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The Crystal Structure of $Hf(OH)_2SO_4$

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Single crystals of an orthorhombic modification of $Hf(OH)_2SO_4$ have been prepared in an autoclave at 325°C and the crystal structure has been determined from three-dimensional X-ray data. The unit cell has the dimensions $a = 11.085$ Å, $b = 5.517$ Å, and $c = 6.647$ Å, the space group being *Pnma*. The atomic positions were obtained from Patterson and Fourier syntheses and the structure was refined to an R value of 0.055, using 405 independent reflexions. $Hf(OH)_2SO_4$ contains infinite chains of composition $[Hf(OH)_2]_n^{2n+}$ which are joined by sulfate groups, each of which connects three chains. The Hf–Hf distance within the chain is 3.562 Å. Hafnium exhibits eightfold oxygen coordination, the coordination polyhedron being a somewhat distorted Archimedean square antiprism. The Hf–O bond distances range between 2.10_6 and 2.25_7 Å with an average distance of 2.17_5 Å.

During an investigation of the $HfO_2-SO_3-H_2O$ system, three basic salts have been prepared by hydrothermal hydrolysis. A note on $Hf(OH)_2SO_4\cdot(H_2O)_2$ [1] and the crystal structure of $Hf(OH)_2SO_4\ H_2O$ [2] have been published earlier, while the structure of $Hf(OH)_2SO_4$ is presented in this paper. For the $ZrO_2-SO_3-H_2O$ system, McWhan and Lundgren reported the structure of $Zr_2(OH)_2(SO_4)_3(H_2O)_4$.[3] Two modifications of $Zr(OH)_2SO_4$,[3] one orthorhombic (I) and one monoclinic (II), were also found and the refined structure of the orthorhombic phase will be published shortly.[4] Since the corresponding hafnium compound could now be prepared it was of interest to determine its structure in order to obtain more information concerning differences or resemblances between zirconium and hafnium.

PREPARATION AND ANALYSIS

The different basic hafnium sulfates have been prepared by means of hydrothermal hydrolysis. After dissolving HfO_2 in boiling concentrated sulfuric acid, the solutions were evaporated to dryness and the residues dissolved in water or dilute sulfuric acid. By varying the acidity and the temperature, hafnium sulfates with different water contents were obtained.

The crystals investigated were formed in 2 M sulfuric acid kept at 325°C for three weeks in an autoclave lined with metallic gold. At 300°C a sample containing crystals of $Hf(OH)_2SO_4$, together with crystals of the monoclinic form of $Hf(OH)_2SO_4H_2O$, was obtained.

The compound was analysed thermogravimetrically, the following results for the *hafnium* content (as HfO_2), the *sulfur* content (as SO_3) and the *water* content thus being obtained:

	%HfO_2	%SO_3	%H_2O	Density (g cm^{-3})
Found:	67.4	26.7	5.9	–
Calc. for $Hf(OH)_2SO_4$:	68.2	26.0	5.8	5.04

UNIT CELL AND SPACE GROUP

From Weissenberg films it was seen that $Hf(OH)_2SO_4$ crystallizes in the orthorhombic system, the following reflexions being systematically absent, $0kl$: $k+l=2n+1$; $hk0$: $h=2n+1$.
These extinctions indicate the space group to be either $Pna2_1$ or $Pnma$.[5]

The cell dimensions were obtained from Guinier powder photographs taken with Cu$K\alpha_1$ radiation and internally calibrated with $Pb(NO_3)_2$ ($a_{Pb(NO_3)_2}$ = 7.8566 Å at 21°C).[6] For the powder investigation crystals were picked out manually, because all the crystals in the sample were not quite transparent and well-developed. 37 reflexions were indexed and a least squares refinement with the programme POWDER [7] gave the following cell dimensions: a = 11.0850 ± 0.0012 Å; b = 5.5170 ± 0.0004 Å; c = 6.6474 ± 0.0007 Å and V = 406.5 Å^3. A list of observed and calculated $\sin^2\theta$ values is given in Table 1.

Assuming [4] that $Z=4$, the analysis and the volume of the cell give a calculated density of 5.04 g cm^{-3}.

