

Solvates of Barium Pentathionates with Acetone and Tetrahydrofuran

OLAV FOSS and OLAV TJOMSLAND

Institutt for uorganisk kjemi, Norges tekniske høgskole, Trondheim, Norway

Barium pentathionate and selenopentathionate crystallize from aqueous acetone as solvates containing one mole of water and one mole of acetone per mole of salt. Analogous solvates, containing tetrahydrofuran instead of acetone, occur when barium pentathionate, selenopentathionate and telluropentathionate crystallize from aqueous tetrahydrofuran.

The solvates with acetone and tetrahydrofuran are isomorphous; the space group is $C_{2h}^2-P2_1/m$ with $Z = 2$. The barium ion, the middle atom of the pentathionate chain, the water molecule and the organic molecule lie in a crystallographic mirror plane. Unit cell dimensions are given for the five solvates, and their structure discussed in relation to the structures of barium pentathionate, selenopentathionate and telluropentathionate dihydrates.

In preparations of the solvates, some of the individual crystals give off the acetone or tetrahydrofuran relatively rapidly, while others are more stable.

In earlier papers on the crystal chemistry of barium salts of pentathionic, selenopentathionic and telluropentathionic acids, five dihydrates have been described, which crystallize in three different space groups. The salts are, triclinic barium pentathionate¹ and telluropentathionate² dihydrates, space group $C_i^1-P\bar{1}$ with $Z = 2$; orthorhombic barium pentathionate³ and selenopentathionate⁴ dihydrates, space group $D_{2h}^{16}-Pnma$ with $Z = 4$; and monoclinic barium telluropentathionate dihydrate², space group C_{2h}^3-A2/m with $Z = 4$. The present paper, on solvates in which one of the water molecules of the dihydrates is replaced by an acetone or tetrahydrofuran molecule, introduces a fourth, closely related structure type, of space group $C_{2h}^2-P2_1/m$ with $Z = 2$.

The solvates of barium pentathionates with acetone and tetrahydrofuran occur very readily, on addition of the solvents to aqueous solutions of the salts. The solvates are relatively stable, although the dissociation pressures of the organic molecules above the solvate crystals appear to be higher than in the case of the corresponding solvates with ethanol⁵. Within a preparation, some individual crystals give off the solvate molecules and become opaque rapidly, while others are quite stable and remain transparent and unchanged for weeks.

The crystals retain the solvate molecules better if immediately after filtering and washing, with the solvate solvent and then with ether, the crop of crystals is spread out on a large surface for drying in air. Crystals, once stable and thus picked and cut for X-ray measurements, mounted on a glass fibre in air in the ordinary way, have not been observed to disintegrate during the exposures to X-rays.

No solvates of barium salts with acetone or tetrahydrofuran appear to have been reported earlier. Deines and Christoph⁶ may have had the solvate of barium pentathionate with acetone in their hands, inasmuch as they in 1933 in a footnote reported on the isolation of barium polythionates, presumably also the pentathionate, from aqueous solutions by addition of ethanol or acetone.

EXPERIMENTAL

Solutions of barium pentathionate¹, selenopentathionate⁴ and telluropentathionate² hydrates, saturated at room temperature, were filtered if necessary and warmed to about 40° C, and from one to two times the volume of acetone or tetrahydrofuran was added with stirring. The solvates crystallized as the solutions were allowed to cool, to room temperature or in ice. Pure water or about 0.2 N perchloric acid was used to dissolve the hydrates, since hydrochloric acid which ordinarily is used to stabilize solutions of the pentathionates, caused contamination of the solvates with barium chloride.

Under the above conditions, the solvates with acetone appear to be less soluble and crystallize more rapidly than those with tetrahydrofuran. As with the hydrates, the solubilities decrease in the order, pentathionate, selenopentathionate and telluropentathionate.

The pentathionates were analyzed iodometrically by means of the sulphite method⁷, some sodium sulphate being added to the sample before the addition of the sodium sulphite reagent in order to remove the barium as sulphate. Two equivalents of iodine correspond to one mole of pentathionate. Absence of tetrathionate was checked through control analyses by means of the cyanide method.

$0.3048 \times \frac{1}{5}$ g, $0.3442 \times \frac{1}{5}$ g, $0.2820 \times \frac{1}{5}$ g substance: 26.38 ml, 27.10 ml, 24.58 ml of 0.01010 N, 0.01099 N, 0.01010 N iodine, respectively.

$\text{BaS}(\text{S}_2\text{O}_3)_2 \cdot \text{H}_2\text{O} \cdot (\text{CH}_3)_2\text{CO}$ (469.8). Mol. weights found, 457.3, 462.3, 454.3.

