Trimeric Anions in $KTeO_2F$

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$KTeO_2F$ was prepared by solid state reaction from KF and TeO_2 at 350 °C. The structure has been determined by single crystal X-ray analysis [$P2_1/n$, $Z = 12$, $a = 1177.8(2)$ pm, $b = 1499.0(3)$ pm, $c = 619.5(2)$ pm, $\beta = 94.11(2)$ °, $R_1 = 0.0266$, $wR_2 = 0.0604$]. A characteristic feature of the structure is the presence of trimeric anions $Te_3O_6F_3^{3-}$ in which the tellurium atoms are bridged by oxygen atoms. The lone pairs are stereoactive leading to pseudotrigonal bipyramidal coordination at the tellurium atoms. Additional weak bonding interactions link these trimeric anions resulting in a layered structure.

Introduction

Acid base reactions between acidic oxides and basic (alkali) metal oxides are well-known and have lead to anions ranging from discrete *ortho* anions like sulfate to polymeric anions with chainlike (Na_3SbO_4[1]), layered (Li_3InO_3[2]) or framework ($NaGaO_2$[3]) structures. When reacting acidic oxides with basic fluorides one can generally expect the resulting fluorooxides to differ in two aspects from the pure oxo compounds. Firstly, the coordination numbers attainable should be higher, and secondly, the fluorooxo compounds should show a higher tendency to form polymeric anions.

The preparation of such fluorooxo compounds can be challenging because the desired products may tend to undergo dismutation reactions.

In the course of our investigations on reactions of fluorides with chalcogen dioxides we have solved the crystal structures of KSO_2F[4] and $KSeO_2F$.[5] Both compounds had been the subject of spectroscopic (IR, Raman)[6–8] and theoretical[8] studies leading to ambiguous results concerning the bonding situations in the complex anions. On the one hand, Seel and Boudier[7] interpreted the IR spectrum of KSO_2F in terms of discrete SO_2F^- anions containing a S–F single bond. On the other, Paetzold and Aurich[6] deduced a weakened S–F and Se–F bond with concomitant interionic bridging from the analysis of the spectra of KSO_2F and $KSeO_2F$, respectively. This weakened S–F bond was also postulated by Kornath et al.[8] who performed quantum mechanical calculations (RHF niveau). Although the crystal structures of KSO_2F and $KSeO_2F$ are closely related (they are both isopunctual) the fluorosulfite anion is discrete containing a S–F single bond, while the fluoroselenite shows weak intermolecular bonding through an asymmetric fluorine bridge, thus linking the SeO_2F^- units to chains.

We here report on the synthesis and characterization of $KTeO_2F$ representing the end member of the KEO_2F series (E = chalcogen).

Results and Discussion

Synthesis and Crystal Structure

$KTeO_2F$ has been obtained by the solid state reaction of potassium fluoride and tellurium dioxide at 350 °C in closed silver crucibles. A colourless crystalline solid that is sensitive to moist air was obtained. Its crystal structure has been solved by single crystal structure analysis (Table 1 and Table 2).

The main feature of the structure of $KTeO_2F$ is the presence of unprecedented trimeric anions $Te_3O_6F_3^{3-}$ in which the tellurium atoms are linked by oxygen atoms forming a six-membered puckered ring (Figure 1). The coordination of the crystallographically independent tellurium atoms by oxygen and fluorine atoms is pseudotrigonal bipyramidal. The terminal oxygen atoms occupy equatorial positions and the fluorine atoms axial positions. The bridging oxygen atoms link an equatorial with an axial vertex of the trigonal bipyramids. The deviations of the bond lengths and angles from perfect trigonal bipyramids can be understood on the basis of the VSEPR model.[9]

These trimeric units are linked by additional oxygen–tellurium interactions to chains running along the crystallographic *c* axis. These oxygen–tellurium contacts [282.2(3) pm] are much shorter than the sum of the van der Waals radii[10] [360 pm; r_{vdW}(Te): 210 pm, r_{vdW}(O): 150 pm] and must be considered as weakly bonding. Further interionic bridging is accomplished by fluorine–tellurium contacts [309.2(3) pm] similarly linking the trimers along the *b* axis [sum of van der Waals radii:[10] 360 pm; r_{vdW}(F): 150 pm]. Thus the anions form weakly bonded corrugated layers in the *bc* plane (Figure 2). The coordination spheres of the tellurium atoms Te1 and Te2 are extended by these intermolecular interactions to strongly distorted pseudooctahedra. The additional ligands are the terminal oxygen and fluorine atoms of Te3. The calculation of the valence

