The Crystal Structure of Cesium Fluorotrioxosulfate(VI), $CsSO_3F$

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Cesium Fluorotrioxosulfate(VI),
Crystal Structure

The crystal structure of $CsSO_3F$ was determined from single-crystal X-ray data as tetragonal, space group $I4_1/amd$, with a = 5.6317(2), c = 14.1991(9) Å and Z = 4. The structure was refined to R = 0.028, R_w = 0.028 for 403 unique reflections.

In contrast to the earlier literature $CsSO_3F$ is not isomorphous with scheelite but with α-$CsReO_4$. The structure contains isolated SO_3F tetrahedra which are linked together by twelvefold coordinated Cs ions. The average S–O,F distance is 1.453(3) Å.

Among the fluorosulfates M^ISO_3F the salts with M^I = K, NH_4, Rb crystallize in the orthorhombic space group Pnma [1]. The crystal structure was determined as the barite type for the potassium [2] and ammonium compound [3]. Cesium fluorosulfate, however, was found to be not isomorphous with the other alkali fluorosulfates. From powder patterns a tetragonal unit cell with cell dimensions a = 5.610(6), c = 14.133(9) Å and c/a = 2.519(2) was assigned to $CsSO_3F$. By an examination of the observed reflection conditions it was proposed that $CsSO_3F$ belongs to the scheelite type although the positions of the oxygen and fluorine atoms had not been established [1].

During our investigations on perrhenates we recently refined the crystal structure of α-$CsReO_4$, the high-temperature modification of cesium perrhenate [4]. The lattice constants were a = 5.9607(4), c = 14.446(1) Å and c/a = 2.423. In contrast to the earlier literature, in which space group $I4_1/a$ (and therefore a scheelite type structure) was assumed for α-$CsReO_4$, we could confirm the space group $I4_1/amd$ to be the right one.

A further compound which crystallizes in the α-$CsReO_4$ structure type is cesium perbromate, $CsBrO_4$ [5] with unit cell parameters a = 5.75, c = 14.82 Å and c/a = 2.58. Though the crystal structure was originally described in space group $I4_1/a$ we found that $I4_1/amd$ is appropriate for $CsBrO_4$ [6].

Regarding the similarities of $CsSO_3F$, α-$CsReO_4$ and $CsBrO_4$ with respect to the unit cell dimensions a scheelite type structure of $CsSO_3F$ became questionable. Since the reflection conditions observed by Seifert [1] were not only fulfilled in space group $I4_1/a$, but in $I4_1/amd$ as well, we decided to reinvestigate the crystal structure of $CsSO_3F$.

Cesium fluorosulfate was prepared by neutralization of a mixture of hydrofluoric acid (40%) and oleum (60% SO_3) with cesium carbonate. Recrystallization of the reaction product from water yielded single crystals of cesium sulfate and cesium fluorosulfate. Due to their different morphology crystals of the title compound could be easily separated. A bipyramidal crystal of $CsSO_3F$ (crystallographic forms {112}, {101} and {001}) of about one mm in diameter was ground to a sphere and used for the structure determination.

Precession photographs exhibited the Laue class 4/mmm and the reflection conditions (hkl): $h+k+l = 2n$, ($hk0$): $h,k = 2n$ and (hkl): $2h+l = 4n$ which uniquely indicated the space group $I4_1/amd$. A scheelite type structure could therefore be excluded with certainty.

Data collection was performed on an Enraf-Nonius CAD-4 diffractometer using MoKα radiation (graphite monochromator in incident beam). The unit cell parameters were obtained by a least-squares refinement based on 25 carefully centred reflections in the range $13.7 \leq \theta \leq 19.0°$. Three standard reflections were measured every 100 min, indicating only random fluctuations in intensity. After reduction of the 1534 recorded data a set of 403 independent reflections with $I > 0\sigma(I)$ remained (R_{int} = 0.021), of which all were used in the subsequent calculations. Crystallographic and experimental data are summarized in Table I.

All calculations were carried out using the programs SHELX-76 [7] and SHELXS-86 [8]. Atomic scattering factors and corrections for anomalous dispersion were taken from the International Tables for X-ray Crystallography [9].

