# Ligand Properties of the $^-OSeF_5$ and $^-OTeF_5$ Groups in Pseudo-trigonal-bipyramidal Molecules

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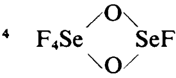
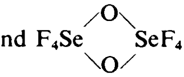
The compounds $F_2Se(OSeF_5)_2$, $F_2Se(OTeF_5)_2$, and $F_2Te(OTeF_5)_2$ have been prepared and their structures investigated by $^{77}Se$ and $^{125}Te$ n.m.r. spectroscopy. All three materials have pseudo-trigonal-bipyramidal structures with axial $^-OSeF_5$ ($-OTeF_5$) ligands, with the fluorine ligands in equatorial positions. This behaviour is discussed in terms of the extreme electronegativity of these ligands. $F_2Te(OTeF_5)_2$ reacts further with $FOTeF_5$ to give *mer*-$F_3Te(OTeF_5)_3$ but no *fac*-$F_3Te(OTeF_5)_3$. Selenium-77 n.m.r. spectroscopic data for numerous selenium fluorides are presented.

The chemistry of the $^-OSF_5$, $^-OSeF_5$, and $^-OTeF_5$ ligands is well documented, and derivatives of many of the main-group and transition elements are known.[1] These ligands, especially $^-OSeF_5$ and $^-OTeF_5$, resemble fluorine in their ability to stabilize high oxidation states, but have the advantage of avoiding bridging which is notorious in fluoride systems. It has been claimed that these groups have a higher (group) electronegativity than fluorine because of their special substitutional behaviour on $IF_5$.[2] However, by careful measurements of $^{125}Te$ and $^{129}Xe$ n.m.r. spectra, and $^{129}Xe$ and $^{127}I$ Mössbauer spectra of various compounds, a (group) electronegativity has been estimated of just a little less than that of fluorine.[3] Other workers have stated that principally the electronegativity of fluorine cannot be exceeded by just accumulating many fluorine atoms around one central atom.[4]

In this paper we describe the substitional behaviour of the $^-OSeF_5$ and $^-OTeF_5$ ligands in trigonal-bipyramidal systems.

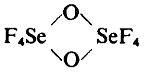
## Experimental

Volatile materials were handled in all-glass vacuum systems by standard techniques. $SeF_4$,[5] $TeF_4$,[6] $SeOF_2$,[5] $SeO_2F_2$,[7,8] $FOSeF_5$,[9,10] $FOTeF_5$,[11] $B(OTeF_5)_3$,[12] $K^+OSeF_5^-$,[13] $Hg(OSeF_5)_2$,[13] $Xe(OSeF_5)_2$,[14]  $F_4Se\genfrac{}{}{0pt}{}{O}{O}SeF_4$,[15] $ClSeF_5$,[16] and $N{\equiv}C{-}O{-}SeF_5$ [17] were prepared according to literature methods. $SeF_6$ and $SeCl_4$ were prepared by exhaustive fluorination and chlorination, respectively, of powdered selenium. $SO_2FCl$, $CFCl_3$, and other fluorinated solvents were purchased and dried over $P_2O_5$ before use, if necessary. Analyses were made by Beller Laboratories, Göttingen. I.r. spectra were recorded on a Beckmann Acculab 10 instrument. Moisture-sensitive compounds were handled in a glove-box with a water content of less than 1 p.p.m. Raman spectra were taken with a Cary 82 (Varian) and Kr-laser excitation. Mass spectra were recorded on a MAT 211 (Varian MAT) at 70 eV excitation energy. N.m.r. spectra were recorded on a JEOL 90 Fourier instrument; $^{19}F$ at 84.25 MHz, $^{125}Te$ at 28.25 MHz, and $^{77}Se$ at 17.03 MHz. In general, $^{19}F$ spectra needed accumulation of a few dozen pulses, $^{125}Te$ of several thousands, and $^{77}Se$ up to 30 000 pulses. In no case was an extra delay time, on top of the aquisition time, allowed between pulses. For $^{19}F$ n.m.r. spectra the conventional standard, $CFCl_3$, was used. Selenium-77 chemical shifts are measured relative to pure $SeOCl_2$, $^{125}Te$ chemical shifts relative to aqueous $H_6TeO_6$; positive signs indicate values to high frequency. The chemicals shifts can be converted to other standards as indicated in the Table.

