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The Crystal Structure of the Asbestos-Like Form of Sulphur Trioxide

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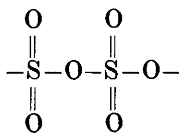
A needle of the asbestos-like form of SO_3 has been successfully isolated. Weissenberg diagrams about the needle axis showed that the crystal was a twin, which gave some difficulties in the interpretation. The cell constants are: $a = 6{\cdot}20$, b (needle axis) $= 4{\cdot}06$, $c = 9{\cdot}31$ Å, $\beta = 109°\ 50'$; space group C_{2h}^5–$P2_1/c$.

The crystal structure was solved by Patterson and Fourier methods. The structure is built up of chains along the needle axis, whose unit length contains two SO_4-tetrahedra so linked that a spiral of –O–S–O–S– is formed. These chains have twofold screw symmetry. The cell contains two chains related by the glide plane c.

There is a significant difference between the S–O distances in the chain (1·61 Å) and the other S–O bonds (1·41 Å), just as was found in the structure of the ice-like modification of this compound.

Introduction

The structure of the so-called ice-like form of SO_3 was determined by us 13 years ago (Westrik & MacGillavry, 1941; Westrik, 1941). At the time we also tried to solve the structure of the asbestos-like modification but failed to obtain single crystals, the needles mostly turning out to be fibre specimens (Westrik, 1941), so that we could determine only the fibre period (4·1 Å). From Raman spectra Gerding & Moerman (1937) concluded that Hägg's original idea (Hägg, 1932) that this form consists of



$$\begin{array}{ccccc} & O & & O & \\ & \| & & \| & \\ - & S & -O- & S & -O- \\ & \| & & \| & \\ & O & & O & \end{array}$$

chains is probably correct.

We have now resumed this investigation and have succeeded in isolating a suitable crystal and in solving the structure.

In the collection of the Laboratory of General and Inorganic Chemistry we found an evacuated bulb, about 25 years old, containing SO_3, in which some good crystals had grown, probably by slow sublimation. The bulb was opened, a few crystals were taken out quickly and inserted into capillary tubes of thin-walled glass, which were immediately sealed off. Under the microscope one of these crystals was selected for X-ray work.

Structure determination

Oscillation diagrams confirmed the fibre period, 4·06 Å. These diagrams also showed the presence of a mirror plane perpendicular to the fibre axis, which is in agreement with the straight extinction observed under the polarization microscope. A Weissenberg diagram of the equator about the needle axis showed that the crystal was a twin, as all reflexions were split save one row which we called $h00$. By considering only spots belonging to one orientation of the twin, the following cell constants were found:

$$a = 6{\cdot}20,\ b \text{ (needle axis)} = 4{\cdot}06,\ c = 9{\cdot}31 \text{ Å}, \\ \beta = 109°\ 50'.$$

Weissenberg diagrams of the 1st, 2nd and 3rd layer line about this axis were also made, using Cu $K\alpha$ radiation. It was impossible to obtain diagrams about other axes than b. Systematic absences were:

$$hkl\text{: none; } h0l\text{: absent with } l = 2n+1\,.$$

To test the $0k0$ reflexions, a crystal was mounted with the needle axis perpendicular to the rotation axis of the camera and oscillation diagrams were made in the regions of 010, 020, 030 and 040. Only 040 was observed so there is probably a twofold screw axis and 020 would be accidentally absent. The space group would then be C_{2h}^5–$P2_1/c$. With 4 molecules in the cell, the calculated density is 2·42 g.cm.$^{-3}$, which is a reasonable value, the density of the ice-like form of SO_3 being 2·29 g.cm.$^{-3}$ (Westrik & MacGillavry, 1941).

The twinning on (100) causes a plane $h,k,2l$ in one orientation to nearly coincide with $-h-l,k,2l$ in the other. Moreover, it was observed in the Weissenberg diagram of the equator, which shows only spots with even l, that spots in twinning positions also have nearly the *same intensity* so that the b-axis projection has strong pseudo-symmetry. This pseudo-symmetry is, of course, lost in the higher layer lines because here reflexions occur with odd l which have no counterpart in the other orientation. It was noticed, however, that in the second layer line intensities of $h,2,2l$ and $-h-l,2,2l$ coincide closely whereas there is no such correspondence in the odd layer lines.

