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THE SYNTHESIS AND CRYSTAL STRUCTURE OF PERFLUOROTELLURANTHRENE, $C_{12}F_8Te_2$

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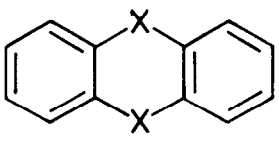
SUMMARY

The reaction of tetrafluoro-1,2-diiodobenzene with tellurium yields an oil which, on treatment with bromine yields perfluorotelluranthrene-9,9,10,10-tetrabromide. The latter is reduced by sodium sulfide to perfluorotelluranthrene. The crystal structure of perfluorotelluranthrene is reported.

INTRODUCTION

Studies of the donor properties of the phenoxachalcogenines [1,2], have stimulated our interest in anthracene derivatives of the type (*1*) where X = O, S, Se and Te. This paper describes the preparation and crystal



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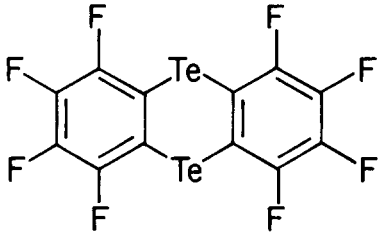

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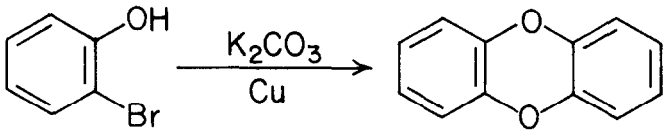
X = O, S, Se, Te

structure of perflurotelluranthrene (*2*). This compound has been of special interest to us because of our inability to reproduce the published synthesis of telluranthrene [3] despite repeated attempts.

The other three dibenzo-1,4-dichalcogenines are readily available. Dibenzo-1,4-dioxane (*3*) has been prepared from 2-halophenols [4,5] by treatment with potassium carbonate and copper metal. Thianthrene (*4*) is



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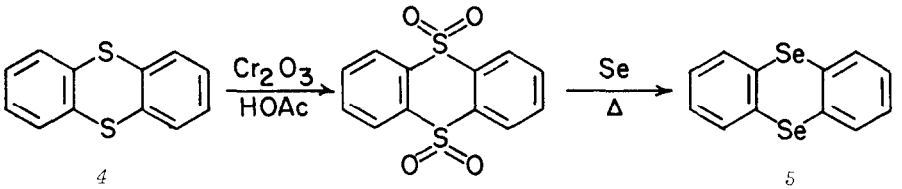
readily available from commercial sources. Selenanthrene has been prepared by a variety of synthetic routes. The first reported synthesis of selenanthrene (*5*) [6,7,8] involves the oxidation of thianthrene (*4*) to the disulphone, which undergoes reaction with elemental selenium when heated to the melting point.



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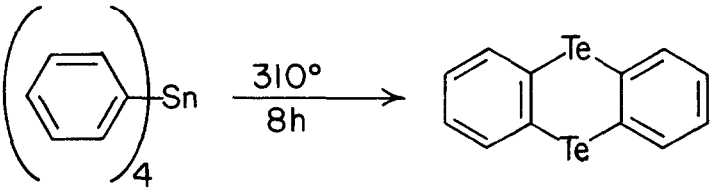
The preparation of telluranthrene (*6*) was claimed by Schuman and Schmidt [3] who treated tetraphenyl tin with tellurium metal in an evacuated glass tube at 310° for eight hours. This synthesis has not been reproducible in our hands despite repeated attempts.



