STRONTIUM AND BARIUM SELENITES. SYNTHESIS AND SOME PROPERTIES

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Dedicated to Professor S. Škramovský on the occasion of his 80th birthday.

The solubility, thermal analysis, powder X-ray diffraction, and infrared spectroscopy methods were applied to a study of selenites $SrSeO_3.n\,H_2O$ ($n = 0{\cdot}6-1{\cdot}0$), anhydrous $SrSeO_3$ (in two modifications), $Sr(HSeO_3)_2$, $SrSe_2O_5$, $BaSeO_3$, and $BaSe_2O_5$. The conditions of their preparation and their bonding parameters are discussed in terms of comparison with magnesium and calcium selenites.

The synthesis and properties of strontium and barium selenites have been the concern of Muspratt[1], Berzelius[2], Nilson[3], Chukhlantsev[4], Leshchinskaya and Selivanova[5,6], Lehner and Wechter[7], Rocchiccioli[8], and Neal and McCrosky[9]; compounds of the composition $SrSeO_3$, $SrSeO_3.3\,H_2O$, $SrSeO_3.n\,H_2O$ ($n = 0{\cdot}6-1{\cdot}0$), $SrSe_2O_5.H_2O$, $BaSeO_3$, $BaSeO_3.H_2O$, and $BaSe_2O_5$ have been described.

The infrared spectra of alkali selenites have been systematically studied by Paetzold and Simon[10-12], who determined the structure and symmetry of the selenite, hydrogen selenite, and diselenite ions and calculated the force constants of the selenium–oxygen bonds. They attribute the point symmetry group C_{3v} to the SeO_3^{2-} anion, the C_s group to the $HSeO_3^-$ anion (with the hydroxyl group bonded at the SeO_2 grouping), and C_{2v} to the $Se_2O_5^{2-}$ anion involving two SeO_2 groups bonded *via* an oxygen bridge.

The objective of the present work was the synthesis of all selenites in the $SrSeO_3$–SeO_2–H_2O system at 25°C based on a solubility study, and investigation of the properties and bonding parameters for these substances as well as for barium selenites synthesized with regard to the solubility diagram[9]. The properties are discussed in terms of comparison with the previously studied[13,24] magnesium and calcium selenites.

EXPERIMENTAL

Chemicals and Procedures

Strontium selenite, $SrSeO_3.n\,H_2O$, was synthesized by precipitation of an aqueous solution of sodium selenite (pure, Lachema, Brno), concentration 0·2 mol l^{-1}, with an aqueous solution of strontium perchlorate of the same concentration; the latter was prepared by dissolving strontium carbonate (pure, Lachema, Brno) in perchloric acid (pure, Laborchemie, Apolda). The deuterate $Sr(DSeO_3)_2$ for infrared spectroscopic study was prepared, based on the solubility diagram, from $SrSeO_3$, SeO_2, and D_2O. Selenium dioxide, pure, was a preparation of Lachema, Brno. Barium selenite was prepared by precipitating sodium selenite (pure, Lachema, Brno) with barium perchlorate (pure, Xenon-Lodž), both in aqueous solutions of concentration 0·2 mol . . l^{-1}. Barium diselenite was obtained from $BaSeO_3$ and SeO_2, making use of the solubility diagram according to Neal and Mc Crosky[9].

The starting materials as well as the products were analyzed gravimetrically. Selenium was determined by a modified method[13] after Bode[15], consisting in reduction with sulphur dioxide to elementary selenium, strontium and barium were determined as sulphates[16]. The results of the analyses were consistent with the selenites composition. The solubility was established by volumetric analysis: selenium was determined according to Ganitskii and Zelinokrayte[17], strontium, complexometrically[18].

The thermal decomposition was examined in the region of 20—600°C by employing a Derivatograph instrument (MOM, Budapest) applying the temperature rise rate of 5°C/min. The powder X-ray diffractograms were obtained on an instrument of Chirana using Siemens chambers of the diameter 57·3 mm; the samples were accomodated on a rod, anhydrous substances, in a Lindenmann glass capillary of the diameter 0·3—0·5 mm; the average exposition time was 45 min, voltage 35 kV, current 20 mA. The infrared spectra were scanned on a UR 20 spectrophotometer (Zeiss, Jena) over the region of 400—4 000 cm^{-1}. The samples were measured in potassium bromide cells as Nujol mulls and, in the region of the hydroxyl group stretching vibrations, as Tripene mulls.

