

TRIS- AND TETRAKIS-(TRIFLUOROMETHYL)FLUOROGERMANATES; THE STRUCTURE OF AN ANION WITH PENTACOORDINATED GERMANIUM

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Summary

Reactions of $(\text{CF}_3)_3\text{GeX}$ ($X = \text{halogen}$) or $(\text{CF}_3)_4\text{Ge}$ with fluoride ions in aqueous or acetonitrile solutions give the trigonal-bipyramidal $(\text{CF}_3)_3\text{GeF}_2^-$ and octahedral *fac*- $(\text{CF}_3)_3\text{GeF}_3^{2-}$ or *cis*- $(\text{CF}_3)_4\text{GeF}_2^{2-}$ anions, respectively. The crystal structure of $[(\text{CH}_3)_4\text{N}][(\text{CF}_3)_3\text{GeF}_2]$ has been determined. The symmetry of the anion (C_s) approximates to C_{3v} , with axial F atoms ($r_{\text{av}}(\text{GeF})$ 1.835(8) Å) and equatorial CF_3 groups ($r_{\text{av}}(\text{GeC})$ 2.000(5) Å) (both distances corrected for libration). The bonding in the anion is discussed on the basis of structural and vibrational spectral data. The configurations of the octahedral complexes have been deduced from their ^{19}F NMR spectra.

Introduction

Pentacoordination is uncommon in germanium chemistry. Most such pentacoordinate species contain chelating ligands and possess geometries between trigonal-bipyramidal and square-pyramidal [1] or display internal coordination via N [2], O [3] or S atoms [4]. Internal Ge–N coordination is also found for some germatranes [5], whereas the trimethylamine adduct of GeCl_4 represents an example of an almost ideal trigonal-bipyramid [6]. The geometry of the structural analogue of SiF_5^- , monomeric GeF_5^- , has been deduced only from vibrational spectra [7], since most structures with a GeF_5^- stoichiometry contain bridged octahedral geometries.

With the highly electronegative CF_3 group as a substituent, the Lewis acid character of the central germanium atom is conserved. The bulk of the CF_3 unit, however, leads to the expectation that pentacoordination might be favored for germanes containing several CF_3 groups; octahedral fluoro complexes have, in fact, been observed upon fluoride addition to CF_3GeF_3 or $(\text{CF}_3)_2\text{GeF}_2$, whereas with $(\text{CF}_3)_3\text{GeF}$ the ^{19}F NMR spectrum is in accord with a pentacoordinated $(\text{CF}_3)_3\text{GeF}_2^-$ anion with the fluorines in the axial positions [8]. In extension of this

work we report on the crystal structure of pentacoordinated $(\text{CF}_3)_3\text{GeF}_2$ as well as ^{19}F NMR spectroscopic evidence for the structures of hexacoordinated $(\text{CF}_3)_3\text{GeF}_3^{2-}$ and $(\text{CF}_3)_4\text{GeF}_2^{2-}$.

The molecular structures of these complexes are also of great interest with respect to the nature of the Ge-C bond. In general, long M-C distances have been reported for M-CF₃ units where M is an electropositive main group element [9]. For example, the Ge-C bond in $\text{Ge}(\text{CF}_3)_4$ is lengthened by 0.044 Å compared with that in $\text{Ge}(\text{CH}_3)_4$ [10] despite the electron withdrawing power of the fluorine atoms, an effect which is ascribed to the Coulomb repulsion between the positively-charged carbon and germanium atoms. Such a repulsive interaction might be reduced in anionic species, since in such cases the charge on the germanium atom should be less positive and might even become negative. Alongside the general bond-lengthening effect associated with complexation a compensating bond-shortening contribution might be expected.

Experimental

The compounds $(\text{CF}_3)_3\text{GeI}$, $(\text{CF}_3)_3\text{GeCl}$ and $(\text{CF}_3)_4\text{Ge}$ were prepared as described previously [11]. Acetonitrile was refluxed and redistilled from P_2O_{10} . Potassium fluoride was dried in vacuo at 400°C for several hours and treated with 1 atm of SiH_3Br .

^{19}F NMR spectra were recorded on a Varian EM 390 spectrometer operating at 84.67 MHz, chemical shifts referring to internal CFCl_3 . Raman spectra were obtained with a Cary 82 instrument equipped with a Kr^+ laser (647.1 nm, 200 mW at the sample). Infrared spectra were recorded on a Perkin-Elmer PE 580B spectrometer.

