

The Crystal Structure of $\text{ZnSO}_3 \cdot 2\frac{1}{2}\text{H}_2\text{O}$

BIRGIT NYBERG

Division of Inorganic Chemistry 2, Chemical Center, Box 740, S-220 07 Lund 7, Sweden

The crystal structure of $\text{ZnSO}_3 \cdot 2\frac{1}{2}\text{H}_2\text{O}$ 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 $\angle \text{O}-\text{S}-\text{O}$ 103.8°.

A preliminary crystal structure determination of $\text{ZnSO}_3 \cdot 2\frac{1}{2}\text{H}_2\text{O}$ has been published earlier.¹ Later a structure determination of the compound $\text{ZnSO}_3 \cdot 2\text{H}_2\text{O}$ 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 $\text{ZnSO}_3 \cdot 2\frac{1}{2}\text{H}_2\text{O}$. 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 $\text{ZnSO}_3 \cdot 2\frac{1}{2}\text{H}_2\text{O}$: 34.32 % Zn, 16.83 % S and 23.65 % H_2O .

Values for the cell dimensions were calculated from an indexed Guinier-Hägg powder photograph. 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 $V = 524.0$ Å³. Observed and calculated $\sin^2 \theta$ values are listed together with calculated structure factors in Table 1.

The cell is not reduced according to Delaunay⁵ 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 photograph of $\text{ZnSO}_4 \cdot 2\frac{1}{2}\text{H}_2\text{O}$. $\text{CuK}\alpha_1$ radiation. KCl was used as an internal standard. $a_{\text{KCl}} = 6.2923 \text{ \AA}$ at 25°C .

hkl	$10^5 \times \sin^2 \theta_{\text{obs}}$	$10^5 \times \sin^2 \theta_{\text{calc}}$	$ F _{\text{calc}}$	I_{obs}
001	—	718	1	
100	1017	1019	101	vst
010	1044	1045	97	st
101	1689	1693	51	m
011		1762	51	
011	1757	1764	54	st
101		1780	55	
110	—	1929	9	
110	—	2199	2	
111	2603	2604	28	w
111	2682	2689	54	m
002	2873	2871	55	
111		2873	50	vst
111	2959	2962	37	vw
102	3806	3803	27	vw
012	3934	3915	31	vw
012		3919	11	.
102	—	3977	5	
200	4074	4074	87	st
020	4196	4182	79	vst
201	4707	4705	51	st
112		4715	78	
210	—	4850	10	
201		4879	55	
112	4892	4885	99	vst
021		4898	30	
021		4902	51	
120	—	4930	33	
112	4995	4981	102	w
112	5163	5160	98	vst
210	—	5390	38	
120	—	5471	25	
211	—	5481	19	
121	5612	5606	113	m
211	—	5653	10	
121	5699	5690	127	st
211	5995	6020	147	st
121	—	6143	24	
211	6202	6196	79	w
121	—	6234	9	
003	—	6460	7	
202	6785	6771	46	vw
022	7052	7049	80	
022		7057	67	m
202	7123	7120	57	
103	—	7348	9	vw
013	—	7503	19	
013	7504	7509	71	
212		7548	76	st
103	7620	7610	74	w
220	7720	7716	78	m
122	—	7722	22	
122	7884	7885	52	
212		7893	90	m

Table 1. Continued.

212	—	8095	45	
122	8259	{ 8251	62	
113		8261	42	w
221	—	8348	34	
122	8425	8433	80	w
212	—	8438	27	
113	—	8517	17	
221	—	8519	9	
113	—	8526	33	
113	—	8793	22	
220	8791	8797	59	vw
300	—	9167	5	
030	—	9409	4	
221	—	9426	3	
221	—	9604	3	
301	9760	9754	52	vw
310	—	9870	11	
301	—	10016	14	
130	—	10022	10	
031	10123	{ 10124	45	
031		10130	34	vw
203	—	10273	11	
311	—	10395	16	
222	—	10416	19	
310	—	10618	5	
023	10642	{ 10636	17	
023		10648	29	vvw
311	—	10655	3	
131	—	10700	21	
222	—	10757	14	
131	10778	{ 10781	40	
203		10796	35	vw
130	—	10834	12	
213		11051		
311		11204		
311	—	11486	1	
004	11471	11485	117	st
222	—	11490	11	
131	—	11505	3	
123	—	11515	40	
213	—	11568	22	
213	—	11586	44	
131	—	11598	12	
302	—	11777	43	
123	—	11794	6	
222	—	11847	35	
213	12117	12115	74	vw
032	—	12275	21	
032	12289	12287	66	w
302	—	12300	7	
104	—	12329	11	
312	12421	12419	103	w
014	—	12526	2	
014	12561	12534	65	vw
320	—	12538	21	
230	—	12673	50	
104	—	12678	34	
132	12824	12812	105	w

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

Table 2. The reduced unit cell according to Delaunay.

$a = 11.734 \text{ \AA}$	$\alpha = 90.06^\circ$
$b = 7.549 \text{ \AA}$	$\beta = 139.32^\circ$
$c = 9.094 \text{ \AA}$	$\gamma = 92.40^\circ$
	$V = 524.0 \text{ \AA}^3$

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 $8.74 \times 10^{-4} \text{ mm}^3$ 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 $\text{CuK}\alpha$ radiation. The collection of data was based on the application of the $\omega - 2\theta$ scan method with an upper limit of $2\theta = 70^\circ$ and a scan range of $(1^\circ + 0.15^\circ \tan \theta)$. 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 ($\mu = 99 \text{ cm}^{-1}$). 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.	
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 $\text{ZnSO}_3 \cdot 2\frac{1}{2}\text{H}_2\text{O}$ 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	<i>x</i>	<i>y</i>	<i>z</i>	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Zn1	0	$\frac{1}{2}$	0	0.0061(2)	0.0103(2)	0.0045(2)	-0.0000(2)	-0.0002(1)	0.0003(1)
Zn2	$\frac{1}{2}$	0	$\frac{1}{2}$	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)	0.25052(7)	0.0075(2)	0.0083(2)	0.0047(1)	0.0005(1)	-0.0002(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)	0.50653(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)	0.045(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)	0.069(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(6)	-0.0004(4)	0.0016(4)
O6	0.4256(5)	0.2497(5)	0.4570(6)	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)	0.060(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)	0.0098(8)	-0.0031(7)	0.0004(7)

Table 6. Observed and calculated structure factors of $\text{ZnSO}_3 \cdot 2\frac{1}{2}\text{H}_2\text{O}$. The reflections are sorted in groups. In each group k and l have constant values. $10 |F_{\text{o}}|$ and $10 |F_{\text{c}}|$ are given after the running index h .

