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A CRYSTALLOGRAPHIC STUDY OF MAGNESIUM AMMONIUM SULFATE HEXAHYDRATE

Berkeley, California

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Thomas N. Margulis
(Ph.D. Thesis)

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by

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July 1962

ABSTRACT

The structure of $Mg(NH_4)_2(SO_4)_2 \cdot 6H_2O$ has been redetermined in order to assign the hydrogen bonds. The crystals are monoclinic, space group $P2_1/a$, with a = 9.324, b = 12.597, c = 6.211 Å, and $\beta = 107.14^\circ$. The structure previously reported by Hofmann has nearly correct coordinates for the Mg, S, and N atoms, but incorrect coordinates for the oxygen atoms. Three-dimensional x-ray diffraction data were taken with the General Electric goniostat. The structure, including hydrogen atoms, was determined by Fourier and least-squares methods. The magnesium atom is surrounded by an octahedron of water molecules, each forming two hydrogen bonds to oxygen atoms of the sulfate ions. Three hydrogen atoms of each ammonium ion are bonded to sulfate oxygen atoms, but the fourth is equidistant from two sulfate oxygen atoms with the geometry which previous authors have called a "bifurcated hydrogen bond". Average interatomic distances (uncorrected for thermal motion) are: Mg-O = 2.07, S-O = 1.47, O-O (hydrogen bonded) = 2.77, N-O (hydrogen bonded) = 2.90, and N-O (bifurcated bond) = 3.08 Å. The average S-O bond length after correction for thermal motion is 1.49 Å.

An attempted calculation of the distribution of electrons in the sulfate ion was unsucessful. Possible reasons for this are discussed.

CRYSTAL STRUCTURE AND HYDROGEN BONDING

Introduction

Magnesium ammonium sulfate hexahydrate, $Mg(NH_4)_2(SO_4)_2 \cdot 6H_2O$, is one of a large number of isomorphous compounds[1] called Tutton's salts.[2] Due to the ease of crystallization these crystals have been studied extensively by paramagnetic resonance (Bowers and Owen, 1955) and other techniques. The crystal structure has been reported by Hofmann (1931) who studied a limited amount of x-ray diffraction data on a number of isomorphs. Upon examination of Hofmann's structure it was found to be impossible to make a reasonable assignment of the hydrogen bonds. For this reason it was decided to attempt to refine the structure using accurate three-dimensional data. The magnesium salt was selected from among the many available isomorphous compounds since it contains relatively light atoms and therefore is well suited for the determination of hydrogen atom positions.

It has been found that Hofmann's coordinates for the magnesium, nitrogen, and sulfur atoms are essentially correct, but that his oxygen positions (for which he claimed little accuracy) are quite poor. The final structure for the oxygen atoms found in this work leads to a satisfactory assignment of hydrogen bonds which is confirmed by evidence of the hydrogen atom positions from the diffraction intensity data. After

[1]Among the divalent ions that can be substituted for Mg^{++} are Mn^{++}, Fe^{++}, Co^{++}, Ni^{++}, Cu^{++}, Zn^{++}, and Cd^{++}. The monovalent ions that can be substituted for NH_4^+ are K^+, Rb^+, Cs^+, and Tl^+. Many of the corresponding selenates are also known.

[2]The mineral $MgK_2(SO_4)_2 \cdot 6H_2O$ is known as schönite.

these calculations were completed, it was learned that Montgomery and Lingafelter (1962) had redetermined the structure of $Zn(NH_4)_2(SO_4)_2 \cdot 6H_2O$ with results in general agreement with this work.[3]

Experimental

A General Electric XRD-5 diffractometer equipped with single crystal orienter and scintillation counter was used for the collection of three-dimensional intensity data and for the measurement of the cell dimensions. All measurements were made on a crystal with dimensions of approximately 0.06 x 0.06 x 0.13 mm. A total of 904 independent reflections including about 120 too weak to be observed were measured with MoKα x-rays (λ = 0.7107 Å). Weissenberg films were also taken in order to have a photographic record of the data. The measured intensities were converted to structure factors in the usual way on the IBM 7090 computer using a program written by Dr. Allan Zalkin. The largest dimension of the crystal corresponds to $\mu R = 0.06$, and therefore absorption effects were neglected.

Unit Cell and Space Group

The cell dimensions of the monoclinic unit cell at room temperature are:

$$a = 9.324 \pm .007 \text{ Å}$$
$$b = 12.597 \pm .009 \text{ Å}$$
$$c = 6.211 \pm .005 \text{ Å}$$
$$\beta = 107.14^\circ \pm .02^\circ$$

These values are in good agreement with those of Hofmann which are:[4]

[3]At this writing, the final refinement of the zinc salt has not been completed.

[4]Converted from kx units to angstroms.

$$a = 9.30 \pm .02 \text{ Å}$$
$$b = 12.60 \pm .025 \text{ Å}$$
$$c = 6.21 \pm .015 \text{ Å}$$
$$\beta = 107.10^{\circ}$$

With two molecules in the unit cell the calculated density is 1.718 g/cc which agrees well with the observed value of 1.72 g/cc (Lange, 1949). Systematic absences of reflections indicate a probable space group of $P2_1/a$ in agreement with Hofmann's choice. The sucessful determination of the structure confirms this choice.

Structure Determination

The space group requires that the magnesium atom be located on a center of symmetry which was chosen at 0,0,0; 1/2, 1/2, 0. All other atoms are in general positions with coordinates $\pm(x, y, z; x + 1/2, -y + 1/2, z)$.

After several attempts to refine Hofmann's structure by the method of least squares proved fruitless it was decided to attack the problem from scratch. A two-dimensional Fourier synthesis was calculated using 16 hk0 reflections whose signs were determined by Hofmann by the isomorphous replacement method. The first Fourier map showed the sulfur atom and magnesium atom with coordinates about the same as Hofmann's. Two more cycles of two-dimensional Fourier refinement led to a trial structure which had the magnesium, sulfur, and nitrogen atoms with about the same x and y coordinates as Hofmann's, but with quite different values for the coordinates of the oxygen atoms. From the two-dimensional structure and Hofmann's values for the z coordinates of the sulfur and nitrogen atoms, it was possible to deduce z coordinates for the oxygen atoms which subsequently proved to be nearly correct.

Refinement of the Structure

The trial structure was refined by full matrix least squares calculations on the IBM 7090 computer using a program written by Gantzel, Sparks, and Trueblood. Atomic scattering factors obtained from Ibers (1962) were used for neutral nitrogen, oxygen, sulfur, and hydrogen, and divalent magnesium. All reflections, including those too weak to be observed, were given equal weighting factors. The function minimized was $\sum(|F_o| - |F_c|)^2 / \sum |F_o|^2$. After about four cycles of refinement of the sulfur, nitrogen, and oxygen coordinates and isotropic temperature factors, the conventional R factor was 0.088.

A difference Fourier synthesis calculated at this point indicated that a refinement using anisotropic temperature factors would be necessary in order to locate the hydrogen atoms. Four more cycles of least squares using individual anisotropic temperature factors in the form $\exp(- (\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}\ell^2 + 2\beta_{12}hk + 2\beta_{13}h\ell + 2\beta_{23}k\ell))$, improved R slightly to a value of 0.075. A difference Fourier calculated after the anisotropy had been accounted for had its eight largest peaks in reasonable positions for hydrogen atoms. Peaks corresponding to the two other hydrogen atoms were found but were not as large as the other eight peaks. A possible reason for this is discussed below.

