Rubidium and cesium acidic selenites

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The solubility diagrams for the Rb_2SeO_3—H_2SeO_3—H_2O and Cs_2SeO_3—H_2SeO_3—H_2O systems were studied for the first time, at 298 K. On the basis of the solubility study results, the conditions for the preparation of the acidic salts, $RbHSeO_3$, $RbH_3(SeO_3)_2$, $CsHSeO_3$, and $CsH_3(SeO_3)_2$, have been refined and the compound, $CsH_5(SeO_3)_3$, that has not yet been described, has been prepared. The thermoanalytical properties and the infrared spectra of the compounds obtained were studied. The results have contributed to the clarification of the behaviour of the protons in the hydrogen bonds of the compounds studied. During the study of the thermoanalytical properties, the diselenites, $Rb_2Se_2O_5$ and $Cs_2Se_2O_5$ were found that have not yet been described.

Впервые изучены диаграммы растворимости систем Rb_2SeO_3—H_2SeO_3—H_2O и Cs_2SeO_3—H_2SeO_3—H_2O при 298 К. На основании результатов изучения растворимости были уточнены условия получения кислых солей $RbHSeO_3$, $RbH_3(SeO_3)_2$, $CsHSeO_3$ и $CsH_3(SeO_3)_2$ и получено до сего времени не описанное соединение $CsH_5(SeO_3)_3$. У полученных соединений исследовались термоаналитические свойства и инфракрасные спектры. Полученные результаты помогли объяснить поведение протонов в водородных связях, присутствующих в изучаемых соединениях. При исследовании термоаналитических свойств были найдены до сих пор не описанные диселениты $Rb_2Se_2O_5$ и $Cs_2Se_2O_5$.

Nilson [1], *Shuvalov* [2], and *Gavrilova-Podolskaya* [3] dealt with the preparation of acidic rubidium and cesium selenites and prepared the compounds, $RbHSeO_3$, $RbH_3(SeO_3)_2$, $CsHSeO_3$, and $CsH_3(SeO_3)_2$.

The thermoanalytical properties were studied for the compound $RbH_3(SeO_3)_2$ [4] and the trihydrogen-bis(selenites) of rubidium [5—8] and cesium [9—11] were characterized using the methods of structural analysis. Molecular spectroscopy methods were applied to study the compounds $CsHSeO_3$ [12], $RbH_3(SeO_3)_2$ and $CsH_3(SeO_3)_2$ [13—18]. A study of NMR [4, 19—21] and of phase transitions [2, 22—24] has contributed to the clarification of the dielectric properties of acidic rubidium and cesium selenites.

Within the framework of a systematic study of acidic selenites, as substances with important dielectric properties, the present work is directed toward charac-

terization of all the acidic salts present in the Rb_2SeO_3—H_2SeO_3—H_2O and Cs_2SeO_3—H_2SeO_3—H_2O systems at 298 K and toward refinement of the conditions for their preparation. The physicochemical properties of the compounds obtained were further studied, with a particular emphasis on the behaviour of the protons in the hydrogen bonds, from the point of view of the occupation of ordered or unordered positions in the structure.

Experimental

Chemicals and methods

Rubidium selenite, Rb_2SeO_3, and cesium selenite monohydrate, $Cs_2SeO_3 \cdot H_2O$, were prepared by neutralization of a 50% solution of selenous acid (Lachema, Brno, pure) with solid rubidium or cesium carbonate (Merck, anal. grade). The strongly hygroscopic products obtained after evaporation of the solution in a vacuum evaporator were washed with ethanol, ether and dried over phosphorus pentoxide. The compound, $Cs_2SeO_3 \cdot D_2O$, was prepared analogously, using deuterium oxide. The deuterated compounds, $RbDSeO_3$, $RbD_3(SeO_3)_2$, $CsDSeO_3$, $CsD_3(SeO_3)_2$, and $CsD_5(SeO_3)_3$, were prepared on the basis of the results of the solubility study, using Rb_2SeO_3, $Cs_2SeO_3 \cdot D_2O$ and SeO_2 (Lachema, Brno, pure).

The composition of the substances obtained was verified gravimetrically. Selenium was determined by the *Bode* method [25], rubidium and cesium in the form of M_2PtCl_6 [26], after separation of selenium. In the solubility study, selenium was determined by iodometric titration [27], rubidium and cesium by atomic absorption spectrometry on a Perkin—Elmer 306 instrument.

