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Properties of trifluoromethylgermanes. Adduct formation and substitution reactions of $(CF_3)_nGeX_{4-n}$ ($n = 2$–4) with NH_3

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Abstract

Crystalline adducts of compositions $(CF_3)_4Ge \cdot nRNH_2$ (R = H: $n = 2$, 3; R = CH_3: $n = 1$, 2) with dissociation vapour pressures at 22°C of 70 (R = H) and 75 mbar (R = CH_3) have been isolated. From their Raman spectra both NH_3 adducts are judged to have a *cis*-configurated octahedral coordination at the germanium atom. Reaction of $(CF_3)_3GeI$ with NH_3 yielded the digermazane $[(CF_3)_3Ge]_2NH$ whereas the cyclic trimers $[(CF_3)_2GeNR]_3$ (R = H, CH_3) were obtained from $(CF_3)_2GeI_2$ and RNH_2. IR spectra show that NH_3 and $[(CF_3)_3Ge]_2NH$ undergo equilibration to give $(CF_3)_3GeNH_2$ in the gas phase, with simultaneous formation of a solid phase with the composition $(CF_3)_3GeNH_2 \cdot 2NH_3$. Addition of trimethyl- or triethyl-amine to $[(CF_3)_3Ge]_2NH$ yields solid 1:1 adducts. The vibration spectra of $[(CF_3)_3Ge]_2NH$, $(CF_3)_3GeNH_2$ and of the NH_3 adducts of $(CF_3)_4Ge$ and of their deuterated analogues have been analyzed. A Ge–N–Ge bond angle of 130° was deduced for $[(CF_3)_3Ge]_2NH$ from model force constant calculations.

Introduction

The high electronegativity of fluorine means that replacement of CH_3 by CF_3 ligands has a marked effect that results in large differences in chemical and physical properties between compounds such as $(CF_3)_{4-n}EX_n$ and $(CH_3)_{4-n}EX_n$. Of the analogous of the CF_3 derivatives of carbon only the germanes (E = Ge) have been systematically prepared [1–4]. The presence of several CF_3 groups leads to a more positively charged central atom E and to highly polar E–X bonds to electronegative substituents X. The accumulation of positive charges in the center of the molecule with a pronounced Coulomb repulsion between the positive C and E atoms is held to be responsible for the observed weakness of the E–CF_3 bond [5–10].

Coulomb forces also influence the geometry of CF_3 derivatives. The repulsive interaction between the negatively charged spheres of adjacent CF_3 groups may account for the planarity of $(CF_3)_3N$ [11] or the large central bond angle of 151° in $(CF_3)_3Ge$–O–$Ge(CF_3)_3$ [12]. The bulk of the CF_3 group will, however, not suppress completely the effects of the high Lewis acidity of the central atom E. Trifluoromethylgermanes are still capable of adding small and hard Lewis-bases to form

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penta- or hexa-coordinate complexes such as the $(CF_3)_3GeF_2^-$ or cis-$(CF_3)_4GeF_2^{2-}$ anions, respectively [13].

While the CF_3 group is similar in electronegativity to a halogen, the F_3C^- anion is less stable than a halide ion and so displacement of a trifluoromethyl group in substitution reactions requires rather strong nucleophiles, e.g. attack by hydroxide leads to quantitative evolution of HCF_3. Such Ge–C bond cleavage is much slower with the less nucleophilic NH_3, and so it can be expected that the chemistry of the $(CF_3)_{4-n}GeX_n/NH_3$ system involves a competition between Ge–C bond cleavage, complex formation, and substitution reactions.

Results and discussion

Reaction of $(CF_3)_{4-n}GeX_n$ *(n = 2–4) with ammonia*

Adduct formation with $(CF_3)_4Ge$. In a first step nucleophiles such as NH_3 or amines add to trifluoromethylated germanes, $(CF_3)_nGeX_{4-n}$, to give complexes containing penta- or hexa-coordinated germanium. The number of donor molecules added and the stability of the complex depend on the Lewis acidity of the germanium atom (and so on the number of CF_3 groups attached to germanium and the electronegativity of the substituents X) and on steric factors. Though displacement of a CF_3 is much slower than that of a halide ligand, some degradation with formation of HCF_3 is always observed if NH functions are present in excess. Thus, $(CF_3)_4Ge$ slowly decomposes in the presence of an excess of NH_3 to form non-volatile *N*-linked polymers. The extent of degradation can be monitored by reaction with gaseous HCl, which cleaves the Ge–N bonds quantitatively to give the monomeric chlorogermanes, $(CF_3)_nGeCl_{4-n}$.

