Crystal structure and hydrogen bonding of magnesium ammonium sulfate hexahydrate*

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With 3 figures

Auszug

Die Struktur von $Mg(NH_4)_2(SO_4)_2 \cdot 6H_2O$ wurde neu bestimmt mit dem Ziel, die Wasserstoffbindungen zu ermitteln. Die Kristalle sind monoklin; sie gehören der Raumgruppe $P2_1/a$ an, mit $a = 9{,}324$ Å, $b = 12{,}597$ Å, $c = 6{,}211$ Å, $\beta = 107{,}14°$. Die von HOFMANN angegebenen Koordinaten für Mg, N und S wurden nahezu bestätigt, nicht jedoch die für die O-Atome. Die Struktur wurde, einschließlich der Lage der H-Atome aus dreidimensionalen Interferenzdaten mittels der Fourier-Methode und der Ausgleichsrechnung bestimmt. Das Mg-Atom ist von Wassermolekülen oktaedrisch umgeben, von denen jedes zwei Wasserstoffbindungen zu den O-Atomen der SO_4-Gruppen aufweist. Mit diesen Atomen sind auch drei H-Atome eines Ammoniumions verbunden, während das vierte H-Atom von zwei O-Atomen gleichweit entfernt ist (gegabelte Bindung). Die mittleren Atomabstände sind ohne Berücksichtigung der Wärmebewegung: Mg—O 2,07 Å, S—O 1,47 Å, O—O (Wasserstoffbindung) 2,77 Å, N—O (Wasserstoffbindung) 2,90 Å, N—O (gegabelte Bindung) 3,08 Å. Der mittlere, auf Wärmebewegung korrigierte Abstand S—O ist 1,49 Å.

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 $\beta = 107.14°$. 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 mole-

cules, 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 Å, S—O = 1.47 Å, O—O (hydrogen bonded) = 2.77 Å, N—O (hydrogen bonded) = 2.90 Å, and N—O (bifurcated bond) = 3.08 Å. The average S—O bond length after correction for thermal motion is 1.49 Å.

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 we found it 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. We selected $Mg(NH_4)_2(SO_4)_2 \cdot 6H_2O$ from among the many available isomorphous compounds since it contains relatively light atoms and therefore is well suited for the determination of the hydrogen atom positions.

We have 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. Our final structure for the oxygen atoms leads to a satisfactory assignment of hydrogen bonds which is confirmed by evidence of the hydrogen atom positions from the diffraction-intensity data. After these calculations were completed, we 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 ours[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

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[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.

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

dimensions. All measurements were made on a crystal with dimensions of approximately $0.06 \times 0.06 \times 0.13$ mm. A total of 904 independent reflections, including about 120 too weak to be observed, were measured with MoKα x-rays ($\lambda = 0.7107$ 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 $\mu R = 0.03$, and therefore absorption effects were neglected.

Unit cell and space group

The cell dimensions of the monoclinic unit cell at room temperature are: $a = 9.324 \pm .007$ Å, $b = 12.597 \pm .009$ Å, $c = 6.211 \pm .005$ Å, $\beta = 107.14° \pm .02°$. These values are in good agreement with those of HOFMANN which are[4]:

$a = 9.30 \pm .02$ Å, $b = 12.60 \pm .025$ Å, $c = 6.21 \pm .015$ Å, $\beta = 107.10°$. With two molecules in the unit cell the calculated density is 1.718 g/cm^3 which agrees well with the observed value of 1.72 g/cm^3 (LANGE, 1949). Systematic absences of reflections indicate a probable space group of $P2_1/a$ in agreement with HOFMANN's choice. The successful 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 $0\ 0\ 0$; $\frac{1}{2}\ \frac{1}{2}\ 0$. All other atoms are in general positions with coordinates $\pm\ (x\ y\ z;\ x + \frac{1}{2},\ -y + \frac{1}{2},\ z)$.

After several attempts to refine HOFMANN's structure by the method of least squares proved fruitless it was decided to attack the problem from the beginning. 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

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[4] Converted from kX units to Ångströms.

