

found 1.80 g/cm³. The systematic absences, $0k0$ when k is odd, indicate that the space group is $C_{2h}^2-P2_1$ or $C_{2h}^2-P2_1/m$. No molecular symmetry is required in either case.

The crystals are thus different from those of the corresponding hexathionate, described above. From hexathionate upwards to about nonathionate, mixed crystals of *trans*-dichlorobis(ethylenediamine)cobalt(III) polythionates, indicating isomorphism, appear to exist².

1. Weitz, E. and Achterberg, F. *Ber.* **61** (1928) 399.
2. Weitz, E. and Spohn, K. *Chem. Ber.* **89** (1956) 2332.
3. Weitz, E., Becker, F. and Gieles, K. *Chem. Ber.* **89** (1956) 2345.
4. Weitz, E., Becker, F., Gieles, K. and Alt, B. *Chem. Ber.* **89** (1956) 2353.
5. Weitz, E., Gieles, K., Singer, J. and Alt, B. *Chem. Ber.* **89** (1956) 2365.
6. Stamm, H., Seipold, O. and Goehring, M. *Z. anorg. allgem. Chem.* **267** (1941) 277.
7. Donnay, J. D. H. and Nowacki, W. *Crystal Data*. The Geological Society of America Memoir 60, New York, 1954.
8. Kurtenacker, A. *Analytische Chemie der Sauerstoffsäuren des Schwefels*, Ferdinand Enke, Stuttgart 1938.
9. Foss, O., Hordvik, A. and Palmork, K. H. *Acta Chem. Scand.* **12** (1958) 1339.
10. Kurtenacker, A. and Laszlo, G. *Z. anorg. allgem. Chem.* **237** (1938) 359.
11. Deines, O. and Christoph, E. *Z. anorg. allgem. Chem.* **213** (1933) 209.
12. Foss, O. and Jahr, J. *Acta Chem. Scand.* **4** (1950) 1560.

Received June 18, 1958.

Structure of the Hexathionate Ion in a Potassium Barium Salt

OLAV FOSS, ASBJØRN HORDVIK and
KARSTEN H. PALMORK

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

The tetra- and pentathionate ions are built up of unbranched and non-planar sulphur chains, with three oxygen atoms bonded to each of the terminal sulphur

atoms, according to crystal structure determinations of barium tetrathionate dihydrate¹, orthorhombic and triclinic barium pentathionate dihydrate^{2,3}, barium pentathionate hydrate acetate⁴, and sodium tetrathionate dihydrate^{5,6}. The present note reports the preliminary results of a structure analysis of a salt of hexathionic acid.

In a preceding note⁷, crystal data were given for a potassium barium hexathionate, $K_2Ba(S_6O_6)_2$. The crystals are monoclinic, with $a = 11.58 \text{ \AA}$, $b = 10.81 \text{ \AA}$, $c = 9.14 \text{ \AA}$, $\beta = 112^\circ$, and two formula units per unit cell. The systematic absences, $h0l$ when l is odd, together with the monoclinic-prismatic morphology of the crystals, indicated that the space group is C_{2h}^4-P2/c . This space group has, beside the fourfold general positions, six set of special, twofold positions, two on twofold axes and four on symmetry centres; the latter are in the glide plane c at $y = 0$ and $\frac{1}{2}$, and atoms in these positions do not contribute to hkl reflections with l odd. It was observed on oscillation photographs about the c axis that reflections on odd layer lines were, particularly for large scattering angles, weak relative to those on even layer lines, and it was therefore proceeded on the assumption that the barium ions lie in symmetry centres of the space group C_{2h}^4-P2/c .

The intensities of the $h0l$ and $hk0$ reflections were estimated visually from zero-layer Weissenberg photographs taken with CuK radiation, and were converted to relative structure amplitudes in the usual way. The signs of the larger terms (74 out of 114 observed $h0l$ reflections and 70 out of 141 observed $hk0$ reflections) were then put positive and Fourier syntheses made. The resulting maps gave the positions of the sulphur atoms, and also showed that the potassium ions lie in two sets of twofold positions, and that the barium ion lies, not in a symmetry centre but on a twofold axis with y equal to or very close to zero. Structure factor calculations including the potassium and sulphur contributions and next also the oxygen contributions led to more refined electron density maps, one of which is shown in Fig. 1. Of the 141 $hk0$ reflections included in the synthesis of this map, only 7 very weak ones have negative signs.