*Selenium*(IV) *Difluoride Bis*[*pentafluoroselenate*(VI)].—$Hg(OSeF_5)_2$ (12 g, 20.6 mmol) was filled into a glass vessel (100 cm$^3$) under strictly dry conditions. Dry $CFCl_3$ (Freon 11; 50 cm$^3$) was condensed under vacuum onto it. Slowly $SeCl_4$ (2 g, 9 mmol) was added, while the mixture was stirred at −10 °C. The reaction mixture was kept stirring for 18 h at −10 °C. Under retained cooling the sediment of $HgCl_2$ was filtered off. The solution was slowly pumped under dynamic vacuum through −30 °C and −196 °C traps. The −196 °C trap contained the solvent and  $F_4Se\genfrac{}{}{0pt}{}{O}{O}SeF_4$, which can be separated from the solvent by a Teflon spinning-band column if necessary. The −30 °C trap contained colourless crystals of the title compound. A second distillation through a −30 °C trap gave improved purity: yield 4.3 g (96%). The material was slightly contaminated with $O{=}Se(OSeF_5)_2$, as shown by n.m.r. spectroscopy and the analysis (Found: F, 44.6; Se, 46.2. $F_{12}O_2Se_3$ requires F, 45.9; Se, 47.8%). $^{19}F$ N.m.r. (−100 °C, $SO_2FCl$ solvent): $AB_4$ spectrum with $\delta_A = 81.2$, $\delta_B = 75.7$ p.p.m., $J(AB) = 218$ Hz, and a single line at δ 14.4 p.p.m. with $^{77}Se$ isotope lines, $J(^{77}Se{-}F) = 1\,128$ Hz. For $^{77}Se$ n.m.r. see Table. Raman spectrum (−60 °C, solid): 823 (w), 725 (vs), 710 (vs), 667 (m), 653 (m), 638 (m), 582 (m), 560 (m), 525 (m), 472 (w), 446 (w), 422 (m), 380 (w), 325 (m, br), 290 (w), 256 (w), 246 (m), 215 (m), 198 (m), 156 (s), 119 (w), and 84 (m) cm$^{-1}$.

*Selenium*(IV) *Difluoride Bis*[*pentafluorotellurate*(VI)].—Under exclusion of moisture $SeF_4$ (1 g, 6.5 mmol) was placed into a fep tube [fep = poly(perfluoroethene–propene)], and freshly sublimed $B(OTeF_5)_3$ (7 g, 9.6 mmol) into another. The tubes were directly interconnected at a glass vacuum line, a few cm$^3$ solvent ($SO_2FCl$) were condensed onto the $SeF_4$, and the $B(OTeF_5)_3$ slowly added to the solution. At first, solidification occurred; at *ca.* −45 °C the solid dissolved with evolution of $BF_3$ and $TeF_6$ (identified by i.r. gas spectra). Further warming to 0 °C completed the reaction. After removal of all volatiles the resulting product was distilled at 55 °C/0.1 mbar, giving a colourless, moisture sensitive liquid (2.7 g, 73%), m.p. 30.8 °C (Found: F, 33.0; Se, 13.05; Te, 43.0. $F_{10}O_3SeTe_2$ requires F, 33.2; Se, 13.8; Te, 44.6%). $^{19}F$ N.m.r.: $AB_4$ spectrum, $\delta_A = 45.05$, $\delta_B = 33.36$ p.p.m., $J(AB) = 185$, $J(^{125}Te{-}F_B) = 3\,741$ Hz. For $^{77}Se$ n.m.r. see Table. Raman spectrum: 1 009 (s, p), 810 (m, p), 731 (sh), 713 (vs, p), 663 (vs, p), 514 (m, p), 478 (s, p), 473 (s, p), 37 (w, p), 322 (m, dp), 308 (m, dp), 279 (m, p), 261 (m, p), 246 (s, p), 231 (s, p), 179 (s, p), 160 (34, p), 110 (m, p), and 83 (m, p) cm$^{-1}$. A similar reaction with half the amount of $B(OTeF_5)_3$ gave evidence for $O{=}SeF{-}OTeF_5$, $F_2Se(OTeF_5)_2$, and $SeF_3^+B(OTeF_5)_4^-$ in the $^{77}Se$ n.m.r. at −60 °C, see the Table.