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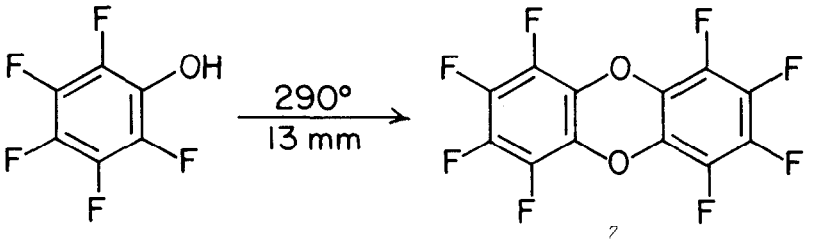
The perfluorinated analogues of the dibenzo-1,4-dichalcogenines have been prepared where the chalcogen atom is O, S, or Se. Octafluorodibenzo-



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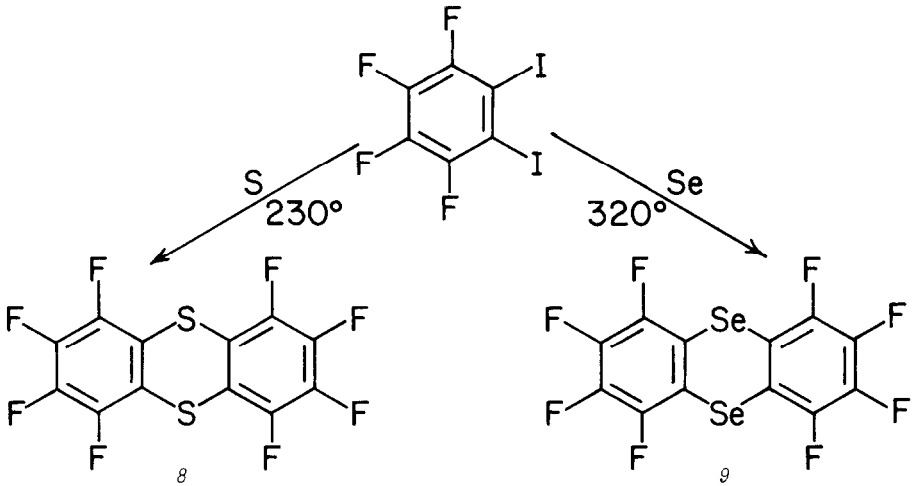
1,4-dioxane (*7*) has been prepared by the thermal decomposition of potassium pentafluorophenolate at 290° (13 mm) [9,10]. Perfluorothianthrene (*8*) and perfluoroselenanthrene (*9*) have both been prepared by reaction of tetrafluoro-1,2-diiodobenzene with either elemental sulfur or selenium in an evacuated sealed glass tube at temperatures of 230° and 320°, respectively [11,12].



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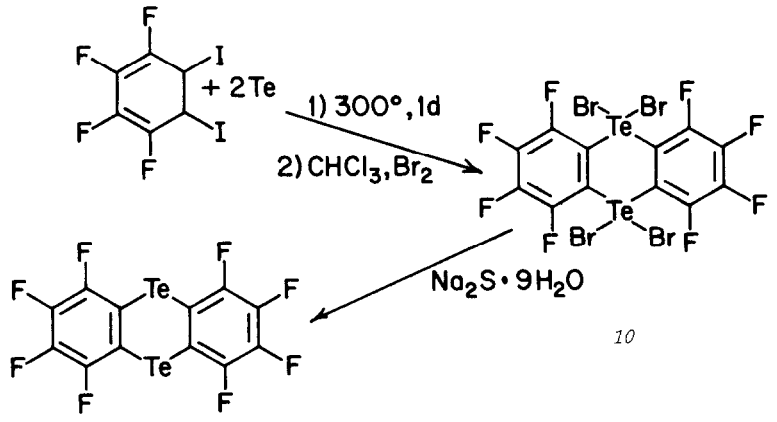
RESULTS AND DISCUSSION

Using a variation of the method of Cohen, Reddy and Massey [11,12], tetrafluoro-1,2-diiodobenzene was allowed to react with tellurium metal



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powder at 300° for 24 h. The product was isolated as perfluorotelluranthrene-9,9,10,10-tetrabromide (*10*) by the addition of bromine to a chloroform extract of the reaction mixture. Perfluorotelluranthrene (*2*) was obtained by the reduction of *10* with sodium sulfide monohydrate. The product was identified as perfluorotelluranthrene by the presence of only three carbon resonances in the ^{13}C NMR spectrum, the observation of a molecular ion of mass 555.80110 (calculated 555.799281 for $C_{12}F_8{}^{130}Te_2$) in the mass spectrum, and by elemental chemical analysis. The mass spectrum for the molecular ion (Figure 1) shows the isotopic distribution expected for a compound having two tellurium atoms [13].

