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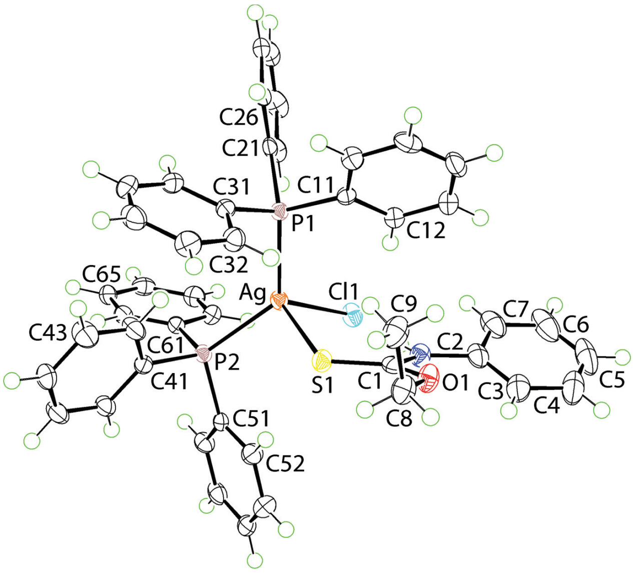
Crystal structure of chlorido-(*O*-ethyl phenylcarbamothioamide-κ*S*)-bis(triphenylphosphane-κ*P*)-silver(I), $C_{45}H_{41}AgClNOP_2S$



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Abstract

$C_{45}H_{41}AgClNOP_2S$, monoclinic, $P2_1/c$ (no. 14), $a = 10.1930(3)$ Å, $b = 18.3087(6)$ Å, $c = 21.3088(6)$ Å, $\beta = 94.516(3)°$, $V = 3964.3(2)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0353$, $wR_{ref}(F^2) = 0.0810$, $T = 100(2)$ K.

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The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list

Table 1: Data collection and handling.

Crystal:	Colourless prism
Size:	$0.60 \times 0.11 \times 0.05$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	0.75 mm^{-1}
Diffractometer, scan mode:	SuperNova, ω
θ_{max}, completeness:	27.6°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	16706, 9086, 0.032
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 7332
$N(param)_{refined}$:	473
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	0.26060(2)	0.23307(2)	0.35902(2)	0.01466(6)
Cl1	0.26896(6)	0.17084(3)	0.25057(3)	0.01943(13)
S1	0.52011(6)	0.24032(3)	0.39628(3)	0.01764(14)
P1	0.23070(6)	0.36667(3)	0.36172(3)	0.01239(13)
P2	0.17069(6)	0.13700(3)	0.42419(3)	0.01308(13)
O1	0.73790(16)	0.26845(9)	0.33888(9)	0.0219(4)
N1	0.5725(2)	0.22098(11)	0.27719(10)	0.0183(5)
H1N	0.4899(12)	0.2077(14)	0.2739(13)	0.022*
C1	0.6146(2)	0.24362(12)	0.33502(13)	0.0172(5)
C2	0.6370(3)	0.22109(13)	0.22008(13)	0.0219(6)
C3	0.7728(3)	0.21608(13)	0.21751(14)	0.0267(6)
H3	0.8292	0.2156	0.2552	0.032*
C4	0.8250(3)	0.21181(15)	0.15912(16)	0.0364(8)
H4	0.9176	0.2086	0.1573	0.044*
C5	0.7446(4)	0.21216(15)	0.10380(15)	0.0398(8)
H5	0.7815	0.2088	0.0643	0.048*
C6	0.6091(3)	0.21753(15)	0.10665(15)	0.0372(8)
H6	0.5529	0.2179	0.0689	0.045*
C7	0.5559(3)	0.22228(14)	0.16412(14)	0.0284(6)
H7	0.4633	0.2264	0.1656	0.034*
C8	0.7959(2)	0.29628(14)	0.39905(13)	0.0230(6)
H8A	0.8927	0.2909	0.4009	0.028*
H8B	0.7631	0.2674	0.4338	0.028*
C9	0.7612(3)	0.37532(14)	0.40696(14)	0.0284(6)
H9A	0.7958	0.3921	0.4487	0.043*
H9B	0.6653	0.3810	0.4028	0.043*
H9C	0.7999	0.4044	0.3745	0.043*
C11	0.3544(2)	0.41694(12)	0.32189(11)	0.0132(5)
C12	0.4062(2)	0.38266(13)	0.27071(12)	0.0174(5)
H12	0.3841	0.3333	0.2611	0.021*
C13	0.4897(2)	0.42037(15)	0.23387(13)	0.0246(6)
H13	0.5250	0.3967	0.1993	0.030*

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Table 2 (continued)

