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The Crystal Structure of Zinc *p*-Toluene Sulphonate Hexahydrate

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The crystal structure of zinc *p*-toluene sulphonate hexahydrate, $(CH_3.C_6H_4.SO_3)_2Zn.6H_2O$, has been determined by two-dimensional Fourier methods. The sulphur atom is surrounded by a tetrahedral arrangement of atoms comprising the three oxygen atoms of the sulphonate group and a carbon atom in the benzene ring. Each oxygen atom of the sulphonate group is linked to two water molecules by hydrogen bonds. The zinc atom is surrounded by regular octahedra of oxygen atoms in the water molecules.

1. Introduction

An X-ray examination of a series of hydrated benzene sulphonates and *p*-substituted salts, begun in this department, led to a preliminary account of the structure of zinc *p*-toluene sulphonate hexahydrate (Hargreaves, 1946) and a detailed description of the structures of zinc and magnesium benzene sulphonate hexahydrates (Broomhead & Nicol, 1948). The work on zinc *p*-toluene sulphonate hexahydrate, $(CH_3.C_6H_4.SO_3)_2Zn.6H_2O$, has now been completed and details of the structure are presented in this paper.

Some X-ray measurements have been made on magnesium *p*-toluene sulphonate hexahydrate; these confirm a previous observation that the magnesium and zinc salts are isomorphous (Groth, 1906–19) and supply data which enable one projection of the structure of the zinc salt to be determined by the isomorphous-replacement method.

2. Experimental

(i) *Crystal data*

X-ray rotation, oscillation and Weissenberg photographs show that the isomorphous hexahydrates of zinc and magnesium *p*-toluene sulphonate are monoclinic with the cell dimensions given in Table 1; the

Table 1. *Crystal data*

	$(CH_3.C_6H_4SO_3)_2Zn.6H_2O$	$(CH_3.C_6H_4SO_3)_2Mg.6H_2O$
a (Å)	$25{\cdot}24 \pm 0{\cdot}01$	$25{\cdot}2 \pm 0{\cdot}1$
b (Å)	$6{\cdot}295 \pm 0{\cdot}002$	$6{\cdot}26 \pm 0{\cdot}04$
c (Å)	$6{\cdot}98 \pm 0{\cdot}04$	$6{\cdot}95 \pm 0{\cdot}04$
β	$91° 18' \pm 15'$	$91° 54' \pm 25'$
$d_{obs.}$ (g.cm.$^{-3}$)	1·55	1·42
$d_{calc.}$ (g.cm.$^{-3}$)	1·54	1·43

lengths of the a and b axes of the zinc salt were obtained by the extrapolation method described by Farquhar & Lipson (1946). The space group is $P2_1/n$ and there are two formula units in each unit cell. For both materials the crystals examined are almost invariably twinned across the plate face (100).

(ii) *Intensity measurements*

The atomic positions in the zinc salt were determined from reflexions $h0l$ and $hk0$ recorded on multiple-film Weissenberg photographs, using unfiltered Cu $K\alpha$ radiation. The intensities of the reflexions were measured by visual comparison with calibration spots obtained by the use of a perforated mask and rotating sector. The crystal specimens used for the Weissenberg photographs were approximately square in the section perpendicular to the axis of oscillation and small enough for absorption errors to be negligible.

The presence of twinned components in the crystal specimens provided no serious difficulties. It was found that the $h0l$ reflexions from the twinned components were completely separated for all but the $h00$ reflexions, for which the overlap was necessarily complete. A correction for the overlap was obtained by measuring the relative intensities of corresponding non-overlapping reflexions from the two components. It was unnecessary to correct the $hk0$ intensities for twinning because of the complete overlap of all pairs of corresponding reflexions from the two components.

The intensities of the $h0l$ reflexions from a crystal of magnesium *p*-toluene sulphonate hexahydrate were similarly (but less accurately) determined, using Weissenberg photographs and visual estimation; these intensities were used only to determine the phase angles of the $h0l$ reflexions for the zinc salt.

