equidistant from $_2C_5$ (4·02 Å) and $_3C_5$ (4·13 Å) and the distance C_5–$_1C_5$ is 3·92 Å. C_5 then lies at distances from $_2C_5$ and $_3C_5$ of 3·78 and 4·81 Å respectively. It is clear that the mobile C_5–S bond can rotate to occupy two positions in which a balanced arrangement of van der Waals forces is achieved, the C_5–S group fitting into the triangle of atoms $_1C_5$, $_2C_5$ and $_3C_5$ in a manner akin to the packing of spheres in a hexagonal lattice. This arrangement may be described as distorted hexagonal packing.

Conclusion

The crystal structures of the dimorphs of methionine have been described. The system of hydrogen bonds binding the molecules in double layers is the same in both. The dimorphism of methionine is ascribed to the free rotation of the terminal CH_3–S group resulting in two different ways of achieving a stable balanced configuration of van der Waals forces. The two forms are therefore almost equally stable. The easy cleavage parallel to (001) is correlated with the weak forces between the double-layer units.

It may be deduced that one or other of these packing arrangements will be utilized in the crystal structures of the other straight-chain aliphatic α-amino acids, their space group being either $P2_1/a$ or $I2/a$ as observed (Dawson & Mathieson, 1951). It is probable that the different shapes of the end portion of the molecules of branched-chain acids do not permit the simple distorted hexagonal packing, and a stable configuration can be achieved only in the lower symmetry of the triclinic system.

On account of the equal stability of the dimorphs of methionine, it might be expected that disorder in stacking of layers could arise. Such disorder has not been observed in methionine, but was noted in the case of norleucine, the crystal structure of which will be reported later.

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The Crystal Structure of Sodium Thiosulphate Pentahydrate

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The crystal structure of sodium thiosulphate pentahydrate has been determined by the use of three-dimensional Patterson methods and refined by two-dimensional Fourier synthesis.

The unit cell dimensions are $a=5{\cdot}94\pm0{\cdot}01$, $b=21{\cdot}57\pm0{\cdot}05$, $c=7{\cdot}53\pm0{\cdot}01$ Å, $\beta=103°\ 58'\pm5'$. The space group is $P2_1/c$. The structure shows a tetrahedral thiosulphate group, with a S–S distance of 1·97 Å and an average S–O distance of 1·48 Å. Each sodium atom is surrounded by an octahedral group of atoms; the external sulphur atom is one member of one such group, but the remainder are oxygens of the thiosulphate groups or are water oxygens. These octahedral groups share edges with each other to form chains parallel to the *a* axis, and these chains are linked together sideways by sharing oxygens with, and by hydrogen bonding to, the S_2O_3 groups.

Introduction

No structure determination of a compound containing the S_2O_3'' group has yet been reported, although determinations of salts of several other sulphur-oxygen anions have been carried through, principally by W. H. Zachariasen and co-workers (Zachariasen, 1932, 1934; Zachariasen & Buckley, 1931; Zachariasen & Ziegler, 1932; Zachariasen & Mooney, 1934; Helwig, 1932; Huggins, 1933). The shapes found for these anions suggest the probable nature of the S_2O_3'' group as a tetrahedron, with a central sulphur atom and with S–O distances of about 1·5 Å and an S–S distance of about 2·0 Å. The present work on the familiar crystals of 'hypo' was undertaken mainly to confirm this suggested shape. It was decided, however, that if possible no chemical evidence would be used in the determination of the structure. From this point of view the work is therefore of interest as a further illustration of certain uses recently developed of the Patterson function (Beevers & Robertson, 1950).

Unit cell and space group

Sodium thiosulphate pentahydrate is, according to Groth (1906–19, vol. 2, p. 670), monoclinic prismatic, with $a:b:c = 0{\cdot}2745:1:0{\cdot}3508$, $\beta = 103°\ 58'$. Crystals grown for this work by slow evaporation of saturated aqueous solution at 18° C. were found to correspond to Groth's description. Three cylindrical specimens of about 0·2 mm. in diameter were cut, one parallel to each principal axis. From these, all the observable layer lines were recorded, using Weissenberg photographs for the a and c axes and oscillation photographs for the (long) b axis. The unit-cell dimensions were obtained from high-order $hk0$, $0kl$ and $h0l$ reflexions on the corresponding Weissenberg photographs by the method of Farquhar & Lipson (1946). The results were:

$$a=5{\cdot}944\pm0{\cdot}01,\quad b=21{\cdot}57\pm0{\cdot}05,\quad c=7{\cdot}525\pm0{\cdot}01\ \text{Å}\,,\quad \beta=103°\ 55'\pm5'\,.$$

This cell contains four molecules, each of composition $Na_2S_2O_3.5H_2O$. The systematic absences are $0k0$ present only with k even, and $h0l$ present only with l even, so that the space group is $P2_1/c\text{–}C^5_{2h}$. This space group has fourfold general positions and thus the positions of two sulphur atoms, two sodium atoms and eight oxygen atoms have to be found in the unique volume of the cell.