Perfluoroselenanthrene was also prepared by this method [11,12] and its crystal structure is reported elsewhere [14].

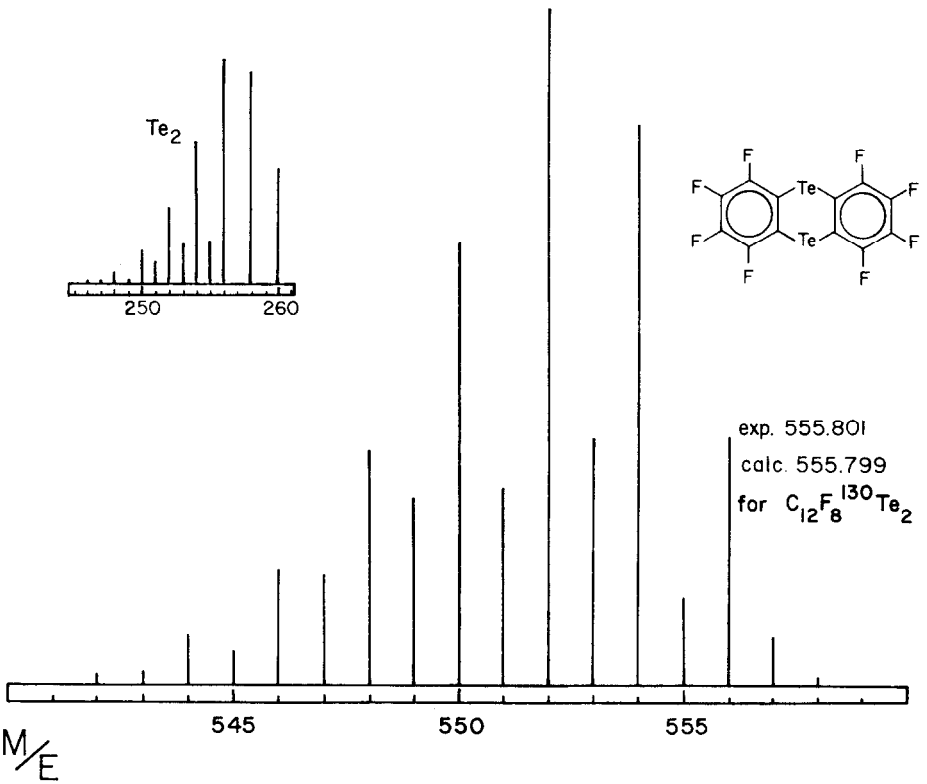

Fig.1. Mass spectrum of molecular ion of perfluorotelluranthrene

Crystal Structure

The atomic coordinates are listed in Table 1, some pertinent distances and angles in Table 2, and an Ortep drawing of the structure is shown in Figure 2.