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Table 1. Data collection and refinement parameters of $KTeO_2F$

Crystal data[a]	
Space group (No.)	$P2_1/n$ (14)
a [pm]	1177.8(2)
b [pm]	1499.0(3)
c [pm]	619.5(2)
β [°]	94.11(2)
V [10^6 pm^3]	1090.9(5)
Z	12
ρ_X [g cm^{-3}]	3.976
μ [mm^{-1}]	9.16
Crystal size [mm]	ca. 0.1 × 0.05 × 0.2
Diffractometer	Smart CCD
Radiation	Mo-K_α
Monochromator	Graphite
Detector distance [mm]	30
Rotation range [°]	3 × 180
Rotation step width [°]	0.3
$2\theta_{max}$ [°]	75.08
Reflections measured	$-20 \le h \le 20$, $-25 \le k \le 25$, $-10 \le l \le 10$
Number of reflections	22026
Completeness of data set	99.2%
Absorption correction	semiempirical (SADABS)
Min./max. transmission	0.151/0.276
Number of unique reflections	5726
R_{int}, R_σ	0.0511, 0.0364
Number of parameters	136
Number of reflections $F_o > 4\sigma(F_o)$	4748
R_1 [$F_o > 4\sigma(F_o)$], R_1 (all)	0.0266, 0.0362
wR_2, a, b	0.0604, 0.0292, 0.000
Goof	0.960
$\Delta\rho_{max}$, $\Delta\rho_{min}$ [10^{-6} e pm^{-3}]	0.98, −1.87 (64 pm from Te3, 35 pm from Te3)

[a] Further details of the crystal-structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository number CSD-411068.

Table 2. Selected interatomic distances [pm] and angles [°]

Te1−O1	180.6(3)	Te2−O2	180.1(3)	Te3−O3	181.5(3)
Te1−O4	191.9(3)	Te2−O6	190.9(3)	Te3−O5	188.4(3)
Te1−O5	209.1(3)	Te2−O4	207.8(3)	Te3−O6	207.2(3)
Te1−F1	211.0(3)	Te2−F2	209.3(2)	Te3−F3	208.2(2)
Te1−O3	282.2(3)	Te2−F3	309.2(3)		
O1−Te1−O4	99.0(2)	O2−Te2−O6	97.8(2)	O3−Te3−O5	102.3(2)
O1−Te1−O5	87.6(2)	O2−Te2−O4	92.9(1)	O3−Te3−O6	93.6(2)
O1−Te1−F1	86.1(1)	O2−Te2−F2	87.3(2)	O3−Te3−F3	88.8(2)
O4−Te1−O5	87.9(1)	O6−Te2−O4	90.9(2)	O5−Te3−O6	89.7(2)
O4−Te1−F1	87.5(2)	O6−Te2−F2	85.7(2)	O5−Te3−F3	81.9(1)
O5−Te1−F1	171.5(1)	O4−Te2−F2	176.5(1)	O6−Te3−F3	171.6(1)
K1−F2	254.5(3)	K2−O2	267.6(3)	K3−O1	278.3(3)
K1−F3	256.3(3)	K2−F1	267.9(3)	K3−F2	280.0(3)
K1−O1	261.4(3)	K2−F2	272.5(3)	K3−O3	281.3(3)
K1−O2	264.0(3)	K2−O5	280.3(3)	K3−F1	288.7(3)
K1−F1	264.1(3)	K2−O3	285.9(3)	K3−O5	308.0(3)
K1−O4	296.8(3)	K2−O6	288.6(3)	K3−O4	309.5(3)
		K2−F3	303.7(3)	K3−O2	309.7(3)
		K2−F3	318.4(3)	K3−O1	313.2(3)
				K3−O1	322.1(3)

sums[11,12] gives support to assuming weak bonding contributions of these intermolecular Te−O/Te−F contacts since this leads to virtually equal valence sums for the three different tellurium atoms (Te1: 4.12, Te2: 4.17, Te3: 4.17).

The three potassium atoms are coordinated by six, eight and nine oxygen and fluorine atoms, respectively. K1 is situated between two layers and is coordinated by three ligands from each layer. K2 and K3 are located in voids within the layers that are formed by the anions, and are coordinated by six and seven ligands from that layer and two ligands from an adjacent layer. These electrostatic interactions of potassium with oxygen or fluorine hold together the anionic layers along the a axis.

