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A germanium–silver complex containing a Ge—Ag bond, $Ag[Ge(OC_6HPh_4\text{-}2,3,5,6)_3\text{-}(AgOSO_2CF_3)]\cdot 4C_6H_6$

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Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.004 Å
R factor = 0.039
wR factor = 0.074
Data-to-parameter ratio = 18.6

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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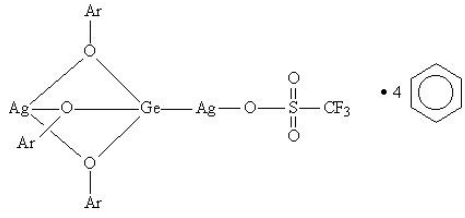
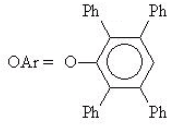
The title compound, tris[μ-2,3,5,6-tetraphenylphenoxy(1−)-1:3κ^2O,1κC^2](trifluoromethylsulfonato-2κO)disilvergermanium(Ag—Ge) benzene tetrasolvate, $Ag[Ge(OC_6HPh_4\text{-}2,3,5,6)_3(AgOSO_2CF_3)]\cdot 4C_6H_6$ or $[Ag_2Ge(CF_3O_3S)(C_{30}H_{21}O)_3]\cdot 4C_6H_6$, is a rare example of a compound containing a $Ge^{II}—Ag^{I}$ bond. The anion consists of a Ge atom bound to three tetraphenylphenoxide ligands and to a molecule of silver trifluoromethanesulfonate. The Ag^{I} counter-ion is encapsulated by the three O atoms of the tetraphenylphenoxide ligands and exhibits π-interactions with the *ortho*-phenyl rings of these ligands.

Comment

The title compound, (I), was isolated from the reaction of $[Ge(OC_6HPh_4\text{-}2,3,5,6)_2]$ with $Ph_3Ge(OSO_2CF_3)$. The Ag atoms undoubtedly result from residual silver in the preparation of $Ph_3Ge(OSO_2CF_3)$ from Ph_3GeCl and $Ag(OSO_2CF_3)$. These complications can be circumvented by the use of triflic acid in place of silver trifluoromethanesulfonate (Uhlig, 1991*a*,*b*). The reaction mixture consisted of an intractable mixture of products, from which only (I) could be isolated and characterized.





(I)

Compound (I) contains a four-coordinate Ge^{II} metal center, consisting of a $[Ge(OC_6HPh_4\text{-}2,3,5,6)_3]^-$ anion with a coordinated $Ag(OSO_2CF_3)$ group and an Ag^+ cation (Fig. 1). The complex cocrystallizes with four molecules of benzene. The average Ge—O bond length of 1.848 (2) Å is a typical value. The Ge—Ag bond for the coordinated silver trifluoromethanesulfonate is 2.4672 (3) Å. To date, compound (I) represents one of three discrete molecular compounds containing a Ge—Ag bond. The complexes $[HB\{3,5\text{-}(CF_3)_2Pz\}_3]AgGeCl[(Me)_2ATl]$, (II), and $[HB\{3,5\text{-}(CF_3)_2Pz\}_3]AgGe(OSO_2CF_3)[(Me)_2ATl]$, (III) $\{[HB\{3,5\text{-}(CF_3)_2Pz\}_3]$ is hydro-

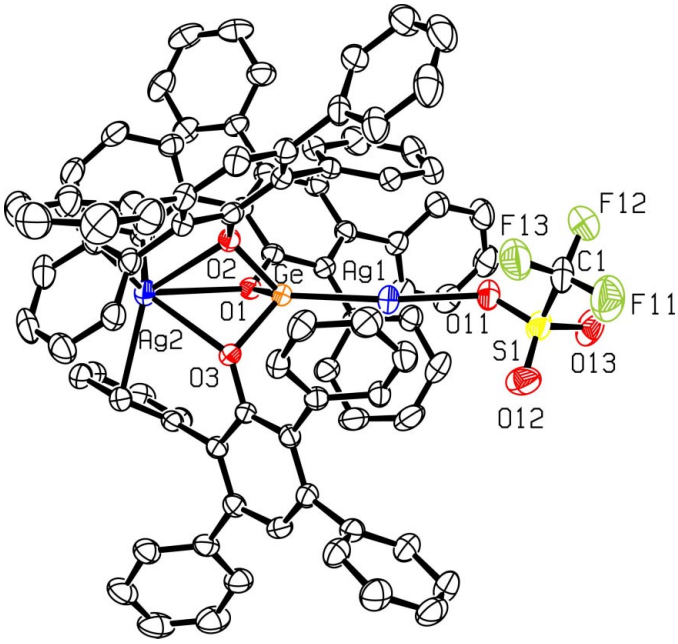


Figure 1
*ORTEP*II (Johnson, 1976) plot highlighting the environment about the silver cation of (I). Displacement ellipsoids are drawn at the 50% probability level. H atoms and the benzene solvent molecules have been omitted.

tris[3,5-bis(trifluoromethyl)pyrazolyl]borate and [(Me)$_2$ATI] is *N*-methyl-2-(methylamino)troponiminate}, have been reported (Rasika Dias & Wang, 2000). Both of these species exhibit Ge—Ag distances similar to (I); the Ge—Ag distance is 2.4215 (9) Å for (II) and 2.412 (1) Å for (III). Complex (III) also contains a trifluoromethanesulfonate anion that is bound to the Ge metal center, rather than to the Ag atom as in (I). Other Ge^{II}/M^{I} compounds (where M^{I} is a group 11 metal) have been structurally characterized. These contain Ge^{II} bound to Cu^{I} (Orlov *et al.*, 1997; Orlov *et al.*, 1998) and Au^{I} metal centers (Bauer *et al.*, 1995, 1997; Bauer & Schmidbaur, 1996, 1997; Contel *et al.*, 1996; Tripathi *et al.*, 1998).