The cations are in the following twofold positions of the space group C_{2h}^4-P2/c : The barium ion and one of the potassium ions on a twofold axis at $0, y, \frac{1}{2}$ with $y = 0$

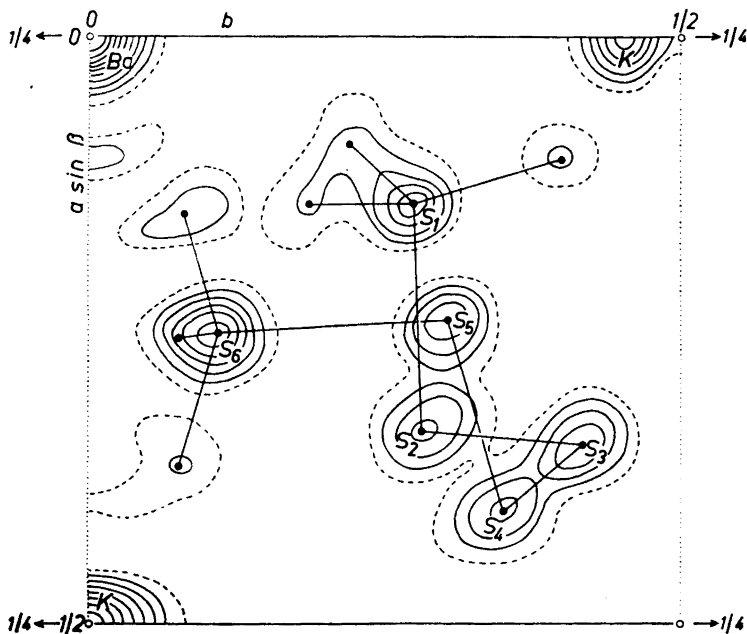


Fig. 1. Electron density projection of potassium barium hexathionate, $K_2Ba(S_6O_6)_2$, along the c axis. The 7-electron line is dashed, and contours are at intervals of $20 e \cdot \text{\AA}^{-2}$ for the barium peak and $5 e \cdot \text{\AA}^{-2}$ for the other atoms.

and $y = 0.45$, respectively, and the other potassium ion in a symmetry centre at $\frac{1}{2}, 0, 0$. The sulphur coordinates are at present as listed in Table 1. The reliability index R , with approximate oxygen contributions and temperature corrections included in the calculated structure factors, is 14% for the $hk0$ reflections. Refinement of the structure is in progress.

In elemental sulphur and in sulphur chain compounds, a dihedral angle of about 90° occurs between successive planes through three and three sulphur atoms. Given a

chain of four, a fifth sulphur atom may occupy a *cis* or a *trans* position relative to the first. This leads to two possible rotational-isomeric forms of the pentathionate ion⁸, one *cis* form in which the first and fifth sulphur atoms are on the same side of the plane through the three middle ones, and a *trans* form in which they are on opposite sides. In the three barium pentathionates referred to above²⁻⁴, the *cis* form occurs. For the hexathionate ion, with a sulphur chain of six, three forms should be possible, one *cis-cis* in which the fifth and sixth atoms are in *cis* positions relative to the first and second, respectively, one *cis-trans* or *trans-cis*, and one *trans-trans*. All three forms may be right- or left-handed; a *cis-trans* form is the mirror-image of a *trans-cis*. The *cis-cis* form represents a segment of the S_8 ring of orthorhombic sulphur, and the *trans-trans* form corresponds to the helical chains of fibrous sulphur and hexagonal selenium and tellurium; these two forms of the six-membered chain possess a twofold axis of symmetry provided that

Table 1. Sulphur coordinates, in fractions of monoclinic cell edges. Origin at a centre of symmetry.

	x	y	z
S_1	0.141	0.273	0.055
S_2	0.335	0.281	0.169
S_3	0.348	0.416	0.321
S_4	0.404	0.350	0.548
S_5	0.242	0.303	0.581
S_6	0.252	0.108	0.590

bond lengths and angles are equal in the two halves.