The bond distances and angles in the structure agree well among themselves and appear to be normal. The (weighted) average values are <Te-C> = 2.114, <C-F> = 1.343, <C-C> = 1.380 A; <C-C-C> = 120.0, <C-C-F> = 119.7, <Te-C-C> (interior) = 122.5, <Te-C-C> (exterior) = 118.2°, and <C-Te-C> = 92.9(1)°. For comparison, in phenoxatellurine [17], $C_{12}H_8OTe$, <Te-C> = 2.099 A, C-Te-C = 89.4(3)°, and in perfluoroselenanthrene [14], $C_{12}F_8Se_2$, <C-F> = 1.345, <C-C> = 1.379 A; <C-C-C> = 119.9, <C-C-F> = 119.8, <Se-C-C> (interior) = 121.7, <Se-C-C> (exterior) = 119.1, <C-Se-C> = 96.5°. Corresponding bond distances in the molecules agree well, while the bond angles seem to follow a regular progression if one considers both the larger size of Te compared to other chalcogens, and the regular decrease in angle in bonds of the type A-X-B, as X varies through the series O, S, Se, Te. Least squares planes drawn through the individual phenyl carbon skeletons show maximum deviations from planarity of 0.01 A for C, and 0.03 A for F. The angle between these planes is θ_1 = 111.5°. The central ring is folded with the Te atoms 0.9 A from the same side of the best plane through C11, C12, C11', C12'. The angle between the planes (C11, C12, Te, Te') and (C11', C12', Te, Te') is θ_2 = 118.4°. These dihedra angles seem exceptional for two reasons. First, they are smaller than corresponding angles in similar molecules, and second, $\theta_1 < \theta_2$. For example, in phenoxthionine [17], $C_{12}H_8OS$, θ_1 = 151°, θ_2 = 141°; in $C_{12}H_8OTe$, θ_1 = 145°, θ_2 = 138°; in $C_{12}F_8Se_2$, θ_1 = 126°, θ_2 = 123°; and in dibenzo-*p*-dioxin [18], $\theta_1 \simeq \theta_2 \simeq 180°$. A trend seems clear. As one moves through the series, O, S, Se, Te, both angles tend to become smaller, i.e., the central boat is more sharply folded. A possible reason for $\theta_1 < \theta_2$ in $C_{12}F_8Te_2$ is that the shortest distances between the benzene rings are longer here than they are in the other molecules. At short ring to ring distances, there may be a net repulsion between them, so that $\theta_1 > \theta_2$, whereas at longer distances there may be a net attraction, so that in $C_{12}F_8Te_2$, $\theta_1 < \theta_2$. (All of the F atoms on a given ring in $C_{12}F_8Te_2$ lie on the same side of the best plane through their carbon atoms, by distances that vary from 0.015 to 0.028 A. The deviations are small, but systematic, and bring the F atoms of one ring closer to the F atoms of the other ring than they would be if they had been exactly in the plane of their carbon rings.)

TABLE 1

Atomic coordinates ($x10^4$). The e.s.d. is given in parenthesis.

Atom	x/a(σ)	y/b(σ)	z/c(σ)
Te	286.3(2)	141.7(6)	3800.0(2)
F1	833(2)	3883(8)	839(2)
F2	1994(1)	6749(8)	1999(2)
F3	2443(1)	6682(8)	3918(2)
F4	1705(1)	3705(9)	4697(2)
C1	1034(2)	3724(10)	1797(3)
C2	1631(3)	5235(9)	2383(4)
C3	1867(2)	5209(10)	3346(5)
C4	1483(2)	3646(10)	3743(3)
C11	652(2)	2206(8)	2171(3)
C12	872(2)	2169(8)	3156(3)

TABLE 2

Distances (A) and Angles (°). The e.s.d. is given in parenthesis.

Te'-C11	2.117(4)A	C1-C2	1.374(7)A
Te-C12	2.111(4)	C2-C3	1.348(9)
C1-F1	1.352(5)	C3-C4	1.405(7)
C2-F2	1.345(5)	C4-C12	1.386(6)
C3-F3	1.331(6)	C12-C11	1.385(5)
C4-F4	1.339(5)	C11-C1	1.368(6)
C12-Te-C11'	92.9(1)°	C11-C1-C2	121.1(4)
Te'-C11-C12	122.4(3)	C12-C4-C3	120.7(4)
Te-C12-C11	122.6(3)	F1-C1-C2	117.1(4)
Te'-C11-C1	118.0(3)	F4-C4-C3	118.6(4)
Te-C12-C4	118.4(3)	C1-C2-C3	121.0(4)
C1-C11-C12	119.6(4)	C2-C3-C4	118.7(4)
C11-C12-C4	118.9(4)	C1-C2-F2	120.1(5)
C11-C1-F1	121.7(4)	C4-C3-F3	120.0(5)
C12-C4-F4	120.6(4)	F2-C2-C3	118.9(4)
		F3-C3-C2	121.3(5)

