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The Structure of 1-(Trifluoromethyl)germatrane

Reint Eujen[*], **Achim Roth,** and **David J. Brauer**

Fachbereich 9 – Anorganische Chemie, Universität-GH Wuppertal, D-42097 Wuppertal, Germany

Summary. 1-(Trifluoromethyl)germatrane ($CF_3Ge(OCH_2CH_2)_3N$) has been prepared from $CF_3Ge(OCH_3)_3$ and triethanolamine and characterized by NMR, vibrational, and mass spectroscopy. The compound crystallizes in the monoclinic space group $P2_1/n$ with $a = 785.73(6)$, $b = 1257.8(1)$, $c = 999.92(9)$ pm, $\beta = 90.871(7)°$, and $Z = 4$. The equatorial Ge–O bond lengths of the almost perfect trigonal bipyramid average to 178.7(3) pm, whereas the axial Ge–C bond length is 200.6(2) pm. The transannular Ge–N contact (210.8(2) pm) is considerably shorter than in other organylgermatranes.

Keywords. Germanium; Germatrane; Trifluoromethyl compounds.

Die Struktur von 1-(Trifluoromethyl)germatran

Zusammenfassung. 1-(Trifluormethyl)germatran ($CF_3Ge(OCH_2CH_2)_3N$) wurde aus $CF_3Ge(OCH_3)_3$ und Triethanolamin gewonnen und durch NMR-, Schwingungs- und Massenspektroskopie charakterisiert. Die Verbindung kristallisiert in der monoklinen Raumgruppe $P2_1/n$ mit $a = 785.73(6)$, $b = 1257.8(1)$, $c = 999.92(9)$ pm, $\beta = 90.871(7)°$ und $Z = 4$. Die equatorialen Ge–O-Abstände der nahezu perfekten trigonalen Bipyramide betragen im Schnitt 178.7(3) pm, der axiale Ge–C-Abstand 200.6(2) pm. Der transannulare Ge–N-Kontakt (210.8(2) pm) ist beträchtlich kürzer als in anderen Organylgermatranen.

Introduction

Recently we have reported about the synthesis and structure of 1-(trifluoromethyl)silatrane [1]. Its most interesting structural feature is the transannular Si–N contact of 202.4 pm which is considerably shorter than that of other organylsilatranes and which closely resembles that of the 1-chloro- or 1-fluorosilatrane. We now extend this work to the corresponding germatrane, $CF_3Ge(OCH_2CH_2)_3N$. The synthesis of this compound has been reported before [2] along with some spectroscopic data, but no structural information is available. As for silatranes, germatranes have been studied with respect to their biological activity and structural characteristics. The Ge–N contact is usually considered to reflect the electronic influence of the substituent on the germanium atom and is found to vary between 216 and 224 pm for alkyl- or aryl-germatranes [3–6], whereas it is somewhat shorter in *O*-bonded derivatives (210–215 pm [7, 8]),

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[*] Corresponding author

1-bromogermatrane (209 pm [6]), or 1-isothiocyanatogermatrane (208 pm [9]). A surprinsingly short Ge–N distance of 201 pm has recently been reported for 1-fluorogermatrane [10].

Results and Discussion

1-(Trifluoromethyl)germatrane has been obtained from $CF_3Ge(OCH_3)_3$ and triethanolamine in tetrahydrofurane according to Eq. (1).

$$CF_3Ge(OCH_3)_3 + N(CH_2CH_2OH)_3 \xrightarrow[-CH_3OH]{THF/RT} CF_3Ge(OCH_2CH_2)_3N \qquad (1)$$

Recrystallization from methanol or acetone gave colourless crystals which are stable in air and insoluble in non-polar solvents, but readily soluble in polar solvents like dimethylformamide, dimethylsulfoxide, or N-methylpyrrolidone. The thermal stability is higher than that of the silatrane. Crystals decompose without melting in two exothermic steps, the first occurring at 245°C with loss of *ca*. 19% of its weight (loss of CF_2: 17.4%), the second starting at 335°C leading to complete degradation. Heating to 250° gives 1-fluorogermatrane which was clearly identified by NMR spectroscopy due to characteristic fluorine couplings [10] (^{1}H(acetone-d$_6$): $\delta = 3.80$ (t, 5.7 Hz; d, 1.5 Hz), 3.06 (t, 5.7 Hz) ppm; ^{19}F: $\delta = -153.8$ ppm (Ge isotope shift: 1.4 ppb/mass unit); ^{13}C: $\delta = 58.4$ (d, 1.0 Hz), 53.0 ppm.