The thermoanalytical properties of the compounds were studied by thermogravimetry (TG), differential thermal analysis (DTA), differential compensation calorimetry (DSC), and the gradual temperature increase method. The measurements were carried out using a Derivatograph OD 102 (MOM, Budapest) at temperatures from 298 to 873 K, with a linear temperature increase of 5 K min^{-1} The DSC curves were obtained using a Perkin—Elmer DSC-4 calorimeter, a thermoanalytical regulator 7/4 and a TADS data station. The measurement was performed within a temperature interval from 303 to 575 K, at a heating rate of 10 K min^{-1} The thermoanalytical curves were obtained by the method of gradually increased temperature in a controllable electric oven, in an interval of 298 to 728 K, increasing the temperature by 10 K every 24 hours.

The X-ray powder patterns were obtained on a Mikrometa 2 instrument (Chirana, Czechoslovakia), using a chamber with a diameter of 57.3 mm and an iron filter, with exposure times of 100 to 120 min, a voltage of 35 kV and a current of 20 mA.

The infrared spectra were measured on a UR-20 instrument (Zeiss, Jena) over a range of $\tilde{v} = 4000$ to 400 cm^{-1}, in a nujol mull, using potassium bromide cells. Measurements were also carried out in a range of $\tilde{v} = 1600$ to 4000 cm^{-1} by the tripene mull method.

Solubility study in the Rb_2SeO_3—H_2SeO_3—H_2O system at 298 K

The Schreinemakers method was used and the resultant phase diagram is given in Fig. 1. It follows from the diagram that, in addition to the initial substances (crystallization fields *I* and *VI*), two acidic salts are formed in the system: rubidium trihydrogen--bis(selenite), $RbH_3(SeO_3)_2$ (crystallization field *II*) and rubidium hydrogen selenite, $RbHSeO_3$ (crystallization field *IV*). Fields *III* and *V* describe an equilibrium between two solid phases and solutions with compositions determined by invariant points *A* (w_i: 54.8% Rb_2SeO_3, 33.2% H_2SeO_3, 12.0% H_2O) and *B* (w_i: 71.2% Rb_2SeO_3, 15.3% H_2SeO_3 and 13.5% H_2O). A melt exists in the system within $w_i = 71.6$—75.6% H_2SeO_3.
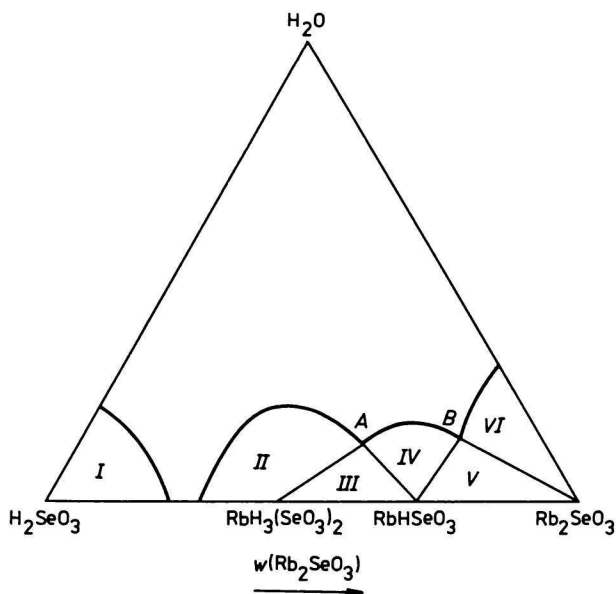
Fig. 1. Solubility diagram in the Rb_2SeO_3—H_2SeO_3—H_2O system at 298 K.

The ratios of mass amounts of the initial compounds, $n(Rb_2SeO_3):n(H_2SeO_3):$ $:n(H_2O)$, leading in the preparation to the highest yields of acidic rubidium selenites, were determined from the solubility diagram and amounted to 1 3.1 7.5 for $RbH_3(SeO_3)_2$ and $1:0.95:3.5$ for $RbHSeO_3$. The compounds obtained were filtered off under a nitrogen atmosphere, washed with chloroform and dried over phosphorus pentoxide. The isolated substances are crystalline, colourless and $RbHSeO_3$ is hygroscopic. The gravimetrical results correspond to the calculated values. For $RbH_3(SeO_3)_2$ w_i (found): 24.78% Rb and 46.1% Se; w_i(calc.): 24.96% Rb and 46.12% Se. For $RbHSeO_3$ w_i (found): 39.92% Rb and 36.79% Se; w_i(calc.): 40.04% Rb and 36.99% Se.

