

The Crystal Structure of Lecontite, $\text{NaNH}_4\text{SO}_4 \cdot 2\text{H}_2\text{O}$ *

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The crystal structure of lecontite, $\text{NaNH}_4\text{SO}_4 \cdot 2\text{H}_2\text{O}$, has been determined from three-dimensional X-ray data, obtained by the equi-inclination Weissenberg technique, and refined by the full-matrix least-squares method to a final R index of 0.08 for 607 measured reflexions. The unit cell is orthorhombic with $a=8.216$, $b=12.854$, $c=6.232$ Å and space group $P2_12_12_1$. The structure shows chains of Na octahedra sharing one face with each other (the Na–Na distance is 3.15 Å). The SO_4 tetrahedron is regular. The NH_4^+ ion coordinates seven oxygen atoms forming a very irregular polyhedron.

Introduction

The present investigation forms a part of a series of crystal structure determinations on sulphate minerals.

Faust & Bloss (1963) showed that synthetic $\text{NaNH}_4\text{SO}_4 \cdot 2\text{H}_2\text{O}$ is identical with natural lecontite, on the basis of the close agreement of the optical properties, physical properties, and diffraction data. They carried out a diffractometric study on both natural and synthetic lecontite, giving the cell dimensions $a=8.23$; $b=12.88$; $c=6.26$ Å, and the space group $P2_12_12_1$.

Experimental

Crystals suitable for structural study were prepared by evaporation of an aqueous solution of sodium sulphate and ammonium sulphate.

The lattice constants were determined by measuring, at room temperature, the 2θ values of appropriate reflexions for each of the constants to be determined, and extrapolating the corresponding interplanar distances,

plotted against $\frac{1}{2} \left(\frac{\cos^2\theta}{\sin\theta} + \frac{\cos^2\theta}{\theta} \right)$, to $2\theta=180^\circ$.

The measurements were made with a Wooster single-crystal diffractometer.

The calculated density of 1.747 g.cm^{-3} on the basis of 4 stoichiometric units in the unit cell agrees very well with the one observed on synthetic crystals of 1.745 g.cm^{-3} (Faust & Bloss, 1963).

Crystals of cylindrical shape, produced by grinding, were found to be satisfactory for intensity measurements. The crystal used in this investigation had an average diameter of 0.42 mm and the cylinder axis corresponded to the z direction.

There are no systematic absences among the reflexions hkl , $h0l$, $0kl$ and $hk0$. Reflexions $h00$ with h odd,

$0k0$ with k odd and $00l$ with l odd are absent. This leads to the space group $P2_12_12_1$. As in this space group all atoms must occupy general positions, the asymmetric unit is $\text{NaNH}_4\text{SO}_4 \cdot 2\text{H}_2\text{O}$.

Crystal data

Orthorhombic,
 $a=8.216 \pm 0.008$, $b=12.854 \pm 0.0011$, $c=6.232 \pm 0.008$ Å
 $U=658.2$ Å³
 Space group $P2_12_12_1$
 $D_m=1.745 \text{ g.cm}^{-3}$ $D_x=1.747 \text{ g.cm}^{-3}$
 $Z=4$
 $\mu=47.9 \text{ cm}^{-1}$.

Three-dimensional intensity data were collected by equi-inclination Weissenberg photographs taken around the c axis (l from 0 to 4) using the multiple film technique with Cu $K\alpha$ radiation ($\lambda=1.5418$ Å). A total of 664 reflexions was recorded, but 57 of them were too weak to be measured. The integrated intensities were evaluated by means of a microdensitometer, and converted to F^2 values by the application of the Lorentz–polarization and absorption corrections with the use of a program written by Albano, Bellon & Pompa (1963) for the IBM 1620 computer. A correction for the incipient but incomplete α_1 – α_2 splitting was also applied.

Wilson's method was then used to estimate an approximate scale factor and an overall temperature parameter for each level. The analytic constants for the calculation of the atomic scattering factors in the process of solution and refinement of the structure are those given by Moore (1963) for neutral atoms.

