Inorganica Chimica Acta, 24 (1977) 13–23
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The Crystal Structure of $Mg_2EDTA \cdot 9H_2O$

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Received November 6, 1976

The crystal structure of $Mg_2EDTA \cdot 9H_2O$ has been determined using 2102 independent reflections measured by a single crystal counter diffractometer (CuKα radiation). The general conclusions are similar to those of an independent determination using film data [2] but the present investigation is very much more accurate, and all the hydrogen atoms have been located. The crystals are orthorhombic, space group Pbcn, *with* a = *11.617(1)*Å, b = *9.495(1)*Å, c = *19.238(2)*Å. *The structure was refined to a conventional R of 0.048 and wR of 0.037. Standard deviations in bond distances are 0.002–0.003*Å *for C–C and C–O bonds and 0.03–0.04*Å *for C–H and O–H bonds.*

The structure consists of a cation, $Mg(H_2O)_6^{2+}$, which is very close to regular octahedral geometry, and an anion, $(MgEDTA\ OH_2)^{2-}$ in which the Mg atom is heptacoordinated by four O and 2 N atoms of the EDTA and one water molecule. The anion coordination sphere is close to pentagonal bipyramidal geometry and the details of the structure are discussed in comparison with other heptacoordinated EDTA complexes. One water molecule is not included in either the cation or the anion, and the whole structure is linked by a tight network of hydrogen bonds, utilizing every proton of the water molecules.

Introduction

Crystals of $MgYH_2 \cdot 6H_2O$* and $Mg[Mg(OH_2)Y] \cdot 8H_2O$ were grown at different pH values (4.5 and 10, respectively). These compounds differed markedly in solubility and other properties, suggesting a different type of coordination of the metal atoms. An X-ray crystallographic investigation was therefore begun in order to elucidate the details of coordination and conformation in both crystals. Both structures were solved. The low pH crystal, where growth conditions would inhibit ionization of the carboxylic acid residues, is a very interesting one with a cation $Mg(H_2O)_6^{2+}$ and an anion YH_2^{2-} which is hydrogen bonded to the water molecules of the cation coordination sphere and not directly bonded to the magnesium atom. However, while refinement was in progress, a very accurate structure determination of this crystal was published by Hoard [1] and our work was discontinued as being merely duplicative.

At about the same time Pozhidaev *et al.* [2] published a structure determination of $Mg[Mg(OH_2)Y] \cdot 8H_2O$ based on visual intensity estimates of film X-ray data. Since the accuracy of work was quite low (the final R was 0.113 and the hydrogen atoms were not located) and the analysis of the results was not extensive, our determination based on counter-diffractometer data was refined to completion and is reported on fully in the present paper. In this compound the cation is $Mg(H_2O)_6^{2+}$ while the anion $[Mg(OH_2)Y]^{2-}$ is a 7-coordinate hexadentate chelate with one water molecule occupying a site of the coordination sphere and the other water molecules involved in hydrogen bonding only and not direct coordination.

A structurally similar but non-identical anion has been found in $Na_2[Mg(OH_2)Y] \cdot 5H_2O$ [3]. Our results are compared in some detail with those obtained from this structure. Other 7-coordinate complexes involving EDTA are those formed with Fe [4] and Mn [5]. In addition DCTA* also forms a 7-coordinate complex with Fe [6].

Experimental

Crystal Data: $Mg_2C_{10}N_2O_{17}H_{30}$, M = 470.95. Orthorhombic, *a* = 11.617(1)Å,** *b* = 9.495(1)Å, *c* = 19.238(2)Å; systematically absent spectra: 0*kl* with *k* odd, *h*0*l* with *l* odd, *hk*0 with *h* + *k* odd; space group *Pbcn*; d_{obs} = 1.55 g cm^{-3}, d_{calc} = 1.55 g

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*Y represents ethylenediaminetetraacetate.

*DCTA represents 1,2-diaminocyclohexane-N,N′-tetraacetic acid.

**Here and throughout this paper numbers included in brackets represent standard deviations referred to the last figure quoted of the immediately preceding number.

cm^{-3}; Z = 4. F(000) = 1000; μ (CuKα radiation) = 17.9 cm^{-1}.

The crystals were hard, white and roughly cube-shaped. The density was determined by flotation using solutions of n-hexane and carbon tetrachloride. This, and all other experimental measurements, were carried out at room temperature (~27 °C). Accurate cell dimensions were determined by a least square fit of high angle reflections on the Enraf-Nonius CAD4 single crystal automated diffractometer.

For intensity data collection a crystal measuring 0.10 X 0.15 X 0.17 mm was selected and determined to be of good quality by photographic methods.

The ω–2θ scanning mode was used with Ni-filtered CuKα radiation and all symmetry independent reflections were measured up to $\sin \theta/\lambda = 0.627$. The intensities of two periodically monitored reflections showed no systematic trend and had random variations of ±2%. The net intensities were reduced to relative amplitudes by Lorentz-Polarization corrections. Absorption corrections were not applied in view of the small crystal size. Calculation from the crystal shape showed that the maximum errors in F due to absorption would be ±3% for a few low angle reflections.

The intensities of 2333 reflections were measured. Using the criterion $I/\sigma_I > 3.0$, 114 of these were rejected as not being significantly above background leaving 2219 observed reflections. The ratio of observed data to structural parameters (anisotropic thermal parameters, positional parameters and scale factor for non-hydrogen atoms only) was 2219/216 = 10.27. The overall isotropic temperature factor with B = 2.13Å^2 was determined from a Wilson plot [7].

Structure Determination and Refinement

A three-dimensional Patterson map sharpened to point atoms was calculated. Since the unit cell contains 8 Mg atoms there could be either equivalent Mg atoms in general positions or two nonequivalent Mg atoms in special positions. No set of vectors could be found corresponding to the first possibility, but peaks in the Patterson map were consistent with a structure in which one Mg atom was at 0,0,0 (at a symmetry center) and the other at 1/2, 0.092, 1/4 (on a 2-fold axis). An electron density map was then calculated based on the phase angles calculated from the positions of the two Mg atoms. Since the scattering power of the Mg atoms is only 16.3% of that of the whole structure, the first electron density map was very rough. For selection of other atoms the criteria of chemical plausibility, agreement with the Patterson map and significant reduction of R were used. After several repetitions of the process, adding new postulated atoms into the phasing calculations and generating new electron density maps, all the non-hydrogen atoms were located.

Full matrix least squares refinement was then carried out using the Busing–Levy program [8]. At the beginning of the refinement R was 0.359. After 3 cycles refining scale, overall B and position parameters, R was reduced to 0.126. Individual B's for each atom were then refined, together with scale and positional parameters and 2 cycles reduced R to 0.071.

An error analysis of the observed and calculated structure factor agreement as a function of $\sin^2\theta$ was then made [9]. This indicated that the low angle data was less reliable than the rest and the reflections for which $\sin^2\theta$ were less than 0.2 were removed from the refinement process. In addition, 14 other reflections which looked suspicious, probably because of extinction or Renninger effects, were removed leaving a total of 2102 reflections. Three cycles of refinement reduced R to 0.052 and the esd's of the atomic positions improved considerably. A difference electron density map was calculated in order to locate the hydrogen atoms. For the six hydrogen atoms in the asymmetric unit attached to carbon atoms, the positions of which are predictable assuming tetrahedral bonding, the program CALCAT [10] was used. The calculated positions agreed very well with the electron density maxima and CALCAT coordinates were used in refinement. Nine remaining hydrogen atoms, in water molecules, were located from the difference map.

The 15 hydrogen atoms were then added into the structure factor calculations and one refinement cycle was carried out varying the isotropic thermal parameters for the hydrogen atoms alone. Refinement was next carried out using isotropic thermal parameters for the hydrogen atoms, but resetting these to the current value of the corresponding isotropic thermal parameter of the C or O atom to which the H atoms were bonded. Anisotropic thermal parameters for all other atoms, and all positional parameters were allowed to vary. Convergence was reached after 2 cycles with a final R of 0.048 and wR of 0.037. Introduction of the unobserved reflections into the refinement made the standard deviations slightly worse and therefore the results of the previous refinement were taken as the final ones. The weighting scheme used was based on the weights calculated from counting statistics and the function minimized was $w(F_{obs} - k\ |F_{calc}|)^2$.

Final values of the observed and calculated structure factors are given in Table I. The atomic scattering factors used are those given in the International Tables [11]. The refined positional and thermal parameters for all non-hydrogen atoms are given in Table II. The refined hydrogen atoms positions and isotropic thermal parameters are given in Table III.

TABLE I.

