

671. *A Detailed Refinement of the Crystal Structure of Sodium Hydroxymethanesulphinic Dihydrate (Rongalite).*

By MARY R. TRUTER.

Anisotropic refinement of the crystal structure ¹ of Na[HO·CH₂·SO₂], 2H₂O has been carried out and the co-ordinates have been corrected for rotational oscillation of the anion. The bond lengths are S-O = 1.513 ± 0.006 Å, S-C = 1.83 ± 0.01 Å, and C-O = 1.40 ± 0.01 Å. The hydrogen atoms in the anion have been located and a more extensive system of hydrogen bonding has been found than was reported previously.

WHEN the structure analysis of this compound was originally undertaken, in 1955, the formula appeared in the chemical literature as NaHSO₂·H·CHO·2H₂O, the constitution of the anion being uncertain; the analysis showed ¹ that the sulphur was present in the oxidation state IV and pyramidally bonded to two oxygen atoms (S-O = 1.50 Å) and one carbon atom with a long S-C bond, 1.84 Å, and therefore the anion should be written HO·CH₂·SO₂⁻.

Advances in crystallographic technique, such as the determination of anisotropic thermal motion ² and correction for systematic errors introduced by rotational oscillation ³ have increased the precision of the results. A complete anisotropic refinement of this structure has yielded results which are comparable with those of the more recent determination of potassium methylenedisulphonate which forms the subject of the preceding paper.⁴

Refinement omitting Hydrogen Atoms.—There are 8 formula units, Na[HO·CH₂·SO₂], 2H₂O, in an orthorhombic unit cell ($a = 6.78$, $b = 10.835$, $c = 15.97$ Å) with space group *Pbca*, so that all the atoms are in general positions and there are two independent water molecules, H₂O(1) and H₂O(2). When isotropic refinement of the structure had been completed an unsuccessful attempt had been made to locate the hydrogen atoms. Fig. 1 gives a view of the structure and the designations of the atoms; it also contains information discovered during the present refinement.

For the present refinement the starting point was the published set of co-ordinates for the atoms other than hydrogen and the final isotropic temperature factors which corresponded to mean-square amplitudes of vibration of 0.01 Å² for Na⁺ and S, 0.015 Å² for C and 0.02 Å² for O. Variations from unity in the ratios of the observed to the calculated values of $\partial^2\rho/\partial x^2$, $\partial^2\rho/\partial y^2$, and $\partial^2\rho/\partial z^2$ had indicated ¹ some anisotropy of the thermal motion. These ratios for each atom (unpublished) were used to derive approximate values for U_{11} , U_{22} , and U_{33} , the mean-square amplitudes of vibration parallel to the a^* -, b^* -, and c^* -axes, to give the first set of anisotropic temperature factors. Comparison with the final values (Table 2, below) showed that the anisotropy was underestimated by this method.

For the first set of structure factors R was 0.15; this was the same as at the end of isotropic refinement despite the changes in temperature factors and in the scattering factors. Refinement was carried out by the method of least squares; the parameters were the scale of $|F_{\text{obs.}}|$, and the co-ordinates and anisotropic vibration parameters for each atom. After four cycles, R was 0.130 and the largest shift in a parameter was 0.4 times the corresponding standard deviation, indicating that refinement of the heavy-atom positions was complete.

Location of the Hydrogen Atoms and Further Refinement.—A three-dimensional difference Fourier synthesis was computed with coefficients from reflections with $\sin \theta < 0.5$. There were no peaks which obviously corresponded to hydrogen atoms. However, the positions of the hydrogen atoms on the anion could be deduced geometrically. For H(1) and H(2) the co-ordinates were calculated on the assumption that the C-H bond length was 1.0 Å and that the bonds round the carbon atom were directed tetrahedrally. The electron-density difference at these positions was positive and as large as in any other region. Similarly, the approximate

¹ Truter, *J.*, 1955, 3064.

² Cruickshank, *Acta Cryst.*, 1956, 9, 754.

³ Cruickshank, *Acta Cryst.*, 1961, 14, 896.

