

The Crystal Structure of $\text{Hf}(\text{OH})_2\text{SO}_4\text{H}_2\text{O}$

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The crystal structure of $\text{Hf}(\text{OH})_2\text{SO}_4\text{H}_2\text{O}$ has been determined by means of three-dimensional single crystal methods. The crystals are monoclinic with the unit cell dimensions $a=6.4652\pm 0.0004$ Å, $b=12.4476\pm 0.0010$ Å, $c=6.7973\pm 0.0005$ Å, $\beta=96.198^\circ\pm 0.004^\circ$, and belong to the space group $C2/c$. Refinement of the structure by least squares methods gave a final R value of 0.066. The crystal structure of $\text{Hf}(\text{OH})_2\text{SO}_4\text{H}_2\text{O}$ is built up from almost planar, infinite $[\text{Hf}(\text{OH})_2]_n^{2n+}$ chains in which the Hf-Hf distance is 3.553 Å. Hafnium is pentagonal bipyramidally coordinated to two sulphate groups, four hydroxide groups and one water molecule, the Hf-O distances lying within the range 2.07₆-2.18₂ Å with an average of 2.11₉ Å.

The relative stabilities of several zirconium and hafnium complexes have previously been investigated by ion exchange methods.¹ Whereas the corresponding chloride and nitrate complexes of hafnium and zirconium were found to have comparable stabilities, large differences were observed in the stabilities of the sulphate complexes.

McWhan and Lundgren² have recently investigated the $\text{ZrO}_2\text{-SO}_3\text{-H}_2\text{O}$ system in order to elucidate the compositions of and the atomic arrangements in products obtained by hydrothermal hydrolysis. Three basic sulphates were prepared: $\text{Zr}_2(\text{OH})_2(\text{SO}_4)_3(\text{H}_2\text{O})_4$, which was found to be monoclinic, and two modifications of $\text{Zr}(\text{OH})_2\text{SO}_4$, one orthorhombic and one monoclinic. A corresponding investigation of the $\text{HfO}_2\text{-SO}_3\text{-H}_2\text{O}$ system has now been started at this department, and three different basic salts have been prepared by means of hydrothermal hydrolysis.³ The results of an X-ray investigation of one of these compounds, $\text{Hf}(\text{OH})_2\text{SO}_4(\text{H}_2\text{O})_2$, have been published recently,⁴ while the crystal structure of another, the monoclinic salt $\text{Hf}(\text{OH})_2\text{SO}_4\text{H}_2\text{O}$, will be described in this paper. The latter compound has been prepared previously, though using a different method, by Motov and Ripper⁵ who formulated the product as $\text{HfOSO}_4(\text{H}_2\text{O})_2$ but performed no structural investigation.

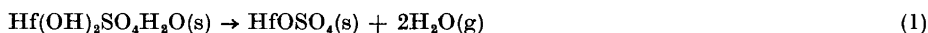
PREPARATION AND ANALYSIS

Crystals were prepared by means of hydrothermal hydrolysis in the following way: 0.5 g HfO_2 was dissolved in boiling concentrated sulphuric acid and the resulting solution was slowly evaporated to dryness. The residue was dissolved in 10 ml 2 M sulphuric acid, sealed in a thick-walled Pyrex tube and kept at 200°C for a month after which time a crystalline precipitate was formed. After cooling, the crystals were filtered off, carefully washed with water and alcohol and dried in air. Most of the crystals were colourless, transparent prisms, but some had the form of thick plates with well-developed faces of the type (010), (110), ($\bar{1}\bar{1}$ 0), (011), (0 $\bar{1}$ 1) and those related by a centre of symmetry.

The amount of hafnium in the product was determined as HfO_2 by ignition to constant weight. The water and sulphur contents, the latter as SO_3 , were both determined by differential thermal analysis and thermogravimetric analysis using a Mettler Recording Thermoanalyzer, with Al_2O_3 as reference. The experimental density was determined by the method of flotation using a mixture of thallium(I) formate, thallium(I) malonate and water. The following results were obtained:

	% HfO_2	% SO_3	% H_2O	Density (g cm^{-3})
Found:	64.9	24.1	10.9	3.94 ± 0.05
Calculated for $\text{Hf}(\text{OH})_2\text{SO}_4\text{H}_2\text{O}$:	64.5	24.5	11.0	3.99

The curves obtained with the thermoanalyzer are shown in Fig. 1. The left-hand part of the figure (at $563\text{--}640^\circ\text{K}$) corresponds to the reaction



and the right-hand part (at $1003\text{--}1043^\circ\text{K}$) to the reactions



Of the last reactions number (2) is the dominating one, but it is not possible to say exactly to which degree it dominates, since the experiment was carried out in a stream of air, using a platinum micro crucible.

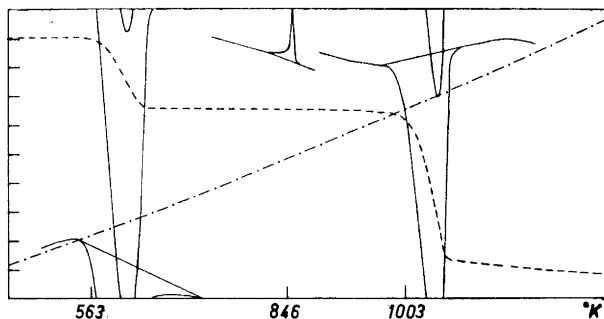


Fig. 1. Thermogravimetric and differential thermal analysis of $\text{Hf}(\text{OH})_2\text{SO}_4\text{H}_2\text{O}$. The small curve in the middle of the figure corresponds to the transition $\alpha\text{-SiO}_2 \rightarrow \beta\text{-SiO}_2$, when SiO_2 was used as reference. (---Temp., --- TG, — DTA. TG range: 10 mg, DTA range: $20 \mu\text{V}$, heating rate: $8^\circ/\text{min}$).

