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Solvates of Barium Pentathionates with Ethanol

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Barium pentathionate and selenopentathionate crystallize from aqueous ethanol as solvates containing one mole of water and one mole of ethanol per mole of salt. The crystals are isomorphous, and have eight-molecule unit cells based on the space group, $D_{2h}^{15}-Pcab$, with a = 9.18 Å, b = 13.27 Å, c = 21.25 Å for the pentathionate and a = 9.19 Å, b = 13.30 Å, c = 21.37 Å for the selenopentathionate. The solvates are relatively stable.

Barium telluropentathionate gives a solvate which probably contains one mole of ethanol but no water.

In 1847, one year after the discovery of pentathionic acid by Wackenroder[1], Lenoir[2] reported the isolation of barium pentathionate by crystallization from aqueous ethanol. Although the salt by analysis was found to contain 2.93 % of ethanol, the ethanol was regarded as an impurity, and the salt described as a dihydrate. Fordos and Gélis[3], in 1848, stated that barium pentathionate always retain some ethanol when precipitated from water by means of ethanol, but no particular significance was attached to the ethanol content.

It is the purpose of this article to show that barium pentathionate and selenopentathionate, when crystallized from aqueous ethanol, are obtained as solvates containing one mole of water and one mole of ethanol per mole of salt. The formulae are:

$$BaS(S_2O_3)_2 \cdot H_2O \cdot C_2H_5OH; \qquad BaSe(S_2O_3)_2 \cdot H_2O \cdot C_2H_5OH$$

The crystals of the two solvates are isomorphous. Lenoir[2] described his crystals as quadratic prisms, and they are later[4] referred to as tetragonal. In fact, the solvates usually occur as prisms having frequently a quadratic cross-section, but they are orthorhombic bipyramidal, not tetragonal. The correct percentage of ethanol in the pentathionate is 10.1 and thus considerably higher than found by Lenoir.

The ethanol appears to be relatively firmly held in the crystal lattice. When kept in closed bottles, the majority of the individual crystals remain unchanged for months, as revealed by microscopic and X-ray examination, although on opening the bottles, an odour of ethanol is perceptible. With regard to the ordinary decomposition reactions of the pentathionates, *i. e.*, the liberation of sulphur or selenium, the solvates are at least as stable as the corresponding hydrates.

These are apparently the first recorded instances of solvates of barium salts with ethanol. According to Sidgwick[5], "the halides (and sometimes the hydroxide and nitrate as well) of barium will combine with glycerol, sugar alcohols, sugars, carboxylic acids, and aminoacids; strontium halides will also combine with alcohol and acetone". As will be shown later, barium pentathionates form well-defined solvates also with acetone and other simple organic solvents.

EXPERIMENTAL

To solutions of crude barium pentathionate[6] and barium selenopentathionate[7] in about 0.01 N hydrochloric acid, saturated at 40–50° C, and filtered if necessary and still warm, were added about equal volumes of ethanol. On cooling, first at room temperature and afterwards in ice, the solvates slowly crystallized. The crops of crystals were filtered with suction on sintered glass filters, washed with ethanol and then with ether, and dried for less than an hour in a vacuum over sulphuric acid. The same procedure was used for recrystallizations.

The crystals of the pentathionate are colourless and those of the selenopentathionate pale greenish.

The pentathionate was analyzed iodometrically by means of the sulphite method[8], after removal of the barium by addition of sodium sulphate[6]. Two equivalents of iodine correspond to one mole of pentathionate. Through control analyses by means of the cyanide method, the salt was found to be free from tetrathionate.

0.3007 × $\frac{1}{5}$ g substance: 26.04 ml of 0.01010 N iodine.

$BaS(S_2O_3)_2 \cdot H_2O \cdot C_2H_5OH$ (457.8): Mol. weight found, 457.3.

The selenopentathionate was oxidized with potassium bromate and subsequently analyzed iodometrically by means of the Norris and Fay method, as described earlier[9].

0.2011 g substance: 16.10 ml of 0.09954 N sodium thiosulphate.

$BaSe(S_2O_3)_2 \cdot H_2O \cdot C_2H_5OH$ (504.7): Mol. weight found, 501.8.

In order to check the presence of ethanol in the crystals, aqueous solutions were oxidized with chromic acid — sulphuric acid. Acetaldehyde was thereafter distilled off and characterized by means of 2,4-dinitrophenylhydrazine.

Experiments made with barium telluropentathionate have shown that also this salt gives a solvate with ethanol. The yellow crystals, obtained from the trihydrate[10] as described for the above solvates, were small and not suited for single-crystal X-ray work. According to analyses, performed by direct titration with iodine[11], the composition corresponds to one mole of ethanol per mole of barium telluropentathionate, but no water. The presence of ethanol in the crystals was checked as described above.

0.2012 g substance: 15.04 ml of 0.1001 N iodine.

$BaTe(S_2O_3)_2 \cdot C_2H_5OH$ (535.3): Mol. weight found, 534.6.

In lack of X-ray data, there remains some doubt concerning the absence of water in this solvate, since some ethanol or water may have escaped from the crystal lattice before the analysis. Similar analytical results have been obtained with some of the solvates of barium pentathionates with acetone and tetrahydrofuran, and there, isomorphism of the whole series of solvates indicates that the questionable mole of water is present, regardless of the analytical results.

CRYSTALLOGRAPHIC DATA

The solvates of barium pentathionate and selenopentathionate with ethanol are orthorhombic, and ordinarily occur as prisms, elongated in the direction of the *a* axis and bounded by {010} and {001}. The cross-section is frequently quadratic or nearly so. There is perfect cleavage along the *c* plane.

Oscillation and Weissenberg photographs were made on single-crystal specimens, using copper radiation, $\lambda(\mathrm{Cu}K_{\alpha}) = 1.542$ Å. Densities were measured by a flotation method. The following unit cell dimensions, believed to be accurate to within 0.5 %, were derived.

	a	*b*	*c*
$BaS(S_2O_3)_2 \cdot H_2O \cdot C_2H_5OH$	9.18 Å	13.27 Å	21.25 Å
$BaSe(S_2O_3)_2 \cdot H_2O \cdot C_2H_5OH$	9.19	13.30	21.37

There are eight molecules per unit cell; densities, calc. 2.35 and 2.57 g/cm^3, respectively; found, 2.34 and 2.59 g/cm^3. Systematic absences, $0kl$ when l is odd, $h0l$ when h is odd, $hk0$ when k is odd. The space group is thus unambiguously determined as D_{2h}^{15}—*Pcab*. The unit cell dimensions, the space group extinctions, and the relative intensities of the reflections show that the two salts are isomorphous.

The number of general positions of the space group being eight, the asymmetric unit corresponds to one formula unit. No detailed structure analysis of any of the salts is contemplated at present.

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