

Refinement of the Crystal Structure of Thenardite, $\text{Na}_2\text{SO}_4(\text{V})$

ANDERS G. NORD

*Institute of Inorganic and Physical Chemistry, University of Stockholm,
Box 6801, S-113 86 Stockholm, Sweden*

The crystal structure of thenardite, $\text{Na}_2\text{SO}_4(\text{V})$, has been analysed and refined by the method of least squares on the basis of three-dimensional X-ray diffractometer data down to a final R value of 3.6% for about 800 independent reflections. At 25°C the orthorhombic ($Fddd$) unit cell has the dimensions $a = 5.8596$, $b = 12.3044$, $c = 9.8170$ Å. The investigation has confirmed the general features of the atomic arrangement reported in 1932 by Zachariasen and Ziegler. The crystal structure may be described in terms of distorted NaO_6 octahedra and nearly regular SO_4 tetrahedra. All S-O distances in these are 1.476 ± 0.001 Å.

This investigation was performed in order to elucidate the size and configuration of the sulphate ion as precisely as possible. For this reason the thenardite phase is convenient since all S-O distances are equal due to the space group ($Fddd$) where the sulphur atom is fixed in a special point position with 222 point symmetry. Moreover, it is interesting to compare the regularity and dimensions of the sulphate ion in different sulphates.

The phase diagram of sodium sulphate shows some very interesting features. According to Gmelin¹ there are eight different anhydrous phases of sodium sulphate. The crystallographic data of most of these phases are quite unsatisfactory and insufficient. The phase $\text{Na}_2\text{SO}_4(\text{V})$ is usually called thenardite after the mineral. It is reported to be stable between 32°C and about 180°C.¹ It seems that the presence of traces of H_2O in inclusions changes the conditions for the stability of thenardite.²

The present results have confirmed the general features of the atomic arrangement reported in 1932 by Zachariasen and Ziegler.³

EXPERIMENTAL

Preparation of the crystals. When a water solution of sodium sulphate is evaporated above 32°C, crystals of thenardite are formed (but below 32°C $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ crystals are obtained). There are several contradictory recommendations in the literature as to

proper conditions for the evaporation process.^{1,2} A fairly quick evaporation overnight at 70°C gave the most well-developed crystals. This was the best result from a series of experiments. These crystals also gave the most distinct powder diffraction pattern. The sample contained small amounts of moisture; on ignition the loss of H₂O was 0.14 %.

X-Ray powder diffraction data. The powder pattern of the sample was found to be in good accordance with the data given by Swanson and Fuyat.⁴ Values for the cell dimensions were calculated from a photograph taken with strictly monochromatized CuK α_1 radiation ($\lambda=1.54050$ Å) in a Guinier-Hägg type focusing camera. Potassium chloride ($a=6.29228$ Å)⁵ was used as an internal standard. The lattice parameters were

Table 1. X-Ray powder data for Na₂SO₄(V) at 25°C. CuK α_1 radiation ($\lambda=1.54050$ Å).

<i>hkl</i>	sin ² θ obs	sin ² θ calc	<i>I</i> _{obs}	<i>d</i> (Å) obs	<i>d</i> (Å) calc
111	0.02736	0.02735	60	4.6567	4.6572
022	0.04028	0.04030	16	3.8378	3.8369
131	0.05873	0.05870	47	3.1784	3.1791
040	0.06278	0.06270	41	3.0742	3.0761
113	0.07660	0.07660	100	2.7830	2.7830
220	0.08478	0.08479	45	2.6453	2.6452
202	0.09370	0.09374	1	2.5163	2.5158
004	0.09859	0.09850	1	2.4531	2.4542
133	0.10799	0.10795	5	2.3439	2.3443
222	0.10931	0.10940	22	2.3297	2.3287
151	0.12142	0.12140	4	2.2105	2.2106
044	0.16124	0.16120	4	1.9182	1.9185
311	0.16562	0.16559	2	1.8927	1.8929
153	0.17070	0.17065	47	1.8643	1.8646
115	0.17508	0.17510	6	1.8408	1.8407
224	0.18336	0.18330	6	1.7988	1.7991
260	0.21026	0.21019	21	1.6798	1.6801
313	0.21490	0.21484	12	1.6616	1.6618
244	0.23030	0.23031	6	1.6050	1.6050
262	0.23472	0.23481	3	1.5898	1.5895
026	0.23732	0.23730	3	1.5811	1.5812
333	0.24618	0.24619	20	1.5524	1.5524
351	0.25967	0.25964	3	1.5116	1.5116
173	0.26471	0.26470	10	1.4971	1.4971
400	0.27651	0.27647	1	1.4648	1.4649
206	0.29073	0.29074	11	1.4285	1.4285
371	0.35370	0.35369	4	1.2951	1.2951