CRYSTAL DATA

Rotation and Weissenberg photographs ($0kl-5kl$), registered with $\text{CuK}\alpha$ radiation, indicated that the crystals were of monoclinic symmetry. The observed conditions of reflection are

$$\begin{aligned} hkl: h + k &= 2n \\ h0l: l &= 2n \end{aligned}$$

which is in accordance with the space groups No. 15 $C2/c$ and No. 9 Cc .⁶ Since it was possible to obtain a plausible structure based on space group $C2/c$, the space group of lower symmetry, Cc , was not taken into consideration.

Accurate cell dimensions were determined from Guinier powder photographs using $\text{CuK}\alpha_1$ radiation and $\text{Pb}(\text{NO}_3)_2$ as an internal standard ($a_{\text{Pb}(\text{NO}_3)_2} = 7.8566 \text{ \AA}$ at 21°C ⁷). By means of the programme Powder⁸ for IBM 360/50 the following cell dimensions and standard deviations were obtained:

$$\begin{aligned} a &= 6.4652 \pm 0.0004 \text{ \AA} & \beta &= 96.198^\circ \pm 0.004^\circ \\ b &= 12.4476 \pm 0.0010 \text{ \AA} & V &= 543.8 \text{ \AA}^3 \\ c &= 6.7973 \pm 0.0005 \text{ \AA} \end{aligned}$$

The observed and calculated values of $\sin^2\theta$ are listed in Table 1. The values obtained for the cell volume and the experimental density indicate that there are four formula units of $\text{Hf}(\text{OH})_2\text{SO}_4\text{H}_2\text{O}$ per unit cell, which corresponds to a calculated density of 3.99 g cm^{-3} (*cf.* above).

DETERMINATION OF THE STRUCTURE

Since the crystals contain a large amount of hafnium, the films obtained with $\text{CuK}\alpha$ radiation showed a high absorption effect. A series of Weissenberg photographs were therefore also registered using $\text{MoK}\alpha$ radiation which ought to give reflections less affected by absorption than those obtained with $\text{CuK}\alpha$ radiation. Since the resulting spots on the films were, however, very small, it was difficult to estimate their relative intensities with sufficiently large accuracy. Intensity data were therefore collected with an automatic single crystal diffractometer (Philips PAILRED), using $\text{MoK}\alpha$ radiation, in order to obtain as high a precision as possible. The crystal used to collect the diffractometer data was plate-like with the dimensions $0.08 \times 0.06 \times 0.04 \text{ mm}$. The a axis was chosen as rotation axis and the layers for which $h = 0, 1, 2, \dots, 10$ were registered. In this way 1467 independent reflections were recorded.

After correcting for Lorentz and polarization effects, a three-dimensional Patterson synthesis was calculated. The four hafnium atoms were then found to occupy the four-fold position $C2/c: 4(e)$ with $y \approx 0.96$. The Patterson synthesis and a three-dimensional electron density map, based on the hafnium parameters, were used to locate the sulphur atoms. They were then found to be situated in the position $C2/c: 4(e)$ with $y \approx 0.38$.

The hafnium and sulphur parameters were refined by least-squares methods using all observed hkl values. Individual scale factors for each layer line were also calculated and refined in order to check the adjustment of the crystal.

Table 1. Guinier powder photograph of $\text{Hf}(\text{OH})_2\text{SO}_4\cdot\text{H}_2\text{O}$. The first 53 of the 84 indexed lines are listed. $\lambda(\text{CuK}\alpha_1)=1.54050 \text{ \AA}$.

$h k l$	$10^5 \times \sin^2\theta$ obs	$10^5 \times \sin^2\theta$ calc	$ F $ calc	I obs
0 2 0	1535	1532	252	vs
1 1 0	1822	1819	231	vvs
0 2 1	2835	2831	233	vs
1 1 1	3409	3413	36	vvw
1 3 0	4882	4882	224	s
0 0 2	5197	5197	310	vs
2 0 0	5743	5746	—	vvs
1 3 $\bar{1}$	5886	5887	103	vw
0 4 0	6116	6127	80	vvw
1 1 $\bar{2}$	6427	6426	185	m
1 3 1	6481	6476	89	vw
0 2 2	6725	6728	236	vs
2 2 0	7273	7276	170	m
0 4 1	7424	7426	211	s
1 1 $\bar{2}$	7606	7606	159	w
2 2 $\bar{1}$	7984	7985	170	m
2 2 1	9164	9165	148	w
1 3 $\bar{2}$	9488	9489	177	m
2 0 $\bar{2}$	9760	9762	245	s
1 3 2	10662	10669	133	w
0 4 2	11314	11323	130	w
2 4 $\bar{1}$		12578	199	
1 5 1	12588	12603	228	s
0 2 3	13214	13225	184	w
3 1 0	13301	13308	257	vs
2 2 2	13646	13653	186	m
2 4 1	13759	13760	179	m
1 1 3	14392	14397	87	vvw
0 6 1	15086	15084	252	m
3 1 1	15484	15492	77	vw
1 5 $\bar{2}$	15616	15616	136	w
1 3 $\bar{3}$	15687	15690	139	w
2 4 $\bar{2}$	15887	15888	89	vw
3 3 0	16371	16371	202	m
3 1 $\bar{2}$	16740	16735	192	m
1 5 2	16798	16796	151	w
2 2 $\bar{3}$	17202	17199	145	w
1 3 3	17469	17460	108	vvw
0 4 3	17821	17819	261	m
3 3 1	18558	18556	129	w
3 3 $\bar{2}$	19799	19798	197	m
2 6 $\bar{1}$	20256	20239	187	m
0 0 4	20760	20787	280	m
1 7 $\bar{1}$	21198	21203	210	w
1 1 4	21427	21427	203	m
1 5 $\bar{3}$	21807	21817	229	s
3 1 $\bar{3}$	22323	22346	79	w
4 0 0	22972	22978	—	m
3 3 2	23335	23338	153	w
1 5 3	23594	23587	198	w
1 1 4	23790	23786	161	vw
2 0 4	24171	24172	203	w
4 2 0	24505	24510	170	m
3 5 1	24667	24682	239	m

