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The Hydrogendifluoride Anion in an Asymmetric Crystalline Environment: The Crystal and Molecular Structure of Trithioureatellurium(II) Di(Hydrogendifluoride)*

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The crystal structure of $\text{Te}[\text{CS}(\text{NH}_2)_2]_3(\text{FHF})_2$, *I*, was determined at 133K using single crystal x-ray diffraction techniques. A total of 6042 independent reflections were observed for the monoclinic crystals (space group $P2_1/c$, No. 14, $a = 0.5846(3)$, $b = 2.046(1)$, $c = 1.1433(7)$ nm, $\beta = 94.69(5)^\circ$, $V_c = 1.363(1)$ nm³, ($Z = 4$), in the range $4.0^\circ \leq 2\theta \leq 70.0^\circ$ of which 5243 had $F_o^2 > 3\sigma(F_o^2)$. The trithiourea-tellurium (II) molecules crystallize as dimeric distorted square planar cations $[\text{Te}(\text{tu})_3]_2^{4+}$ (tu = thiourea) located about an inversion center. The cations are linked by N—H...F hydrogen bonds. The environment about the two independent $(\text{FHF})^-$ anions is decidedly asymmetric and therefore the hydrogen atoms are not centered between the fluorine atoms.

INTRODUCTION

Structural studies of the hydrogendifluoride or bifluoride anion, $(\text{F—H—F})^-$, containing compounds, $\text{K}(\text{FHF})^1$, $\text{Na}(\text{FHF})^2$, and $(\text{NH}_4)(\text{FHF})^3$, have demonstrated that they contain crystallographically centrosymmetric bifluoride ions. In $\text{Te}(\text{tu})_4(\text{FHF})_2^4$ the environment about the anion is very nearly symmetric. In all of these compounds the bifluoride anion contains a short, very strong, and apparently centered hydrogen bond. In contrast, a neutron diffraction study of p-toluidinium bifluoride⁵ shows the bridging hydrogen atom of the anion to be 0.020 nm closer to one fluorine atom than the other. Only in the latter crystal structure report was the N—H...F environment of the $(\text{FHF})^-$ ion markedly asymmetric. Earlier X-ray structural studies of $\text{Te}(\text{tu})_3(\text{FHF})_2^{6,7}$ indicated that the bifluoride anions in this crystal structure also lack crystallographic symmetry. In order to further explore the hydrogen bonding in this complex, a low temperature single crystal x-ray investigation was undertaken because crystals of sufficient size for a neutron diffraction study could not be grown.

EXPERIMENTAL

Following the method of Foss and Hauge⁶, aqueous solutions with a 3 : 1 molar ratio of thiourea to Te(IV) (1.78 g of thiourea in 6 ml of H₂O and 1.22 g of TeO₂ in 11 g of 36.7% HF by weight) yielded yellow monoclinic crystals. Preliminary

* Dedicated to Professor D. Grdenić on occasion of his 65th birthday.

x-ray precession photographs confirmed the unit cell and space group previously determined.^{6,7} The data crystal, an elongated prism (0.10 × 0.125 × 0.20 mm), was mounted in a glass capillary and cooled to 133(3) K using a cold N₂ stream low temperature device. The unit cell parameters (see Table I for pertinent crystal data)

TABLE I

Crystal Data

Molecular Formula for Trithioureate tellurium(II)

Di(Hydrogendifluoride) Te[CS(NH₂)₂]₃(FHF)₂

Molecular Weight = 433.97

Space Group P2₁/c (c_{2h}⁵, No. 14)

Lattice Parameters (T = 133(3) K)

a = 0.5846(3) nm, *b* = 2.046(1) nm, *c* = 1.1433(7) nm, β = 94.69(5)° *V*_c = 1.363(1) nm³

