922	0.478788	0.115345	0.052 [*]
H10C	0.055923	0.365918	0.121238	0.052 [*]
C11	0.2890(4)	0.7543(3)	0.06469(18)	0.0228(9)
C12	0.3547(5)	0.8043(3)	0.02080(18)	0.0280(9)
H12	0.451066	0.821462	0.030242	0.034 [*]
C13	0.2774(5)	0.8288(3)	−0.03711(18)	0.0312(10)
H13	0.320919	0.864719	−0.066821	0.037 [*]
C14	0.1371(5)	0.8011(3)	−0.05185(18)	0.0295(10)
H14	0.085692	0.816259	−0.091803	0.035 [*]
C15	0.0730(5)	0.7515(3)	−0.0080(2)	0.0293(10)
H15	−0.022807	0.732717	−0.018219	0.035 [*]
C16	0.1463(4)	0.7284(3)	0.05079(19)	0.0257(9)
H16	0.100816	0.695894	0.080979	0.031 [*]
C21	0.4516(4)	0.5858(3)	0.13356(17)	0.0225(8)
C22	0.4278(4)	0.5282(3)	0.07861(18)	0.0258(9)
H22	0.375447	0.560242	0.042615	0.031 [*]
C23	0.4795(5)	0.4241(3)	0.0754(2)	0.0319(10)
H23	0.461801	0.385140	0.037628	0.038 [*]
C24	0.5568(4)	0.3781(3)	0.12777(19)	0.0295(9)
H24	0.592663	0.307281	0.125872	0.035 [*]
C25	0.5822(4)	0.4344(4)	0.1827(2)	0.0311(10)
H25	0.637089	0.402854	0.218286	0.037 [*]
C26	0.5280(4)	0.5366(3)	0.18616(19)	0.0274(9)
H26	0.542643	0.573887	0.224527	0.033 [*]
C31	0.5317(4)	0.8109(3)	0.15445(17)	0.0225(8)
C32	0.5067(4)	0.9193(3)	0.16440(18)	0.0267(9)
H32	0.414612	0.943308	0.165524	0.032 [*]
C33	0.6166(5)	0.9926(4)	0.17272(19)	0.0320(10)

Table 2 (continued)

Atom	x	y	z	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
H33	0.599210	1.066789	0.178958	0.038 [*]
C34	0.7513(4)	0.9577(3)	0.17190(17)	0.0276(9)
H34	0.826199	1.007712	0.177615	0.033 [*]
C35	0.7764(4)	0.8496(3)	0.16274(18)	0.0291(9)
H35	0.868831	0.825697	0.162400	0.035 [*]
C36	0.6672(4)	0.7756(3)	0.15402(18)	0.0258(9)
H36	0.685054	0.701522	0.147831	0.031 [*]

Comment

The most studied case of structural mimicry relates to the chloro/methyl exchange whereby structures that differ only by a chloride versus methyl substituent are evaluated for similarity or otherwise [5]. If the chloro/methyl substituents have no major influence the molecular packing, isomorphous relationships might be apparent as the molecular volumes of a chloride atom and a methyl group are close. In this connection, the title phosphanegold(I) thioamide molecule, Ph₃PAu[SC(OR)=NC₆H₄Y-4], for R = *i*Pr and Y = Cl, (I), has been investigated. Related structures with Y = Cl and R = Me [6] and R = Et, isolated as a dichloromethane hemi-solvate [7], are known. The three structures with Y = Me and R = Me [8], R = Et [9] and R = *i*Pr [10] are also available in the literature. Herein, in order to complete the 2 (Y = Cl and Me) × 3 (R = Me, Et and *i*Pr) matrix of Y and R structures, the crystal and molecular structures of (I) are described.

The molecular structure of (I) is shown in the figure (70% displacement ellipsoids) which shows the gold atom to be coordinated by thiolate-S [Au–S1 = 2.3166(10) Å] and phosphane-P [Au–P1 = 2.2551(10) Å] atoms which define an almost linear geometry [P1–Au–S1 = 173.52(3)°]. The crystal structure of the pure acid, i.e. *i*PrOC(=S)N(H)C₆H₄Cl-4, is available for comparison [11]. The C1–S1 [1.6708(15) Å] and C1–N1 [1.3388(18) Å] bond lengths in the acid are significantly shorter and longer than the comparable bonds in (I) of 1.769(4) and 1.272(5) Å, respectively. The deviation from the ideal 180° for the P1–Au–S1 angle may be traced to the close approach of the O1 atom towards the gold centre with Au...O = 2.900(3) Å.

In the crystal of (I) chlorophenyl-C–H... π (P-phenyl) [C4–H4...Cg(C11–C16)ⁱ: H4...Cg(C11–C16)ⁱ = 2.67 Å with an angle at H4 = 139° for symmetry operation (i): $-x, -1/2 + y, 1/2 - z$], P-phenyl-C–H... π (chlorophenyl) [C14–H14...Cg(C2–C7)ⁱⁱ: H14...Cg(C2–C7)ⁱⁱ = 2.92 Å with angle at H14 = 130° and C32–H32...Cg(C2–C7)ⁱⁱⁱ: H32...Cg(C2–C7)ⁱⁱ = 2.85 Å with an angle at H32 = 150° for (ii) $x, 3/2 - y, -1/2 + z$ and (iii) $-x, 1/2 + y, 1/2 - z$] and end-on C–Cl... π (P-phenyl) [C5–Cl1...Cg(C31–C36)^{iv}: Cl1...Cg(C31–C36)^{iv} = 3.7658(19) Å with an angle at Cl1 = 170.73(14)° for

(iv) $-1+x$, $3/2-y$, $1/2+z$] connect molecules into a three-dimensional structure. In this scheme, the chlorophenyl ring accepts two $C-H \cdots \pi$ contacts.

