Fluoro-Germanium (IV) Cations with Neutral Co-Ligands—Synthesis, Properties and Comparison with Neutral GeF₄ Adducts

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Abstract: The reaction of [GeF₄L₂], L = dms (Me₂SO), dmf (Me₂NCHO), py (pyridine), pyNO (pyridine-N-oxide), OPPh₃, OPMe₂, with Me₃SiO₃SCF₃ (TMSOTf) and monodentate ligands, L, in a 1:1:1 molar ratio in anhydrous CH₂Cl₂ formed the monocations [GeF₃L][OTf]. These rare trifluorogermanium (IV) cations were characterised by microanalysis, IR, ¹H, ¹³F[¹H] and, where appropriate, 3¹P[¹H] NMR spectroscopy. The ¹³F[¹H] NMR data show that in CH₃NO₂ solution the complexes exist as a mixture of mer and fac isomers, with the mer isomer invariably having the higher abundance. The X-ray structure of mer-[GeF₃(OPPh₃)₂][OTf] is also reported. The attempts to remove a second fluoride using a further equivalent of TMSOTf and L were mostly unsuccessful, although a mixture of [GeF₂(OAsPh₃)₄][OTf]₂ and [GeF₃(OAsPh₃)₃][OTf] was obtained using excess TMSOTf and OAsPh₃. The reaction of [GeF₄(MeCN)]₂ with TMSOTf in CH₂Cl₂ solution, followed by the addition of 2,2’,6’,2’’-terpyridine (terpy) formed mer-[GeF₃(terpy)][OTf], whilst a similar reaction with 1,4,7-trimethyl-1,4,7-triazacyclononane (Me₃-tacn) in MeCN solution produced fac-[GeF₃(Me₃-tacn)][OTf]. Dicaticonic complexes bearing the GeF₂⁺ fragment were isolated using the tetra-aza macrocycles, 1,4,7,10-tetramethyl-1,4,7,10-tetraazacyclododecane (Me₄-cyclam) and 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (Me₄-cyclam), which reacted with [GeF₄(MeCN)₂] and two equivalents of TMSOTf to cleanly form the dicaticonic difluoride salts, cis-[GeF₂(Me₄-cyclam)][OTf]₂ and trans-[GeF₂(Me₄-cyclam)][OTf]₂. The ¹³F[¹H] NMR spectroscopy shows that in CH₃NO₂ solution there are four stereoisomers present for trans-[GeF₂(Me₄-cyclam)][OTf]₂, whereas the smaller ring-size of Me₄-cyclam accounts for the formation of only cis-[GeF₂(Me₄-cyclam)][OTf]. and is confirmed crystallographically. New spectroscopic data are also reported for [GeF₄(L)₂] (L = dms, dmf and pyNO). Density functional theory calculations were used to probe the effect on the bonding as fluoride ligands were sequentially removed from the germanium centre in the OPMe₂ complexes.

Keywords: germanium; fluoride; cations; crystal structures

1. Introduction

Transition-metal halides, especially those from the 3d series, are very frequently used as the metal source for the introduction of the transition-metal ion to a wide range of ligand types, from monodentates to chelates, to form coordination complexes, with easy and often spontaneous displacement of the halides [1]. In contrast, the p-block halides often retain the halides, and formation of cationic species with p-block Lewis acids derived from p-block halides is much less common.

The coordination chemistry of p-block elements containing the heavier halide co-ligands (Cl, Br or I) has been studied in great detail for over 50 years [1–5]. In marked
contrast, after some preliminary study, that of the corresponding fluorides (except BF₃), was neglected until recent years [6]. In part, this reflected the limited commercial availability of the fluorides, which even when available, were often of unknown and doubtful purity. Additionally, studies were hindered by the fact that the fluorides of the more metallic elements were strongly polymerised, inert solids, which rarely offered facile routes to their complexes [6,7]. In some cases within Group 13, only the more reactive hydrated MF₃ precursors could be used, and even then they sometimes required hydrothermal conditions [6–9].

Recent studies of the coordination chemistry of p-block fluorides have been driven by the recognition that the complexes of the fluorides often have very different properties than those containing the heavier halides [6,7], and also in part by the search for new carriers of the radioisotope [¹⁸F]⁻, which is widely used in medical diagnostics for PET (positron emission tomography) imaging [7,10,11]. In this regard, the p-block systems have attracted interest due to their high M-F bond dissociation energies, and their ability to incorporate [¹⁸F]⁻ under mild conditions (e.g., aqueous solution, near room temperature and close to neutral pH) and in the final step of the process.

Within Group 14, the development of soluble synthons such as [SnF₃(MeCN)]₂ [12] or [GeF₃(MeCN)]₂ [13], from which the weakly bound MeCN could be readily displaced by other neutral ligands, was a major advance. The [GeF₄(MeCN)]₂ is both easier to handle and to control the stoichiometry, compared to using GeF₄, which is a gas at ambient temperatures (Sub. 236 K) [13]. As a result of these more recent studies, a range of neutral ligand complexes of GeF₄ with N- or O-donor ligands has been thoroughly characterised, e.g., [GeF₄L₂] (L = OPR₃, OASR₃, py) and [GeF₄(L-L)] (L-L = R₂P(O)(CH₂)₆P(O)R₂, bipy (2,2′-bipyridyl), phen (1,10-phenanthroline), Me₂N(CH₂)₂NMe₂). The crystal structures of representative examples have also been reported [13,14].

Examples of soft donor ligand complexes, such as with tertiary phosphines, include cis-[GeF₄(PR₃)]₂ (R = Me, Ph, ¹⁴Pr), cis-[GeF₄(R₂P(CH₂)₂PR₂)] (R = Me, Et, Ph, Cy), and cis-[GeF₄(µ-C₆H₄(PR₃))] (R = Me, Ph) [15,16], while dithioether ligands yield species such as cis-[GeF₄[R(S(CH₂)₂SR)] (R = Me, Et) [17], which have also been thoroughly characterised. Notably, the tri- and tetraphosphines, Me₄(C₂H₅P)₃ and P(CH₂CH₂PPh₂)₃ (L) form complexes of the type [GeF₄(L)], with the polyphosphate κ⁴-coordinated, and the free arms are unable to displace fluoride from the germanium [16].

