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A Neutral Spirocyclic Hexacoordinated Germanium(IV) Complex: Hypervalent Germanium Compounds with Sulfur-Containing Eight-Membered Rings

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Introduction

The conformational analysis of medium-sized heterocycles has only very recently received much attention,[1] stimulated in part by recent studies on eight-membered rings containing phosphorus. In particular, 12*H*-dibenzo[*d,g*][1,3,2]dioxaphosphocin derivatives have been shown to provide unique coordination geometries when employed as ligands for transition-metal-catalyzed hydroformylation reactions.[2−4] The diequatorial aptitude of certain 12*H*-dibenzo[*d,g*][1,3,2]dioxaphosphocins incorporated in pentaoxyphosphoranes has important ramifications to literature proposals describing activated states for cyclic adenosine monophosphites where trigonal bipyramidal geometries about phosphorus are invoked.[5] Certain sterically congested molecules incorporating medium-sized organophosphorus heterocycles exhibit unique spectral properties.[6,7] Several reviews on the conformational analysis of 12*H*-dibenzo[*d,g*]-[1,3,2]dioxaphosphocins have appeared.[8,9] Studies on the conformation of the corresponding silicon-containing 12*H*-dibenzo[*d,g*][1,3,2]dioxasilocin ring system have been reported,[10] including a very recent crystallographic study.[11,12] Quite interestingly, Holmes *et al.*[12] observed bonding of the transannular sulfur to silicon in substituted 12*H*-dibenzo[*d,g*]-[1,3,6,2]dioxathiasilocins, which led to a hypervalent silicon atom. Both pentacoordinate and hexacoordinate silicon[13−16] and phosphorus[17,18] compounds serve as models for intermediates or transition states in nucleophilic substitution reactions of the corresponding tetracoordinate state. Hypervalent silicon species are implicated in synthetically important reactions; for example, a recent report by Denmark described a catalytic enantioselective aldol reaction of trichlorosilyl enolates with aldehydes.[19]

Virtually nothing is known about the corresponding eight-membered-ring systems with germanium except for our very recent reports on the synthesis and characterization of a substituted 12*H*-dibenzo[*d,g*][1,3,2]dioxagermocin[20] and 12*H*-dibenzo[*d,g*][1,3,6,2]dioxathiagermocin,[21] for which NMR spectral evidence suggested bonding of sulfur to germanium. We report herein the *first crystallographic evidence for a neutral hypervalent germanium(IV) complex with sulfur-induced hexacoordination of germanium in a spirocyclic complex with two sterically hindered eight-membered 12H-dibenzo[d,g][1,3,6,2]-dioxathiagermocin rings.*

Experimental Section

All melting points were determined with a Fisher-Johns melting point apparatus and are uncorrected. ^{1}H NMR (300.08 and 499.84 MHz,

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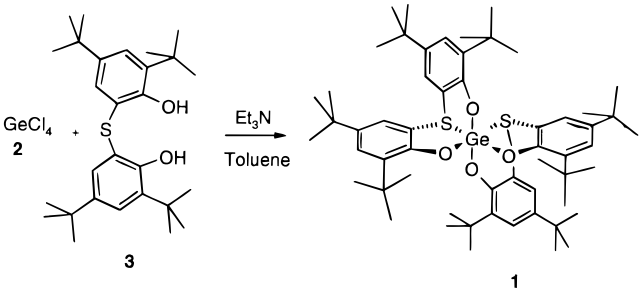
respectively) spectra were taken on Varian Model Gemini-300 and Unity-500 spectrometers. All ^{1}H chemical shifts are reported in ppm relative to tetramethylsilane, where a positive sign is downfield from the standard. Significant ^{1}H NMR data are tabulated in the following order: multiplicity (m, multiplet; s, singlet; d, doublet; t, triplet; dd, doublet of doublets), atom assignments, coupling constant in hertz, and number of protons. Merck precoated (0.25 mm) silica gel F-254 plates were used for TLC. Reagents were purchased from commercial laboratory supply houses. The thiobis(phenol) **1** was prepared according to a literature procedure.[10b] Solvents were dried prior to use, when necessary, with appropriate drying agents. Reactions were carried out in flame-dried apparatus under a dry inert atmosphere of either nitrogen or argon. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY.

