individual $Fe^{3+}-O^{2-}$ distances would cause deviations of almost 4° from the average $Fe^{3+}-O^{2-}-Fe^{3+}$ values.

One conclusion following from Table 8 is that even in $LaFeO_3$, which has an almost cubic unit cell, distortions from the ideal lattice are large, a conclusion reached earlier by Geller (1956) from examination of intensities of X-ray powder and single-crystal photographs.

Finally, the average deviation of the $Fe^{3+}-O^{2-}-R^{3+}$ angles from 90° is less than 9° in both structures, but one of these angles is increased to almost 120° (Table 7).

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The Crystal Structure of Ammonium Sulfite Monohydrate

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The structure of ammonium sulfite monohydrate has been determined in order to provide information about the geometry of the sulfite ion. It forms crystals of space group $P2_1/c$, with $a_0=6{\cdot}34$, $b_0=8{\cdot}08$, $c_0=12{\cdot}39$ Å, $\beta=97{\cdot}9°$, and four formula weights in the unit cell. The structure was readily solved by Patterson methods and was refined by full-matrix least squares; the hydrogen atoms were located in a difference map. Within experimental error, the sulfite ion is a trigonal pyramid, with the S–O distance 1·53 Å and the O–S–O angle 105°. The structure is held together by an efficient network of hydrogen bonds involving every hydrogen atom. This analysis provides another example of increasing bond distance with decreasing oxidation number in the oxyanions of third-row elements, observed earlier with the oxyanions of chlorine.

The geometrical and electronic structures of many of the oxyanions of third-row elements from Si to Cl, and of species related to these ions, have been investigated carefully in recent years (Cruickshank, 1961, 1964; Larson, 1965), but one notable lack has been the absence of any precise determination of the structure of the sulfite ion. The only previously reported structural study of the sulfite ion was that by Zachariasen & Buckley (1931), who determined the structure of anhydrous sodium sulfite. They reported the ion to be a trigonal pyramid, with the S–O distance 1·39 Å, the O–S–O angle 107°, and the sulfur atom displaced 0·51 Å from the plane of the three oxygens. However, their analysis was complicated by the apparent presence of twinning. Tang & Kuei (1956) considered further the nature of the twinning in this crystal, but did not give any structural information about the ion.

The S–O distance reported by Zachariasen & Buckley seems anomalously short, since it is about 0·10 Å shorter than that in the sulfate ion (Larson, 1965), whereas in the corresponding isoelectronic chlorine oxyanions, the Cl–O bond in chlorate ion (Laing & Trueblood, 1965) is about 0·04 Å longer than that in perchlorate (Cruickshank, 1961). It was for this reason that we undertook our study; we hoped at first to redetermine the structure of sodium sulfite, but difficulties with twinning made this impracticable. We therefore turned to $(NH_4)_2SO_3 . H_2O$, described by Groth (1908), after Marignac (1857).

Experimental

Initial attempts to obtain good single crystals of sodium, lithium, magnesium, and ammonium sulfites by recrystallization from aqueous solution failed because of air oxidation (to sulfate), twinning, or both. How-

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* Contribution No. 1725.

ever, good single crystals of ammonium sulfite monohydrate were obtained by cooling a warm saturated solution. About 10 g of powdered reagent-grade $(NH_4)_2SO_3 . H_2O$ was dissolved in 20 ml of water, the solution was warmed gently to 70 °C, and about 50 g more of $(NH_4)_2SO_3 . H_2O$ was added to saturate the solution. The solution was then cooled quickly in an ice-bath, and the white needle-like crystals were removed by filtration. These crystals were dried superficially and were then stored in an evacuated vessel which contained some of the original powdered ammonium sulfite monohydrate in order to maintain the proper humidity; otherwise the crystals effloresced rapidly. If the warm saturated solution was allowed to cool slowly to room temperature, the primary product obtained was ammonium sulfate (as manifested by the acid-insoluble precipitate it formed with barium ion). Consequently, to minimize both efflorescence and oxidation, the crystals used for our X-ray studies were enclosed in thin-walled lithium-glass capillaries.

Weissenberg photographs with Cu K radiation of crystals mounted about **a** and **b** showed the systematic extinctions characteristic of $P2_1/c$ [$h0l$ with l odd, and $0k0$ with k odd]. The unit-cell dimensions, measured on zero-level Weissenberg photographs calibrated with CeO_2 ($a_0=5{\cdot}411$ Å) powder patterns, are: $a_0=6{\cdot}34\pm0{\cdot}01, b_0=8{\cdot}08\pm0{\cdot}02, c_0=12{\cdot}39\pm0{\cdot}03$ Å, $\beta=97{\cdot}9\pm0{\cdot}2°$. The corresponding axial ratios are 0·785:1:1·533; Groth (1908) gives 0·7832:1:1·5257, with $\beta=97°59'$. The observed density is 1·425 g.cm^{-3}; that calculated for four formula weights of $(NH_4)_2SO_3 . H_2O$ in the unit cell is 1·417 g.cm^{-3}.

Intensity estimates were made visually from multiple-film Weissenberg photographs taken with Cu $K\alpha$ radiation. Two different crystals were used: one, mounted about **a**, had a cross-section 0·09 by 0·11 mm, and was used to obtain levels with $h=0$ through 4; the other, mounted about **b**, was 0·15 by 0·18 mm in cross-section, and was used to obtain levels $k=0$ through 4. Because the crystals were small and were enclosed in capillaries, no absorption corrections were applied. After Lorentz, polarization, and Tunell corrections had been made, and the variation of film factor with angle of incidence taken into account, the measurements about different axes were correlated by a least-squares method similar to that suggested by Rollett & Sparks (1960). In all, 1253 unique reflections were observable, corresponding to 82% of the sphere of reflection. Of these, 226 were too weak to be measured; the structure amplitudes for these were later assumed for the least-squares refinements to be $F_{\min}/\sqrt{3}$ (Hamilton, 1955), where $F_{\min}$ is the minimum observable structure amplitude in the corresponding region of reciprocal space.

Twinning is common in these crystals and it was necessary to select single-crystal specimens carefully for data-collection. The predominant form involves a lack of distinction between the positive and negative directions of **a**; as a result, because c^* is approximately four times $a^* \cos\beta^*$, a photograph of the $k=0$ level of the twin appears superficially to have $C_0=2c_0$ and to have the peculiar extinction conditions $00L$ absent with $L\neq4n$, and $H0L$ absent with $L=4n+2$ and $4n+3$.

All calculations were made on an IBM 7094 computer, with programs written in this laboratory. The form factors for nitrogen and oxygen were those of Hoerni & Ibers (1954), that for sulfur was Dawson's (1961), and that for hydrogen was taken from *International Tables for X-ray Crystallography* (1962).