Uniquely, the triaza macrocycle, Me₂-tacn (Me₂-tacn = 1,4,7-trimethyl-1,4,7-triazaacyclononane) reacts with [GeF₄(MeCN)]₂ in CH₂Cl₂ solution to form a cation in the [GeF₃(Me₂-tacn)]₂[GeF₆] salt [14]. The X-ray crystal structure of [GeF₃(Me₂-tacn)]Cl confirms the presence of a fac-octahedral GeF₃N₃ unit in the cation. In contrast, the tetraaza macrocycle Me₄-cyclam (1,4,8,11-tetramethyl-1,4,8,11-tetraazaacyclotetradecane) forms the neutral [GeF₄(κ₂-Me₄-cyclam)] or [GeF₄(µ-κ₂κ′⁻Me₄-cyclam)], in which the macrocyle is bound exodentate to the GeF₄ units [14].

A new route to cationic germanium (IV) fluoride complexes via the oxidation of germanium (II) adducts has also been reported. The tetradentate N-donor ligand, tris(1-ethylbenzoimidazol-2-ylmethyl)amine (BIMEt₃) forms the Ge (II) complex, [Ge(BIMEt₃)][OTf]₂, which, upon treatment with XeF₂ or Selectfluor, produces [GeF₂(BIMEt₃)][OTf]₂ [18]. The X-ray structure of this species reveals a distorted octahedron with cis fluorines. The treatment of [GeF₂(BIMEt₃)][OTf]₂ with TMSOTf (TMSOTf = Me₃SiOTf) generates [GeF(BIMEt₃)][OTf][OTf]₂, in which a coordinated triflate completes the six-coordination at germanium.

Since cationic fluoro-germanium (IV) complexes with most neutral ligands do not form directly from GeF₄, we explored the use of halide abstraction reagents. This approach is exemplified by using AlCl₃ to remove chloride from various tin (IV) phosphine complexes, forming cationic [SnCl₃(PR₃)]₂[AlCl₄], [SnCl₂(PR₃)]₂[AlCl₄]₂ (R = Me, Et), [SnCl₃(µ-C₆H₄(PMe₂)]₂[AlCl₄] and [SnCl₂(µ-C₆H₄(PMe₂)]₂[AlCl₄]₂ [19,20]. A similar reaction using Na[BArF₄] (BArF₄ = B[3,5-C₆F₃(C₆H₄)]₂) and the corresponding neutral tetrahalide complex produced the five-coordinate species [SnCl₃(PEt₃)]₂[BArF₄] and [SnCl₃(AsEt₃)]₂[BArF₄] [20].
In the corresponding tin fluoride systems, AlF$_3$ did not behave as a fluoride abstractor as it is an inert polymer [6], while reactions with Na[BArF$^4$] did not go to completion [21]. Therefore, we explored using TMSOTf. This has previously proved to be an efficient halide abstractor in group 14 halide chemistry, predominantly with the group 14 tetra-chlorides [20,22], and in tin (IV) and germanium (IV) fluoride phosphine systems [16,21]. In the majority of the phosphine cases, the halide abstraction resulted in complexes with weakly coordinated triflate, rather than salts containing genuine cationic species. Examples included [SnF$_4$$_n$-(PMe$_3$)$_2$(OTf)$_n$] ($n$ = 1–3) [21], [GeF$_4$$_n$-(PMe$_3$)$_2$(OTf)$_n$] ($n$ = 1–3), and GeF$_4$$_n$-(o-C$_6$H$_4$(PMe$_2$)$_2$)(OTf)$_n$] ($n$ = 1–3) [16]. In the case of Sn (IV), the reactions of [SnF$_4$L$_2$] (L = dmso, py, pyNO, dmf, OPPh$_3$) with one equivalent each of TMSOTf and L produced [SnF$_3$L$_3$]OTf cations, shown by NMR studies to be a mixture of mer and fac isomers in solution [21]. The attempts to remove a further fluoride using a second equivalent of TMSOTf and more L in most cases resulted in a mixture of [SnF$_3$L$_3$]OTf and [SnF$_2$L$_4$][OTf]$_2$, although [SnF$_3$(OPPh$_3$)$_4$][OTf]$_2$ was isolated and shown by an X-ray structure to be the trans isomer in the solid state. The NMR studies showed a mixture of the cis and trans form of this dication present in solution [21].

Here we report attempts to isolate fluoro-germanium (IV) cations with a range of neutral N- and O-donor ligands, including the N$_3$- and N$_4$-donor macrocyclic ligands. A comparison of the key spectroscopic data for [GeF$_4$L$_2$] and [GeF$_3$L$_3$]$^+$ types with the tin analogues and an exploration of the bonding via DFT calculations are reported, together with the promotion of endocyclic coordination of the tetra-aza macrocycles, yielding germanium difluoride dications.

2. Results

[GeF$_4$L$_2$]: [GeF$_4$L$_2$] (L = dmso, dmf, py, pyNO, OPPh$_3$, OPMe$_3$, OAsPh$_3$) were prepared by the direct reaction of [GeF$_4$(MeCN)$_2$] with the ligands. The complexes with py, OPPh$_3$, OPMe$_3$, OAsPh$_3$ have been previously described [13,14] and the characterisation data in the present study were consistent with the published data. The X-ray crystal structures of trans-[GeF$_4$L$_2$] (L = py, OPPh$_3$, OPMe$_3$) and cis-[GeF$_4$(FCH$_2$CN)$_2$] have also been previously reported [13,14,23]. Their $^{19}$F NMR spectroscopic data are given in Table 1.