The temperature coefficient were refined isotropically. An R factor ($R = \sum |F_o| - |F_c| / \sum |F_o|$) of 0.13 was obtained, which indicated that the deduced hafnium and sulphur positions were almost correct.

The positions of the oxygen atoms present in the unit cell were clearly indicated by a three-dimensional difference Fourier synthesis based on the signs obtained from the hafnium and sulphur parameters. They were found to be arranged in the following way:

$$\begin{array}{ll} 8 \text{ O}_1 \text{ in } C2/c: 8(f) & \text{with } x \approx 0.01 \quad y \approx 0.08 \quad z \approx 0.44 \\ 8 \text{ O}_2 \text{ » } C2/c: 8(f) & \text{» } x \approx 0.05 \quad y \approx 0.31 \quad z \approx 0.42 \\ 8 \text{ O}_3 \text{ » } C2/c: 8(f) & \text{» } x \approx 0.16 \quad y \approx 0.46 \quad z \approx 0.20 \\ 4 \text{ O}_4 \text{ » } C2/c: 4(e) & \text{» } y \approx 0.80 \end{array}$$

The parameters were tested by one cycle of least squares calculations. The reliability index then dropped to 0.105.

Errors in the intensity material due to absorption could not be neglected, since $\text{Hf}(\text{OH})_2\text{SO}_4\text{H}_2\text{O}$ has a linear absorption coefficient of 207 cm^{-1} for $\text{MoK}\alpha$ radiation. A correction for this effect reduced the R factor to 0.075. A final refinement was then performed using the full matrix least squares programme, LALS,⁹ and allowing for anisotropic refinement of the thermal parameters. All structure factors were weighted according to Cruickshank's weighting scheme,¹⁰ ($w = [140 + F_o + 10^{-3}F_o^2]^{-1}$), and the thermal parameters were expressed in the form $\exp(-h^2\beta_{11} - k^2\beta_{22} - l^2\beta_{33} - hk\beta_{12} - hl\beta_{13} - kl\beta_{23})$, β_{12} and

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

Atom and position	x	y	z
Hf in 4(e)	0	0.95841(5)	1/4
S in 4(e)	0	0.3809(3)	1/4
O ₁ in 8(f)	0.0139(17)	0.0887(7)	0.4473(11)
O ₂ in 8(f)	0.0601(19)	0.3156(9)	0.4229(16)
O ₃ in 8(f)	0.1771(16)	0.4540(8)	0.2178(14)
O ₄ in 4(e)	1/2	0.2831(10)	1/4

Table 3. Final anisotropic thermal parameters and their standard deviations. The temperature coefficient is expressed as $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + hk\beta_{12} + hl\beta_{13} + kl\beta_{23})]$.

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Hf	0.00263(10)	0.00091(2)	0.00184(7)	0	0.00007(11)	0
S	0.0051(7)	0.0010(2)	0.0050(5)	0	0.0032(9)	0
O ₁	0.0114(21)	0.0014(4)	0.0031(9)	-0.0015(15)	0.0014(24)	0.0005(10)
O ₂	0.0107(24)	0.0034(6)	0.0096(18)	0.0021(19)	0.0018(34)	0.0088(17)
O ₃	0.0068(18)	0.0019(4)	0.0093(15)	0.0002(17)	0.0044(26)	0.0002(15)
O ₄	0.0132(33)	0.0010(5)	0.0058(18)	0	0.0048(40)	0

Table 4. Observed and calculated structure factors. Non-observed reflexions are indicated by a dash. (The columns are l , F_o , and F_c , respectively.)