Upon controlled addition of ammonia or methylamine, however, the formation of distinct complexes with dissociation vapour pressures at 22°C of 70 and 75 mbar, respectively, is observed. The infrared spectrum of the gas phase above the solid shows only the absorptions of the starting materials.

$$(CF_3)_4Ge + nNH_2R \rightleftharpoons (CF_3)_4Ge(NH_2R)_n \qquad (1)$$

$(R = H,\ n = (1),\ 2,\ 3;\ R = CH_3,\ n = 1,\ 2)$

The adducts form colourless crystals which slowly decompose with evolution of HCF_3 and amine to give cyclic oligomers such $[(CF_3)_2GeNR]_3$ or polymers e.g.:

$$3(CF_3)_4Ge(NH_2R)_2 \rightarrow 6HCF_3 + 3NH_2R + \left[(CF_3)_2GeNR\right]_3 \qquad (2)$$

$(R = H,\ CH_3)$

There is no indication of complex formation with sterically more demanding dimethylamine or trimethylamine. In both cases the vapour pressure increases upon addition of the donor. Similarly, no solid is formed with the less volatile amines pyridine, aniline, or 1,2-diaminobenzene, and $(CF_3)_4Ge$ can be removed quantitatively from the mixture.

The stepwise formation and the composition of the complexes was demonstrated, and their composition established, by vapour pressure measurements, as shown in Fig. 1. Cocondensation of an increasing amount of NH_3 with a constant quantity of $(CF_3)_4Ge$ (p_0 = 100 mbar) followed by equilibration at 0°C results in a decrease in the total pressure and formation of a solid. The irregularity around the 1 : 1 ratio as well as the slight change of the slope may arise from a 1 : 1 complex that is unstable

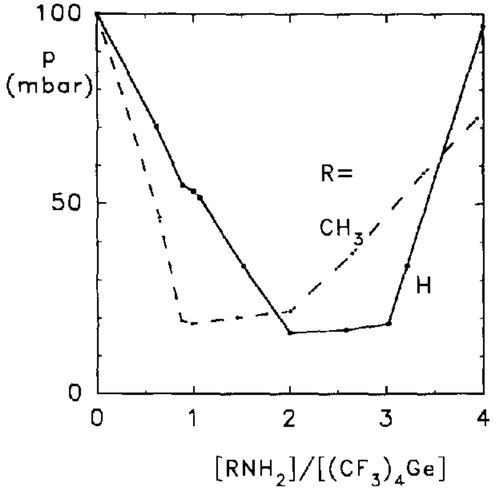

Fig. 1. Vapour pressures at 0 °C of the adducts of $(CF_3)_4Ge$ (starting gas phase pressure $p_0 = 100$ mbar) with NH_3 (———) and CH_3NH_2 (- - - - - -).

with respect to dismutation to the 1 : 2 species and $(CF_3)_4Ge$. Whereas the 1 : 1 and 1 : 2 stoichiometries are readily associated with penta- and hexa-coordinate complexes, the nature of the 1 : 3 species (the stoichiometry $(CF_3)_4Ge(NH_3)_3$ was further confirmed by several independent elemental analyses) is less obvious. The Raman spectra of the 1 : 2 and 1 : 3 NH_3 adducts (see below), however, strongly suggest *cis*-configurated octahedral arrangements and the formulations *cis*-$(CF_3)_4Ge(NH_3)_2$ and *cis*-$(CF_3)_4Ge(NH_3)_2 \cdot NH_3$, respectively.

In keeping with the high dissociation vapour pressure, fast exchange between the donors occurs in solution. At ambient temperature a sharp ${}^{19}F$ NMR line at -58.2 ppm is observed, and this broadens at low temperature but does not show the A_6B_6 pattern expected for a rigid *cis*-complex. The non-cubic symmetry of the complex is evident from the absence of the ten ${}^{73}Ge$ ($I = 9/2$; 7.76%) satellites characteristic of tetrahedral $(CF_3)_4Ge$ [14].

Reaction of $(CF_3)_3GeI$ with ammonia. Hexakis(trifluoromethyl)digermazane, $(CF_3)_3GeNHGe(CF_3)_3$, was obtained by reaction of the germyl iodide with a stoichiometric amount of NH_3:

$$2(CF_3)_3GeI + 3NH_3 \rightarrow [(CF_3)_3Ge]_2NH + 2NH_4I \qquad (3)$$

It was isolated as a colourless liquid with a vapour pressure of 11 mbar at 25 °C and a melting point of -35 °C. Its ${}^{19}F$ NMR spectra consists of a sharp line at -54.4 ppm accompanied by ${}^{13}C$ satellites with ${}^{1}J(CF) = 331$ Hz and unresolved fine structure due to overlapping ${}^{4}J(FF)$ and ${}^{6}J(FF)$ couplings. The ${}^{13}C$ resonance, the X-part of a $A_3B_6C_9X$ system, shows a corresponding quartet at 126.3 ppm (ext. $CDCl_3$, $\delta = 77.0$ ppm), with some further splitting (${}^{3}J(CF)$ ca. 5 Hz), whereas a singlet is observed in the ${}^{15}N$ spectrum at -407.2 ppm (vs ext. CH_3NO_2).