### Table 1. Selected NMR spectroscopic data.

| Complex            | Solvent | Temperature | $^{19}$F{$_1$H} NMR/ppm $^a$ | $^{2}$J$_{FF}$/Hz | $^{31}$P{$_1$H} NMR/ppm | Reference        |
|--------------------|---------|-------------|-----------------------------|-------------------|------------------------|------------------|
| [GeF$_4$(dmso)$_2$] | cis     | CD$_3$NO$_2$ | 253 K                      | $-115.3$ (t), $-129.8$ (t) | $-115.4$ (s) | 61 This work        |
| cis trans          |         |             | $-115.3$ (t), $-129.8$ (t) | $-115.4$ (s)        |            |                  |
| [GeF$_4$(dmso)$_2$] | mer     | CD$_3$NO$_2$ | 253 K                      | $-109.8$ (d), $-121.7$ (t) | $-122.2$ (s) | 71 This work        |
| fac                |         |             | $-109.8$ (d), $-121.7$ (t) | $-122.2$ (s)        |            |                  |
| [GeF$_4$(dmf)$_2$]  | cis     | CD$_3$NO$_2$ | 253 K                      | $-125.4$ (t), $-135.8$ (t) | $-125.4$ (s) | 59 This work        |
| cis trans          |         |             | $-125.4$ (t), $-135.8$ (t) | $-125.4$ (s)        |            |                  |
| [GeF$_4$(dmf)$_3$]  | mer     | CD$_3$NO$_2$ | 253 K                      | $-126.1$ (d), $-135.0$ (t) | $-134.5$ (s) | 64 This work        |
| fac                |         |             | $-126.1$ (d), $-135.0$ (t) | $-134.5$ (s)        |            |                  |
| [GeF$_4$(py)$_2$]   | trans   | CDCl$_3$    | 253 K                      | $-125.7$ (s)        |            | Ref. [14]          |
| [GeF$_3$(py)$_3$]   | mer     | CD$_2$Cl$_2$ | 298 K                      | $-122.0$ (d), $-137.3$ (t) | $-149.2$ (s) | 55 This work        |
| fac                |         |             | $-122.0$ (d), $-137.3$ (t) | $-149.2$ (s)        |            |                  |
| Complex | Solvent Temperature | $^{19}$F\[\text{^1H}\] NMR/ppm | $^2$J_{FF}/Hz | $^{31}$P\[\text{^1H}\] NMR/ppm | Reference |
|---------|---------------------|---------------------|----------------|---------------------|----------|
| [GeF$_4$(pyNO)$_2$]$_{cis}$ | CD$_2$NO$_2$ 298 K 253 K | $-142.8$ (br s) $-136.1$ (t), $-133.1$ (t) $-129.8$ (s) | 58 | | This work |
| [GeF$_3$(pyNO)$_3$]$_{mer}$ | CD$_2$NO$_2$ 298 K 253 K | $-136.8$ (d), $-143.0$ (t) | 65 | | This work |
| [GeF$_4$(OPPh$_3$)$_2$]$_{cis}$ | CDCl$_3$ 298 K 253 K | $-100.9$ (t), $-120.6$ (t) $-105.3$ (s) | 64 | | Ref. [13] |
| [GeF$_3$(OPPh$_3$)$_3$]$_{mer}$ | CD$_2$Cl$_2$ 298 K | $-89.0$(d), $-100.4$(t) $-100.9$(s) | 76 | | This work |
| [GeF$_3$(OPPh$_3$)$_3$]$_{fac}$ | CD$_2$Cl$_2$ 298 K | $-95.6$ (d), $-106.6$ (t) $-93.0$ (s) | 64 | | This work |
| [GeF$_4$(OPMe$_3$)$_2$]$_{cis}$ | CD$_2$Cl$_2$ 298 K | $-107.6$ (t), $-121.6$ (t) $-109.9$ (s) | 60 | | Ref. [13] |
| [GeF$_3$(OPMe$_3$)$_3$]$_{mer}$ | CD$_2$NO$_2$ 298 K 253 K | $-79.3$ (d), $-89.5$ (t) $-89.9$ (s) | 68 | | This work |
| [GeF$_3$(OPMe$_3$)$_3$]$_{fac}$ | CD$_2$NO$_2$ 298 K | $-65.1$ (s) $-59.1$ (s) | | | This work |
| [GeF$_4$(MeCN)$_2$]$_{cis}$ | CD$_2$Cl$_2$ 180 K | $-101.2$ (t), $-134.2$ (t) $-108.2$ (s) | 55 | | Ref. [13] |
| fac-[GeF$_3$(Me$_3$-tacn)]$_{OTf}$ | CD$_2$NO$_2$ 298 K | $-151.7$ (s) | | | This work |
| mer-[GeF$_3$(terpy)]$_{OTf}$ | CD$_2$Cl$_2$ 298 K | $-115.9$ (d), $-153.0$ (t) | 68 | | This work |
| [GeF$_2$(Me$_4$-cyclen)]$_{cis}$ | CD$_2$NO$_2$ 298 K | $-132.3$ (s) | | | This work |
| [GeF$_2$(Me$_4$-cyclam)]$_{trans}$ | CD$_2$NO$_2$ 298 K | $-136.8$ (d) $-134.8$ (d) $-132.7$ (s) $-132.2$ (d) $-130.8$ (d) $-130.5$ (s) | 38 38 52 38 52 52 | | This work |

* triflate resonances omitted; $^b$ not isolated in a pure state, data from a mixture with [GeF$_2$(OAsPh$_3$)$_4$][OTf]$_2$ and [GeF$_3$(OAsPh$_3$)$_3$][OTf].

In solution at low temperatures, the $^{19}$F\[\text{^1H}\] NMR data typically show two 1:1 triplets and a singlet indicating the presence of both cis and trans isomers (Figure 1) [13,14], although the ambient temperature spectra of some are consistent with exchanging systems, (Table 1) and the relative amounts of the isomers vary with the solvent. Full details of the spectra of the new complexes are given in the Experimental section and the SI. The $^{19}$F\[\text{^1H}\] NMR spectra of [GeF$_4$(dmso)$_2$] and [GeF$_4$(dmf)$_2$] in CH$_3$NO$_2$ show one sharp singlet and two
broad lines at 298 K; on cooling to 253 K, the broad lines resolve into the expected triplets (Figures S1.4 and S2.4). This suggests that dissociative neutral ligand exchange is easier in the cis isomers, whilst the trans isomers are not involved.