Table 1. *Observed and calculated structure factors each multiplied by 10*

h	k	l	F_o	F_c	h	k	l	F_o	F_c	h	k	l	F_o	F_c	h	k	l	F_o	F_c	h	k	l	F_o	F_c
0	0	1	267	235	1	2	-2	778	777	1	10	-4	0	-23	2	6	2	149	157	3	3	5	98	-86
0	0	2	301	-312	1	2	-3	24	-20	1	11	0	255	255	2	6	3	229	222	3	3	-1	781	794
0	0	3	598	591	1	2	-4	98	-95	1	11	1	177	-183	2	6	4	102	-102	3	3	-2	46	52
0	0	4	252	268	1	2	-5	274	264	1	11	2	0	-17	2	6	5	37	-42	3	3	-3	36	-18
0	0	5	203	216	1	2	-6	145	137	1	11	3	174	171	2	6	-1	375	379	3	3	-4	220	201
0	0	6	0	-40	1	3	0	860	898	1	11	-1	151	149	2	6	-2	329	325	3	3	-5	290	284
0	1	1	628	597	1	3	1	229	-235	1	11	-2	120	-123	2	6	-3	0	5	3	3	-6	150	156
0	1	2	248	-238	1	3	2	0	6	1	11	-3	0	-11	2	6	-4	214	218	3	4	0	542	535
0	1	3	156	-164	1	3	3	296	299	1	12	0	122	118	2	6	-5	285	287	3	4	1	182	191
0	1	4	70	66	1	3	4	132	136	1	12	1	0	-7	2	7	0	0	21	3	4	2	222	-224
0	1	5	283	278	1	3	5	114	-115	1	12	2	52	-76	2	7	1	0	-4	3	4	3	68	72
0	1	6	36	-12	1	3	6	101	-95	1	12	-1	112	-103	2	7	2	83	-89	3	4	4	89	90
0	2	0	228	202	1	3	-1	372	371	1	12	-2	0	12	2	7	3	72	-86	3	4	5	0	-35
0	2	1	245	235	1	3	-2	138	-148	1	12	-3	170	158	2	7	4	0	6	3	4	-1	205	-200
0	2	2	176	-165	1	3	-3	322	324	1	13	0	74	-60	2	7	-1	302	291	3	4	-2	167	165
0	2	3	116	121	1	3	-4	405	402	1	13	1	156	149	2	7	-2	0	-1	3	4	-3	71	66
0	2	4	108	102	1	3	-5	217	229	1	13	-1	0	-14	2	7	-3	112	-103	3	4	-4	0	-10
0	2	5	0	36	1	3	-6	0	-27	2	0	0	434	412	2	7	-4	56	-65	3	4	-5	202	200
0	2	6	157	159	1	4	0	0	-12	2	0	1	790	-814	2	7	-5	0	-16	3	4	-6	52	-40
0	3	1	432	430	1	4	1	426	425	2	0	2	0	13	2	8	0	90	90	3	5	0	450	458
0	3	2	266	-263	1	4	2	0	-16	2	0	3	111	103	2	8	1	228	-218	3	5	1	507	509
0	3	3	485	-480	1	4	3	0	-10	2	0	4	322	320	2	8	2	165	163	3	5	2	170	189
0	3	4	118	118	1	4	4	370	375	2	0	5	110	-101	2	8	3	298	288	3	5	3	143	158
0	3	5	66	70	1	4	5	92	93	2	0	-1	1033	1045	2	8	4	115	117	3	5	4	49	59
0	3	6	37	-58	1	4	-1	220	211	2	0	-2	698	-697	2	8	-1	225	217	3	5	5	114	114
0	4	0	946	-971	1	4	-2	276	274	2	0	-3	196	193	2	8	-2	42	51	3	5	-1	416	411
0	4	1	236	-218	1	4	-3	26	34	2	0	-4	391	382	2	8	-3	122	-111	3	5	-2	324	327
0	4	2	552	554	1	4	-4	0	23	2	0	-5	77	79	2	8	-4	68	-69	3	5	-3	165	-156
0	4	3	46	30	1	4	-5	157	-163	2	0	-6	0	-16	2	8	-5	143	132	3	5	-4	174	168
