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Crystal Structure of $Te_2O_3F_2$

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$Te_2O_3F_2$ crystallizes with the triclinic symmetry (space group P-1) and the unit cell parameters a = 515.3(1) pm, b = 625.7(1) pm, c = 688.8(1) pm, α = 98.71(1)°, β = 110.31(1)°, γ = 92.72(1)°, Z = 2. Its structure was solved and refined to R values R_1 = 0.024 and wR_2 = 0.059 on the basis of 699 independent reflections recorded on a single crystal with an automatic four-circle diffractometer. The two Te atoms are, respectively, fourfold and fivefold coordinated and their lone pair E is stereochemically active. The bond valence calculation shows a perfect O/F order. The Te(1)O_3FE and Te(2)O_4FE polyhedra form, by sharing O–O edges, bipolyhedral units with a very short Te–Te distance (319 pm). These units, by sharing corners, constitute independent sheets parallel to $x0y$. All the F atoms are nonbridging and orientated, together with the lone pairs E, toward the interlayer space. The structural relationships with the α-TeO_2 structure have been evidenced and analyzed. © 1996 Academic Press, Inc.

INTRODUCTION

Our recent investigation by thermal and X-ray diffraction techniques within the TeO_2–TeF_4 system has allowed us to isolate and characterize two original crystalline Te^{IV} oxidefluorides with the respective formulas $TeOF_2$ and $Te_2O_3F_2$ (1).

The present paper deals with the resolution and the description of the crystal structure of the $Te_2O_3F_2$ compound.

EXPERIMENTAL—DETERMINATION OF THE STRUCTURE

$Te_2O_3F_2$ can be prepared as a white polycrystalline powder (i) either in the solid state, by direct reaction in a sealed platinum tube between TeO_2 and TeF_4, heated for 24 h at 250°C, (ii) or by a wet method, consisting of a dissolution of TeO_2 in an aqueous HF solution (40%), followed by a slow evaporation on a sand bath, the precipitate so obtained being then heated at 200°C during 24 h in a sealed nickel tube.

Single crystals of good quality can be obtained by this last method. One of them, prismatic and 0.14 × 0.07 × 0.05 mm in size, has been selected for this study.

The recording of the integrated intensities of diffraction was performed with a P4-Siemens four-circle automatic diffractometer, using the Mo$K\alpha$ radiation and under the conditions reported in Table 1.

The crystal structure was solved by using the direct methods of the SHELXS-86 program (2) and refined with SHELXL-93 (3). Absorption corrections were performed by the psi-scan method, using the XEMP program (4). The reliability factors R converged to R_1 = 0.024 and wR_2 = 0.060 when all the intensities were used. The refined parameters are reported in Table 2 and the main interatomic distances in Table 3.

A bond valence calculation realized by the Brown's method (5) shows that the O^{2-} and F^- anions are perfectly ordered on the anionic sites (Table 4).

DESCRIPTION OF THE STRUCTURE

The Te(1) atom is surrounded by four anions, three oxygen atoms at distances ranging from 188.2 to 212.4 pm and one fluorine atom F(1). Four other anions (O(1), O(2), F(1), and F(2)) are located at much longer distances. Their contribution to the electrostatic valence around Te(1) is relatively low (see Table 4) and so they can be neglected. The corresponding Te(1)O_3F polyhedron is represented in Fig. 1a. It can be considered as a distorted trigonal bipyramid Te(1)O_3FE whose one equatorial corner is occu-

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TABLE 1
Crystal Data and Structure Refinement Conditions for $Te_2O_3F_2$

Formula weight (g)	341.20
Temperature	293(2) K
Wavelength	71.073 pm
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	$a = 515.3(1)$ pm $\alpha = 98.71(1)°$
	$b = 625.7(1)$ pm $\beta = 110.31(1)°$
	$c = 688.8(2)$ pm $\gamma = 92.72(1)°$
Volume	$204.35(6) \times 10^6$ pm^3
Z	2
Density (calculated)	5.536 Mg/m^3
Absorption coefficient	14.19 mm^{-1}
Absorption correction	psi-scan method
$F(000)$	292
Crystal size	$0.14 \times 0.07 \times 0.05$ mm^3
2θ range for data collection	3.21° to 43.01°
Index ranges	$-1 \le h \le 5$, $-7 \le k \le 7$, $-8 < l \le 8$
Reflections collected	957
Independent reflections	699 [R(int) = 0.0253]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	699/0/65
Goodness-of-fit on F^2	0.850
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0213$, w$R_2 = 0.0584$
R indices (all data)	$R_1 = 0.0242$, w$R_2 = 0.0598$
Extinction coefficient	0.0167(14)
Largest diff. peak and hole	1115 and −885 e·nm^{-3}

pied by the lone pair E of Te(1). This kind of polyhedron is quite classical in the stereochemistry of Te^{IV} and is observed in crystal structures like the α and β form of TeO_2 (6, 7) and $H_2Te_2O_3F_4$ (8).