$\pm 0 \text{ L}^{\pm} 70$	0 151 157	23 151 152	1 172 178	0 200 275	3 167 197	2 278 280	0 15 15
0 237 249	2 212 212	-1 107 107	2 171 178	2 200 200	3 167 177	2 237 230	1 63 63
0 237 249	3 210 214	0 257 235	5 170 170	4 222 235	6 171 171	3 268 265	3 145 150
0 105 113	0 77 77	7 225 225	-7 140 150	4 200 207	6 177 174	1 234 234	5 1 1 L ⁺ 1
1 211 219	0 66 50	5 92 71	-6 117 119	4 198 207	6 177 174	2 186 149	7 63 29
1 137 142	1 240 257	6 165 170	5 310 307	4 200 207	6 177 174	3 168 168	7 63 29
0 236 258	0 48 48	6 180 191	2 210 210	4 225 225	5 275 280	5 272 295	5 26 17
0 167 160	0 66 66	1 120 120	0 247 247	3 111 101	5 165 165	6 97 105	4 157 155
0 237 232	0 350 361	1 207 207	0 219 219	1 200 202	2 268 277	7 270 280	2 743 793
0 64 53	0 43 43	7 355 341	1 207 207	0 245 245	0 255 249	1 793 783	6 63 53
0 125 122	-3 90 92	-7 355 341	2 212 197	2 572 554	1 520 554	0 237 225	2 137 135
0 110 123	-2 105 192	-5 131 120	3 187 187	3 177 172	2 157 160	0 200 187	3 177 158
0 200 202	0 37 36	5 314 326	3 187 187	3 177 172	2 157 160	0 101 93	9 54 51
0 171 171	0 37 36	5 294 296	0 245 245	4 268 268	3 555 555	0 310 304	9 491 465
0 209 209	1 209 209	3 744 736	6 155 156	0 233 232	0 233 232	5 274 274	9 41 43
0 216 182	2 76 35	-2 30 28	6 31 31	5 237 237	6 220 226	3 840 841	6 404 500
0 56 51	3 272 259	-1 225 230	7 102 97	3 177 177	6 40 35	1 108 112	209 209
0 165 162	3 39 34	0 45 46	8 175 180	2 240 240	7 386 374	1 250 242	6 410 404
0 115 115	0 255 227	1004 931	-1 262 257	0 101 93	0 101 93	9 54 51	9 54 51
0 165 73	9 117 113	3 528 496	0 152 154	0 152 154	0 152 154	0 152 154	0 152 154
0 170 172	0 152 154	2 528 496	0 152 154	1 71 71	0 282 282	0 282 282	0 152 154
0 65 75	0 152 154	2 255 232	2 207 210	1 72 72	0 284 284	0 284 284	0 128 115
0 209 209	0 30 12	6 409 610	5 128 122	3 220 215	0 155 155	0 105 105	0 128 115
0 185 192	0 265 270	1 132 116	3 92 94	4 80 79	5 155 155	0 141 152	6 400 418
0 212 192	0 30 39	2 192 165	0 152 154	0 152 154	0 152 154	0 152 154	0 152 154
0 55 53	0 170 165	6 165 170	0 237 227	4 80 79	5 155 155	0 141 152	6 400 418
0 211 191	0 30 39	2 192 165	0 152 154	0 152 154	0 152 154	0 152 154	0 152 154
0 155 155	0 334 331	5 155 155	0 152 154	0 152 154	0 152 154	0 152 154	0 152 154
0 155 155	2 151 155	-7 140 152	1 975 915	0 100 105	3 212 215	0 141 152	6 400 418
0 104 117	3 71 71	0 104 104	2 205 192	0 44 41	4 420 445	6 175 175	1 648 941
0 155 155	4 370 333	0 78 76	3 55 61	3 268 355	9 127 132	6 174 174	0 91 106
0 155 155	6 66 53	0 78 76	3 55 61	2 490 493	6 174 174	2 269 260	1 748 793
0 155 155	0 250 239	6 538 594	-1 128 125	0 152 154	0 152 154	0 152 154	0 152 154
0 227 227	0 152 154	0 152 154	6 160 177	0 271 278	0 152 154	0 152 154	0 152 154
0 131 130	0 56 40	0 351 330	2 270 270	0 152 154	0 152 154	0 152 154	0 152 154
0 245 256	0 121 122	1 41 38	0 152 154	2 473 425	0 217 220	1 446 571	9 407 395
0 267 270	0 127 138	2 73 82	-7 25 15	9 418 425	0 92 73	3 185 180	6 555 533
0 236 236	0 56 63	0 743 851	25 102 86	5 26 41	1 354 350	2 262 287	7 365 346
0 34 35	0 152 154	9 92 102	-137 142	6 25 20	1 118 118	2 209 202	0 267 249
0 212 212	0 253 247	9 145 148	7 40 40	3 265 245	0 152 154	0 152 154	0 152 154
0 192 192	1 151 154	6 53 53	0 215 217	3 265 245	0 152 154	0 152 154	0 152 154
0 192 192	2 73 73	0 152 154	2 150 154	1 510 456	4 142 145	0 58 63	0 285 307
0 41 41	0 229 268	0 78 81	1 212 212	0 177 169	6 152 141	0 152 154	0 152 154
0 41 41	4 52 50	0 56 56	2 117 105	7 245 350	0 152 154	0 152 154	0 152 154
0 27 25	0 132 137	0 270 265	9 357 181	0 152 154	0 152 154	0 152 154	0 152 154
0 70 83	9 240 234	-2 242 280	5 349 356	4 260 325	3 71 78	2 197 190	0 83 708
0 280 235	0 305 302	7 310 297	-2 355 340	0 190 175	0 152 154	0 152 154	0 152 154
0 124 138	0 66 66	0 280 266	7 310 297	0 190 175	0 152 154	0 152 154	0 152 154
0 64 61	199 199	1 269 285	8 42 48	-1 848 788	1 98 98	-1 499 590	4 245 255
0 447 472	0 331 330	7 71 71	0 152 154	0 780 641	2 112 112	0 192 148	6 96 97
0 247 247	0 130 130	2 160 162	4 61 61	3 140 100	3 88 87	1 102 90	2 235 237
0 170 168	0 443 464	1 167 164	-7 146 156	4 61 61	4 376 354	2 234 241	7 74 78
