The Crystal Structure of $Hf_{18}O_{10}(OH)_{26}(SO_4)_{13}(H_2O)_{33}$

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$Hf_{18}O_{10}(OH)_{26}(SO_4)_{13}(H_2O)_{33}$ crystallizes in space group $P6_3/m$ (No. 176) with $a=b=34\cdot09$ (2), $c=17\cdot664$ (7) Å, $Z=6$. The positions of the Hf atoms were deduced by direct methods and the lighter atoms from successive Fourier calculations. The determination was based on 2240 observed Weissenberg intensities and refined to an R of $0\cdot075$. Aggregates with the composition $Hf_{18}O_{10}(OH)_{26}(SO_4)_{13}(H_2O)_{20}$ constitute the building units of the structure, which is held together in the z direction by sulphate groups and by hydrogen-bonded water molecules. The Hf atoms are coordinated to seven or eight O atoms in such a way that each Hf atom is linked to 2,3,4 or 7 neighbouring Hf atoms by double oxygen bridges. The polyhedra formed by the coordinated O atoms are, for eight coordination, either dodecahedra or square antiprisms, and for seven-coordination, capped trigonal prisms.

Introduction

The determination of $Hf_{18}O_{10}(OH)_{26}(SO_4)_{13}(H_2O)_{33}$ forms part of a systematic investigation of crystalline basic phases appearing in the two systems $Zr(Hf)O_2-SO_3-H_2O$ (McWhan & Lundgren, 1966; Hansson, 1969, 1973*a, b*; Hansson, Lundgren & McWhan; to be published) and $Zr(Hf)O_2-CrO_3-H_2O$ (Mark, 1972, 1973; Hansson & Mark, 1973).

The aim of the investigation is to establish the effects of variations in acidity and temperature on the polynuclear species formed by hydrothermal hydrolysis. The degree of polymerization and the coordination of atoms around the metal ions have been subjects of special interest as well as the differences in the chemical behaviour and the coordination distances.

Preparation and analyses

The products in the system $HfO_2-SO_3-H_2O$ were prepared by hydrothermal hydrolysis of a solution obtained in the following way. Pure HfO_2 (99·8 %) was dissolved in boiling concentrated H_2SO_4 and the solution was evaporated to dryness. The residues were dissolved in water or dilute H_2SO_4 with a molarity varying between 0·1 and 10 *M*. By keeping the solutions at different temperatures in the range 0–350° C during the hydrolysis, more than 100 samples were obtained, most of which were amorphous or unstable.

The preparation of the compound presented in this paper has been reported earlier (Hansson & Lundgren, 1968). Samples showing identical Guinier powder photographs with this compound were synthesized by hydrolysis in water or in 0·1 *M* H_2SO_4 in the temperature range 75–100° C.

The proposed composition of the present compound, which can also be written $18HfO_2.13SO_3.46H_2O$, is based on the thermogravimetric determination of the

SO$_3$ and H$_2$O contents as well as on the structure determination. As the crystals effloresce in air and some of the water molecules are loosely bound in the structure, the water analysis is not very accurate. The analyses were performed on a Mettler recording thermoanalyser, which yielded the following results (heating rate $6°\text{min}^{-1}$):

	%SO$_3$	%H$_2$O
Found	18·5	14·4
Calculated for		
$18HfO_2.13SO_3.46H_2O$	18·4	14·7

The removal of H$_2$O took place in the temperature range 50–650° C, while SO$_3$ evaporated between 740 and 830° C.

Crystal data

Weissenberg and precession photographs taken with Cu $K\alpha$ radiation showed that the crystals had hexagonal symmetry, belonging to the Laue group $6/m$. Since the only systematically absent reflexions are $00l$ with $l=2n+1$ the space group is either $P6_3$ (No. 173) or $P6_3/m$ (No. 176).

The cell dimensions determined from Guinier powder photographs (Hansson & Lundgren, 1968), are: $a=b=34\cdot09$ (2), $c=17\cdot664$ (7) Å, $V=1\cdot775\times10^4$ Å^3.

The same authors determined the density by flotation which gave values between 3·07 and 3·30 g cm^{-3} with a mean of 3·19 g cm^{-3}. This indicates six formula units of $18HfO_2.13SO_3.46H_2O$ ($\varrho_c=3\cdot19$ g cm^{-3}) in the cell, corresponding to 108 Hf atoms per cell. The lower and higher limits of the observed density would correspond to 104 and 112 Hf atoms per cell, respectively. The structure determination is consistent with 108 Hf atoms.

The crystal used for data collection was mounted in a sealed capillary along the c axis. Weissenberg photographs were taken for $hk0-hk9$ with Cu $K\alpha$ ra-

diation, and 2240 independent reflexions were measured visually. The intensities were not corrected for absorption.

Structure determination and refinement

Owing to the large unit cell it was impossible to resolve the different Hf–Hf vectors in a Patterson map. Efforts were made, therefore, to solve the structure by direct methods.

The data set used in the determination consisted of 2240 observed and 1259 unobserved reflexions within the limits $0 < 2\theta < 45°$. The absolute scale was determined by a Wilson plot (Wilson, 1942) and normalized structure factors were calculated (Karle & Karle, 1966). The $|E|$ statistics are given in Table 1. A centrosymmetric structure is indicated, although, since the data set consisted of independent reflexions only, there is a slight ambiguity. Since the space group $P6_3$ is noncentrosymmetric $P6_3/m$ was used in the subsequent calculations.