Structure determination

The approximate position of the sulphur atom and of the four tetrahedrally coordinated oxygen atoms around it were derived readily from a three-dimensional Patterson synthesis. At the same time, and independently, a statistical test for giving the signs to the struc-

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ture factors of reflexions of the $hk0$ centrosymmetric section was carried out, according to Cochran & Woolfson's probability formula (Woolfson, 1961). The $hk0$ Fourier synthesis, computed by the signs given by the statistical method, showed the SO_4 group to be in the same position as the one obtained by the interpretation of the Patterson synthesis. The Na atom and the remaining two oxygen atoms were found by means of a three-dimensional Fourier synthesis, computed on the basis of the contribution of the SO_4 group. Two further and more detailed Fourier syntheses were then computed to locate the Na atom and to refine the positions of all atoms previously placed. At this stage the reliability index R was 0.25.

The structure was refined by the method of least squares, using first a program written by Albano, Bellon, Pompa & Scatturin (1963) for the IBM 1620 computer. This program uses 3×3 blocks for positional parameters and 1×1 blocks for individual isotropic thermal parameters. By four subsequent cycles of isotropic refinement, each followed by a proper re-scaling of F_o 's, the R value decreased to 0.13.

The refinement including anisotropic thermal parameters was then continued by means of a program written by Sgarlata (1965) for the Elea 6001 digital computer, which minimizes the unweighted differences $F_o - F_c$ and takes into account the full matrix. After three cycles the R index dropped to 0.092 for all the observed reflexions, and to 0.080 with the exclusion of 5 reflexions affected by extinction.

By the atomic coordinates obtained from the last cycle of least squares, a three-dimensional difference Fourier synthesis was computed in order to locate the hydrogen atoms, the positions of which were checked also by steric considerations and charge balances. Both the water hydrogen atoms and the NH_4 hydrogen atoms were found in this map, and they were given a general isotropic thermal parameter of 5.0 \AA^2 . Because in the Fourier difference map the peaks belonging to the hydrogen atoms of the water molecule and of the NH_4^+ ion [especially H(6) and H(8)] were poorly defined and somewhat spread out, the positions of the hydrogen atoms were determined according to the scheme of Fig. 1, *i.e.* near the lines $\text{H}_2\text{O}-\text{SO}_4$ and NH_4-O . The data were not of sufficient quality to warrant an attempt to refine the hydrogen parameters, but their presumed positions were included in the structure factor calculations for the final least-squares refinement cycle of the heavy atoms. The b_{33} coefficient of the Na atom, which persisted in being negative during these cycles, was forced to become slightly positive each time, but even in the last cycle it did not reach a positive value, and it was held at a near zero value. During the fourth and last cycle there were no variations in the atomic coordinates, but only slight variations in the thermal parameters. The standard deviations in the b_{ij} and positional parameters were computed, according to Cruickshank (1949, 1956), with the program written by Nardelli, Andreotti, Do-

miano & Musatti (1965) for the Elea 6001 computer. The final atomic positional parameters and their standard deviations are given in Table 1. The anisotropic thermal parameters are shown in Table 2, and in Table 3 are given the thermal ellipsoids related to the crystallographic axes. The observed and calculated structure factors are listed in Table 4.

Description of the structure

The structure is illustrated in Fig. 1. The bond distances and bond angles, calculated from the positional parameters of Table 1, are given in Table 5.

The SO_4 group has the usual regular tetrahedral coordination, with a mean S-O distance of 1.47 \AA , and angles with small deviations from the tetrahedral ones.

Table 1. Final atomic coordinates and their standard deviations

(σ) applies to the rightmost digit of the quantity in question

	x/a	y/b	z/c
S	0.0842 (2)	0.1277 (1)	0.3733 (6)
Na	0.2652 (4)	0.4847 (2)	0.9133 (8)
O(1)	0.0690 (9)	0.2001 (6)	0.1890 (28)
O(2)	0.0617 (12)	0.1894 (3)	0.5740 (27)
O(3)	0.2450 (10)	0.0807 (5)	0.3719 (24)
O(4)	0.0392 (10)	0.5455 (5)	0.1380 (20)
O(5)	0.2115 (7)	0.6350 (4)	0.6949 (16)
O(6)	0.0793 (6)	0.4039 (4)	0.6625 (19)
N	0.1719 (8)	0.8541 (5)	0.3678 (24)
H(1)	0.910	0.145	0.700
H(2)	0.710	0.190	0.780
H(3)	0.570	0.175	0.370
H(4)	0.480	0.090	0.360
H(5)	0.395	0.200	0.855
H(6)	0.410	0.060	0.860
H(7)	0.230	0.160	0.990
H(8)	0.240	0.160	0.780