![Figure 1. The $^{19}$F$^1$H NMR spectrum of the cis/trans-isomer mixture from $[\text{GeF}_4(\text{dmf})_2]$ in CH$_3$NO$_2$ at 253 K.](image)

$[\text{GeF}_3\text{L}_3]\text{[OTf]}$: The general approach to the synthesis of the trifluoro-germanium cations utilised the reaction of $[\text{GeF}_4\text{L}_2]$ with one equivalent of TMSOTf in anhydrous CH$_2$Cl$_2$, followed by the addition of a further equivalent of L (Scheme 1).

![Scheme 1. Synthesis of the complexes produced in this work containing monodentate ligands L or L'.](image)

The reaction of $[\text{GeF}_4(\text{MeCN})_2]$ with TMSOTf in MeCN caused decomposition, but with the other ligands ($L = \text{dms}, \text{dmf}, \text{py}, \text{pyNO}, \text{OPPh}_3, \text{OPMe}_3$) the products were $[\text{GeF}_3\text{L}_3]\text{[OTf]}$. Crystals of $[\text{GeF}_3(\text{OPPh}_3)_3]\text{[OTf]}$ were obtained from CH$_2$Cl$_2$ solution by slow evaporation and the X-ray structure analysis revealed them to be the mer isomer (Figure 2).

The structure reveals a near regular octahedral geometry with the d(Ge-F) and d(Ge-O) showing no significant effect of the trans ligands. A comparison with the structure of $[\text{GeF}_4(\text{OPPh}_3)_2]$ [13] shows that the d(Ge-F) are identical, but the d(Ge-O) is slightly longer in the latter.

The cations were generally poorly soluble in chlorocarbons, and data were mostly obtained from the CH$_3$NO$_2$ / CD$_3$NO$_2$ solutions, which have the limitation of a high M.P. (245 K), hence precluding lower temperature studies, but stronger donor solvents were avoided since they tend to displace the neutral ligands. The $^{19}$F$^1$H NMR spectra show the presence of both mer and fac isomers with the former producing a doublet [2F] and a triplet [F] and the latter a singlet; usually the mer isomer is the more abundant. Figure 3 shows a typical example. The $^{19}$F$^1$H NMR resonances (Table 1) occur in the range of $\delta = -80$ to $-155$ depending upon the isomer and the neutral ligand present, and overlap with those of $[\text{GeF}_4\text{L}_2]$, although the $\delta$($F$) trans $F$ are always at a higher frequency than the $\delta$($F$) trans N/O for a particular complex.
Figure 2. View of the molecular structure of the cation in mer-[GeF₃(OPPh₃)]_2[Otf] showing the atom numbering scheme. A second similar, but crystallographically independent, molecule of mer-[GeF₃(OPPh₃)]_2[Otf] in the asymmetric unit, and the H atoms are omitted for clarity. Ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (°): Ge1-F3 = 1.7598 (11), Ge1-F1 = 1.7679 (11), Ge1-F2 = 1.7628 (11), Ge1-O2 = 1.8950 (13), Ge1-O3 = 1.9076 (13), Ge1-O1 = 1.8990 (13), P3-O3 = 1.5287 (14), P2-O2 = 1.5298 (13), P1-O1 = 1.5232 (13), F3-Ge1-F2 = 91.99 (5), F2-Ge1-F1 92.69 (5), O2-Ge1-O3 = 88.38 (6), O2-Ge1-O1 = 89.30 (6).

Figure 3. The ¹⁹F[¹H] NMR spectrum of the mer/fac-isomer mixture in [GeF₃(OPPh₃)]_2[Otf] (CD₂Cl₂, 298 K); the Otf resonance is omitted for clarity.

[GeF₃(pyNO)]_2[Otf] appears to be somewhat unstable in CD₂NO₂ solution, decomposing slowly at room temperature over the period of the NMR acquisition, and the ¹⁹F[¹H] NMR spectra usually show some [GeF₄(pyNO)]₂ present (SI Figure S7.2). The [GeF₃(OPPh₃)]_2[Otf] (R = Me, Ph) complexes were obtained in good yield and were stable in CD₂NO₂ solution; the mer isomer is the major form in both (Figure 3). In addition to the 2JFF coupling, the ¹⁹F[¹H] and ³¹P[¹H] NMR spectra of [GeF₃(OPMe₃)]_2[Otf] (Figure S9) show further small couplings of ~ 7 Hz which were tentatively assigned as 3JFF. Similar couplings are evident, but less well resolved, in the spectra of [GeF₃(OPPh₃)]_2[Otf].