**Table.** Selenium-77 n.m.r. data for some selenium fluorides and chlorides

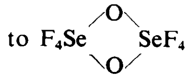
| Compound | Solvent | Temp. (°C) | Chemical shift [a] (δ/p.p.m.) | Coupling constant [b] [$^1J(^{77}Se-F)$/Hz] |
|---|---|---|---|---|
| $SeOCl_2$ | — | 25 | 0 | |
| $SeOF_2$[c] | — | 25 | −101 | 867 |
| $SeO_2F_2$[c] | — | 25 | −531 | 1 577 |
| $SeF_4$ | $CH_3F$ | −135 | −396 | 1 206 (e), 284 (a) [d] |
| $SeF_6$[c] | — | 25 | −879 | 1 423 |
| $SeF_3^+B(OTeF_5)_4^-$ | $SO_2FCl$ | −60 | −343 | 1 184 [e] |
| $K^+SeOF_5^-$ | $CH_3CN$ | | −847 | 1 288 (e), 1 075 (a) |
| $F-O-SeF_5$ | — | 25 | −850 | 1 430 (e), 1 387 (a), $^2J(^{77}Se-^{19}F) = 110$ |
| $F_5Se-O-SeF_5$ | — | 25 | −882 | 1 407 (e), 1 390 (a) |
| $F_5Se-O-O-SeF_5$ | — | 25 | −845 | 1 473 (e), 1 368 (a) |
|  | — | 25 | −877 | 1 403, 1 302, $^3J(^{77}Se-^{19}F) = 7.3$ |
| $ClSeF_5$ | — | 25 | −880 | 1 300 (e), 1 325 (a) |
| $N\equiv C-O-SeF_5$ | — | −15 | −913 | 1 470 (e), 1 423 (a) |
| $C(OSeF_5)_4$ | $CFCl_3$ | 25 | −872 | 1 414 (e), 1 384 (a) |
| $Hg(OSeF_5)_2$ | $CH_2Cl_2$ | 25 | −843 | 1 299 (e), 1 287 (a) |
| $Xe(OSeF_5)_2$ | $CFCl_3$ | 25 | −871 | 1 323 (e), 1 323 (a), $^2J(^{129}Xe-^{77}Se) = 153.8$ |
| $O=Se(OSeF_5)_2$ | $CFCl_3$ | 25 | −117 ($Se^{IV}$),<br>−875 ($Se^{VI}$) | 1 335 (e), 1 328 (a), $^3J(^{77}Se-F) = 24.7$ |
| $F_2Se(OSeF_5)_2$ | $SO_2FCl$ | −100 | −452.4 ($Se^{IV}$),<br>−873 ($Se^{VI}$) | 1 339 (e), 1 311 (a), 1 113 ($Se^{IV}-F$), $^3J(^{77}Se-F_e) = 26.9$,<br>$^3J(^{77}Se-F) = 9.9$, $^2J(^{77}Se-^{77}Se) = 340$<br>$^3J(^{77}Se-F_e) = 16.4$ |
| $O=Se(OTeF_5)_2$ | $SO_2FCl$ | −60 | −132 | 834.9, $^3J(^{77}Se-F_e) = 12.8$ |
| $O=SeF-OTeF_5$ | $SO_2FCl$ | −60 | −148 | 1 074, $^3J(^{77}Se-F_e) = 8.0$ |
| $F_2Se(OTeF_5)_2$ | $SO_2FCl$ | −60 | −355 | |

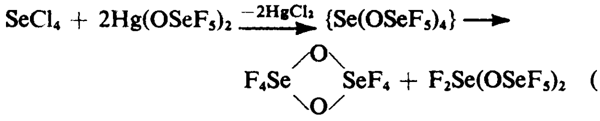
[a] $SeOCl_2$ was used as external standard. Chemical shifts can be converted to values relative to $(CH_3)_2Se$ by adding 1 479 p.p.m., see ref. 42. [b] e = Equatorial, a = axial fluorine atom. [c] See also ref. 43. [d] The previous values of $^1J(^{77}Se-F)$ (1 200 and 302 Hz; ref. 19) in the $^{19}F$ n.m.r. spectrum have been remeasured and found to be 1 204 and 286 Hz. [e] A value of 1 212.6 Hz has been reported for $SeF_3^+BF_4^-$ (M. Brownstein and R. J. Gillespie, *J. Chem. Soc., Dalton Trans.*, 1973, 67).

*Tellurium*(IV) *Difluoride Bis*[*pentafluorotellurate*(VI)].—A reaction vessel (100 cm$^3$) equipped with a cold-finger for sublimation was filled with $TeF_4$ (4 g, 19.7 mmol) and $B(OTeF_5)_3$ (9.5 g, 13.1 mmol). The vessel was connected to a glass vacuum line. A pressure of *ca.* 500 mbar Ar was retained, and the solid mixture was slowly heated to 60—70 °C. A colourless solution was obtained and $BF_3$ evolved. This was subsequently pumped off if the total gas pressure increased beyond 600 mbar. After completion of the reaction the mixture was cooled, all volatiles pumped off, and the product sublimed to the cold-finger with a bath temperature of 60 °C. $F_2Te(OTeF_5)_2$ (12 g, 95%) was obtained as a colourless, crystalline moisture-sensitive product, m.p. 63—64 °C. It is very soluble in $CFCl_3$, $CF_2Cl-CFCl_2$, $CH_2Cl_2$, and $SO_2FCl$ (Found: F, 34.7; Te, 60.5. $F_{12}O_2Te_3$ requires F, 35.2; Te, 59.8%). $^{19}F$ N.m.r.: $AB_4$ spectrum, $\delta_A = -37.7$, $\delta_B = -41.0$ p.p.m., $J(AB) = 185$ Hz, and a broad single line at δ −48.3 p.p.m. $^{125}Te$ N.m.r. ($SO_2FCl$ solution at −100 °C; see also Figure 2): $\delta(Te^{VI}) = 135.9$ p.p.m., $^1J(^{125}Te-F_e) = 3\,647$, $^1J(^{125}Te-F_a) = 3\,419$ Hz, $\delta(Te^{IV}) = 532.5$ p.p.m., $^1J(^{125}Te-F) = 2\,812$, $^2J(^{125}Te-^{125}Te) = 1\,400$ Hz. I.r. absorptions (NaCl): 888 (m), 872 (m), 845 (m), 790 (m), 715 (sh), 688 (s), 670 (s), 645 (sh) cm$^{-1}$. Raman spectrum (solid): 834 (s), 756 (w), 731 (m), 717 (s), 685 (vs), 674 (vs), 654 (w), 645 (w), 610 (s), 439 (m), 306 (m), 331 (m), 248 (w), 237 (m), 208 (w), 159 (m), 139 (s), 123 (w), 113 (w), 77 (w), and 31 (s) cm$^{-1}$. Mass spectrum: $m/z = 631$, $(M - F)^+$; plus smaller fragments, all with the correct isotopic distribution.

