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The Crystal Structure of $ZnSO_3.2\frac{1}{2}H_2O$

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The crystal structure of $ZnSO_3.2\frac{1}{2}H_2O$ has been determined from three-dimensional X-ray diffractometer data. The unit cell is triclinic, space group $P\bar{1}$, with the following dimensions: $a = 7.651(2)$, $b = 7.549(2)$, $c = 9.094(2)$ Å, $\alpha = 90.06(2)$, $\beta = 88.53(2)$, $\gamma = 93.75(3)°$. There are four formula units in the cell. The structure was refined by full-matrix least-squares calculations to an R value of 0.059 for 1855 observed reflections. Pyramidal sulfite groups link the structure together, which may be described as built up of ZnO_4 tetrahedra (mean distance Zn – O 1.99 Å) and ZnO_6 octahedra (mean distance Zn – O 2.10 Å). The average dimensions of the sulfite group are: S–O distance 1.525 Å, O–O distance 2.403 Å, and ∠O–S–O 103.8°.

A preliminary crystal structure determination of $ZnSO_3.2\frac{1}{2}H_2O$ has been published earlier.[1] Later a structure determination of the compound $ZnSO_3.2H_2O$ was reported by Quinones and Baggio.[2] The cell dimensions, cell content and atomic positions of all atoms, besides one half water molecule, the lattice water, make it possible that the very same compound has been investigated in both cases. Independent solution and refinement have, however, been made with diffractometer data in the hope of obtaining a more accurate structure determination.

EXPERIMENTAL

The sample of zinc sulfite hydrate was prepared according to Pannetier *et al.*[3] The analyses confirm the formula $ZnSO_3.2\frac{1}{2}H_2O$. The amount of zinc was determined by titration with EDTA and the amount of sulfur was determined gravimetrically as $BaSO_4$. The water content was determined at 390°C by controlled potential coulometry according to Karlsson and Karrman.[4] The analyses gave: 34.4(1) % Zn, 16.7(2) % S and 23.6(1) % H_2O; calculated for $ZnSO_3.2\frac{1}{2}H_2O$: 34.32 % Zn, 16.83 % S and 23.65 % H_2O.

Values for the cell dimensions were calculated from an indexed Guinier-Hägg powder photogram. Least-squares refinement of the cell parameters gave $a = 7.651(2)$ Å, $b = 7.549(2)$ Å, $c = 9.094(2)$ Å, $\alpha = 90.06(2)°$, $\beta = 88.53(2)°$, $\gamma = 93.75(3)°$ and $V = 524.0$ Å^3. Observed and calculated $\sin^2\theta$ values are listed together with calculated structure factors in Table 1.

The cell is not reduced according to Delaunay [5] because of the pseudotetragonal character of the selected unit cell. In Table 2 the dimensions of the reduced cell are given.

The observed density, 2.43 g cm^{-3}, found from the apparent loss of weight in benzene, gives four formula units in the cell (calculated density 2.41 g cm^{-3}).

Table 1. Guinier-Hägg powder photogram of $ZnSO_3.2\frac{1}{2}H_2O$. Cu$K\alpha_1$ radiation. KCl was used as an internal standard. $a_{KCl} = 6.2923$ Å at 25°C.