Determination and refinement of the structure

The structure was readily solved by analysis of a sharpened three-dimensional Patterson distribution for which the coefficients had been modified simply by a positive exponential, exp $(+6s^2)$, where $s=\sin\theta/\lambda$. The sulfur atom was found, within 0·05 Å of its final position, primarily by inspection of the Harker line $(0, v, \frac{1}{2})$ and section $(u, \frac{1}{2}, w)$, and the three S–O bond vectors corresponded to the only peaks at about 1·5 Å from the origin. A difference Fourier synthesis phased on the four atoms of the sulfite ion, each assigned an isotropic temperature factor of 3·0 Å^2, showed three additional peaks of height 4 to 6 e.Å^{-3}, presumably corresponding to the two ammonium ions and the water molecule, and one small sharp peak slightly below 2 e.Å^{-3} in height, which was shown to be spurious both by calculation of inter-peak distances and by the fact that it disappeared in a subsequent difference map phased on the other seven atoms. The peaks ascribed to the ammonium ions and the water molecule could be differentiated, even at this stage, on the basis of their hydrogen-bonding environment, that is, the number and disposition of their potential hydrogen-bonding neighbors at about 2·8 Å. The arrangement depicted in Fig. 1 was already apparent and made it quite clear which was the water molecule.

Least-squares refinement was then begun, using the program of Gantzel, Sparks & Trueblood (ACA No. 317), which refines $\Sigma w(F_o-G|F_c|)^2$ where G is a scale factor. Hughes's (1941) weights were used throughout, with $4F_{\min}=6{\cdot}6$. After three cycles of full-matrix isotropic refinement, and then three cycles of full-matrix anisotropic refinement, a difference map was calculated in order to locate the ten hydrogen atoms. The eight on the two ammonium ions showed up well, and were the highest peaks on the map, between 0·5 and 0·8 e.Å^{-3}; they were all within 0·1 Å of the positions expected from the hydrogen-bonding arrangement of Fig. 1. The hydrogen atoms of the water molecule were less well defined, the corresponding peaks being somewhat smeared out and only slightly higher than the e.s.d. of the electron density, which was close to 0·3 e.Å^{-3}. However, the positions were in accord with the scheme of Fig. 1, *i.e.* near the lines from the water molecule to O(1) of one sulfite ion and to O(2) of another.

Table 1. *Observed and calculated structure factors*

The three columns are, in order, l, F_o and F_c. The letters E and U identify extinct and unobserved reflections, as discussed in the text.