mer-*Tellurium*(VI) *Trifluoride Tris*[*pentafluorotellurate*(VI)].—Powdered $F_2Te(OTeF_5)_2$ (3.2 g, 5 mmol) was filled into a glass ampoule of 10 mm external diameter. $CFCl_3$ (1 g) and $FOTeF_5$ (0.77 g, 3 mmol) were condensed on it using the glass vacuum line. The sealed ampoule was shaken for 9 d at −20 °C. Then the ampoule was opened and the contents distilled in dynamic vacuum through 0, −40, and −196 °C cold traps. The −40 °C fraction contained 2 g (45%) almost pure *mer*-$F_3Te(OTeF_5)_3$ with traces of *cis*- and *trans*-$F_2Te(OTeF_5)_4$ and *trans*-$F_4Te(OTeF_5)_2$, as detected by $^{19}F$ n.m.r. *mer*-Tellurium(VI) trifluoride tris[pentafluorotellurate(VI)] is a colourless, stable liquid, m.p. −5 °C, b.p. 140—145 °C, with decomposition above 180 °C (Found: F, 37.2; Te, 57.5. $F_{18}O_3Te_4$ requires F, 37.8; Te, 56.9%). $^{19}F$ N.m.r. (neat liquid): two closely overlapping $AB_4$ spectra with $\delta_A = -51.4$ and −51.6, $\delta_B = -41.3$ p.p.m., $J(AB) = 183$ Hz, and a $C_2D$ pattern, $\delta_C = -12.6$, $\delta_D = -17.3$ p.p.m., $J(CD) = 189.8$ Hz. $^{125}Te$ N.m.r.: for the ligands $OTeF_5$, doublet of quintets, $\delta = -168.5$ p.p.m., $^1J(^{125}Te-F_a) = 3\,647$, $^1J(^{125}Te-F_e) = 3\,705$, $^3J(^{125}Te-F) = 40$ Hz; for the central atom, doublet of triplets, $\delta = 174.4$ p.p.m., $J(^{125}Te-F) = 3\,647$ and 3 595 Hz. I.r. absorptions (liquid): 920 (w), 873 (m), 850 (m), 749 (s), 728 (s), 708 (w), and 678 (w) cm$^{-1}$. Raman spectrum (liquid): 738 (w, p), 719 (s, p), 695 (m, p), 677 (vs, p), 663 (m, p), 652 (w, p), 450 (m, p), 320 (w, p), 313 (w, p), 248 (w, p), 175 (w, p), 138 (m, p), and 113 (w, p) cm$^{-1}$. Mass spectrum: $m/z = 891$, $(M - F)^+$; 669, $(M - OTeF_5)^+$; plus smaller fragments, all with the correct isotopic distribution.

## Results and Discussion

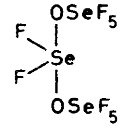
*The* $Se^{IV}-OSeF_5$ *System.*—$Hg(OSeF_5)_2$ and $SeCl_4$ react at low temperatures, but $Se(OSeF_5)_4$ is not observed. $SeOF_4$ is eliminated and dimerises to ; [15] $F_2Se(OSeF_5)_2$ is also formed [equation (1)]. The latter is a colourless liquid which hydrolyses rapidly. The first product of hydrolysation is $O=Se(OSeF_5)_2$. This has been prepared previously by a



