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The Crystal Structure of Magnesium Chloride Dodecahydrate, $MgCl_2 . 12H_2O$

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Magnesium chloride dodecahydrate crystallizes in the monoclinic space group $P2_1/c$ with unit-cell dimensions $a=8{\cdot}59$, $b=14{\cdot}40$, $c=8{\cdot}75$ Å, $\beta=129{\cdot}6°$, $D_x=1{\cdot}241$ g.cm^{-3}, $Z=2$.

The phase problem was solved by the direct method. The positions of all atoms except the hydrogen atoms were deduced from the three-dimensional Fourier synthesis, and refined by anisotropic least squares. All the hydrogen atoms are involved in hydrogen bonding and their approximate positions could be deduced from geometrical considerations.

The structure consists of $[Mg^+(H_2O)_6]$ and $[Cl^-(H_2O)_6]$ octahedra which are corner-linked in layers and hydrogen-bonded together between these layers. The ionic-bonded cationic octahedra are regular, while the larger hydrogen-bonded anion octahedra are considerably distorted.

Introduction

Magnesium chloride forms five hydrates, stable over the following temperature ranges, (van't Hoff & Meyerhoffer, 1898),

$$MgCl_2 . 12H_2O \xrightarrow{-16.4°C} MgCl_2 . 8H_2O \xrightarrow{-3.4°C} MgCl_2 . 6H_2O \xrightarrow{116.7°C} MgCl_2 . 4H_2O \downarrow{}^{181°C} MgCl_2 . 2H_2O$$

Only the structure of the room temperature form has been determined (Andress & Gundermann, 1934). The octahydrate is reported to be dimorphic (van't Hoff & Meyerhoffer, 1898). No hydrate is reported for MgF_2, but $MgBr_2$ forms hexa- and deca-hydrates, and MgI_2 octa- and deca-hydrates (Panfilow, 1894). In this work, we have determined the structure of $MgCl_2 . 12H_2O$ as part of a program for investigating the structural behavior of ions and molecules in the presence of a majority of water molecules.

Experimental

The crystals of $MgCl_2 . 12H_2O$ were obtained from a stoichiometric aqueous solution by cooling to $-20°$ to -25 °C in a bromobenzene bath, (van't Hoff & Meyerhoffer, 1898). Nucleation was promoted by wetting a thread with solution, pre-cooling it in dry ice and immersing into the cool solution. The well-developed crystals of ~0·3 mm diameter, which formed on the thread, were separated and inserted into capillary tubes in a cold-box at -35 °C. The X-ray data were obtained with Cu $K\alpha$ radiation and a Weissenberg camera operating in the cold-box, as described by Allen, Jeffrey & McMullan (1963).

The crystal data are as follows,

Monoclinic, m.p. $-16{\cdot}4$ °C

$a=8{\cdot}59\pm0{\cdot}05$, $b=14{\cdot}40\pm0{\cdot}03$, $c=8{\cdot}75\pm0{\cdot}05$ Å,

$\beta=129{\cdot}6\pm0{\cdot}2°$, $D_x=1{\cdot}241$ g.cm^{-3}, $Z=2$,

μ(Cu $K\alpha$) = 42·58 cm^{-1}.

The space group is $P2_1/c$, from systematic extinctions $h0l$ absent for l odd, $0k0$ absent for k odd. Hence the formula unit is centrosymmetrical, and the Mg ions are on the twofold centers of symmetry.

The intensities were recorded by the multiple-film technique on 0 to 5, 0 to 6, and 0 and 1 layers about the *a*, *b* and *c* axes respectively. The intensities were eye-estimated, correlated and Lp-corrected with the use of IBM 1620 programs. Of the 2260 possible reflections within the Cu $K\alpha$ sphere, 1609 were recorded. Of these, 206 were not observed and were given values of zero. The approximate absolute scale and mean isotropic temperature factors were determined from a Wilson plot.

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Table 1. *Structural parameters for* $MgCl_2 . 12H_2O$, *with the standard deviations referred to the last significant digits in parentheses*

The b_{ij} are defined by: $T=\exp\{-[10^{-4}(b_{11}h^2+b_{22}k^2+b_{33}l^2+2b_{12}hk+2b_{13}hl+2b_{23}kl)]\}$.

Atom	x	y	z	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Mg	0	0	0	38 (6)	11 (1)	57 (6)	—	33 (5)	—
Cl	0·2628 (3)	0·3100 (1)	0·2505 (3)	102 (4)	20 (1)	98 (4)	−1 (2)	65 (3)	−2 (1)
O(1)	0·2390 (8)	0·0493 (4)	0·0225 (9)	74 (11)	33 (3)	148 (13)	−2 (5)	78 (10)	27 (5)
O(2)	−0·0082 (9)	0·1222 (4)	0·1175 (9)	170(14)	18 (3)	175 (14)	−10 (5)	145 (12)	−15 (5)
O(3)	0·2060 (9)	−0·0565 (4)	0·2798 (8)	122 (12)	23 (3)	80 (11)	18 (5)	55 (10)	15 (4)
O(4)	0·4357 (10)	−0·2104 (5)	0·3427 (10)	135 (13)	28 (3)	141 (14)	14 (6)	84 (12)	24 (5)
O(5)	0·3518 (9)	−0·4889 (4)	0·1626 (8)	107 (12)	28 (3)	105 (11)	−5 (5)	63 (10)	−1 (5)
O(6)	0·1475 (9)	−0·3482 (5)	0·1812 (9)	103 (12)	36 (3)	127 (13)	10 (6)	72 (11)	17 (5)

