Polyhedron 27 (2008) 1841–1847

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Synthesis and crystal structure of a germanium(II) calix[6]arene containing unusual diamidosilyl ether groups

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ARTICLE INFO

Article history:
Received 5 December 2007
Accepted 15 February 2008
Available online 1 April 2008

Keywords:
Germanium
Macrocycles
X-ray crystal structure
Calixarenes
Silyl ether
Silyl amide

ABSTRACT

The reaction of $Ge[N(SiMe_3)_2]_2$ with calix[6]arene furnishes a novel macrocyclic product having two divalent germanium atoms incorporated into a Ge_2NO rhombus which contains a μ_2-oxygen atom and a μ_2-NH_2 group. The crystal structure of the product indicates the presence of a conformationally rigid molecule where three of the six oxygen atoms of the calix[6]arene are bound to the germanium atoms while the remaining three have been converted into $–OSiMe_3$ or unusual $–OSi(H)(NH_2)_2$ groups. Spectral (^1H, ^{13}C, and ^{29}Si NMR) data in solution are consistent with the solid-state structure and indicate the germanium calix[6]arene retains its structure in solution.

1. Introduction

Calix[*n*]arenes are an important class of macrocycles which contain four or more phenol moieties connected together by methylene bridges. These species have applications in the areas of catalysis, self-assembly, and molecular or ionic recognition, and can also serve as platforms for the support of multiple transition- or main group-metal centers [1–24], including silicon- [13,16,17,21], phosphorus- [10–15,18,20,22–24], and arsenic [19]. Variation of the number of phenolic subunits present in the molecule allows control over the cavity size in these systems, which in turn has a profound effect on their properties and reactivity. The presence or absence of conformational rigidity, which is typically influenced by the attachment of peripheral substituents to the *para*-positions (or upper rim) of the aromatic rings, is also important in this regard [2,6,7,25–27].

Calix[6]arenes have been confirmed to be more flexible than calix[4]- and calix[8]arenes bearing identical *para*-substituents by variable temperature NMR spectral studies [28,29]. Several oxygen-functionalized calix[6]arenes have been employed for the complexation of metal ions [30–43] and some bimetallic complexes containing group 2 or 4 metals [44–46] bound directly to the oxygen atoms have been prepared. The latter types of complexes are uncommon, presumably due to the high conformational mobility of the hexamers versus the related tetramers and octamers. We recently described the syntheses and structures of calix[4]- and calix[8]arene complexes containing two or four germanium(II) sites (respectively) bound to the oxygen atoms of the macrocycles which were prepared via the protonolysis reaction of $Ge[N(SiMe_3)_2]_2$ with the *para*-unsubstituted parent calixarenes [47]. The structures of these two compounds were similar in that the germanium atoms were incorporated into Ge_2O_2 rhombi each having one terminal and two bridging Ge–O attachments. The calix[8]arene species was also shown to undergo an oxidative addition reaction with $Fe_2(CO)_9$ resulting in an octa-iron compound containing four $GeFe_2$ triangles.

In light of these results, we attempted to prepare a similar complex by treatment of the *para*-unsubstituted calix[6]arene with three equivalents of $Ge[N(SiMe_3)_2]_2$, and we now wish to report the outcome of this investigation. Instead of forming a complexe containing a Ge_2O_2 rhombus as observed in reactions with calix[4]- and calix[8]arene, reaction of the germanium amide with the calix[6]arene substrate furnished a Ge_2NO rhombus which contains a bridging amide group and has the two germanium atoms bound to three of the six oxygen atoms present in the macrocycle. One of the remaining three oxygen atoms has been incorporated into a $–OSiMe_3$ moiety while the other two have been incorporated into structurally unprecedented $–OSi(H)(NH_2)_2$ groups.