Table 1. *Statistics for the normalized structure factors and the basic set in the structure determination*

	Experimental	Theoretical Centric	Theoretical Acentric
$\langle|E|\rangle$	0·84	0·80	0·89
$\langle|E^2-1|\rangle$	0·83	0·97	0·74
$\langle|E|^2\rangle$	1·00	1·00	1·00
$|E|>1$	30·67	31·73	36·79
$|E|>2$	3·29	4·55	1·83
$|E|>3$	0·23	0·27	0·01

Basic set

h	k	l	E	
7	6	1	3·29	⎫
13	5	6	3·13	⎬ Defining origin
3	7	4	3·09	⎭
9	10	4	−2·98	
19	7	1	−2·97	
3	13	6	2·84	
22	7	1	2·76	
6	10	5	−2·75	
2	24	5	−2·73	

$\langle|E|\rangle^2$ was normalized to 1·00 and the 366 reflexions with $|E| > 1·5$ were used in listing the phase-determining $\sum_2$ relationship. The signs of 357 reflexions were determined with the $\sum_2$ summation. A basic set of nine reflexions (Table 1) with their signs obtained by the symbolic addition procedure was used as a start.

E maps from Fourier summation of the 357 *E* values showed peaks, corresponding to all 108 Hf atoms, and satisfying the metal–metal distance criterion of 3·4–3·6 Å. The Hf parameters were refined to an R of 0·177, and the unit cell turned out to consist of six separate clusters each containing 18 Hf atoms. Subsequent Fourier calculations successively revealed the remaining light atoms. The atoms are situated either in the general position 12(i) or in 6(h) $(x,y,\frac{1}{4})$ of $P6_3/m$.

Peaks corresponding to 216 O atoms coordinated to two, three or four different Hf atoms were obtained

from difference maps. These O atoms constitute double oxygen bridges which link the Hf atoms to form aggregates, each composed of 18 Hf and 36 O atoms. In Fig. 1 such a framework of the structure is shown in perspective. It can be seen that this part of the structure has an additional mirror plane perpendicular to xy which would result in the symmetry of space group $P6_3/mcm$.

Moreover, the positions of 72 S atoms at appropriate distances from the Hf atoms could be deduced and also 288 O atoms coordinated to S, each aggregate of 18 Hf thus containing 12SO_4 groups. An empirical formula $3HfO_2.2SO_3.xH_2O$ would be in accordance with these results. Some of the S-coordinated O atoms are also coordinated to Hf but in no case to two different Hf atoms. One peak in the Fourier maps with the same electron density as the O atoms could not, owing to too short distances to the neighbouring atoms O(18) and O(32), be explained as an O atom. When it was taken into account in the refinement as an S atom [S(9)] with the occupation number 0·5, R decreased markedly and the atomic parameters converged. The contribution of the statistically distributed S(9) and its coordinated oxygens O(62) and O(63) gives the aggregate the more complicated composition $18HfO_2.13SO_3.yH_2O$. Also, the SO_4 groups have no mirror plane perpendicular to xy and hence the symmetry of $P6_3/m$ is correct for the total structure.

Additional O atoms (132) were located, which were coordinated to one Hf atom only, and were presumably O atoms of H_2O molecules. The composition of the cluster could thus be written $18HfO_2.13SO_3.33H_2O$ or, more consistent with the actual structure, $Hf_{18}O_{10}(OH)_{26}(SO_4)_{13}(H_2O)_{20}$. This formulation assumes that O atoms coordinated to only one Hf are O atoms of H_2O molecules, that those coordinated to two Hf are OH^-, while some of those coordinated to three Hf are OH^- and some are O^{2-} and those coordinated to four Hf are O^{2-}.

Finally, the H_2O molecules of crystallization between the clusters could be found in the difference maps. Their O atoms are denoted O(101)–O(108) and yield 13 waters of crystallization per aggregate. The total composition of one cluster is thus $18HfO_2.13SO_3.46H_2O$ or $Hf_{18}O_{10}(OH)_{26}(SO_4)_{13}(H_2O)_{33}$. Some of these atoms, *i.e.* O(103) and O(108), have high temperature factors, which might indicate an occupation number less than 1·0, and thus statistically distributed water molecules. Owing to the low accuracy of the data compared with the large number of light atoms, it was not considered profitable to try different occupation numbers in the refinement. Moreover, the H_2O molecules between the clusters are probably loosely bound in the structure, since evaporation starts at a low temperature.

Refinement of the atomic parameters, including isotropic temperature factors, was performed with the least-squares block-diagonal approximation. The structure factors were weighted according to Hughes (1941)

which gave the weighting scheme shown in Table 2. The scattering factors were those given by Cromer & Waber (1965) for Hf, by Doyle & Turner (1968) for S and in *International Tables for X-ray Crystallography* for O. The Hf and S scattering factors were corrected for the real part of the anomalous dispersion according to Cromer (1965). The final R was 0·075 for the 2240 observed reflexions and 0·161 including the non-observed reflexions ($\sum 3349$). A difference synthesis gave a maximum residual electron density of 2·2 e Å^{-3}.

Table 2. *Weight analysis after the final cycle of refinement*

The quantities $w\Delta^2$ are normalized sums, $K_{norm} \cdot (\sum w|F_o - |F_c||^2)$ and the number of reflexions within each F_o interval is 224.