Solubility study in the Cs_2SeO_3—H_2SeO_3—H_2O system at 298 K

It can be seen from the phase diagram (Fig. 2) that, in addition to the initial substances (crystallization fields *I* and *IX*), three acidic salts are formed in the system: cesium pentahydrogen-tris(selenite), $CsH_5(SeO_3)_3$ (crystallization field *III*), cesium trihydrogen--bis(selenite), $CsH_3(SeO_3)_2$ (crystallization field *V*), and cesium hydrogen selenite, $CsHSeO_3$. Fields *II, IV, VI*, and *VIII* represent an equilibrium between two solid phases and solutions with compositions determined by invariant points *A* (w_i: 19% Cs_2SeO_3, 74.2% H_2SeO_3, 6.8% H_2O), *B* (w_i: 31.00% Cs_2SeO_3, 48.5% H_2SeO_3, 20.5% H_2O), *C* (w_i: 59.9% Cs_2SeO_3, 22.1% H_2SeO_3, 18.0% H_2O), and *D* (w_i: 79.0% Cs_2SeO_3, 8.0% H_2SeO_3, 13.0% H_2O).
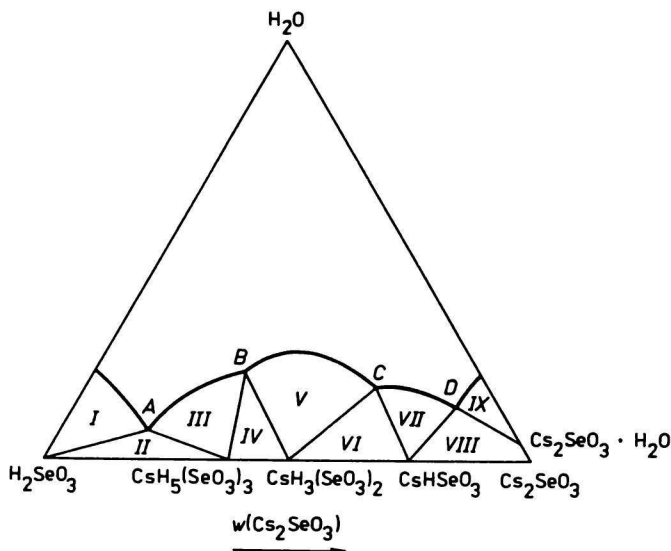
Fig. 2. Solubility diagram in the Cs_2SeO_3—H_2SeO_3—H_2O system at 298 K.

From the solubility diagram, the mass amount ratios, $n(Cs_2SeO_3 \cdot H_2O) : n(H_2SeO_3) : n(H_2O)$, were obtained that lead to the highest yields of cesium acidic selenites, namely, 1 : 7.5 : 14.3 for $CsH_5(SeO_3)_3$, 1 : 2.7 : 12.5 for $CsH_3(SeO_3)_2$, and 1 : 0.8 : 5.1 for $CsHSeO_3$. The compounds obtained by heterogeneous reactions, except for $CsHSeO_3$, were filtered off in the air, washed with ethanol and ether. The strongly hygroscopic compound $CsHSeO_3$ was filtered off and stored under a nitrogen atmosphere. The isolated compounds are crystalline and colourless substances and the gravimetrical results correspond to the calculated values. For $CsH_5(SeO_3)_3$ w_i(found): 25.53% Cs and 45.58% Se; w_i (calc.): 25.62% Cs and 45.60% Se. For $CsH_3(SeO_3)_2$ w_i (found): 33.97% Cs and 40.49% Se; w_i(calc.): 34.09% Cs and 40.51% Se. For $CsHSeO_3$ w_i(found): 50.79% Cs and 30.11% Se; w_i(calc.): 50.94% Cs and 30.27% Se.