L	FO	FC
H= 0, K= 0		
2	471	-540
4	1466	1891
6	73	10
8	425	376
10	1076	1003
12	507	-481
14	76	7
16	200	206
18	111	-114
H= 0, K= 0		
-20	560	551
-22	132	-111
-24	45	53
H= 1, K= 0		
2	79	98
4	232	258
6	1055	-1134
8	271	342
10	367	280
12	196	180
14	348	342
16	108	-114
18	69	-52
20	80	-85
H= 1, K= 0		
20	98	-85
22	49	-31
24	53	52
H= 2, K= 0		
0	1269	1577
2	105	202
4	436	-278
6	322	-257
8	1300	1356
10	116	52
12	555	578
14	405	-408
16	279	269
18	165	-162
20	407	416
H= 2, K= 0		
20	442	416
22	79	-70
H= 3, K= 0		
2	1279	1621
4	230	-290
6	520	-419
8	368	-307
10	225	222
12	104	99
14	80	-61
15	72	-35
H= 3, K= 0		
22	168	151
H= 4, K= 0		
0	727	-490
2	1427	-1404
4	273	308
6	1119	-1102
8	902	927
10	62	-57
12	723	729
14	108	112
16	168	178
18	314	327
20	102	109
H= 4, K= 0		
18	337	327
20	111	109
H= 5, K= 0		
2	1121	1083
4	496	-669
6	243	145
8	533	-537
10	233	-248
12	175	142
14	526	-518
16	208	213
18	96	-70
H= 5, K= 0		
18	81	-70
20	78	61
22	242	225
H= 6, K= 0		
0	982	980
2	165	-255
4	1150	1214
6	367	-293
8	93	82
10	325	328
12	462	473
14	191	198
16	501	504
18	113	119
H= 6, K= 0		
18	132	119
20	409	392
H= 7, K= 0		
2	512	-437
4	44	34
6	147	-145
8	70	-67
10	374	358
12	79	-69
14	337	326
16	132	-138
20	65	67
H= 7, K= 0		
16	132	-139
20	70	67
H= 8, K= 0		
0	634	633
2	382	348
4	873	896
6	61	-52
8	724	722
10	50	26
12	428	413
14	221	-222
20	168	178
H= 8, K= 0		
20	179	178
H= 9, K= 0		
2	212	-212
4	533	547
6	171	166
8	253	275
10	37	31
12	75	77
14	145	155
16	126	-123
H= 9, K= 0		
16	131	-123
H= 10, K= 0		
0	605	621
4	218	215
6	272	-260
8	443	420
10	118	-108
12	245	238
14	208	-215
16	49	-23
H= 11, K= 0		
2	200	199
4	54	-70
6	318	318
8	332	-326
10	71	52
14	30	-25
H= 12, K= 0		
0	703	702
2	202	-201
4	114	121
6	64	-61
8	102	120
10	96	95
12	133	135
H= 13, K= 0		
4	89	-76
6	308	-302
8	215	-213
10	57	-45
H= 14, K= 0		
0	307	296
2	143	-148
4	266	267
6	80	81
H= 1, K= 1		
0	768	-874
1	299	344
2	1051	1232
3	332	318
4	495	461
5	36	31
6	590	556
7	767	-713
8	541	501
9	489	392
10	642	677
11	726	-714
12	446	489
13	184	202
14	271	256
15	204	-194
17	100	96
18	355	372
19	227	-248
19	238	-248
20	38	35
21	119	124
22	179	175
23	70	66
H= 2, K= 1		
1	33	-70
2	951	-1007
3	369	-365
4	67	56
5	551	586
6	76	-76
7	667	-591
8	283	-275
9	390	320
10	446	-429
11	443	435
12	340	-332
13	79	66
15	463	496
16	81	74
17	288	312
18	167	166
19	137	147
15	144	142
20	241	229
21	46	-42
22	86	81
23	69	-58
H= 3, K= 1		
0	1125	1121
2	592	622
3	396	-371
4	246	-171
5	142	90
6	365	-292
7	766	-702
8	202	-212
9	646	601
10	368	376
11	201	-174
12	223	-201
13	557	561
14	191	198
15	81	-72
16	142	-152
17	88	90
18	318	331
19	51	-54
19	61	-54
20	106	98
22	126	123
H= 4, K= 1		
1	900	-827
2	737	-715
3	206	-186
4	287	-261
5	86	-61
6	50	-60
7	70	-79
8	171	-162
9	82	100
10	103	-80
11	188	215
12	48	62
13	179	-186
14	108	120
16	53	-51
17	74	85
18	63	-63
18	64	-63
19	48	-46
21	43	-52
22	85	-82
H= 5, K= 1		
0	850	822
1	195	198
2	507	493
3	127	95
4	730	-724
5	533	557
6	562	517
8	153	162
9	126	150
10	773	783
11	108	-114
13	388	382
14	103	-98
15	425	-431
16	82	77
17	263	259
18	36	24
18	42	24
19	65	-62
20	251	254
21	141	133
22	142	139
H= 6, K= 1		
1	183	184
2	218	204
3	43	25
4	648	624
5	154	119
7	262	-261
8	129	124
9	82	-99
10	153	156
11	267	-252
12	68	60
13	122	-139
14	176	168
15	108	-116
16	192	-190
17	124	-130
17	130	-130
18	115	-115
18	124	-115
19	36	-26
20	47	-45
21	108	-99
H= 7, K= 1		
0	671	706
1	491	452
2	257	278
3	270	-236
4	103	-107
5	498	478
6	357	356
7	68	-103
8	475	469
10	662	675
11	39	24
12	136	-132
13	147	139
14	387	375
15	326	-327
17	62	50
17	47	50
18	326	342
18	355	342
19	110	-110
20	38	30
21	50	51
H= 8, K= 1		
1	471	445
2	601	590
3	218	194
4	190	191
5	238	229
7	68	67
8	50	-23
11	92	-105
12	298	303
13	72	67
14	85	-82
15	64	62
15	66	62
16	44	53
16	37	53
17	134	-126
17	128	-126
18	85	-83
18	83	-83
19	47	40
19	50	40
H= 9, K= 1		
0	61	-51
2	444	528
3	141	-143
4	119	-118
6	293	273
7	325	-345
9	154	171
10	149	140
11	157	-151
12	78	68
13	277	276
14	181	174
15	149	-145
15	151	-145
16	178	179
16	178	179
17	58	54
17	51	54
18	129	136
18	145	136
H= 10, K= 1		
1	132	-137
2	284	286
4	364	-365
6	77	-88
7	182	193
8	262	-271
9	55	55
10	98	82
12	156	163
13	152	155
14	36	-39
16	37	42
17	91	-83
17	99	-83
H= 11, K= 1		
0	56	57
1	119	126
2	63	83
3	65	-42
4	229	218
5	54	57
6	262	262
7	240	-241
8	121	-104
9	86	95
10	193	194
11	252	-242
12	153	-146
13	79	86
14	100	111
15	31	-12
H= 12, K= 1		
1	185	-174
2	98	-101
3	144	-134
4	166	166
5	61	-40
6	260	-260
7	119	-119
8	94	98
9	85	-69
10	119	-115
11	113	-101
12	58	-50
13	64	71
H= 13, K= 1		
0	134	-126
1	124	124
2	412	409
3	109	-115
4	70	80
5	69	75
6	158	164
7	101	-105
8	101	103
9	122	116
10	91	87
H= 14, K= 1		
4	28	5
5	65	66
6	115	132
H= 0, K= 2		
0	1429	1975
1	213	75
2	118	-153
3	1077	-1201
4	55	175
5	1005	-1040
7	1068	-985
9	1093	-1127
10	1008	1080
11	463	464
13	66	-61
14	87	-67
15	139	-133
16	169	180
17	202	-202
18	152	144
H= 0, K= 2		
19	274	271
20	275	274
21	73	-70
22	80	79
H= 1, K= 2		
1	99	-15
2	265	-232
3	596	523
4	1123	1189
5	48	-25
6	556	-571
7	1044	997
8	539	481
9	183	170
11	147	157
12	149	124
13	249	242
14	184	179
15	166	-183
16	209	-204
17	88	-80
18	36	16
21	148	142
22	35	-36
23	111	114
H= 2, K= 2		
0	397	-358
1	37	-83
2	1262	1352
3	898	761
4	513	-497
5	33	-86
7	85	15
8	706	641
9	545	-564
10	192	210
11	280	255
12	584	592
13	37	-29
14	191	-201
15	195	-188
16	264	283
18	153	150
19	122	109
20	195	186
21	128	115
22	83	76
23	38	36
H= 3, K= 2		
1	135	152
2	436	458
3	148	235
4	394	396
5	137	-217
6	271	236
7	373	391
8	145	-146
9	88	-68
10	282	272
11	244	-225
12	252	240
13	517	521
14	138	131
16	204	-201
17	117	-127
19	75	86
21	94	86
22	52	-38
23	113	115
H= 4, K= 2		
1	664	554
2	704	618
3	808	883
4	127	143
5	501	487
6	171	178
7	490	496
8	674	650
9	179	169
11	525	511
12	441	424
13	35	-8
14	144	127
15	264	287
16	106	104
17	257	-257
18	262	248
18	241	248
19	59	-58
21	41	-28
22	162	154
H= 5, K= 2		
1	332	-365
2	315	281
3	422	-418
4	319	-284
5	277	-239
6	80	64
7	396	-362
8	211	-276
9	364	-360
10	201	-158
