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Hexacoordinated Spirocyclic Germanium(IV) Complex: Synthesis and Structural Characterization

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ABSTRACT: *The spiro-dibenzogermocine [O(o-$C_6H_4S)_2]_2$Ge (**1**) was prepared in a reaction between O(o-$C_6H_4SH)_2$ and Ge($O^iPr)_4$, and its molecular structure was determined by X-ray diffraction studies. In the solid state,* **1** *shows the existence of two weak O → Ge transannular interactions, resulting in a hexacoordinated germanium atom that displays the geometry of a distorted bicapped tetrahedron.* © 2009 Wiley Periodicals, Inc. Heteroatom Chem 20:45–49, 2009; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20510

INTRODUCTION

Only three spiro-dibenzogermocine complexes of the type [D(*o*-$C_6H_4E)_2]_2$Ge (D = Se, S, P-Ph; E = O, S) [1–3] and two spiro-germocane complexes [D($CH_2CH_2S)_2]_2$Ge (D = O, S) [4] (Fig. 1) in which the germanium atom is hexacoordinated have been structurally characterized. It was found that in the above-mentioned compounds, the secondary bonding [5] between the donor and the germanium atoms causes the hypercoordination phenomenon of these complexes, resulting in a hexacoordinated germanium atom with a distorted octahedral geometry. To continue with our research about the influence of the combination of the donor atoms in the ligand and its rigidity on the strength of the transannular bond, we decided to use the O(*o*-$C_6H_4SH)_2$ ligand [6].

The ligands based on diphenylether should exhibit smaller flexibility than those derived from diphenylthioether due to the shorter C—O bonds, which should have together with the short C—O bond length and thus larger distance between the oxygen and germanium atoms a large effect on the transannular O → Ge distance in the spiro-dibenzogermocine compounds. Herein, we report the synthesis, characterization, and structural study of a spiro-dibenzogermocine [O(*o*-$C_6H_4S)_2]_2$Ge (**1**).

RESULTS AND DISCUSSION

Attempts to synthesize compound **1** by salt metathesis reaction between the lithium salt O(*o*-$C_6H_4SLi)_2$ and $GeCl_4$, or with the use of $GeCl_4$, the free ligand O(*o*-$C_6H_4SH)_2$ and an amine as an HCl acceptor (methods used in other cases) were unsuccessful [1–3]. Therefore, we decided to use Ge($O^iPr)_4$ as the source of germanium because its reactivity is lower than that of $GeCl_4$ and thus the reaction can be easily controlled. Furthermore, the only byproduct of the reaction of Ge($O^iPr)_4$ with the ligand O(*o*-$C_6H_4SH)_2$ would be isopropanol that is volatile and easy to remove, facilitating thus the isolation and

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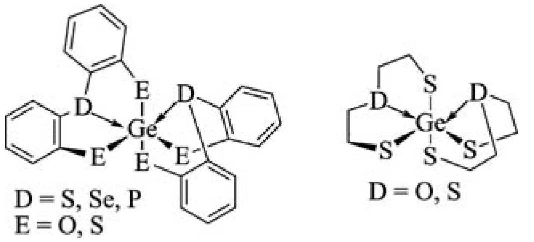


FIGURE 1 Spiro-dibenzogermocine and spiro-germocane complexes.

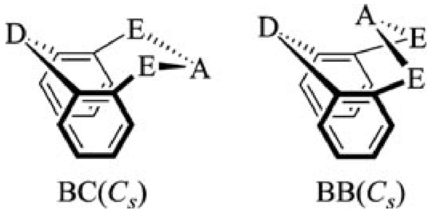


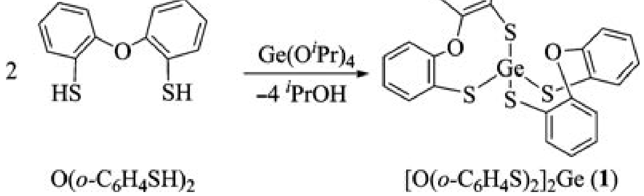
FIGURE 2 Conformational representations of eight-membered rings with *Cs* symmetry; boat–chair (BC) and boat–boat (BB) in dibenzometallocines.

purification of the product. Therefore, the reaction between $Ge(O^iPr)_4$ and the free ligand $O(o\text{-}C_6H_4SH)_2$ [6] in a molar ratio 1:2 in refluxing benzene leads to the formation of **1** in high yield (Scheme 1). Compound **1** is air-stable, soluble in benzene, toluene, dichloromethane, and chloroform but insoluble in pentane, hexane, and isopropanol.