0 43 43	1 264 308	0 160 162	4 61 61	3 550 530	3 330 326	8 128 126	0 142 144
0 137 122	0 109 405	6 100 100	170 164	4 388 400	0 10 10	4 40 31	9 142 144
0 137 122	1 30 30	7 132 132	1 160 160	5 748 611	0 93 101	9 56 60	0 152 154
0 227 227	0 261 261	0 152 154	5 65 61	6 262 260	1 435 444	6 61 56	0 152 154
0 235 235	0 331 333	0 152 154	6 65 61	7 245 239	0 405 390	7 358 355	0 232 237
0 235 235	4 400 400	0 152 154	6 65 61	8 160 147	1 202 200	0 152 154	0 152 154
0 210 212	5 226 217	0 255 252	0 734 606	3 170 167	0 152 154	0 152 154	0 152 154
0 210 212	6 364 353	0 66 73	1 160 162	3 170 167	0 152 154	0 152 154	0 152 154
0 910 920	-1 71 76	2 766 726	0 262 250	0 152 154	0 152 154	0 152 154	0 152 154
0 130 130	0 200 270	2 162 190	-7 122 136	0 209 282	0 88 107	0 156 165	0 156 165
0 124 127	0 200 270	1 122 118	2 212 217	0 265 555	0 130 137	0 479 505	0 124 127
0 284 275	0 151 155	2 170 150	6 349 339	2 743 735	0 287 300	0 223 222	0 223 222
0 274 277	-1 207 205	4 70 71	7 259 249	0 93 96	0 83 92	0 229 195	1 230 214
0 222 230	0 227 222	9 175 175	3 380 340	1 91 95	0 473 453	1 455 450	2 305 315
0 172 172	1 332 320	6 307 295	0 1018 873	2 91 93	0 152 154	0 152 154	0 152 154
0 227 227	3 321 323	0 152 154	6 65 61	6 262 260	1 435 444	6 61 56	0 152 154
0 235 235	4 400 400	0 152 154	6 65 61	7 245 239	0 405 390	7 358 355	0 232 237
0 235 235	5 226 217	0 255 252	0 734 606	3 170 167	0 152 154	0 152 154	0 152 154
0 310 312	6 364 353	0 66 73	1 160 162	0 152 154	0 152 154	0 152 154	0 152 154
0 910 920	-1 71 76	2 766 726	0 262 250	0 152 154	0 152 154	0 152 154	0 152 154
0 130 130	0 200 270	2 162 190	-7 122 136	0 209 282	0 88 107	0 156 165	0 156 165
0 124 127	0 200 270	1 122 118	2 212 217	0 265 555	0 130 137	0 479 505	0 124 127
0 284 275	0 151 155	2 170 150	6 349 339	2 743 735	0 287 300	0 223 222	0 223 222
0 274 277	-1 207 205	4 70 71	7 259 249	0 93 96	0 83 92	0 229 195	1 230 214
0 222 230	0 227 222	9 175 175	3 380 340	1 91 95	0 473 453	1 455 450	2 305 315
0 172 172	1 251 157	5 349 363	1 165 152	5 95 97	0 2 2 L ⁺ 2	0 925 405	0 391 403
0 227 280	3 97 96	6 61 63	4 73 73	7 255 234	0 20 29	1 170 169	0 157 138
0 227 280	4 107 116	7 50 73	7 255 234	0 101 90	0 223 111	2 294 290	0 51 50
0 235 235	0 152 154	6 65 61	6 65 61	6 268 260	3 20 21	7 226 222	0 210 209
0 135 131	0 245 255	-2 179 180	0 152 154	1 101 90	0 250 345	4 383 394	2 270 292
0 165 162	-1 92 93	-2 289 270	-5 100 103	1 63 55	0 103 123	6 454 429	0 204 212
0 107 112	0 101 110	0 376 385	-5 120 123	2 804 730	0 278 349	5 53 56	0 157 138
0 227 227	1 311 325	1 55 61	-3 305 315	3 260 249	0 176 180	6 420 422	0 220 220
0 93 70	0 107 112	0 255 252	1 165 152	5 165 152	0 152 154	0 152 154	0 152 154
0 222 230	3 230 222	3 127 127	-1 162 175	5 157 167	1 180 220	3 250 257	0 321 323
0 172 172	4 95 93	5 157 162	0 51 55	6 170 170	2 220 174	-2 63 51	0 152 154
0 222 230	5 95 93	5 157 162	0 51 55	7 240 41	3 25 17	-1 232 242	0 152 154
0 165 162	0 245 255	5 157 162	0 51 55	7 240 41	3 25 17	-1 232 242	0 152 154
0 227 227	5 95 93	5 157 162	0 51 55	7 240 41	3 25 17	-1 232 242	0 152 154
0 227 227	6 107 116	7 50 73	7 255 234	0 101 90	0 223 111	2 294 290	0 51 50
0 235 235	0 152 154	6 65 61	6 65 61	6 268 260	3 20 21	7 226 222	0 210 209
0 135 131	0 245 255	-2 179 180	0 152 154	1 101 90	0 250 345	4 383 394	2 270 292
0 165 162	-1 92 93	-2 289 270	0 152 154	1 63 55	0 103 123	6 454 429	0 204 212
0 107 112	0 101 110	0 376 385	-5 120 123	2 804 730	0 278 349	5 53 56	0 157 138
0 227 227	1 311 325	1 55 61	-3 305 315	3 260 249	0 176 180	6 420 422	0 220 220
0 93 70	0 107 112	0 255 252	1 165 152	5 165 152	0 152 154	0 152 154	0 152 154
0 222 230	3 230 222	3 127 127	-1 162 175	5 157 167	1 180 220	3 250 257	0 321 323
0 172 172	4 95 93	5 157 162	0 51 55	6 170 170	2 220 174	-2 63 51	0 152 154
0 222 230	5 95 93	5 157 162	0 51 55	7 240 41	3 25 17	-1 232 242	0 152 154
0 165 162	0 245 255	5 157 162	0 51 55	7 240 41	3 25 17	-1 232 242	0 152 154
0 227 227	6 107 116	7 50 73	7 255 234	0 101 90	0 223 111	2 294 290	0 51 50
0 235 235	0 152 154	6 65 61	6 65 61	6 268 260	3 20 21	7 226 222	0 210 209
0 135 131	0 245 255	-2 179					