11	308	-292
12	361	338
13	189	196
14	278	-275
15	177	138
16	68	82
17	59	-58
17	58	-58
18	43	-13
20	36	-2
22	148	141
H= 6, K= 2		
0	612	594
1	264	-225
2	247	247
3	396	375
4	268	259
5	373	-371
6	518	502
7	133	-105
9	258	248
10	258	252
11	131	113
12	107	104
13	147	131
14	69	65
15	360	343
16	252	241
16	241	241
17	318	-308
17	301	-308
19	97	-97
19	98	-97
19	128	-115
20	244	243
21	182	-179
H= 7, K= 2		
1	342	-335
2	256	-233
3	36	60
4	114	111
5	321	287
6	379	-386
7	248	239
8	36	-17
11	134	104
12	248	-229
13	123	-130
14	120	121
16	118	-107
16	105	-107
18	105	109
19	175	-162
20	57	51
H= 8, K= 2		
0	279	280
1	296	-305
2	350	356
3	341	315
4	175	-176
5	275	-278
6	58	81
7	144	-156
8	292	307
9	194	-167
10	63	42
11	266	-275
12	212	211
13	109	-190
14	61	59
15	114	104
15	102	104
17	108	-95
17	94	-95
18	104	103
18	100	103
19	94	93
19	74	93
H= 9, K= 2		
1	276	277
2	73	-61
3	373	361
4	129	124
5	384	385
6	180	-180
8	175	169
9	74	73
10	75	-58
11	89	-67
12	42	-30
13	58	-58
14	53	42
15	21	22
16	52	-51
16	59	-51
17	130	138
17	138	138
18	49	44
H= 10, K= 2		
0	61	45
1	51	65
2	282	284
3	107	-109
5	106	-103
7	123	127
8	275	277
9	297	-289
10	123	113
11	175	180
12	298	302
13	206	-201
15	39	47
16	87	97
16	90	97
H= 11, K= 2		
1	46	6
2	175	173
3	45	-46
6	126	117
7	142	-149
8	46	-44
9	128	-122
10	50	57
12	116	114
13	162	-152
14	33	-2
15	50	58
15	42	58
H= 12, K= 2		
0	238	238
1	125	-130
2	35	-2
3	55	57
4	105	107
5	130	-118
6	85	81
7	134	136
8	64	77
9	88	-84
10	254	253
11	217	209
12	103	101
13	79	72
H= 13, K= 2		
1	274	-212
2	47	41
3	231	-226
4	151	149
5	36	-48
6	104	-107
7	47	-41
9	69	72
H= 14, K= 2		
0	130	119
2	84	81
3	158	161
4	149	157
5	29	32
H= 1, K= 3		
0	502	578
1	970	925
2	240	-258
3	270	289
4	659	-523
5	644	657
6	313	348
7	193	-227
10	226	229
11	65	37
12	53	29
13	170	173
14	459	455
15	37	19
16	231	241
17	158	-177
18	135	143
19	327	-316
20	183	176
21	161	154
22	99	95
23	35	-28
H= 2, K= 3		
1	320	205
2	378	351
3	615	-584
4	267	-330
5	854	838
6	44	15
7	349	-338
8	377	353
9	240	202
10	413	402
11	321	292
12	119	-112
14	49	25
15	606	622
16	47	57
17	213	220
18	128	-112
19	58	50
20	185	-167
21	33	-22
22	76	-64
23	139	-131
H= 3, K= 3		
0	256	272
1	113	127
2	870	768
3	392	-367
4	375	335
5	45	-17
6	755	688
7	902	-928
8	673	673
9	289	271
10	536	543
11	88	-78
12	251	254
13	308	319
14	130	139
15	136	122
17	98	-118
18	131	139
19	69	82
20	98	99
21	65	54
22	137	134
H= 4, K= 3		
1	538	-532
2	644	691
4	104	91
5	201	-232
6	173	182
7	387	386
8	412	402
9	127	-122
10	65	-32
11	49	-24
13	129	-138
14	204	-212
15	57	-62
16	163	166
17	140	138
17	146	138
18	38	26
19	190	-175
20	63	-55
21	35	-48
22	128	125
H= 5, K= 3		
0	687	664
1	552	540
2	811	837
3	184	-178
4	568	553
6	170	181
7	252	-238
8	34	-25
9	223	-208
10	449	432
11	52	4
12	70	67
14	47	32
15	334	-330
16	41	30
17	235	241
17	247	241
18	192	176
20	65	62
21	240	236
H= 6, K= 3		
1	107	99
2	55	60
3	146	154
4	136	-140
5	54	-69
6	87	-72
7	58	-56
8	263	-254
9	248	-244
10	134	140
11	184	-194
12	108	-97
13	125	-126
14	131	123
15	144	-136
16	39	-22
17	79	-68
17	65	-68
19	95	-82
20	99	86
21	27	-37
H= 7, K= 3		
0	41	-55
1	848	865
2	300	314
3	283	-289
4	186	208
5	353	343
6	111	-90
7	39	-36
9	122	-130
10	172	159
11	311	304
13	91	-90
15	194	-203
15	199	-203
16	47	-52
16	49	-52
18	231	235
19	124	-130
H= 8, K= 3		
1	163	176
2	301	-294
3	121	138
4	78	52
5	158	169
6	329	-348
7	49	-6
8	169	-168
9	62	-60
10	216	-207
11	79	83
12	132	120
13	97	98
15	107	102
15	96	102
16	84	-88
16	88	-88
17	76	-74
17	89	-74
18	30	-14
19	30	30
H= 9, K= 3		
0	258	-269
2	201	209
3	97	93
5	120	114
6	253	256
7	272	-280
8	251	250
9	252	253
10	193	198
12	217	217
13	315	317
14	111	114
15	72	-83
15	83	-83
16	117	124
16	114	124
17	50	-34
17	48	-34
H= 10, K= 3		
1	322	-326
2	40	56
3	153	144
5	94	-107
6	226	226
7	257	267
8	211	-194
9	74	-72
11	68	71
13	231	227
14	38	-14
16	50	-47
16	40	-47
H= 11, K= 3		
0	449	439
1	164	172
2	47	-17
4	179	176
5	154	150
6	230	229
7	222	-228
8	46	53
9	46	34
10	234	236
11	142	-140
12	56	50
13	107	106
14	298	305
H= 12, K= 3		
1	178	-185
2	60	-57
3	60	57
4	131	131
8	158	156
9	196	-189
10	85	91
11	147	-145
12	75	71
H= 13, K= 3		
0	63	57
1	97	100
2	175	180
3	176	-170
4	48	-43
5	76	74
6	169	167
7	88	-96
8	60	66
H= 14, K= 3		
1	28	28
2	45	45
H= 0, K= 4		
0	1394	-1365
2	745	-690
3	773	782
4	173	110
5	770	-720
6	136	68
7	125	103
8	45	-33
9	105	-80
10	592	617
11	360	363
12	91	86
13	245	-217
14	316	303
15	127	145
16	125	-143
17	149	-153
H= 0, K= 4		
18	238	240
19	268	263
21	100	-103
22	127	123
H= 1, K= 4		
1	327	327
2	430	-405
3	562	531
4	885	866
6	314	-296
7	97	-91
8	233	248
9	59	-80
10	430	-426
11	98	-88
12	169	-144
14	38	-52
15	294	-298
16	125	-109
17	39	-41
18	67	72
19	69	-66
22	36	34
H= 2, K= 4		
0	42	18
1	223	-260
2	722	704
3	941	945
4	457	434
5	575	-584
6	294	230
7	153	169
8	49	7
9	203	-200
10	313	306
11	423	399
12	130	126
13	114	-104
14	425	440
15	63	47
16	55	55
17	166	-168
18	349	337
19	37	43
20	36	37
22	68	69
H= 3, K= 4		
1	216	211
2	501	-447
3	816	807
4	88	58
6	318	316
7	67	-88
8	304	-293
9	185	-162
10	146	120
12	154	-142
13	106	-81
14	217	211
15	308	-310
16	90	-95
17	155	-157
17	161	-157
18	72	-70
19	41	-30
20	103	110
22	169	-163
H= 4, K= 4		
0	1136	1172
2	757	791
3	570	535
4	583	586
5	182	-179
6	626	653
7	117	107
8	205	210
9	587	-564
10	314	327
11	465	460
12	79	-77
13	55	-82
14	363	363
15	135	145
17	325	-330
17	344	-330
18	230	221
21	68	-45
H= 5, K= 4		
1	277	-302
2	276	-238
3	39	-67
4	280	291
6	141	137
7	205	-235
8	72	87
9	60	38
10	96	88
12	244	247
13	89	99
14	104	84
15	115	112
16	72	72
16	70	72
17	46	-33
18	80	-64
H= 6, K= 4		
0	342	367
1	555	-536
2	146	-103
3	487	485
4	131	-146
5	261	-273
6	668	643
7	85	-68
9	484	-473
10	422	436
11	97	95
12	208	-205
13	99	103
14	104	99
15	119	124
15	137	124
16	34	43
17	235	-229
18	136	-121
19	113	101
20	100	107
H= 7, K= 4		
1	374	-372
2	186	179
3	258	-258
4	145	136
5	94	104
6	63	55
7	85	59
9	136	-122
10	43	-40
12	172	-174
13	145	142
14	61	-81
15	267	269
15	271	269
16	36	1
17	150	139
18	36	36
19	55	-52
H= 8, K= 4		
0	283	277