⁴ Truter, preceding paper.

position of H(3) could be calculated on the assumption that the H(3) to O(1) bond length was 1.0 Å and that H(3) was situated along the line joining O(1) and O(2)' which, being separated by only 2.64 Å, suggests the presence of a hydrogen bond. Once again, this position was in a region of positive electron density in the difference synthesis. Round the oxygen atoms of the water molecules the electron density difference was zero or negative within a sphere of radius 1.5 Å, so for the moment, these hydrogen atoms were ignored.

In the next calculation of structure factors, in which the three hydrogen atoms were included, with isotropic temperature factors, R fell to 0.128₀; least-squares refinement gave the most significant shifts in the heavy atom parameters as z for O(2) and y for C which were,

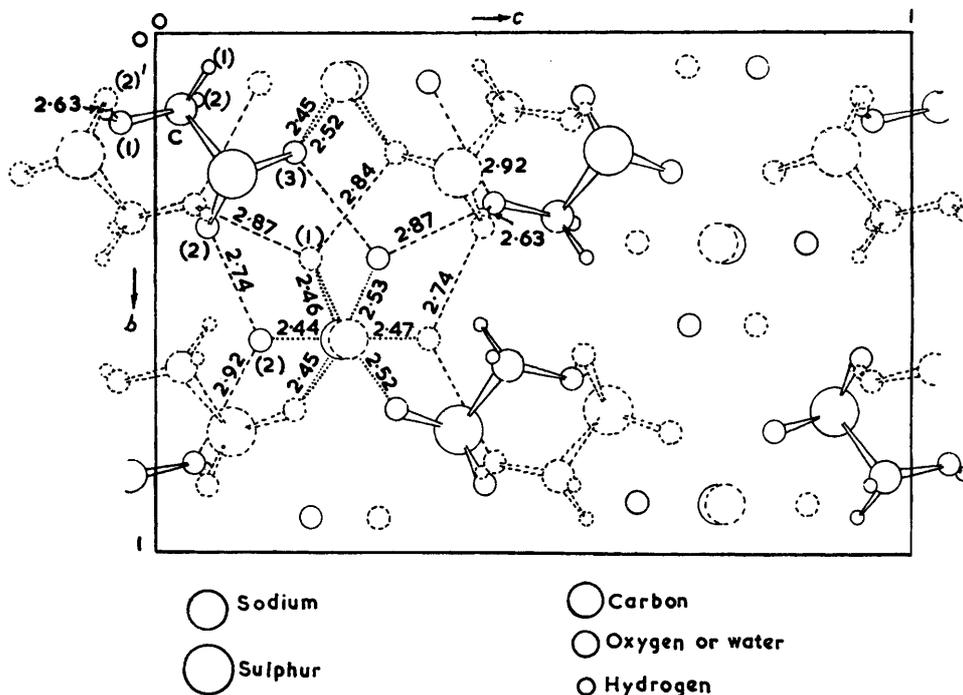


FIG. 1. Projection of the structure along [100]. Anions and water molecules at $x/a \sim 0$ and sodium ions at $x/a \sim \frac{1}{4}$ are shown by full circles; anions and water molecules at $x/a \sim \frac{1}{2}$ and sodium ions at $x/a \sim \frac{3}{4}$ are shown by broken circles. Probable hydrogen bonds are indicated by broken lines and the distances in Å between the oxygen atoms are marked. Contacts round the sodium ions are shown by dotted lines; the six distances in Å round one sodium ion with $x/a \sim \frac{1}{4}$ are shown. Each O(3) or water molecule is nearly equidistant from two sodium ions, as indicated specifically for O(3).

respectively, 0.96 and 0.86 times the corresponding standard deviations. A further cycle of refinement gave a slight improvement in R (0.127₀); the most significant shift in a heavy-atom parameter was 0.2 times its standard deviation, so that refinement was complete but for the four hydrogen atoms which had been omitted.

Hydrogen Atoms of the Water Molecules.—The absence of any indication of hydrogen atoms in the electron-density difference synthesis would be explained if the water molecules are rotating. On the other hand, if their environment indicates that they participate in hydrogen bonding, it is unlikely that they are rotating, and so their positions can be deduced.