Determination of the structure

The intensities of all reflexions were obtained by comparison with multiple-exposure photographs. The usual correction factors were applied by means of the charts given by Cochran (1949); no corrections were made for absorption or the temperature effect. The intensities of the three two-dimensional zones were then converted separately to the absolute scale by the method of Wilson (1942), a procedure which gives some correction for absorption and temperature effects. The corrected general intensities were then obtained on the same scale by comparison with the spots of the two-dimensional zones.

An attempt was first made to solve the structure using only the two-dimensional data, and the Patterson projections on (001) and (100) were calculated. Then the sulphur parameters were sought by choosing likely vectors to be those between atoms of the same set and testing these by working out the vectors between the two different sulphur sets of equivalent points. The vectors between sulphur of the same set are:

$$\begin{aligned}&0,\ \tfrac{1}{2}+2y_1,\ \tfrac{1}{2}\ \text{(single weight)}\\&2x_1,\ 2y_1,\ 2z_1\ \text{(single weight)}\\&2x_1,\ \tfrac{1}{2},\ \tfrac{1}{2}+2z_1\ \text{(double weight)}\end{aligned}$$

and similarly for sulphur 2. The vectors between sulphurs of different sets are

$$\begin{aligned}&x_1-x_2,\ y_1-y_2,\ z_1-z_2\\&x_1-x_2,\ \tfrac{1}{2}+y_1+y_2,\ \tfrac{1}{2}+z_1-z_2\\&x_1+x_2,\ y_1+y_2,\ z_1+z_2\\&x_1+x_2,\ \tfrac{1}{2}+y_1-y_2,\ \tfrac{1}{2}+z_1-z_2\end{aligned}$$

all of double weight. The Patterson summation possesses mirror planes at $y = 0$ and $\frac{1}{2}$, and centres of symmetry at 0 and $\frac{1}{2}$ along all axes. The sulphur parameters found in this way were eventually abandoned after it was found that Fourier syntheses based on the signs obtained from these positions did not lead to a satisfactory structure.

The Patterson function was then computed in three dimensions, as sections parallel to the $a\,b$ plane at the following values of z: 0, 3, 7, 10, 13, 17, 20, 23, 27 and 30 sixtieths of c. The Patterson–Harker section at $y = \frac{1}{2}b$ was also computed in steps of 30ths of a and c[*] It was found that two outstandingly heavy peaks are present on the latter at $(\frac{17}{60}, \frac{1}{2}, \frac{2}{60})$ and $(\frac{12}{60}, \frac{1}{2}, \frac{42}{60})$. Taking these to be peaks of the type $(2x, \frac{1}{2}, \frac{1}{2}+2z)$, the probable x and z parameters of the sulphurs are (in 60ths):

x	z
6 or 36	6
9 or 39	17

The corresponding $(2x, 2y, 2z)$ peaks were sought for in the body of the Patterson summation. The suggested $2y$ values thus found were then verified by looking along the lines $0, y, \frac{1}{2}$ for the third type of peak at $(0, \frac{1}{2}-2y, \frac{1}{2})$. The y values were strongly supported by these lines and the positions of the sulphurs were thus determined with considerable confidence. The vectors between atoms of the same set leave some ambiguities, such as the possibility of x and $\frac{1}{2}\pm x$, etc., but the vectors between sulphurs of the two different sets remove all these. The final parameters chosen were as follows (in 60ths of the cell edges):

x	y	z
6	4	6
9	9	17

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[*] The labour of calculating the three-dimensional Patterson function was rendered feasible by the use of a machine, built in this laboratory by Dr F. Stern, for one-dimensional summation. This machine is of the Hägg–Laurent type, but was constructed of standard telephone equipment. All four quadrants of a sine–cosine summation with wave-numbers up to 15 can be obtained in 60ths with one setting of amplitudes; wave numbers up to 30 are obtainable with two amplitude settings. The time required to compute the average two-dimensional summation is reduced by the use of this machine to 4–5 hr.