ρ calc = 2.115 Mg/m³

λ (MoK_α) = 0.071073 nm

μ (MoK_α1) = 27.43 cm⁻¹

T_{max} = exp(-μ_rmin) = 0.820

T_{min} = exp(-μ_rmax) = 0.715

No. of unique data = 6042

No. of data with *I* > 3σ(*I*) = 5243

Data to parameter ratio = 27 : 1 (all data)

23 : 1 (*I* > 3σ(*I*))

were determined by a least squares fit of 25 medium intensity reflections in the range 12.0° < 2θ < 36.0°. A total of 6910 intensities were observed with the ω — 2θ scan technique using graphite monochromatized MoK_α radiation (Syntex P2₁ automated four-circle diffractometer). Step scans were collected at variable rates from 2.0 — 12.0°/min., from 1.0° below K_α1, to 1.3° above K_α2 to compensate for α₁ — α₂ splitting. Backgrounds were observed for one-half the total scan time. A total of 6042 unique reflections were observed in the range 4.0° < 2θ < 70.0° and of these 5243 had *I* > 3σ_{*I*}. The »agreement factors« for averaging the data are:

$$R_F = 0.027 = \sum_j \|F_j\| - |F_{av}| / \sum |F_{av}| \quad \text{and} \quad R_{WF} = 0.074 = \\ = \left\{ \sum_j [(F_j^2 - F_{av}^2)^2 / \sigma_j^2 (F_j^2 - F_{av}^2)] / \sum_j [F_{av}^4 / \sigma_j^2 (F_j^2 - F_{av}^2)] \right\}^{1/2}$$

determined from the 0k1 zone and check reflections. The intensities of 7 check reflections measured after every 93 reflections showed a linear decay of 14.0% over the 204 hours of data collection. All data were corrected for intensity decay. The systematic absences (0k0, k = odd absent and h01, l = odd absent) determine the space group unambiguously as P2₁/c. All data were corrected for Lorentz and polarization effects and treated for absorption using an analytical absorption correction.⁸ Weights were derived from the observed backgrounds, B1 and B2, and net intensity *I*, as follows: σ(*I*) = [0.5²(B1 + B2) + *pI*]^{1/2}, where *p* is a 2% factor used to account for the experimental uncertainty.

Atom positional parameters and thermal parameters were refined using full matrix least-squares techniques. Hydrogen atom positional parameters determined from a subsequent difference Fourier map, were included later in the refinement with isotropic temperature factors. In the final stages of the refinement a secondary extinction parameter was included.⁹ The final R-factors for all data were:

$$(1) R(F_o) = \sum \|F_o\| - |F_c| / \sum |F_o| = 0.038$$

$$(2) R_w(F_o) = \left\{ \sum w(F_o^2 - F_c^2)^2 / \sum w F_o^4 \right\}^{1/2} = 0.087$$

$$(3) \text{ »Goodness of fit« } = \left\{ \sum w(F_o^2 - F_c^2)^2 / (n_o - np) \right\}^{1/2} = 2.70$$

The function minimized in the least-squares refinement was Σ{(F_o² — F_c²)/σ²(F_o²)}. A difference Fourier map contained a few peaks of approximate magnitude 1.0 e/Å³

near the Te atom and the map had a general noise level of $\pm 0.40 \text{ e}/\text{\AA}^3$.¹⁰ The final refined values of the positional parameters and temperature factors appear in Table II.