hkl	$10^5 \times \sin^2 \theta_{obs}$	$10^5 \times \sin^2 \theta_{calc}$	$\|F\|_{calc}$	I_{obs}
001	–	718	1	
100	1017	1019	101	vst
010	1044	1045	97	st
101	1689	1693	51	m
011		1762	51	
$0\bar{1}1$	1757	1764	54	st
$\bar{1}01$		1780	55	
$\bar{1}10$	–	1929	9	
110	–	2199	2	
$1\bar{1}1$	2603	2604	28	w
$\bar{1}11$	2682	2689	54	m
002	2873	2871	55	
111		2873	50	vst
$\bar{1}\bar{1}1$	2959	2962	37	vw
102	3806	3803	27	vw
012	3934	3915	31	vw
$0\bar{1}2$		3919	11	
$\bar{1}02$	–	3977	5	
200	4074	4074	87	st
020	4196	4182	79	vst
201	4707	4705	51	st
$1\bar{1}2$		4715	78	
$\bar{2}10$	–	4850	10	
$\bar{2}01$	4892	4879	55	vst
$\bar{1}12$		4885	99	
021		4898	30	
$0\bar{2}1$		4902	51	
$\bar{1}20$	–	4930	33	
112	4995	4981	102	w
$\bar{1}\bar{1}2$	5163	5160	98	vst
210	–	5390	38	
120	–	5471	25	
$2\bar{1}1$	–	5481	19	
$1\bar{2}1$	5612	5606	113	m
$\bar{2}11$	–	5653	10	
$\bar{1}21$	5699	5690	127	st
211	5995	6020	147	st
121	–	6143	24	
$\bar{2}\bar{1}1$	6202	6196	79	w
$\bar{1}\bar{2}1$	–	6234	9	
003	–	6460	7	
202	6785	6771	46	vw
022	7052	7049	80	m
$0\bar{2}2$		7057	67	
$\bar{2}02$	7123	7120	57	vw
103	–	7348	9	
013	–	7503	19	
$0\bar{1}3$	7504	7509	71	st
$2\bar{1}2$		7548	76	
$\bar{1}03$	7620	7610	74	w
$\bar{2}20$	7720	7716	78	m
$1\bar{2}2$	–	7722	22	
$\bar{1}22$	7884	7885	52	m
$\bar{2}12$		7893	90	

Table 1. Continued.

212	–	8095	45	
122	8259	8251	62	
1$\bar{1}$3		8261	42	w
2$\bar{2}$1	–	8348	34	
1$\bar{2}$2	8425	8433	80	w
2$\bar{1}$2	–	8438	27	
$\bar{1}$13	–	8517	17	
$\bar{2}$21	–	8519	9	
113	–	8526	33	
1$\bar{1}$3	–	8793	22	
220	8791	8797	59	vw
300	–	9167	5	
030	–	9409	4	
221	–	9426	3	
2$\bar{2}$1	–	9604	3	
301	9760	9754	52	vw
3$\bar{1}$0	–	9870	11	
3$\bar{0}$1	–	10016	14	
$\bar{1}$30	–	10022	10	
031	10123	10124	45	vw
0$\bar{3}$1		10130	34	
203	–	10273	11	
3$\bar{1}$1	–	10395	16	
2$\bar{2}$2	–	10416	19	
310	–	10618	5	
023	10642	10636	17	vvw
0$\bar{2}$3		10648	29	
3$\bar{1}$1	–	10655	3	
1$\bar{3}$1	–	10700	21	
2$\bar{2}$2	–	10757	14	
$\bar{1}$31	10778	10781	40	vw
2$\bar{0}$3		10796	35	
130	–	10834	12	
2$\bar{1}$3		11051		
311		11204		
3$\bar{1}$1	–	11486	1	
004	11471	11485	117	st
222	–	11490	11	
131	–	11505	3	
$\bar{1}$23	–	11515	40	
2$\bar{1}$3	–	11568	22	
213	–	11586	44	
$\bar{1}$31	–	11598	12	
302	–	11777	43	
123	–	11794	6	
2$\bar{2}$2	–	11847	35	
2$\bar{1}$3	12117	12115	74	vw
032	–	12275	21	
0$\bar{3}$2	12289	12287	66	w
3$\bar{0}$2	–	12300	7	
104	–	12329	11	
3$\bar{1}$2	12421	12419	103	w
014	–	12526	2	
0$\bar{1}$4	12561	12534	65	vw
3$\bar{2}$0	–	12538	21	
2$\bar{3}$0	–	12673	50	
$\bar{1}$04	–	12678	34	
1$\bar{3}$2	12824	12812	105	w

The powder was completely indexed to $\sin^2\theta = 0.16$.