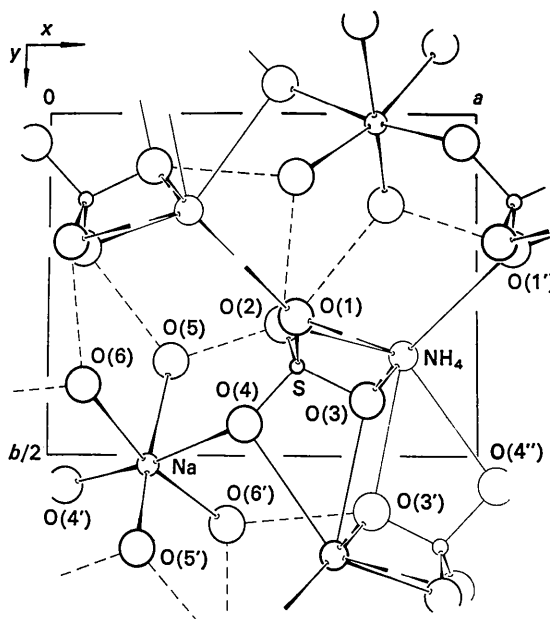


Fig. 1. Structure of lecontite viewed along $[001]$.

Table 2. *The final anisotropic temperature factors and their standard deviations*

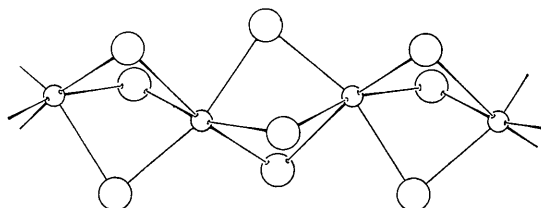
Thermal parameters are in the form $\exp[-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)]$
(σ) applies to the rightmost digit of the quantity in question

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
S	0.0048 (1)	0.0026 (0)	0.0069 (16)	-0.0010 (3)	0.0004 (10)	0.0001 (6)
Na	0.0091 (2)	0.0041 (1)	0.0000 (24)	-0.0017 (7)	-0.0005 (19)	0.0009 (12)
O(1)	0.0146 (5)	0.0048 (4)	0.0245 (78)	-0.0013 (22)	-0.0011 (63)	0.0127 (45)
O(2)	0.0171 (9)	0.0055 (1)	0.0191 (66)	-0.0080 (16)	0.0132 (63)	-0.0074 (24)
O(3)	0.0051 (1)	0.0055 (3)	0.0386 (71)	0.0007 (15)	-0.0073 (41)	0.0007 (36)
O(4)	0.0066 (4)	0.0043 (3)	0.0108 (51)	0.0038 (16)	0.0017 (42)	0.0035 (30)
O(5)	0.0103 (6)	0.0038 (2)	0.0041 (41)	0.0016 (14)	0.0019 (39)	-0.0051 (20)
O(6)	0.0073 (3)	0.0048 (2)	0.0164 (50)	-0.0005 (14)	-0.0024 (36)	-0.0042 (24)
N	0.0108 (3)	0.0030 (2)	0.0198 (62)	-0.0011 (15)	-0.0165 (38)	0.0010 (30)

Table 3. *Root mean square thermal vibrations along the ellipsoid axes (\AA), magnitude of the principal axes (\AA^2) and angles ($^\circ$) between the crystallographic axes and the principal axes of the vibration ellipsoids*

	r.m.s.	B_j	α	β	γ
S	0.12	1.22	28	68	74
	0.15	1.81	113	23	90
	0.12	1.06	105	96	16
Na	0.17	2.20	35	55	89
	0.19	2.97	125	35	87
	0.01	0.01	89	93	3
O(1)	0.22	3.91	10	86	81
	0.27	5.59	99	50	42
	0.13	1.42	87	40	130
O(2)	0.17	2.42	46	50	110
	0.29	6.74	44	124	65
	0.16	2.06	95	57	33
O(3)	0.21	3.64	86	4	91
	0.28	6.12	99	88	9
	0.13	1.25	10	94	81
O(4)	0.14	1.55	123	91	33
	0.21	3.46	64	32	72
	0.13	1.29	45	122	63
O(5)	0.18	2.57	45	129	70
	0.20	3.06	45	46	100
	0.06	0.29	97	69	22
O(6)	0.17	2.32	127	64	49
	0.21	3.60	88	33	123
	0.15	1.77	37	72	59
N	0.16	1.96	90	8	98
	0.24	4.72	133	84	44
	0.13	1.30	43	85	47

