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Barium Salts of Telluropentathionic Acid

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A study has been made of the crystal chemistry of barium telluropentathionate hydrates. On crystallization from water, a monoclinic trihydrate (I) occurs. Two dihydrates were obtained, one triclinic (II) by crystallization from aqueous methanol, and one monoclinic (III) by crystallization from aqueous acetone. The unit cell dimensions and space groups are:

I, $a = 11.16$ Å, $b = 5.24$ Å, $c = 21.30$ Å, $\beta = 107°$; space group, $C_{2h}{}^{5} - P2_1/c$ with $Z = 4$.

II, $a = 4.99$ Å, $b = 10.57$ Å, $c = 12.38$ Å, $\alpha = 106°$, $\beta = 101\frac{1}{2}°$, $\gamma = 90°$; space group, $C_i{}^{1} - P\bar{1}$ with $Z = 2$.

III, $a = 4.99$ Å, $b = 10.59$ Å, $c = 23.61$ Å, $\beta = 98°$; space group, $C_{2h}{}^{3} - A2/m$ with $Z = 4$.

Isomorphism of II with triclinic barium pentathionate dihydrate, and the requirement in III of a mirror plane of molecular symmetry, show that the telluropentathionate ion occurs in a *cis* form in these salts.

The first salts of telluropentathionic acid, those of sodium and potassium, were isolated in 1949[1]. Later, the ammonium, rubidium and cesium salts were prepared, and unit cells and space groups determined for these and the potassium salt[2]. Detailed crystal structure analyses of ammonium telluropentathionate[3], as well as of orthorhombic[4] and triclinic[5] barium pentathionate dihydrate and orthorhombic barium selenopentathionate dihydrate[6], were subsequently carried out.

Pentathionate chains may occur in two rotational-isomeric forms, which have been termed *cis* and *trans*[7]. The telluropentathionate ion in the ammonium salt occurs in the *trans* form, whereas the *cis* form was found for the pentathionate and selenopentathionate ions in the barium salts. It was of interest to see whether in barium salts also the telluropentathionate ion would have the *cis* form. This has now been found to be the case, in two crystalline modifications of barium telluropentathionate dihydrate. Together with the earlier structure determination of the ammonium salt, the work on barium salts serves to establish the occurrence of different rotational-isomeric forms of the telluropentathionate ion in different salts.

SYNTHESIS OF SALTS

Three distinct barium telluropentathionate hydrates were obtained, on recrystallization under various conditions of crude samples prepared from the sodium salt[1] by metathesis with a slight excess of barium perchlorate. The sodium and barium perchlorates being readily soluble in water, barium telluropentathionate crystallized readily on mixing concentrated solutions of the reactants, and cooling. This procedure was used also for the preparation of crude barium selenopentathionate[6].

When crystallized from water, without the use of an organic solvent to depress the solubility, barium telluropentathionate separates as a trihydrate. Under such conditions also barium selenopentathionate gives a trihydrate, whereas barium pentathionate comes out as a triclinic dihydrate.

From aqueous methanol, barium pentathionate and selenopentathionate separate as orthorhombic dihydrates. Attempts to prepare an orthorhombic barium telluropentathionate dihydrate in this way have failed so far; instead, a triclinic dihydrate, isomorphous with the triclinic pentathionate, was obtained. On crystallization from aqueous acetone, barium pentathionate and selenopentathionate give solvates, whereas barium telluropentathionate crystallized as a monoclinic dihydrate.

The order of decreasing stability of the crystals of the three barium telluropentathionate hydrates, with respect to liberation of tellurium on keeping, appears to be: Trihydrate, monoclinic dihydrate, and triclinic dihydrate. The two former salts are stable for months, and also crystallize readily, with well developed forms free from twinning, whereas the triclinic dihydrate shows a pronounced tendency of irregular growth and twinning. Although crystals of the dihydrates, when moistened, gradually dissolve and recrystallize as the trihydrate, no transition of one crystalline hydrate to another has been observed on keeping at room temperature and ordinary humidity conditions.

The trihydrate has a yellowish green colour, whereas the dihydrates are yellow. The crystals of the monoclinic dihydrate, in daylight and more rapidly on exposure to X-rays, develop an orange colour but give unchanged X-ray photographs.