refined from 27 reflections (Table 1) by the method of linear regression using the program POWDER.⁶ The dimensions of the orthorhombic unit cell (with standard deviations) at 25°C are:

$$\left. \begin{array}{l} a = 5.8596 \pm 5 \text{ \AA} \\ b = 12.3044 \pm 12 \text{ \AA} \\ c = 9.8170 \pm 10 \text{ \AA} \end{array} \right\} \begin{array}{l} (5.863) \\ (12.304) \\ (9.821) \end{array} \text{ Ref. 4.}$$

From X-ray photographic methods (oscillations and Weissenberg photographs around the *a* and *c* axes) the space group was, from the reflections systematically absent, uniquely determined as No. 70, *Fddd*⁷ in agreement with Zachariassen and Ziegler. The crystal selected for collection of X-ray data had the dimensions 0.15 mm (in the direction of the *c* axis) \times 0.06 mm \times 0.03 mm and was mounted along the *c* axis. The X-ray intensity data were collected with $\theta-2\theta$ scan technique on an automatic single-

crystal diffractometer Siemens AED (Automatischer Einkristall-Diffraktometer) equipped with a graphite monochromator and a scintillation detector. MoK α radiation was used. All independent reflections with $\theta \lesssim 50^\circ$ were measured at a temperature of 22°C. Punched paper tape was used as input/output medium for the diffractometer. The computer programs used for the calculations involved in the present work are summarized in Table 9. A survey of the IBM 360/75 programs used at this institute is also given in a paper by Brandt and Nord.⁸

All reflections with $\sigma(I_{\text{net}})/I_{\text{net}} < 0.50$ were accepted leaving 812 reflections from about 900 measured ones. The net intensities were corrected for Lorentz, polarization and absorption ($\mu = 10.3 \text{ cm}^{-1}$) effects.

REFINEMENT OF THE CRYSTAL STRUCTURE

All atom position parameters were readily determined from peaks in a three-dimensional Patterson function $P(uvw)$. These parameters agreed within a few per cent with those given by Zachariasen and Ziegler. The crystal structure was then refined by the full-matrix least-squares program LALS minimizing $\sum w(|F_{\text{obs}}| - |F_{\text{calc}}|)^2$. Hughes' weighting function⁹ with $h = 4$ was used in the final refinements. The atomic scattering curves applied were those for S⁰, Na⁺, and O⁻. Correction was made for the real part of the anomalous dispersion. After a few cycles with isotropic temperature factors the reliability index $R = \sum ||F_{\text{obs}}| - |F_{\text{calc}}|| / \sum |F_{\text{obs}}|$ dropped to 5.0%. When all atoms in the model were allowed to vibrate anisotropically (within the restrictions fixed by the space group symmetry) the final R was reduced to 3.6% for all 812 reflections. This large drop in weighted and unweighted R values from the isotropically to the anisotropically refined model enables the Hamilton test¹⁰ to show, that the model with anisotropically vibrating atoms is the more realistic one. The weighting scheme obtained in the final cycle of the anisotropic refinement is shown in Table 2. Reflections with $1.20 < |F_{\text{obs}}/F_{\text{calc}}| < 0.70$ were given zero weight in the refinement.

A list of the observed and calculated structure factors is presented in Table 3. The atomic parameters arrived at in the last cycle of anisotropic refinement are listed in Table 4. The temperature factors obtained in the

Table 2. Weight analysis obtained in the final cycle of the anisotropic least-squares refinement of thenardite. w = weighting factor, $\Delta = ||F_{\text{obs}}| - |F_{\text{calc}}||$.

