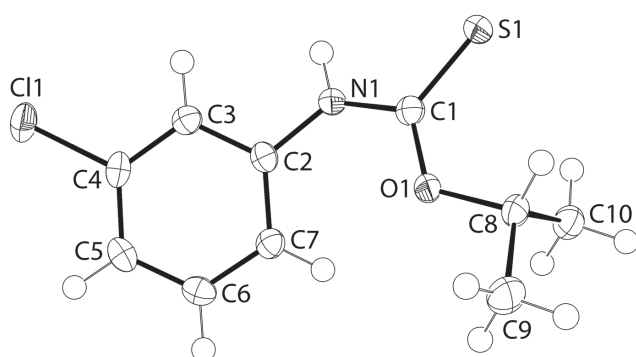




Chien Ing Yeo and Edward R.T. Tiekink*

Crystal structure of *N*-(3-chlorophenyl)(propan-2-yloxy)carbothioamide, C₁₀H₁₂ClNOS

**Table 1:** Data collection and handling.

Crystal:	Colourless block
Size:	0.25 × 0.09 × 0.06 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	5.1 cm ⁻¹
Diffractometer, scan mode:	Bruker SMART APEX, ω scans
2 θ _{max} , completeness:	55°, >99%
$N(hkl)$ _{measured} , $N(hkl)$ _{unique} , R_{int} :	12986, 2497, 0.033
Criterion for I_{obs} , $N(hkl)$ _{gt} :	$I_{obs} > 2 \sigma(I_{obs})$, 2196
$N(param)$ _{refined} :	132
Programs:	Bruker programs [1, 2], SHELX [3, 4], ORTEP [5]

<https://doi.org/10.1515/ncrs-2017-0411>

Received December 16, 2017; accepted March 16, 2018; available online April 6, 2018

Abstract

C₁₀H₁₂ClNOS, monoclinic, $P2_1/n$ (no. 14), $a = 13.2003(12)$ Å, $b = 6.0448(6)$ Å, $c = 13.9403(13)$ Å, $\beta = 101.9180(10)^\circ$, $V = 1088.36(18)$ Å³, $Z = 4$, $R_{gt}(F) = 0.0291$, $wR_{ref}(F^2) = 0.0807$, $T = 100(2)$ K.

CCDC no.: 1830415

The asymmetric unit of the title crystal structure is shown in the figure. Tables 1 and 2 contain details of the measurement method and a list of the atoms including atomic coordinates and displacement parameters.

Source of materials

3-Chlorophenyl isothiocyanate (Sigma Aldrich; 2.5 mmol, 0.33 mL) was added to NaOH (Merck; 2.5 mmol, 0.10 g) in iPrOH (Merck; 5 mL) and the mixture was left for stirring at room temperature for 2 h. This was followed by the addition of excess 5 M HCl solution. The resulting mixture was stirred for another 1.5 h. The final product was extracted with chloroform (Merck; 20 mL) and left for evaporation at room temperature, yielding colourless crystals after 5 weeks. M.p.

*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

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	<i>x</i>	<i>y</i>	<i>z</i>	U_{iso}^*/U_{eq}
Cl1	0.45970(3)	0.03216(7)	0.10488(3)	0.02439(11)
S1	0.38771(3)	0.47645(6)	0.59269(3)	0.01761(11)
O1	0.29120(7)	0.10134(17)	0.52802(7)	0.0161(2)
N1	0.40998(9)	0.2174(2)	0.44643(8)	0.0154(2)
H1N	0.4559(11)	0.318(2)	0.4410(12)	0.018*
C1	0.36131(11)	0.2534(2)	0.52058(10)	0.0143(3)
C2	0.39332(10)	0.0544(2)	0.37143(10)	0.0139(3)
C3	0.42858(10)	0.1094(2)	0.28661(10)	0.0155(3)
H3	0.4605	0.2485	0.2814	0.019*
C4	0.41646(11)	-0.0411(2)	0.21042(10)	0.0165(3)
C5	0.36997(11)	-0.2446(2)	0.21476(10)	0.0174(3)
H5	0.3616	-0.3452	0.1614	0.021*
C6	0.33581(11)	-0.2972(2)	0.29969(10)	0.0172(3)
H6	0.3040	-0.4367	0.3043	0.021*
C7	0.34692(10)	-0.1511(2)	0.37813(10)	0.0151(3)
H7	0.3232	-0.1906	0.4357	0.018*
C8	0.23245(11)	0.1151(2)	0.60690(10)	0.0161(3)
H8	0.2111	0.2715	0.6149	0.019*
C9	0.13810(12)	-0.0270(3)	0.57210(12)	0.0254(3)
H9A	0.0989	0.0304	0.5096	0.038*
H9B	0.0944	-0.0245	0.6210	0.038*
H9C	0.1597	-0.1794	0.5631	0.038*
C10	0.29920(12)	0.0325(2)	0.70175(11)	0.0194(3)
H10A	0.3590	0.1306	0.7213	0.029*
H10B	0.3232	-0.1177	0.6922	0.029*
H10C	0.2585	0.0312	0.7531	0.029*

(Krüss KSP1N): 347–349 K. IR (Perkin Elmer Spectrum 400 FT Mid-IR/Far-IR; cm⁻¹): 3220 (s) ν (N–H), 1478 (s) ν (C–N), 1203 (s) ν (C=S), 1095 (s) ν (C–O). Elem. Anal. (Perkin Elmer PE 2400 CHN): Calc. for C₁₀H₁₂ClNOS: C, 52.04; H, 5.14; N, 6.33%. Found: 52.28; H, 5.27; N, 6.10%.