F_o interval	$w\Delta^2$	F_o interval	$w\Delta^2$
0–254	0·71	411–477	1·14
254–295	1·22	477–554	0·91
295–333	0·87	554–648	1·06
333–367	0·66	648–802	1·05
367–411	0·69	802–	1·68

Table 3. *Atomic coordinates and isotropic thermal parameters in* Å^2 *for* $Hf_{18}O_{10}(OH)_{26}(SO_4)_{13}(H_2O)_{33}$

O(101)–O(108) are oxygen atoms of water molecules of crystallization. (Standard deviations are given in parentheses.)

	x	y	z	B
Hf(1)	0·08517 (10)	0·40546 (12)	0·35046 (23)	1·69 (8)
Hf(2)	0·11547 (10)	0·31801 (12)	0·34904 (23)	1·77 (8)
Hf(3)	0·18162 (10)	0·26398 (12)	0·35432 (25)	1·94 (8)
Hf(4)	0·18144 (15)	0·42117 (17)	$\frac{1}{4}$	1·56 (11)
Hf(5)	0·07879 (15)	0·21755 (18)	$\frac{1}{4}$	1·88 (11)
Hf(6)	0·02433 (15)	0·30629 (17)	$\frac{1}{4}$	1·68 (11)
Hf(7)	0·14315 (11)	0·48318 (12)	0·50835 (24)	1·96 (8)
Hf(8)	0·19246 (11)	0·34126 (12)	0·50845 (25)	1·99 (8)
Hf(9)	0·00774 (15)	0·42024 (17)	$\frac{1}{4}$	1·71 (11)
Hf(10)	0·09025 (11)	0·51315 (12)	0·35448 (25)	2·03 (8)
Hf(11)	0·23089 (11)	0·45797 (13)	0·55534 (29)	2·09 (8)
S(1)	0·2845 (6)	0·3408 (7)	0·4392 (13)	2·8 (5)
S(2)	−0·0223 (7)	0·4554 (8)	0·4059 (15)	4·2 (6)
S(3)	0·0087 (5)	0·2267 (6)	0·3755 (13)	1·8 (4)
S(4)	−0·0782 (9)	0·3090 (11)	$\frac{1}{4}$	3·7 (8)
S(5)	0·2132 (12)	0·4489 (14)	$\frac{3}{4}$	6·4 (11)
S(6)	0·2342 (8)	0·5211 (9)	$\frac{1}{4}$	2·2 (6)
S(7)	0·1943 (7)	0·5925 (8)	0·4373 (16)	4·8 (6)
S(8)	0·2702 (11)	0·4246 (13)	$\frac{1}{4}$	5·3 (9)
S(9)	0·0972 (11)	0·1569 (13)	0·3900 (24)	2·3 (9)*
O(1)	0·1484 (17)	0·3498 (20)	$\frac{1}{4}$	1 (1)
O(2)	0·0359 (16)	0·3766 (18)	$\frac{1}{4}$	1 (1)
O(3)	0·1223 (17)	0·4273 (20)	$\frac{1}{4}$	1 (1)
O(4)	0·1249 (19)	0·5231 (22)	$\frac{1}{4}$	2 (2)
O(5)	0·0457 (22)	0·5011 (25)	$\frac{1}{4}$	4 (2)
O(6)	0·1777 (27)	0·4606 (31)	$\frac{3}{4}$	6 (2)
O(7)	0·1487 (17)	0·2169 (19)	$\frac{1}{4}$	1 (1)
O(8)	0·0723 (17)	0·2791 (20)	$\frac{1}{4}$	1 (1)
O(9)	0·2090 (20)	0·2969 (23)	$\frac{1}{4}$	3 (2)
O(10)	−0·0554 (26)	0·3562 (30)	$\frac{1}{4}$	6 (2)
O(11)	0·2793 (41)	0·3834 (48)	$\frac{1}{4}$	13 (4)
O(12)	0·2833 (30)	0·5479 (35)	$\frac{1}{4}$	8 (3)
O(13)	0·1902 (25)	0·3943 (30)	$\frac{3}{4}$	5 (2)
O(14)	−0·0436 (23)	0·2917 (27)	$\frac{1}{4}$	4 (2)
O(15)	0·2163 (28)	0·5538 (33)	$\frac{1}{4}$	7 (3)
O(16)	0·3129 (39)	0·4688 (44)	$\frac{1}{4}$	11 (4)
O(17)	0·0543 (12)	0·2631 (14)	0·4122 (27)	1 (1)
O(18)	0·1430 (13)	0·1989 (15)	0·4084 (30)	2 (1)
O(19)	0·0640 (11)	0·3354 (13)	0·3375 (23)	1 (1)
O(20)	0·0992 (12)	0·4130 (14)	0·4671 (28)	1 (1)
O(21)	0·2904 (13)	0·3134 (15)	0·4977 (28)	2 (1)
O(22)	0·2013 (16)	0·4798 (18)	0·4682 (35)	4 (1)
O(23)	0·0940 (11)	0·5005 (13)	0·4726 (28)	1 (1)
O(24)	−0·0196 (14)	0·2002 (16)	0·4328 (32)	3 (1)
O(25)	0·1855 (11)	0·3327 (12)	0·3814 (25)	0 (1)
O(26)	0·2279 (15)	0·3270 (17)	0·6033 (30)	3 (1)
O(27)	−0·0112 (11)	0·2481 (13)	0·3288 (25)	1 (1)
O(28)	0·0495 (12)	0·4410 (14)	0·3282 (27)	1 (1)
O(29)	0·0828 (15)	0·5756 (18)	0·3459 (32)	4 (1)
O(30)	0·1195 (13)	0·2596 (15)	0·3314 (28)	2 (1)
O(31)	0·2173 (17)	0·2270 (19)	0·3486 (35)	5 (2)
O(32)	0·0654 (17)	0·1600 (20)	0·3214 (41)	5 (2)
O(33)	−0·0186 (17)	0·4253 (19)	0·4643 (37)	5 (1)
O(34)	0·2574 (13)	0·3132 (15)	0·3776 (30)	2 (1)

Table 3 (cont.)