Table 2. The reduced unit cell according to Delaunay.

$a = 11.734$ Å	$\alpha = 90.06°$
$b = 7.549$ Å	$\beta = 139.32°$
$c = 9.094$ Å	$\gamma = 92.40°$
	$V = 524.0$ Å^3

The methods of data collection and of structure determination used in the preliminary structure investigation have already been reported.[1] In Table 3 the statistical averages and distribution of the $|E|$ values from the first study are compared with the theoretical values expected for centrosymmetric and non-centrosymmetric structures according to Karle and Karle.[6] These values support the choice of the space group $P\bar{1}$.

Table 3. Statistical averages and distribution of normalized structure factors.

	Observed	Theoretical	
		Centric	Non-centric
Average $\|E\|$	0.72	0.798	0.886
Average $\|E\|^2$	1.0	1.0	1.0
Average $\|E^2-1\|$	1.018	0.968	0.736
$\|E\| > 1$	31.15 %	31.73 %	36.79 %
$\|E\| > 2$	4.82 %	4.55 %	1.83 %
$\|E\| > 3$	0.34 %	0.27 %	0.01 %

In order to collect further X-ray data a crystal with the volume 8.74×10^{-4} mm^3 was mounted along its c axis. The dimension in the b axis direction was 0.0258 mm and in the a axis direction 0.0450 mm. The intensities were recorded at room temperature using a CAD-4 four-circle diffractometer with Cu$K\alpha$ radiation. The collection of data was based on the application of the $\omega - 2\theta$ scan method with an upper limit of $2\theta = 70°$ and a scan range of $(1° + 0.15° \tan\theta)$. Reflections with $I < 3\sigma(I)$, where $\sigma(I)$ is based on counting statistics, were considered to be insignificantly different from the background. The 040 and $1\bar{2}1$ reflections were used as standards and one of them was remeasured after every 20 reflections. The structure factors were derived by means of a data reduction program which performed Lorentz and polarization corrections and absorption corrections ($\mu = 99$ cm^{-1}). Many dependent intensities were recorded, and after averaging the equivalent ones the data set consisted of 1855 reflections. A list of the programs used in the calculations is given in Table 4.

Table 4. Computer programs used for the crystallographic calculations.

Program name and function	Authors
CELSIUS. Refinement of direct cell dimensions by the method of least-squares.	J. Tegenfeldt, Uppsala, Sweden.
CELL. Calculation of direct and reciprocal cell parameters and the constants in the quadratic formula. Transformation of the unit cell to the reduced cell according to Delaunay.	G. Malmros, B. Nyberg and C. Svensson, Lund, Sweden.

Table 4. Continued.

CADDY. Reads CAD-4 reflection data and decodes them to card images.	C. Särnstrand and C. Svensson, Lund, Sweden.
DATAPC. Processes data obtained with CAD-4. Performs corrections for Lorentz, polarization and absorption. Calculates extinction components for the program LINUS.	Originally written by P. Coppens; modified by W. C. Hamilton, New York, USA. (DATAPH). Modified by C. Svensson, Lund, Sweden.
SORTA. Sorting and averaging of equivalent reflections.	J.-O. Lundgren, Uppsala, Sweden.
LINUS. Full-matrix least-squares refinement of atomic parameters with extinction refinement.	P. Coppens and W. C. Hamilton. Modification of the program ORFLS originally written by W. R. Busing, K. O. Martin and H. A. Levy, Tennessee, USA. Further modified by P.-G. Jönsson, Uppsala, Sweden.
DISTAN. Calculation of interatomic distances, angles and their standard deviations.	A. Zalkin, Berkeley, USA.
DRF. Data reduction and Fourier calculations.	A. Zalkin, Berkeley, USA.
SACTA. Prints structure factor tables for publication.	J. Albertsson, Lund, Sweden.

