

molecules per unit cell; density, calc. 2.01, found 2.03 g/cm³. Space group, from systematic absences, $C_{2h}^2 - P2_1/c$.

The crystals were obtained as long, red prisms, bounded by {001} and {100}, with the latter occasionally dominant.

Tellurium dibenzenethiosulphonate, $\text{Te}(\text{S}_2\text{O}_2\text{C}_6\text{H}_5)_2$, monoclinic dimorph. $a = 13.93 \text{ \AA}$, $b = 7.71 \text{ \AA}$, $c = 15.72 \text{ \AA}$, $\beta = 96^\circ$. Density, calculated for four molecules per unit cell, 1.88 g/cm³, as compared with 1.86 g/cm³ for the orthorhombic dimorph⁶. The space group, from systematic absences, is $C_{2h}^2 - P2_1/c$.

The orthorhombic dimorph (I) of this compound, the crystal structure of which was described recently⁷, was obtained on crystallization from chloroform⁶. The monoclinic dimorph (II) usually occurred when benzene was used as a crystallization medium instead of chloroform, and also when the compound was crystallized from dilute chloroform solutions on addition of ether. Occasionally, mixtures were obtained, small amounts of I separating along with II from benzene, and II together with I from chloroform. Chemical analysis of the X-ray sample of II gave 26.6% Te, calc. 26.9%. The dimorphs appear to be about equally stable, no transition between them being observed at room temperature or on heating to about 150°C.

Tetragonal crystals, containing 75 mole % of tellurium dibenzenethiosulphonate and 25 mole % of sulphur dibenzenethiosulphonate, have been observed. The latter compound, and also the selenium analogue, crystallize in a tetragonal space group^{8,9}.

*Sulphur dibenzenethiosulphonate*⁹, $\text{S}_2(\text{S}_2\text{O}_2\text{C}_6\text{H}_5)_2$. Orthorhombic bipyramidal, $a = 11.36 \text{ \AA}$, $b = 12.90 \text{ \AA}$, $c = 22.47 \text{ \AA}$. Density, calculated for eight molecules per unit cell, 1.66 g/cm³. This figure may be compared with the X-ray densities, 1.58, 1.57 and 1.62 g/cm³, respectively, of the analogues containing one, two and three sulphur atoms less^{8,10}. The space group, from systematic absences, is $D_{2h}^{15} - Pbca$.

This hexathionic compound crystallized as plates {001} with plate edges parallel to the *ab* diagonals.

Strontium selenopentathionate dihydrate, $\text{SrSe}(\text{S}_2\text{O}_3)_2 \cdot 2\text{H}_2\text{O}$. Orthorhombic bipyramidal, $a = 4.94 \text{ \AA}$, $b = 10.19 \text{ \AA}$, $c = 21.83 \text{ \AA}$. Density, calculated for four formula units per unit cell, 2.58 g/cm³. Systematic absences, $0kl$ when $k + l$ is odd, $hk0$ when h is odd. These data indicate that the salt is isomorphous with orthorhombic barium

pentathionate¹¹ and selenopentathionate¹² dihydrates, the space group of which is $D_{2h}^{16} - Pnma$. The crystals have the same morphology as the barium salts, and show the same perfect cleavage along the *c* plane.

The crystals were obtained by recrystallization from aqueous methanol of a crude sample prepared from the sodium salt¹³ by metathesis with strontium perchlorate. No chemical analysis was made, but the X-ray data in connection with the known composition of the barium salts appear sufficient to establish the formula given above.

No further crystallographic work on the compounds is contemplated.

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The Nature of the Sulphur-Sulphur Bond in Thiosulphate and Thiosulphonate Ions

OLAV FOSS and ASBJØRN HORDVIK

Chemical Institute, University of Bergen, Bergen, Norway

Thiosulphate and thiosulphonate ions, $[\text{S}-\text{SO}_3]^-$ and $[\text{S}-\text{SO}_2\text{R}]^-$, are apparently (beside the polysulphide ions) the only relatively stable species with sulphur-sulphur bonds where one of the sulphur

atoms forms one bond only. Bonds of this type may be coordinate bonds, or double bonds. It was predicted by one of us¹ in 1950, on the basis of a discussion of the non-existence of branched sulphur chains, that the sulphur-sulphur bonds of thio-sulphate and thiosulphonate ions possess a considerable degree of double-bond character. The argument was¹ that, since a sulphur atom, as acceptor, can be expected to add to another sulphur atom, as donor, only if the donor is *less* electronegative than the acceptor, and since the sulphur atom of sulphite and sulphinate ions is, presumably, *more* electronegative than electroneutral sulphur, the bonds cannot be pure coordinate bonds.

In the same year, Gerding and Eriks², on the basis of force constants from Raman spectra of aqueous sodium thiosulphate solutions, concluded that in the thiosulphate ion "the sulphur-sulphur bond undoubtedly possesses a strong double bond character".

Taylor and Beevers³, in 1952, determined the crystal structure of sodium thio-sulphate pentahydrate and found the sulphur-sulphur bond to be 1.97 Å, with a maximum error given as 0.06 Å. The present authors have now⁴ made a crystal structure determination of sodium methanethiosulphonate monohydrate, CH₃·SO₂·SNa·H₂O. The crystals⁵ are orthorhombic bipyramidal, space group *D*_{2h}¹⁶—*Pnma* with four formula units per unit cell, and the methanethiosulphonate ion possesses mirror plane symmetry in the crystals. The sulphur-sulphur bond was found to be 1.98 Å and the sulphur-oxygen bonds 1.45 Å, with standard deviations of probably less than 0.01 Å and 0.02 Å, respectively.

There is some uncertainty as to the length of a S—S single bond. Abrahams⁶ has recently proposed 2.08 Å, and the true value may be a little larger. The double-bond length is probably⁶ as in the S₂ molecule in the ground state, 1.89 Å. The S—S bonds in the thiosulphate and thio-sulphonate ions, of lengths 1.97—1.98 Å, are next to that in the S₂ molecule the shortest S—S bonds measured, and correspond, according to Abrahams' tentative bond order-bond length curves⁶⁻⁸, to between 50 % and 60 % double-bond character.

There may, of course, be various causes for the shortening of the sulphur-sulphur

bonds of the thiosulphate and thiosulphonate ions. One picture is that, as predicted, double bonds (π bonds) exist to a considerable degree, arising from overlap of the $p\pi$ electron pairs of the outer sulphur atom with available 3*d* orbitals of the central sulphur atom. In view of the smaller tendency of the $p\pi$ electron pairs of a larger atom to participate in π -bond formation (cf. Ref.⁹), the amount of π -bond character of the sulphur-sulphur bonds should be smaller than in the sulphur-oxygen bonds of the same ions. The S—O distance in the methanethiosulphonate ion, 1.45 Å, corresponds^{6,10} to about 90 % π -bond character. The estimate arrived at above for the S—S bond does thus not appear unreasonable.

It is interesting to note that when the thiosulphate and methanethiosulphonate ions undergo oxidation to the corresponding tetrathionic compounds, the double-bond character of the outer S—S bonds is lost, the length changing from 1.97—1.98 Å to 2.10—2.12 Å. The latter figures are from crystal structure determinations of barium tetrathionate dihydrate¹¹ and dimethanesulphonyl disulphide¹². On the other hand, the new S—S bond formed on oxidation, *i. e.*, the middle S—S bond of the tetrathionic compounds, is about 2.04 Å and thus shorter than the outer bonds, probably due to pd π -bond formation now occurring between the divalent sulphur atoms.

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