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Crystal Structure of Germanium(II) Dichloride Solvated by Tetrahydrofuran

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ABSTRACT: *The thermally highly unstable tetrahydrofuran solvate of germanium(II) dichloride ($GeCl_2 \cdot 2THF$) was crystallized, and its crystal structure was determined. It consists of a chain of $GeCl_2$ units connected by secondary $Cl \cdots Ge$ contacts [3.846(2) Å] in which each Ge atom is coordinated to two molecules of THF. Two weak hydrogen bonds of the $C{-}H \cdots Cl{-}Ge$ type in $GeCl_2 \cdot 2THF$ were also detected both with lengths of 2.90(3) Å.* © 2005 Wiley Periodicals, Inc. Heteroatom Chem 16:361–363, 2005; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20105

INTRODUCTION

Dicoordinated germylenes are very sensitive to air and moisture, whereas the adduct of germanium dichloride with 1,4-dioxane is quite stable under inert gas environments at ambient conditions and even can be handled in air for a brief period of time [1–4]. Thus $GeCl_2 \cdot 2$Dioxane became one of the most favorite starting compound for the synthesis of other divalent germanium species. The $GeCl_2 \cdot 2$Dioxane adduct can be easily dissolved in donor solvents such as NEt_3 [5], especially in ethers such as 1,4-dioxane, Et_2O, and THF. With regard to this high solubility, the knowledge of the species present in solution is desirable for their preparative application. Earlier investigations have established the structure of a germanium dichloride solvate with 1,4-dioxane [4,6,7], in which the Ge atoms located at the center of a pseudo-octahedron formed by two oxygen atoms and four chlorine atoms (two covalent Ge—Cl bonds and two secondary Ge ··· Cl bonds). To our knowledge, the THF solvate of $GeCl_2$ has not been reported so far.

RESULTS AND DISCUSSION

We got hold of a crystal of $GeCl_2 \cdot 2THF$ first during our attempts to react $GeCl_2 \cdot 2$Dioxane with formamidinium chloride $[(Me_2N)_2CH]Cl$ in THF to give compounds of the type $(R_2N)_2CHMCl_3$ (M = Ge, Sn) [8]. The unreacted $GeCl_2$ formed a solvated adduct with THF solvent molecules. During the crystallization at −78°C, a colorless crystalline material was formed. It turned out to be unstable and visibly decomposed with gas evolution at temperatures higher than −30°C. This adduct could be resynthesized by directly dissolving $GeCl_2 \cdot 2$Dioxane in THF. We managed to mount such a crystal under an inert perfluoropolyether and to transfer it to the diffractometer under permanent cooling, and thus were able to determine its crystal structure.

Molecules of $GeCl_2 \cdot 2THF$ are present as chain polymers in the monoclinic crystals with the space group $P2_1/c$. The structure and the cell components are shown in Figs. 1 and 2, respectively; Table 1 gives the selected bond lengths and angles. No crystallographic symmetry is imposed on the $GeCl_2 \cdot 2THF$ unit. In this respect, $GeCl_2 \cdot 2THF$ and its dioxane analogue $GeCl_2 \cdot 2$Dioxane behave differently.

Dedicated to Professor Dr. Alfred Schmidpeter on the occasion of his 75th birthday.

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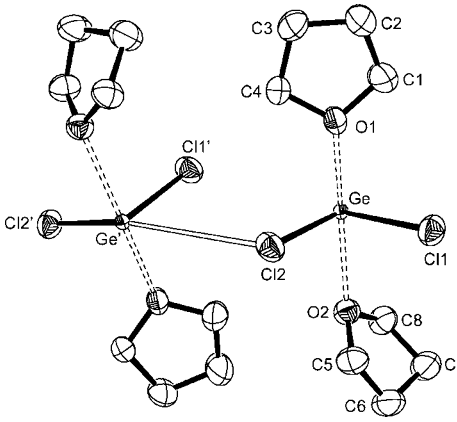

FIGURE 1 Crystal structure of the chain aggregation for **1** (ORTEP drawing with 50% probability ellipsoids). The open drawn bond represents the Ge ··· Cl secondary interaction, the dashed bonds represent secondary Ge ··· O contacts. Hydrogen atoms are omitted for clarity.

