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The Crystal Structure of Potassium Aminedisulphonate

By G. A. Jeffrey* and D. W. Jones†

Chemistry Department, The University, Leeds 2, England

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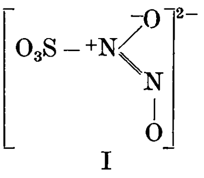
$K_2.NH.(SO_3)_2$ is monoclinic, $C2/c$, with cell dimensions $a = 12{\cdot}430$, $b = 7{\cdot}458$, $c = 7{\cdot}175$ Å, $\beta = 91°\ 11'$; $Z = 4$; molecular symmetry, 2. The cation and sulphur atomic coordinates were obtained by comparison of the Patterson projections with those of the pseudo-isomorphous ammonium and rubidium salts. The approximate positions of the light atoms were determined by difference syntheses of the Fourier projections. Three-dimensional data were used for the accurate atomic parameters, the final refinement of which was two cycles of observed and calculated differential syntheses computed on the Manchester electronic computer.

The dimensions of the anion are as follows: bond lengths, S–N 1·655 Å, e.s.d. 0·007 Å; S–O, 1·454, 1·438, 1·448 Å, mean e.s.d. 0·009 Å; bond angles, S–N–S 124° 40′; O–S–O 113° 30′, 112° 50′, 112° 20′; N–S–O 107° 10′, 102° 55′, 106° 55′.

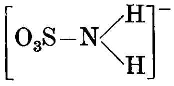
The ionic coordination is 12:6. The shorter cation to anion separations are K · · · O, which range between 2·70 and 3·23 Å.

Introduction

In the study of the structures of the dinitrososulphite, I, and sulphamate, II, ions by Jeffrey & Stadler (1951), attention was drawn to the disparity in the lengths of the S–N bonds. In I, the length of 1·79 Å was close to what might reasonably be associated with a single bond, whereas in II the length of 1·60 Å was close to that for a double bond. There is similarly a striking difference in the chemistry of these ions with respect to acid hydrolysis. The sulphamate ion is the most stable of the three amine sulphonates, II, III, IV, with only slight hydrolysis by acids at room temperature. In contrast, the S–N link in the dinitrososulphite ion is disrupted in moist air; this fact was largely responsible for the uncertainty about the existence of a direct S–N linkage and consequently about the configuration of the ion (see Cox, Jeffrey & Stadler, 1949).



I



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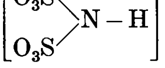

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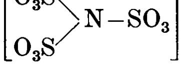

IV

A multiple S–N bond in the sulphamate ion would seem to require a planar configuration for the $S\text{–}NH_2$ atoms, but owing to the difficulty of locating the hydrogen atoms there was no direct confirmation of this (Brown & Cox, 1940; Jeffrey & Stadler, 1951). We have therefore determined the structure of the aminedisulphonate ion, III, in the potassium salt, with the object of measuring the S–N bond length and if possible establishing the configuration of the nitrogen valencies. The ammonium salt would have been more suitable for precision analysis, but for its more complex structure (Jones, 1955).

Experimental

Potassium aminedisulphonate, $K_2NH(SO_3)_2$, was prepared through the trisulphonate by the reactions

$$KNO_2 + 3\ KHSO_3 \rightarrow K_3N(SO_3)_3 + H_2O + KOH\ ,$$

$$K_3N(SO_3)_3 + H_2O \xrightarrow[\text{hydrolysis}]{\text{acid}} K_2NH(SO_3)_2 + KHSO_4\ .$$

This is followed by the further hydrolysis to potassium sulphamate,

$$K_2NH(SO_3)_2 + H_2O \rightarrow KNH_2SO_3 + KHSO_4\ ,$$

but this reaction is slow, and with low acid concentration the yield is mostly the disulphonate (Yost & Russell, 1944; Sisler & Audrieth, 1938; Wagner, 1896; Berglund, 1876). The product, in the form of a pasty mass of crystals, was washed with iced water and recrystallized from an aqueous solution of 16% concentrated ammonia to give small colourless tablets.

The crystals are monoclinic with well developed {100} and {010} forms. The cell dimensions measured by the Straumanis method and by the Weisz, Cochran & Cole (1947) θ-method are

$$a = 12{\cdot}430,\quad b = 7{\cdot}458,\quad c = 7{\cdot}175\ \text{Å},\quad \beta = 91°\ 11',$$

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* Present address: The University of Pittsburgh, Pittsburgh 13, Pa., U.S.A.

