[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE STATE UNIVERSITY OF IOWA]

The Crystal Structure of Potassium Hydroxylamine-N-sulfonate[1]

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The crystal structure of potassium hydroxylamine-N-sulfonate, KSO_3NHOH, was determined from Weissenberg and precession data. The crystals are orthorhombic with cell dimensions $a = 7.06$, $b = 12.02$, $c = 5.58$ Å., $Z = 4$, space group $P2_12_12_1$. Patterson and Fourier methods were used to locate the atoms and further refinement was accomplished by three-dimensional least squares. S–O bond lengths are 1.46, 1.46 and 1.48 Å. while the S–N distance is 1.67 Å. The N–O distance is 1.51 Å. The structure is discussed and compared to other compounds having nearly the same arrangement.

Introduction

Potassium hydroxylamine-N-sulfonate is one of a group of derivatives of hydroxylamine formed by the substitution of a sulfonic acid group for the hydrogens of hydroxylamine. The O-sulfonic acid is the only member having a stable acid and the remaining derivatives have all been studied as salts. A good discussion of chemical properties has been given in the book by Yost and Russell,[2] but none of the crystal structures of the hydroxylamine sulfonates has been reported. Jeffrey and Jones[3] have determined the crystal structure of potassium amine disulfonate, $K_2NH(SO_3)_2$, and postulated that the stability to acid hydrolysis parallels the bond order of the S–N bonds in the amine sulfonates. As further support they cited the data of Brown and Cox[4] who determined the crystal structure of potassium sulfamate, KSO_3NH_2. The suggestion was made that the bond character of the S–N bond in the hydroxylamine sulfonates would undergo a similar change. Partly with this view in mind, we have determined the crystal structure of potassium hydroxylamine-N-sulfonate.

Experimental

Potassium hydroxylamine-N-sulfonate was prepared by the controlled hydrolysis of the N,N-disulfonate. The latter compound was synthesized by the method of Rollefson and Oldershaw[5] except that potassium salts were used for all reactants. The hydrolysis was effected according to the procedure of Raschig,[6] and separation of the product was accomplished by repeated fractional recrystallization. Washing the final product again with ice-water to remove completely any bisulfate seemed to give better results. The compound was analyzed for potassium by ignition to potassium sulfate. The crystals were colorless, slightly hygroscopic, and had an uncorrected melting point of 115°. No marked cleavage properties were noted.

Anal. Calcd. for KSO_4NH_2: K, 25.95. Found: K, 25.90.

Weissenberg and precession films showed that the crystals were orthorhombic with unit cell dimensions, $a = 7.06 \pm 0.02$, $b = 12.02 \pm 0.02$, $c = 5.58 \pm 0.02$ Å. A measured density of 2.05 g. cm.$^{-3}$ by pycnometer agreed with the calculated value of 2.11 g. cm.$^{-3}$ assuming four formula weights per unit cell. A zero and three upper layer Weissenberg photographs were recorded by rotation about the *c* axis using the multiple film technique. Zero layer precession films at an angle of 30° were obtained by precession about the *a* and *b* axes. Several timed exposures were made for intensity measurements. Systematic absences indicate the most probable space group is $P2_12_12_1$. Intensities were estimated visually by comparison with standard scales prepared from the same crystal. All data were corrected for Lorentz and polarization effects but the absorption correction was not calculated because of the irregular shape of the crystal. About 465 independent reflections were observed and measured in the reciprocal space investigated.

Structure Determination.—Patterson functions were calculated for projections on (001), (100) and (010). The larger peaks on the (001) projection were interpreted as those due to K–K, S–S or K–S vectors. From trial calculations using several sensitive reflections, the *x* and *y* coördinates suggested by the Patterson maps were correctly assigned to the sulfur and potassium atoms (initial *R* value was 0.43). The Patterson projections on (100) and (010) led to suitable *z* parameters for these atoms also [*R* values for (0*kl*) and (*h*0*l*) data after one stage of Fourier refinement were near 0.30]. This rough agreement enabled sufficient signs of the structure factors to be determined that the refinement could be effected by further electron density projections.