There were no signals observed belonging to either the S—H protons or the protons from the ^{i}PrO moieties in the ^{1}H NMR spectrum of **1** [6], confirming a complete substitution of the ^{i}PrO groups on the Ge center by sulfur atoms. The four C_6H_4S moieties are equivalent in solution showing an ABCD pattern for the aromatic protons. The ortho proton H-1 is shifted toward low frequencies when compared with complexes where the germanium atom is pentacoordinated [$O(o\text{-}C_6H_4S)_2GeEtCl$ and $O(o\text{-}C_6H_4S)_2GePh_2$] [7], but has a similar shift with respect to the free ligand [$O(o\text{-}C_6H_4SH)_2$] [6].

The chemical shifts in the proton decoupled ^{13}C spectrum of **1** are similar as those reported for the dibenzogermocine [$O(o\text{-}C_6H_4S)_2GeEtCl$ and $O(o\text{-}C_6H_4S)_2GePh_2$] [7] complexes. The signal for the ipso carbon atom C-4a was found at 154.7 ppm, which is 2.6 ppm at higher frequency with respect to the free ligand [$O(o\text{-}C_6H_4SH)_2$] [6]. Such trends have also been observed in other dibenzometallocines [6,8].

The study in solution by ^{1}H and ^{13}C NMR spectroscopy at ambient temperature suggests that either the system is highly symmetric or that the conformational interconversion is very fast on the NMR time scale to be determined under these conditions. The chemical shifts also suggest that the O → Ge transannular interactions in complex **1** are very weak or completely lacking in solution; a similar phenomenon has been observed in the dibenzogermocine [$O(o\text{-}C_6H_4S)_2GeEtCl$ and $O(o\text{-}C_6H_4S)_2GePh_2$] [7] complexes under these conditions. Thus, the existence of the boat–chair conformer (BC) in solution can be suggested [2] (Fig. 2). This conformation is more stable than the boat–boat conformation required for the presence of the transannular bond.



$O(o\text{-}C_6H_4SH)_2$

$[O(o\text{-}C_6H_4S)_2]_2Ge$ (**1**)

SCHEME 1

The mass spectrum of **1** exhibits the molecular ion (M^+) for $[O(o\text{-}C_6H_4S)_2]_2Ge$ with the appropriate isotopic pattern at *m/z* 538 albeit at low intensity, confirming the binding of germanium to sulfur atoms and the stability of the spiro-dibenzogermocine. The peak at *m/z* 506 corresponds to the fragment $M^+ - S$, the fragment at *m/z* 430 can be ascribed to $M^+ - SPh$ and the peaks at *m/z* 306 and 232 are assigned to the $O(C_6H_4S)_2Ge$ and $O(C_6H_4S)_2$ fragments, respectively. The base peak was assigned to the $O(C_6H_4)_2S$ moiety and appears at *m/z* 200.

X-ray Structure Description of Compound 1

The molecular structure of **1** has been determined by single-crystal X-ray diffraction analysis. Compound **1** crystallizes in the monoclinic space group $P2_1/c$ with one molecule of **1** and a solvating benzene molecule in the asymmetric unit. Selected crystallographic data are given in Table 1, and selected bond lengths, angles, and torsion angles are given in Table 2. The ORTEP drawing of **1** is depicted in Fig. 3.

The Ge—S(thiolate) bond lengths are in a good agreement with those reported for dibenzogermocine complexes [$D(o\text{-}C_6H_4S)_2GeL^1L^2$] (D = S, O; L^1 = Ph, Cl Br; L^2 = Et, Ph) (2.216(2)–2.255(1) Å) [7], the spiro-germocane $[O(CH_2CH_2S)_2]_2Ge$ [2.210(3)–2.236(3) Å], and $[S(CH_2CH_2S)_2]_2Ge$ [2.217(2)–2.222(1) Å] complex [4]. However, when compared

