

with other literature values, because different impurity levels of the crystal specimen examined may shift the minimum in the c axis *vs.* temperature curve. For example, Erfling (1939) found a c axis expansivity value for beryl that, at about 100°C, was $-2.0 \times 10^{-6} \text{°C}^{-1}$ and which decreased to $-1.43 \times 10^{-6} \text{°C}^{-1}$ at room temperature, while the expansivity along the a axis changed from $-0.52 \times 10^{-6} \text{°C}^{-1}$ at -200°C to $+1.05 \times 10^{-6} \text{°C}^{-1}$ at room temperature. Room-temperature values for emerald from the *Handbook of Chemistry and Physics* (1957) are $1.00 \times 10^{-6} \text{°C}^{-1}$ and $-1.35 \times 10^{-6} \text{°C}^{-1}$ for a axis and c axis expansivities; these compare better with Erfling's beryl values than with the present values of either beryl or emerald, and suggest the importance of impurities in affecting the thermal expansion behavior of this silicate system.

Returning to the question of atomic movements, it is known that the lattice constants for beryl and emerald can be determined with a greater precision than the atomic locations, and these constants appear to corroborate the above mentioned hypothesis on the movement of the silicate rings with temperature. Note that the lattice constants for beryl and emerald at room temperature differ by $\sim 5 \times 10^{-4} \text{Å}$, and that the radii of Al^{3+} and Cr^{3+} can be taken as 0.61 and 0.70 Å respectively (Shannon & Prewitt, 1969). Further, an Al^{3+} ion constitutes about 15% of a linear dimension in the cell, while the difference of the radii is about 15% with a concentration dopant level of Cr ions of about 3%; this suggests a difference ($0.15 \times 0.15 \times 0.03 \approx 6 \times 10^{-4}$) in the lattice constants of beryl and emerald can be expected, and is found to be of the same order of magnitude as that observed. The introduction of Cr^{3+} ions into the beryl structure results in a corresponding expansion of the lattice, as indicated in the above mentioned hypothesis, *i.e.* the

rings are moved away from each other to accommodate the larger Cr^{3+} radius. This implies that the thermal expansion behavior of emerald may be similar to beryl, but with a shift on the temperature scale. Indeed, the minimum on the c axis expansivity is shifted in temperature some 200°. The added lengthening on the Be–O separations (as well as the Al–O separations, which are also lengthened) probably tend to resist the rotation of the rings, yielding a shallower minimum in the c axis *vs.* temperature curve for emerald than for beryl.

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The Crystal Structure of Ammonium Sulphamate

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Ammonium sulphamate, $\text{NH}_4\text{NH}_2\text{SO}_3$, crystallizes in the orthorhombic space group $Pbca$, with eight formula units in a unit cell of dimensions $a=7.558$ (6), $b=7.835$ (9), and $c=14.49$ (2) Å. The crystal structure has been determined by the symbolic addition method and refined by full-matrix least squares to an R value of 0.095. The sulphamate tetrahedron is slightly distorted, the S–O distances being 1.45 (1), 1.46 (1) and 1.49 (1) Å. The S–N bond distance is 1.63 (1) Å, which is in between single and double bond values, indicating ($p \rightarrow d$) π -bonding. The sulphamate and ammonium ions are arranged in columns parallel to the a and c directions and are held together by a network of hydrogen bonds.

Introduction

A neutron-diffraction study of potassium sulphamate, KNH_2SO_3 , by Cox, Sabine, Padmanabhan, Ban,

Chuang & Surjadi (1967) indicated that the nitrogen atom is tetrahedrally surrounded by one sulphur and two hydrogen atoms, with a lone pair of electrons in the fourth tetrahedral direction. The N–S bond length

was observed to be 1.666 Å, which is in between the single (1.74 Å) and double (1.54 Å) bond lengths calculated from covalent radii. A similar length (1.655 Å) for the N-S bond was obtained for potassium amine-disulphonate, $K_2NH(SO_3)_2$, by Jeffrey & Jones (1956). Though they could not locate the hydrogen atom position, they arrived at a planar configuration about the nitrogen atom, basing their inference on the observed N-S bond lengths, which they explained in terms of ($p \rightarrow d$) π -bonding. Similar conclusions were earlier drawn for the sulphamate ion in potassium sulphamate (Brown & Cox, 1940; Jeffrey & Stadler, 1951). In sulphamic acid, $N^+H_3SO_3^-$, which exists as a zwitterion in the solid state (Sass, 1960), the nitrogen atom has no electrons available for π bonding and thus has a tetrahedral configuration, with a single N-S bond (1.764 Å). Recently, however, Tillack & Kennard (1970) have found a N-S bond length of 1.72 Å, close to the single bond value, in potassium nitrilotrisulphonate dihydrate, $K_3N(SO_3)_3 \cdot 2H_2O$. But the geometry of NS_3 is planar in this case. The present crystal structure investigation of ammonium sulphamate was undertaken with the purpose of getting more information about the sulphamate ion.

