

The molecules are oriented nearly parallel to the (100) plane, and a rough calculation of the atomic positions indicates short intramolecular O—H...O distances and rather close intermolecular approach. The length of the hydrogen bond is of great interest in connection with the recent studies of the infrared spectra of hydroxy-quinones³⁻⁵, but further discussion will have to await the final refinements of the calculations.

1. Palacios, J. and Salvia, R. *Anales soc. españ. fís. y quim.* **32** (1934) 49.
2. Rogers, M. T. *J. Am. Chem. Soc.* **69** (1947) 1506.
3. Josien, M.-L., Fuson, N., Lebas, J.-M. and Gregory, T. M. *J. Chem. Phys.* **21** (1953) 331.
4. Hadzi, D. and Sheppard, N. *Trans. Faraday Soc.* **50** (1954) 911.
5. Flett, M. St. C. *J. Chem. Soc.* **1948** 1441.

Received May 28, 1956.

X-Ray Crystallographic Data on Sodium and Potassium Thiosulphonates

OLAV FOSS

*Chemical Institute, University of Bergen,
Bergen, Norway*

A study of unit cells and space groups of some alkali methane- and *p*-toluene-thiosulphonates has been made, with the following results. The axial lengths, from oscillation and Weissenberg photographs taken with copper radiation, $\lambda(\text{CuK}\alpha) = 1.542 \text{ \AA}$, are probably correct to within 0.5%. Densities were determined by a flotation method.

Sodium methanethiosulphonate monohydrate, $\text{CH}_3\text{SO}_2\text{SNa} \cdot \text{H}_2\text{O}$. Orthorhombic, $a = 6.49 \text{ \AA}$, $b = 5.55 \text{ \AA}$, $c = 16.23 \text{ \AA}$. Four formula units per unit cell; density, calc. 1.73, found 1.72 g/cm³. Systematic absences, $0kl$ when $k + l$ is odd, $h k 0$ when h is odd. These absences are characteristic of the space groups, $D_{2h}^{10} - Pnma$ and $C_{2h}^2 - Pn2_1a$. If the former is the correct one, the carbon and both sulphur atoms of the methanethiosulphonate ion lie in a crystallographic mirror plane of symmetry.

From water, the salt crystallized as plates {001} with plate edges parallel to the a and b axes. There is perfect cleavage along the plate face, and also a pronounced tendency of cleavage along another, not identified plane parallel to the a axis.

Potassium methanethiosulphonate, $\text{CH}_3\text{SO}_2\text{SK}$. Monoclinic prismatic, $a = 8.76 \text{ \AA}$, $b = 8.12 \text{ \AA}$, $c = 7.42 \text{ \AA}$, $\beta = 92^\circ$. Four formula units per unit cell; density, calc. 1.89, found 1.88 g/cm³. Systematic absences, $h0l$ when l is odd, $0k0$ when k is odd. The space group is thus $C_{2h}^2 - P2_1/c$.

The salt crystallized from water or methanol as thick plates {100} bounded by {011}, {010} and occasionally {111}. There is perfect cleavage along the plate face.

Potassium p-toluenethiosulphonate monohydrate, $\text{C}_7\text{H}_7\text{SO}_2\text{SK} \cdot \text{H}_2\text{O}$. Monoclinic, $a = 8.56 \text{ \AA}$, $b = 9.67 \text{ \AA}$, $c = 13.01 \text{ \AA}$, $\beta = 95^\circ$. Four formula units per unit cell; density, calc. 1.51, found 1.49 g/cm³. Systematic absences, hkl when $h + k$ is odd. The monoclinic prismatic morphology^{1,2} of the crystals points to the centrosymmetric space group, $C_{2h}^2 - C2/m$, the correctness of which would imply that the *p*-toluenethiosulphonate ion possesses mirror plane symmetry in the crystals.

The salt was first prepared by Blomstrand³ and Wahlstedt⁴, and by these authors noted to crystallize particularly well. Brugnatelli^{1,2} described the crystals as monoclinic prismatic, with $a : b : c = 0.8854 : 1 : 1.5436$ and $\beta = 119^\circ 52'$. Transforming according to the matrix, $100/010/101$, these data become $a : b : c = 0.8854 : 1 : 1.344$; $\beta = 94.9^\circ$, as compared with $a : b : c = 0.8853 : 1 : 1.345$; $\beta = 95^\circ$ from the X-ray data.

There is perfect cleavage along the c plane.

Sodium p-toluenethiosulphonate, $\text{C}_7\text{H}_7\text{SO}_2\text{SNa}$. Monoclinic, $a = 7.36 \text{ \AA}$, $b = 9.72 \text{ \AA}$, $c = 12.96 \text{ \AA}$, $\beta = 93^\circ$. Four formula units per unit cell; density, calc. 1.51, found 1.51 g/cm³. Systematic absences, hkl when $h + k$ is odd.

Except for the length of the a axis, the cell dimensions are close to those found for potassium *p*-toluenethiosulphonate monohydrate. The systematic absences are the same, and the intensity distribution of the $0kl$ reflections of the two salts are very similar. It appears likely that the space group of the sodium salt is that of the potassium salt, and thus probably $C_{2h}^2 - C2/m$.

