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New oxyfluorotellurates(IV): $M\text{TeO}_3\text{F}$ ($M = \text{Fe}^{\text{III}}$, Ga^{III} and Cr^{III})

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The crystal structures of the new isomorphous compounds iron(III) oxyfluorotellurate(IV), FeTeO_3F , gallium(III) oxyfluorotellurate(IV), GaTeO_3F , and chromium(III) oxyfluorotellurate(IV), CrTeO_3F , consist of zigzag chains of MO_4F_2 distorted octahedra alternately sharing O–O and F–F edges and connected *via* TeO_3 trigonal pyramids. A full O/F anionic ordering is observed and the electronic lone pair of the Te^{IV} cation is stereochemically active.

Comment

In recent years, a systematic investigation of tellurium(IV) fluorides and oxyfluorides has been performed in our laboratory in order to develop our knowledge in four directions: (i) synthesis of new phases of potential interest for their nonlinear optical properties; (ii) characterization of new structure types in order to determine the influence of the electronic lone pair of Te^{IV} atoms (E) on their structural framework, especially in fluorides and oxyfluorides, compounds very sensitive to the stereochemical activity of this electronic lone pair; (iii) determination of the main rules governing the O/F anionic long-range or short-range ordering in oxyfluorides; and (iv) crystal growth in hydrofluoric acid medium of tellurates and oxyfluorotellurates(IV), which could be promising for nonlinear optics.

Following on from the structural characterization of the TeOF_2 (Guillet *et al.*, 1999), $\text{Te}_2\text{O}_3\text{F}_2$ (Ider *et al.*, 1996) and $\text{KTe}_3\text{O}_6\text{F}$ (Laval *et al.*, 2002) phases, this paper deals with the syntheses and crystal structure determination of a new isomorphous series of oxyfluorides, $M\text{TeO}_3\text{F}$, with $M = \text{Fe}^{\text{III}}$, Ga^{III} and Cr^{III} .

The Te atom is bonded to three O atoms at distances of *ca* 1.9 Å (Tables 1 and 2). It occupies the center of a trigonal pyramid with the stereochemically active electronic lone pair E pointing in the direction of the fourth corner (Fig. 1). If three weak extra bonds with lengths of *ca* 2.7 Å are considered, the anionic polyhedron can be described as a distorted

octahedron. The lone pair E occupies the volume formed between the Te atom and the weakly bonded anions. The M atom is sixfold coordinated, slightly shifted from the center of a distorted MO_4F_2 octahedron (Fig. 2, and Tables 1 and 2). Bond-valence calculations (Brown, 1981) are consistent with the description $M^{\text{III}}\text{Te}^{\text{IV}}(\text{O}^{2-})_3\text{F}^-$ showing a full O/F ordering (Tables 3 and 4).

FeTeO_3F , GaTeO_3F and CrTeO_3F [with lattice parameters refined on the basis of powder X-ray diffraction data of $a = 5.028$ (1) Å, $b = 5.073$ (1) Å, $c = 12.307$ (2) Å and $\beta = 97.40$ (4)°, using the refinement program *CHEKCELL* (Laugier & Bochu, 2000)] are isomorphous, with ‘zigzag’ chains of MO_4F_2 ($M = \text{Fe}^{\text{III}}$, Ga^{III} and Cr^{III}) distorted octahedra sharing alternately O–O and F–F edges and interconnected *via* TeO_3 trigonal pyramids (Fig. 3*a*). A projection on to (010) shows large tunnels parallel to [010], towards which point the lone pairs E (Fig. 3*b*). The description considering the Te anionic environment as a distorted octahedron (Fig. 1) allows an interesting comparison with the $\alpha\text{-PbO}_2$ (Fig. 4) structure (Hyde & Andersson, 1989). Indeed, the structure of $M\text{TeO}_3\text{F}$ ($M = \text{Fe}^{\text{III}}$, Ga^{III} and Cr^{III} ; Fig. 3*a*) is thus based on parallel zigzag chains of corner-sharing octahedra, two adjacent chains being shifted by $a/2$ along the [001] direction. The idealized $M\text{TeO}_3\text{F}$ structure appears as a superstructure of $\alpha\text{-PbO}_2$ with doubling of the c axis (Table 5). However, the hexagonal close packed (hcp) anionic array and

Figure 1

The anionic polyhedron (distorted octahedron) around the Te atom in the FeTeO_3F structure. The arrow indicates the direction towards which the lone pair E points. The Ga and Cr analogs are isomorphous. [Symmetry codes: (i) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{3}{2}$; (ii) $-x + \frac{3}{2}, y - \frac{1}{2}, -z + \frac{3}{2}$.]

