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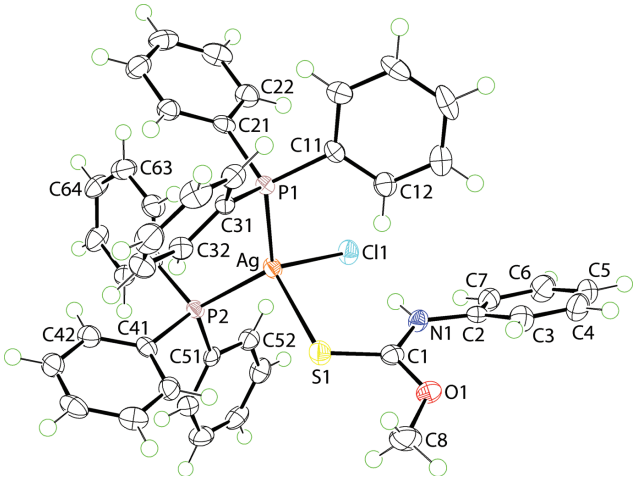
Crystal structure of chlorido-(*O*-methyl phenylcarbamothioamide-κ*S*)-bis(triphenylphosphane-κ*P*)silver(I), $C_{44}H_{39}AgClNOP_2S$



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Abstract

$C_{44}H_{39}AgClNOP_2S$, triclinic, $P\bar{1}$ (no. 2), $a = 10.2520(3)$ Å, $b = 13.2252(4)$ Å, $c = 14.9378(3)$ Å, $\alpha = 78.424(2)°$, $\beta = 78.388(2)°$, $\gamma = 84.534(3)°$, $V = 1940.35(9)$ Å^3, $Z = 2$, $R_{gt}(F) = 0.0382$, $wR_{ref}(F^2) = 0.0807$, $T = 100(2)$ K.

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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.

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Table 1: Data collection and handling.

Crystal:	Colourless prism
Size:	0.10 × 0.05 × 0.05 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	0.76 mm^{-1}
Diffractometer, scan mode:	SuperNova, ω
θ_{max}, completeness:	27.6°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	30490, 8967, 0.056
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 7094
$N(param)_{refined}$:	464
Programs:	CrysAlis^{PRO} [1], SHELX [2, 3], WinGX/ORTEP [4]

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Ag	0.86583(2)	0.75024(2)	0.25301(2)	0.01561(6)
Cl1	1.11233(6)	0.76342(5)	0.25111(4)	0.02003(15)
S1	0.84634(7)	0.85009(6)	0.07791(4)	0.02095(16)
P1	0.81885(7)	0.57098(5)	0.25117(4)	0.01358(14)
P2	0.73868(7)	0.85804(5)	0.36090(4)	0.01349(14)
O1	1.01595(19)	0.89720(14)	−0.08262(11)	0.0218(4)
N1	1.1105(2)	0.82275(17)	0.03710(13)	0.0162(5)
H1N	1.103(3)	0.806(2)	0.0975(7)	0.019*
C1	0.9976(3)	0.8567(2)	0.00793(16)	0.0169(6)
C2	1.2433(3)	0.81508(19)	−0.01460(17)	0.0172(6)
C3	1.2723(3)	0.7920(2)	−0.10352(18)	0.0222(6)
H3	1.2023	0.7859	−0.1349	0.027*
C4	1.4042(3)	0.7781(2)	−0.14591(18)	0.0265(7)
H4	1.4243	0.7629	−0.2069	0.032*
C5	1.5071(3)	0.7860(2)	−0.10078(19)	0.0267(7)
H5	1.5971	0.7753	−0.1302	0.032*
C6	1.4778(3)	0.8095(2)	−0.01215(19)	0.0268(7)
H6	1.5480	0.8153	0.0192	0.032*
C7	1.3465(3)	0.8246(2)	0.03047(17)	0.0212(6)
H7	1.3267	0.8415	0.0908	0.025*
C8	0.9032(3)	0.9457(2)	−0.12306(18)	0.0288(7)
H8A	0.9348	0.9810	−0.1870	0.043*
H8B	0.8559	0.9961	−0.0862	0.043*
H8C	0.8425	0.8928	−0.1234	0.043*
C11	0.9458(3)	0.5006(2)	0.17872(16)	0.0154(5)
C12	1.0384(3)	0.5580(2)	0.11114(16)	0.0188(6)
H12	1.0325	0.6313	0.1030	0.023*
C13	1.1397(3)	0.5086(2)	0.05535(18)	0.0236(6)
H13	1.2026	0.5483	0.0095	0.028*
C14	1.1492(3)	0.4022(2)	0.06628(19)	0.0272(7)
H14	1.2178	0.3687	0.0278	0.033*
C15	1.0578(3)	0.3447(2)	0.13389(19)	0.0271(7)

Table 2 (continued)