0	0	L	8	122	-124	1	3	L	-2	145	149	-2	-	37	-10	48	-94	4	114	-111	
2	288	-310	9	-	-2	13	51	51	-1	138	-133	-1	115	110	-11	50	55	2	55	-103	
4	269	280	10	83	81	12	68	63	0	122	-119	0	56	-60	-12	67	67	2	127	140	
6	236	-234	11	-	-5	11	60	-52	1	129	114	1	106	-104	-13	51	-52	1	116	121	
8	147	141	12	82	-76	10	47	-78	2	145	141	2	-	-35	-	-	-	0	96	-98	
10	131	-131				9	64	59	3	73	-49	3	83	93		2	4	L	L	L	
12	95	91				8	98	89	4	103	-107	4	45	-47	-13	79	-66	-2	117	118	
			0	14	L	7	38	-87	5	115	107	5	88	-89	-12	45	36	-3	96	105	
0	2	L	1	105	-98	6	176	-126	6	96	94	6	-	-40	-11	78	73	-4	100	-108	
0	202	252	2	129	119	5	73	66	7	69	-67	7	91	75	-10	-	-34	-5	56	-56	
1	207	233	3	74	69	4	150	158	8	100	-83	8	-	-21	-7	104	-101	-6	32	84	
2	223	-236	4	107	-109	3	118	-168	9	62	60	9	64	-62	-8	51	57	-7	66	69	
3	185	-182	5	91	-82	2	141	-131	10	72	62				-7	110	111	-8	73	-84	
4	200	198	6	97	93	1	85	89	11	61	-58		1	15	L	1	1	-8	65	-67	
5	134	122	7	54	57	0	197	224	12	94	-96	0	77	73	-5	123	-116	-10	66	62	
6	136	-137	8	68	-75	-1	76	-103	13	-	-	0	-	-21	-4	66	64	-11	53	51	
7	122	-112	9	44	-45	-2	106	-177	14	11	L	1	11	L	1	1	1	-12	65	-59	
8	115	111	10	61	66	-3	141	139	12	74	-65	4	-	-20	-2	53	-49				
9	75	79				-4	142	145	11	-	-15	2	55	95	-1	114	-112		2	12	L
10	85	-94				-5	93	-84	10	73	72	2	-	-22	0	53	53	-12	55	-74	
11	-	-57	0	49	-51	-6	141	-142	9	-	-20	1	98	-97	1	175	175	-11	-	1	
12	98	65	1	123	-114	-7	105	104	8	103	-93	0	-	-25	2	107	-102	-10	76	83	
13	47	49	2	45	44	-8	103	105	7	-	-13	-1	55	54	3	207	-201	-9	-	1	
			3	107	102	-9	71	-70	6	116	109	-2	-	-27	4	70	65	-6	110	-120	
0	4	L	4	61	-50	-10	80	-81	5	-	-23	3	94	-100	5	131	118	-7	-	15	
C	1	201	5	108	-103	-11	52	54	4	124	-118	-4	-	24	6	70	-62	-6	110	118	
2	137	-130	7	74	75	-12	72	67	3	-	-25	7	161	-83	7	161	-137	-5	-	-	
3	248	-261	8	-	-33				2	136	139	-6	42	-26	8	67	58	-4	133	-145	
4	71	78	9	70	-66				1	-	-24	-7	60	-79	9	107	100	-3	-	7	
5	137	132				-13	73	-78	0	140	-141	-8	-	20	10	-	-36	-2	156	169	
6	97	-61				-12	-	-32	-1	39	-24	-5	55	65	11	33	-74	-1	-	18	
7	138	-132	0	-	-7	-11	-	-100	-2	153	157	-3	-	-23	12	100	93	-140	-	151	
8	63	60	1	95	-91	-10	62	-39	-5	-	-22		1	21	L	1	1	1	171	174	
9	105	103	2	-	-21	-8	65	66	-9	49	-25	-7	65	-48				3	-	-3	
10	-	-34	3	88	97	-7	162	165	-9	123	125	-5	-	-44	13	46	65	4	139	-143	
11	72	-71	4	-	-14	-6	43	-50	-7	-	-13	-4	54	61	12	76	-2	5	-	8	
12	47	46	5	70	-73	-5	105	-107	-8	99	-106	-3	59	-60	11	76	-66	6	130	133	
13	47	66	6	-	-5	-4	96	98	-9	-	-18	-2	56	-57	10	-	-8	7	-	-3	