The gas phase reaction of the digermazane with an excess of NH_3 leads to an equilibrium with the germylamine $(CF_3)_3GeNH_2$, which is analogues to the formation of the unstable $(CF_3)_3GeOH$ from the corresponding digermoxane and water [12]:

$$[(CF_3)_3Ge]_2NH + NH_3 \rightleftharpoons 2(CF_3)_3GeNH_2 \qquad (4)$$

When the NH_3 pressure is increased the NH stretch at 3375 cm^{-1} and the $\nu_{as}(Ge_2N)$ band at 871 cm^{-1} disappear, and new strong absorptions appear at 3490 and 3400 cm^{-1} (ν_s and $\nu_{as}(NH_2)$) and at 740 cm^{-1} ($\nu(GeN)$). With a 4 : 1 excess of NH_3 the digermazane is no longer detectable in the gas phase. The simultaneously formed condensed phase appears to be in equilibria with various adducts. With increase in the amounts of NH_3 its consistency changes from liquid corresponding formally to $(CF_3)_3GeNH_2$ to a crystalline sublimable material with the composition $(CF_3)_3GeNH_2 \cdot 2NH_3$, which has a dissociation vapour pressure of 80 mbar at 22 °C and decomposes to GeN polymers, NH_3, and HCF_3.

The digermazane is readily hydrolyzed by moisture to the digermoxane $[(CF_3)_3Ge]_2O$. When the reaction is carried out in the gas phase with water vapour, however, colourless sublimable crystals are deposited on the glass walls; these are also obtained by treating the digermoxane with ammonia:

$$[(CF_3)_3Ge]_2NH + H_2O \rightarrow [(CF_3)_3Ge]_2O + NH_3 \qquad (5)$$

$$[(CF_3)_3Ge]_2O + 2NH_3 \rightarrow [(CF_3)_3Ge(NH_3)]_2O \qquad (6)$$

The nature of this NH_3 complex, which exists in a room temperature and a low temperature phase, was established by an X-ray diffraction study, which revealed the presence of a pseudo-linear N–Ge–O–Ge–N chain with penta-coordinated germanium for the high temperature phase. Upon cooling a more ordered conformation is formed with a Ge–O–Ge bond angle of 150 ° [15].

In contrast to the halides $(CF_3)_3GeX$, to $(CF_3)_4Ge$ or $[(CF_3)_3Ge]_2O$, the digermazane forms crystalline 1 : 1 adducts with triethylamine (mp. 63 °C, dissociation vapour pressure at 25 °C 3 mbar) or trimethylamine (m.p. 28 °C; p_{25} 17 mbar):

$$[(CF_3)_3Ge]_2NH + NR_3 \rightarrow [(CF_3)_3Ge]_2NH \cdot NR_3$$

$(R = CH_3, C_2H_5)$

The Raman spectra of the colourless solids show an almost undisturbed pattern fo the free digermazane (see below) except that (i) the NH stretch can no longer be detected and (ii) the $\nu(GeN)$ stretch is blue-shifted to 580 cm^{-1}. Furthermore, there was no clear evidence for the $\nu_{as}(Ge_2N)$ band in the IR spectra. For the electronically similar $(Cl_3Si)_2NH$, the frequency of the asymmetric SiN stretch increases significantly upon deprotonation [16]. A corresponding shift would place the asymmetric GeN stretch, expected to give a rather strong IR band, in the region of the very strong CF absorptions. Such an increase in $\nu_{as}(Ge_2N)$, associated with a modest increase in $\nu_s(Ge_2N)$, is in accord with an increase of the Ge–N bond strength associated with a linearization of the Ge–N–Ge skeleton. Some additional transfer of electron density to the $(CF_3)_3Ge$ fragments is furthermore indicated by a red-shift of 8 cm^{-1} for the $\delta_s(CF_3)$ mode. The ^1H NMR signal is shifted from 2.0 ppm in the digermazane to 12.5 ppm for the trimethylamine adduct (recorded at 35 °C as a liquid without solvent) or to 7.5 ppm for the triethylamine adduct (in CH_3CN). On the other hand the Raman lines associated with the NEt_3 part of the spectrum are quite different from those of free NEt_3 and those of the NEt_3H^+

cation. These observations lead to the conclusion that the species are strongly associated via N $\cdots$ H $\cdots$ N bridges.

Despite the apparent acidity of the digermazane, all attempts to deprotonate the digermazane with alkali metals, sodium amide, lithium alkyls, $(CH_3)_3COK$, or sodium ketyl in various solvents led either to recovery of the starting material (e.g. Na in toluene at 110 °C for 4 h), replacement of CF_3 groups by alkyl groups and polymerization (methyl- or butyl-lithium at or below room temperature), or complete decomposition. We also failed to prepare the trigermylamine $[(CF_3)_3Ge]_3N$. Substitution reactions of $(CF_3)_3GeX$ with primary and secondary amines will be described elsewhere [17].