In the crystals of potassium barium hexathionate the configuration of the sulphur chain is *cis-cis*. Thus, in the pentathionates and the one hexathionate for which structural data so far are available, the sulphur chain has the same configuration as in orthorhombic sulphur. Whether or not this is the preferred form of the ions, or due in some measure to the presence of oxygen-coordinating barium ions in the crystals, must await a study of other salts. A *trans* five-membered sulphur chain occurs in sulphur dimethanethio-sulphonate⁹, and a *trans-trans* six-membered one in cesium hexasulphide¹⁰.

1. Foss, O., Furberg, S. and Zachariassen, H. *Acta Chem. Scand.* **8** (1954) 459.
2. Foss, O. and Zachariassen, H. *Acta Chem. Scand.* **8** (1954) 473.
3. Foss, O. and Tjomsland, O. *Acta Chem. Scand.* **10** (1956) 288.
4. Foss, O. and Tjomsland, O. *Acta Chem. Scand.* **12** (1958) 44.
5. Foss, O. *Acta Chem. Scand.* **6** (1952) 802.
6. Foss, O. and Hordvik, A. *To be published.*
7. Foss, O. and Palmork, K. H. *Acta Chem. Scand.* **12** (1958) 1337.
8. Foss, O. *Acta Chem. Scand.* **7** (1953) 1221.
9. Foss, O., Furberg, S. and Hadler, E. *Acta Chem. Scand.* **5** (1951) 1417.
10. Abrahams, S. C. and Grison, E. *Acta Cryst.* **6** (1953) 206.

Received June 18, 1958.

Preliminary Note on the Solubility of Oxygen in α -Zirconium

BO HOLMBERG and ARNE MAGNÉLI
*Institute of Inorganic and Physical Chemistry,
University of Stockholm, Stockholm, Sweden*

In the course of studies on the crystal chemistry of titanium and vanadium oxides at elevated temperatures which are

being carried out at this Institute with the sponsorship of the Office, Chief of Research and Development, U.S. Department of Army, through its European Office, ordered phases have been found to occur in the solid solubility range of oxygen in α -titanium¹. In connection with these studies an investigation has also been started of the corresponding region of the zirconium-oxygen system.

The solubility limit for samples heat-treated at 800°C has been found to be close to the composition $ZrO_{0.40}$ in agreement with data reported by previous authors². The length of the *a* axis reaches a maximum at the approximate composition $ZrO_{0.25}$ ($a(Zr) = 3.232 \text{ \AA}^3$, $a(ZrO_{0.25}) = 3.256 \text{ \AA}$, $a(ZrO_{0.40}) = 3.245 \text{ \AA}$), while the length of the *c* axis increases with increasing oxygen content over the whole solubility range ($c(Zr) = 5.148 \text{ \AA}^3$, $c(ZrO_{0.25}) = 5.188 \text{ \AA}$, $c(ZrO_{0.40}) = 5.207 \text{ \AA}$). The behaviour is similar to that observed for the titanium-oxygen system⁴.

When annealed at 800°C the sample $ZrO_{0.30}$ gives X-ray powder photographs which show the oxygen atoms to be distributed at random in the interstices of the zirconium lattice. The preparation $ZrO_{0.35}$, similarly heat-treated, gives a powder pattern essentially corresponding to a structure of *anti*-Cd(OH)₂ type. The oxygen atoms should thus occur only in every second layer of octahedral holes extending normally to the *c* axis. About 30 % of these holes must thus be vacant. The metal atoms are slightly forced apart by the interstitial atoms. The *z* parameter of the zirconium atoms thus acquires the value of 0.26 as compared to 0.25 for the ideal structure. There are, however, also indications of the vacancies in the oxygen positions being ordered. Research on this matter will be continued.

1. Andersson, S., Åsbrink, S. Holmberg, B. and Magnéli, A. *Symposium on Crystal Physics, National Institute of Sciences (India), Gulmarg, Kashmir, June 1958.*
2. Domagala, R. F. and McPherson, D. J. *J. Metals* **6** Trans. (1954) 238.
3. Treco, R. M. *J. Metals* **5** Trans. (1953) 344.
4. Andersson, S., Collén, B., Kuylenstierna, U., and Magnéli, A. *Acta Chem. Scand.* **11** (1957) 1641.

Received July 17, 1958.