likely to be found when R is a strongly electron-releasing group.[5b]

The composition of the π-MOs of **1** ($R = NH_2$) is also shown in Figure 5. There are five occupied π-type orbitals, of which three are entirely associated with the heterocyclic ring. The other two orbitals have contributions from both endocyclic and exocyclic atoms. The $1b_1$ orbital is totally bonding with respect to the CNSNSN ring but also exhibits some electron density on the exocyclic NH_2 group. Conversely, the $3b_1$ orbital is primarily a lone pair located on the exocyclic nitrogen atom with smaller contributions from the three endocyclic nitrogen atoms. To a first approximation the $3b_1$ orbital can be regarded as an n_π (NH_2) orbital, and the contribution of the exocyclic nitrogen to $1b_1$ can be neglected with the result that the ring in **1** ($R = NH_2$) can be regarded as an eight-π-electron system.

Reactions of $(R_2NCN)(NSCl)_2$ with Halide Ion Acceptors. The dication of **1**, $(RCN)(SN)_2^{2+}$, should be an electron-precise six-π-electron system.[1] The treatment of solutions of **3** ($R = Me_2N$, Et_2N, i-Pr_2N) in carbon tetrachloride or n-hexane with various halide ion acceptors resulted in the immediate precipitation of yellow-orange solids, e.g.

$$(R_2NCN)(NSCl)_2 + SbCl_5 \rightarrow [(R_2NCN)(NSCl)(NS)][SbCl_6]$$

As indicated in Table II, these products were identified as monocations rather than dications on the basis of elemental analyses and IR spectroscopic data. The infrared band at 1550–1570 cm^{-1} attributed to $\nu(CN_2)$ in **3** ($R = Me_2N$, Et_2N, i-Pr_2N)[6] is shifted by 40–45 cm^{-1} in the monocations, which also exhibit a strong band in the 445–455-cm^{-1} region assigned to ν(S–Cl).

In contrast to the reactions of **3** with halide ion acceptors, the addition of antimony pentachloride to a solution of the eight-membered ring, 1,5-$(Me_2NCN)_2(NSCl)_2$,[6a] in carbon tetrachloride produces the dication 1,5-$(Me_2NCN)_2(SN)_2^{2+}$ (Table II).

Summary and Conclusions

The six-membered rings $(RCS_2N_3)_n$ ($R = Et_2N$, i-Pr_2N) were obtained as dark purple solids characterized as adducts with norbornadiene. HFS-SCF MO calculations for **1** ($R = NH_2$) indicate that the heterocyclic ring is an eight-π-electron system and reveal a quasi-degeneracy of the HOMO (π^*) and LUMO (π^*) levels ($\Delta\epsilon = 0.3$ eV). The first example of the $RCS_2N_2^+$ ring in which R is an electron-releasing substituent was prepared by the azide reduction of **3** ($R = Et_2N$). The purple color of such derivatives ($\lambda_{max} \sim 530$ nm) is attributed to an $n_\pi(R_2N) \rightarrow \pi^*$ transition. The cations $(RCN)(NSCl)(NS)^+$ ($R = Me_2N$, Et_2N, i-Pr_2N) and 1,5-$(Me_2NCN)_2(SN)_2^{2+}$ are readily produced by treatment of the appropriate mixed thiazyl–cyanuric ring with a halide ion acceptor. The resulting salts are soluble in SO_2 and could serve as precursors of polymers containing an –(R)CNSN– backbone via electrochemical reduction (cf. preparation of $(SN)_x$ from $S_5N_5^+$ salts).[40]

Acknowledgment. We are grateful for useful discussions with Professor W. G. Laidlaw and financial support of the NSERC (Canada), CNPq, and FAPESP (Brazil). We also thank Professor R. Mews for helpful correspondence and a preprint of ref 33.

Supplementary Material Available: Listings of positional and isotropic thermal parameters for hydrogen atoms, anisotropic thermal parameters for non-hydrogen atoms, bond lengths, and bond angles associated with hydrogen atoms in i-$Pr_2NCS_3N_5$, and IR spectral data for salts of the $(R_2NCN)(NSCl)(NS)^+$ and 1,5-$(Me_2NCN)_2(SN)_2^{2+}$ cations (4 pages). Ordering information is given on any current masthead page.