Calculation of all the interatomic distances of less than 3.5 Å showed (Fig. 1) that the water molecules do appear to be taking part in hydrogen bonding. For H₂O(1) the bond lengths are 2.84 and 2.87 Å and the angle between the bonds is 101°; for H₂O(2) the bond lengths are 2.92 and 2.73 Å and the angle is 124°. However, when hydrogen atoms were included in the

3402 Truter: A Detailed Refinement of the Crystal Structure of

calculations at positions chosen to give O-H = 1.0 Å and H-O-H = 110° and O-H...O as close as possible to O...O, the value of *R* increased to 0.129. Large increases in the temperature factor for these four hydrogen atoms were also indicated by the refinement and this is the usual response to a wrongly-placed atom. Although on chemical grounds the postulated positions for H(4)—H(7) in Table 1 are reasonable, it has not been possible to prove their existence crystallographically. The final results are those obtained by including the hydrogen atoms of the anion and excluding those of the water molecules.

Results.—The final parameters for the heavy atoms and the three hydrogen atoms located are shown with their standard deviations in Tables 1 and 2. The terms U_{12} , U_{23} , and U_{13} in Table 2 together with U_{11} , U_{22} , and U_{33} define the ellipsoid of vibration of each atom with respect to the crystallographic axes.

TABLE 1.

Atomic co-ordinates in Å (a) before and (b) after correction for rotational oscillation.

| | X(a) | X(b) | $\sigma(X)$ | Y(a) | Y(b) | $\sigma(Y)$ | Z(a) | Z(b) | $\sigma(Z)$ |
|---|--------|--------|-------------|-------|-------|-------------|--------|--------|-------------|
| Na | 1.865 | | 0.005 | 1.000 | | 0.004 | 4.083 | | 0.004 |
| S | 0.721 | 0.722 | 0.003 | 2.970 | 2.971 | 0.003 | 1.619 | 1.620 | 0.002 |
| C | 0.293 | 0.292 | 0.012 | 1.559 | 1.555 | 0.010 | 0.541 | 0.539 | 0.010 |
| O(1) | 0.613 | 0.614 | 0.009 | 1.822 | 1.820 | 0.009 | -0.795 | -0.800 | 0.007 |
| O(2) | -0.203 | -0.205 | 0.010 | 4.035 | 4.040 | 0.009 | 1.088 | 1.087 | 0.007 |
| O(3) | 0.183 | 0.182 | 0.009 | 2.478 | 2.476 | 0.008 | 2.939 | 2.945 | 0.007 |
| H ₂ O(1) | 3.231 | | 0.011 | 4.715 | | 0.008 | 3.324 | | 0.007 |
| H ₂ O(2) | -0.095 | | 0.009 | 6.522 | | 0.008 | 2.221 | | 0.007 |
| H(1) | 0.95 | | 0.2 | 0.7 | | 0.2 | 1.2 | | 0.2 |
| H(2) | -0.7 | | 0.2 | 1.4 | | 0.2 | 0.9 | | 0.2 |
| H(3) | 1.5 | | 0.2 | 1.7 | | 0.2 | -1.1 | | 0.2 |
| <i>Probable positions for hydrogen atoms on water molecules</i> | | | | | | | | | |
| H(4) | 3.5 | | | 4.1 | | | 2.4 | | |
| H(5) | 3.3 | | | 3.9 | | | 3.9 | | |
| H(6) | -0.3 | | | 7.4 | | | 1.7 | | |
| H(7) | -0.1 | | | 5.6 | | | 1.8 | | |

TABLE 2.