Table 2. *Observed and calculated structure factors*

K= 0 H= 0
2 504+ 712-
4 331 362
6 60 57
8 173 192
K= 1 H= 0
1 325 308
2 279 265-
3 561+ 673
5 53 38-
6 62 50
7 126 119
K= 2 H= 0
0 176 122
1 214 233
2 443+ 596
3 428+ 503-
4 66 65
5 236 244
6 219 257
7 139 159-
K= 3 H= 0
1 261 252
2 80 50-
3 258 264
4 107 110-
5 190 198
6 75 68-
7 95 95
8 52 60
K= 4 H= 0
0 255 268
1 349+ 428-
2 126 116
3 113 93
4 199 212
5 147 146-
6 128 158
7 82 119
8 47 51
K= 5 H= 0
1 208 159-
2 135 131-
3 379+ 480
4 120 145
5 110 119
6 140 166-
K= 6 H= 0
0 474+ 594
1 544+ 771
2 171 142-
3 239 279-
4 143 169
5 86 72
6 60 55
7 151 158-
8 85 97
K= 7 H= 0
1 131 115
2 131 123
3 81 84
4 70 45-
6 83 72-
K= 8 H= 0
0 255 207-
1 289 282-
2 381 433
4 300 344-
5 75* 69
6 200 283
7 63 62-
K= 9 H= 0
1 70 54
2 120 108
3 57* 29
4 133 119-
5 86 64
K= 10 H= 0
0 265 239
1 255 266-
2 153 164-
3 119 102
4 106 93
5 93 89-
7 102 121
K= 11 H= 0
2 126 104-
5 105 112
6 79 66
K= 12 H= 0
0 136 118-
1 170 147
2 122 88
3 151 142-
4 72* 60
5 133 174
6 75 72
K= 13 H= 0
2 165 158
3 139 146
4 67* 54-
K= 14 H= 0
0 88 73
1 235 257-
2 115 96
3 195 247
4 69 56-
5 87 89-
K= 15 H= 0
1 73 62
2 109 104
3 103 92
4 53 36-
K= 16 H= 0
0 269 287
2 83 88-
4 136 176
K= 17 H= 0
1 112 117
K= 18 H= 0
2 94 13
K= 0 H= 1
0 333 267
2 71 62
4 164 125
6 37* 24
K= 1 H= 1
0 249 267-
1 547 607
2 254 256
4 81 77-
4 404 414-
5 52 33-
6 226 224
7 103 77
K= H= 1
0 333 316
1 614 622-
2 77 14
4 163 109
5 84 50-
6 112 92
7 31* 18
K= 3 H= 1
0 301 292
1 432 429-
2 636+ 728-
3 466 492
4 204 164
5 149 114-
6 129 92-
7 193 178
K= 4 H= 1
0 484 422-
1 183 136
2 282 266
3 195 168-
4 276 227
5 147 114-
6 61 36
7 65 39
K= 5 H= 1
0 66 50
1 613+ 719
2 335 330-
3 335 296-
4 162 136
5 345 342
6 175 166-
7 47 35-
K= 6 H= 1
0 135 86
1 179 147-
2 60* 7-
3 87 53
4 282 269
5 131 95-
6 71 52
7 30* 11-
K= 7 H= 1
0 258 247-
1 325 348
2 198 148
3 239 238
4 246 224-
5 98 79-
6 88 99
7 124 155
K= 8 H= 1
0 284 271
1 79 42-
2 77 41
3 77 61
4 155 157
5 136 126-
6 62* 32
K= 9 H= 1
0 369 351
1 286 313
2 375 430-
4 171 151
5 117 105
6 76 80-
K= 10 H= 1
0 127 89-
1 115 110-
2 207 216
4 138 139
K= 11 H= 1
0 162 149-
1 323 382
2 139 137
3 125 120-
4 150 150-
5 229 243
6 102 107
K= 12 H= 1
0 97 64
1 71 60
4 160 175
K= 13 H= 1
0 77* 55-
1 122 98-
2 87 83
3 233 277
4 50* 6
5 95 84-
K= 14 H= 1
2 60* 38-
3 151 147
4 63* 53
5 111 111
K= 15 H= 1
0 104 76
1 130 126-
2 119 125
4 147 162
5 71 78-
K= 16 H= 1
0 86 40-
1 121 128
2 80 47
K= 17 H= 1
0 131 109
2 82 71
3 62 57
K= 18 H= 1
0 127 123-
1 67 58
2 114 121
K= 0 H= 2
0 75 72
1 40 42
K= 1 H= 2
0 525 540-
2 448 454
4 335 318-
6 182 210
K= 2 H= 2
0 187 138
2 340 305-
3 100 48-
4 146 119
5 87 62
7 149 16
K= 3 H= 2
0 112 28
1 440 430-
2 225 183
3 256 250
4 95 61
5 217 200-
6 88 78-
K= 4 H= 2
0 155 95-
1 144 118
2 271 229
3 206 161-
4 53* 12
5 218 214
6 103 93
K= 5 H= 2
0 260 243-
1 73 41-
2 205 182
3 233 208
4 54 48
5 103 85
K= 6 H= 2
0 70 68-
1 128 93-
2 334 344
3 245 227
4 55* 23
5 180 170-
6 111 87
K= 7 H= 2
0 71 36
1 338 337
4 105 81
5 123 135
K= 8 H= 2
0 566+ 689
1 79 52-
2 84 50-
3 60* 66
4 269 308
6 115 133-
K= 9 H= 2
0 52* 9
1 230 216
3 161 153
4 87 58-
5 68 61
6 48 42
K= 10 H= 2
0 151 145
1 211 201
2 305 305
3 238 257-
4 78 58-
5 114 113
K= 11 H= 2
0 176 169-
2 60* 38-
3 151 147
4 71 63
5 111 111
K= 12 H= 2
1 187 222
3 71 54-
K= 14 H= 2
0 168 147
1 193 237
3 142 155-
4 115 141