The projection of the electron density on (001) was interpreted as having two peaks which arose from the overlap of

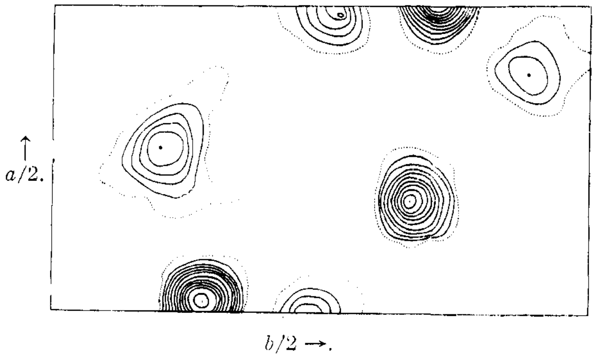

Fig. 1.—Electron density projected on to (001).

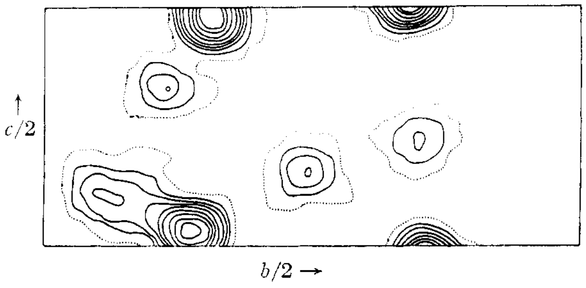

Fig. 2.—Electron density projected on to (100).

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[2] D. M. Yost and H. R. Russell, "Systematic Inorganic Chemistry of the Fifth and Sixth Group Nonmetallic Elements," Prentice-Hall, Inc., New York, N. Y., 1944, pp. 90–96.

[3] G. A. Jeffrey and D. W. Jones, *Acta Cryst.*, **9**, 283 (1956).

[4] C. J. Brown and E. G. Cox, *J. Chem. Soc.*, 1 (1940).

[5] G. K. Rollefson and C. F. Oldershaw, THIS JOURNAL, **54**, 977 (1932).

[6] F. Raschig, "Schwefel- und Stickstoffstudien," Leipzig, 1924 pp. 154–155.

two pairs of atoms: an oxygen and a sulfur at $x = 0$, $y = 0.14$, and a nitrogen and oxygen at $x = 0.24$, $y = 0.11$. Successive Fourier syntheses reduced the R value from 0.43 to 0.16 for observed reflections only. The final electron density plot is given in Fig. 1. Although he x and y coördinates were known, and rough values of the z coördinates of potassium and sulfur, different orientations of the atoms around the sulfur were possible. Several of these gave superficial agreement with the intensity data. However, an arrangement compatible with both the $(0kl)$ and $(h0l)$ data was found which could be refined. Four syntheses reduced the discrepancy factor, R, to 0.18 for the $(0kl)$ data. The final electron density projection on (100) is shown in Fig. 2. The peak at $y = 0.14$, $z = 0.03$ is distorted from partial superposition of nitrogen and sulfur atoms. A separate refinement was carried out on the $(h0l)$ data and the R value was lowered to 0.19. Because the overlap was so much greater, only some of the parameters were improved.

To remove all overlap errors and improve the accuracy of all parameters, the refinement was continued by the least squares method of Shoemaker, *et al.*[7] They minimized the function

$$R_2 = \sum w(|F_0|^2 - |F_c|^2)^2$$

where w = weight assigned to a reflection

$|F_0|^2$ = square of magnitude of obsd. structure factor

$|F_c|^2$ = square of magnitude of calcd. structure factor

The calculations were performed on an IBM 604 punched card electronic calculator. A single cycle was run and corrections to the initial parameters were computed from the equations by omitting non-diagonal elements of the determinant. During the interval that refinements were being carried out, a least squares procedure was developed by Sayre, *et al.*,[8] employing one of the newest IBM computers. This machine is able to handle large groups of data and perform a number of least squares cycles more simply and less expensively than others. Therefore the final stages of the refinement were run on an IBM 704 computer using Sayre's method.[8] The last in a series of five least squares cycles yielded the parameters listed in Table I ($R = 0.148$). A complete list of observed and calculated structure factors derived from the final least squares coördinates has been deposited with the American Documentation Institute.[9] No significant discrepancies between calculated and observed amplitudes occur.