The Ag^{I} cation of compound (I) is encapsulated by the O atoms of the three tetraphenylphenoxide ligands. The average Ag—O distance is 2.631 (3) Å. There are also short Ag—C contacts of 2.522 (2), 2.536 (2) and 2.522 (3) Å with three of the *ortho*-C atoms of the phenyl rings of the tetraphenylphenoxide ligands. These contacts arise from interaction of the Ag atom with the $p\pi$ electrons of the aromatic rings. Thus, the Ag^{I} cation is in a six-coordinate environment.

Experimental

Compound (I) was isolated from the reaction of 0.23 g (0.26 mmol) of [Ge(OC$_6$HPh$_4$-2,3,5,6)$_2$] with 0.14 g (0.31 mmol) of Ph$_3$Ge(O-SO$_2$CF$_3$) in benzene, yielding 0.020 g of (I). Ph$_3$Ge(OSO$_2$CF$_3$) was prepared from Ph$_3$GeCl (1.00 g, 2.94 mmol) and Ag(OSO$_2$CF$_3$) (0.84 g, 3.3 mmol) in benzene in the absence of light and was judged to be pure by ^{1}H and ^{19}F NMR spectroscopic analysis.

Crystal data

[Ag$_2$Ge(CF$_3$O$_3$S)(C$_{30}$H$_{21}$O)$_3$]·4C$_6$H$_6$
M_r = 1942.36
Monoclinic, $P2_1/n$
a = 13.9593 (2) Å
b = 24.3433 (3) Å
c = 26.9406 (4) Å
β = 92.1511 (5)°
V = 9148.4 (4) Å^3
Z = 4
D_x = 1.41 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 63826 reflections
θ = 2.1–27.9°
μ = 0.83 mm^{-1}
T = 150 K
Irregular block, colorless
0.30 × 0.30 × 0.25 mm

Data collection

Nonius KappaCCD diffractometer
ω scans
Absorption correction: multi-scan (Otwinowski & Minor, 1997)
T_{min} = 0.574, T_{max} = 0.814
63826 measured reflections
21443 independent reflections
15451 reflections with $I > 2\sigma(I)$
R_{int} = 0.060
θ_{max} = 27.9°
$h = 0 \rightarrow 18$
$k = 0 \rightarrow 30$
$l = -35 \rightarrow 35$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.074
S = 0.91
21401 reflections
1153 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0352P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.003
$\Delta\rho_{max}$ = 0.38 e Å^{-3}
$\Delta\rho_{min}$ = −0.67 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Ag(1)—O(11)	2.2654 (19)	S(1)—O(13)	1.434 (2)
Ag(1)—Ge	2.4672 (3)	S(1)—O(11)	1.450 (2)
Ag(2)—C(222)	2.522 (2)	S(1)—C(1)	1.802 (4)
Ag(2)—C(122)	2.546 (2)	F(11)—C(1)	1.338 (4)
Ag(2)—C(322)	2.552 (3)	F(12)—C(1)	1.339 (4)
Ge—O(2)	1.8458 (16)	F(13)—C(1)	1.339 (4)
Ge—O(3)	1.8467 (16)	O(1)—C(11)	1.380 (3)
Ge—O(1)	1.8507 (16)	O(2)—C(21)	1.378 (3)
S(1)—O(12)	1.429 (2)	O(3)—C(31)	1.369 (3)
O(11)—Ag(1)—Ge	169.03 (5)	O(13)—S(1)—C(1)	102.95 (15)
C(222)—Ag(2)—C(122)	112.03 (9)	O(11)—S(1)—C(1)	101.67 (14)
C(222)—Ag(2)—C(322)	115.17 (9)	C(11)—O(1)—Ge	122.48 (15)
C(122)—Ag(2)—C(322)	115.72 (8)	C(21)—O(2)—Ge	123.82 (14)
O(2)—Ge—O(3)	90.20 (7)	C(31)—O(3)—Ge	122.55 (14)
O(2)—Ge—O(1)	90.21 (7)	S(1)—O(11)—Ag(1)	137.01 (12)
O(3)—Ge—O(1)	91.26 (7)	F(11)—C(1)—F(13)	106.9 (3)
O(2)—Ge—Ag(1)	126.36 (5)	F(11)—C(1)—F(12)	106.7 (3)
O(3)—Ge—Ag(1)	123.20 (5)	F(13)—C(1)—F(12)	106.3 (3)
O(1)—Ge—Ag(1)	125.05 (5)	F(11)—C(1)—S(1)	112.3 (2)
O(12)—S(1)—O(13)	116.91 (13)	F(13)—C(1)—S(1)	112.6 (2)
O(12)—S(1)—O(11)	113.69 (13)	F(12)—C(1)—S(1)	111.6 (2)
O(13)—S(1)—O(11)	114.37 (13)	O(1)—C(11)—C(16)	119.7 (2)
O(12)—S(1)—C(1)	104.73 (15)	O(1)—C(11)—C(12)	118.3 (2)

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* and *SCALEPACK*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976) and *PLUTON* (Spek, 1997); software used to prepare material for publication: *CIF VAX* in *MolEN* (Fair, 1990).

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