K= 15 H= 2
0 80 66-
1 51* 37
2 45* 25
3 95 97
K= 16 H= 2
0 93 90-
1 46* 43
2 209 266
K= 17 H= 2
1 52 17
K= 0 H= 3
0 239 196
2 215 203
4 90 96
K= 1 H= 3
0 548 626
1 239 219
2 331 334-
3 146 126
4 180 150
5 74 50
6 71 68-
K= 2 H= 3
0 317 244
1 47 29
4 81 57
5 51 37
6 136 145
K= 3 H= 3
0 222 186-
1 338 332
2 240 210
3 90 67
4 94 68-
5 173 177
6 106 104
K= 4 H= 3
0 245 216
1 46* 43-
2 74 47
3 127 99
4 104 75
5 54 22
6 100 104
K= 5 H= 3
0 108 62-
1 328 311-
2 387 406
3 349 354
4 136 130-
5 68 60-
K= 6 H= 3
0 274 243
3 171 132
4 140 120
5 100 96
K= 7 H= 3
0 320 323
1 325 335
3 66* 47
4 143 141
5 47* 19
K= 8 H= 3
0 335 335
1 127 120
2 80* 48
K= 9 H= 3
0 216 207-
1 98 63
2 167 163
3 122 116
K= 10 H= 3
0 309 335
1 126 120-
K= 11 H= 3
0 181 188
1 161 159-
2 131 115-
3 250 283
K= 12 H= 3
0 93 74
1 64* 25-
3 93 81-
4 71 63
K= 13 H= 3
1 187 222
3 71 54-
K= 14 H= 3
0 104 115
K= 0 H= 4
0 534 526
2 105 72-
4 288 351
K= 1 H= 4
0 305 285-
1 455 508
2 81 54
5 104 100
K= 2 H= 4
1 307 306
2 318 304
3 273 271-
4 72 53
5 108 105
K= 3 H= 4
0 113 76
1 172 141
2 103 81-
3 169 156
5 56 29
K= 4 H= 4
0 93 70
1 281 268-
3 227 198
4 211 197
5 109 110-
K= 5 H= 4
0 42* 6-
1 239 258
2 107 72
3 37* 18
4 49 33-
5 64 71
K= 6 H= 4
0 113 83
1 287 277
2 55* 20
3 166 158-
4 156 140
K= 7 H= 4
0 155 118-
2 111 83
K= 8 H= 4
0 241 219-
1 82 61
2 280 298
4 128 128-
K= 9 H= 4
0 159 140
1 117 101
2 133 137-
K= 10 H= 4
0 200 182
1 112 117-
2 149 148-
3 71 71
K= 11 H= 4
2 66* 33-
K= 12 H= 4
0 118 106-
1 113 102
2 131 113
3 55 51-
K= 13 H= 4
0 94 79
K= 14 H= 4
0 102 88-
1 106 106-
2 99 102
K= 15 H= 4
1 121 146
K= 16 H= 4
0 170 235
K= 0 H= 5
0 277 265
2 262 269
4 95 97-
K= 1 H= 5
0 253 235-
1 122 80
2 118 97
3 57 40
4 126 121-
K= 2 H= 5
0 274 259
1 90 52-
2 61* 1
3 90 66-
4 118 112
K= 3 H= 5
0 69 52-
1 117 80-
2 147 134-
3 219 209
4 65 57
K= 4 H= 5
0 54* 16-
1 96 66-
2 215 223
3 59 46
K= 7 H= 5
2 120 123
3 109 98
K= 8 H= 5
0 149 140
1 60* 38
2 110 83
3 110 111-
K= 9 H= 5
0 97 64
1 58* 30
2 136 133-
3 62 56
K= 10 H= 5
2 137 150
K= 11 H= 5
0 88 71-
1 107 125-
K= 14 H= 5
0 87 96
K= 0 H= 6
0 80 42-
2 116 128
K= 1 H= 6
0 55 40
1 60 41-
2 40* 29-
3 109 113
K= 2 H= 6
0 260 252
1 175 171-
2 134 91-
3 50 44
K= 3 H= 6
0 44* 22
1 90 94
2 63 41-
K= 4 H= 6
0 200 182
1 142 142
3 70 62-
K= 5 H= 6
0 38* 35
1 50 31
2 46 30-
K= 6 H= 6
0 83 63
1 141 142-
2 137 114
K= 7 H= 6
0 73* 72
1 123 120
K= 8 H= 6
0 260 347
K= 9 H= 6
1 173 228
K= 11 H= 6
1 52 56
K= 12 H= 6
0 104 137
K= 0 H= 7
0 157 176
K= 1 H= 7
0 177 191
1 47 32
2 113 112-
4 144 148-
K= 3 H= 7
1 190 204
K= 4 H= 7
0 60 29-
1 70 59-
K= 5 H= 7
0 33* 5
1 71 59-
K= 6 H= 7
0 140 135
1 109 119
K= 7 H= 7
0 137 161
1 122 173
K= 9 H= 7
0 87 98-
K= 10 H= 7
0 93 130
K= 0 H= 8
0 190 216
K= 1 H= 8
0 39 40-
K= 2 H= 8
0 58 40
K= 3 H= 8
0 53 35
K= 4 H= 8
0 53 39
K= 5 H= 8
0 35 27-
K= 0 H= -1
2 409+ 501
4 146 162
6 36* 26
K= 1 H= -1
3 117 115
4 237 219
5 202 176
6 220 233-
7 195 193
8 222 231
9 26* 14
K= 2 H= -1
1 93 86-
2 283 335
3 326 335-
4 217 211
5 306 314
6 53 35
8 185 199
K= 3 H= -1
1 477+ 742
2 248 274
3 253 332-
4 92 82-
5 458+ 621
6 191 209
7 105 92-
8 70 63-
9 73 109
K= 4 H= -1
1 482+ 567
2 304 335
3 107 84
4 345 434
5 55* 42
8 76 92
K= 5 H= -1
1 331 366-
4 401+ 470
5 105 69-
6 342 393
7 219 220
8 142 138
9 87 84-
K= 3 H= -2
1 461 494
2 186 182
4 47 32-
5 82 63-
6 150 136
7 198 206
9 32* 8
K= 4 H= -2
1 188 229
2 129 103-