EXPERIMENTAL

Sodium telluropentathionate dihydrate was prepared from tellurium dioxide and sodium thiosulphate as described earlier[1]. To 25 g of the crude sodium salt, dissolved in 40 ml of 0.2 N hydrochloric acid by gentle heating, and filtered and cooled in ice, was added a solution of 25 g of barium perchlorate trihydrate in 15 ml of water. Crystals of barium telluropentathionate rapidly began to separate out. After a few minutes, the product was filtered off, and washed with methanol and ether. Yield, about 18 g. The recrystallizations were performed as follows.

Trihydrate (I). The crude barium salt was dissolved in four to five times the amount of 0.2 N hydrochloric acid at 40—50° C, and the solution was filtered and allowed to cool, first at room temperature and then in ice.

Triclinic dihydrate (II). To a solution prepared as above, but about half as concentrated, of the crude salt or the trihydrate was added about twice the amount of methanol. The crystallization took place at or slightly above room temperature. If the solution is cooled in ice, the preparation will have a composition intermediate between di- and trihydrate.

Monoclinic dihydrate (III). 1 g of the trihydrate was dissolved in 8 ml of 0.2 N perchloric acid, and the solution was filtered and warmed to 40—50° C. Then 8 ml of acetone was added from a pipet, with stirring, and the solution was allowed to cool to room temperature.

The crops of crystals were filtered with suction on sintered glass filters, and I, II and III were washed with ethanol, methanol and acetone, respectively, and then with ether. They were dried for a short time in a vacuum over sulphuric acid; small crops were dried on a plate in air. On prolonged keeping over sulphuric acid, the water of crystallization is given off.

The salts were analyzed by direct titration with iodine, as described earlier [1]. Absence of tetrathionate was checked through subsequent analysis of the titrated solutions by means of the sulphite method [1].

0.3322 g of I: 24.60 ml of 0.09954 N iodine.
$BaTe(S_2O_3)_2 \cdot 3H_2O$ (543.3). Mol. weight found, 542.6.
0.2744 g of II: 21.01 ml of 0.09954 N iodine.
$BaTe(S_2O_3)_2 \cdot 2H_2O$ (525.3). Mol. weight found, 524.9.
0.1530 g of III: 11.70 ml of 0.09954 N iodine.
$BaTe(S_2O_3)_2 \cdot 2H_2O$ (525.3). Mol. weight found, 525.5.

As mentioned above, barium selenopentathionate on crystallization from water occurs as a trihydrate, like barium telluropentathionate. This trihydrate has not been described, and is therefore included here. Crude barium selenopentathionate [6] was dissolved in about three times the amount of 0.2 N hydrochloric acid at 40—50° C, and the solution was filtered and cooled in ice. It was advantageous, for better crystallization, to add a little barium perchlorate before cooling. The salt was oxidized with potassium bromate and subsequently analyzed iodometrically by means of the Norris and Fay method, as described earlier [8].

0.1989 g substance: 16.10 ml of 0.09954 N sodium thiosulphate.
$BaSe(S_2O_3)_2 \cdot 3H_2O$ (494.6). Mol. weight found, 496.4.

The salt is more stable than the orthorhombic dihydrate [6]; thus, a sample kept in a dark bottle was found unchanged after five years. The pale greenish crystals occur as prisms, of much the same habit as the trihydrate I above, but often flattened almost to leaves and with a tendency of irregular growth. It appears probable that the salt may be isomorphous with I, but no X-ray measurements have been made.

CRYSTALLOGRAPHIC DATA

The crystals of the barium telluropentathionate hydrates were characterized by means of X-ray oscillation and Weissenberg photographs. Copper radiation was used, $\lambda(\mathrm{Cu}K_\alpha) = 1.542$ Å. The axial lengths recorded below are believed to be accurate to within 0.5 %. The densities of the crystals were determined by flotation in suitable solvents.

Barium telluropentathionate trihydrate, $BaTe(S_2O_3)_2 \cdot 3H_2O$ (I). Monoclinic, $a = 11.16$ Å, $b = 5.24$ Å, $c = 21.30$ Å, $\beta = 107°$. Four molecules per unit cell; density, calc. 3.03, found 3.0 g/cm^3. Systematic absences, $h0l$ when l is odd, $0k0$ when k is odd. The space group is thus C_{2h}^5—$P2_1/c$. The crystals occur as flat prisms, extended along the b axis and with $\{100\}$ predominant.

Barium telluropentathionate dihydrate, $BaTe(S_2O_3)_2 \cdot 2H_2O$ (II). Triclinic, $a = 4.99$ Å, $b = 10.57$ Å, $c = 12.38$ Å, $\alpha = 106°$, $\beta = 101\frac{1}{2}°$, $\gamma = 90°$. Two molecules per unit cell; density, calc. 2.84, found 2.84 g/cm^3. No systematic absences. The crystals occur as prisms, extended along the a axis and usually flattened along the b axis. There is perfect cleavage along the c plane.

