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Multinuclear Nuclear Magnetic Resonance and Mössbauer Study of OTeF5 Derivatives of Tellurium, Iodine, and Xenon. Spectroscopic Determination of the Relative Electronegativities of F and OTeF5

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A series of OTeF5 compounds of tellurium, iodine, and xenon and their fluorine analogues have been studied by [125]Te and [129]Xe NMR and by [127]I and [129]Xe Mössbauer spectroscopy. The NMR chemical shifts and Mössbauer quadrupole splittings of the central xenon, iodine, and tellurium atoms have been used to assess the relative electronegativities of F and OTeF5. In all cases examined, F is found to be more electronegative than the OTeF5 group; the latter has a value of 3.87 (Pauling scale) as estimated from [129]Xe Mössbauer quadrupole splittings.

Introduction

Since the first synthesis of HOTeF5 by Engelbrecht and Sladky,[2] a substantial number of derivatives of the elements containing OTeF5 groups have been prepared.[3] In general, the OTeF5 group appears to be capable of stabilizing the same oxidation states as F, and indeed nearly all of the chemistry of OTeF5 compounds has been developed by analogy with the existing fluorides. For example, the OTeF5 analogues of XeF2,[4,5] XeF4,[6] XeOF4,[7] and XeF6[7] have all been reported though Xe(OTeF5)6 has not been fully characterized.

In view of the large number of OTeF5 compounds, the question of the effective group electronegativity of OTeF5 relative to that of F has been speculated upon a number of times. An estimate of the electronegativity of the OTeF5 group has been made with ^{1}H NMR spectroscopy by the application of the equation of Dailey and Shoolery[8] (reevaluated here with Pauling electronegativities). A linear plot of the difference between the chemical shifts of the methyl and methylene protons of XCH2CH3 (X = I, Br, Cl, OTeF5, or F)[9] yields a group electronegativity of 3.88 for OTeF5 (coefficient of determination, R^2 = 0.99). Although HF is capable of displacing HOTeF5 from its compounds, it has been argued that the OTeF5 group posssesses an electronegativity greater than that of F.[10] The latter electronegativity order is based upon the observation that in the reaction of IF5 with the ligand-transfer agent B(OTeF5)3, the square-pyramidal shapes of the resulting structures, i.e., $F_aIF_{4-n}(OTeF_5)_n$, were maintained, but no axial fluorine substitution was observed. These results seem to conform to the valence-shell electron-pair-repulsion (VSEPR) predictions,[11] although nowhere in the literature is it clearly noted that the least electronegative ligand occupies the axial position of a square-based pyramidal molecule. This conclusion regarding the stereochemistry observed in AX5E-type molecules has apparently been inferred by extending arguments pertaining to trigonal-bipyramidal molecules, which conform without exception to VSEPR predictions. Steric effects resulting from mutual hindrance of the OTeF5 groups, which might account for preferential occupation of the equatorial positions by OTeF5 groups, appear to have been ruled out on

the basis of the crystal structures of the related *trans*-F2Te-(OTeF5)4[12] and Te(OTeF5)6[13] compounds.

Attempts to quantify relative group electronegativities by examining the P=O stretching frequencies, ^{31}P chemical shifts, and [31]P–[19]F spin–spin coupling constants of the series O=PF2X (X = F, OTeF5, OSeF5, Cl) have led to the ambivalent conclusion that the electronegativities of OSeF5 and OTeF5 are approximately equal to that of F.[10]

The cation FXeFXeOTeF5+ has recently been observed in solution in the presence of its V-shaped fluorine analogue FXeFXeF+.[14] Simultaneous obsevation of both species in the same sample using [129]Xe NMR spectroscopy demonstrated that the FXe group of FXeFXeOTeF5+ was labile but those of Xe2F3+ were not. It was concluded that of the two principal contributing valence-bond structures (Ia and Ib), structure Ia was dominant and stabilized by a lower effective group electronegativity for OTeF5 than for the terminal fluorine on xenon.

Ia   Ib
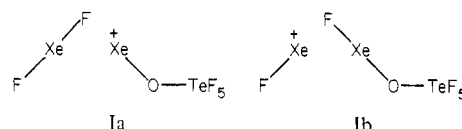
In order to conclusively establish the relative electronegativity of OTeF5 vs. F, we have chosen to examine a series of compounds using [129]Xe and [125]Te NMR and [129]Xe and [127]I Mössbauer spectroscopy. Both techniques are sensitive to changes in electron density at the nucleus of interest and are therefore ideally suited to an investigation of relative effective electronegativities of the directly bonded ligands. In the case of the [129]Xe nucleus, the Mössbauer results are complimented by NMR results on the same nucleus.