Additional analysis of the molecular packing was conducted whereby the Hirshfeld surfaces were calculated along with the full and delineated two-dimensional fingerprint plots. This was achieved with Crystal Explorer 17 [12] following literature procedures [13]. The analysis shows that over 97% of all surface contacts involve hydrogen with the major contribution coming from non-directional $H \cdots H$ contacts at 47.3%. Significant contributions are apparent from $H \cdots C/C \cdots H$ [26.1%] contacts reflecting, in part, the specified $C-H \cdots \pi$ interactions. Other notable contributions to the calculated surface occur at separations at or beyond the sums of the respective van der Waals radii, e.g. $H \cdots S/S \cdots H$ [7.1%] and $H \cdots Cl/Cl \cdots H$ [9.7%]. It is noted $C \cdots Cl/Cl \cdots C$ contacts contribute 1.8% to the surface.

The unit cell parameters for (I) and the methyl isostere, i.e. $Ph_3PAu[SC(O-iPr)=NC_6H_4Me-4]$ [10], (II), indicate an isostructural relationship. The molecular structures closely resemble each other but, in the molecular packing of (II), the tolyl-methyl group sits in an hydrophobic pocket and does not participate in a directional intermolecular contact in contrast to the chloride atom in (I). This difference is reflected in the calculated Hirshfeld surface of (II) where the $H \cdots H$ contacts amount to 58.3% of all contacts, which is close to the sum of $H \cdots H + H \cdots Cl/Cl \cdots H$ contacts of (I). It is noted a isostructural relationship also exists for the two $R = Me$, $Y = Cl$ [6] and $Y = Me$ [8] compounds but, not for the pair of $R = Et$ structures as the $Y = Cl$ species is a hemi-dichloromethane solvate [7] while the $Y = Me$ compound was characterised solvent-free.

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

References

1. Agilent Technologies: CrysAlis^{PRO}. Agilent Technologies, Santa Clara, CA, USA (2014).
2. Sheldrick, G. M.: A short history of SHELX. *Acta Crystallogr. A* **64** (2008) 112–122.
3. Sheldrick, G. M.: Crystal structure refinement with SHELXL. *Acta Crystallogr. C* **71** (2015) 3–8.
4. Farrugia, L. J.: WinGX and ORTEP for Windows: an update. *J. Appl. Cryst.* **45** (2012) 849–854.
5. Edwards, M. R.; Jones, W.; Motherwell, W. D. S.; Shields, G. P.: Crystal engineering and chloro-methyl interchange—a CSD analysis. *Mol. Cryst. Liq. Cryst., Sect. A* **356** (2001) 337–353.
6. Tadbuppa, P. P.; Tiekink, E. R. T.: [(Z)-N-(4-Chlorophenyl)-O-methylthiocarbamato-κS](triphenylphosphine-κP)-gold(I). *Acta Crystallogr. E* **65** (2009) m1700.
7. Tadbuppa, P. P.; Tiekink, E. R. T.: [(Z)-O-Ethyl N-(4-chlorophenyl)thiocarbamato-κS](triphenylphosphine-κP)-gold(I) dichloromethane hemisolvate. *Acta Crystallogr. E* **66** (2010) m687.
8. Kuan, F. S.; Ho, S. Y.; Tadbuppa, P. P.; Tiekink, E. R. T.: Electronic and steric control over $Au \cdots Au$, $C-H \cdots O$ and $C-H \cdots \pi$ interactions in the crystal structures of mononuclear triarylphosphinegold(I) carbonimidothioates: $R_3PAu[SC(OMe)=NR']$ for $R = Ph$, *o*-tol, *m*-tol or *p*-tol, and $R' = Ph$, *o*-tol, *m*-tol, *p*-tol or $C_6H_4NO_2-4$. *CrystEngComm* **10** (2008) 548–564.
9. Tadbuppa, P. P.; Tiekink, E. R. T.: [(Z)-O-Ethyl-N-(*p*-tolyl)thiocarbamato-κS](triphenylphosphine-κP)gold(I). *Acta Crystallogr. E* **65** (2009) m1587.
10. Yeo, C. I.; Sim, J.-H.; Khoo, C.-H.; Goh, Z.-J.; Ang, K.-P.; Cheah, Y.-K.; Fairuz, Z. A.; Halim, S. N. B. A.; Ng, S. W.; Seng, H.-L.; Tiekink, E. R. T.: Pathogenic Gram-positive bacteria are highly sensitive to triphenylphosphane-gold(O-alkylthiocarbamates), $Ph_3PAu[SC(OR)=N(p\text{-tolyl})]$ ($R = Me$, *Et* and *iPr*). *Gold Bull.* **46** (2013) 145–152.
11. Kuan, F. S.; Mohr, F.; Tadbuppa, P. P.; Tiekink, E. R. T.: Principles of crystal packing in *O*-isopropyl-*N*-aryl-thiocarbamides: $iPrOC(=S)N(H)C_6H_4-4-Y$: $Y = H$, *Cl*, and *Me*. *CrystEngComm* **9** (2007) 574–581.
12. Turner, M. J.; McKinnon, J. J.; Wolff, S. K.; Grimwood, D. J.; Spackman, P. R.; Jayatilaka, D.; Spackman, M. A.: Crystal Explorer v17. The University of Western Australia, Australia (2017).
13. Tan, S. L.; Jotani, M. M.; Tiekink, E. R. T.: Utilizing Hirshfeld surface calculations, non-covalent interaction (NCI) plots and the calculation of interaction energies in the analysis of molecular packing. *Acta Crystallogr. E* **75** (2019) 308–318.