† Present address: The British Rayon Research Association, Heald Green Laboratories, Wythenshawe, Manchester, England.

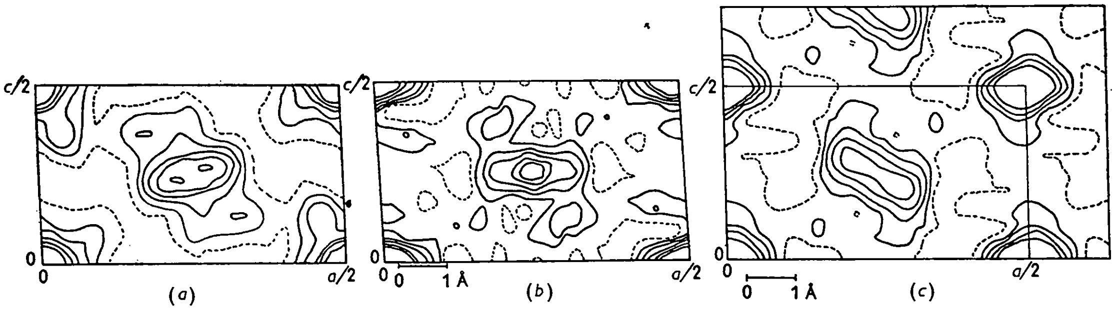


Fig. 1. Patterson (*xz*) projections: (*a*) NH_4 salt; (*b*) K salt; (*c*) Rb salt. Contours at equal intervals, negative contours being broken.

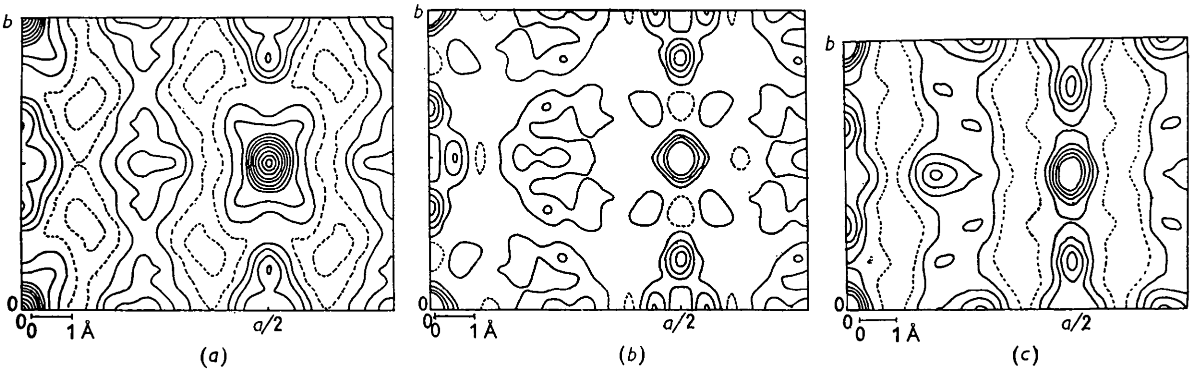


Fig. 2. Patterson (*xy*) projections: (*a*) NH_4 salt; (*b*) K salt; (*c*) Rb salt.

in good agreement with the axial ratios reported by Münzing (1888) and Zirngiebl (1902). With four molecules in the unit cell the calculated density is 2·47 g.cm.$^{-3}$ compared with an observed value of 2·49 g.cm.$^{-3}$. The systematic extinctions characterized the space group as *Cc* or *C*2/*c*. No pyro- or piezo-electrical effects could be detected and the provisional assignment of a centrosymmetrical structure was confirmed during the course of the analysis by a statistical treatment of the observed intensities by the methods of Wilson (1949) and Rogers (1949).

