

## The Crystal Structure of the Compound $\text{HNO}_3 \cdot 2\text{SO}_3$

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The compound  $\text{HNO}_3 \cdot 2\text{SO}_3$  forms crystals belonging to the triclinic system, space group  $P\bar{1}$ . The unit cell, which contains two units of  $\text{HNO}_3 \cdot 2\text{SO}_3$ , has the following dimensions:

$$a = 8.11, b = 8.43, c = 5.55 \text{ \AA}, \\ \alpha = 71.6^\circ, \beta = 82.4^\circ, \gamma = 81.7^\circ.$$

The compound  $\text{HNO}_3 \cdot 2\text{SO}_3$  is ionic and should be formulated as  $\text{NO}_2^+ \text{HS}_2\text{O}_7^-$ .

### Introduction

In the system  $\text{HNO}_3\text{-SO}_3$  some crystalline compounds have been isolated, e.g.  $\text{HNO}_3 \cdot 2\text{SO}_3$  and  $\text{HNO}_3 \cdot 3\text{SO}_3$  (Heertjes & Revallier, 1950). According to modern views these compounds are considered to be salts of the nitronium ion. By analysis of the Raman spectra of the molten compounds, we have in fact proved that they are to be considered as  $\text{NO}_2^+ \text{HS}_2\text{O}_7^-$  and  $\text{NO}_2^+ \text{HS}_3\text{O}_{10}^-$  (Gerding, Heertjes, Revallier & Steeman, 1952). Millen (1950) was able to account for the Raman spectrum of solid  $\text{HNO}_3 \cdot 2\text{SO}_3$  by assuming the presence of the nitronium ion.

It seemed important to confirm these conclusions by X-ray analysis of some nitronium compounds.

### Experimental

The compound  $\text{HNO}_3 \cdot 2\text{SO}_3$  was prepared by mixing the calculated quantities of nitric acid and sulphur trioxide. The compound was purified either by repeated fractional crystallization from the melt or by crystallization from 5% oleum.

The crystals obtained are either regularly shaped parallelepipeds or needles along the  $c$  or  $b$  axis, depending on the method of preparation.

Because of the very hygroscopic and reactive properties of the compound it was necessary to handle it in thin-walled glass capillaries. Using two needles, one along the  $c$  axis, the other along the  $b$  axis, it was possible to photograph all reflexions within the limiting sphere with two crystal settings. A Weissenberg diagram of the  $0kl$  reflexions was also made, and with this diagram the other diagrams were put on the same relative scale.

### Crystallographic properties

The compound  $\text{HNO}_3 \cdot 2\text{SO}_3$  forms colourless crystals. Weissenberg photographs showed the crystal to be triclinic, the unit-cell dimensions being:

$$a = 8.11 \pm 0.1, b = 8.43 \pm 0.1, c = 5.55 \pm 0.1 \text{ \AA}, \\ \alpha = 71.6 \pm 1^\circ, \beta = 82.4 \pm 1^\circ, \gamma = 81.7 \pm 1^\circ.$$

With two units of  $\text{HNO}_3 \cdot 2\text{SO}_3$  in the unit cell the density of the crystals is calculated to be  $2.13 \text{ g.cm.}^{-3}$ . Amelin & Borostodova (1949) measured the density of the molten compound at  $120^\circ \text{C.}$  and found  $2.15 \text{ g.cm.}^{-3}$ ; this figure is slightly higher than our value for the density of the crystals at  $20^\circ \text{C.}$ ; the difference should not be considered significant, however.

No systematic absences of reflexions were found, so the axes we assumed form a primitive system. It is not known, however, whether the substance crystallizes in the space group  $P1$  or  $P\bar{1}$ .

### Determination of the structure

#### 1. Patterson analysis

To solve the structure it is necessary to know if the structure is centrosymmetric. Wilson (1949) has shown that there is a remarkable difference between centric and acentric crystals as regards the distribution of the magnitudes of the structure factors. If this method is to be applied, however, it is essential that there shall be a sufficiently large number of equal atoms in general position in the unit cell. In our case there are only four sulphur atoms in the cell, which give a very important contribution to the structure factor, so the statistical method is not strictly applicable.

Because of this uncertainty it was decided to start the structure determination with a three-dimensional Patterson analysis. From the number and the positions of the high peaks, which had to be attributed to S-S vectors, the conclusion could be drawn that the structure is centric, and the approximate positions of most of the atoms could be derived. The space group  $P\bar{1}$  was further confirmed by Wilson tests (for details see Steeman, 1953).