Experimental

Crystals of ammonium sulphamate were grown by slow evaporation from the aqueous solution obtained by neutralizing sulphamic acid with ammonium hydroxide. The unit-cell dimensions, first determined from Weissenberg photographs, were refined by least squares, using data collected with the neutron diffractometer SAND at the CIRUS reactor ($\lambda = 1.041$ Å).

Crystal data

Ammonium sulphamate, $NH_4NH_2SO_3$, M.W. 114.1.

$a = 7.558$ (6) Å $D_m = 1.78$ g.cm⁻³
 $b = 7.835$ (9) $Z = 8$
 $c = 14.49$ (2) $D_x = 1.768$ g.cm⁻³

Systematic absences: $0kl$, k odd; $h0l$, l odd; $hk0$, h odd
 Space group: $Pbca$ (No. 61)
 Linear absorption coefficient (for Cu $K\alpha$) $\mu = 58.3$ cm⁻¹

Multiple-film equi-inclination Weissenberg photographs were taken along the b axis for the zero to the third layer and along the a axis for the zero and the first layer. Cylindrical specimens were used for both the zones, with diameters 0.28 and 0.43 mm respectively. The relative intensities of 553 independent reflexions were visually estimated by comparison with a calibrated film strip. Of these, 345 were observable. Corrections were applied for absorption and for the Lorentz and polarization factors. The data for the two zones were brought to the same scale by comparing the intensities of common reflexions. A Wilson plot was then made to place the observed intensities on an absolute scale.

Sign determination

The symbolic addition method (Karle & Karle, 1966) was employed for determining the signs of structure factors. Normalized structure amplitudes, $|E_h|$, were computed from the observed structure amplitudes and reflexions with $|E_h| \geq 1.2$ were used for determining their signs. Table 1 shows the sign assignments of reflexions which were chosen for specifying the origin and for initiating the sign-determination procedure by the application of the Σ_2 formula:

$$sE_h \simeq s(E_k E_{h-k}),$$

where h , k are vectors with reflexion indices for their components, and s means 'sign of'. The symbols A , B , C and D in Table 1 are unknown to start with. Signs of other reflexions, in terms of products involving the symbols A , B , C , D , were determined from the Σ_2 formula using a computer program written by Sikka (1970). A number of reflexions, the signs of which were determined by many different combinations, gave strong indications for the following results: $A \cdot D = +1$, $B \cdot C = -1$. As the analysis went further, the relations $A = +1$, $D = +1$, and $B = -1$, $C = +1$, also became evident. Signs of 153 independent reflexions were determined in this way. A Fourier synthesis was now made, with normalized structure factors for the coefficients (E map). This E map, as it later turned out, had five strong, genuine peaks. But, as there were also at least four other false, strong peaks, only the strongest peak was accepted and attributed to the sulphur atom. Assuming the presence of the sulphur atom alone, signs of structure factors were calculated for the 345 observable reflexions and a second Fourier synthesis was made (F map). This gave the sulphur peak and four other strong peaks. From stereochemical considerations, two of these were tentatively attributed to oxygen atoms of the sulphamate group and one to the ammonium ion. A third Fourier synthesis, with signs determined by contributions from these four atoms, revealed the positions of the remaining two atoms also.

Table 1. Sign assignments for specifying the origin and implementing the Σ_2 formula

h	Sign	E_h
6 1 4	+	2.22
1 2 11	+	3.37
1 1 10	+	2.87
1 3 7	A	2.41
1 3 11	B	2.86
0 2 13	C	2.61
1 4 8	D	2.24

Refinement

A full-matrix least-squares refinement of the atomic parameters was now carried out using the computer

program *ORFLS** (Busing, Martin & Levy, 1962). Initially, all observable structure amplitudes were given unit weights, with zero weights for the unobservable ones. Individual scale factors were assigned to the data from each layer and were treated as variables during the refinement. The quantity minimized was $\sum w(|F_o| - K|F_c|)^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes, respectively, and w is the weight assigned to a particular observation $|F_o|$; K is the scale factor pertaining to the layer to which a given $|F_o|$ belongs. A value of 0.17 was obtained for the conventional R index after a few cycles.