TABLE I

FINAL COÖRDINATES OF KSO_3NHOH COMPUTED FROM IBM 704 LEAST SQUARES PROGRAM

Atom	x	y	z
K	0.185	0.340	0.519
S	.015	.140	.032
N	.235	.094	.077
O_1	.284	.115	.336
O_2	.984	.246	.156
O_3	.013	.153	.772
O_4	.893	.051	.126

Discussion of Structure

A list of bond distances and angles calculated from the final parameters is given in Table II. A drawing of one molecule is shown in Fig. 3. The sulfur atom is surrounded by a distorted tetrahedron of atoms consisting of three oxygens at a mean distance of 1.47 Å. and a nitrogen at a distance of 1.67 Å. The fourth oxygen atom is attached directly to the nitrogen at a distance of 1.51 Å. The potassium ion has eight nearest neighbors, all oxygen atoms, four located at a mean distance of 2.96 Å. and four others at a mean distance of 2.77 Å. Hydrogen bonds connect the tetrahedra of anions in a three-dimensional network (Fig. 4). Although the hydrogen atoms cannot be located directly, bond distances and angles are such that the formation of hydrogen bonds is to be expected. These bonds are of two types: the first is of length 2.86 Å. and is an N–H. . .O type where the nitrogen is a hydrogen donor to an oxygen in a neighboring tetrahedron; the second is of length 2.90 Å. and is an O–H. . .N type where the oxygen provides the hydrogen bridge to a nitrogen in a neighboring group. The 2.86 Å. hydrogen bonds bind the tetrahedra in two-

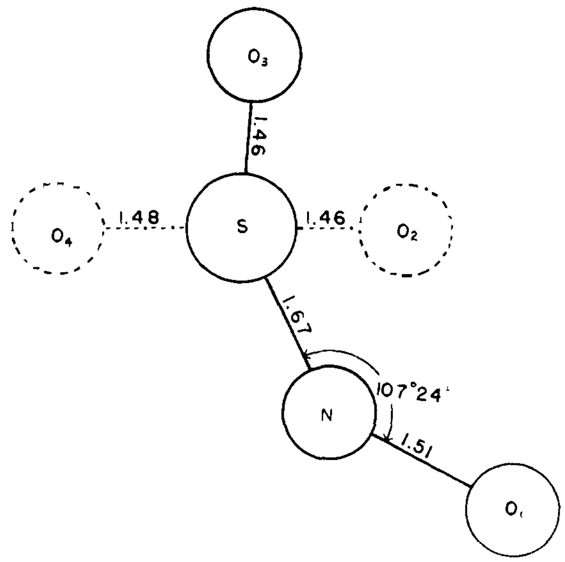

Fig. 3.—One unit of $[SO_3NHOH]^-$.

TABLE II

BOND DISTANCES AND ANGLES FOR KSO_3NHOH

Atoms	Distances, Å.	Stand. dev.	Atoms	Distances, Å.	Stand. dev.
$S-O_2$	1.46	0.02	$K-O_1$	2.97	0.02
$S-O_3$	1.46	.02	$K-O_3$	2.92	.02
$S-O_4$	1.48	.02	$K-O_2$	2.72	.02
S–N	1.67	.02	$K-O_1$	2.99	.02
$N-O_1$	1.51	.02	$K-O_2$	2.97	.02
$N-O_2$	2.59	.03	$K-O_3$	2.83	.02
$N-O_3$	2.42	.03	$K-O_4$	2.80	.02
$N-O_4$	2.49	.03	$K-O_4$	2.71	.02
O_2-O_3	2.43	.03	$N-H\ldots O_2$	2.86	.03
O_2-O_4	2.44	.03	$O_1-H\ldots N$	2.90	.03
O_3-O_4	2.48	.03			

Angles	Value	Error
$N-S-O_2$	111° 11′	1°
$N-S-O_3$	101° 0′	1°
$N-S-O_4$	104° 25′	1°
O_2-S-O_3	112° 8′	1°
O_2-S-O_4	112° 14′	1°
O_3-S-O_4	115° 1′	1°
$S-N-O_1$	107° 24′	1°

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(7) D. P. Shoemaker, J. Donohue, V. Schomaker and R. B. Corey, THIS JOURNAL, **72**, 2328 (1950).

(8) D. Sayre, W. Love and P. H. Friedlander, *Acta Cryst.*, **8**, 732 (1955).

(9) The list has been deposited as Document number 4995 with the ADI Auxiliary Publication Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting $1.25 for photoprints, or $1.25 for 35 mm. microfilm in advance by check or money order payable to: Chief, Photoduplication Service, Library of Congress.