Experimental details

The C-bound H atoms were geometrically placed (C–H = 0.95–1.00 Å) and refined as riding with $U_{\text{iso}}(\text{H}) = 1.2\text{--}1.5 U_{\text{eq}}(\text{C})$. The N-bound H-atom was located in a difference Fourier map but was refined with a distance restraint of N–H = 0.88 + –0.01 Å, and with $U_{\text{iso}}(\text{H})$ set to 1.2 $U_{\text{eq}}(\text{N})$. Owing to poor agreement, a reflection, i.e. (10 0 8), was omitted from the final cycles of refinement.

Comment

The motivation for the preparation of the title compound was the observation that alkoxythiocarbamides, i.e. ROC(=S)N(H)R' for R/R' = alkyl/aryl, when complexed to phosphanegold(I), generate bioactive compounds in the context of both cancer [6] and bacterial infection [7], and the structure determination follows on-going systematic structural investigations in this area [8, 9].

The molecular structure of *iPrOC(=S)N(H)C₆H₄Cl₃* is shown in the Figure (70% displacement ellipsoids) and comprises a planar CNOS core [r.m.s. deviation = 0.0052 Å] which forms a dihedral angle of 20.50(8)° with the N-bound 3-chlorophenyl group, there being a twist about the N1–C2 bond; the C1–N1–C2–C3 torsion angle is 156.74(14)°. The thioamide-N–H and thione-S atoms are syn, and to a first approximation, the chlorine atom lies to the same side of the molecule as does the thione-S atom.

In the molecular packing, the syn-disposition of the thioamide-N–H and thione-S atoms facilitates the formation of thioamide-N–H...S(thione) hydrogen bonds and eight-membered {···HNCS}₂ synthons [N1–H1n...S1ⁱ: 2.535(14) Å and 164.6(12)° for symmetry operation *i*: 1 – *x*, 1 – *y*, 1 – *z*]. Interestingly, weak Cl...Cl halogen bonding is also apparent [Cl1...Cl1ⁱⁱ = 3.3345(7) Å for symmetry operation *ii*: –*x*, –*y*, 1 – *z*]. These serve to link the dimeric aggregates into supramolecular chains parallel to $[\bar{1} 1 5]$.

While there are no direct precedents for the title compound in the crystallographic literature [8, 9], the structure of the ethoxy derivative has been reported recently [10]. In the latter, the same syn disposition of the thioamide-N–H and thione-S atoms in the molecular structure and supramolecular {···HNCS}₂ synthon in the molecular packing are

observed. The key difference in structures is found in the relative dispositions of the thione-S and chloro atoms which lie to opposite sides in the molecule of the ethoxy derivative as opposed to the conformation observed in the title compound.

Acknowledgements: The University of Malaya's X-ray laboratory is thanked for the data collection. Sunway University is thanked for support of biological and crystal engineering studies of metal alkoxy-carbothioamides.

References

1. Krause, L.; Herbst-Irmer, R.; Sheldrick, G. M.; Stalke, D.: Comparison of silver and molybdenum microfocus X-ray sources for single-crystal structure determination. *J. Appl. Cryst.* **48** (2015) 3–10.
2. Bruker: APEX2 and SAINT. Bruker AXS Inc., Madison, WI, USA (2008).
3. Sheldrick, G. M.: A short history of SHELX. *Acta Crystallogr.* **A71** (2015) 3–8.
4. Sheldrick, G. M.: Crystal structure refinement with SHELXL. *Acta Crystallogr.* **C71** (2015) 3–8.
5. Farrugia, L. J.: WinGX and ORTEP for Windows: an update. *J. Appl. Cryst.* **45** (2012) 849–854.
6. Ooi, K. K.; Yeo, C. I.; Mahandaran, T.; Ang, K. P.; Akim, A. M.; Cheah, Y.-K.; Seng, H.-L.; Tiekink, E. R. T.: G₂/M cell cycle arrest on HT-29 cancer cells and toxicity assessment of triphenylphosphanegold(I) carbonimidothioates, Ph₃PAu[SC(OR)=NPh], R = Me, Et, and *iPr*, during zebrafish development. *J. Inorg. Biochem.* **166** (2017) 173–181.
7. 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 triphenylphosphanegold (O-alkylthiocarbamates), Ph₃PAu[SC(OR)=N(*p*-tolyl)] (R = Me, Et and *iPr*). *Gold Bull.* **46** (2013) 145–152.
8. Jotani, M. M.; Yeo, C. I.; Tiekink, E. R. T.: A new monoclinic polymorph of *N*-(3-methylphenyl) ethoxycarbothioamide: crystal structure and Hirshfeld surface analysis. *Acta Crystallogr.* **E73** (2017) 1889–1897.
9. Yeo, C. I.; Tiekink, E. R. T.: Crystal structure of *N*-(2-chlorophenyl)-methoxycarbothioamide, C₈H₈ClNOS. *Z. Kristallogr. – NCS* **233** (2018) 517–518.
10. Tan, Y. S.; Yeo, C. I.; Tiekink, E. R. T.: Crystal structure of *N*-(3-chlorophenyl)ethoxycarbothioamide, C₉H₁₀ClNOS. *Z. Kristallogr. – NCS* **233** (2018) 511–512.