Tetramethylammonium difluoro-tris(trifluoromethyl)germanate, $[(\text{CH}_3)_4\text{N}][(\text{CF}_3)_3\text{GeF}_2]$

$(\text{CF}_3)_3\text{GeCl}$ was treated with excess of concentrated aqueous NaF solution. The water was removed in vacuo and the residue extracted with ethanol. Evaporation of the extract gave $\text{Na}[(\text{CF}_3)_3\text{GeF}_2] \cdot \text{H}_2\text{O}$. Treatment with $[(\text{CH}_3)_4\text{N}]\text{Cl}$ in ethanol then gave $[(\text{CH}_3)_4\text{N}][(\text{CF}_3)_3\text{GeF}_2]$, which crystallized as colorless needles.

Potassium trifluoro-tris(trifluoromethyl)germanate, $\text{K}_2[(\text{CF}_3)_3\text{GeF}_3]$ and potassium difluoro-tetrakis(trifluoromethyl)germanate, $\text{K}_2[(\text{CF}_3)_4\text{GeF}_2]$

A suspension of carefully dried KF (2 g) in CH_3CN was stirred for 5 min with 1 mmol of $(\text{CF}_3)_3\text{GeCl}$ or $(\text{CF}_3)_4\text{Ge}$. The solution was filtered in vacuo and evaporated to form white $\text{K}_2[(\text{CF}_3)_3\text{GeF}_3]$ or $\text{K}_2[(\text{CF}_3)_4\text{GeF}_2]$.

X-Ray structural analysis

A needle-shaped crystal ($0.15 \times 0.20 \times 1.16$ mm) of $[(\text{CH}_3)_4\text{N}][(\text{CF}_3)_3\text{GeF}_2]$ was sealed in a glass capillary under argon. The orthorhombic space groups consistent with the symmetry and systematic absences revealed by Weissenberg photographs were $Pnma$ and $Pn2_1a$, and the former was confirmed by the refinement. Crystal data determined at 23°C with a Siemens AED I diffractometer employing Zr-filtered $\text{Mo-K}\alpha$ radiation (λ 0.71073 Å) are a 13.964(3), b 10.877(2), c 9.402(1) Å, $Z = 4$ and $d_x = 1.822$ g/cm³.

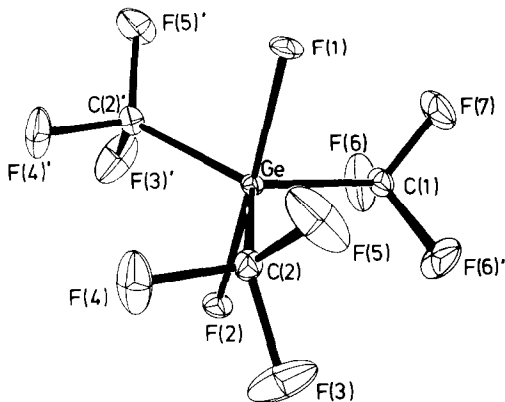
TABLE 1

 POSITIONAL AND ISOTROPIC OR EQUIVALENT ISOTROPIC THERMAL ^a PARAMETERS FOR [(CH₃)₄N][(CF₃)₃GeF₂]

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i>
Ge	0.25659(4)	0.7500	0.19306(7)	0.0540(2)
F(1)	0.3253(3)	0.7500	0.3555(5)	0.093(2)
F(2)	0.1924(3)	0.7500	0.0252(4)	0.092(2)
F(3)	0.2547(5)	0.5154(7)	0.074(2)	0.192(6)
F(3A)	0.281(2)	0.503(3)	0.194(4)	0.08(1)
F(4)	0.3865(5)	0.5981(5)	0.054(1)	0.138(3)
F(4A)	0.401(2)	0.579(3)	0.165(4)	0.09(1)
F(5)	0.347(1)	0.5255(7)	0.2468(8)	0.192(5)
F(5A)	0.307(2)	0.566(3)	0.004(3)	0.08(1)
F(6)	0.0824(5)	0.6542(9)	0.2714(9)	0.203(5)
F(6A)	0.122(2)	0.843(3)	0.385(3)	0.09(1)
F(7)	0.1431(6)	0.7500	0.4367(8)	0.148(6)
F(7A)	0.060(3)	0.7500	0.227(4)	0.07(1)
N	0.4580(4)	0.7500	0.6721(5)	0.052(2)
C(1)	0.1341(6)	0.7500	0.298(1)	0.091(4)
C(2)	0.3137(5)	0.5895(6)	0.1392(7)	0.080(2)
C(3)	0.5216(6)	0.7500	0.7978(8)	0.088(3)
C(4)	0.3558(6)	0.7500	0.7177(9)	0.086(4)
C(5)	0.4769(4)	0.6386(5)	0.5835(5)	0.079(2)