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
C14	0.5216(2)	0.49251(15)	0.24745(13)	0.0240(6)
H14	0.5769	0.5186	0.2214	0.029*
C15	0.4733(2)	0.52651(13)	0.29863(13)	0.0214(6)
H15	0.4972	0.5756	0.3084	0.026*
C16	0.3897(2)	0.48901(13)	0.33590(12)	0.0183(5)
H16	0.3564	0.5126	0.3710	0.022*
C21	0.0811(2)	0.40822(13)	0.32497(11)	0.0149(5)
C22	0.0016(2)	0.36693(14)	0.28270(12)	0.0192(5)
H22	0.0196	0.3165	0.2775	0.023*
C23	−0.1049(3)	0.39909(15)	0.24767(13)	0.0258(6)
H23	−0.1587	0.3708	0.2185	0.031*
C24	−0.1316(2)	0.47260(16)	0.25584(13)	0.0263(6)
H24	−0.2033	0.4947	0.2318	0.032*
C25	−0.0546(2)	0.51393(14)	0.29878(12)	0.0225(6)
H25	−0.0750	0.5639	0.3049	0.027*
C26	0.0523(2)	0.48239(13)	0.33293(12)	0.0173(5)
H26	0.1061	0.5111	0.3618	0.021*
C31	0.2443(2)	0.40207(12)	0.44189(11)	0.0141(5)
C32	0.3681(2)	0.40655(13)	0.47514(12)	0.0193(5)
H32	0.4451	0.3967	0.4542	0.023*
C33	0.3790(3)	0.42526(14)	0.53846(13)	0.0222(6)
H33	0.4636	0.4284	0.5604	0.027*
C34	0.2682(3)	0.43933(14)	0.56994(13)	0.0233(6)
H34	0.2764	0.4520	0.6133	0.028*
C35	0.1444(3)	0.43469(14)	0.53740(12)	0.0229(6)
H35	0.0678	0.4442	0.5587	0.027*
C36	0.1325(2)	0.41622(13)	0.47406(12)	0.0187(5)
H36	0.0476	0.4131	0.4523	0.022*
C41	0.1762(2)	0.15424(12)	0.50868(11)	0.0143(5)
C42	0.1888(3)	0.22594(13)	0.53028(12)	0.0216(6)
H42	0.1972	0.2645	0.5011	0.026*
C43	0.1890(3)	0.24162(14)	0.59411(13)	0.0260(6)
H43	0.1974	0.2907	0.6082	0.031*
C44	0.1770(2)	0.18604(14)	0.63708(12)	0.0218(6)
H44	0.1765	0.1969	0.6807	0.026*
C45	0.1657(3)	0.11417(14)	0.61638(12)	0.0222(6)
H45	0.1584	0.0758	0.6459	0.027*
C46	0.1651(2)	0.09833(13)	0.55262(12)	0.0176(5)
H46	0.1571	0.0491	0.5388	0.021*
C51	0.2510(2)	0.04768(12)	0.41970(11)	0.0146(5)
C52	0.3885(2)	0.04606(13)	0.42407(12)	0.0197(5)
H52	0.4365	0.0906	0.4272	0.024*
C53	0.4556(3)	−0.01980(14)	0.42392(13)	0.0254(6)
H53	0.5491	−0.0203	0.4276	0.030*
C54	0.3861(3)	−0.08489(14)	0.41848(12)	0.0226(6)
H54	0.4319	−0.1301	0.4186	0.027*
C55	0.2498(3)	−0.08394(13)	0.41281(12)	0.0204(6)
H55	0.2022	−0.1285	0.4083	0.024*
C56	0.1824(2)	−0.01811(13)	0.41364(12)	0.0177(5)
H56	0.0889	−0.0179	0.4100	0.021*
C61	−0.0017(2)	0.11610(12)	0.40149(11)	0.0135(5)
C62	−0.0339(2)	0.09880(13)	0.33824(12)	0.0181(5)
H62	0.0318	0.1006	0.3090	0.022*
C63	−0.1624(2)	0.07896(13)	0.31807(12)	0.0200(5)
H63	−0.1831	0.0654	0.2754	0.024*
C64	−0.2597(2)	0.07883(13)	0.35966(12)	0.0192(5)
H64	−0.3474	0.0660	0.3454	0.023*
C65	−0.2292(2)	0.09739(13)	0.42214(12)	0.0183(5)
H65	−0.2963	0.0980	0.4507	0.022*
C66	−0.1000(2)	0.11527(12)	0.44331(12)	0.0171(5)
H66	−0.0792	0.1269	0.4864	0.021*

of the atoms including atomic coordinates and displacement parameters.

Source of material

To AgCl (Sigma Aldrich; 0.36 g, 2.5 mmol) in acetonitrile (25 mL) was added an equimolar quantity of EtOC(=S)N(H)Ph [5] (0.45 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: 1.85 g (87%). **M. pt** (Krüss KSP1N melting point meter): 403–406 K. **Elemental Analysis** for $C_{45}H_{41}AgClNOP_2S$ (Perkin Elmer PE 2400 CHN Elemental Analyser; %): C, 63.65; H, 4.87; N, 1.65. Found: C, 63.82; H, 4.88; N, 1.66. **IR** (Perkin Elmer Spectrum 400 FT Mid-IR/Far-IR spectrophotometer; cm^{-1}): 3433 (br) ν(N—H), 1433 (s) ν(C—N), 1215 (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), 7.41–7.18 (m, br, 35H, Ph_3P, aryl-H), 4.53 (q, 2H, OCH_2, $^3J_{HH} = 7.10$), 1.34 (t, 3H, CH_3, $^3J_{HH} = 7.10$ Hz). **^{13}C{^{1}H} NMR** (as for ^{1}H NMR): δ 187.0 (C_q), 137.5 (Ph, C_{ipso}), 134.0 (d, m-PC_6H_5, $^3J_{CP} = 16.65$ Hz), 133.1 (d, i-PC_6H_5, $^1J_{CP} = 21.34$ Hz), 129.8 (s, p-PC_6H_5), 128.8 (Ph, C_{meta}), 128.7 (d, o-PC_6H_5, $^2J_{CP} = 9.28$ Hz), 125.1 (Ph, C_{para}), 122.2 (Ph, C_{ortho}), 68.4 (CH_2), 14.1 (CH_3). **^{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 5.3.