The structure was solved by Patterson methods, followed by successive difference Fourier syntheses. The final full-matrix least-squares refinement (including anisotropic displacement factors and an extinction correction of the form $F_{corr} = F_c(1-gF_c^2/\sin\theta)$) converged at R = 0.028 and R_w = 0.028. Atomic positions and displacement factors

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Table I. Crystal data, data collection and refinement parameters for $CsSO_3F$[a].

Formula	$CsSO_3F$
Molecular weight	231.97 $g \cdot mol^{-1}$
Space group	$I4_1/amd$ (Nr. 141)
Cell dimensions	a = 5.6317(2) Å
	c = 14.1991(9) Å
	c/a = 2.521
	V = 450.34(3) Å^3
Z	4
Density (calcd)	3.421 $g \cdot cm^{-3}$
μ (MoKα)	8.50 mm^{-1}
F(000)	416
Temperature	295(1) K
Radiation	MoKα (λ = 0.71073 Å)
Scan mode	$\omega - 2\theta$
Scan width	$(0.6+0.35 \tan\theta)^\circ$
2θ range	$2^\circ \leq 2\theta \leq 80^\circ$
hkl limits	$-10 \leq h \leq 10; 0 \leq k \leq 10; 0 \leq l \leq 25$
$(\sin\theta/\lambda)_{max}$	0.90 Å^{-1}
Recorded reflections	1534
Unique reflections, R_{int}	403, 0.021
Reflections used in least-squares refinement	403
Parameters refined	13
$(\Delta/\sigma)_{max}$	0.002
Weighting scheme	$w = 1.1164 \cdot (\sigma^2(F_o) + 0.000007 F_o^2)^{-1}$
Final R, R_w	0.028, 0.028
$(\Delta \varrho)_{max, min}$	+0.4, −0.7 $e \cdot$ Å^{-3}
Extinction coefficient g	$6.0(1) \cdot 10^{-7}$

[a] Here, as in the following tables, the standard deviations are given in parentheses.

for $CsSO_3F$ are given in Table II, derived atomic distances and angles in Table III*.

The results of the structure refinement show that $CsSO_3F$ and α-$CsReO_4$ are indeed isostructural. Therefore, the oxygen and fluorine atoms are statistically distributed on the 16 h site.

The structure of $CsSO_3F$ consists of isolated SO_3F tetrahedra which are linked together by cesium ions. Cesium is twelvefold coordinated by oxygen and fluorine with an average Cs−O,F distance of 3.290(2) Å. The S−O,F distance of 1.453(3) Å is in agreement with the mean values of 1.447(3) Å in $CsH(SO_3F)_2$ [10], 1.455(20) Å in KSO_3F [2], 1.465(4) Å in $LiSO_3F$ [11], 1.466(4) Å in NH_4SO_3F [3] and 1.473(1) Å in HSO_3F [12].

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* Lists of structure factors, bond distances and bond angles have been deposited at the Fachinformationszentrum Karlsruhe GmbH, D-W-7514 Eggenstein-Leopoldshafen 2. Copies may be obtained by quoting the depository number CSD 57082, the name of the authors and literature citation.

Table II. Atomic positional parameters and displacement factores [Å^2] for $CsSO_3F$. Fractional atomic coordinates and equivalent isotropic displacement parameters[a]. Origin at centre (2/m).

Atom	Site	x/a	y/b	z/c	U_{eq}
Cs	4a	0	3/4	1/8	0.0282(1)
S	4b	0	1/4	3/8	0.0414(4)
O,F	16h	0	0.5371(6)	0.6828(2)	0.0584(9)

Anisotropic displacement factors

Atom	U_{11}	U_{22}	U_{33}	U_{23}
Cs	0.0285(1)	U_{11}	0.0275(2)	0
S	0.0442(5)	U_{11}	0.0357(7)	0
O,F	0.049(1)	0.066(2)	0.060(2)	0.037(1)

$U_{12} = U_{13} = 0$

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table III. Selected interatomic distances [Å] and bond angles [°].

S−O,F	1.453(3) (4×)	O,F−S−O,F	111.3(3) (2×)
O,F−O,F	2.359(4) (4×)	O,F−S−O,F	108.6(1) (4×)
O,F−O,F	2.399(4) (2×)		
Cs−O,F	3.172(3) (4×)	Cs−S	3.982
Cs−O,F	3.349(3) (8×)	Cs−Cs, S−S	4.508

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