Reaction of $(CF_3)_2GeI_2$ with NH_3 and CH_3NH_2. The reaction of $(CF_3)_2GeI_2$ with NH_3 leads to the formation of six-membered ring species in moderate yields:

$$3(CF_3)_2GeI_2 + 9RNH_2 \rightarrow [(CF_3)_2GeNR]_3 + 6RNH_3^+I^- \qquad (8)$$

(R = H(45%); CH_3(31%))

No mono- or dimeric species have been detected, but the presence of more complex structures arising from CF_3-elimination are apparent from the NMR spectra. An independent preparation of the *cyclo*-trigermazane (R = H) has been described recently [18]. The cyclic compounds form colourless sublimable crystals (m.p.: 96 °C (R = H); 70 °C (R = CH_3)), which are slowly hydrolysed when exposed to air, and are cleaved to $(CF_3)_2GeCl_2$ by gaseous HCl.

Vibrational spectra and structure

$[(CF_3)_3Ge]_2NH$. The infrared and Raman spectra of $[(CF_3)_3Ge]_2NH$ (Table 1) closely resemble those of the "isoelectronic" digermoxane, $[(CF_3)_3Ge]_2O$ [12]. The modes associated with the $(CF_3)_3Ge$ fragment hardly change upon deuteration and its structural parameters may confidently be taken to be similar to those in the digermoxane [12]. Differences arise for the Ge_2NH skeleton because of the additional modes due to the presence of the N–H bond and an evidently smaller Ge–E–Ge bond angle. The large H/D shift of ca 100 cm^{-1} for the $\nu_{as}(Ge_2N)$ mode clearly indicates a strong vibrational coupling of the asymmetric Ge–N(D) stretch with the a''-GeND deformation at 1007 cm^{-1} in the deuterated species. The corresponding GeNH deformation is not directly observable. The small but significant inverse isotope effect noticed for the ν(CF) stretches points to the presence of a coupling mode at a somewhat higher energy in the NH species. Calculations place the GeNH deformation at ca 1250 cm^{-1}, and its assignment to the IR band at 1252 cm^{-1}, overlapping with the combination $\delta_s + \delta_{as}(CF_3)$ (1257 cm^{-1} in the ND compound), seems reasonable.

Evidence for the in-plane a'(GeNH) deformation is given by the inverse isotope shift of 2 cm^{-1} for the $\nu_s(Ge_2N)$, which is in good agreement with force constant calculations based on the assignment to a rather weak feature around 495 cm^{-1} in the deuterated species. The NH and ND stretches appear as rather strong IR absorptions and weak Raman bands at nearly the same frequency as in their methyl analogues [19].

Since the $(CF_3)_3Ge$ modes are well separated from the skeletal vibrations, a four-mass model can be used to evaluate the GeN force constant and to predict the central Ge–N–Ge bond angle with the same reliability as for the digermoxane, for which the gas phase structure was determined experimentally [12]. The value of the

Table 1

Infrared and Raman spectra of $[(CF_3)_3Ge]_2NH$ and $[(CF_3)_3Ge]_2ND$ [a]

$[(CF_3)_3Ge]_2NH$			$[(CF_3)_3Ge]_2ND$		Assignment
IR	Raman		IR	Raman	
gas	liq.	sol. [b]	gas	liq.	
	56m			56m	
		67m			$\delta(CGeC)$
	ca 80sh			ca 80sh	
		91m			$\delta(GeNGe)$ [c]
	157m,p	162m		157m	$\rho(CGeN)$
	223m	223m		223m	$\rho(CF_3)$
	244s,p	248s		244s,p	$\nu_s(GeC_3)$
	251m			251m	$\rho(CF_3)$
305m	316w,p	316w	305m	315w–m,p	$\rho(CF_3)$
349sh	347w	347w	345m–s	346w	
361s	360vw,p		360s	361vw,p	$\nu_{as}(GeC_3)$
			495sh		$\delta(GeND)$ (a') [c]
	510sh			510sh	$\delta_{as}(CF_3)$
525w	525w	523w	528w	525w	
558m	560vw,p	573vw	560m	562w,p	$\nu_s(Ge_2N)$
732m	731s,p	729s	732m	731s,p	$\delta_s(CF_3)$
871s	865vvw	867vvw	770s		$\nu_{as}(Ge_2N)$
			1007s		$\delta(GeND)$ (a'')
1125sh			1120sh		
			1135sh		
1155sh	1156m,b	1155m	1156vs	1158m,b	$\nu_{as}(CF_3)$
		1164sh			
1172vs		1170sh	1177vs		
1198s		1200vw	1198vs		$\nu_s(CF_3)$
	1208vw,p	1212vw		1208w,p	
1252m			1257m		[c]
2246w			2246w		
			2275w		
2295w			2292w		
2360vw			2362vw		
3374m	3367w,p	3375vw	2497m	2490w,p	$\nu(NH/D)$

[a] In cm^{-1}. [b] At −100 °C. [c] See text.