^a $U = \frac{1}{3} \sum_i U_{ii}$ for anisotropically refined atoms.

Intensity data (hkl , $4^\circ \leq 2\theta \leq 65^\circ$) were collected by the 2θ - ω step-scan technique as described previously [12]. The data were corrected for coincidence losses, the slow decay (4.5%) of standard reflections checked hourly, and absorption (μ 22.2 cm⁻¹, transmission 0.617 and 0.733). Of the 2697 unique reflections measured, only 1169 with $|F_o| \geq 4\sigma(|F_o|)$ were deemed “observed” and used in the refinement.


 Fig. 1. A perspective drawing of the anion in [(CH₃)₄N][(CF₃)₃GeF₂].

The structure was solved by the heavy atom method and refined by full-matrix least squares techniques. Following anisotropic refinement of the non-hydrogen atoms, the residual electron density in a difference Fourier map suggested a second orientation of low occupancy for each CF_3 group as well as the positions of the hydrogen atoms. With the latter introduced at ideal positions (C-H 0.95 Å, H-C-H 109.5°, staggered), the positional and isotropic thermal parameters of the new fluorine atoms along with appropriately constrained occupancy factors were also refined. Refinement converged, $|S'/\sigma|_{\text{max}} = 0.59$, at $R = \sum \|F_o\| - |F_c| \| / \sum |F_o| = 0.055$ and $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2} = 0.061$ where $w = (\sigma^2(|F_o|) + 0.0004|F_o|^2)^{-1}$. Densities in the final difference Fourier synthesis ranged from 0.63 to $-0.37 \text{ e}/\text{Å}^3$ and are of no chemical significance. Positional parameters are given in Table 1, the numbering scheme of the anion being defined in Fig. 1. Similar degrees of disorder (0.86(2): 0.14(2)) are found for both crystallographically independent CF_3 groups, and the fluorine atoms of low occupancy are designated with an "A". SHELX-76 [13], ORTEP-II [14] and local programs were used in the calculations [15].

Description of the crystal structure

The crystals are composed of discrete $[(\text{CH}_3)_4\text{N}]^+$ cations and $[(\text{CF}_3)_3\text{GeF}_2]^-$ anions. Interionic contacts are not unusual, the shortest being F(1)–H(5C) ($1/2 + x$, $1 - y$, $1/2 + z$) 2.40 Å. Each cation is surrounded by a nearly cubic array of eight anions but the arrangement of eight anions about each cation is much less regular. Both ions are located on crystallographic mirror planes. These planes pass through N, C(3), H(3B), C(4) and H(4B) of the cation and Ge, F(1), F(2), C(1), F(7) and F(7A) of the anion.

Bond distances and angles are tabulated in Tables 2 and 3. The CF_3 groups containing the F atoms of low occupancy are related to those in the dominant configuration by a rotation of $\sim 60^\circ$ about the Ge–C bonds. Examination of intermolecular distances reveals that the volume occupied by the anion is sufficiently large to accommodate both rotamers. Because of the low precision obtained for the "A" coordinates they are not considered in the discussion below.