Thermal parameters (all units are 10⁻³ Å²).

| | U_{11} | σ | U_{22} | σ | U_{33} | σ | U_{12} | σ | U_{23} | σ | U_{13} | σ |
|---------------------------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|
| Na | 11 | 2 | 18 | 2 | 10 | 2 | -1 | 3 | 2 | 3 | -3 | 2 |
| S | 5 | 1 | 12 | 1 | 7 | 1 | 0 | 1 | 0 | 1 | 1 | 1 |
| C | 19 | 6 | 7 | 4 | 9 | 4 | 3 | 6 | -2 | 4 | 10 | 5 |
| O(1) | 21 | 4 | 22 | 4 | 7 | 3 | 5 | 4 | -1 | 3 | -5 | 4 |
| O(2) | 22 | 4 | 17 | 4 | 18 | 4 | -7 | 5 | 8 | 3 | -2 | 4 |
| O(3) | 24 | 5 | 18 | 3 | 9 | 3 | -5 | 5 | 4 | 3 | -1 | 4 |
| H ₂ O(1) | 31 | 5 | 19 | 4 | 13 | 3 | -1 | 5 | -4 | 3 | -5 | 4 |
| H ₂ O(2) | 14 | 4 | 16 | 4 | 12 | 3 | -6 | 4 | -3 | 3 | 9 | 4 |

For hydrogen, isotropic temperature factor $\bar{U} = 0.04 \text{ \AA}^2$.

Although the vibration parameters are small, an analysis of the thermal motion of the anion was carried out by Cruickshank's revised procedure³ to determine the corrections in the atomic co-ordinates required to allow for the systematic error due to rotational oscillation. (It is necessary to assume rigid-body motion, and internal consistency showed that the assumption was justified.) Table 3 shows the principal values of the mean-square amplitude of translational motion and the corresponding direction cosines; the principal values of the mean-square angular oscillation are presented in Table 3. It can be seen that the direction of a principal translatory motion does not coincide with any of the principal axes of rotation. In Fig. 2 the principal axes are illustrated with respect to one anion. The largest oscillation takes place about an axis which makes an angle of 10° to the axis about which the moment of inertia is a minimum.

Table 1 shows the co-ordinates after correction for rotational oscillation; the largest correction for any co-ordinate is 0.005 Å.

Interatomic Distances and Angles.—From the corrected co-ordinates, given by the computer to four decimal places, the bond lengths and angles were calculated and are shown, with their standard deviations, in Table 4.

TABLE 3.

| Principal axes of translation and rotational oscillation. | | | |
|---|---|--------|--------|
| Mean-square amplitude of translation and its standard deviation | Direction cosines with respect to the crystallographic axes, <i>a</i> , <i>b</i> , and <i>c</i> | | |
| $0.005 \pm 0.002 \text{ \AA}^2$ | -0.546 | -0.499 | 0.673 |
| 0.012 ± 0.004 | 0.349 | -0.866 | -0.359 |
| 0.008 ± 0.002 | 0.762 | 0.039 | 0.647 |
| Mean-square angular oscillation and its standard deviation | | | |
| $7^\circ \pm 4^\circ$ | -0.772 | -0.601 | 0.207 |
| $22^\circ \pm 10^\circ$ | -0.202 | 0.542 | 0.816 |
| $13^\circ \pm 4^\circ$ | -0.602 | 0.588 | -0.540 |

TABLE 4.

| Bond lengths (Å) and angles in the hydroxymethanesulphinate ion. | | | | | |
|--|--------------------|---------------------------------|-------------|-----------------------------|-----------------------|
| S-O(2) | 1.513 ± 0.009 | } $1.513 \pm 0.006 \text{ \AA}$ | O(2)-S-O(3) | 108.7° | } all $\pm 0.5^\circ$ |
| S-O(3) | 1.513 ± 0.008 | | O(2)-S-C | 101.2 | |
| | | O(3)-S-C | 100.4 | | |
| S-C | $1.83_3 \pm 0.010$ | | S-C-O(1) | $111.3^\circ \pm 0.6^\circ$ | |
| C-O(1) | $1.40_3 \pm 0.012$ | | H(1)-C-S | 96° | } all $\pm 12^\circ$ |
| C-H(1) | 1.2 | } ± 0.2 | H(2)-C-S | 97 | |
| C-H(2) | 1.1 | | H(1)-C-O(1) | 119 | |
| O(1)-H(3) | 1.0 | | H(2)-C-O(1) | 125 | |
| | | | H(1)-C-H(2) | $102^\circ \pm 16^\circ$ | |
| | | | H(3)-O(1)-C | $122^\circ \pm 12^\circ$ | |