TABLE I *(continued)*

L	FO	FC
4	504	503
6	43	-23
7	65	-78
9	155	-157
10	47	-15
11	50	37
12	71	57
14	83	92
15	42	-39
16	183	-184
17	72	-69
18	103	94
19	52	-47
H= 3, K= 7		
0	95	-88
1	99	-108
2	36	-17
3	308	285
4	228	234
5	122	127
6	53	-69
7	46	63
8	143	134
9	94	92
10	214	-223
12	242	238
13	127	-133
14	229	230
16	229	222
17	166	-160
18	175	164
H= 4, K= 7		
1	130	-147
2	94	-102
3	308	320
4	167	-176
5	57	-77
8	256	-254
10	63	56
11	98	-112
12	157	160
13	299	318
14	38	-28
15	50	-58
16	40	-32
17	107	108
18	52	-36
H= 5, K= 7		
0	140	-135
1	70	-76
2	242	-235
3	45	-42
4	227	212
5	149	135
6	326	326
7	235	245
8	182	174
10	66	-54
11	197	192
12	177	185
13	50	-52
14	282	284
15	137	143
15	144	143
16	226	240
16	233	240
17	150	-137
H= 6, K= 7		
2	56	-62
3	115	184
4	176	-185
5	87	-81
6	84	89
7	226	229
8	70	-54
9	72	-61
10	53	-48
11	156	167
12	90	-94
14	98	-96
16	58	60
16	71	69
H= 7, K= 7		
0	514	524
1	98	-113
2	60	-67
3	84	-68
4	481	484
5	47	27
6	350	331
7	56	65
8	132	138
9	65	-76
10	60	83
11	78	56
12	46	51
13	44	-36
14	254	259
15	126	137
15	130	137
H= 8, K= 7		
1	129	120
2	110	-97
3	238	-233
4	97	95
5	148	133
6	39	36
7	134	-134
8	318	314
9	62	76
11	59	-46
12	179	-181
13	156	-151
14	37	26
H= 9, K= 7		
0	218	232
1	140	-144
2	285	280
3	123	115
4	180	186
5	73	-79
6	38	38
7	86	-75
8	129	126
9	100	-102
10	90	-86
11	88	-90
12	145	153
H= 10, K= 7		
1	94	97
4	165	-166
5	121	-118
6	161	159
7	69	66
8	78	71
9	144	-137
10	126	129
H= 11, K= 7		
0	38	40
1	127	124
3	61	-46
4	51	101
5	106	-100
6	57	-57
H= 0, K= 8		
0	223	210
1	52	-45
2	183	175
3	388	-397
4	429	434
5	367	369
6	409	410
7	121	-78
8	42	-25
10	141	137
11	192	-194
12	53	51
13	113	110
14	595	566
H= 0, K= 8		
15	160	-160
16	184	184
17	42	-34
H= 1, K= 8		
1	56	-22
2	42	-29
3	430	-411
4	323	-333
5	96	91
6	127	127
7	100	-99
9	107	105
10	87	75
12	137	128
13	53	48
15	140	133
15	144	133
16	132	137
16	142	137
H= 2, K= 8		
0	144	-150
1	176	-179
2	69	73
3	133	-133
4	123	131
5	175	163
6	479	476
7	137	-138
8	61	-69
9	136	120
10	219	215
11	263	-266
12	38	-13
13	173	176
14	218	226
15	125	-125
15	130	-125
16	99	104
16	111	104
17	104	102
H= 3, K= 8		
3	346	-345
4	190	-196
5	222	-233
6	215	236
7	204	194
8	113	104
9	59	25
11	87	92
12	51	-35
14	102	-101
15	181	190
15	194	190
16	117	124
16	121	124
17	68	68
H= 4, K= 8		
0	141	134
1	210	209
2	56	45
3	119	-126
4	151	147
5	46	53
6	166	171
7	142	-160
8	86	-74
9	218	197
10	205	215
11	176	-172
12	149	-151
13	86	92
14	156	163
15	74	-71
15	82	-71
16	140	-139
16	152	-139
H= 5, K= 8		
1	191	190
2	40	-20
3	63	-67
4	119	100
3	43	17
8	118	103
9	47	52
10	79	-92
11	123	-120
12	129	-130
13	33	-20
14	71	-63
15	37	-25
15	36	-25
H= 6, K= 8		
0	170	158
1	324	317
2	506	513
4	157	156
5	42	-23
6	135	126
8	100	107
9	186	191
10	101	90
12	93	87
13	38	46
14	213	217
H= 7, K= 8		
1	108	112
3	121	120
4	143	-152
5	138	135
7	40	-44
8	143	-136
9	53	-44
10	93	92
13	148	-149
H= 8, K= 8		
0	111	-92
1	162	161
2	189	184
4	106	106
5	87	87
6	268	263
7	103	-108
8	157	158
9	192	193
10	177	168
11	91	-90
H= 9, K= 8		
1	102	-92
3	157	155
4	58	48
7	59	-55
H= 10, K= 8		
0	36	-32
2	84	-86
3	96	-107
4	43	55
5	42	40
6	161	162
H= 1, K= 9		
0	93	-71
1	250	-250
2	209	199
3	250	269
5	424	-408
6	255	247
7	131	137
8	190	202
9	111	-117
10	123	123
11	35	-15
12	239	225
13	236	-225
14	256	254
H= 2, K= 9		
1	200	208
3	248	253
4	350	341
5	139	161
6	111	-114
7	138	-124
8	214	216
10	46	54
11	55	64
12	86	-79
14	188	181
15	29	-23
H= 3, K= 9		
0	69	-53
1	282	-293
2	269	273
3	174	162
5	170	-168
6	129	130
7	232	222
9	41	34
10	127	-115
11	199	189
12	64	57
13	51	-58
14	111	114
H= 4, K= 9		
1	167	-162
2	42	27
3	54	33
5	61	45
7	88	-92
8	41	35
9	65	69
10	108	110
12	35	-41
14	98	98
H= 5, K= 9		
0	67	-65
1	337	-330
2	269	269
3	279	261
4	225	214
5	47	-48
6	330	322
7	336	339
9	163	-166
10	71	66
11	87	80
13	41	-42
H= 6, K= 9		
1	115	-110
2	70	-62
3	118	-127
4	79	-72
5	71	-66
7	85	-87
8	54	43
10	95	-93
12	53	-55
H= 7, K= 9		
0	248	227
1	254	-240
2	62	57
4	264	268
5	100	-100
6	268	264
7	111	111
9	227	-221
10	277	283
H= 8, K= 9		
1	154	160
2	140	-136
3	66	-65
4	41	-28
5	76	67
6	30	-4
7	41	-27
8	41	41
H= 9, K= 9		
0	63	-66
1	285	-278
2	171	174
3	75	79
4	74	-62
5	223	-229
H= 0, K= 10		
0	79	85
1	386	370
3	358	-352
4	344	355
5	182	173
6	44	-43
7	155	152
8	229	223
10	57	-44
11	220	213
12	157	161
13	77	-73
H= 1, K= 10		
1	43	15
2	54	48
3	39	-23
5	192	186
6	176	168
7	60	62
8	35	8
9	172	175
11	56	50
12	107	105
H= 2, K= 10		
0	140	151
4	257	258
5	87	79
6	38	11
7	86	85
8	173	177
9	68	70
11	123	-124
12	235	240
H= 3, K= 10		
3	134	132
6	166	159
7	106	116
8	30	34
10	57	39
12	117	123
H= 4, K= 10		
0	293	293
3	228	-214
4	239	231
5	57	50
7	117	-120
8	224	227
9	45	50
11	155	-150
H= 5, K= 10		
1	33	14
2	72	-87
3	44	50
5	209	-206
6	65	-61
7	53	-58
8	30	-4
9	74	-78
10	28	-15
H= 6, K= 10		
0	137	146
1	29	24
2	122	122
3	247	-240
4	166	159
5	70	-68
7	52	-62
8	284	297
H= 7, K= 10		
2	30	16
3	88	-80
5	37	-37
6	69	-71
H= 1, K= 11		
0	57	59
1	138	-131
2	80	86
3	114	-99
4	43	28
5	159	153
6	112	122
7	70	62
8	79	-77
9	93	83
H= 2, K= 11		
1	308	282
2	101	-88
3	32	33
4	130	-125
6	130	-129
7	72	63
8	90	-85
H= 3, K= 11		
0	64	66
1	98	101
2	202	196
3	201	-191
4	109	116
5	37	38
6	254	253
7	27	3
H= 4, K= 11		
1	86	85
3	132	-121
6	41	43
H= 5, K= 11		
0	121	98
1	101	93
2	167	178
H= 3, K= 9		
4	107	103
H= 8, K= 4		
1	439	-442
2	54	-25
3	244	240
4	39	-54
5	208	-200
6	89	86
8	61	-53
9	187	-188
10	185	190
11	57	65
12	83	-73
13	42	-49
14	355	350
15	181	176
15	181	176
16	68	62
16	66	62
17	166	-175
17	182	-175
18	199	216
18	225	216
H= 9, K= 4		
1	63	-81
2	162	166
4	360	-350
5	49	22
6	69	-59
7	147	152
8	136	-140
9	60	-72
11	228	-222
13	97	91
14	126	-129
15	62	52
15	59	52
16	77	80
16	99	80
17	60	63
17	61	63
H= 10, K= 4		
2	422	424
3	131	128
4	110	99
5	148	-141
6	292	277
7	358	355
8	143	132
9	125	-138
10	213	212
11	252	249
12	172	176
13	175	-187
14	190	190
15	64	63
15	57	63
H= 11, K= 4		
1	158	143
2	52	81
4	148	-154
5	131	131
10	44	39
11	53	-63
12	157	115
13	93	-91
H= 12, K= 4		
0	31	-2
1	68	-78
2	127	132
3	220	222
4	210	200
5	120	-132
6	179	179
7	208	200
9	60	72
10	217	224
H= 13, K= 4		
1	76	70
2	52	42
4	134	134
5	62	72
6	127	132
7	69	-69
H= 1, K= 5		
0	1321	1349
1	234	238
2	160	-164
3	253	189
4	727	759
5	403	392
6	60	-51
7	80	73
8	235	232
9	191	-176
10	110	-119
11	450	437
12	66	83
13	476	486
14	227	-237
15	155	-167
16	358	379
17	38	-25
18	160	-152
19	186	-180
20	186	188
21	40	54
H= 2, K= 5		
1	152	-142
2	119	120
3	581	-601
4	105	-58
5	331	331
6	97	-107
7	134	108
8	45	-32
9	143	-118
10	133	142
11	242	-202
12	122	132
13	226	-214
15	146	152
16	135	-147
16	145	-147
17	239	-237
19	88	-97
20	93	-93
21	35	-6
H= 3, K= 5		
0	55	-40
1	424	-395
3	499	505
4	603	613
6	154	139
7	540	-514
8	926	935
9	131	137
10	108	-106
11	510	-500
12	719	737
13	96	120
15	193	-193
16	399	415
16	421	415
17	83	-80
19	121	113
20	118	124
21	41	17
H= 4, K= 5		
1	282	294
2	363	316
3	282	283
4	84	-77
5	99	-40
6	110	56
7	272	244
8	57	-46
9	105	-120
10	146	-155
11	462	-453
12	180	175
13	300	305
14	256	-269
15	37	20
15	50	20
16	58	54
16	64	54
17	70	61
18	115	105
H= 5, K= 5		
0	172	168
1	87	91
2	252	-249
3	148	-161
4	589	617
5	490	-474
6	116	-95
7	314	-317
8	390	392
9	58	43
10	178	-185
11	171	-162
12	492	494
14	251	244
15	84	-80
15	90	-80
16	346	362
16	368	362
17	61	68
18	44	42
19	45	-40
20	196	191
H= 6, K= 5		
1	45	34
3	149	150
4	273	-273
5	43	16
6	94	90
7	213	193
8	160	-168
10	104	106
11	90	97
12	81	-87
13	44	38
14	45	27
15	54	35
16	67	68
18	59	63
19	30	14
H= 7, K= 5		
0	282	256
1	298	273
2	101	-112
4	540	528
5	96	-109
6	132	-134
7	54	-39
8	243	245
9	138	130
10	309	-316
11	80	60
12	253	247
16	122	129
16	134	129
17	79	78
18	70	-63
H= 8, K= 5		
1	216	-226
2	328	-330
3	343	-355
4	217	212
5	222	223
6	193	-198
7	393	-402
8	309	310
9	176	170
10	45	-59
11	109	120
12	85	-82
13	90	-85
14	118	113
15	74	63
15	57	63
16	46	-55
16	64	-55
17	94	-103
17	108	-103
H= 9, K= 5		
0	230	244
1	89	-72
2	176	176
3	385	387
4	408	400
5	133	151
6	48	53
7	90	-83
8	439	441
9	212	205
10	142	-135
11	101	-110
12	314	321
13	186	182
14	144	-144
15	85	-76
15	74	-76
16	116	120
16	118	120
H= 10, K= 5		
1	133	-125
3	86	101
4	59	58
5	47	-39
6	255	251
7	131	-126
8	42	53
9	111	-117
10	71	68
12	164	-161
13	32	29
14	29	33
H= 11, K= 5		
0	554	550
1	94	96
2	71	-72
3	73	-66
4	349	346
5	88	85
6	34	-23
7	94	-96
8	231	233
9	67	-60
10	73	77
11	71	79
12	179	185
H= 12, K= 5		
2	58	-52
3	153	147
5	208	212
7	86	83
8	28	20
H= 13, K= 5		
0	177	180
2	113	-107
3	54	-59
H= 0, K= 6		
0	379	-358
1	246	241
2	487	503
3	177	177
4	209	215
5	354	346
6	626	670
7	74	-75
8	166	181
9	388	360
10	217	-212
11	296	-296
12	199	221
14	505	508
H= 0, K= 6		
16	40	34
17	38	16
18	101	94
19	102	97
20	112	-116
H= 1, K= 6		
1	108	97
2	223	-238
3	288	-275
4	236	-224
5	55	-31
6	358	-342
7	562	-562
9	53	-46
10	239	-241
11	145	-156
12	113	-137
13	41	-36
14	39	-47
16	127	120
16	113	120
17	54	51
18	44	51
19	39	16
20	42	-2
H= 2, K= 6		
0	289	-291
1	101	175
2	578	593
3	176	-175
4	139	126
5	52	1
6	665	667
7	293	-310
9	201	211
11	47	-40
12	109	109
13	99	104
14	280	288
16	105	102
16	120	102
17	44	-50
19	87	-88
H= 3, K= 6		
1	101	-112
2	199	-226
3	49	-17
4	441	-425
5	190	-190
6	199	-207
7	44	-48
8	59	-64
9	85	-90
10	142	-141
11	210	216
12	412	-431
13	215	-220
16	187	179
19	65	-64
20	45	40
H= 4, K= 6		
0	38	5
1	418	397
2	360	364
3	255	-237
4	152	143
5	67	66
6	348	339
7	294	-292
8	46	-46
9	156	-160
10	283	276
11	113	106
13	85	102
14	143	140
15	112	-108
15	113	-108
16	76	85
16	89	85
17	35	-34
18	162	157
19	130	-121
H= 5, K= 6		
1	49	56
2	96	-110
3	62	60
4	183	193
5	368	368
7	105	94
8	358	361
9	232	246
10	65	-58
11	146	149
12	92	-90
15	64	56
15	62	56
H= 6, K= 6		
0	237	-247
1	295	296
2	365	353
3	137	130
4	90	-72
5	239	242
6	251	230
7	45	-42
9	140	-146
10	361	362
12	145	148
13	122	123
14	74	78
15	214	-216
15	226	-216
16	218	216
16	235	216
17	113	106
18	180	182
H= 7, K= 6		
1	55	43
2	66	58
3	57	48
4	177	180
5	83	86
6	202	209
7	56	-63
8	156	162
9	205	-206
10	142	139
11	115	-112
12	147	141
13	46	56
14	46	44
15	135	136
15	140	136
16	59	-50
16	51	-50
17	54	48
H= 8, K= 6		
0	136	-123
1	126	132
2	235	225
3	219	-199
4	62	59
5	125	120
6	268	266
7	158	-151
8	82	74
9	123	113
10	247	260
11	77	79
12	67	63
13	97	91
14	167	179
15	30	17
16	123	114
16	127	114
H= 9, K= 6		
1	274	-275
3	68	73
5	220	-217
6	37	40
7	163	160
8	35	-35
9	184	-188
10	40	-51
11	174	-176
12	180	171
13	98	106
14	89	-85
H= 10, K= 6		
2	308	309
3	120	-111
4	108	108
6	339	331
9	43	40
10	43	49
11	80	-80
H= 11, K= 6		
2	107	-120
5	68	70
6	107	-103
7	73	58
8	30	-15
9	75	78
10	108	-104
H= 12, K= 6		
0	58	59
1	98	93
2	218	221
3	62	-51
4	92	82
5	97	94
6	206	211
H= 1, K= 7		
0	505	486
1	403	382
2	231	257
3	141	-142
4	706	690
5	389	-387
6	231	232
7	82	-76
8	223	224
9	362	-376
10	272	286
11	300	295
12	89	67
13	176	-171
15	45	38
15	47	38
16	112	114
16	127	114
17	46	47
H= 2, K= 7		
1	407	-409
3	67	-60