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Crystal and Molecular Structures of *mer*-Ph_3TeF_3 and Stereoselective Fluorine Exchange in the *mer*-Ph_3TeF_3–$Ph_3TeF_2^+$ System

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Triphenyltellurium(VI) trifluoride, $(C_6H_5)_3TeF_3$, was prepared by the reaction of triphenyltellurium(IV) fluoride with xenon difluoride. The crystal and molecular structures of *mer*-Ph_3TeF_3 were determined by X-ray diffraction techniques. *mer*-Ph_3TeF_3 crystals are monoclinic, $P2_1/n$, $Z = 4$, with unit cell dimensions of $a = 10.640$ (2) Å, $b = 12.144$ (2) Å, $c = 12.445$ (2) Å, and $\beta = 100.10$ (1)°. The structure has been refined by full-matrix least-squares methods to values of R and R_w of 0.031 and 0.020, respectively. The molecule has Te with a slightly distorted octahedral coordination and has an approximate C_2 symmetry axis. The phenyl groups are rotated with respect to each other as a result of intramolecular steric repulsion. Te–F and Te–C bond distances lie in the ranges 1.915 (2)–1.954 (2) and 2.110 (3)–2.129 (3) Å, respectively. Crystals contain molecules packed in a chainlike pattern. The *mer* structure is retained in solution, as confirmed by ^{19}F and ^{125}Te NMR. Reaction of *mer*-Ph_3TeF_3 with PF_5 gave $Ph_3TeF_2^+PF_6^-$, which was characterized by ^{19}F and ^{125}Te NMR and chemical reaction. Intermolecular fluorine exchange occurred on addition of $Ph_3TeF_2^+$ to *mer*-$Ph_3TeF^aF^b_2$. On the basis of both ^{19}F and ^{125}Te NMR, it was possible to demonstrate that only the F^a ligand undergoes fluorine exchange, consistent with a mechanism involving five- and six-coordinate tellurium species and the fluorine-bridged intermediate $[Ph_3TeF^b_2–F^a–TeF^b_2Ph_3]^+$, in which only the F^a ligand occupies the bridging position. The intermolecular (bond-breaking) process is not accompanied by an intramolecular scrambling of F^a and F^b ligands. An intermolecular exchange process involving only the PF_6^- anion can be initiated by adding PF_5 to $Ph_3TeF_2^+PF_6^-$.

Introduction

The synthesis of a variety of phenyltellurium(VI) fluorides by the oxidative fluorination of Te(I), Te(II), and Te(IV) compounds with xenon difluoride[2]

$$Ph_3TeF + XeF_2 \rightarrow Ph_3TeF_3 + Xe$$

has made these compounds available for structural and NMR studies. In this paper we describe the crystal structure of *mer*-Ph_3TeF_3, which is the first example of an organotellurium(VI) crystal structure investigation, as far as we know, and correlate our findings with NMR studies of fluorine exchange in *mer*-Ph_3TeF_3.

Intermolecular fluorine exchange is known to be rapid in systems such as SiF_5^-–SiF_6^{2-},[3] $PhPF_3H$–$PhPF_4H^-$,[4] and

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$PhPF_4$–$PhPF_5^-$.[5] A fluorine-bridged intermediate appears reasonable in each system, but an accompanying intramolecular ligand-exchange process scrambles the axial and equatorial ligands in trigonal-bipyramidal SiF_5^-, $PhPF_3H$, and $PhPF_4$. Both intramolecular and intermolecular processes can be monitored simultaneously, as demonstrated in the $PhPF_3H$–$PhPF_4H^-$ study,[4] but in order to establish which fluorines are preferentially lost from specific sites in five- or six-coordinate compounds, a system is required in which rapid bond breaking is not accompanied by intramolecular scrambling of ligands. The *mer*-Ph_3TeF_3–$Ph_3TeF_2^+$ system, described in this paper, appears to meet this criterion.

Experimental Section

Xenon difluoride (PCR Research Chemicals Inc.), Ph_3TeCl (K & K Laboratories), and PF_5 (PCR Research Chemicals Inc.) were commercial samples. Ph_3TeF was prepared in poly(tetrafluoroethylene) equipment with use of the method of Emeleus and Heal.[6] Attempts to prepare this compound in standard glassware invariably produced large amounts of $Ph_3Te^+BF_4^-$. Anal. Calcd for $C_{18}H_{15}F_4BTe$: C, 48.5; H, 3.4. Found: C, 47.6; H, 3.3.

Preparation of *mer*-Triphenyltellurium(VI) Trifluoride, *mer*-Ph_3TeF_3. Solid XeF_2 (62 mg, 0.36 mmol) was added to a stirred solution of Ph_3TeF (116 mg, 0.30 mmol) in chloroform (3 mL). The reaction mixture was stirred for an additional 8 h at room temperature, and a pale yellow solution was formed. The solid product was precipitated by adding about 15 mL of *n*-hexane and recrystallized from chloroform/*n*-hexane. In some instances, the product was purified by sublimation at 102 °C (10^{-3} cmHg). Anal. Calcd for $C_{18}H_{15}F_3Te$: C, 51.2; H, 3.6. Found: C, 52.2; H, 3.7.

mer-Ph_3TeF_3 was also recovered from the reaction of Ph_3TeCl (158 mg, 0.40 mmol), suspended in $CHCl_3$ (3 mL), with an excess of solid XeF_2 (128 mg, 0.75 mmol); this mixture was stirred for 48 h until the solution turned a pale yellow and the product purified as described above.