In marked contrast, the reaction of [GeF₄(MeCN)]_2, TMSOTf and OasPh₃ in a 1:1:3 molar ratio in CH₂Cl₂ precipitated a white solid. The ¹⁹F[¹H] NMR spectrum (CD₃NO₂) shows the expected resonances for [GeF₃(OasPh₃)]_2[Otf], viz., δ = −89.9 (s), fac isomer; −89.5 (t, 2JFF = 66 Hz), −79.3 (2JFF = 67 Hz), mer isomer, and −79.9 (s, Otf), along with two strong singlets at δ = −65.1 and −59.1. By comparison with the spectra of [GeF₂(tetra-azamacrocyle)₂][Otf]₂ (vide infra), these were assigned to cis- and trans-[GeF₂(OasPh₃)]_2[Otf]₂ (Figure 4). Integration of the ¹⁹F[¹H] NMR spectrum of the mixture suggested that the ratio of the complexes [GeF₃(OasPh₃)]_2[Otf]₂: [GeF₂(OasPh₃)]_4[Otf]₂ was ~3:1. Attempts to obtain a pure sample of either were unsuccessful, although their identities are not in doubt.
This complex was insoluble in common solvents, but a crystal fortuitously obtained from the filtrate proved to be \([\text{GeF}_3(\text{Me}_3\text{tacn})]\)Cl, whilst a few crystals grown from the filtrate proved to be \([\text{GeF}_3(\text{Me}_3\text{tacn})]\)OTf (Scheme 2), which was more soluble and allowed the solution NMR data for the cation to be obtained. The \(^{19}\text{F}\{^1\text{H}\}\) spectrum, which shows a singlet at \(-151.7\) ppm, is consistent with the expected fac geometry. In the earlier study \cite{14}, the direct reaction of \(\text{GeF}_4\) with terpy in \(\text{CH}_2\text{Cl}_2\) yielded an insoluble product of the composition \([\text{GeF}_3(\text{terpy})]\), and since the IR spectrum of this complex did not show features characteristic of \([\text{GeF}_3]^2-\) \cite{27}, it was suggested to be oligomeric with both bridging and chelating terpy ligands. Here we found that the sequential reaction of \([\text{GeF}_4(\text{MeCN})]\) with TMSOTf and terpy (terpy = terpyridine) in \(\text{CH}_2\text{Cl}_2\) solution (Scheme 2), afforded white \([\text{GeF}_3(\text{terpy})]\)OTf, whose \(^{19}\text{F}\{^1\text{H}\}\) NMR spectrum contains (in addition to the OTf resonance) resonances at \(-115.9\) (d, \(2\text{F}\), \(J_{\text{FF}} = 68\) Hz) and \(-153.0\) (t, \(\text{F}\), \(2\)\(^{19}\text{F}\) = 68 Hz), showing the presence of the expected \textit{mer} cation. However, the product did not fully dissolve for the NMR spectra (see Materials and Methods section).

\([\text{GeF}_2(\text{L}''')][\text{OTf}]_2\) \((\text{L}''' = \text{Me}_4\text{-cyclen} \text{ or Me}_4\text{-cyclam})\): The direct reaction of \([\text{GeF}_4(\text{MeCN})]\) with \(\text{Me}_4\text{-cyclam}\) in \(\text{CH}_2\text{Cl}_2\) precipitated a white powder, identified as \([\text{GeF}_2(\mu-\text{Me}_4\text{-cyclam})]\) \cite{14}. In contrast, the reaction of \([\text{GeF}_4(\text{MeCN})]\) with two molar equivalents of TMSOTf in MeCN, followed by addition of \(\text{Me}_4\text{-cyclen} \text{ or Me}_4\text{-cyclam}\) afforded the dications \([\text{GeF}_2(\text{L}'''')][\text{OTf}]_2\) in good yields (Scheme 3). For \([\text{GeF}_2(\text{Me}_4\text{-cyclen})]][\text{OTf}]_2\) the \(^1\text{H}\) NMR spectrum exhibits two Me resonances of equal intensity and a singlet resonance in the \(^{19}\text{F}\{^1\text{H}\}\) NMR spectrum, indicating that the 12-membered ring generated the \textit{cis}-octahedral isomer. This was confirmed by an X-ray crystal structure analysis of \([\text{GeF}_2(\text{Me}_4\text{-cyclen})][\text{OTf}]_2\times\text{CH}_3\text{NO}_2\) (see Materials and Methods section for discussion of this inversion twin) (Figure 5).
In contrast, the corresponding spectra of \([\text{GeF}_2(\text{Me}_4\text{-cyclam})][\text{OTf}]_2\) exhibit six $^{19}\text{F}[^1\text{H}]$ resonances (Figure 6), four doublets and two singlets. These may be attributed to the presence of four of the five possible stereoisomers (with the Me groups ‘all up’, ‘up,up,up,down’, ‘up,up,down,down’—2 variants and ‘up,down,up,down’ relative to the GeN$_4$ plane) of a trans octahedral geometry with slow pyramidal inversion at N; the larger (14-membered) ring of Me$_4$-cyclam allowing the germanium to sit within the ring. The coordinated fluorides are inequivalent in the ‘all up’ and ‘up,up,up,down’ forms, accounting for the four doublets, whilst the two singlets probably correspond to the equivalent fluorines in the other two stereoisomers. We cannot rule out the possibility that one of the singlets corresponds to a cis isomer, but this seems less likely.

Scheme 2. Routes used to prepare complexes with the tridentate Me$_3$-tacn and terpy ligands.

Scheme 3. Synthesis of the tetra-aza macrocyclic complexes.
Scheme 3. Synthesis of the tetra-aza macrocyclic complexes.

DFT Calculations

The DFT calculations were performed on the neutral complexes cis/trans-[GeF₄(OPMe₃)₂], the monocations, mer/fac-[GeF₃(OPMe₃)₃]⁺, and the dication cis/trans-[GeF₂(OPMe₃)₄]²⁺ using the B3LYP-D3 functional and 6-311G(d) basis set. For trans-[GeF₄(OPMe₃)₂] the initial geometry was taken from the published crystal structure [13], whereas for the cis isomer the structure was constructed starting from the trans geometry. Both structures were optimised, and the calculations converged with no imaginary frequencies. For the monocationic mer/fac-[GeF₃(OPMe₃)₃]⁺, the geometry of the mer isomer was taken from the structure of [GeF₃(OPPh₃)₃]⁺ with the Ph groups modified to Me. For the fac isomer the converged structure of mer-[GeF₃(OPMe₃)₃]⁺ was taken as a starting point. The dicationic complexes trans/cis-[GeF₂(OPMe₃)₄]²⁺ were also modelled, with trans-[SnF₂(OPPh₃)₄]²⁺ [21] taken as the starting geometry for the trans isomer. For the cis isomer the initial geometry was taken from the optimised geometry of trans-[GeF₂(OPMe₃)₄]²⁺ and the structure was modified to yield the cis geometry.

