

A Neutron Diffraction Study of Potassium Sulphamate, KSO_3NH_2

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A single-crystal neutron diffraction investigation of potassium sulphamate has been made in which the intensities of 501 reflexions were measured. The structure was refined by a least-squares technique with individual anisotropic temperature factors. The non-hydrogen atom positions obtained agree well with those of Jeffrey & Stadler (*J. Chem. Soc.* 1951, p.1467). The hydrogen atom positions differ substantially from those postulated from the X-ray work and the nitrogen atom is in sp^3 configuration. The sulphamate ions are packed one above the other with hydrogen bonds linking them in infinite chains parallel to the c axis.

Introduction

The crystal structure of potassium sulphamate has been studied by Brown & Cox (1940) and by Jeffrey & Stadler (1951) by X-ray methods. In both cases the authors suggest that the nitrogen valency directions are coplanar and that the hydrogen atoms lie in the mirror plane of symmetry of the molecule.

Experimental procedure

Crystals of potassium sulphamate were grown by slow evaporation from a solution of pure sulphamic acid neutralized with pure potassium hydroxide. The crystal data (from Jeffrey & Stadler) are given in Table 1. Large crystals can be grown easily and a specimen of size $4 \times 3 \times 3$ mm was cut and mounted on a two-circle goniometer set so that the c axis of the crystal was along the φ axis of the goniometer and the scattering vector remained in the χ plane for all reflexions. The intensity data were collected on a neutron diffractometer on the Australian Atomic Energy Commission's reactor HIFAR. The beam current at the specimen was approximately 6×10^6 neutrons $\text{cm}^{-2}\text{sec}^{-1}$, at a wavelength of 1.09 Å. The integrated intensities of 501 reflexions with $\sin \theta/\lambda < 0.65$ were measured. Of these, 81 were recorded as unobserved. There was no evidence of severe extinction effects. The crystal angles were set by hand and the intensity data recorded by

step scanning through the peak in the $\theta-2\theta$ mode. The scan was made in steps of 0.03° of 2θ under monitor control.

Table 1. *Crystal data*

Crystal system: Orthorhombic
 Space group: $Pbcm$ (D_{2h}^{11}) (no. 57)
 Cell parameters $a=5.907$, $b=8.333$, $c=8.302$ Å
 $Z=4$ molecules per unit cell
 $D_x=2.2$ g.cm^{-3}
 Mass=32.5 mg
 Linear absorption coefficient, $\mu=0.702$ cm^{-1}

Miller indices of face	Perpendicular distance of face from an origin inside the crystal
	mm
0 0 1	1.70
0 0 -1	1.70
-1 0 0	1.14
0 1 0	1.49
1 2 0	1.04
1 1 0	0.97
1 0 0	1.14
1 -2 0	1.68
0 -1 0	1.75
-1 -1 0	0.69

Volume calculated from dimensions, 15.85 mm^3
 Volume calculated from mass, 14.77 mm^3

Analysis of data

The data were corrected for absorption and reduced to F_o and $\sigma(F_o)$ by the program CDRABS written by one of us (G.W.C.). The absorption cross sections were taken as the sum of the cross section due to true absorption and that due to incoherent scattering. The

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carded and the reliability factor converged to values of 0.079, 0.067 and 0.073 for all reflexions, excluding unobserved reflexions, and for weighted structure amplitudes respectively. The observed and calculated structure amplitudes are given in Table 2. The final positional parameters and their standard deviations are listed in Table 4. The coordinates of non-hydrogen atoms agree well with those reported from X-ray studies. A Fourier section of the nuclear density at $z=0.25$ is shown in Fig. 1, from which it is clear that the hydrogen atoms are not in the mirror plane.

Interatomic distances and bond angles were calculated from the parameters listed in Table 1, using the program ORFFE (Busing, Martin & Levy, 1962*b*). These values are given in Table 3, together with the values for sulphamic acid reported by Sass (1960).