STRUCTURE DETERMINATION AND REFINEMENT

The parameters for Zn, S, and O from the preliminary structure determination were used in a full-matrix least-squares refinement with isotropic temperature factors for the water oxygen atoms and anisotropic ones for the other atoms. This resulted in a discrepancy factor $R = 0.075$.

A new refinement with anisotropic temperature factors for all the non-hydrogen atoms and an isotropic extinction parameter, g, according to Coppens and Hamilton,[7] gave an R-value of 0.059 and a g-value of $1.2(1) \times 10^{-4}$.

From a three-dimensional difference map small residual maxima not above 15 % of the heights of the oxygen peaks in an F_o synthesis were found. Some of these could indicate hydrogen atoms as well as background peaks.

A weighting scheme with $w^{-1} = \sigma^2(F_o) + 0.005\ F_o^2$ was used. Atomic scattering factors for neutral atoms were applied.[8]

In Table 5 the final values of the atomic parameters and their standard deviations are presented. The observed and calculated structure factors are listed in Table 6.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

A schematic drawing of the structure of $ZnSO_3.2\frac{1}{2}H_2O$ is shown in Fig. 1. The interatomic distances and angles are listed in Table 7.

The structure may be described in terms of pyramidal sulfite groups, ZnO_4 tetrahedra, and ZnO_6 octahedra. The tetrahedral coordination around half the zinc atoms is provided by four oxygen atoms belonging to four different sulfite groups. The mean Zn – O distance (1.99 Å) is in good agreement with

Table 5. Final atomic parameters and their standard deviations. The anisotropic temperature factors are of the form $\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$.

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Zn1	0	½	0	0.0061(2)	0.0103(2)	0.0045(2)	−0.0000(2)	−0.0002(1)	0.0003(1)
Zn2	½	0	½	0.0096(2)	0.0071(2)	0.0041(2)	0.0021(2)	−0.0004(1)	0.0003(1)
Zn3	0.48793(8)	0.49657(8)	0.25042(7)	0.0075(2)	0.0083(2)	0.0047(1)	0.0005(1)	0.0006(1)	−0.0002(1)
S1	0.62763(15)	0.25797(14)	0.98344(12)	0.0042(2)	0.0047(2)	0.0018(2)	0.0016(2)	−0.0001(1)	0.0002(1)
S2	0.73830(14)	0.65656(15)	0.50643(12)	0.0037(3)	0.0046(2)	0.0019(2)	−0.0002(2)	−0.0002(1)	0.0007(1)
O1	0.2534(5)	0.5792(5)	0.0465(5)	0.0045(6)	0.0106(7)	0.0061(5)	−0.0009(5)	−0.0019(4)	0.0030(5)
O2	0.5221(5)	0.7171(5)	0.1225(4)	0.0069(6)	0.0064(6)	0.0029(4)	−0.0010(5)	−0.0019(4)	−0.0006(4)
O3	0.5448(5)	0.2865(5)	0.1343(4)	0.0121(8)	0.0068(6)	0.0022(4)	0.0018(5)	0.0019(4)	0.0001(4)
O4	0.7010(5)	0.5534(5)	0.3638(4)	0.0050(6)	0.0119(7)	0.0025(4)	0.0007(5)	−0.0013(4)	−0.0006(4)
O5	0.2693(4)	0.4889(4)	0.3731(3)	0.0042(6)	0.0083(7)	0.0014(4)	0.0011(5)	−0.0004(4)	0.0016(4)
O6	0.4256(5)	0.2497(5)	0.4570(5)	0.0090(7)	0.0066(7)	0.0067(5)	0.0034(5)	0.0019(5)	0.0016(5)
O7	0.8911(5)	0.7549(6)	0.0396(5)	0.0060(7)	0.0107(8)	0.0077(6)	0.0003(5)	−0.0001(5)	−0.0014(5)
O8	0.2615(5)	0.8694(6)	0.4205(6)	0.0087(8)	0.0092(8)	0.0111(7)	0.0009(6)	−0.0043(6)	0.0001(6)
O9	0.9709(5)	0.4176(5)	0.2169(4)	0.0064(6)	0.0109(7)	0.0028(4)	0.0000(5)	0.0004(4)	0.0006(4)
O10	0.6214(5)	0.0018(5)	0.2918(4)	0.0095(7)	0.0070(6)	0.0049(5)	0.0015(5)	0.0002(5)	0.0006(4)
O11	0.0080(6)	0.0100(6)	0.2431(6)	0.0129(11)	0.0131(10)	0.0110(8)	0.0009(8)	−0.0031(7)	0.0004(7)