Discussion

NMR Spectroscopy. Both tellurium and xenon possess isotopes having nuclear spins of $^1/_2$ and natural abundances and sensitivities which allow ready observation by FT NMR spectroscopy, i.e., [123]Te, 0.87%, D^C = 0.89; [125]Te, 6.99%, D^C = 12.5; [129]Xe, 26.44%, D^C = 31.8 (D^C = natural abundance sensitivity relative to natural abundance ^{13}C). It can generally be assumed that the paramagnetic term makes the dominant contribution to [125]Te ([123]Te) and [129]Xe shieldings. Presently known [129]Xe and [125]Te chemical shifts range over ~7500[15] and ~3000 ppm,[16] respectively. The large ranges of chemical

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(2) Engelbrecht, A.; Sladky, F. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 383.
(3) Engelbrecht, A.; Sladky, F. *MTP Int. Rev. Sci.: Inorg. Chem., Ser. One* **1972**, *2*, Chapter 5.
(4) Sladky, F. *Monatsh. Chem.* **1970**, *101*, 1578.
(5) Sladky, F. *Monatsh.* **1970**, *101*, 1559.
(6) Lentz, D.; Seppelt, K. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 356.
(7) Lentz, D.; Seppelt, K. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 66.
(8) Dailey, B. P.; Shoolery, J. N. *J. Am. Chem. Soc.* **1955**, *77*, 3977.
(9) Sladky, F.; Kropshofer, H. *Inorg. Nucl. Chem. Lett.* **1972**, *8*, 195.
(10) Lentz, D.; Seppelt, K. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 355.
(11) Gillespie, R. J. "Molecular Geometry"; Van Nostrand-Reinhold: London, 1972.

(12) Lentz, D.; Pritzkow H.; Seppelt, K. *Inorg. Chem.* **1978**, *17*, 1926.
(13) Pritzkow, H.; Seppelt, K. *Inorg. Chem.* **1977**, *16*, 2685.
(14) Keller, N.; Schrobilgen, G. J. *Inorg. Chem.* **1981**, *20*, 2118.
(15) (a) Schrobilgen, G. J.; Holloway, J. H.; Granger, P.; Brevard, C. *Inorg. Chem.* **1978**, *17*, 980. (b) Schrobilgen, G. J. In "N.M.R. and the Periodic Table"; Harris, R. K., Mann, B. E., Eds.; Academic Press: London, 1978; Chapter 14.
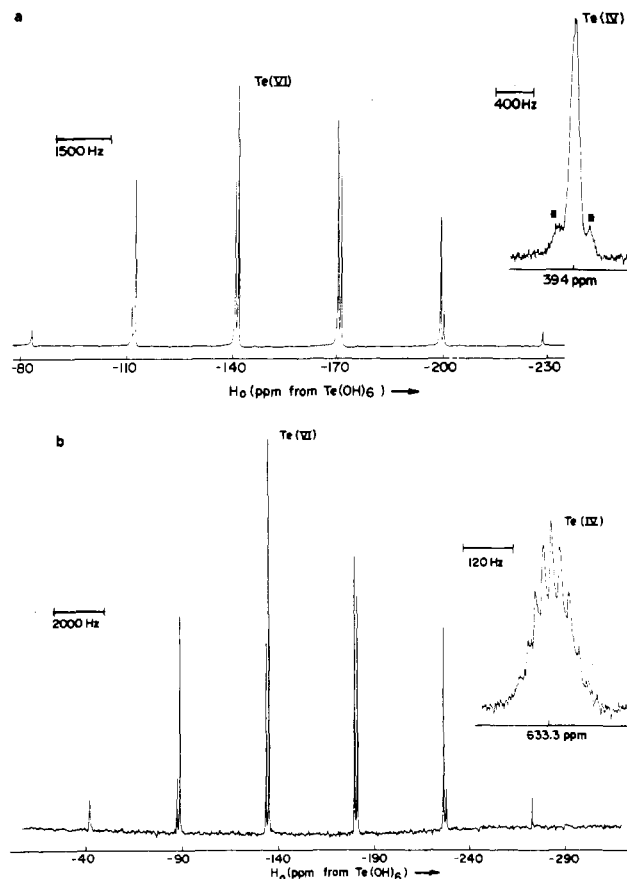
Figure 1. ^{125}Te NMR spectra of Te(OTeF₅)₄: (a) CH₃CN solvent (0.996 *m*, 24 °C) (asterisks denote ^{125}Te satellites); (b) SO₂ClF solvent (0.185 *m*, 24 °C).

Figure 2. ^{125}Te NMR spectrum of Te(OTeF₅)₆ in 1,1,2-trichloro-trifluoroethane solvent (0.329 *m*, 110 °C): (A) OTeF₅ groups; (a) ^{125}Te satellites; (B) central Te environment. Asterisks denote Te-(OTeF₅)₄ impurity lines.

Figure 3. ^{125}Te NMR spectrum of TeF₆ in 1,1,2-trichlorofluoroethane solvent (1.323 M, 24 °C).

shifts in different xenon and tellurium species are anticipated in view of existing trends among other nuclei. The present body of experimental data shows that the range of chemical shifts not only increases with Z for a particular group but also increases with Z for a particular period. It may also be anticipated that the chemical shifts of these heavy nuclei will exhibit greater sensitivity to the effects of substituents than lighter NMR nuclei. It is partly for this reason that we have chosen ^{125}Te and ^{129}Xe as NMR probes for assessing the relative electronegativities of F and OTeF₅.