$0.1834 \times \frac{1}{5}$ g, $0.2525 \times \frac{1}{5}$ g, $0.2497 \times \frac{1}{5}$ g substance: 13.99 ml, 18.97 ml, 19.08 ml, respectively, of 0.01099 N iodine.

$\text{BaS}(\text{S}_2\text{O}_3)_2 \cdot \text{H}_2\text{O} \cdot (\text{CH}_2)_4\text{O}$ (483.8). Mol. weights found, 477.0, 484.4, 476.3.

The selenopentathionates were titrated with potassium bromate and subsequently analyzed iodometrically by means of the Norris and Fay method, as described earlier⁸. The bromate titration values served as a check on the absence of tetrathionate⁹.

0.2808 g, 0.2474 g, 0.2765 g substance: 22.43 ml, 19.15 ml, 21.91 ml, respectively, of 0.09954 N sodium thiosulphate.

$\text{BaSe}(\text{S}_2\text{O}_3)_2 \cdot \text{H}_2\text{O} \cdot (\text{CH}_3)_2\text{CO}$ (516.7). Mol. weights found, 503.0, 519.2, 507.1.

0.1983 g, 0.2066 g substance: 15.02 ml, 15.64 ml, respectively, of 0.09954 N sodium thiosulphate.

$\text{BaSe}(\text{S}_2\text{O}_3)_2 \cdot \text{H}_2\text{O} \cdot (\text{CH}_2)_4\text{O}$ (530.7). Mol. weights found, 530.6, 530.8.

The telluropentathionate was analyzed by direct titration with iodine, as described earlier⁹. Absence of tetrathionate was checked through subsequent analyses of the titrated solutions by means of the sulphite method⁷.

0.3360 g, 0.1500 g, 0.2496 g substance: 24.26 ml, 10.98 ml, 17.70 ml, respectively, of 0.1001 N iodine.

$\text{BaTe}(\text{S}_2\text{O}_3)_2 \cdot \text{H}_2\text{O} \cdot (\text{CH}_2)_4\text{O}$ (579.4). Mol. weights found, 553.5, 546.0, 563.4.

Different analyses reported for a substance were on different preparations.

The presence of organic molecules in the solvates was apparent from the strong characteristic odours of acetone or tetrahydrofuran which appeared when the solvates were dissolved in a little water. The acetone was, furthermore, characterized by means of 2,4-dinitrophenylhydrazine.

The solvate of barium selenopentathionate with tetrahydrofuran is the only one which gave consistent analytical results in agreement with the theoretical composition of the solvate. In the case of the other solvates, the results indicate that some water or, more likely, some acetone or tetrahydrofuran may have escaped from the crystal lattices before analysis. There is also a possibility that the solvates are non-stoichiometric, in the sense that, regarding them as derived from dihydrates, a water molecule of the latter is not completely, but only partly replaced by the organic molecule. That is, in the crystal lattice of the solvates some of the acetone or tetrahydrofuran positions are occupied by water.

CRYSTALLOGRAPHIC DATA

The solvates of barium pentathionates with acetone and tetrahydrofuran occur as plates {001}, bounded by {110}. The plates are usually rhomb-shaped and very thin, but do on slow crystallization grow thicker. There is perfect cleavage along (001), and some tendency of cleavage along another plane parallel to the *b* axis, probably (100). Twinning on (001) frequently occurs. The acetone solvates have also been obtained as prisms elongated in the direction of the *a* axis and with, also here, {001} predominant.

The unit cell dimensions were determined from oscillation and Weissenberg photographs about the *a* and *b* axes, using copper radiation. The axial lengths given in Table 1 are based on $\lambda(\text{Cu}K\alpha) = 1.542 \text{ \AA}$ and are believed to be correct to within 0.5 %.

Table 1. Unit cell dimensions of isomorphous acetone and tetrahydrofuran solvates.

	<i>a</i>	<i>b</i>	<i>c</i>	β
$\text{BaS}(\text{S}_2\text{O}_3)_2 \cdot \text{H}_2\text{O} \cdot (\text{CH}_2)_2\text{CO}$	5.04 Å	10.47 Å	13.61 Å	104°
$\text{BaSe}(\text{S}_2\text{O}_3)_2 \cdot \text{H}_2\text{O} \cdot (\text{CH}_2)_2\text{CO}$	5.02	10.56	13.78	105°
$\text{BaS}(\text{S}_2\text{O}_3)_2 \cdot \text{H}_2\text{O} \cdot (\text{CH}_2)_4\text{O}$	5.03	10.56	13.81	104°
$\text{BaSe}(\text{S}_2\text{O}_3)_2 \cdot \text{H}_2\text{O} \cdot (\text{CH}_2)_4\text{O}$	5.03	10.69	13.97	105°
$\text{BaTe}(\text{S}_2\text{O}_3)_2 \cdot \text{H}_2\text{O} \cdot (\text{CH}_2)_4\text{O}$	5.00	10.82	14.21	106°