Table 6. Continued.

0 235 235	27 192 195	5 77 76	+ 1 192 189	+ 2 230 222	0 255 222	3 190 170	5 252 255
0 175 175	26 302 312	5 252 234	+ 2 232 225	+ 3 180 73	1 380 370	4 323 325	6 444 433
0 91 111	25 249 300	5 252 234	+ 3 183 87	+ 1 1351 1266	2 237 209	5 320 245	7 311 126
0 476 456	24 257 227	+ 0 L ⁺ 10	+ 2 165 169	0 403 302	3 340 383	6 210 202	8 215 214
0 231 220	+ 0 101 911	+ 2 166 227	+ 1 264 255	2 200 233	9 180 116	7 135 128	8 162 151
0 31 21	+ 0 105 105	+ 2 166 227	+ 0 264 255	2 200 233	5 185 182	6 162 151	+ 0 L ⁺ 1
0 231 220	+ 0 163 734	+ 1 151 152	+ 2 173 781	3 464 350	4 161 30	+ 0 L ⁺ 4	+ 7 217 219
0 78 71	1 137 179	1 117 110	5 166 93	7 335 341	+ 5 205 190	+ 0 162 165	+ 3 317 320
0 840 883	2 117 107	3 174 160	+ 0 332 351	+ 5 205 190	+ 5 141 194	+ 0 40 48	+ 3 317 320
0 145 162	3 801 885	5 166 93	7 335 341	+ 5 205 190	+ 5 141 194	+ 0 40 48	+ 3 317 320
0 145 162	3 801 885	5 166 93	7 335 341	+ 5 205 190	+ 5 141 194	+ 0 40 48	+ 3 317 320
0 227 210	5 145 915	+ 0 L ⁺ 11	+ 0 332 351	+ 5 205 190	+ 5 141 194	+ 0 40 48	+ 3 317 320
0 267 287	4 137 163	0 87 80	8 90 87	+ 0 97 88	+ 0 290 620	+ 1 230 182	+ 1 307 279
0 58 60	7 200 312	+ 0 L ⁺ 0	+ 0 166 6	+ 0 312 319	+ 1 280 262	0 162 150	0 350 305
0 41 66	6 111 107	+ 0 167 162	+ 0 166 6	+ 0 325 326	0 302 287	1 232 182	1 440 201
0 161 197	9 103 97	+ 0 135 135	+ 0 329 309	+ 0 44 39	1 46 30	2 570 545	3 282 272
0 220 210	+ 0 398 400	+ 0 398 400	+ 0 51 51	+ 0 56 53	2 245 259	3 282 272	4 35 36
0 178 179	+ 0 L ⁺ 6	+ 0 398 400	+ 0 51 51	+ 0 56 53	2 245 259	3 282 272	4 35 36
0 115 162	+ 0 177 149	+ 0 493 176	+ 0 124 133	+ 0 474 743	4 374 384	5 44 40	6 124 116
0 115 162	+ 0 177 149	+ 0 493 176	+ 0 124 133	+ 0 474 743	4 374 384	5 44 40	6 124 116
0 115 162	+ 0 391 424	+ 0 170 103	+ 0 395 420	+ 1 547 520	6 345 324	7 140 142	8 290 299
0 247 270	+ 0 71 35	+ 0 192 91	+ 0 458 603	+ 0 986 800	+ 0 205 190	+ 0 205 190	+ 0 205 190
0 30 43	+ 0 86 815	0 1203 946	0 470 390	1 466 419	+ 0 L ⁺ 5	+ 0 L ⁺ 5	+ 0 L ⁺ 2
0 222 104	+ 0 116 125	1 117 115	5 76 78	2 131 170	4 40 48	+ 7 150 152	8 21 52
0 222 104	+ 0 116 125	1 117 115	5 76 78	2 131 170	4 40 48	+ 7 150 152	8 21 52
0 217 199	+ 0 303 334	3 48 50	3 370 920	4 260 250	+ 2 38 38	+ 4 48 51	+ 9 132 125
0 285 315	0 1190 1148	9 456 453	120 127	5 242 252	+ 1 361 371	+ 2 240 279	+ 2 240 280
0 87 78	1 73 106	5 73 6	5 964 481	6 177 180	0 121 212	+ 3 76 73	+ 3 215 215
0 160 160	2 671 756	6 113 116	6 182 180	7 117 117	1 267 265	+ 2 329 323	+ 3 122 105
0 685 70	4 425 471	7 81 87	7 333 330	8 93 61	2 65 70	+ 1 215 137	+ 2 123 135
0 6 215 230	+ 0 229 207	+ 0 76 76	+ 0 229 207	+ 0 110 95	3 135 155	4 161 155	+ 3 315 335
0 5 212 222	+ 0 229 207	+ 0 76 76	+ 0 229 207	+ 0 110 95	3 135 155	4 161 155	+ 3 315 335
0 115 162	0 483 486	+ 0 L ⁺ 1	+ 0 182 170	+ 0 181 107	5 87 87	+ 1 187 157	+ 0 41 50