Spectra

The NMR data of 1-(trifluoromethyl)germatrane using *DMSO*-d$_6$ as solvent (^{1}H: $\delta(OCH_2) = 3.71$ ppm, $\delta(NCH_2) = 2.97$ ppm, $^3J(HH) = 5.7$ Hz; ^{13}C: $\delta(OCH_2) = 56.1$ppm, $\delta(NCH_2) = 50.6$ ppm, $\delta(CF_3) = 131.2$ ppm, $^1J(CF) = 341.8$ Hz; ^{19}F: $\delta(CF_3) = -60.5$ ppm) are in good agreement with those reported for acetone solution [1].

The mass spectrum is dominated by peaks with the characteristic germanium isotope pattern. The base peak ($C_6H_{12}NO_3Ge^+$, $m/z = 220$) is formed by loss of the CF_3 group from the molecular ion ($m/z = 289$; 50%). Further peaks are constituted by loss of CH_2O moieties: $[M\text{-}CH_2O]^+$, $m/z = 259$ (40%); $[M\text{-}CF_3\text{-}CH_2O]^+$, $m/z = 190$ (94%); $[M\text{-}CF_3\text{-}2\,CH_2O]^+$, $m/z = 160$ (84%).

The infrared and *Raman* spectra show the characteristics of both the CF_3 group and an atrane. The modes of the CF_3 group ($\nu_s(CF_3) = 1067$ (IR, vs) $\nu_{as}(CF_3) = 1023$ (IR, vs), $\delta_s(CF_3) = 716$ (IR, m/*Ra*, m), $\delta_{as}(CF_3) = 520$ (*Ra*, w)cm^{-1}) are hardly shifted with respect to the silatrane. In contrast, the a_1 skeleton frequencies of the germatrane are lowered by *ca*. 10 to 50 cm^{-1}, the strongest *Raman* lines being at 613 and 545 cm^{-1}. The Ge-CF_3 stretch is assigned to a *Raman* line at 270 cm^{-1} which is somewhat lower than ν(Ge–CF_3) in $CF_3Ge(CH_3)_3$ (292 cm^{-1} [[11]).

Crystal structure

Crystals of 1-trifluoromethylgermatrane are isomorphous with those of its silicon homologue. The structure of the germatrane is shown in Fig. 1, and selected bond

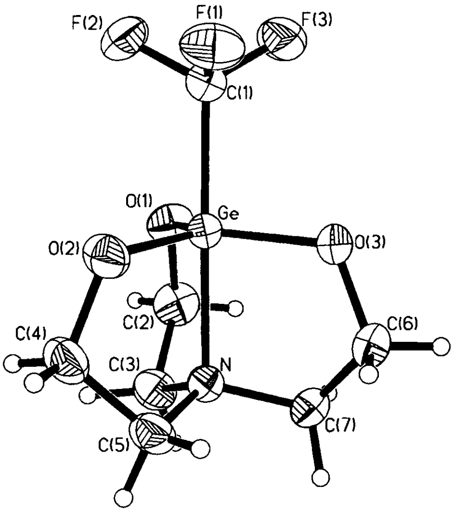

Fig. 1. A perspective drawing of 1-(trifluoromethyl)germatrane with 50% probability thermal ellipsoids for the non-hydrogen atoms