3. Determination of the structure

(i) *The* [010] *projection*

It can be deduced from the space group ($P2_1/n$) and the unit-cell contents (two formula units) that the structure is centrosymmetrical with the metal atoms lying at the symmetry centres (0, 0, 0) and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. Therefore it would be possible to determine the signs of the structure factors $F(h0l)$ by the isomorphous-replacement method in the way described by Robertson (1936) for the perfectly analogous case of the phthalocyanines. It is more convenient, however, to use a graphical modification of the method which

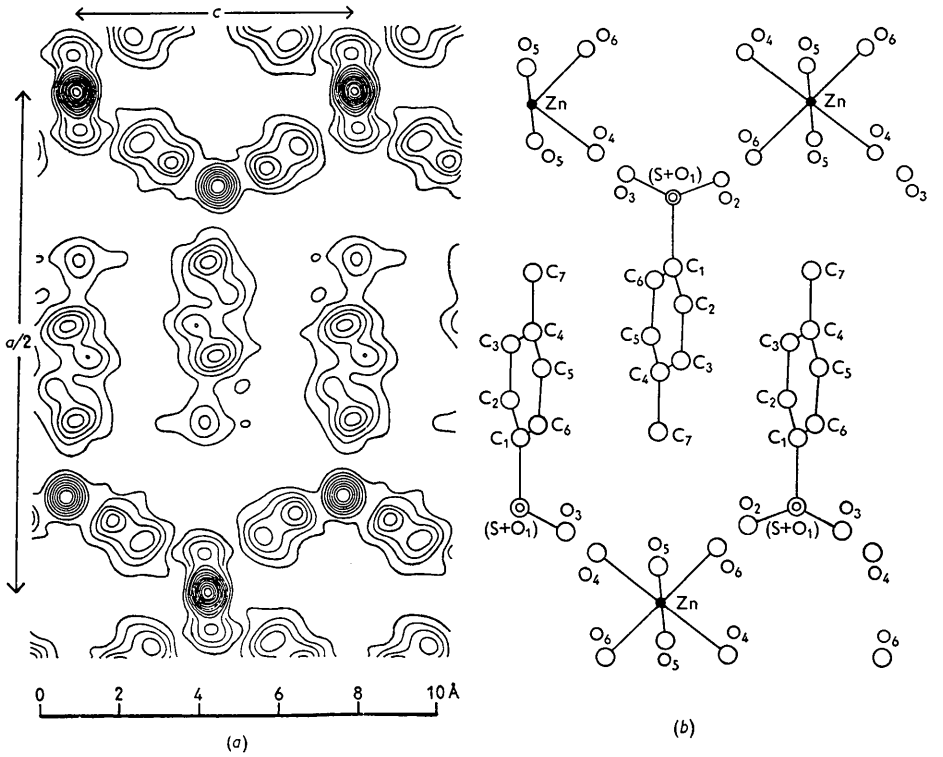

Fig. 1. (*a*) Projection of the electron density along [010]. Contours at 2, 4, 6, ... e.Å^{-2}, except for the zinc atom and the (S+O$_1$) group where they are at 2, 6, 10, ... e.Å^{-2}. (*b*) The structure viewed along [010].

renders unnecessary the type of auxiliary X-ray measurements required by Robertson for determining the absolute values of the structure amplitudes. Details of the graphical method and its application in determining the signs of $F(h0l)$ for zinc *p*-toluene sulphonate hexahydrate are given in another paper (Hargreaves, 1957). The signs were determined with sufficient certainty to permit the inclusion of all the 165 measured $F(h0l)$'s in the first Fourier synthesis, the result of which is given in Fig. 1. The complete projection was therefore deduced from the experimental data alone; no assumptions were made about the stereochemistry of the structure.