Of the known xenon fluorides and oxyfluorides, XeF₂, XeF₄, and XeOF₄ have been shown to possess well-defined OTeF₅ analogues, i.e., Xe(OTeF₅)₂,[5] Xe(OTeF₅)₄,[6] and O=Xe(OTeF₅)₄.[7] Fluorine-19 and xenon-129 NMR parameters have been reported for these species. However, a common solvent for the fluoride and its OTeF₅ analogue has not been used in the majority of cases, and in the case of Xe(OTeF₅)₄ and O=Xe(OTeF₅)₄, two different chemical shift conventions seem to have been used. It has been demonstrated that xenon chemical shifts are very sensitive to solvent effects and that this sensitivity increases with increasing number of xenon lone pairs. In some instances, solvent effects can account for up to 200 ppm shifts[15a] (cf. chemical shifts of XeF₂ and Xe(O-TeF₅)₂ in CFCl₃ and SO₂ClF solvents at room temperature (Table I)). In order to compare the relative effective electronegativities of F and OTeF₅, in a meaningful way, we have remeasured the ^{129}Xe chemical shifts of the F and OTeF₅ analogues in the same solvent at the same temperature and have referenced them to pure liquid XeOF₄, the accepted reference for ^{129}Xe chemical shifts.[15b] We have also accurately
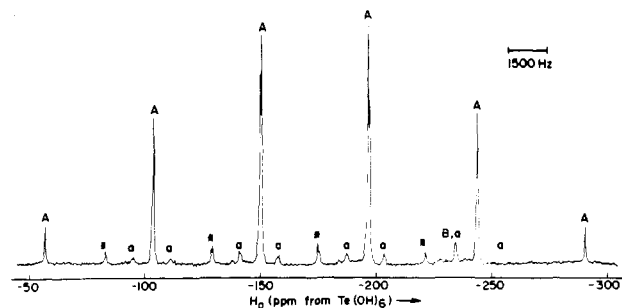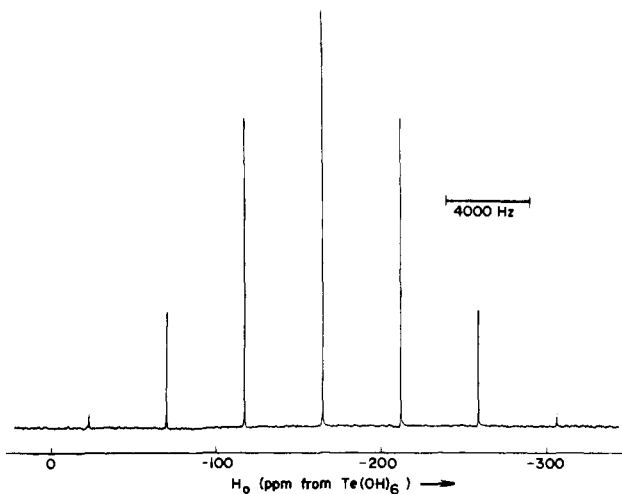
measured the ^{125}Te chemical shifts of TeF₄, Te(OTeF₅)₄ (Figure 1a,b), and Te(OTeF₅)₆ (Figure 2) for the first time (Table I). The ^{125}Te NMR parameters for TeF₆ (Figure 3) have been reported previously elsewhere[14] but have been remeasured here under the same temperature and solvent conditions as for Te(OTeF₅)₆.
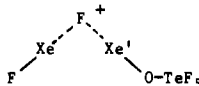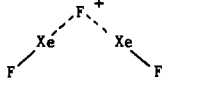
Differences between ^{125}Te and ^{129}Xe chemical shifts for the F and OTeF₅ analogues consistently show that the OTeF₅ group is significantly more shielding toward the central NMR nucleus than F (Table I). This strongly argues in favor of an OTeF₅ group that is less electronegative than F.

The ^{129}Xe chemical shift differences ($\Delta\delta = \delta$(F derivative) − δ(OTeF₅ derivative)) for XeF⁺ and XeOTeF₅⁺ (898 ppm) and that for Xe(OTeF₅)₂ and XeF₂ (438 ppm; 219 ppm/group) not only reflect the lower effective electronegativity of OTeF₅ but they are also in accord with the anticipated relative bond orders derived from a simplified MO treatment;[17] i.e., XeX⁺ (X = F or OTeF₅) is described in terms of a two center–two electron bond (bond order 1) and XeX₂ in terms of a linear three center–four electron bond in which two electrons occupy a bonding MO (bond order $^1/_2$). Hence, the chemical shift changes per group are greater for systems of greater bond order, e.g., 2c–2e bonds such as in XeX⁺ and TeX₄ (in the case of TeF₄ and Te(OTeF₅)₄, the chemical shift contribution from one 3c–4e bond is averaged with contributions from two 2c–2e bonds). The bonding in the TeX₆-type molecules may be approximately described in terms of three 3c–4e bonds; consequently, the ^{125}Te chemical shift difference for TeX₄ (166 ppm; 41.5 ppm/group) is expected to be larger than for TeX₆ (71.5 ppm; 11.9 ppm/group) owing to the

(16) Schrobilgen, G. J.; Burns, R. C.; Granger, P. *J. Chem. Soc., Chem. Commun.* **1978**, 957.

(17) Rundle, R. E. *J. Am. Chem. Soc.* **1963**, *85*, 112.