Table 1

Thermal analysis of rubidium selenites using the TG, DTA, and DSC methods

TG	DTA	DSC	Assignment
w/mass % T/K	Effect T/K	Effect T/K	
		RbHSeO$_3$	
1.05 335—400	*endo* 335—355	*endo* 340—345	incongruent fusion and evaporation of part of H$_2$O
4.45 400—470	*endo* 400—415 460—465	*endo* 395—405	H$_2$O evaporation with formation of Rb$_2$Se$_2$O$_5$
	endo 555—575	*endo* 545—555	polymorphous transition
14.80 665	*endo* 675—875		decomposition and partial oxidation to Rb$_2$SeO$_4$, sublimation of SeO$_2$
		RbH$_3$(SeO$_3$)$_2$	
0.70 315—405	*endo* 315—335	*endo* 320—325	incongruent fusion and evaporation of part of H$_2$O
8.05 405—455	*endo* 405—435	*endo* 405—420	evaporation of H$_2$O with formation of Rb$_2$Se$_2$O$_5$ and SeO$_2$
53.50 525—875	*endo* 525—655 815—875		SeO$_2$ sublimation, decomposition and partial oxidation to Rb$_2$SeO$_4$

Thermoanalytical properties, infrared spectra, and X-ray powder patterns

The results of the study of the thermoanalytical properties of the studied compounds are given in Tables 1 to 4. The intermediates and the final products were identified analytically, by X-ray powder patterns and by infrared spectroscopy.

The infrared spectra of the studied compounds are given in Tables 5 to 10, using common abbreviations; "X" denotes a hydrogen or deuterium atom and $^+$SeO$_3^{2-}$ a selenite anion bonded by a hydrogen bond with protons in unordered positions. The newly prepared compounds, except for cesium diselenite that did not yield a powder pattern, were characterized by X-ray patterns. The interplanar distances are given in pm and the numbers in parentheses specify the relative intensities, 1 to 5, determined visually.

CsH$_5$(SeO$_3$)$_3$: 611 (2), 377.0 (7), 349.3 (10), 306.9 (9), 287.6 (2), 279.7 (1), 269.0 (1), 249.5 (2), 240.4 (3), 226.5 (5), 223.3 (3), 212.7 (4), 204.5 (3), 201.9 (2), 192.9 (1), 184.5 (4), 182.1 (1), 175.2 (3), 168.1 (1), 161.6 (3), 157.5 (3), 154.2 (2), 150.1 (2), 148.2 (2), 144.3 (1),

Thermal analysis of rubidium selenites by the method of gradually increased temperature

T/K	$w/mass \%$	Assignment
	$RbHSeO_3$	
320—355	4.65	decomposition to $Rb_2Se_2O_5$ and H_2O, evaporation of H_2O
600—725	25.5	decomposition and partial oxidation to Rb_2SeO_4, sublimation of SeO_2
	$RbH_3(SeO_3)_2$	
320—405	8.15	decomposition to $Rb_2Se_2O_5$, SeO_2, and H_2O, evaporation of H_2O
455—585	39.95	SeO_2 sublimation
585—615	$Rb_2Se_2O_5$	
615—725	54.90	decomposition and partial oxidation to Rb_2SeO_4, SeO_2 sublimation

142.3 (1), 139.1 (1), 134.9 (2), 132.8 (3), 129.4 (1), 124.9 (1), 122.0 (1), 118.8 (1), 115.7 (1), 113.8 (1), 110.6 (1), 108.7 (1), 105.8 (1).

$Rb_2Se_2O_5$: 453 (1), 337.6 (1), 311.0 (10), 301.8 (1), 286.7 (7), 278.0 (1), 268.3 (1), 261.4 (3), 257.1 (3), 235.0 (1), 225.4 (1), 204.5 (4), 187.0 (5), 169.2 (8), 161.8 (1), 157.5 (3), 152.6 (2), 146.9 (2), 145.5 (2), 142.9 (1), 139.3 (2), 134.9 (2), 131.9 (2), 125.5 (1), 122.9 (1), 121.1 (2), 120.1 (2), 116.8 (1), 115.4 (2), 108.1 (2).

Discussion

In the Rb_2SeO_3—H_2SeO_3—H_2O system, congruently soluble compounds with the compositions, $n(Rb):n(Se):n(H_2O) = 2:2:1$ and $2:4:3$, have been found at 298 K. The analysis of the infrared spectra and the thermoanalytical curves has demonstrated that the compounds are rubidium hydrogen selenite and trihydrogen-bis(selenite) that have been described in the literature [1].