Fig. 1 shows all the distances of less than 3.0 Å between atoms other than hydrogen (apart from separations within the anions). Round the water molecules the environment is approximately tetrahedral; the closest neighbours are two sodium ions and two oxygen atoms, and the angles subtended range from 86° to 116° for H₂O(1) and from 89° to 124° for H₂O(2),

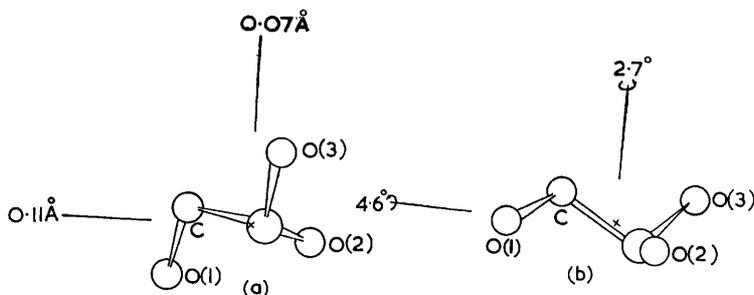


FIG. 2. The anion viewed along the intermediate of the principal axes of (a) translation and (b) oscillation, showing the directions of maximum and minimum (a) translation and (b) oscillation with the corresponding r.m.s. amplitudes. The mass centre is marked *x*.

the smallest being $\text{Na} \cdots \text{O} \cdots \text{Na}$. A more distorted tetrahedron is found round O(3); the neighbours are two sodium ions ($\text{Na} \cdots \text{O} \cdots \text{Na} = 86^\circ$), one water molecule and the sulphur atom; the largest angle is 142° for $\text{Na} \cdots \text{O}-\text{S}$. For O(2), however, there are only three nearest neighbours, a water molecule, the hydrogen atom, H(3) attached to O(1) and the sulphur atom with angles $\text{S}-\text{O} \cdots \text{O}(1) 121^\circ$, $\text{S}-\text{O} \cdots \text{H}_2\text{O}(2) 118^\circ$ and $\text{O}(1) \cdots \text{O} \cdots \text{H}_2\text{O}(2) 104^\circ$. For O(1) again the environment is approximately tetrahedral, the neighbours being the carbon atom, the hydrogen atom H(3) which forms the $\text{O}(1) \cdots \text{O}(2)$ hydrogen bond and two water molecules; the angles range from 82° for $\text{H}_2\text{O} \cdots \text{O} \cdots \text{H}_2\text{O}(2)$ to 134° for $\text{C}-\text{O} \cdots \text{H}_2\text{O}(1)$.

3404 *Truter: A Detailed Refinement of the Crystal Structure of*

Around the sodium the arrangement is approximately octahedral; the angles which would be 90° in a regular octahedron range from 75° to 104° .

Discussion.—The structure consists of sodium ions, hydroxymethanesulphinate ions, and water molecules. There is an extensive system of electrostatic and hydrogen bonds; their components in the bc plane are shown in Fig. 1. The anions and the water molecules lie at approximately $x/a = 0$ or $\frac{1}{2}$; the sodium ions lie at $x/a = \frac{1}{4}$ or $\frac{3}{4}$, so that each O(3) atom and each water molecule is about equidistant from two sodium ions separated by $a/2$; there is thus a system of electrostatic bonding parallel to a . Also parallel to a are the hydrogen bonds from O(1) to O(2)' which join the anions in helices. There is only one of these hydrogen bonds within the unit cell for each pair of anions; the other two hydrogen bonds are to anions in the unit cell below and the unit cell above the one shown.

In anions of the type $Y-SO_3^-$, the Y-S-O angles are less, and the O-S-O angles greater, than those of a regular tetrahedron, the distortion being attributable to repulsion between the charged oxygen atoms. In this compound the C-S-O angles are significantly less than, but the O-S-O angle is not significantly different from, the tetrahedral.