0	4	4	148	-161	1	4	-6	0	-3	2	1	0	610	601	2	9	0	199	195	3	5	-5	207	206
0	4	5	83	83	1	5	0	106	-100	2	1	1	591	591	2	9	1	31	-35	3	5	-6	0	31
0	4	6	93	94	1	5	1	139	141	2	1	2	201	184	2	9	2	317	-323	3	6	0	108	110
0	5	1	214	215	1	5	2	72	71	2	1	3	104	115	2	9	3	0	-42	3	6	1	0	-14
0	5	2	382	-370	1	5	3	28	35	2	1	4	238	234	2	9	4	160	156	3	6	2	434	-443
0	5	3	338	339	1	5	4	55	57	2	1	5	85	78	2	9	-1	0	-31	3	6	3	0	34
0	5	4	62	-59	1	5	5	0	20	2	1	-1	268	-264	2	9	-2	220	-214	3	6	4	194	194
0	5	5	255	-257	1	5	-1	49	-53	2	1	-2	193	177	2	9	-3	93	-98	3	6	-1	0	19
0	6	0	184	-198	1	5	-2	302	-291	2	1	-3	410	398	2	9	-4	166	166	3	6	-2	98	-84
0	6	1	260	260	1	5	-3	54	-48	2	1	-4	263	276	2	9	-5	0	-43	3	6	-3	41	-44
0	6	2	213	212	1	5	-4	265	265	2	1	-5	55	-68	2	10	0	32	-31	3	6	-4	131	119
0	6	3	164	168	1	5	-5	118	122	2	1	-6	186	-179	2	10	1	221	217	3	6	-5	0	-11
0	6	4	230	225	1	5	-6	0	12	2	2	0	105	98	2	10	2	0	0	3	7	0	108	97
0	6	5	0	-17	1	6	0	109	-97	2	2	1	513	504	2	10	3	36	-29	3	7	1	508	509
0	7	1	37	44	1	6	1	285	285	2	2	2	88	-82	2	10	-1	161	-154	3	7	2	0	-1
0	7	2	237	244	1	6	2	207	-195	2	2	3	180	192	2	10	-2	253	254	3	7	3	198	-204
0	7	3	117	117	1	6	3	467	-462	2	2	4	200	192	2	10	-3	159	151	3	7	4	137	141
0	7	4	115	108	1	6	4	168	167	2	2	5	111	108	2	10	-4	64	-63	3	7	-1	208	-210
0	7	5	0	-2	1	6	5	36	55	2	2	-1	0	-28	2	11	0	34	-16	3	7	-2	115	122
0	8	0	156	157	1	6	-1	226	-224	2	2	-2	88	85	2	11	1	0	2	3	7	-3	248	246
0	8	1	148	150	1	6	-2	419	-408	2	2	-3	34	-23	2	11	2	62	74	3	7	-4	46	59
0	8	2	0	19	1	6	-3	103	94	2	2	-4	202	203	2	11	3	126	122	3	7	-5	36	14
0	8	3	0	-2	1	6	-4	44	38	2	2	-5	106	-127	2	11	-1	59	65	3	8	0	156	-156
0	8	4	193	186	1	6	-5	182	-179	2	2	-6	51	39	2	11	-2	85	68	3	8	1	165	-169
0	8	5	75	78	1	7	0	115	-114	2	3	0	205	-195	2	11	-3	36	-43	3	8	2	183	174
0	9	1	73	64	1	7	1	288	289	2	3	1	537	528	2	12	0	71	72	3	8	3	69	-71
0	9	2	31	33	1	7	2	505	502	2	3	2	255	255	2	12	1	141	152	3	8	4	141	-139
0	9	3	189	-191	1	7	3	255	-252	2	3	3	68	-76	2	12	2	53	49	3	8	-1	51	-41
0	9	4	51	-47	1	7	4	59	-63	2	3	4	217	224	2	12	-1	0	22	3	8	-2	177	180
0	10	0	0	-44	1	7	5	275	263	2	3	5	0	-4	2	12	-2	36	54	3	8	-3	106	94
0	10	1	304	309	1	7	-1	26	33	2	3	-1	276	-279	2	12	-3	162	156	3	8	-4	178	-186