The structure, including all ten hydrogen atoms (with isotropic temperature parameters arbitrarily fixed at 4.0 $Å^2$), was then refined to a final R factor of 0.061. The final R factor of the non zero reflections is about 0.04. The observed and calculated structure factors are listed in Table 1. The final atomic coordinates and their standard deviations are given in Table 2, and the final anisotropic temperature parameters are in Table 3.

h	k	ℓ	F_o	F_c
0	0	1	267	235
0	0	2	301	-312
0	0	3	598	591
0	0	4	252	268
0	0	5	203	216
0	0	6	0	-40
0	1	1	628	597
0	1	2	248	-238
0	1	3	156	-164
0	1	4	70	66
0	1	5	283	278
0	1	6	36	-12
0	2	0	228	202
0	2	1	245	235
0	2	2	176	-165
0	2	3	116	121
0	2	4	108	102
0	2	5	0	36
0	2	6	157	159
0	3	1	432	430
0	3	2	266	-263
0	3	3	485	-480
0	3	4	118	118
0	3	5	66	70
0	3	6	37	-58
0	4	0	946	-971
0	4	1	236	-218
0	4	2	552	554
0	4	3	46	30
0	4	4	148	-161
0	4	5	83	83
0	4	6	93	94
0	5	1	214	215
0	5	2	382	-370
0	5	3	338	339
0	5	4	62	-59
0	5	5	255	-257
0	6	0	184	-198
0	6	1	260	260
0	6	2	213	212
0	6	3	164	168
0	6	4	230	225
0	6	5	0	-17
0	7	1	37	44
0	7	2	237	244
0	7	3	117	117
0	7	4	115	108
0	7	5	0	-2
0	8	0	156	157
0	8	1	148	150
0	8	2	0	19
0	8	3	0	-2
0	8	4	193	186
0	8	5	75	78
0	9	1	73	64
0	9	2	31	33
0	9	3	189	-191
0	9	4	51	-47
0	10	0	0	-44
0	10	1	304	309
0	10	2	286	284
0	10	3	49	-48
0	10	4	0	9
0	11	1	224	-212
0	11	2	0	4
0	11	3	0	16
0	12	0	70	90
0	12	1	79	54
0	12	2	97	93
0	13	1	212	-195
1	1	0	112	-123
1	1	1	548	553
1	1	2	47	-43
1	1	3	306	309
1	1	4	172	181
1	1	5	111	103
1	1	6	244	233
1	1	-1	20	-16
1	1	-2	792	797
1	1	-3	95	102
1	1	-4	168	-168
1	1	-5	101	-104
1	1	-6	119	120
1	2	0	435	-423
1	2	1	418	-417
1	2	2	48	-43
1	2	3	266	262
1	2	4	42	48
1	2	5	209	-210
1	2	6	0	14
1	2	-1	577	553

h	k	ℓ	F_o	F_c
1	2	-2	778	777
1	2	-3	24	-20
1	2	-4	98	-95
1	2	-5	274	264
1	2	-6	145	137
1	3	0	860	898
1	3	1	229	-235
1	3	2	0	6
1	3	3	296	299
1	3	4	132	136
1	3	5	114	-115
1	3	6	101	-95
1	3	-1	372	371
1	3	-2	138	-148
1	3	-3	322	324
1	3	-4	405	402
1	3	-5	217	229
1	3	-6	0	-27
1	4	0	0	-12
1	4	1	426	425
1	4	2	0	-16
1	4	3	0	-10
1	4	4	370	375
1	4	5	92	93
1	4	-1	220	211
1	4	-2	276	274
1	4	-3	26	34
1	4	-4	0	23
1	4	-5	157	-163
1	4	-6	0	-3
1	5	0	106	-100
1	5	1	139	141
1	5	2	72	71
1	5	3	28	35
1	5	4	55	57
1	5	5	0	20
1	5	-1	49	-53
1	5	-2	302	-291
1	5	-3	54	-48
1	5	-4	265	265
1	5	-5	118	122
1	5	-6	0	12
1	6	0	109	-97
1	6	1	285	285
1	6	2	207	-195
1	6	3	467	-462
1	6	4	168	167
1	6	5	36	55
1	6	-1	226	-224
1	6	-2	419	-408
1	6	-3	103	94
1	6	-4	44	38
1	6	-5	182	-179
1	7	0	115	-114
1	7	1	288	289
1	7	2	505	502
1	7	3	255	-252
1	7	4	59	-63
1	7	5	275	263
1	7	-1	26	33
1	7	-2	311	305
1	7	-3	164	165
1	7	-4	131	-135
1	7	-5	51	98
1	8	0	19	-4
1	8	1	142	-139
1	8	2	0	-6
1	8	3	108	92
1	8	4	276	-278
1	8	-1	188	-175
1	8	-2	0	24
1	8	-3	244	-247
1	8	-4	83	-79
1	8	-5	153	145
1	9	0	162	162
1	9	1	139	149
1	9	2	165	166
1	9	3	68	72
1	9	4	73	75
1	9	-1	384	397
1	9	-2	159	166
1	9	-3	81	77
1	9	-4	79	76
1	10	0	38	6
1	10	1	107	-102
1	10	2	235	230
1	10	3	163	168
1	10	4	54	-63
1	10	-1	234	217
1	10	-2	0	22
1	10	-3	0	4

h	k	ℓ	F_o	F_c
1	10	-4	0	-23
1	11	0	255	255
1	11	1	177	-183
1	11	2	0	-17
1	11	3	174	171
1	11	-1	151	149
1	11	-2	120	-123
1	11	-3	0	-11
1	12	0	122	118
1	12	1	0	7
1	12	2	52	-76
1	12	-1	112	-103
1	12	-2	0	12
1	12	-3	170	158
1	13	0	74	-60
1	13	1	156	149
1	13	-1	0	-14
2	0	0	434	412
2	0	1	790	-814
2	0	2	0	13
2	0	3	111	103
2	0	4	322	320
2	0	5	110	-101
2	0	-1	1033	1045
2	0	-2	698	-697
2	0	-3	196	193
2	0	-4	391	382
2	0	-5	77	79
2	0	-6	0	-16
2	1	0	610	601
2	1	1	591	591
2	1	2	201	184
2	1	3	104	115
2	1	4	238	234
2	1	5	85	78
2	1	-1	268	-264
2	1	-2	193	177
2	1	-3	410	398
2	1	-4	263	276
2	1	-5	55	-68
2	1	-6	186	-179
2	2	0	105	98
2	2	1	513	504
2	2	2	88	-82
2	2	3	180	192
2	2	4	200	192
2	2	5	111	108
2	2	-1	0	-28
2	2	-2	88	85
2	2	-3	34	-23
2	2	-4	202	203
2	2	-5	106	-127
2	2	-6	51	39
2	3	0	205	-195
2	3	1	537	528
2	3	2	255	255
2	3	3	68	-76
2	3	4	217	224
2	3	5	0	-4
2	3	-1	276	-279
2	3	-2	236	-226
2	3	-3	568	561
2	3	-4	175	169
2	3	-5	152	-160
2	3	-6	0	4
2	4	0	193	190
2	4	1	602	618
2	4	2	382	384
2	4	3	173	-170
2	4	4	32	-11
2	4	5	161	157
2	4	-1	219	-211
2	4	-2	375	376
2	4	-3	467	461
2	4	-4	83	-76
2	4	-5	105	107
2	4	-6	184	179
2	5	0	163	-181
2	5	1	362	-351
2	5	2	236	233
2	5	3	0	-32
2	5	4	332	-329
2	5	5	52	46
2	5	-1	387	-370
2	5	-2	187	192
2	5	-3	67	43
2	5	-4	370	-381
2	5	-5	117	111
2	5	-6	172	164
2	6	0	156	161
2	6	1	26	-11