On the other hand, the coordination polyhedron of the NH_4^+ ion is very irregular, both in its shape and in the $\text{NH}_4\text{-O}$ distances. Five $\text{NH}_4\text{-O}$ distances range from 2.82 to 3.01 \AA , two more are at 3.27 and 3.32 \AA ; an eighth distance $\text{NH}_4\text{-O}(5'')$, of 3.49 \AA , seems to be too long to be an ammonium-oxygen bond distance

Fig. 2. Chains of NaO_6 octahedra parallel to c .

(*International Tables for X-ray Crystallography*, 1962). Among these bonds, four are arranged nearly tetrahedrally, with distances ranging from 2.82 to 3.01 \AA , and they were assigned to hydrogen bridges N-H-O . As it was said before, the peaks belonging to H(6) and H(8) were scarcely defined in the difference map; according to the assumed positions for these hydrogen atoms the NH_4^+ tetrahedron would be pretty distorted. Since the same ion has five neighbour oxygen atoms at distances less than 3 \AA , and there are only four hydrogen atoms, this suggests a kind of partially statistical distribution of regular tetrahedral NH_4^+ ions within the structure, possibly with some preferred orientation for either H(7) or H(5), pointing toward O(1) and O(1') respectively. The coordination polyhedra of the NH_4^+ ion are linked together by the sharing of one edge O(3)-O(3'), to form zigzag chains, elongated in the c direction; these chains are connected to one another by the sharing of one corner O(1), to form a three-dimensional network, with channels in the c direction, along the screw axis $\frac{1}{2}0z$.

The Na atoms, which are lying nearly on the screw axis, share opposite faces of their coordination octahedra in order to form infinite straight chains, parallel to the c axis, filling the channels of the ammonium-oxygen network. These chains are not evident in Fig. 1 because they are perpendicular to the plane of the drawing. One of the chains is shown in Fig. 2. This kind of connexion of Na octahedra is rather unusual, but already known, for instance in the isostructural sodium sulphate (Frevel, 1940) and sodium chromate (Miller, 1936), as well as in sodium thioantimonate (Grund & Preisinger, 1950). Thus the distance Na-Na is forced to be very short (3.15 \AA), even shorter than that found in the above structures (3.30 \AA). The nearness of pairs of Na^+ ions is the reason for deformation of the Na polyhedron, elongated in the Na-Na direction because of the electrostatic repulsion between the cations (the Na-Na distance would be about 2.8 \AA for regular Na octahedra sharing one face). A significant feature is the b_{33} thermal parameter of sodium, which remained at slightly negative values during all the cycles of refinement; such irregular behaviour can be explained by the lack of freedom of Na, which is not allowed to vibrate in the c direction (see also Table 3), and by the use of scattering factors which

Table 4. *Observed and calculated structure factors* ($\times 10$)