			7	71	73	-3	216	229	-10	63	76	-1	56	52	9	97	100	8	122	-118	
0	40	-30	8	-	-10	-2	135	-136	-11	-	-17	0	66	62	8	-	-3	9	-	-2	
C	1	232	9	54	-62	-1	240	-254	-12	63	-75	1	53	-54	7	176	-122	10	70	81	
2	2	2				0	36	41				3	61	-64	6	-	-3				
3	182	-183	0	-	-35	1	223	228	1	132	L	3	43	58	9	167	160		2	14	L
4	-	-21	1	57	-63	2	161	-151	-10	67	68	4	91	55	4	-	-9	11	58	42	
5	180	170	2	-	-34	3	202	-198	-9	-	-22	5	-	-42	3	158	-154	10	-	68	
6	-	-5	3	69	63	4	78	75	-6	82	-85	6	45	-45	2	-	6	9	-	-46	
7	133	-129	4	-	-30	5	176	176	-7	67	68	7	60	40	1	167	174	8	77	-74	
8	-	0	5	-	-51	6	45	-49	-6	69	65	-3	61	-63	0	63	-73	7	63	53	
9	99	97	6	-	-26	7	152	-140	-5	46	46	4	122	L	-1	176	-117	6	110	93	
10	-	-82	7	58	55	8	73	69	-4	102	-108	4	61	59	-2	-	-4	5	54	-79	
11	81	-82	8	-	-17	9	118	113	-3	-	-19	3	61	-7	3	178	137	4	109	-106	
12	-	-	9	66	66	10	55	-30	-2	113	114	-2	-	-55	-4	-	-20	3	69	61	
13	49	65	0	71	67	11	96	-93	-1	-	-62	1	-	-10	-6	133	-133	2	111	103	
			1	48	-45	12	-	-31	0	67	-91	-1	71	-	-6	-	4	1	72	-71	
0	8	L	2	53	-52	13	71	73	1	-	-33	-1	-	-11	-7	114	118	0	111	-115	
0	124	-121	3	48	47	2	106	113	2	106	113	-2	61	-63	-8	-	-4	-1	77	82	
1	173	177	4	-	-59	3	15	-15	-3	15	-	-3	-	-65	-5	94	-94	-2	107	107	
2	67	64	5	-	-40	13	76	-82	4	94	-92	-4	61	63	-10	14	-2	-	-	-56	
3	129	-129	6	50	-52	12	12	-20	5	45	-39	8	-	-39	-8	141	139	-4	98	-94	
4	49	-62				6	83	-87	6	75	75	-12	51	55	-12	43	-67	-4	71	68	
5	145	147				10	43	40	7	-	-12	-12	51	55	-12	43	-67	-6	84	92	
6	59	66	0	24	L	9	114	116	8	84	-81	-10	125	-127	-8	125	-127	-7	-	-53	
7	94	-90	1	-	-3	8	-	-34	9	-	-21	-8	161	139		2	8	1	80	-74	
8	40	36	0	65	72	7	137	-130	10	57	61	-4	155	209	-11	75	73	-9	62	62	
9	50	85				5	172	160	11	15	L	-2	240	-245	-5	71	-78	-10	80	82	
10	-	-36				4	73	-69	19	46	50	2	223	-211	-8	-	-36		2	16	L
11	79	-72	-12	71	74	3	197	-192	9	48	-44	4	271	263	-7	86	85	-9	69	61	
12	-	-32	-11	-	-17	2	64	58	8	58	-58	6	224	-205	-6	54	54	-8	-	-28	
13	81	47	-10	111	-105	1	206	214	7	-	-39	8	141	139	-5	127	-126	-7	63	-72	
			-9	42	-33	0	102	-98	6	80	74	10	136	-133	-4	-	-32	-6	44	58	
0	10	L	-8	120	118	-1	191	-210	5	64	-69	12	88	89	-3	93	96	-5	81	90	
0	135	-129	-7	40	33	-2	58	66	4	81	-77	-2	49	50	-2	49	50	-4	54	-48	
1	122	127	-6	158	-160	-3	206	217	3	51	49	-1	141	-143	-3	74	-78	-3	74	-89	
2	163	163	-5	-	-25	-4	87	-81	2	79	82	12	62	67	0	72	-78	-2	-	38	
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6	88	96	-1	-	-4	-8	40	-38	-2	87	86	8	118	114	4	58	-65	2	-	43	
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Table 4. Continued.