TABLE II
Final Least Squares Parameter Values

	X	Y	Z	U11	U22	U33	U12	U13	U23
TE	-12559(3)	9506(1)	5032(1)	76(1)	101(1)	70(1)	0(1)	-5(0)	0(1)
S1	-28201(11)	13645(4)	23621(5)	73(2)	221(3)	71(2)	23(2)	5(2)	-15(2)
Cl	-4303(42)	14068(11)	33913(20)	112(9)	80(9)	82(8)	18(7)	15(7)	1(7)
N1	-8517(40)	13273(11)	44996(18)	108(9)	158(9)	77(8)	-8(7)	14(7)	3(7)
N2	16508(38)	15239(12)	31017(19)	86(8)	190(10)	95(8)	-20(8)	5(7)	11(7)
S2	-14867(10)	20254(3)	-5048(5)	80(2)	97(2)	86(2)	-10(2)	-9(2)	5(2)
C2	-38146(42)	18910(12)	-15654(20)	93(9)	95(9)	98(9)	6(7)	-1(7)	8(7)
N3	-59114(38)	18777(12)	-12523(19)	80(8)	208(11)	114(9)	0(8)	2(7)	11(8)
N4	-33411(40)	18172(12)	-26647(19)	108(9)	216(11)	77(8)	13(8)	4(7)	-12(7)
S3	6962(10)	4151(3)	-14802(5)	77(2)	136(3)	69(2)	-7(2)	1(2)	-8(2)
C3	-15848(42)	2376(12)	-25023(20)	90(9)	112(10)	91(9)	0(8)	-2(7)	8(7)
N5	-36945(39)	1623(13)	-21932(20)	79(9)	244(11)	118(9)	-32(8)	7(7)	0(8)
N6	-11600(41)	1792(12)	-36162(19)	119(9)	209(11)	74(8)	-11(8)	0(7)	-36(7)
F1	11590(29)	18680(9)	-33530(14)	130(7)	208(8)	121(7)	9(6)	6(6)	0(6)
F2	27923(31)	28124(9)	-39669(15)	156(7)	197(8)	130(7)	4(6)	17(6)	7(6)
F3	46340(30)	12687(9)	-48742(14)	122(7)	253(9)	122(7)	-18(6)	8(6)	11(6)
F4	33380(29)	2877(9)	-42390(14)	124(7)	233(8)	126(7)	-3(6)	14(6)	-12(6)

	X	Y	Z	B(Å ²)
H1A	265(62)	1450(17)	5062(28)	0.54(0.60)
H1B	-2160(73)	1273(20)	4685(33)	1.44(0.76)
H2A	2742(68)	1493(18)	3559(30)	0.79(0.64)
H2B	1824(72)	1584(19)	2392(33)	1.50(0.77)
H3A	-6269(75)	1896(21)	-439(33)	2.82(0.82)
H3B	-7071(75)	1834(20)	-1853(33)	2.71(0.76)
H4A	-4407(66)	1783(18)	-3225(30)	1.00(0.68)
H4B	-1951(72)	1860(19)	-2857(31)	1.42(0.75)
H5A	-3744(68)	217(18)	-1365(31)	1.82(0.69)
H5B	-4803(70)	194(19)	-2723(32)	1.31(0.73)
H6A	259(76)	216(20)	-3846(33)	2.06(0.78)
H6B	-2059(69)	50(18)	-4168(31)	1.83(0.69)
H7	2318(75)	2551(20)	-3821(32)	2.87(0.80)
H8	4330(76)	908(18)	-4603(32)	2.25(0.75)

UIJ has been multiplied by 10**4. The conversion of BIJ to UIJ I.NE.J includes multiplication by 1/2.

^a The form of the anisotropic temperature factor is $\exp[(-2\pi^2(U_{11}h^2a^{*2} + \dots + 2U_{23}klb^*c^*))]$. ^b Positional parameters have been multiplied by 10⁵, estimated standard deviations are given in parentheses.