For the intensity measurements approximately spherical specimens 0·06 mm. in diameter were prepared by cutting and partially dissolving a small crystal in dilute acid. Absorption errors were thereby minimized (μ for Cu $K\alpha$ = 181 cm.$^{-1}$) and no corrections were applied. The intensities were recorded on multiple-film equi-inclination Weissenberg photographs for layer lines zero to eighth about the *a* axis and zero to fifth about the *b* and *c* axes. Over nine thousand individual estimations of intensities were made by direct visual comparison against standard calibrated spots. The compression and elongation of low-order reflexions on non-zero layers was compensated for by averaging estimates from upper and lower halves of the film. After application of the *Lp* and angle factors by means of the Cochran (1948) charts, the mean intensities were reduced to a common arbitrary scale by internal correlation and then placed on an approximately absolute scale by Wilson's procedure (1942). This also gave a mean temperature factor of $B = 2{\cdot}75$ Å^{-2}. The most intense reflexions were from the planes 202, $\bar{2}02$, 400 and 021. Apart from the systematically absent spectra, 71 reflexions within the range of Cu $K\alpha$ radiation were too weak to be observed; the number of independent non-zero structure amplitudes recorded was 681.

As reported elsewhere by Jones (1955), ammonium and rubidium aminedisulphonates are pseudo-isomorphous with the potassium salt, having similar *a*- and *c*-axis lengths but with their *b* axes respectively three and five times as long as that of the potassium salt. All the reflexions on the additional layer lines were very weak and a limited use of the isomorphous-replacement methods could be made by indexing the reflexions as for the simpler lattice of the potassium salt. The intensities on the principal zones and such others as were required in the structure determination were estimated with no special efforts for maximum accuracy.

Determination of the structure

With four molecules of $K_2[NH.(SO_3)_2]$ in the unit cell, the cations lie in general positions and the anions are oriented with their diad symmetry axis along the N–H bond at $(0, y, \frac{1}{4})$ and $(0, y, \frac{3}{4})$. Excluding the hydrogen atom, there are 17 independent atomic parameters to be determined.

In the initial stage of analysis, data from the am-

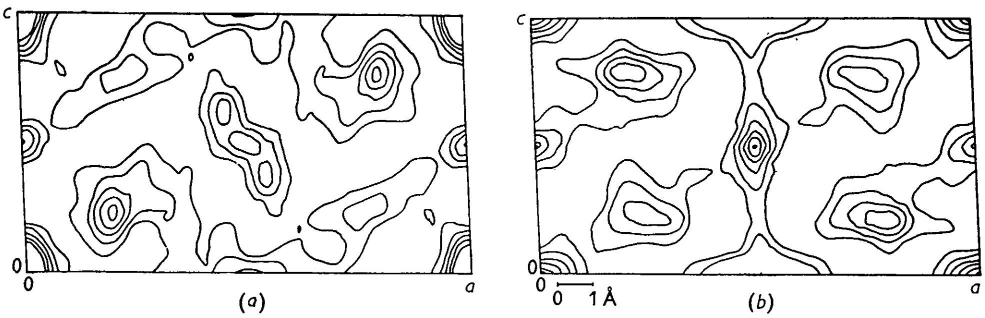


Fig. 3. (a) Patterson section at $y = 0$, NH_4 salt. (b) Patterson section at $y = \frac{1}{2}$, Rb salt. Contours at ($\frac{1}{2}, \frac{1}{2}, 0$) peak not shown.