TABLE II. Positional and Thermal Parameters of the Non-hydrogen Atoms. The Temperature Factor Used is $\exp\{-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{23}kl + 2\beta_{13}hl)\}$. Values of β_{ij} are multiplied by 10^5.

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mg_1	0.0	0.0	0.0	273(5)	421(7)	127(2)	−005(5)	−016(2)	021(3)
Mg_2	0.0	0.58948(7)	0.25000	252(5)	371(7)	146(2)	0	049(2)	0
N	0.08083(12)	0.38807(14)	0.30703(7)	415(9)	507(14)	115(3)	008(9)	018(4)	031(5)
O_1	0.15171(9)	0.56165(12)	0.19975(5)	325(8)	625(12)	142(3)	103(7)	040(3)	073(5)
O_2	0.32815(11)	0.47209(15)	0.1978(7)	370(8)	1120(17)	273(4)	233(10)	093(5)	161(6)
O_3	0.08118(11)	0.65264(12)	0.35663(6)	598(10)	499(12)	185(3)	030(1)	−014(4)	044(5)
O_4	0.12442(10)	0.58559(13)	0.46473(6)	502(9)	640(13)	169(3)	014(9)	−070(4)	−036(5)
O_{w1}	0.0	0.80626(18)	0.25000	386(11)	466(16)	183(4)	0	024(5)	0
O_{w2}	0.10000(12)	0.16557(14)	0.03153(7)	376(8)	532(13)	232(3)	−050(8)	−071(4)	045(6)
O_{w3}	0.51696(13)	0.43274(15)	0.10279(6)	628(11)	732(14)	145(3)	−076(10)	−036(4)	073(5)
O_{w4}	0.35722(12)	0.37361(14)	−0.00650(7)	335(8)	598(14)	280(4)	076(8)	032(4)	087(6)
O_{w5}	0.17258(11)	0.62737(14)	0.06136(8)	480(8)	648(13)	152(3)	−021(9)	037(4)	056(5)
C_1	0.22921(13)	0.47895(17)	0.22166(8)	318(10)	551(17)	141(3)	070(10)	007(5)	−005(6)
C_2	0.20084(16)	0.38277(23)	0.28241(10)	445(1)	886(2)	201(5)	222(13)	045(6)	123(9)
C_3	0.09728(13)	0.56128(17)	0.40217(8)	272(10)	546(16)	150(4)	−007(10)	−003(5)	017(6)
C_4	0.07856(17)	0.40902(18)	0.38253(8)	587(14)	540(17)	115(4)	−051(13)	−004(6)	031(7)
C_5	0.01497(18)	0.26073(17)	0.28829(8)	736(15)	393(16)	147(4)	−031(13)	−009(6)	010(6)

TABLE III. Positional and Isotropic Thermal Parameters for the Hydrogen Atoms. The B values correspond to those in the final isotropic temperature factors of the C or O atoms to which the hydrogen atoms are bonded.