The Ge atom is trigonal-bipyramidally coordinated, with F(1) and F(2) in axial positions and C(1), C(2) and C(2)' in equatorial positions. The thermal parameters of these six atoms are well fitted by a TLS rigid-body-motion model [16]. Since the

TABLE 2
SELECTED BOND DISTANCES (Å) IN $[(\text{CH}_3)_4\text{N}][(\text{CF}_3)_3\text{GeF}_2]^-$

Ge–F(1)	1.804(4)	C(1)–F(6A)	1.31(3)
Ge–F(2)	1.815(4)	C(1)–F(7A)	1.23(4)
Ge–C(1)	1.975(9)	C(2)–F(3A)	1.16(3)
Ge–C(2)	1.985(6)	C(2)–F(4A)	1.25(3)
C(1)–F(6)	1.291(8)	C(2)–F(5A)	1.30(3)
C(1)–F(7)	1.31(1)	N–C(3)	1.478(9)
C(2)–F(3)	1.302(9)	N–C(4)	1.489(7)
C(2)–F(4)	1.299(7)	N–C(5)	1.494(6)
C(2)–F(5)	1.314(9)		

* These values have not been corrected for librational shortening.

TABLE 3
SELECTED BOND ANGLES ($^{\circ}$) IN $[\text{Me}_4\text{N}][(\text{CF}_3)_3\text{GeF}_2]$

F(1)–Ge–F(2)	177.4(2)	Ge–C(2)–F(5)	114.3(5)
F(1)–Ge–C(1)	92.2(3)	Ge–C–F(A) ^b	115(1)
F(1)–Ge–C(2)	90.2(2)	F(6)–C(1)–F(6)'	107.5(9)
F(2)–Ge–C(1)	90.4(3)	F(6)–C(1)–F(7)	104.3(7)
F(2)–Ge–C(2)	88.6(2)	F(3)–C(2)–F(4)	104.5(7)
C(1)–Ge–C(2)	118.4(2)	F(3)–C(2)–F(5)	104.9(8)
C(2)–Ge–C(2) ^a	123.2(3)	F(4)–C(2)–F(5)	103.6(7)
Ge–C(1)–F(6)	112.8(6)	F(A)–C–F(A) ^b	103(1)
Ge–C(1)–F(7)	114.5(7)	C(3)–N–C(4)	110.2(6)
Ge–C(2)–F(3)	114.2(5)	C(3)–N–C(5)	109.8(4)
Ge–C(2)–F(4)	114.1(5)	C(4)–N–C(5)	109.3(4)
		C(5)–N–C(5)'	108.4(5)

^a x' , y' , $z' = x$, $1.5 - y$, z . ^b These are averaged bond angles involving the fluorine atoms of low occupancy.

librational corrections to the Ge–F and Ge–C bond lengths are statistically significant, corrected values are used in the following discussion. The mean Ge–F bond distance, 1.835(8) Å, agrees excellently with those *trans* F in *cis*- $[(\text{CF}_3)_2\text{GeF}_4]^{2-}$, corrected 1.835(2) Å [8]. Although the Ge–F bonds in these anions are more than 0.1 Å longer than those determined in the gas phase for $(\text{CF}_3)_2\text{GeF}_2$, 1.697(3) Å [17], the mean Ge–C distance in $[(\text{CF}_3)_3\text{GeF}_2]^-$, 2.000(6) Å, agrees well with the gas phase value for $(\text{CF}_3)_4\text{Ge}$, 1.989(5) Å [10], and $(\text{CF}_3)_2\text{GeF}_2$, 2.000(5) Å [17], but is significantly shorter than those in *cis*- $[(\text{CF}_3)_2\text{GeF}_4]^{2-}$, corrected 2.051(4) Å [8].

Depending on the orientation of the CF_3 groups, the highest possible symmetry for the $[(\text{CF}_3)_3\text{GeF}_2]^-$ anion is not trigonal-bipyramidal D_{3h} but either C_{3h} or C_{3v} . In the solid state the symmetry is lower (C_s), and only roughly approximates to C_{3v} . The F(1)–Ge–F(2) bond angle, 177.4(2) $^{\circ}$, is slightly non-linear, a distortion which tilts the Ge–F(1) bond further away from the C(1)–F(7) bond with which it is eclipsed. The C(1)–Ge–C(2) bond angle, 118.4(2) $^{\circ}$, is smaller than that across the mirror plane (i.e., C(2)–Ge–C(2) 123.2(3) $^{\circ}$). On the other hand, the C(1), C(2), C(2)' and Ge atoms all lie within 0.02 Å of the trigonal plane.