H= 0, K= 0		
2	21.5	-19.3
4	67.4E	-104.6
6	23.6	-20.6
8	20.6	21.3
10	13.8	12.9
12	11.2	-9.7
14	1.0U	-1.7
H= 0, K= 1		
1	41.4	39.1
2	38.6	41.5
3	60.0	-64.9
4	36.4	39.1
5	19.6	16.8
6	0.9U	-0.1
7	14.4	11.5
8	24.0	-23.2
9	12.7	9.2
10	7.7	-5.7
11	17.4	-17.9
12	5.9	5.8
13	6.3	-6.6
14	1.0U	-0.7
15	8.3	7.8
H= 0, K= 2		
0	57.7	51.0
1	29.1	25.3
2	41.7	-41.8
3	13.0	11.5
4	18.8	-17.1
5	5.0	-5.4
6	9.1	8.7
7	10.3	-8.8
8	31.7	31.1
9	1.2U	0.2
10	8.6	9.2
11	9.5	9.7
12	28.7	-26.7
13	4.6	-4.3
14	9.0	-8.4
15	9.4	-9.4
H= 0, K= 3		
1	7.8	7.7
2	18.3	17.8
3	22.3	-20.4
4	42.1	-37.5
5	6.5	4.7
6	11.4	-10.4
7	1.1U	1.9
8	16.6	15.9
9	22.7	23.8
10	15.0	15.3
11	11.8	-10.5
12	1.2U	-1.1
13	13.0	-12.1
14	10.9	-10.3
H= 0, K= 4		
0	65.7	58.7
1	63.5	59.2
2	4.9	-5.1
3	26.9	26.0
4	24.4	-22.2
5	39.8	-39.3
6	18.8	-17.9
7	18.2	-17.4
8	14.3	14.4
9	14.0	13.6
10	7.8	7.9
11	21.7	15.7
12	9.6	-9.3
13	1.4	-0.9
14	0.7U	1.1
H= 0, K= 5		
1	15.9	12.6
2	36.7	34.8
3	13.7	-12.0
4	13.2	-11.8
5	1.2U	1.7
6	16.3	-14.6
7	1.2U	1.4
8	1.3U	1.2
9	1.3U	1.7
10	13.3	12.3
11	15.1	-13.5
12	1.0U	-0.1
13	5.2	4.8
H= 0, K= 6		
0	14.8	13.9
1	30.3	30.7
2	4.0	-3.7
3	17.0	21.7
4	1.2U	-0.6
5	12.0	-10.1
6	4.9	-5.7
7	18.0	-17.5
8	4.4	-4.7
9	5.7	5.5
10	1.1U	-0.2
11	15.6	14.0
12	2.8	-2.7
H= 0, K= 7		
1	8.3	-8.6
2	21.2	20.8
3	3.8	4.6
4	1.3U	1.4
5	4.6	4.8
6	6.1	-11.7
7	4.3	-4.3
8	6.4	-6.8
9	7.2	7.4
10	14.7	13.9
11	2.7	-2.9
H= 0, K= 8		
0	19.3	-19.7
1	19.3	19.0
2	3.3	-3.5
3	12.1	12.2
4	18.5	18.2
5	14.8	-13.3
6	1.1U	-1.7
7	17.1	-15.9
8	3.8	-3.3
9	10.4	10.2
H= 0, K= 9		
1	5.9	-5.6
2	9.4	9.3
3	7.3	7.9
4	7.9	-8.6
5	5.7	5.2
6	10.7	-10.2
7	9.0	-9.3
H= 0, K= 10		
0	4.1	-3.7
1	10.4	10.9
2	0.7U	0.4
3	7.3	8.3
H= 1, K= 0		
-14	10.3	11.0
-12	2.8	-2.9
-10	28.3	-26.9
-8	30.4	30.9
-6	31.1	35.1
-4	37.6	-43.0
-2	41.1	-52.9
0	16.1	13.6
2	54.9	50.6
4	8.2	-6.4
6	5.7	-3.7
8	27.0	-24.1
10	33.1	29.8
12	1.0U	2.2
14	28.5	-26.0
H= 1, K= 1		
-15	9.6	9.2
-14	7.3	-6.6
-13	12.3	9.8
-12	1.0U	1.4
-11	13.7	-13.5
-10	10.7	10.7
-9	21.6	-21.5
-8	9.3	-8.2
-7	34.2	36.6
-6	5.0	-4.2
-5	3.8	5.0
-4	29.0	32.2
-3	19.8	-21.8
-2	2.0	-0.9
-1	28.5	-39.4
0	37.0	-34.8
1	29.4	42.1
2	13.8	11.3
3	6.8	-2.8
4	8.4	-6.3
5	5.9	3.7
6	9.8	-6.3
7	8.9	-7.5
8	13.2	10.9
9	1.0U	-0.6
10	10.0	9.3
11	23.0	18.9
12	1.0U	0.6
13	17.7	-15.8
14	7.9	-6.7
15	6.5	-7.0
H= 1, K= 2		
-15	0.6U	0.5
-14	5.9	5.9
-13	1.5U	-0.3
-12	1.0U	-1.0
-11	4.5	3.4
-10	31.1	-32.3
-9	12.2	-11.3
-8	15.6	12.7
-7	13.8	-10.7
-6	41.6	43.3
-5	39.9	46.3
-4	21.2	-18.4
-3	24.3	25.7
-2	47.8E	-74.0
-1	48.1E	-79.5
0	39.1	40.4
1	37.9	-30.8
2	53.9E	84.8
3	23.1	35.1
4	46.6	-45.3
5	12.9	10.3
6	35.8	-29.8
7	0.9U	0.0
8	13.7	-11.6
9	9.9	-9.5
10	30.6	31.3
11	1.1U	2.7
12	9.2	8.1
13	6.3	5.3
14	13.1	-13.3
15	3.1	-3.7
H= 1, K= 3		
-15	6.4	7.7
-14	5.8	5.3
-13	14.4	14.3
-12	11.9	11.8
-11	10.6	-10.2
-10	1.1U	0.3
-9	32.4	-34.4
-8	24.8	-23.0
-7	15.9	13.7
-6	0.8U	1.2
-5	24.8	24.5
-4	18.7	18.7
-3	17.5	15.6
-2	9.2	-9.4
-1	20.4	-22.9
0	8.6	-10.4
1	35.1	30.0
2	22.1	20.0
3	28.4	-24.6
4	4.5	4.5
5	30.9	-25.9
6	2.0	1.8
7	9.6	7.5
8	15.4	-13.7
9	14.8	14.2
10	10.6	-10.4
11	10.8	10.1
12	17.8	15.7
13	14.2	-12.9
14	4.7	3.7
H= 1, K= 4		
-14	3.5	3.4
-13	18.4	17.6
-12	0.9U	-0.3
-11	12.0	13.0
-10	15.2	-14.0
-9	22.7	-22.0
-8	15.2	15.6
-7	20.6	-19.1
-6	11.5	10.7
-5	15.3	-15.1
-4	10.7	-10.2
-3	7.9	6.7
-2	25.9	-25.7
-1	13.9	-13.2
0	0.7	-2.2
1	13.2	14.4
2	41.6	38.6
3	26.0	22.6
4	13.0	-10.6
5	0.9U	-1.1
6	7.8	-7.1
7	15.5	-13.7
8	6.2	-6.6
9	23.7	-25.9
10	13.8	13.2
11	15.5	14.1
12	0.9U	-0.7
13	20.7	21.0
14	7.0	-8.4
H= 1, K= 5		
-13	0.7U	-0.4
-12	15.7	13.3
-11	6.0	-6.3
-10	1.0U	-1.3
-9	9.5	8.7
-8	22.4	-24.0
-7	19.4	18.3
-6	8.4	7.8
-5	17.7	-16.8
-4	21.2	23.7
-3	5.6	-4.7
-2	5.6	-5.2
-1	23.8	-25.8
0	23.8	-24.9
1	12.4	10.9
2	9.1	7.3
3	23.4	20.6
4	9.7	9.2
5	7.9	7.4
6	1.5	2.6
7	8.4	-8.6
8	10.5	-10.3
9	7.9	-6.5
10	4.9	-4.8
11	6.2	4.7
12	16.1	14.8
13	5.5	-5.2
H= 1, K= 6		
-12	0.7U	0.6
-11	6.4	4.4
-10	5.5	-4.7
-9	22.3	-21.8
-8	8.7	8.2
-7	4.0	-4.8
-6	9.5	-9.2
-5	37.5	42.8
-4	2.4	1.1
-3	18.4	18.2
-2	8.0	8.3
-1	43.3	-49.3
0	11.3	-9.7
1	29.9	-31.3
2	8.1	7.6
3	30.8	32.3
4	4.1	-4.6
5	19.7	19.6
6	1.0U	0.2
7	7.8	-6.6
8	1.0U	-1.2