h	k	ℓ	F_o	F_c
2	6	2	149	157
2	6	3	229	222
2	6	4	102	-102
2	6	5	37	-42
2	6	-1	375	379
2	6	-2	329	325
2	6	-3	0	5
2	6	-4	214	218
2	6	-5	285	287
2	7	0	0	21
2	7	1	0	-4
2	7	2	83	-89
2	7	3	72	-86
2	7	4	0	6
2	7	-1	302	291
2	7	-2	0	-1
2	7	-3	112	-103
2	7	-4	56	-65
2	7	-5	0	-16
2	8	0	90	90
2	8	1	228	-218
2	8	2	165	163
2	8	3	298	288
2	8	4	115	117
2	8	-1	225	217
2	8	-2	42	51
2	8	-3	122	-111
2	8	-4	68	-69
2	8	-5	143	132
2	9	0	199	195
2	9	1	31	-35
2	9	2	317	-323
2	9	3	0	-42
2	9	4	160	156
2	9	-1	0	-31
2	9	-2	220	-214
2	9	-3	93	-98
2	9	-4	166	166
2	9	-5	0	-43
2	10	0	32	-31
2	10	1	221	217
2	10	2	0	0
2	10	3	36	-29
2	10	-1	161	-154
2	10	-2	253	254
2	10	-3	159	151
2	10	-4	64	-63
2	11	0	34	-16
2	11	1	0	2
2	11	2	62	74
2	11	3	126	122
2	11	-1	59	65
2	11	-2	85	68
2	11	-3	36	-43
2	12	0	71	72
2	12	1	141	152
2	12	2	53	49
2	12	-1	0	22
2	12	-2	36	54
2	12	-3	162	156
2	13	0	100	-108
2	13	-1	92	89
3	1	0	226	229
3	1	1	123	-103
3	1	2	56	56
3	1	3	229	230
3	1	4	138	142
3	1	5	126	109
3	1	-1	456	-460
3	1	-2	30	-32
3	1	-3	590	600
3	1	-4	63	-60
3	1	-5	223	-218
3	1	-6	61	60
3	2	0	130	-151
3	2	1	178	189
3	2	2	258	268
3	2	3	0	-11
3	2	4	170	-162
3	2	5	127	127
3	2	-1	547	-539
3	2	-2	89	-47
3	2	-3	75	-83
3	2	-4	470	-469
3	2	-5	32	12
3	2	-6	209	199
3	3	0	89	102
3	3	1	243	-241
3	3	2	229	224
3	3	3	142	137
3	3	4	0	-12

h	k	ℓ	F_o	F_c
3	3	5	98	-86
3	3	-1	781	794
3	3	-2	46	52
3	3	-3	36	-18
3	3	-4	220	201
3	3	-5	290	284
3	3	-6	150	156
3	4	0	542	535
3	4	1	182	191
3	4	2	222	-224
3	4	3	68	72
3	4	4	89	90
3	4	5	0	-35
3	4	-1	205	-200
3	4	-2	167	165
3	4	-3	71	66
3	4	-4	0	-10
3	4	-5	202	200
3	4	-6	52	-40
3	5	0	450	458
3	5	1	507	509
3	5	2	170	189
3	5	3	143	158
3	5	4	49	59
3	5	5	114	114
3	5	-1	416	411
3	5	-2	324	327
3	5	-3	165	-156
3	5	-4	174	168
3	5	-5	207	206
3	5	-6	0	31
3	6	0	108	110
3	6	1	0	-14
3	6	2	434	-443
3	6	3	0	34
3	6	4	194	194
3	6	-1	0	19
3	6	-2	98	-84
3	6	-3	41	-44
3	6	-4	131	119
3	6	-5	0	-11
3	7	0	108	97
3	7	1	508	509
3	7	2	0	-1
3	7	3	198	-204
3	7	4	137	141
3	7	-1	208	-210
3	7	-2	115	122
3	7	-3	248	246
3	7	-4	46	59
3	7	-5	36	14
3	8	0	156	-156
3	8	1	165	-169
3	8	2	183	174
3	8	3	69	-71
3	8	4	141	-139
3	8	-1	51	-41
3	8	-2	177	180
3	8	-3	106	94
3	8	-4	178	-186
3	8	-5	0	-33
3	9	0	205	-216
3	9	1	0	33
3	9	2	0	-8
3	9	3	0	26
3	9	-1	44	-43
3	9	-2	189	177
3	9	-3	67	-87
3	9	-4	124	125
3	10	0	204	-209
3	10	1	112	114
3	10	2	213	215
3	10	3	0	0
3	10	-1	147	152
3	10	-2	89	93
3	10	-3	0	23
3	10	-4	37	50
3	11	0	49	-45
3	11	1	123	-124
3	11	2	203	204
3	11	-1	323	314
3	11	-2	50	52
3	11	-3	63	-72
3	12	0	103	110
3	12	1	53	-51
3	12	-1	0	2
3	12	-2	238	-239
4	0	0	358	-367
4	0	1	0	-1
4	0	2	110	103
4	0	3	115	109