O(35)	0·1579 (15)	0·5729 (17)	0·3748 (36)	4 (1)
O(36)	0·0214 (14)	0·1997 (16)	0·3254 (32)	3 (1)
O(37)	0·1540 (12)	0·4002 (14)	0·3602 (30)	2 (1)
O(38)	0·2372 (15)	0·4214 (18)	0·3192 (38)	4 (1)
O(39)	0·1812 (16)	0·6205 (18)	0·4983 (34)	4 (1)
O(40)	0·1292 (12)	0·3311 (14)	0·4663 (28)	1 (1)
O(41)	0·1793 (15)	0·2727 (18)	0·4697 (35)	4 (1)
O(42)	0·2649 (15)	0·3671 (17)	0·4718 (34)	4 (1)
O(43)	0·2228 (15)	0·4126 (17)	0·4632 (33)	4 (1)
O(44)	0·0133 (14)	0·3682 (16)	0·4117 (32)	3 (1)
O(45)	0·0225 (16)	0·4992 (18)	0·4056 (34)	4 (1)
O(46)	0·1403 (20)	0·2952 (23)	0·5965 (40)	7 (2)
O(47)	0·2921 (13)	0·4535 (14)	0·5916 (28)	2 (1)
O(48)	0·1695 (15)	0·4539 (18)	0·5922 (34)	4 (1)
O(49)	−0·0559 (19)	0·4683 (22)	0·4212 (45)	7 (2)
O(50)	0·1373 (12)	0·4835 (14)	0·3877 (25)	1 (1)
O(51)	0·2186 (13)	0·4897 (15)	0·3206 (33)	2 (1)
O(52)	−0·0341 (13)	0·4330 (15)	0·3277 (30)	2 (1)
O(53)	0·2916 (18)	0·4977 (20)	0·4628 (39)	6 (2)
O(54)	0·3285 (16)	0·3751 (19)	0·4059 (34)	4 (1)
O(55)	0·1992 (12)	0·3875 (13)	0·5971 (25)	1 (1)
O(56)	0·0939 (24)	0·4564 (28)	0·6048 (47)	9 (2)
O(57)	0·2677 (15)	0·5302 (17)	0·5941 (32)	3 (1)
O(58)	0·2386 (16)	0·6159 (19)	0·3961 (33)	4 (1)
O(59)	−0·1007 (18)	0·2936 (22)	0·1788 (44)	6 (2)
O(60)	0·2349 (14)	0·4639 (15)	0·6688 (29)	2 (1)
O(61)	0·1927 (17)	0·5524 (20)	0·4813 (38)	5 (1)
O(62)	0·0606 (40)	0·1529 (44)	0·4749 (88)	7 (4)*
O(63)	0·0919 (29)	0·1168 (33)	0·3902 (60)	3 (3)*
O(101)	0·3471 (24)	0·3685 (27)	$\frac{1}{4}$	5 (2)
O(102)	0·1607 (23)	0·2761 (27)	$\frac{1}{4}$	4 (2)
O(103)	0·0086 (38)	0·4647 (44)	$\frac{3}{4}$	11 (4)
O(104)	0·0678 (16)	0·3338 (19)	0·5562 (34)	4 (1)
O(105)	0·0610 (22)	0·2240 (25)	0·5521 (43)	8 (2)
O(106)	−0·0033 (21)	0·4217 (24)	0·6065 (42)	7 (2)
O(107)	0·2983 (24)	0·5961 (29)	0·4779 (52)	10 (2)
O(108)	0·1091 (32)	0·6374 (37)	0·4850 (66)	16 (4)

* Occupation number 0·5

The highest peak obtained could not be explained as the O atom of a statistically distributed H_2O molecule, owing to improbable O–O distances.

The final atomic parameters are listed in Table 3.*

All calculations were performed on an IBM 360/65 computer with the program library of the Department of Inorganic Chemistry, Göteborg. DATAP2 (data reduction) was originally written by Coppens, Leiserowitz & Rabinovich (1965), GAASA I–V ('direct methods') by Lindgren, Lindqvist & Nyborg (1970) and BLOCK by Lindgren, while DRF (Fourier) and DISTAN were written by Zalkin, Berkeley, California.