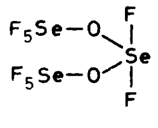
(1)

direct method from $SeOCl_2$.[18] $F_2Se(OSeF_5)_2$ can have several different structures. Since it is a derivative of $SeF_4$, we have to deal with a pair of axial ligands and a pair of equatorial ligands and a non-bonding electron pair in an equatorial position. The whole situation is more commonly known for sulphur tetrafluoride and its derivatives. Also, rapid ligand exchange has to be taken into account: in $SeF_4$ ligand exchange is frozen out only at −140 °C,[19] in very pure $SF_4$ it occurs at −20 °C.[20,21]

Solutions of $F_2Se(OSeF_5)_2$ in $SO_2FCl$ show sharp $^{19}F$ and $^{77}Se$ n.m.r. spectra at −100 °C, see Figure 1. The interpretation is straightforward: since only one type of $OSeF_5$ ligand and one type of directly bonded fluoride is observed, only the two pseudo-trigonal-bipyramidal configurations (A) and (B) are possible.



(A)



(B)

These two configurations should differ in the $^{19}F$ chemical shift of the centrally bonded fluorine atoms and even more so in their coupling constant $^1J(^{77}Se-F)$. In $SeF_4$, the coupling constants are 1 206 Hz for the equatorial (downfield) fluorine atoms and 284 Hz for the axial (upfield) fluorine atoms;[19] the value of 1 113 Hz is only compatible with fluorine atoms in equatorial positions. The same result is suggested by the chemical shift of these fluorine atoms (14.4 p.p.m.), as compared with the axial (37.7 p.p.m.) and equatorial (12.1 p.p.m.) fluorine atoms in $SeF_4$.[19] So $F_2Se(OSeF_5)_2$ has structure (A). Structure (A) can be interconverted to structure (B) by allowing intramolecular ligand exchange, as in a Berry pseudo-rotation. However, on warming to −20 °C the n.m.r. spectra do not change; only a little broadening is observed, but without change of the coupling constant $^1J(^{77}Se-^{19}F)$ on the central atom. So if an intramolecular exchange occurs, structure (B) is much less populated, *i.e.* it is significantly less stable than structure (A).

*The* $Te^{IV}$–$OTeF_5$ *System.*—$Te(OTeF_5)_4$ has been prepared previously,[22] and its structure has been analysed in terms of a pseudo-trigonal-bipyramidal configuration using low-temperature $^{125}Te$ n.m.r. spectroscopy.[3] This was an important finding since crystalline $TeF_4$ is strongly bridged[23] and the ligand exchange of dissolved $TeF_4$ in $CH_3F$ is not frozen out even at −140 °C.

The preparation of $Te(OTeF_5)_4$ from $TeF_4$ and $B(OTeF_5)_3$ is certainly a stepwise process, all species $F_{4-x}Te(OTeF_5)_x$ should exist at least as intermediates: equation (2). Such

$$TeF_4 + \frac{x}{3}B(OTeF_5)_3 \longrightarrow F_{4-x}Te(OTeF_5)_x + \frac{4-x}{3}BF_3 \quad (2)$$

partial substitution reactions have already been observed, *e.g.* in the systems $UF_6$–$U(OTeF_5)_6$[24] and $OXeF_4$–$OXe(OTeF_5)_4$.[25,26] In the systems $XeF_2$–$FXeOTeF_5$–$Xe(OTeF_5)_2$[27] and $WF_6$–$F_xW(OTeF_5)_{6-x}$–$W(OTeF_5)_6$[28–30] intermediates have been isolated.

In the case of $Te^{IV}$ it was surprising that at room temperature only $F_2Te(OTeF_5)_2$ was observed. It can be obtained pure if the correct ratio of starting materials are reacted. Since the structure should be similar to $F_2Se(OSeF_5)_2$ this is easily explained: two $OTeF_5$ groups prefer the axial positions, so the combination $F_2Te(OTeF_5)_2$ is more stable than $F_3Te(OTeF_5)$ and $FTe(OTeF_5)_3$.

The $^{125}Te$ n.m.r. spectrum of $F_2Te(OTeF_5)_2$, Figure 2, shows a striking similarity to the $^{77}Se$ n.m.r. spectrum of $F_2Se(OSeF_5)_2$. A large coupling constant $^1J(^{125}Te-F)$ for the central tellurium atom is observed. Since highly resolved n.m.r. spectra of $TeF_4$ have not been obtained, we have to compare this coupling constant with the $Se^{IV}$ system. $^1J(^{77}Se-F_e)$ = 1 113 Hz of $F_2Se(OSeF_5)_2$ is multiplied by the ratio of the gyromagnetic factors $^{125}Te : ^{77}Se = 0.8871 : 0.534 = 1.66$. An estimated value of 1 848 Hz for $^1J(^{125}Te-F_e)$ is obtained.* On such heavy elements this must further be corrected for relativistic effects on the *s*-electron density.[32] By comparison of isostructural Se and Te compounds an estimated value of *ca.* 2 950 Hz is obtained, which fits nicely with the experimental value of 2 812. For axial fluorine on $Te^{IV}$, however, a coupling constant well below 1 000 Hz is expected.† So $F_2Te(OTeF_5)_2$ also has structure (A).