Table I. ^{125}Te and ^{129}Xe NMR Data for F and $OTeF_5$ Derivatives of Tellurium and Xenon

solute	δ_{125Te} [a,b]	δ_{129Xe} [a,c]	$^{125}Te-^{19}F$ [d]	$^{129}Xe-^{19}F$ [d]	$^{125}Te-^{125}Te$	$^{125}Te-^{129}Xe$	solvent	temp. °C	concn. molal
$Te(OTe'F_5)_4$	Te, 394.0; Te', −157.6		F, 3639; F', 3403		544		CH_3CN	24	1.00
$Te(OTe'F_5)_4$	Te, 633.3; Te', −160.8		F, 31.8; F', h; F, 3665; F', 3555				SO_2ClF	24	0.18
$Te(OTe'F_5)_4$	Te, 630; Te'(A) −154.3 [f]; Te'(E) −167.1 [f]		F, 3600; F', 3600; F, 3725; F', 3650				SO_2ClF	−110	0.18
TeF_4	559.8		e				CH_3CN	24	4.35
$Te(OTe'F_5)_6$	Te, −235.8; Te', −174.5		F, 3710; F', 3662		1302		$C_2F_3Cl_3$ [g]	110	0.33
TeF_6	−164.3; −164.9		3727; 3736				$C_2F_3Cl_3$ [g]; $C_2F_3Cl_3$ [g]	110; 24	1.32
$Xe(OTeF_5)_2$		−2447.4	F, 31; F', h		476		$CFCl_3$	26	0.61
XeF_2		−2009		5579			$CFCl_3$	26	satd
$Xe(OTeF_5)_2$		−2327	F, 30; F', h		470		SO_2ClF	26	1.54 [j]
$FXeOTeF_5$		−2051	F, 34; F', h	5743 [j]		560±20	SO_2ClF	26	1.54 [j]
XeF_2		−1913		5621			SO_2ClF	26	1.54 [j]
$XeOTeF_5^+$ [k]	−134.9	−1472	F, 18.5; F', h				SbF_5	26	0.74
XeF^+ [j]		−574		7210			SbF_5	26	0.71
(F bridged Xe–F–Xe', O–TeF5 structure) [j]		Xe, −1146; Xe', −1633		5747 [m]			BrF_5	−60	0.30 [n]
(F bridged Xe–F–Xe, F terminal structure)		−1059		F_b, 4828 [o]; F_t, 6662			BrF_5	−60	0.30 [n]
$Xe(OTeF_5)_4$		−662.8	F, 63; F', h		988		$CFCl_3$	24	~0.2
XeF_4		166.1		3801			$CFCl_3$	24	satd
$O=Xe(OTeF_5)_4$		−211.8	F, 54; F', h		1304		$CFCl_3$	24	~0.4
$O=XeF_4$		0.0		1123			neat	24	16.4

Table II. Mössbauer Data for F and OTeF₅ Derivatives of Xenon and Iodine

compd	$S,^a$ mm s⁻¹	$\Delta E_Q,^e$ mm s⁻¹	$\Gamma,^f$ mm s⁻¹
XeF₂^b	0.2 (2)	39.7 (4)	
Xe(OTeF₅)₂^b	0.1 (3)	38.3 (3)	
XeF₄^b	0.40 (4)	41.04 (7)	
Xe(OTeF₅)₄	0.9 (1)	36.1 (2)	8.8 (2)
O=XeF₄^b	0.5 (3)	18.1 (5)	
O=Xe(OTeF₅)₄	0.7 (1)	15.7 (1)	8.8 (2)
IF₅	−1.34 (4)^c	+1170 (56)^d	2.88 (19)
FI(OTeF₅)₄	−1.33 (4)^c	+910 (37)^d	1.98 (18)

^{a} ¹²⁹Xe isomer shifts (S) are relative to the xenon β-hydroquinone clathrate. ^{b} Data from ref 18. ^{c} ¹²⁷I isomer shifts are relative to Na₂H₃IO₆. ^{d} ¹²⁷I quadrupole couplings are given in the more usual form of $e^{127}Q_gV_{zz}/h$ in units of MHz; for ¹²⁷I, 1 mm s⁻¹ = 46.46 MHz. ^{e} Quadrupole splitting. ^{f} Line width.

higher average bond orders anticipated for TeX₄ species. It is interesting to note that the ¹²⁹Xe chemical shift difference per group for XeF₄ and Xe(OTeF₅)₄ (207 ppm/ group) is nearly identical with that for XeX₂ (213 ppm/group). This is in accord with a description of the bonding in XeX₄ in terms of two 3c–4e bonds. Although the Xe–X bonds of XeOX₄ may be described in terms of two 3c–4e bonds, the value derived for XeOX₄ is small (53 ppm/group) compared to those of XeX₂ and XeX₄. The Xe=O bond serves to diminish the difference in deshielding effects between OTeF₅ and F. The less electronegative OTeF₅ groups place more electron density onto the central xenon. A greater contribution from the valence-bond structure ⁺Xe–O⁻ results and serves to remove much of the additional electron density on the xenon of the OTeF₅ compound. This is supported by a somewhat lower Xe=O stretching frequency for the OTeF₅ compound (O= XeF₄, 920 cm⁻¹; O=Xe(OTeF₅)₄, 882 cm⁻¹ (this work)).