9	18.0	-14.9
10	7.3	5.7
11	7.9	7.0
12	2.3	-2.3
H= 1, K= 7		
-11	0.6U	-1.2
-10	3.7	3.9
-9	8.4	-7.9
-8	19.0	-20.4
-7	5.4	-4.9
-6	2.4	1.0
-5	1.0U	-1.1
-4	17.8	18.8
-3	18.8	21.8
-2	8.2	1.7
-1	2.8	-2.3
0	23.2	-23.4
1	2.5	-2.4
2	8.8	8.1
3	9.2	-9.0
4	13.4	12.7
5	8.8	-8.1
6	10.4	-7.9
7	8.1	7.4
8	11.0	-9.0
9	6.8	6.0
10	5.0	4.2
11	0.5U	-1.2
H= 1, K= 8		
-9	14.5	-15.1
-8	0.8U	0.2
-7	8.7	-7.9
-6	8.5	-8.5
-5	11.1	10.3
-4	5.0	5.0
-3	7.6	7.3
-2	6.3	6.4
-1	12.3	-11.2
0	4.6	-4.8
1	7.8	-7.8
2	1.0U	2.8
3	21.8	20.2
4	5.2	-5.7
5	4.6	4.7
6	3.1	3.2
7	15.6	-14.0
8	0.7U	0.8
9	12.5	-12.6
H= 1, K= 9		
-7	4.1	-4.1
-6	6.6	5.9
-5	8.7	-8.2
-4	6.2	5.2
-3	9.9	9.0
-2	0.9U	2.4
-1	0.9U	-2.3
0	12.5	-11.2
1	2.8	-4.2
2	0.8U	1.5
3	0.8U	-0.5
4	12.7	11.8
5	6.7	6.2
6	0.6U	0.7
7	6.9	4.8
H= 1, K= 10		
-4	0.4U	3.8
-3	3.9	3.3
-2	14.2	15.0
-1	7.3	-6.7
0	7.2	-7.0
1	9.0	-10.0
2	11.6	-12.1
3	8.0	9.3
H= 2, K= 0		
-14	1.1U	2.5
-12	8.7	8.7
-10	12.1	-14.7
-8	36.9	-42.1
-6	58.9	75.2
-4	49.7	53.4
-2	49.1	-56.3
0	68.8E	-101.6
2	10.5	10.5
4	56.8	59.3
6	1.5U	-0.9
8	23.7	-22.0
10	1.9U	-1.3
12	25.1	20.5
14	7.3	-6.8
H= 2, K= 1		
-15	1.1U	-4.1
-14	1.4U	2.5
-13	11.3	12.1
-12	7.3	8.1
-11	16.2	20.1
-10	7.4	-4.2
-9	25.8	-34.0
-8	25.4	-27.0
-7	11.9	-13.7
-6	1.6U	-2.8
-5	36.2	40.0
-4	26.4	31.9
-3	1.1U	-0.5
-2	16.1	16.9
-1	9.1	6.7
0	22.1	22.0
1	32.6	-37.0
2	25.7	-20.9
3	18.0	18.5
4	42.4	-37.0
5	5.4	5.2
6	6.9	5.6
7	7.5	-7.3
8	15.9	14.0
9	10.5	-9.7
10	2.2U	-3.7
11	20.3	16.9
12	2.0U	0.7
13	5.3	5.4
14	4.1	4.3
H= 2, K= 2		
-15	8.1	-8.0
-14	11.4	11.4
-13	1.8U	-1.9
-12	19.1	19.9
-11	12.0	12.5
-10	6.3	-5.1
-9	2.0U	-1.0
-8	27.2	-32.3
-7	22.7	-23.6
-6	24.7	26.2
-5	11.4	11.6
-4	18.8	-17.0
-3	9.0	8.3
-2	6.4	-5.5
-1	3.5	-0.8
0	6.3	4.3
1	12.9	10.3
2	22.4	19.0
3	16.5	-14.2
4	33.9	31.2
5	1.6U	-0.5
6	17.9	-16.3
7	12.7	12.2
8	30.3	-32.7
9	11.5	-11.4
10	2.1U	-2.6
11	10.1	-8.0
12	32.3	30.1
13	15.3	13.5
H= 2, K= 3		
-14	13.2	-13.7
-13	11.7	13.2
-12	2.1U	-0.5
-11	6.3	7.1
-10	20.5	26.5
-9	21.2	-24.6
-8	2.1U	0.1
-7	1.9U	-0.5
-6	19.0	-19.4
-5	14.5	15.3
-4	6.6	6.4
-3	12.9	-11.1
-2	10.3	-8.1
-1	11.2	7.8
0	5.7	-4.9
1	26.9	-23.3
2	1.4U	-2.1
3	25.1	22.6
4	15.3	10.9
5	13.2	12.1
6	16.6	15.3
7	8.3	-7.6
8	7.1	-5.6
9	24.3	-21.1
10	19.5	-17.1
11	9.9	8.1
12	1.8U	3.5
13	12.3	10.3
H= 2, K= 4		
-13	1.3U	-4.7
-12	1.5U	3.1
-11	18.7	17.5
-10	6.8	-6.2
-9	11.1	12.4
-8	24.8	-15.9
-7	31.9	-34.8
-6	27.2	26.7
-5	3.9	3.2
-4	10.1	9.4
-3	36.0	35.5
-2	7.5	-5.9
-1	6.8	-5.8
0	37.7	-31.8
1	38.5	-38.9
2	8.4	6.7
3	12.5	-11.5
4	28.6	23.6
5	37.0	34.4
6	5.3	-6.0
7	19.5	19.3
8	7.3	-6.7
9	19.1	-17.3
10	3.4	-2.5
11	17.8	-15.3
12	14.0	11.1
13	7.1	7.1
H= 2, K= 5		
-11	9.3	9.3
-10	20.2	21.0
-9	7.9	-8.0
-8	10.7	-11.5
-7	8.6	-9.3
-6	25.8	-24.0
-5	14.9	13.8
-4	15.1	14.6
-3	14.0	13.2
-2	16.7	13.9
-1	7.0	-5.5
0	2.1U	2.0
1	22.8	-20.8
2	22.4	-19.3
3	15.3	13.4
4	2.3U	-0.6
5	13.7	-12.7
6	15.7	14.7
7	2.4U	1.4
8	2.4U	0.2
9	13.8	9.6
10	16.1	-13.6
11	4.7	4.5
12	7.1	3.8
H= 2, K= 6		
-11	16.6	15.6
-10	2.1U	4.4
-9	2.3U	1.2
-8	2.4U	-3.8
-7	30.8	-27.6
-6	2.4U	4.1
-5	2.4U	4.1
-4	2.4U	0.6
-3	18.2	20.6
-2	2.3U	2.4
-1	11.4	10.4
0	15.2	-14.8
1	15.7	-13.0
2	9.1	8.9
3	15.7	-15.7
4	7.4	6.5
5	12.8	11.8
6	10.3	-10.3
7	10.9	10.2
8	2.2U	4.5
9	15.7	-13.9
10	1.8U	-1.4
11	11.4	-10.1
H= 2, K= 7		
-10	14.0	12.9
-9	1.9U	2.5
-8	14.2	-13.1
-7	2.3U	0.8
-6	14.5	-14.6
-5	7.8	-7.3
-4	13.7	11.9
-3	2.4U	-1.8
-2	15.1	13.4
-1	7.1	6.1
0	2.4U	3.2
1	2.4U	-2.6
2	19.4	-19.9
3	10.4	9.3
4	2.4U	-1.6
5	8.8	-4.8
6	15.5	13.3
7	2.1U	1.3
8	1.9U	2.3
9	1.7U	-3.0
10	13.4	-13.3
H= 2, K= 8		
-7	18.3	-17.0
-6	7.8	-7.5
-5	2.1U	-0.4
-4	17.7	-16.2
-3	17.2	14.4
-2	11.6	11.5
-1	2.3U	4.0
0	11.7	10.5
1	26.0	-21.4
2	2.3U	0.2
3	6.8	-6.2
4	8.8	-7.6
5	25.1	21.4
6	1.9U	-3.7
7	9.3	7.8
8	5.6	7.1
H= 2, K= 9		
-6	12.1	-13.1
-5	6.2	-6.5
-4	1.7U	-0.6
-3	1.8U	-1.1
-2	8.4	8.0
-1	9.0	8.0
0	1.9U	-2.9
1	1.9U	-2.3
2	12.1	-11.6
3	1.7U	-4.3
4	12.1	12.3
5	7.1	-6.5
H= 3, K= 0		
-14	8.0	-8.6
-12	21.2	18.4
-10	8.7	9.6
-8	29.7	-27.2
-6	14.3	-14.1
-4	20.3	23.5
-2	2.9	-0.4
0	36.2	35.0
2	39.0	-43.4
4	9.8	8.0
6	26.9	24.3
8	19.0	-20.9
10	20.2	-18.1
12	13.5	13.2
14	3.1	19.0
H= 3, K= 1		
-14	7.0	0.7