0 115 162	0 483 486	+ 0 L ⁺ 1	+ 0 182 170	+ 0 181 107	5 87 87	+ 1 187 157	+ 0 41 50
0 307 92	+ 0 L ⁺ 9	+ 0 265 277	+ 0 297 290	+ 0 105 120	5 205 219	5 257 237	6 222 229
0 386 376	+ 0 71 54	+ 0 97 97	+ 0 260 297	+ 0 366 390	+ 0 170 170	7 51 41	9 322 317
0 113 92	+ 0 209 187	+ 0 150 151	+ 0 290 310	+ 0 51 51	+ 0 187 187	+ 0 187 187	+ 0 187 187
0 205 170	+ 0 485 504	+ 0 200 205	+ 0 297 322	+ 0 73 80	+ 0 197 197	+ 0 197 197	+ 0 197 197
0 205 170	+ 0 485 504	+ 0 200 205	+ 0 297 322	+ 0 73 80	+ 0 197 197	+ 0 197 197	+ 0 197 197
0 272 307	+ 0 520 581	1 66 72	1 285 295	+ 0 237 167	+ 1 317 319	+ 0 236 236	+ 0 L ⁺ 3
0 88 63	+ 0 282 310	3 41 29	2 504 571	+ 1 128 161	2 51 58	+ 0 588 578	+ 0 L ⁺ 3
0 93 40	+ 0 661 773	7 73 102	3 46 41	+ 2 343 329	+ 0 404 419	+ 0 230 228	+ 0 107 107
0 35 15	0 43 43	+ 0 558 536	9 117 127	+ 3 492 500	+ 0 346 346	+ 0 268 219	+ 0 51 50
0 1 250 285	+ 0 620 600	+ 0 500 500	+ 0 400 297	+ 4 60 61	+ 0 43 43	+ 0 271 257	+ 0 271 257
0 229 229	+ 0 194 194	+ 0 300 800	+ 0 165 167	+ 4 61 61	+ 0 43 43	+ 0 271 257	+ 0 271 257
0 229 229	+ 0 194 194	+ 0 300 800	+ 0 165 167	+ 4 61 61	+ 0 43 43	+ 0 271 257	+ 0 271 257
0 272 270	+ 0 152 197	+ 0 117 97	+ 0 217 207	+ 6 115 125	+ 7 71 60	+ 0 325 287	+ 0 290 299
0 1 272 270	+ 0 152 197	+ 0 117 97	+ 0 217 207	+ 6 115 125	+ 7 71 60	+ 0 325 287	+ 0 290 299
1 307 319	7 53 51	5 66 46	+ 0 267 285	7 567 573	+ 5 117 127	2 169 145	+ 1 102 111
2 205 224	8 100 100	6 270 266	+ 0 267 285	8 512 511	+ 2 205 223	3 405 461	+ 0 176 161
3 249 456	7 100 100	6 270 266	+ 0 267 285	8 512 511	+ 2 205 223	3 405 461	+ 0 176 161
4 123 115	+ 0 L ⁺ 6	9 167 145	+ 0 268 202	+ 7 92 84	+ 1 166 103	6 61 58	3 349 361
0 180 174	+ 0 192 167	+ 0 L ⁺ 2	+ 0 215 187	+ 6 163 526	0 122 125	7 105 179	4 102 87
0 180 174	+ 0 192 167	+ 0 L ⁺ 2	+ 0 215 187	+ 6 163 526	0 122 125	7 105 179	4 102 87
0 98 122	+ 0 197 205	+ 2 192 207	+ 6 193 465	+ 3 196 465	2 111 66	+ 0 3 L ⁺ 7	+ 0 215 215
0 351 361	+ 0 197 205	+ 2 192 207	+ 6 193 465	+ 3 196 465	2 111 66	+ 0 3 L ⁺ 7	+ 0 215 215
1 781 844	+ 0 189 210	+ 0 227 227	+ 6 202 312	+ 6 208 371	+ 3 227 285	+ 0 236 236	+ 0 236 236
3 36 46	+ 0 254 325	+ 0 365 365	+ 6 43 33	+ 1 341 319	+ 2 225 245	+ 2 191 239	+ 0 L ⁺ 5
4 106 1083	1 38 48	+ 167 157	+ 2 291 267	+ 2 291 267	+ 0 30 28	+ 0 200 277	+ 0 225 245
6 312 320	2 31 41	+ 0 625 903	+ 0 L ⁺ 9	+ 3 573 600	+ 0 3 L ⁺ 1	+ 1 207 192	+ 0 245 245
6 272 287	2 290 331	+ 0 629 886	+ 0 151 153	+ 4 593 600	+ 0 3 L ⁺ 1	+ 1 207 192	+ 0 245 245
7 72 71	7 55 51	+ 0 629 886	+ 0 151 153	+ 4 593 600	+ 0 3 L ⁺ 1	+ 1 207 192	+ 0 245 245
8 191 679	8 211 192	+ 0 349 307	+ 0 167 123	+ 4 593 611	+ 2 62 71	+ 0 96 93	+ 0 636 503
9 197 215	4 115 125	1 949 1021	+ 2 245 267	7 237 230	+ 5 297 297	5 61 61	1 553 526
0 158 160	2 429 446	+ 0 247 246	+ 2 247 246	8 115 125	+ 7 376 365	6 87 87	2 761 766
0 252 270	+ 0 L ⁺ 7	+ 0 995 1076	+ 0 81 87	+ 3 106 88	+ 0 3 L ⁺ 7	+ 0 198 198	+ 0 248 248
