ACTA CHEMICA SCANDINAVICA 27 (1973) 3467–3476

The Crystal Structure of a Basic Hafnium Chromate

MARGARETA HANSSON and WANDA MARK

Department of Inorganic Chemistry, Chalmers University of Technology and The University of Göteborg, P.O. Box, S-402 20 Göteborg 5, Sweden

Hafnium chromate of approximate formula $Hf_4(OH)_8(CrO_4)_4.H_2O$ crystallizes in space group *Pnnm* with $a = 11.543$, $b = 13.587$, $c = 6.847$ Å and $Z = 2$. It is isotypic with a corresponding zirconium compound with the formula $Zr_4(OH)_6(CrO_4)_5.H_2O$.

The crystal structure of the hafnium compound has been determined from X-ray single crystal data by means of three dimensional Fourier syntheses. Least squares refinement of the structural parameters based on 818 independent reflexions yielded a final R value of 0.061.

The hafnium atoms are joined by double oxygen bridges to form planar infinite chains with the composition $[Hf(OH)_2]_n^{2n+}$. The chains are connected by chromate groups to form a three-dimensional structure. Seven oxygen atoms are coordinated to each hafnium atom in a pentagonal bipyramidal arrangement. The Hf–O distances range from 2.01 to 2.25 Å.

Some investigations have been performed in order to elucidate the differences between zirconium and hafnium with respect to their chemical behaviour and atomic sizes. The hydrolysis systems $ZrO_2-SO_3-H_2O$ and $HfO_2-SO_3-H_2O$ have been investigated by McWhan, Lundgren and Hansson [1,2] and the two systems show discrepancies as regards the conditions under which the different phases are formed.

In the hydrolysis system $ZrO_2-CrO_3-H_2O$, three principally different crystalline phases are obtained.[3] In attempts to prepare the corresponding phases in the $HfO_2-CrO_3-H_2O$ system, only one crystalline phase was found, namely $4HfO_2.4.3CrO_3.5.4H_2O$, the corresponding phase in the zirconium system having the composition $4ZrO_2.4.9CrO_3.3.7H_2O$.[3] Apart from the different compositions of the products, crystallization is more readily brought about in the zirconium system. The crystalline hafnium chromate is formed in very low yield and the crystals are small.

EXPERIMENTAL

The hafnium chromate investigated was prepared by hydrothermal hydrolysis of an amorphous hafnium chromate in a 10 M chromium trioxide solution at 165°C.

Due to the small amount obtained, the hafnium and chromium contents were determined by electron probe microanalysis. The results indicate an approximate formula of $Hf_4(OH)_8(CrO_4)_4.H_2O$, which can also be written $4HfO_2.4CrO_3.5H_2O$. By refining the structure with three-dimensional X-ray data, it was possible to establish the composition $4HfO_2.4.3CrO_3.5.4H_2O$. The experimental and calculated hafnium and chromium contents are:

	% Hf	% Cr
Experimental	53.9	16.2
Calculated for:		
$4HfO_2.4CrO_3.5H_2O$	53.6	15.6
$4HfO_2.4CrO_3.6H_2O$	52.9	15.4
$4HfO_2.4.3CrO_3.5.4H_2O$	52.2	16.3

PROCESSING OF DATA

From Guinier and Weissenberg photographs it was evident that the hafnium chromate structure is very nearly isomorphous with that of the corresponding zirconium chromate.

The crystals are red truncated double pyramids, that used for the structure determination having a basal plane of 0.03×0.05 mm^2 (y and z directions) and a height of 0.05 mm.

Due to the positions of the hafnium atoms in the structure, reflexions with $k = 2n$ are very strong while those with $k = 2n+1$ are very weak. The crystal was therefore mounted along the y axis in a single crystal diffractometer (Philips PAILRED) and reflexions from the reciprocal layers $h0l - h14l$ and $\bar{h}0l - \bar{h}14l$ with k even were registered with Mo$K\alpha$ radiation. The ω scanning speed was 1°/min, and the total time for registration of one reflexion was 3 min for the lower levels and 6 min for the higher levels. A total of 1196 reflexions were collected with k even. The intensities of the reflexions with k odd are on an average one tenth of those with k even. In order to be able to estimate these weak reflexions with a better accuracy, they were registered with multiple film Weissenberg techniques and Cu$K\alpha$ radiation. Each layer ($h1l - h9l$, $k = 2n+1$) was exposed for 2 – 3 weeks and the intensities of the 311 independent reflexions thus obtained were estimated visually by comparison with an intensity scale.

UNIT CELL DIMENSIONS

The crystals have orthorhombic symmetry and the conditions for reflexion are:

$h0l$ with $h + l = 2n$
$0kl$ with $k + l = 2n$

The conditions are in accordance with space groups No. 34, *Pnn*2, and No. 58, *Pnnm*.