Atom	x	y	z	U_{iso}*/U_{eq}
H15	1.0644	0.2714	0.1418	0.033*
C16	0.9567(3)	0.3931(2)	0.19013(18)	0.0227(6)
H16	0.8949	0.3529	0.2364	0.027*
C21	0.7937(3)	0.48227(19)	0.36336(16)	0.0146(5)
C22	0.9039(3)	0.4540(2)	0.40765(17)	0.0206(6)
H22	0.9896	0.4765	0.3770	0.025*
C23	0.8880(3)	0.3936(2)	0.49585(18)	0.0247(7)
H23	0.9631	0.3741	0.5251	0.030*
C24	0.7633(3)	0.3612(2)	0.54176(18)	0.0246(7)
H24	0.7529	0.3199	0.6024	0.029*
C25	0.6543(3)	0.3891(2)	0.49909(18)	0.0244(7)
H25	0.5688	0.3673	0.5307	0.029*
C26	0.6689(3)	0.4493(2)	0.40979(17)	0.0185(6)
H26	0.5935	0.4677	0.3807	0.022*
C31	0.6617(3)	0.56835(19)	0.21201(16)	0.0142(5)
C32	0.5636(3)	0.6443(2)	0.23418(17)	0.0192(6)
H32	0.5830	0.6962	0.2644	0.023*
C33	0.4379(3)	0.6453(2)	0.21282(18)	0.0257(7)
H33	0.3707	0.6961	0.2300	0.031*
C34	0.4115(3)	0.5712(2)	0.16602(19)	0.0282(7)
H34	0.3258	0.5715	0.1508	0.034*
C35	0.5091(3)	0.4968(2)	0.14138(18)	0.0247(7)
H35	0.4909	0.4474	0.1080	0.030*
C36	0.6334(3)	0.4941(2)	0.16531(16)	0.0191(6)
H36	0.6994	0.4417	0.1499	0.023*
C41	0.5712(3)	0.89356(19)	0.33661(17)	0.0150(5)
C42	0.4550(3)	0.8737(2)	0.40218(18)	0.0196(6)
H42	0.4602	0.8454	0.4651	0.023*
C43	0.3315(3)	0.8951(2)	0.37592(19)	0.0229(6)
H43	0.2526	0.8805	0.4209	0.028*
C44	0.3224(3)	0.9375(2)	0.28490(19)	0.0232(6)
H44	0.2375	0.9518	0.2673	0.028*
C45	0.4375(3)	0.9590(2)	0.21940(18)	0.0224(6)
H45	0.4312	0.9888	0.1569	0.027*
C46	0.5615(3)	0.9377(2)	0.24410(17)	0.0194(6)
H46	0.6400	0.9528	0.1988	0.023*
C51	0.8055(3)	0.9804(2)	0.36421(15)	0.0147(5)
C52	0.9378(3)	0.9765(2)	0.37567(17)	0.0199(6)
H52	0.9898	0.9129	0.3785	0.024*
C53	0.9935(3)	1.0659(2)	0.38290(17)	0.0230(6)
H53	1.0833	1.0631	0.3914	0.028*
C54	0.9188(3)	1.1587(2)	0.37783(17)	0.0241(7)
H54	0.9570	1.2193	0.3834	0.029*
C55	0.7887(3)	1.1636(2)	0.36475(18)	0.0265(7)
H55	0.7381	1.2278	0.3601	0.032*
C56	0.7310(3)	1.0743(2)	0.35826(17)	0.0209(6)
H56	0.6412	1.0777	0.3498	0.025*
C61	0.7131(3)	0.79487(19)	0.48370(16)	0.0140(5)
C62	0.7242(3)	0.6876(2)	0.50624(17)	0.0218(6)
H62	0.7431	0.6482	0.4580	0.026*
C63	0.7080(3)	0.6375(2)	0.59847(18)	0.0274(7)
H63	0.7141	0.5641	0.6133	0.033*
C64	0.6828(3)	0.6948(2)	0.66869(18)	0.0255(7)
H64	0.6735	0.6606	0.7318	0.031*
C65	0.6711(3)	0.8014(2)	0.64752(18)	0.0259(7)
H65	0.6534	0.8404	0.6960	0.031*
C66	0.6852(3)	0.8519(2)	0.55508(17)	0.0197(6)
H66	0.6759	0.9252	0.5406	0.024*