RESULTS AND DISCUSSION

The coordination geometry about the Te atoms found in earlier studies was verified in this study. Figure 1 shows the $[\text{Te}_2(\text{tu})_6]^{4+}$ cation; the geometry is distorted square-planar at each Te atom. The molecules are linked by short $\text{N—H}\dots\text{F}$ hydrogen bonds to the bifluoride anions. The resulting packing in the unit cell is illustrated in Figure 2. Hydrogen bonding interactions are summarized in Table III and also presented in Figure 3. The hydrogen bonding environment about each of the bifluoride ions in the crystal is asymmetric. In the case of $[\text{F}(1)\text{H}(7)\text{F}(2)]^-$, the $\text{N—H}\dots\text{F}$ hydrogen bonding arrangement is very asymmetric. F(1) is involved in three normal $\text{N—H}\dots\text{F}$ hydrogen bonds (average $\text{H}\dots\text{F}$ distance 0.197(4) nm while F(2) is observed to form only two $\text{N—H}\dots\text{F}$ bonds. As a result of this pronounced asymmetry, the hydrogen

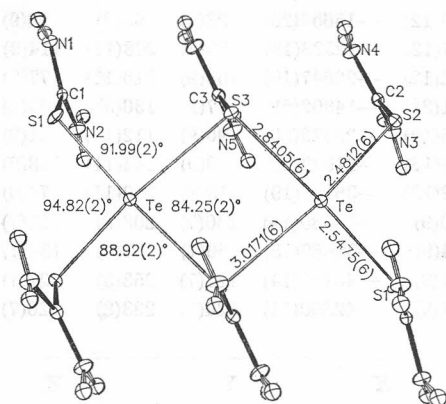


Figure 1. The $[\text{Te}_2(\text{tu})_6]^{4+}$ cation viewed normal to the plane formed by the Te and S atoms. An inversion center is located at the center of the molecule. The atoms are shown at the 50% probability level with the temperature factors for H atoms arbitrarily assigned $B_{\text{iso}} = 1.00 \text{ \AA}^2$. All distances are given in \AA units.

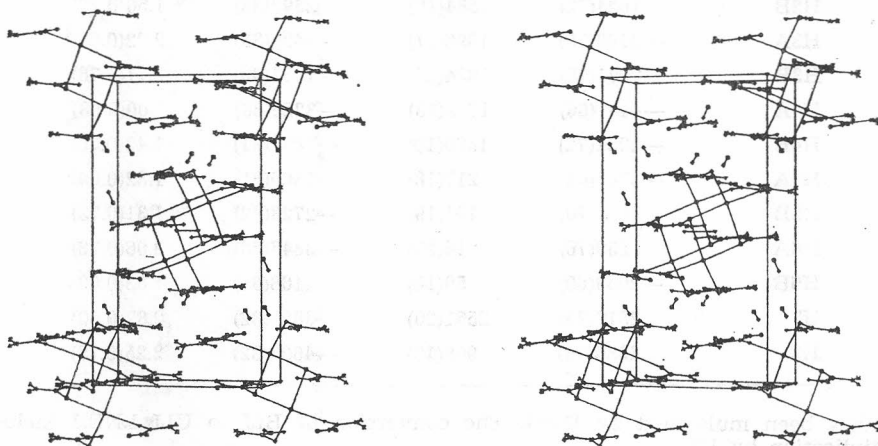


Figure 2. The unit cell drawing for $[\text{Te}_2(\text{tu})_6](\text{FHF})_4$ viewed down the a -axis (c up, b across). The $[\text{Te}_2(\text{tu})_6]^{4+}$ dimers are connected by hydrogen bonds to bifluoride anions.

TABLE III
Hydrogen Bonding Distances for Te₂(tu)₆(FHF)₄

F...H—N	F—H (nm)	F—N (nm)	Angle F—H—N ^o
F(1)...H(1A)—N(1)	0.203(3)	0.2857(3)	149(5) ^o
F(1)...H(3B)—N(3)	0.192(4)	0.2833(3)	164(10) ^o
F(1)...H(4B)—N(4)	0.195(4)	0.2809(3)	175(4) ^o
F(2)...H(2B)—N(2)	0.210(4)	0.2853(3)	150(5) ^o
F(2)...H(3A)—N(3)	0.191(4)	0.2851(3)	163(10) ^o
F(3)...H(1B)—N(1)	0.198(4)	0.2793(3)	172(5) ^o
F(3)...H(2B)—N(2)	0.208(4)	0.2830(3)	158(8) ^o
F(3)...H(4A)—N(4)	0.219(4)	0.2925(3)	143(4) ^o
F(4)...H(5B)—N(5)	0.197(4)	0.2808(3)	164(10) ^o
F(4)...H(6A)—N(6)	0.189(4)	0.2789(3)	176(4) ^o
F(4)...H(6B)—N(6)	0.203(3)	0.2834(3)	162(9) ^o