Interval F_{obs}	$\overline{w\Delta^2}$	Number of independent reflections	Interval $\sin \theta$	$\overline{w\Delta^2}$	Number of independent reflections
0.0 - 7.4	1.08	75	0.000 - 0.362	1.35	84
7.4 - 9.3	1.15	76	0.362 - 0.456	1.31	93
9.3 - 11.5	1.08	76	0.456 - 0.522	1.11	81
11.5 - 13.6	0.91	75	0.522 - 0.575	0.96	85
13.6 - 16.5	0.88	77	0.575 - 0.619	0.88	81
16.5 - 20.3	0.90	75	0.619 - 0.658	0.77	82
20.3 - 26.4	0.86	75	0.658 - 0.693	0.85	70
26.4 - 35.9	1.31	74	0.693 - 0.724	0.97	66
35.9 - 51.8	0.97	75	0.724 - 0.753	0.81	68
51.8 - 206.1	0.87	76	0.753 - 0.780	0.72	44

Table 3. Observed and calculated structure factors of thenardite, Na₂SO₄(V).

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
1	0	0	100	100															
2	0	0	400	400															
3	0	0	900	900															
4	0	0	1600	1600															
5	0	0	2500	2500															
6	0	0	3600	3600															
7	0	0	4900	4900															
8	0	0	6400	6400															
9	0	0	8100	8100															
10	0	0	10000	10000															
11	0	0	12100	12100															
12	0	0	14400	14400															
13	0	0	16900	16900															
14	0	0	19600	19600															
15	0	0	22500	22500															
16	0	0	25600	25600															
17	0	0	28900	28900															
18	0	0	32400	32400															
19	0	0	36100	36100															
20	0	0	40000	40000															
21	0	0	44100	44100															
22	0	0	48400	48400															
23	0	0	52900	52900															
24	0	0	57600	57600															
25	0	0	62500	62500															
26	0	0	67600	67600															
27	0	0	72900	72900															
28	0	0	78400	78400															
29	0	0	84100	84100															
30	0	0	90000	90000															
31	0	0	96100	96100															
32	0	0	102400	102400															
33	0	0	108900	108900															
34	0	0	115600	115600															
35	0	0	122500	122500															
36	0	0	129600	129600															
37	0	0	136900	136900															
38	0	0	144400	144400															
39	0	0	152100	152100															
40	0	0	160000	160000															
41	0	0	168100	168100															
42	0	0	176400	176400															
43	0	0	184900	184900															
44	0	0	193600	193600															
45	0	0	202500	202500															
46	0	0	211600	211600															
47	0	0	220900	220900															
48	0	0	230400	230400															
49	0	0	240100	240100															
50	0	0	250000	250000															
51	0	0	260100	260100															
52	0	0	270400	270400															
53	0	0	280900	280900															
54	0	0	291600	291600															
55	0	0	302500	302500															
56	0	0	313600	313600															
57	0	0	324900	324900															
58	0	0	336400	336400															
59	0	0	348100	348100															
60	0	0	360000	360000															
61	0	0	372100	372100															
62	0	0	384400	384400															
63	0	0	396900	396900															
64	0	0	409600	409600															
65	0	0	422500	422500															
66	0	0	435600	435600															
67	0	0	448900	448900															
68	0	0	462400	462400															
69	0	0	476100	476100															
70	0	0	490000	490000															
71	0	0	504100	504100															
72	0	0	518400	518400															
73	0	0	532900	532900															
74	0	0	547600	547600															
75	0	0	562500	562500															
76	0	0	577600	577600															
77	0	0	592900	592900															
78	0	0	608400	608400															
79	0	0	624100	624100															
80	0	0	640000	640000															
81	0	0	656100	656100															
82	0	0	672400	672400															
83	0	0	688900	688900															
84	0	0	705600	705600															
85	0	0	722500	722500															
86	0	0	739600	739600															
87	0	0	756900	756900															
88	0	0	774400	774400															
89	0	0	792100	792100															
90	0	0	810000	810000															
91	0	0	828100	828100															
92	0	0	846400	846400															
93	0	0	864900	864900															