Anisotropic temperature factors were next in-

troduced and the following weighting scheme was employed: $w^{1/2} = 0$ for unobservable reflexions; $w^{1/2} = 1$ for observable reflexions with $|F_o| \leq 20$; $w^{1/2} = 20/|F_o|$ for observable reflexions with $|F_o| > 20$. A few cycles of refinement, excluding about ten reflexions suspected to be severely affected by extinction, brought the R index down to 0.11 and gave a value of 0.15 for the weighted R index, WR [defined as $WR = \{\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2\}^{1/2}$].

To ascertain the correctness of the choice of sulphamate nitrogen position, its atomic parameters were interchanged with those of each of the three oxygen atoms in turn and the refinement was repeated. All three trials gave a significantly higher value for the quantity minimized, compared with its value from the original choice. The original choice was further confirmed by the bond length values.

It was found at this stage that for one of the oxygen

* This and all other computations were carried out on the CDC 3600 computer at the Tata Institute of Fundamental Research, Bombay.

Table 2. *Observed and calculated structure factors for ammonium sulphamate*

Successive columns contain $h, k, l, |F_o|$ and F_c . A minus sign with $|F_o|$ means 'less than'.

(This table contains a large grid of data points for structure factors, organized in columns corresponding to h, k, l, |F_o|, and F_c. The data is too dense to transcribe fully here.)

Table 3. *Fractional coordinates and thermal parameters with their standard deviations in parentheses*

The thermal parameters are defined by $T = \exp \{ -(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl) \}$. All values are multiplied by 10^4

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
S	3819 (5)	1494 (5)	1394 (2)	95 (7)	117 (9)	25 (2)	14 (10)	-11 (3)	5 (3)
O(1)	2766 (14)	972 (16)	603 (6)	138 (20)	200 (26)	34 (4)	32 (29)	-8 (8)	5 (8)
O(2)	2687 (19)	2017 (16)	2184 (6)	222 (24)	184 (24)	30 (5)	80 (29)	38 (10)	-4 (8)
O(3)	5085 (12)	2806 (15)	1140 (7)	80 (15)	121 (19)	56 (6)	-38 (24)	23 (8)	14 (10)
N(1)*	4918 (17)	-195 (19)	1720 (8)	113 (20)	134 (27)	49 (6)	67 (30)	21 (10)	14 (10)
N(2)	3706 (16)	1358 (18)	4180 (7)	108 (19)	153 (27)	34 (5)	-19 (30)	-11 (11)	0 (9)

* N(1) denotes the sulphamate-ion nitrogen atom, and N(2) the ammonium-ion nitrogen atom.

atoms [designated O(3) in Table 3], the matrix representing the thermal ellipsoid is not positive-definite, indicating some serious systematic error. Extinction was suspected, and an approximate correction for isotropic, secondary extinction was applied, using Zachariasen's (1967) general theory of extinction. \bar{T} , the absorption-weighted mean path length in the crystal, was calculated for each reflexion from the following relation (Coppens & Hamilton, 1970):

$$\bar{T} \approx \log A^*/\mu,$$

A^* being the absorption correction factor. Two cycles of refinement, with the extinction constant g' (Coppens & Hamilton, 1970) as a variable parameter, gave $R=0.11$, $WR=0.12$.

An error analysis of the data at this stage indicated the following weighting scheme:

$$w^{-1/2} = 2.65 + 0.0005 F_c^2/\sin 2\theta.$$

The refinement was repeated with this weighting scheme. The final value of the R index was 0.095, with $WR=0.11$. The extinction constant, g' , had the value 4.68, corresponding to a value of 1.24 seconds for the equivalent mosaic spread parameter, η . For the worst affected reflexion (021), F_o^2/F_c^2 was found to be 0.15.

Table 2 gives the observed and the calculated structure factors for the various reflexions. Table 3 gives the coordinates and anisotropic temperature factors for non-hydrogen atoms, and Table 4 the bond lengths and angles for the sulphamate ion, calculated by using the program *ORFFE* (Busing, Martin & Levy, 1964).