h	k	l	F_o	F_c	F_e	h	k	l	F_o	F_c	F_e	h	k	l	F_o	F_c	F_e	h	k	l	F_o	F_c	F_e									
2	0	0	9	9		0	16	0	117	117		3	13	1	88	94	42	85	1	12	2	43	0	43	2	12	3	132	124	106	-65	
4			272	291	291	1			36	31	31	4			60	61	60	15	2		39	-30	26	3			60	50	50	15		
6			628	692	692	2			51	55	55	5			103	110	100	88	3		225	228	-228	4			46	46	-45	-15		
8			146	136	-136	1	0	1	500	484	484	6			92	99	-33	-94	4		115	112	21	-111	5		91	97	58	78		
10			11	-11		2			564	669	-669	0	14	1	57	62	62		5		29	20	17	11	6		33	32	-19	26		
1	0	84	51	-51		3			54	44	44	1			49	46	-1	46	6		34	36	-22	29	0	13	3	12	12	-12		
2			332	315	-315	4			130	120	-120	2			132	120	-120	-35	0	13	2	2	2	2	0	13	3	60	-36	72	-33	
3			256	312	-312	5			112	105	-105	3			152	159	-159	-14	1		177	175	-174	-21	2		1	60	72	-1	-72	
4			522	730	-730	6			102	91	-91	4			91	89	-89	11	2		61	67	18	65	3		50	43	-25	35		
5			168	160	-160	7			114	103	-103	5			50	45	4	-45	3		12	3	12	4	4		34	42	19	36		
6			86	87	-87	8			256	247	247	0	15	1	125	129	129		4		41	44	-35	-28	5		37	74	38	64		
7			190	171	171	9			76	85	85	2			92	94	-81	40	5		26	26	95	-16	0	14	3	54	52	16	16	
8			141	126	-126	1	1	1	450	434	-434	3			91	96	-96	-4	2		80	72	28	2	2		76	87	79	37		
9			139	126	136	2			512	585	-440	-386	4			36	39	-39	-3	3		55	58	9	-58	3		80	87	79	37	
0	2	0	194	254		3			106	116	-116	3	1	1	94	91	55	73	4		67	60	57	-21	0	15	3	64	77	-77	-77	
1			321	846	846	4			96	100	-91	42	2		60	61	-1	-61	2		57	64	-5	-64	1		82	84	51	67		
2			310	399	-399	110			212	210	144	-154	0	2	2	623	499	499	55	0	15	2	2	2	0	4	0	402	399	399		
3			127	110		6			238	235	40	232	2		79	62	-62	7	1		88	66	-86	7	2		72	73	-73			
4			350	389	389	7			117	113	4	113	3		448	431	-431	2	3		16	16	2	3	3		142	147	-147			
5			153	128	-128	8			169	162	156	45	4		74	68	68		3		34	39	25	-30	4		54	52	16	16		
6			154	133	-133	9			103	91	65	78	5		40	37	37	20	1		80	77	28	2	2		86	87	79	37		
7			322	318	-318	10			105	123	122	-18	6		40	16	16		2		359	356	7	-356	6		61	67	-67			
8			147	135	135	0	2	1	510	494	-494		7		282	298	-298		3		184	198	-198		7	6	7	64	67	-67		
9			54	57	-57	1			309	261	261	-9	8		86	79	79		4		66	51	-51	8	8		75	68	68			
10			497	24	-61	2			497	24	-52	56	9		44	62	-62	9	5		60	58	58	9	5		5	6	6			
1	3	0	383	688	-688	3			56	43	-43	43	10		25	33	-33		6		11	-11	0	1	4	0	4	456	5	456		
2			66	66	-66	4			192	185	81	167	1	1	2	203	121	-121	-5	7		152	166	-166	1		83	49	5	49		
3			385	433	-433	5			259	254	213	139	2		346	327	6	-327	8		193	223	-223	2		297	261	168	-200			
4			217	217	-209	6			374	380	380	0	3		149	137	137	147	9		37	73	73	3	29		184	149	29	-147		
5			369	379	-379	7			171	174	-174	-9	4		197	187	114	149	0	1	3	64	20	20	4		287	279	123	181		
6			185	180	180	8			117	113	37	107	5		60	59	-53	-24	1		262	175	137	109	5		105	94	-77	54		
7			90	66	66	9			89	91	-84	35	6		149	161	-59	128	2		196	180	-43	-175	6		130	136	-49	-135		
8			188	184	184	64			30	27	-4	-27	7		131	105	-90	55	3		71	78	7	10	7		147	157	-157	2		
0	4	0	113	120	120	1			292	294	262	-135	9		71	68	59	-34	5		69	57	-57	7	0		109	120	-40	119		
1			474	735	-735	10			545	602	562	-210	10		210	217	-217	-39	6		212	211	151	-176	2	4	0	357	270	-270	-270	
2			276	233	-233	1			293	285	144	246	0	2	2	245	159	159	-39	7		97	102	100	100	0	2	4	402	399	399	-241
3			80	82	-82	4			107	104	96	40	1		475	381	381	21	8		50	31	31	0	1		97	72	72	3		
4			108	101	-101	5			88	83	-83	-8	2		269	234	-190	137	9		49	66	-30	59	3		155	147	-116	-91		
5			355	433	350	6			263	271	168	213	3		340	340	-314	43	0	2	3	418	229	-229	-175	4		228	229	-175	-175	
6			240	242	242	7			190	188	-136	130	4		332	333	83	323	0	3	351	269	-148	225	5		227	227	135	202		
7			191	199	199	8			140	130	-127	30	5		218	202	193	-62	2		102	97	89	41	6		111	116	81	86		
8			124	103	103	9			43	41	17	38	6		136	125	-65	-107	3		192	155	153	30	7		175	174	-38	170		
9			185	172	172	10			40	10	50	-49	7		175	143	-163	76	4		4	-66	52	4	4		4	4	-41	-62		
10			39	32	-32	0	4	1	503	527	-527	-11	8		225	247	-247		5		108	101	-68	75	9		42	40	33	-23		
1	5	0	234	251	-251	1			168	165	165	0	9		108	116	37	-14	6		222	223	-222	-27	0	3	4	54	47	47		
2			403	472	472	2			436	430	355	402	10		406	39	-3	-116	7		173	188	156	-105	1		396	335	6	335		
3			401	455	455	4			369	377	-373	14	0	3	2	602	419	419	14	8		51	203	203	2	2		208	209	-175	-175	
4			430	472	209	5			296	297	-181	236	1		448	416	320	-266	0	3	59	78	72	31	3		163	147	40	142		
5			100	95	-95	6			222	210	-41	206	2		504	491	-18	-491	1		107	56	51	-25	5		203	168	147	83		
6			40	37	37	7			68	67	66	-14	3		211	209	111	178	1		107	56	51	-25	5		100	179	-67	167		
7			194	200	200	8			107	97	-98	8	4		149	130	-68	-97	2		353	333	133	263	6		60	64	62	62		
8			103	93	-93	9			67	56	40	40	5		149	130	-68	-97	3		215	215	102	-190	7		130	134	-53	53		
9			62	44	-44	10			122	128	40	-122	7		214	202	-127	-199	4		44	38	-19	-34	8		143	168	-152	73		
0	6	0	267	287	287	0	5	1	199	184	-11	184	9		149	132	-126	42	5		241	24	-24	-247	0	4	4	322	252	252	-252	
1			191	170	170	2			283	285	272	86	10		36	65	-16	64	8		80	78	17	77	2		212	203	203	-203		
2			158	165	-165	3			213	216	-117	162	0	4	2	341	324	-324		9		49	67	3	67	4		81	100	-100	-3	
3			163	159	159	4			126	126	59	-105	0	4	3	47	36	6	36	0	4	3	460	407	-407	5		246	251	-251	251	
4			57	57	57	5			198	199	-21	198	2		335	326	-224	238	1		227	221	-55	-215	6							