In potassium metabisulphite,⁵ $K_2S_2O_5$, and in sodium dithionite,⁶ $Na_2S_2O_4$, both of which contain the $-SO_2^-$ group, the relevant O-S-O angles are 110.3° and 108.2° , respectively, and the S-S-O angles are 100.5° in $S_2O_5^{2-}$ and 99.4° and 98.0° in $S_2O_4^{2-}$. These are the same, within experimental error, as the corresponding ones found in the hydroxymethanesulphinate ion.

Although the difference in the environment (see Fig. 1) of O(2) and O(3) suggests that the bonds round sulphur could be represented as $C-S \begin{matrix} \diagup O \\ \diagdown O \end{matrix}$, *i.e.*, that O(3) should carry the negative charge, the S-O bond lengths are in fact equal. Evidently the hybridisation is more important than the electrostatic environment in the determination of bond lengths. In the $S_2O_5^{2-}$ and $S_2O_4^{2-}$ ions the comparable bond lengths are also 1.50—1.51 Å, so that in the three known YSO_2^- groups the bond angles and S-O bond lengths are the same. A similar constancy has been found experimentally in $\equiv C-SO_3^-$ groups in sulphonates, the S-O bond length being 1.46 Å while for sulphones R_2SO_2 the S-O bond lengths are again constant at 1.43 Å.

There is as yet no theory which accounts satisfactorily for the bond lengths in all the oxy-compounds of sulphur. The simplest view of compounds in which sulphur has 2, 3, and 4 neighbours in the oxidation states II, IV, and VI, respectively, is that they are all based on sp^3 -hybridisation. This would give two lone pairs in sulphur(II), one lone pair and one electron in the d -orbitals in neutral compounds of sulphur(IV) (but 2 d -electrons in YSO_2^-), and 2 electrons in the d -orbitals of sulphur(VI).

Cruickshank⁷ has discussed the bond lengths of XO_4^{n-} and related ions where X is Si, P, S, or Cl, in terms of π -bonding between electrons in the $3d$ -orbitals, predominantly the d_{z^2} - and $d_{x^2-y^2}$ -orbitals, of X and the $p\pi$ - and $p\pi'$ -orbitals of oxygen. For compounds in which sulphur is bonded only to oxygen, he finds a linear relation between the S-O bond length and the π -bond order. If atoms other than oxygen are attached to sulphur, the "effective nuclear charge" for the d -orbitals is altered, and this, in turn, is reflected in a lengthening of the S-O bonds when the other atoms are less electronegative than oxygen. For example, in $CH_2(SO_3)_2^{2-}$ no π -bonding is possible from sulphur to carbon, so that each of the two π -bonding orbitals extends over three oxygen atoms, giving the S-O bonds a π -bond order of $2/3$. The predicted bond length, 1.40 Å is, as expected, shorter than the observed value,⁴ 1.462 ± 0.005 Å.

In Cruickshank's treatment, the hydroxymethanesulphinate ion is regarded as a sulphur-oxygen compound with one tetrahedral position occupied by an atom less electronegative

⁵ Lindqvist and Mörtzell, *Acta Cryst.*, 1957, **10**, 406.

⁶ Dunitz, *Acta Cryst.*, 1956, **9**, 579.

⁷ Cruickshank, *J.*, 1961, 5486.

than oxygen and another occupied by a lone pair of electrons. The lone pair produces a greater decrease in the "effective nuclear charge" than a carbon atom, thus explaining the observation that the S-O bond lengths (1.51 Å) are longer than those in sulphones (1.43 Å) in which the π -bond order for the S-O bonds is also $\frac{1}{2} + \frac{1}{2} = 1$. By inclusion of the lone-pair effect, Cruickshank implies that the oxidation state is not important but he adds that the length of the C-S bond suggests that the σ -bond length may be changed by the presence of the lone pair.