1	81	-84	-7	152	151	-7	-	-23	4	C	L	-5	59	55	4	46	-38	-8	59	48					
0	-	-2	-6	53	-50	-6	80	81	-12	87	93	-5	120	-125	5	69	-77	-7	129	127					
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-7	62	-65	1	234	239	1	45	-35	4	217	209	2	-	34	7	5E	66	0	60	60					
-8	-	-8	2	14C	-131	2	17E	122	6	156	-154	3	1C1	-104	6	-	-2	1	151	139					
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			5	183	174	5	4E	-40	12	6E	75	6	-	39	3	75	74	4	4E	42					
			6	61	-53	6	45	82	6	65	-82	7	79	-74	2	-	-15	5	135	130					
			7	147	-137	7	-	14	8	4	2	L	8	-	31	1	84	-79	6	7E					
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			12	-	-	12	-	30	8	76	93	4	10	L	-4	-	13	5	7	L					
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			28	59	-59	28	59	-59	-9	70	-79	-9	70	-79	-5	94	-9E	4	2	-7	117	116			
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Table 4. Continued.

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-5	-	50	6	-	8	-	-	8	7	63	61	-1	48	-49	-1	48	-49	-5	59	-55			
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-8	5 17	L	9	65	80	-4	-	10	4	82	-75	-10	64	-65	-4	77	-69	-	9 11	L			
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-60	7	68	-71	-2	126	135	6	73	-72	-1	-	50	5	80	75	7	-	-53	5	-	42	-	
-61	8	86	84	-3	-	10	7	61	-59	C	-	-66	6	-	-30	8	61	57	6	70	-63	-	
-62	9	57	53	-4	118	-128	8	63	66	1	95	-46	5	64	-57	-	-	-	7	-	-43	-	
-63	10	62	-69	-6	90	102	-7	5	L	78	4	61	-59	5	49	-43	-	-	8	53	53	-	
-64	9	55	70	-7	-	8	9	70	78	4	61	-59	5	49	-43	-	-	-	-	-	-	-	
-65	8	-	41	-8	99	-96	8	7	90	-94	5	7	17	L	3	47	-65	4	55	30	4	48	32
-66	7	106	-104	-10	67	74	6	55	-42	-2	64	62	3	47	-54	4	55	30	4	48	32	-	
-67	6	-	-49	-	-	-	5	104	104	3	65	-	2	71	78	3	113	-167	3	83	-70	-	
-68	5	105	104	-9	6	L	4	-	34	2	-	27	C	82	-73	1	121	115	1	95	80	-	
-69	4	56	51	-8	53	39	3	130	-128	1	69	-72	-1	61	-69	0	45	42	0	-	35	-	
-70	3	132	-127	-8	75	-68	2	59	-58	0	-	-33	-2	79	71	-1	127	-111	-1	93	-83	-	
-71	2	68	-67	-7	-	-45	1	125	135	-1	74	78	-3	-	-55	-2	51	-41	-2	41	-37	-	
-72	1	152	157	-6	61	74	C	54	54	-2	-	31	-4	63	-69	-3	115	114	-3	47	82	-	
-73	C	56	58	-5	67	58	-1	132	-141	-3	72	-80	-5	65	-63	-4	48	39	-	-	-	-	
-74	-1	125	-131	-4	81	-84	-2	44	-51	-4	-	-27	-6	64	63	-5	111	-97	-	10	6	L	-80
-75	-2	67	-63	-3	57	-57	-3	142	149	-5	69	71	-7	50	52	-6	-	-35	0	82	-80	-	
-76	-3	131	136	-2	163	56	-4	52	55	-4	-	-	-8	66	-61	-7	70	85	C	-	-	-	
-77	-4	56	57	-1	86	72	-5	137	-127	-10	6	L	87	-90	-	-	-	-	9	7	L	-4	
-78	-5	118	-118	0	92	-92	-6	46	-45	-8	103	101	-7	83	L	-78	-5	64	-100	3	75	-75	
-79	-6	50	-41	1	-	-62	-7	128	117	-6	128	-117	-7	-	-	-4	43	-30	4	-	-6	-	
-80	-7	89	94	2	55	91	-8	51	41	-4	130	127	-6	85	83	-3	95	99	5	81	66	-	
-81	-8	-	43	3	52	58	-9	104	-98	-4	142	-139	-5	-	-71	-2	-	-35	6	61	66	-	
-82	-9	85	-79</																				

at (0.01, 0.09, 0.45) and (−0.01, 0.09, 0.05) and can probably be attributed to diffraction effects.

The final positional parameters and anisotropic temperature coefficients are given with their standard deviations in Tables 2 and 3. A comparison between observed and calculated structure factors is given in Table 4. Interatomic distances and angles together with their standard deviations, calculated with the programme DISTAN,⁹ are listed in Table 5.

The Lorentz and polarisation correction, calculated with the programme DATA P2,⁹ the Patterson synthesis, all structure factor calculations, the Fourier syntheses, calculated with the programme DRF,⁹ and the least squares refinement, calculated with the programme LALS,⁹ were performed on an IBM 360/50 computer at the Göteborg Universities' Computing Centre.

THE POSITIONS OF THE HYDROGEN ATOMS

According to the analysis of the compound there are sixteen hydrogen atoms in the unit cell. Since the oxygen atoms occupying the O₂ and O₃ positions belong to sulphate groups, the hydrogen atoms ought to be situated close to O₁ and O₄.¹ The oxygen atoms O₁ are in close contact with the hafnium ions, so that it seems most plausible that they are the OH[−] ions and that the remaining four oxygen atoms, O₄, are the water molecules. This is supported by short O—O distances indicating hydrogen bonding (*cf.* Table 5).

DISCUSSION OF THE STRUCTURE

The hafnium and hydroxide ions form almost planar infinite [Hf(OH)₂]_n²ⁿ⁺ chains, running parallel to the *c* axis. Such an arrangement with double hydroxide bridges between metal atoms is a characteristic feature of all basic

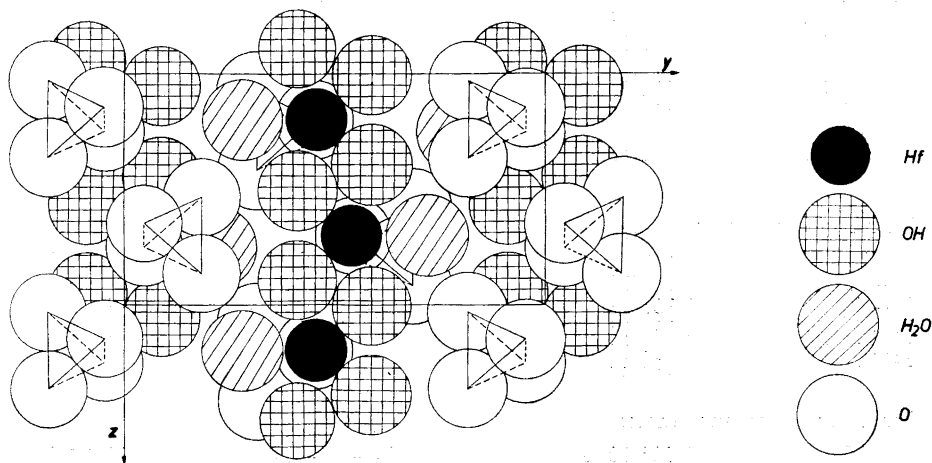


Fig. 2. Projection of the structure of $\text{Hf}(\text{OH})_2\text{SO}_4 \cdot \text{H}_2\text{O}$ perpendicular to the *yz* plane. The unit cell and the sulphate tetrahedra are indicated.