The densities of the first and third of the solvates were measured by flotation in bromoform-carbon tetrachloride mixtures and found to be 2.25 and 2.27 g/cm³, respectively, as compared with the calculated values of 2.24 and 2.26 g/cm³ for two molecules per unit cell. The only systematic absences are, for all five solvates, *0k0* when *k* is odd. A comparison of the intensities of the *0kl* and *h0l* zones of reflections, and the close correspondence of unit cell dimensions, leave no doubt that the solvates are isomorphous. The diffraction symmetry being monoclinic, there are two space groups compatible with the systematic absences, of which the centrosymmetric one, $C_{2h}^2 - P2_1/m$, has been found to be the correct one through Patterson and Fourier projections along the *a* and *b* axes of the solvate of barium pentathionate with acetone.

With two formula units per unit cell, either centres of symmetry or mirror planes are required as molecular symmetry elements. Since pentathionate ions, water molecules and acetone or tetrahydrofuran molecules cannot reasonably be centrosymmetric, they must lie in mirror planes, as does also the barium ion according to the projections mentioned above.

The work so far done on the crystal structure of the solvate of barium pentathionate with acetone shows, as was expected from the unit cell dimensions and space group and the known structures of barium pentathionate, selenopentathionate and telluropentathionate dihydrates, that the solvate crystals are built up of layers which have the same internal structure as in the dihydrates, but for the substitution of a water molecule by an organic molecule. In the dihydrate structures¹⁻⁴, one of the water molecules, $(\text{H}_2\text{O})_{\text{I}}$, is firmly bound, being coordinated to two barium ions and forming hydrogen bonds to two oxygen atoms, whereas the other water molecule, $(\text{H}_2\text{O})_{\text{II}}$, is coordinated to one barium ion only, forms no hydrogen bonds and has a relative spacious environment. It is this water molecule, $(\text{H}_2\text{O})_{\text{II}}$, of the dihydrates which in the solvates is replaced by acetone or tetrahydrofuran, the internal structure of the layers otherwise being the same.

The dihydrates crystallize in three different space groups¹⁻⁴, *viz.*, $C_i^1-P\bar{1}$ with $Z = 2$, $D_{2h}^{16}-Pnma$ with $Z = 4$, and C_{2h}^3-A2/m with $Z = 4$. The space group, $C_{2h}^2-P2_1/m$ with $Z = 2$, of the acetone and tetrahydrofuran solvates represents a fourth structure type. The unit cell dimensions of the dihydrates and the solvates are very like, with $a = 5.0 \text{ \AA}$ and $b = 10.3-10.8 \text{ \AA}$, and c spacings as discussed below. The isostructural layers are parallel to the c planes, and the crystals show a corresponding perfect cleavage along this plane. The internal layer symmetry, $2_1/m$, is crystallographically required by all space groups except the triclinic one, but is realized even there¹. The structure types differ only in the way in which the layers are arranged relative to each other. In the crystals of space group $C_i^1-P\bar{1}$, there is a repetition of layers with relative displacements in the directions of the a and b axes; in $C_{2h}^2-P2_1/m$, there is a repetition with displacements in the direction of the a axis only; in $D_{2h}^{16}-Pnma$, successive layers are related through glide planes a in their interface, and in C_{2h}^3-A2/m , through twofold rotation axes parallel to the b axis in the interface.

In the solvates, the oxygen atom of the organic molecule coordinates to the barium ion, like the oxygen atom of the replaced water molecule, and is located between the barium ion and the nearest layer interface, with the rest of the molecule directed towards the interface. It is interesting to compare the space requirements of the water and organic molecules with the observed variations of layer thicknesses. The layer thickness is equal to the c spacing when there are two formula units per unit cell, and half the c spacing when there are four. The distances from the centre of the oxygen atom, along the molecular axis to the van der Waals sphere of the methyl or methylene groups, are calculated as 4.0 \AA for acetone and 4.3 \AA for tetrahydrofuran, using dimensional data from electron diffraction studies^{10,11} and taking the van der Waals radius of methyl and methylene groups¹² as 2.0 \AA . For water, the corresponding distance is 1.8 \AA . The observed c spacings of the solvates with tetrahydrofuran are, in fact, a little larger than of those with acetone, *viz.*, 0.19 \AA for the pentathionates and 0.18 \AA for the selenopentathionates. Also, the c spacings of the solvates are larger, by $2.0-2.4 \text{ \AA}$, than the c spacings, or half these values, of the corresponding dihydrates¹⁻⁴. Although the molecules probably do not point directly towards the layer interface, but are more or less inclined to it in the direction of the a axis, it appears that there is a

dependence of layer thickness on the space requirements of the replaceable molecules.

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