0	10	2	286	284	1	7	-2	311	305	2	3	-2	236	-226	2	13	0	100	-108	3	8	-5	0	-33
0	10	3	49	-48	1	7	-3	164	165	2	3	-3	568	561	2	13	-1	92	89	3	9	0	205	-216
0	10	4	0	9	1	7	-4	131	-135	2	3	-4	175	169	3	1	0	226	229	3	9	1	0	33
0	11	1	224	-212	1	7	-5	51	98	2	3	-5	152	-160	3	1	1	123	-103	3	9	2	0	-8
0	11	2	0	4	1	8	0	19	-4	2	3	-6	0	4	3	1	2	56	56	3	9	3	0	26
0	11	3	0	16	1	8	1	142	-139	2	4	0	193	190	3	1	3	229	230	3	9	-1	44	-43
0	12	0	70	90	1	8	2	0	-6	2	4	1	602	618	3	1	4	138	142	3	9	-2	189	177
0	12	1	79	54	1	8	3	108	92	2	4	2	382	384	3	1	5	126	109	3	9	-3	67	-87
0	12	2	97	93	1	8	4	276	-278	2	4	3	173	-170	3	1	-1	456	-460	3	9	-4	124	125
0	13	1	212	-195	1	8	-1	188	-175	2	4	4	32	-11	3	1	-2	30	-32	3	10	0	204	-209
1	1	0	112	-123	1	8	-2	0	24	2	4	-1	219	-211	3	1	-3	590	600	3	10	1	112	114
1	1	1	548	553	1	8	-3	244	-247	2	4	-2	375	376	3	1	-4	63	-60	3	10	2	213	215
1	1	2	47	-43	1	8	-4	83	-79	2	4	-3	467	461	3	1	-5	223	-218	3	10	3	0	0
1	1	3	306	309	1	8	-5	153	145	2	4	-4	83	-76	3	1	-6	61	60	3	10	-1	147	152
1	1	4	172	181	1	9	0	162	162	2	4	-5	105	107	3	2	0	130	-151	3	10	-2	89	93
1	1	5	111	103	1	9	1	139	149	2	4	-6	184	179	3	2	1	178	189	3	10	-3	0	23
1	1	6	244	233	1	9	2	165	166	2	5	0	163	-181	3	2	2	258	268	3	10	-4	37	50
1	1	-1	20	-16	1	9	3	68	72	2	5	1	362	-351	3	2	3	0	-11	3	11	0	49	-45
1	1	-2	792	797	1	9	4	73	75	2	5	2	236	233	3	2	4	170	-162	3	11	1	123	-124
1	1	-3	95	102	1	9	-1	384	397	2	5	3	0	-32	3	2	5	127	127	3	11	2	203	204
1	1	-4	168	-168	1	9	-2	159	166	2	5	4	332	-329	3	2	-1	547	-539	3	11	-1	323	314
1	1	-5	101	-104	1	9	-3	81	77	2	5	5	52	46	3	2	-2	89	-47	3	11	-2	50	52
1	1	-6	119	120	1	9	-4	79	76	2	5	-1	387	-370	3	2	-3	75	-83	3	11	-3	63	-72
1	2	0	435	-423	1	10	0	38	6	2	5	-2	187	192	3	2	-4	470	-469	3	12	0	103	110
1	2	1	418	-417	1	10	1	107	-102	2	5	-3	67	43	3	2	-5	32	12	3	12	1	53	-51
1	2	2	48	-43	1	10	2	235	230	2	5	-4	370	-381	3	2	-6	209	199	3	12	-1	0	2
1	2	3	266	262	1	10	3	163	168	2	5	-5	117	111	3	3	0	89	102	3	12	-2	238	-239
1	2	4	42	48	1	10	4	54	-63	2	5	-6	172	164	3	3	1	243	-241	4	0	0	358	-367
1	2	5	209	-210	1	10	-1	234	217	2	6	0	156	161	3	3	2	229	224	4	0	1	0	-1
1	2	6	0	14	1	10	-2	0	22	2	6	1	26	-11	3	3	3	142	137	4	0	2	110	103
1	2	-1	577	553	1	10	-3	0	4						3	3	4	0	-12	4	0	3	115	109