Additional support for the relative electronegativities of F and OTeF₅ can be derived from the exchange behavior of TeF₄ and Te(OTeF₅)₄. At room temperature we observed no ¹²⁵Te–¹⁹F spin–spin coupling in the ¹²⁵Te spectrum of TeF₄ in CH₃CN, whereas a long range ¹²⁵Te–¹²⁵Te coupling is observed for Te(OTeF₅)₄ (Figure 1a) under the same solvent and temperature conditions (Table I). This indicates that intermolecular fluorine exchange occurs at an appreciable rate in the case of TeF₄, as has been noted previously for SF₄, SeF₄, and TeF₄ by Muetterties and Phillips[18] using ¹⁹F NMR spectroscopy at low-field dispersions (30 and 40 MHz). Intermolecular fluorine exchange for TeF₄ was found to be rapid in toluene solvent down to ∼−100 °C. It was proposed that exchange occurs by means of a fluorine-bridged intermediate. The apparent absence of an analogous fast exchange process for Te(OTeF₅)₄ in the present work may be explained by the greater covalent bond character of the Te^{IV}–O bond when compared to the Te^{IV}–F bond and may be a direct consequence of the lower effective electronegativity of the OTeF₅ group. This observation could also be a result of the bulk of the OTeF₅ groups which might preclude bridge formation in the transition state.[18]

A comparison of the chemical shifts of Te(IV) in Te(OTeF₅)₄ in CH₃CN solvent and in the very weakly basic solvent SO₂ClF (Figure 1b) (TeF₄ is insoluble in SO₂ClF) reveals that the central tellurium atom is considerably more shielded in CH₃CN (Table I). Acetonitrile is apparently a relatively strong electron-pair donor toward Te(OTeF₅)₄ and strongly solvates the Te(IV) site.

In the absence of ligand exchange and pseudorotation, both TeX₄ molecules are expected to exhibit geometries based on trigonal-bipyramidal arrangements of four bond pairs and one lone pair (AX₄E). According to the VSEPR rules, the static

structures would be expected to exhibit two longer axial bonds and two shorter equatorial bonds. The presence of a long range ¹⁹F–¹²⁵Te coupling on Te(IV) and a single Te(VI) environment in the room-temperature ¹²⁵Te NMR spectrum in SO₂ClF (Figure 1b and Table I) as well as a single AB₄ pattern in the room-temperature ¹⁹F spectrum[13] of Te(OTeF₅)₄ indicates that the two nonequivalent OTeF₅ environments are exchange averaged due to pseudorotation. Owing to its high solubility in SO₂ClF, it was possible to cool a solution of Te(OTeF₅)₄ to −110 °C and slow the intramolecular pseudorotation sufficiently on the NMR time scale to observe the two nonequivalent Te(VI) environments of structure II (Table I).

II
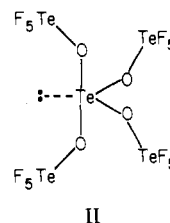
Mössbauer Spectroscopy. Table II summarizes the ¹²⁹Xe and ¹²⁷I Mössbauer data for pairs of structurally related molecules in which the axial fluorines in XeF₂ and the equatorial fluorines in XeF₄, O=XeF₄, and IF₅ molecules are replaced by the OTeF₅ group. The geometry remains the same in each pair, and the Mössbauer parameters should then reflect the effect of replacing a fluorine by the OTeF₅ group. The influence that these ligands have upon the parameters will depend upon their relative electron-withdrawing powers, i.e., upon their relative electronegativities and upon the nature of the bonding in these molecules. Three types of molecules are represented here which may be described according to VSEPR rules[11] as AX₂E₃, AX₄E₂ and AX₅E. In valence-bond terms the bonding could be described as sp³d and sp³d². However, it has already been established,[19] on the basis of the trends in the isomer shifts of a large series of xenon compounds, that the bonds between the central xenon and the ligands only have a very small degree of s character. The isomer shifts reported here, which are a measure of s-electron density, confirm this conclusion.

With one exception, the isomer-shift differences between the fluorides and the OTeF₅ analogues lie within the errors of measurement for both the xenon and iodine compounds. In all cases the changes in isomer shift are only a small fraction of the widths of the observed resonance, and as a result no realistic interpretation can be given for the changes in this parameter.

Fortunately, the changes in the quadrupole splitting are much greater than the errors in the measurement, and this parameter is therefore much more useful as a structural tool. The fact that the quadrupole splittings for the F and OTeF₅ analogues are very similar is added confirmation that their structures are of the same type; i.e., Xe(OTeF₅)₂ is linear like XeF₂ while FI(OTeF₅)₄ has a square-based pyramidal geometry like IF₅. The largest quadrupole splittings are observed in those cases where the bonding ligands F or OTeF₅ are along one axis (Xe(OTeF₅)₂) or in the same plane (Xe(OTeF₅)₄) while nonbonding electron pairs occupy the remaining positions in the structure. These arrangements create the largest electric field gradients and have the largest quadrupole splittings. The quadrupole coupling constants in the XeX₂ and XeX₄ (X = F or OTeF₅) compounds should of course have opposite signs since V_{zz} is in the equatorial plane for XeF₂ but in the axial direction for XeX₄. In going from Xe(OTeF₅)₄ to O= Xe(OTeF₅)₄, the quadrupole splitting drops by 20.4 mm s⁻¹

(18) Muetterties, E. L.; Phillips, W. D. *J. Am. Chem. Soc.* **1959**, *81*, 1084.