* Unobserved or very weak reflections omitted from final refinement calculations.
\+ Reflections omitted because of extinction.

Table 2 (*cont.*)

3 172	207-	4 270	271-	K= 12 H= -3		6 214	232-	10 61	42-	K= 0 H= -6		4 84	51-	8 142	134				
4 335	395	6 109	94	2 185	165	7 128	110	K= 4 H= -5		2 201	206	5 109	73	9 77	67				
5 330	377	8 93	87	3 93	77-	9 96	77	1 238	232	4 258	267-	6 67	34	K= 0 H= -9					
6 123	108	10 46*	7-	4 124	107	K= 8 H= -4		2 72	60	6 238	239	7 227	205	2 201	246				
7 169	172-	K= 1 H= -3		5 161	150	1 147	119	3 118	100-	8 58	47	8 80	63	4 138	149-				
8 69*	32-	1 170	151	6 119	107	2 315	343	4 273	316	10 211	181	9 195	206-	6 262	344				
9 153	192	2 214	274	7 111	104-	3 97	78-	5 303	310	K= 1 H= -6		10 74	67-	8 131	127				
K= 5 H= -2		3 118	107-	8 83	83	4 200	208-	6 224	228	1 101	101	11 124	177	10 123	119				
1 100	61	4 219	205-	K= 13 H= -3		5 182	165-	7 187	187-	2 144	154	K= 4 H= -7		K= 1 H= -9					
2 169	157	5 143	147	1 165	155-	6 189	189	8 61*	37-	3 49	45-	1 191	193-	2 139	143-				
3 265	272	6 188	159	2 147	138	7 127	124	9 76	72	4 278	275-	2 153	143	3 171	197				
4 107	65-	7 144	134-	3 284	313	9 88	86-	10 71	69	5 100	105	3 119	102	4 166	184				
5 162	167	8 168	158-	4 102	58-	K= 9 H= -4		K= 5 H= -5		6 311	315	4 192	193	5 110	94				
6 199	213	9 186	184	7 144	158	1 117	81	1 46	18-	7 54	43	5 159	157-	6 111	113-				
7 53*	30	10 132	149	K= 14 H= -3		3 155	141-	2 266	280	8 48*	38-	7 127	117	7 154	166				
8 78	69-	K= 2 H= -3		1 106	90	4 60*	40	3 417	507	9 174	153	8 71	54	8 110	113				
9 48	43	1 188	119-	2 134	107	5 186	186	4 91	60	11 61	49	9 93	85-	9 120	97				
K= 6 H= -2		2 318	368	4 99	65	6 64*	51	5 246	225-	K= 2 H= -6		10 53	38	10 132	140-				
1 251	279-	3 361	400-	6 90	85	8 87	98-	6 98	90-	1 252	274-	K= 5 H= -7		K= 2 H= -9					
2 370	401	4 376	410-	7 50	42-	9 85	89	7 276	296	2 177	160-	1 196	201	2 46*	27				
3 663*	786	5 52	29	K= 15 H= -3		K= 10 H= -4		8 51	45	3 214	215	2 122	117-	3 31	29				
4 54*	15	6 288	288	1 172	168	1 175	167-	9 73	57-	4 193	173	3 38*	14-	4 175	200				
5 298	339-	7 165	143	4 189	172	2 87	37-	10 31*	1	5 71	64	4 71	58	5 47	26-				
6 237	237	8 39*	1	5 109	95	3 130	93	K= 6 H= -5		7 145	118	5 276	306	6 60	55				
7 123	98	9 95	69-	6 175	196-	4 172	154	1 222	218	8 273	276	6 101	88-	7 152	143				
8 81	71-	10 31	20	K= 16 H= -3		5 101	80-	2 93	73	9 45*	41-	7 122	106-	8 162	178				
K= 7 H= -2		K= 3 H= -3		1 74	62	6 142	133-	3 68	57	10 148	127-	8 79	53-	9 171	165-				
1 341	355	1 561*	676-	3 49*	40-	7 134	135	4 163	141	11 44	41	9 187	155	10 66	49				
2 242	245	2 552*	638-	5 71	63	8 223	249	6 141	133	K= 3 H= -6		10 92	84	K= 3 H= -9					
3 163	158	3 749	930	K= 17 H= -3		9 58	60-	7 45*	36	1 96	110-	K= 6 H= -7		2 63	53				
5 80	55-	4 47	44	2 163	169	K= 11 H= -4		8 69	49-	2 51*	2	1 127	115	3 50	42				
6 105	86	5 194	167-	4 134	139-	1 64*	1-	9 64	34-	3 243	269	2 59	32	5 188*	207				
7 193	199	6 71*	6	K= 0 H= -4		2 63*	23-	10 112	120	4 135	123	3 90	80-	6 41	18				
K= 8 H= -2		7 165	141	2 248	254	3 90	70	K= 7 H= -5		5 140	122	4 218	215	9 156*	151				
1 92	82	8 54*	35	4 377	410	5 97	76	1 289	303	6 135	112	5 144	118-	10 26	13-				
2 252	243-	9 78	56-	6 275	287-	6 98	97	2 148	106-	8 92	70	6 45*	30	K= 4 H= -9					
3 149	120-	10 34	44-	8 378	443	7 79	67	3 212	192-	10 34*	31-	7 70	46-	2 89	79				
4 409	462	K= 4 H= -3		10 32*	29-	K= 12 H= -4		4 232	272	11 95	149	8 147	128	3 78	79-				
5 148	130	1 519	595-	K= 1 H= -4		1 211	203	5 140	140	K= 4 H= -6		9 138	114	4 110	94				
6 136	118-	2 66	50-	1 208	226	2 125	77	6 196	205-	1 355	355	10 74	53	5 135	140				
8 198	188	3 266	315	2 439	539-	3 223	224-	8 146	153	2 244	241	K= 0 H= -8		6 129	123				
K= 9 H= -2		4 220	239	3 170	140	4 139	134	9 135	130	3 290	313-	2 36*	4-	7 92	98-				
1 260	259	5 245	254-	4 126	121	5 242	267	10 94	98-	4 82	58	4 179	183	8 51	34				
2 86	68-	6 222	239	5 171	163	7 162	144-	K= 8 H= -5		5 344	386	6 38*	45	10 61	59				
3 278	267	8 57*	49-	6 57	26	K= 13 H= -4		2 56*	10-	6 108	83	8 181	185	K= 5 H= -9					
4 102	58	K= 5 H= -3		7 263	273	1 126	120	3 200	197	7 134	119-	10 34*	29-	2 47	40				
5 73*	54-	1 434	465	8 51	18	2 100	105	4 55*	43	8 107	89	K= 1 H= -8		3 224*	225				
7 174	192	2 51	39-	9 36*	15-	3 62*	42-	7 61*	51-	9 191	199	1 86	68	4 31*	11-				
8 73	54	3 42	15	10 84	69-	4 80	65	8 91	103	K= 5 H= -6		2 73	67-	5 40*	21				
K= 10 H= -2		4 165	145-	K= 2 H= -4		5 182	167	9 92	78	1 93	76	3 171	191	6 33	17				
1 100	88	5 350	385	1 179	153	K= 14 H= -4		K= 9 H= -5		2 167	174	4 48*	45	7 71	74				
K= 11 H= -2		6 131	112-	2 500	540	1 56*	38-	1 173	168	3 78	60	6 138	129-	8 53	46-				