-13	5.8	5.4
-12	5.3	-5.8
-11	16.4	17.9
-10	1.3U	2.9
-9	1.3U	1.5
-8	12.5	12.4
-7	32.9	-34.5
-6	7.4	-6.3
-5	7.7	8.1
-4	17.5	-20.2
-3	10.8	11.4
-2	4.0	-5.4
-1	24.3	30.7
0	13.0	13.1
1	14.0	-12.8
2	6.7	6.0
3	42.6	-40.2
4	3.8	3.2
5	33.2	32.0
6	10.0	8.8
7	4.7	3.4
8	8.7	-8.4
9	11.2	-12.9
10	12.4	-11.4
11	6.5	-5.4
12	1.1U	1.0
13	10.8	11.7
H= 3, K= 2		
-15	0.7U	0.2
-14	7.4	-8.5
-13	6.2	-5.8
-12	10.1	8.2
-11	5.2	3.9
-10	15.4	16.0
-9	14.9	15.2
-8	13.3	-12.8
-7	8.5	-6.8
-6	17.0	-17.8
-5	25.1	-26.7
-4	29.6	35.0
-3	0.8U	-1.0
-2	4.5	3.8
-1	22.2	24.3
0	22.1	-19.9
1	22.2	21.6
2	48.5	-50.0
3	24.6	-22.6
4	30.2	34.5
5	9.0	-7.1
6	33.5	34.8
7	15.7	14.6
8	12.5	-13.1
9	1.3U	-1.8
10	19.1	-16.6
11	7.5	-6.3
12	1.0U	-0.7
13	0.8U	-0.6
H= 3, K= 3		
-14	10.9	-10.5
-13	5.8	-5.2
-12	8.5	-8.6
-11	12.3	12.5
-10	11.4	10.6
-9	20.9	22.0
-8	6.4	6.3
-7	21.2	-21.7
-6	10.0	-9.2
-5	5.8	-5.5
-4	4.5	3.6
-3	4.3	4.0
-2	4.1	-2.8
-1	2.9	2.4
0	14.3	13.3
1	17.7	-14.8
2	3.3	1.3
3	7.4	-5.8
4	31.2	-33.0
5	29.5	30.8
6	7.8	7.5
7	5.7	-5.7
8	22.1	19.3
9	10.0	-9.4
10	1.2U	-1.4
11	4.3	-3.7
12	8.6	-8.2
13	0.8U	6.6
H= 3, K= 4		
-13	17.1	-19.3
-12	4.7	4.3
-11	1.2U	-0.4
-10	8.5	6.8
-9	16.6	13.6
-8	7.2	-7.7
-7	1.3U	-0.9
-6	14.2	-15.2
-5	1.2U	0.7
-4	17.1	17.9
-3	7.1	6.8
-2	5.3	4.1
-1	6.8	-5.7
0	9.1	4.1
1	7.7	7.3
2	20.0	-19.5
3	24.9	-25.6
4	8.6	9.7
5	9.1	-10.1
6	8.1	7.1
7	30.0	29.3
8	7.3	-7.3
9	10.0	8.5
10	8.1	-6.6
11	16.3	-16.5
12	3.6	3.8
H= 3, K= 5		
-13	7.7	9.0
-12	9.9	-9.7
-11	1.1U	0.2
-10	15.7	13.3
-9	5.1	-4.7
-8	12.8	14.2
-7	21.0	-18.6
-6	18.2	-14.6
-5	6.1	6.2
-4	13.3	-12.4
-3	15.0	14.2
-2	1.2U	1.0
-1	13.4	12.7
0	22.1	21.1
1	3.0	-2.4
2	3.9	4.2
3	18.2	-18.9
4	21.1	-25.5
5	1.3U	1.3
6	8.5	7.3
7	4.8	3.4
8	15.2	13.0
9	1.1U	2.2
10	5.8	-5.9
11	5.2	-4.7
H= 3, K= 6		
-11	4.7	4.7
-10	1.0U	0.9
-9	21.5	20.5
-8	3.1	2.7
-7	5.6	-4.3
-6	3.8	-3.5
-5	36.4	-34.3
-4	3.8	4.6
-3	1.3U	-1.6
-2	7.3	-7.9
-1	24.0	27.9
0	3.8	3.8
1	15.7	17.6
2	1.3U	0.2
3	27.5	-26.1
4	4.1	4.2
5	9.4	-8.2
6	3.2	-2.4
7	18.0	17.1
8	1.1U	-0.9
9	1.0U	1.1
10	3.1	-2.7
H= 3, K= 7		
-10	4.4	4.6
-9	11.8	12.7
-8	16.1	18.5
-7	1.1U	0.4
-6	9.2	-9.4
-5	1.2U	-1.2
-4	18.1	-17.3
-3	4.2	-4.4
-2	6.9	5.9
-1	9.1	-8.2
0	15.7	15.6
1	1.3U	1.2
2	6.5	-5.1
3	9.1	8.4
4	14.2	-14.1
5	3.1	2.9
6	10.4	11.5
7	5.8	-5.9
8	6.9	6.8
9	2.8	3.3
H= 3, K= 8		
-8	5.5	6.6
-7	4.5	4.5
-6	1.0U	-1.4
-5	10.4	-11.3
-4	3.0	2.9
-3	3.6	3.3
-2	4.6	-5.4
-1	9.3	9.8
0	2.7	-2.7
1	1.1U	0.8
2	2.3	2.4
3	15.0	-18.5
4	3.5	3.7
5	0.9U	-1.7
6	6.1	-6.7
7	10.5	15.8
H= 3, K= 9		
-6	5.1	-7.5
-5	1.5	1.7
-4	5.3	-6.3
-3	3.3	-3.3
-2	5.4	6.2
-1	0.9U	-0.6
0	8.7	9.1
1	5.9	6.5
2	2.2	-3.0
3	0.7U	1.5
4	9.4	-14.2
H= 4, K= 0		
-14	14.1	-13.7
-12	1.2U	1.9
-10	12.6	14.5
-8	18.2	19.6
-6	24.4	-30.6
-4	28.7	-40.3
-2	32.9	34.2
0	48.8	36.5
2	19.5	-17.5
4	29.1	-26.3
6	26.7	27.3
8	3.0	1.4
10	9.7	-8.8
12	6.8	-7.4
H= 4, K= 1		
-14	6.6	-6.0
-13	13.8	-14.9
-12	10.7	-9.0
-11	5.0	3.7
-10	7.8	8.6
-9	14.6	14.4
-8	10.6	11.7
-7	12.9	14.0
-6	6.0	4.4
-5	29.4	-35.0
-4	4.1	-4.8
-3	6.0	-6.3
-2	13.5	-19.8
-1	13.3	22.3
0	15.1	-10.2
1	14.1	15.1
2	17.5	15.6
3	20.3	-30.1
4	4.3	6.9
5	3.2	3.3
6	4.9	-4.0
7	17.7	18.2
8	1.3U	0.5
9	6.7	-6.2
10	1.1U	2.5
11	6.5	-6.2
12	0.8U	-1.9
H= 4, K= 2		
-14	14.4	-16.4
-13	7.1	-6.5
-12	6.5	-4.5
-11	6.3	-5.6
-10	1.3U	1.4
-9	3.6	3.4
-8	10.8	10.7
-7	7.0	5.4
-6	3.5	-2.7
-5	9.2	8.1
-4	5.2	-3.9
-3	6.7	-6.9
-2	12.0	13.2
-1	11.5	-11.1
0	6.8	5.1
1	8.9	7.0
2	18.0	-16.0
3	2.6	2.0
4	27.1	-27.3
5	10.8	-10.7
6	23.4	25.4
7	5.6	5.5
8	15.7	13.1
9	10.5	8.8
10	8.3	-7.1
11	0.9U	-0.5
12	8.1	-11.5
H= 4, K= 3		
-13	11.1	-9.9
-12	8.2	-7.0
-11	7.8	6.6
-10	9.2	-8.8
-9	5.5	5.3
-8	1.3U	-1.5
-7	3.0	2.4
-6	12.6	12.6
-5	18.3	-19.2
-4	5.3	-5.0
-3	9.0	9.4
-2	14.0	-12.8
-1	16.6	14.9
0	20.5	17.7
1	13.7	11.9
2	17.7	14.8
3	26.5	-27.4
4	20.7	-20.8
5	13.2	-12.5
6	9.3	-8.9
7	20.1	18.1
8	10.4	9.3
9	8.3	6.8
10	4.6	3.8
11	4.2	-4.0
12	0.4U	0.1
H= 4, K= 4		
-12	0.9U	0.3
-11	10.3	-9.3
-10	5.8	5.2
-9	1.2U	-0.8
-8	11.2	11.4
-7	14.2	14.7
-6	13.4	-14.8
-5	1.2U	-1.7
-4	12.4	-12.1
-3	26.6	-29.6
-2	12.8	12.7
-1	7.5	7.3
0	7.1	5.9
1	34.0	38.2
2	1.7	-0.3
3	1.7	-2.2
4	12.9	-13.3
5	32.8	-30.1
6	13.5	10.8
7	1.2U	0.2