INTENSITY DATA

$Hf(OH)_2SO_4$ crystallizes as rather large multi-faced crystals. The crystal chosen for the structure determination was cut off from an aggregate and had the maximum dimensions (in mm): 0.21 × 0.14 × 0.05. Three-dimensional X-ray data were collected with a Philips automatic four-circle diffractometer, PW 1100. Reflexions were registered with monochromated Cu$K\alpha$ radiation in the θ-interval 0 – 70°. The net intensities, I_{net}, and their estimated standard deviations, $\sigma(I_{net})$, based on counter statistics, were calculated. Only the 420 most significant reflexions with $\sigma(I_{net})/I \leq 0.25$ were used in the subsequent calculations. Corrections for Lorentz and polarization effects were performed with the program DATAP1.[8]

The absorption coefficient, $\mu_{CuK\alpha}$ = 530.1 cm^{-1}, was calculated from the values for the different elements given in the International Tables (1962), and a correction for absorption effects was performed with the program DATAPH.[8] Since the crystal had 18 faces a paper model was constructed to obtain an adequate picture of the crystal, and thus enable a correct calculation of the absorption factors. Because of requirements of the program used, the boundary planes were approximated to be 15. For the same reason fifteen reflexions measured at $\psi = 90°$, were not included in this correction. The remaining 405 reflexions were used in the final refinement of the structure.

Table 1. Guinier powder photograph of $Hf(OH)_2SO_4$.

$h\ k\ l$	$10^5 \sin^2\theta$ obs	$10^5 \sin^2\theta$ calc	F calc	I obs
1 0 1	1825	1825	112	s
2 0 0	1931	1931	184	s
0 1 1	3299	3292	174	vvs
1 1 1	3782	3775	126	vs
2 1 0	3881	3881	86	w
2 1 1	5221	5223	127	s
3 0 1	5696	5688	105	m
3 1 1	7640	7637	144	s
0 2 0 1 1 2	7807	7797 7803	225 212	vvs
4 0 1	9065	9068	109	m
2 1 2	9250	9251	55	w
4 1 0	9678	9674	222	s
2 2 0	9730	9728	135	m
2 2 1	11079	11071	108	m
3 1 2	11675	11665	50	vw
1 0 3	12570	12566	180	m
1 2 2	13651	13650	109	m
0 1 3	14036	14033	112	w
1 1 3	14509	14516	53	vw
2 1 3	15971	15964	77	w
3 0 3	16437	16429	95	w
4 2 1	16870	16865	171	s
3 2 2	17522	17513	184	s
3 1 3	18377	18378	133	w
0 3 1	18894	18886	157	m
1 3 1 5 1 2	19377	19368 19390	79 79	m
1 2 3	20356	20363	169	m
6 1 1	20669	20674	98	w
2 2 3	21821	21812	123	m
3 3 1	23243	23231	109	m
1 3 2	23402	23396	158	s
4 3 0	25261	25268	162	s
4 2 3	27606	27606	96	vvw
0 2 4	29283	29279	138	vw
7 1 2	30989	30978	111	m
2 4 0	33116	33119	111	w
4 4 1	40257	40255	86	vw

SOLUTION AND REFINEMENT OF THE STRUCTURE

From a three-dimensional Patterson synthesis, calculated with data yet uncorrected for absorption, the Hf and S parameters were obtained. A subsequent electron density calculation revealed the oxygen atoms and all parameters were seen to be consistent with the corresponding parameters in the structure of $Zr(OH)_2SO_4$.[4] A preliminary refinement of the atomic positions and isotropic temperature factors gave an R value of 0.143 ($R = \sum|F_o -$

$|F_c||/\sum F_o$). The Fourier summations were performed with the program *DRF*.[9]

After correction for absorption effects the isotropic refinement was repeated, including separate scale factors for three different θ-intervals in which the data were registered. The R value then dropped to 0.098.