*The* $Se^{IV}$–$OTeF_5$ *System.*—The reaction between $SeF_4$ and varying amounts of $B(OTeF_5)_3$ is complex. At temperatures below −78 °C a sediment is obtained, which is probably $SeF_3^+BF(OTeF_5)_3^-$. $B(OTeF_5)_3$ is known to be a very strong Lewis acid.[33] On warming this dissolves under evolution of $BF_3$ and $TeF_6$. With excess of $B(OTeF_5)_3$ at room temperature $O{=}Se(OTeF_5)_2$ is obtained as the only product: equation (3).

$$SeF_4 + B(OTeF_5)_3 \longrightarrow O{=}Se(OTeF_5)_2 + TeF_6 + BF_3 \quad (3)$$

Smaller amounts of $B(OTeF_5)_3$ and by keeping the reaction mixture below −20 °C affords $O{=}SeF{-}OTeF_5$, $F_2Se(OTeF_5)_2$, and $SeF_3^+B(OTeF_5)_4^-$, as shown by $^{77}Se$ n.m.r. spectroscopy, see the Table. The large coupling constant $^1J(^{77}Se-F)$ = 1 074 Hz in $F_2Se(OTeF_5)_2$ again indicates a structure of type (A).

*The (Group) Electronegativity of the* $-OSeF_5$ *and* $-OTeF_5$ *Groups.*—The axial preference of these groups cannot be explained by any bridging or lack of it, since we are using dilute solutions in rather non-polar solvents; nor can it be explained by steric effects. Assuming a bond angle on oxygen of *ca.* 140°, as in $F_5Te{-}O{-}TeF_5$,[34] $F_2Te(OTeF_5)_4$,[35] or $Te(OTeF_5)_6$,[36] no steric interaction is observed in either structure (A) or (B).

With virtually no exception, fluorine always occupies axial positions in trigonal-bipyramidal species.‡ The principal explanation (by means of the v.s.e.p.r. theory) is that fluorine atoms, because of their high electronegativity, have less electron density close to the central atom than all other possible ligands; thus they occupy the sterically tighter axial positions. In the $OSeF_5$ and $OTeF_5$ ligands the electron density on the oxygen atoms is diminished by the interaction of the non-

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* The background to this calculation is the 'theory of reduced coupling constants'.[31]

† $(CF_3)_2TeF_2$ should have the centrally bonded fluorine atoms in axial positions, and a very small coupling constant $^1J(Te-F)$ = 234 Hz is indeed observed (D. Naumann and S. Herberg, *J. Fluorine Chem.*, 1982, **19**, 205). However, since this measurement was taken in acetonitrile which might influence the co-ordination sphere, we hesitate to use this value as a reference for a typical coupling constant of axially bonded fluorine.

‡ The partial deviation from this rule in the phosphoranes $(CF_3)_xPF_{5-x}$ is well explained by steric effects (H. Oberhammer, G. Grobe, and D. Le Van, *Inorg. Chem.*, 1982, **21**, 275).

