

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

MARGARETA HANSSON

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

The crystal structure of $\text{Zr}(\text{OH})_2\text{SO}_4\cdot\text{H}_2\text{O}$ has been determined from three-dimensional X-ray data. The symmetry is monoclinic, space group $C2/c$, with $a=6.497 \text{ \AA}$, $b=12.460 \text{ \AA}$, $c=6.826 \text{ \AA}$, $\beta=96.31^\circ$ and $Z=4$. Intensity data were collected with an automatic single crystal diffractometer, and, using a total of 986 independent reflexions, least squares full matrix refinements yielded a final R value of 0.060.

The structure consists of almost planar, infinite $[\text{Zr}(\text{OH})_2]_n^{2n+}$ chains, which are joined in one direction by sulfate groups, thus constituting layers held together merely by hydrogen bonds and van der Waals contacts. Zr exhibits sevenfold oxygen coordination, the coordination polyhedron being a somewhat distorted pentagonal bipyramid. The Zr-O bond distances range between 2.10, and 2.19, \AA with an average distance of 2.13, \AA .

The crystal structure of $\text{Hf}(\text{OH})_2\text{SO}_4\cdot\text{H}_2\text{O}$ has recently been determined.¹ The close resemblance between Hf and Zr suggested that the isomorphous compound $\text{Zr}(\text{OH})_2\text{SO}_4\cdot\text{H}_2\text{O}$ ought to exist. During an investigation of the $\text{ZrO}_2-\text{SO}_3-\text{H}_2\text{O}$ system, McWhan and Lundgren found other zirconium hydroxide salts,² but not $\text{Zr}(\text{OH})_2\text{SO}_4\cdot\text{H}_2\text{O}$. The experiments were, however, carried out using more basic solutions than those used for the preparation of $\text{Hf}(\text{OH})_2\text{SO}_4\cdot\text{H}_2\text{O}$. Attempts were therefore made to prepare the zirconium salt under conditions more alike those under which the hafnium compound is obtained.

PREPARATION AND ANALYSIS

Solutions of 0.8 g $\text{ZrOCl}_2\cdot 8\text{H}_2\text{O}$ in concentrated sulfuric acid were evaporated to dryness and the residues dissolved in 2 M sulfuric acid. After heating in sealed Pyrex glass tubes for a month, no crystals were obtained. Experiments with solutions containing both hafnium and zirconium indicates, however, that the distribution factor for the crystals obtained, was in favour of Hf under these conditions. Guinier powder photographs showed the phase to be identical with $\text{Hf}(\text{OH})_2\text{SO}_4\cdot\text{H}_2\text{O}$, and electron probe microanalysis indicated that with a Zr:Hf mol ratio of 3:1 in the original solution, the elements were distributed statistically in approximately equal amounts in the crystals.

Some experiments were then carried out in which only the volume of dilute sulfuric acid was varied, between 3 and 12 ml. In the more dilute zirconium solutions, crystals of $\text{Zr}_2(\text{OH})_2(\text{SO}_4)_3(\text{H}_2\text{O})_4$ were obtained,² while in the more concentrated ones $\text{Zr}(\text{OH})_2\text{SO}_4\text{H}_2\text{O}$ crystallized as elongated prisms.

The compound was analysed with a Mettler Recording Thermoanalyzer, the following results for the *zirconium* content (as ZrO_2), the *sulfur* content (as SO_3) and the amount of *water* thus being obtained:

	% ZrO_2	% SO_3	% H_2O	Density (g cm^{-3})
Found:	52.0	33.3	14.8	2.88
Calc. for $\text{Zr}(\text{OH})_2\text{SO}_4\text{H}_2\text{O}$:	51.5	33.5	15.0	2.89

The density was determined by the flotation method.

UNIT CELL AND SPACE GROUP

From rotation and Weissenberg photographs it was seen that $\text{Zr}(\text{OH})_2\text{SO}_4\text{H}_2\text{O}$ crystallizes in the monoclinic system, the following reflexions being systematically absent: hkl , $h+k=2n+1$; $h0l$, $l=2n+1$. These extinctions are characteristic for space groups Nos. 9, Cc , and 15, $C2/c$.³

Accurate cell dimensions were obtained from Guinier powder photographs taken with $\text{CuK}\alpha_1$ radiation and internally calibrated with $\text{Pb}(\text{NO}_3)_2$ ($a=7.8566 \text{ \AA}$ at 21°C).⁴ 52 reflexions were indexed and least squares refinement with the program POWDER⁵ gave the following cell dimensions:

$$\begin{aligned} a &= 6.4969 \pm 0.0004 \text{ \AA} & \beta &= 96.311^\circ \pm 0.004^\circ \\ b &= 12.4598 \pm 0.0010 \text{ \AA} & V &= 549.2 \text{ \AA}^3 \\ c &= 6.8262 \pm 0.0004 \text{ \AA} \end{aligned}$$

A list of observed and calculated $\sin^2 \theta$ values is given in Table 1. Assuming that $Z=4$, the calculated density of $\text{Zr}(\text{OH})_2\text{SO}_4\text{H}_2\text{O}$ is 2.89 g cm^{-3} which is in good agreement with the experimental value (*cf.* above).