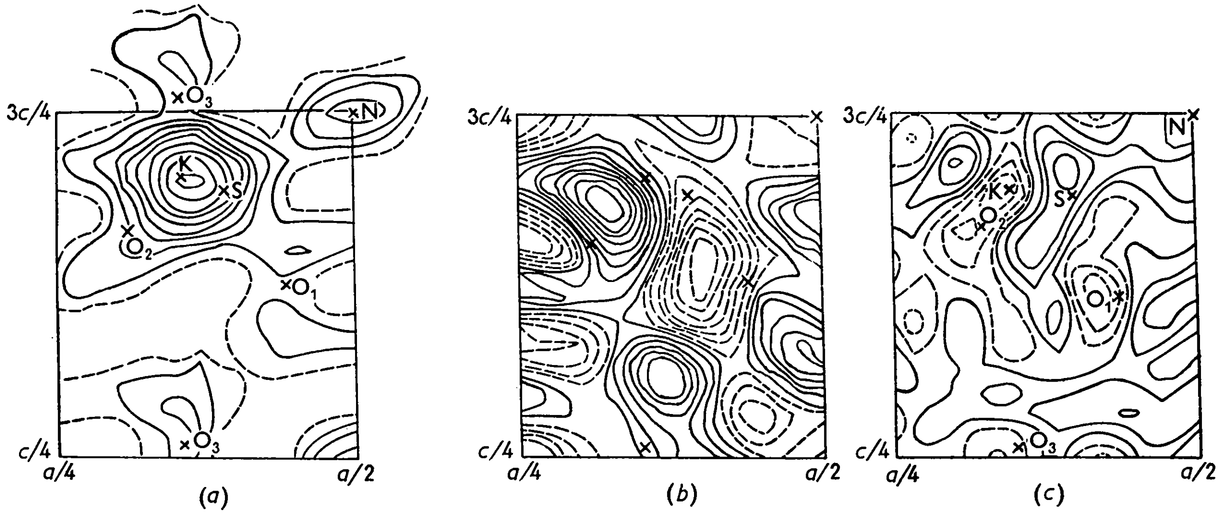


Fig. 4. (a) K salt Fourier projection on (010). (b, c) K salt ($\varrho_o - \varrho_c$) projections on (010): (b) $R = 0{\cdot}26$; (c) $R = 0{\cdot}14$. Negative contours broken; contour interval approximately 0·6 e.Å^{-2}.

monium and rubidium salts were also used. As previously mentioned, the structure of these salts appears to be closely related to that of the potassium compound. When all three sets of structure amplitudes were indexed on the simple potassium lattice the similarity in structures was apparent from the Patterson projections on (010) and (001) (Figs. 1 and 2).

Although these syntheses indicated considerable overlap of the sulphur and cations, particularly in the ($h0l$) projection, this zone was studied first since the nitrogen coordinates were fixed. A peak at 3 Å from the origin on the projection was confirmed as containing the S–S intramolecular vector by a Patterson section at $y = 0$ on the ammonium salt. Approximate coordinates for the cation were taken from a section at $y = \frac{1}{2}$ on the rubidium salt (Fig. 3).

As far as possible these coordinates for the sulphur and cations were refined by trial-and-error calculations on the $h00$ and $00l$ orders, and finally gave a disagreement index of 0·32 for the ($h0l$)'s of the ammonium salt. The analysis was then continued solely with the potassium salt. Since the oxygen positions were ill defined on the Fourier projection with the 55 terms available (see Fig. 4(a), on which the final positions are indicated on the map), the refinement was carried further by difference syntheses. Successively the disagreement index dropped to 0·14 with corresponding improvement in the difference map (Fig. 4(b, c)). The scale factor and an isotropic temperature factor uniform for all atoms were adjusted simultaneously with the parameter refinement by checking the $\ln \Sigma|F_o|/\Sigma|F_c|$ versus $\sin^2\theta$ plot at each refinement stage. In the later stages, extinction errors (see below) masked the true coordinate shifts, and better refinement (as judged by a reduction in the disagreement index) was realized by using syntheses computed from the reflexions for which $\sin\theta > 0{\cdot}5$.

The y parameters were obtained from the $hk0$ data. Again the projection showed poor resolution, particularly of the oxygen atoms, and successive refinement by difference syntheses was carried out until the disagreement index was 0·13.

The parameters obtained from the ($hk0$) and ($h0l$) data are given in column (1), Table 1. The uniform temperature factor was $B = 2{\cdot}35$ Å^{-2}.

Extinction corrections

For a small number of intense low-order reflexions the disagreement between observed and calculated

Table 1. *Atomic parameters and molecular dimensions obtained during analysis*

	(1) From Fourier projections			(2) From 3-dimensional Fourier synthesis			(3) Final values from observed and calculated differential synthesis		
	x/a	y/b	z/c	x/a	y/b	z/c	x/a	y/b	z/c
K	0·349	0·644	0·644	0·3479	0·6407	0·6426	0·3476	0·6414	0·6428
S	0·399	0·177	0·639	0·3990	0·1787	0·6385	0·3985	0·1783	0·6397
N	0·500	0·077	0·750	0·500	0·073	0·750	0·5000	0·0753	0·7500
O_1	0·441	0·280	0·483	0·442	0·269	0·485	0·4422	0·2711	0·4810
O_2	0·328	0·037	0·589	0·328	0·035	0·589	0·3276	0·0330	0·5879
O_3	0·351	0·276	0·770	0·352	0·299	0·763	0·3522	0·3000	0·7721