Those ^{19}F NMR samples of *mer*-Ph_3TeF_3 that showed line-broadening effects were treated by adding a small amount of NaF, with gentle shaking, and filtering off the NaF.

Preparation of Difluorotriphenyltellurium(VI) Hexafluorophosphate, $Ph_3TeF_2^+PF_6^-$. An excess of PF_5 (0.55 mmol) was condensed onto a solution of *mer*-Ph_3TeF_3 (0.12 mmol) in dichloromethane (2 mL) in a stoppered reaction tube. The mixture was slowly allowed to warm to room temperature. After 1 h, the excess PF_5 was removed and the solution transferred to an NMR tube, which was flame-sealed and used for NMR studies as required.

The reaction of $Ph_3TeF_2^+PF_6^-$ with an excess of NaF in dichloromethane for 1 day, with occasional shaking, gave *mer*-Ph_3TeF_3 in about 80% yield, as judged by ^{19}F NMR. Similarly, reaction of $Ph_3TeF_2^+PF_6^-$ with an excess of benzyltriethylammonium chloride for 20 min, with gentle shaking, gave Ph_3TeF_2Cl[2] in about 80% yield.

^{19}F NMR spectra were recorded on a Bruker WH90 spectrometer at 84.66 MHz with the use of C_6F_6 (−162.9 ppm with respect to $CFCl_3$) as an internal reference. ^{125}Te NMR spectra were recorded on a Bruker AM300 spectrometer at 94.76 MHz using Ph_2Te (692 ppm with respect to Me_2Te) as an external reference. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

Colorless crystals of the title compound suitable for X-ray diffraction analysis were afforded by slow evaporation from a chloroform/*n*-hexane solution at room temperature. A single crystal was chosen and mounted in a general orientation on a Nicolet R3m automated diffractometer; an orientation matrix was determined from the setting angles of 25 centered reflections. From the indices and refined angles, final unit cell parameters (Table I) were obtained by a least-squares fit of 25 reflections with $24° < 2\theta < 58°$.

Data were collected with use of Mo Kα (λ = 0.71073 Å) radiation with a graphite monochromator in the incident beam; peak backgrounds and scans were counted for equal times; scan widths were given by 2.00 + $(2\theta_{K\alpha_2} - 2\theta_{K\alpha_1})°$. Corrections for Lorentz and polarization effects as well as an empirical absorption correction (based on reflection intensity measurements at 36 different azimuthal angles for 10 reflections) were applied to the data with use of programs supplied in the SHELXTL software package. An intensity decay correction was not warranted as the maximum decay in the three standard reflections' intensities was less than 5% during the total exposure time of 49.4 h. A total of 77% of the unique data were considered observed with $I \geq 1.5\sigma(I)$, where $\sigma(I) = R[S + BL + BR]^{1/2}$, R = scan rate, S = total scan count, and BL, BR = left and right background counts.

Table I

formula	$(C_6H_5)_3TeF_3$
fw	415.93
$F(000)$	808
space group	$P2_1/n$ (alternative setting of No. 14, $P2_1/c$)
systematic absences	$0k0$ ($k = 2n + 1$), $h0l$ ($h + l = 2n + 1$)
a, Å	10.640 (2)
b, Å	12.144 (2)
c, Å	12.445 (2)
β, deg	100.10 (1)
V, Å^3	1583.1 (4)
Z	4
d_{calcd}, g/cm^3	1.745
cryst size, mm	0.13 × 0.20 × 0.40
μ(Mo Kα), cm^{-1}	19.6
transmission factors	0.544–0.626
temp, °C	22 ± 1
scan type	ω–2θ
scan rate, deg/min	8.4–29.3
data collecn range, 2θ, deg	3–60
data collected	$\pm h,+k,+l$
unique data	4633
data with $F_o \geq 3\sigma(F_o)$	3740
parameters refined	260
GOF	1.478
max shift/esd final cycle	0.40
max residual peak, e/Å	0.22