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doi:10.1016/j.poly.2008.02.027

2. Results and discussion

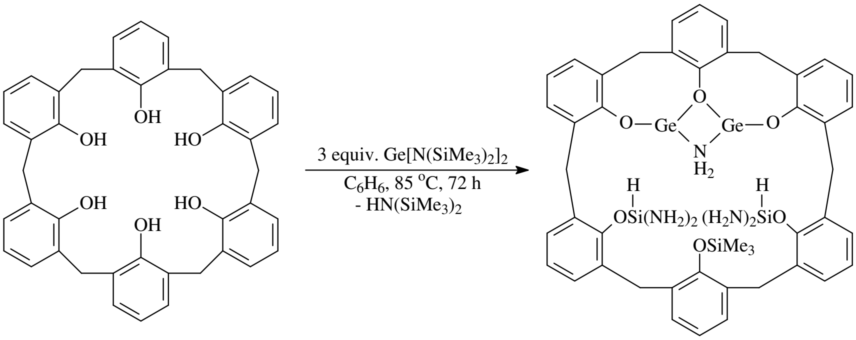
2.1. Synthesis and structure of compound ***1***

Treatment of calix[6]arene with three equivalents of Ge[N(SiMe$_3$)$_2$]$_2$ yielded complex **1** in 41% yield as shown in Eq. (1). The identity of **1** was ascertained by obtaining its X-ray crystal structure, and an ORTEP diagram of **1** is shown in Fig. 1 while selected bond distances and angles are collected in Table 1. Of the six phenolic oxygen atoms present in **1**, three are bound to the two Ge atoms in either a terminal or bridging fashion while the remaining three oxygen atoms have been incorporated into to either –OSiMe$_3$ or –OSi(H)(NH$_2$)$_2$ groups. We have previously observed the transformation of hydroxyl groups to trimethylsiloxy groups in the reactions of 3,3′-disubstituted binaphthols with metal(II) amides M[N(SiMe$_3$)$_2$]$_2$ (M = Be, Zn, Ge, Sn) [48]; however, the conversion of –OH groups to silylamides has not been previously described.

Table 1
Selected bond distances (Å) and angles (°) for compound **1** · 0.5 (C$_6$H$_6$)

Ge(1)–O(1)	1.860(3)	O(1)–Ge(1)–O(3)	91.4(1)
Ge(1)–O(3)	1.992(3)	O(1)–Ge(1)–N(5)	89.7(1)
Ge(1)–N(5)	2.011(4)	O(2)–Ge(2)–O(3)	91.6(1)
Ge(2)–O(2)	1.835(3)	O(2)–Ge(2)–N(5)	91.4(1)
Ge(2)–O(3)	1.993(3)	O(3)–Ge(1)–N(5)	77.1(1)
Ge(2)–N(5)	1.995(4)	O(3)–Ge(2)–N(5)	77.4(1)
Si(1)–O(6)	1.664(3)	Ge(1)–O(3)–Ge(2)	103.0(1)
Si(2)–O(5)[a]	1.696(5)	Ge(1)–N(5)–Ge(2)	102.3(2)
Si(2)–N(3)[a]	1.816(8)	O(5)–Si(2)–N(3)[a]	111.6(3)
Si(2)–N(4)[a]	1.715(8)	O(5)–Si(2)–N(4)[a]	108.2(3)
Si(3)–O(4)[a]	1.712(4)	N(3)–Si(2)–N(4)[a]	122.8(5)
Si(3)–N(1)[a]	1.700(8)	O(4)–Si(3)–N(1)[a]	112.4(4)
Si(3)–N(2)[a]	1.806(9)	O(4)–Si(3)–N(2)[a]	108.8(4)
		N(1)–Si(3)–N(2)[a]	119.6(4)

[a] The atoms Si(2) and Si(3) are disordered over two positions. The tabulated values are for the average of the two positions.