Bond lengths

	(1)	(2)	(3)	E.s.d.
S–N	1·64 Å	1·665 Å	1·655 Å	0·0067 Å
S–O_1	1·47	1·413	1·454	0·0088
S–O_2	1·40	1·425	1·438	0·0103
S–O_3	1·35	1·409	1·448	0·0082

Valency angles

	(1)	(2)	(3)	E.s.d.
S–N–S	—	—	124° 40′	30′
O_1–S–O_2	—	—	113° 31′	1° 3′
O_2–S–O_3	—	—	112° 50′	1° 1′
O_3–S–O_1	—	—	112° 18′	55′
N–S–O_1	—	—	107° 11′	55′
N–S–O_2	—	—	102° 55′	45′
N–S–O_3	—	—	106° 54′	45′

Intramolecular distances between non-bonded atoms

O_1–O_2	2·41 Å	N–O_2	2·42 Å	O_3–O_3'	3·69 Å
O_2–O_3	2·40	N–O_3	2·50	S–S′	2·93
O_3–O_1	2·41	O_1–O_1'	4·07		
N–O_1	2·51	O_1–O_3'	3·06		

structure factors was exceptionally large with the observed value always the lesser. This was treated as due to secondary extinction and was corrected empirically from the plot of observed versus calculated intensities shown in Fig. 5. The majority of the planes conform to a linear region close to the origin and their intensities were unmodified. The group of strong reflexions which included 020, 202, 400 and $\bar{2}02$ was corrected by a factor corresponding to the separation of the mean line from the corresponding point for I_c on the extrapolated zero-extinction straight line. With these corrections the disagreement index for both projections was reduced to 0·11.

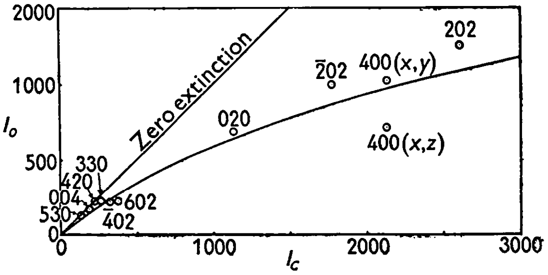


Fig. 5. Graph showing extinction of planes in *hk*0 and *h*0*l* zones.

The three-dimensional refinement

Although a comparatively low value for the disagreement index was obtained for the *hk*0 and *h*0*l* zones, the number of experimental observations was only about five times the number of parameters for each projection separately. Taking into account also the predominance of the potassium and sulphur atomic scattering, it was not unexpected that a comparison of the x coordinates from the two projections showed a discrepancy of 0·06 Å in one oxygen parameter. There was also an apparent variation in S–O distances from 1·35 to 1·47 Å, which was correctly ascribed to experimental error at this stage in the analysis. A three-dimensional refinement was therefore undertaken in order to obtain the molecular dimensions with sufficient accuracy to form a basis for discussion of the molecular structure.

The first set of general *hkl* structure factors, which was calculated from the mean projection coordinates using B.T.M. punched card equipment, gave a disagreement index of 0·21 for the 681 observed structure amplitudes. A three-dimensional Fourier synthesis was then computed in blocks at intervals of sixtieths in the region of each atomic peak; the calculations were also carried out by punched-card methods. The consequent improvement in parameters, which were interpolated from the electron-density values by the three-point parabola method, together with an adjustment of the scale and uniform temperature factor, reduced the disagreement index to 0·14 on the second general structure-factor calculation. These coordinates, which are of course uncorrected for series-termination errors, are listed in column (2), Table 1.

There was evidence from this set of structure-factor calculations that different temperature factors for the potassium and sulphur atoms would be more appropriate. These were deduced from plots of ln $\Sigma|F_c|/|F_o|$ against mean $\sin^2\theta$ for groups of planes for which the potassium and sulphur atoms separately made the predominant contribution (see Fig. 6). Experimental scattering-factor curves were also derived on a similar basis. That for the K^+ corresponded closely to the theoretical Hartree curve with a temperature factor $B = 3{\cdot}3$ Å^{-2}, while for the S atom a mean of the Hartree and Viervoll–Ögrim curves with $B = 2{\cdot}9$ Å^{-2} gave the best agreement. However, the differences were small, and the Hartree curves were used in the subsequent calculations to obtain the final coordinates corrected for series errors. For the O and N atoms, scattering factors with a mean B factor of 2·9 Å^{-2} were used (this was later modified from a comparison of peak curvatures to a value of $B = 3{\cdot}2$ Å^{-2} for the O atoms).