Table II. Final Positional Parameters (Fractional, ×10^5 for Te and F, ×10^4 for C) and Isotropic Thermal Parameters (10^3 Å^2) with Estimated Standard Deviations in Parentheses

atom	x	y	z	U_{eq}[a]
Te	6750 (2)	71199 (2)	75433 (2)	36
F(1)	−10063 (16)	64927 (15)	72972 (14)	48
F(2)	23962 (16)	76617 (15)	78450 (15)	50
F(3)	13340 (20)	56610 (14)	80078 (15)	56
C(1)	544 (3)	7318 (2)	9210 (2)	40
C(2)	1046 (4)	8264 (3)	9743 (3)	52
C(3)	939 (4)	8395 (3)	10833 (3)	63
C(4)	344 (4)	7616 (3)	11355 (3)	60
C(5)	−153 (4)	6682 (3)	10820 (3)	59
C(6)	−44 (4)	6528 (3)	9738 (3)	53
C(7)	950 (3)	6594 (2)	5984 (2)	38
C(8)	2154 (3)	6323 (3)	5804 (3)	51
C(9)	2307 (4)	6024 (3)	4766 (3)	56
C(10)	1285 (4)	5986 (3)	3934 (3)	54
C(11)	79 (4)	6253 (3)	4116 (3)	51
C(12)	−92 (3)	6580 (3)	5146 (3)	45
C(13)	−42 (3)	8702 (2)	7007 (2)	39
C(14)	776 (4)	9506 (3)	6763 (3)	50
C(15)	276 (5)	10505 (3)	6352 (3)	60
C(16)	−1007 (5)	10688 (3)	6182 (3)	68
C(17)	−1813 (5)	9891 (4)	6437 (4)	80
C(18)	−1345 (4)	8886 (3)	6842 (4)	64

[a] U_{eq} is equal to one-third the trace of the diagonalized anisotropic temperature factor matrix.

Coordinates for the Te atom were obtained from a Patterson map and refined. The remaining atoms were located in subsequent difference Fourier maps, and the structure was refined by full-matrix least-squares techniques[7] with anomalous dispersion correction for the Te atom.[8] The heavy atoms were refined with anisotropic temperature factors, and isotropic thermal motion was assumed for hydrogens. An isotropic type I

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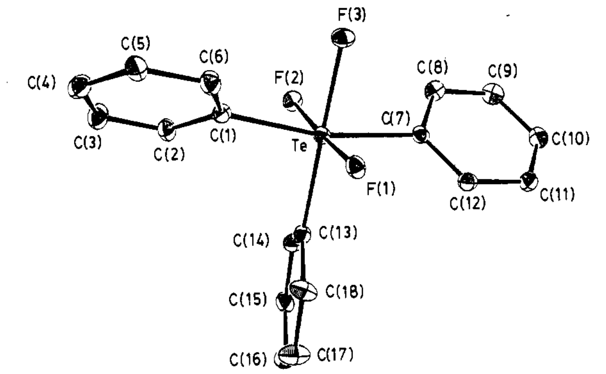

Figure 1. ORTEP drawing of the Ph_3TeF_3 molecule. Atoms are represented by thermal ellipsoids at the 50% probability level.

Table III. Bond Lengths (Å) with Estimated Standard Deviations in Parentheses

bond	uncor	cor	bond	uncor	cor
Te–F(1)	1.915 (2)	1.923	Te–C(1)	2.113 (3)	2.116
Te–F(2)	1.916 (2)	1.924	Te–C(7)	2.110 (3)	2.114
Te–F(3)	1.954 (2)	1.960	Te–C(13)	2.129 (3)	2.134

Table IV. Bond Angles (deg) with Estimated Standard Deviations in Parentheses

bonds	angle	bonds	angle
F(1)–Te–F(2)	176.18 (8)	F(3)–Te–C(13)	178.95 (10)
F(1)–Te–F(3)	87.82 (8)	C(1)–Te–C(7)	167.98 (11)
F(1)–Te–C(1)	89.16 (10)	C(1)–Te–C(13)	97.14 (11)
F(1)–Te–C(7)	90.54 (10)	C(7)–Te–C(13)	94.87 (11)
F(1)–Te–C(13)	92.11 (10)	Te–C(1)–C(2)	118.8 (2)
F(2)–Te–F(3)	88.50 (8)	Te–C(1)–C(6)	120.0 (2)
F(2)–Te–C(1)	89.44 (10)	Te–C(7)–C(8)	120.3 (2)
F(2)–Te–C(7)	90.10 (10)	Te–C(7)–C(12)	118.3 (2)
F(2)–Te–C(13)	91.58 (10)	Te–C(13)–C(14)	120.3 (2)
F(3)–Te–C(1)	83.91 (10)	Te–C(13)–C(18)	119.1 (3)
F(3)–Te–C(7)	84.08 (10)		