0 25 12	+ 0 111 102	5 83 82	+ 2 305 350	+ 3 106 88	+ 0 3 L ⁺ 7	+ 0 198 198	+ 0 248 248
0 49 60	+ 0 140 140	+ 0 227 227	+ 4 160 142	+ 3 332 339	+ 0 533 459	+ 0 100 100	7 141 142
0 53 54	+ 0 142 245	7 440 435	6 88 87	+ 1 341 319	+ 1 51 35	+ 0 260 272	+ 0 245 245
0 440 449	+ 0 242 256	9 220 207	+ 6 193 189	+ 2 349 349	+ 1 177 197	+ 0 177 197	+ 0 L ⁺ 5
0 51 191	+ 0 130 157	+ 0 242 256	+ 6 193 189	+ 3 145 145	+ 3 145 145	+ 0 177 197	+ 0 L ⁺ 5
-2 540 546	+ 2 97 87	+ 0 L ⁺ 3	+ 3 380 398	+ 3 103 123	+ 4 386 396	+ 2 134 120	+ 2 220 231
-1 501 551	+ 0 108 123	+ 0 242 256	+ 2 180 195	+ 4 386 396	+ 2 134 120	+ 2 134 120	+ 2 220 231
0 20 12	+ 0 130 123	+ 0 242 256	+ 2 180 195	+ 4 386 396	+ 2 134 120	+ 2 134 120	+ 2 220 231
-1 51 17	+ 0 140 51	+ 0 451 461	+ 0 343 300	+ 0 120 107	7 73 68	+ 4 102 95	+ 2 235 217
-2 495 505	+ 2 339 333	+ 0 449 470	1 515 500	+ 1 405 360	+ 2 333 325	+ 4 102 95	+ 2 235 217
-3 913 515	3 141 192	+ 0 242 256	+ 2 187 217	+ 2 81 71	+ 2 315 317	+ 4 102 95	+ 2 235 217
-5 279 277	5 336 343	+ 0 180 170	+ 4 25 20	+ 4 303 300	+ 2 322 220	+ 2 108 105	+ 0 87 82
-6 302 315	7 76 66	+ 0 170 165	+ 4 25 20	+ 5 102 102	+ 2 320 225	+ 1 113 105	+ 5 190 195
-7 28 26	+ 0 170 165	+ 0 170 165	+ 4 25 20	+ 5 102 102	+ 2 310 225	+ 1 113 105	+ 5 190 195
-8 180 182	+ 0 L ⁺ 6	+ 0 437 493	+ 0 106 117	+ 7 270 267	+ 6 688 726	+ 0 320 300	+ 6 56 56
-9 113 101	+ 0 351 101	+ 0 182 195	+ 0 127 175	+ 7 270 267	+ 6 688 726	+ 0 31 91 91	+ 7 80 76
-0 230 220	+ 0 274 257	+ 0 160 209	+ 0 74 40	+ 0 L ⁺ 6	+ 0 830 833	+ 2 24 30	+ 4 199 199
-7 192 167	+ 0 274 257	+ 0 160 209	+ 0 74 40	+ 0 L ⁺ 6	+ 0 830 833	+ 2 24 30	+ 4 199 199
-1 111 117	+ 0 274 257	+ 0 160 209	+ 0 74 40	+ 0 L ⁺ 6	+ 0 830 833	+ 2 24 30	+ 4 199 199
-3 135 17	+ 0 748 803	+ 0 126 115	+ 2 799 783	+ 3 220 202	+ 3 771 756	+ 2 235 200	+ 3 200 195
-4 102 90	+ 1 330 910	+ 0 445 441	+ 1 355 331	+ 2 197 190	+ 4 267 275	+ 0 191 191	+ 4 191 191
-5 102 90	+ 1 330 910	+ 0 445 441	+ 1 355 331	+ 2 197 190	+ 4 267 275	+ 0 191 191	+ 4 191 191
-3 245 235	+ 0 L ⁺ 9	1 53 25	6 364 375	+ 4 101 101	+ 4 300 300	+ 2 199 199	+ 4 L ⁺ 7
-4 147 142	+ 2 380 440	+ 0 140 162	+ 0 768 775	+ 1 386 365	+ 4 366 350	+ 1 381 350	+ 4 L ⁺ 7
-5 147 142	+ 2 382 445	+ 2 420 421	+ 7 145 128	+ 5 207 182	+ 4 366 350	+ 1 381 350	+ 4 L ⁺ 7
-6 120 330	+ 0 145 147	+ 2 420 421	+ 8 265 252	+ 7 165 190	+ 5 208 200	+ 4 366 350	+ 4 L ⁺ 7
-7 207 195	+ 2 73 67	5 143 157	+ 0 L ⁺ 5	+ 0 100 85	+ 3 381 350	+ 1 381 350	+ 4 L ⁺ 7
-8 209 214	+ 2 239 240	6 64 63	+ 0 98 369	+ 5 128 117	+ 2 564 559	+ 0 1366 131	+ 4 191 191
-9 78 80	0 48 35	8 155 140	+ 0 132 123	+ 5 135 147	+ 1 191 191	+ 2 564 559	+ 4 191 191
-0 180 265	2 323 349	+ 0 L ⁺ 5	+ 0 170 165	+ 5 102 101	+ 3 104 92	+ 0 157 142	+ 4 L ⁺ 7
-0 262 265	3 137 146	+ 0 217 215	+ 0 835 841	+ 1 383 370	+ 2 154 120	+ 0 200 214	+ 4 L ⁺ 7