From the intensities at low sin θ-values and the irregular shape of the crystal the diffraction from the crystal of $Hf(OH)_2SO_4$ could be suspected to be associated with extinction effects. A refinement of an isotropic secondary extinction factor, the scale factors and the atomic parameters, including isotropic thermal vibrations, was performed with the program LINUS.[9] An R value of 0.070 was obtained when the atomic scattering factors [10] for Hf and S were corrected for anomalous dispersion.[11] The final value of the isotropic extinction parameter was $g = (0.68 \pm 0.03) \times 10^4$.

Finally, the refinement was extended to include anisotropic thermal parameters, the scale factors being kept constant. The R value converged to 0.055, and the final parameters are given in Tables 2a,b. A weighting scheme according to Cruickshank was used in the refinements ($w = [60.0 + F_o + 0.018\ F_o^2 + 10^{-4}F_o^3]^{-1}$). The observed and calculated structure factors are compared in Table 3.

The accuracy of the structure was tested by means of a difference electron density calculation with the program FFT [9] which handles correction for

Table 2a. Atomic coordinates, expressed as fractions of the cell edges, and their standard deviations.

Atom and position	x	y	z
Hf in 4(*c*)	0.06016(8)	1/4	0.1366(1)
S in 4(*c*)	0.3635(4)	1/4	0.9435(7)
O_1 in 8(*d*)	0.4179(11)	−0.0004(33)	0.3938(16)
O_2 in 4(*c*)	0.4794(13)	1/4	0.0525(22)
O_3 in 4(*c*)	0.2615(14)	1/4	0.0855(21)
O_4 in 8(*d*)	0.3515(9)	0.0357(22)	0.8152(15)

Table 2b. Anisotropic thermal parameters and their standard deviations. The temperature coefficient is expressed as $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Hf	0.0025(1)	0.0085(6)	0.0015(4)	0	−0.0001(1)	0
S	0.0021(4)	0.0106(16)	0.0012(11)	0	0.0003(5)	0
O_1	0.0034(8)	0.0166(48)	0.0068(24)	−0.0002(19)	−0.0006(11)	0.0009(30)
O_2	0.0030(12)	0.0121(47)	0.0069(40)	0	0.0001(19)	0
O_3	0.0048(13)	0.0094(52)	0.0006(27)	0	0.0018(18)	0
O_4	0.0023(8)	0.0179(42)	0.0081(20)	0.0004(16)	−0.0017(12)	−0.0048(31)

Table 3. Observed and calculated structure factors for $Hf(OH)_2SO_4$. (The columns are h, F_o and F_c, respectively.)

H 0 0	4 15 16	3 94 90
2 235 184	5 91 91	4 6 7
4 57 51	6 70 67	5 140 144
6 110 111	7 32 33	6 11 12
8 108 113	8 88 90	7 60 58
10 120 127	9 10 10	8 30 30
12 13 14	10 64 65	9 25 26
	11 48 48	
H 1 0		H 5 2
2 119 86	H 4 1	1 116 120
4 271 222	1 74 74	2 26 23
6 155 157	2 84 85	3 26 26
8 11 8	3 60 60	4 18 17
10 98 102	4 79 87	5 42 44
12 81 77	5 37 37	6 4 6
	6 54 55	7 63 66
H 2 0	7 96 100	
0 294 225	8 25 26	H 6 2
2 186 135	9 67 67	0 6 7
4 54 49	10 35 31	1 36 40
6 84 87		2 12 13
8 94 97	H 5 1	3 80 85
10 97 100	0 81 81	4 9 8
12 39 40	1 54 59	
	2 68 70	H 0 3
H 3 0	3 76 79	1 173 180
2 121 100	4 23 27	2 58 63
4 181 163	5 55 55	3 92 95
6 110 117	6 58 61	4 67 68
8 10 7	7 26 26	5 53 57
10 83 85	8 74 74	6 32 34
		7 107 119
H 4 0	H 6 1	8 31 28
0 281 242	1 34 38	9 94 90
2 127 112	2 55 62	10 23 21
4 19 17	3 33 38	11 44 43
6 70 78	4 71 77	12 61 58
8 80 84	5 10 10	
10 91 92		H 1 3
	H 0 2	0 117 112
H 5 0	0 15 16	1 55 53
2 45 47	1 28 30	2 75 77
4 118 126	2 11 8	3 130 134
6 90 98	3 104 110	4 58 58
8 6 11	4 8 8	5 138 141