94	0	0	883600	883600															
95	0	0	902500	902500															
96	0	0	921600	921600															
97	0	0	940900	940900															
98	0	0	960400	960400															
99	0	0	980100	980100															
100	0	0	100000	100000															
101	0	0	102000	102000															
102	0	0	104000	104000															
103	0	0	106000	106000															
104	0	0	108000	108000															
105	0	0	110000	110000															
106	0	0	112000	112000															
107	0	0	114000	114000															
108	0	0	116000	116000															
109	0	0	118000	118000															
110	0	0	120000	120000															
111	0	0	122000	122000															
112	0	0	124000	124000															
113	0	0	126000	126000															
114	0	0	128000	128000															
115	0	0	130000	130000															
116	0	0	132000	132000															
117	0	0	134000	134000															
118	0	0	136000	136000															
119	0	0	138000	138000															
120	0	0	140000	140000															
121	0	0	142000	142000															
122	0	0	144000	144000															
123	0	0	146000	146000															
124	0	0	148000	148000															
125	0	0	150000	150000															
126	0	0	152000	152000															
127	0	0	154000	154000															
128	0	0	156000	156000															
129	0	0	158000	158000															
130	0	0	160000	160000															
131	0	0	162000	162000															
132	0	0	164000	164000															
133	0	0	166000	166000															
134	0	0	168000	168000															
135	0	0	170000	170000															
136	0	0	172000	172000															
137	0	0	174000	174000															
138	0	0	176000	176000															
139	0	0	178000	178000															
140	0	0	180000	180000															
141	0	0	182000	182000															
142	0	0	184000	184000															
143	0	0	186000	186000															
144	0	0	188000	188000															
145	0	0	190000	190000															
146	0	0	192000	192000															
147	0	0	194000	194000															
148	0	0	196000	196000															
149	0	0	198000	198000															
150	0	0	200000	200000															
151	0	0	202000	202000															
152	0	0	204000	204000															
153	0	0	206000	206000															
154	0	0	208000	208000															
155	0	0	210000	210000															
156	0	0	212000	212000															
157	0	0	214000	214000															
158	0	0	216000	216000															
159	0	0	218000	218000															
160	0	0	220000	220000															
161	0	0	222000	222000															
162	0	0	224000	224000															
163	0	0	226000	226000															
164	0	0	228000	228000															
165	0	0	230000	230000															
166	0	0	232000	232000															
167	0	0	234000	234000															
168	0	0	236000	236000															
169	0	0	238000	238000															
170	0	0	240000	240000															
171	0	0	242000	242000															
172	0	0	244000	244000															
173	0	0	246000	246000															
174	0	0	248000	248000															
175	0	0	250000	250000															
176	0	0	252000	252000															
177	0	0	254000	254000															
178	0	0	256000	256000															
179	0	0	258000	258000															
180	0	0	260000	260000															
181	0	0	262000	262000															
182	0	0	264000	264000															
183	0	0	266000	266000															
184	0	0	268000	268000															
185	0	0	270000	270000															
186	0	0	272000	272000															
187	0	0	274000	274000															
188	0	0	276000	276000															
189	0	0	278000	278000															
190	0	0	280000	280000															
191	0	0	282000	282000															
192	0	0	284000	284000															
193	0	0	286000	286000															
194	0	0	288000	288000															
195	0	0	290000	290000															
196	0	0	292000	292000															
197	0	0	294000	294000															
198	0	0	296000	296000															
199	0	0	298000	298000															
200	0	0	300000	300000															