Accurate cell dimensions were obtained by least squares refinement of the cell parameters using the program POWDER.[4] For this purpose 41 lines were indexed on a Guinier powder photograph taken with Cu$K\alpha_1$ radiation, using lead nitrate as an internal standard ($a_{Pb(NO_3)_2} = 7.8566$ Å at 21°C).[5] The cell dimensions and their standard deviations were found to be (for com-

Table 1. Guinier powder data. $\lambda_{CuK\alpha_1} = 1.54050$ Å.

h k l	$10^5 \sin^2 \theta$ obs	$10^5 \sin^2 \theta$ calc	*d* Å calc	*I* obs
1 0 1	1715	1711	5.8892	st
1 2 0	1734	1731	5.8549	st
2 0 0	1785	1781	5.7715	st
1 3 0	3346	3338	4.2162	vvw
3 1 0 2 2 1	4341	4329 4332	3.7021 3.7008	w
2 3 0	4683	4673	3.5630	vw
0 0 2	5069	5062	3.4237	vst
0 4 0	5146	5142	3.3968	vst
3 0 1	5274	5273	3.3544	vst
3 2 0	5299	5293	3.3480	vst
1 2 2	6801	6792	2.9555	vvw
2 0 2 1 4 1	6851	6843 6852	2.9446 2.9425	m
2 4 0	6934	6923	2.9275	st
4 2 1	9682	9675	2.4763	st
0 4 2	10195	10203	2.4114	vw
3 2 2	10359	10354	2.3937	vw
3 4 1	10412	10415	2.3868	vw
1 0 3	11840	11834	2.2391	w
2 4 2	11990	11984	2.2250	vw
1 6 0	12035	12014	2.2222	w
4 4 0	12276	12266	2.1993	vw
5 2 0	12433	12417	2.1859	m
2 6 1	14619	14615	2.0148	w
3 0 3	15420	15396	1.9631	w
3 6 0	15587	15576	1.9516	m
1 4 3	16969	16975	1.8695	w
1 6 2	17077	17076	1.8640	vvw
5 2 2	17484	17479	1.8424	w
6 2 1	18581	18580	1.7869	m
4 2 3	19784	19798	1.7311	w
4 6 1	19944	19959	1.7241	w
0 0 4	20250	20246	1.7118	vw
0 8 0 3 6 2	20593	20567 20638	1.6984 1.6955	w
1 2 4 2 0 4	22013	21977 22027	1.6431 1.6412	vw
1 8 1	22273	22278	1.6319	vvw
2 8 0	22351	22348	1.6293	w
5 6 0	22727	22701	1.6166	w
7 0 1 7 2 0	23090	23083 23103	1.6032 1.6025	m
2 6 3	24740	24738	1.5486	vvw
3 2 4 0 8 2	25571	25539 25629	1.5242 1.5215	vw
2 4 4	27176	27169	1.4777	vvw
5 6 2	27741	27762	1.4619	vvw
6 2 3	28716	28703	1.4377	vw
6 6 1	28880	28864	1.4337	vw

parison those of the corresponding zirconium compound are given within brackets):

$a = 11.543 \pm 0.002$ Å (11.629)
$b = 13.587 \pm 0.002$ Å (13.653)
$c = 6.847 \pm 0.001$ Å (6.882)
$V = 1073.9 \pm 0.3$ Å^3 (1092.7)

The observed and calculated values of $\sin^2\theta$ less than 0.30 are listed in Table 1, together with the calculated inter-planar spacings. As the experimental density could not be determined, the number of formula units per unit cell was assumed to be $Z = 2$ as in the corresponding zirconium chromate structure. On the basis of this assumption, the calculated density is 4.18 g/cm^3, which seems reasonable.

STRUCTURE DETERMINATION AND REFINEMENT

The two sets of data were corrected for Lorentz, polarization and absorption effects with the programs DATAP1 and DATAP2,[6] respectively. To bring the different data sets on to the same scale, a structure factor calculation was performed, which was based on the hafnium atoms, assuming that the positional parameters were the same as in $4ZrO_2.4.9CrO_3.3.7H_2O$. Successive three dimensional Fourier syntheses were calculated (program DRF [6]) to obtain the positions of the chromium and oxygen atoms. In the calculations, the space group *Pnnm* was used and the positions of the atoms labelled Cr_1, Cr_2, $O_1 - O_{10}$, and O_{12} could be determined without any ambiguity. All atoms occupy the special position 4(*g*) except O_1 and O_2 which are situated in the general position 8(*h*). This implies the composition $Hf_4(OH)_8(CrO_4)_4.2H_2O$ or $4HfO_2.4CrO_3.6H_2O$. The O_{12} atoms correspond to the two water molecules of crystallization per formula unit. A Fourier synthesis, based on the refined atomic parameters, showed small excesses of electron density at very nearly the same positions as the Cr_3 atoms in the zirconium chromate structure. It was therefore considered likely that the hafnium compound contained a small additional amount of chromate (Cr_3). These chromate groups must be statistically distributed between four equivalent positions, as will be seen later. As the additional chromate oxygen atoms (O_{11}) could not be located from the Fourier syntheses, they were assumed to occupy the same positions as in the zirconium structure. Refinement of the parameters was performed with the program BLOCK,[6] different occupation numbers being assigned to Cr_3. In the different refinements, the occupation number of O_{11} was assigned the same value, q, as that of Cr_3. The occupation number for O_{12}, $(1-q)$, (*cf.* later) was deduced from the positional relationship between Cr_3 and O_{12}. The best fit with the experimental data was obtained for an occupation number of 0.14 for Cr_3 and thus of 0.86 for O_{12}.