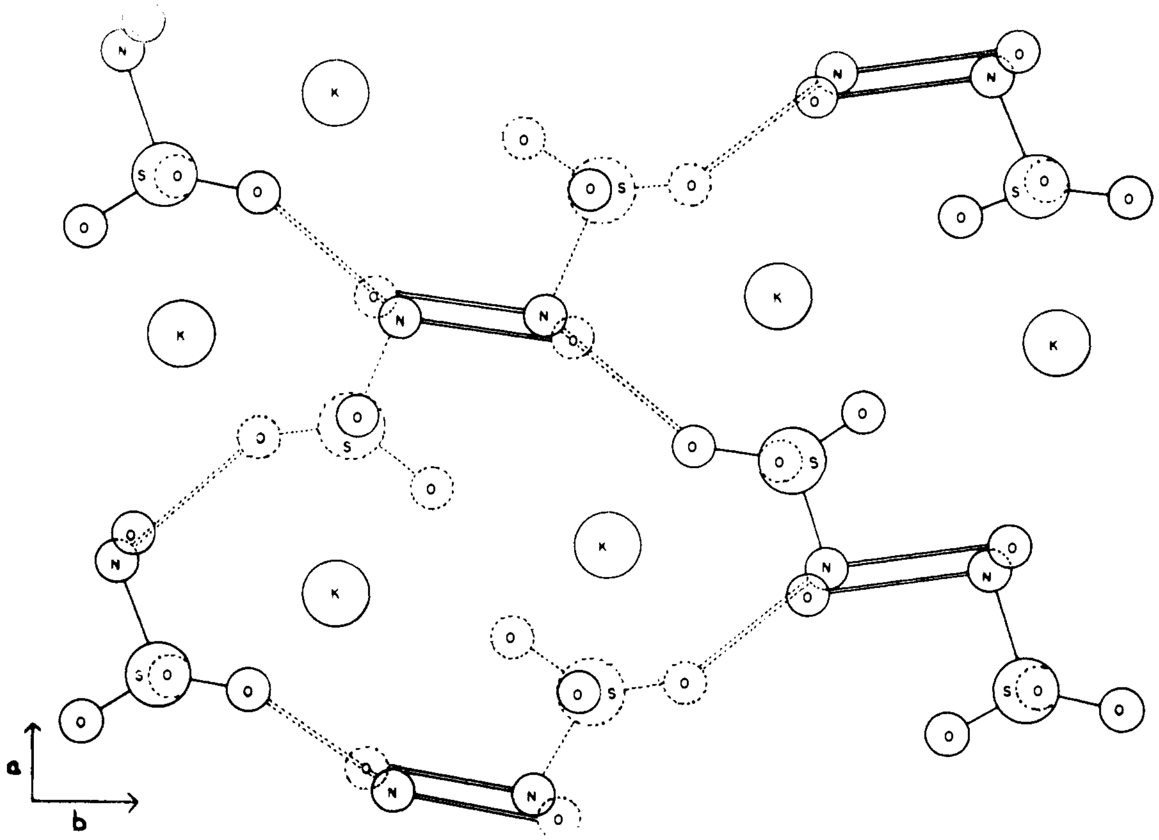

Fig. 4.—Hydrogen-bonding network in KSO_3NHOH—denoted by the doubled lines.

dimensional sheets while the 2.90 Å. hydrogen bonds serve to unite the sheets in three dimensions by cross linkages.

The N–O bond length in KSO_3NHOH is longer than that found in hydroxylammonium chloride by Jerslev[10] who reported a value of 1.47 Å. In solid hydroxylamine Meyers and Lipscomb[11] found a distance of 1.48 Å. The change of bond character about the nitrogen probably lengthens the N–O bond. In hydroxylamine the nitrogen forms a sp^3 type tetrahedral hybrid and in the KSO_3NHOH there is undoubtedly π as well as σ bonding between the nitrogen and sulfur. The S–N bond length of 1.67 Å. for KSO_3NHOH is longer than that given by Brown and Cox[4] in their structure of sulfamate. The remaining tetrahedral distances are equivalent within the limits of error. However, the two structures differ in coördination and in the lack of hydrogen bonding in the potassium sulfamate. Naiditch and Yost[12] have made a kinetic study on the rate of acid hydrolysis of hydroxylamine disulfonate, and it is known to hydrolyze faster than the monosulfonate. From the ideas of Jeffrey and Jones,[3] the S–N bond length in the disulfonate would be expected to be longer than the 1.67 Å. found in the monosulfonate.

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(10) B. Jerslev, *Acta Cryst.*, **1**, 21 (1948).

(11) E. A. Meyers and W. N. Lipscomb, *ibid.*, **8**, 583 (1953).

(12) S. Naiditch and D. M. Yost, THIS JOURNAL, **63**, 2123 (1941).