Table 1. Bond lengths (pm) and angles (°) for 1-(trifluoromethyl)germatrane

Ge–C(1)	200.6(2)	F(1)–C(1)	135.6(2)
Ge–N	210.8(2)	F(2)–C(1)	135.5(2)
Ge–O(1)	178.59(13)	F(3)–C(1)	134.6(2)
Ge–O(2)	178.99(14)	O(1)–C(2)	142.2(2)
Ge–O(3)	178.51(13)	O(2)–C(4)	142.8(2)
N–C(3)	147.7(3)	O(3)–C(6)	142.6(2)
N–C(5)	147.9(3)	C(2)–C(3)	152.0(3)
N–C(7)	147.8(3)	C(4)–C(5)	151.6(3)
		C(6)–C(7)	151.2(3)
O(1)–Ge–O(2)	118.16(7)	C(1)–Ge–N	179.18(7)
O(1)–Ge–O(3)	120.24(7)	Ge–N–C[a]	104.4(2)
O(2)–Ge–O(3)	120.02(7)	C–N–C[a]	114.0(4)
O(1)–Ge–C(1)	94.63(7)	Ge–O–C[a]	116.0(3)
O(2)–Ge–C(1)	94.44(7)	Ge–C–F[a]	113.6(6)
O(3)–Ge–C(1)	93.50(7)	F–C–F[a]	105.0(2)
O(1)–Ge–N	85.84(6)	O–C–C[a]	109.9(2)
O(2)–Ge–N	85.93(6)	N–C–C[a]	107.7(2)
O(3)–Ge–N	85.68(6)		

[a] Average angle with the standard deviation defined as the larger one of the estimates derived from the spread and from the mean value

distances and angles are listed in Table 1. No crystallographic symmetry being imposed on the molecule, the structural parameters deviate only slightly from ideal C_3 symmetry. For example, the largest deviation is the small 2.0° spread of the O–Ge–O angles; because a similar variation was found for the O–Si–O angles of the silatrane, the distortion is likely to be due to packing forces. The CF_3 group of

Table 2. Atomic coordinates and equivalent isotropic displacement parameters (pm^2) for 1-(trifluoromethyl)germatrane

	x	*y*	*z*	*U*(eq)[a]
Ge	0.05412(2)	0.10480(2)	0.25395(2)	247(1)
N	0.2607(2)	−0.00213(13)	0.2546(2)	282(3)
F(1)	−0.26216(15)	0.18220(12)	0.15770(14)	500(4)
F(2)	−0.1020(2)	0.30786(10)	0.23329(14)	475(3)
F(3)	−0.2315(2)	0.20526(12)	0.36913(13)	522(4)
O(1)	0.1833(2)	0.18491(11)	0.36247(14)	361(3)
O(2)	0.0860(2)	0.11488(12)	0.07755(14)	389(3)
O(3)	−0.0659(2)	−0.00315(11)	0.3199(2)	363(3)
C(1)	−0.1446(2)	0.2049(2)	0.2542(2)	332(4)
C(2)	0.3344(3)	0.1363(2)	0.4133(2)	409(5)
C(3)	0.4049(2)	0.0597(2)	0.3104(2)	377(5)
C(4)	0.2368(3)	0.0658(2)	0.0289(2)	401(5)
C(5)	0.2799(3)	−0.0314(2)	0.1124(2)	370(5)
C(6)	0.0159(3)	−0.1043(2)	0.3215(2)	394(5)
C(7)	0.2057(3)	−0.0902(2)	0.3417(2)	369(5)

[a] *U*(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor

the germatrane is not exactly staggered with respect to the GeO_3 fragment but is rather rotated about its Ge–C bond by 12.3(6)° away from this arrangement (cf. the 9.4(2)° displacement in the silatrane).

The germatrane possesses the expected trigonal-bipyramidal structure with an essentially linear C(1)-Ge–N fragment (179.18(7)°). Undoubtedly the high electronegativity of the CF_3 group leads to a Ge–N separation (210.8(2) pm) which is markedly shorter than the values found for this linkage in other organogermatranes (216.0(2) [4] – 224 pm [6]). The strength of this interaction is further underscored by the relatively small displacement of the Ge atom (13.0(1) pm) from the plane defined by the oxygen atoms; for example, displacements between 19 and 27 pm are reported for other carbyl substituted germatranes [4, 6]. While the Ge–N contact is similar to those of the bromo or thiocyanato derivatives, it is much longer than the distance reported for the 1-fluorogermatrane (201 pm [10]). A closer inspection of this structure reveals some unusual features such as a variation of 8 pm within both the O–C and C–N bond distances, an unusual large equivalent isotropic thermal parameter for the fluorine atom, and an unexpectedly large standard deviation for the absolute structure parameter. All these evidences suggest that this structure should be confirmed.