The study of the Cs_2SeO_3—H_2SeO_3—H_2O system has shown that the heterogeneous reaction at 298 K produces congruently soluble compounds with the composition $n(Cs):n(Se):n(H_2O) = 2:2:1$, $2:4:3$, and $2:6:5$. It follows from the physicochemical study that the former two substances are cesium hydrogen selenite, $CsHSeO_3$, and trihydrogen-bis(selenite), $CsH_3(SeO_3)_2$, known from the literature [2]. The latter compound is cesium pentahydrogen-tris(selenite), $CsH_5(SeO_3)_3$, that has not yet been described in the literature.

In dependence on the type of the salts formed, the studied systems can be

Table 3

Thermal analysis of cesium selenites using the TG, DTA, and DSC methods

TG	DTA	DSC	Assignment
w/mass % T/K	Effect T/K	Effect T/K	
		$CsHSeO_3$	
0.70 350—365	*endo* 345—365	*endo* 355—365	incongruent melting and evaporation of part of H_2O
3.65 370—460	*endo* 375—385 445—455	*endo* 375—385 390—400	H_2O evaporation with formation of $Cs_2Se_2O_5$
	endo 505—535	*endo* 495—500	polymorphous transition
14.95 655—875	*endo* 665—875		decomposition and oxidation to Cs_2SeO_4, SeO_2 sublimation
		$CsH_3(SeO_3)_2$	
0.40 320—400	*endo* 330—355	*endo* 350—355	incongruent melting and evaporation of part of H_2O
7.25 400—455	*endo* 400—425	*endo* 395—400	H_2O evaporation with formation of $Cs_2Se_2O_5$ and SeO_2
48.55 525—875	*endo* 815—875		SeO_2 sublimation, decomposition and oxidation to Cs_2SeO_4
		$CsH_5(SeO_3)_3$	
	endo 315—335	*endo* 325—335	incongruent melting
8.50 335—430	*endo* 385—430	*endo* 345—395	H_2O evaporation with formation of $Cs_2Se_2O_5$ and SeO_2
60.15 515—825	*endo* 545—575 655—705		SeO_2 sublimation, decomposition and oxidation to Cs_2SeO_4

compared with the systems of the selenites of the other alkali metals [28—30] and the ammonium cation [31], with which, similar to rubidium and cesium, acidic salts of the types, $MHSeO_3$ and $MH_3(SeO_3)_2$, have been found at 298 K. An acidic selenite with the ratio $n(Se):n(M) > 2:1$, analogous to the newly obtained salt $CsH_5(SeO_3)_3$, has only been known with sodium, with the composition $NaH_7(SeO_3)_4$.

The study of the thermoanalytical curves for $RbHSeO_3$ and $CsHSeO_3$ has shown that the thermal decomposition of these substances is characterized by a

Table 4

Thermal analysis of cesium selenites using the method of gradually increasing temperature

T/K	w/mass %	Assignment
	CsHSeO$_3$	
345—425	3.60	decomposition to Cs$_2$Se$_2$O$_5$ and H$_2$O, H$_2$O evaporation
480—725	20.95	decomposition and oxidation to Cs$_2$SeO$_4$, SeO$_2$ sublimation
	CsH$_3$(SeO$_3$)$_2$	
335—425	6.85	decomposition to Cs$_2$Se$_2$O$_5$, SeO$_2$, and H$_2$O, H$_2$O evaporation
455—695	48.60	SeO$_2$ sublimation, decomposition and oxidation to Cs$_2$SeO$_4$
	CsH$_5$(SeO$_3$)$_3$	
315—430	8.85	decomposition to Cs$_2$Se$_2$O$_5$, SeO$_2$, and H$_2$O, H$_2$O evaporation
445—675	60.85	SeO$_2$ sublimation, decomposition and oxidation to Cs$_2$SeO$_4$