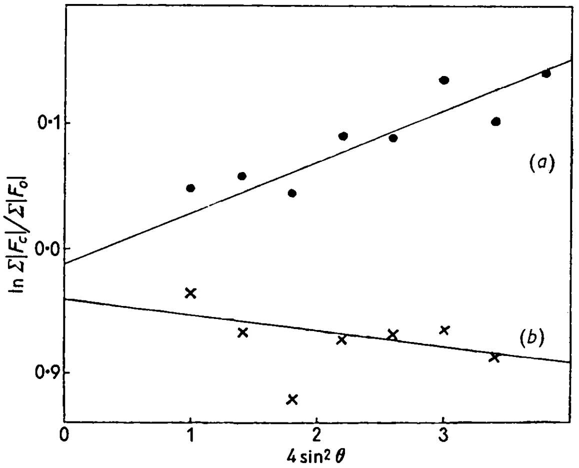


Fig. 6. Graphs of ln $\Sigma|F_c| \div \Sigma|F_o|$ versus 4 $\sin^2\theta$ for planes with (a) large K contributions and (b) large S contributions.

An attempt was made to locate the hydrogen electron of the N–H bond by computing a difference synthesis along the line $(0, y, \frac{1}{4})$. A peak of 0·3 e.Å^{-3} did appear on this line at 0·97 Å from the nitrogen atom, but this was considered inconclusive since there was an apparent residual excess electron density of 0·75 e.Å^{-3} at the nitrogen position and several obviously spurious peaks of $\sim 0{\cdot}3$ e.Å^{-3} also along this line.

The final refinement of the atomic parameters was carried out on the Manchester electronic computer, using the methods of Ahmed & Cruickshank (1953) for computing observed and calculated differential syntheses. The first cycle of structure-factor and synthesis calculations gave rise to shifts as large as 0·058 Å on one of the oxygen atoms. From a comparison of the ratios in the observed and calculated syntheses of the peak heights and curvatures, only the oxygen scattering curve was altered. A second cycle reduced the corrections to less than 0·0075 Å for the light atoms and less than 0·0015 Å for the potassium and sulphur atoms. At this stage the refinement was terminated; the final atomic coordinates are given in column (3), Table 1. The disagreement index for the observed and calculated structure factors at the penultimate stage of the refinement was $R = 0{\cdot}12$, which included a scale error of 2%.

The lower part of Table 1 shows a comparison of the results for the S–O and S–N bond lengths at various stages in the progress of the analysis. It emphasizes the necessity for elaborate structure refinement in order to obtain meaningful interatomic distances between comparatively light and heavy atoms. The last column gives the estimated standard deviations of the bond lengths calculated by the method of Cruickshank & Robertson (1953) from the standard deviations of the atomic coordinates obtained by the procedures of Cruickshank (1949) and Cruickshank & Rollett (1953).

Table 2. *Peak heights, ϱ, and mean curvatures, A, from final differential synthesis*

Atom	$\varrho_{\text{obs.}}$ (e.Å^{-3})	$-A_{\text{obs.}}$ (e.Å^{-5})	$\dfrac{\varrho_{\text{calc.}}}{\varrho_{\text{obs.}}}$	$\dfrac{A_{\text{calc.}}}{A_{\text{obs.}}}$	B (Å^{-2})
K	38·4	379	1·03	1·02	3·3
S	37·7	389	1·05	1·03	2·4
N	11·8	107	0·90	0·89	2·9
O_1	12·3	102	1·10	1·11	3·2
O_2	11·8	88	1·10	1·15	3·2
O_3	12·6	109	1·03	1·08	3·2
Mean O	12·2	100	1·08	1·11	3·2

In Table 2, the peak heights and curvatures from the observed final synthesis are given and compared with those of the calculated synthesis. The isotropic thermal parameters are given in the last column. The estimated standard deviation of the electron density at a general position (i.e. S, O, K atoms) was 0·33 e.Å^{-3}, and 0·49 e.Å^{-3} at the special N positions. The difference in peak heights between the oxygen atoms was therefore not significant and the nitrogen atom was indistinguishable in height from the oxygen atoms. Only in the case of the sulphur atom was there a significant difference between the observed and calculated peak heights (i.e. $\Delta p/\sigma = 3{\cdot}7$).