(' = $\bar{x}$, y, ½-z)

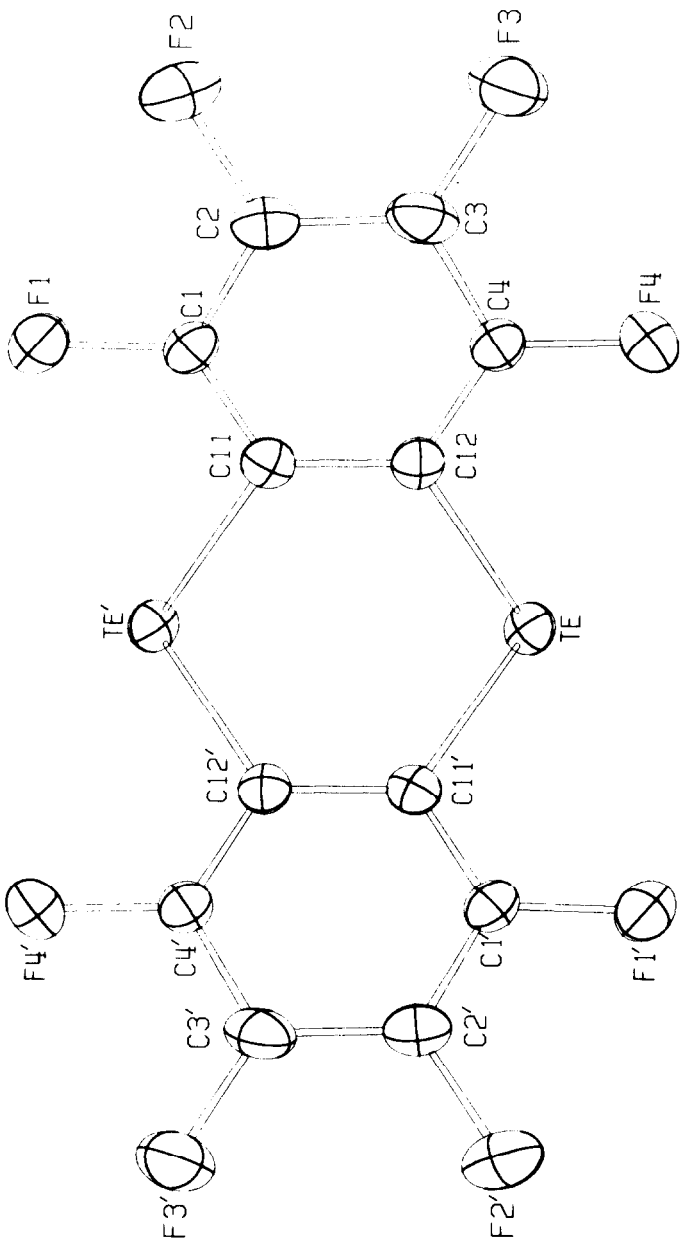

Fig. 2. Ortep drawing of structure of perfluorotelluranthrene.

The closest intermolecular constants are (Te...Te) = 4.39, (Te...F) = 3.36, (Te...C) = 3.84, (F...F) = 2.95, (F...C) = 3.08, (C...C) = 3.68 A. None of them seems to be exceptionally short.

EXPERIMENTAL

General Methods

^{13}C NMR spectra were recorded on a Jeol Model JNM-PS-100 high resolution NMR spectrometer equipped with a Nicolet 1080 E data processing system in the T-1 mode. A sweep width of 5617.977 Hz (224.4 ppm), a sweep frequency of 25.0344 MHz (obs), and an irradiating frequency of 99.5388 MHz at 10 watts power were used. $CDCl_3$ was the source of an internal deuterium lock. Infrared spectra were recorded on a Beckman IR-4260 Research Infrared Spectrophotometer. Mass spectra were measured by G. M. Gable and R. D. Grigsby who recorded them on a CEC 21-110B mass spectrometer employing an accelerating voltage of 8 kV. The molecules were bombarded with 70 eV electrons. The nominal masses were determined by reference to a perfluorokerosene standard. Melting points were measured on a Büchi SMP-20 melting point apparatus and are uncorrected. Elemental analyses were performed by Galbraith Laboratories Inc., Knoxville, Tennessee.