The Te(2) atom is surrounded by five anions (O(1), O(1′), O(2), O(3″), and F(2)) which constitute a distorted Te(2)O_4FE octahedron, the sixth corner being occupied by the lone pair E of Te(2). This polyhedron, which is drawn on Fig. 1b, is commonly observed in fluorinated compounds of Te^{IV} as, for instance, TeF_4 (9) and $KTeF_5$ (10).

Like for the TeO_4E polyhedron observed in tellurite α-TeO_2 (6) (Fig. 1c), and because of the repulsion effect of the nonbonding lone pair E, bond angles logically deviate from the ideal values for regular trigonal bipyramid or octahedron, i.e., respectively, 180°, 120°, 90° and 180°, 90° (see Table 5).

Each Te(1)O_3FE and Te(2)O_4FE polyhedron shares an edge (O(3)–O(3) and O(1)–O(1), respectively) with another identical polyhedron to constitute bipolyhedral units $Te(1)_2O_4F_2E_2$ and $Te(2)_2O_6F_2E_2$ (Figs. 1a and 1b), both characterized by very short and identical Te–Te distances (319 pm).

These units are distributed within layers parallel to $x0z$, alternately along $0y$ at $y \approx 0$ for Te(2) units and $y \approx 0.5$ for Te(1) units. From one layer to another they are connected by O(2) and O(3) atoms, so forming independent $Te_2O_3F_2$ sheets parallel to $x0y$. One of these sheets, which repeat regularly along $0z$, is represented in Fig. 2. As shown on Fig. 3 these sheets are severely twisted along $0y$. In contrast to O(2) and O(3) atoms, fluorine atoms F(1) and F(2) are nonbridging and, like the lone pairs E, are directed toward the interlayer space. They can be considered as terminal anions. However, they contribute to the cohesion of the three-dimensional net-

TABLE 2
Atomic Coordinates (×10^4) and Equivalent Isotropic Temperature Factors B_{eq} (pm^2 × 10^{-4})

	x	y	z	B_{eq}
Te(1)	1323(1)	4784(1)	2419(1)	0.79
Te(2)	3907(1)	967(1)	7879(1)	0.87
F(1)	1032(10)	6996(7)	4717(7)	1.34
F(2)	6728(9)	9559(7)	7100(7)	1.42
O(1)	6371(11)	1843(8)	661(8)	1.18
O(2)	5211(11)	3672(9)	7071(8)	1.11
O(3)	1136(11)	3505(8)	9325(7)	0.95

TABLE 3
Bond Lengths (pm) for $Te_2O_3F_2$

Te(1)–O(2)	188.2(5)	Te(2)–O(1)	187.1(5)
Te(1)–O(3′)	191.2(5)	Te(2)–F(2)	192.3(5)
Te(1)–F(1)	199.0(4)	Te(2)–O(2)	201.5(5)
Te(1)–O(3)	212.4(5)	Te(2)–O(1′)	217.5(5)
		Te(2)–O(3″)	250.6(5)
Te(1)–O(1)	284.4(4)		
Te(1)–F(1)	296.4(5)	Te(2)–F(1)	297.8(5)
Te(1)–F(2)	296.8(4)	Te(2)–F(1)	302.3(5)
Te(1)–O(2)	333.1(5)	Te(2)–F(2)	328.8(6)
		Te(1)–Te(1′)	318.7(1)
		Te(2)–Te(2′)	318.8(1)

TABLE 4
Bond Valence Analysis of $Te_2O_3F_2$

	Te(1)	Te(2)	Sum	Expected
F(1)	0.724 0.052	0.050 0.044	0.87	1
F(2)	0.051	0.866 0.022	0.94	1
O(1)	0.096	1.330 0.586	2.01	2
O(2)	0.026 1.293	0.903	2.22	2
O(3)	0.672 1.192	0.240	2.10	2
Sum	4.106	4.041		
Expected	4	4		