h	k	ℓ	F_o	F_c
4	0	4	164	-161
4	0	5	194	-193
4	0	-1	190	-174
4	0	-2	128	-110
4	0	-3	0	5
4	0	-4	129	125
4	0	-5	281	275
4	0	-6	148	143
4	1	0	216	225
4	1	1	136	-142
4	1	2	192	-187
4	1	3	0	18
4	1	4	0	23
4	1	5	170	-164
4	1	-1	105	-95
4	1	-2	103	-104
4	1	-3	73	-81
4	1	-4	41	22
4	1	-5	238	235
4	1	-6	113	-101
4	2	0	647	644
4	2	1	277	283
4	2	2	0	8
4	2	3	229	230
4	2	4	0	20
4	2	5	66	64
4	2	-1	273	-265
4	2	-2	197	211
4	2	-3	276	289
4	2	-4	168	171
4	2	-5	103	98
4	2	-6	0	-17
4	3	0	207	-198
4	3	1	332	338
4	3	2	264	-262
4	3	3	44	40
4	3	4	49	58
4	3	-1	287	-272
4	3	-2	0	-11
4	3	-3	382	-371
4	3	-4	0	10
4	3	-5	46	-35
4	3	-6	36	-53
4	4	0	448	457
4	4	1	280	283
4	4	2	29	-27
4	4	3	0	15
4	4	4	315	311
4	4	-1	287	288
4	4	-2	36	-14
4	4	-3	363	366
4	4	-4	86	86
4	4	-5	135	-132
4	4	-6	37	49
4	5	0	300	-278
4	5	1	274	271
4	5	2	252	244
4	5	3	232	-225
4	5	4	0	3
4	5	-1	258	-265
4	5	-2	238	243
4	5	-3	241	233
4	5	-4	246	-249
4	5	-5	138	-147
4	5	-6	125	115
4	6	0	246	-240
4	6	1	137	-118
4	6	2	208	190
4	6	3	68	63
4	6	4	0	32
4	6	-1	410	417
4	6	-2	361	356
4	6	-3	241	-250
4	6	-4	46	-47
4	6	-5	137	140
4	7	0	66	-39
4	7	1	68	77
4	7	2	32	-47
4	7	3	35	27
4	7	4	0	21
4	7	-1	109	110
4	7	-2	288	291
4	7	-3	154	155
4	7	-4	139	149
4	7	-5	63	47
4	8	0	217	-228
4	8	1	32	18
4	8	2	338	336
4	8	3	63	58
4	8	-1	411	419
4	8	-2	235	224
4	8	-3	57	-58
4	8	-4	49	52
4	8	-5	150	150
4	9	0	224	225
4	9	1	233	-237
4	9	2	93	-83
4	9	3	184	184
4	9	-1	186	191
4	9	-2	221	-227
4	9	-3	145	-141
4	9	-4	102	102
4	10	0	145	141
4	10	1	127	119
4	10	2	0	-10
4	10	-1	163	-153
4	10	-2	91	-98
4	10	-3	227	205
4	10	-4	155	153
4	11	0	36	18
4	11	1	64	-80
4	11	-1	0	6
4	11	-2	162	-152
4	11	-3	65	-56
4	12	0	130	133
4	12	-1	53	-48
4	12	-2	0	-33
5	1	0	534	540
5	1	1	176	195
5	1	2	131	-124
5	1	3	124	113
5	1	4	182	174
5	1	-1	275	275
5	1	-2	57	-57
5	1	-3	205	214
5	1	-4	409	405
5	1	-5	94	72
5	1	-6	63	60
5	2	0	58	-51
5	2	1	305	319
5	2	2	132	-130
5	2	3	434	-428
5	2	4	97	88
5	2	-1	145	-149
5	2	-2	148	-138
5	2	-3	28	12
5	2	-4	125	-139
5	2	-5	294	-298
5	2	-6	127	123
5	3	0	387	-377
5	3	1	103	99
5	3	2	193	188
5	3	3	95	87
5	3	4	0	8
5	3	-1	69	76
5	3	-2	321	321
5	3	-3	146	-143
5	3	-4	175	-180
5	3	-5	48	38
5	3	-6	123	114
5	4	0	55	30
5	4	1	152	-158
5	4	2	137	-147
5	4	3	142	-153
5	4	4	0	24
5	4	-1	136	119
5	4	-2	157	-156
5	4	-3	29	-36
5	4	-4	44	-45
5	4	-5	109	114
5	4	-6	113	108
5	5	0	0	30
5	5	1	42	37
5	5	2	236	238
5	5	3	78	78
5	5	4	0	0
5	5	-1	75	76
5	5	-2	312	317
5	5	-3	151	158
5	5	-4	56	-41
5	5	-5	61	71
5	6	0	95	82
5	6	1	31	-43
5	6	2	66	73
5	6	3	260	257
5	6	-1	202	200
5	6	-2	67	60
5	6	-3	125	-121
5	6	-4	94	91
5	6	-5	108	108
5	7	0	309	289
5	7	1	79	81
5	7	2	0	7
5	7	3	0	12
5	7	-1	81	74
5	7	-2	230	-220
5	7	-3	253	246
5	7	-4	237	231
5	7	-5	0	0
5	8	0	65	-53
5	8	1	144	143
5	8	2	189	194
5	8	3	0	-40
5	8	-1	112	-92
5	8	-2	32	36
5	8	-3	233	233
5	8	-4	0	-6
5	8	-5	93	-103
5	9	0	108	116
5	9	1	70	61
5	9	2	111	105
5	9	-1	0	-15
5	9	-2	76	82
5	9	-3	0	26
5	9	-4	0	32
5	10	0	0	-70
5	10	1	0	30
5	10	-1	170	-170
5	10	-2	62	67
5	10	-3	0	35
5	11	0	74	-80
5	11	-1	192	179
5	11	-2	245	240
6	0	0	49	38
6	0	1	477	482
6	0	2	283	281
6	0	3	0	-24
6	0	-1	83	85
6	0	-2	216	216
6	0	-3	230	229
6	0	-4	63	-59
6	0	-5	113	-108
6	0	-6	279	268
6	1	0	239	-205
6	1	1	385	-393
6	1	2	32	28
6	1	3	50	50
6	1	-1	162	155
6	1	-2	0	11
6	1	-3	0	4
6	1	-4	226	-217
6	1	-5	124	124
6	1	-6	37	134
6	2	0	314	320
6	2	1	0	12
6	2	2	113	123
6	2	3	35	24
6	2	-1	176	167
6	2	-2	40	-41
6	2	-3	280	285
6	2	-4	183	185
6	2	-5	84	81
6	2	-6	65	71
6	3	0	0	-18
6	3	1	236	-239
6	3	2	0	-14
6	3	3	130	121
6	3	-1	0	0
6	3	-2	330	335
6	3	-3	0	62
6	3	-4	205	-205
6	3	-5	60	66
6	3	-6	85	82
6	4	0	100	93
6	4	1	95	-110
6	4	2	127	-118
6	4	3	190	169
6	4	-1	200	193
6	4	-2	164	-177
6	4	-3	31	-30
6	4	-4	305	313
6	4	-5	0	14
6	5	0	88	95
6	5	1	252	265
6	5	2	0	-10
6	5	3	129	-123
6	5	-1	205	-197
6	5	-2	30	-37
6	5	-3	331	327
6	5	-4	33	-30
6	5	-5	170	-177
6	6	0	101	-101
6	6	1	58	44
6	6	2	118	122
6	6	3	66	73
6	6	-1	100	-102
6	6	-2	297	292
6	6	-3	46	-20
6	6	-4	196	-200
6	6	-5	117	116
6	7	0	47	46
6	7	1	49	60
6	7	2	0	-12
6	7	-1	202	-203
6	7	-2	109	-108
6	7	-3	0	-27
6	7	-4	0	10
6	7	-5	0	13
6	8	0	49	-31
6	8	1	212	222
6	8	2	113	120
6	8	-1	90	88
6	8	-2	420	412
6	8	-3	61	58
6	8	-4	0	-30
6	9	0	0	-2
6	9	1	117	-103
6	9	-1	227	231
6	9	-2	0	-6
6	9	-3	179	-179
6	9	-4	0	21
6	10	0	240	230
6	10	-1	181	179
6	10	-2	0	-42
6	10	-3	0	12
7	1	0	391	396
7	1	1	161	-157
7	1	2	35	-55
7	1	3	207	206
7	1	-1	388	373
7	1	-2	0	-18
7	1	-3	31	24
7	1	-4	110	101
7	1	-5	113	119
7	2	0	305	305
7	2	1	273	276
7	2	2	250	-248
7	2	3	0	-21
7	2	-1	177	-183
7	2	-2	111	117
7	2	-3	275	277
7	2	-4	226	235
7	2	-5	0	-2
7	3	0	45	42
7	3	1	249	253
7	3	2	118	115
7	3	-1	190	-196
7	3	-2	188	189
7	3	-3	269	264
7	3	-4	90	-99
7	3	-5	63	-70
7	4	0	86	-80
7	4	1	34	45
7	4	2	0	-23
7	4	-1	132	-121
7	4	-2	71	65
7	4	-3	33	-18
7	4	-4	109	-113
7	4	-5	52	45
7	5	0	111	-132
7	5	1	121	123
7	5	2	128	123
7	5	-1	118	-125
7	5	-2	104	95
7	5	-3	179	168
7	5	-4	106	102
7	5	-5	106	97
7	6	0	84	-88
7	6	1	0	-36
7	6	2	92	90
7	6	-1	0	-2
7	6	-2	135	142
7	6	-3	170	-164
7	6	-4	177	-171
7	7	0	0	-4
7	7	1	36	39
7	7	-1	294	284
7	7	-2	0	16
7	7	-3	186	-183
7	7	-4	279	274
7	8	0	36	53
7	8	1	53	72
7	8	-1	0	0
7	8	-2	140	-130
7	8	-3	0	0
7	9	0	85	85
7	9	-1	140	140
7	9	-2	106	105
7	9	-3	0	22
8	0	0	159	155
8	0	1	299	296
8	0	2	0	-8
8	0	-1	275	-270
8	0	-2	211	210
8	0	-3	367	365
8	0	-4	0	4
8	0	-5	261	-252
8	1	0	278	-266
8	1	1	112	95
8	1	2	196	199
8	1	-1	57	57
8	1	-2	172	164
8	1	-3	33	-6
8	1	-4	111	-112
8	1	-5	83	-85
8	2	0	59	23
8	2	1	0	17
8	2	2	38	31
8	2	-1	33	45
8	2	-2	33	42
8	2	-3	102	89
8	2	-4	50	50
8	2	-5	37	56
8	3	0	147	-148
8	3	1	62	73
8	3	2	175	168
8	3	-1	0	8
8	3	-2	255	258
8	3	-3	91	86
8	3	-4	80	-68
8	3	-5	0	25
8	4	0	50	62
8	4	1	0	-43
8	4	-1	280	278
8	4	-2	91	92
8	4	-3	192	-201
8	4	-4	193	183
8	5	0	95	90
8	5	1	53	56
8	5	-1	0	7
8	5	-2	86	-98
8	5	-3	0	-1
8	5	-4	162	156
8	6	0	142	142
8	6	1	138	136
8	6	-1	36	104
8	6	-2	0	8
8	6	-3	172	169
8	6	-4	38	33
8	7	0	0	19
8	7	-1	37	-48
8	7	-2	117	-117
8	7	-3	75	-79
8	8	-1	38	-46
8	8	-2	0	39
9	1	0	104	-77
9	1	-1	134	123
9	1	-2	0	27
9	1	-3	95	-94
9	1	-4	37	33
9	2	0	222	208
9	2	-1	0	0
9	2	-2	227	-234
9	2	-3	0	3
9	2	-4	135	132
9	3	0	248	244
9	3	-1	51	24
9	3	-2	0	-1
9	3	-3	252	258
9	3	-4	182	178
9	4	0	0	-18
9	4	-1	74	-67
9	4	-2	0	-30
9	4	-3	52	59
9	5	-1	37	45
9	5	-2	53	51
9	5	-3	126	114
10	0	-2	179	-173
10	1	-2	76	81