Description of the structure

The unit cell contains six aggregates of hydrolysed Hf and SO_4 ions with the composition $Hf_{18}O_{10}(OH)_{26}(SO_4)_{13}(H_2O)_{20}$. The Hf arrangement is most easily interpreted from Fig. 2 which shows the ar-

rangement of Hf and S only. A ring of ten Hf [2Hf(3), 2Hf(8), 2Hf(11), 2Hf(7), 2Hf(10)], joined by double oxide or hydroxide bridges, encircles the remaining eight Hf. The ring is folded along a line Hf(11)–Hf(11) so that two planes are formed at an angle of ~120°. The angles within this ten-ring are given in Table 4. In the middle of the ring, there are six Hf [2Hf(1), 2Hf(2), Hf(4), Hf(6)] arranged very nearly as an ideal octahedron. Hf(5) and Hf(9) are part of the Hf skeleton and form square pyramids with 2Hf(2), 2Hf(3) and 2Hf(1), 2Hf(10), respectively.

Table 4. Angles within the ten-membered Hf ring constituting part of each cluster

Hf(3)—Hf(3)—Hf(8)	137·77 (9)°
Hf(3)—Hf(8)—Hf(11)	144·21 (15)
Hf(7)—Hf(11)—Hf(8)	108·88 (12)
Hf(7)—Hf(10)–Hf(10)	137·64 (9)
Hf(10)–Hf(7)—Hf(11)	144·95 (15)

Each Hf is connected to 2, 3, 4 or 7 other Hf by double oxygen bridges, some of which are O^{2-} and some OH^-. In Fig. 1 an aggregate is shown, only those O atoms which bridge the Hf being outlined. The central part of this Hf–O aggregate has a fluorite-like

type of structure, although the rows of close-packed O atoms are bent.

The coordination number of Hf is either 7 or 8. For Hf(1), Hf(2), Hf(3), Hf(8) and Hf(10) the eight-coordinated O atoms are arranged dodecahedrally (Fig. 3) and for Hf(4), Hf(5) and Hf(11) they form square antiprisms. The different sites and edges are labelled according to Hoard & Silverton (1963) in Fig. 3. For the seven-coordinated Hf(6) and Hf(9) the coordination polyhedra are capped trigonal prisms. Hf(7) is also coordinated to seven O atoms, but, in this case these occupy seven corners of a square antiprism. One of its O atoms, O(56), has higher standard deviations than the remainder and, moreover, there is a peak in the difference map corresponding to the eighth corner of an antiprism. However, the parameters of an O atom in this position gave very high standard deviations in the refinement and this possibility was therefore discarded. There is, however, a possibility that the O coordination of Hf(7) is not always the same.

Most SO$_4$ groups share two corners with two different Hf polyhedra [S(1), S(2), S(4), S(5), S(7), S(9)]. In Fig. 2 the Hf–S lines indicate single oxide bridges, whereas the lines between the Hf atoms denote double oxygen bridges. The same is true for S(3), which shares three O atoms with three different Hf atoms [Hf(2), Hf(5), Hf(6)]. The SO$_4$ groups corresponding to S(6) and S(8) are, on the other hand, connected to Hf(4) by the sharing of an edge.

In Fig. 4, one cluster is outlined schematically, viewed along c, with the Hf coordination polyhedra denoted. Table 5 gives the Hf–O and S–O coordination distances and also the average Hf–Hf distance. The O–O distances within the different polyhedra are shown in Table 6.

Infinite rows of condensed clusters are formed in the c direction since the SO$_4$ groups [S(5), O(6), O(13), $2 \times$ O(60)] are shared between two clusters. H$_2$O molecules [O(101)–O(108)] are situated between the clusters, giving the total empirical formula 18HfO$_2$.13SO$_3$.46H$_2$O. O(101) and O(103)–O(106) have typical hydrogen-bond distances to O atoms in one cluster and O(103)–O(106) also have somewhat longer distances to O atoms in symmetry-related clus-
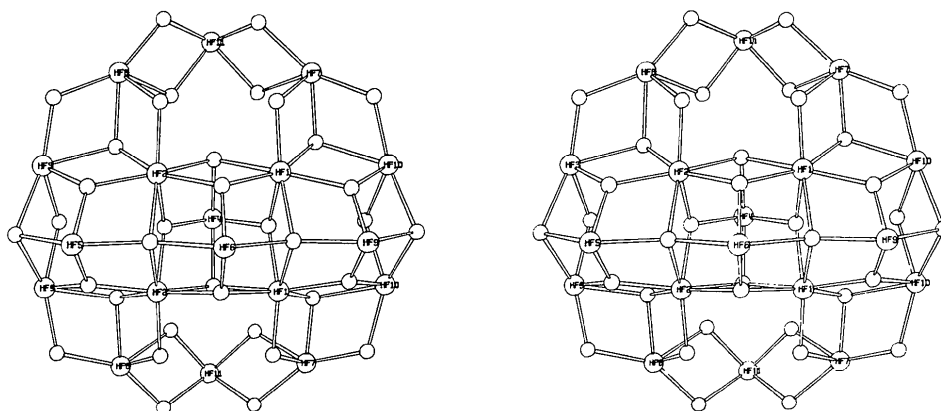