As can be seen from Fig. 1, each GeCF_3 fragment exhibits large torsional amplitudes about its Ge–C bond. Rigid-body-motion calculations yield librationaly-corrected average C–F distances of 1.397(6) Å. Since the corrections are large (0.1 Å), they should not be accepted uncritically. While corrected distances found in crystal structures of *cis*- $[(\text{CF}_3)_2\text{GeF}_4]^{2-}$ [8] and $(\text{CF}_3)_3\text{GeMn}(\text{CO})_5$ [18] are not significantly shorter (1.39(1) and 1.38(1) Å, respectively), much shorter C–F bond lengths were found in the gas phase for $(\text{CF}_3)_4\text{Ge}$, 1.330(2) Å [10], and $(\text{CF}_3)_2\text{GeF}_2$, 1.336(2) Å [17]. The larger C–F distances are, however, in accord with the averaged C–F stretch frequencies, which are red-shifted by ca. 40 cm^{-1} with respect to $(\text{CF}_3)_4\text{Ge}$ [19] or $(\text{CF}_3)_2\text{GeF}_2$ [20]. Furthermore, the mean F–C–F angle, 104.7(4) $^{\circ}$, found here is closer to those for *cis*- $[(\text{CF}_3)_2\text{GeF}_4]^{2-}$, 103.8(3) $^{\circ}$ [8], and $(\text{CF}_3)_3\text{GeMn}(\text{CO})_5$, 105.2(8) $^{\circ}$ [18], than to the larger values for $(\text{CF}_3)_4\text{Ge}$, 108.3(3) $^{\circ}$ [10], and $(\text{CF}_3)_2\text{GeF}_2$, 108.6(3) $^{\circ}$ [17]. Since the C–F distances tend to increase as the F–C–F angles decrease [21], the changes in trends in the bond angles are consistent with the variations in the bond distances.

Results and discussion

Upon treatment with F^- in aqueous solution $(CF_3)_3GeX$ ($X = \text{halogen}$) forms a stable complex anion, $[(CF_3)_3GeF_2]^-$, the structure of which may be described as an almost ideal trigonal bipyramid with equatorial Ge-C and axial Ge-F bonds (Fig. 1). The Ge-CF₃ bond length shows no simple correlation with the coordination number of the Ge; for example, shorter distances are found in the pentacoordinated anion $[(CF_3)_3GeF_2]^-$ than in either the tetracoordinated species of $(CF_3)_3GeMn(CO)_5$, corrected 2.024(4) Å [18], or the hexacoordinated anion $[(CF_3)_2GeF_4]^{2-}$ (vide supra). Instead, this distance seems to reflect the effective charge of the Ge atom. Increase in its electron density should (1) increase the effective covalent radius of the germanium atom and (2) lead to Ge-C bond strengthening by decreasing the Coulomb repulsion present in uncharged species such as $(CF_3)_4Ge$. For the pentacoordinated anion the two effects seem approximately to cancel out, whereas the additional negative charge of the dianion $[(CF_3)_2GeF_4]^{2-}$ will contribute to the first but only slightly to the second effect. The comparatively long distance in the pentacarbonyl manganese derivative is associated with an ionic contribution of $(CF_3)_3Ge^- Mn(CO)_5^+$ in the VB description [18]. Indeed, a very weak Ge-C bond with an extrapolated length of 2.12 Å has been indicated by vibrational data for the $(CF_3)_3Ge^-$ anion [22].

A greater variation is found in the Ge-F distances, which are very similar in the $(CF_3)_3GeF_2^-$ and *cis*- $(CF_3)_2GeF_4^{2-}$ anions but much longer than those in the GeF_6^{2-} moiety, e.g. 1.72(1) Å in $(NH_4)_2GeF_6$ [23], 1.77 Å in K_2GeF_6 [24], or 1.785(3) Å in $(SF_3)_2GeF_6$ [25].