Table 2. Atomic Coordinates and their Standard Deviations

Atom	x	y	z	Sigma (x)	Sigma (y)	Sigma (z)
Mg_1	0	0	0	----	----	----
S_2	.0953	-.3605	.2575	.0002	.0001	.0002
O_3	-.0469	-.4174	.2116	.0005	.0004	.0008
O_4	.2185	-.4328	.3718	.0004	.0003	.0007
O_5	.1185	-.3211	.0456	.0005	.0003	.0007
O_6	.0951	-.2702	.4089	.0005	.0003	.0007
O_7	.1603	-.1094	-.0307	.0005	.0004	.0007
O_8	.1685	.1042	.1656	.0005	.0004	.0008
O_9	-.0017	-.0687	.2986	.0005	.0003	.0007
N_{10}	.1321	.3509	.3611	.0007	.0005	.0011
H_{11}	.21	.100	.30	.01	.008	.02
H_{12}	.02	-.131	.32	.01	.008	.02
H_{13}	.26	-.090	.05	.01	.007	.01
H_{14}	.06	.332	.21	.01	.007	.02
H_{15}	.15	-.178	-.01	.01	.008	.01
H_{16}	.21	.305	.40	.01	.008	.01
H_{17}	.17	.422	.36	.01	.008	.01
H_{18}	.40	-.438	.31	.01	.007	.01
H_{19}	.23	.120	.10	.01	.008	.02
H_{20}	.09	.346	.45	.01	.008	.02

Table 3. Anisotropic temperature parameters and their standard deviations.

	β_{11}	β_{22}	β_{33}	$2\beta_{12}$	$2\beta_{13}$	$2\beta_{23}$	$\sigma(\beta_{11})$	$\sigma(\beta_{22})$	$\sigma(\beta_{33})$	$\sigma(2\beta_{12})$	$\sigma(2\beta_{13})$	$\sigma(2\beta_{23})$
Mg_1	0.0056	.0032	.0129	-0.0008	.0043	- .0002	.0004	.0002	.0008	.0004	.0008	.0006
S_2	.0056	.0036	.0160	.0007	.0056	.0009	.0002	.0001	.0005	.0002	.0005	.0003
O_3	.0077	.0071	.033	- .0015	.005	.005	.0006	.0004	.002	.0008	.002	.001
O_4	.0071	.0040	.022	.0037	.006	.003	.0006	.0003	.001	.0007	.001	.001
O_5	.0105	.0043	.016	.0018	.010	.003	.0006	.0003	.001	.0007	.002	.001
O_6	.0130	.0043	.020	.0024	.010	- .002	.0007	.0003	.001	.0008	.002	.001
O_7	.0059	.0035	.024	.0011	.006	.002	.0006	.0003	.002	.0007	.002	.001
O_8	.0079	.0049	.016	- .0031	.004	- .002	.0006	.0003	.001	.0007	.001	.001
O_9	.0080	.0034	.017	.0006	.008	.002	.0006	.0003	.001	.0007	.001	.001
N_{10}	.0100	.0054	.022	- .0006	.012	- .001	.0009	.0005	.002	.001	.002	.002

Results and Discussion

Accuracy

The standard deviations given in the tables are calculated by the least squares method with the assumption of random errors in the intensity data. They are probably reasonable for the atomic coordinates and for bond distances and angles. The temperature parameters are subject to many non-random errors and should therefore be looked upon with caution. For a discussion of the uncertainties in anisotropic temperature parameters see Lonsdale and Milledge (1961).

Description of the Structure

Interatomic distances and angles are listed in Tables 4 and 5. All water molecules are coordinated to magnesium ions, six to each one. The crystal structure (Fig. 1) consists of a packing of these octahedrally hydrated magnesium ions and unhydrated ammonium ions among the tetrahedral sulfate ions. Hofmann found these same features of the structure except that he had a different orientation for both the sulfate tetrahedron and the water octahedron. The orientations which we found permit satisfactory hydrogen bonding which is confirmed by the locations found for the hydrogen atoms.

The Sulfate Ion

The shape of the sulfate ion is close to that of a regular tetrahedron. The O-S-O angles range from 108.4° to 110.7° with standard deviations of 0.3°. The S-O distance, before correction for thermal motion, range from 1.459 to 1.481 Å with standard deviations of 0.005 Å; the average is 1.473 Å.

Table 4. Interatomic distances and their standard deviations in Å*

SO_4^{-} tetrahedron:			
$S-O_3$	1.459 ± 0.005	O_3-O_5	2.419 ± 0.006
$S-O_4$	1.474 ± 0.005	O_3-O_6	2.396 ± 0.007
$S-O_5$	1.481 ± 0.005	O_4-O_5	2.417 ± 0.006
$S-O_6$	1.476 ± 0.005	O_4-O_6	2.393 ± 0.006
O_3-O_4	2.387 ± 0.006	O_5-O_6	2.417 ± 0.006
$Mg(H_2O)_6^{++}$ octahedron:			
$Mg-O_7$	2.083 ± 0.005	O_7-O_9	2.924 ± 0.007
$Mg-O_8$	2.073 ± 0.005	O_7-O_9'	2.922 ± 0.007
$Mg-O_9$	2.051 ± 0.005	O_8-O_9	2.953 ± 0.007
O_7-O_8	2.945 ± 0.007	O_8-O_9'	2.879 ± 0.007
O_7-O_8'	2.932 ± 0.007		
H_2O hydrogen bonding			
O_7-O_3	2.722 ± 0.006	O_8-H_{19}	0.8 ± 0.1
O_7-O_5	2.756 ± 0.006	O_9-H_{12}	0.8 ± 0.1
O_8-O_4	2.792 ± 0.006	O_9-H_{18}	0.9 ± 0.1
O_8-O_5	2.844 ± 0.006	O_3-H_{13}	1.8 ± 0.1
O_9-O_4	2.777 ± 0.006	O_4-H_{11}	2.0 ± 0.1
O_9-O_6	2.713 ± 0.006	O_5-H_{15}	1.9 ± 0.1
O_7-H_{13}	1.0 ± 0.1	O_6-H_{12}	1.9 ± 0.1
O_7-H_{15}	0.9 ± 0.1	O_4-H_{18}	1.9 ± 0.1
O_8-H_{11}	0.8 ± 0.1	O_5-H_{19}	2.0 ± 0.1
NH_4^{+} hydrogen bonding			
$N-O_3$	3.102 ± 0.009	$N-H_{17}$	1.0 ± 0.1
$N-O_4$	2.837 ± 0.008	$N-H_{20}$	0.8 ± 0.1
$N-O_5$	2.916 ± 0.008	O_5-H_{14}	2.0 ± 0.1
$N-O_6$	2.949 ± 0.008	O_6-H_{16}	2.1 ± 0.1
$N-O_6'$	3.057 ± 0.009	O_4-H_{17}	1.9 ± 0.1
$N-H_{14}$	1.0 ± 0.1	O_3-H_{20}	2.4 ± 0.1
$N-H_{16}$	0.9 ± 0.1	$O_6'-H_{20}$	2.3 ± 0.1

*Uncorrected for thermal motion.