(ii) *The* [001] *projection*

The isomorphous-replacement method was not used for the [001] projection because the replaceable zinc and magnesium atoms make no contribution to $hk0$ reflexions with $(h+k)$ odd. Approximate positions for the sulphur and oxygen atoms in this projection were deduced by combining the information given in a Patterson projection along [001] with that already obtained from the [010] projection. A Fourier synthesis then revealed approximate positions for all the carbon atoms, even though the signs given to $F(hk0)$ in the synthesis were calculated from the contributions of the zinc, sulphur and oxygen atoms only. Refinement of the projection by three more Fourier syntheses gave the electron-density map shown in Fig. 2.

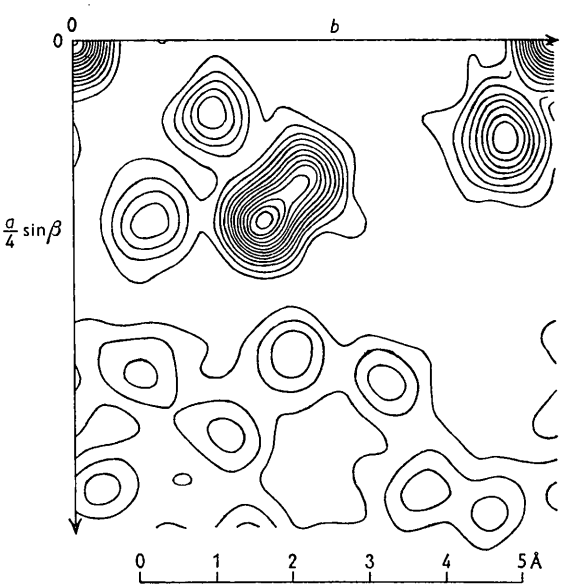

Fig. 2. Projection of the electron density along [001]. Contours at 2, 4, 6, ... e.Å^{-2}, except for the zinc atom where they are at 2, 6, 10, ... e.Å^{-2}.

(iii) *Atomic co-ordinates: accuracy*

The final atomic co-ordinates, deduced from Figs. 1 and 2, are given in Table 2.

Table 2. *Atomic co-ordinates*

Atom	x (Å)	y (Å)	z (Å)
Zn	0·000	0·000	0·000
S	2·403	2·466	3·596
O_1	2·398	0·999	3·596
O_2	1·951	3·022	4·802
O_3	1·790	3·001	2·414
$O_4(H_2O)$	1·267	5·657	1·635
$O_5(H_2O)$	0·954	1·813	0·082
$O_6(H_2O)$	1·391	5·665	5·601
C_1	4·104	2·839	3·612
C_2	5·116	1·967	3·879
C_3	6·121	5·414	6·617
C_4	5·803	0·332	0·045
C_5	5·873	4·568	3·050
C_6	4·480	4·079	3·217
$C_7(CH_3)$	4·310	0·871	0·163

The observed and calculated structure factors are compared in Table 3. The calculated structure factors were computed on the Manchester University Electronic Digital Computer; atomic scattering factors were taken from *International Tables* (1935). The value of the agreement residual $R = \Sigma|F_o - F_c| \div \Sigma|F_o|$ is 0·15 for the $h0l$ reflexions; in evaluating R accidentally absent reflexions were excluded. The observed intensities of the six strongest reflexions (002, $\bar{3}01$, 200, 301, 501 and $\bar{5}01$) are low, probably because of extinction, and if they are omitted R falls to 0·13. For $hk0$ reflexions R is 0·15 and extinction effects appear to be negligible.

The calculated structure factors for the reflexions $\bar{1}8,0,2$ and 14,5,0 have signs which differ from those used in the final syntheses, and the sign of 16,0,0 is doubtful; these reflexions are all very weak, however, and changes in the signs of their structure factors would not change the Fourier maps sufficiently to cause an appreciable improvement in the accuracy of the atomic co-ordinates read from them.

