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The Crystal Structure of Magnesium Thiosulphate Hexahydrate

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Magnesium thiosulphate hexahydrate, $Mg(OH_2)_6S_2O_3$, crystallizes in the space group D_{2h}^{16}-*Pnma*, with unit-cell dimensions $a = 9{\cdot}32$, $b = 14{\cdot}36$, $c = 6{\cdot}87$ Å, and with $Z = 4$. The structure consists of alternating layers of $Mg(OH_2)_6^{2+}$ octahedra and $S_2O_3^{2-}$ tetrahedra perpendicular to the b axis. Each octahedron is linked by OH $\cdots$ O hydrogen bonding to four surrounding octahedra in the same layer and to four tetrahedra in the two adjacent layers. An OH $\cdots$ S type of interaction, probably due to hydrogen bonding, is observed.

Introduction

An X-ray study of magnesium thiosulphate hexahydrate, $Mg(OH_2)_6S_2O_3$, was carried out by Brunt (1946), but the proposed model was not consistent with the tetrahedral structure of the $S_2O_3^{2-}$ ion.

A new determination of the structure is reported in the present paper. The results are consistent with those found by Taylor & Beevers (1952) in $Na_2S_2O_3.5H_2O$, by Sándor & Csordás (1960) in $Na_2S_2O_3$, and by us in $BaS_2O_3.H_2O$ (to be published).

Experimental

$Mg(OH_2)_6S_2O_3$ crystallizes in colourless flat prisms. As the crystals are hygroscopic, the one used for X-ray analysis was sealed in a Lindemann tube.

The crystal data, deduced from rotation and Weissenberg photographs (Cu $K\alpha$) around the elongation axis [001], agree with those reported by Brunt and with the axial ratio found by Fock & Klüss (1891):

$$a = 9{\cdot}32 \pm 0{\cdot}01,\ b = 14{\cdot}36 \pm 0{\cdot}04,\ c = 6{\cdot}87 \pm 0{\cdot}01\ \text{Å}\ ,$$
$$V = 919\ \text{Å}^3,\ Z = 4,\ D_c = 1{\cdot}766,\ D_o = 1{\cdot}818\ \text{g.cm.}^{-3}$$

(Oliver, reported in Groth, 1909), $\mu = 62{\cdot}2$ cm.$^{-1}$, $F(000) = 512$.

Space group (from systematic absences): D_{2h}^{16}-*Pnma* or C_{2v}^{9}-$Pn2_1a$.

The intensity data were obtained photometrically from $hk0$, $hk1$ and $hk2$ multiple-film, Weissenberg photographs. 62$hk0$ (possible 87), 103$hk1$ (possible 174) and 115$hk2$ (possible 168) independent reflections were observed.

Corrections for absorption were calculated assuming a cylindrical sample of mean radius 0·03 cm. A preliminary scale factor was obtained by Wilson's method.

Structure determination and refinement

To solve the phase problem, the coincidences method of Grant, Howells & Rogers (1957) was applied to the $hk0$ reflections adopting, as a starting hypothesis, the space group *Pnma*. Using the 29 reflections with $0{\cdot}20 \le U \le 0{\cdot}51$, a rough Fourier projection was calculated. The successive results showed that the space group and the signs were correct, except for three weak reflections.

The first value of $R(hk0)$, 0·243, indicated a correct interpretation of the Fourier projection. A new electron-density projection was then evaluated to improve the x and y coordinates.

An initial set of z coordinates was derived by considering the packing of the ionic polyhedra and assuming for $S_2O_3^{2-}$ the dimensions found in $Na_2S_2O_3.5H_2O$ by Taylor & Beevers. These coordinates gave the following R values:

$$R(hk0) = 0{\cdot}223,\quad R(hk1) = 0{\cdot}192,\quad R(hk2) = 0{\cdot}175\ .$$

In Fig. 1 the final projection $\varrho_0(X, Y)$ is shown.