Reagents

Selenium and tellurium metal (99.9% pure) were furnished as gifts from the Canadian Coppers Refiners Limited. 1,2-Diiodotetrafluorobenzene was purchased from Columbia Organic Chemicals Co., Inc. It had a melting point of 56° and was used without further purification. Other solvents and reagents (reagent grade) and NMR solvents (spectral grade) were purchased from commercial sources.

Perfluoroselenanthrene

Following the method of Cohen and co-workers [11,12], 10.0 g (24.9 mmol) of 1,2-diiodotetrafluorobenzene and 3.0 g (38.0 mmol) of selenium powder were heated in a 20-cm evacuated (0.2 mm Hg) sealed tube at 320° for two days. After the heating period, the tube was cooled and broken. The contents were extracted with CH_2Cl_2 (300 ml) and filtered to remove unreacted selenium. The CH_2Cl_2 extracts were then washed with saturated

sodium thiosulfate solution (2x50 ml) and distilled water (50 ml), and then dried over anhydrous sodium sulfate. The dichloromethane was removed *in vacuo* to leave 5.10 g (11.2 mmol, 90.3%) of product; m.p. 117-121°. This impure compound was sublimed and then recrystallized from absolute methanol to give clear white crystals; m.p. 121° (lit. [12] m.p. 119°); IR (KBr) 1596, 1485 (b, vs), 1260 (w), 1090, 1012 (s), 837, 772, 727 (w), 635 (w), and 380 cm^{-1}; ^{13}C NMR ($CDCl_3$) δ (ppm) 150.885 (m), 146.065 (m), 141.133 (m), 135.654 (m), 116.204 (m). The multiplets in the ^{13}C NMR spectrum are due to ^{19}F coupling.

Perfluorotelluranthrene-9,9,10,10-tetrabromide

Following the general procedure for the preparation of perfluoroselenanthrene [11,12], 10.0 g (24.9 mmol) of 1,2-diiodotetrafluorobenzene and 5.0 g (39.2 mmol) of tellurium powder were placed in a 20-cm tube which was evacuated (0.2 mm Hg) and sealed. The tube was placed in an oven for one day at 300° after which time it was cooled and broken. The residue in the tube consisted of a liquid and a solid. The residue was extracted with CH_2Cl_2 and filtered to remove any unreacted tellurium. The filtrate was washed with concentrated sodium thiosulfate (50 ml) and distilled water (50 ml), and dried over anhydrous sodium sulfate. The CH_2Cl_2 was removed *in vacuo* to leave a dark brown oil. All attempts to crystallize the oil failed. The oil was taken up in $CHCl_3$ and bromine was added. This resulted in the formation of a bright yellow precipitate. Bromine was added until the color of bromine persisted. The precipitate was collected by filtration at reduced pressure and washed with $CHCl_3$ to yield 3.15 g (3.62 mmol, 29.1%), of perfluorotelluranthrene-9,9,10,10-tetrabromide; m.p. 280-281°, IR (KBr) 1594, 1490, 1431 (vs), 1350 (w), 1311, 1269, 1111, 1098, 1010, 824, 758 (m), 718 (m), 639 (w), and 372 cm^{-1}; m/e 637 (35.9), 636 (20.5), 635 (79.5), 634 (17.9), 633 (100), 632 (25.6), 631 (87.2), 630 (33.3), 629 (56.4), 628 (30.8), 627 (35.9), 626 (15.4), 625 (15.4%). The mass spectrum does not show a molecular ion for the tetrabromide. The mass fragment, $C_{12}F_8Te_2Br^+$ is the heaviest observed. The observed isotopic cluster distribution is consistent with that expected for an isotopic cluster Te_2Br^+ as reported by Irgolic and Haller [13]. The remainder of the mass spectrum is the same as the mass spectrum observed for perfluorotelluranthrene. Anal.: Calc'd. for $C_{12}F_8Te_2Br_4$: C, 16.54; Br, 36.70. Found: C, 16.54; Br, 36.54.