Table 6. Observed and calculated structure factors of $ZnSO_3.2\frac{1}{2}H_2O$. The reflections are sorted in groups. In each group k and l have constant values. 10 $|F_o|$ and 10 $|F_c|$ are given after the running index h.

Table 6. Continued.

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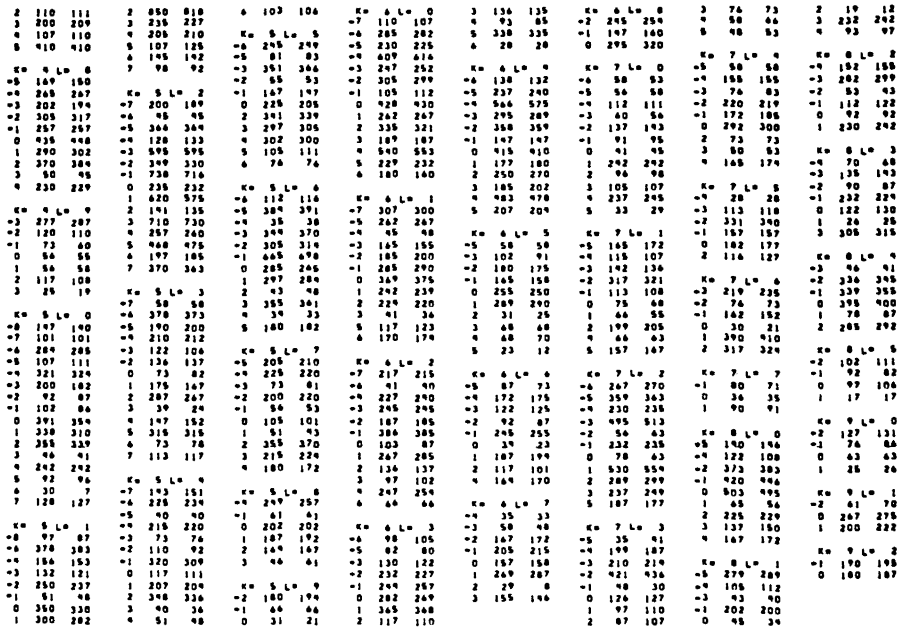

Table 7. Interatomic distances (Å) and angles (°) with standard deviations. The distances are not corrected for thermal motion.

Metal-oxygen distances			
Zn1 – O1	2.045(4)	Zn2 – O6	2.045(4)
– O9	2.071(4)	– O10	2.087(4)
– O7	2.172(4)	– O8	2.157(4)
Zn3 – O3	1.970(4)		
– O5	1.975(4)		
– O4	1.984(3)		
– O2	2.031(4)		
Sulfite groups			
S1 – O1	1.502(4)	S2 – O6	1.509(4)
– O3	1.518(4)	– O4	1.535(4)
– O2	1.537(4)	– O5	1.549(3)
O1 – O2	2.362(5)	O4 – O6	2.430(6)
O1 – O3	2.405(6)	O4 – O5	2.432(5)
O2 – O3	2.404(5)	O5 – O6	2.367(5)
O1 – S1 – O2	102.0(2)	O6 – S2 – O4	105.9(2)
O1 – S1 – O3	105.6(2)	O6 – S2 – O5	101.4(2)
O2 – S1 – O3	103.8(2)	O4 – S2 – O5	104.1(2)
Short O–O distances indicating possible hydrogen bonds			
O11 – O7	2.791(6)	O4 – O9	2.689(5)
O11 – O8	2.815(7)	O5 – O9	2.744(5)
O2 – O10	2.721(5)	O5 – O8	2.909(6)
O2 – O7	2.899(5)		
O3 – O10	2.689(5)		

