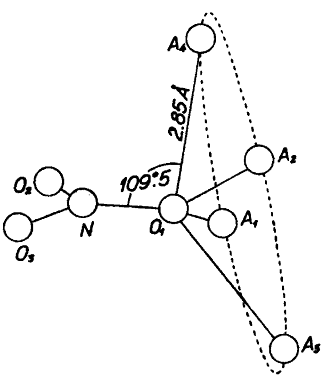

*Fig. 3. Nitrate group* (*$NO_1O_2O_3$*) *with hydrogen bond to ammonium group or water molecule* (*A*)*. The broken circle illustrates the rotation possibility of A.*

an oxygen atom ($O_1$) of the nitrate ion by a hydrogen bond. With bond length 2.85 Å and bond angle 110°, the distance A—N in Fig. 3 is 3.47 Å. The distances $A-O_2$ and $A-O_3$ in Fig. 3 vary with the position of A on the broken circle in the figure. In positions $A_1$ or $A_2$ the hydrogen bond lies in the plane of the nitrate group and the distances are 3.2 and 4.7 Å. In positions $A_3$ or $A_4$ the hydrogen bond lies in a plane perpendicular to the nitrate group and both distances are about 4 Å. From the shape of our distribution curves in relation to that of water, we conclude that the latter structure is present, but evidently the presence of the first one cannot be eliminated. An equilibrium between the two and the intermediate positions, caused by a rotation around the bond $N-O_1$, is not unlikely.

The displacements of the maxima at 4.5 and 7.0 Å (water) to 4.7 and 7.2 Å in the present case are explained by analogeous reasoning.

However, we may mention that other possible arrangements may be partly responsible for the displacements of the maxima on the distribution curves: Water molecules packed around the nitrate group give distances from 3.2 Å upwards. The ammonium groups may have greater packing radii than the water molecules. And lastly, the hydrogen bonds may be longer in the present case than in the case of liquid water. Investigations of crystal structures indicate that this is possible for hydrogen bonds between nitrate and ammonium ions [7], but hardly between nitrate ions and water, where our value seems perhaps too great [5].

The author is much obliged to the following institutions and persons: *Fridtjof Nansens fond* and *Norges Teknisk-Naturvitenskapelige Forskningsråd* for financial aid, Professor Chr. Finbak for suggesting the work and Dr. O. Bastiansen for helpful advice.

1. Michelsen, K. In publication.
2. Finbak, Chr. *Acta Chem. Scand.* **3** (1949) 1279, 1293.
3. Viervoll, H. *Acta Chem. Scand.* **1** (1947) 120.
4. Wyckoff, R.W.G. *Crystal Structures.* (1948). New York, Interscience Publishers, Inc.
5. Luzatti, V. *Acta Cryst.* **4** (1951) 120, 193.
6. Grison, E., Eriks, K., and de Kies, J. L. *Acta Cryst.* **3** (1950) 290.
7. Duke, J. R. C., and Llewellyn, F. J. *Acta Cryst.* **3** (1950) 305.
8. Finbak, Chr., and Viervoll, H. *Tids. Kjemi, Bergvesen, Met.* **5** (1943) 36.

Received April 22, 1952.

# X-ray Crystallographic Data on Tetrathionates

OLAV FOSS

*Universitetets Kjemiske Institutt,*
*Blindern — Oslo, Norway*

This note completes a preliminary X-ray survey on the crystal structure of polythionic compounds. Earlier reports give unit cell and space group data on salts of pentathionic, selenopentathionic and telluropentathionic acids [1], divalent sulphur, selenium and tellurium methanethiosulphonates [2], selenium and diselenium disulphinates [3], and divalent selenium and tellurium benzene- and *p*-toluenethiosulphonates and the corresponding triselenium disulphinates[4]. The use of tellurium as a heavy atom has made possible a structure determination of the methanethiosulphonates[5].

Single-crystal oscillation and Weissenberg photographs were taken with $CuK_\alpha$ radiation, $\lambda = 1.54$ Å. The values recorded below for axial lengths are believed to be accurate to within 0.5 %. Density determinations were made by a flotation method.