Three cycles of Booth's differential synthesis were carried out, the atomic coordinates and the isotropic thermal parameters being determined from the observed and calculated values of the electron densities and from their first and second derivatives. Anisotropic

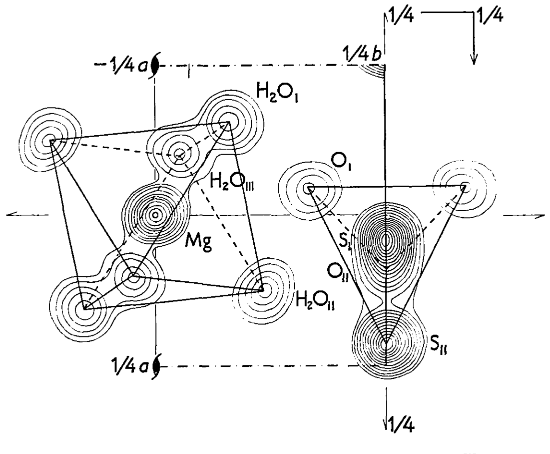


Fig. 1. Electron-density projection $\varrho_0(X, Y)$. Contour interval 2 e.Å^{-2}, first line at 4 e.Å^{-2}.

Table 1. *Observed and calculated structure factors*

A minus sign for F_o means 'less than'. (°) reflections corrected for secondary extinction. (*) reflection shaded by the beam stop