(19) de Waard, H.; Bukshpan, S.,; Schrobilgen, G. J.; Holloway, J. H.; Martin, D. *J. Chem. Phys.* **1979**, *70*, 3247.
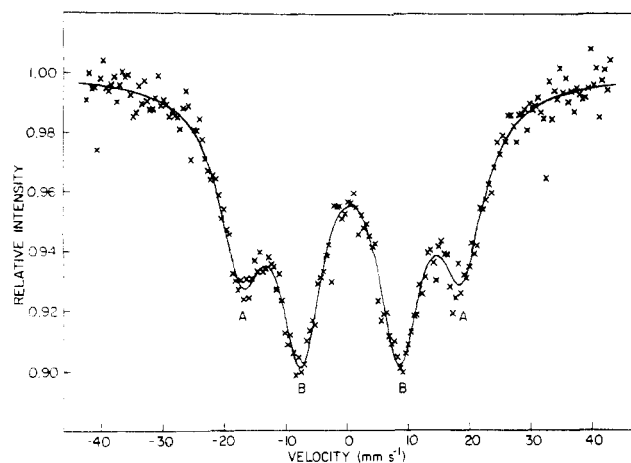
Figure 4. ^{129}Xe Mössbauer spectrum of a O=Xe(OTeF$_5$)$_4$/Xe-(OTeF$_5$)$_4$ (~2:1) mixture at 4 K (denoted by doublets B and A, respectively). The solid line represents the best fit to the data.

while in the XeF$_4$/XeOF$_4$ pair the drop is 23.9 mm s^{-1}. This is the effect of replacing a nonbonded electron pair (zero electronegativity[11]) by an electronegative oxygen. Figure 4 shows the ^{129}Xe Mössbauer spectrum of a mixture of Xe(O-TeF$_5$)$_4$ and O=Xe(OTeF$_5$)$_4$. The identity of these species was confirmed by NMR as discussed earlier.

One can see from Table II that for a given fluoride, replacement of F by OTeF$_5$ results in a decrease in the magnitude of the quadrupole splitting. This occurs whether the central atom is xenon or iodine and is a reflection of the relative electron-withdrawing power of the F compared to the OTeF$_5$ group. The greater the electron withdrawal in the x and y directions as compared to the z direction (which contains the nonbonding electron pair(s) in the AX$_4$E$_2$ or AX$_5$E compounds), the greater the quadrupole splitting. The reverse is true for XeF$_2$ and Xe(OTeF$_5$)$_2$, where the ligands are along the z axis and the nonbonded electron pairs are in the xy plane. Clearly, these results establish that F is a more electronegative ligand than OTeF$_5$. From the nearly linear relationship between the quadrupole splittings of XeF$_2$, XeCl$_2$, and XeBr$_2$[20] and the Pauling electronegativities of the ligand atoms (coefficient of determination, R^2 = 0.98), we have estimated the corresponding Pauling electronegativity of OTeF$_5$. The interpolated value for OTeF$_5$ derived from the observed quadrupole splitting for Xe(OTeF$_5$)$_2$ is 3.87 compared to 3.98 for F. This compares to a value of 3.88 obtained from the NMR method as mentioned previously.

The Mössbauer spectrum of IF$_5$ has been reported by Bukshpan et al.,[21] who used the ^{129}I isotope. This isotope gives much better resolved spectra than the ^{127}I isotope, but because the earlier workers were not sure of the purity of their sample, we have recorded the spectrum of a pure sample using the natural isotope. The Mössbauer parameters obtained for IF$_5$ agree reasonably well with the earlier data after converting the ^{129}I data to their ^{127}I equivalents. The computed line width for the ^{127}IF$_5$ spectrum is substantially greater than the natural line width, i.e., 2.88 compared to 1.25 mm s^{-1}. We attribute this large line width to the fact that in the solid state at −80 °C there are three crystallographically discrete, albeit chemically equivalent, iodine sites.[22] This interpretation is consistent with the results obtained by Kuz'min et al.,[23] who
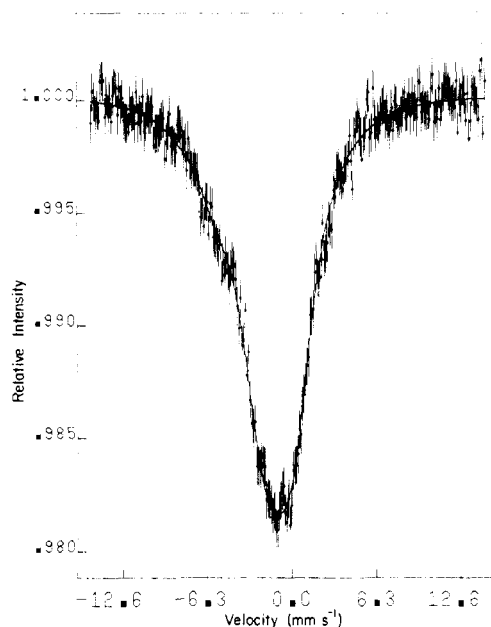