Comparing the geometric isomers of [GeF₄(OPMe₃)₂], the cis isomer is only very slightly lower in energy by 1.31 kJ/mol (compared to RT = 2.48 kJ/mol) in the gas phase (Table S2). This is consistent with the experimental observation that both isomers are seen in solution, although in this case the position of the equilibrium will be affected by the chosen solvent. For the trifluoro monocations, the mer isomer is slightly more stable than the fac by 3.19 kJ/mol, which is also consistent with the solution state data, which indicate that mer-[GeF₃(OPMe₃)₃]⁺ is the more abundant isomer. For the dica
The calculations show that the cis isomer is much more stable than the trans isomer (18.50 kJ/mol lower in energy) (although we were unable to isolate these dications). For both isomers of [GeF₄(OPMe₃)₂] the HOMO, HOMO-1 and HOMO-2 are combinations of lone pairs based on the fluorine ligands and the oxygens of the OPMe₃ ligand (Figure S7). The LUMO and LUMO+2 have a Ge-F σ* character with the LUMO+1 being entirely based on the OPMe₃ ligand.

The HOMO, HOMO-1, and HOMO-2 of the geometric isomers of [GeF₃(OPMe₃)₃]⁺ are also based on combinations of lone pairs on the F and O atoms. For these complexes the LUMO is mostly Ge-F antibonding and LUMO+1/2 are mostly ligand-based. For both isomers of [GeF₂(OPMe₃)₄]²⁺ the HOMO and HOMO-1/-2 are based on the lone pairs of the O and F atoms with the LUMO being mostly Ge-F antibonding and the LUMO+1/+2 mostly ligand-based (Figure 7 and SI).

![Figure 7. Representations of the HOMO and LUMO of cis- and trans-[GeF₄(OPMe₃)₂]](image_url)

3. Materials and Methods

The syntheses were carried out using standard Schlenk and vacuum line techniques, with samples handled and stored in a glove box under a dry dinitrogen atmosphere.
TMSOTf was obtained from Sigma-Aldrich and distilled before use. Germanium tetrafluoride was obtained from Fluorochem and used as received. CH₂Cl₂ and MeCN were dried by distillation from CaH₂ and n-hexane from sodium wire. Neutral ligands were obtained from Sigma-Aldrich unless otherwise stated and dried in vacuo (solids) or over molecular sieves (liquids) before use. 

Tacn (1,4,7-triazacyclononane) was prepared by the literature method [28] and the methylated versions, Me₃-tacn, Me₆-cyclen and Me₆-cyclam, were prepared from the parent macrocycles using the Eschweiler–Clarke reaction [29]. The germanium (IV) fluoride complexes, [GeF₄(MeCN)₂]⁺, [GeF₄(py)₂]⁻, [GeF₄(OPPh₃)₂], [GeF₄(OPMe₃)₂]⁻ and [GeF₄(OAsPh₃)₂]⁻, were made by following the literature methods [13,14].

Infrared spectra were recorded as Nujol mulls between CsI plates using a PerkinElmer Spectrum 100 spectrometer over the range 4000–200 cm⁻¹. The ¹H ¹⁹F[¹H] and ³¹P[¹H] NMR spectra were recorded from CH₃NO₂/CD₃NO₂ or CH₂Cl₂/CD₂Cl₂ solutions unless otherwise stated, using a Bruker AV400 spectrometer and are referenced to Me₄Si (via the residual solvent resonance), CFCl₃, and 85% H₃PO₄, respectively. ESI⁺ mass spectra were obtained in MeCN solution using a Waters Acquity Platform. Microanalyses were undertaken by Medac.

3.1. X-ray Experimental

Crystals of mer-[GeF₃(OPPh₃)₂][OTf] and cis-[GeF₂(Me₄-cyclen)][OTf]₂ xCH₃NO₂ were grown from CH₂Cl₂ solution and CH₃NO₂ solution, respectively. Data collection used a Rigaku AFC12 goniometer equipped with an enhanced sensitivity (HG) Saturn724+ detector mounted at the window of an FR-E+ SuperBright molybdenum (λ = 0.71073 Å) rotating anode generator with VHF Varimax optics (70 μm focus) with the crystal held at 100 K. Structure solution and refinement were performed using SHELXS(L)97, SHELX-2013, or SHELX-2014/7.41 and OLEX [30–32]. H atoms bonded to C were placed in calculated positions using the default C–H distance and refined using a riding model. Analysis of the data for [GeF₂(Me₄-cyclen)][OTf]₂ xCH₃NO₂ revealed an inversion twin with a surprisingly large unit cell in space group P2₁, with the asymmetric unit containing 14 cations, 28 anions and four CH₃NO₂ solvent molecules that were resolved, and a further 5.5 CH₃NO₂ solvent molecules per asymmetric unit were accounted for by solvent masking. There appeared to be no plausible higher symmetry space group and no missed symmetry. While the [GeF₂(Me₄-cyclen)]²⁺ cations were generally well-defined, some of the OTf groups showed evidence of some rotational disorder, most of which were modelled satisfactorily. Given the very large cell and the inversion twin, while the identity of the complex and the cis octahedral coordination geometry at Ge are not in doubt, detailed comparisons of the geometric parameters are not justified. Details of the crystallographic parameters are given in Table S1. CCDC reference numbers for the crystallographic information files in cif format are 2174295 ([GeF₃(OPPh₃)₂][OTf]) and 2177877 ([GeF₂(Me₄-cyclen)][OTf]₂ xCH₃NO₂).

3.2. DFT Calculations

The electronic structures of the series [GeF₄(OPMe₃)₂], [GeF₃(OPMe₃)₃]⁺ and [GeF₂(OPMe₃)₄]²⁺ were investigated by density functional theory (DFT) calculations using the Gaussian 16W program [33] and visualised using GaussView 5.0. The density functional chosen was B3LYP-D3 [34] with the basis set as 6-311G(d) [35]. Energy minima were confirmed by the absence of imaginary frequencies.