8	3.9	2.7
9	9.6	8.2
10	5.1	-5.1
11	3.4	4.4
H= 4, K= 5		
-12	9.5	-11.3
-11	3.0	-2.9
-10	8.7	-7.4
-9	11.3	10.2
-8	10.0	8.1
-7	9.4	9.0
-6	21.4	19.1
-5	19.3	-21.3
-4	14.9	-11.5
-3	1.2U	1.5
-2	19.0	-20.8
-1	1.2U	0.4
0	9.6	9.9
1	4.4	4.0
2	19.1	19.6
3	1.2U	0.6
4	14.3	-12.4
5	6.8	5.4
6	13.0	-9.9
7	4.2	3.2
8	10.3	9.1
9	9.5	-8.5
10	3.5	4.0
H= 4, K= 6		
-11	8.7	-10.1
-10	3.4	-2.9
-9	2.9	2.0
-8	6.8	6.6
-7	16.7	15.0
-6	7.5	-7.2
-5	5.4	4.9
-4	1.2U	-1.0
-3	16.6	-16.3
-2	8.7	7.7
-1	9.5	-6.9
0	6.0	-4.8
1	9.5	11.1
2	2.6	1.8
3	5.6	4.3
4	4.7	-3.5
5	16.1	-15.5
6	5.5	4.1
7	5.4	4.9
8	0.8U	-0.4
9	9.3	13.7
H= 4, K= 7		
-9	3.7	-4.1
-8	9.5	10.0
-7	1.0U	-0.3
-6	14.0	11.9
-5	1.1U	-0.2
-4	15.7	-12.8
-3	12.6	11.0
-2	15.7	-12.9
-1	6.3	-6.0
0	7.0	5.3
1	1.2U	0.3
2	17.6	16.8
3	1.1U	-1.2
4	5.7	-5.7
5	7.0	-6.5
6	14.9	-13.8
7	2.0	2.0
H= 4, K= 8		
-7	8.4	11.6
-6	5.6	5.5
-5	2.5	-3.3
-4	9.4	10.0
-3	11.6	-14.9
-2	7.2	-6.6
-1	5.1	5.8
0	11.0	-12.4
1	13.0	15.0
2	9.9	9.4
3	2.5	1.9
4	2.7	2.3
5	12.0	-17.7
H= 5, K= 0		
-12	15.6	-16.0
-10	5.4	-3.8
-8	6.3	6.2
-6	30.5	27.9
-4	18.2	-17.6
-2	12.3	-12.0
0	9.0	7.7
4	7.7	-7.9
6	6.9	-5.9
8	18.3	16.9
10	8.6	7.9
H= 5, K= 1		
-12	7.0	5.5
-11	10.1	-9.2
-10	7.2	-4.8
-9	1.7U	1.0
-8	12.7	-13.0
-7	28.4	22.3
-6	6.4	5.2
-5	1.7U	2.9
-4	13.4	14.6
-3	33.6	-36.7
-2	1.7U	-3.6
-1	10.8	11.2
0	1.7U	2.2
1	16.4	14.9
2	1.7U	1.4
3	1.7U	2.8
4	12.0	-11.3
5	19.4	-16.6
6	5.4	-4.6
7	1.6U	-0.3
8	6.3	6.2
9	11.8	10.8
10	4.9	5.1
11	0.7U	3.1
H= 5, K= 2		
-12	9.3	-9.5
-11	1.3U	-3.0
-10	1.4U	-4.2
-9	12.5	-10.4
-8	8.7	6.9
-7	1.6U	0.3
-6	20.3	16.9
-5	26.5	22.4
-4	36.7	-34.3
-3	1.6U	-4.2
-2	7.6	-5.4
-1	18.5	-18.9
0	29.4	32.3
1	6.5	7.1
2	8.0	9.4
3	11.8	6.6
4	16.9	-15.7
5	1.6U	-4.1
6	15.8	-14.4
7	1.5U	-3.8
8	9.1	7.2
9	1.2U	0.1
10	5.6	5.6
H= 5, K= 3		
-11	10.0	-10.2
-10	5.4	-4.4
-9	6.4	-6.7
-8	6.2	-4.7
-7	18.1	14.8
-6	9.5	9.3
-5	1.8U	1.2
-4	8.7	9.8
-3	21.9	-22.1
-2	20.0	-21.1
-1	15.8	16.5
0	6.9	-7.8
1	11.3	10.9
2	13.7	14.1
3	1.8U	-3.1
4	11.7	11.6
5	17.8	-14.7
6	1.7U	-4.0
7	1.6U	3.1
8	12.0	-10.2
9	5.4	5.6
10	0.9U	-0.6
H= 5, K= 4		
-11	1.1U	-0.8
-10	1.4U	-1.6
-9	6.7	-5.1
-8	1.6U	3.4
-7	6.5	-4.6
-6	14.3	12.8
-5	13.1	10.6
-4	11.7	-11.4
-3	7.2	-5.2
-2	1.7U	-3.7
-1	12.9	-13.4
0	1.7U	3.3
1	7.8	8.2
2	1.7U	3.4
3	13.8	13.1
4	1.7U	-4.1
5	1.6U	0.3
6	5.4	-5.0
7	12.5	-12.6
8	10.4	10.0
9	0.9U	-2.4
H= 6, K= 0		
-10	22.3	-20.5
-8	9.7	-7.6
-6	27.9	24.3
-4	14.7	13.6
-2	29.6	-28.5
2	6.9	7.3
6	8.9	-8.8
8	4.3	-8.1
H= 6, K= 1		
-11	8.6	-7.8
-10	1.3U	-3.2
-9	15.5	-14.3
-8	7.3	-6.7
-7	1.6U	2.7
-6	1.7U	-2.6
-5	23.7	22.6
-4	1.7U	3.9
-3	13.1	-10.7
-2	6.7	5.2
-1	14.5	-12.9
0	1.7U	1.6
1	11.8	9.2
2	5.4	-3.9
3	7.0	5.0
4	1.6U	-1.0
5	1.5U	2.2
6	6.3	4.9
7	15.7	-14.2
8	4.0	-3.7
9	0.6U	2.4
H= 6, K= 2		
-11	7.4	6.8
-10	9.6	-8.3
-9	1.3U	-2.5
-8	1.4U	-7.2
-7	7.7	-7.6
-6	7.2	6.6
-5	1.6U	-0.2
-4	6.1	5.6
-3	5.0	4.4
-2	19.0	-17.9
-1	1.6U	-1.0
0	1.6U	2.1
1	1.6U	1.3
2	7.4	6.8
3	1.5U	-0.4
4	12.3	10.8
5	1.4U	4.1
6	8.9	-8.1
7	1.1U	-0.8
8	10.6	-10.0
H= 6, K= 3		
-10	5.7	6.3
-9	1.3U	-1.4
-8	10.6	-9.4
-7	6.1	4.5
-6	1.6U	-3.6
-5	14.2	12.0
-4	17.5	14.5
-3	10.3	-9.5
-2	1.7U	-1.4
-1	17.0	-15.4
0	13.8	-12.2
1	1.7U	3.6
2	1.7U	-0.6
3	12.9	12.2
4	1.5U	4.4
5	9.4	8.0
6	7.9	7.3
7	15.0	-13.8
H= 6, K= 4		
-10	6.9	-8.5
-9	6.2	-6.8
-8	1.3U	-1.7
-7	14.3	-13.1
-6	6.2	6.1
-5	15.8	13.6
-4	9.7	9.0
-3	20.3	17.8
-2	12.0	-11.7
-1	15.8	-15.8
0	1.6U	0.1
1	15.0	-13.2
2	1.5U	3.0
3	1.5U	1.8
4	1.4U	3.6
5	11.5	10.5
6	5.1	-5.7
7	3.7	4.5
H= 7, K= 0		
-8	9.2	-9.0
-6	4.2	-4.7
-4	1.2U	2.0
-2	9.3	7.5
0	1.2U	-5.2
2	1.1U	-1.7
4	8.2	7.7
H= 7, K= 1		
-3	13.0	12.7
1	12.5	-10.1
2	1.4U	0.5
3	6.1	1.3
4	5.2	4.9
H= 7, K= 2		
-9	5.3	6.5
-8	11.7	-11.4
-7	7.5	-6.9
-6	1.2U	2.8
-5	5.2	-5.2
-4	15.8	15.2
-3	1.3U	3.8
-2	1.3U	3.0
-1	5.1	4.9
0	18.4	-17.5
1	1.3U	-2.5
2	5.4	-4.2
3	5.3	-4.8
4	5.4	7.0
5	6.5	1.8
H= 7, K= 3		
-8	4.4	-4.5
-7	1.1U	-4.3
-6	7.1	-7.2
-5	1.3U	3.3
-4	1.3U	0.5
-3	9.2	10.5
-2	8.2	8.8
-1	9.8	-9.2
0	6.8	6.1
1	6.5	-6.0
2	9.5	-7.9
3	1.1U	3.6
4	0.9U	-9.4
5	4.7	5.2
H= 7, K= 4		
-7	3.3	-4.8
-6	4.2	-3.9
-5	1.1U	-2.2
-4	4.4	4.2
-3	1.2U	1.6
-2	4.6	4.1
-1	7.5	7.6
0	5.7	-6.7
1	1.1U	-0.5
2	1.0U	2.1
3	8.5	-9.8