The unit cell dimensions are not far from those of triclinic barium pentathionate dihydrate [5]. The γ angle of 90°, and the characteristic cleavage, are retained, and the b axis and c spacing are a little larger, as may be expected when tellurium is substituted for sulphur. A comparison of the intensities of the $0kl$ and $h0l$ reflections of the two triclinic dihydrates adds further support to the assumption that the salts are isomorphous. The space group of II has therefore been taken as C_i^1—$P\bar{1}$.

Barium telluropentathionate dihydrate, $BaTe(S_2O_3)_2 \cdot 2H_2O$ (III). Monoclinic, $a = 4.99$ Å, $b = 10.59$ Å, $c = 23.61$ Å, $\beta = 98°$. Four molecules per unit cell; density, calc. 2.82, found 2.80 g/cm^3. Systematic absences, hkl when $k + l$ is odd. The crystals occur as prisms, extended along the a axis and ordinarily flattened along the b axis. The habit is monoclinic prismatic, and the forms $\{001\}$, $\{011\}$ and $\{110\}$ occur, with the former the more predominant one. There is a pronounced cleavage along the c plane.

On the basis of the systematic absences, three space groups are possible, *viz.*, C_{2h}^3—$A2/m$ and two of lower symmetries. In the crystals of orthorhombic barium pentathionate [4] and selenopentathionate [6] dihydrates, of space group D_{2h}^{16}—$Pnma$ with four molecules per unit cell, $0kl$ reflections are present only when $k + l$ is even, as in III, and the a axis projections of these and of III have also very like dimensions. A comparison of the intensities of the $0kl$ reflections, allowing for the different scattering powers of sulphur, selenium and tellurium, shows that the $0kl$ zone of III has the same intensity distribution as the $0kl$ zones of the orthorhombic dihydrates. The space group and $0kl$ zones of the latter being centrosymmetric, the same applies, beyond reasonable doubt, to the $0kl$ zone of III. The space group is therefore the centrosymmetric one, C_{2h}^3—$A2/m$.

In III, the telluropentathionate ion lies in a crystallographic mirror plane of symmetry, and has thus a *cis* configuration, as contrasted with the *trans* configuration found earlier in the crystals of ammonium telluropentathionate [3]. The crystals of II being isomorphous with those of triclinic barium pentathionate dihydrate, the *cis* configuration occurs also in II. The triclinic space group possesses no crystallographic mirror plane, but the pentathionate ion has mirror plane symmetry also in those crystals [5].

The orthorhombic structure of barium pentathionate and selenopentathionate dihydrate, of space group D_{2h}^{16}—$Pnma$, is built up of layers related to each other through glide planes a in their interface [4,6]. From the correspondence of unit cell dimensions, the cleavage, and the similar intensities of the $0kl$ zones of reflections, it is to be expected that the monoclinic structure of barium telluropentathionate dihydrate, of space group C_{2h}^3—$A2/m$, is built up of layers which have the same internal structure as in the orthorhombic analogues, but are related to each other through twofold rotation axes instead of glide planes. A complete structure determination of III will be made.

The unit cell dimensions of triclinic and monoclinic barium telluropentathionate dihydrate show close correspondence, with $a = 4.99$ Å, $b = 10.57$ Å and 10.59 Å, and $d_{001} = 11.64$ Å and 2×11.69 Å, respectively. The intensities of the $00l$ reflections, with the l indices of III halved, are very similar. The structural difference should be the same as between triclinic and orthorhombic barium pentathionate dihydrate [4,5], and thus consist in a different arrangement of like layers relative to each other.

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REFERENCES

1. Foss, O. *Acta Chem. Scand.* **3** (1949) 708.
2. Foss, O. and Jahr, J. *Acta Chem. Scand.* **4** (1950) 1560.
3. Foss, O. and Larssen, P. A. *Acta Chem. Scand.* **8** (1954) 1042.
4. Foss, O. and Zachariasen, H. *Acta Chem. Scand.* **8** (1954) 473.
5. Foss, O. and Tjomsland, O. *Acta Chem. Scand.* **10** (1956) 288.
6. Foss, O. and Tjomsland, O. *Acta Chem. Scand.* **8** (1954) 1701.
7. Foss, O. *Acta Chem. Scand.* **7** (1953) 1221.
8. Foss, O. *Acta Chem. Scand.* **3** (1949) 435.

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