TABLE 1 Selected Bond Lengths Å and Angles of $GeCl_2 \cdot 2THF$ (°)

Ge—Cl1	2.442 (2)	Cl1—Ge—O1	84.9 (7)
Ge—Cl2	2.438 (2)	Cl1—Ge—O2	85.2 (7)
Ge ··· Cl2′	3.846 (2)	Cl2—Ge—O1	84.0 (7)
Ge ··· O1	2.410 (2)	Cl2—Ge—O2	85.2 (7)
Ge ··· O2	2.459 (2)	O1—Ge—O2	163.1 (7)
Cl1—Ge—Cl2	95.1 (1)	Ge—Cl2—Ge′	104.4 (7)

The latter crystallizes also in the monoclinic crystal system, but with space group $C2/c$ and the molecules obey crystallographic C_2 symmetry [4]. This makes the skeleton of $GeCl_2 \cdot 2$Dioxane more regular than that of $GeCl_2 \cdot 2THF$.

The Ge atom in $GeCl_2 \cdot 2THF$ unit is $[2+3]$ coordinate by two covalent Ge—Cl bonds and three dative bonds: one Ge ··· Cl bond to a Cl atom from a neighbour $GeCl_2$ unit and two Ge ··· O secondary bonds with oxygen atoms from two THF molecules. The $GeCl_2 \cdot 2THF$ units aggregate as a polymer with a chain structure build up by the Ge ··· Cl interactions, while in the $(2+4)$ coordination environment of Ge atom in $GeCl_2 \cdot 2$Dioxane an additional Ge ··· Cl bond is involved [4]. In the latter case, there are two aggregation connections: besides the chain structure of $GeCl_2$ units connected by two-coordinate Cl atoms, infinite $[O(CH_2CH_2)_2O \cdots GeCl_2]_n$ chains exit caused by two dative bonds from the oxygen atoms in one dioxane molecule. They are almost vertical to each other [4]. Expectedly, the Cl1—Ge—Cl2 angle in $GeCl_2 \cdot 2THF$ at 95.1(1)° is larger than that in $GeCl_2 \cdot 2$Dioxane at 94.30(2)°. Both Ge—Cl bonds in $GeCl_2 \cdot 2THF$ [2.438(2) and 2.442(2) Å] and the Ge ··· O bonds [2.410(2) and 2.459(2) Å] are slightly longer than the corresponding values in $GeCl_2 \cdot 2$Dioxane [Ge—Cl 2.281(1) Å, the shortest Ge ··· O at 2.399(1) Å] [4]. The secondary Ge ··· Cl bond has a length of 3.846(2) Å, which is reasonably less than the van der Waals distance of 3.90 Å [$r_{\mathrm{Cl,VdW}} = 1.75$ Å [9], $r_{\mathrm{Ge,VdW}} = 2.15$ Å [16]], but almost 0.4 Å longer than the Ge ··· Cl length in $GeCl_2 \cdot 2$Dioxane at 3.463(1) Å. The O1—Ge—O2 angle in $GeCl_2 \cdot 2THF$ has a value of 163.1(7)° and is more than 10° smaller than the same angle in $GeCl_2 \cdot 2$Dioxane at 173.1(1)° [4].

There are two further contacts detected in $GeCl_2 \cdot 2THF$, which can be classified as weak hydrogen bonds of the C—H ··· Cl—Ge type, both with

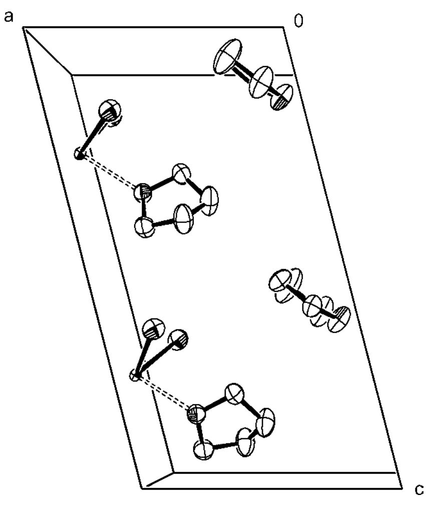

FIGURE 2 The cell contents of **1** projected on (010) (ORTEP drawing with 50% probability ellipsoids). Only the front half of the components is depicted for clarity.