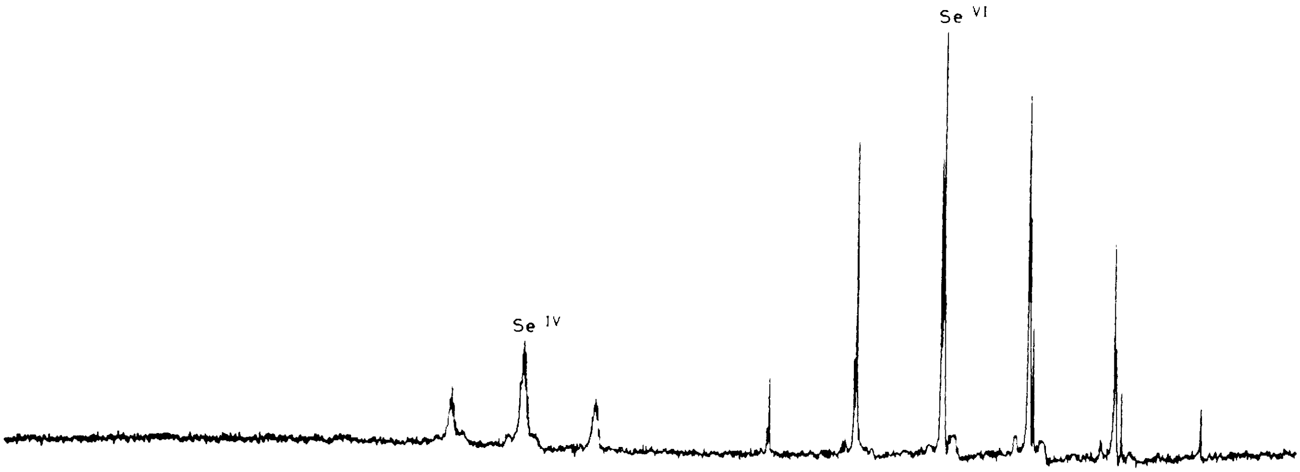


**Figure 1.** Selenium-77 n.m.r. spectrum of $F_2Se(OSeF_5)_2$ at −100 °C, in $SO_2ClF$. Within the $Se^{IV}$ pattern, satellites due to $^{77}Se-^{77}Se$ coupling are visible. The $Se^{VI}$ signal shows second-order splittings, see text

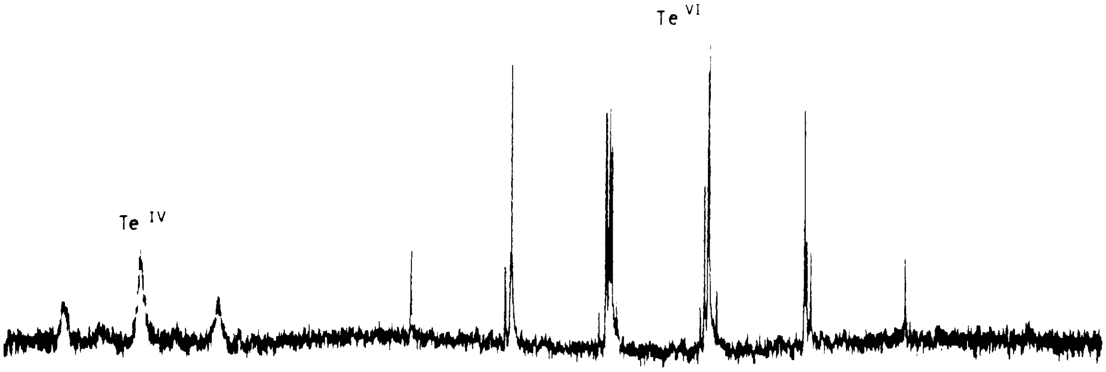


**Figure 2.** Tellurium-125 n.m.r. spectrum of $F_2Te(OTeF_5)_2$ at −100 °C, in $SO_2ClF$. Within the $Te^{IV}$ pattern, satellites due to $^{125}Te-^{125}Te$ coupling are visible

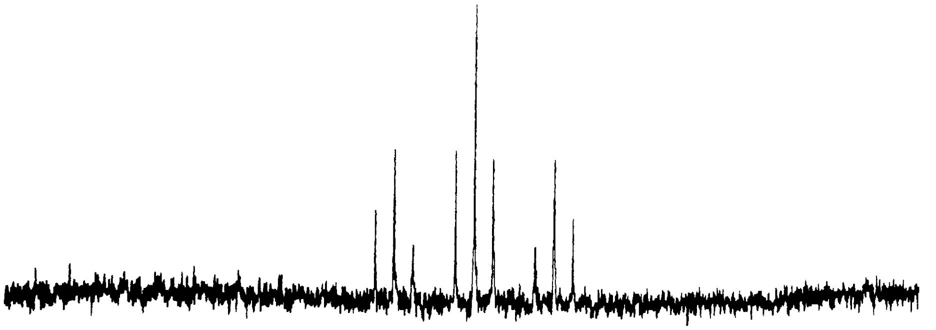


**Figure 3.** Selenium-77 n.m.r. spectrum of $SeF_4$ in a dilute solution of $CH_3F$ at −135 °C. On warming, this multiplet collapses to a broad single line. The coalescence point is close to −80 °C (ref. 19)

bonding electron pairs with the ligand groups $^{-}SeF_5$ and $^{-}TeF_5$. This is commonly called a (*pd*)-π interaction and is important mainly in systems of very high oxidation states.

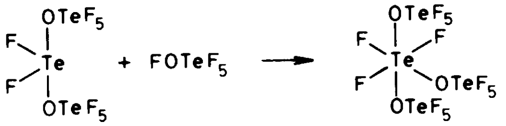
Fluorine, though a more electronegative atom than oxygen, needs here more space than oxygen for its non-bonding electron pairs. Similar considerations have been used to explain the equatorial preference of these groups in the $IF_5$ system,[2] and also in the explanation for the higher Lewis acidity of $B(OTeF_5)_3$ over $BF_3$.[12,33]