The coordinates calculated by analysis from the

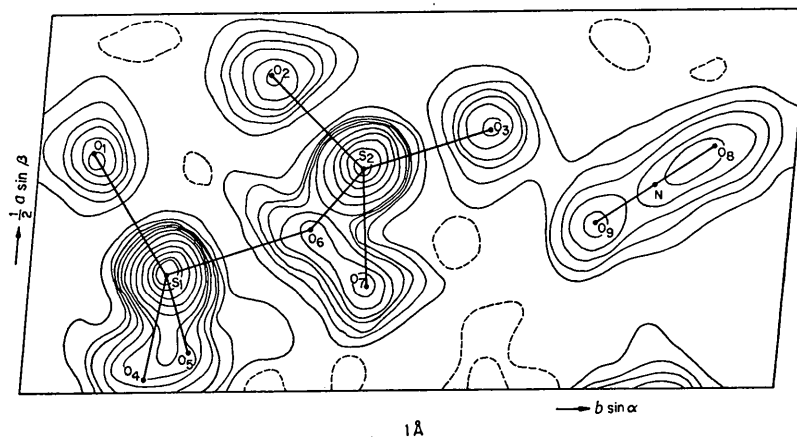
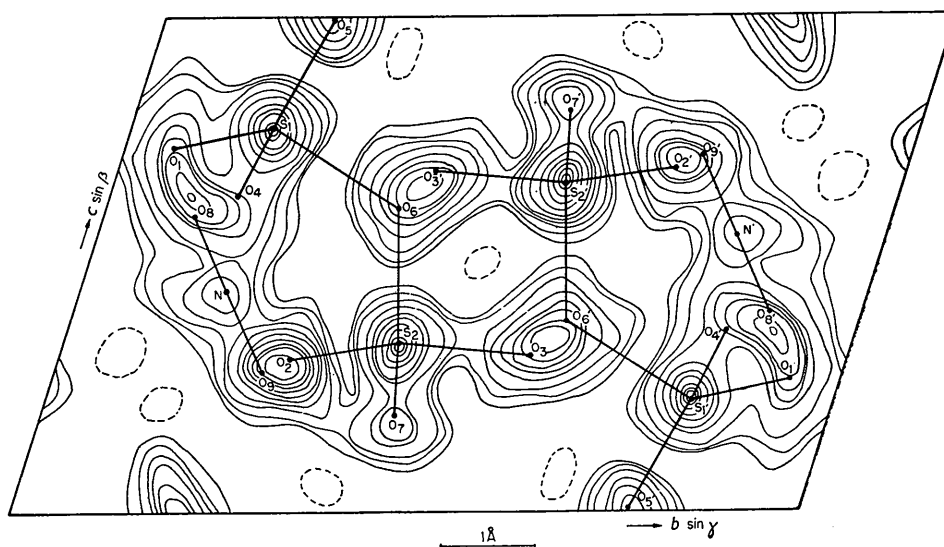
Fig. 1.  $\text{HNO}_3 \cdot 2\text{SO}_3$ : c-axis projection.Fig. 2.  $\text{HNO}_3 \cdot 2\text{SO}_3$ : a-axis projection.

Table 1. Atomic coordinates

	From Patterson analysis			From Fourier synthesis		
	$x$ ( $^\circ$ )	$y$ ( $^\circ$ )	$z$ ( $^\circ$ )	$x$ ( $^\circ$ )	$y$ ( $^\circ$ )	$z$ ( $^\circ$ )
$\text{S}_1$	54	64	278	57	64	272
$\text{S}_2$	104	153	121	107	153	124
$\text{O}_1$	116	22	264	109	25	262
$\text{O}_2$	151	105	110	154	104	111
$\text{O}_3$	124	214	111	127	214	99
$\text{O}_4$	5	58	232	10	73	228
$\text{O}_5$	20	78	358	23	79	330
$\text{O}_6$	78	133	220	81	134	205
$\text{O}_7$	48	162	68	53	158	87
$\text{O}_8$	244	40	214	268	43	213
$\text{N}$	263	67	157	288	79	154
$\text{O}_9$	282	94	100	308	115	93

Patterson synthesis are given in Table 1, together with the final coordinates obtained by repeated Fourier syntheses and steepest-descent refinement.

## 2. Refinement of the structure

To refine the coordinates obtained by analysis of the three-dimensional Patterson synthesis, we used the Fourier method in two projections. After some cycles no further refinement was obtained. For further refinement we then used  $(F_o - F_c)$  syntheses (Booth, 1949). The results of the final Fourier syntheses are shown in Figs. 1 and 2.

## 3. Calculation of the structure factors

For the calculation of the structure factors, the scattering powers of the S, O and N atoms were assumed to be those of the un-ionized atoms given in the *International Tables*. To correct for the thermal movements of the atoms, we used the Debye formula with  $B = 1.5 \times 10^{-16}$  cm.<sup>2</sup>. A list of calculated and observed structure factors may be found in the doctorate thesis of the junior author (Steeman, 1953).

The reliability index, defined as  $\Sigma(|F_o| - |F_c|) \div \Sigma|F_o|$ , was calculated to be:

$hk0$  reflexions: 0.135;  
 $h0l$  reflexions: 0.158;  
 $0kl$  reflexions: 0.155;  
 $hkl$  reflexions: 0.170;  
 average for about 500 reflexions: 0.155.

The good agreement between the observed and the calculated structure factors confirms the proposed structure.