The data were not of sufficient quality to warrant an attempt to refine the hydrogen-atom parameters, but the presumed hydrogen positions, with isotropic temperature factors of 3 Å^2, were included in the structure factor calculations for two final least-squares refinement cycles of the heavy atoms. The final shifts were all smaller than 10^{-4} Å; the usual discrepancy index, *R*, was 0·13 for all reflections and 0·11 if the unobserved (marked *U* in Table 1) and the five strongest (marked *E* in Table 1) were omitted. The final parameters are given in Table 2.

Results and discussion

The structure is illustrated in Fig. 1, in which the hydrogen-bonding network is shown by dashed lines. The hydrogen-bond distances and angles are listed in Table 3. The four hydrogen-bonded neighbours of each of the two ammonium ions form a nearly tetrahedral arrangement, the six angles subtended at the nitrogen atoms by their closest neighbours varying from 93 to 124° at N(1) and from 100 to 123° at (N2) Ammonium-1 links four different sulfite ions and ammonium-2 links three sulfite ions and the water molecule. The water molecule's hydrogen-bonded neighbors are ammonium-2 and two sulfite ions. The three hydrogen-bonded neighbors of the water molecule are in a plane, with the angle subtended by the acceptor atoms, O(1) and O(2), 106°. Each of the three sulfite oxygen atoms accepts three hydrogen bonds, and these, together with the S–O bonds, form an approximately

Table 2. *Final parameters*

All $\times 10^4$ except for those of the H atoms, which are $\times 10^3$. H(3) to H(6) are on N(1); H(7) to H(10) are on N(2). The e.s.d.'s of the positions are essentially isotropic for all but the water oxygen (*W*); for it, $\sigma(x)$ is 0·011 Å, $\sigma(y) = \sigma(z) = 0{\cdot}007$ Å. The e.s.d.'s of the B_{ii} average about 5 % of the corresponding value for S and between 7 and 10 % for the other atoms.
The thermal parameters are of the form

$$\exp\left(-B_{11}h^2 - B_{22}k^2 - B_{33}l^2 - B_{12}hk - B_{23}kl - B_{13}hl\right)$$

	x	y	z	e.s.d.
S	2213	5390	3776	0·0015 Å
O(1)	2933	7086	4231	0·005
O(2)	−0079	5618	3270	0·005
O(3)	3436	5144	2804	0·005
N(1)	3079	8087	1522	0·006
N(2)	2731	3011	0940	0·006
W	−1667	5352	1075	*
H(1*W*)	−110	550	180	
H(2*W*)	−210	410	100	
H(3)	320	710	200	
H(4)	300	800	075	
H(5)	420	880	180	
H(6)	200	890	160	
H(7)	180	210	120	
H(8)	420	260	090	
H(9)	240	350	025	
H(10)	300	370	150	

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
S	132	53	22	−5	22	−7
O(1)	183	80	35	28	4	29
O(2)	150	120	49	6	7	26
O(3)	148	81	41	−46	59	1
N(1)	181	85	30	16	37	−19
N(2)	181	83	34	−8	33	2
W	758	130	47	209	−91	−43

Table 3. *Distances and angles*

The values in parentheses after the S–O distances are before correction for libration; the other distances and angles have not been corrected. The e.s.d.'s of the S–O distances are about 0·006 Å and of the O–S–O angles about 0·4°. The e.s.d.'s of the hydrogen-bond distances and angles are 0·008–0·009 Å and about 0·6°. The positions of hydrogen-bonded atoms are indicated by a number if other than (x, y, z) and by the translation involved if in a neighboring unit cell. Positions: 2, $-x, -y, -z$; 3, $-x, \frac{1}{2}+y, \frac{1}{2}-z$; 4, $x, \frac{1}{2}-y, \frac{1}{2}+z$. The angles for each set of hydrogen bonds are given in the right-hand column, only the subtending atoms being listed.