Table 5

Infrared spectra of RbHSeO$_3$ and RbDSeO$_3$

RbHSeO$_3$ $\tilde{v}$(I)/cm^{-1}	RbDSeO$_3$ $\tilde{v}$(II)/cm^{-1}	$\tilde{v}$(I)/$\tilde{v}$(II)	Assignment
406 s	400 s	1.02	δ(SeO$_2$)
617 s	605 s	1.02	v(SeO)(SeOX)
795 s	797 s	1.00	v_{as}(SeO)(SeO$_2$)
855 s	860 s	0.99	v_s(SeO)(SeO$_2$)
1178	875 sh	1.35	δ(SeOX)
1640—1720 w	1220—1260 w	1.33	
2100—2500 m, b (max. 2350)	1550—1900 m, b (max. 1750)	1.34	v(OX)(SeOX)
2600—3200 s, b (max. 3000)	1940—2400 s, b (max. 2250)	1.34	

Table 6

Infrared spectra of $CsHSeO_3$ and $CsDSeO_3$

$CsHSeO_3$ $\tilde{\nu}(I)/cm^{-1}$	$CsDSeO_3$ $\tilde{\nu}(II)/cm^{-1}$	$\tilde{\nu}(I)/\tilde{\nu}(II)$	Assignment
421 w	412 w	1.02	$\delta(SeO_2)$
590 s	577 s	1.02	
608 s	598 s	1.02	$\nu(SeO)(SeOX)$
779 s	780 s	1.00	$\nu_{as}(SeO)(SeO_2)$
855 s	845 s	1.00	$\nu_s(SeO)(SeO_2)$
960 sh			$\gamma(OX)(SeOX)$
1278 m	933 m	1.36 ⎫	$\delta(SeOX)$
1310 sh		⎭	
1620—1720 w	1200—1260 w	1.35 ⎫	
2100—2600 s, b	1700—1900 s, b	1.32 ⎪	
(max. 2400)	(max. 1830)	⎬	$\nu(OX)(SeOX)$
2650—3200 s, b	1950—2400 s, b	1.34 ⎪	
(max. 2820)	(max. 2100)	⎭	

Table 7

Infrared spectra of $RbH_3(SeO_3)_2$ and $RbD_3(SeO_3)_2$

$RbH_3(SeO_3)_2$ $\tilde{\nu}(I)/cm^{-1}$	$RbD_3(SeO_3)_2$ $\tilde{\nu}(II)/cm^{-1}$	$\tilde{\nu}(I)/\tilde{\nu}(II)$	Assignment
410 s	415 s	0.99	$\delta(SeO_2)(XSeO_3^-)$
435 m	435 m	1.00	$\delta(SeO_2)(X_2SeO_3)$
	505 m		
665 s	661 s	1.01	$\nu(SeOX)(XSeO_3^-)$, $\nu_s(SeO_2)(X_2SeO_3)$
680 sh	685 sh	0.99	$\nu_{as}(SeO_2)(X_2SeO_3)$
770 s	780 s	0.99	$\nu_{as}(SeO_2)(XSeO_3^-)$
840 s	845 s	0.99	$\nu_s(SeO)(X_2SeO_3)$
885 s	890 s	0.99	$\nu_s(SeO_2)(XSeO_3^-)$
1160 w	915 m	1.28 ⎫	$\delta(SeOX)$
1220 w	955 m	1.28 ⎭	
1620 w, b	1230 w, b	1.31 ⎫	
1900—2500 s, b	1700—1900 s, b	1.32 ⎪	
(max. 2350)	(max. 1780)	⎬	$\nu(OX)(SeOX)$
2650—3300 s, b	1900—2500 s, b	1.34 ⎪	
(max. 2750)	(max. 2050)	⎭	

Table 8

Infrared spectra of $CsH_3(SeO_3)_2$ and $CsD_3(SeO_3)_2$

$CsH_3(SeO_3)_2$ $\tilde{\nu}(I)/cm^{-1}$	$CsD_3(SeO_3)_2$ $\tilde{\nu}(II)/cm^{-1}$	$\tilde{\nu}(I)/\tilde{\nu}(II)$	Assignment
405 s	402 s	1.00	$\delta(SeO_2)$
655 s	655 s	1.00	$\nu(SeO)(SeOX)$, $\nu_{s,\,as}(SeO_2)(^+SeO_3^{2-})$
770 s	775 s	0.99	$\nu_{as}(SeO)(SeO_2)$
835 s	835 s	1.00	$\nu_s(SeO)(SeO_2)$, $\nu_s(SeO)(^+SeO_3^{2-})$
1175 sh			$\delta(SeOX)$
1230 m	925 m	1.33	
1620 w, b	1230 w, b	1.32	
2000—2550 s, b (max. 2350)	1700—1900 s, b (max. 1780)	1.32	$\nu(OX)(SeOX)$
2600—3300 s, b (max. 2750)	1950—2500 s, b (max. 2100)	1.31	