3.3. Complex Syntheses

[GeF₄(dmso)₂]: GeF₄ was gently bubbled through a stirred solution of dmso (1 mL) in n-hexane for 2 min. The solution was then stirred for 1 h at room temperature. The resulting white solid was filtered off and dried in vacuo. Yield 0.43 g. C₄H₁₂F₄GeO₅S₂(304.88): calcd. C 15.76, H 3.97; found C 15.91, H 3.31%. ¹H NMR (400 MHz, CD₃NO₂, 298 K): δ = 2.90 (br s, CH₃); (253 K): δ = 3.03 (br s, CH₃); 2.91 (s, CH₃). ¹⁹F[¹H] NMR (CD₃NO₂, 298 K): δ = −112.5 (br), −112.8 (s), −128.2 (br); (253 K): δ = −115.3 (t, ²FF = 61 Hz), −115.4 (s),
Inorganics 2022, 10, 107

(0.50 g, 2.2 mmol) was added, and the reaction mixture was stirred for 72 h. The solid was collected by filtration, washed with n-hexane (3 × 2 mL) and dried in vacuo. Yield 0.320 g, 41%. C_{10}H_{10}F_{4}GeN_{2}O_{5} (423.8): calcld. C, 31.46, H 2.64, N 6.48; found C, 31.62, H 2.94, N 7.18%. 1H NMR (400 MHz, CD_{3}NO_{2}, 298 K): δ = 8.7 (m), 8.3 (m), 8.1 (m), 7.9 (m). 19F[{H}] NMR (CD_{3}NO_{2}, 298 K): δ = −79.1 (s), −109.8 (d, 3_{FF} = 65 Hz), −141.8 (s), −143.0 (t, 3_{FF} = 65 Hz). IR (Nujol): ν = 639 (s), 590 (w) (Ge-F) cm⁻¹.

[GeF_{6}(dmsO)]·[OTf]: TMSOTf (0.024 g, 0.11 mmol) was added to a solution of [GeF_{6}(pyNO)_{2}] (0.095 g, 0.11 mmol) in MeCN (1 mL) was added. The reaction mixture was stirred for 2 h. The resulting white precipitate was collected by filtration, washed with n-hexane (15 mL) and dried in vacuo. Yield 0.54 g, 77%. C_{10}H_{10}F_{4}GeN_{2}O_{5}SCH_{2}Cl_{2} (648.9): calcld. C, 31.46, H 2.64, N 6.48; found C, 31.62, H, 2.94, N, 7.18%. 1H NMR (400 MHz, CD_{3}NO_{2}, 298 K): δ = 8.7 (m), 8.3 (m), 7.9 (m). 19F[{H}] NMR (CD_{3}NO_{2}, 298 K): δ = −79.1 (s), −109.8 (d, 3_{FF} = 65 Hz), −141.8 (s), −143.0 (t, 3_{FF} = 65 Hz). IR (Nujol): ν = 639 (s), 590 (w) (Ge-F) cm⁻¹.

[GeF_{3}(dmf)]·[OTf]: TMSOTf (0.051 g, 0.23 mmol) was added to a solution of [GeF_{3}(dmsO)]·[OTf] (0.070 g, 0.23 mmol) in MeCN (10 mL) at room temperature. After stirring for 2 h, the reaction mixture was stirred for 2 h. The resulting white precipitate was collected by filtration, washed with n-hexane (15 mL) and dried in vacuo. Yield 0.082 g, 69%. C_{5}H_{6}F_{6}GeO_{3}SCH_{2}Cl_{2} (549.1): calcld. C, 31.03, H 4.04; found C, 15.03, H 4.14. 1H NMR (400 MHz, CD_{3}NO_{2}, 298 K): δ = 3.06 (s, CH_{3}), 2.99 (s, CH_{3}), 2.98 (s, CH_{3}), 2.98 (s, CH_{3}), 2.00 (s, H_{2}O). 19F[{H}] NMR (CD_{3}NO_{2}, 298 K): δ = −79.1 (s), −109.8 (d, 3_{FF} = 71 Hz), −121.7 (t, 3_{FF} = 71 Hz), −122.2 (s). IR (Nujol): ν = 3437 (br) 1651 (m) 932 (m), 920 (m) (S-O), 639 (s), 590 (w) (Ge-F) cm⁻¹.

[GeF_{3}(dmsO)]·[OTf]: TMSOTf (0.128 g, 0.50 mmol) was added to a solution of [GeF_{3}(pyNO)]·[OTf] (0.056 g, 0.20 mmol) in MeCN (10 mL) at room temperature. After stirring for 2 h, the reaction mixture was stirred for 15 h. The solid was collected by filtration, washed with n-hexane (5 mL) and dried, and the reaction mixture was stirred for 2 h. The resulting white precipitate was collected by filtration, washed with n-hexane (15 mL) and dried in vacuo. Yield 0.150 g, 67%. C_{5}H_{6}F_{6}GeO_{3}S 1.5CH_{2}Cl_{2} ...
ν was washed with n-hexane (10 mL) and dried in vacuo. Yield 0.160 g, 72%. C_10 (0.120 g, 0.52 mmol) was added, and the reaction mixture was stirred for 15 h. A white precipitate gradually formed, and this was collected by filtration, washed with n-hexane (10 mL) and dried in vacuo. Yield 0.260 g, 53%. C_10 (0.302 g, 1.1 mmol) in MeCN (10 mL) at room temperature and stirred for 2 h. MeCN was added, and the reaction mixture was stirred for 2 h. To this, OAsPh_4 was added, and the reaction mixture was stirred for 15 h. A white precipitate was collected by filtration, washed in hexane and dried in vacuo. Yield 0.10 g, 47%. C_10 and dried in vacuo. Yield 0.150 g. Despite attempts on different batches both before and after filtration, satisfactory elemental analyses for this compound could not be obtained, most likely due to the very poor solubility of the complex and co-precipitation of inorganic materials with the complex. However, the spectroscopic data are consistent with that expected for the formulation, mer-[GeF_3(py)_2]OTf. H NMR (400 MHz, CD_2Cl_2, 298 K): δ = 7.9 (m, [2H]), 8.9 (m, [2H]), 8.8 (m, [2H]), 8.7 (m, [H]), 8.6 (m, [2H]), 8.2 (m, [2H]). F{^19} NMR (CD_2Cl_2, 298 K): δ = 79.0 (s), −92.0 (t, ^{2}J_{FF} = 55 Hz), −137.3 (d, ^{2}J_{FF} = 35 Hz), −149.2 (s). IR (Nujol): ν = 627 (br), 615 (br) (Ge-F) cm^{-1}. Since the ^19F NMR spectrum showed that both complexes were present (see Results and Discussion), microanalytical data were not recorded.