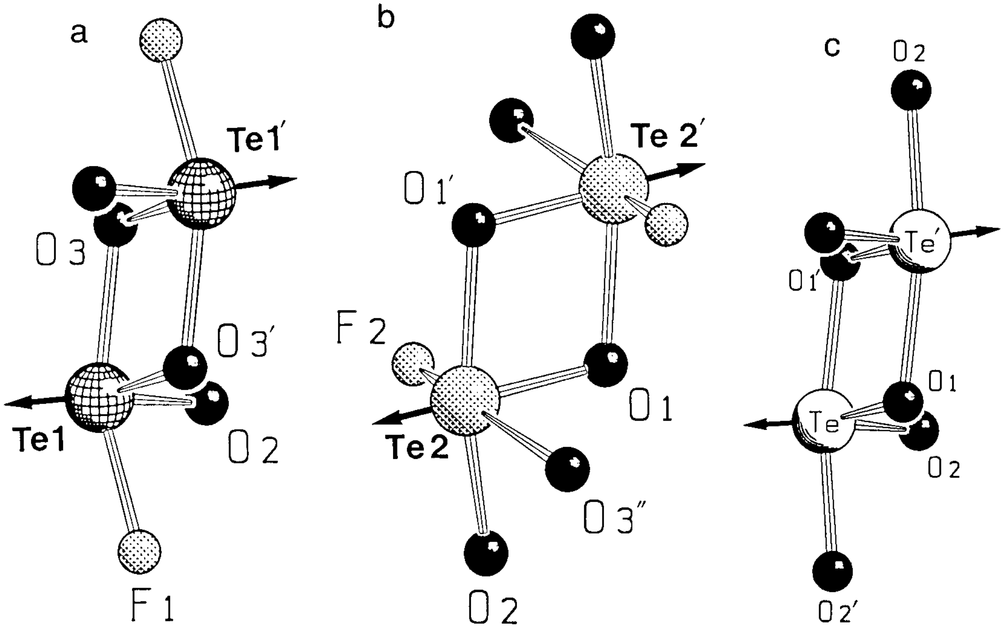

FIG. 1. Anionic polyhedra (a) Te(1)O_3FE, forming bipolyhedra $Te(1)_2O_4F_2E_2$; (b) Te(2)O_4FE, forming bipolyhedra $Te(2)_2O_6F_2E_2$; (c) TeO_4E (α-TeO_2) forming bipolyhedra $Te_2O_6E_2$ (for comparison). Arrows visualize the direction toward which probably point the lone pairs E of Te^{IV}.

work through weak Te–F bonds between successive sheets.

COMPARISON WITH α-TeO_2 CRYSTAL STRUCTURE

The α-form of TeO_2 crystallizes with tetragonal symmetry (space group $P4_12_12$, a = 481.2(2) pm, b = 761.5(7) pm, Z = 4) (6). Its structure exhibits great analogies with the $Te_2O_3F_2$ structure:

—the building units $Te_2O_6E_2$ (Fig. 1c) are nearly identical to the $Te_2O_4F_2E_2$ bipolyhedral units (Fig. 1a), with quite the same very short Te–Te distance (317 pm), and

—these units constitute, by sharing corners, isolated twisted $(Te_2O_4)_n$ sheets very similar structurally to the independent $Te_2O_3F_2$ sheets, as shown by a comparison of Figs. 4a and 4b with, respectively, Figs. 2 and 3.

The repetition of these sheets and their twisted character

TABLE 5
Comparison of Characteristic Angles in Te_2O_6, $Te(2)O_6F_2$, and $Te(1)_2O_4F_2$ Bipolyhedra, Respectively, in α-TeO_2 (Tellurite) and $Te_2O_3F_2$ Structures

		$Te_2O_3F_2$			
TeO_2		Te(1)		Te(2)	
O(1)–Te–O(2)	101.0°	O(3′)–Te(1)–O(2)	100.7(2)°	O(1)–Te(2)–O(3″)	79.3(2)°
				O(1)–Te(2)–F(2)	91.2(2)°
O(1)–Te–O(1′)	78.3°	O(3)–Te(1)–O(3′)	75.8(2)°	O(1)–Te(2)–O(1′)	76.3(2)°
O(1)–Te–O(2′)	90.2°	F(1)–Te(1)–O(3′)	82.5(2)°	O(1)–Te(2)–O(2)	90.8(2)°
O(2)–Te–O(1′)	90.0°	O(2)–Te(1)–O(3)	89.0(2)	O(3″)–Te(2)–O(1′)	102.0(2)°
O(2)–Te–O(2′)	89.6°	F(1)–Te(1)–O(2)	86.3(2)°	O(3″)–Te(2)–O(2)	83.0(2)°
				O(2)–Te(2)–F(2)	87.6(2)°
				F(2)–Te(2)–O(1′)	84.8(2)°
O(2′)–Te–O(1′)	168.9°	O(3)–Te(1)–F(1)	156.5(2)°	O(2)–Te(2)–O(1′)	164.8(2)°
				F(2)–Te(2)–O(3″)	166.6(2)°
Te–O(1)–Te′	102.0°	Te(1)–O(3)–Te(1′)	104.2(2)°	Te(2)–O(1)–Te(2′)	103.7(2)°