Source of material

To AgCl (Sigma Aldrich; 0.36 g, 2.5 mmol) in acetonitrile (25 mL) was added an equimolar quantity of MeOC(=S)N(H)Ph [5] (0.42 g, 2.5 mmol) in acetonitrile (25 mL), followed by addition of two moles equivalent of triphenylphosphane (Merck; 1.31 g, 5.0 mmol) in acetonitrile (25 mL). The resulting mixture was stirred for 3 h at 323 K, giving a white suspension. An equal volume of dichloromethane (75 mL) was added to the suspension and the clear solution that resulted was left for slow evaporation at room temperature, yielding colourless crystals after 1 week. Yield: 1.86 g (89%). **M. pt.** (Krüss KSP1N melting point meter): 425–427 K. **Elemental Analysis** for $C_{44}H_{39}AgClNOP_2S$ (Perkin Elmer PE 2400 CHN Elemental Analyser; %): C, 63.29; H, 4.71; N, 1.68. Found: C, 63.05; H, 4.62; N, 1.68. **IR** (Perkin Elmer Spectrum 400 FT Mid-IR/Far-IR spectrophotometer; cm^{-1}): 3434 (br) ν(N—H), 1436 (s) ν(C—N), 1224 (s) ν(C—O), 1095 (s) ν(C=S). **^{1}H NMR** (Bruker Avance 400 MHz NMR spectrometer with chemical shifts relative to tetramethylsilane in $CDCl_3$ solution at 298 K, ppm): δ 11.17 (s, br, 1H, NH), 7.41–7.20 (m, br, 35H, Ph_3P, aryl-H), 4.02 (s, 3H, Me). **^{13}C{^{1}H} NMR** (as for ^{1}H NMR): δ 187.9 (C_q), 137.4 (Ph, C_{ipso}), 134.0 (d, m-PC_6H_5, $^3J_{CP}$ = 16.47 Hz), 133.1 (d, i-PC_6H_5, ^1JCP = 21.49 Hz), 129.8 (s, p-PC_6H_5), 128.8 (Ph, C_{meta}), 128.7 (d, o-PC_6H_5, $^2J_{CP}$ = 9.23 Hz), 125.3 (Ph, C_{para}), 122.4 (Ph, C_{ortho}), 58.4 (OMe). **^{31}P{^{1}H} NMR** (as for ^{1}H NMR but with chemical shift referenced to 85% aqueous H_3PO_4 as the external reference): δ 5.4.

A preliminary screen for anti-bacterial activity was performed, again following literature protocols [6]. Compound (I) proved ineffective against the studied bacteria.

Experimental details

The C-bound H atoms were geometrically placed (C—H = 0.95–0.98 Å) and refined as riding with U_{iso}(H) = 1.2–1.5U_{eq}(C). The N-bound H atom was refined with N—H = 0.88 ± 0.01 Å, and with 1.2U_{eq}(N).

Comment

The synthesis and characterisation of the title compound, $(Ph_3P)_2Ag[S{=}C(OMe)N(H)Ph]Cl$, (I), was motivated by the biological potential exhibited by their phosphanegold(I) thiolate counterparts of general formula $R_3PAu[SC(OR')=NAr]$. These have proven to be potent against bacteria, especially Gram-positive bacteria [7] and against a number of cancer cell lines, inducing cell death via apoptotic pathways [8].

The molecular structure of (I) is shown in the figure (70% displacement ellipsoids). The Ag atom is tetrahedrally coordinated by the Cl [2.5438(7) Å], thione-S [2.7201(7) Å] and two phosphane-P atoms [Ag—P1, P2 = 2.4702(7), 2.4600(7) Å]. The C1 = S1 and C1—N1 bond lengths in (I) of 1.685(3) and 1.326(3) Å, respectively, are similar to those of the

uncoordinated acid, i.e. S=C(OMe)N(H)Ph [5], of 1.6708(11) and 1.3288(15) Å, respectively, confirming the thione form of the ligand in (I). The range of tetrahedral angles is from a small 100.95(2)°, for Cl1—Ag—S1, to a wide 125.07(2)° for P1—Ag—P2. The thiocarbamide molecule is orientated to place the amide-N—H in a position to form an intramolecular amide-N—H···Cl hydrogen bond [N1—H1n···Cl1: H1n···Cl1 = 2.270(12) Å, N1···Cl1 = 3.139(2) Å with angle at H1n = 173(3)°] to form a quasi six-membered ring.

The most closely related structure in the literature is found in the accompanying report which describes the structure of the O-ethyl analogue of (I) which displays the same basic molecular structure [9]. Further, there is the direct copper(I) analogue of (I) which, while not isostructural features a very similar geometry [10].

The molecular packing of (I) features phenyl-C—H···Cl interactions [C24—H24···$Cl1^i$: H24···$Cl1^i$ = 2.81 Å, C24···$Cl1^i$ = 3.613(3) Å with angle at H24 = 143° and C33—H33···$Cl1^{ii}$: H33···$Cl1^{ii}$ = 2.69 Å, C33···$Cl1^{ii}$ = 3.536(3) Å with angle at H33 = 149° for symmetry operations (i) $2-x$, $1-y$, $1-z$ and (ii) $-1+x$, y, z]. These interactions serve to link molecules into a linear, supramolecular chain along the *a*-axis. As there are no apparent directional interactions between the chains, a further analysis of the molecular packing was conducted by calculating the Hirshfeld surface and two-dimensional fingerprint plots with the aid of Crystal Explorer 17 [11] following established procedures [12].

The distinctive feature of the fingerprint plot are symmetric spikes due to the specified H···Cl/Cl···H interactions. Yet, these contacts contribute only 4.0% to the overall Hirshfeld surface. By far, the most prominent contacts are H···H contacts, contributing 62.8% followed by H···C/C···H contacts, at 28.0%. Finally, reflecting the lack of π···π stacking, C···C contacts contributed only 1.5% to the overall surface.

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