The intensities belonging to one orientation were estimated by visual comparison, using the multiple-film technique. The reflexions $h00$ of both orientations coincide; their intensities were split in the mass ratio of the two orientations, as determined from the average intensity ratio of a number of $h0l$ reflexions from the one and the other orientation.

The strong fibre character and the largest refractive index in the direction of the fibre point to a chain nature as supposed by Hägg (1932) and by Gerding & Moerman (1937).

The x and z parameters

A Patterson projection along the b axis was computed (Fig. 1). This map can be interpreted as a vector projection of a chain along a twofold axis linked in such a way that a spiral of -O-S-O-S- is formed (Fig. 2). The cell contains two of these chains related by the glide plane c. As each chain period contains two asymmetric units, it must have either symmetry centres or a screw axis. Clearly, centres are incompatible with the chain model, which can on the other hand have twofold screw symmetry. The positions of the chain axes in the unit cell are thus fixed; according to the vector map, Fig. 1, the azimuth is such that the vector S-S is practically perpendicular to the c axis.

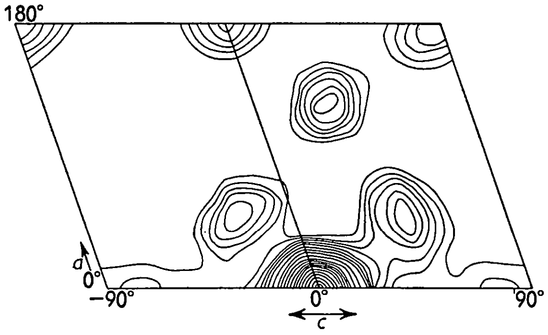


Fig. 1. Patterson projection along the b axis. Contour lines are at equal intervals on an arbitrary scale.

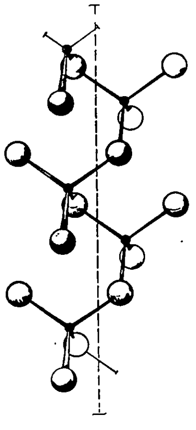


Fig. 2. Model of a chain of $(SO_3)_n$.

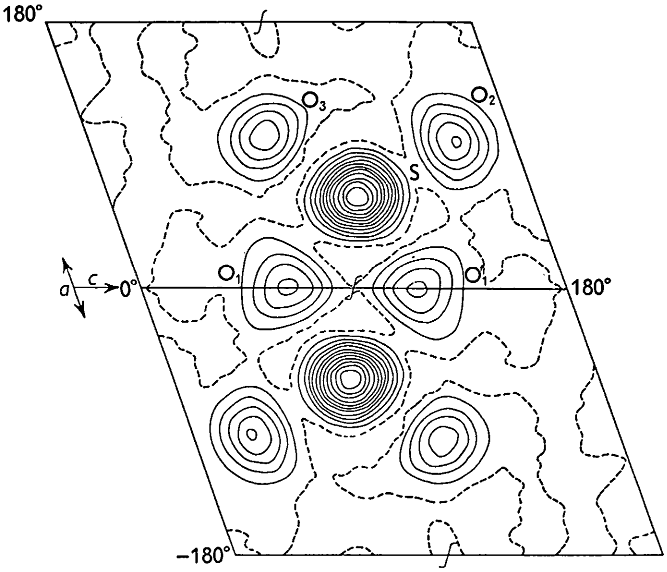


Fig. 3. Electron-density map of β-SO_3 projected along the b axis. Contours are drawn at intervals of 1 e.Å^{-2}, the zero contour line being broken.

After refinement by ordinary Fourier methods the electron-density map, Fig. 3, was obtained. The x and z coordinates were subsequently corrected for back-shift.

The y parameters

Inspection of the Weissenberg diagrams of the higher layer lines shows a preference for $k+l$ even, especially at higher diffraction angles where f_O has fallen off

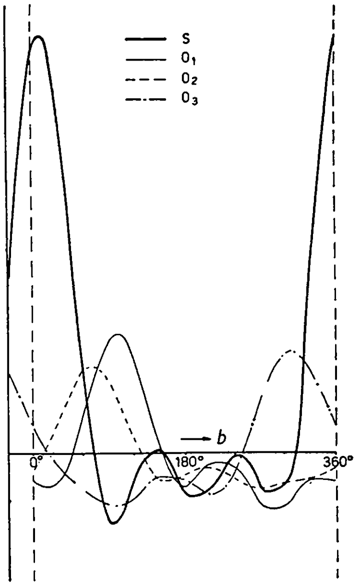


Fig. 4. Fourier syntheses along lines in the b direction through atomic centres found in the [010] projection.

considerably. Thus the arrangement of the S atoms is approximately centred in the y–z plane, i.e., $y_S \doteqdot 0$. The y coordinates of the O atoms then follow from the model and interatomic distances. They were refined by three-dimensional Fourier summations along lines parallel to b through the atomic centres found in the [010] projection; the result is seen in Fig. 4. As the maximum value of k is 3, these line syntheses show strong diffraction effects.