Table 3. *Bond lengths and bond angles*

Standard deviations are shown in brackets.

Bond lengths		
	Potassium sulphamate	Sulphamic acid
S-N	1.666 (0.006) Å	1.764 (0.02) Å
S-O(1)	1.459 (0.007)	1.421 (0.02)
S-O(2)	1.454 (0.004)	1.452 (0.02)
N-H	1.007 (0.006)	1.024 (0.02) (average)
O(2)···H	2.147 (0.006)	
N-H···O(2)	3.080 (0.006)	
Bond angles		
	Potassium sulphamate	Sulphamic acid
H-N-H	110.1 (0.7)°	107.6° (average)
H-N-S	110.2 (0.4)	111.3 (average)
N-S-O(1)	108.5 (0.4)	103.2 (average)
N-S-O(2)	103.9 (0.3)	
O(1)-S-O(2)	112.1 (0.3)	115.1 (average)
O(2)-S-O(2')	115.5 (0.5)	
S-N-O(2)	105.2 (0.1)	
N-H-O(2)	153.2 (0.5)	

Discussion

The nitrogen atom configuration

This investigation shows conclusively that the two hydrogen atoms do not lie in the plane containing the S, N and O(1) atoms. The bond angles around the nitrogen atom are S-N-H 110.2° and H-N-H 110.1°. These are so close to the ideal tetrahedral angle of

109.5° that it must be assumed the nitrogen atom has an sp^3 configuration with a lone pair of electrons in the fourth tetrahedral position. This conclusion is in disagreement with the expected relationship between bond length and bond order for the S-N bond. The theoretical single and double bond lengths are 1.74 and 1.54 Å from the covalent radii given by Pauling (1945). A single bond is associated with a tetrahedral configuration and Sass has found that in sulphamic acid the bond length is 1.764 Å and the nitrogen has an sp^3 configuration. In most other substances (see review by Trueblood & Mayer, 1956) a shorter bond has been observed and attributed to the availability of p electrons from the nitrogen to form π bonds with sulphur d -orbitals (Sass & Donohue, 1958). The nitrogen is then expected to be trigonally bonded with sp^2 hybridization. Recently, O'Connor & Maslen (1965) have found the S-N bond to be 1.61 Å in β -sulphanilamide and the configuration sp^2 while Alléaume & Decap

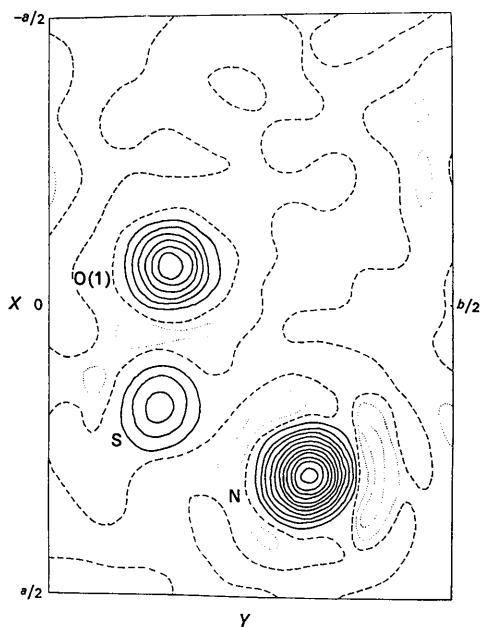


Fig. 1. Fourier section of neutron scattering density at $z=0.25$. The full, broken and dotted lines represent positive, zero and negative densities respectively. The negative densities are plotted with half the contour interval of the positive ones.

Table 4. *Atomic parameters and their estimated standard deviations*

Positional parameters are expressed as fractions of the lattice parameters.
Thermal parameters are in the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.
All parameters are given $\times 10^4$.