An estimate of the accuracy of the structure is obtained from the consistency in the lengths of similar bonds. The three sulphur–oxygen linkages, which should provide the most reliable bond lengths, agree to within ±0·03 Å (§ 4). The six water–oxygen distances, which may, of course, have real deviations from equality, agree to within ±0·05 Å. This suggests that the accuracy of the co-ordinates of the oxygen atoms is about ±0·03 Å. The carbon atoms have lower peak heights than the oxygen atoms in the electron-density maps and their co-ordinates may be considerably less accurate.

4. Description of the structure

The sulphonate group is attached to the benzene ring through the linkage S–C_1 (Fig. 1(*b*)); dimensions are given in Fig. 3(*a*). The atom C_1 and the three oxygen atoms of the sulphonate radical form a tetrahedral group with the sulphur atom at the centre. The bond angles O–S–O are approximately 4° larger than those which would be present in a perfectly regular tetrahedral arrangement. This may be caused by the repulsive forces arising from the short distances (2·40 Å) between the oxygen atoms and from the similar charges which they carry: the hydrogen bonds which link the oxygen atoms of the sulphonate group with those of the water molecules are directed so that they tend to decrease rather than increase the O–S–O bond angles. The mean length of the S–O bonds is 1·43 Å, a value commonly observed in this type of group; it agrees with the value of 1·41 Å determined by Broomhead & Nicol (1948) for the mean S–O distance in the very similar structures of magnesium and zinc benzene sulphonate hexahydrate.

Each oxygen atom of the sulphonate group is linked to two water molecules and vice versa by hydrogen bonds; the lengths of the hydrogen bonds and the angular separation between the bonds in each pair

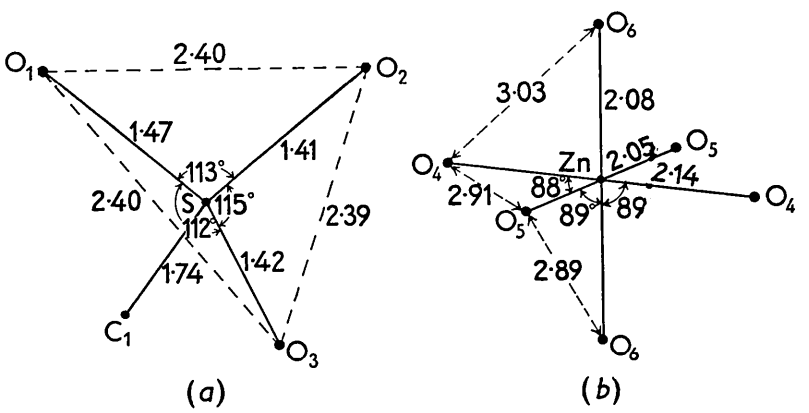

Fig. 3. (*a*) Dimensions of the sulphonate group, (*b*) configuration of the hydrated zinc ion $[Zn(H_2O)_6]^{++}$; distances in Ångström units.