Table 5 shows the bond lengths in a number of compounds in which S-Y is probably a single bond. The experimental evidence strongly suggests that the σ -bond radius does vary with the oxidation state of sulphur. Lindqvist and Mörtzell⁵ discussed the S-S and

TABLE 5.
S-Y bond lengths (Å).

| Bond | Length | Source | Ref. | Calc. | Bond | Length | Source | Ref. | Calc. |
|---------------------------|---------------|---|------|-------|---------------------------|-------------|--|------|-------|
| S(vi)-S(vi) | 2.15 ± 0.01 | S ₂ O ₆ ²⁻ | 8 | 2.16 | S(iv)-C(sp ³) | 1.83 ± 0.01 | Present work | — | 1.83 |
| S(iv)-S(iv) | 2.39 ± 0.01 | S ₂ O ₄ ²⁻ | 6 | 2.38 | S(II)-C(sp ³) | 1.82 | (CH ₃) ₂ S | 10 | 1.80 |
| S(II)-S(II) | 2.048 ± 0.005 | S ₈ | 9 | 2.06 | S(iv)-C(sp ³) | 1.76 ± 0.02 | Ph ₂ SO | 12 | 1.80 |
| S(iv)-S(vi) | 2.209 ± 0.005 | S ₂ O ₆ ²⁻ | 5 | 2.22 | S(II)-C(sp ³) | 1.75 | (<i>p</i> -C ₆ H ₄ Me) ₂ S | 13 | 1.77 |
| S(II)-S(vi) | 2.04 - 2.13 | S ₂ O ₆ ²⁻ | 11 | 2.04 | S(vi)-Cl | 1.99 ± 0.02 | SO ₂ Cl ₂ | 11 | 1.96 |
| S(vi)-C(sp ³) | 1.770 ± 0.005 | CH ₂ (SO ₃) ₂ ²⁻ | 4 | 1.78 | S(iv)-Cl | 2.07 ± 0.03 | SOCl ₂ | 11 | 2.01 |

S-O bond lengths, in compounds 1—4 of Table 5, in terms of the ratio of *s*- and *p*-character in the hybridisation of the orbitals round sulphur. It is implicit in their treatment that the bond angles result solely from the hybridisation and are unaffected by electrostatic forces and π -bonding. In the same way we calculated the hybridisation ratio for the other compounds in Table 5. Although the treatment is applied in the same way to all oxidation states, the angles observed are such that the YSO₂⁻ groups have an S → Y orbital of predominantly *p*-character, the sulphur(II) orbitals are close to *sp*³, and the S → Y orbital in YSO₃⁻ is intermediate in character. The S-S bond lengths in Table 5 were used to construct a curve relating *p*-character to σ -bond radius for sulphur and, from this and the radii Cl = 1.00 Å, C(*sp*³) = 0.77 Å, and C(*sp*²) = 0.74 Å, the S-Cl and S-C bond lengths were calculated. For sulphur(II) the agreement with the observed values was good, but for sulphur(IV) and sulphur(VI) the S-C bond lengths were too long by 0.07 Å, suggesting the need for an additional postulate, namely, that the electronegativity of these states is 1.7 instead of 2.5 and the bond lengths must be corrected by the Stevenson-Schomaker rule. But the S-Cl bond lengths were not consistent with this postulate, the uncorrected values being 2.00 Å in thionyl chloride and 2.02 Å in sulphuryl chloride. For the S-O bonds all the orbitals were close to *sp*³ and the corresponding radius of sulphur, 1.10 Å, did not differ significantly from one compound to another, so that the variation in S-O bond lengths cannot be explained in this way. An unsatisfactory feature of this approach is that bond angles which are not significantly different experimentally may correspond to large changes in the σ -bond radius; *e.g.*, in S₂O₄²⁻, S₂O₅²⁻, and HO·CH₂·SO₂⁻ the calculated radii of sulphur in the direction Y for the YSO₂⁻ groups are 1.19, 1.14, and 1.12 Å, respectively.

Theories which imply a gradation from sulphur(II) to sulphur(VI) do not explain the essentially anomalous properties of sulphur(IV). Chemically it is the least stable and tends to become oxidised to sulphur(VI); it also has the longest single bonds and the smallest bond angles. A possible explanation is that the hybridisation is essentially the

⁸ Stanley, *Acta Cryst.*, 1956, **9**, 897.

⁹ Abrahams, *Acta Cryst.*, 1955, **8**, 661; Cooper, Bond, and Abrahams, *Acta Cryst.*, 1961, **14**, 1008.

¹⁰ Siebert, *Z. anorg. Chem.*, 1952, **271**, 65.