In this context, a simple bonding scheme which distributes the four Ge valencies of these $[(CF_3)_nGeF_m]^{4-n-m}$ compounds so that totals of n and $4-n$ are found in the Ge-C and Ge-F linkages, respectively, must be considered. This scheme assigns valencies of 1, 0.67, 0.5 and 0.5 to the Ge-F bonds of $(CF_3)_3GeF_2^-$, GeF_6^{2-} , $[(CF_3)_3GeF_2]^-$ and $[(CF_3)_2GeF_4]^{2-}$, respectively; thus these predictions follow the variations in the bond lengths. This model, which involves transmission of the negative charge mainly into the Ge-F bonds, is also supported by the vibrational data (Table 4). The rather isolated Ge-C stretching modes at 363 (e) and 235 cm^{-1} (a_1) are very similar to those for uncharged $(CF_3)_3Ge$ species, whereas the averaged Ge-F stretching frequency of ca. 515 cm^{-1} is clearly lower than that of GeF_6^{2-} [26] or GeF_5^- [7], 563 and 644 cm^{-1} , respectively, a difference which cannot be ascribed to the different coupling patterns. With the reasonable assumption of isolated Ge-F stretching modes, a value of 2.4 $N\ cm^{-1}$ can be calculated for $f(Ge-F)$ compared with 2.9 $N\ cm^{-1}$ for GeF_6^{2-} . A sensitive probe for the environment of the CF₃ group is the frequency of the δ_s mode that appears as a strong, highly polarized Raman line. The value of 727 cm^{-1} is close to that found for the halides $(CF_3)_3GeX$, e.g. 732 cm^{-1} for $X = Cl$ [27], and clearly larger than those for $(CF_3)_3GeMn(CO)_5$, 721 cm^{-1} [18], or the $(CF_3)_3Ge^-$ anion, 701 cm^{-1} [22], and these values reflect the bonding situation in these molecules.

While C_{3h} rather than C_{3v} symmetry was assumed in the electron diffraction study of $(CF_3)_3PF_2$ [28], its structure can be regarded as isostructural with that of $[(CF_3)_3GeF_2]^-$. Since these compounds are in a sense isoelectronic, comparison of their MCF₃ and MF structural parameters after size corrections may reveal the influence of charge on these interactions. Size corrections are facilitated by subtrac-

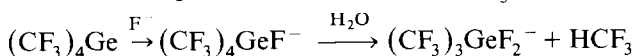
TABLE 4
VIBRATIONAL SPECTRA OF THE $(\text{CF}_3)_3\text{GeF}_2^-$ ION

IR _{KBr} ^a	Ra _{sol} ^b	Ra _{aq} ^c	Assignment
	140w	(145vw)	$\delta(\text{CGeF})$
	239vs	235s,p	$\nu_3(\text{GeC}_3)$
	260m	255m	$\rho(\text{CF}_3)$
	275m	275m	
363s	370vw		$\nu_{as}(\text{GeC}_3)$
465vw	460w	475m,p	$\nu_3(\text{GeF}_2)$
508w			
527m	531m	530m	$\delta_{as}(\text{CF}_3)$
556s	555sh		$\nu_{as}(\text{GeF}_2)$
728vw	729s	727s,p	$\delta_s(\text{CF}_3)$
1078vs	1080w,b	1075vw	$\nu_{as}(\text{CF}_3)$
1123vs	1120w,b	1120vw	
1177vs	1180wm	1182w	$\nu_s(\text{CF}_3)$
1208s	1208w	1208vw,(p)	

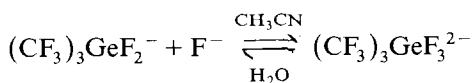
^a As KBr pellet of $[(\text{CH}_3)_4\text{N}][(\text{CF}_3)_3\text{GeF}_2]$. ^b From crystalline $\text{Na}[(\text{CF}_3)_3\text{GeF}_2]$. ^c Aqueous solution of $\text{Na}[(\text{CF}_3)_3\text{GeF}_2]$.

tion of the corresponding covalent radius of M from the M–C and M–F bond lengths. For the Ge–F and P–F bonds, the differences are 0.62 and 0.50 Å, respectively, whereas for the Ge–C and P–C bonds, the corresponding differences are almost identical viz., 0.78 and 0.79 Å, respectively. These values reveal that with the same kind of hybridization the negative charge of the anion mainly effects the Ge–F bond, the character of the Ge–C bond remaining comparable with that of the uncharged species. Some delocalization of electron density into the C–F bond is, however, indicated by the larger C–F distances, the lower C–F stretching frequencies, and the smaller F–C–F bond angles.

In aqueous solution tris- and tetrakis(trifluoromethyl)germanes show no tendency to form hexacoordinated species. An intermediate complex formed from $(\text{CF}_3)_4\text{Ge}$ and F^- decomposes with evolution of HCF_3 .