Atom	x	y	z	B(Å^2)
H_1	0.2518(30)	0.4148(34)	0.3210(16)	2.62
H_2	0.2210(29)	0.2913(40)	0.2682(16)	2.62
H_3	0.0051(31)	0.3845(31)	0.3980(15)	2.17
H_4	0.136(27)	0.3504(32)	0.4049(15)	2.17
H_5	−0.0589(29)	0.2611(32)	0.3161(15)	2.31
H_6	0.0554(28)	0.1725(37)	0.2972(15)	2.31
H_7	0.0531(29)	0.8596(35)	0.2364(15)	2.11
H_8	0.1037(27)	0.2365(41)	0.008(17)	2.31
H_9	0.1673(34)	0.1501(33)	0.0468(17)	2.31
H_{10}	0.4617(32)	0.4467(35)	0.1312(18)	2.61
H_{11}	0.5397(29)	0.3568(42)	0.1186(17)	2.61
H_{12}	0.2960(35)	0.3934(36)	−0.0174(17)	2.46
H_{13}	0.3533(27)	0.2992(40)	0.0185(17)	2.46
H_{14}	0.1668(27)	0.6109(34)	0.1014(20)	2.33
H_{15}	0.1486(27)	0.5611(38)	0.0354(17)	2.33

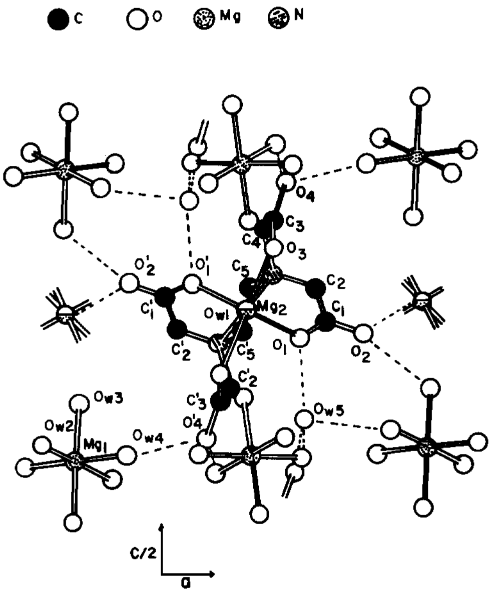

Figure 1. The arrangement of one anion and six cations viewed in the direction of the crystal *b* axis. To minimize overlap the second anion in the half cell is indicated only by the central Mg atom and O_{w_1} with bonds from the Mg atom. Hydrogen bonds are shown by broken lines.

The O–H and C–H distances indicated a systematic error displacing the hydrogen atom towards the O or C atoms due to close overlap of the H 1s orbital and the p or sp^3 orbital of the other atom. Therefore the hydrogen-acceptor distances (Table IV) are probably slightly lengthened by this experimental effect.

Description of the Structure

Molecular Packing

The relative arrangement of anions and cations in the structure is determined by a complex three-dimensional network of hydrogen bonds. This is illustrated in Figure 1 which is a perspective view of one anion and neighbouring cations viewed in the direction of the crystal *b* axis. Details of the hydrogen bond distances are given in Table IV.

The efficiency of the hydrogen bonding system is illustrated by the fact that every proton of the five independent waters is utilized in H bonding. The oxygen atom O_{w_5} belongs to an isolated water mole-

TABLE IV. Distances and Angles Involved in Hydrogen Bonding.

D–H•••A[a]	Distance D•••A (Å)	Distance H•••A (Å)	Angle D–H–A (Degrees)
O_{w_1}–$H_7 \cdots O_2$	2.734(2)	1.90(3)	175(3)
O_{w_2}–$H_8 \cdots O_4$	2.705(2)	1.90(4)	171(3)
O_{w2}–$H_9 \cdots O_{w5}$	2.728(2)	1.89(4)	168(4)
O_{w3}–$H_{10} \cdots O_2$	2.880(2)	2.03(4)	178(3)
O_{w3}–$H_{11} \cdots O_3$	2.870(2)	2.05(4)	170(3)
O_{w_4}–$H_{12} \cdots O_4$	2.787(2)	2.03(4)	169(4)
O_{w_4}–$H_{13} \cdots O_{w5}$	2.700(2)	1.85(4)	170(3)
O_{w_5}–$H_{14} \cdots O_1$	2.745(2)	1.96(4)	178(3)
O_{w5}–$H_{15} \cdots O_4$	2.803(2)	1.97(3)	168(3)

[a] Donor atoms are represented by D and acceptor atoms by A.

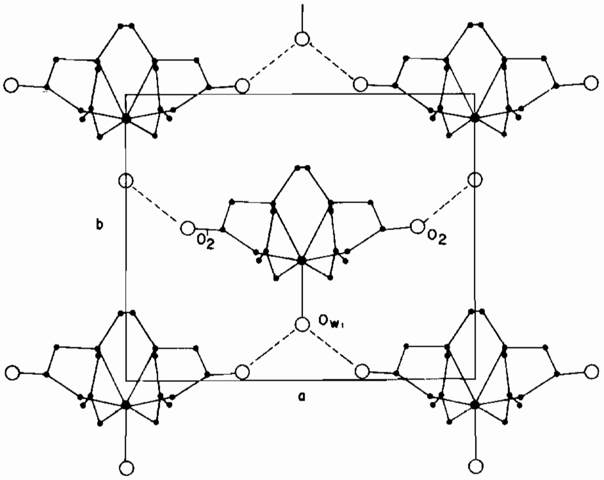

Figure 2. A sheet of anions linked directly by hydrogen bonding via O_2 and O_{w_1} as viewed in the direction of the crystal *c* axis.

cule outside the coordination spheres of both anion and cation. However, this water molecule has a key position in the structure since it is tetrahedrally hydrogen bonded to O_{w2} and O_{w4} of the cation and O_1 and O_4 of the anion.

Atom O_{w1} lies on a 2-fold axis and is in the water molecule bonded to Mg_2 and completes the anion coordination sphere. This water molecule forms two hydrogen bonds to the atoms O_2 in neighbouring anions. Thus a chain of anions directly connected by hydrogen bonding runs through the crystal in the *x* direction as illustrated in Figure 2. The hardness of the crystals and relatively small values of the thermal vibration parameters are undoubtedly due to the tightness of the hydrogen bonded system.

Molecular Geometry

The cation $Mg(H_2O)_6^{2+}$ is very close to regular octahedral geometry. The dimensions are given in Table V. The Mg–O bond distances average 2.061 Å with an average deviation of 0.017 Å, while the average deviation of the O–Mg–O bond angles from 90° is 1.2°.

The geometry of the anion is more complex. Mg_2 is heptacoordinated by four oxygen atoms O_1, O_3, O_1'* and O_3' and two nitrogen atoms N and N′ of the EDTA. The coordination is completed by O_{w1} which lies on a crystallographic 2-fold axis as does Mg_2. These coordinating atoms lie at the vertices of a pentagonal bipyramid (Figure 3).

The anion includes five rings which are located on one side of a plane passing through Mg_2 and parallel to (010). The other side of this plane is occupied only by O_{w1}. Following the standard notation described for EDTA complexes [12, 13] these may be divided into an E ring (ethylenediamine and metal ring), two G rings and two R rings. Both the G and R rings are formed by the glycinate arm of the EDTA complexing to the metal through nitrogen and oxygen. In an R ring the metal–oxygen bond is roughly perpendicular to the nitrogen–metal–nitrogen plane while in a G ring it is roughly parallel to this plane. In the case of $Mg(OH_2)Y^{2-}$ there are only three crystallographically independent rings since the two

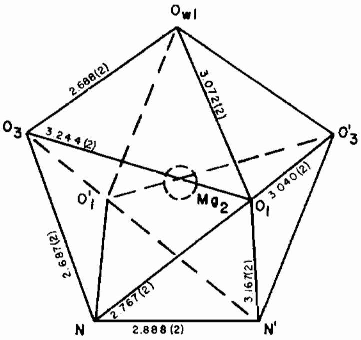

Figure 3. Coordination sphere atoms forming a pentagonal bipyramid around the central Mg atom.

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*In the anion primed atomic names are used to indicate atoms in the same ion related by the 2-fold axis, in the cation atoms in the same ion related by the symmetry center.