A few cycles of refinement with the least squares full matrix program LINUS [6] showed that secondary extinction effects were of little importance. The final cycles of refinement were performed with the program LALS.[6]

Table 2. Observed and calculated structure factors for $\sim Hf_4(OH)_8(CrO_4)_4.H_2O$.

H 0 0			H 0 11			9 125 -125			H 4 8			H 6 8			H 8 9		
2 513 457			1 105 111			13 84 89			0 237 -228			3 155 152			1 154 162		
6 150 -131			3 105 100						2 141 -149			5 175 173			9 96 -101		
8 211 -187			9 95 -87			H 2 9			10 154 157			7 119 129					
10 350 -335						4 160 -165			12 129 136			9 94 88			H 8 10		
12 289 -266			H 0 12			6 192 -196									0 132 152		
14 104 -93			0 126 144			8 99 -59			H 4 9			H 6 9			2 122 115		
20 87 82			10 95 -84						1 148 -153			2 94 92			10 126 -101		
22 78 90			12 80 -75			H 2 10			3 125 -129			4 153 160					
						3 146 -136			7 97 87			6 156 158			H 8 11		
H 0 1			H 0 13			5 118 -137			9 127 125			8 101 88			1 105 112		
1 448 432			1 94 84			7 111 -110			11 113 113								
3 478 455									13 86 80			H 6 10			H 10 0		
5 70 65			H 0 14			H 2 11						3 118 126			3 214 -216		
7 359 -314			0 96 99			4 109 -113			H 4 10			5 133 143			5 405 -394		
9 270 -258						6 131 -137			0 189 -187			7 110 103			7 285 -283		
11 187 -184			H 2 0						2 119 -122			9 94 63			9 105 -108		
13 181 -169			1 291 -296			H 2 12			10 118 126						13 93 97		
15 134 -116			3 501 -493			3 85 -83						H 6 11			15 151 141		
			5 490 -453						H 4 11			4 104 109			17 121 122		
H 0 2			7 314 -314			H 4 0			1 110 -104			6 118 111					
0 803 816			9 271 -255			2 377 -383			3 98 -90						H 10 1		
2 294 300			13 204 188			4 215 -208						H 8 0			1 33 -25		
8 110 -113			15 184 177			6 86 74			H 4 12			2 334 333			2 204 -213		
10 294 -282			17 106 110			8 228 223			0 133 -119			4 179 180			4 253 -245		
12 256 -245						10 343 331			2 95 -76			6 98 -89			6 254 -252		
14 103 -100			H 2 1			12 273 260						8 250 -231			8 236 -219		
			2 108 -112			14 94 94			H 6 0			10 261 -252			10 107 -91		
H 0 3			4 372 -380						1 206 249			12 204 -191			12 113 92		
1 453 454			6 524 -509			H 4 1			3 476 454			14 114 -105			14 154 137		
3 399 405			8 236 -223			1 315 -345			5 442 426			20 99 80			16 111 116		
5 65 51			14 123 120			3 329 -337			7 270 269								
7 317 -310			16 194 183			5 161 -144			9 169 164			H 8 1			H 10 2		
9 267 -265			18 120 118			7 192 187			13 133 -129			1 350 378			1 68 -26		
11 177 -186						9 295 282			15 159 -153			3 222 220			3 155 -153		
13 148 -153			H 2 2			11 253 243			17 148 -125			7 144 -130			5 325 -327		
15 125 -100			1 205 -212			13 156 159						9 219 -209			7 240 -248		
19 88 93			3 298 -311			15 84 81			H 6 1			11 235 -232			9 105 -107		
21 82 80			5 319 -316			19 93 -84			2 232 233			13 158 -151			13 97 79		
			7 249 -255						4 396 393						15 141 128		
H 0 4			9 268 -248			H 4 2			6 377 374			H 8 2			17 128 119		
0 631 661			13 166 158			0 457 -461			8 165 170			0 374 369					
2 256 304			15 157 159			2 250 -264			16 178 -157			2 248 258			H 10 3		
6 85 -72			17 105 108			4 161 -171			18 109 -106			4 148 159			2 208 -213		
8 135 -132			19 88 77			8 158 153						8 193 -179			4 241 -259		
10 251 -263						10 287 282			H 6 2			12 185 -176			6 244 -249		
12 212 -221			H 2 3			12 257 240			1 192 189			14 127 -109			8 211 -205		
14 95 -85			2 173 -161			14 117 101			3 313 321						10 87 -75		
			4 412 -415						5 320 326			H 8 3			12 110 95		
H 0 5			6 478 -480			H 4 3			7 215 225			1 383 383			14 147 135		
1 250 266			8 209 -211			1 382 -384			9 177 163			3 206 214			16 115 111		
3 255 269			12 89 78			3 309 -320			15 146 -138			7 137 -144					
5 80 61			14 122 122			5 111 -108			17 141 -122			9 205 -212			H 10 4		
7 195 -193			16 176 172			7 201 207						11 220 -224			3 149 -163		
9 182 -189			18 104 107			9 277 280			H 6 3			13 151 -139			5 301 -303		
11 136 -144						11 236 234			2 242 241			17 89 33			7 225 -227		
13 134 -135			H 2 4			13 133 145			4 384 399						9 85 -93		
15 100 -96			1 188 -189						6 344 362			H 8 4			15 116 119		
19 80 79			3 321 -317			H 4 4			8 166 167			0 346 347			17 104 108		
			5 304 -310			0 440 -443			14 132 -120			2 247 250					
H 0 6			7 233 -240			2 275 -272			16 173 -149			4 149 139			H 10 5		
0 430 466			9 207 -205			4 139 -139						8 179 -175			2 145 -148		
2 230 239			13 163 150			8 155 160			H 6 4			10 202 -204			4 178 -181		
8 96 -113			15 146 148			10 261 262			1 164 161			12 168 -160			6 178 -187		
10 200 -216			17 99 96			12 214 215			3 303 302						8 166 -165		
12 182 -183						14 87 86			5 304 312			H 8 5			14 114 108		
			H 2 5						7 218 214			1 249 261					
H 0 7			2 80 -80			H 4 5			9 136 138			3 154 155			H 10 6		
1 233 245			4 254 -260			1 227 -237			13 94 -104			7 97 -89			3 130 -139		
3 198 213			6 337 -338			3 213 -223			15 126 -129			9 157 -156			5 235 -246		
7 169 -169			8 163 -165			5 91 -93			17 114 -110			11 189 -179			7 191 -187		
9 171 -173			14 99 91			7 128 129						13 120 -122			15 109 101		
11 124 -128			16 149 147			9 199 201			H 6 5								
13 105 -106						11 175 182			2 142 148			H 8 6			H 10 7		
15 87 -70			H 2 6			13 124 129			4 249 261			0 258 275			2 116 -132		
			1 146 -140			15 88 69			6 258 261			2 199 202			4 158 -170		
H 0 8			3 249 -250						8 132 136			4 106 111			6 162 -165		
0 263 295			5 226 -246			H 4 6			14 102 -92			8 154 -145			8 131 -134		
2 142 160			7 190 -195			0 343 -346			16 133 -127			10 166 -170					
8 79 -70			9 146 -162			2 220 -219			18 96 -88			12 153 -134			H 10 8		
10 149 -156			13 109 125			4 94 -104									5 164 -174		
12 133 -140			15 124 125			8 133 132			H 6 6			H 8 7			7 131 -137		
						10 215 216			1 112 118			1 227 232					
H 0 9			H 2 7			12 181 177			3 240 235			3 105 133			H 10 9		
1 151 165			2 88 -96			14 82 71			5 241 251			9 148 -142			4 122 -121		
3 140 146			4 244 -242						7 169 177			11 157 -153			6 101 -118		
7 114 -114			6 277 -280			H 4 7			9 109 111						8 101 -100		
9 136 -122			8 137 -135			1 221 -224			15 94 -110			H 8 8					
			16 129 123			3 182 -185						0 177 184			H 10 10		
H 0 10						7 148 126			H 6 7			2 134 141			3 85 -84		
0 226 229			H 2 8			9 182 178			2 134 137			4 81 82			5 140 -141		
2 130 131			1 87 -94			11 134 154			4 229 233			8 90 -99					
10 121 -126			3 151 -161			13 91 102			6 228 224			10 112 -124			H 10 11		
12 108 -107			5 145 -164						8 125 116			12 98 -103			2 79 -65		
			7 139 -139						16 101 -106						6 98 -84		