TABLE 1 Crystal Data and Summary of Data Collection and Refinement for **1**

Compound	**1** · C_6H_6
Formula	$C_{30}H_{22}GeO_2S_4$
Formula weight	615.31
Temperature (K)	173(2)
Radiation (Å)	0.71073 (Mo K_α)
Crystal size (mm)	0.35 × 0.24 × 0.21
Crystal system, space group	Monoclinic, $P2_1/c$
a (Å)	9.008(2)
b (Å)	30.612(3)
c (Å)	9.873(2)
β (°)	101.60(2)
V (Å^3)	2667(1)
Z	4
D_{calc}.(g cm^{-3})	1.532
Absorption coefficient μ (mm^{-1})	1.490
F(000)	1256
θ Range for data collection (°)	2.21 to 25.38
Index ranges	$-10 \leq h \leq 10$ $-36 \leq k \leq 36$ $-11 \leq l \leq 11$
Collected reflections	15684
Independent reflections/R_{int}.	4868/0.0326
Data/restraints/parameters	4868/324/389
Goodness-of-fit on F^2	1.043
R_1,[a] wR_2^b ($I > 2.\sigma(I)$)	0.0379, 0.0918
R_1,[a] wR_2^b (all data)	0.0468, 0.0965
Max./min. electron density (e Å^{-3})	0.781/–0.235

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
[b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma(F_o^2)^2]^{1/2}$.

to the Ge—S bond lengths in $[PhP(o\text{-}C_6H_4S)_2]_2Ge$ [2.343(1)–2.400(1) Å] they are significantly shorter [3].

In addition to the four Ge—S bonds, two weak transannular O → Ge interactions are observed. The O → Ge distances in **1** [2.782(2) and 2.827(2) Å] are in the middle of the range between the sum of the covalent radii of these elements [Σ_{rCov}(O,Ge) = 1.88 Å] [5] and the sum of their van der Waals radii [Σ_{rVdW}(O,Ge) = 3.47 Å] [9]. They are significantly longer than those in $O(CH_2CH_2S)_2GeCl_2$ [2.36(1) and 2.39(1) Å] [10], $O(CH_2CH_2S)_2GeSO(C_2H_4)$ [2.492(3) Å] [11], $O(CH_2CH_2S)_2GeS_2(C_2H_4)$ [2.616(1) Å] [10], and in $O(C_6H_4S)_2GeEtCl$ [2.656(3) Å] [7], but shorter than those reported for $[O(CH_2CH_2S)_2]_2Ge$ [2.915(3), 3.040(3), 2.955(3) and 2.946(3) Å] [4] and $O(o\text{-}C_6H_4S)_2GePh_2$ [2.872(3)Å] [7].

TABLE 2 Selected Bond Lengths (Å), Angles, and Torsion Angles (°) for **1**

	Bond Length		
O1 → Ge1	2.782(2)	Ge1–S2	2.219(1)
O2 → Ge1	2.827(2)	Ge1–S3	2.218(1)
Ge1–S1	2.232(1)	Ge1–S4	2.224(1)
	Bond Angles		
S3–Ge1–S2	113.4(1)	S1–Ge1–S4	94.0(1)
S3–Ge1–S4	114.9(1)	O1–Ge1–S4	164.5(1)
S2–Ge1–S4	108.7(1)	O2–Ge1–S1	163.2(1)
S1–Ge1–S3	108.9(1)	O1–Ge1–O2	122.8(1)
S1–Ge1–S2	115.6(1)		
	Torsion Angles		
C1–O1–C7–C8	142.2(1)	C13–O2–C19–C20	−81.3(1)
C7–O1–C1–C2	−79.5(1)	C19–O2–C13–C14	139.9(1)
S1–Ge1–S2–C8	−22.3(1)	S3–Ge1–S4–C20	91.9(1)
S2–Ge1–S1–C2	95.0(1)	S4–Ge1–S3–C14	−19.2(1)