extinction correction[9,10] was applied with a final value of $g = 0.57$ (3) $\times 10^4$. Convergence was reached at $R = 0.031$ and $R_w = 0.020$, where $R = \sum||F_o| - k|F_c||/\sum|F_o|$ and $R_w = [\sum w(|F_o| - k|F_c|)^2/\sum w|F_o|^2]^{1/2}$. For the complete data set $R = 0.044$ and $R_w = 0.020$. The function minimized throughout refinement was $w(|F_o| - k|F_c|)^2$ with $w = 1/\sigma^2(F)$ (where $\sigma^2(F)$ is derived from the previously defined $\sigma(I)$) for the observed data and $w = 0$ for data classified as unobserved. A weighting analysis confirmed the suitability of the chosen weights by showing uniform average values of $w(|F_o| - k|F_c|)^2$ over ranges of F_o. Atomic scattering factors were from ref 11 and 12. Final atomic positional parameters are given in Table II. Complete tables of anisotropic thermal parameters and structure factor data are available as supplementary material.

The thermal motion[13] has been analyzed in terms of rigid-body modes of translation, libration, and screw motion. Analysis of all non-hydrogen atoms indicated significant independent motion of the PhTe groups and the C_3TeF_3 moiety.

Discussion

Molecules of *mer*-Ph_3TeF_3 (Figure 1) are best described as having three phenyls and three fluorines bonded in a slightly distorted octahedral arrangement about the central Te atom. Important bond lengths and angles are given in Tables III and IV, respectively. Both the Te and C(13) atoms lie off the plane of F(1), F(2), and F(3) by 0.02 and 0.08 Å, respectively, with the rest of the C(13) ring rotated along the C(13)–Te bond so as to give a C(18)–C(13)–Te–F(1) torsion angle[14] of about 10°. The remaining two phenyl groups, which are trans to each other, are twisted in a propeller fashion with a dihedral angle of 109°, and each is roughly perpendicular to the plane of the third phenyl ring. As one looks down the C(1)···C(7) direction, F(3) bisects the wider opening between the two projected ring planes. The molecules can be classified as having an approximate C_2 axis along the F(3)–Te bond direction with minor deviations in the phenyl rings preventing the exhibition of true C_2 symmetry.

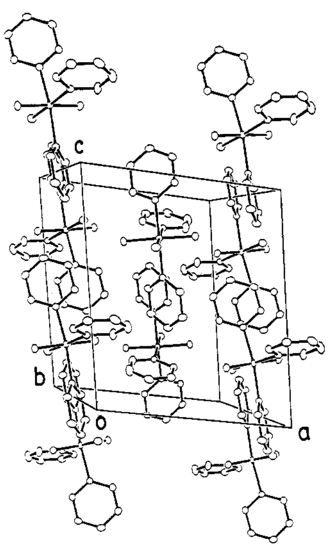

Figure 2. ORTEP drawing of the packing arrangement of Ph_3TeF_3 molecules shown with atoms with 50% probability ellipsoids.

The relative orientations of the three phenyl rings are those that would be predicted almost solely on the basis of steric arguments. The propeller-like twist of the trans phenyl groups, tending to maximize the intramolecular contact distances of carbons 2, 6, 8, and 12 and their associated hydrogens, alleviates, somewhat, the steric repulsion from the fluorines and the bulky third phenyl group. If the rings had been coplanar with the fluorines F(1) and F(2), there would have been close contacts of approximately 2.3 Å between ortho hydrogens and the fluorines; the van der Waals radii sum for these two atoms is 2.67 Å using the values 1.47 Å for F and 1.20 Å for H.[15] The slight rotation of the third phenyl ring, C(13), C(14), ..., C(18), about the approximate twofold axis leaves carbons 14 and 18 in less hindered positions under the uptilted ortho carbons 8 and 6, respectively, of the other rings. The bulkiness of the phenyls is further accommodated by the bending of the trans phenyl groups and trans fluorines toward the less congested region around F(3), which results in decreases in the C(1)–Te–C(7) and F(1)–Te–F(2) angles from ideal linear values to 167.98 (11) and 176.18 (8)° (Table IV), respectively.