H 6 3	2 62 63	
1 72 79	3 45 43	
2 53 52	4 150 146	
	5 9 6	
H 0 4	6 121 119	
0 209 209	7 42 43	
1 15 15	9 40 39	
2 121 128		
3 73 75	H 3 5	
4 7 8	0 151 142	
5 27 26	1 42 41	
6 106 115	2 84 81	
7 7 4	3 49 46	
8 131 130	4 29 29	
9 15 13	5 42 41	
10 80 78	6 58 57	
11 20 19	7 15 16	
	8 83 76	
H 1 4		
1 43 44	H 4 5	
2 120 122	1 58 55	
3 53 54	2 58 55	
4 160 160	3 20 20	
5 12 10	4 114 105	
6 98 100	5 23 26	
7 51 54	6 97 91	
8 21 20		
9 31 31	H 5 5	
10 60 56	0 99 100	
11 6 4	1 17 18	
	2 59 58	
H 2 4		
0 145 138	H 0 6	
1 42 41	0 33 34	
2 97 96	1 68 70	
3 59 61	2 40 45	
4 27 26	3 113 117	
5 21 21	4 4 3	
6 80 78	5 69 72	
7 18 18	6 15 18	
8 116 105	7 41 43	
9 20 20	8 58 58	
10 82 81		
	H 1 6	
H 3 4	1 109 110	

H 6 0	5 199 225	6 66 68
0 115 121	6 8 7	7 54 59
2 59 65	7 86 82	8 86 79
4 8 4	8 40 39	9 38 39
	9 35 35	10 38 37
H 0 1	10 13 13	11 78 76
1 106 112	11 75 72	12 6 7
2 140 158	12 7 5	
3 94 105		H 2 3
4 66 109	H 1 2	1 174 169
5 69 69	1 203 212	2 122 123
6 71 66	2 55 55	3 35 34
7 157 156	3 51 50	4 98 96
8 47 50	4 30 28	5 38 36
9 89 92	5 76 79	6 22 23
10 43 42	6 10 9	7 68 63
11 1 3	7 119 111	8 10 10
12 88 87	8 17 16	9 100 96
13 10 9	9 131 127	10 37 35
	10 13 11	11 60 63
H 1 1	11 65 66	
0 180 174	12 21 21	H 3 3
1 119 126		0 80 77
2 122 127	H 2 2	1 31 28
3 138 144	0 43 40	2 67 65
4 43 46	1 113 109	3 106 103
5 109 106	2 30 30	4 53 51
6 110 98	3 186 184	5 136 131
7 43 43	4 22 22	6 59 61
8 114 114	5 188 189	7 47 48
9 15 18	6 40 42	8 75 71
10 62 64	7 69 65	9 42 41
11 57 58	8 48 50	10 31 29
12 7 7	9 43 43	
	10 10 9	H 4 3
H 2 1	11 96 92	1 124 122
1 58 60	12 8 7	2 57 55
2 111 108		3 52 51
3 64 60	H 3 2	4 52 50
4 167 171	1 167 158	5 40 39
5 19 19	2 58 56	6 21 23
6 98 93	3 60 57	7 85 78
7 91 92	4 16 14	8 23 22
8 6 7	5 61 62	9 72 68
9 83 90	6 8 2	

1 26 25	2 56 56	
2 103 99	3 80 82	
3 59 58	4 51 52	
4 142 133	5 21 23	
5 10 8	6 30 34	
6 86 86	7 114 110	
7 60 58	8 9 11	
8 17 17		
9 23 23	H 2 6	
	0 32 30	
H 4 4	1 62 62	
0 144 138	2 57 58	
1 23 21	3 129 123	
2 89 88	4 13 10	
3 55 53	5 96 92	
4 17 6	6 47 47	
5 12 12	7 31 32	
6 81 79		
7 6 5	H 3 6	
8 100 91	1 107 100	
	2 55 54	
H 5 4	3 66 63	
1 27 27	4 42 42	
2 77 74	5 21 21	
3 26 27	6 26 24	
4 102 102		
5 5 6	H 4 6	
	0 25 24	
H 0 5	1 51 51	
1 84 87	2 34 35	
2 78 79	3 90 83	
3 19 18		
4 137 141	H 0 7	
5 35 37	1 145 138	
6 112 122	2 15 14	
7 42 47	3 31 34	
8 13 13	4 34 38	
9 53 52	5 33 40	
10 62 62	6 39 41	
H 1 5	H 1 7	
0 167 163	0 53 54	
1 36 37	1 22 21	
2 93 97	2 13 13	
3 49 49	3 102 101	