INTENSITY DATA

Three-dimensional X-ray data were collected with a Philips PAILRED single crystal diffractometer. A single crystal of the dimensions (in mm): $0.087 \times 0.062 \times 0.062$ was mounted along the a -axis in a sealed glass capillary, and reflexions from the layer lines $0kl-9kl$ were recorded with $\text{MoK}\alpha$ radiation. The intensities were processed using the program DATAP1.⁶ Standard deviations, $\sigma(I)$, based on counter statistics, were evaluated, and the reflexions with $\sigma(I)/I \leq 0.5$ were regarded as observed, thus yielding a data set of 1050 reflexions to be used in the subsequent calculations. Corrections for Lorentz', polarization and absorption effects were calculated with the programs DATAP1 and DATAP2,⁶ the linear absorption coefficient being 23.0 cm^{-1} .

SOLUTION AND REFINEMENT OF THE STRUCTURE

A three-dimensional Patterson function and a subsequent electron density calculation (program DRF⁶) yielded parameters for all atoms in accordance with the corresponding parameters in the structure of $\text{Hf}(\text{OH})_2\text{SO}_4\text{H}_2\text{O}$. The

Table 1. Guinier powder photograph of $Zr(OH)_2SO_4 \cdot H_2O$.

hkl	$10^5 \sin^2 \theta$ obs	$10^5 \sin^2 \theta$ calc	d (calc) Å	I obs
0 2 0	1531	1529	6.230	s
1 1 0	1804	1805	5.733	vs
0 2 1	2821	2817	4.589	vvs
1 3 0	4865	4862	3.493	s
0 0 2	5163	5155	3.392	s
2 0 0	5684	5691	3.229	vvs
1 1 2	6360	6365	3.053	m
0 2 2	6675	6684	2.979	s
2 2 0	7219	7219	2.867	m
0 4 1	7408	7403	2.831	s
2 2 1	7918	7913	2.738	s
2 2 1	9109	9104	2.553	m
1 3 2	9421	9422	2.509	m
2 0 2	9660	9655	2.479	m
0 4 2	11272	11270	2.294	vw
1 5 1	11966	11968	2.227	s
2 0 2	12039	12037	2.220	vvw
1 1 3	12511	12511	2.178	w
1 5 1	12557	12563	2.173	m
0 2 3	13135	13128	2.126	m
3 1 0	13190	13187	2.121	s
2 2 2	13561	13565	2.091	w
2 4 1	13694	13690	2.082	w
1 1 3	14302	14297	2.037	vw
0 6 1	15055	15046	1.986	s
1 5 2	15546	15536	1.954	m
3 3 0	16251	16244	1.911	s
3 1 2	16553	16556	1.893	m
1 5 2	16725	16727	1.883	m
2 2 3	17039	17032	1.866	w
0 4 3	17718	17714	1.830	s
3 3 2	19615	19613	1.739	m
3 1 2	20129	20128	1.717	m
2 2 3	20608	20605	1.697	s
1 7 1	21142	21139	1.675	w
1 1 4	21239	21235	1.672	vw
2 4 3	21625	21618	1.657	w
1 5 3	21676	21683	1.654	w
1 7 1	21733	21735	1.652	w
0 2 4	22142	22149	1.637	m
{ 3 5 1	22754	{ 22754	{ 1.615	vvs
{ 4 0 0		{ 22764	{ 1.614	
3 3 2	23191	23185	1.600	vw
1 5 3	23466	23469	1.590	m
2 0 4	23934	23930	1.575	vw
{ 1 3 4	24293	{ 24292	{ 1.563	m
{ 4 2 0		{ 24293	{ 1.563	
3 5 1	24541	24540	1.555	m
2 4 3	25190	25191	1.535	m
4 0 2	25544	25538	1.524	w
{ 3 5 2	25735	{ 25728	{ 1.518	m
{ 0 8 1		{ 25747	{ 1.518	
2 0 4	28699	28693	1.438	m
2 2 4	30222	30222	1.401	w
4 2 3	32311	32319	1.355	w

Table 2. Continued.