Figure 5. ^{127}I Mössbauer spectrum of FI(OTeF$_5$)$_4$ at 4 K. The solid line represents the best fit to the data.

measured the ^{127}I NQR spectrum of IF$_5$ at 77 K. These workers were able to resolve three crystallographically non-equivalent iodine atom positions having a population ratio of ca. 3:4:3, whose resonance frequencies were 1025, 1031, and 1067 MHz. The ^{127}I spectrum of FI(OTeF$_5$)$_4$ shown in Figure 5 gives a more acceptable line width, suggesting that only one iodine site is present. The shape of the iodine spectrum immediately gives the sign of the quadrupole coupling constant, which is positive, indicating that there is an excess of electron density in the z direction, i.e., that direction which contains the nonbonded electron pair and the axial fluorine. In the case of the xenon spectra, the sign of the interactions cannot be determined by inspection and must be inferred from the geometry of the compound.

Conclusions

We have shown by NMR and Mössbauer spectroscopy that F is more electronegative than OTeF$_5$. On the basis of the observed geometry of FI(OTeF$_5$)$_4$ and VSEPR implications, it was previously concluded that OTeF$_5$ is more electronegative than F. In the case of the trigonal bipyramid where the axial and equatorial regions of space are clearly geometrically unique, there appears to be no exception to VSEPR which predicts that the axial position is always occupied by the most electronegative ligand.[11] In the case of the square-based pyramid, however, which may be regarded as a pseudoocta-hedron, the differences between equatorial and axial positions are more subtle, such that a ligand's preference for a particular region of space is less demanding, thereby making predictions more difficult.

It is difficult to find many suitable examples with which to compare FI(OTeF$_5$)$_4$ and *trans*-F$_2$Te(OTeF$_5$)$_4$. It has been found for the series of compounds RIF$_4$(R = OCH$_3$, CF$_3$, C$_2$F$_5$, etc.) that the least electronegative R group remains axial,[24] as might have been expected. However, there also exist examples in the main group, where VSEPR has enjoyed most of its success, in the transition metals, and even in the actinides, where the most electronegative ligand in fact occupies the axial position of a pseudooctahedral molecule, to which the square-based pyramid may be classed. In IO$_2$F$_4^-$,[25] both cis

(20) Perlow, G. J.; Yoshida, H. *J. Chem. Phys.* **1968**, *49*, 1474.
(21) Bukshpan, S.; Goldstein, C.; Soriano, J.; Shamir, J. *J. Chem. Phys.* **1969**, *51*, 3976.
(22) Burbank, R. D.; Jones, G. R. *Inorg. Chem.* **1974**, *13*, 1071.
(23) Kuz'min, A. I.; Shpanko, V. I.; Evidadza, G. N.; Sukhoverkhov, V. F.; Barkman, V. S.; Dzevitskii, B. E. *Russ. J. of Inorg. Chem.* (*Engl. Transl.*) **1977**, *22*, 1290.

(24) (a) Oates, G.; Winfield, J. M.; Chambers, O. R. *J. Chem. Soc., Dalton Trans.* **1974**, 1380. (b) Oates, G.; Winfield, J. M. *Ibid.* **1974**, 119.
(25) Engelbrecht, A.; Peterfy, P. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 768.

and trans isomers are known to exist despite the fact that doubly bonded oxygen normally prefers to adopt pseudoaxial positions (double-bonded oxygen is thought to exhibit steric characteristics similar to a nonbonded pair of electrons).[26] Similarly, the reactions of TeF$_6$ with various alcohols[27] result in the formation of disubstituted products where, although the cis isomer predominates, some trans isomer is also formed. The reaction of telluric acid with anhydrous HF[28] results in fluoro-substituted species whose ^{19}F NMR spectra are consistent with the presence of (HO)$_5$TeF, *trans*-(HO)$_4$TeF$_2$, *fac*-(HO)$_3$TeF$_3$, and *mer*-(HO)$_3$TeF$_3$. Tötsch and Sladky[29] have recently isolated *cis*- and *trans*-(HO)$_2$TeF$_4$, HOTeF$_4$OCH$_3$, and (CH$_3$O)$_2$TeF$_4$ and have demonstrated that the isomer ratio of (HO)$_2$TeF$_4$ is kinetically and not thermodynamically controlled. In the tungsten hexahalide system WF$_x$Cl$_{6-x}$,[30] all compounds in the series are known, including all geometric isomers. Fluorine-19 NMR studies[31] have also shown that all isomers of the F$_x$U(OTeF$_5$)$_{6-x}$ system exist in solution.

Thus, in pseudooctahedral molecules there appears to be no strong preference for the least electronegative ligand to remain in the pseudoaxial position. The above examples suggest that it is perhaps not a good idea to base electronegativity differences of attached ligands solely upon the observed stereochemistry and VSEPR arguments since other effects (kinetic, thermodynamic, etc.) may become important, particularly when these differences are small.

Experimental Section

Apparatus and Materials. Manipulations were carried out under anhydrous conditions on a vacuum line constructed from 316 stainless steel, nickel, Teflon, and FEP. Solids were transferred into sample containers or reaction vessels in a drybox. All preparative work involving xenon and tellurium compounds was carried out in 50-mL glass vessels equipped with Teflon Rotaflo valves.