Fig. 1. Stereoscopic picture of the Hf–O framework of a cluster in Hf$_{18}$O$_{10}$(OH)$_{26}$(SO$_4$)$_{13}$(H$_2$O)$_{33}$.
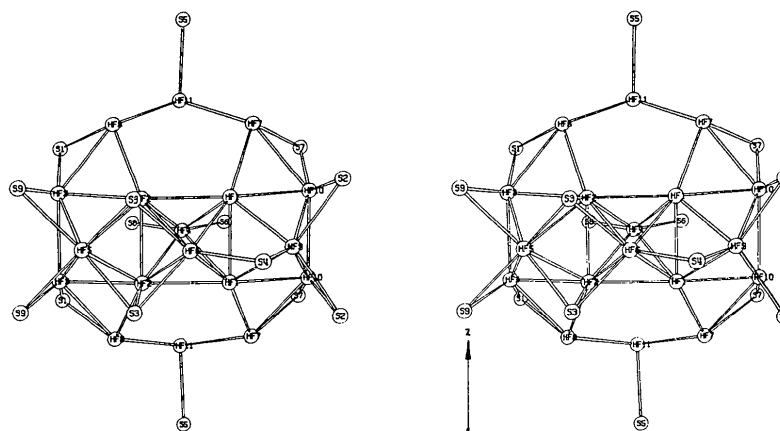
Fig. 2. Stereoscopic view of the mutually connected Hf and S atoms in a cluster of Hf$_{18}$O$_{10}$(OH)$_{26}$(SO$_4$)$_{13}$(H$_2$O)$_{33}$. Double oxygen bridges between the Hf atoms are replaced by straight lines.

ters. The O–O distances for the water O atoms are listed in Table 7. It can be seen that the clusters are held together by weak hydrogen bonds from the H_2O of crystallization and most firmly by O(106).

Discussion

Structures determined so far in the two systems $Zr(Hf)O_2$–SO_3–H_2O and $Zr(Hf)O_2$–CrO_3–H_2O are all very closely related. The building units in these structures are Zr(Hf)–O chains linked by SO_4 or CrO_4 groups. In the structure of $Zr(OH)_2CrO_4$ (Mark, 1972), which is obtained at lower acidity than the other chromate compounds, the chains are condensed perpendicular to each other to form infinite nets. The structure of $Hf_{18}O_{10}(OH)_{26}(SO_4)_{13}(H_2O)_{33}$ is therefore unique regarding the condensation of Hf atoms. It fits well with the theory that more highly polymerized species are formed at low acidities. Clearfield & Vaughan (1956) have found tetranuclear species of $Zr_4(OH)_8(H_2O)_{16}^{8+}$ in $ZrOCl_2(H_2O)_8$ and $ZrOBr_2(H_2O)_8$. Studies of Zr^{IV} and Hf^{IV} in aqueous solutions were undertaken by Kraus & Johnson (1953), Johnson & Kraus (1956) and Clearfield (1964). The authors came to the conclusion that the degree of polymerization lies between three and four in HCl and $HClO_4$ media of 0.2–$2.0 M$ and increases rapidly as the acid concentration decreases below $0.2 M$. It would therefore be of interest to study the solution from which the investigated compound is synthesized in order to ascertain which kind of polynuclear species exists in solution.

Owing to the difficulty in obtaining low standard deviations of the O atomic positions, the main purpose of this work has been to establish unambiguously the configuration of this unusual complex rather than to obtain accurate interatomic distances. A brief discussion of the different distances will, however, be given with reference to a paper on eight-coordination by Hoard & Silverton (1963).

By comparing pairs of isostructural compounds as for example $Zr(OH)_2SO_4$, $Hf(OH)_2SO_4$ (Hansson, 1973a, b) and $Zr_4(OH)_6(CrO_4)_5H_2O$ (Mark, 1973), $Hf_4(OH)_8$ $(CrO_4)_4H_2O$ (Hansson & Mark, 1973) Hf has been seen to have slightly shorter coordination distances to O than has Zr. The mean Hf–O distances in the dodecahedra of $Hf_{18}O_{10}(OH)_{26}(SO_4)_{13}(H_2O)_{33}$ are, however, longer than the Zr–O distances usually obtained in Zr compounds. This is obviously because of the strain implied on the actual configuration. If on the other hand the two different types of bonds, Hf–O(A) and Hf–O(B), are compared (Table 5) it can be seen that the mean Hf–O(A) bonds are all longer than normal while the mean Hf–O(B) bonds tend to be normal or even shorter than normal. In the two mutually perpendicular trapezoids which form the dodecahedron, the coordinated O atoms situated at the top of one trapezoid are denoted O(A) and those at the base O(B). The ratio Me–O(A)/Me–O(B) is 1.03 for the most favourable model calculated for a dodecahedron by Hoard & Silverton.

In the present structure, this value varies between 1.03 and 1.13, indicating that strains enforced on the structure weigh most heavily on the Hf–O(A) bonds.

Table 5. *Oxygen coordination distances in Å for hafnium and sulphur, and the average Hf–Hf distance*

The standard deviations are given in parentheses.

Hf: eight-coordination (dodecahedra)