Experimental

Chemicals were obtained from commercial sources and used without further purification. *Raman* spectra were measured on a Cary 82 spectrometer with Kr^+ excitation at 647.1 nm. Infrared spectra were recorded with a Bruker IFS 25 spectrometer as KBr pellets. Combined calorimetric and thermogravimetric analyses (DSC/TGA) were performed with a simultaneous DSC/TG instrument (Netzsch STA 409). NMR spectra were recorded with a Bruker AC 250 instrument (^1H, 250.13 MHz;

^{19}F, 235.36 MHz; ^{13}C, 62.90 MHz; ^{29}Si, 49.69 MHz) and referenced to internal *DMSO*-d_6 at 2.58 ppm (^{1}H) and 39.50 ppm (^{13}C), external *TMS* (^{29}Si) and $CFCl_3$ (^{19}F), corrections being made for the shift of the lock substance.

(Trifluoromethyl)trimethoxygermane

To CF_3GeCl_3, three equivalents of methanol were added at −30°C. The mixture was warmed to ambient temperature and stirred for 3 h. The product was purified by fractional condensation.

NMR: ^{1}H: 4.78 ppm; ^{13}C: 125.2 ppm (q, $^{1}J(CF) = 335.7$ Hz), 52.5 ppm; ^{19}F: −61.4 ppm.

1-(Trifluoromethyl)germatrane

To 1.2 g (5.0 mmol) of $CF_3Ge(OCH_3)_3$ in 5 ml of *THF*, 0.75 g of $N(CH_2CH_2OH)_3$ (5.0 mmol) in 3 ml of *THF* were added dropwise. The reaction mixture was stirred for 2 h at ambient temperature. The white precipitate was filtered off and recrystallized from methanol yielding 0.8 g (55%) of 1-(trifluoromethyl)germatrane.

Raman (solid)/IR (KBr pellet): 2996(m)/2993(m), 2951(s)/2947(m), 2890(s)/2885, 2876(s), 1486(s)/1489(m), 1456(m)/1451(s), 1277(s)/1280, 1270(m), 1249(m)/1246(m), 1197(m)/1196(s), 1167(w)/1163(w), 1098(w)/1105(s), 1067(m)/1067(vs), 1042(w)/1039, 1023(s), 933(m)/933(m), 900(w)/905, 896(m), 870(w)/871, 864(w), 716(m)/-, -/646, 637(s), 613(s)/614(s), 600(sh)/600(s), 546(s)/545(m), 522(w)/-, 421(w)/419(w), 327(m)/-, 270(s)/-, 220(s)/-, 245(vw)/-, 178(s)/- cm^{-1}.

X-Ray structural investigation

Crystals of (trifluoromethyl)germatrane were grown from a solution in methanol, and a specimen with the dimensions 0.15×0.29×0.32 mm was glued to a glass fiber. X-Ray measurements were performed at 22°C with a Siemens P3 diffractometer equipped with a graphite monochromator and employing MoK_α radiation. The compound crystallizes in the monoclinic space group $P2_1/n$ with $a = 785.73(6)$, $b = 1257.8$, $c = 999.92(9)$ pm, $\beta = 98.871(7)°$, $Z = 4$, and $D_{calc} = 1.934\ g \cdot cm^{-3}$. A quadrant of data ($hkl$, $\bar{h}kl$, $5° \leq 2\theta \leq 60°$) was collected by the θ–2θ scan technique. The intensities were derived by profile analysis, corrected for the small fluctuations (±1%) of the three periodically monitored standards, and by integration for absorption (transmission: 0.4527–0.6915) and converted into structure factor amplitudes. Of the 3033 intensities measured, 2889 are unique; 2185 of them have $I > 2\sigma(I)$. The structure was solved by direct methods and refined conventionally with anisotropic and isotropic temperature factors, respectively, for the non-hydrogen and hydrogen atoms which were placed geometrically. The refinement on F^2 of the 149 parameters, which included an extinction correction, converged with a conventional residual $R_1 = 0.025$ for the observed reflections and a weighted residual $(F^2)wR_2 = 0.058$ for all reflections. The final difference density map contains features between 0.46 and $-0.46\ e \cdot Å^{-3}$ and confirms the structure. Coordinates of the non-hydrogen atoms are listed in Table 2 [12]. Direct methods, least-squares refinement, and the ORTEP drawing were made with the SHELXTL program package (Version 5.03).

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[12] Further crystallographic details may be obtained from Cambridge Crystallographic Data Centre under the deposition number CCDC-116151.

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