1 246	258	7 156	147-	3 275	317-	2 200	210	2 154	132	4 107	94	7 173	160	9 44	32-				
K= 10 H= -2		8 45*	21	5 80	65	3 158	175	3 58*	25-	5 314	326	8 178	157	10 31	31				
2 278	253	9 192	215	6 348	379	5 165	153-	4 238	251-	6 81	63-	9 129	126	K= 6 H= -9					
3 151	141-	K= 6 H= -3		7 74	42-	6 89	66	6 282	343	7 107	94-	10 149	147-	2 125	143				
5 114	89	1 178	143-	8 117	102-	7 123	135	7 60*	16-	8 127	125	11 28	20-	3 142	135				
6 246	259	2 166	151	9 44*	33	K= 15 H= -4		8 152	145-	9 105	85	K= 2 H= -8		4 80	63-				
7 73	62-	3 97	65-	10 184	203	2 86	77	9 142	167	10 33*	23	1 32*	8-	5 166	141-				
8 81	78-	4 178	169	K= 3 H= -4		3 64*	73	K= 10 H= -5		K= 6 H= -6		2 163	176	6 149	121				
K= 11 H= -2		5 71	63-	1 169	164	6 63	62	2 136	125	1 96	79-	3 167	176-	7 76	63				
2 258	260-	6 90	84	2 277	308-	K= 16 H= -4		3 81	55-	2 240	216	4 51	22-	8 78	50				
3 211	186	7 100	72-	3 292	332	1 77	66	4 114	99-	3 230	218	5 182	174	9 50	38-				
5 95	71	8 185	169	4 141	122	2 100	88-	5 97	86	4 107	82-	6 321	326	K= 0 H=-10					
6 102	104	K= 7 H= -3		5 284	256	4 131	137	6 186	193	5 43*	21-	7 133	117-	6 80	75				
7 152	137	1 143	85-	6 129	106-	K= 17 H= -4		7 58*	28	6 320	314	8 110	107-	8 72	61				
8 49	37-	2 292	308	7 75	55	2 49	39-	8 93	66-	7 84	60	10 156	151	10 156	192				
K= 12 H= -2		3 270	294	8 63	50-	3 76	85	9 36*	28	8 123	102-	11 58	67-	K= 1 H=-10					
1 247	249-	4 288	298-	9 94	97	K= 0 H= -5		K= 11 H= -5		9 68	32-	K= 3 H= -8		4 36	24-				
2 81	49	5 134	126	K= 4 H= -4		2 169	144-	1 118	107-	10 152	142	1 206	209	5 90	93				
3 244	243	6 91	63	1 290	279-	4 351	396	2 150	131-	K= 11 H= -6		2 71	64-	6 81	83				
4 275	305	7 148	140	2 335	372	6 247	290	3 247	226	1 89	87	3 94	76	7 129	118				
5 217	224-	9 190	165-	3 93	72	8 64	29	4 106	108	K= 12 H= -6		4 94	78-	8 64	61-				
6 87	68	K= 8 H= -3		4 208	228	10 213	221	5 90	61-	1 133	138-	5 160	167	9 63	60				
7 99	101	1 66	48-	5 323	366-	K= 1 H= -5		7 134	104	K= 0 H= -7		6 91	69	10 74*	84				
K= 13 H= -2		2 183	180	6 127	116	1 284	310	8 69	68	2 77	74-	8 136	132-	K= 2 H=-10					
1 72	50	5 117	101-	7 226	243	2 346	420-	9 52	60-	6 46*	20-	9 135	146	3 15	31				
3 175	188	6 164	141	8 103	85	3 269	331	K= 12 H= -5		8 173	175	K= 4 H= -8		4 126	134				
5 94	93	8 196	165	9 229	268-	4 382	439	1 150	153-	10 83	68-	1 183	168-	6 58	47-				
6 78	80-	K= 9 H= -3		10 36*	38	5 198	184-	2 90	75	K= 1 H= -7		2 43*	44	7 169	162				
7 60	61	1 201	200	K= 5 H= -4		6 171	166-	3 101	96	1 130	147	3 166	184	8 174	175				
K= 14 H= -2		2 345	379-	1 124	74-	7 437	491	4 131	129	2 125	124	4 227	260	9 109*	114-				
1 218	242	3 263	261	3 146	156	8 157	137	5 72*	74-	3 142	148-	5 306	358-	10 19	11				
3 162	166-	4 221	203	4 99	83-	9 58	37	7 49*	60	4 209	206-	6 75	56	K= 3 H=-10					
4 146	147	5 64*	55-	5 325	338	10 141	133-	K= 13 H= -5		5 153	132	7 168	165	4 113	112				
5 94	84	6 209	189-	6 195	179-	K= 2 H= -5		1 222	222	6 277	289	9 193	171-	5 45	40-				
K= 15 H= -2		7 212	233	7 116	92	1 41*	30-	3 85	71-	7 73	45-	10 113	99	6 51	28				
1 130	133	8 171	158	8 50	25-	2 71	48	4 86	70-	8 207	199-	K= 5 H= -8		7 168	161				
2 78	69-	9 61	55	9 61	50-	3 83	68	5 200	195	9 159	140	1 43	14	8 76	75				
3 53*	23	K= 10 H= -3		10 27*	24-	4 349	415	7 82	72-	10 127	102	2 56	45-	9 63	65-				
4 60*	41	1 131	108-	K= 6 H= -4		5 46	14-	K= 14 H= -5		11 63	53-	3 173	201	K= 4 H=-10					
5 80	83	2 115	102-	1 260	237	6 76	62	2 50*	52-	K= 2 H= -7		4 105	105-	4 126	120				
6 72	76-	3 146	141-	2 86	28	7 157	152	3 77	58	1 64	51-	5 46*	31-	5 137	154				
K= 16 H= -2		4 256	273	3 134	136-	8 211	196	4 164	167	2 225	262	6 37*	22-	6 49	33				
2 191	187	5 114	96	4 376	409	9 58	51-	5 74	51-	3 136	128-	7 206	219	7 96*	91-				
3 73	65	6 134	121	6 218	212-	10 81	65	7 84	79-	5 143	142	8 138	141-	8 31	22-				
4 101	74-	8 109	91	7 272	276-	K= 3 H= -5		K= 15 H= -5		6 57	32-	9 60	41-	9 151	176				
5 87	94-	K= 11 H= -3		8 258	279	1 302	306	2 91	82	7 79	57-	10 60	55	K= 5 H=-10					
K= 17 H= -2		1 248	248	9 91	87	2 87	60	3 174	156	8 55	41	K= 6 H= -8		4 50	51				
1 144	157	2 222	210	10 40*	22-	3 39*	34	4 146	144-	9 85	78	1 47	29	5 142	158				
4 53	43-	3 65*	54	K= 7 H= -4		4 107	96-	5 87	80-	10 120	104	2 97	60-	8 97	105				
K= 18 H= -2		4 188	166-	1 365	384	5 418	472	6 107	103	11 83	90-	3 86	70-	9 71	88				
1 102	121-	5 291	302	2 199	173-	6 210	230	K= 16 H= -5		K= 3 H= -7		4 185	182	K= 6 H=-10					
2 66	69-	6 100	97	3 241	263-	7 89	71-	2 94	101	1 44*	23-	6 58	38	6 74	69				
K= 0 H= -3		7 78	64-	4 140	139	8 61*	26-	3 59	37	2 100	85-	7 193	195-	7 74	79				
2 184	156	9 62	37-	5 168	166	9 190	213	5 64	76-	3 70	57								