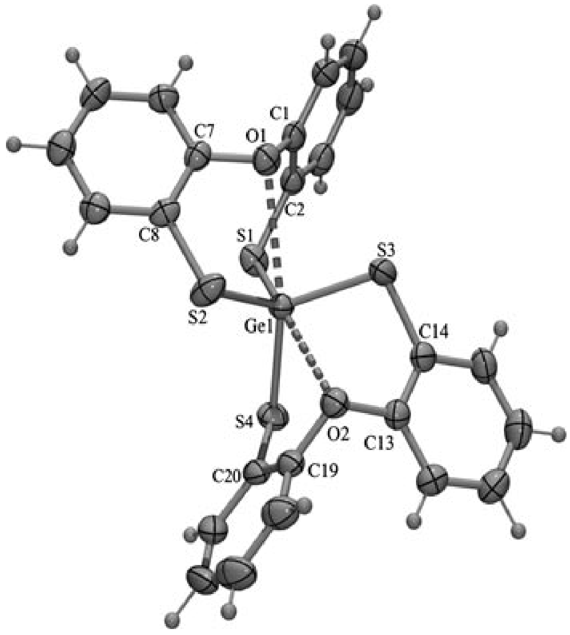


FIGURE 3 ORTEP diagram of $[O(o\text{-}C_6H_4S)_2]_2Ge \cdot C_6H_6$ (**1**) (50% probability ellipsoids, benzene molecule is omitted).

The geometry around the germanium atom in compound **1** can best be described as a distorted bicapped tetrahedron [11,12], if the two weak transannular O → Ge interactions are taken into account. The tetrahedron is determined by the four covalent Ge—S bonds (S1—Ge1, S2—Ge1, S3—Ge1, and S4—Ge1), being distorted through the capping of the S1—S2—S3 and S2—S3—S4 faces by the O1 and O2 atoms, respectively, as shown in the Fig. 4. The relatively wide S3—Ge1—S2 [113.4(1)°] and rather acute S1—Ge1—S4 [94.0(1)° compared to the value for an ideal tetrahedral angle 109.5°] bond angles are attributed to the presence of the two transannular O → Ge interactions.

In the solid state, the eight-membered ring conformation in **1** can be described as a twisted boat (C_1 symmetry) according to the observed torsion angles [2].

TABLE 3 Comparison of D → Ge Geometrical Bond Parameters in Spirocyclic Germanium Compounds, Bond Lengths (Å), Bond Angles (°), and the Pauling Bond Order (BO)

Compound	*D*	*E*	*D → Ge*	*D-Ge-D*	*Δd*[a]	*BO*[b]*D → Ge*	*Reference*
$[D(CH_2CH_2E)_2]_2Ge$	O	S	2.914(3)	118.9	1.034	0.036	[4,11]
			3.040(3)	118.4	1.16	0.023	
			2.946(3)		1.07	0.030	
			2.955(3)		1.06	0.030	
$[D(CH_2CH_2E)_2]_2Ge$	S	S	3.453(3)	111.0	0.977	0.042	[4,11]
			3.237(3)		1.193	0.020	
$[D(o\text{-}C_6H_4E)_2]_2Ge$	O	S	2.782(2)	122.8(1)	0.902	0.053	This work
			2.827(2)		0.947	0.046	
$[D(o\text{-}C_6H_4E)_2]_2Ge$	S	O	2.477(1)	97.19(6)	0.237	0.463	[3]
$[D(o\text{-}C_6H_4E)_2]_2Ge$	Se	O	2.5959(6)	96.00(2)	0.2359	0.465	[1]
$[PhD(o\text{-}C_6H_4E)_2]_2Ge$	P	S	2.4131(10)	100.34(3)	0.3331	0.339	[2]
			2.4173(12)		0.3373	0.335	

[a] Bond lengths, $\Delta d = (d\,\text{exp} - \Sigma_{\text{rCov}})$, according to standard bond lengths Σ_{rCov} (O,Ge) = 1.88; Σ_{rCov} (S,Ge) = 2.24; Σ_{rCov} (Se,Ge) = 2.36, Σ_{rCov} (P,Ge) = 2.08 Å [5,8,15].
[b] Mode of calculation $BO = 10^{-(1.41\cdot\Delta d)}$ [13,14].

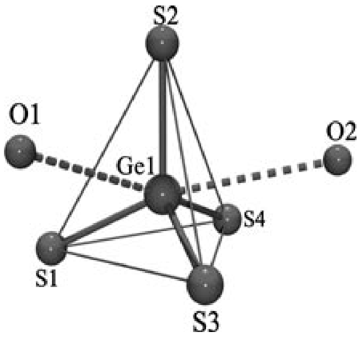


FIGURE 4 View of the hexacoordinate geometry at germanium atom in **1**.

To evaluate the magnitude of the transannular interactions (D → Ge) in the spiro-dibenzogermocines $[D(o\text{-}C_6H_4E)_2]_2Ge$ (D = Se, S, P-Ph; E = O, S) and spiro-germocanes, the Pauling-type bond order (BO) was calculated [13,14]. These results are presented in Table 3.

