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A Crystalline Diethyl Ether Adduct of Tetrafluorogermane

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Introduction

During our studies of intramolecular interactions between geminal donor and acceptor centers, we have found three-membered-ring structures in aminoxysilanes of the general formula $R_3SiONR'_2$,[1,2] whereby the strongest Si···N interactions were found in $F_3SiONMe_2$.[3] In an attempt to synthesize analogous germanium compounds we were looking for a suitable laboratory scale synthesis of GeF_4 without the necessity of employing either the corrosive hydrogen fluoride (with $Ge(OMe)_4$),[4] the highly reactive agents elemental fluorine, ClF_3 (with elemental Ge),[5] BrF_3 (with GeO_2),[6] or NOF_3 (with elemental Ge),[7] or high temperatures (up to 1000 °C), as required for the decomposition of $BaGeF_6$.[8] It seems highly desirable that a new preparation procedure starts with the readily accessible $GeCl_4$. A way to find suitable synthons for GeF_4 could be to generate a soluble adduct of medium stability, as was achieved for H_2SiCl_2 with its teraethylethylenediamine adduct,[9] which is applied as a synthon for SiH_2Cl_2. However, most amine adducts of GeF_4 and SiF_4 are only sparingly soluble and thus constitute no suitable reagents for syntheses. Ether adducts could be a class of compounds with more favorable properties. Quite a number of them have been synthesized, but many are unstable toward decomposition. Oxirane, for instance, is decomposed by GeF_4 to give 1,4-dioxane and dark purple solids,[10] and $GeF_4(OMe_2)_2$ decomposes already at temperatures as low as −78 °C.[11] Nevertheless, complexes of Me_2O and $(H_2C)_2O$ with GeF_4 have been studied by vibrational spectroscopy using matrix isolation techniques.[12,13]

Results

A facile way for producing small quantities of SiF_4 is the reaction of $SiCl_4$ with SbF_3 in diethyl ether in an evacuated bulb and trap-to-trap fractionation of the volatile products. This reaction does occur not to work satisfactorily for $GeCl_4$ in inert solvents like hexane or toluene under a variety of conditions including temperatures up to 200 °C and under prolonged ultrasonification. Frequently the only volatile fluorinated product obtained under such conditions is SiF_4 formed by the reaction of the reagents with the glassware, and only traces of GeF_4 could be obtained in this way.

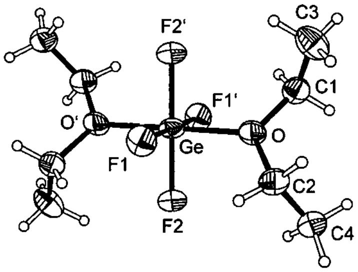

Figure 1. Molecular structure of $GeF_4{\cdot}(OEt_2)_2$ in the crystal as determined by low-temperature X-ray crystallography.

When we carried out a similar reaction using diethyl ether as a solvent, we observed the formation of beautiful large crystals at the glass walls of the reaction vessel above a brown liquid at the bottom. These crystals turned out to be the bis(diethyl ether) adduct of germanium tetrafluoride, as was shown by a crystal structure determination (vide infra). The ether solution also contains this adduct, which is somewhat volatile, but it is almost impossible to separate the ether from GeF_4 in the way described for SiF_4. The condensate always consists of the ether adduct, and only minute quantities of pure GeF_4 can be obtained. At ambient temperature the solid $GeF_4{\cdot}(OEt_2)_2$ is only stable under an atmosphere of Et_2O. Handling under inert gas conditions is therefore difficult, but can be managed if the substance is quickly manipulated under cooling. Although $GeF_4{\cdot}(OEt_2)_2$ is a possible reagent to replace the gaseous GeF_4 in synthesis, the described properties make it difficult to measure exact quantities.

The compound $GeF_4{\cdot}(OEt_2)_2$ is soluble in ethers and hydrocarbon solvents. A ^1H NMR spectrum could be obtained from a solution in benzene-d^6. It shows signals at 1.16 and 3.36 ppm due to the ethyl groups of the coordinate diethyl ether molecules, which are at slightly higher frequencies as compared to noncoordinate ether in benzene (1.10 and 3.25 ppm). A mass spectrum recorded in the CI mode does not allow one to detect the peak of the molecular ion, but does allow one to detect the peaks of the fragments GeF_3^+ and GeF_2^+ at $m/z = 131$ and 112. The absence of impurities of any antimony-containing compounds could be proved on the basis of a total reflection X-ray fluorescence analysis (TRFA), which shows germanium to be the element with the highest atomic weight present in the sample.

The crystal structure of $GeF_4{\cdot}(OEt_2)_2$ was elucidated by X-ray diffraction at low temperature. $GeF_4{\cdot}(OEt_2)_2$ crystallizes in the tetragonal space group $P4_2/n$. Figure 1 shows the structure of the complex, and some selected geometry parameters are listed in Table 1 along with data from quantum chemical calculations for comparison.