Table 4. Bond lengths and angles in the sulphamate ion

S-O(1)	1.45 (1) Å	O(1)-S-O(2)	111.7 (7)
S-O(2)	1.49 (1)	O(1)-S-O(3)	111.1 (6)
S-O(3)	1.45 (1)	O(2)-S-O(3)	112.3 (7)
S-N(1)	1.63 (1)	O(1)-S-N(1)	106.1 (7)
		O(2)-S-N(1)	107.1 (7)
		O(3)-S-N(1)	108.2 (7)

Table 5. Intermolecular distances less than 3.40 Å and the relevant angles

N(1 ⁱ)...O(2 ^{vi})	3.02 (2) Å	S ⁱ —N(1 ⁱ)-O(2 ^{vi})	108.6 (6)°
N(1 ⁱ)...O(2 ^{viii})	3.15 (2)	S ⁱ —N(1 ⁱ)-O(2 ^{viii})	92.2 (5)
N(1 ⁱ)...O(2 ⁱⁱⁱ)	3.25 (2)	S ⁱ —N(1 ⁱ)-O(2 ⁱⁱⁱ)	165.8 (6)
N(2 ⁱ)...O(3 ⁱⁱⁱ)	2.97 (2)	O(3 ⁱⁱⁱ)-N(2 ⁱ)-O(3 ^{viii})	127.7 (5)
N(2 ⁱ)...O(1 ^{iv})	2.97 (1)	O(3 ⁱⁱⁱ)-N(2 ⁱ)-O(3 ^{vii})	103.8 (4)
N(2 ⁱ)...O(3 ^{viii})	3.00 (1)	O(3 ⁱⁱⁱ)-N(2 ⁱ)-N(1 ⁱⁱⁱ)	129.3 (4)
N(2 ⁱ)...O(1 ^{vii})	3.02 (1)	O(3 ^{viii})-N(2 ⁱ)-O(3 ^{vi})	111.7 (4)
N(2 ⁱ)...O(1 ^{viii})	3.10 (2)	O(3 ^{viii})-N(2 ⁱ)-O(3 ⁱⁱⁱ)	85.0 (4)
N(2 ⁱ)...O(3 ^{vii})	3.10 (1)	O(3 ^{vii})-N(2 ⁱ)-N(1 ⁱⁱⁱ)	95.0 (4)
N(2 ⁱ)...N(1 ⁱⁱⁱ)	3.17 (2)	O(3 ⁱⁱⁱ)-N(2 ⁱ)-O(1 ^{vi})	146.0 (5)
N(2 ⁱ)...N(1 ^{viii})	3.37 (2)	O(3 ^{viii})-N(2 ⁱ)-O(1 ^{vii})	78.2 (4)
		O(1 ^{vi})-N(2 ⁱ)-O(1 ⁱⁱⁱ)	76.6 (5)

Code for symmetry-related atoms:

Superscript	Atom at	Superscript	Atom at
i	x, y, z	v	$\bar{x}, \bar{y}, \bar{z}$
ii	$\frac{1}{2} + x, \frac{1}{2} - y, \bar{z}$	vi	$\frac{1}{2} - x, \frac{1}{2} + y, z$
iii	$\bar{x}, \frac{1}{2} + y, \frac{1}{2} - z$	vii	$x, \frac{1}{2} - y, \frac{1}{2} + z$
iv	$\frac{1}{2} - x, \bar{y}, \frac{1}{2} + z$	viii	$\frac{1}{2} + x, y, \frac{1}{2} - z$

Discussion

The dimensions of the sulphamate tetrahedron are similar to those reported for potassium sulphamate (Cox *et al.*, 1967). The three S-O bonds are normal, with lengths 1.45, 1.46, and 1.49 Å, averaging 1.47 Å. The O-S-O angles are also normal and range between 111.1 and 112.3°, deviating slightly from the tetrahedral value. The N-S bond length (1.63 Å), as in potassium sulphamate, is considerably shorter than the single bond (1.74 Å) value, and lies in between single and double bond (1.54 Å) values. As mentioned earlier, the shortening may be attributed to $d_{\pi}-p_{\pi}$ overlap of d orbitals of sulphur with p orbitals of nitrogen, resulting in the delocalization of electron density around the N-S bond, with an appropriate increase in the double-bond character. The three chemically equivalent angles, O-S-N, are systematically smaller than the tetrahedral value. The effect of this distortion is to equalize the non-bonded O-N distances (Donohue, 1965; Shaefer & Marsh, 1966). The average such O-N distance is 2.49 Å, with a root-mean-square deviation of 0.02 Å.