The atomic coordinates are:

	x	y	z
S	0·171	0·02^5	0·294
O_1	0·001	0·27^5	0·169
O_2	0·270	0·20	0·431
O_3	0·281	−0·15	0·207

The standard deviations of the x and z parameters, calculated according to Cruickshank (1949), are 0·01 Å for S and 0·02 Å for O; σ_y has not been estimated; it may well be twice as large as σ_x and σ_z. The reliability factor in the [010] projection is 0·14.

Discussion of the structure

Interatomic distances are:

S · · · S	2·85 Å	O_1–O_1'	2·53 Å
S–O_1	1·63	O_2–O_3	2·54
S–O_1'	1·59	O_1–O_2	2·45
S–O_2	1·41	O_1'–O_3	2·42
S–O_3	1·41	O_3–O_1	2·39
		O_1'–O_2	2·37

The smallest intermolecular O–O distance is 3·09 Å. Valence angles are:

O_2–S–O_3 = 128°
O_1–S–O_1' = 102
O_1–S–O_3 = 103^5
S–O–S = 121

The difference in distance between S–O in the chain and the other S–O bonds is significant, those between the O atoms are probably not. The same difference in S–O distances was found in the ice-like form of SO_3.

In the present structure, oxygen forms a cubic close packing slightly deformed by the sulphur atoms. In fact, one single $(SO_3)_n$ chain may be considered as a strip cut out of a zincblende type structure (see Fig. 5(*a*)).

From Fig. 5(*b*) it may be seen that the 'cell dimensions' of the deformed cubic structure of the oxygens are:

$$\tfrac{2}{3}d_{(100)} = 3{\cdot}89,\ b = 4{\cdot}06,\ \tfrac{1}{2}c = 4{\cdot}66\ \text{Å}\,.$$

Twinning on (100) leaves this oxygen packing nearly unchanged throughout the crystal (see Fig. 5*b*). This explains the frequency of this twinning.

We have now studied both forms of SO_3, the ice-like (γ) form consisting of trimers S_3O_9 and the present β form composed of polymer chains. These structure types reveal a formal resemblance with silicate anions. The γ form resembles benitoite in that both structures have rings of three linked tetrahedra, whereas the β form corresponds to the pyroxenes. However, these rings and chains in SO_3 have a configuration appreciably different from that in the silicates.

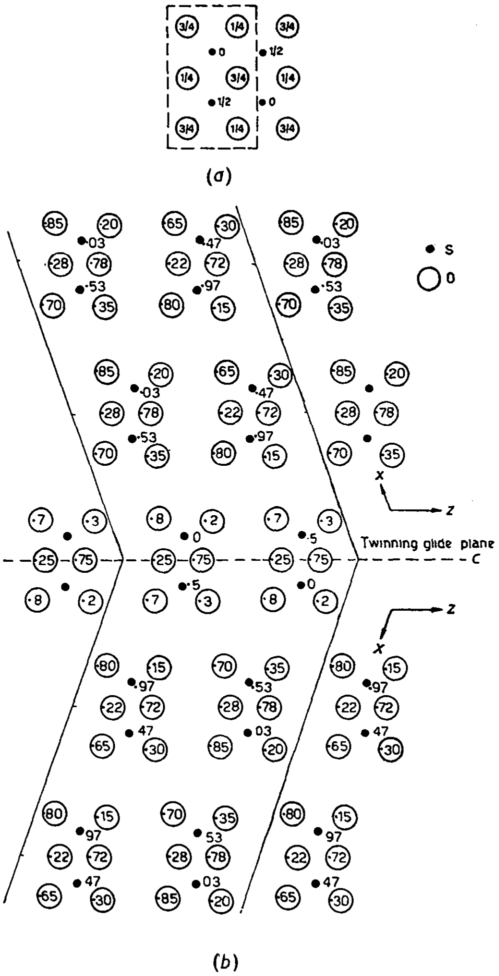


Fig. 5. (*a*) Zincblende structure displaced $-\frac{1}{4}c$ with respect to the conventional origin. Enclosed in broken lines is the part corresponding to one idealised SO_3 chain.
(*b*) Possible twinning mechanism of β-SO_3. The numbers are y parameters.