(1)

Compound **1** contains an unusual bridging –NH$_2$– group between the two germanium centers, and the structure of **1** can be compared to the two related calixarene complexes {calix[4]}Ge$_2$ (**2**) and {calix[8]}Ge$_4$ (**3**) [47] as well as the dimeric species [(C$_6$H$_3${C$_6$H$_3$Pr$^i_2$-2,6}$_2$-2,6)GeNH$_2$]$_2$ (**4**) which also contains bridging –NH$_2$– moieties [49]. Similar to the Ge$_2$O$_2$ rhombus in compound **2** the Ge$_2$NO rhombus adopts a planar geometry. The Ge(1)–O(3)–Ge(2) angle of 103.0(1)° is significantly more acute than the Ge–O$_{br}$–Ge angles in **2** and **3** which range from 106.1(1) to 107.89(6)° [47]. Furthermore, the Ge(1)–N(5)–Ge(2) angle measures 102.3(2)° which is more obtuse than the average Ge–N$_{br}$–Ge angles in **4** (100.0(1)°) [49]. The O(3)–Ge(1)–N(5) and O(3)–Ge(2)–N(5) angles average 77.3(1)° which are wider than the O$_{br}$–Ge–O$_{br}$ angles in **2** and **3** but more acute than the N$_{br}$–Ge–N$_{br}$ ligands angles in **4**. These structural differences can be attributed to the presence of two different types of bridging atoms in **1** and the internal angles in the Ge$_2$NO rhombus can be regarded as being intermediate between the Ge$_2$O$_2$ rhombi of **2** and **3** and the Ge$_2$N$_2$ rhombus of **4**.

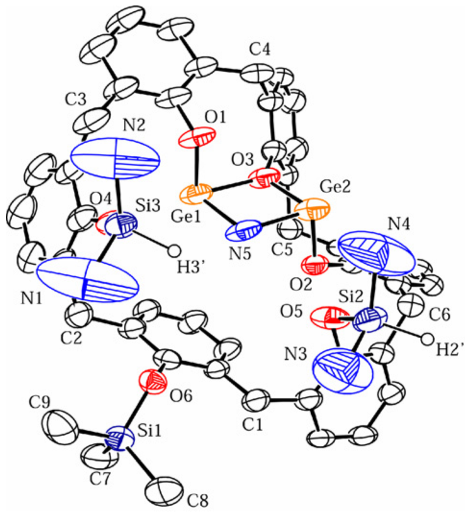


Fig. 1. ORTEP diagram of compound **1**. Thermal ellipsoids are drawn at 50% probability.

The terminal Ge(1)–O(1) and Ge(2)–O(2) bond lengths in **1** are typical for germanium(II)–oxygen distances and are comparable to those in compounds **2** and **3** [47] as well as in other Ge(II) aryloxides [50–54]. The bridging Ge(1)–O(3) and Ge(2)–O(3) bond lengths in **1** are 1.992(3) and 1.993(3) Å (respectively) which fall between the average Ge–O$_{br}$ bond distances in **2** (1.988 Å) and **3** (2.000 Å) [47]. The bridging N atom is not symmetrically disposed between the two germanium atoms in **1** as indicated by the two Ge–N bond lengths measuring 2.011(4) and 1.995(4) Å. These distances are shorter than those found in the structure of **4** which has an average Ge–N distance of 2.013(3) Å [49]. The Ge–N distances in **1** are longer than those in germanium(II) compounds bearing ligands with terminal Ge–N bonds, including the well-known bulky bisamide Ge[N(SiMe$_3$)$_2$]$_2$ which has Ge–N bond lengths of 1.873(5) and 1.878(5) Å [55] and the bis(piperidinato) complex Ge[NC$_5$H$_6$Me$_4$-2,2,6,6]$_2$ which has distances of 1.87(1) and 1.90(1) Å [56]. However, the Ge–N distances in **1** are considerably shorter than those in divalent germanium compounds having dative N → Ge bonds including those in [Ge(2-{(Me$_3$Si)$_2$C}-C$_5$H$_4$N)R] which measure 2.082(4) or 2.089(7) Å (R = Cl or CH(PPh$_2$)$_2$, respectively) [57]. These distances are also shorter than those in the divalent binhapthoxide complex