Figure 2

The coordination polyhedron of the Fe atom in FeTeO_3F . [Symmetry codes: (i) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{3}{2}$; (ii) $-x + \frac{3}{2}, y - \frac{1}{2}, -z + \frac{3}{2}$; (iii) $-x + 1, -y + 2, -z + 1$; $-z + 1$; (iv) $x - \frac{1}{2}, -y + \frac{3}{2}, z - \frac{1}{2}$.]

Figure 3

(a) The (100) layer of 'zigzag' $(\text{FeO}_3\text{F})_n$ chains of FeO_4F_2 octahedra connected via TeO_3 . (b) A projection on to (010), showing the tunnels towards which the lone pairs E point.

Figure 4

The ideal structure of $\alpha\text{-PbO}_2$ for comparison with the structure of FeTeO_3F (see Fig. 3a).

the positions of the cations are more distorted than in $\alpha\text{-PbO}_2$ as a consequence of the cationic ordering, of the difference in size between M^{III} and Te^{IV} cations, and of the stereochemical activity of the lone pair E . A strong monoclinic distortion of the lattice also occurs in the $M\text{TeO}_3\text{F}$ phases, but the analogy is worth noting.

The new $M\text{TeO}_3\text{F}$ structure type is important because it shows that oxyfluorotellurates associating the Te^{IV} cation with trivalent cations presenting octahedral coordination can adopt a structure type derived from a classical oxide such as $\alpha\text{-PbO}_2$, with a distorted hcp anionic array and full cationic ordering in parallel zigzag rows. It also corresponds to an intergrowth of MOF and TeO_2 slabs with F^- anions only bonded to M^{III} cations. There is no strong $\text{Te}-\text{F}$ bond, sensitive to hydrolysis, so this kind of phase is air stable and could be of interest for applications in optical devices. Moreover, the unusual environment of M^{III} cations, interconnected by alternate $\text{F}-\text{F}$ and $\text{O}-\text{O}$ edges, offers the potential of promising magnetic properties.

Experimental

Fe_2O_3 , Cr_2O_3 and Ga_2O_3 were commercial products (Aldrich, 99.9%) and TeO_2 was prepared by decomposition of commercial H_6TeO_6 (Aldrich, 99.9%) at 823 K under flowing oxygen. FeTeO_3F and GaTeO_3F were prepared in two steps: first an intimate mixture (mol%) of $\frac{1}{2}\text{Fe}_2\text{O}_3-4\text{TeO}_2$ (or $\frac{1}{2}\text{Ga}_2\text{O}_3-2\text{TeO}_2$) was dissolved in hydrofluoric acid (40%) in a Teflon beaker and heated at 453 K, and then, after slow evaporation, the product was crushed and heated in a sealed platinum tube. The temperature was progressively increased to 723 K (923 K for the Ga phase) (5 K min^{-1}), kept stable for 96 h, slowly decreased to 673 K (0.05 K min^{-1} for Fe and 0.1 K min^{-1} for Ga) and finally stabilized for 10 h. After that, the tube was water-quenched to room temperature. Green crystals of FeTeO_3F and colorless crystals of GaTeO_3F , air stable and suitable for X-ray diffraction study, were obtained. The chromium phase was obtained in powder form by direct heating of a $\text{Cr}_2\text{O}_3-\text{CrF}_3-3\text{TeO}_2$ mixture in a sealed platinum tube. The temperature was progressively increased to 973 K (5 K min^{-1}) and kept stable for 96 h. The tube was then water-quenched.

Compound (I)

Crystal data

FeTeO_3F
 $M_r = 250.45$
 Monoclinic, $P2_1/n$
 $a = 5.0667(7)\text{ \AA}$
 $b = 5.0550(7)\text{ \AA}$
 $c = 12.3975(15)\text{ \AA}$
 $\beta = 97.630(13)^\circ$

$V = 314.72(7)\text{ \AA}^3$
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 13.73\text{ mm}^{-1}$
 $T = 293(2)\text{ K}$
 $0.10 \times 0.04 \times 0.02\text{ mm}$

Data collection

Nonius KappaCCD diffractometer
 Absorption correction: multi-scan
 (SADABS; Bruker 2004)
 $T_{\min} = 0.337$, $T_{\max} = 0.763$

10518 measured reflections
 903 independent reflections
 757 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.058$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.021$
 $wR(F^2) = 0.036$
 $S = 0.99$
 903 reflections

56 parameters
 $\Delta\rho_{\text{max}} = 0.88\text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.95\text{ e \AA}^{-3}$

Table 1

Selected bond lengths (Å) for (I).