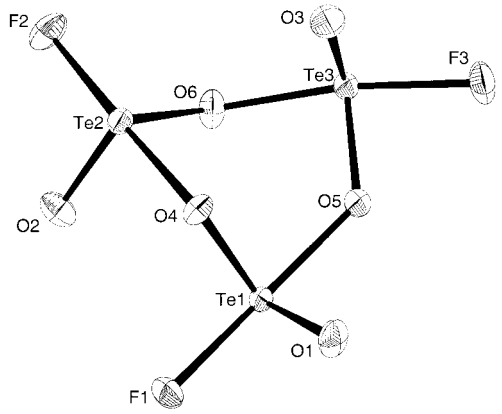

Figure 1. Trimeric cyclic anion $Te_3O_6F_3^{3-}$

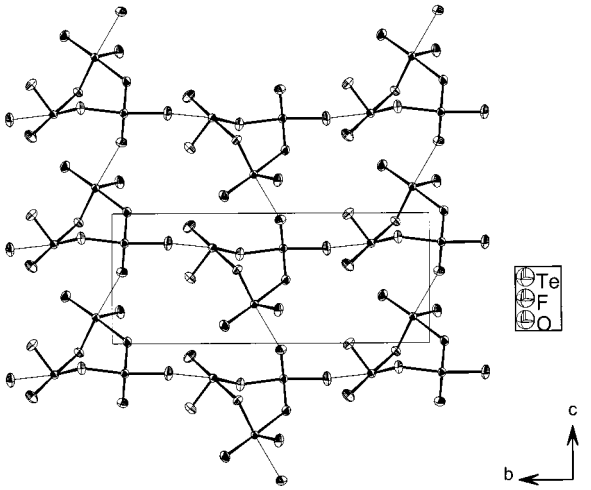

Figure 2. View along [100] showing the association of $Te_3O_6F_3^{3-}$-trimers building infinite layers

When comparing the structures of $KTeO_2F$ and its homologues one observes an increase in coordination number of the chalcogen atom as one would expect when moving from KSO_2F (C.N. 3) via $KSeO_2F$ (C.N. 3 + 1) to $KTeO_2F$ [C.N. 4 (Te3) and C.N. 4 + 1(Te1, Te2)]. However, the tendency towards intermolecular interactions through fluorine bridges, as exhibited by the selenium compound, is not continued. Instead polymerization is accomplished almost exclusively through oxygen atoms.

Since $KTeO_2F$ is the first fluorooxotellurite whose structure has been determined, it is interesting to compare it to those of pure oxotellurites. In contrast to, for example, the oxide adducts of SiO_2 or P_2O_5 in which the silicon and phosphorus atoms are fourfold coordinated, and which contain vertice-sharing tetrahedra like in the binary oxides, the tellurium-oxygen network is significantly changed when reacting TeO_2 with alkali metal oxides. The fourfold coor-

dination (pseudotrigonal bipyramidal) of the tellurium atoms is partly ($K_2Te_4O_9$, $K_2Te_2O_5$)[13] or fully (K_2TeO_3)[14] reduced to threefold pseudotetrahedral coordination. However, the structure of $KTeO_2F$ shows that, upon fluoride addition to tellurium dioxide, both the fourfold coordination of the tellurium atoms and the linkage scheme of the polyhedra (bridging oxygen atoms link equatorial and axial vertices) are preserved. It will be interesting to obtain structural information on other fluoride adducts of TeO_2 which contain more fluoride than $KTeO_2F$. Preliminary X-ray investigations on $Rb_2TeO_2F_2$[15] indicate the existence of discrete pseudotrigonal bipyramidal $TeO_2F_2^{2-}$ anions, thus confirming the preservation of the tellurium coordination when adding fluoride to TeO_2.

Vibrational Spectroscopy and Thermal Analysis

The vibrational spectra of $KTeO_2F$ are given in Table 3. For a twelve-atom molecule of C_1 symmetry, 30 absorptions are expected though additional absorptions could be present due to combination vibrations, overtones or factor group splitting. No assignment was made because of the complexity of the spectra. Theoretical studies appear to be necessary in order to reach an unambiguous assignment of the absorptions. However, the spectra do not agree with the spectra given by Milne[16] who has claimed to have synthesized $KTeO_2F$.

Table 3. Infrared and Raman spectra of $KTeO_2F$ [cm^{-1}]

IR	Raman	IR	Raman
817 (vs)	817 (vs)		360 (w)
793 (vs)	795 (vs)	343 (vs)	341 (vw, sh)
	767 (w)	330 (vs)	332 (w)
752 (w)		317 (s)	322 (w, sh)
736 (w)	737 (w)		312 (w)
	709 (m)	300 (m, sh)	304 (m)
692 (vs)	690(m)	291 (m, sh)	294 (w, sh)
682 (vs)			285 (w)
662 (vs)	660 (w)	263 (w)	269 (w)
610 (w)	609 (w, sh)	232 (m)	225 (w)
587 (m)	586 (s)	210 (m)	209 (m)
460 (s)	453 (m)	194 (w)	199 (m)
439 (m, sh)	440 (w, sh)	175 (vw, sh)	173 (m)
	412 (w)	157 (w)	162 (w, sh)
393 (m)			151 (w)
368 (s)	375 (w)		

DTA measurements show one endothermic signal at 376 °C indicating the melting point.