Preliminary screening (disc diffusion) for anti-bacterial activity was performed following literature precedents [6]. Compound (I) did not produce zones of inhibition, indicating a lack of *in vitro* antibacterial activity.

Experimental details

The C-bound H atoms were geometrically placed (C—H = 0.95–0.99 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 molecular structure of $(Ph_3P)_2Cu[S{=}C(OEt)N(H)Ph]Cl$, i.e. the direct copper(I) analogue of the silver(I) title compound, (I), was particularly noteworthy in that it provided evidence for an intramolecular phenyl-C—H⋯π(quasi chelate-ring) interaction where the six-membered "quasi" ring was closed by a N—H⋯Cl hydrogen bond, i.e. {⋯ClCuSCNH} [7]. DFT calculations showed this favourable contact has an energy of stabilisation of about 3.5 kcal/mol [7]. Subsequent work showed that intermolecular versions of these interactions occurred in approximately 30% structures where they could potentially form and sustained zero-, one-, two- and even three-dimensional architectures [8]. Over and above structural considerations, it is noted that phosphanegold(I) thiolate analogues of these compounds, i.e. $R_3PAu[SC(OR'){=}NAr]$, exhibit biological potential against several strains of bacteria [9] as well as anti-cancer potential [10].

The molecular structure of (I) is shown in the figure (70% displacement ellipsoids) and features a tetrahedrally coordinated Ag atom within a ClP_2S donor set defined by Cl [2.5841(6) Å], thione-S [2.7046(6) Å] and two phosphane-P [Ag—P1, P2 = 2.4661(6), 2.4622(6) Å] atoms. The crystal structure of the parent acid, i.e. $S{=}C(OEt)N(H)Ph$, is available for comparison [5]. Here, there are three independent molecules in the asymmetric unit with the C1 = S1 bond lengths lying in the range 1.636(5) to 1.651(5) Å, and C1—N1 in the range 1.319(7) to 1.324(7) Å [5]. These values compare with the C1 = S1 and C1—N1 bond lengths in (I) of 1.684(3) and 1.338(3) Å, respectively, and therefore, confirm the ligand as being in the thione form. The tetrahedral angles at Ag(I) range from 93.69(2)°, for S1—Ag—P1, to 130.03(2)° for P1—Ag—P1. A quasi six-membered ring is formed owing to the presence of an intramolecular amide-N—H⋯Cl hydrogen bond [N1—H1n⋯Cl1: H1n⋯Cl1 = 2.366(15) Å, N1⋯Cl1 = 3.234(2) Å with angle at H1n = 173(3)°].

The most closely related structure to (I) is the O-methyl analogue [11]. Here, the Ag—Cl1 [2.5438(7) Å] and Ag—S1 [2.7201(7) Å] have contracted and elongated, respectively compared with the equivalent bonds in (I). Also, the range of angles subtended at the Ag atom is significantly reduced, i.e. 100.95(2)°, for Cl1—Ag—S1, to 125.07(2)° for P1—Ag—P2. As mentioned above, the copper(I) analogue of (I), which adopts a very similar coordination geometry, features an intramolecular phenyl-C—H⋯π (quasi chelate-ring) interaction. In (I), the separation between the proximate phenyl-C—H12 atom and the ring centroid is short at 2.47 Å and the angle at the H12 atom is 131°. However, this H12 atom appears to be directed towards the Cl1 atom with the C12—H12⋯Cl1 angle being 168° even though the H12⋯Cl1 separation is long at 3.20 Å.

The only directional interaction in the molecular packing of (I) is a methyl-C—H⋯Cl interaction [C9—H9c⋯Cg(C31–C36)^{i}: H9c⋯Cg(C31–C36)^{i} = 2.70 Å with angle at H9c = 157° for symmetry operation (i) $1+x, y, z$]. These interactions connect molecules into a linear, supramolecular chain along the a-axis. The chains assemble in the crystal with no directional interactions between them. This is confirmed by an analysis of the calculated Hirshfeld surface and two-dimensional fingerprint plots which were conducted with Crystal Explorer 17 [12] in accord with literature procedures [13]. This analysis shows that 62.3% of all contacts are of the type H⋯H followed by H⋯C/C⋯H contacts, at 30.6%. The only other contacts of note are H⋯Cl/Cl⋯H contacts, contributing 3.9%.

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