Table 5. Bond angles in degrees.*

O-S-O Angles			
O_3-S-O_4	108.9	O_4-S-O_5	109.7
O_3-S-O_5	110.7	O_4-S-O_6	108.4
O_3-S-O_6	109.4	O_5-S-O_6	109.6
O-Mg-O Angles			
O_7-Mg-O_8	90.3	O_8-Mg-O_9	91.5
O_7-Mg-O_9	90.0		
H_2O Hydrogen bond angles			
O_3-O_7-O_5	101.2	O_3-O_7-H_{13}	8
O_4-O_8-O_5	115.3	O_5-O_7-H_{15}	2
O_4-O_9-O_6	102.9	O_4-O_8-H_{11}	7
H_{13}-O_7-H_{15}	110	O_5-O_8-H_{19}	5
H_{11}-O_8-H_{19}	111	O_4-O_9-H_{18}	6
H_{12}-O_9-H_{18}	106	O_6-O_9-H_{12}	6
NH_4^+ Hydrogen bond angles			
O_3-N-O_4	82.1	O_6-N-O_6'	102.7
O_3-N-O_5	115.7	H_{17}-N-O_4	6
O_3-N-O_6	97.3	H_{14}-N-O_5	12
O_3-N-O_6'	45.8	H_{16}-N-O_6	14
O_4-N-O_5	107.1	H_{20}-N-O_3	27
O_4-N-O_6	106.7	H_{20}-N-O_6'	19
O_4-N-O_6'	122.6	S-H_{20}-N	171
O_5-N-O_6	135.2	O_3-H_{20}-O_6'	60
O_5-N-O_6'	82.7		

* Standard deviations are 0.3° for bond angles not involving hydrogen atoms. For bond angles involving hydrogen, the standard deviations are 10° or less.

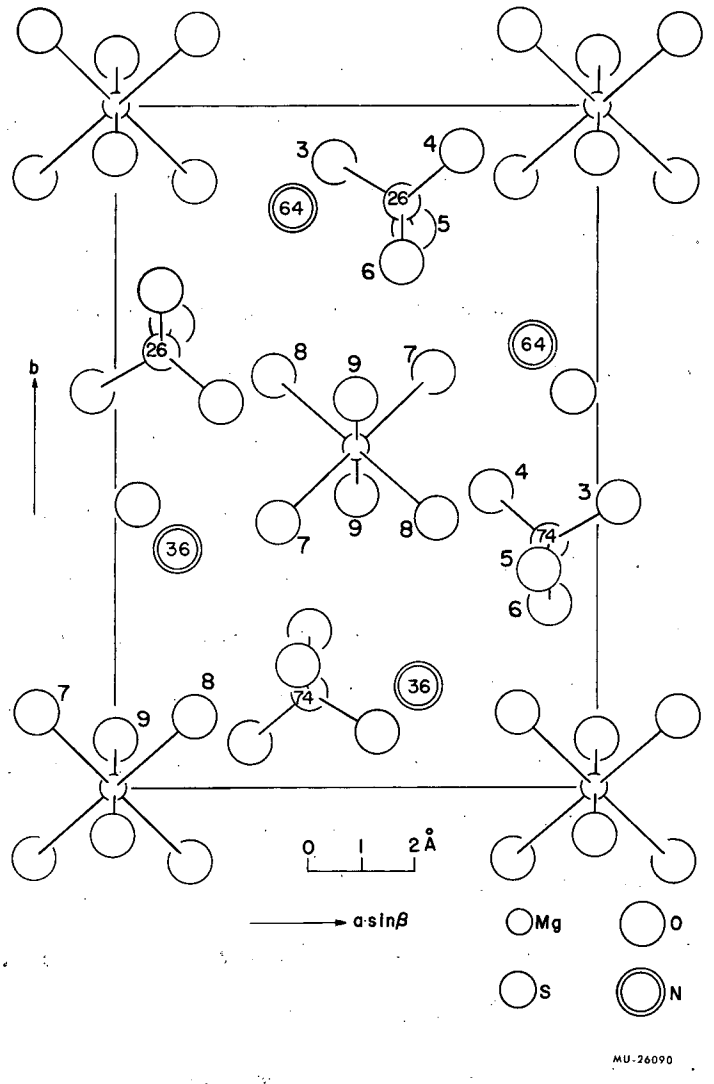

Fig. 1. Crystal structure of $Mg(NH_4)_2(SO_4)_2 \cdot 6H_2O$: The numbers inside the sulfur and nitrogen atoms indicate their z coordinates. The numbers beside some of the oxygen atoms correspond to the numbering of Table 2.

The thermal motion of the oxygen atoms exceeds that of the sulfur atom. As a result, the time average of an S-O distance is larger than the distance between the average positions which is determined by the x-ray method. The extent of this effect depends on the details of the motion which was analyzed by the program of Busing and Levy (1959). The rms amplitudes in the principal vibration directions calculated from the anisotropic thermal parameters are listed in Table 6. The sulfur atom moves almost isotropically with the amplitude 0.16 Å. The amplitudes of the oxygen atoms in the directions of minimum motion are very similar to this value. The directions of this minimum motion are at angles 21°, 10°, 17°, and 11° to the corresponding S-O bonds for atoms O_3 to O_6. The larger amplitudes of these oxygen atoms are approximately perpendicular to the S-O bonds. Thus the thermal parameters are consistent with the model of a rigid sulfate ion which vibrates with some angular oscillation (libration). For this model of the motion, the correction to the distance is calculated with the two atoms moving in phase (oxygen "riding on" sulfur). The results (Table 7) show a spread in the four values of only 0.010 Å, compared with a spread of 0.022 Å in the uncorrected distances.

The correction assuming in-phase motion is the smallest that can be applied. Any out-of-phase motion transverse to the bond increases the effect. With random phases, one calculates distances of about 1.52 Å (Table 7) for the S-O bonds. For a tightly bound ion such as sulfate it seems likely that the motion will be largely in-phase, and therefore 1.49 Å is reported as the most likely interpretation of the results for the S-O bond distance in sulfate.

The Hydrated Magnesium Ion

The Mg-O distances range from 2.051 to 2.063 Å, each $\pm$ 0.005 Å (Table 8),

Table 6. Principal rms amplitudes, Å

Atom	u_1	u_2	u_3
Mg_1	.15	.15	.16
S_2	.15	.17	.17
O_3	.17	.22	.27
O_4	.14	.20	.21
O_5	.16	.18	.21
O_6	.17	.20	.24
O_7	.15	.17	.21
O_8	.15	.18	.21
O_9	.16	.17	.19
N_{10}	.18	.20	.21

Table 7. Comparison of sulfur-oxygen bond lengths with and without thermal motion corrections*

Atoms	Uncorrected bond length	Bond length with in-phase correction	Bond length with random-phase correction
$S-O_3$	1.459 Å	1.481 Å	1.518 Å
$S-O_4$	1.474	1.482	1.520
$S-O_5$	1.481	1.490	1.525
$S-O_6$	1.476	1.491	1.525

* Standard deviations are all 0.005 Å.

Table 8. Comparison of magnesium-oxygen interatomic distances with and without thermal motion corrections*

Atoms	Uncorrected distance	Distance with in-phase correction	Distance with random-phase correction
$Mg-O_7$	2.083 Å	2.089 Å	2.110 Å
$Mg-O_8$	2.073	2.080	2.104
$Mg-O_9$	2.051	2.055	2.078

* Standard deviations are all 0.005 Å.

before correction for thermal motion. The motion of the magnesium atom is practically isotropic with an amplitude equal to the minimum amplitude for the water molecules. The water molecules have their largest motion approximately transverse to the bonds to magnesium, but the motion is not as anisotropic as that of the sulfate oxygen atoms. The directions of minimum motion are at angles 26°, 18°, and 18° to the corresponding Mg-O bonds. These parameters are approximately consistent with rigid-molecule libration. The amplitude of this libration is less than in the case of the sulfate ion. The correction of the Mg-O distance for thermal motion has been made with both in-phase and random-phase assumptions (Table 8). As in the case of the sulfate ion, the in-phase correction is considered to be the best interpretation of the data, but there is less basis for this choice here than for the sulfate.