Bond lengths (Table III) between Te and F in this compound have intermediate values ranging from 1.915 (2) to 1.954 (2) Å compared with those of Te–F bonds in the (tetravalent) perfluoroethyltellurium(IV) trifluoride[16] of 1.870 (7) to 2.196 (8) Å and are significantly smaller than the Te–F distance of 2.006 (2) Å in diphenyltellurium(IV) difluoride.[17] Seppelt and coworkers[18-21] have completed structural investigations on some pentafluorotellurium(VI) oxides, where they have found Te–F bond lengths to be in the range 1.80–1.86 Å. As far as we are aware, ours is the first study to find a hexavalent tellurium to

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Table V. NMR Data for the *mer*-$Ph_3TeF^aF^b_2$–$Ph_3TeF_2^+$ System[a]

sample	Te	F^a	F^b	$J(F^a–F^b)$	$J(^{125}Te–F^a)$	$J(^{125}Te–F^b)$
mer-$Ph_3TeF^aF^b_2$	+786	−2.5	−97.6	40	2860	2081
$Ph_3TeF_2^+PF_6^-$	+896		−122			1600
mer-Ph_3TeF_3–$Ph_3TeF_2^+$ (molar ratio 1:4)			−116			1739
mer-Ph_3TeF_3–$Ph_3TeF_2^+$ (molar ratio 1:0.9)	+810					1985

[a] Solvent CD_2Cl_2; chemical shift values are in ppm and coupling constants in Hz.

fluorine bond length of greater than the previously known upper limit of 1.86 Å. The increase of 0.05 and 0.09 Å (or 0.06 and 0.10 Å with use of libration-corrected values) in the Te–F bonds in the current study are probably a reflection of the decrease in electron-withdrawing power of the phenyls compared with the fluorines and oxygen in the pentafluorotellurium(VI) oxides. Te–C bond lengths in the present structure are found to be comparable to those in the tetravalent tellurium analogue Ph_2TeF_2[17] as well as those in other diphenyltellurium(IV) dihalides.[22-24]

Two phenyl rings are planar within experimental error; however, the other ring, comprised of carbons 7–12, shows evidence of slight puckering. A mean plane calculated through carbons 7–11 shows a maximum deviation of 0.004 (4) Å from the plane; C(12) lies off this plane by 0.024 Å. A mean plane through all six ring atoms leaves C(11) and C(12) on opposite sides of the plane at distances of 0.010 (4) and 0.012 (3) Å, respectively. The reason for the slight deformation from planarity is unclear but may be, in part, due to the overlap of this ring with its symmetrically related partner (vide infra).

Crystals of Ph_3TeF_3 contain molecules that pack in a chainlike pattern along the *c* axis (Figure 2) with the trans phenyl groups appearing as the link termini. There is little interaction along the chain between the parallel, symmetrically related phenyl rings (x, y, z; $-x$, $1 - y$, $2 - z$) containing carbons 1–6; however, the parallel, offset stacking and the 3.50-Å plane separation between symmetrically related rings (x, y, z; $-x$, $1 - y$, $1 - z$) containing carbons 7–12 suggests some orbital interaction, which most likely plays a key role in determining the chainlike packing arrangement. Similar phenyl–phenyl interactions linking chains of molecules have been observed in Ph_2TeCl_2. In the present structure the rings overlap each other to the extent of approximately 30%, i.e. C(11) and C(12) lie about a third of the way into the other ring when both rings are projected onto one another in a plane parallel to the ring planes. The slight puckering observed in these rings (vide supra) is such that the C(12) atoms are bent away from each other.

The ab_2 ^{19}F and ^{125}Te NMR spectra of Ph_3TeF_3 (Table V) confirm the *mer*-$Ph_3TeF^aF^b_2$ structure in solution. There is no NMR evidence of intramolecular scrambling of F^a and F^b ligands, and therefore the *mer* isomer is "rigid" in solution. A *fac* isomer, where phenyl crowding would be more severe, has not been detected by NMR.

In order to study rapid intermolecular fluorine exchange in six-coordinate phenyltellurium(VI) fluorides, it was necessary to prepare a five-coordinate Te species and this was accomplished by reaction of *mer*-Ph_3TeF_3 with PF_5:

$$mer\text{-}Ph_3TeF_3 + PF_5 \rightarrow Ph_3TeF_2^+PF_6^-$$

The resulting $Ph_3TeF_2^+$ cation was identified by ^{19}F and ^{125}Te NMR (Table V). Chemical reaction with NaF and R_4NCl provided further evidence for the identity of the $Ph_3TeF_2^+$ cation:

$$Ph_3TeF_2^+ \xrightarrow{NaF} Ph_3TeF_3$$

$$Ph_3TeF_2^+ \xrightarrow{PhCH_2(Et)_3NCl} Ph_3TeF_2Cl$$

When known amounts of *mer*-$Ph_3TeF^aF^b_2$ and $Ph_3TeF_2^+PF_6^-$ were mixed and the ^{19}F and ^{125}Te NMR spectra were recorded, the following results were obtained:

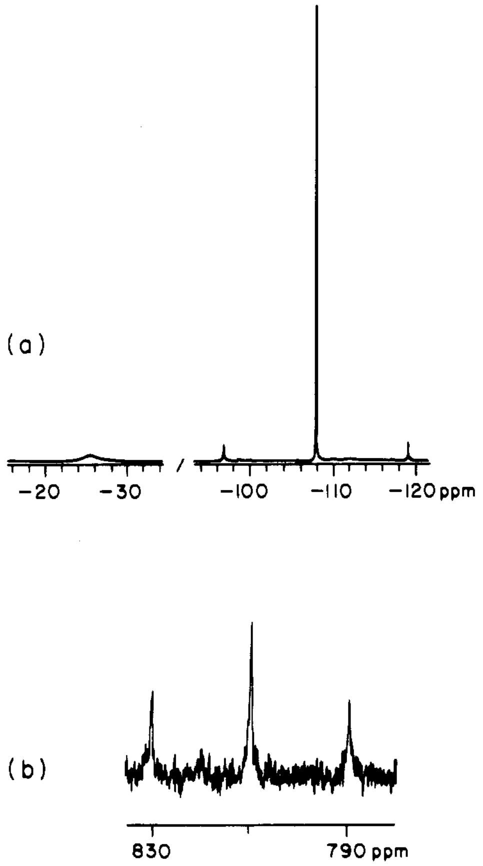

Figure 3. (a) ^{19}F NMR spectrum of a mixture of *mer*-$Ph_3TeF^aF^b_2$ and $Ph_3TeF_2^+PF_6^-$ (2.6:1.0 molar ratio) in CD_2Cl_2 at 24 °C showing averaged F^a (−25.2 ppm) and F^b (−108 ppm) peaks with retention of F^b–Te coupling (1904 Hz). The PF_6^- doublet is not shown. (b) ^{125}Te NMR spectrum of a mixture of *mer*-$Ph_3TeF^aF^b_2$ and $Ph_3TeF_2^+PF_6^-$ (5.0:1.0 molar ratio) showing averaged Te peak (808 ppm) with retention of Te–F^b (1985 Hz) coupling.

(1) The F^b–F^a coupling is lost but the Te–F^b coupling is retained as $Ph_3TeF_2^+$ is added to *mer*-$Ph_3TeF^aF^b_2$ (Figure 3).

(2) The average fluorine chemical shift of F^b moves toward high field as $Ph_3TeF_2^+$ is added, but Te–F^b coupling is retained (Figure 3).

(3) The ^{125}Te NMR spectrum of *mer*-$Ph_3TeF^aF^b_2$ is a doublet of triplets (Table V). On addition of $Ph_3TeF_2^+$, the coupling to F^a is lost but a triplet, due to coupling of Te to two F^b ligands, remains (Figure 3).

(4) The F^a peak at −2.5 ppm in *mer*-$Ph_3TeF^aF^b_2$ (Table V) moves significantly to high field as $Ph_3TeF_2^+$ is added, and the F^a–Te coupling is lost. At a 2.6:1.0 molar ratio of *mer*-$Ph_3TeF^aF^b_2$:$Ph_3TeF_2^+$ the averaged F^a peak has shifted to −25.2 ppm (Figure 3).

These results demonstrate that exchange does not lead to scrambling of F^a and F^b ligands but that intermolecular fluorine exchange in the *mer*-$Ph_3TeF^aF^b_2$–$Ph_3TeF^b_2{}^+$ system is rapid on the NMR time scale and involves cleavage of the Te–F^a bond, but not that of the Te–F^b bonds. A mechanism involving rapid coordination changes for Te ($5 \rightleftharpoons 6$) and F^a ($1 \rightleftharpoons 2$) and a fluorine-bridged intermediate in which only the F^a ligand occupies the bridging position is consistent with all our experimental results:

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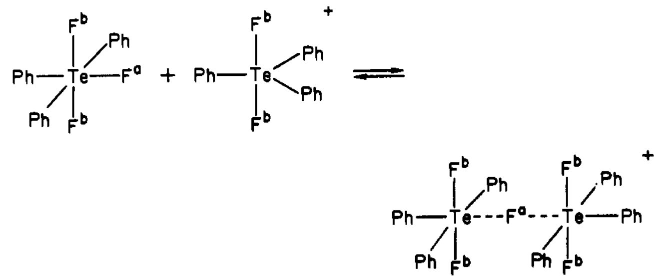

The stereoselective exchange of F^a ligands is opposed by statistical factors (2 F^b vs. 1 F^a) but must be favored by the significantly longer Te–F^a bond length (1.960 Å) compared to the Te–F^b bond lengths (1.923 and 1.924 Å) in the solid-state structure. In addition, an intermediate with F^a in the bridging position minimizes the steric interactions among the six phenyl substituents.