Table 9

Infrared spectra of $CsH_5(SeO_3)_3$ and $CsD_5(SeO_3)_3$

$CsH_5(SeO_3)_3$ $\tilde{\nu}(I)/cm^{-1}$	$CsD_5(SeO_3)_3$ $\tilde{\nu}(II)/cm^{-1}$	$\tilde{\nu}(I)/\tilde{\nu}(II)$	Assignment
432 s	427 s	1.01	$\delta(SeO_2)(XSeO_3^-)$, (X_2SeO_3)
615 s	615 s	1.00	$\nu(SeOX)(XSeO_3^-)$
653 s	660 s	0.99	
678 s	683	0.99	$\nu_s(SeO_2)(X_2SeO_3)$
725 s	725 m	1.00	$\nu_{as}(SeO_2)(X_2SeO_3)$
824 m	833 m	0.99	$\nu_{as}(SeO_2)(XSeO_3^-)$, $\nu_s(SeO)(X_2SeO_3)$
860 s	860 s	1.00	$\nu_s(SeO_2)(XSeO_3^-)$
886 sh	895 m	0.99	
1050 m			$\delta(SeOX)$
1170 w			
1248 m	928 sh	1.34	
1650 w, b	1250 w, b	1.32	
2000—2500 s, b (max. 2450)	1700—1900 s, b (max. 1800)	1.35	$\nu(OX)(SeOX)$
2600—3400 s, b (max. 2750, 3270)	1950—2500 s, b (max. 2100, 2450)	1.33	

Table 10

Infrared spectra of $Rb_2Se_2O_5$ and $Cs_2Se_2O_5$

$Rb_2Se_2O_5$ $\tilde{v}/cm^{-1}$	$Cs_2Se_2O_5$ $\tilde{v}/cm^{-1}$	Assignment
	400 s	$\delta(SeO_2)$
450 s	439 m	$v_s(SeO)(SeOSe)$
525 s	535 s	$v_{as}(SeO)(SeOSe)$
	643 sh	
823 s	800 s ⎫	
838 s	835 s ⎬	$v_{as}(SeO)(SeO_2)$
865 s	890 m	$v_s(SeO)(SeO_2)$

process during which they are converted into diselenites that have not yet been described in the literature, with liberation of water

$$2MHSeO_3 \quad \rightarrow \quad M_2Se_2O_5 + H_2O \qquad (A)$$
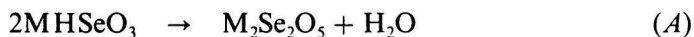
The temperatures found for this decomposition correspond to the stability of the hydrogen bonds present in the hydrogen selenites. The lower value of the wavenumber of the bonding vibration of hydroxyl group, $\delta(SeOH)$, found in the infrared spectrum of $RbHSeO_3$, compared with that of $CsHSeO_3$, is caused by a greater length of the hydrogen bond [32] and the lower temperature of the decomposition of the rubidium salt. The infrared spectra of the newly obtained diselenites, $Rb_2Se_2O_5$ and $Cs_2Se_2O_5$, are given in Table 10. The thermal decomposition of the diselenites formed from the acidic salts proceeds through a polymorphous transition, which has also been confirmed by the gradual temperature increase method. The following decomposition of the new modifications is accompanied by the oxidation of the compound to selenate, as verified analytically, by X-ray patterns and by the infrared spectra. Whereas the oxidation of the rubidium salt is only partial within the studied temperature range, it is complete for the cesium salt.