The octahedron of water molecules is slightly distorted from regular. The Mg-O distances differ by up to 0.03 Å, independent of how the thermal correction is applied, while each has a standard deviation of 0.005 Å. One of the O-Mg-O angles is $91.5 \pm 0.3^{\circ}$. These small distortions are attributed to the lack of symmetry of the neighbors to which the water molecules are hydrogen bonded.

Hydrogen Bonding

One can assign each hydrogen atom of the water molecules to a hydrogen bond on the basis that each near oxygen neighbor of the water molecule, unless it is coordinated to the same magnesium ion, is hydrogen bonded. This procedure gives a configuration (Fig. 2) in which the hydrogen bonds all involve oxygen atoms of neighboring sulfate ions. This configuration is confirmed by the hydrogen positions which were calculated in the refinement of the structure; the O-H vectors make angles of 2° to

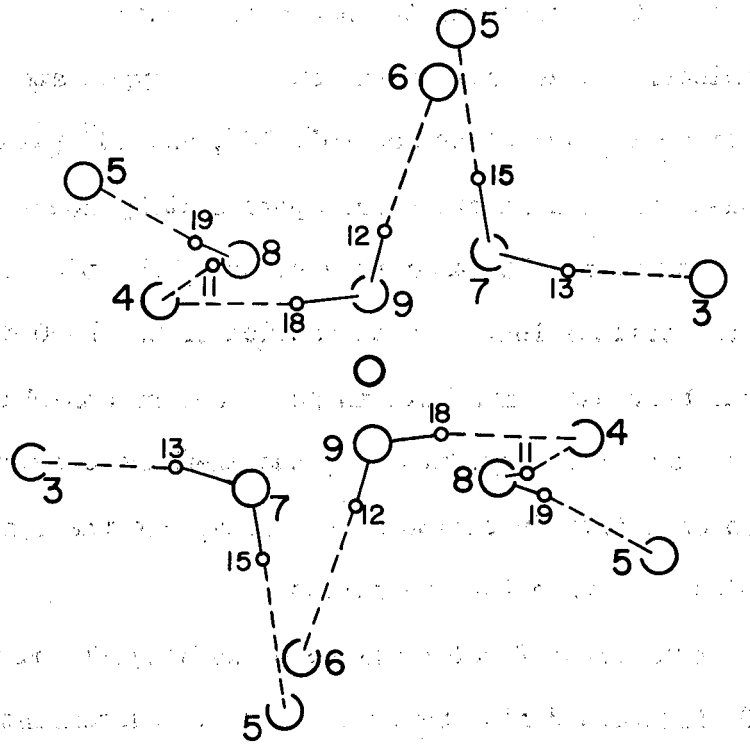

Fig. 2. Hydrogen bonding of the water molecules: The central atom is Mg at 1/2, 1/2, 0. The numbering corresponds to that of Table 2. The projection is the same as that of Figure 1.

8° with the corresponding O-O vectors. Furthermore, the H-O-H angles and O-H distances are reasonable for water molecules when the experimental accuracy is considered. The O-H bonds of the water molecules make angles of 108° to 121° with the respective O-Mg vectors. It is of interest to note that H_{19}, the hydrogen atom in the longest of these hydrogen bonds, was one of the two hydrogen atoms that were difficult to locate in the difference Fourier. It is possible that this hydrogen bond is weaker than the others and thus H_{19} has more freedom of thermal motion.

The hydrogen bonding of the NH_4^+ ion is shown in Fig. 3. The nitrogen atom has five sulfate oxygen neighbors within 3.102 Å. The closest neighbor of O_4 at 2.837 Å. Atom H_{17} is placed such that the H_{17}-N-O_4 angle is 6°, thus forming a fairly strong hydrogen bond. Two other oxygen neighbors, O_5 and O_6, are at 2.916 and 2.949 Å respectively from the nitrogen atom. The angles H_{14}-N-O_5 and H_{16}-N-O_6 are 12° and 14° respectively. These are still reasonable hydrogen bonds although somewhat longer and weaker than the N-O_4 bond.

Oxygen atoms O_3 and O_6' which belong to the same sulfate ion are still further away from the nitrogen atom at 3.102 and 3.057 Å respectively, forming a bifurcated hydrogen bond. The hydrogen atom, H_{20}, involved in this interaction is pointed almostly directly at the sulfur atom, with an N-H_{20}-S angle of 171°. The least squares refinement leads to an N-H_{20} bond length of about 0.8 Å and H_{20}-O distances of 2.4 and 2.3 Å for O_3 and O_6' respectively. It is interesting to note that H_{20} was the other hydrogen atom which was difficult to find in the difference map. Therefore this bifurcated configuration may involve little bonding and permit greater thermal motion. It is encouraging that all of the H-N-H bond angles are within 5° of the expected tetrahedral angles.

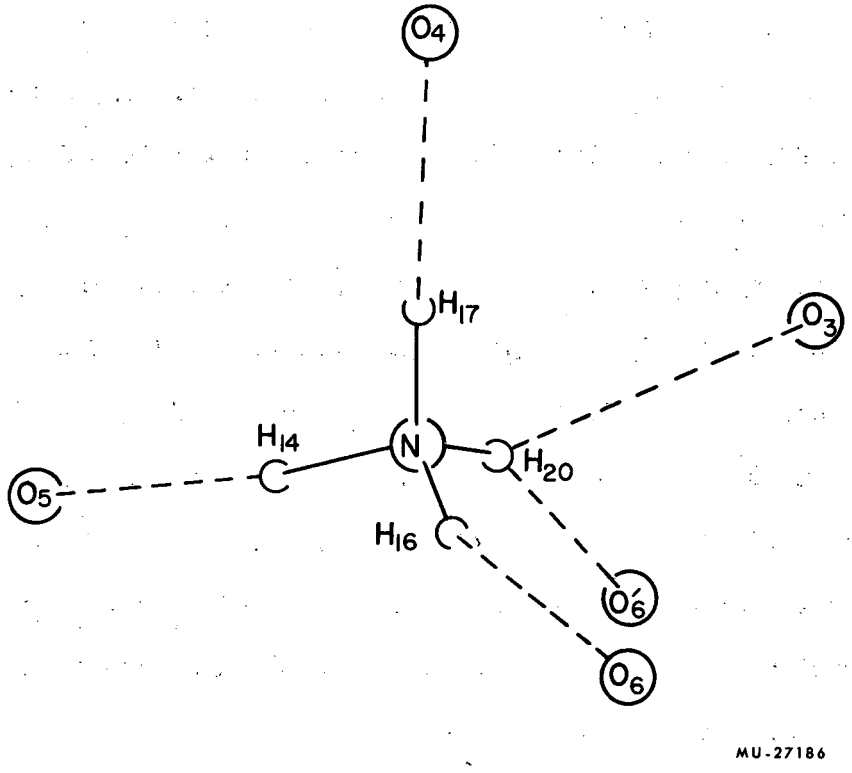

Fig. 3. Hydrogen bonding of the NH_4^+ ion: Projected down [100].

ATTEMPTED CALCULATION OF THE ELECTRON DISTRIBUTION OF THE SULFATE ION IN MAGNESIUM AMMONIUM SULFATE HEXAHYDRATE

Introduction

With the hope of contributing to a better understanding of the chemical bonding in the sulfate ion, an attempt was made to calculate the electron distribution of this ion as it exists in $Mg(NH_4)_2(SO_4)_2 \cdot 6H_2O$. To accomplish this a computer program was written to integrate the electron density of a crystal as determined by x-ray diffraction methods.