Synthesis of [2,2′-S(4,6-^{t}Bu$_2$C$_6$H$_2$O)$_2$]$_2$Ge (1). To a room-temperature solution of 1.22 g (5.68 mmol) of germanium(IV) chloride (**2**) in 12 mL of toluene was added dropwise over a 30 min period a solution of 5.00 g (11.3 mmol) of 2,2′-thiobis(4,6-di-*tert*-butylphenol) (**3**) and 4.57 g (45.2 mmol) of triethylamine in 19 mL of toluene. The reaction mixture was heated to 60 °C and held at this temperature overnight. The reaction mixture was cooled to room temperature, and then the suspension of triethylamine hydrochloride was removed by filtration. The volatiles were removed *in vacuo*, and the residue was recrystallized from a mixture of acetonitrile and toluene to give 2.86 g (53.1%) of a white solid, mp 339−341 °C. ^{1}H NMR (C$_6$D$_6$, 300.075 MHz, 27 °C): δ 1.10 (s, 18 H), 1.14 (s, 18 H), 1.25 (s, 18 H), 1.72 (s, 18 H), 7.41 (d, J = 2.4 Hz, 2 H), 7.50 (d, J = 2.4 Hz, 2 H), 7.52 (d, J = 2.4 Hz, 2 H), 7.55 (d, J = 2.4 Hz, 2 H). MS: 950, 951, 952, 953, 954, 955, 956, 957 (M$^{\bullet+}$) observed in the ratio calculated for the naturally abundant isotopic mixture of ^{32}S,^{33}S, ^{34}S, ^{70}Ge, ^{72}Ge, ^{73}Ge, ^{74}Ge, and ^{76}Ge. Anal. Calcd for C$_{56}$H$_{80}$O$_4$S$_2$Ge: C, 70.50; H, 8.45. Found: C, 70.68; H, 8.59.



X-ray Structural Analysis. Crystals suitable for X-ray crystallographic analysis were grown by slow diffusion of acetronitrile vapor into a toluene solution of **1**. Crystal data for **1**: C$_{56}$H$_{80}$O$_4$S$_2$Ge, MW = 953.96; crystal/habit = colorless blocks, orthorhombic; crystal size (mm) 0.30 × 0.30 × 0.20; space group = *Pccn* (No. 56); cell parameters a = 19.604(2) Å, b = 15.489(2) Å, c = 18.478(2) Å, V = 5610(1) Å^3, Z = 4; d_{calc} = 1.129 Mg·m^{-3}. Data collection: Enraf-Nonius diffractometer; Mo Kα (λ = 0.710 69 Å) radiation; graphite monochromator; scan type $\omega-2\theta$; scan width = (1 + 0.34 tan θ)°; $2\theta_{\text{max}}$ 49.9°; number of variables 285; number of observed reflections 2655 ($I > 3.0\sigma(I)$); R = 0.045, R_w = 0.042, GOF = 1.85. Refinement: method full-matrix; hydrogen atoms located, not refined; maximum and minimum density in final difference map (e Å^{-3}) 0.30 and 0.49, respectively.

Results and Discussion

The spirocyclic germanium compound **1** was prepared as a white crystalline solid (53% recrystallized) by the reaction of the germanium(IV) chloride **2** with the tetra-*tert*-butyl-substituted thiobis(phenol) **3** using triethylamine as an acid acceptor. Crystals suitable for X-ray crystallographic analysis were grown by slow diffusion of acetronitrile vapor into a toluene solution of **1**. In the solid-state X-ray structure of **1**, a distorted octahedral geometry about germanium is observed. In addition to the expected bonding of the four oxygen atoms to germanium, bonding of the transannular sulfur atoms in the eight-membered rings is observed (see Figure 1). The sulfur atoms lie in a plane with one oxygen atom of each eight-membered ring and are cis to one another. The O(2)−Ge−O(2*), O(2)−Ge−S, and S−Ge−S* bond angles in the hypothetical plane passing through the S, S*, O(2), and O(2*) atoms are 90.50(2), 86.28(9), and 97.19(6)°, respectively. The sum of the appropriate bond angles in the plane is 360.25°. The remaining ligand oxygen atoms from each eight-membered ring are perpendicular to the plane defined by the S, S*, O(2), and O(2*) atoms and are trans to one another. The trans oxygen atoms are bent slightly toward one another [O(1)−Ge−O(1*) = 163.2(2)°]. The bonding parameters for both eight-membered rings are identical and both rings are interchanged by a C_2 symmetry operation. The eight-membered rings assume a C_s symmetric boat−boat conformation in the solid-state structure of **1**,[6b,20−26] which brings the transannular sulfur and germanium atoms to within bonding distance of each other. See Table 1 for selected bond distances and angles.