Table 2. Continued.

H 12 C					
2	256	-265			
4	180	-169			
6	89	83			
8	218	215			
10	182	181			
12	110	132			
H 12 1					
1	316	-332			
3	133	-131			
7	75	74			
9	168	160			
11	218	208			
13	122	126			
H 12 2					
0	257	-241			
2	218	-222			
4	141	-155			
8	183	180			
10	147	157			
12	111	122			
H 12 3					
1	330	-326			
3	132	-131			
7	83	85			
9	177	161			
11	207	201			
13	115	117			
H 12 4					
0	233	-232			
2	207	-209			
4	135	-138			
6	79	61			
8	171	172			
10	149	150			
H 12 5					
1	248	-241			
3	110	-98			
9	126	122			
11	169	164			
13	111	103			
H 12 6					
0	179	-192			
2	186	-172			
4	112	-113			
8	135	149			
10	119	127			
12	104	95			
H 12 7					
1	210	-210			
3	84	-88			
9	128	111			
11	159	141			
H 12 8					
0	131	-132			
2	115	-124			
8	85	103			
H 12 9					
1	145	-151			
3	71	-63			
H 12 10					
0	100	-111			
2	97	-101			
H 14 0					
1	31	47			
3	188	186			
5	296	294			
7	201	206			
15	106	-108			
H 14 1					
2	193	196			
4	225	214			
6	168	168			
8	136	149			
10	97	77			
14	110	-113			
16	108	-90			
H 14 2					
3	142	149			
5	258	256			
7	184	184			
15	102	-98			
H 14 3					
2	191	192			
4	224	215			
6	177	167			
8	138	143			
14	128	-111			