The germanium atom is located on a molecular and crystallographic inversion center of the molecule. It is pseudo-octahedrally coordinated by four shorter Ge−F bonds of 1.754(2) and 1.747(2) Å and two longer Ge−O bonds [1.975(2) Å]. The Ge−F bonds in $GeF_4{\cdot}(OEt_2)_2$ are thus considerably longer than in crystalline GeF_4 [1.661(1) Å][14] or gaseous GeF_4 [1.67(3) Å].[15] However, they are similar to those in the 2,2′-

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Table 1. Selected Geometric Parameters for $GeF_4 \cdot (OEt_2)_2$ as Obtained by Low-Temperature Crystallography, by ab Initio and DFT Calculations

	XRD	MP2/6-31G(d)	B3LYP/6-31G(d)
Ge−F(1)	1.754(2)	1.783	1.776
Ge−F(2)	1.747(2)	1.779	1.774
Ge−O	1.975(2)	1.982	2.010
O−C(1)	1.459(4)	1.455	1.455
O−C(2)	1.464(4)	1.455	1.455
O−Ge−F(1)	90.0(1)	90.0	90.0
O−Ge−F(2)	90.0(1)	90.0	90.0
F(1)−Ge−F(2)	89.7(1)	89.9	89.2
Ge−O−C(1)	122.1(2)	121.0	120.8
Ge−O−C(2)	121.8(2)	121.0	120.7
C(1)−O−C(2)	116.1(3)	118.0	118.5

bipyridine adduct of GeF_4 (1.756−1.777 Å) despite the different coordination mode of the latter, where the nitrogen atoms occupy two neighboring sites of a pseudo-octahedral germanium coordination sphere.[16] The Ge−O bonds in $GeF_4 \cdot (OEt_2)_2$ are much shorter than in two intramolecular five-coordinate adducts of organohydridogermanes (2.357 and 2.747 Å), which contain 1-methoxy-naphth-8-yl ligands as oxygen donor functionalities.[17] The oxygen atoms in $GeF_4 \cdot (OEt_2)_2$ are positioned at opposite sites of the octahedron, or, in other words, they are axial ligands. The F−Ge−F and O−Ge−F angles are almost exactly 90°, which shows how near to ideal the coordination geometry of the germanium atom is. The oxygen atoms adopt completely planar coordination geometries, as is obvious from the sum of the valence angles about these centers, which are exactly 360°. These valence angles at oxygen are almost equally distributed, with the smallest being the C−O−C angle of 116.1(3)°.

The structural characterization of the first isolated ether adduct of GeF_4 is important with respect to a recent study about adduct formation of silanes and germanes, which questions the thermodynamic stability of these adducts as free molecules, i.e., if they are not part of a crystal lattice.[18] GeF_4 is said to be a stronger Lewis acid than SiF_4 due to the more facile deformation of the GeF_4 skeleton (not due to the stronger interaction with the donor).[18] This could explain why, in the analogous synthesis of SiF_4, the latter is easily separated from the ether, whereas GeF_4 crystallizes as the diether adduct.

We have carried out ab initio and DFT calculations on $GeF_4 \cdot (OEt_2)_2$ up to the MP2/6-31G(d) and B3LYP/6-31G(d) levels of theory. They consistently predict $GeF_4 \cdot (OEt_2)_2$ to be a minimum on the potential hypersurface. The calculated geometry parameters are given in Table 1. They show not unexpectedly that the MP2 method is better suited to reproduce the length of the Ge−O bond than the DFT method. The value at the MP2/6-31G(d) level is still somewhat longer than found in the crystal structure, but this might be attributed to the general finding that partial polar bonds of Lewis base−acid adducts are driven toward completion upon incorporation of the molecules into the lattices of crystals or other polar media, due to the strengthening of the polar bonds by dipolar interactions with the surroundings.[19] Otherwise the parameters of the calculations are very similar to those found experimentally in the crystal structure, which indicates the absence of pronounced molecular structure deforming forces in the crystal.

Table 2. Crystallographic Data for $GeF_4 \cdot (OEt_2)_2$

$C_8H_{20}F_4O_2Ge$	$M_r = 296.84$
$a = 13.851(2)$ Å	$P4_2/n$ (No. 86)
$b = 13.851(2)$ Å	$T = 143(2)$ K
$c = 6.3120(13)$ Å	$\gamma = 0.71073$ Å
$V = 1210.9(4)$ Å^3	$D_{calc} = 1.628$ g cm^{-3}
$Z = 4$	$\mu = 2.562$ mm^{-1}
	$R1(F_o^2) = 0.0418$ $(F_o > 4\sigma(F_o))^a$
	$wR2(F_o^2) = 0.1214^b$

^{a} $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

Experimental Section

Synthesis. A 2 L bulb was charged with 6.0 g of SbF_3 (34 mmol) and evacuated and its coldfinger immersed in liquid nitrogen. Diethyl ether (30 mL) was condensed into the bulb followed by 4.3 g of $GeCl_4$ (20 mmol). The mixture was allowed to warm to ambient temperature and left overnight, while the solution turned brown and a considerable amount of crystals formed on the glass wall. These crystals were quickly removed using a spoon spatula while the glass wall was cooled to −78 °C.

^{1}H NMR (C_6D_6, 21 °C): $\delta = 1.16$ (t, $^3J_{HCCH} = 7$ Hz), 3.36 ppm (q, $^3J_{HCCH} = 7$ Hz). MS (CI): $m/z = 131, 112$.

Crystal Structure Determination of $GeF_4 \cdot (OEt_2)_2$. Single crystals of $GeF_4 \cdot (OEt_2)_2$ were quickly removed from the diethyl ether atmosphere at dry ice temperature and immersed in Fomblin perfluoropolyether oil at ca. −40 °C. A suitable crystal was selected and transferred at dry ice temperature to a Nonius Turbo-CAD4 diffractometer. Structure solution and refinement were undertaken with the program SHELXTL 5.01.[20] Further details are listed in Table 2.

Ab Initio Calculations. Ab initio molecular orbital calculations were carried out using the Gaussian 94 program.[21] Geometry optimizations were performed at the SCF, B3LYP, and MP2 levels of theory. Calculations were undertaken at the SCF level using the standard 3-21G-(d) and 6-31G(d) basis sets, while the larger basis set was used for calculations at the B3LYP and MP2 levels of theory. The nature of the stationary points was checked by vibrational frequency calculations up to the B3LYP/6-31G(d) level of theory.

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Supporting Information Available: Tables listing detailed crystallographic data, atomic positional parameters, and bond lengths and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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