Table 4. The crystal structure of $\text{Na}_2\text{SO}_4(\text{V})$, thenardite.Space group: (No. 70) $Fddd$.Unit cell dimensions: $a = 5.8596 \pm 5 \text{ \AA}$
 $b = 12.3044 \pm 12 \text{ \AA}$
 $c = 9.8170 \pm 10 \text{ \AA}$ $V = 707.8 \text{ \AA}^3$. $D_{\text{calc}} = 2.666 \text{ g/cm}^3$, $D_{\text{obs}} = 2.65 \text{ g/cm}^3$.Cell content: $8\text{Na}_2\text{SO}_4$.

Arrangement of atoms (f denotes translations characteristic of a face centered lattice):

8 S in 8(a): $\pm(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})_f$
16 Na in 16(g): $\pm(\frac{1}{2}, \frac{1}{2}, z)_f$, $\pm(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}-z)_f$
32 O in 32(h): $\pm(x, y, z)_f$, $\pm(x, \frac{1}{2}-y, \frac{1}{2}-z)_f$, $\pm(\frac{1}{2}-x, y, \frac{1}{2}-z)_f$, $\pm(\frac{1}{2}-x, \frac{1}{2}-y, z)_f$

Fractional atomic coordinates

Atom	$x \pm \sigma(x)$	$y \pm \sigma(y)$	$z \pm \sigma(z)$
S	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$
Na	$\frac{1}{2}$	$\frac{1}{2}$	0.4414 ± 1
O	-0.0203 ± 2	0.0572 ± 1	0.2137 ± 1

Anisotropic thermal parameters ($\times 10^5$).

$$\hat{T} = \exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)].$$

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
S	518 ± 6	113 ± 2	206 ± 3	0	0	0
Na	926 ± 11	192 ± 3	432 ± 5	35 ± 8	0	0
O	1041 ± 12	207 ± 3	345 ± 5	-297 ± 10	319 ± 12	65 ± 5

isotropic refinement were $B_{\text{S}} = 0.74 \pm 0.01$, $B_{\text{Na}} = 1.30 \pm 0.02$, $B_{\text{O}} = 1.29 \pm 0.02 \text{ \AA}^2$. A three-dimensional ΔF Fourier synthesis was then computed with the anisotropic model. This showed no peak or hole greater than 0.6 e\AA^{-3} . A close inspection of Table 3 shows that the extinction effects are so small that they are negligible.

DESCRIPTION AND DISCUSSION OF THE CRYSTAL STRUCTURE

The crystal structure may be described in terms of nearly regular SO_4 tetrahedra and distorted NaO_6 octahedra. In fact, the NaO_6 octahedra are more distorted than Zachariasen and Ziegler reported. The interatomic distances and standard deviations (σ) and some angles of interest are listed in Table 5. No corrections have been made for the thermal vibration.

The sodium atoms are each surrounded by 6 oxygen atoms, two at 2.334 \AA , two at 2.426 \AA , and two at 2.534 \AA , forming distorted NaO_6 octahedra with a 2-fold axis parallel to the c axis. These Na-O distances are quite in accordance with those reported in other compounds, e.g. $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$.¹¹ All the sulphate ions are separated from each other by distances $> 3 \text{ \AA}$ for two oxygen

Table 5. Interatomic distances (Å) with standard deviations and some angles in $\text{Na}_2\text{SO}_4(\text{V})$. All angles have standard deviations of $\pm 0.05^\circ$ or less. No corrections have been made for thermal vibration. Atom denotations used in Table 5, Table 7, and Fig. 2: S, Na, and O(1) in (x, y, z) , O(2): $(x, \frac{1}{2}-y, \frac{1}{2}-z)$, O(3): $(\frac{1}{2}-x, y, \frac{1}{2}-z)$, O(4): $(\frac{1}{2}-x, \frac{1}{2}-y, z)$, O(5): $(\frac{1}{2}+x, \frac{1}{2}-y, \frac{3}{2}-z)$, O(6): $(\frac{1}{2}+x, -y, \frac{1}{2}+z)$, O(7): $(-\frac{1}{2}-x, y, \frac{1}{2}-z)$, O(8): $(-x, \frac{1}{2}+y, \frac{1}{2}+z)$. Oxygen-oxygen edges shared by SO_4 and NaO_6 are marked (*).

SO ₄ group	S—O(1,2,3,4)	1.476 ± 1	O(1)—S—O(2)	109.55°
	O(1)—O(2)	2.412 ± 2	O(1)—S—O(3)	111.15°
	O(1)—O(3)	2.435 ± 2	O(1)—S—O(4)	107.74°
	O(1)—O(4)*	2.384 ± 2	Average:	109.48°
NaO ₆ group	Na—O(1,4)	2.534 ± 1	O(1)—Na—O(4)	56.13°
	Na—O(5,7)	2.426 ± 1	O(1)—Na—O(6)	81.64°
	Na—O(6,8)	2.334 ± 1	O(6)—Na—O(7)	81.89°
			O(1)—Na—O(7)	86.43°
	O(1)—O(4)*	2.384 ± 2	O(7)—Na—O(8)	93.97°
	O(6)—O(7)	3.120 ± 2	O(1)—Na—O(8)	108.09°
	O(1)—O(6)	3.186 ± 2	O(5)—Na—O(7)	134.82°
	O(1)—O(7)	3.397 ± 2	O(1)—Na—O(5)	137.74°
	O(7)—O(8)	3.481 ± 2	O(6)—Na—O(8)	169.27°
	O(1)—O(8)	3.942 ± 2		
	O(5)—O(7)	4.479 ± 2		
	O(1)—O(5)	4.626 ± 2		
	O(6)—O(8)	4.648 ± 2		