S–O(1)	1·532 (1·528) Å		O(1)–S–O(2)	105·4°
S–O(2)	1·520 (1·513)		O(1)–S–O(3)	104·4
S–O(3)	1·535 (1·532)		O(2)–S–O(3)	104·6
N(1)	··· O(1), 4, $00\bar{1}$	2·83 Å	O(1), O(2)	101
	··· O(2), 3, $0\bar{1}0$	2·83	O(1), O(3)	120
	··· O(3)	2·85	O(1), O(3′)	104
	··· O(3), 3, $1\bar{1}0$	2·80	O(2), O(3)	124
			O(2), O(3′)	93
			O(3), O(3′)	109
N(2)	··· O(1), 3, 100	2·88	O(1), O(2)	118
	··· O(2), 3	2·82	O(1), O(3)	100
	··· O(3)	2·87	O(1), *W*	100
	··· *W*, 2, 010	2·82	O(2), O(3)	100
			O(2), *W*	123
			O(3), *W*	115
W	··· O(1), 3	2·77	O(1), O(2)	106
	··· O(2)	2·78	O(1), N(2)	107
	··· N(2), 2, 010	2·82	O(2), N(2)	147

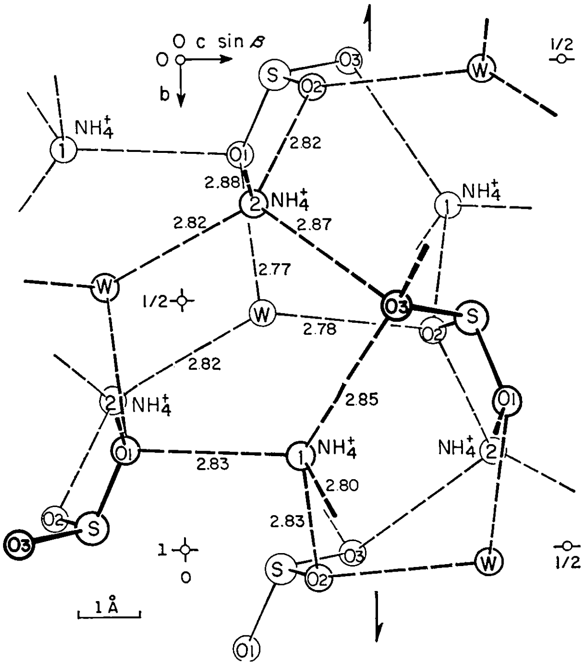

Fig. 1. A view of a portion of the structure down **a**, showing the lengths of the hydrogen bonds (Å). *W* represents the water molecule.

tetrahedral array at each of these atoms as well. It is, in all, a remarkably efficient packing scheme, as manifested by the comparatively low temperature factors of all the atoms but the oxygen of the water molecule. Its motion is very markedly anisotropic; the r.m.s. amplitude of vibration normal to the plane of its three nearest neighbors (and thus almost in the direction of viewing in Fig. 1) is 0·39 Å, about twice that in any direction in the plane, where its motion is nearly isotropic and comparable to that of the ammonium ions. We suspected at first that this high apparent vibration amplitude, analogous to that of a drumhead, might be merely a manifestation of some disorder, but inspection of the final difference map along the line (*x*, 0·54, 0·11), and indeed elsewhere as well, revealed no unaccounted peaks even as high as 0·5 e.Å^{-3}.

The geometry of the sulfite ion is summarized in Table 3. The libration corrections, which are small and do not affect the angles significantly, were estimated by averaging the differences in the amplitudes of vibration of the sulfur and oxygen atoms in two perpendicular directions normal to the S–O bonds, and then applying the Pythagorean theorem, a procedure analogous to that of Leung & Marsh (1958). The average S–O distance is 1·529 Å, and the average angle is 104·8°. The distance is compared with those in some related oxyanions in Table 4; it is in good accord with expectation on the basis of analogy with the chlorate-perchlorate comparison. Robinson (1964) predicted a bond length of 1·54 Å in the sulfite ion by consideration of the S–O stretching frequency and a linear relationship between bond orders and force constants for S–O bonds.

Table 4. *Distances in some third-row oxyanions**

	P–O (n=3)	S–O (n=2)	Cl–O (n=1)
XO$_4^{n-}$	1·54^a	1·48^b	1·46^a
XO$_3^{n-}$		1·53^c	1·50^d
XO$_2^{n-}$			1·57^e

(*a*) Cruickshank (1961)
(*b*) Larson (1965)
(*c*) This work
(*d*) Laing & Trueblood (1965)
(*e*) Gillespie, Sparks, & Trueblood (1959)

* The e.s.d. of each distance is 0·01 Å or less, except for that in ClO$_2^-$, where it is about 0·03 Å.

The increase in distance with decreasing number of oxygen atoms may be regarded as a consequence of a greater effect of the decreasing nuclear charge on the 3*d* orbitals than of the increasing π-bond order of the X–O bonds, as discussed by Cruickshank (1961). On the other hand, Robinson (1964) suggests that the bond order in sulfite is only 1·33, as compared with 1·50 in sulfate, with the lone pair replacing one of the two resonating double bonds in the valence-bond formulation of sulfate; he attributes this effect to a reduction of the electronegativity of the central atom by the lone pair (Robinson, 1963). The effect of the unshared electron pair is manifested also in the decrease of the O–S–O bond angle by nearly 5° below the tetrahedral value; the corresponding decrease in ClO$_3^-$ is nearly 3° (Laing & Trueblood, 1965). These angles are in marked contrast to the O–S–O angles in methylenedisulfonate ion, CH$_2$(SO$_3$)$_2^{2-}$, which average 113° (Truter, 1962*a*), significantly greater than the tetrahedral value; the difference from sulfite seems most simply ascribable to a difference in lone pair–bonded pair and bonded pair–bonded pair repulsions (Gillespie & Nyholm, 1957). An alternative interpretation of the results, in accord with a suggestion of Truter (1962*b*), is that the bonding orbitals used by S(IV) and Cl(V) may have significantly more *p*-character than do sp^3 orbitals, with consequently greater bond distances and smaller bond angles. However, we prefer the former interpretation.

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