Te1—O3	1.870 (2)	Fe1—O1 ⁱ	1.923 (2)
Te1—O1	1.884 (2)	Fe1—O3	1.941 (2)
Te1—O2	1.904 (2)	Fe1—O2 ⁱⁱ	1.965 (2)
Te1—O1 ⁱ	2.695 (2)	Fe1—F1	1.974 (2)
Te1—O3 ⁱⁱⁱ	2.746 (2)	Fe1—F1 ⁱⁱⁱ	2.040 (2)
Te1—F1 ⁱ	2.850 (3)	Fe1—O2 ^{iv}	2.054 (2)

 Symmetry codes: (i) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{3}{2}$; (ii) $-x + \frac{3}{2}, y - \frac{1}{2}, -z + \frac{3}{2}$; (iii) $-x + 1, -y + 2, -z + 1$; (iv) $x - \frac{1}{2}, -y + \frac{3}{2}, z - \frac{1}{2}$.

Compound (II)

Crystal data

GaTeO ₃ F	$V = 304.22 (7) \text{ Å}^3$
$M_r = 264.32$	$Z = 4$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 5.0625 (7) \text{ Å}$	$\mu = 18.29 \text{ mm}^{-1}$
$b = 4.9873 (7) \text{ Å}$	$T = 293 (2) \text{ K}$
$c = 12.1662 (15) \text{ Å}$	$0.10 \times 0.04 \times 0.02 \text{ mm}$
$\beta = 97.952 (13)^\circ$	

Data collection

Nonius KappaCCD diffractometer	8547 measured reflections
Absorption correction: multi-scan (<i>SADABS</i> ; Bruker 2004)	867 independent reflections
$T_{\min} = 0.257, T_{\max} = 0.697$	831 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.036$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.017$	56 parameters
$wR(F^2) = 0.042$	$\Delta\rho_{\max} = 1.25 \text{ e Å}^{-3}$
$S = 1.21$	$\Delta\rho_{\min} = -1.71 \text{ e Å}^{-3}$
867 reflections	

Table 2

Selected bond lengths (Å) for (II).

Te1—O3	1.865 (2)	Ga1—O1 ⁱ	1.918 (2)
Te1—O1	1.884 (2)	Ga1—O3	1.911 (2)
Te1—O2	1.918 (2)	Ga1—O2 ⁱⁱ	1.923 (2)
Te1—O1 ⁱ	2.632 (2)	Ga1—F1	1.929 (2)
Te1—O3 ⁱⁱⁱ	2.731 (2)	Ga1—F1 ⁱⁱⁱ	2.009 (2)
Te1—F1 ⁱ	2.830 (2)	Ga1—O2 ^{iv}	1.987 (2)

 Symmetry codes: (i) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{3}{2}$; (ii) $-x + \frac{3}{2}, y - \frac{1}{2}, -z + \frac{3}{2}$; (iii) $-x + 1, -y + 2, -z + 1$; (iv) $x - \frac{1}{2}, -y + \frac{3}{2}, z - \frac{1}{2}$.

Table 3

Bond valences for (I).

	Fe1	Te1	V_{ij}
O1	0.600	1.286/0.144	2.03
O2	0.536/0.421	1.218	2.18
O3	0.576	1.335/0.125	2.04
F1	0.417/0.349	0.071	0.84
V_{ij}	2.90	4.18	—

Table 4

Bond valences for (II).

	Ga1	Te1	V_{ij}
O1	0.602	1.286/0.17	2.06
O2	0.594/0.499	1.173	2.27
O3	0.613	1.354/0.13	2.10
F1	0.480/0.386	0.096	0.96
V_{ij}	3.17	4.21	—

Table 5

 Comparison of lattice parameters (Å) of FeTeO₃F and α -PbO₂.

FeTeO ₃ F	α -PbO ₂
$a = 5.067$	$a = 4.989$
$b = 5.055; \beta = 97.63$	$c = 5.466$
$c = 12.398 = 2 \times 6.199$	$b = 5.947$
Monoclinic, $P2_1/n$	Orthorhombic, <i>Pbcn</i>

For both compounds, data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DIRAX/LSQ* (Duisenberg *et al.*, 2000); data reduction: *EVALCCD* (Duisenberg *et al.*, 2000); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2001); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3115). Services for accessing these data are described at the back of the journal.

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