Group electronegativity is not properly defined. If it were defined in terms of axial/equatorial preference in such systems, the title ligands would be more electronegative than fluorine. However, if the group electronegativity is estimated by the ligand impact on *s*-electron densities on various nuclei (n.m.r. shift and Mössbauer values), fluorine is estimated to be a little more electronegative than $OTeF_5$.[3] However, the differences between F and these groups are subtle indeed: $^1H$ n.m.r. correlations on $EtOTeF_5$ and $MeOTeF_5$ give a group electronegativity a little less than that of fluorine;[37,38] the same correlation carried out on $MeOSeF_5$ gives a group electronegativity for $OSeF_5$ a little larger than that of fluorine.[39]

$^{77}Se$ *N.M.R. Spectra.*—125-Tellurium n.m.r. spectra of fluorine-containing systems have been measured recently.[3,40,41] This is not the case for $^{77}Se$ n.m.r. spectra. Fundamental work has been carried out in this area,[42] where also the known data for SeF systems are reviewed.[43] Recently the spectra of mainly fluoro-organic selenium compounds have been measured.[44] The nucleus $^{77}Se$ (7% natural abundance, spin $\frac{1}{2}$, gyromagnetic factor 0.534) is only little less sensitive than $^{125}Te$. Because of lower molecular weight, more concentrated samples can be obtained. In the Table $^{77}Se$ n.m.r. data of various selenium fluorides are given and the $^{77}Se$ spectrum of $SeF_4$ is shown in Figure 3. The remeasurement for compounds previously studied[43] ($SeF_6$, $SeO_2F_2$, and $SeOF_2$) resulted in only small numerical discrepancies.

It is remarkable that $Se^{IV}$ fluorides are less shielded than $Se^{VI}$ fluorides. Selenium(VI)–fluorine coupling constants are usually of the order of 1 400 Hz, and $^{77}Se^{IV}-^{19}F$ of the order of 1 200 Hz. Only the axial F in $SeF_4$ has the low value of 284 Hz, which is in accord with the usual bonding explanations, *e.g.* three-centre bonding within the axis *versus* two-centre bonding within the equatorial frame.* The $^{-}OSeF_5$ ligand shows in almost all cases a double quintet, due to the coupling with four equatorial and one axial fluorine atom. In some cases, especially in $F_5Se-O-O-SeF_5$ and $F_2Se(OSeF_5)_2$, and also in $F_2Te(OTeF_5)_2$ (see Figures 1 and 2), higher order splitting is observed. This is because the $^{19}F$ spectra are extremely degenerated. This phenomenon can be substantiated by simulation of the $^{77}Se$ spectrum as a $XAB_4$ system with a very small chemical shift difference between A and B. Within the ligand $^{-}OSeF_5$ the coupling constant to the equatorial fluorine atoms is a little larger than the coupling constant to the axial fluorine. Exceptions are $Cl-SeF_5$, where the axial coupling constant is larger, and $Xe(OSeF_5)_2$, where both are the same within the precision of the measurement (2 Hz).

*mer*-$F_3Te(OTeF_5)_3$.—In the series $F_xTe(OTeF_5)_{6-x}$ the members $TeF_6$, $F_5TeOTeF_5$, *cis*- and *trans*-$F_4Te(OTeF_5)_2$, *cis*- and *trans*-$F_2Te(OTeF_5)_4$, $FTe(OTeF_5)_5$, and $Te(OTeF_5)_6$ have been obtained already.[36] These are stable materials and do not exchange ligands below 170 °C. $F_2Te(OTeF_5)_2$ reacts with $F-OTeF_5$ according to equation (4). Only the meridional (asymmetric) isomer was obtained. The structural proof is simple: the fluorine atoms on the central tellurium show an $AB_2$ pattern in the $^{19}F$ n.m.r. spectrum. In the case of the facial (symmetric) isomer the three fluorine atoms should be equivalent. The $^{125}Te$ n.m.r. spectrum of the central tellurium shows the expected doublet of triplets (instead a simple quartet), see Experimental section. If the non-bonding (equatorial) electron pair in $F_2Te(OTeF_5)_2$ is replaced by F and $OTeF_5$, only the meridional isomer can result, see equation (4). Certainly *fac*-$F_3Te(OTeF_5)_3$ could exist also, but an alternative method of preparation is required.



(4)

## Acknowledgements

We are indebted to the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial help with this project.

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* The large difference between axial (284 Hz) and equatorial (1 206 Hz) $^{77}Se-^{19}F$ coupling constants is paralleled by a similar difference in $^{129}Xe-^{19}F$ coupling constants of the pseudo-octahedral $XeF_5^+$ cation: 159 Hz for the four equatorial atoms, 1 400 Hz for the axial fluorine atom (G. J. Schrobilgen, J. H. Holloway, P. Granger, and C. Brevard, *Inorg. Chem.*, 1978, **17**, 980). Therefore it is not surprising that in the substitution of the isoelectronic $IF_5$ by $-OTeF_5$ and $-OSeF_5$ the equatorial positions are preferred, see ref. 2.

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*Received 5th March* 1984; *Paper* 4/367