H 14 4					
3	141	145			
5	228	239			
7	169	171			
H 14 5					
2	153	146			
4	157	160			
6	121	128			
8	125	119			
H 14 6					
3	125	122			
5	204	200			
7	146	144			
H 14 7					
2	133	128			
4	130	145			
6	107	115			
8	106	100			
H 14 8					
5	152	148			
7	98	109			
H 14 9					
2	90	93			
4	105	105			
6	88	84			
H 1 0					
2	30	30			
3	100	-71			
4	-	-12*			
5	99	-70			
6	-	-1*			
7	27	-16			
8	61	53			
9	64	-48			
10	94	81			
11	-	2*			
12	56	57			
13	62	58			
14	16	18			
H 1 1					
0	21	-25			
1	19	-23			
2	10	-11			
3	72	-56			
4	17	21			
5	38	33			
6	99	-74			
7	70	55			
8	66	-53			
9	31	12			
10	-	7*			
11	40	44			
12	23	20			
13	45	47			
14	18	21			
H 1 2					
1	24	29			
2	32	40			
3	51	-47			
4	-	-11*			
5	39	-34			
6	-	-10*			
7	-	-8*			
8	29	20			
9	51	-45			
10	66	58			
11	-	-14*			
12	44	46			
13	43	39			
14	17	23			
H 1 3					
0	18	-22			
1	28	-29			
2	-	-10*			
3	42	-44			
4	-	-5*			
5	22	25			
6	75	-73			
7	63	60			
8	46	-48			
9	31	29			
10	-	10*			
11	37	48			
12	21	30			
13	30	44			
H 1 4					
1	-	15*			
2	-	20*			
3	40	-41			
4	-	-10*			
5	33	-37			
6	-	-1*			

7	-	-16*			
8	26	30			
9	39	-36			
10	50	59			
11	-	-4*			
12	33	45			
13	21	42			
H 1 5					
0	-	-9*			
1	-	-12*			
2	-	-6*			
3	25	-25			
4	-	5*			
5	-	15*			
6	38	-44			
7	29	33			
8	27	-34			
9	-	10*			
10	-	0*			
11	19	30			
H 1 6					
1	-	8*			
2	-	10*			
3	-	-29*			
4	-	-7*			
5	-	-29*			
6	-	1*			
7	-	-16*			
8	-	26*			
9	20	-28			
10	30	45			
H 1 7					
0	-	-7*			
1	-	-12*			
2	-	-7*			
3	18	-19			
4	-	-7*			
5	-	9*			
6	27	-40			
7	22	33			
8	17	-27			
H 3 0					
1	70	68			
2	117	-104			
3	41	-34			
4	-	7*			
5	61	39			
6	68	52			
7	108	84			
8	21	17			
9	57	53			
10	64	47			
11	51	-50			
12	93	85			
13	69	-60			
14	29	31			
H 3 1					
0	78	-88			
1	62	70			
2	31	28			
3	-	13*			
4	114	93			
5	102	-90			
6	44	29			
7	28	18			
8	-	2*			
9	89	71			
10	-	12*			
11	68	62			
12	-	-1*			
13	21	15			
14	36	-43			
H 3 2					
1	56	59			
2	83	-83			
3	35	-37			
4	-	-2*			
5	-	3*			
6	46	36			
7	80	64			
8	-	-7*			
9	53	48			
10	45	30			
11	29	-30			
12	76	76			
13	43	-39			
14	24	36			
H 3 3					
0	51	-61			
1	38	44			
2	23	20			
3	-	11*			
4	91	92			
5	67	-69			
6	44	41			

7	33	28			
8	-	8*			
9	76	75			
10	-	6*			
11	56	62			
12	-	-14*			
13	12	15			
H 3 4					
1	34	41			
2	53	-62			
3	-	-15*			
4	-	-2*			
5	21	15			
6	30	35			
7	59	60			
8	-	6*			
9	34	40			
10	34	34			
11	29	-34			
12	54	69			
H 3 5					
0	33	-38			
1	26	31			
2	18	16			
3	-	6*			
4	43	52			
5	39	-52			
6	24	20			
7	-	9*			
8	-	0*			
9	42	48			
10	-	11*			
11	31	45			
H 3 6					
1	19	28			
2	32	-42			
3	-	-6*			
4	-	-3*			
5	-	14*			
6	22	26			
7	36	46			
8	-	8*			
9	24	32			
10	17	28			
H 3 7					
0	18	-24			
1	-	16*			
2	-	12*			
3	-	4*			
4	33	46			
5	24	-34			
6	21	26			
7	14	16			
H 5 0					
1	33	-42			
2	36	-46			
3	70	67			
4	-	17*			
5	108	82			
6	31	27			
7	-	-3*			
8	74	-58			
9	-	13*			
10	132	-114			
11	40	28			
12	48	-47			
13	32	-30			
H 5 1					
0	-	16*			
1	11	12			
2	32	22			
3	74	65			
4	39	-46			
5	43	-42			
6	77	56			
7	83	-59			
8	91	74			
9	-	-11*			
10	-	3*			
11	50	-44			
12	38	-36			
13	55	-60			
H 5 2					
1	48	-52			
2	50	-61			
3	55	50			
4	-	11*			
5	71	58			
6	34	31			
7	-	-5*			
8	33	-29			
9	-	17*			
10	98	-88			
11	42	41			
12	37	-35			