Discussion of the structure

The detail of the stereochemistry of the $[NH.(SO_3)_2]^{2-}$ ion is shown in Fig. 7.

Although the space-group symmetry requires a twofold rotation axis in the molecule, this does not necessarily exclude a pyramidal distribution of nitrogen valencies, since the hydrogen atoms could be statistically distributed on either side of the diad axis. Unfortunately it was not possible to locate the hydrogen electron density unequivocally by difference synthesis, and the planar configuration about the nitrogen atom can be inferred only from the N–S bond lengths. When the bond length of 1·66 Å is compared with that of 1·79 Å in the dinitrososulphite ion, the standard deviations, σ and σ', give a value of $\Delta/(\sigma^2+\sigma'^2)^{\frac{1}{2}}=9{\cdot}7$, where Δ is the difference between the two bond lengths. This corresponds to a highly significant difference, and the same is true when the comparison is made with a value of 1·74 Å, which is the single-bond length from the Pauling covalent radii. As in the sulphamate ion, this is evidence of both σ and π bonding between the trigonal [sp^2], p, hybridized nitrogen orbitals and the tetrahedral [sp^3] and d sulphur atomic orbitals. The corresponding valence bond resonance diagrams are of the type V and VI with fully equivalent S–O bonds.

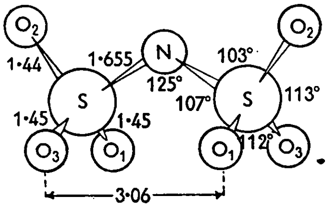
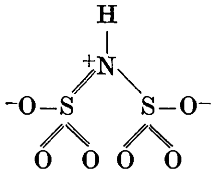
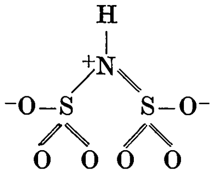


Fig. 7. Dimensions of anion.



V



VI

For the sulphur to nitrogen double-bond length the Pauling covalent radii give a value of 1·54 Å. Alternatively, if the well-established sulphur to oxygen distance of 1·44 Å is increased by the difference between oxygen and nitrogen double-bond radii, a value of 1·48 Å is obtained. In either case the bond in the aminedisulphonate ion is significantly longer. Assuming a linear relationship between bond order and length, the S–N total bond order is about 1·4. On the same basis, the bond orders in the dinitrososulphite and sulphamate ions are 1·0 and about 1·7 respectively. This variable degree of multiple bonding runs parallel with the stability to acid hydrolysis, and suggests a correlation which can be extended to the third member of the amine sulphonate series, $N(SO_3)^{3-}$, to predict a S–N bond length of about 1·70 Å. A similar variation in bond character is expected to occur in the two hydroxylamine sulphonates, $HO.NH.SO_3^-$ and $HO.N.(SO_3)_2^{2-}$, of which the monosulphonate is the more stable, although less so than the sulphamate ion.

The three S–O bond lengths are equal within the experimental error of the analysis. The mean value of 1·447 Å (σ = 0·0053 Å), although considerably shorter than the Pauling radius sum for a double bond, is in agreement with the values from the dinitrososulphite and sulphamate structures (1·46, 1·43, 1·43; 1·42, 1·45, 1·45 Å), and from many other structures containing S=O bonds. These structures display a constancy in the sulphur to oxygen bond character which is in striking contrast to the situation with respect to sulphur–nitrogen multiple bonds.

The S–N–S angle of 124° exceeds the ideal value of 120° owing to the repulsion of the oxygens in the