In both cases, the valence angle of the oxygen atom connecting two tetrahedra in sulphur trioxyde is smaller than in the corresponding silicates, which might be interpreted as due to a more covalent bond in SO_3. Relatively small oxygen valence angles, 115° and 122° respectively, were also found in the structures of $HNO_3.2SO_3$ (Steeman & MacGillavry, 1954) and of $N_2O_5.3SO_3$ (Eriks & MacGillavry, 1954).

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The Crystal Structure of β-Nitropropionic Acid

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β-Nitropropionic acid is monoclinic, $A2/a$–C_{2h}^6 with eight molecules of $C_3H_5NO_4$ in a unit cell of dimensions $[a] = 20·02$, $[b] = 5·20$, $[c] = 9·57$ Å, $\beta = 92° 26'$. Two molecules are linked through the carboxyl groups by hydrogen bonds of length 2·66 Å across a centre of symmetry, and adjacent pairs are further linked by a zigzag arrangement of weak contacts of length 3·06 Å.

Introduction

The identity of β-nitropropionic acid and hiptagenic acid has been established by means of mixed melting points, dissociation constants, optical properties and X-ray powder photographs. Because of the unusual reactions given by hiptagenic acid, a naturally occurring product, many workers have regarded it as a 1:2-disubstituted propionic acid; in order to determine its constitution, the crystal structure has been investigated.

Experimental

β-Nitropropionic acid was prepared by a variation of the method of Lewkowitsch (1879) by the action of silver nitrite on 2-iodopropionic acid.

The crystals obtained from chloroform solution are very thin monoclinic plates elongated along [*b*] with {100} predominant and {001} and {101} occasionally developed. When carefully cut the crystals cleave along {101}. They are optically positive and biaxial with the optic axes lying in the (*ac*) plane and with γ vibrating 25° away from [*c*] in the acute angle β. The refractive indices, using the NaD line, are

$$\alpha = 1·463,\ \beta = 1·499,\ \gamma = 1·558\ .$$
$$2V = 78° 46'.$$

The unit-cell dimensions and space group were obtained from rotation and oscillation photographs:

$$[a] = 20·02,\ [b] = 5·20,\ [c] = 9·57\ \text{Å};\ \beta = 92° 26'.$$

Systematic absences are $\{hkl\}$ when $k+l \neq 2n$ and $\{h0l\}$ when $h \neq 2n$ and $l \neq 2n$. The space group is therefore either $A2/a$–C_{2h}^6 or Aa–C_s^4; these can accommodate eight and four molecules respectively in general positions. The density measured by flotation is 1·59 g.cm.$^{-3}$; the value calculated for eight molecules of $C_3H_5NO_4$ per cell is 1·589 g.cm.$^{-3}$. The space group was therefore taken as $A2/a$. Absorption coefficient for Cu $K\alpha$ X-rays, $\mu = 15·0$ cm.$^{-1}$.

The intensities of all $\{hkl\}$ reflexions obtainable with Cu $K\alpha$ radiation were recorded on equi-inclination Weissenberg photographs, using the multiple-film technique. The crystals, which are deliquescent and volatile, were enclosed in perspex capsules (Llewellyn, 1951). The intensities were measured visually, a total of 512 planes out of a possible 1148 being observed, and then converted to structure amplitudes; these were placed on an approximately absolute scale, first by a photographic method in which a few planes from β-nitropropionic acid were compared with planes from *p*-dinitrobenzene (Llewellyn, 1947) and secondly by the method of Harker (1948).

Later, when the crystal structure would not refine, the $\{h0l\}$ and $\{hk0\}$ planes were corrected for absorption, using the intensities from the [*b*] and [*c*] axes zero-layer-line Weissenberg photographs, by a modification of the method of Albrecht (1939); only one value of the path length of the X-rays through the crystal was calculated, by taking one measurement through the geometric centre of the crystal. This was considered justifiable as the differences between this method and the more laborious Albrecht method were found to be small for the planes tried. The dimensions of the crystals were $0·05 \times 0·76 \times 0·20$ mm. for [*b*]- and $0·06 \times 0·34 \times 0·35$ mm. for [*c*]-axis photographs.