	$x, \sigma(x)$	$y, \sigma(y)$	$z, \sigma(z)$	$\beta_{11},$ $\sigma(\beta_{11})$	$\beta_{22},$ $\sigma(\beta_{22})$	$\beta_{33},$ $\sigma(\beta_{33})$	$\beta_{12},$ $\sigma(\beta_{12})$	$\beta_{13},$ $\sigma(\beta_{13})$	$\beta_{23},$ $\sigma(\beta_{23})$
S	1775 (10)	1370 (7)	2500	86 (17)	22 (7)	59 (9)	-9 (9)	0	0
N	2914 (4)	3198 (3)	2500	141 (6)	39 (3)	59 (3)	-10 (4)	0	0
O(1)	-684 (6)	1532 (5)	2500	92 (10)	76 (6)	91 (6)	1 (6)	0	0
O(2)	2611 (5)	650 (3)	3981 (3)	201 (8)	67 (3)	43 (3)	10 (4)	-26 (4)	17 (3)
K	6644 (10)	2500	0	136 (19)	51 (6)	44 (7)	0	0	8 (6)
H	2438 (10)	3803 (7)	1506 (7)	285 (20)	131 (7)	119 (9)	-23 (10)	-35 (10)	57 (7)

All parameter changes in the last cycle of least-squares refinement were less than 1×10^{-4} .

(1965) have made a similar observation for γ -sulphanilamide in which they have found an S–N bond of 1.67 Å. Sabine & Cox (1967) have found the S–N bond in $S_4N_4H_4$ to be 1.65 Å and a trigonal nitrogen configuration.

In potassium sulphamate the S–N bond is not significantly longer but the configuration is sp^3 . The sulphamate ion configuration is the same as that of the sulphamic acid molecule except for the absence of one of the hydrogen atoms from the nitrogen atom.

Hydrogen bonding

The intermolecular O...H distance of 2.15 Å is significantly less than the van der Waals contact distance of 2.8 Å and constitutes a weak hydrogen bond joining the sulphamate molecules in infinite chains parallel to the c axis. The N–H bonds are staggered from the S–O bonds with respect to rotation about the S–N bond with a dihedral angle of 60.8° between the SNO(1) and SNH planes.

The potassium ion environment

The potassium ions are located between the chains of sulphamate molecules. Each potassium ion is surrounded by six oxygen atoms, two at each of the distances 2.729 [O(1)], 2.729 [O(2)] and 2.961 Å [O(2)]. The average S–O distance of 1.455 Å is close to the value 1.439 Å for sulphamic acid found by Sass.

Thermal vibrations

A detailed analysis of the thermal vibration parameters was not made; however, inspection of Table 4 shows that the maximum vibration is along a , which is normal to the direction of hydrogen bonding.

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The Crystal and Molecular Structure of a Dimethyl Sulfoxide Complex of Iron(III) Chloride

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A three-dimensional X-ray structure determination of the dimethyl sulfoxide (DMSO) compound of empirical formula $FeCl_3(DMSO)_2$ has shown it to be composed of *trans*- $[FeCl_2(DMSO)_4]^+$ and $FeCl_4^-$ ions. It crystallizes in the space group $I4_1/a$ of the tetragonal system with unit-cell dimensions $a = 11.60 \pm 0.01$, $c = 20.33 \pm 0.01$ Å. There are four of the true (ionic) formula units in each cell, with all iron atoms occupying positions of $\bar{4}$ symmetry. The DMSO molecules are coordinated through their oxygen atoms. The S–O distance (1.541 ± 0.006 Å) is slightly but significantly greater than that in DMSO itself.

Introduction

The pronounced ability of dimethyl sulfoxide (hereafter abbreviated DMSO) to function as a donor or Lewis base toward a wide variety of acceptors or Lewis acids was clearly demonstrated by the isolation of a

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large number of complexes several years ago (Cotton & Francis, 1960). Subsequent studies showed that other sulfoxides possess similar bonding capacities (Francis & Cotton, 1961; Francis, 1964) but not to the same degree as DMSO.