¹¹ Sutton *et al.*, "Interatomic Distances," *Chem. Soc. Special Publ.* No. 11, 1958.

¹² Abrahams, *Acta Cryst.*, 1957, **10**, 417.

¹³ Blackmore and Abrahams, *Acta Cryst.*, 1955, **8**, 329.

same in sulphur(II) and sulphur(VI), *i.e.*, sp^3 , but different in sulphur(IV), the small angles round sulphur(IV) indicating a tendency to pure p -bonds with the lone pair in the s -shell. The p -bonds would result in a larger radius and a smaller electronegativity for sulphur(IV).

As a purely empirical treatment, we postulated a specific radius and electronegativity for each oxidation state and found the values which gave the best agreement when used to calculate the bond lengths by the Stevenson-Schomaker equation. These values were 1.03, 1.19, and 1.08 Å for the radii of sulphur(II), sulphur(IV), and sulphur(VI), respectively, with the electronegativities 2.5 (the usual value for sulphur), 1.0, and 1.7. Again the increase in radius, and presumably of p -character is correlated with a decrease in electronegativity. The calculated values are shown in Table 5 to be consistent with the experimental values. This empirical approach allows for the bond angles to be influenced by electrostatic repulsions as well as hybridisation, and so the comparatively constant O-S-O angles do not imply constant S-O σ -bond lengths; the calculated single-bond lengths are S(IV)-O = 1.71 Å and S(VI)-O = 1.67 Å. This difference of 0.04 Å in the σ -bond length accounts in part for the observed difference between the S(VI)-O bond lengths, 1.43 Å in sulphones, R₂SO₂, and the S(IV)-O bond lengths, 1.51 Å, in the YSO₂⁻ groups.

It is not certain that the remainder of the difference can be attributed to a decreased "effective nuclear charge" because in the sulphoxides, Y₂SO, the S-O bond length is only 1.47 Å (*e.g.*, in diphenyl sulphoxide¹²); sulphoxides can be regarded as related to YSO₂⁻ by replacement of an oxygen atom by a less electronegative carbon atom and removal of one d -electron, leaving one electron in a $d\pi$ -bonding orbital to give a π -bond order of one for the one S-O bond.

It is evident that many factors contribute to the observed bond lengths; they include the oxidation state of sulphur, its hybridisation, the electronegativities of all the atoms, and the existence of π -bonding, and they are not independent.

Experimental.—The observed structure factors have been published.¹ After two cycles of refinement had been carried out, an empirical extinction correction was applied to reflections with $\sin \theta < 0.25$; this correction was of the form $I_{\text{obs.}} = I_{\text{true}} \exp(-0.000145I_{\text{calc.}})$. The scale factor was one of the parameters in the refinement, the final value being 1.078.

The scattering factors used were the same as those for potassium methylenedisulphonate⁴ with the addition of Na from Berghuis *et al.*¹⁴

In the least-squares refinement the function minimised was $R' = \sum w(|F_o| - |F_c|)^2$, where the weighting factor w was taken as $1/(|F_o| + 0.3|F_c|)^2$; this proved satisfactory by the criterion that R'/n , where n is the number of planes within a given range of $|F_o|$, should be constant for different ranges.

All computations for refinement, Fourier syntheses, analysis of thermal vibrations, and determination of interatomic distances were carried out on the Leeds University Ferranti Pegasus computer with programmes written by Cruickshank, Pilling, *et al.*¹⁵

I am grateful to my colleagues for the use of their programmes and to the Director and Staff of the Leeds University Computing Laboratory for the use of their facilities.

DEPARTMENT OF INORGANIC & STRUCTURAL CHEMISTRY,
THE UNIVERSITY, LEEDS, 2.

[Received, March 15th, 1962.]

¹⁴ Berghuis, Haanappel, Potters, Loopstra, MacGillavry, and Veenendaal, *Acta Cryst.*, 1955, **8**, 478.

¹⁵ Cruickshank, Pilling, and, in part, Bujosa, Lovell, and Truter. "Computing Methods and the Phase Problem in X-ray Crystal Analysis," Pergamon Press, Oxford, 1961.