GeN/GeN interaction constant is extremely sensitive to changes in the bond angle, an increase by one degree corresponding to an increase of 0.1 N cm^{-1}. A negative value, such that calculated in Ref. 19 for hexamethyldigermazane, clearly indicates that the bond angle chosen for the calculation is too small. With the assumption that $f(GeN/GeN)$ is positive and has a value approximately 10% of that of $f(GeN)$, a Ge–N–Ge bond angle of 130° is derived. On the other hand the size of the Ge–N–H bond angle hardly affects the calculations, and was fixed of 105°. The results of the normal coordinate analysis with calculated frequencies and force constants are set out in Table 2.

$(CF_3)_3GeNH_2$. For the primary amine $(CF_3)_3GeNH_2$ only the gas phase IR spectrum (Table 3) is interpreted since the liquid phase contains a complex mixture of adducts, presumably with both coordinative Ge–NH_3 and hydrogen-bonded GeN–H ··· NH_3 interactions.

Table 2

Calculated frequencies [a], potential energy distribution (PED) [b] and force constants [c] of the Ge_2NH skeleton of $[(CF_3)_3Ge]_2NH$

$[(CF_3)_3Ge]_2NH$		$[(CF_3)_3Ge]_2ND$		PED	
exp.	calc.	exp.	calc.		
a′					
3374	3393	2497	2482	100(NH)	
–	647			77(GeNH), 19(GeNH/GeNH)	
		(495)	495	75(GeNH), 19(GeNH/GeNH), 7(GeN)	
558	558			84(GeN), 13(GeNGe), 8(GeN/GeN), −7(GeN/GeNGe)	
		560	560	79(GeN), 11(GeNGe), 8(GeN/GeN), −6(GeN/GeNGe)	
157	157	157	157	88(GeNGe), 6(GeN)	
a″					
(1252)	1251			133(GeNH), −33(GeNH/GeNH), 8(GeN)	
		1007	1007	80(GeNH), 60(GeN), −20(GeNH/GeNH), −11(GeN/GeNH)	
871	871			104(GeN), −10(GeN/GeN)	
		770	770	55(GeNH), 52(GeN), −14(GeN/GeN), 9(GeN/GeNH), −5(GeN/GeN)	
f(NH)		6.37		*f*(GeN/GeN)	0.40
f(GeN)		4.13		*f*(GeN/GeNGe)	0.10
f(GeNGe)		0.46		*f*(GeN/GeNH)	0.04
f(GeNH)		0.66		*f*(GeN/GeNH′)	−0.13
				f(GeNH/GeNH)	0.17

[a] In cm^{-1}. [b] Contributions exceeding 5%. [c] In N cm^{-1}, deformation constants normalized to 100 pm. Assumed geometry: *r*(GeN) 180 pm; *r*(NH) 101.5 pm; α(GeNGe) 130° (see text); β(GeNH) 105°.

Table 3

Infrared gas spectra of $(CF_3)_3GeNH_2$ and $(CF_3)_3GeND_2$ [a]

$(CF_3)_3GeNH_2$	$(CF_3)_3GeND_2$	Assignment
350s	347s	$\nu_{as}(GeC_3)$
525vw	524w	$\delta_{as}(CF_3)$
	687m	$\nu(GeN(D_2))$
729s	732w	$\delta_s(CF_3)$
740s		$\nu(GeN(H_2))$
1125v	1125vs	$\nu_{as}(CF_3)$
1151vs	1148vs	
1173vs	1173vs	$\nu_s(CF_3)$
1207s	1207s	
1545m	1376w*	$\delta(NH_2)$
2230vw	2230vw	
2265vw	2265vw	
2300vw	2300vw	
2376vw	2376vw	
3400m	2490m	
	2540w*	$\nu(NH)$
3487w–m	2598w	
	3443w*	

[a] In cm^{-1}; bands marked with asterisk are due to $(CF_3)_3GeNHD$.

Table 4

Raman spectra of the $NH_3(ND_3)$ adducts of $(CF_3)_4Ge$ [a]

liq. [6a]	$(CF_3)_4Ge$ $\cdot 2NH_3$	$\cdot 2ND_3$	$\cdot 3NH_3$	$\cdot 3ND_3$
	187m	186m	192m	188m
(225)	217m	217m	218m	217m
232	244vs	245vs	245vs	245vs
247	~ 265sh	~ 265sh		~ 265sh
255	276s	276s	276s	276s
	328m,b	314s	320m,b	314s
359			345m,b	330sh
528	527w	527w	529m	529m
733	715vs	716vs	715vs	714vs
		975vw		982vw
1125	1050vw,sh	1045vw,sh	1050vw,b	1050w,b
1158	1095w,b	1095w,h	1105w	1100m
1190	1145m	1145m	1151m	1148m
1208	1170w	1170w	1170sh	1167vw
		2350vw,b		
	3310m	2405m	3325w	2406w
		2435vw		2420sh
		2530vw		2530vw

[a] In cm^{-1}.