Determination and refinement of the structure

The phase problem was solved directly with the three-dimensional sign-correlation IBM 1620 program of Beurskens (1964). The first application of this method gave 284 signs, all of which were for the reflections $h+k=2n$. The resulting E-map showed twice the proper number of atomic peaks and a false twofold symmetry axis at $\frac{1}{4}$, y, $\frac{1}{4}$. A sign determination of the weaker reflections of the type $h+k=2n+1$ gave 47 assignments of high probability but low frequency. Inclusion of these in the E-map increased some peaks and diminished others, thereby permitting an identification of the asymmetric unit of structure. The coordinates of all the atoms in the general positions, except the hydrogen atoms, were derived and the initial isotropic structure factor calculations gave an agreement index of $R=0{\cdot}24$. For the calculation of structure factors, the atomic scattering factors of magnesium and chlorine ions, and oxygen atoms were taken from *International Tables for X-Ray Crystallography*.

The structure refinement was carried out with the full-matrix least-squares IBM 7090 program of Busing & Levy (1959). The function minimized was $\Phi=\sum_{hkl}\omega(|F_{obs}|-G|F_{calc}|)^2$, where G is the overall scale factor which varies between cycles and $\omega=1/(a+b|F_{obs}|+c|F_{obs}|^2)$ with $a=4$, $b=1$, $c=0{\cdot}029$. Four cycles in the isotropic mode reduced R to 0·13, and three anisotropic cycles gave a further small reduction to 0·11. The hydrogen atoms could not be directly located, since the three-dimensional difference Fourier synthesis showed twice as many weak maxima as hydrogen atoms. Although it was possible to predict the donor/acceptor positions of all the hydrogen atoms in hydrogen bonds, the inclusion of these atoms had no affect on the agreement indices and therefore they were not included in the final refinement calculations. The standard deviations quoted in Table 1 are directly from the least-squares program output and take no account of the omission of the hydrogen scattering.

The atomic parameters are given in Table 1. The structure factors are given in Table 2. Those marked with asterisks were omitted from the final refinement calculation because they were suspected to be unreliable, either by reason of extinction, or because they corresponded to unobserved reflections or to very weak spots on the photographs. The ionic and hydrogen bond angles are given in Tables 3, 4 and 5.

Table 4. *Hydrogen bond distances and angles within the* $Cl(H_2O)_6$ *octahedron*

From atoms in positions	to atoms	in positions	Distance
Cl	O(1)	$x, \frac{1}{2}-y, \frac{1}{2}+z$	3·230 (7) Å
(x, y, z)	O(5)	x, y, z	3·211 (7)
	O(4)	$1-x, \frac{1}{2}+y, \frac{1}{2}-z$	3·186 (8)
	O(2)	x, y, z	3·261 (8)
	O′(4)	$1-x, -y, 1-z$	3·112 (8)
	O(6)	$-x, -y, -z$	3·166 (8)

Atoms	Angle
O(2) –Cl–O(5)	152·5 (0·2)°
O(1) –Cl–O(4)	133·6 (0·2)
O′(4)–Cl–O(6)	158·0 (0·2)

Atoms	Angle
O(1) –Cl–O(5)	75·4 (0·2)
O(5) –Cl–O(4)	70·5 (0·2)
O(4) –Cl–O(2)	110·1 (0·2)
O(2) –Cl–O(1)	114·6 (0·2)
O(1) –Cl–O′(4)	81·0 (0·2)
O′(4)–Cl–O(4)	91·8 (0·2)
O(4) –Cl–O(6)	100·3 (0·2)
O(6) –Cl–O(1)	103·0 (0·2)
O(2) –Cl–O′(4)	84·9 (0·2)
O′(4)–Cl–O(5)	122·5 (0·2)
O(5) –Cl–O(6)	79·1 (0·2)
O(6)–Cl–O(2)	73·7 (0·2)

Discussion

The structure consists of corner-sharing $[Mg^+ . 6H_2O]$ and $[Cl^- . 6H_2O]$ octahedra as shown in Figs. 1, 2 and 3. The Mg^+ hydration polyhedra are centrosymmetric and regular with Mg · · · O distances of $2{\cdot}062 \pm 0{\cdot}003$ Å and O · · · O edges of $2{\cdot}916 \pm 0{\cdot}026$ Å. Within the experimental errors, these are perfect octahedra. In contrast, the Cl^- hydration polyhedra are very distorted

Table 3. *Bond distances and angles within the* $Mg(H_2O)_6$ *octahedron and between the corners of the octahedron and hydrogen-bonded neighbouring atoms*

Standard deviations are in parentheses referred to the last digits.

From atom in position (x, y, z)	to atoms	in positions	Distance	Atoms	Angle
Mg	O(1)	x, y, z	2·059 (7) Å	O(1)–Mg –O(2)	90·4 (0·3)°
	O(2)	x, y, z	2·061 (7)	O(1)–Mg –O(3)	88·5 (0·3)
	O(3)	x, y, z	2·065 (7)	O(2)–Mg –O(3)	91·2 (0·3)
O(1)	Cl′	$x, \frac{1}{2}-y, -1+\frac{1}{2}+z$	3·230 (7)	Cl′–O(1)–O(5)	102·6 (0·3)
	O(5)	$1-x, \frac{1}{2}+y, \frac{1}{2}-z$	2·811 (10)		
O(2)	Cl	x, y, z	3·261 (8)	Cl —O(2)–O(6)	98·5 (0·3)
	O(6)	$-x, \frac{1}{2}+y, \frac{1}{2}-z$	2·721 (10)		
O(3)	O(4)	x, y, z	2·779 (10)	O(4)–O(3)–O′(5)	103·2 (0·3)
	O′(5)	$x, -1+\frac{1}{2}-y, \frac{1}{2}+z$	2·805 (10)		

(Fig. 4). The $Cl^- \cdots O$ distances range from 3·11 Å to 3·26 Å and the $O \cdots O$ edges from 3·86 Å to 5·55 Å. There are correspondingly wide deviations from orthogonal coordination angles at the chlorine, as shown in Table 3.

The hydration octahedra share corners so as to form layers which extend parallel to (100). These layers are shown most clearly, separated by zigzag channels, in projection on (010) on the right hand side of Fig. 1. The layers of corner-linked octahedra are then hydrogen-bonded together between corners and across the channels as indicated by the heavy lines on the left hand side of the figure. The hydrogen bonds form links between the corners of anionic and cationic octahedra, and pairs of anionic octahedra, but not between pairs of cationic octahedra. It can also be seen in Fig. 1 that all like octahedra form chains in the *c*-axis direction with the Cl^- octahedra sharing a common corner. The

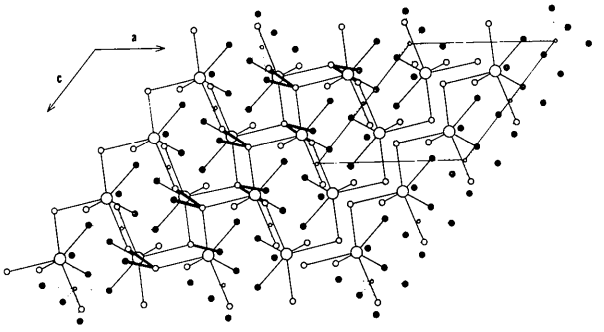


Fig. 1. The structure of magnesium dodecahydrate in orthogonal projection on the (100) plane. Smallest open circles, Mg^+; filled circles, water oxygen belonging to magnesium octahedron; large open circles, Cl^-; medium open circles, water oxygen belonging to chloride octahedron. The magnesium and chloride octahedral coordinations are indicated by dotted and full lines respectively. Zigzag channels separate the layers of corner-sharing octahedra. The heavy lines across these channels are the hydrogen bonds between the layers.