Perfluorotelluranthrene

Perfluorotelluranthrene-9,9,10-10-tetrabromide 0.5 g (0.57 mmol) was placed in a flask with excess sodium sulfide nonahydrate. The reaction mixture was heated to 90° in a water bath for 20 m after which time it was cooled. The reaction mixture was extracted with diethyl ether (2x25 ml). The ether extracts were dried (Na_2SO_4) and evaporated *in vacuo* to leave 65 mg of a crude yellow solid (0.11 mmol, 20%). The crude solid was sublimed and then recrystallized from absolute methanol to yield clear yellow crystals; m.p. 119°; IR (KBr) 1585, 1470 (broad vs, d), 1425 (broad vs, d), 1306 (m, d), 1270 (m, d), 1090 (vs), 1009 (vs), 819, 753, 698 (w), 640 (m), and 370 cm^{-1}; ^{13}C NMR ($CDCl_3$) δ (ppm) 152.658 (m), 145.122 (m), 143.128 (m), 134.927 (m), 119.413 (m); m/e 557 (47.7), 555 (87.5), 552 (97.7), 551 (28.4), 550 (64.8), 549 (27.3), 548 (35.2), 547 (17.0), 546 (18.2%). This isotopic cluster for the molecular ion $C_{12}F_8Te_2$ is consistent with that calculated for Te_2^+ as reported [13]. A high resolution measurement of the 556 peak was found to be 555.80110, (calcd. 555.799281 for $C_{12}F_8{}^{130}Te_2$ at 3.3 ppm). Analysis: Calculated for $C_{12}F_8Te_2$: C, 26.12; Te, 46.30. Found: C, 27.62; Te, 47.51.

Crystal structure determination

Single crystal X-ray data were collected by the Molecular Structure Corporation, College Station, Texas. The sample was a pale-yellow prism, $(0.15 \times 0.20 \times 0.25)mm^3$, mounted on a glass fiber. Cell constants were obtained from measurements of 25 reflections, t = 23°, MoKα radiation (λ = 0.71073 A): $\underline{a}$ = 21.332(2), $\underline{b}$ = 4.4626(4), $\underline{c}$ = 15.465(1) A, β = 115.93(1)°; monoclinic, C2/c, 4/cell. Intensity data were collected with an Enraf-Nonius CAD4 diffractometer equipped with a graphite monochromator. The intensities were measured for 1076 reflections for which $I>1.5\sigma(I)$ by scanning in 2θ. (MoKα radiation, $0 < 2\theta < 50°$, $\sigma^2(I) = \sigma^2(PK) + (0.05I)^2$, where $\sigma^2(PK)$ was estimated from counting statistics). Lorentz and polarization factors, and an empirical absorption correction were applied to the data.

A Patterson function was calculated and a trial position for Te obtained. The space group extinctions allowed two possibilities, C2/c or Cc. Analysis was begun and successfully accomplished in C2/c, which required that the center of the molecule be located on a two-fold axis. Successive Fourier syntheses of the electron density and block-diagonal

least-squares refinement of the atomic parameters, including anisotropic temperature factors yielded the final results:

$R_1 = [\Sigma\omega||Fo|-|Fc||/\Sigma\omega|Fo|] = 0.032$

$R_2 = [\Sigma\omega(|Fo|-|Fc|)^2/\Sigma\omega|Fo|^2]^{\frac{1}{2}} = 0.048$

σ = 1.58 (Standard error in an observation of unit weight).

The scattering factors were taken from the tables of Cromer [15] and Cromer and Waber [16], and included corrections for anomalous dispersion. The least-squares refinement was terminated when each parameter shifted by less than 10% of its estimated standard deviation. The magnitude of the largest residue on a final difference electron density map was 10, compared to the Te peak height of 1470 on the same scale.

ACKNOWLEDGEMENTS

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