It is perhaps worth mentioning that the solution achieved from the projections alone had given the above values, but with the two y parameters interchanged. This was due to the fact that the single weight $(2x, 2y, 2z)$ vectors were not sufficiently outstanding in the projections, although the other peaks had been correctly identified.

A complete solution of the structure might now have been possible by Fourier methods, but it was thought that the use of the vector convergence method (Beevers & Robertson, 1950), using the eight sulphur atoms to 'search' the three-dimensional Patterson summation, would be more elegant. The method consists in building up a function which represents the addition of eight Patterson summations with their origins placed each time at the position of the searcher atom concerned. New atomic sites are then expected to appear as eightfold coincidences of vectors. In practice this was done by marking the centres of every peak judged sufficiently high to be an S–O vector, but indicating the actual height by the size of the symbol used. In addition to this, the contribution of each searcher atom was marked with a distinctive symbol in order to assist the identification of genuine coincidences. The function required only the most casual inspection to reveal the ten required oxygen positions. The eightfold coincidences were easily distinguishable from any chance clusters of peaks, and no extra eightfold coincidences were found.

The resulting structure was at once tested by building a model and by calculating structure factors. The model showed immediately that the structure was acceptable from the chemical point of view. A tetrahedral thiosulphate group was present as expected. The two sodium atoms, distinguished from the oxygens by the heavier vectors composing their coincidences, were surrounded by the expected octahedral arrangement of six atoms—all oxygens in one case, five oxygens and the external sulphur in the other. The structure was in fact that shown in the final diagram except for minor shifts produced by refinement. A set of $F(hkl)$ values was then calculated from the suggested parameters and the results were in very satisfactory agreement with the observed F's, giving a factor $R = \Sigma||F_o|-|F_c||\div\Sigma F_o$ of 0·35. Values of this factor obtained for the zones $(0kl)$ and $(hk0)$ gave values 0·48 and 0·48 respectively. After four successive Fourier refinements on each zone, the R values had fallen to 0·35 and 0·32 and the refinement at this point seemed to be at a standstill. It was thought that the principal source of error at this stage was the lack of convergence of the series, due to absence of a temperature correction. Instead of applying a temperature factor, however, it was decided to use a method suggested by Cochran (1951) to correct for lack of convergence, namely the synthesis using as coefficients (F_o-F_c).

Such difference syntheses were computed on the (001) and (100) projections and their results were interpreted according to the formula given by Cochran, $\Delta = (dD/dr)/2p\varrho_o$, where dD/dr is the slope of the difference synthesis at the original atomic position, ϱ_o is the height of the atom concerned, and the value $p = 4·9$ (given by Cochran for nitrogen and carbon) was assumed to hold here. After re-calculation of the $(0kl)$ and $(hk0)$ F's with the resulting positions it was found that the respective values of R were now 0·29 and 0·26, and the value for the $(h0l)$ F's was 0·31. Further F_o-F_c syntheses on the same two projections showed no further shifts.

The final co-ordinates of the atoms are given in Table 1. It is considered that these have a maximum error of 0·03 Å; the maximum error in bond lengths is therefore 0·06 Å, and that in the bond angles is estimated at 5°.

Table 1. *Final co-ordinates*

	x (Å)	y (Å)	z (Å)
S_1	0·62	1·50	0·82
S_2	0·86	3·06	2·07
Na_1	4·13	7·38	0·56
Na_2	1·44	8·83	1·57
O_1	1·92	2·64	3·26
O_2	5·28	3·30	2·57
O_3	1·15	4·20	1·38
$(H_2O)_4$	3·55	5·04	0·88
$(H_2O)_5$	0·58	6·72	2·13
$(H_2O)_6$	3·60	7·97	2·69
$(H_2O)_7$	4·98	9·60	0·88
$(H_2O)_8$	3·74	0·30	1·88

Discussion of the structure

The structure is shown in projection down the a axis in Fig. 1. The tetrahedral S_2O_3 group has the following dimensions:

$$S_1–S_2 = 1·97\ \text{Å}$$
$$S_2–O_1 = 1·46$$
$$S_2–O_2 = 1·59$$
$$S_2–O_3 = 1·40$$

The bond angles range from 104° to 115°. The bonds external to the group are:

S_1 to O: 2·74, 2·74, 2·85 Å
O to O: 2·43, 2·44, 2·48 Å

The differences in length shown by the S–O bonds is difficult to explain by differing external bonding of the three oxygen atoms, and it is concluded that maximum errors may be present in these oxygen positions. The average S–O distance, however, is probably fairly accurate.