13	16	-17			
H 5 3					
0	23	28			
1	24	26			
2	-	18*			
3	57	57			
4	20	-28			
5	43	-36			
6	68	57			
7	74	-63			
8	72	66			
9	25	-25			
10	-	-3*			
11	42	-50			
12	33	-42			
13	35	-57			
H 5 4					
1	40	-37			
2	39	-43			
3	47	50			
4	-	13*			
5	52	53			
6	20	20			
7	-	-1*			
8	39	-38			
9	-	13*			
10	75	-85			
11	25	29			
12	25	-36			
H 5 5					
0	-	18*			
1	-	15*			
2	-	6*			
3	34	35			
4	24	-31			
5	25	-32			
6	40	41			
7	34	-38			
8	46	53			
9	-	-4*			
10	-	4*			
11	21	-31			
H 5 6					
1	24	-28			
2	27	-31			
3	29	39			
4	-	10*			
5	30	40			
6	-	15*			
7	-	0*			
8	23	-34			
9	-	11*			
H 5 7					
0	-	19*			
1	-	18*			
2	-	7*			
3	-	28*			
4	-	-16*			
5	18	-24			
6	24	37			
7	23	-37			
H 7 0					
1	67	-80			
2	111	115			
3	38	36			
4	-	-4*			
5	34	-23			
6	80	-67			
7	103	-83			
8	-	-12*			
9	36	-35			
10	24	-7			
11	70	62			
12	83	-71			
13	34	41			
H 7 1					
0	54	66			
1	46	-55			
2	41	-33			
3	16	-26			
4	132	-110			
5	111	91			
6	-	1*			
7	-	0*			
8	26	20			
9	80	-65			
10	-	-21*			
11	70	-61			
H 7 2					
1	76	-77			
2	104	105			
3	38	38			
4	-	8*			
5	-	4*			

6	62	-51			
7	80	-65			
8	-	4*			
9	34	-30			
10	-	0*			
11	43	44			
12	62	-66			
H 7 3					
0	54	54			
1	40	-41			
2	34	-25			
3	-	-25*			
4	105	-106			
5	84	72			
6	-	-13*			
7	-	-8*			
8	-	12*			
9	67	-66			
10	25	-14			
11	52	-59			
H 7 4					
1	54	-58			
2	78	79			
3	19	23			
4	-	5*			
5	-	-8*			
6	45	-47			
7	60	-62			
8	-	-5*			
9	26	-26			
10	-	-5*			
11	34	46			
H 7 5					
0	33	36			
1	27	-29			
2	20	-23			
3	-	-14*			
4	63	-69			
5	54	60			
6	-	1*			
7	-	3*			
8	-	16*			
9	42	-46			
H 7 6					
1	35	-42			
2	47	57			
3	-	14*			
4	-	5*			
5	-	-10*			
6	30	-36			
7	39	-49			
8	-	-7*			
H 7 7					
0	21	26			
1	-	-19*			
2	-	-16*			
3	-	-12*			
4	39	-58			
5	28	40			
H 9 0					
1	51	60			
2	61	59			
3	65	-67			
4	27	-26			
5	77	-62			
6	-	-12*			
7	-	5*			
8	79	71			
9	29	-15			
10	82	88			
11	40	-34			
12	-	23*			
H 9 1					
0	33	-40			
1	29	-33			
2	-	0*			
3	55	-51			
4	75	67			
5	89	72			
6	75	-60			
7	52	43			
8	96	-83			
9	-	2*			
10	-	-8*			
11	50	44			
12	35	40			
H 9 2					
1	71	67			
2	70	66			
3	58	-53			
4	25	-18			
5	62	-51			
6	-	-14*			
7	-	2*			

Table 2. Continued.

8	53	46		3	44	-46		H	9	4		5	-	-14*		5	42	49	
9	23	-20		4	53	50		1	48	48		10	43	67		6	36	-43	
10	64	67		5	65	60		2	49	47						7	23	30	
11	41	-41		6	59	-55		3	46	-47			H	9	5	8	49	-61	
				7	48	48		4	-	-16*		0	-	-22*					
	H	5	3	8	73	-72		5	48	-45		1	-	-19*			H	9	6
0	36	-41		9	-	16*		6	-	-8*		2	-	3*		1	31	35	
1	34	-35		10	-	-3*		7	-	0*		3	30	-28		2	28	33	
2	-	-4*		11	35	48		8	44	50		4	33	43		3	25	-36	

4	22	-11																	
5	31	-36																	
6	-	-5*																	

These were based on a data set consisting of 509 strong structure factors with $k=2n$ and 313 weak structure factors with $k=2n+1$. Mean values of F_{hkl} and $F_{\bar{h}kl}$ for $k=2n$ were used, those reflexions that did not occur twice being eliminated. Positional parameters, including isotropic temperature factors, and layer scale factors were refined, only one of the four oxygen atoms O_7-O_{10} being refined at a time. These four oxygen atoms were refined alternately until the shifts were negligible. This method of refinement was necessary owing to coupling between the x and y parameters of O_7-O_{10}. Cruickshank's weighting scheme was used, and the refinement yielded a final R value of 0.061. The final R factor based on the strong structure factors was 0.046, while that based on the weak structure factors was 0.158.

No correction was made for anomalous dispersion since the data set consisted partly of reflexions obtained with copper and partly of reflexions obtained with molybdenum radiation.

The positional parameters were also refined with all atoms occupying the general position 4(*c*) in space group *Pnn*2. After several cycles of refinement, the parameter shifts had still not converged. The space group *Pnnm* was therefore considered to be the correct one.