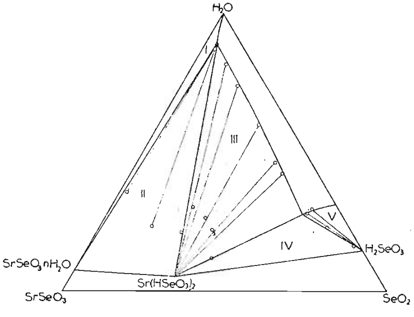

FIG. 1

Solubility diagram for the $SrSeO_3$–SeO_2–H_2O system at 25°C

Solubility in the $SrSeO_3$–SeO_2–H_2O *System at* 25°C

Schreinemaker's method was applied to the solubility study of the $SrSeO_3$–SeO_2–H_2O system; the equilibrium established within several days.

The solubility diagram, constructed according to Gibbs and Roozeboom, is shown in Fig. 1. In the crystallization region III the incongruently soluble anhydrous strontium hydrogen selenite, $Sr(HSeO_3)_2$, is formed. The crystallization regions I and V belong to the starting materials, the regions II and IV pertain to the equilibria between the two solids and the solutions of the compositions corresponding to the peritonic point *P* and the eutonic point *E*, respectively, which are 7·3% $SrSeO_3$, 3·1% SeO_2, and 89·6% H_2O, and 12·0% $SrSeO_3$, 60·2% SeO_2, and 27·8% H_2O, respectively. In the region II, with the liquid phase composition corresponding to point *P*, a phase reaction occurs resulting in the formation of the hydrogen selenite: $SrSeO_3 + SeO_2 + H_2O \rightleftharpoons Sr(HSeO_3)_2$.

Based on this solubility diagram, anhydrous strontium hydrogen selenite was prepared. The substance was collected on an S3 glass filter, washed with ethanol and ether, and dried on air at ambient temperature to give fine colourless crystals, steady on air at room temperature.

Thermal Analysis, Powder X-Ray Diffraction, and Infrared Spectroscopy Measurements

The results of the thermal decomposition study for $SrSeO_3.n\,H_2O$, $Sr(HSeO_3)_2$, and $BaSe_2O_5$ are given in Table I.

The powder X-ray diffraction patterns of $SrSeO_3$ prepared by decomposition of $SrSeO_3.n\,H_2O$, taken before and after the *exo* effect at 340–355°C, are substantially different, although the composition does not vary.

$Sr(HSeO_3)_2$ affords at 360–410°C anhydrous $SrSeO_3$ whose diffraction patterns are identical with those of anhydrous $SrSeO_3$ obtained by heating $SrSeO_3.n\,H_2O$ above 355°C.

The powder diffraction patterns of $BaSeO_3$ are consistent with the ASTM data[26].

$BaSe_2O_5$ transforms at 360–445°C into $BaSeO_3$ whose powder diffractogram is identical with that of $BaSeO_3$ prepared by precipitation in aqueous solution.

The powder diffractograms of $SrSeO_3$ II and $BaSeO_3$ differ only in the 2Θ values, the number of lines and their relative intensities are the same.

The infrared spectra were run for $SrSeO_3.n\,H_2O$, $Sr(HSeO_3)_2$, $Sr(DSeO_3)_2$, anhydrous $SrSeO_3$ I, $SrSe_2O_5$, $BaSeO_3$, and $BaSe_2O_5$; the data are summarized in Tables II–IV. The band assignment is based on works of Paetzold and Simon[10–12], the spectrum of $BaSeO_3$ is consistent with the data reported by Rocchiccioli[8].