The NH stretches are found at significantly higher frequencies than those for the digermazane or other trialkylgermylamines [20]; from the difference $\nu_{as}-\nu_s(NH)$ a H–N–H bond angle of 112.5° can be evaluated [20]. The isolated NH and ND stretches are readily observed in the NHD species and correspond with the average of the ν_{as} and ν_s values. The NH_2 deformation at 1545 cm^{-1} is lowered to 1376 cm^{-1} in the NHD isotopomer, and is calculated (but not observed) to be around 1170 cm^{-1} for the ND_2 species where it interacts slightly with the very intense CF stretch at ca 1150 cm^{-1}.

A strong interaction of the Ge–N stretch with the nearby symmetric CF_3 deformation, essentially as found for the Ge–F and Ge–O stretches in $(CF_3)_3GeF$ [7a] and $(CF_3)_3GeOH$ [12], respectively, is apparent for the germyl amine: The $\delta_s(CF_3)$ mode at 732 cm^{-1} is red-shifted by 3 cm^{-1} and simultaneously steals considerable intensity from $\nu(GeN)$ at 740 cm^{-1}. The H/D isotope shift of ca 50 cm^{-1} cannot be due to the mass effect but must arise from coupling of $\nu(GeN)$ in the deuterated species with the $a'(GeND)$ deformation at somewhat higher energy. This region is, however, virtually inaccessible owing to the ever-present NH_3 or ND_3 absorptions.

NH_3 adducts of $(CF_3)_4Ge$. Complexation of $(CF_3)_4Ge$ is expected to lead to Ge–C bond weakening and lengthening, as confirmed by the structures of *cis*-$(CF_3)_4Ge(OSMe_2)_2$ and *cis*-$(CF_3)_4Ge(OPHMe_2)_2$ [15b], e.g. $r(GeC)$ increases from 198 pm in $(CF_3)_4Ge$ to an average value of ca 207 pm. Weakening of the C–F bonds in the complexed species is evident from the decrease of both the $\nu(CF)$ and $\delta_s(CF_3)$ frequencies [6a] around 1100 and 720 cm^{-1}, respectively (Table 4). In contrast, an increase of the frequencies in the $\nu(GeC)$ region between 200 and 300 cm^{-1} is observed upon complexation. This increase, however, must not be taken as

evidence for stronger Ge–C bonds, but is a consequence of a change in the geometry, with lowering of the symmetry and coupling of the ν(GeC) to the $\rho(CF_3)$ modes. The assignment of the rather indistinct features around 320 cm^{-1} to the GeN stretches is based on the fact that, along with the NH stretches, these are the only modes clearly affected by deuteration. For a *trans*-configurated complex with D_{4h} symmetry of the skeleton, coupling of the Raman intense a_{1g} $\nu(GeC_4)$ mode with a $\rho(CF_3)$ mode is impossible, and only one intense line should appear in the Raman spectrum. For a *cis*-complex, however, such a coupling will occur, as found for $(CF_3)_3GeCl$ [7a] or $(CF_3)_2GeCl_2$ [7b], yielding a pair of strong Raman lines. Further evidence for the *cis*-configuration arises from a comparison with the spectra of the *cis*-configurated $OPHMe_2$ and $OSMe_2$ adducts, which show almost identical patterns in this frequency region.

From these observations we deduce that all these adducts contain the *cis*-$(CF_3)_4GeL_2$ unit, and that the differences in the Raman spectra of the 1 : 2 and 1 : 3 ammonia adducts associated with the GeN- and NH-pattern are due to the formation of the adduct $(CF_3)_4Ge(NH_3)_2 \cdot NH_3$.

Experimental

Volatile materials were manipulated in a vacuum line equipped with greaseless stopcocks. Starting materials were purified and dried by standard methods. Products were purified by trap-to-trap condensation. $(CF_3)_3GeI$ was obtained from GeI_4 and $(CF_3)_2Hg$ [3]. Vapour pressures were monitored with a MKS Baratron 315 BHS pressure gauge. NMR spectra were recorded with a Varian EM 390 (^1H: 90.00 MHz, relative to external TMS; ^{19}F: 84.67 MHz, relative to external $CFCl_3$) and a Bruker AC 250 spectrometer (^{13}C: 62.90 MHz, relative external C_6D_6 at 128.0 ppm; ^{15}N: 25.36 MHz, relative to external CH_3NO_2). Infrared spectra were recorded on a Perkin–Elmer PE 580 B spectrometer with 10 cm gas cells, with KBr pellets or Nujol mulls, and Raman spectra with a Cary 82 (excitation Kr^+ 647.1 nm). Mass spectra were obtained with a MAT 311 spectrometer (E.I., 70 eV). Force constant calculations were carried out with the program NORCOR [21].