10 55 57	7 110 102	H 5 3
11 22 22	8 21 22	0 59 60
12 67 65	9 106 104	1 35 35
	10 10 10	2 45 44
H 3 1	11 56 54	3 82 81
0 170 157		4 26 28
1 80 79	H 4 2	5 79 82
2 94 92	0 14 11	6 42 42
3 114 109	1 33 33	7 38 36
	2 13 12	

4 32 32	4 14 16	
5 60 61	5 115 119	
6 67 69		
7 14 16	H 2 7	
8 97 90	1 141 129	
9 4 5	2 28 27	
10 86 79	3 34 36	
	4 42 43	
H 2 5		
1 28 27	H 3 7	
	0 38 39	
	1 23 19	

Table 4. Interatomic distances (Å) and angles (°) with their standard deviations in parentheses.

Within the antiprism:

$Hf-2O_1$	2.136(14)	O_1-Hf-O_1 (2x)	65.8(5)
$Hf-2O_1$	2.106(15)	O_1-Hf-O_1	82.0(8)
$Hf-O_2$	2.251(15)	O_1-Hf-O_1	80.3(8)
$Hf-O_3$	2.257(16)	$O_2-Hf-2O_1$	77.9(4)
$Hf-2O_4$	2.203(11)	$O_3-Hf-2O_1$	76.9(4)
Mean	2.175	$O_2-Hf-2O_4$	71.5(5)
		$O_3-Hf-2O_4$	69.0(4)
O_1-O_1 (2x)	2.763(37)	O_2-Hf-O_3	122.1(5)
O_1-O_1 (2x)	2.303(24)	O_4-Hf-O_4	91.4(6)
O_2-2O_4	2.601(16)		
O_3-2O_4	2.527(16)		
O_2-2O_1	2.742(19)		
O_3-2O_1	2.733(19)		
O_1-O_4 (2x)	2.903(15)		
O_1-O_4 (2x)	2.916(16)		

Within the sulfate group:

$S-O_2$	1.476(16)	O_2-S-O_3	110.8(9)
$S-O_3$	1.473(16)		
$S-2O_4$	1.464(12)	O_4-S-O_4	107.7(9)
O_2-O_3	2.428(22)		
O_4-O_4	2.364(25)	O_2-S-O_4 (2x)	111.4(5)
O_2-2O_4	2.429(17)		
O_3-2O_4	2.371(17)	O_3-S-O_4 (2x)	107.7(9)

Other distances:			
(within the chain)		(different chains):	
Hf–Hf	3.562(1)	O_1-O_4	3.038(16)
O_4-O_4	3.153(25)	O_1-O_3	3.020(19)

extinction effects. No unexpected maxima or minima were obtained, and the maximum electron density found was 4 e/Å^3.

Interatomic distances and angles were calculated with the program DISTAN [9] and the results are given in Table 4.

DISCUSSION

The structure may be considered to be composed of layers of zig-zag chains of somewhat distorted square antiprisms, the layers being connected by sulfate groups. Two chains of antiprisms from different layers are shown in Fig. 1 together with some of the connecting sulfate tetrahedra. This arrangement is also found in the isomorphous salts $Zr(OH)_2SO_4$(I),[4] $Th(OH)_2SO_4$,[12] and $U(OH)_2SO_4$,[13] and all of the structures have the characteristic $[Me(OH)_2]_n^{2n+}$ chains running along the *b* axis.