h	k	l	$10\|F_o\|$	$10F_c$
0	2	0	(°)406	-467
	4		(°)762	1013
	6		(°)672	-607
	8		(°)1144	1116
	10		438	-354
	12		826	786
	14		540	-386
	16		411	503
	18		164	-202
2	0	0	(°)755	910
	1		(°)553	-543
	2		175	138
	3		(°)1000	976
	4		490	419
	5		109-	-40
	6		(°)839	741
	7		(°)1063	987
	8		346	280
	9		542	-419
	10		162-	66
	11		200	115
	12		276	229
	13		178-	-36
	14		175-	62
	15		460	402
	16		146-	74
	17		122-	-114
	18		81-	118
4	0	0	335	-153
	1		113-	32
	2		544	-528
	3		120-	50
	4		(°)713	742
	5		313	-320
	6		346	286
	7		519	461
	8		316	297
	9		166-	171
	10		209	-162
	11		178	109
	12		462	450
	13		173-	31
	14		164-	24
	15		148-	13
	15		213	240
	17		101	-77
6	0	0	226	98
	1		294	-257
	2		383	342
	3		553	541
	4		195	-156
	5		765	-853
	6		168-	99
	7		373	358
	8		176-	-11
	9		327	-347
	10		322	315
	11		373	339
	12		239	167
	13		305	-302
	14		246	244
	15		135	144
8	0	0	191	143
	1		209	211
	2		394	415
	3		178-	-19
	4		178-	-58
	5		178-	-22
	6		182	213
	7		175-	-140
	8		178	120
	9		164-	-118
8	10	0	279	238
	11		213	-202
	12		124-	-76
	13		100-	43
10	0	0	162-	45
	1		259	-239
	2		257	203
	3		157-	95
	4		266	240
	5		204	-132
	6		193	185
	7		237	247
	8		157	140
	9		129	-158
	10		74-	87
0	1	1	(*) -	-232
	3		46-	26
	5		64-	62
	7		507	388
	9		498	416
	11		415	295
	13		109-	51
	15		105-	-56
	17		77-	0
1	0	1	137	-200
	1		288	278
	2		(°)1312	1273
	3		(°)574	-529
	4		397	-305
	5		(°)716	744
	6		197	156
	7		338	-276
	8		219	171
	9		169	81
	10		689	693
	11		402	-364
	12		238	-189
	13		224	203
	14		388	347
	15		100-	-56
	16		91-	28
	17		155	151
	18		169	190
2	0	1	210	-160
	1		(°)525	-519
	2		169	-80
	3		(°)679	731
	4		(°)726	-699
	5		283	-251
	6		388	-301
	7		434	390
	8		265	-188
	9		347	-288
	10		188	151
	11		297	279
	12		109-	116
	13		192	-163
	14		151	121
	15		215	202
	15		86-	40
	17		73-	-110
	18		46-	28
3	0	1	(°)648	-627
	1		475	-432
	2		392	412
	3		229	-197
	4		(°)725	745
	5		374	332
	6		444	401
	7		86-	-30
	8		242	174
	9		100-	-92
3	10	1	242	213
	11		109-	-44
	12		109-	55
	13		109-	-32
	14		242	196
	15		96-	47
	16		82-	81
	17		64-	42
4	0	1	(°)779	-853
	1		260	202
	2		127	113
	3		151	-175
	4		457	-472
	5		160	125
	6		420	415
	7		324	-331
	8		260	-259
	9		192	-141
	10		233	209
	11		238	-249
	12		229	-214
	13		109-	32
	14		183	171
	15		91-	-27
	16		77-	-80
	17		55-	55
5	0	1	297	-225
	1		251	227
	2		589	622
	3		397	-388
	4		192	175
	5		347	367
	6		444	475
	7		498	-521
	8		137	-112
	9		370	389
	10		374	346
	11		109-	-29
	12		109-	18
	13		100-	116
	14		292	290
	15		270	-265
	16		64-	-48
6	0	1	169	130
	1		91-	-59
	2		96-	-54
	3		315	-286
	4		238	242
	5		179	-156
	6		105-	42
	7		109-	-102
	8		109-	89
	9		109-	1
	10		141	-109
	11		109-	-48
	12		100-	24
	13		91-	-71
	14		82-	-81
	15		64-	-71
7	0	1	727	732
	1		233	197
	2		105-	17
	3		104-	-77
	4		256	246
	5		274	294
	6		127	-95
	7		338	-348
	8		315	382
	9		156	155
	10		105-	10
	11		100-	-41
	12		301	266
7	13	1	77-	89
	14		64-	-43
8	0	1	109-	109
	1		109-	41
	2		333	324
	3		109-	9
	4		127	-106
	5		109-	12
	6		127	114
	7		109-	-3
	8		238	-155
	9		100-	41
	10		156	131
	11		86-	17
	12		73-	-80
	13		59-	17
9	0	1	210	222
	1		109-	-16
	2		109-	94
	3		109-	-90
	4		105-	63
	5		174	168
	6		238	207
	7		96-	-46
	8		201	158
	9		86-	7
	10		118	88
	11		64-	-73
10	0	1	100-	81
	1		174	136
	2		96-	-70
	3		96-	16
	4		96-	66
	5		165	164
	6		86-	-42
	7		77-	-31
	8		73-	75
	9		59-	82
11	0	1	279	269
	1		77-	53
	2		118	-124
	3		179	-174
	4		292	301
	5		100	104
	6		55-	-16
0	2	2	365	-494
	4		374	-357
	6		310	290
	8		500	501
	10		93-	82
	12		339	330
	14		100-	4
	16		188	290
1	0	2	218	131
	1		230	210
	2		(°)600	644
	3		364	-337
	4		(°)562	-552
	5		164	-113
	6		69-	9
	7		154	-111
	8		268	-277
	9		255	213
	10		321	290
	11		100-	-52
	12		103-	-108
	13		103-	53
	14		188	165
	15		129	-137
	16		80-	-128
	17		64-	22
2	0	2	(°)764	740
	1		265	-201
	2		82	-81
	3		(°)600	-578
	4		202	184
	5		324	-262
	6		366	321
	7		201	134
	8		236	248
	9		196	-214
	10		97-	49
	11		239	-266
	12		337	376
	13		99-	-76
	14		99-	68
	15		89-	56
	16		122	158
	17		61-	-69
3	0	2	(°)672	658
	1		(°)627	598
	2		321	-318
	3		150	-149
	4		381	367
	5		487	523
	6		488	-456
	7		343	-322
	8		361	362
	9		96-	100
	10		252	-237
	11		339	-355
	12		202	215
	13		256	257
	14		188	-211
	15		85-	-69
	16		211	166
	17		131	161
4	0	2	(°)788	691
	1		167	146
	2		249	207
	3		73-	57
	4		623	806
	5		321	-350
	6		249	257
	7		119	63
	8		220	194
	9		233	-187
	10		102-	-51
	11		103-	-89
	12		384	360
	13		97-	-53
	14		89-	33
	15		79-	50
	16		63-	62
5	0	2	387	-303
	1		268	-234
	2		192	-163
	3		128	124
	4		271	246
	5		167	-143
	6		138	108
	7		221	240
	8		139	102
	9		123	-109
	10		103-	-96
	11		102-	120
	12		99-	-48
	13		90-	-94
	14		82-	-56
	15		69-	101
	16		48-	40
6	0	2	500	440
6	1	2	118	61
	2		346	288
	3		509	458
	4		385	410
	5		353	-355
	6		237	233
	7		242	241
	8		272	264
	9		128	-84
	10		102-	92
	11		250	210
	12		90-	87
	13		82-	-63
	14		70-	29
	15		52-	81
7	0	2	174	156
	1		174	155
	2		148	-146
	3		327	-279
	4		163	160
	5		147	112
	6		221	-235
	7		157	-148
	8		102-	87
	9		271	245
	10		96-	-100
	11		87-	-59
	12		166	144
	13		69-	85
	14		51-	-51
8	0	2	158	126
	1		103-	-85
	2		266	252
	3		182	171
	4		103-	-8
	5		154	-136
	6		161	130
	7		331	284
	8		195	157
	9		89-	-9
	10		223	217
	11		135	122
	12		63-	-17
9	0	2	282	233
	1		199	-212
	2		167	-136
	3		401	328
	4		99	102
	5		188	-205
	6		258	-219
	7		174	152
	8		103	130
	9		237	-245
	10		64-	-88
	11		158	155
10	0	2	129	-113
	1		154	-104
	2		228	189
	3		85-	35
	4		82-	-23
	5		79-	-52
	6		122	107
	7		163	143
	8		58-	-4
	9		45-	-74
11	0	2	256	-115
	1		66-	-21
	2		64-	51
	3		61-	6
	4		57-	-54
	5		51-	12