Bis-tris(trifluoromethyl)germylamine

In a 100 ml glass ampoule 2.0 g (4.9 mmol) of $(CF_3)_3GeI$ were cocondensed with 7.4 mmoles of $NH_3(ND_3)$. The mixture was allowed to warm to ambient temperature and stirred for 15 min. The volatile materials were then transferred to a new ampoule and kept for another 30 min. Trap-to-trap condensation resulted in collection of 0.9 g (77%) $[(CF_3)_3Ge]_2NH(D)$ in a −35°C trap. Mol. weight, found: 579 (calc. 574.2). Anal. Found: C, 12.73; H 0.23; F 59.0; N 2.53. $C_6F_{18}Ge_2HN$ calc.: C, 12.55; H, 0.18; F, 59.55; N, 2.44%. MS ($m_{Ge} = 74$): *m/e* 508 $[(CF_3)_5Ge_2NH]^+$ 1; 458 $[(CF_3)_4Ge_2FNH]^+$ 12; 408 $[(CF_3)_3Ge_2F_2NH]^+$ 15; 246 $[(CF_3)_2GeFNH]^+$ 20; 231 $[(CF_3)_2GeF]^+$ 50; 181 $[CF_3GeF_2]^+$ 25; 93 $[GeF]^+$ 35; 69 $[CF_3]^+$ 70; 66 $[CF_2NH_2]^+$ 100%.

Tris(trifluoromethyl)germylamine

The formation of $(CF_3)_3GeNH_2$ in the gas phase was monitored by IR spectroscopy. Cocondensation of 0.5 g (0.9 mmol) of $[(CF_3)_3Ge]_2NH$ with various amounts (0.9, 1.8, 2.7, 4.5 mmol) of NH_3, followed by fractional condensation yielded a liquid phase in a trap at −45 °C, mainly consisting of the starting digermazane (0.45, 0.30, 0.15, 0.03 g), and an increasing amount of solid material in a trap at −126 °C (0.04, 0.21, 0.36, 0.50 g), e.g. a crystalline phase for the 1 : 5 ratio, p(22 °C) 80 mbar; MS ($m_{Ge} = 74$): m/e 281 $[(CF_3)_3Ge]^+$ 3; 247 $[(CF_3)_2GeFNH_2]^+$ 7; 228 $[(CF_3)_2GeNH_2]^+$ 60; 178 $[(CF_3)GeFNH_2]^+$ 45; 128 $[GeF_2NH_2]^+$ 65; 93 $[GeF]^+$; 90 $[GENH_2]^+$ 50; 69 $[CF_3]^+$ 60; 66 $[CF_2NH_2]^+$ 100%.

Trialkylamine adducts of $[(CF_3)_3Ge]_2NH$

1.0 g (1.7 mmol) of $[(CF_3)_3Ge]_2NH$ were treated with 1.9 mmoles of trimethyl- or triethylamine. The volatile adduct was separated from the excess of amine by fractional condensation, in which it was trapped at −10 °C, yield 80%.

$[(CF_3)_3Ge]_2NH \cdot N(CH_3)_3$: Anal. Found: C, 17.2; H, 1.65; N, 4.60. $C_9F_{18}Ge_2H_{10}N_2$ calc.: C, 17.06; H, 1.58; N, 4.42%. Raman (cm^{-1}): 2980m, 2910w, 2880w, 2820w, 1475w, 1450w, 1168w–m, 1100w/b, 824m. 722vs, 580m/sh, 563m, 524w, 418w, 355w, 335w, 315w, 303m, 245vs, 223s, 158s, 80sh, 73vs.

$[(CF_3)_3Ge]_2NH \cdot N(C_2H_5)_3$: Anal. Found: C, 21.5; H, 2.65; N, 4.3. $C_{12}F_{18}Ge_2H_{16}N_2$ calc.: C, 21.35; H, 2.39; N, 4.15%. Raman (cm^{-1}): 3000m, 2960w, 2895w, 1465w, 1162w, 723s, 581m, 523m, 410m, 355m, 332w–m, 310m, 245vs, 222s, 158s, 73vs.

Amine adducts of $(CF_3)_4Ge$

Calibrated volumes of volatile donors (NH_3, CH_3NH_2, $(CH_3)_2NH$, $(CH_3)_3N$, PH_3, $(CH_3)_3P$, PF_3) were cocondensed with 100 mbar $(CF_3)_4Ge$ in a fixed volume. The vapour pressure was recorded after equilibration at 0 °C. A decrease of the vapour pressure and formation of a crystalline material was observed only in the case of NH_3 (subl. pt. 65 °C) and CH_3NH_2 (m.p. 2–12 °C).