-5	29	27	0.06	-4	47	46	0.05	-3	64	64	0.05	5	40	52	3.05	7	37	31	-3.07
-10	28	24	0.09	-1	31	31	0.05	-4	31	27	0.04	7	32	35	-3.06	7	46	45	-3.05
	8	16	L	-2	52	50	-3.10	-4	44	49	-3.08	9	33	30	0.04	6	26	29	0.06
-5	29	28	0.04	-1	16	18	-3.05	-6	21	22	-3.09		9	a	L		9	13	L
-3	30	29	-3.06	0	42	43	0.05	-7	47	42	0.07	8	23	23	-3.06	8	22	18	-3.03
1	28	30	-3.06	1	29	30	0.05	-8	27	23	0.04	4	34	37	0.06	4	23	23	0.09
3	35	31	0.07	2	51	51	-3.10	-9	34	37	-3.07	4	34	37	-3.04	-2	24	25	-3.09
	9	1	L	3	28	28	-3.08		9	7	L	3	25	25	-3.04		9	15	L
4	23	24	0.10	4	40	40	0.05	-11	31	33	0.08	2	40	44	3.05	-4	29	25	0.07
4	41	42	0.06	6	32	31	-3.07	-9	28	31	-3.05	1	22	22	0.01	-4	25	25	-3.07
2	33	36	-3.04	8	27	28	0.07	-7	40	44	0.07	0	47	47	-3.09	0	30	28	-3.04
0	48	51	0.05		9	5	L	-6	26	23	0.04	-1	29	27	-3.08		9	17	L
-2	34	40	-3.08	9	34	29	0.03	-5	52	56	-3.09	-2	45	44	0.05	1	31	32	-3.07
-4	32	31	0.07	7	30	39	-3.07	-4	24	18	-3.09	-3	24	21	0.04	-1	30	31	0.08
-6	36	36	-3.08	5	40	45	0.06	-3	52	49	0.06	-4	36	40	-3.08	-3	35	34	-3.07
-12	24	19	0.12	3	57	59	-3.09	-1	72	69	-3.10	-6	29	34	0.07	-5	25	24	-3.03
	9	3	L	2	28	27	-3.10	0	26	30	-3.11	-8	23	27	-3.06				
-10	26	24	-3.06	1	63	64	0.05	1	61	60	0.05		9	11	L				
-8	32	33	0.07	0	30	24	0.04	2	21	19	0.05	-8	26	30	-3.07				
-7	17	12	0.13	-1	60	60	-3.09	3	49	51	-3.08	-4	37	38	-3.05				
-6	31	32	-3.07	-2	30	27	-3.10	4	28	23	-3.10	-2	38	39	0.06				

space group was therefore assumed to be $C2/c$. Preliminary refinement of the scale factors between the layers and the atomic parameters gave an R value of 0.069. After correction for absorption effects there were still some discrepancies between observed and calculated structure factors with high values, and a secondary extinction factor was therefore included in the refinement. The following parameters were thus refined with the program LINUS:⁶ scale factors, atomic positions including isotropic thermal vibrations and an isotropic secondary extinction factor. An R value of 0.065 was obtained when the scattering factors⁷ for Zr and S were corrected for anomalous dispersion.⁸

Since the crystal was very symmetric in shape, the values of the average path lengths in the crystal, used to calculate the extinction corrections, are approximately the same for the reflexions $0kl$ and $0k\bar{l}$. Hence, mean values of F_{0kl} and $F_{0k\bar{l}}$ could be calculated, giving a final data set of 986 independent reflexions. The final refinement was then extended to include anisotropic thermal parameters while the scale factors were held constant. When the shifts of the parameters were less than 2% of the standard deviations the refinement was terminated, the R value having converged to 0.060. A weighting scheme according to Cruickshank was used in the refinement, which yielded a weighted R value of 0.074. The final value of the isotropic extinction parameter was $g = (1.12 \pm 0.10) \times 10^4$. Observed and calculated structure factors are listed in Table 2. Because of the small size of the crystal used in the collection of the intensity data, there were more reflexions with $\sigma(I)/I > 0.5$ than for the hafnium salt. Calculated structure factors for the unobserved reflexions

Table 3a. Atomic coordinates, expressed as fractions of the cell edges, and their standard deviations.