refinement was not considered, discontinuous absorption effects and reflections with $l>2$ being neglected.

A comparison of the F_o and F_c showed that secondary extinction was present. Extinction is also indicated by the lower R value for layers with higher l. It was corrected by the method of Pinnock, Taylor & Lipson (1956) and the R's dropped to the following values (calculated with the observed reflections only):

Table 2. *Atomic coordinates and thermal parameters with their s.d.*

	x/a	y/b	z/c	x (Å)	y (Å)	z (Å)	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$	B (Å^2)	$\sigma(B)$
								(Å × 10^3)			
Mg	0	0	0	0	0	0	—	—	—	1·30	0·29
S_{I}	0·0417	0·2500	0·4390	0·389	3·590	3·016	3	—	9	1·79	0·23
S_{II}	0·2148	0·2500	0·6160	2·002	3·590	4·232	3	—	8	1·79	0·23
O_{I}	−0·0427	0·1649	0·4823	−0·398	2·368	3·313	11	13	26	3·25	0·57
O_{II}	0·0922	0·2500	0·2348	0·859	3·590	1·613	15	—	41	3·25	0·57
H_2O_{I}	−0·1546	0·0821	0·1462	−1·441	1·179	1·004	7	7	18	2·40	0·40
H_2O_{II}	0·1269	0·1172	−0·0304	1·183	1·683	−0·209	8	8	21	2·40	0·40
H_2O_{III}	−0·0980	0·0275	−0·2638	−0·913	0·395	−1·812	11	9	22	2·40	0·40