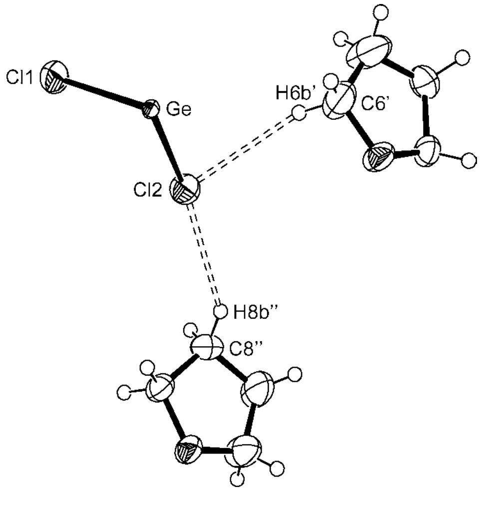

FIGURE 3 View of the secondary hydrogen bonds in $GeCl_2 \cdot 2THF$ (ORTEP drawing with 50% probability ellipsoids). Weak contacts between H and Cl atom are represented as dashed lines.

TABLE 2 Crystal and Refinement Data of $GeCl_2 \cdot 2THF$

Crystal system	Monoclinic	$T_{min/max}$	0.3959/0.8648
Space group	$P2_1/c$	$2\theta_{max}$ (°)	60.04
a (Å)	8.463 (2)	Measd. refl.	13090
b (Å)	9.891 (2)	Unique refl.	3438
c (Å)	14.733 (3)	Observed refl	3091
β(°)	105.23 (1)	R_{int}	0.0417
V (Å^3)	1189.9 (4)	Parameters	118
ρ_{calc} (g cm^{-3})	1.606	$R[I > 2\delta(I)]/wR^2$	0.0849/0.1972
Z	4	ρ_{fin} (min/max) (eÅ^3)	−1.615/2.072
μ (mm^{-1})	2.993	CCDC-no.	252126
Temp. (K)	123 (2)		

lengths of 2.90(3) Å (Fig. 3). As these hydrogen bonds are long-range interactions, the acceptor can attract more than one hydrogen atom simultaneously [11]. Their values fit quite well in the range of weak hydrogen bond lengths reported, C—H ··· Cl—Ge 2.81(2)–2.87(2) Å [8,12] and C—H ··· Cl—Sn 2.78–2.90 Å [13].

EXPERIMENTAL

All manipulations were carried out under a dry nitrogen atmosphere with Schlenk techniques using standard double manifolds. THF was distilled and dried over K/Na alloy. A Bruker Apex X-ray diffractometer ($\lambda = 0.71073$ Å) was used to collect the scattering intensities for single crystal structure determination. $GeCl_2 \cdot 2$Dioxane was prepared by a literature method [14].

Preparation of $GeCl_2 \cdot 2THF$

50 mL THF was added to $GeCl_2 \cdot 2$Dioxane (0.3 g, 1.0 mmol) in one portion at ambient temperature and refluxed for 60 min. The obtained clear solution was slowly cooled down to −78°C. After storage at this temperature for 3 days, the colourless crystalline material $GeCl_2 \cdot 2THF$ was formed.

Crystal Structure Analysis

A single crystal of $GeCl_2 \cdot 2THF$ was mounted under inert perfluoropolyether at the tip of a glass fibre and was cooled in the cryostream of the diffractometer. Absorption corrections were applied using the program SADABS [15]. Structure solutions were carried out using direct methods, and the refinements of the structures were undertaken with the program SHELXTL 5.01 [16]. Non-hydrogen atoms were refined with anisotropic thermal displacement parameters, and hydrogen atoms isotropically with a riding model. Further details of data collection and refinement are listed in Table 2. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications (see Table 2). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: (+44)1223-336-033; email: deposit@ccdc.cam.ac.uk].

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