Table 5. *Interatomic distances (Å) and bond angles (°) with their standard deviations*

(σ) applies to the rightmost digit of the quantity in question

Na-O(4)	2.453 (10)	S-O(1)	1.483 (14)	O(4'')-NH ₄ -O(3')	46.8 (2)
Na-O(5)	2.404 (8)	S-O(2)	1.492 (14)	O(4')-NH ₄ -O(3)	85.6 (4)
Na-O(6)	2.468 (9)	S-O(3)	1.452 (8)	O(4'')-NH ₄ -O(3'')	84.3 (4)
Na-O(4')	2.382 (11)	S-O(4)	1.466 (7)	O(4'')-NH ₄ -O(1)	127.3 (5)
Na-O(5')	2.341 (9)			O(4'')-NH ₄ -O(2)	125.7 (5)
Na-O(6')	2.419 (9)	O(1)-S-O(2)	107.8 (6)	O(4'')-NH ₄ -O(1')	99.7 (3)
		O(1)-S-O(3)	109.4 (6)	O(3')-NH ₄ -O(3)	72.8 (7)
O(4)-Na-O(5)	85.9 (3)	O(1)-S-O(4)	110.9 (6)	O(3')-NH ₄ -O(3'')	73.5 (7)
O(4)-Na-O(6)	81.3 (3)	O(2)-S-O(3)	109.8 (7)	O(3')-NH ₄ -O(1)	94.5 (4)
O(4)-Na-O(4')	166.7 (7)	O(2)-S-O(4)	109.8 (6)	O(3')-NH ₄ -O(2)	92.4 (3)
O(4)-Na-O(5')	81.0 (3)	O(3)-S-O(4)	109.1 (4)	O(3')-NH ₄ -O(1')	146.1 (4)
O(4)-Na-O(6')	91.6 (3)			O(3)-NH ₄ -O(3'')	141.7 (5)
O(5)-Na-O(6)	89.1 (3)			O(3)-NH ₄ -O(1)	44.2 (3)
O(5)-Na-O(4')	81.2 (3)	NH ₄ -O(4'')	3.009 (9)	O(3)-NH ₄ -O(2)	119.3 (4)
O(5)-Na-O(5')	165.3 (6)	NH ₄ -O(3')	2.973 (9)	O(3)-NH ₄ -O(1')	116.1 (6)
O(5)-Na-O(6')	82.2 (3)	NH ₄ -O(3)	3.322 (20)	O(3'')-NH ₄ -O(1)	122.7 (4)
O(6)-Na-O(4')	101.4 (3)	NH ₄ -O(3'')	3.274 (20)	O(3'')-NH ₄ -O(2)	45.4 (4)
O(6)-Na-O(5')	82.4 (3)	NH ₄ -O(1)	3.004 (16)	O(3'')-NH ₄ -O(1')	102.0 (5)
O(6)-Na-O(6')	169.1 (4)	NH ₄ -O(2)	2.908 (16)	O(1)-NH ₄ -O(2)	80.9 (4)
O(4')-Na-O(5')	112.2 (3)	NH ₄ -O(1')	2.821 (10)	O(1)-NH ₄ -O(1')	114.7 (7)
O(4')-Na-O(6')	83.7 (3)			O(2)-NH ₄ -O(1')	108.3 (5)
O(5')-Na-O(6')	104.7 (3)				