The two sodium atoms each have around them a distorted octahedral co-ordination group. In the case of Na_1 this is composed of two thiosulphate and four water oxygens at distances of between 2·38 and 2·53 Å. The bond angles at this sodium vary from 84° to 107°. Na_2 forms its co-ordination group of one oxygen, four water oxygens and the external sulphur atom of the thiosulphate group. Na to O distances lie between 2·33

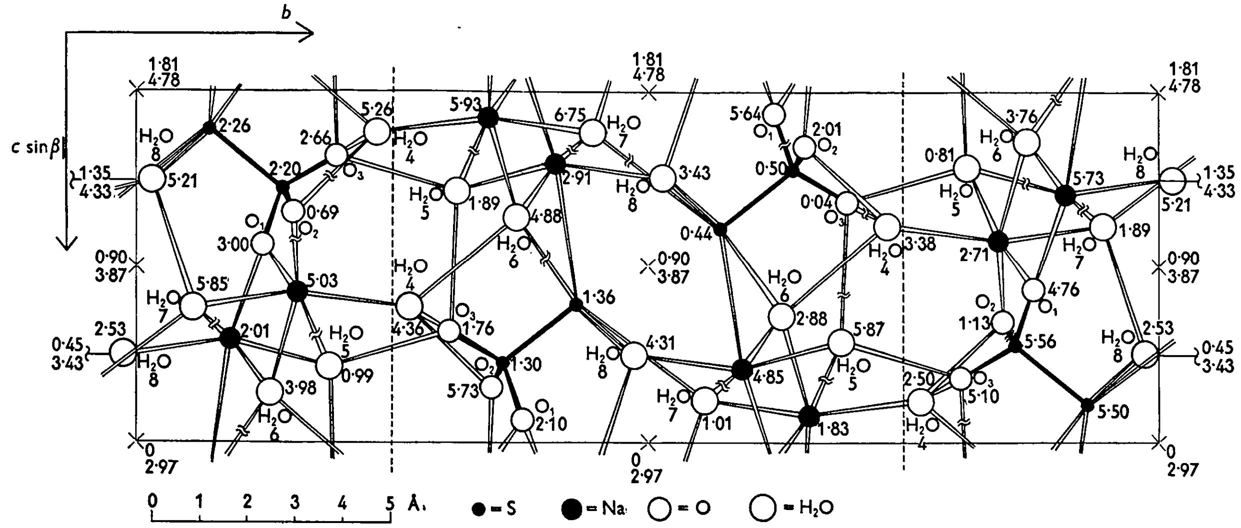

Fig. 1. The complete unit cell. The heights of the atoms and of the centres of symmetry are shown in Ångström units above a standard plane perpendicular to the a axis.

and 2·41 Å. The Na to S distance, however, is 3·55 Å. The bond angles at Na_2 range from 73° to 103°. The sodium octahedra form continuous linked chains parallel to the a axis, by sharing edges, i.e. two atoms, between adjacent octahedra. The pairs of shared atoms are O_1 and $(H_2O)_6$; $(H_2O)_5$ and $(H_2O)_7$ respectively. Other hydrogen bonds are those shown in the 'bond diagram' (Fig. 2), and in the case of those directed to other oxygens the lengths show a variation from 2·74 to 2·92 Å. The role of the external sulphur atom S_1 seems to be an important one. It forms five contacts in addition to the S_1–S_2 bond; these slope away from the latter at angles of 97–118°, and are arranged with respect to one another with roughly equal adjacent angles of 57–84°. One of these contacts has already been mentioned and is to Na_2, of length 3·55 Å. The other four are directed to water oxygens; they vary from 3·31 to 3·38 Å. Two such groups around S_1 face each other across centres of symmetry. The columns of linked sodium octahedra are thus held together laterally by the co-ordination with the thiosulphate groups and by bonds between the water molecules and the thiosulphate groups.

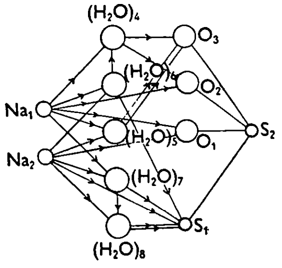

Fig. 2. Bond structure, showing contacts made by the atoms. Each water molecule has two incoming and two outgoing (hydrogen) bonds.

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