Table 3. *Observed and calculated structure factors*

h k l	F_o	F_c	*h k l*	F_o	F_c	*h k l*	F_o	F_c	*h k l*	F_o	F_c
2 0 0	60	84	$\bar{18}$ 0 2	7	−7	$\bar{1}$ 0 5	—	5	13 1 0	12	7
4 0 0	45	45	$\bar{20}$ 0 2	25	20	$\bar{3}$ 0 5	27	27	15 1 0	23	23
6 0 0	67	−73	$\bar{22}$ 0 2	25	22	$\bar{5}$ 0 5	59	52	17 1 0	40	49
8 0 0	52	−40	$\bar{24}$ 0 2	9	14	$\bar{7}$ 0 5	46	41	19 1 0	21	27
10 0 0	17	24	$\bar{26}$ 0 2	—	3	$\bar{9}$ 0 5	17	14	21 1 0	21	26
12 0 0	79	74	$\bar{28}$ 0 2	—	3	$\bar{11}$ 0 5	23	−24	23 1 0	7	11
14 0 0	—	4	$\bar{30}$ 0 2	15	16	$\bar{13}$ 0 5	—	−3	25 1 0	7	8
16 0 0	9	0				$\bar{15}$ 0 5	17	8	27 1 0	5	5
18 0 0	23	26	1 0 3	19	21	$\bar{17}$ 0 5	28	22			
20 0 0	26	28	3 0 3	65	64	$\bar{19}$ 0 5	15	17	0 2 0	62	70
22 0 0	31	31	5 0 3	65	65				2 2 0	71	72
24 0 0	11	14	7 0 3	20	21	0 0 6	52	44	4 2 0	6	11
26 0 0	—	1	9 0 3	9	7	2 0 6	10	10	6 2 0	8	4
28 0 0	—	1	11 0 3	—	6	4 0 6	11	−11	8 2 0	13	8
30 0 0	15	15	13 0 3	35	36	6 0 6	5	1	10 2 0	24	23
			15 0 3	41	36	8 0 6	21	13	12 2 0	60	55
1 0 1	15	−6	17 0 3	25	21	10 0 6	30	26	14 2 0	47	50
3 0 1	99	127	19 0 3	24	−25	12 0 6	22	16	16 2 0	28	28
5 0 1	103	126	21 0 3	—	0	14 0 6	—	0	18 2 0	24	22
7 0 1	64	70	23 0 3	—	6	16 0 6	—	−8	20 2 0	4	7
9 0 1	13	−10	25 0 3	25	26	18 0 6	15	15	22 2 0	—	7
11 0 1	46	−46	27 0 3	18	20	$\bar{2}$ 0 6	50	42	24 2 0	—	9
13 0 1	15	6	$\bar{1}$ 0 3	23	15	$\bar{4}$ 0 6	12	8	26 2 0	5	9
15 0 1	43	43	$\bar{3}$ 0 3	64	56	$\bar{6}$ 0 6	—	−3			
17 0 1	50	51	$\bar{5}$ 0 3	66	61	$\bar{8}$ 0 6	—	−2	1 3 0	11	9
19 0 1	—	4	$\bar{7}$ 0 3	47	42	$\bar{10}$ 0 6	15	13	3 3 0	23	27
21 0 1	—	8	$\bar{9}$ 0 3	12	10	$\bar{12}$ 0 6	36	32	5 3 0	65	61
23 0 1	—	8	$\bar{11}$ 0 3	25	−18	$\bar{14}$ 0 6	14	12	7 3 0	47	43
25 0 1	22	21	$\bar{13}$ 0 3	33	33	$\bar{16}$ 0 6	—	2	9 3 0	55	49
27 0 1	16	17	$\bar{15}$ 0 3	39	40	$\bar{18}$ 0 6	—	−3	11 3 0	20	16
29 0 1	4	1	$\bar{17}$ 0 3	32	34	$\bar{20}$ 0 6	8	6	13 3 0	—	−1
$\bar{1}$ 0 1	16	−21	$\bar{19}$ 0 3	—	5	$\bar{22}$ 0 6	8	6	15 3 0	4	8
$\bar{3}$ 0 1	92	111	$\bar{21}$ 0 3	17	−20				17 3 0	7	8
$\bar{5}$ 0 1	102	130	$\bar{23}$ 0 3	—	5	1 0 7	7	5	19 3 0	13	15