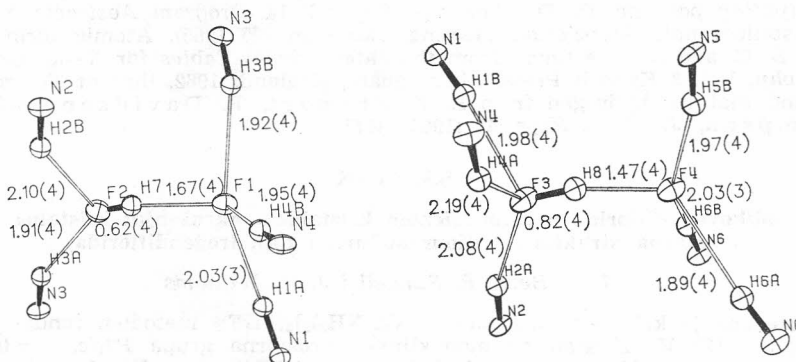


Figure 3. Hydrogen bonding interactions to the two asymmetric bifluoride anions. The origin of the (F—H...F)⁻ anion asymmetry is the asymmetric N—H...F hydrogen bonding environment about the F atoms of the bifluoride anions (see text). The temperature factors are plotted at the 50% probability level with H-atoms assigned $B_{\text{iso}} = 1.0 \text{ \AA}^2$. All distances are given in \AA units.

atom H(7), is bound much more tightly to atom F(2) than F(1) viz., (F—H = 0.06 nm vs 0.17 nm). The F—H distances discussed here, and shown in the figures, are »observed distances« and are shorter than expected being an artifact of the x-ray diffraction experiment, H-atom scattering factor table, etc. Nevertheless, the asymmetry in the (F—H...F)⁻ anions is obvious and only neutron diffraction studies will provide correct H—F distances. In the case of the [F(3)—H(8)—F(4)]⁻ anion, three hydrogen bonds form with each of the two fluorine atoms and the bridging proton of the anion is, as expected, more nearly centered between F(3) and F(4). For both bifluoride anions the F...F distances are in the normal range, F(1)...F(2) = 0.2291(3) nm and F(3)...F(4) = 0.2285(3) nm as compared to F...F = 0.2264(3) nm in NaFHF₂, with the

slightly longer F...F distances caused by the numerous N—H...F hydrogen bonds.

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SAŽETAK

Anion vodikovog diflorida u asimetričnom kristalnom okruženju: kristalna i molekularna struktura tritioureatelur(II) di(hidrogendiflorida)

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Određena je kristalna struktura $\text{Te}[\text{CS}(\text{NH}_2)_2]_3(\text{FHF})_2$ metodom rendgenske difrakcije na 133 K. Kristali su monoklinski, prostorna grupa $P2_1/c$, $a = 0,5846(3)$, $b = 2,046(1)$, $c = 1,1433(7)$ nm, $\beta = 94,69(5)^\circ$, $V_c = 1,363(1)$ nm³, $Z = 4$. Molekule tritioureatelura(II) kristaliziraju kao dimerni, nepravilni kvadratno-planarni kationi $\text{Te}_2[\text{CS}(\text{NH}_2)_2]_6^{4+}$ koji su međusobno povezani N—H...F vodikovim vezama. Okoliš dva neovisna $(\text{FHF})^-$ aniona jest asimetričan, pa prema tome vodikovi atomi nisu smješteni u centru među fluorovim atomima.