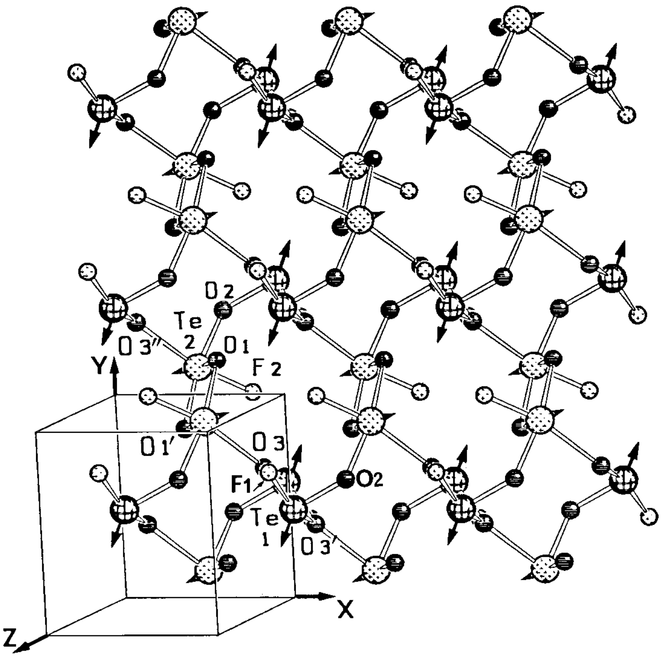

FIG. 2. One of the independent $Te_2O_3F_2$ sheets parallel to $x0y$.

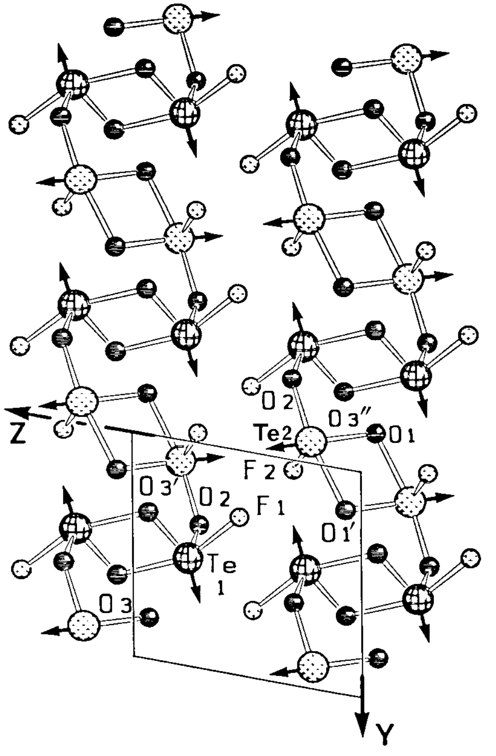

FIG. 3. Projection of the $Te_2O_3F_2$ structure onto the yz plane, showing the succession of the sheets along $0z$ axis and their twisted character.

are comparable in both structures. Some differences, mainly in the structure of these sheets, can, however, be pointed out when comparing Figs. 2 and 4a.

In both structures, four building units constitute, by sharing corners (O(2) corners in the case of $Te_2O_6E_2$ units, O(1) and O(3) corners in the case of $Te_2O_4F_2E_2$ units), rectangular holes placed at right angles to each other. These rectangular holes accommodate the lone pairs E of Te^{IV} in TeO_2 and both the lone pairs E and the nonbridging atoms F(2) in $Te_2O_3F_2$. However, in TeO_2 the lone pairs are directed toward the center of all the rectangular cavities (two lone pairs per cavity) which are therefore all identical, whereas in $Te_2O_3F_2$, only one half of the cavities is occupied by the lone pairs E and the fluorine atoms F(2) (four lone pairs E and two F(2) per cavity) and therefore strongly distended with respect to the unoccupied ones.