Method of Calculation

The well-known formula for the electron density at any point x, y, z, in the unit cell of a crystal is given by

$$\rho_{xyz} = 1/V \sum_{h=-\infty}^{+\infty} \sum_{k=-\infty}^{+\infty} \sum_{\ell=-\infty}^{+\infty} F_{hk\ell} \exp(-2\pi i(hx + ky + \ell z)) \qquad (1)$$

where V is the volume of the cell, $F_{hk\ell}$ is the structure factor of a plane in the crystal specified by h, k, ℓ, the Miller indices. To obtain the number of electrons, E, in a given volume, v, this Fourier series must be integrated over that volume giving

$$E = \int_v \rho_{xyz}\, dv. \qquad (2)$$

Carrying out the integration over a sphere of radius R, with origin at X, Y, Z, E is obtained as a summation of terms

$$E = \sum_{h=-\infty}^{+\infty} \sum_{k=-\infty}^{+\infty} \sum_{\ell=-\infty}^{+\infty} E_{hk\ell} \qquad (3)$$

in which each term $E_{hk\ell}$ is given by

$$E_{hk\ell} = 2RF_{hk\ell}/|h| \left[\frac{\mathrm{Sin}(2\pi|h|R)}{2\pi|h|R} - \mathrm{Cos}(2\pi|h|R) \right] \exp(-2\pi i(hx + ky + \ell z)) \qquad (4)$$

where $|h| = 1/d = 2\mathrm{Sin}\theta/\lambda$.

To reduce series termination errors the calculation was made using $\Delta F_{hk\ell}$, the difference between the observed and calculated structure factors, in place of $F_{hk\ell}$. The summation using $\Delta F_{hk\ell}$ is called E'. If E' is a positive number when calculated in a sphere corresponding to a given atom, then the atomic scattering factor assumed for that atom is too small. In other words the atom was assumed to have too few electrons. Alternatively if E' is a negative number the atom was assumed to have too many electrons.

A computer program called COUNT was written for the IBM 7090 to calculate E' in space group $P2_1/a$. The program requires as input the output tape of the UCLA least squares program (LALS1). E' can be evaluated for any number of atoms in spheres of any specified radii.

Three calculations were made using the data for $Mg(NH_4)_2(SO_4)_2 \cdot 6H_2O$, described above. In each case the structure was first refined by full matrix least squares using anisotropic temperature factors for all atoms as described above. The only difference between the three refinements was the atomic scattering factors used for sulfur and oxygen. Case A considers sulfur and oxygen to be both neutral, Case B uses S^{+6} and O^{-2}, and Case C uses neutral sulfur and $O^{-1/2}$. The neutral atom scattering factors were obtained from Ibers (1962), S^{+6} from James and Brindley (1931), and $O^{-1/2}$ by averging Ibers' values for O^{o} and O^{-1}.

After refinement, E' was calculated taking the refined coordinates of the sulfur and sulfate oxygen atoms sucessively as origin of the sphere. The calculation was made for a number of different radii around each atom. E' was also evaluated around the Mg^{++} ion in the hope that this would provide a check of consistancy between different calculations.

Results and Discussion

Table 8 shows the partial results of the three least squares refinements. Table 9 lists selected values of E' in spheres of radius R around the magnesium, sulfur, and oxygen atoms after each refinement.

The results of the three cases are in direct conflict! The result for Case A around sulfur indicates that the sulfur atom is very nearly neutral but Case B indicates that it is about +6. The values obtained around oxygen are always small (under 0.4) no matter if oxygen is put in as O^{o}, O^{-2}, or $O^{-1/2}$. In cases B and C, O_4 and O_5 have negative values of E' whereas O_3 and O_6 have positive values.

The reason for the failure of this calculation is probably the effectiveness of the least squares method in finding a good fit between the observed and calculated structure factors when given enough parameters to vary. The clearly ridiculous case of S^{+6} and O^{-2} (Case B) still gives an R factor of .068, not so much worse than that of 0.060 obtained in Case C where sulfur and oxygen are both neutral. The least squares program has thus managed to adjust the scale factor, atomic coordinates, and anisotropic temperature factors to give a reasonable fit to the data.

One possible method of solving this difficulty might be to carry out a complete neutron diffraction study of the structure. Since the scattering factors for neutrons are less complex than those for x-rays, it might be possible to obtain more reliable anisotropic temperature factors from such a study. These temperature factors could then be held fixed in the refinement of the x-ray data and thus, hopefully, a better scale factor could be obtained. Another possible experiment is that of taking low temperature x-ray diffraction data to reduce the temperature factors to small values.

Table 8

Partial results of the least squares refinements. Standard deviations are the same as those given in Part I.

Atom	Case	X	Y	Z	β_{11}	β_{22}	β_{33}	$2\beta_{12}$	$2\beta_{13}$	$2\beta_{23}$
S	A	.0953	-.3605	.2575	.0056	.0035	.0160	.0007	.0057	.0009
S	B	.0953	-.3605	.2574	.0059	.0038	.0171	.0006	.0060	.0008
S	C	.0953	-.3605	.2575	.0053	.0034	.0156	.0007	.0055	.0008
O_3	A	-.0468	-.4174	.2116	.0077	.0071	.033	-.0015	.005	.005
O_3	B	-.0447	-.4166	.2123	.0084	.0068	.031	-.0002	.005	.005
O_3	C	-.0467	-.4174	.2115	.0095	.0079	.036	-.0016	.007	.004
O_4	A	.2185	-.4328	.3718	.0071	.0040	.022	.0037	.006	.003
O_4	B	.2170	-.4321	.3707	.0072	.0038	.021	.0025	.007	.002
O_4	C	.2184	-.4327	.3715	.0086	.0049	.026	.0038	.008	.003
O_5	A	.1185	-.3211	.0456	.0105	.0043	.016	.0018	.010	.003
O_5	B	.1183	-.3215	.0483	.0097	.0038	.017	.0020	.007	.002
O_5	C	.1185	-.3210	.0459	.0122	.0051	.020	.0021	.011	.003
O_6	A	.0951	-.2702	.4089	.0130	.0043	.020	.0024	.010	-.002
O_6	B	.0950	-.2714	.4071	.0117	.0044	.019	.0024	.009	.0001
O_6	C	.0951	-.2703	.4089	.0150	.0052	.024	.0025	.011	-.002
Mg	A	0	0	0	.0056	.0032	.013	-.0008	.004	-.0002
Mg	B	0	0	0	.0069	.0039	.016	-.0009	.006	-.0002
Mg	C	0	0	0	.0054	.0031	.012	-.0008	.004	-.0003

R Factor-Case A	.060	Scale Factor-Case A	5.590
R Factor-Case B	.068	Scale Factor-Case B	5.232
R Factor-Case C	.061	Scale Factor-Case C	5.667

Table 9

Selected Values of E'

Atom	Case	R in Å					
		.6	.7	.8	.9	1.0	1.1
S	A	-.04	-.06	-.1	-.15	-.20	-.25
S	B	.19	.29	.42	.57	.72	.88
S	C	-.01	-.02	-.05	-.09	-.15	-.23
O_3	A	.09	.14	.20	.26	.30	.31
O_3	B	.06	.09	.13	.16	.20	.23
O_3	C	.05	.08	.12	.15	.18	.18
O_4	A	.03	.06	.09	.12	.16	.20
O_4	B	-.006	-.011	-.012	-.005	.017	.054
O_4	C	-.012	-.018	-.019	-.009	.016	.05
O_5	A	.03	.05	.08	.11	.14	.15
O_5	B	-.0007	-.0006	+.001	.005	.014	.28
O_5	C	-.016	-.021	-.021	-.016	-.003	+.012
O_6	A	.06	.09	.13	.15	.16	.16
O_6	B	.03	.04	.06	.07	.08	.09
O_6	C	.017	.018	.015	.010	.003	-.004
Mg	A	-.07	-.10	-.13			
	B	-.23	-.33	-.42			
	C	-.029	-.033	-.038			

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