DISCUSSION

A selenite of the composition Sr : Se : H_2O = 1 : 2 : 1 has been identified in the $SrSeO_3$–SeO_2–H_2O system at 25°C. The authors of previous works were unable to decide whether this compound was anhydrous strontium hydrogen selenite or strontium diselenite monohydrate. As to analogous systems involving metals of the 2nd main subgroup, the occurrence of the hydrogen selenites $Mg(HSeO_3)_2.4\,H_2O$ and

TABLE I

Thermal decomposition of the selenites

Temperature °C	TGA	DTA	Assignment
	$SrSeO_3.n\,H_2O$		
160—200	loss	*endo*	dehydration
220—340	−7·99% plateau	—	$SrSeO_3$ anhydrous, crystalline I
340—355	—	*exo*	recrystallization
355—higher	—	—	$SrSeO_3$ anhydrous, crystalline II
	$Sr(HSeO_3)_2$		
180—195	loss	*endo*	dehydration
210—360	−5·72% plateau	—	$SrSe_2O_5$
360—410	loss	*endo*	loss of SeO_2
420—higher	−38·0%	—	$SrSeO_3$ anhydrous, crystalline II
	$BaSeO_3$		
510—higher	start of a small increment		start of oxidation to selenate
	$BaSe_2O_5$		
360—445	loss	*endo*	loss of SeO_2
450—510	−31·0% plateau	—	$BaSeO_3$
510—higher	start of a small increment	*exo*	start of oxidation to selenate

$Ca(HSeO_3)_2.H_2O$ and the diselenite $BaSe_2O_5$ has been established for magnesium[13], calcium[14], and barium[9], respectively. In the case in question, a solution to the problem can be gained from the infrared spectrum: the presence of the

TABLE II

Infrared spectra of $Sr(HSeO_3)_2$ and $Sr(DSeO_3)_2$. Band positions ($\tilde{\nu}$) in cm^{-1}, relative intensities: s strong, m medium, w weak; b broad, sh shoulder. Vibrational assignment: ν_s symmetric stretching, ν_{as} antiasymmetric stretching, δ bending, ϱ rocking

$\tilde{\nu}_{Sr(HSeO_3)_2}$	$\tilde{\nu}_{Sr(DSeO_3)_2}$	$\tilde{\nu}_{Sr(HSeO_3)_2}/\tilde{\nu}_{Sr(DSeO_3)_2}$	Assignment
431 s	427 m	1·01	δ SeO_2
454 m	448 m	1·01	
618 s	617 m	1·00	ν SeO(SeOH)
637 s	627 m	1·02	
800 s	794 s	1·01	ν_{as} SeO_2
830 s	823 s	1·01	ν_s SeO_2
873 s	870 s	1·00	
1 160 w	865 sh	1·34	δ OH(SeOH)
1 229 w	908 m	1·35	
2 415 w, b	2 240—2 370 m, b	1·08	ν OH(SeOH)
3 050 m, b		1·33	

TABLE III

Infrared spectra of hydrated and anhydrous $SrSeO_3$. Symbols as in Table II

$SrSeO_3.n\ H_2O$	Assignment	$SrSeO_3$ anhydrous crystalline I	Assignment
412 m	δ SeO_3	419 m	δ SeO_3
460 m		463 m	
627 m	ϱ H_2O	476 m	
720 s	ν_s SeO_3	757 s	ν_s SeO_3
763 s		785 s	
803 sh	ν_{as} SeO_3	800 sh	ν_{as} SeO_3
838 s		812 sh	
1 699 w, b	δ H_2O		
3 164 s, b	ν H_2O		

ν_{OH}(SeOH) and δ_{OH}(SeOH) bands and absence of the $\nu_{OH}(H_2O)$ and $\delta_{OH}(H_2O)$ bands gives evidence that the compound formed in the system under study is anhydrous strontium hydrogen selenite.

Thermal decomposition of $SrSeO_3.n\,H_2O$ leads to the formation of the first crystal modification $SrSeO_3$ I, which at 345 – 355°C is transformed into the second, as yet not described modification $SrSeO_3$ II. Decomposition of strontium hydrogen selenite at 185 – 195°C results in the formation of strontium diselenite, which at 360 to 410°C loses SeO_2, thereupon converting into the second crystal modification $SrSeO_3$ II. $BaSeO_3$ is thermally stable up to 510°C, where it starts to partially oxidize to selenate. This temperature is 140°C lower than that reported by Rocchiccioli[8]. By thermal decomposition of $BaSe_2O_5$, barium selenite is formed at 360 – 445°C, a temperature region 20 – 50°C lower than as given by Rocchiccioli[8].