Table 3. *Comparison of peak heights and curvatures from differential synthesis*

	ϱ (e.Å^{-3})		$-A_{hh}$ (e.Å^{-5})		$-A_{kk}$ (e.Å^{-5})		$-A_{ll}$ (e.Å^{-5})	
	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.
Mg	15·3	15·9	196·7	187·9	175·2	175·6	24·2	24·6
S_{I}	19·8	20·3	229·8	224·5	239·5	232·0	29·5	29·5
S_{II}	19·1	19·5	234·0	224·2	206·7	202·9	30·8	30·8
O_{I}	6·4	6·8	61·9	62·2	48·3	42·0	9·9	10·0
O_{II}	6·4	6·8	45·8	46·3	64·5	55·6	6·1	6·5
H_2O_{I}	8·8	8·3	94·7	81·0	92·2	85·4	13·9	13·1
H_2O_{II}	8·0	8·0	92·1	89·2	78·7	78·7	12·2	12·4
H_2O_{III}	7·5	7·7	64·0	63·8	71·9	72·5	11·7	12·3

$R(hk0)=0{\cdot}117,\ R(hk1)=0{\cdot}102,\ R(hk2)=0{\cdot}116\,.$

F_o and F_c are listed in Table 1, where F_c is calculated from the final atomic coordinates and thermal parameters in Table 2. The atomic scattering factors used were those of Berghuis *et al.* (1955) for O and Mg^{2+}, and those of Dawson (1960) for S.

The standard deviations of atomic coordinates and thermal parameters have been estimated by the method of Cruickshank (1949, 1956) for observed reflections only. The largest values are for the $\sigma(z)$'s, owing to the small number of reciprocal lattice layers considered. This is also responsible for the particularly small values of $A_{ll}=(\partial^2\varrho/\partial z^2)_{r=0}$; but the agreement between the observed and calculated values for the electron densities and their second derivatives at the atomic peaks is good (Table 3). The standard deviation of the electron density is $\sigma(\varrho)=0{\cdot}206$ e.Å^{-3}.