In fact, we can consider that the $Te_2O_3F_2$ structure formally derives from the α-TeO_2 type simply by an ordered (i) addition of a terminal F(2) anion to one half of the $Te_2O_6E_2$ units (formation of the $Te(2)_2O_6F_2E_2$ units), and (ii) substitution of a F(1) anion for an oxygen atom for the other half of the $Te_2O_6E_2$ units (formation of the $Te(1)_2O_4F_2E_2$ units).

This operation is not possible without a change in the connection between the building units so constituted: the substituted F(1) anions are nonbridging, the connection being realized by the O(3) anions.

CONCLUSION

$Te_2O_3F_2$ is the first simple Te^{IV} oxidefluoride isolated and characterized up to now.

Its original crystal structure exhibits great analogies with that of the α-form of TeO_2.

Actually, in both structures nearly identical $Te_2X_6E_2$ bipolyhedral units and independent twisted sheets are observed. In both structures too, the lone pairs E of Te^{IV} atoms are stereochemically active and point toward the intersheet space.

The main differences result from the well defined structural role respectively played in $Te_2O_3F_2$ by the strictly ordered O and F atoms: in contrast to O atoms, F atoms are nonbridging and mainly located within the intersheet space, so ensuring the cohesion between the highly covalent sheets.

As observed for Bi^{III} (11) and Sb^{III} (12–14), the O/F long range order seems to be a fundamental feature of Te^{IV} oxidefluorides. The determination in progress of the crystal structure of the second oxidefluoride $TeOF_2$ will allow us to check this hypothesis.

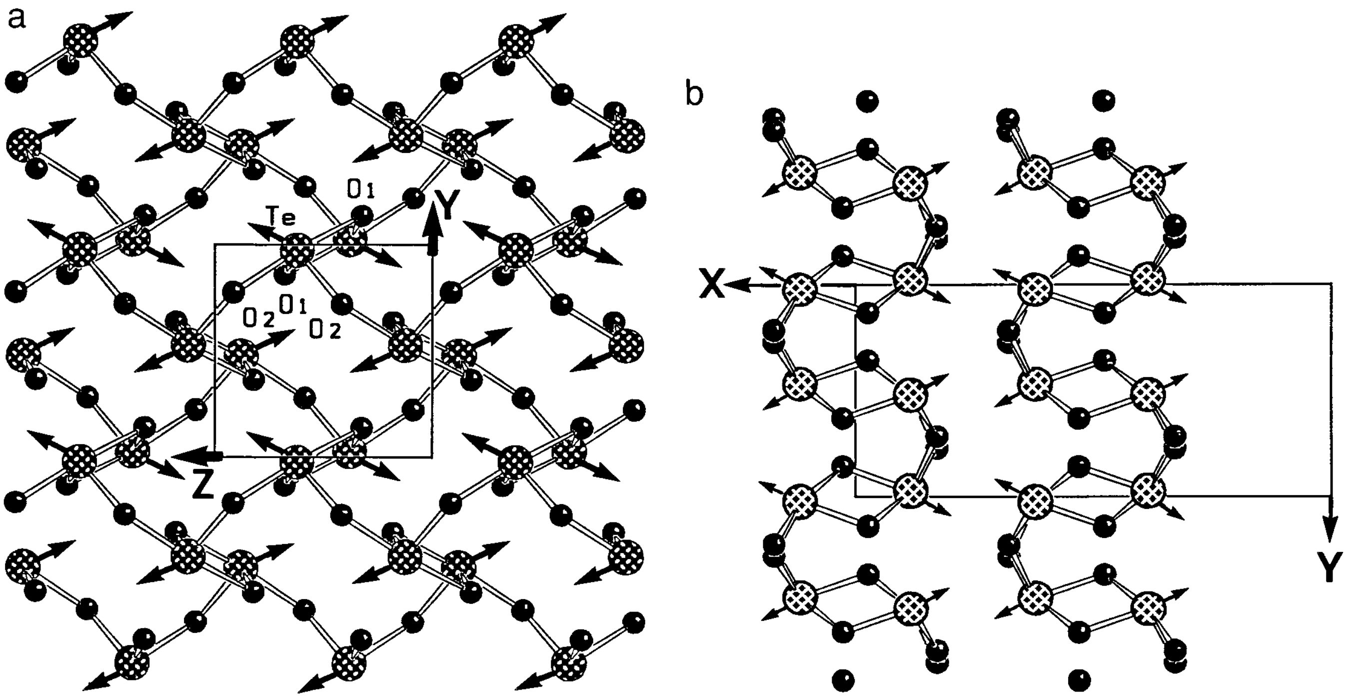

FIG. 4. The independent TeO_2 sheets in α-TeO_2. (a) View of one along O*x*; (b) their succession along O*z*.

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