

Crystal Data on Salts of Hexathionic Acid

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The existence of hexathionic acid, $\text{H}_2\text{S}_6\text{O}_6$, was first established by Weitz and Achterberg¹ in 1928, through the isolation of the potassium salt from the reaction of potassium thiosulphate and potassium nitrite with hydrochloric acid. Although the polythionate series extends far higher, up to and including the hydrophilic Odén's sulphur sols which appear to be sodium polythionates $\text{Na}_2\text{S}_x\text{O}_6$ with $50 < x < 100$, hexathionates are the highest polythionates which have been isolated in a pure state and not as mixtures with higher and lower homologues²⁻⁵.

The present authors have made a preparative and X-ray crystallographic study of salts of hexathionic acid, for subsequent attempts at structure analyses, and the results are given below. Unit cell and space group data have been obtained for two salts the crystals of which are, in view of the rather unstable nature and poor crystallization power of hexathionates, surprisingly well developed and stable. The salts are, *trans*-dichlorobis(ethylenediamine)cobalt(III) hexathionate, first prepared by Weitz and Achterberg¹, and a potassium barium double salt found in the present work. As starting material for their preparation served the potassium salt, prepared by Weitz and Achterberg's procedure¹ as slightly modified by Stamm, Seipold and Goehring⁶.

The X-ray data were derived from oscillation and Weissenberg photographs of single-crystal specimens, using CuK radiation, $\lambda(a) = 1.542 \text{ \AA}$, and for the cobalts salts FeK radiation, $\lambda(a) = 1.937 \text{ \AA}$. The axial lengths were calibrated against potassium chloride powder lines superimposed on zero-layer Weissenberg photographs, and are believed to be accurate to within 0.5%. Density determinations were made by flotation in bromoform-carbon tetrachloride mixtures.

Potassium hexathionate, $\text{K}_2\text{S}_6\text{O}_6$. The salt crystallizes in small, very thin plates^{1,2}, and only in one sample was a crystal found large enough for some photographs to be taken. The crystals are triclinic, with $a = 7.37 \text{ \AA}$, $b = 7.43 \text{ \AA}$ (from layer-line separa-

tions on oscillation photographs), $d_{100} = 7.07 \text{ \AA}$, $d_{010} = 7.15 \text{ \AA}$, $d_{001} = 10.42 \text{ \AA}$, $\alpha^* = 74\frac{1}{2}^\circ$, $\beta^* = 73\frac{1}{2}^\circ$ (from zero-layer Weissenberg photographs about the a and b axes). The a and b axes lie in the plane of the plate and make an angle of about 90° with each other. This gives a cell volume of about 570 \AA^3 and a density of about 2.13 g/cm^3 for two formula units per unit cell; found, 2.15 g/cm^3 .

trans-Dichlorobis(ethylenediamine)cobalt(III)hexathionate, $[\text{Coen}_2\text{Cl}_2]_2\text{S}_6\text{O}_6 \cdot \text{H}_2\text{O}$. Green, long, orthorhombic prisms {110}, with $a = 12.12 \text{ \AA}$, $b = 19.13 \text{ \AA}$, $c = 6.43 \text{ \AA}$, and two formula units per unit cell; density, calc. 1.80, found 1.80 g/cm^3 . Systematic absences, $0kl$ when k is odd, $h0l$ when h is odd. Of the two space groups compatible with these absences, $C_{2v}^8 - Pba2$ is probably the correct one; it requires that the hexathionate ion lies on a twofold axis of symmetry. The other possible place group, $D_{2h}^9 - Pbam$, would require the symmetry $2/m$ for the ion, which is quite improbable. The space group $Pba2$ appears to be rare, no example being listed by Donnay and Nowacki⁷ (1954).

Although no mentioning of water of crystallization was made by Weitz and co-workers^{1,2}, the density and the analytical data point to the presence of one mole of crystal water in the salt. The water molecule would lie on the second set of twofold positions (twofold axes) of the space group. In a vacuum over phosphorus pentoxide the finely powdered salt lost 1.3% weight in the course of three weeks; calc. for monohydrate, 2.2%.

The salt was prepared from equal volumes of about 0.2 M aqueous *trans*-dichlorobis(ethylenediamine)cobalt(III) chloride and about 0.13 M potassium hexathionate in 0.5 N hydrochloric acid, by mixing at about 50°C , and cooling. For analysis, 0.6055 g was dissolved in water, and the solution run through a 'Zeo-Karb' 225 ion exchange column (acid form) and then made up to 250 ml in a volumetric flask. Four 25 ml samples were pipetted out and analyzed for hexathionate by means of the sulphite method⁸: $22.98 \pm 0.02 \text{ ml}$ of 0.00982 N iodine; calc. for monohydrate, 22.94 ml. Cobalt and total sulphur were determined gravimetrically in separate samples, sulphur as barium sulphate, and cobalt as sulphate after ignition of the substance and treatment of the residue with sulphuric acid, in both cases as described by Weitz and Spohn². (Found:

S 23.81, Co 14.62. Calc. for monohydrate, S 23.86, Co 14.62.)