In aprotic solvents, such as acetonitrile, both $(\text{CF}_3)_3\text{GeX}$ (X = halogen) and $(\text{CF}_3)_4\text{Ge}$ add fluoride ions to form octahedral species which are unstable in water, e.g.



For both $(\text{CF}_3)_3\text{GeF}_3^{2-}$ and $(\text{CF}_3)_4\text{GeF}_2^{2-}$ the ^{19}F NMR spectra (Table 5) offer conclusive evidence for the presence of only the relevant *cis* isomer:

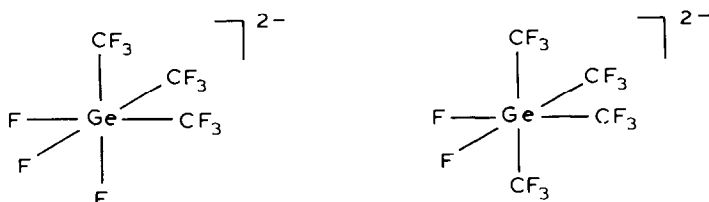


TABLE 5

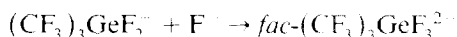
¹⁹F NMR DATA FOR TRIS- AND TETRAKIS(TRIFLUOROMETHYL)FLUOROGERMANATES^a

Ion	$\delta(\text{CF}_3)$	$\delta(\text{F})$	$J(\text{FF})$
$(\text{CF}_3)_3\text{GeF}_2$	-58.0	-137.6	11.6
<i>fac</i> - $(\text{CF}_3)_3\text{GeF}_3^{2-}$	-59.0	-124.5	0
<i>cis</i> - $(\text{CF}_3)_4\text{GeF}_2^{2-}$	56.5	-121.0	0

^a In CH_3CN ; chemical shifts in ppm vs. internal CFCl_3 , coupling constants in Hz. ^b $A_3A'_3A''_3XX'X''$ spin system, $^3J(\text{FF}_{trans}) + 2^3J(\text{FF}_{cis}) = 23.4 \text{ Hz}$. ^c $A_3A'_3B_6XX'$ spin system, $\delta_A - \delta_B = 0.35 \text{ ppm}$; $^3J(\text{F}_A\text{F}_B)$ ca. 10 Hz.

Though the line widths of the NMR signals of ca. 2 Hz do not allow a detailed analysis, the observed "pseudo-quartet" structure of the CF_3 resonance of $(\text{CF}_3)_3\text{GeF}_2^{2-}$ is in agreement with an $A_3A'_3A''_3XX'X''$ spin system. Homonuclear decoupling leads to singlets for both the A and X parts. Similarly, instead of the simple $A_{12}X_2$ spectrum for a possible *trans*- $(\text{CF}_3)_4\text{GeF}_2^{2-}$, an asymmetric pattern of resonances arises for the CF_3 groups attributed to a $A_3A'_3B_6XX'$ spin system, which on decoupling of the X part symmetrizes to a poorly resolved A_6B_6 system.

Fluoride addition in CH_3CN occurs stepwise. Addition of small amounts of KF to $(\text{CF}_3)_3\text{GeCl}$ gives rise to two additional broad signals, at -57.3 (CF_3) and -134.5 ppm (GeF), which upon cooling below 0°C split into a doublet and decet, respectively ($J(\text{FF})$ 10 Hz). These signals can not be attributed to $(\text{CF}_3)_3\text{GeF}$, since a chemical shift of -219 ppm has been reported for the GeF resonance of neat $(\text{CF}_3)_3\text{GeF}$ [29], and this is shifted to -174 ppm in CH_3CN solution. Instead, the similarity of chemical shifts suggests a pentacoordinated $(\text{CF}_3)_3\text{GeFCl}$ species, with F and Cl in the axial positions. Further KF addition leads to precipitation of KCl and formation of the stable $(\text{CF}_3)_3\text{GeF}_2^{2-}$, and ultimately to *fac*- $(\text{CF}_3)_3\text{GeF}_3^{2-}$ anions:



Similarly, F^- addition to $(\text{CF}_3)_4\text{Ge}$ in CH_3CN gives rise to additional signals at -54.8 and -114.6 ppm, the former being resolved to a doublet at ca. -40°C ($J(\text{FF})$ 11 Hz). The equivalence of the CF_3 groups as well as the quite different GeF shift indicates a fluxional $(\text{CF}_3)_4\text{GeF}^-$ ion.