Conclusion

$KTeO_2F$ can be synthesized by standard solid-state techniques from KF and TeO_2. The crystal structure represents a new structure type, the characteristic feature of which is the presence of trimeric anions $Te_3O_6F_3^{3-}$. The tellurium atoms exhibit pseudotrigonal bipyramidal coordination; they are linked by oxygen atoms forming a puckered six-membered ring. The trimeric anions are linked to layers by secondary bonding interactions.

When compared to the homologous sulfur and selenium compounds, $KTeO_2F$ shows both expected and unexpected features. While the increase in coordination number agrees with the trend known from KSO_2F and $KSeO_2F$, the bridging by oxygen atoms in $KTeO_2F$ is different from the weak bridging by fluorine atoms in $KSeO_2F$.

In contrast to the significant change of the tellurium coordination when basic oxides are reacted with TeO_2, the characteristic pseudotrigonal bipyramidal coordination of the tellurium atoms is preserved upon fluoride addition to tellurium dioxide.

Experimental Section

Synthesis: The handling of all substances was performed under carefully dried argon by standard Schlenk techniques or in an argon filled drybox (< 0.1 ppm H_2O).

KF (Merck, p. a., > 99%) was finely ground and dried in vacuum at 200 °C before use. It was then stored in sealed glass ampoules.

TeO_2 was prepared following a literature method[17] by oxidation of powdered tellurium (Merck, 99%) with nitric acid (Baker, p.a., 65%) and subsequent thermal decomposition of the basic nitrate $Te_2O_3(OH)(NO_3)$. It was stored in sealed glass ampoules.

Single-phase $KTeO_2F$ was prepared by heating a compacted stoichiometric mixture of KF and TeO_2, in a closed silver crucible encapsulated in duran glass, under argon to 350 °C for 14 days. This was then cooled to room temperature at 10 °C/h. The powder diffraction measurements of the samples were performed in sealed glass capillaries of 0.1 mm diameter. Single crystals were obtained from mixtures containing 2% KF in excess and heating for 30 days. Crystals suitable for structure determination were selected in a drybox and sealed into glass capillaries of 0.3 mm diameter.

X-ray Diffraction Analysis: Powder diffraction measurements were carried out on a powder diffractometer (STOE StadiP) with a linear position sensitive detector using Cu-$K_{\alpha 1}$ radiation (Ge monochromator). Silicon was used as an external standard. Indexing of the powder pattern yielded a monoclinic cell. Systematic absences indicated the space group $P2_1/n$ (No. 14).

Precession photographs of the single crystal used for structure determination proved the unit cell dimensions and the space group. The intensity data collection was carried out with a Smart CCD system (Bruker AXS) using Mo-K_α radiation (graphite monochromator). The data were corrected semi-empirically for absorption (SADABS[18]) improving the residual value R_{int} from 0.0866 to 0.0511. The tellurium and potassium atoms were found by the Patterson method (SHELXS-97[19]), and oxygen and fluorine atoms by a subsequent difference Fourier synthesis (SHELXL-97[20]). The distinction between oxygen and fluorine was made by chemical arguments [bond lengths, valence sums, most electronegative ligand in apical position (Bent's rule)]. Fluorine in the bridging position was tested but this assignment was rejected because the displacement parameters of the bridging atoms were larger than those of the terminal ligands. Moreover, the final difference Fourier map showed the largest peaks at the terminal apical oxygen atoms and the R-values were significantly larger (wR_2 = 0.0825). The structure refinement converged at R_1 = 0.0266, wR_2 = 0.0604. Further information on the structure determination is given in Table 1 and structural parameters are listed in Table 2.

Vibrational spectroscopy: Infrared spectra were recorded on a Bruker IFS113v with a DTGS detector using CsI pellets prepared in a drybox.

Raman spectra were recorded on a Dilor multichannel XY system (microscope technique, Kr laser, 647.1 nm, ca. 10 mW). The samples were sealed in melting point capillaries.

Thermal Analysis: Combined DTA/TG measurements were performed on a Netzsch STA 409 in an argon atmosphere using corundum crucibles.

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