*Sodium tetrathionate dihydrate*[6–8], $Na_2S_4O_6 \cdot 2H_2O$. Monoclinic crystals, submicroscopically twinned on (100) and having an orthorhombic appearance. $a = 14.46$ Å, $b = 6.37$ Å, $c = 5.44$ Å, $\beta = 105\frac{1}{2}°$. Two molecules per unit cell; density, calc. 2.11, found 2.10. Absent reflections, $(hkl)$ when $h + k$ is odd. Of the three possible space groups, $C_s^3-Cm$ and $C_{2h}^3-C2/m$ would require that the tetrathionate ions lie in symmetry planes, while $C_2^3-C2$ requires that the tetrathionate ions possess a two fold axis of symmetry. The last requirement appears to be more probable. The salt, at first erroneously named 'disulphopersulphate' and listed as such by Groth[9], was described by Villiers[7] as orthorhombic.

*Ammonium tetrathionate*[8], $(NH_4)_2S_4O_6$. Monoclinic prismatic, $a = 5.56$ Å, $b = 11.86$ Å, $c = 14.10$ Å, $\beta = 106°$. Four molecules per unit cell; density, calc. 2.08, found 2.03. Absent reflections, $(h0l)$ when $l$ is odd, $(0k0)$ when $k$ is odd. Space group, $C_{2h}^5-P2_1/c$. The crystals occur as prisms, elongated along the $a$ axis and bounded by $\{011\}$.

*Rubidium tetrathionate*[10], $Rb_2S_4O_6$. $a = 22.74$ Å, $b = 8.23$ Å, $c = 10.44$ Å, $\beta = 104°$. Eight molecules per unit cell; density, calc. 2.77, found 2.77. Absent reflections, $(hkl)$ when $h + k$ is odd, $(h0l)$ when $h$ is odd or when $l$ is odd. The habit of the crystals is monoclinic domatic, which indicates that the space group is $C_s^4-Cc$. The salt is isomorphous with potassium tetrathionate[11].

*Barium tetrathionate dihydrate*[6,12], $BaS_4O_6 \cdot 2H_2O$. Monoclinic prismatic, $a = 5.17$ Å, $b = 9.46$ Å, $c = 19.07$ Å, $\beta = 96°$. Four molecules per unit cell; density, calc. 2.84, found[12] 2.777. Absent reflections, $(h0l)$ when $l$ is odd, $(0k0)$ when $k$ is odd. Space group, $C_{2h}^5-P2_1/c$. The crystals were in most cases observed as prisms, elongated along the $a$ axis.

Furthermore, data on a pentathionate are reported here.

Cesium pentathionate, $Cs_2S(S_2O_3)_2$, was prepared from the potassium salt by metathesis with sodium perchlorate and subsequently with cesium chloride, as described previously for rubidium pentathionate[1]. The cesium salt is apparently orthorhombic, with the unit cell dimensions, $a = 6.30$ Å, $b = 18.01$ Å, $c = 9.68$ Å. Four molecules per unit cell; density, calc. 3.16, found 3.12. The absent reflections are the same as for cesium selenopentathionate[1], and the two salts appear to be isomorphous.

Some of the salts will be the subject of further study.

1. Foss, O., and Jahr, J. *Acta Chem. Scand.* **4** (1950) 1560.
2. Foss, O. *Acta Chem. Scand.* **5** (1951) 115.
3. Foss, O. *Acta Chem. Scand.* **6** (1952) 508.
4. Foss, O. *Acta Chem. Scand.* **6** (1952) 521.
5. Foss, O., Furberg, S., and Hadler, E. *Acta Chem. Scand.* **5** (1951) 1417.
6. Fordos, M. J., and Gelis, A. *J. prakt. Chem.* **28** (1843) 471.
7. Villiers, A. *Compt. rend.* **106** (1888) 1354, **108** (1889) 402.
8. Kurtenacker, A., and Laszlo, G. *Z. anorg. u. allgem. Chem.* **237** (1938) 359.
9. Groth, P. *Chemische Krystallographie.* **2** (1908) 727. Leipzig.
10. Meyer, J., and Eggeling, H. *Ber.* **40** (1907) 1351.
11. Tunell, G., Merwin, H. E., and Ksanda, C. J. *Am. J. Sci.* [5] **35 A** (1938) 361.
12. Portillo, R. *An. Españ.* **27** (1929) 236.

Received April 24, 1952.