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References

- 1 R.O. Day, J.M. Holmes, A.C. Sau and R.R. Holmes, *Inorg. Chem.*, 21 (1982) 281; R.R. Holmes, R.O. Day, A.C. Sau, C.A. Poutasse and J.M. Holmes, *Inorg. Chem.*, 24 (1985) 193.
- 2 C. Breliere, F. Carre, R.J.P. Corriu, A. De Saxe, M. Poirier and G. Royo, *J. Organomet. Chem.*, 205 (1981) C1.

- 3 M. Dräger, *Z. Anorg. Allg. Chem.*, 423 (1976) 53.
- 4 M. Dräger, *Chem. Ber.*, 108 (1975) 1723.
- 5 L.O. Atovmyan, Ya.Ya. Bleidelis, A.A. Kemme and R.P. Shibaeva, *Zh. Strukt. Khim.*, 11 (1978) 318; A.A. Kemme, Ya.Ya. Bleidelis, R.P. Shibaeva and L.O. Atovmyan, *Zh. Strukt. Khim.*, 14 (1973) 103; S.N. Gurkova, A.I. Gusev, I.R. Segel'man, N.V. Alekseev, T.K. Gar and N.V. Khromova, *Zh. Strukt. Khim.*, 22 (1981) 181.
- 6 M.S. Bilton and M. Webster, *J. Chem. Soc., Dalton Trans.*, (1972) 722.
- 7 T.E. Mallouk, B. Desbat and N. Bartlett, *Inorg. Chem.*, 23 (1984) 3160.
- 8 D.J. Brauer, H. Bürger and R. Eujen, *Angew. Chem.*, 92 (1980) 859.
- 9 H. Oberhammer, *J. Fluor. Chem.*, 23 (1983) 147, and references cited herein.
- 10 H. Oberhammer and R. Eujen, *J. Mol. Struct.*, 51 (1979) 211.
- 11 R.J. Lagow, R. Eujen, L.L. Gerchman and J.A. Morrison, *J. Amer. Chem. Soc.*, 100 (1978) 1722.
- 12 D.J. Brauer, H. Bürger, G.R. Liewald and J. Wilke, *J. Organomet. Chem.*, 287 (1985) 305.
- 13 G.M. Sheldrick, SHELX-76, Program for crystal structure determination, University of Cambridge, England (1976).
- 14 C.K. Johnson, ORTEP-II, Report ORNL-5138, Oak Ridge National Laboratory, Tennessee (1976).
- 15 F_o , F_c lists, tables of hydrogen coordinates and anisotropic thermal parameters may be obtained from Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen 2, by quoting the deposit number CSD-51976, the names of the authors and the literature reference.
- 16 V. Schomaker and K.N. Trueblood, *Acta Crystallogr. B*, 24 (1968) 63.
- 17 H. Oberhammer and R. Eujen, unpublished results.
- 18 D.J. Brauer and R. Eujen, *Organometallics*, 2 (1983) 263.
- 19 R. Eujen and H. Bürger, *Spectrochim. Acta A*, 35 (1979) 541.
- 20 H. Bürger and R. Eujen, *Spectrochim. Acta A*, 31 (1975) 1655.
- 21 A. Yokozeki and S.H. Bauer, *Top. Curr. Chem.*, 53 (1975) 71.
- 22 R. Eujen, *Spectrochim. Acta*, in press.
- 23 B.K. Vainshtein and R.N. Kurdumova, *Krystallografiya*, 3 (1958) 29.
- 24 J.L. Hoard and W.B. Vincent, *J. Amer. Chem. Soc.*, 61 (1939) 2849.
- 25 T.E. Mallouk, G.L. Rosenthal, G. Müller, R. Brusasco and N. Bartlett, *Inorg. Chem.*, 23 (1984) 3167.
- 26 G.M. Begun and A.C. Rutenberg, *Inorg. Chem.*, 6 (1967) 2212.
- 27 R. Eujen and H. Bürger, *Spectrochim. Acta A*, 35 (1979) 549.
- 28 H. Oberhammer, J. Grobe and D. LeVan, *Inorg. Chem.*, 21 (1982) 275.
- 29 R. Eujen and R. Mellies, *J. Fluor. Chem.*, 22 (1983) 263.