have a spherical symmetry, which, of course, is not exactly proper for such an atom as Na in this structure.

The SO₄ tetrahedra make ammonium-sulphur-ammonium bridges, by the sharing of three of their edges with three surrounding NH₄ polyhedra, and one corner with another NH₄. Furthermore, the SO₄ groups make indirect connexions between the Na chains and the NH₄ network.

The two water molecules belong to the Na polyhedron [oxygen atoms indicated by the symbols O(5) and O(6)] and make additional hydrogen bridges between Na and NH₄ polyhedra. The distances between oxygen atoms connected by hydrogen bridges range from 2.77 to 2.81 Å, in close agreement with the lengths of hydrogen bonds given in the literature (*International Tables*, 1962). The atomic coordinates of the four hydrogen atoms belonging to the water molecules are not refined in the same way as the four hydrogen atoms of the NH₄⁺ ion, and lead therefore to a lack of accuracy in the bond lengths and angles.

References

- AHMED, F. R. & CRUICKSHANK, D. W. J. (1953). *Acta Cryst.* **6**, 385.
- ALBANO, V., BELLON, P. L. & POMPA, F. (1963). *Ric. Sci.* (III-A), 285.
- ALBANO, V., BELLON, P. L., POMPA, F. & SCATTURIN, V. (1963). *Ric. Sci.* (III-A), 1067.
- CRUICKSHANK, D. W. J. (1949). *Acta Cryst.* **2**, 65.
- CRUICKSHANK, D. W. J. (1949). *Acta Cryst.* **2**, 154.
- CRUICKSHANK, D. W. J. (1950). *Acta Cryst.* **3**, 72.
- CRUICKSHANK, D. W. J. (1952). *Acta Cryst.* **5**, 511.
- CRUICKSHANK, D. W. J. (1956). *Acta Cryst.* **9**, 747.
- FAUST, R. J. & BLOSS, F. D. (1963). *Amer. Min.* **48**, 180.
- FREVEL, L. K. (1940). *J. Chem. Phys.* **8**, 290.
- GRUND, A. & PREISINGER, A. (1950). *Acta Cryst.* **3**, 363.
- International Tables for X-ray Crystallography* (1962). Vol. III, p.259. Birmingham: Kynoch Press.
- MILLER, J. J. (1936). *Z. Kristallogr.* **94**, 131.
- MOORE, F. H. (1963). *Acta Cryst.* **16**, 1169.
- NARDELLI, M., ANDRETTI, G., DOMIANO, P. & MUSATTI, A. (1965). *Ric. Sci.* **35**, (I-A), 477.
- SGARLATA, F. (1965). *Per. Min.* **24**, 401.
- WOOLFSON, M. M. (1961). *Direct Methods in Crystallography*. Oxford: Clarendon Press.