Table 3. Atomic coordinates, expressed as fractions of the cell edges, and isotropic thermal parameters in Å². Standard deviations are given within brackets.

Atom	Occ. number	x	y	z	B
Hf_1	1	0.0505(1)	0.1246(3)	0	0.95(2)
Hf_2	1	0.0421(1)	0.6269(3)	0	0.88(2)
Cr_1	1	0.3716(5)	0.1608(6)	0	1.1(1)
Cr_2	1	0.3622(5)	0.5910(6)	0	1.1(1)
Cr_3	0.14	0.191(3)	0.872(5)	0	1.2(6)
O_1	1	0.068(1)	0.134(2)	0.304(2)	1.3(3)
O_2	1	0.049(1)	0.628(3)	0.303(3)	1.7(3)
O_3	1	0.243(2)	0.110(2)	0	0.6(3)
O_4	1	0.227(2)	0.637(3)	0	1.5(4)
O_5	1	0.354(3)	0.276(3)	0	2.8(7)
O_6	1	0.351(4)	0.476(4)	0	4.4(11)
O_7	1	0.107(2)	0.271(2)	0	1.6(4)
O_8	1	0.089(2)	0.775(2)	0	1.7(5)
O_9	1	0.092(3)	0.963(2)	0	1.9(5)
O_{10}	1	0.093(3)	0.467(2)	0	1.9(5)
O_{11}	0.14	0.282(12)	0.868(16)	0.184(22)	2.2(23)
O_{12}	0.86	−0.305(5)	0.122(5)	0	5.6(13)

Table 4. Distances (Å) and angles (°) in $\sim Hf_4(OH)_8(CrO_4)_4.H_2O$. Standard deviations are given within parentheses.

Within the HfO_7 pentagonal bipyramids:				
axial oxygen atoms:	Hf_1-2O_1	2.10(2)	Hf_2-2O_2	2.08(2)
equatorial oxygen atoms:	Hf_1-O_3	2.24(2)	Hf_2-O_4	2.13(3)
	Hf_1-O_7	2.09(3)	Hf_2-O_7	2.21(3)
	Hf_1-O_8	2.12(3)	Hf_2-O_8	2.08(3)
	Hf_1-O_9	2.25(3)	Hf_2-O_{10}	2.25(3)
	Hf_1-O_9'	2.03(3)	Hf_2-O_{10}'	2.01(3)
	$O_1-Hf_1-O_1$	167(1)	$O_2-Hf_2-O_2$	176(1)
	$O_3-Hf_1-O_7$	77(1)	$O_4-Hf_2-O_8$	71(1)
	$O_7-Hf_1-O_8$	68(1)	$O_8-Hf_2-O_7$	66(1)
	$O_8-Hf_1-O_9'$	76(1)	$O_7-Hf_2-O_{10}$	78(1)
	$O_9'-Hf_1-O_9$	66(1)	$O_{10}-Hf_2-O_{10}'$	66(1)
	$O_9-Hf_1-O_3$	73(1)	$O_{10}'-Hf_2-O_4$	78(1)
ax.–eq.:	O_1-O_3	2.92(2)	O_2-O_4	2.92(3)
	O_1-O_7	2.82(3)	O_2-O_7	3.07(3)
	O_1-O_8	3.03(3)	O_2-O_8	2.92(4)
	O_1-O_9	3.13(4)	O_2-O_{10}	3.06(4)
	O_1-O_9'	3.08(3)	O_2-O_{10}'	2.94(3)
eq.–eq.:	O_3-O_7	2.70(4)	O_4-O_8	2.46(5)
	O_7-O_8	2.34(4)	O_8-O_7	2.34(4)
	O_8-O_9'	2.56(5)	O_7-O_{10}'	2.67(5)
	$O_9'-O_9$	2.34(6)	$O_{10}'-O_{10}$	2.33(6)
	O_9-O_3	2.65(4)	$O_{10}-O_4$	2.78(5)
Within the CrO_4 tetrahedra sharing vertices with HfO_7:				
	Cr_1-2O_2	1.69(2)	Cr_2-2O_1	1.67(2)
	Cr_1-O_3	1.63(2)	Cr_2-O_4	1.68(3)
	Cr_1-O_5	1.57(4)	Cr_2-O_6	1.56(5)
	$O_2-Cr_1-O_2$	106(1)	$O_1-Cr_2-O_1$	107(1)
	$O_2-Cr_1-O_3$	112(1)	$O_1-Cr_2-O_4$	108(1)
	$O_3-Cr_1-O_5$	108(2)	$O_4-Cr_2-O_6$	107(2)
	$O_5-Cr_1-O_2$	109(1)	$O_6-Cr_2-O_1$	113(1)
Within the CrO_4 tetrahedra sharing an edge with HfO_7:				
	Cr_3-O_8	1.78(6)	$O_8-Cr_3-O_9$	95(2)
	Cr_3-O_9	1.69(6)	$O_9-Cr_3-O_{11}$	118(7)
	Cr_3-2O_{11}	1.64(15)	$O_{11}-Cr_3-O_8$	113(7)
			$O_{11}-Cr_3-O_{11}$	101(10)
Other distances:				
	$O_{12}(H_2O)-O_8$	2.86(7)	Hf_1-Hf_1	3.581(9)
	$O_{12}(H_2O)-O_9'$	2.71(7)	Hf_1-Hf_2	3.542(8)
			Hf_2-Hf_2	3.583(9)

The observed and calculated structure factors together with those corresponding to the unobserved $k=2n+1$ reflexions are listed in Table 2. The atomic positions and their standard deviations are given in Table 3.