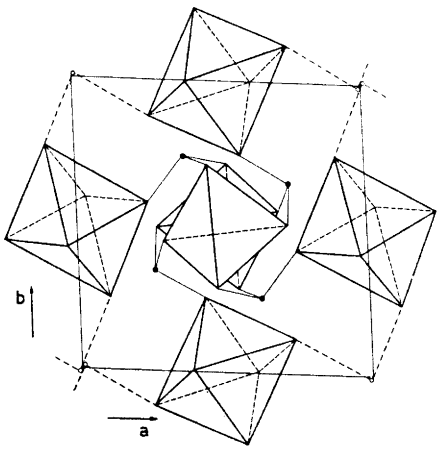

Fig. 1. The structure of $ZnSO_3.2\frac{1}{2}H_2O$. Schematic drawing showing the ZnO_4 tetrahedra and the ZnO_6 octahedra. The structure is viewed along the *c* axis. Filled circles denote sulfur atoms and unfilled circles oxygen atoms from the lattice water molecules. Possible hydrogen bonds between the lattice water and the other oxygen atoms are indicated by dotted lines.

the sum of the effective ionic radii (1.98 Å) according to Shannon and Prewitt [9] for four-coordinated zinc. The octahedral coordination around the rest of the zinc atoms is provided by two oxygen atoms from two different sulfite groups and four oxygen atoms belonging to water molecules. The two ZnO_6 groups in the structure are independent. The mean distance calculated for both groups is 2.10 Å in agreement with a greater distance for six-coordinated zinc. The value from the work of Shannon and Prewitt is 2.14 Å.

The zinc polyhedra have no corner in common, and the structure is held together by linking the sulfite groups to the polyhedra (Fig. 1). Possible O–H···O distances are given in Table 7. The assumed linking of the lattice water molecule to the polyhedra is illustrated in Fig. 1.

The dimensions of the sulfite group are consistent with a structure in which this group is coordinated through oxygen.[10] Two independent sulfite groups exist, but their oxygen atoms have similar surroundings. A sulfite group is connected to two different zinc tetrahedra and to one zinc octahedron.

The oxygen atoms O2 and O5, from two sulfite groups, are bonded to four-coordinated zinc and also probably have two hydrogen bonds to the water molecules. They have the longest S–O distance in each group (S1–O2 1.537 Å and S2–O5 1.549 Å).

The oxygen atoms in the sulfite groups with the shortest S–O distances are O1 and O4 (S1–O1 1.502 Å and S2–O6 1.509 Å). These oxygen atoms are bonded only to six-coordinated zinc and the S–O distances are not significantly different from the distance of 1.504 found in Na_2SO_3 [11] for the free anion.

O3 and O4 are both bonded to four-coordinated zinc and probably to one water molecule. They have S–O bonds between the values for the other two distances in the group (S1–O3 1.518 Å and S2–O4 1.535 Å).

The differences in lengths between the longest and shortest S–O bond in the groups are 0.035 Å (S1) and 0.040 Å (S2), corresponding to differences of

8σ and 10σ in the bond lengths. Similar variations of individual S – O bonds, because of coordination effects on oxygen, have been observed in $(NH_4)_9[Fe(SO_3)_6]$ [12] and $Tl_2[Cu(SO_3)_2]$.[13]

The average S – O distance (1.525 Å) in the sulfite groups is approximately the same as in other sulfites with oxygen engaged in metal bonding and/or hydrogen bonding. In $(NH_4)_2SO_3.H_2O$ [14] the same distance is 1.524 Å and in $(NH_4)_9[Fe(SO_3)_6]$ 1.517 Å.

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