Table 6. Continued.

110	111	850	910	6	103	106	K+	6	L+	0	3	136	135	K+	6	L+	0	3	74	73	K+	2	19	12			
200	209	3	235	227	-	-	K+	6	L+	0	-7	110	107	K+	6	L+	0	-7	110	107	K+	3	232	22			
107	110	4	205	210	K+	6	L+	0	-6	285	282	K+	6	330	335	K+	6	245	250	K+	6	40	33				
9	410	410	5	107	125	-	-	K+	6	235	237	K+	6	230	225	K+	6	197	160	K+	4	93	77				
5	4	4	145	142	-	-	K+	6	145	142	-	-	235	237	-	-	235	237	-	-	K+	6	145	142			
5	4	4	9	92	-	-	K+	6	351	346	-	-	237	243	-	-	237	243	-	-	K+	6	9	92			
5	4	4	9	92	-	-	K+	6	25	53	-	-	205	209	-	-	205	209	-	-	K+	6	25	53			
5	4	4	147	147	K+	6	L+	2	-1	167	167	K+	6	105	112	K+	6	130	132	K+	6	58	53				
5	4	4	245	247	K+	6	L+	2	-1	200	185	K+	6	225	205	K+	6	237	240	K+	6	56	50				
5	4	4	202	195	-	-	K+	6	225	205	-	-	925	930	-	-	565	575	-	-	K+	6	112	122			
5	4	317	317	-	-	K+	6	45	45	-	-	285	287	-	-	285	287	-	-	K+	6	45	45				
5	4	237	237	-	-	K+	6	165	165	-	-	265	267	-	-	265	267	-	-	K+	6	165	165				
5	4	355	355	-	-	K+	6	129	133	-	-	205	207	-	-	187	187	-	-	K+	6	73	73				
5	4	290	302	-	-	K+	6	595	595	5	105	111	5	167	167	K+	6	115	910	K+	6	50	53				
5	4	370	384	-	-	K+	6	349	330	-	-	200	200	-	-	177	180	-	-	K+	6	292	292				
5	4	50	49	-	-	K+	6	730	716	6	74	76	5	227	232	K+	6	250	270	K+	6	96	98				
5	4	230	229	-	-	K+	6	230	229	-	-	180	180	-	-	250	270	-	-	K+	6	180	182				
5	4	230	229	-	-	K+	6	230	229	-	-	180	180	-	-	250	270	-	-	K+	6	180	182				
5	4	191	191	-	-	K+	6	112	112	-	-	180	180	-	-	250	270	-	-	K+	6	112	112				
5	4	277	287	-	-	K+	6	191	195	-	-	285	291	-	-	207	307	300	5	207	209	K+	6	122	130		
5	4	120	110	-	-	K+	6	257	260	-	-	349	370	-	-	45	48	K+	6	L+	5	K+	6	157	157		
5	4	173	160	-	-	K+	6	466	475	-	-	205	208	-	-	165	165	K+	6	55	56	K+	6	182	177		
5	4	156	156	-	-	K+	6	197	185	-	-	205	205	-	-	180	180	K+	6	142	136	K+	2	114	114		
5	4	56	58	-	-	K+	6	270	263	-	-	285	245	-	-	265	290	-	-	K+	6	33	29				
5	4	217	198	-	-	K+	6	297	295	-	-	205	205	-	-	365	375	-	-	K+	6	231	231				
5	4	25	19	-	-	K+	6	5	5	3	43	40	1	294	299	K+	6	255	250	K+	6	113	108				
5	4	58	58	-	-	K+	6	358	358	3	355	341	2	225	220	K+	6	289	290	K+	6	75	68				
5	4	157	150	-	-	K+	6	150	150	-	-	205	205	-	-	21	21	K+	6	157	150	K+	6	205	205		
5	4	101	101	-	-	K+	6	210	212	-	-	180	182	-	-	117	123	-	-	K+	6	48	70				
5	4	284	285	-	-	K+	6	122	105	K+	6	L+	7	-	-	-	23	23	12	-	K+	6	157	147			
5	4	107	111	-	-	K+	6	136	137	-	-	205	210	-	-	217	215	K+	6	4	6	K+	6	7	6		
5	4	322	324	-	-	K+	6	73	82	-	-	205	220	-	-	207	217	K+	6	136	135	K+	6	70	72		
5	4	200	192	-	-	K+	6	125	125	-	-	205	205	-	-	197	207	K+	6	137	135	K+	6	92	82		
5	4	92	87	-	-	K+	6	287	247	-	-	200	220	-	-	227	240	K+	6	97	75	K+	6	36	35		
5	4	102	94	-	-	K+	6	39	27	-	-	56	53	-	-	245	245	K+	6	122	125	K+	6	239	235		
5	4	391	359	-	-	K+	6	197	192	0	105	101	-	2	167	165	K+	6	92	87	K+	6	95	91			
5	4	1330	310	-	-	K+	6	315	315	1	51	51	3	384	385	K+	6	245	255	K+	6	56	63				
5	4	381	229	-	-	K+	6	73	73	-	-	325	320	0	102	97	0	19	222	222	K+	6	140	136			
5	4	113	117	-	-	K+	6	215	215	-	-	325	325	-	-	117	120	-	-	K+	6	49	43				
5	4	242	242	-	-	K+	6	180	172	-	-	136	137	-	-	117	101	-	-	K+	6	530	554				
5	4	92	96	-	-	K+	6	5	5	5	97	102	3	97	102	K+	6	144	170	K+	6	289	299				
5	4	30	7	-	-	K+	6	153	151	K+	6	L+	8	4	247	254	K+	6	237	249	K+	6	903	995			
5	4	120	127	-	-	K+	6	226	231	-	-	205	257	6	64	66	K+	6	L+	7	5	187	177	K+	6	65	56
5	4	59	51	-	-	K+	6	125	125	-	-	205	205	-	-	245	254	K+	6	35	33	K+	6	225	220		
5	4	97	87	-	-	K+	6	73	76	-	1	187	192	-	-	98	105	K+	6	147	172	K+	6	35	31		
5	4	370	383	-	-	K+	6	110	92	-	2	165	147	-	-	62	80	K+	6	205	215	K+	6	199	187		
5	4	156	153	-	-	K+	6	120	309	3	46	61	-	2	130	122	K+	6	197	158	K+	6	210	219			
5	4	121	121	-	-	K+	6	101	111	-	-	205	205	-	-	187	192	K+	6	147	172	K+	6	167	170		
5	4	250	254	-	-	K+	6	101	111	-	-	205	205	-	-	232	237	K+	6	269	267	K+	6	267	269		
5	4	51	46	-	-	K+	6	238	236	-	2	180	172	-	-	66	66	K+	6	229	249	K+	6	126	123		
5	4	350	320	-	-	K+	6	90	36	-	1	66	66	1	365	368	K+	6	197	110	K+	6	202	200			
5	4	300	282	-	-	K+	6	51	48	0	31	21	2	117	110	K+	6	87	107	K+	6	49	39				