The distortion of the antiprismatic configuration about Hf is mainly due to the double oxygen bridges between the hafnium atoms. The short distances between the oxygen atoms in the bridges (cf. Table 4) cause a compression of the oxygen square on one side of the metal atom. In $Hf(OH)_2SO_4$ the O_1-O_1

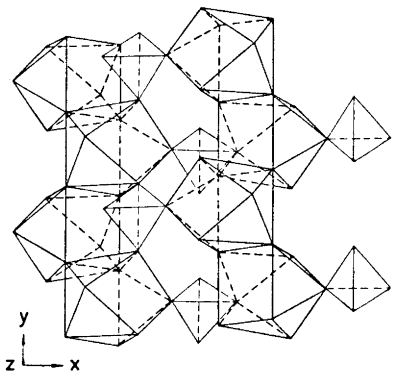

Fig. 1. Parts of two infinite chains of distorted square antiprisms connected by sulfate groups.

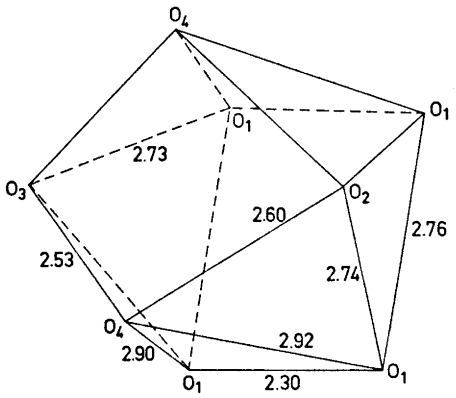

Fig. 2. Antiprismatic configuration of oxygen atoms about hafnium in $Hf(OH)_2SO_4$. (Distances in Å).

bridge distance is noticeably short, *i.e.* 2.30 ± 0.02 Å. This can be compared with the distances in $Zr(OH)_2SO_4$[4] (2.40 Å), $Zr_2(OH)_2(SO_4)_3(H_2O)_4$[3] (2.34 Å), $Hf(OH)_2SO_4H_2O$[2] (2.33 Å), $Zr(OH)_2CrO_4$[14] (2.35 Å) and $Zr_4(OH)_6(CrO_4)_5H_2O$[15] (2.37 – 2.40 Å). The shortest distances mentioned above (2.33 – 2.35 Å) are, however, found in structures with planar $[Me(OH)_2]_n^{2n+}$ chains.

On the other side of the hafnium atom an approximate square rotated through 45° is built up from oxygen atoms (O_2, O_3, $2O_4$), belonging to four different sulfate ions (*cf.* Fig. 2). Since this square was not quite planar, the plane of best fit was calculated by the program PLANEFIT,[9] the following equation being obtained (in Å and fractional coordinates): $6.720x + 5.286z = 2.441$. The distances of the sulfate oxygen atoms and of the hafnium atom from the plane are: O_2 0.21 Å; O_3 0.23 Å; $2 \times O_4$ −0.22 Å; and Hf 1.31 Å. The distance of Hf from the plane through the O_1 atoms was found to be 1.13 Å and the angle between the two planes 0.5°. These values are in agreement with those found for $Zr(OH)_2SO_4$(I),[4] the angles between the two planes differing, however, slightly in the two compounds. The angle is a little larger (1.2°) in the zirconium salt, but the difference is not quite significant.

The sulfate tetrahedra in the two isomorphous hafnium and zirconium salts are somewhat distorted but not in the same manner. The sulfate groups are bonded through all four vertices to four different metal atoms belonging to three different chains (*cf.* Fig. 1). In $Zr(OH)_2SO_4$ the tetrahedra are elongated along the chains, the distance between the two O_4 atoms belonging to the same chain being 2.48 Å. The distance between the layer-connecting oxygens, O_2 and O_3, is 2.37 Å. Corresponding distances in $Hf(OH)_2SO_4$ are 2.36 and 2.43 Å, respectively.

Despite the short distance between the bridging oxygen atoms, the distance between the bridged Hf-atoms, 3.562 Å, is shorter than the corresponding distance in $Zr(OH)_2SO_4$, *i.e.* 3.576 Å. Moreover, the planar chains in $Hf(OH)_2SO_4H_2O$ exhibit the shortest Me – Me distance (3.553 Å) found in basic compounds containing $[Me(OH)_2]_n^{2n+}$ chains (Me = Hf,Zr).

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