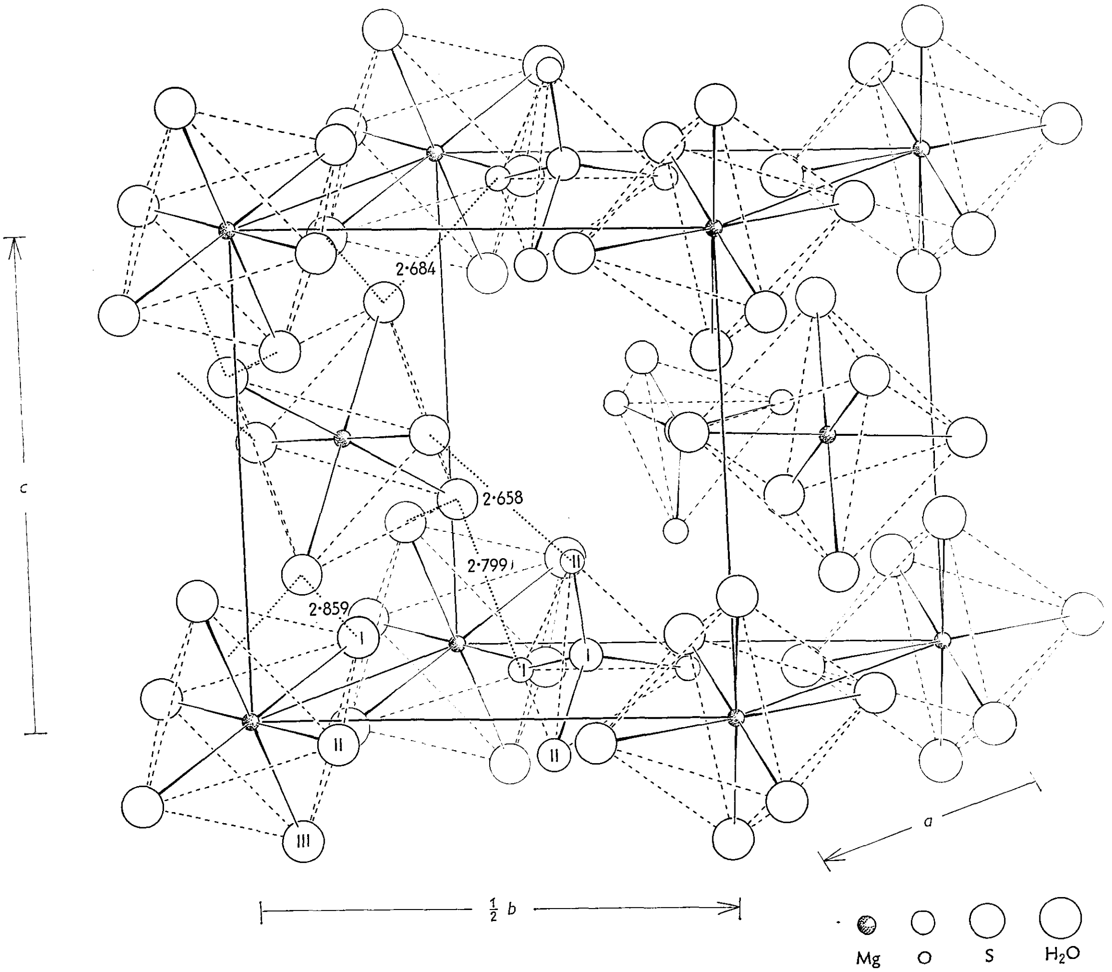


Fig. 2. Clinographic projection of the structure of $Mg(OH_2)_6S_2O_3$.

Discussion

Fig. 2 is a clinographic projection of one half of the unit cell. Each Mg atom is surrounded by six water molecules arranged at the corners of a nearly regular octahedron, as the following values of bond distances and angles indicate:

$Mg–H_2O_I$	$2·115 \pm 0·011$ Å
$Mg–H_2O_{II}$	$2·068 \pm 0·008$
$Mg–H_2O_{III}$	$2·068 \pm 0·020$
$H_2O_I–Mg–H_2O_{II}$	$89·1 \pm 0·4°$
$H_2O_I–Mg–H_2O_{III}$	$90·5 \pm 0·6$
$H_2O_{II}–Mg–H_2O_{III}$	$90·5 \pm 0·6$

The standard deviations are calculated from the formulae of Ahmed & Cruickshank (1953) for bond lengths and by Darlow (1960) for angles.

The distances Mg–OH₂ agree well with those already found for $Mg(OH_2)_6^{2+}$; e.g. 2·04 Å (mean value) in magnesium benzene sulphonate hexahydrate (Broomhead & Nicol, 1948), 2·08 and 2·12 Å in magnesium phosphite hexahydrate (Corbridge, 1956).

The distances and angles in the tetrahedral thiosulphate group are in good agreement with those found in sodium thiosulphate pentahydrate by Taylor & Beevers (1952) and in anhydrous sodium thiosulphate by Sándor & Csordás (1960):

