Structure of the Tetrathionate Ion in the Sodium Salt

OLAV FOSS and ASBJØRN HORDVIK

Chemical Institute, University of Bergen, Bergen, Norway

A crystal structure analysis of barium tetrathionate dihydrate five years ago [1] led to an unbranched, non-planar structure for the sulphur chain of the tetrathionate ion, and gave the following values (±0.03 Å and ± 2°) for bond lengths and angles: $S_1-S_2 = 2.10$ Å, $S_2-S_3 = 2.02$ Å, $S_3-S_4 = 2.13$ Å, $\angle S_1-S_2-S_3 = 104°$, $\angle S_2-S_3-S_4 = 102°$. The dihedral angle, $S_1S_2S_3/S_2S_3S_4$, was found to be 90°. These results have now been confirmed through a more accurate structure analysis of sodium tetrathionate dihydrate, $Na_2S_4O_6 \cdot 2H_2O$.

This salt is monoclinic [2], with $a = 14.50$ Å, $b = 6.37$ Å, $c = 5.47$ Å, $\beta = 105.6°$, and two formula units per unit cell. The space group is C_2^3-C2, which requires that the tetrathionate ion lies on a twofold axis of symmetry. The b and c-axis projections were solved through Patterson and Fourier syntheses and refined through repeated difference syntheses, based on 81 observed $h0l$ reflections and 56 observed $hk0$ reflections out of 90 and 61, respectively, accessible with Cu$K\alpha$ radiation. The intensities were estimated visually from zero-layer Weissenberg photographs of an approximately spherical crystal with a diameter of 0.12 mm. Individual temperature corrections, anisotropic for some atoms, were applied in calculating $h0l$ structure factors, whereas an overall, isotropic temperature correction was used for the $hk0$ data. The final atomic coordinates are listed in Table 1; the reliability index R is 0.076 for both zones.

Table 1. Atomic coordinates for sodium tetrathionate dihydrate, in fractions of monoclinic cell edges. Origin on a twofold axis.

	x	y	z
S_2	0.0234	0	0.342
S_1	0.1340	0.227	0.420
O_1	0.090	0.435	0.379
O_2	0.180	0.169	0.223
O_3	0.192	0.193	0.678
Na	0.271	0.406	0.020
H_2O	0.123	0.619	—0.088

These coordinates give a length of 2.019 Å for the middle S—S bond across the twofold axis, and 2.116 Å for the end S—S bonds, with estimated standard deviations of 0.01 Å. There is thus no doubt that the middle bond, between the two divalent sulphur atoms of the tetrathionate ion, is shorter than the two other S—S bonds. The S—S—S bond angles are 103.8° ± 0.5° and the dihedral angle SSS/SSS is 90.4° ± 1°.

The SO_3 groups have trigonal symmetry within the accuracy of the analysis, with S—O bond lengths of 1.45, 1.46 and 1.46 Å (± 0.02 Å) and O—S—O angles of 112.6°, 113.5° and 114.8° (± 1.5°). The axis of the trigonal pyramid does not coincide with the direction of the O_3S-S bond, the O—S—S angles being 108.1°, 98.6° and 107.6° (± 1°).

Details of the structure will be published later.

1. Foss, O., Furberg, S. and Zachariasen, H. *Acta Chem. Scand.* **8** (1954) 459.
2. Foss, O. *Acta Chem. Scand.* **6** (1952) 802.

Received September 20, 1958.