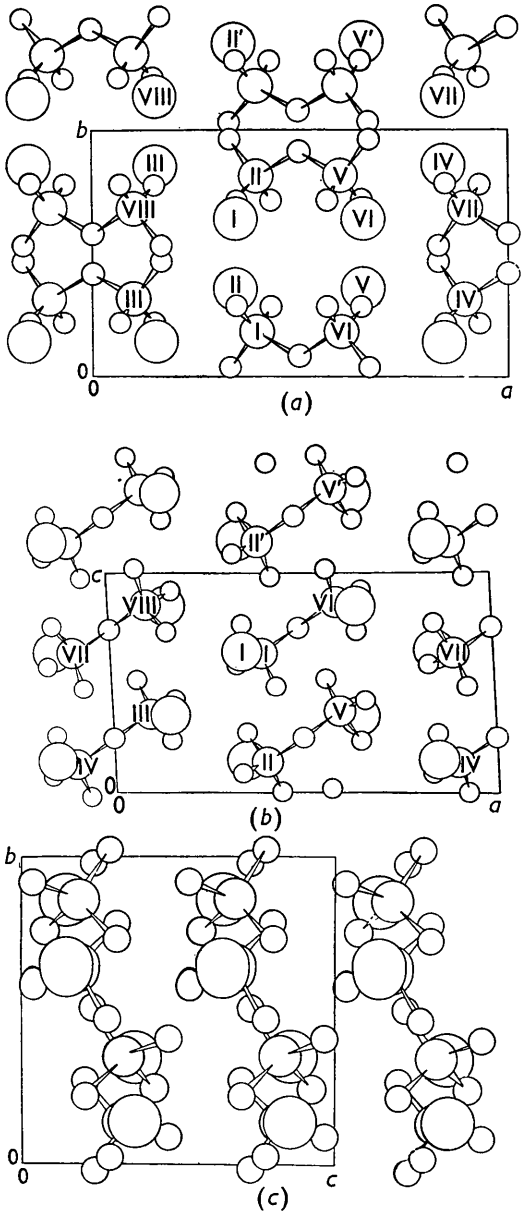


Fig. 8. Structure of $NH(SO_3K)_2$ projected (a) on (001), (b) on (010), (c) on (100).

sulphonate groups, so that the closest oxygen to oxygen approach between groups is 3·06 Å. Similarly the O–S–O angles (mean 112° 45′) exceed the tetrahedral angle at the expense of the N–S–O angles (mean 105° 40′), so that the oxygen to oxygen separation within the sulphonate group is 2·40 Å, 0·1 Å less than the corresponding oxygen to nitrogen distance. The same effect was observed in the dinitrososulphite (O–S–O 115° 5′, O–S–N 104° 0′) and sulphamate (O–S–O 111° 30′, O–S–N 107° 30′) ions.

The interionic structure is illustrated in Fig. 8 which shows the projections down the principal crystallographic axes. The coordination of the ions is 12:6. An amine disulphonate ion II/V in Fig. 7(*a*), for example, is surrounded by twelve potassium ions: I, II, III, IV, V and VI in the same cell, II′, V′, VII and VIII in an adjacent cell, I and VI in the cell below. The closest interionic separations are the K · · · O values which range from 2·70 to 3·23 Å. The K · · · S distances are 3·50 Å and longer, and the K · · · N separations are somewhat greater (Table 3).

Table 3. *The shorter cation–anion interatomic distances*

(All values in Ångström units)

$K \cdots O_1$	3·23(I)	2·74(II)	2·87(V)	
$K \cdots O_2$	2·96(I′)	2·99(III)	3·07(VIII)	
$K \cdots O_3$	2·71(I)	2·70(II)	2·84(VIII)	
$K \cdots S$	3·51(I)	4·06(I′)	3·93(II)	3·84(II′)
	4·33(III)	4·04(V′)	3·49(VIII)	
$K \cdots N$	3·82(I)	4·05(II)		

These distances refer to the cation K(I) and the roman numerals to those on the anions in Fig. 8 (a).

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Ordering of Atoms in the σ Phase*

By J. S. Kasper and R. M. Waterstrat

General Electric Research Laboratory, Schenectady, N.Y., U.S.A.

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A neutron diffraction study has been made of the ordering of component atoms in the following three σ phases: Ni–V, Fe–V, Mn–Cr. Definite evidence for ordering is found in all three systems, with different degrees of precision for the three systems. These results, with some X-ray investigations, enable a generalization to be made regarding the scheme of the ordering for binary σ phases of the first row transition elements (also those containing molybdenum).

Introduction

In recent years there have been detailed X-ray diffraction investigations of the structure of the σ phase in which the locations of the atoms in the unit cell have been made with considerable precision (Bergman & Shoemaker, 1954; Dickins, Douglas & Taylor, 1956; Kasper & Decker, 1955). It has not been possible in these studies, however, to decide whether there is a definite ordering of the respective atoms among the different sites in the unit cell

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* The neutron diffraction data were obtained at the Brookhaven National Laboratory Reactor, Upton, L. I., N.Y., U.S.A.