zirconium and thorium¹²⁻¹⁵ salts reported to date and of $\text{U}(\text{OH})_2\text{SO}_4$.¹⁶ Two main types of arrangement of metal and hydroxide ions have been found in the infinite chains: In the isomorphous sulphates $\text{Me}(\text{OH})_2\text{SO}_4$ with $\text{Me} = \text{zirconium},^2$ thorium,¹³ and uranium¹⁶ and in $\text{Th}(\text{OH})_2\text{CrO}_4\text{H}_2\text{O}$ ¹² the hydroxide ions form two parallel rows with the metal atoms situated on alternate sides of the rows. In $\text{Hf}(\text{OH})_2\text{SO}_4\text{H}_2\text{O}$ and $\text{Zr}_4(\text{OH})_6(\text{CrO}_4)_5(\text{H}_2\text{O})_2$,¹⁹ however, the metal atoms and the bridging oxygen atoms all lie in the same plane forming two different zigzag chains which cross one another (*cf.* Fig. 2).

The Hf—Hf distances within the chains are 3.553 Å, which can be compared with the Me—Me distances 3.545–3.60 Å in basic zirconium compounds,² 3.97–4.09 Å in basic thorium compounds,¹²⁻¹⁵ and 3.90 Å in $\text{U}(\text{OH})_2\text{SO}_4$.¹⁶ The O—O distance in the hydroxide bridge is very short, 2.33 ± 0.02 Å, but this seems to be a significant feature of other $\text{Me}(\text{OH})_2\text{—Me}$ arrangements. In $\text{Zr}_2(\text{OH})_2(\text{SO}_4)_3(\text{H}_2\text{O})_4$,² $\text{Zr}(\text{OH})_2\text{SO}_4$,² and $\text{Zr}(\text{OH})_2(\text{NO}_3)_2(\text{H}_2\text{O})_4$,² the O—O distances in the bridges lie within the range 2.34–2.44 Å, in $\text{NaAl}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}(\text{SeO}_4)_4(\text{H}_2\text{O})_x$ ¹⁸ the O—O distance is 2.34 Å and in $\text{Al}_2(\text{OH})_2(\text{H}_2\text{O})_{10}(\text{SO}_4)_2(\text{H}_2\text{O})_2$ and the corresponding selenate it is 2.40 Å.¹⁹

The $[\text{Hf}(\text{OH})_2]_n^{2n+}$ chains in $\text{Hf}(\text{OH})_2\text{SO}_4\text{H}_2\text{O}$ are held together in the *x* direction by sulphate groups, each of which is in contact with hafnium atoms in two different chains (*cf.* Fig. 2). The bond distances within the sulphate group are listed in Table 5, and these are in good agreement with the S—O distances 1.44–1.53 Å reported for SO_4^{2-} in Int. Tab. III.²⁰ The water molecules and the hydroxide ions form an almost planar pentagon around each hafnium atom, which is thus coordinated to a pentagonal bipyramidal arrangement of seven oxygen atoms, whose departure from the ideal D_{5h} symmetry is illustrated in Fig. 3. The shortest Hf—O distances are those to

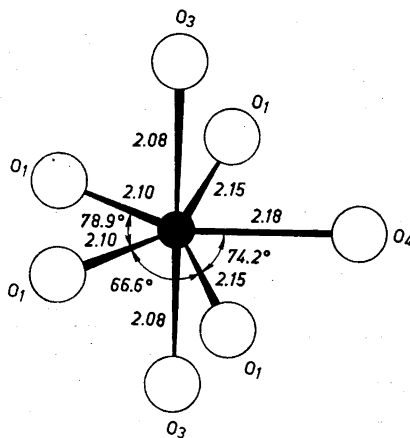


Fig. 3. The coordination polyhedron of $\text{Hf}(\text{OH})_2\text{SO}_4\text{H}_2\text{O}$. The Hf—O distances (in Å) and some O—Hf—O bond angles are indicated.

the sulphate oxygens, while, as expected, the longest is that to the water molecule. The mean value of the Hf—O distances is 2.11₉ Å. A similar coordination polyhedron was found in $\text{Zr}_4(\text{OH})_6(\text{CrO}_4)_5(\text{H}_2\text{O})_2$,¹⁷ where the shortest Zr—Zr distance is 3.59₅ Å and the Zr—O distances in the bipyramid are

within the range 1.97–2.21 Å, which can be compared with the distances in Table 5.

In zirconium hydroxide chromate¹⁷ the oxygen pentagon surrounding the zirconium atom is exactly planar since the oxygen atoms are situated in a mirror plane of the space group. This is, however, not the case for $\text{Hf}(\text{OH})_2\text{SO}_4\text{H}_2\text{O}$. The plane of best fit through the oxygen atoms of the pentagon surrounding hafnium was therefore calculated by least squares methods. Since both Hf and O_4 are situated on a twofold axis, the plane must pass through this axis. Its equation should thus have the form $Ax + Bz = C$. The programme PLANEFIT⁹ gave $A = 6.332$ Å, $B = 0.805$ Å, and $C = 3.267$ Å, x and z being the fractional coordinates. The distances of the hydroxide ions (O_1) from this plane are 0.10₅ Å (for two O_1) and 0.06₇ Å (for two O_1), whereas the hafnium atom and the water molecule (O_4) are situated in the plane. The pentagon of oxygen atoms surrounding the hafnium atom does thus not deviate appreciably from planarity.