Table 1. *(Continued)*

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

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 GANT-ZEL, SPARKS, and TRUEBLOOD. Atomic scattering factors obtained from IBERS (1962) were used for neutral nitrogen, oxygen, sulfur, and

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	.333	.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

hydrogen, and divalent magnesium. All reflections, including those too weak to be observed, were given equal weighting factors. The function minimized was $\Sigma (|F_o| - |F_c|)^2 / \Sigma |F_o|^2$. 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

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	.001	.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	.001	.0007	.001	.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

form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ 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 Å²), 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.

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

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.

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.

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_{13}	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.

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 distances, 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.

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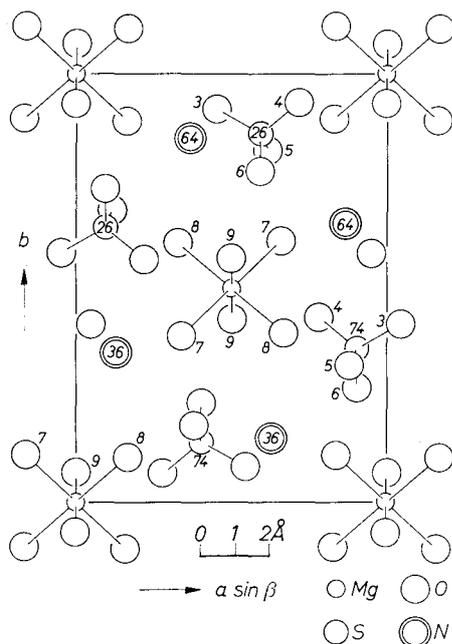
Fig. 1. Crystal structure of $Mg(NH_4)_2(SO_4)_2 \cdot 6H_2O$: The numbers at the sulfur and nitrogen atoms indicate their z coordinates. The numbers beside some of the oxygen atoms correspond to the numbering of Table 2.

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.

Table 6. *Principal rms amplitudes*

Atom	u_1	u_2	u_3
Mg_1	.15 Å	.15 Å	.16 Å
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.

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 we report 1.49 Å as the most likely interpretation of our results for the S—O bond distance in sulfate.

The hydrated magnesium ion

The Mg—O distances range from 2.051 to 2.083 Å, each ± 0.005 Å (Table 8), 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 ampli-

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.

tude 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, we consider the in-phase correction to be the best interpretation of the data, but we have 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 ± 0.3°. We attribute these small distortions 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 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.

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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.
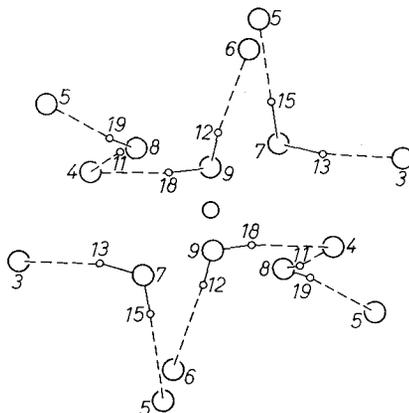
Fig. 2. Hydrogen bonding of the water molecules: The central atom is Mg at $\frac{1}{2}$ $\frac{1}{2}$ 0. The numbering corresponds to that of Table 2. The projection is the same as that of Figure 1.
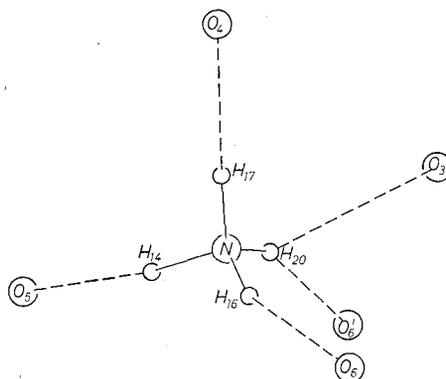
Fig. 3. Hydrogen bonding of the NH_4^+ ion: Projected along [100]

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 is 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.

Acknowledgements

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