Mg^+ octahedra are not directly linked, but are invariably interspersed by those of the anions, as shown in Figs. 2 and 3. They are, in fact, as removed from each other in the structure as possible. The distortions of the $[Cl^- . 6H_2O]$ from octahedral symmetry are unsymmetrical and each individual polyhedron is enantiomorphic, so that left- and right-handedly distorted octahedra alternate along the corner-sharing chain in the *c*-axis direction. This is a consequence of the particular arrangement of the polyhedra, as seen by consideration of Fig. 2, for example.

If it is assumed that each water molecule in the structure forms two hydrogen bonds and that these are directed either toward the anions or toward other

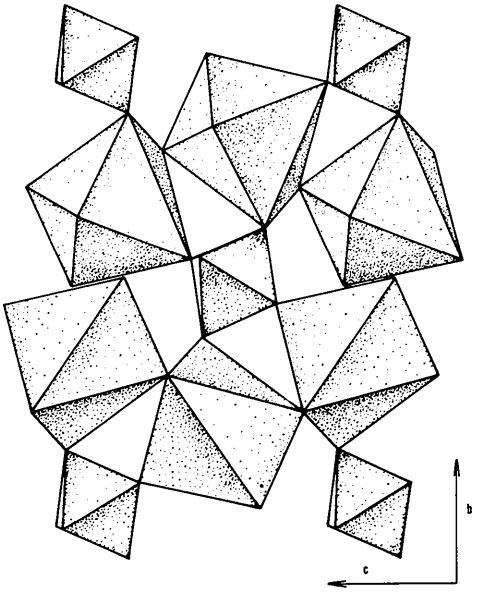


Fig. 2. The corner-sharing magnesium and chloride hydration octahedra which form the layer of the structure parallel to (100), in orthogonal projection on the (100) plane.

Table 5. *Hydrogen-bond distances and angles of the water molecules*

The angles are calculated assuming linear hydrogen bonds.

Central atom in (x, y, z)	to atom forming tetrahedron	in positions	Distance	Atoms	Angle	σ
O(4)	Cl	$1-x, \quad -y, \quad 1-z$	3·112 (8) Å	Cl —O(4)–Cl′	96·6°	0·2°
	Cl′	$1-x, \quad -1+(\frac{1}{2}+y), \quad \frac{1}{2}-z$	3·186 (8)	Cl —O(4)–O(3)	124·2	0·3
	O(3)	$x, \quad y, \quad z$	2·779 (11)	Cl —O(4)–O(6)	94·3	0·3
	O(6)	$x, \quad y, \quad z$	2·758 (11)	Cl′—O(4)–O(3)	117·8	0·3
				Cl′—O(4)–O(6)	123·1	0·3
				O(3)–O(4)–O(6)	100·4	0·3
O(5)	Cl	$x, \quad -1+y, \quad z$	3·211 (7)	Cl —O(5)–O(1)	106·4	0·3
	O(1)	$1-x, \quad -1+(\frac{1}{2}+y), \quad \frac{1}{2}-z$	2·811 (10)	Cl —O(5)–O(3)	120·2	0·3
	O(3)	$x, \quad -1+(\frac{1}{2}-y), \quad -1+(\frac{1}{2}+z)$	2·805 (10)	Cl —O(5)–O(6)	113·1	0·3
	O(6)	$x, \quad y, \quad z$	2·752 (10)	O(1)–O(5)–O(3)	116·9	0·3
				O(1)–O(5)–O(6)	104·1	0·3
				O(3)–O(5)–O(6)	94·7	0·3
O(6)	Cl	$-x, \quad -y, \quad -z$	3·166 (8)	Cl —O(6)–O(2)	100·7	0·3
	O(2)	$-x, \quad -1+(\frac{1}{2}+y), \quad \frac{1}{2}-z$	2·721 (10)	Cl —O(6)–O(5)	108·9	0·3
	O(5)	$x, \quad y, \quad z$	2·752 (10)	Cl —O(6)–O(4)	116·1	0·3
	O(4)	$x, \quad y, \quad z$	2·758 (11)	O(2)–O(6)–O(5)	118·9	0·3
				O(2)–O(6)–O(4)	113·7	0·3
				O(5)–O(6)–O(4)	99·3	0·3

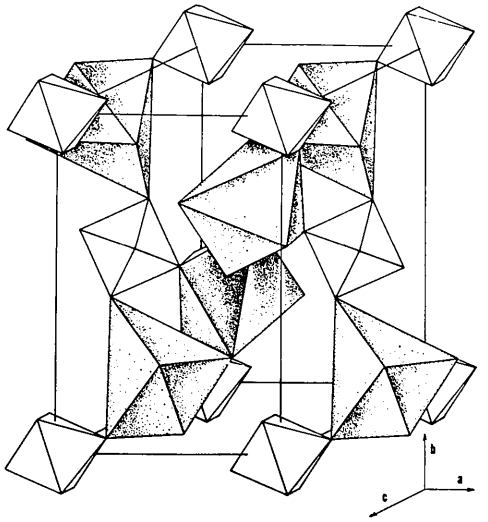
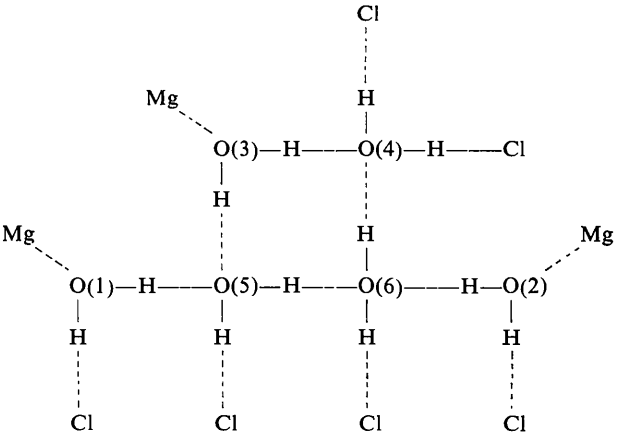


Fig. 3. The unit cell of magnesium chloride dodecahydrate, viewed in perspective, with two additional chloride octahedra at the top of left and bottom of right sides. The small octahedra are $[Mg^+ . 6H_2O]$ and the large octahedra are $[Cl^- . 6H_2O]$.

water molecules, every proton in the structure can be associated with a hydrogen-bond distance and its donor/acceptor position can be uniquely predicted. This hydrogen-bond distribution and proton assignment is represented diagramatically below.