Hf–O(A)		Hf–O(B)		
Hf(1)–O(2)	2·30 (3)	Hf(1)–O(3)	2·09 (3)	
–O(37)	2·38 (5)	–O(19)	2·14 (4)	
–O(44)	2·45 (4)	–O(20)	2·10 (5)	
–O(50)	2·44 (4)	–O(28)	2·14 (4)	
Av.	2·39	Av.	2·12	Mean value 2·25
Hf(2)–O(8)	2·24 (3)	Hf(2)–O(1)	2·07 (3)	
–O(17)	2·28 (4)	–O(19)	2·12 (3)	
–O(25)	2·26 (3)	–O(30)	2·09 (4)	
–O(37)	2·44 (4)	–O(40)	2·12 (5)	
Av.	2·30	Av.	2·10	Mean value 2·20
Hf(3)–O(7)	2·33 (4)	Hf(3)–O(9)	2·12 (3)	
–O(18)	2·15 (5)	–O(30)	2·09 (4)	
–O(25)	2·33 (4)	–O(31)	2·15 (5)	
–O(34)	2·31 (4)	–O(41)	2·07 (6)	
Av.	2·28	Av.	2·10	Mean value 2·19
Hf(8)–O(25)	2·26 (4)	Hf(8)–O(40)	2·14 (4)	
–O(26)	2·25 (5)	–O(41)	2·25 (5)	
–O(43)	2·26 (5)	–O(42)	2·26 (5)	
–O(46)	2·29 (7)	–O(55)	2·15 (4)	
Av.	2·27	Av.	2·20	Mean value 2·23
Hf(10)–O(5)	2·29 (4)	Hf(10)–O(4)	2·12 (3)	
–O(35)	2·21 (5)	–O(23)	2·15 (5)	
–O(45)	2·30 (5)	–O(28)	2·19 (4)	
–O(50)	2·36 (4)	–O(29)	2·27 (5)	
Av.	2·29	Av.	2·18	Mean value 2·24

Hf: eight-coordination (antiprisms)

Hf(4)–O(1)	2·11 (6)	Hf(5)–O(7)	2·40 (5)
–O(3)	2·13 (5)	–O(8)	2·22 (6)
–2× O(37)	2·12 (5)	–2× O(30)	2·01 (5)
–2× O(38)	2·26 (5)	–2× O(32)	2·18 (7)
–2× O(51)	2·38 (5)	–2× O(36)	2·19 (5)
Av.	2·22	Av.	2·17
Hf(11)–O(22)	2·17 (6)	Hf(11)–O(53)	2·45 (6)
–O(43)	2·16 (6)	–O(55)	2·21 (4)
–O(47)	2·26 (4)	–O(57)	2·24 (5)
–O(48)	2·13 (5)	–O(60)	2·01 (5)
		Av.	2·20

Hf: seven-coordination (capped trigonal prisms)

Hf(6)–O(2)	2·23 (5)	Hf(9)–O(2)	2·14 (5)
–O(8)	2·25 (5)*	–O(5)	2·39 (7)*
–O(14)	2·11 (7)	–O(10)	2·17 (8)
–2× O(19)	1·96 (4)	–2× O(28)	1·85 (4)
–2× O(27)	2·22 (4)	–2× O(52)	2·18 (5)
Av.	2·14	Av.	2·11

Hf: seven coordination ('missing' antiprism)

Hf(7)–O(20)	2·22 (4)	Hf(7)–O(50)	2·14 (5)
–O(22)	2·16 (5)	–O(56)	2·24 (8)
–O(23)	2·13 (4)	–O(61)	2·16 (6)
–O(48)	2·21 (5)	Av.	2·18

* capped.

Table 5 (cont.)

S:(tetrahedra)

S(1)–O(21)	1·48 (5)	S(2)–O(33)	1·50 (7)	S(3)–O(17)	1·56 (4)
–O(34)	1·43 (5)	–O(45)	1·51 (6)	–O(24)	1·38 (6)
–O(42)	1·48 (6)	–O(49)	1·44 (6)	–O(27)	1·47 (4)
–O(54)	1·49 (6)	–O(52)	1·53 (6)	–O(36)	1·49 (5)
Av.	1·47	Av.	1·50	Av.	1·48
S(4)–O(10)	1·39 (10)	S(5)–O(6)	1·45 (9)	S(6)–O(12)	1·45 (9)
–O(14)	1·56 (8)	–O(13)	1·62 (10)	–O(15)	1·51 (10)
–2 × O(59)	1·43 (7)	–2 × O(60)	1·58 (5)	–2 × O(41)	1·55 (6)
Av.	1·45	Av.	1·56	Av.	1·52
S(7)–O(35)	1·54 (6)	S(8)–O(11)	1·58 (14)	S(9)–O(18)	1·54 (6)
–O(39)	1·64 (6)	–O(16)	1·48 (13)	–O(32)	1·67 (8)
–O(58)	1·50 (6)	–2 × O(38)	1·63 (6)	–O(62)	1·91 (15)
–O(61)	1·55 (7)	Av.	1·58	–O(63)	1·29 (11)
Av.	1·56			Av.	1·60

Mean Hf–Hf distance: 3·54 (3·41–3·69).

The dodecahedral edges, a, m, b and g (Fig. 3 and Table 6) should according to the ideal symmetry, have the relative lengths $a = m < b < g$. In this particular case, a is always longer than m and b. This is the consequence of the long Hf–O(A) bonds, as the d orbitals are strongly directed.

The average Hf–O distances and lengths of the edges in the square antiprisms are about those which are to be expected (Tables 5 and 6).

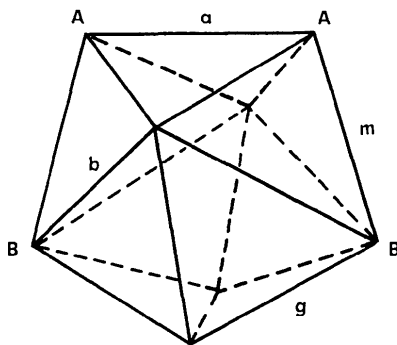The most favourable polyhedra formed by seven-coordinated atoms are the pentagonal bipyramid and

Fig. 3. Idealized dodecahedron with symbols according to Hoard & Silverton.