TABLE V. Dimensions of the Cation, $Mg(H_2O)_6^{2+}$ and of the Anion, $Mg(OH_2)Y^{2-}$.

a) *Cation*

Atoms	Bond Distance (Å)	Atoms	Angle (Degrees)
$Mg_1-O_{w_2}$	2.047(1)	$O_{w_1}-Mg_1-O_{w_3}$	90.45(5)
$Mg_1-O_{w_3}$	2.087(1)	$O_{w_2}-Mg_1-O_{w_4}$	89.51(5)
$Mg_1-O_{w_4}$	2.051(1)	$O_{w_3}-Mg_1-O_{w_4}$	92.57(5)
$O_{w_1}-H_7$	0.84(3)	$O_{w_2}-O_{w_3}-O_{w_4}$	58.26(5)
$O_{w_2}-H_8$	0.81(4)	$O_{w_3}-O_{w_2}-O_{w_4}$	61.85(5)
$O_{w_2}-H_9$	0.85(4)	$O_{w_3}-O_{w_4}-O_{w_2}$	59.89(5)
$O_{w_3}-H_{10}$	0.85(4)	Atoms	Second Neighbour Distance (Å)
$O_{w_3}-H_{11}$	0.83(4)		
$O_{w_4}-H_{12}$	0.76(4)	$O_{w_2}-O_{w_3}$	2.935(2)
$O_{w_4}-H_{13}$	0.86(4)	$O_{w_2}-O_{w_4}$	2.885(2)
$O_{w_5}-H_{14}$	0.79(4)	$O_{w_3}-O_{w_4}$	2.991(2)
$O_{w_5}-H_{15}$	0.85(3)	$O_{w_2}-O_{w_3}$	2.912(2)
		$O_{w_2}-O_{w_4}$	2.910(2)
		$O_{w_3}-O_{w_4}$	2.860(2)

b) *Anion*

Atoms	Bond Distances (Å)	Atoms	Angles (Degrees)
$Mg_2-O_{w_1}$	2.058 (2)	$O_1-Mg_2-O_3$	95.81 (5)
Mg_2-O_1	2.027 (1)	$O_1-Mg_2-O_{w_1}$	97.49 (4)
Mg_2-O_3	2.336 (1)	$O_3-Mg_2-O_{w_1}$	75.13 (4)
Mg_2-N	2.396 (1)	O_1-Mg_2-N	76.92 (5)
C_1-O_1	1.267 (2)	O_3-Mg_2-N	69.18 (5)
C_1-O_2	1.239 (2)	$Mg_2-O_1-C_1$	122.7 (1)
C_3-O_3	1.247 (2)	$Mg_2-O_3-C_3$	119.9 (1)
C_3-O_4	1.265 (2)	$O_1-C_1-O_2$	124.7 (2)
C_1-C_2	1.519 (3)	$O_3-C_3-O_4$	125.4 (1)
C_3-C_4	1.510 (2)	$O_1-C_1-C_2$	118.3 (1)
C_5-C_5'	1.514 (2)	$O_3-C_3-C_4$	118.0 (1)
C_2-N	1.473 (2)	$C_2-C_1-O_2$	117.0 (1)
C_4-N	1.466 (2)	$C_4-C_3-O_4$	116.7 (1)
C_5-N	1.476 (2)	$N-C_2-C_1$	115.6 (2)
C_2-H_1	1.00 (3)	$N-C_4-C_3$	112.0 (1)
C_2-H_2	0.94 (4)	Mg_2-N-C_2	104.5 (1)
C_4-H_3	0.93 (4)	Mg_2-N-C_4	109.8 (1)
C_4-H_4	0.97 (3)	Mg_2-N-C_5	109.8 (1)
C_5-H_5	1.01 (3)	C_2-N-C_5	112.6 (1)
C_5-H_6	0.98 (3)	C_4-N-C_5	110.1 (1)
		$N-C_5-C_5'$	110.9 (1)
		$N-Mg_2-N'$	74.10 (5)

fold axis through the center of the ion relates the two G rings and the two R rings to each other. These rings are shown in Figures 1 and 4 and consist of the following atoms: E ring–Mg_2, N, C_5, C_5', N′; G ring–Mg_2, N, C_4, C_3, O_3; R ring–Mg_2, N, C_2, C_1, O_1. The least squares mean plane for the three rings and also for the equatorial plane of the pentagonal bipyramid are given in Table VI. All these groups show considerable deviations from planarity. The relief of strain by these deviations is discussed further below. The conformations of the rings are most conveniently expressed by the torsion angles about each bond and these are given in Table VII.

A notation specifically developed for analysis of the conformational types of EDTA complexes has been given by Lee [14]. The different five membered

TABLE VI. Weighted Least Squares Mean Planes. The Equations of the Planes are AX + BY + CZ + D = 0, where X, Y, and Z are the Crystallographic Directions in Å, and A, B, C are the Direction Cosines of the Plane Normal.

Plane 1 E ring

	Atoms	Displacements (Å)
A 0.795	Mg_2	0.0
B 0.0	N	0.081 (1)
C −0.606	N′	−0.081 (1)
D 2.918	C_5	−0.309 (2)
	C_5'	0.309 (2)

Plane 2 G ring

	Atoms	Displacements (Å)
A 0.920	Mg_2	−0.0120 (1)
B 0.116	O_3	−0.160 (1)
C −0.373	C_4	−0.322 (2)
D 1.134	C_3	−0.096 (1)
	N	0.221 (1)

Plane 3 R ring

	Atoms	Displacements (Å)
A −0.410	Mg_2	−0.0065 (4)
B −0.629	O_1	0.076 (1)
C −0.660	C_1	−0.078 (1)
D 6.691	C_2	−0.140 (2)
	N	0.087 (1)

Plane 4 R ring carboxylate

	Atoms	Displacements (Å)
A −0.304	C_1	0.007 (2)
B −0.703	C_2	−0.003 (2)
C −0.643	O_1	−0.001 (1)
D 6.754	O_2	−0.002 (1)

Plane 5 G ring carboxylate

	Atoms	Displacements (Å)
A 0.965	C_3	0.013 (2)
B −0.066	C_4	−0.005 (2)
C −0.253	O_3	−0.003 (1)
D 1.237	O_4	−0.003 (1)

Plane 6 Equatorial planes of pentagonal bipyramid

	Atoms	Displacements (Å)
A 0.873	N	0.284
B 0.0	N′	−0.284
C −0.488	O_{w_1}	0
D 2.347	O_3	−0.179
	O_3'	0.179

TABLE VII. Torsion Angles in the Three Anion Rings.

	Bonded Atoms	Attached Atoms	Torsion Angle (Degrees)
E ring	Mg_2–N	N′, C_5	−14.5
	N–C_5	Mg_2, C_5'	41.7
	C_5–C_5'	N,N′	−57.4
G ring	Mg_2–N	O_3, C_4	27.9
	N–C_4	Mg_2, C_3	−34.5
	C_4–C_3	N, O_3	18.9
	C_3–O_3	C_4, Mg_2	8.4
	O_3–Mg_2	C_3, N	−20.6
R ring	Mg_2–N	O_1, C_2	11.6
	N–C_2	Mg_2, C_1	−11.6
	C_2–C_1	N,O_1	4.3
	C_1–O_1	C_2, Mg_2	8.4
	O_1–Mg_2	C_1, N	−11.5

rings in a complex are classified according to relations between "ruffling parameters", *i.e.* rotations of certain bonds out of the rings plane about another bond. On this basis the anion is described as δλλλλ, the same conformation found in $Fe(OH_2)Y^{2-}$ [4] which also has a pentagonal bipyramidal structure. The coordinates given above actually define the enantiomer of this configuration but because of the glide planes both enantiomers exist in the crystal.

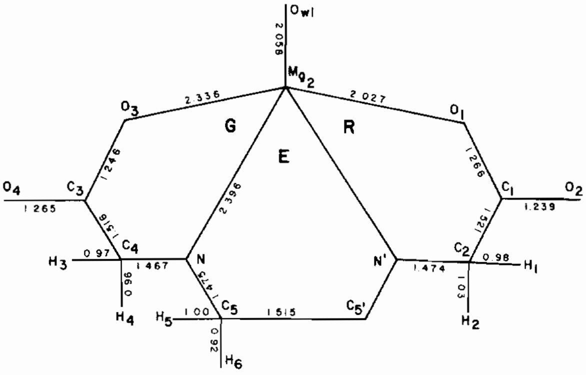

Figure 4. Schematic diagram showing the E, G and R Rings of the anion.