The reagents HOTeF$_5$,[32] B(OTeF$_5$)$_3$,[33] XeF$_2$,[34] XeF$_4$,[35] XeOF$_4$,[36] and IF$_5$ (commercial sample obtained from Matheson and purified by the procedure outlined for BrF$_5$[37]) used in the preparation of the OTeF$_5$ derivatives have been prepared and purified as previously described. The synthetic procedures used to prepare the OTeF$_5$ derivatives of tellurium,[13] iodine,[10] and xenon[5-7] studied in this paper

have also been previously described.

The solvents CH$_3$CN, C$_2$F$_3$Cl$_3$ (1,1,2-trichlorotrifluoroethane), and CFCl$_3$ were dried over P$_2$O$_5$ for several days prior to use and vacuum distilled into glass storage vessels equipped with Teflon Rotaflo valves.

Nuclear Magnetic Resonance Spectroscopy. Tellurium-125 and xenon-129 NMR spectra were obtained on natural-abundance compounds with a Bruker WM-250 Fourier-transform multinulcear spectrometer. All spectra were run unlocked (field drift <1 Hz/h) and accumulated in 16K of memory. Xenon-129 and tellurium-125 spectra were obtained at 69.20 and 78.97 MHz, respectively, in 5000–10000 scans with a spectral width of 45 KHz (2.8 Hz/data point; pulse repetition time 0.18 s) for ^{129}Xe, a spectral width of 83 KHz (5.1 Hz/data point; pulse repetition time 0.20 s) for ^{125}Te, and pulse widths of 20 μs for both nuclei. Line broadenings of 3 Hz (^{129}Xe) and 5 Hz (^{125}Te) were applied in the exponential smoothing of the free-induction decays.

Nuclear magnetic resonance samples were prepared in 10-mm o.d. precision glass NMR tubes (Wilmad) joined by $^1/_4$-in. o.d. standard wall tubing and attached by means of $^1/_4$-in. Teflon nuts and ferrules to a Teflon diaphragm valve. Samples were prepared by distilling the appropriate solvent through all Kel-F and Teflon connections into a sample tube containing the solute at −196 °C. Samples were sealed under vacuum and stored at −196 °C until their spectra could be recorded.

Xenon-129 spectra were referenced externally with respect to pure XeOF$_4$ liquid at 24 °C. Tellurium-125 spectra were referenced externally with respect to saturated aqueous Te(OH)$_6$ at 24 °C.

Mössbauer Spectroscopy. Samples were thoroughly mixed with dried, prefluorinated Teflon powder and were placed in either Teflon or Kel-F containers in a dry inert-atmosphere glovebox and were immediately immersed in liquid nitrogen upon removal from the glovebox. Mössbauer spectra were recorded with both source and absorber immersed in liq. helium.

The Mössbauer measurements were carried out as described in the literature.[19,38] Isomer shifts are given relative to the xenon β-hydroquinone clathrate for ^{129}Xe and Na$_2$H$_3$IO$_6$ for the ^{127}I isotope. All spectra were computer fitted, with those involving the ^{127}I isotope using the full-transmission integral procedure described by Ruebenbauer and Birchall.[39] It is particularly important that this procedure be used for fitting ^{127}I spectra since the multiline spectra which result from compounds containing iodine in noncubic environments are rarely well resolved.

(26) Christe, K. O., Oberhammer, H. *Inorg. Chem.* **1981**, *20*, 296.
(27) Fraser, G. W.; Millar, J. B. *J. Chem. Soc., Dalton Trans.* **1974**, 2029.
(28) Elgad, U.; Selig, H. *Inorg. Chem.* **1975**, *14*, 140.
(29) Tötsch, W.; Sladky, F. *J. Chem. Soc., Chem. Commun.* **1980**, 927.
(30) Fraser, G. W.; Gibbs, C. J. W.; Peacock, R. D. *J. Chem. Soc. A* **1970**, 1708.
(31) Seppelt, K. *Chem. Ber.* **1976**, *109*, 1046.
(32) Seppelt, K.; Nöthe, D. *Inorg. Chem.* **1973**, *12*, 2727.
(33) Sladky, F.; Kropshofer, H.; Leitzke, O. *J. Chem. Soc., Chem. Commun.* **1973**, 134.
(34) Williamson, S. M. *Inorg. Synth.* **1968**, *11*, 147.
(35) Malm, J. G.; Chernick, C. L. *Inorg. Synth.* **1966**, *8*, 254.
(36) Chernick, C. L.; Classen, H. H.; Malm, J. G.; Plurien, P. L. In "Noble-Gas Compounds"; Hyman, H. H., Ed.; University of Chicago Press: Chicago, IL,, 1963; p 106.
(37) Gillespie, R. J.; Schrobilgen, G. J. *Inorg. Chem.* **1974**, *13*, 1230.

(38) Birchall, T.; Myers, R. D. *J. Chem. Soc., Dalton Trans.* **1980**, 1060.
(39) Ruebenbauer, K.; Birchall, T. *Hyperfine Interact.* **1979**, *7*, 125.