[GeF_3(OAsPh_3)_2]OTf and [GeF_3(OAsPh_3)_3]OTf: TMSOTf (0.089 g, 0.40 mmol) was added to a solution of [GeF_3(OmpMe_3)] (0.092 g, 0.40 mmol) in CH_2Cl_2 (10 mL) at room temperature. After stirring for 2 h, pyridine (0.03 g, 0.43 mmol) was added to the solution and the reaction mixture was stirred for 15 h. The solvent was concentrated to ca. 5 mL, n-hexane (15 mL) was added, and the solid was filtered off and dried in vacuo. Yield 0.160 g, 72%. C_10 (0.120 g, 0.52 mm mol) was added, and the reaction mixture was stirred for 15 h. A white precipitate was collected by filtration, washed in hexane and dried in vacuo. Yield 0.21 g. 1H NMR (CD_2Cl_2, 298 K): δ = 8.93 (m), 8.76 (m), 8.20 (m), 7.91 (m), 7.82 (m), 7.73 (m), 7.73 (m). ^19F NMR (CD_2Cl_2, 298 K): δ = 79.0 (s), −122.0 (t, ^{2}J_{FF} = 55 Hz), −137.3 (d, ^{2}J_{FF} = 55 Hz), −149.2 (s). IR (Nujol): ν = 627 (br), 615 (br) (Ge-F) cm^{-1}.
which showed that the M-OAs bond length was shorter than that for M-OP, suggesting with crystallographic data on isostructural early transition-metal pnictine oxide complexes, spectroscopic data: Figure S1. [GeF₄(Nujol): $\tilde{v} = 639$ (s) (Ge-F) cm$^{-1}$]

Conclusions
A series of fluoro-germanium (IV) cations [GeF₃L₃][OTf] with neutral N- and O-donor co-ligands (L = dmso, dmf, pyNO, OPh₃, OPMe₃, py) was prepared and fully characterised. In solution they exist as mixtures of mer and fac isomers, with the mer dominating. The attempts to prepare dicyclics by removal of a further fluoride were only successful for L = OAsPh₃ (partially) and for the two tetra-aza macrocycles. The [GeF₃L₃][OTf] are similar to [SnF₃L₃][OTf] [21], but appear to be less stable in solution, and whilst mixtures of [SnF₃L₃][OTf] and [SnF₂L₄][OTf] were formed by the reaction of [SnF₄L₂] or [SnF₃L₃][OTf] with TMSOTf and more L (although only [SnF₂(OPPh₃)₃][OTf] was isolated in a pure form), the similar removal of a second fluoride in the germanium systems did not occur for most of the L investigated. Standard sources [36] suggest that Sn-F and Ge-F bonds differ little in energy (456 and 464 kJ/mol, respectively), and there may be a significant kinetic factor in the germanium case. Such a situation is much more common in transition-metal rather than main-group chemistry, where partially filled d-orbitals and significant interactions of the ligands with the transition-metal d-orbitals can give rise to very significant kinetic barriers. Notably, in the present study the tetra-aza macrocyclic complex syntheses, [GeF₂L²][OTf]$_2$, required some 3 days to go to completion. Further, the ability of OAsPh₃ to form [GeF₂(OAsPh₃)₂][OTf]$_2$ contrasts with OPR$_3$, suggesting that OAsPh₃ is a stronger donor towards the fluoro-germanium (IV) centre. This is consistent with crystallographic data on isostructural early transition-metal pnictine oxide complexes, which showed that the M-OAs bond length was shorter than that for M-OP, suggesting stronger binding of the OAsPh₃ towards hard acceptors.

The DFT calculations provided evidence for trends in the stability of the isomers, although it should be remembered that the calculations are for gas-phase ions, and cation/anion interactions, packing effects in the solids, and solvation in solution will significantly affect the stabilities.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/inorganics10080107/s1, spectroscopic data: Figure S1. [GeF₄(dmso)$_2$]; Figure S2. [GeF₄(dmf)$_2$]; Figure S3. [GeF₄(pyNO)$_2$]; Figure S4. [GeF₃(dmso)$_3$][OTf]; Figure S5.
[GeF₃(dmf)₃][OTf]; Figure S6. [GeF₃(py)₃][OTf]; Figure S7. [GeF₃(pyNO)₃][OTf]; Figure S8. [GeF₃(OPPh₃)₃][OTf]; Figure S9. [GeF₃(OPMe₃)₃][OTf]; Figure S10. [GeF₃(OAsPh₃)₃][OTf] and [GeF₂(OAsPh₃)₂][OTf]; Figure S11. [GeF₃(terpy)][OTf]; Figure S12. [GeF₃(Me₅-tacn)][OTf]; Figure S13. [GeF₂(Me₅-cyclen)][OTf]; Figure S14. [GeF₂(Me₅-cyclam)][OTf]; Table S1. X-ray crystallographic data; Figure S15. Frontier orbitals of cis-trans-[GeF₄(OPMe₃)₂]; Figure S16. Frontier orbitals of fac/mer-[GeF₃(OPMe₃)₃]⁺; Figure S17. Frontier orbitals of cis/trans-[GeF₂(OPMe₃)₄]³⁻. Table S2. The x,y,z coordinates used in the DFT calculations are also included.

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