DESCRIPTION OF THE STRUCTURE

$4HfO_2.4.3CrO_3.5.4H_2O$ is isomorphous with $4ZrO_2.4.9CrO_3.3.7H_2O$ apart from the different Cr_3 chromate and water contents. The most important distances and angles are given in Table 4. To facilitate a comparison between the structures of the zirconium and hafnium chromates the labelling of the atoms and the lay-out of the table are the same as for $4ZrO_2.4.9CrO_3.3.7H_2O$.

The hafnium atoms are joined by double hydroxide bridges involving the oxygen atoms $O_7 - O_{10}$. Planar infinite chains of composition $[Hf(OH)_2]_n^{2n+}$, running parallel to the y axis, are thus formed. In addition, there are three oxygen atoms from three different chromate groups coordinated to each hafnium atom. All the hafnium atoms are thus seven coordinated the oxygen atoms being situated at the vertices of distorted pentagonal bipyramids. The chromate groups Cr_1 and Cr_2 each share three vertices with three HfO_7 polyhedra belonging to different chains. The chains are thus connected in the x and z directions to form a three-dimensional network. The structure described has the composition $4HfO_2.4CrO_3.6H_2O$ if the two water molecules of crystallization are taken into account. The additional chromate groups, corresponding to the Cr_3 atoms, are situated in the same holes in the structure as the water molecules, though not simultaneously. Each CrO_4^{2-} entering such a hole expels $2OH^-$ in the $[Hf(OH)_2]_n^{2n+}$ chain and thus shares one tetrahedron edge with a pentagonal bipyramid. The occupation number of O_{12}, as deduced from the Fourier synthesis, is very nearly 1 and the compound can therefore be formulated as $4HfO_2.(4+x)CrO_3.(6-2x)H_2O$. The x value may vary between 0 and 2 without changing the structure, since $Z = 2$. For this crystal x was found to be 0.28.

In Fig. 1, approximately one formula unit of the structure is depicted in perspective with distances given in Å. The Hf – Hf distances are on an average 3.56_2 Å and are significantly shorter than the average Zr – Zr distance

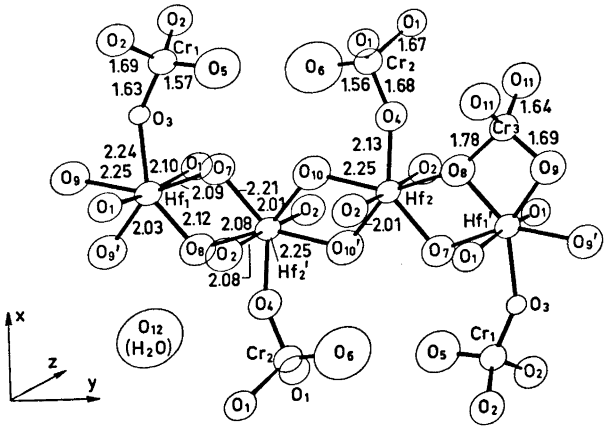

Fig. 1. One approximate formula unit of $4HfO_2.4.3CrO_3.5.4H_2O$ shown in perspective. The thermal motions are outlined as spheres and the distances are given in Å.

(3.597 Å) in zirconium chromate. Assuming that the O – Me – O angles in the Me – $(OH)_2$ bridges are not altered, the short Hf – Hf distance results in a displacement of the bridging oxygen atoms in opposite directions in order to avoid too close an oxygen-oxygen contact. The Hf – O distances are hence alternately short and long, as can be seen from Table 4 and Fig. 1.

Since the structure is held together by chromate groups, there may be structural constraints on the chains due, for example, to the close contact (2.73 Å) between the chromate oxygen atoms O_5 and O_6. However, due to experimental difficulties, the results obtained do not permit a more detailed comparison between this hafnium chromate and the structures of other similar zirconium and hafnium compounds.

Acknowledgements. The authors thank Professor Georg Lundgren for his interest in this work. Thanks are also due to Dr. Susan Jagner for revising the English text.

The work has been supported financially by the *Swedish Natural Science Research Council* (NFR, Contract No. 2318).

REFERENCES

1. McWhan, D. B. and Lundgren, G. *Inorg. Chem.* **5** (1966) 284.
2. Hansson, M. *Acta Chem. Scand. To be published.*
3. Mark, W. *Acta Chem. Scand.* **27** (1973) 177.
4. Lindqvist, O. and Wengelin, F. *Arkiv Kemi* **28** (1967) 179.
5. *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham 1962, Vol. III, p. 122.
6. The program library of the Dept. of Inorg. Chem. Göteborg. DATAP1 and BLOCK have been written locally by O. Lindgren, DATAP2 was originally written by Coppens, Leiserowitz and Rabinowich (1965), DRF by A. Zalkin, Berkeley, California, and LALS by P. Gantzel, R. Sparks and K. Trueblood.

Received June 19, 1973.