Thermal Motion

Figure 5 shows the ellipsoids expressing anisotropic thermal vibration for the non-hydrogen atoms of the anion as given by ORTEP [15]. No corrections for thermal motion were made to the bond distances, since neither the anion nor the cation can be regarded as simple librating molecules because of the strong hydrogen bonding involved. In any case the bond distances found in other structures with which our values are compared in the succeeding section are also not corrected for thermal motion. Every atom in the

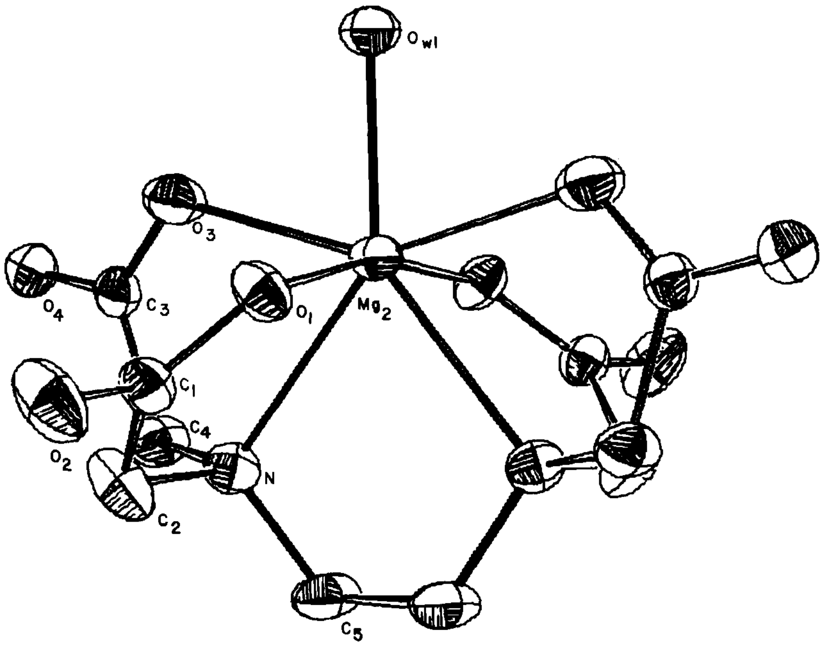

Figure 5. ORTEP drawing of the anion showing the ellipsoids corresponding to the anisotropic vibration parameters of Table II.

R ring vibrates with a larger amplitude than its counterpart in the G ring except for atoms O_1 and O_3 which have isotropic B's of 1.94 Å and 2.51 Å respectively. This reversal is due to the relative strength of the bonds formed with Mg_2. The larger thermal parameters of the R ring atoms result from the lower strain in the R ring relative to the G ring.

Discussion

The coordination of magnesium in the cation is completely normal, illustrating the very strong tendency of magnesium to form octahedral bonds. In fact, as noted above, in $MgYH_2 \cdot 6H_2O$ [1] this is the only coordination type of the magnesium atoms. The influence of the cation on the geometry of the anion can therefore be only indirect, *via* the hydrogen bond network, but it may nevertheless be profound. The anion itself exists because of the high complexing power of EDTA, in this instance a hexadentate ligand. The formation of six bonds between the metal atom and EDTA necessarily introduces some strain into the ion, since complete planarity of the rings would introduce large repulsive forces.

In a crystal structure of this type the conformation adopted is a compromise between strain minimization and maximum hydrogen bonding. The more fundamental question is the preferred conformation of the anion outside of a rigid hydrogen bonding system *i.e.* in solution. The relative stabilities of two basic conformations, the pentagonal bipyramid and the capped trigonal prism have been discussed for several 7-coordinate ions by Hoard [3, 4, 6]. We now compare the results of the present structure analysis with those obtained from these closely related structures.

Comparison with $Na_2Mg(OH_2)Y$

$Na_2Mg(OH_2)Y$ and $Mg[Mg(OH)_2Y] \cdot 8H_2O$, have chemically identical complex anions.* However, the conformational differences between the anions are extensive. The anion of MgI is a capped trigonal prism whereas that of MgII is a distorted pentagonal bipyramid. In Figure 1 the line N–N′ would be parallel to the bisector of O_1–O′, and O_3–O_3′ for the monocapped trigonal prism and at 45° to it for the pentagonal bipyramid. The measured angle is 30.8° indicating slightly greater than two-thirds pentagonal bipyramidal character. This distortion in the direction of the monocapped trigonal prism is also shown by the criteria of Muetterties and Guggenberger [16]. The average dihedral angle between adjacent faces on the same side of the girdle is 51.1° rather than the ideal value of 54.4°. The difference between the two anions must be due to differences in the three dimensional networks in the two structures.

In MgII these networks are formed entirely by hydrogen bonding. However, in MgI three of the four crystallographically independent carboxylate atoms are bonded to Na^+ ions. Two of these are also bonded

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*To distinguish between the two crystal structures $Na_2[Mg(OH_2)Y] \cdot 5H_2O$ will be designated MgI and $Mg[Mg(OH_2)Y] \cdot 8H_2O$ will be designated MgII.

to Mg atoms. Thus there is a much more direct cation–anion influence in MgI than in MgII and the anion in the former structure must be regarded as more constrained. The oxygen atoms O_3 and O_4 of the same carboxyl group are coordinated directly in MgI to Na^+ ions. This in turn places limits on the rotation of the E ring about the two-fold axis which would be required to bring the two anions into geometrical coincidence.

In discussing the relative stabilities of the two structures three major contributions must be taken into account. These are: (a) strain energy, including both repulsive interactions and angular strain *i.e.* deviations of the rings from planarity; (b) the relative strengths of the bonds formed within the two anions; (c) bond energies external to the anion, in this case hydrogen bonding for MgII and Na–O bonds for MgI.

Repulsive energies may be compared by totalling the differences from the sum of the van der Waals [17] radii for all contacts within the coordination polyhedra which are less than the sum of the radii in one or both of the anions. These totals are 1.063 Å for MgI and 1.036 Å for MgII. The angular distortion strain may be evaluated by comparing the sums of the angles of the G, E and R rings in MgII with the corresponding rings in MgI. The ideal sum of the internal bond angles is 540°.

The total deviation from 540 in all three rings is 13.8° for MgI and 12.6° for MgII. One further steric effect is the fact that in MgII the Mg atom is not significantly displaced from the mean plane of the pentagonal bipyramid girdle resulting in the very long Mg–N distance of 2.396 Å.

One marked difference between the two structures is the inequality in the carbon-oxygen distances within each carboxyl group in MgII. These are 1.267 Å and 1.239 Å for C_1–O_1 and C_1–O_2 respectively, and 1.247 Å and 1.265 Å for C_3–O_3 and C_3–O_4 respectively, whereas in MgI these pairs are very close to equality. Such inequalities are usually indicative of high complexing power since the longer C–O bond is to the more negatively charged oxygen atom which in turn can form a stronger bond to the positive metal. This is well illustrated in the case of $Fe(OH_2)Y^{2-}$ [4] where all four oxygen atoms of the longer C–O bonds form tight bonds to the Fe atom. However, the situation in MgII is rather different. Atoms O_1 and O_1' do form very strong bonds measuring 2.027 Å to Mg_2. These are the strongest Mg–O bonds in either complex being 0.051 Å shorter than the corresponding bonds in MgI. In the G ring on the other hand, where bonds to the metal are usually weaker, it is O_3 and O_3', the less negative of the carboxyl oxygens which bond to Mg_2, forming bonds of 2.336 Å, 0.066 Å longer than the corresponding bonds in MgI. For all seven Mg–O bonds in the complex those in MgII average 0.009 Å longer in MgII than in MgI. Using the empirical constants of Brown and Wu [18], in MgII the bond valences of the bonds from Mg_2 to O_1, O_3 and O_{w1} are 0.38, 0.21 and 0.36 respectively, and by subtraction the bond valence of Mg_2–N is 0.23.

In MgII the more negative oxygen atom on C_3, O_4 exhibits its complexing power not by binding to Mg_2 but by forming three hydrogen bonds to O_{w2} (2.705 Å), O_{w4} (2.787 Å) and O_{w5} (2.803 Å). The first of these is the shortest hydrogen bond found in the whole structure. Thus there is, in fact an external compensation for the weakening of the Mg–O_3 bond in the anion itself.

In summary we conclude that the anion in MgII is less strained than that of MgI. This is achieved at the cost of a slight weakening of the average bonding to Mg_2 itself, although the strongest Mg–O bond in either anion is found in MgII, and by increasing the inequality of the ligands. In neither crystal structure is there really a completely free anion. That in MgII is much closer to this concept since it does not have the constraints imposed by bonding to Na^+ ions that occur in MgI. Nevertheless, in the overall minimization of the crystal energy of MgII with respect to MgI (experimentally the former is more stable since the crystals did not require to be sealed in capillaries to prevent deterioration) the rigid hydrogen bonding framework may be decisive. It does not therefore seem possible to answer the question of whether the capped trigonal prism or the pentagonal bipyramid is more stable in solution.

Comparison of MgII to Other 7-Coordinate Complexes

The structures of $Mn(OH)_2Y^{2-}$ [5], $Mg(OH_2)Y^{2-}$ (MgI) [3] and $Fe(OH_2)DCTA^-$ [6] are monocapped trigonal prismatic. Those of $Fe(OH_2)Y^{2-}$ [4] and $Mg(OH_2)Y^{2-}$ (MgII) are pentagonal bipyramidal. In general the differences between the G and R rings increase on changing from the monocapped trigonal prism to the pentagonal bipyramid as shown by the differences between M–O_1, and M–O_3. This is a maximum in MgII but is actually less in $Fe(OH_2)Y^{2-}$ than in MgI in contrast to the general trend. The closest equality of the ligands is found in $Mn(OH_2)Y^{2-}$ but this is believed to be due to a large amount of electrostatic bonding and the stability of the complex arises from the larger size of the Mn^{2+} ion which can accommodate itself to the monocapped trigonal prismatic geometry with little strain. The M–N distance in MgII is the largest found in any of these complexes.

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