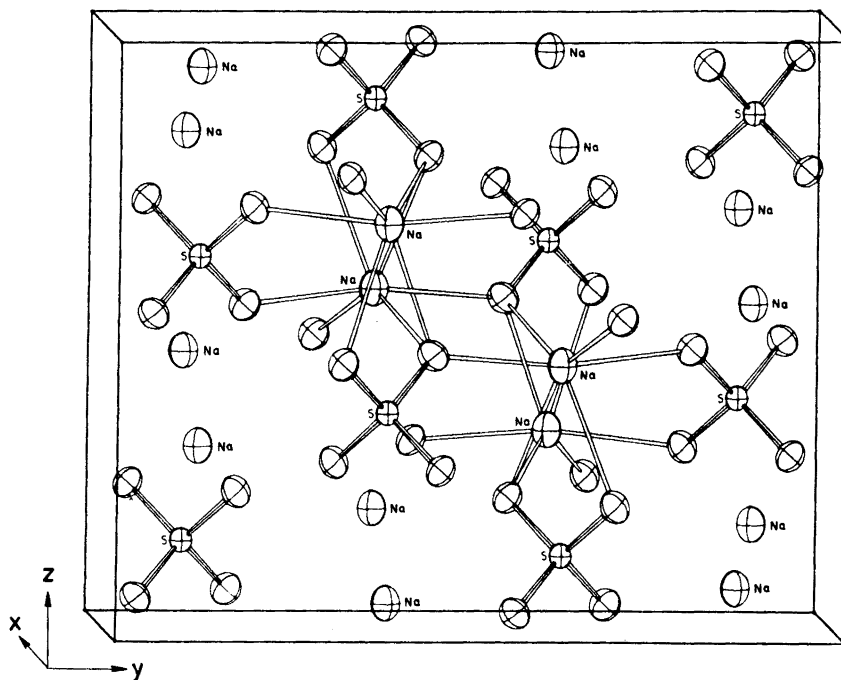


Fig. 1. The crystal structure of thenardite. One unit cell with eight sulphate ions and four NaO_6 octahedra is shown.

atoms belonging to different sulphate groups (Table 5). The SO_4 tetrahedra are nearly regular. All S–O distances are equal, $1.476 \pm 0.001 \text{ \AA}$, due to the space group since the sulphur atom is fixed in a special point position with 222 point symmetry. Each SO_4 tetrahedron shares two of its edges with two different NaO_6 octahedra. The longest Na–O distance of 2.534 \AA represents the distances to oxygens forming the shared tetrahedral edge. The remaining corners of the NaO_6 octahedron are shared with another four SO_4 tetrahedra thus giving a three-dimensional framework. Fig. 1 shows a three-dimensional model of the crystal structure. It has been produced by the plot program ORTEP.¹² Fig. 2 is an ORTEP plot picture showing one NaO_6 octahedron.

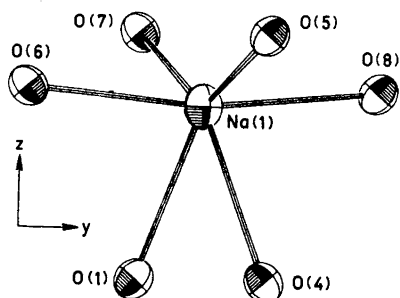


Fig. 2. One NaO_6 octahedron showing the coordination of oxygen atoms around a sodium atom in thenardite. The atoms have been numbered as in Tables 5 and 7.

Table 6. Analysis of anisotropic thermal parameters.

Atom	Axis	Root of mean square amplitude (\AA)	R.m.s. radial thermal displacement (\AA)
S	1	0.093	0.167
	2	0.095	
	3	0.100	
Na	1	0.120	0.228
	2	0.128	
	3	0.145	
O	1	0.094	0.226
	2	0.136	
	3	0.154	

Table 7. Some interatomic distances (\AA) in thenardite.