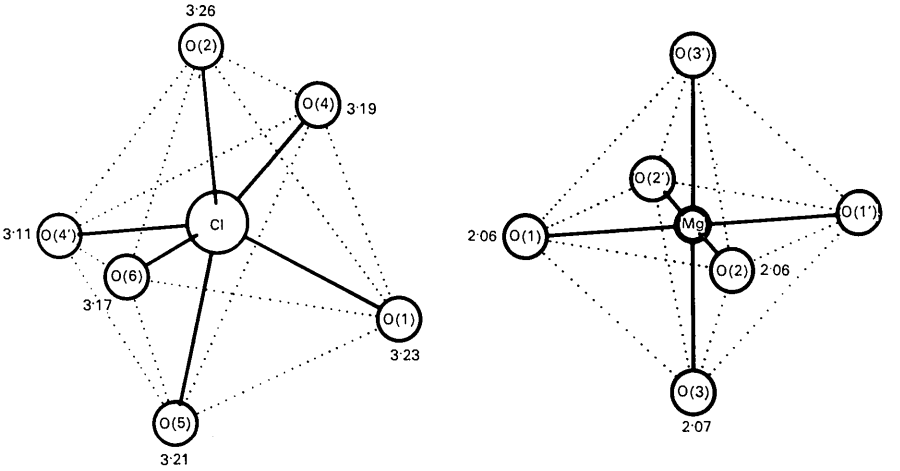


Fig. 4. The distances of the water molecules from the central ions in the hydration polyhedra.

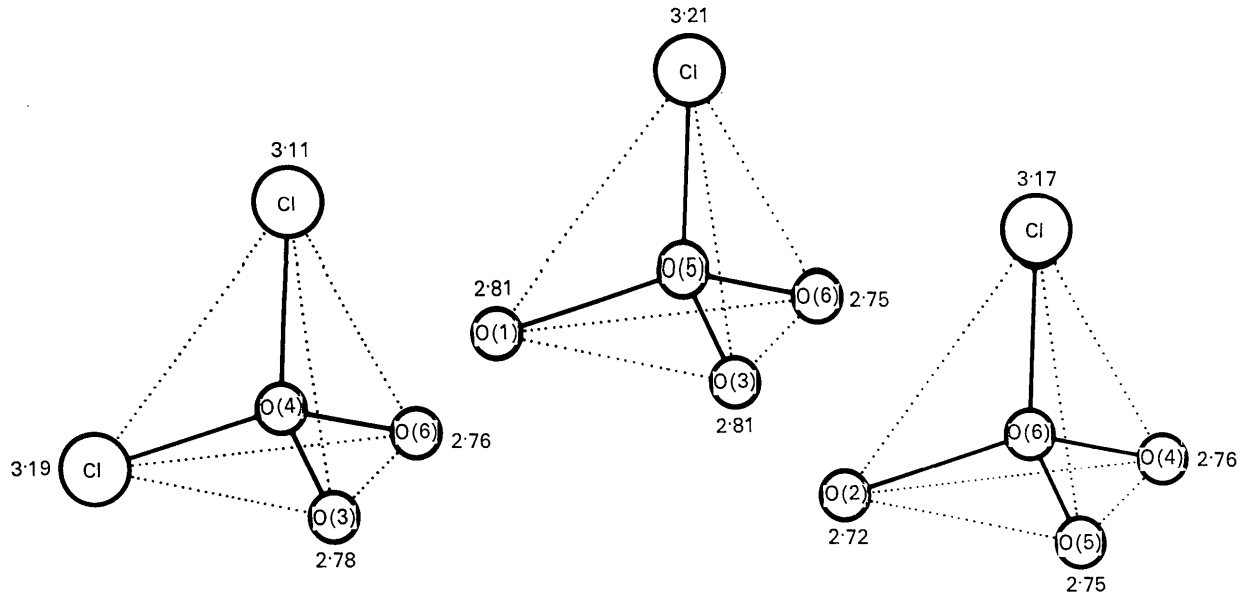


Fig. 5. The tetrahedral environment of the three four-coordinated water molecules with their hydrogen-bond distances.

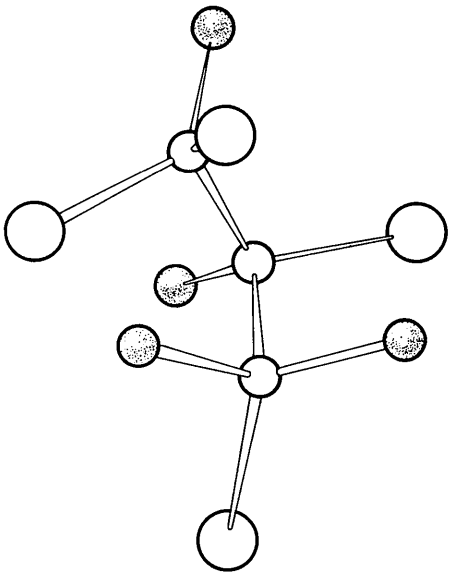


Fig. 6. The orthogonal projection of the three water molecules O(4), O(5) and O(6) with their tetrahedrally coordinated neighbours. The large spheres are chloride ions and the small ones are the water molecules. The dotted spheres are water molecules belonging to magnesium octahedra.

It is probable that the hydrogen atoms do not lie very far from the line of centers of the heavier atoms, since the hydrogen-bond angles, assuming linearity of the bond, do not deviate by more than 16° from tetrahedral. This approximately tetrahedral environment of the three four-coordinated water molecules, O(4), O(5) and O(6) is illustrated in Figs. 5 and 6.

This is clearly a very reasonable structure for a hydrated phase in which the stoichiometry is such that each ion can have a complete hydration polyhedron and there is no direct anion-cation contact. It is interesting to note that all the distortions from regularity necessary to form this pattern of associated octahedra are to be found in the hydrogen-bonded $[Cl^- . 6H_2O]$ octahedra, and that this distortion has an enantiomorphic sense even though the whole crystal structure is centrosymmetrical. The more tightly bound ionic $[Mg^+ . 6H_2O]$ octahedra are completely undistorted within the accuracy of the structure determination.

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The Evaluation of Phases for Structure Determination by Neutron Diffraction

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The formulas for phase determination often used for X-ray diffraction data are not immediately applicable to neutron diffraction data when atoms with both positive and negative scattering factors are present. A formula is presented from which normalized structure factors for the squared structure may be calculated from the normalized scattering data, as obtained from a neutron diffraction experiment. Since the squared structure is defined as the structure which scatters with the square of the scattering factor for each atom in the original structure, the computed structure factors for the squared structure will always represent a positive structure and the formulas for phase determination used for X-ray data will be applicable. Test calculations are presented.

Introduction

The positions of the atoms in the unit cell of a crystal can be calculated by Fourier series methods, provided that both the amplitudes and phases of the scattered neutron waves are known. The amplitudes and phases form the coefficients of a Fourier series representing the neutron scattering density in the unit cell, and the main maxima of such a function correspond to the positions of the atomic nuclei. Fourier series methods have been employed for several years starting with the investigations of Bacon & Pease (1953) and Peterson, Levy &