$\bar{7}$ 0 1	102	107	$\bar{25}$ 0 3	14	14	3 0 7	25	19	21 3 0	20	20
$\bar{9}$ 0 1	26	22	$\bar{27}$ 0 3	19	21	5 0 7	34	31	23 3 0	8	12
$\bar{11}$ 0 1	52	−47				7 0 7	—	4			
$\bar{13}$ 0 1	11	2	0 0 4	107	103	9 0 7	—	4	0 4 0	4	−5
$\bar{15}$ 0 1	28	26	2 0 4	29	21	11 0 7	—	−1	2 4 0	21	20
$\bar{17}$ 0 1	39	42	4 0 4	—	1	13 0 7	6	7	4 4 0	42	39
$\bar{19}$ 0 1	16	15	6 0 4	3	5	15 0 7	12	10	6 4 0	42	31
$\bar{21}$ 0 1	—	1	8 0 4	28	15	$\bar{1}$ 0 7	—	−6	8 4 0	18	22
$\bar{23}$ 0 1	11	13	10 0 4	34	33	$\bar{3}$ 0 7	—	−3	10 4 0	5	7
$\bar{25}$ 0 1	15	17	12 0 4	20	19	$\bar{5}$ 0 7	25	19	12 4 0	12	9
$\bar{27}$ 0 1	15	18	14 0 4	8	−5	$\bar{7}$ 0 7	25	21	14 4 0	40	38
$\bar{29}$ 0 1	—	7	16 0 4	17	−12	$\bar{9}$ 0 7	16	16	16 4 0	27	20
			18 0 4	28	32	$\bar{11}$ 0 7	—	0	18 4 0	7	6
0 0 2	130	156	20 0 4	18	15	$\bar{13}$ 0 7	—	5	20 4 0	—	−8
2 0 2	41	−26	22 0 4	22	21	$\bar{15}$ 0 7	9	5	22 4 0	—	−3
4 0 2	28	30	$\bar{2}$ 0 4	60	56	$\bar{17}$ 0 7	11	10	24 4 0	7	7
6 0 2	46	48	$\bar{4}$ 0 4	30	26	$\bar{19}$ 0 7	7	6	26 4 0	18	20
8 0 2	71	74	$\bar{6}$ 0 4	11	10						
10 0 2	72	78	$\bar{8}$ 0 4	19	15	0 0 8	17	10	1 5 0	8	4
12 0 2	44	41	$\bar{10}$ 0 4	33	21	2 0 8	—	6	3 5 0	—	5
14 0 2	19	−26	$\bar{12}$ 0 4	42	36	4 0 8	—	0	5 5 0	—	−2
16 0 2	26	−33	$\bar{14}$ 0 4	15	−18	6 0 8	7	7	7 5 0	31	27
18 0 2	32	28	$\bar{16}$ 0 4	14	−8	8 0 8	15	9	9 5 0	40	36
20 0 2	28	24	$\bar{18}$ 0 4	—	3	10 0 8	9	8	11 5 0	41	36
22 0 2	30	31	$\bar{20}$ 0 4	26	31	$\bar{2}$ 0 8	19	17	13 5 0	14	12
24 0 2	—	9	$\bar{22}$ 0 4	26	27	$\bar{4}$ 0 8	—	2	15 5 0	—	−1
26 0 2	—	−3	$\bar{24}$ 0 4	12	14	$\bar{6}$ 0 8	—	3	17 5 0	—	−1
28 0 2	—	3				$\bar{8}$ 0 8	—	4	19 5 0	14	10
30 0 2	16	18	1 0 5	14	15	$\bar{10}$ 0 8	14	9	21 5 0	13	12
$\bar{2}$ 0 2	37	−14	3 0 5	49	41	$\bar{12}$ 0 8	15	11	23 5 0	4	8
$\bar{4}$ 0 2	21	19	5 0 5	57	51						
$\bar{6}$ 0 2	23	19	7 0 5	4	2	1 1 0	12	10	0 6 0	15	10
$\bar{8}$ 0 2	61	63	9 0 5	6	−12	3 1 0	71	81	2 6 0	10	6
$\bar{10}$ 0 2	74	79	11 0 5	16	−18	5 1 0	92	97	4 6 0	13	9
$\bar{12}$ 0 2	90	88	13 0 5	9	9	7 1 0	59	61	6 6 0	14	14
$\bar{14}$ 0 2	13	−15	15 0 5	32	27	9 1 0	34	35	8 6 0	8	7
$\bar{16}$ 0 2	11	−17	17 0 5	31	29	11 1 0	24	−25	10 6 0	13	13