Amine contents were determined by decomposition of the complexes with NaOH, absorption of the evolved amine by sulfuric acid, and retitration. An additional analysis was performed for $(CF_3)_4Ge \cdot 3NH_3$: Found: C, 12.17; H, 2.22; N, 10.40; F, 57.0. $C_4F_{12}GeN_3H_9$ calc.: C, 12.02; H, 2.27; N, 10.51; F, 57.04%.

Hexakis(trifluoromethyl)-cyclo-*trigermazane, $[(CF_3)_2GeNR]_3$ ($R = H, CH_3$)*

A solution of 5.0 g (10.8 mmol) of $(CF_3)_2GeI_2$ [30] in 20 ml of diethyl ether was treated with 0.55 g (32.4 mmol) NH_3 (1.0 g CH_3NH_2) for 3 h at ambient temperature. Ammonium iodide was filtered off, the ether removed *in vacuo*, and the residue sublimed at 45–55 °C and 10^{-2} mbar.

$[(CF_3)_2GeNH]_3$: Yield 1.1 g (45%), m.p. 95 °C. ^1H NMR: δ 0.47 ppm. ^{19}F NMR: δ −59.7 ppm. IR (cm^{-1}): 3358m, 3180m, 3005m, 2815m, 1475m, 1432s, 1183vs, 1132vs, 1070vs, 1042s, 927s, 792vs, 723w, 542s, 522sh, 420m, 304m. Raman (cm^{-1}): 3395w, 1168w, 728s, 575w/b, 525m, 335w, 311w, 253s, 222m, 192s, 162m, 140m. MS ($m_{Ge} = 74$): m/e 612 $[(CF_3)_5Ge_3(NH)_3]^+$ 2; 562 $[(CF_3)_4FGe_3(NH)_3]^+$ 17; 512 $[(CF_3)_3F_2Ge_3(NH)_3]^+$ 19; 497 $[(CF_3)_3F_2Ge_3(NH)_2]^+$ 10; 462 $[(CF_3)_2F_3Ge_3(NH)_3]^+$ 11; 447 $[(CF_3)_2F_3Ge_3(NH)_2]^+$ 13; 412 $[(CF_3)F_4Ge_3(NH)_3]^+$ 25; 397 $[(CF_3)F_4Ge_3(NH)_2]^+$ 26; 362 $[F_5Ge_3(NH)_3]^+$ 13; 347 $[F_5Ge_3(NH)_2]^+$ 53; 93 $[GeF]^+$ 100; 69 $[CF_3]^+$ 87%.

$[(CF_3)_2GeNCH_3]_3$: Yield 0.8 g (31%), m.p. 69 °C. ^1H NMR: δ 3.1 ppm. ^{19}F NMR: δ −54.1 ppm. IR (cm^{-1}): 2970w, 1175vs, 1122vs, 1025s, 855vs, 528w, 483m. Raman (cm^{-1}): 2960vw, 2850vw, 1491vw, 1452vw, 1192w, 1162w, 725s, 528w, 425m, 378w, 330w, 252vs, 220m, 180s, 146w. MS ($m_{\mathrm{Ge}} = 74$): m/e 723 M^+ 3; 673 $[(CF_3)_5FGe_3(NCH_3)_3]^+$ 3; 654 $[(CF_3)_5Ge_3(NCH_3)_3]^+$ 3; 604 $[(CF_3)_4FGe_3(NCH_3)_3]^+$ 21; 554 $[(CF_3)_3F_2Ge_3(NCH_3)_3]^+$ 34; 525 $[(CF_3)_3F_2Ge_3(NCH_3)_2]^+$ 10; 504 $[(CF_3)_2F_3Ge_3(NCH_3)_3]^+$ 35; 475 $[(CF_3)_2F_3Ge_3(NCH_3)_2]^+$ 14; 454 $[(CF_3)F_4Ge_3$-$(NCH_3)_3]^+$ 43; 425 $[(CF_3)F_4Ge_3(NCH_3)_2]^+$ 26; 413 $[(CF_3)_3Ge_2(NCH_3)_2]^+$ 13; 375 $[F_5Ge_3(NCH_3)_2]^+$ 58; 363 $[(CF_3)_2FGe_2(NCH_3)_2]^+$ 35; 313 $[(CF_3)F_2Ge_2(NCH_3)_2]^+$ 55; 263 $[F_3Ge_2(NCH_3)_2]^+$ 45; 260 $[(CF_3)_2FGeNCH_3]^+$ 82; 210 $[(CF_3)F_2GeNCH_3]^+$ 95; 93 $[GeF]^+$ 86; 69 $[CF_3]^+$ 47; 60 $[CFNCH_3]^+$ 100%. Anal. Found: C, 14.8; H, 1.45; N 5.9. $C_3H_3F_6GeN$ calc.: C, 15.03; H, 1.26; N, 5.85%.

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