It was also found that "ion selective" fluorine exchange can be carried out; i.e., fluorine exchange in either the tellurium cation or phosphorus anion can be initiated without affecting intermolecular exchange in the other ion. Exchange in the *mer*-Ph_3TeF_3–$Ph_3TeF_2^+$ system does not involve the anion PF_6^- as the ^{19}F signal of PF_6^- remains a sharp doublet throughout the exchange process. When excess PF_5 is added to $Ph_3TeF_2^+PF_6^-$, however, a single line is observed in the phosphorus–fluoride region, due to rapid fluorine exchange in the PF_5–PF_6^- system,[25] but the tellurium species remain unaffected, as confirmed by fluorine NMR.

All intermolecular fluorine exchange in the *mer*-Ph_3TeF_3–$Ph_3TeF_2^+$ system is stopped by adding NaF or R_4NCl because any five-coordinate Te(VI) species is converted to a six-coordinate Te(VI) species. This observation was applied to the purification of *mer*-Ph_3TeF_3 and other phenyltellurium(VI) fluorides: washing samples with NaF was sufficient to convert line-broadened NMR spectra to spectra characteristic of "rigid" compounds.

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Registry No. *mer*-Ph_3TeF_3, 99893-86-4; PF_5, 7647-19-0; $Ph_3TeF_2^+$-PF_6^-, 102109-26-2; $Ph_3TeF_2^+$, 102109-25-1; $[Ph_3TeF_2–F–TeF_2Ph_3]^+$, 102109-27-3; PF_6^-, 16919-18-9; $Ph_3Te^+BF_4^-$, 26202-89-1; Ph_3TeF, 34814-96-5; Ph_3TeCl, 31426-14-9; ^{125}Te, 14390-73-9; F_2, 7782-41-4.

Supplementary Material Available: Tables of hydrogen coordinates and isotropic thermal parameters, anisotropic thermal parameters, and bond lengths and angles involving phenyl carbons and hydrogens and complete lists of torsion angles (8 pages). Ordering information is given on any current masthead page.

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Synthesis and Characterization of the Three Geometrical Isomers of Difluoro(1,3-propanediamine-*N*,*N'*-diacetato)chromate(III). Crystal Structure of *trans*-Li[CrF_2(1,3-pdda)]·$2H_2O$

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The synthesis and isolation of chromium(III) complexes of the linear tetradentate ligand 1,3-propanediamine-*N*,*N'*-diacetate (1,3-pdda) with monodentate (F^-) and bidentate (malonate, oxalate) ligands are reported. The three geometrical isomers (sym-cis, unsym-cis, trans) of $[CrF_2(1,3\text{-pdda})]^-$ and the unsym-cis isomer of the corresponding malonate and oxalate complexes were isolated. Characterization was accomplished with UV/visible spectroscopy, ^2H NMR spectroscopy, and single-crystal X-ray diffraction analysis. The complex *trans*-Li[CrF_2(1,3-pdda)]·$2H_2O$ ($LiCrF_2O_4N_2C_7H_{12}\cdot 2H_2O$) crystallizes in the space group *Pnma* of the orthorhombic crystal system with a = 12.137 (6) Å, b = 15.450 (6) Å, c = 7.050 (3) Å, $\alpha = \beta = \gamma = 90°$, and Z = 4. A residual of 0.053 was obtained for 1985 independent "observed" reflections collected at ambient temperature with use of a full-matrix least-squares refinement procedure. The complex has distorted-octahedral geometry around the chromium, with two fluorines trans to one another and a F–Cr–F angle of 176.67 (9)°. The Cr–F distances are 1.878 (2) and 1.901 (2) Å. The independent Cr–O and Cr–N distances are 1.992 (2) and 2.060 (2) Å, respectively. The stability of *trans*-$[CrF_2(1,3\text{-pdda})]^-$ was established by ^2H NMR and is attributed in part to the chair conformation of the ligand diamine hydrocarbon "backbone". A new synthetic scheme for incorporating deuterons into polyamino poly(carboxylic acid) ligands is also reported.

Introduction

The study of geometrical isomerism in substitution-inert transition-metal complexes has been an area of intense activity and has provided much of the basic structural information for the study of transition-metal chemistry in general. Most of the classical stereochemical work has been done with more easily made and characterized Co(III) complexes. Investigation of isomerism for Cr(III) complexes has been hampered by the lack of an NMR technique due to the extreme broadening of most nuclei brought about by the paramagnetic Cr(III) center. Recently, deuteron nuclear magnetic resonance (^2H NMR) spectroscopy was shown to be a powerful technique for studying chromium(III) complexes in solution.[2-5] In order to determine whether ^2H NMR could

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