	Uncorrected	"Independent"
S–O(1,2,3,4)	1.476	1.497
O(1)–O(2), O(3)–O(4)	2.412	2.427
O(1)–O(3), O(2)–O(4)	2.435	2.451
O(1)–O(4), O(2)–O(3)	2.384	2.401
Na–O(1)	2.534	2.546
Na–O(5)	2.426	2.440
Na–O(6)	2.334	2.350

Table 8. Data for sulphate groups. Uncorrected and corrected S—O bond distances (in Å) are given for six carefully determined sulphate structures. The corrected distances have all been calculated in the same manner, *i.e.* assuming the riding motion model.

Compound: Ref.:	Na ₂ SO ₄ (V) This work	Li ₂ SO ₄ ·H ₂ O Larson ¹⁴	MgSO ₄ ·4H ₂ O Baur ¹⁵	MgSO ₄ ·7H ₂ O Baur ¹⁶	FeSO ₄ ·7H ₂ O Baur ¹⁷	β-K ₂ SO ₄ McGinnety ¹⁸
Uncorr. bond dist.						
Shortest	1.476 ± 1	1.462 ± 2	1.466 ± 5	1.460 ± 4	1.462 ± 4	1.459 ± 4
Longest	1.476 ± 1	1.482 ± 2	1.480 ± 4	1.482 ± 4	1.488 ± 4	1.473 ± 4
Average	1.476	1.472	1.473	1.471	1.474	1.469
Corrected bond dist.						
Average	1.484	1.480	1.479	1.486	1.486	1.486

Table 9. Computer programs used for the crystallographic calculations. All programs are written in FORTRAN IV for an IBM 360/75 computer except program SIMSA.

Program name and function	Authors
1. LAZY. Calculation of sin ² θ- and <i>d</i> -values from a Guinier powder photograph after internal standard correction.	A. G. Nord, Stockholm, Sweden.
2. POWDER. Refinement of cell constants. Ref. 6.	O. Lindqvist and F. Wengelin, Göteborg. Modified by A. G. Nord and B. G. Brandt, Stockholm, Sweden.
3. SIP. Generation of steering paper tape for Siemens AED.	R. Norrestam, Stockholm, Sweden.
4. SIMSA. Interpretation and evaluation of paper tape output from Siemens AED. IBM 1800.	R. Norrestam, Stockholm, Sweden.
5. DATAP2. Lp- and absorption correction.	P. Coppens, L. Leiserowitz and D. Rabinovich, Rehovath, Israel. Modified by O. Olofsson and M. Elfström, Uppsala. Further modifications by S. Åsbrink, B. G. Brandt and A. G. Nord, Stockholm, Sweden.
6. DRF. Fourier summations and structure factor calculations.	A. Zalkin, Berkeley, USA. Local modification.
7. LALS. Full matrix least squares refinement of positional and thermal parameters.	P. K. Gantzel, R. A. Sparks, and K. N. Trueblood, Los Angeles, USA. Modified by A. Zalkin, J. O. Lundgren, R. Liminga, C. I. Brändén, A. G. Nord and B. G. Brandt.
8. DISTAN. Calculation of interatomic distances and bond angles with <i>e.s.d.</i>	A. Zalkin, Berkeley, USA. Local modification.
9. ORFFE. Crystallographic function and error program. Ref. 13.	W. R. Busing, K. O. Martin, and H. A. Levy, Oak Ridge, USA. Modified by L. Kihlberg, Stockholm, Sweden.
10. ORTEP. Thermal ellipsoid plot program for crystal structure illustrations. Ref. 12.	C. K. Johnson, Oak Ridge, USA.

The anisotropic thermal parameters were analysed to find the axes of the ellipsoids. Some results from program ORFFE are presented in Table 6. The character of thermal vibration may also be studied in Figs. 1–2. Table 7 contains some bond lengths in thenardite corrected due to thermal motion. The effect of thermal motion on the distances is calculated assuming the “independent motion” model.¹³

Pertinent data relating to the sulphate group in some compounds are given in Table 8. All “corrected” S–O distances have been calculated in the same manner, *i.e.* assuming the “riding motion” model.¹³ Although the ligand atoms of the different sulphate groups vary, all uncorrected S–O distances as well as all corrected ones are nearly identical. The S–O distances within each sulphate group are also very similar, but the differences exceed the reported standard deviations. However, all these facts show that the sulphate ion in the compounds discussed is fairly stable and it also possesses a high degree of regularity.

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