Atom and position	x	y	z
Zr in 4(e)	0.0	0.95831(7)	1/4
S in 4(e)	0.0	0.3800(2)	1/4
O ₁ in 8(f)	0.0142(8)	0.0894(4)	0.4460(7)
O ₂ in 8(f)	0.0606(11)	0.3160(6)	0.4237(11)
O ₃ in 8(f)	0.1733(8)	0.4510(6)	0.2105(9)
O ₄ in 4(e)	1/2	0.2826(8)	1/4

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

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Zr	0.0014(1)	0.00051(3)	0.0007(1)	0	0.00011(6)	0
S	0.0035(4)	0.0013(1)	0.0057(4)	0	0.0014(3)	0
O ₁	0.0089(10)	0.0010(3)	0.0041(8)	-0.0004(4)	0.0013(6)	0.0008(3)
O ₂	0.0097(13)	0.0033(5)	0.0111(12)	-0.0006(5)	0.0014(9)	0.0025(6)
O ₃	0.0038(9)	0.0036(4)	0.0085(9)	0.0002(5)	0.0014(7)	0.0001(5)
O ₄	0.0146(21)	0.0019(5)	0.0082(16)	0	0.0042(14)	0

have not therefore been included in the table. The final atomic parameters, together with their standard deviations, are given in Table 3a, b.

Finally, a three-dimensional electron difference density calculation was performed with the program FFT.⁶ Only negligible rest peaks around the zirconium atoms were obtained.

Interatomic distances and angles were calculated with the program DISTAN⁶ and the results are given in Table 4.

Table 4. Interatomic distances and angles with their standard deviations in parentheses.

Zr-Zr	3.568(1) (Å)		
Within the bipyramid:			
Zr-2O ₁	2.107(5) (Å)	O ₁ -Zr-O ₁	78.4(3)°
Zr-2O ₁	2.170(5)	O ₁ -Zr-O ₁ (2 ×)	66.9(2)
Zr-2O ₃	2.112(5)	O ₁ -Zr-O ₃ (2 ×)	88.8(2)
Zr-O ₄	2.190(10)	O ₁ -Zr-O ₃ (2 ×)	90.8(2)
	Mean 2.138	O ₁ -Zr-O ₃ (2 ×)	95.0(2)
O ₁ -O ₁	2.662(10)	O ₁ -Zr-O ₃ (2 ×)	87.9(2)
O ₁ -O ₁ (2 ×)	2.359(11)	O ₄ -Zr-2O ₁	74.1(1)
O ₁ -O ₃ (2 ×)	3.049(8)	O ₄ -Zr-2O ₃	87.5(2)
O ₁ -O ₃ (2 ×)	2.971(8)	O ₃ -Zr-O ₄	175.1(4)
O ₁ -O ₃ (2 ×)	2.952(8)		
O ₁ -O ₃ (2 ×)	3.111(8)		
O ₄ -2O ₁	2.627(8)		
O ₄ -2O ₃	2.977(10)		
Within the sulfate group:			
S-2O ₂	1.448(8)	O ₂ -S-O ₂	113.1(6)°
S-2O ₃	1.480(6)	O ₃ -S-O ₃	106.6(6)
O ₂ -O ₃	2.415(15)	O ₂ -S-O ₃ (2 ×)	108.9(4)
O ₂ -O ₃ (2 ×)	2.382(10)	O ₂ -S-O ₃ (2 ×)	109.6(4)
O ₂ -O ₃ (2 ×)	2.392(10)		
O ₃ -O ₃	2.372(11)		
Other distances and angles (different layers):			
O ₄ -2O ₂	2.611(9)	O ₂ -O ₄ -O ₂	123.9(5)°
O ₁ -O ₂	2.846(9)	Zr-O ₁ -O ₂	109.8(2)

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The zirconium atoms constitute, together with the oxygen atoms, O_1 , infinite, almost planar zigzag chains lying in the yz plane and running parallel to the z direction. The metal atoms are joined by double hydroxide bridges and the Zr–Zr distance within the chains are 3.568 Å (*cf.* Table 4). This is significantly longer than the corresponding distance (3.553 Å) in $\text{Hf}(\text{OH})_2\text{SO}_4\text{H}_2\text{O}$.¹

The $[\text{Zr}(\text{OH})_2]^{2n+}$ chains are connected in the x direction by sulfate groups, each of which is in contact with zirconium atoms in two different chains. A water oxygen atom, O_4 , completes the pentagonal bipyramidal arrangement about zirconium. This oxygen atom is at coordination distance from Zr and lies in the same plane as the metal atom and the hydroxide oxygen atoms, O_1 . The structure can thus be visualised as being composed of chains of condensed pentagonal bipyramids linked in one direction by sulfate tetrahedra. These layers, which are parallel to the xz plane, are held together only by means of hydrogen bonds (2.61 Å and 2.85 Å) and van der Waals contacts. The structure is described in more detail in the paper on $\text{Hf}(\text{OH})_2\text{SO}_4\text{H}_2\text{O}$.¹