Crystallized from 96% ethanol above room temperature, the salt occurred as

fatty leaves or thin plates {001}. There is perfect cleavage along (001) and along planes parallel to the *ab* diagonals.

Sodium p-toluenethiosulphonate dihydrate, $C_7H_7SO_3SNa \cdot 2H_2O$. Monoclinic prismatic, $a = 13.59 \text{ \AA}$, $b = 6.47 \text{ \AA}$, $c = 12.95 \text{ \AA}$, $\beta = 91\frac{1}{2}^\circ$. Four formula units per unit cell; density, calc. 1.44, found 1.43 g/cm³. Systematic absences, $h0l$ when l is odd, $0k0$ when k is odd. The space group is thus $C_{2h}^5 - P2_1/c$.

The dihydrate^{3,5} was obtained by crystallization from 96 % ethanol at low room temperature, and occurred as plates {100} which were often prismatic along the *b* axis. There is a pronounced tendency of cleavage along the plate face. In air, the crystals keep well at temperatures below 10° C, but give off the water of crystallization rapidly above 20° C.

A salt, originally⁶ listed as sodium *p*-toluenethiosulphonate dihydrate but later² reported to be the monohydrate, was described by Weibull^{2,6} as monoclinic prismatic with $a : b : c = 0.8869 : 1 : 2.774$ and $\beta = 103^\circ 52'$. With the transformation, $\bar{1}00/0\bar{1}0/\frac{1}{2}, 0, \frac{1}{2}$, Weibull's data become $a : b : c = 0.8869 : 1 : 1.351$; $\beta = 94.6^\circ$, which do not agree with the X-ray data for the dihydrate nor the anhydrous salt. A monohydrate has not been observed in the present work. Weibull's transformed data are almost identical with those which apply to potassium *p*-toluenethiosulphonate monohydrate.

Further work on the crystal structures of some of the salts will be made, with a view of determining the length of a thio-sulphonate sulphur-sulphur bond. As pointed out earlier⁷, this bond is probably a predominantly double bond.

1. Brugnatelli, L. *Ber.* **24** (1891) 494.
2. Groth, P. *Chemische Kristallographie* Bd. 4, Leipzig 1917, p. 424.
3. Blomstrand, W. *Ber.* **3** (1870) 957.
4. Wahlstedt, A. *Acta Univ. Lund.* **16** (1879—80) Part II No. 2.
5. Otto, R. and Rössing, A. *Ber.* **24** (1891) 3874. Footnote pp. 3877—8.
6. Weibull, M. Z. *Kryst.* **15** (1889) 234.
7. Foss, O. *Acta Chem. Scand.* **4** (1950) 404.

Received June 13, 1956.

Structure of Thiuret Hydroiodide

OLAV FOSS and OLAV TJOMSLAND

Chemical Institute, University of Bergen, Bergen, Norway

Thiuret hydroiodide, or 3,5-diimino-1,2,4-dithiazolidine hydroiodide, occurs on oxidation of dithiobiuret with iodine¹, and is a five-membered cyclic disulphide^{1,2}.

The unit cells and space groups of some simple 1,2,4-dithiazolidine derivatives, including thiuret hydroiodide, were reported by one of us in a preceding note³. The preliminary results of a complete crystal structure determination of thiuret hydroiodide are given here. The disulphide group has been found to lie across a crystallographic mirror plane of symmetry, and is thus exactly planar. This appears to be the first crystal structure determination reported for a cyclic disulphide, and the first recorded instance of a planar disulphide group.

Open-chain disulphides, X—S—S—X, have always been found to be non-planar⁴ with a dihedral angle of about 90° between the X—S—S and S—S—X planes, there being a barrier to internal rotation about an S—S bond of from 10 to 14 kcal/mole⁵⁻⁷. The formation of a five-membered cyclic disulphide requires the rotation of the S—S bond to a dihedral angle of nearly 0°, where the barrier probably has its highest value. The nevertheless relatively high stabilities of unsaturated five-membered cyclic disulphides, such as 1,2-dithiacenaphthene⁸ and the trithiones^{9,10}, and of 1,2,4-dithiazolidine derivatives with double-bonded substituents in the 3 and 5 positions, must be due to some extent to resonance stabilization of the ring, a resonance involving the unshared *p* electron pairs of the sulphur atoms. The barrier to internal rotation about an S—S bond being thought to be due principally to the mutual repulsion of these electron pairs¹¹, one on each sulphur atom, their participation in π bonding with the adjacent carbon atoms would tend to lower the barrier height.

The yellow crystals of thiuret hydroiodide, $S_2(C:NH)_2NH \cdot HI$, occur as prisms, bounded by {001} and {011} and showing perfect cleavage along the *c* plane. The four-molecule unit cell has the dimensions³, $a = 5.38 \text{ \AA}$, $b = 9.24 \text{ \AA}$, $c = 13.98 \text{ \AA}$, and the space group is $D_{2h}^{16} - Pnma$. The intensities of the $0kl$ reflections were