The initial process in the thermal decomposition of the acidic selenites, $RbH_3(SeO_3)_2$ and $CsH_3(SeO_3)_2$ can be expressed by the equation

$$2MH_3(SeO_3)_2 \quad \rightarrow \quad M_2Se_2O_5 + 2SeO_2 + 3H_2O \qquad (B)$$
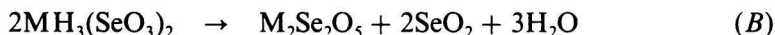
The studied compounds first melt incongruently and the water liberated is only evaporated at a higher temperature. A further increase in the temperature leads to the sublimation of selenium dioxide that strongly affects the shapes of the thermoanalytical curves. As the sublimation is not complete at the onset of the diselenite decomposition, no lags corresponding to the existence of these sub-

stances were found on the TG curves, except for the thermoanalytical curve of $RbH_3(SeO_3)_2$ obtained by the gradual temperature increase method. However, pure $Cs_2Se_2O_5$ cannot be prepared from $CsH_3(SeO_3)_2$ even when using the latter method.

The $CsH_5(SeO_3)_3$ decomposition is characterized in the initial stage, similar to the above acidic salts, by incongruent melting followed by evaporation of water with the formation of the diselenite, according to the equation

$$2CsH_5(SeO_3)_3 \quad \rightarrow \quad Cs_2Se_2O_5 + 4SeO_2 + 5H_2O \qquad (C)$$

The further decomposition is analogous to that of $CsH_3(SeO_3)_2$ and again a lag corresponding to the existence of the diselenite alone has not been found.

The study of the infrared spectra of rubidium and cesium acidic selenites was mainly directed toward the clarification of the behaviour of protons in the hydrogen bonds, from the point of view of their ordering, as they decisively influence the dielectric properties of the compounds. In the spectra of $RbHSeO_3$ and $CsHSeO_3$, bands characteristic of symmetric and antisymmetric stretching vibrations of the SeO_2 group were found, together with a stretching vibration band of the SeO(H) group. These bands indicate the presence of the $HSeO_3^-$ anion with the C_s symmetry. Moreover, the characteristic intense band of bending vibration of the HO(Se) group that was found with both the salts fully corresponds to an asymmetric location of a proton along a hydrogen bond in an ordered position, *i.e.* at lower levels of a two-minimum potential function. A low probability of proton tunnelling [33] corresponds to this arrangement.

The infrared spectra of the compounds $RbH_3(SeO_3)_2$ and $CsH_3(SeO_3)_2$ markedly differ in the number of the absorption bands. In the spectrum of the rubidium salt, bands corresponding to the vibrations of the $HSeO_3$ and H_2SeO_3 groups are found, which can only be present when the protons occupy ordered positions in the structure, with a minimum probability of tunnelling. This conclusion is also confirmed by the three Se—O distances obtained in the study of the structure [5—8], corresponding to the values found for the Se—OH group. In the $CsH_3(SeO_3)_2$ structure [9—11], the SeO_3 groups are connected by 4 hydrogen bonds with the protons in unordered positions with a high probability of tunnelling. The fifth hydrogen bond has a proton in an unordered position, but the probability of its occurrence at one of the oxygen atoms predominates at a ratio of 68:32. This fact is reflected in the $CsH_3(SeO_3)_2$ spectrum by bands characteristic of the $HSeO_3$ group and simultaneously of the selenite anion with oxygen atoms to which belong protons exhibiting a tunnel effect.

The $CsH_5(SeO_3)_3$ spectrum contains absorption bands corresponding to vibrations of the $HSeO_3$ and H_2SeO_3 groups. The protons are, therefore, located symmetrically along the hydrogen bond, with a minimum possibility of tunnelling. This is also indicated by the three absorption bands in the region of the

bending vibrations of the (Se)OH group, that belong to variously long hydrogen bonds with the protons in ordered positions. On the other hand, broad bands corresponding to the selenite anion with protons in unordered positions have not been found in the spectrum.

In the region of stretching vibrations of the Se(OH) group, three broad absorption bands were found for all the studied acidic salts; these bands have also been found with other acidic selenites of the alkali metals that belong among the KDP type ferroelectrics [15]. The similarity of the spectra of these substances within the region discussed is caused by a slow interbond tunnel effect [34].

The character of the infrared spectra of $Rb_2Se_2O_5$ and $Cs_2Se_2O_5$ has fully demonstrated that the molecules contain bridging diselenite groups, Se—O—Se. Further, the spectra indicate a decrease in the C_{2v} symmetry of the anion, which is reflected in splitting of the degenerate vibration of the group, $v_{as}(SeO_2)$.

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