The deviation of the Zr coordination polyhedron from the ideal D_{5h} symmetry is illustrated in Figs. 1 and 2. A comparison with Fig. 3 and Table 5

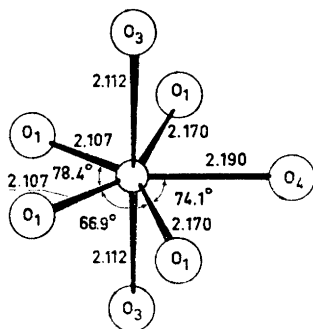


Fig. 1. The coordination polyhedron of $\text{Zr}(\text{OH})_2\text{SO}_4\text{H}_2\text{O}$. The Zr–O distances (in Å) and some O–Zr–O bond angles are indicated.

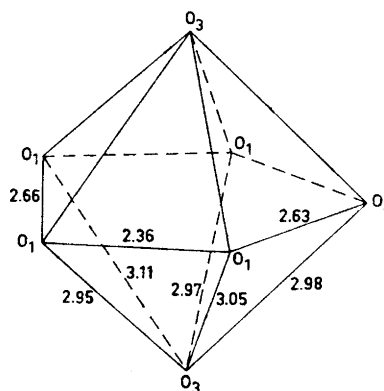


Fig. 2. Pentagonal bipyramidal configuration of oxygen atoms about zirconium in $\text{Zr}(\text{OH})_2\text{SO}_4\text{H}_2\text{O}$. (Distances in Å.)

in the paper on $\text{Hf}(\text{OH})_2\text{SO}_4\text{H}_2\text{O}$ shows the distortion of the bipyramids to be about the same in the two compounds. There are, however, some differences. The Me–O distances are, for example, on the whole slightly longer in the zirconium compound, and the difference is significant for the axially coordinated O_3 atoms, the distances being 2.11₂ and 2.07₆ Å in the zirconium and hafnium compounds, respectively. This is reflected in the somewhat smaller O_3 –Me– O_3 angle in the zirconium compound, 175.1°, compared with 177.0° in the hafnium salt, as well as in the discrepancies in the O_1 – O_3 bond distances, as can be seen from the tables.

The plane of best fit through the four O₁ oxygen atoms around Zr was calculated with the program PLANEFIT,⁶ the following equation being obtained (Cartesian coordinates, Å):

$$0.9926X + 0.1216Z = 3.2443$$

Transformation to fractional coordinates is performed by $X = 6.4969x$, $Z = -0.7504x + 6.7848z$.

Two O₁ atoms are situated 0.10₇ Å and 0.06₇ Å above the plane while the other two are at the same distances under the plane. This is in good agreement with corresponding values in the structure of the hafnium compound. The metal atoms and the water oxygen atoms are situated on a twofold axis and thus lie in the plane.

The sulfate tetrahedra in the two isomorphous zirconium and hafnium compounds are somewhat deformed due to their chain-connecting function. The type of distortion appears to be slightly different in the two compounds, but the differences in the geometry are not quite significant.

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

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

REFERENCES

1. Hansson, M. *Acta Chem. Scand.* **23** (1969) 3541.
2. McWhan, D. B. and Lundgren, G. *Inorg. Chem.* **5** (1966) 284.
3. *International Tables for X-Ray Crystallography*, 2nd Ed., Kynoch Press, Birmingham 1965, Vol. I.
4. *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham 1962, Vol. III, p. 122.
5. Lindqvist, O. and Wengelin, F. *Arkiv Kemi* **28** (1967) 179.
6. The program library of the Dept. of Inorg. Chem. Göteborg. DATAP1 has been written locally by O. Lindgren, DATAP2 was originally written by Coppens, Leiserowitz and Rabinowich (1965), DRF and DISTAN by A. Zalkin, Berkeley, California, FFT by Ten Eyck, L. and PLANEFIT by Wengelin, F. LINUS is the Busing, Martin and Levy (1962) LS program modified for refinement of extinction parameters by Coppens and Hamilton, 1970.
7. Cromer, D. T. and Waber, J. T. *Acta Cryst.* **18** (1965) 104.
8. Cromer, D. T. *Acta Cryst.* **18** (1965) 17.

Received March 23, 1973.