Table 3 (*cont.*)

h k l	F_o	F_c	*h k l*	F_o	F_c	*h k l*	F_o	F_c	*h k l*	F_o	F_c
12 6 0	17	13	18 1 0	29	31	10 3 0	16	14	14 5 0	5	1
14 6 0	12	10	20 1 0	5	7	12 3 0	8	−11	16 5 0	—	1
16 6 0	14	10				14 3 0	37	−45	18 5 0	8	−8
			1 2 0	25	27						
1 7 0	11	8	3 2 0	76	68	1 4 0	18	15	1 6 0	—	−2
3 7 0	10	6	5 2 0	70	68	3 4 0	32	36	3 6 0	5	1
5 7 0	12	10	7 2 0	2	1	5 4 0	—	1	5 6 0	5	−9
7 7 0	11	9	9 2 0	4	−3	7 4 0	6	−6	7 6 0	14	18
9 7 0	9	8	11 2 0	—	−6	9 4 0	21	−19	9 6 0	—	−3
11 7 0	3	4	13 2 0	3	−12	11 4 0	15	−17	11 6 0	4	−2
			15 2 0	—	−6	13 4 0	10	11	13 6 0	4	−2
2 1 0	64	−63	17 2 0	10	−9						
4 1 0	20	−24	19 2 0	24	−22	2 5 0	—	−1	2 7 0	—	−2
6 1 0	22	21	21 2 0	10	14	4 5 0	—	1	4 7 0	—	−1
8 1 0	32	31				6 5 0	11	−9	6 7 0	11	−10
10 1 0	15	9	2 3 0	29	−23	8 5 0	17	−9	8 7 0	8	−3
12 1 0	45	−45	4 3 0	13	14	10 5 0	5	3	10 7 0	—	0
14 1 0	25	−26	6 3 0	40	38	12 5 0	7	11	12 7 0	9	9
16 1 0	8	−13	8 3 0	48	49						

are listed in Table 4. The mean length of 2·78 Å is, within experimental error, the same as the average value of 2·77 Å observed for the similar hydrogen bonding in magnesium and zinc benzene sulphonate hexahydrates.

Table 4. *The hydrogen bonds*

(i) Lengths of the bonds		(ii) Angular separation between the bonds in each pair	
O_1–$O_4(H_2O)$	2·78 Å	O_1–$(H_2O)_6$–O_2	105°
O_1–$O_6(H_2O)$	2·79	O_1–$(H_2O)_4$–O_3	107
O_2–$O_5(H_2O)$	2·77	O_2–$(H_2O)_5$–O_3	113
O_2–$O_6(H_2O)$	2·82		
O_3–$O_4(H_2O)$	2·81	$(H_2O)_4$–O_3–$(H_2O)_5$	97
O_3–$O_5(H_2O)$	2·73	$(H_2O)_4$–O_1–$(H_2O)_6$	91
		$(H_2O)_5$–O_2–$(H_2O)_6$	96

The positions occupied by the water molecules are such that the oxygen atoms are distributed in an almost regular octahedral arrangement about the zinc ion; dimensional details are given in Fig. 3(*b*). The average Zn–O distance of 2·09 Å agrees with the value of 2·08 Å observed in zinc benzene sulphonate hexahydrate.

The average distance between the carbon atoms in the benzene ring is 1·39 Å with individual values varying from 1·32 Å to 1·48 Å; it is doubtful whether the variations are significant. The length of the carbon–methyl bond is 1·59 Å.

The shortest intermolecular contacts are between pairs of carbon atoms in different benzene rings; all exceed 3·5 Å.

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