Table 6. *The mean values of oxygen–oxygen distances (in Å) within the different polyhedra*

(The nomenclature is according to Hoard & Silverton.)

Dodecahedra

Oxygens coordinated to	O–O edge			
	a	m	g	b
Hf(1)	3·07	2·71	2·57	3·26
Hf(2)	2·97	2·61	2·69	3·16
Hf(3)	2·85	2·51	2·72	3·07
Hf(8)	2·69	2·60	2·65	3·33
Hf(10)	2·81	2·64	2·68	3·20

Antiprisms

Oxygens coordinated to	O–O edge		
	l Trigonal faces	s Square faces	l/s
Hf(4)	2·91	2·58	1·13
Hf(5)	2·85	2·53	1·13
Hf(11)	2·81	2·63	1·07

the capped trigonal prism. The pentagonal bipyramid is the polyhedron adopted in all compounds investigated by the authors, although the capped trigonal prism has been suggested by Herak, Malčič & Manojlović (1965) for Na$_5$Zr$_2$F$_{13}$. In Hf$_{18}$O$_{10}$(OH)$_{26}$(SO$_4$)$_{13}$(H$_2$O)$_{33}$ Hf(6) and Hf(9) are seven-coordinated by O atoms forming quite regular capped trigonal prisms. Seven-coordination has been dealt

Table 7. *Distances in Å from oxygen atoms of water molecules of crystallization to nearest neighbouring oxygen atoms in different clusters*

Standard deviations are given in parentheses. The symmetry-related clusters are denoted: C1(x, y, z), C2$(\bar{x}, \bar{y}, \bar{z})$, C3$(x - y, x, \frac{1}{2} + z)$ and C4$(y - x, \bar{x}, z)$, where C1 corresponds to the parameters given in Table 3.

O(101)–O(11)	(C1)	2·60 (15)	O(105)–O(46)	(C1)	2·69 (9)
–2 × O(54)	(C1)	2·86 (6)	–O(62)	(C1)	2·78 (16)
O(102)–2 × O(46)	(C1)	2·95 (8)	–O(17)	(C1)	2·87 (9)
O(103)–O(5)	(C2)	2·63 (14)	–O(31)	(C3)	2·89 (9)
–2 × O(106)	(C1)	2·85 (10)	O(106)–O(33)	(C1)	2·58 (10)
O(104)–O(40)	(C1)	2·67 (7)	–O(54)	(C3)	2·76 (9)
–O(20)	(C1)	2·83 (7)	–O(103)	(C1)	2·85 (10)
–O(21)	(C3)	2·84 (7)	–O(29)	(C2)	2·88 (8)
			O(107)–O(57)	(C1)	2·83 (10)
			–O(58)	(C1)	2·84 (10)
			O(108)–O(39)	(C1)	2·80 (11)
			–O(47)	(C4)	2·87 (12)
			–O(33)	(C2)	2·88 (11)

with extensively in a review of high coordination numbers by Muetterties & Wright (1967). The interconversions between the different proposed polyhedra are easily established, however, since the energy differences between them are relatively small. Thus, the seven O atoms surrounding Hf(7) could also be regarded as the corners of a tetragonal base–trigonal base polyhedron, which is found in monoclinic ZrO_2 (Mc-Cullough & Trueblood, 1959; Smith & Newkirk, 1965) and HfO_2 (Adam & Rogers, 1959). The uncertainty concerning the coordination of Hf(7) is emphasized by the average Hf–O distance of 2·18 Å, which lies between the values obtained for seven- and eight-coordination.

Some of the SO_4 groups have longer average S–O distances than normal (Table 5). When studying these, one has to bear in mind that at least two of the S-coordinated O atoms are also coordinated to different Hf atoms. The two S–O distances of 1·91 and 1·29 in the SO_4 group S(9) must be considered to be less reliable since O(62) and O(63) have an occupation number of 0·5.

Fig. 4. Schematic outline of a building unit $Hf_{18}O_{10}(OH)_{26}(SO_4)_{13}(H_2O)_{20}$ viewed along the c axis. The different coordination polyhedra established for hafnium are depicted by D (dodecahedron), A (antiprism) and C (capped trigonal prism). The z coordinates of the atoms are given in the Figure unless $z = 0.25$.

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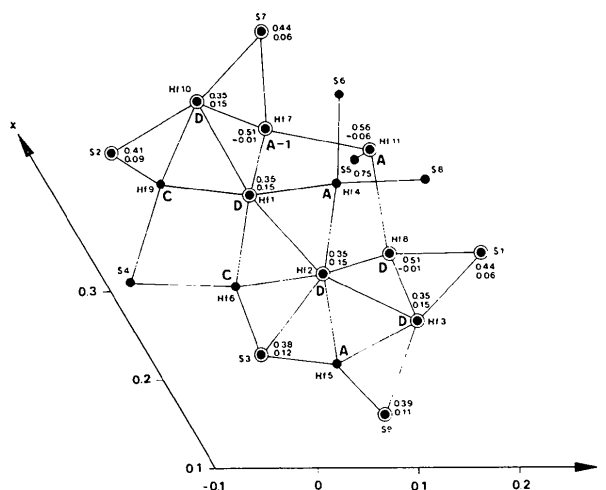WILSON, A. C. J. (1942). *Nature, Lond.* **150**, 151–152.