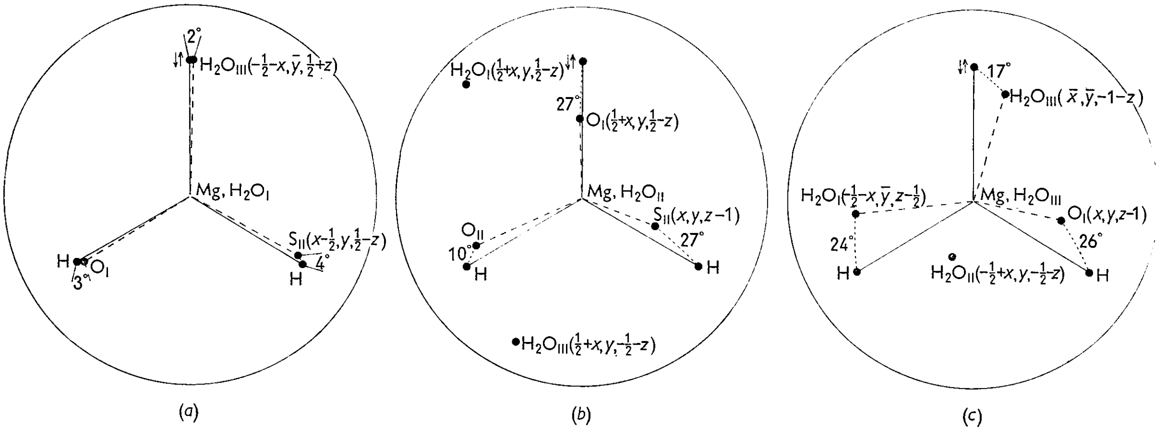
	Present study	Taylor & Beevers	Sándor & Csordás
$S_I–S_{II}$	$2·020 \pm 0·008$ Å	1·97 Å	2·01 Å
$S_I–O_I$	$1·484 \pm 0·014$	1·46 1·59 1·40	$1·46 \pm 0·05$
$S_I–O_{II}$	$1·479 \pm 0·040$		
$O_I–S_I–O_I'$	$110·9 \pm 1·1°$	104–115°	$110·5 \pm 1·5°$
$O_I–S_I–O_{II}$	$111·0 \pm 1·1$		
$O_I–S_I–S_{II}$	$107·6 \pm 0·8$		$108·5 \pm 1·5$
$O_{II}–S_I–S_{II}$	$108·5 \pm 0·8$		

The other interatomic distances shorter than 3·5 Å are as follows. (When the coordinates are not indicated the atom is at x, y, z.)

$H_2O_I–O_I$	$2·799 \pm 0·027$ Å
$H_2O_I–O_{II}$	$3·387 \pm 0·015$
$H_2O_I–O_{II}(x-\frac{1}{2}, y, \frac{1}{2}-z)$	$3·470 \pm 0·016$
$H_2O_I–S_{II}(x-\frac{1}{2}, y, \frac{1}{2}-z)$	$3·246 \pm 0·013$
$H_2O_I–H_2O_{III}(-\frac{1}{2}-x, \bar{y}, \frac{1}{2}+z)$	$2·859 \pm 0·014$
$H_2O_{II}–O_{II}$	$2·658 \pm 0·032$
$H_2O_{II}–O_I(\frac{1}{2}+x, y, \frac{1}{2}-z)$	$3·172 \pm 0·014$
$H_2O_{II}–S_{II}(x, y, z-1)$	$3·195 \pm 0·018$
$H_2O_{II}–H_2O_I(\frac{1}{2}+x, y, \frac{1}{2}-z)$	$3·371 \pm 0·023$
$H_2O_{II}–H_2O_{III}(\frac{1}{2}+x, y, -\frac{1}{2}-z)$	$3·199 \pm 0·018$
$H_2O_{III}–O_I(x, y, z-1)$	$2·684 \pm 0·024$

The distances shorter than 3 Å are probably hydrogen bonds. The packing of the octahedral cations and the tetrahedral anions is determined by these interactions. The structure as a whole is built up from alternating layers of octahedra and tetrahedra; the layers are parallel to (010) and succeed each other at intervals of $\frac{1}{4}b$. Each octahedron is bonded to the four surrounding octahedra in the same layer by a hydrogen bond (2·86 Å) and with six hydrogen bonds directed towards the oxygens in the adjacent layers of tetrahedra. These hydrogen bonds are stronger than the previous ones within the layers, as indicated by the shorter distances (2·66, 2·68, 2·80 Å).