It can be observed that the Pauling bond order of the transannular interactions D → Ge for spiro-diberzogermocine $D(o\text{-}C_6H_4E)_2]_2Ge$ (D = Se, S, P-Ph, O; E = O, S) compounds indicates that the interaction between the donor atom (D) and the germanium atom increases in the order O < P-Ph < S ≤ Se.

The comparison of the bond lengths and the Pauling bond orders at O → Ge in $[O(o\text{-}C_6H_4S)_2]_2Ge$ shows that the transannular interactions O → Ge are stronger than those in a similar spiro-germocane $[O(CH_2CH_2S)_2]_2Ge$ complex [3,11].

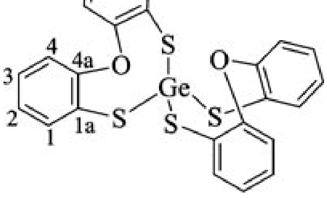
CONCLUSION

We have synthesized a novel homospiro-dibenzogermocine that exhibits two weak transannular O → Ge interactions resulting in a hypercoordinated germanium atom. $Ge(O^iPr)_4$ has proven to be an excellent starting material for the synthesis of spirocyclic germanium compounds.

EXPERIMENTAL SECTION

General Procedures

All manipulations were performed under a dry, oxygen-free atmosphere using standard Schlenk techniques. Solvents were dried by standard methods and distilled prior to use. The melting point was determined on a Mel-Temp II instrument. EI-MS (70 eV); spectrum was recorded with a JEOL JMS-AX505HA. NMR spectra were recorded at ambient temperature and measured on a Varian Inova 500 and a Bruker Avance 300 spectrometers using the solvent signals as internal reference (^1H and $^{13}C\{^1H\}$) (numbering scheme for the assignment of the NMR signals are shown in Scheme 2). The IR spectrum was recorded in the 4000–400 cm^{-1} range on a Bruker tensor 27 spectrometer, as KBr pellet. $O(o\text{-}C_6H_4SH)_2$ was synthesized according to the



SCHEME 2

literature method [6]. Ge(O^{i}Pr)$_4$ was purchased from Aldrich and used as supplied.

[O(*o*-C_6H_4S)$_2$]$_2$Ge (**1**): A solution of O(*o*-C_6H_4SH)$_2$ (1.52 g, 6.40 mmol) in benzene (20 mL) was added via a syringe to Ge(O^{i}Pr)$_4$ (1.0 mL, 3.20 mmol). The colorless reaction mixture was refluxed for 16 h, and then the resultant solution was cooled to room temperature. The solution was reduced to 5 mL of the volume, and the resulting colorless crystals of **1** were separated by suction filtration. Yield: 1.32 g (77%) mp = 142–146°C. MS-EI (70 eV): *m/z* (%) = 538 (8) (M)$^+$, 506 (5) (M – S)$^+$, 430 (7) (M – SPh)$^+$, 306 (8) (M – S – SPhO)$^+$, 232 (25) (M – S – SPhO – Ge)$^+$, 200 (100) (M– S – SPhO – Ge – S)$^+$. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.35$ (dd, $^3J = 8.0$, $^4J = 2.0$, H-1), 7.22 (ddd, $^3J = 8.0$, $^4J = 2.0$, H-3), 7.11 (dd, $^3J = 8.0$, $^4J = 2.0$, H-4), 7.05 (ddd, $^3J = 8.0$, $^4J = 2.0$, H-2) ppm. $^{13}C\{^1H\}$ NMR (300 MHz, $CDCl_3$): $\delta = 154.7$ (C-4a), 133.2 (C-1), 128.8 (C-3), 126.1 (C-1a), 125.1 (C-2), 120.4 (C-4) ppm. IR (KBr pellet): 3062, 1569, 1463, 1438, 1258, 1219, 1120, 1060, 1032, 872, 799, 751, 733, 676 cm^{-1}.

X-Ray Crystallography

Suitable single crystals of complex **1** were grown by slow evaporation from a benzene solution. X-ray diffraction data on **1** were collected at 170 K on a Bruker-APEX three-circle diffractometer through the use of Mo K_α radiation ($\lambda = 0.71073$ Å, graphite monochromator). The structure was solved by direct methods (SHELXS-97) [16] and refined against all data by full-matrix least squares on F^2 [17]. CCDC-696800 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via http:/www.ccdc.cam.ac.uk/const/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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