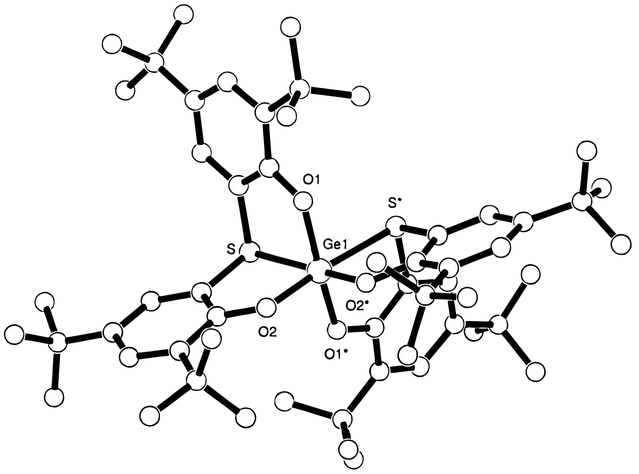


Figure 1. Molecular structure of **1** showing the crystallographic numbering scheme.

Table 1. Selected Bond Lengths and Angles in **1**[a]

	Bond Lengths (Å)		
Ge−S	2.477(1)	S−C(8)	1.778(4)
Ge−O(1)	1.862(3)	O(1)−C(1)	1.352(4)
Ge−O(2)	1.799(3)	O(2)−C(7)	1.342(5)
S−C(2)	1.779(4)		
	Bond Angles (deg)		
S−Ge−S*	97.19(6)	C(2)−S−C(8)	105.1(2)
O(2)−Ge−S	86.28(9)	Ge−S−C(2)	92.9(2)
O(2)−Ge−O(2*)	90.50(2)	Ge−S−C(8)	90.8(1)
O(1)−Ge−O(1*)	163.2(2)		

[a] Numbering of carbon atoms may be found in the Supporting Information.

The Ge−O bonds (1.862 Å) trans to an oxygen atom are longer than the Ge−O bonds (1.799 Å) trans to a sulfur atom. The Ge−O bond lengths are shorter than that observed by Denmark *et al.* in anionic pentacoordinate complexes (1.994

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Å).[27] The Ge−S bond lengths are 2.477 Å, which are 11% longer than the sum of the covalent radii of Ge and S (2.24 Å)[28] but significantly shorter than the sum of the van der Waals radii (3.75 Å).[29,30] The observed Ge−S bond length in **1** is significantly shorter than that reported by Dräger[30,31] and co-workers for neutral pentacoordinate germanium complexes (3.005 Å).[32] Ge−S Bond lengths ranging from 2.250 to 2.343 Åwere reported by Holmes *et al.* for an anionic rectangular pyramidal germanium complex.[33] Although neutral hexacoordinate germanium complexes have been suggested,[34] few complexes have been characterized by crystallography,[35−38] of which none involve the bonding of sulfur to germanium. The unsymmetrical bonding of the oxygen atoms of the eight-membered rings to germanium in **1** is in contrast to the diequatorial bonding observed in related hexacoordinate hypervalent phosphorus compounds reported by Holmes *et al*.[39] This result underscores the conclusion reached by Holmes and co-workers that related eight-membered rings display considerable conformational flexibility with small energy differences between the various conformers[40] and our calculations on the corresponding silicon-containing eight-membered ring.[11b]

In the ^{1}H NMR spectrum of **1**, four singlets were observed that were assigned to the protons of four nonequivalent pairs of *tert*-butyl substituents. Similarly, four doublets were observed that were assigned to the protons of four nonequivalent pairs of aromatic protons. The ^{1}H NMR spectrum observed is that expected if the bonding of sulfur to germanium observed in solid state is maintained in solution. Furthermore, the observation of four pairs of both nonequivalent *tert*-butyl substituents and aromatic protons strongly suggests that ligand permutation by psuedorotational processes, which are often observed for ligands of hypervalent phosphorus species,[17,18] are either absent or slow on the NMR time scale. Indeed, Corriu and co-workers suggested the involvement of hexacoordinated germanium in the racemization of enantiomerically pure chlorogermanes.[41,42]

This report constitutes the first crystallographic evidence for sulfur-induced hexacoordination in a neutral germanium complex. Furthermore, the observation of neutral hypervalent germanium molecules containing medium-sized rings provides valuable mechanistic insights into the possible bonding and structure of transition states and intermediates involved in nucleophilic substitution reactions at germanium.

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Supporting Information Available: A description of the structure solution of **1** and listings of crystal data, X-ray experimental details, bond angles, bond lengths, thermal parameters, and atomic parameters and an ORTEP diagram giving complete non-H atomic labeling for **1** (10 pages). Ordering information is given on any current masthead page.

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