The structure, projected down the b axis, is shown in Fig. 1. Sulphamate and ammonium ions are arranged one above the other in columns running parallel to the c and a directions. These columns are linked by a network of hydrogen bonds. There are three types of hydrogen bond in the structure: (i) N-H...O type, where the nitrogen atom belongs to the NH₂ group of the sulphamate ion, (ii) N-H...O type in which the nitrogen atom is from the ammonium ion, and (iii) N-H...N type, the acceptor nitrogen being from the NH₂ group of the sulphamate ion. The nitrogen atom of the NH₂ group has three neighbouring oxygen atoms belonging to different sulphamate ions. These are at reasonable distances (< 3.3 Å), and are in satisfactory directions (the S-N...O angles ranging between 92.2 and 165.8°) to form hydrogen bonds

(Table 5). As attempts at locating hydrogen atom positions from difference Fourier syntheses did not give definite results, it is not possible to say which of these oxygen atoms are involved in hydrogen bonding. For types (ii) and (iii) of hydrogen bond, in which the ammonium-ion nitrogen atom acts as the donor, there are nine possible acceptor atoms (seven oxygen and two nitrogen) at distances less than 3.4 Å (Table 5). Of these, hydrogen bonds to three oxygen atoms [all O(3)'s] and one nitrogen atom, at distances 2.97, 3.00, 3.10 and 3.17 Å, will have the minimum amount of deviation from linearity, the angles subtended varying between 85.0 and 129.3°. Alternatively, one may consider the oxygen [O(1)] at a distance of 3.02 Å from N(2) as a possible acceptor atom, instead of one of the O(3)'s, which is at a greater distance (3.10 Å). The latter possibility has been shown in Fig. 1, where these bonds have been indicated by dashed lines as

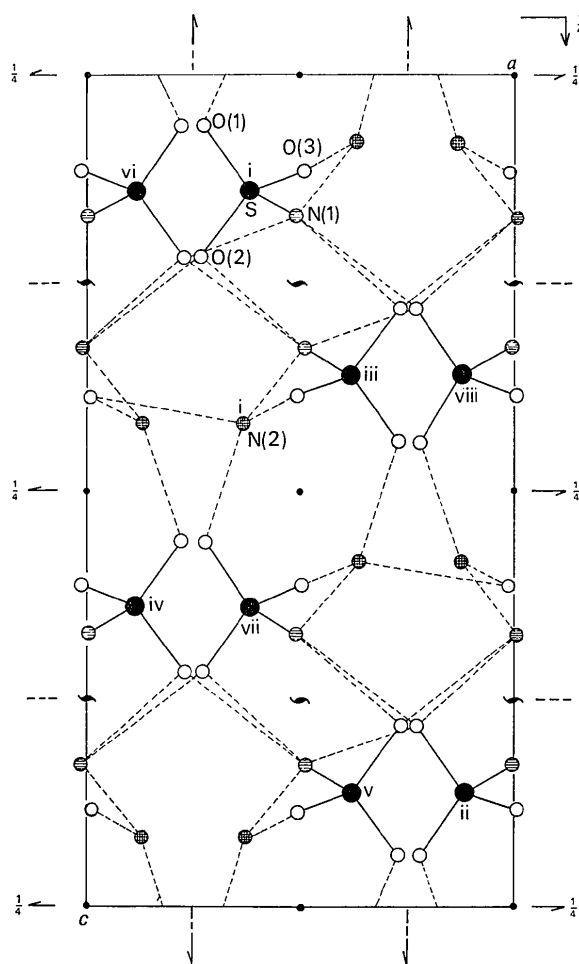


Fig. 1. Projection of the structure of $\text{NH}_4\text{NH}_2\text{SO}_3$ viewed down the b axis. Broken lines indicate hydrogen bonds.

also the possible hydrogen bonds in which the NH_2 nitrogen acts as a donor atom. It is possible that a single proton may be shared by two acceptor oxygen atoms to form bifurcated hydrogen bonds.

For saying something conclusive about the configuration around the NH_2 nitrogen atom, a knowledge of the exact hydrogen position would be essential. A three-dimensional neutron diffraction study of the structure has therefore been started.

The r.m.s. components of atomic thermal displacement along ellipsoid principal axes ($1 < 2 < 3$), along with their e.s.d.'s, are given in Table 6. In general, the atoms O(2) and O(3) exhibit considerable anisotropy.

Table 6. The r.m.s. components of thermal displacement along ellipsoid principal axes

	Axis	Component		Axis	Component
S	1	0.139 (9) Å	O(3)	1	0.110 (32) Å
	2	0.182 (7)		2	0.210 (18)
	3	0.200 (8)		3	0.255 (12)
O(1)	1	0.176 (19)	N(1)	1	0.127 (39)
	2	0.204 (16)		2	0.204 (20)
	3	0.257 (18)		3	0.263 (17)
O(2)	1	0.130 (27)	N(2)	1	0.161 (23)
	2	0.218 (18)		2	0.200 (18)
	2	0.298 (16)		3	0.223 (21)

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