The experimental data are insufficient to determine the distribution of H atoms. Nevertheless, a plausible guess for this distribution can be made by considering an idealized tetrahedral model of the H's and lone pairs in the water molecule. Assuming one lone pair directed towards Mg^{2+}, the H's will probably orientate towards those atoms which are in the best condition for hydrogen bonding. The environments for H_2O_I, H_2O_{II} and H_2O_{III} are shown in Fig. 3(*a*), (*b*) and (*c*) respectively. In these figures probable orientations of H's and lone pairs are also indicated. The lone pairs have been directed in the first case (Fig. 3(*a*)) towards a water molecule behaving as a proton donor, in the others towards an oxygen atom (Fig. 3(*b*)) and a water molecule (Fig. 3(*c*)) which are rather distant



(*a*) (*b*) (*c*)

Fig. 3. Stereographic projection of the environment of (*a*) H_2O_I, (*b*) H_2O_{II}, (*c*) H_2O_{III} viewed down the H_2O–Mg bonds. The orientation of H's and lone pairs (↓↑) is hypothetical.

(3·17 and 3·81 Å respectively). The hydrogen bonding $H_2O_I \cdots S_{II}$ satisfies particularly well the angular criterion of Donohue (1952) but the same cannot be said for $H_2O_{II} \cdots S_{II}$.

The calculations at the refinement stage were performed on the IBM 650 computer of the *Centro Calcoli e Servomeccanismi della Università di Bologna* using the programmes of L. H. Jensen for the structure factors calculations and those of R. Shiono for the differential synthesis. The cost of the computing work was borne by the *Consiglio Nazionale delle Ricerche*. It is a pleasure to thank all these people and Prof. L. Cavalca for his valuable interest.

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The Structures of Substituted Triazolopyrimidines. Part I. 2-Amino 5-propyl 7-methyl s-triazolo [2,3-c] Pyrimidine Hydrochloride

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The molecular structure of $C_9H_{13}N_5.HCl$, a biologically active triazolo–pyrimidine, has been determined by X-ray methods. The crystals are monoclinic, with the unit-cell parameters

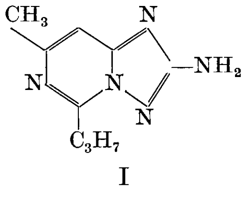
$$a = 22{\cdot}30 \pm 0{\cdot}07,\ b = 6{\cdot}41 \pm 0{\cdot}02,\ c = 16{\cdot}76 \pm 0{\cdot}05\ \text{Å},\ \beta = 107{\cdot}7 \pm 0{\cdot}5^\circ .$$

There are eight molecules in the unit cell, and the space-group is $C2/c$. The three-dimensional Patterson synthesis confirmed this space group, and excluded the alternative, Cc. The structure was solved by the use of Buerger's minimum function, which was derived graphically from the Patterson synthesis. Refinement by Fourier and least-squares methods was continued until the final average standard deviation of the atomic positions was 0·017 Å.

The substance was shown to be a triazolo [2,3-*c*] pyrimidine, with the structure I. The two fused rings are planar and inclined at 6° to each other. The bonds in the fused ring system are all shorter than normal single-bonds, but simple resonance theory is not adequate to explain them. The molecules are linked by a spiral chain of hydrogen bonds 3·18 and 3·30 Å long between the chloride ion and the primary amine group N10; there are also other inter-ionic contacts less than 3·5 Å long which cannot all be hydrogen bonds.

Introduction

In the course of work on a variety of substituted triazolopyrimidines which have interesting biological properties, a substance with the empirical formula $C_9H_{13}N_5$ was isolated, and was thought to be the triazolo [2,3-*c*] pyrimidine, I, or the [4,3-*c*] isomer, II, (Davies, Miller & Rose 1960; Miller & Rose 1960). The chemical and spectroscopic evidence was not conclusive however, and the X-ray analysis described in this paper was therefore undertaken.



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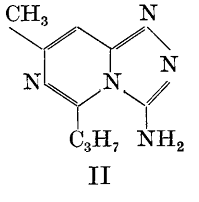

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