In the monoclinic form of ZrO_2 (naturally occurring as baddeleyite) the Zr–O distances within the seven-coordinated polyhedron are 2.04–2.26 Å²¹ and Adam and Rogers²² have shown that HfO_2 is isomorphous with this form of ZrO_2 .

The Me–O distances (Å) in some dodecahedral eight-coordinated zirconium complexes are:

$\text{Zr}_2(\text{OH})_2(\text{SO}_4)_3(\text{H}_2\text{O})_4^2$	2.09 – 2.26	Mean 2.19
$\text{Zr}(\text{OH})_2(\text{NO}_3)_2(\text{H}_2\text{O})_4^2$	2.12 – 2.37	Mean 2.22
$\text{Na}_4\text{Zr}(\text{C}_2\text{O}_4)_4(\text{H}_2\text{O})_3^{23}$	2.144 – 2.244	Mean 2.199
Zr cupferrate ²⁴	2.162 – 2.226	Mean 2.191

The values given in Int. Tab. III²⁵ for Zr–O and Hf–O in eight-coordinated polyhedra are 2.18 Å and 2.215 Å, respectively.

The structure of $\text{Hf}(\text{OH})_2\text{SO}_4\text{H}_2\text{O}$ can be visualised as being built up from layers parallel to the xz plane, formed from bipyramids linked together by sulphate groups and double hydroxide bridges. These layers are held together by means of hydrogen bonds ($\text{O}_4 \cdots \text{O}_2 = 2.61$ Å, $\text{O}_1 \cdots \text{O}_2 = 2.85$ Å) and van der Waals contacts only.

The stereochemistry of compounds exhibiting high coordination numbers has been discussed on the basis of different theories. One approach to the problem is to assume that molecular geometry is governed by steric forces. In a detailed review by Gillespie and Nyholm²⁶ it is stated that the most probable arrangement of seven bonding pairs of electrons with electronic configuration $d_e^2d_\gamma^4s^2p^6$ is a pentagonal bipyramid. Kettle,²⁷ on the other hand, by neglecting steric interactions and basing his calculations on molecular orbital theory only (π -bonding effects are not considered), has arrived at results which are not in agreement with the configurations commonly observed.

Claxton and Benson²⁸ have confirmed Gillespie's²⁹ proposal that for seven-coordination the most probable arrangement, for an interparticle potential proportional to r^{-n} , is the C_{3v} structure when n is large. (C_{3v} corresponds to an octahedron with an additional ligand capping one face). For $n = 1$ the D_{5h} structure may be energetically more favorable but for $2 < n < 5.6$, and probably even for $n = 1$, the configuration of minimum energy is that with C_2 symmetry.

However, since the three arrangements do not differ too greatly, it seems possible that transitions from one structure to another may occur through a complete spectrum of intermediate configurations, and it is difficult to predict which factor is the decisive one for a specific compound. It can be noted that for any number of ligands from two to eight, except seven, the arrangement of minimum energy is independent of the force law.²⁹⁻³¹ Examples of the three types of stereochemistry for seven coordination (D_{5h} , C_{3v} and C_{2v}) are listed in *Coord. Chem. Rev.*³²

The IR-spectrum of $\text{Hf}(\text{OH})_2\text{SO}_4\cdot\text{H}_2\text{O}$, registered using the potassium bromide technique, is shown in Fig. 4. It is not possible to analyze it with

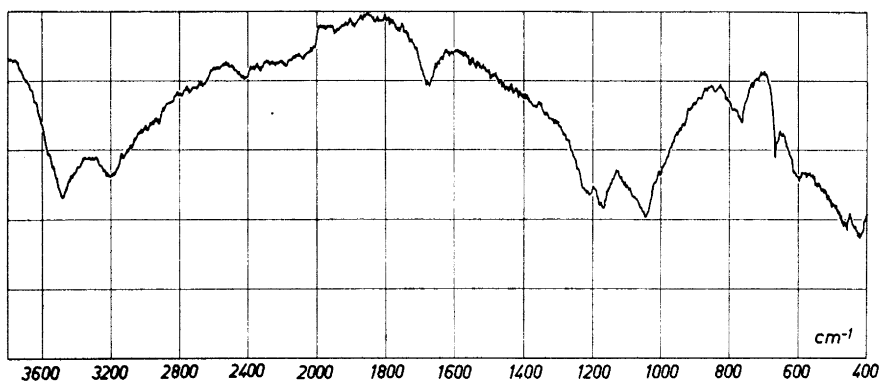


Fig. 4. Infrared spectrum of $\text{Hf}(\text{OH})_2\text{SO}_4\cdot\text{H}_2\text{O}$.

certainty since no spectra of the basic salts of zirconium, thorium, or uranium are yet available. There are, however, bands in the region 3500–2000 cm^{-1} which may be accounted for by the presence of hydrogen bonding. The band at 1050 cm^{-1} can originate from the Me–O–H bending in the metal-hydroxide bridges. Nakamoto *et al.*³³ have observed such a band at approximately 1100 cm^{-1} in a Co(III) polynuclear complex with bridging OH groups. Sartori *et al.*³⁴ have calculated the vibrational frequencies of coordinated water molecules and according to their calculations, the Me–O rocking, wagging and stretching vibrations should appear at 900, 768, and 673 cm^{-1} , respectively. There are some bands in this region of the spectrum which may be due to coordinated water molecules, but, since these frequencies are very sensitive to the strength of the coordinate bond as well as to hydrogen bonding, it is not possible to identify them unequivocally.

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