Comparing the decomposition temperatures of selenite hydrates and hydrogen selenites over the Mg through Ba series, we find them decreasing, which can be explained in terms of the diminishing polarizing effect of the cation upon the hydrogen bond between the water molecule and the anion.

The force constants of the Se–O bonds in the selenites under study were calculated from the infrared spectra; the values are given in Table V. The calculations were based on the equations derived for a biatomic model using Lehmann's relation for wavelength averaging in a manner reported previously for magnesium[13] and calcium[14] selenites. The force constants of Se–O bonds in $MSeO_3$ selenites (M = Mg, Ca, Sr, Ba) and their hydrates lie in the range of 485 – 498 $N\,m^{-1}$. No substantial differences in the bond force constants were observed between the hydrates and the

TABLE IV

Infrared spectra of $SrSe_2O_5$ and $BaSe_2O_5$. Symbols as in Table II

$SrSe_2O_5$	Assignment	$BaSe_2O_5$	Assignment
433 m	δ SeO_2	399 m	δ SeO_2
445 sh		426	
550 sh	ν Se–O–Se	525 sh	ν Se–O–Se
583 s		547 s	
595 sh		590 s	
770 w	ν_{as} SeO_2	787 sh	ν_{as} SeO_2
830 s		800 s	
872 sh	ν_s SeO_2	822 s	
900 sh		836 s	ν_s SeO_2
917 m		862 s	

anhydrous salts. The Se–O bond force constants in the SeO_2 groups lie in the regions of 528 – 535 and 540 – 567 $N m^{-1}$ for the hydrogen selenites and diselenites, respectively. The Se–O bond force constants in the SeOH groups of hydrogenselenites fall in the range 308 – 337 $N m^{-1}$, the force constants of the Se–O–Se bridge bonds in diselenites are between 229 – 268 $N m^{-1}$.

The spectra were also evaluated to obtain the hydrogen bond energies and lengths from the positions of the hydroxyl group stretching vibration bands. The energies were calculated by the method of Sokolov[20], similarly as in the case of calcium selenites[14]; the value obtained for $SrSeO_3.n H_2O$ was 38 $kJ mol^{-1}$. The hydrogen bond lengths were read from the $R_{O...O}$ *vs* $\tilde{\nu}_{OH}$ correlation diagrams[21–25]; the $R_{O...O}$ distance obtained for $SrSeO_3.n H_2O$ was 273 pm, the values for $Sr(HSeO_3)_2$ were 270 and 257 pm. For all the magnesium through strontium selenite hydrates and hydrogenselenites, the longest hydrogen bonds are found between the hydrate water molecules, the shortest, between the hydrogen selenite anions. Regarding the hydrogen bond strength, the selenite and hydrogen selenite anions can be classed among positively hydrating anions, where the hydrogen bonding between the water molecules and the anion is stronger than that between the water molecules themselves.

For the anhydrous selenites in the Mg through Ba series prepared by thermal decomposition of the selenite hydrates and diselenites, and in the case of calcium[14] also the triselenite, polymorphism is observed. In view of the marked similarity of the powder X-ray diffraction patterns of some of the anhydrous selenites, the substances can be considered to be of similar structure. Especially pronounced is the similarity between $SrSeO_3$ II (high-temperature modification) and $BaSeO_3$. In addi-

TABLE V

Force constants of the Se–O bonds in the substances studied

Substance	Grouping	k_{Se-O} $N m^{-1}$
$SrSeO_3.n H_2O$	SeO_3	496
$SrSeO_3$ anhydrous, cryst. I	SeO_3	495
$Sr(HSeO_3)_2$	SeO_2	535
	SeOH	308
$SrSe_2O_5$	SeO_2	565
	Se–O–Se	268
$BaSeO_3$	SeO_3	491
$BaSe_2O_5$	SeO_2	540
	Se–O–Se	241

tion to the temperature and way of preparation, the formation of the various modifications is obviously governed by the polarizing ability of the cation. As the polarizing ability decreases, modifications appear that for cations with a higher polarizing ability are only formed at higher temperatures.

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