Table 7. Interatomic distances (\AA) and angles ($^\circ$) 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)		

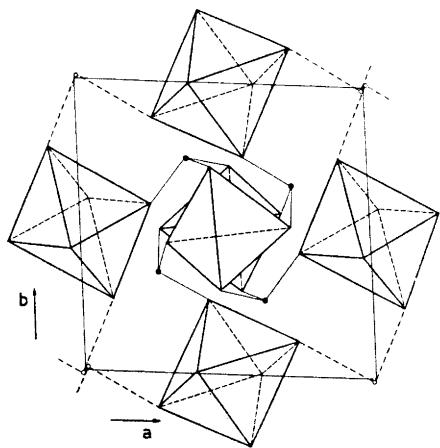


Fig. 1. The structure of $\text{ZnSO}_3 \cdot 2\frac{1}{2}\text{H}_2\text{O}$. Schematic drawing showing the ZnO_4 tetrahedra and the ZnO_6 octahedra. The structure is viewed along the c axis. Filled circles denote sulfur atoms and unfilled circles oxygen atoms from the lattice water molecules. Possible 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 \AA) according to Shannon and Prewitt⁹ 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 \AA in agreement with a greater distance for six-coordinated zinc. The value from the work of Shannon and Prewitt is 2.14 \AA .

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 \AA and S₂—O₅ 1.549 \AA).

The oxygen atoms in the sulfite groups with the shortest S—O distances are O₁ and O₄ (S₁—O₁ 1.502 \AA and S₂—O₆ 1.509 \AA). 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 \AA 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 \AA and S₂—O₄ 1.535 \AA).

The differences in lengths between the longest and shortest S—O bond in the groups are 0.035 \AA (S₁) and 0.040 \AA (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 $(\text{NH}_4)_9[\text{Fe}(\text{SO}_3)_6]$ ¹² and $\text{Ti}_2[\text{Cu}(\text{SO}_3)_2]$.¹³

The average S—O distance (1.525 \AA) in the sulfite groups is approximately the same as in other sulfites with oxygen engaged in metal bonding and/or hydrogen bonding. In $(\text{NH}_4)_2\text{SO}_3 \cdot \text{H}_2\text{O}$ ¹⁴ the same distance is 1.524 \AA and in $(\text{NH}_4)_9[\text{Fe}(\text{SO}_3)_6]$ 1.517 \AA .

Acknowledgement. The author expresses her sincere gratitude to Professor Bengt Aurivillius for his encouraging interest in this work and for invaluable advice. Her thanks are due also to Mr. Christer Särnstrand and Mr. Christer Svensson for their valuable help during the data collecting with CAD-4. The skilful technical assistance of Miss Kerstin Renhult is gratefully acknowledged. The author thanks Dr. Karin Aurivillius for critically reading the manuscript.

The investigation has received financial support from the *Swedish Natural Science Research Council*.

REFERENCES

1. Nyberg, B. *Acta Chem. Scand.* **26** (1972) 857.
2. Quinones, H. and Baggio, S. *J. Inorg. Nucl. Chem.* **34** (1972) 2153.
3. Pannetier, G., Djega-Madriadassou, G. and Bregault, J. M. *Bull. Soc. Chim. France* **1964** 1749.
4. Karlsson, R. and Karrman, K. J. *Talanta* **18** (1971) 459.
5. *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham 1962, Vol. I, p. 550.
6. Karle, J. and Karle, I. L. *Acta Cryst.* **21** (1966) 849.
7. Coppens, P. and Hamilton, W. C. *Acta Cryst. A* **26** (1970) 71.
8. Doyle, P. A. and Turner, P. S. *Acta Cryst. A* **24** (1968) 390.
9. Shannon, R. D. and Prewitt, C. T. *Acta Cryst. B* **25** (1969) 925.
10. Kierkegaard, P., Larsson, L. O. and Nyberg, B. *Acta Chem. Scand.* **26** (1972) 218.
11. Larsson, L. O. and Kierkegaard, P. *Acta Chem. Scand.* **23** (1969) 2253.
12. Larsson, L. O. and Niinistö, L. *Acta Chem. Scand.* **27** (1973) 859.
13. Hjertén, I. and Nyberg, B. *Acta Chem. Scand.* **27** (1973) 345.
14. Battle, L. F. and Trueblood, K. N. *Acta Cryst.* **19** (1965) 531.

Received November 17, 1972.