### Description of the structure

From the results given in Table 1 and the Fourier projections shown in Figs. 1 and 2, it is clear that we may consider the structure of the compound  $\text{HNO}_3 \cdot 2\text{SO}_3$  to be composed of nitronium and pyrosulfate ions, so the formula should be written  $\text{NO}_2^+ \cdot \text{HS}_2\text{O}_7^-$ .

Both ions are elongated approximately along the  $[\bar{1}24]$  axis. The stacking of the ions resembles that of the NaCl structure; in the direction of the  $a$  and  $b$  axes there is an alternation of  $\text{NO}_2^+$  and  $\text{HS}_2\text{O}_7^-$  ions,

Table 2. *Interatomic distances*

Distances inside the tetrahedra of the  $\text{HS}_2\text{O}_7^-$  group

$\text{S}_1-\text{O}_1 = 1.64 \text{ \AA}$	$\text{S}_2-\text{O}_2 = 1.46 \text{ \AA}$
$\text{S}_1-\text{O}_4 = 1.43$	$\text{S}_2-\text{O}_3 = 1.51$
$\text{S}_1-\text{O}_5 = 1.43$	$\text{S}_2-\text{O}_7 = 1.52$
$\text{S}_1-\text{O}_6 = 1.68$	$\text{S}_2-\text{O}_6 = 1.52$
$\text{O}_1-\text{O}_4 = 2.56$	$\text{O}_2-\text{O}_3 = 2.56$
$\text{O}_1-\text{O}_5 = 2.87$	$\text{O}_2-\text{O}_6 = 2.44$
$\text{O}_1-\text{O}_6 = 2.51$	$\text{O}_5-\text{O}_7 = 2.56$
$\text{O}_4-\text{O}_5 = 2.24$	$\text{O}_3-\text{O}_6 = 2.40$
$\text{O}_4-\text{O}_6 = 2.50$	$\text{O}_3-\text{O}_7 = 2.50$
$\text{O}_5-\text{O}_6 = 2.44$	$\text{O}_6-\text{O}_7 = 2.39$

Distances between the tetrahedra of the  $\text{HS}_2\text{O}_7^-$  group

$\text{S}_1-\text{S}_2 = 2.68 \text{ \AA}$	$\text{O}_4-\text{O}_7 = 3.02 \text{ \AA}$
$\text{O}_1-\text{O}_2 = 2.65$	

Distance in the  $\text{NO}_2^+$  ion

$\text{N}-\text{O}_8 = 1.09 \text{ \AA}$
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Distances between the  $\text{NO}_2^+$  and  $\text{HS}_2\text{O}_7^-$  groups

$\text{O}_3-\text{O}_8^- = 2.68 \text{ \AA}$	$\text{O}_1-\text{O}_8^- = 2.66 \text{ \AA}$
$\text{O}_3-\text{N} = 2.58$	$\text{O}_1-\text{N} = 2.62$
$\text{O}_3-\text{O}_9^- = 2.84$	$\text{O}_1-\text{O}_9^- = 2.09$
$\text{O}_4-\text{O}_8 = 2.88$	$\text{O}_5-\text{O}_8 = 2.66$
$\text{O}_4-\text{N} = 2.67$	$\text{O}_5-\text{N} = 3.90$
$\text{O}_4-\text{O}_9 = 2.80$	$\text{O}_5-\text{O}_9 = 4$

Distances between the  $\text{HS}_2\text{O}_7^-$  groups

$\text{O}_1-\text{O}_2 = 2.95 \text{ \AA}$	$\text{O}_7-\text{O}_7^- = 3.10 \text{ \AA}$
$\text{O}_5-\text{O}_7 = 2.54$	$\text{O}_2-\text{O}_2^- = 3.07$
$\text{O}_4-\text{O}_4 = 3.62$	$\text{O}_2-\text{O}_3 = 3.41$

whereas the  $c$  axis of the present structure may be compared with a face diagonal of the unit cell of NaCl. The two pronounced cleavages along (100) and (001) enhance this similarity, since these are comparable with the cube cleavage planes of NaCl. A third cleavage plane, which should be along (021), has not been observed.

From the coordinates of the atoms given in Table 1 we calculated some interatomic distances (see Table 2). A calculation of the root-mean-square error in those distances resulted in the following approximate values:

0.02 Å for a S-S distance, 0.03 Å for a S-O distance and 0.04 Å for a O-O distance.

It appears that many differences found in Table 2, between chemically comparable distances, need not be significant.

There is one very short interionic O-O distance, namely between  $\text{O}_5$  and  $\text{O}_6$  of the  $\text{HS}_2\text{O}_7^-$  groups shifted along the  $c$  axis. This might be a hydrogen bridge, which would then cause strings of pyrosulfate ions to be bound along the  $c$  axis. This interpretation is, however, not corroborated by the pronounced cleavage plane along (100).

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The calculations necessary for the three-dimensional Patterson synthesis and the Fourier syntheses were all carried out on I.B.M. accounting machines, using a modified Pauling-Schomaker system (Steeman, 1953). We wish to express our thanks to Messrs Reichward, Westra and van Dooyeweert of the Municipal Electricity Board, Amsterdam, for their gracious cooperation with respect to this accounting equipment.

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