Potassium barium hexathionate, $K_2Ba(S_6O_6)_2$. Monoclinic prismatic, $a = 11.58 \text{ \AA}$, $b = 10.81 \text{ \AA}$, $c = 9.14 \text{ \AA}$, $\beta = 112^\circ$. There are two formula units per unit cell; density, calc. 2.48, found 2.49 g/cm^3 . The space group is C_{2h}^4-P2/c , which requires that the barium ions lie in special, twofold positions.

The salt crystallized, very slowly, as well developed prisms extended along the c axis, bounded by $\{100\}$ (dominant) and $\{110\}$ and terminated by $\{111\}$. It has a faint yellowish colour, discernible only in the larger crystals.

The crystal structure has been solved⁹, through Fourier projections along the b and c axes by use of the heavy atom technique in the first stages. All the cations lie in special, twofold positions, the barium ion and one of the potassium ions on a twofold axis at $0, y, \frac{1}{2}$ with $y = 0$ and $y = 0.45$, respectively, and the other potassium ion in a symmetry centre at $\frac{1}{2}, 0, 0$. The hexathionate ions occupy general, fourfold positions. The sulphur chain of the hexathionate ion is unbranched and non-planar, and the configuration of the chain is *cis-cis*, *i. e.*, as in the S_8 ring of orthorhombic sulphur.

Crystals of the salt, admixed with crystals of barium chloride, were first observed in an attempt to prepare barium hexathionate from crude potassium hexathionate, containing potassium chloride, through metathesis with barium perchlorate. A subsequent experiment using pure, recrystallized potassium hexathionate (5 g) and half the equimolar amount (2.66 g) of barium perchlorate trihydrate, in which, after addition of methanol, and standing, 1.4 g of potassium hexathionate first crystallized and then 0.35 g of the double salt, led to the following procedure: 3.6 g of potassium hexathionate was dissolved in 6 ml of 0.5 N hydrochloric acid at about 50°C , and the solution added to 2.66 g of barium perchlorate trihydrate in 1 ml of water. The mixture was cooled and the potassium perchlorate filtered off, and 5 ml of methanol was added to the filtrate. Yield, after two days in a refrigerator, 0.9 g of the double salt.

Barium was determined gravimetrically as sulphate, and potassium as tetraphenylborate. 0.1242 g substance gave 0.0372 g $BaSO_4$ and 0.1110 g $KB(C_6H_5)_4$ (Found: Ba 17.6, K 9.75. Calc. for $K_2Ba(S_6O_6)_2$;

Ba 17.3, K 9.87.) Polythionate analysis was made by the sulphite method: One fifth of 0.1307 g substance gave 19.85 ml of 0.01 N iodine; calc. 19.79 ml.

In the course of the work, unit cell and space group data were obtained also for three pentathionates.

Sodium pentathionate dihydrate, $Na_2S_5O_6 \cdot 2H_2O$. Orthorhombic prisms extended along the c axis, with $a = 8.94 \text{ \AA}$, $b = 22.86 \text{ \AA}$, $c = 5.53 \text{ \AA}$. There are four formula units per unit cell; density, calc. 1.99, found 2.05 g/cm^3 . Systematic absences, $0kl$ when $k+l$ is odd, $h0l$ when l is odd. In view of the shortness of the c axis and the known configuration and dimensions of the pentathionate ion, the existence of a mirror plane normal to the c axis appears unlikely, so that the space group is probably C_{2v}^6-Pnc2 .

The salt was prepared from potassium pentathionate through metathesis with sodium perchlorate. It was described as a dihydrate by Kurtenacker and Laszlo¹⁰, and as a trihydrate by Deines and Christoph¹¹. Iodometric analysis of the X-ray sample by the sulphite method indicated two moles of water, and in a vacuum over phosphorus pentoxide the sample lost 9.5 % weight; calc. for dihydrate, 10.6 %.

Ammonium pentathionate hemitrihydrate, $(NH_4)_2S_5O_6 \cdot 1\frac{1}{2}H_2O$. Orthorhombic bipyramidal, $a = 20.59 \text{ \AA}$, $b = 9.33 \text{ \AA}$, $c = 12.61 \text{ \AA}$. The space group, from systematic absences, is $D_{2h}^{14}-Pbcn$. These X-ray data indicate that the salt is isomorphous with a series of pentathionate, selenopentathionate and telluropentathionate hemitrihydrates described earlier¹². They contain eight formula units per unit cell. Iodometric analysis by the sulphite method gave a formula weight agreeing with that of a hemitrihydrate.

The salt was obtained as long prisms by recrystallization from 2 N hydrochloric acid of a sample of ammonium hexathionate (containing about 35 mole % of pentathionate) prepared from benzidine hexathionate as described by Weitz and Spohn². It appears that the '*überraschend gut ausgebildete, bis zu 1 cm lange Stäbchen*' of alleged ammonium hexathionate obtained in the same way by Weitz and Spohn² may have been the pentathionate.

trans-Dichlorobis(ethylenediamine)cobalt(III) pentathionate, $[Co en_2Cl_2]_2S_5O_6$. Green, monoclinic prisms extended along the c axis, with $a = 23.30 \text{ \AA}$, $b = 18.46 \text{ \AA}$, $c = 6.53 \text{ \AA}$, $\beta = 97^\circ$, and four formula units per unit cell; density, calc. 1.80,

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.

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Structure of the Hexathionate Ion in a Potassium Barium Salt

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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 $y = 0$