

Lithium and thallium(I) selenites

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The solubility diagrams of the $\text{Li}_2\text{SeO}_3\text{—H}_2\text{SeO}_3\text{—H}_2\text{O}$ and $\text{Tl}_2\text{SeO}_3\text{—H}_2\text{SeO}_3\text{—H}_2\text{O}$ systems were studied for the first time at 298 K. On the basis of the study of solubility, the conditions for the preparation of the substances were refined and the following lithium compounds were prepared: $\text{Li}_2\text{SeO}_3 \cdot \text{H}_2\text{O}$, LiHSeO_3 , and $\text{LiH}_3(\text{SeO}_3)_2$; the prepared thallium compounds involved $\text{TlH}_3(\text{SeO}_3)_2$ and the compound $\text{Tl}_2\text{Se}_2\text{O}_5$ that has not yet been described. The thermoanalytical properties and the IR spectra were studied for all the compounds prepared. On the basis of the results obtained, hydrogen bonding in $\text{Li}_2\text{SeO}_3 \cdot \text{H}_2\text{O}$ was characterized and the behaviour of protons in the hydrogen bonds in acid salts was described from the point of view of the occupation of ordered or disordered positions.

Впервые изучены при 298 К диаграммы растворимости $\text{Li}_2\text{SeO}_3\text{—H}_2\text{SeO}_3\text{—H}_2\text{O}$ и $\text{Tl}_2\text{SeO}_3\text{—H}_2\text{SeO}_3\text{—H}_2\text{O}$. На основании изучения растворимости были уточнены условия получения веществ и были приготовлены следующие соединения лития: $\text{Li}_2\text{SeO}_3 \cdot \text{H}_2\text{O}$, LiHSeO_3 и $\text{LiH}_3(\text{SeO}_3)_2$; полученные соединения таллия включали $\text{TlH}_3(\text{SeO}_3)_2$ и соединение $\text{Tl}_2\text{Se}_2\text{O}_5$, не описанное ранее. Изучены термоаналитические свойства и ИК-спектры всех полученных соединений. На основе полученных результатов была охарактеризована водородная связь в $\text{Li}_2\text{SeO}_3 \cdot \text{H}_2\text{O}$, а также поведение протонов в водородных связях в кислых солях было описано с точки зрения занятости упорядоченных или неупорядоченных положений.

Lithium selenites were prepared for the first time by Nilson [1], Rosenheim and Krause [2] who described substances with the compositions of Li_2SeO_3 , $\text{Li}_2\text{SeO}_3 \cdot \text{H}_2\text{O}$, $\text{Li}_2\text{SeO}_3 \cdot 3/4\text{H}_2\text{O}$, LiHSeO_3 , and $\text{LiH}_3(\text{SeO}_3)_2$. A recent study of lithium selenites added lithium diselenite, $\text{Li}_2\text{Se}_2\text{O}_5$, to this series and refined some preparation methods [3—6]. The preparation of thallium(I) selenites was first dealt with by Kuhlmann [7] and Nilson [8], who obtained the compounds Tl_2SeO_3 , TlHSeO_3 , and $\text{TlH}_3(\text{SeO}_3)_2$.

The properties of lithium selenites have been predominantly studied with acid salts. The crystal structures of the compounds LiHSeO_3 [9] and $\text{LiH}_3(\text{SeO}_3)_2$ [10—13] were described, as well as their IR and Raman spectra [14—17]. The thermoanalytical properties of acid lithium selenites were studied by *Selivanova* and *Roshchina* [18, 19]. Among the properties of thallium(I) selenites, the molar conductivity of aqueous solutions [20] and some thermodynamic properties of Tl_2SeO_3 [21, 22] were studied.

In the framework of a systematic study of selenites as potential ferroelectrics the present paper deals with characterization of all selenites present in the $\text{Li}_2\text{SeO}_3\text{—H}_2\text{SeO}_3\text{—H}_2\text{O}$ and $\text{Tl}_2\text{SeO}_3\text{—H}_2\text{SeO}_3\text{—H}_2\text{O}$ systems at 298 K and with a refinement of the conditions for their preparation. The physicochemical properties of the compounds obtained were further studied, with a special emphasis on the behaviour of protons in hydrogen bonds.

Experimental

Chemicals and methods

Lithium selenite monohydrate, $\text{Li}_2\text{SeO}_3 \cdot \text{H}_2\text{O}$, was prepared by neutralization of a 30 % solution of selenious acid (Lachema, Brno, pure) with solid lithium carbonate (Lachema, Brno, anal. grade). The product separated was washed with ethanol and ether and was dried in the air at laboratory temperature. Anhydrous thallium(I) selenite, Tl_2SeO_3 , was prepared by neutralization of a saturated solution of thallium(I) carbonate (Merck) by a 1 % excess of a 30 % solution of selenious acid at 353 K. The crystals that separated on cooling were filtered off, washed with chloroform and dried in the air at laboratory temperature. The deuterated compounds, $\text{Li}_2\text{SeO}_3 \cdot \text{D}_2\text{O}$, LiDSeO_3 , $\text{LiD}_3(\text{SeO}_3)_2$, and $\text{TlD}_3(\text{SeO}_3)_2$, were prepared on the basis of the results of the solubility study, using the above salts of the studied metals, SeO_2 (Lachema, Brno, pure) and D_2O .

The composition of the substances obtained was verified gravimetrically. Selenium was determined by a modified *Bode* method [23], lithium and thallium were determined in the form of Li_3PO_4 [24] and TlI [25], after separation of selenium. Titration analysis was used in the solubility study. Selenium(IV) was determined iodometrically [26], thallium(I) was oxidized to thallium(III) by bromine water after addition of potassium tartrate and, after pH adjustment, titrated with EDTA using Methylthymol Blue as the indicator [27]. Lithium was determined by atomic absorption spectrometry (AAS) on a Perkin—Elmer 306 instrument at 670.8 nm, in an acetylene—air flame.

The IR spectra were obtained on a UR-20 instrument (Zeiss, Jena), from 400 to 4000 cm^{-1} in a nujol mull and using potassium bromide cells. The measurements in tripene were also carried out within a region from 1600 to 4000 cm^{-1} .

The thermoanalytical properties of the compounds were studied thermogravimetrically (TG), by differential thermal analysis (DTA) and by the method of gradually increased temperature. The measurements were carried out using a Derivatograph type OD 102

instrument (MOM, Budapest), at temperatures from 298 to 873 K, with a linear temperature increase of 5 K min^{-1} . A regulated electric oven was used in the method of gradually increased temperature. The temperature was increased by 10 K per 24 h, over a range from 298 to 728 K.

Solubility study in the $\text{Li}_2\text{SeO}_3\text{—H}_2\text{SeO}_3\text{—H}_2\text{O}$ system at 298 K

The Schreinemakers method was used to study the solubility and the resultant phase diagram is given in Fig. 1. It follows from the diagram that, in addition to the initial substances — selenious acid (crystallization field *I*) and lithium selenite monohydrate (crystallization field *VII*), two acid salts are formed in the system, namely, lithium trihydrogen-bis(selenite), $\text{LiH}_3(\text{SeO}_3)_2$ (crystallization field *III*) and lithium hydrogen selenite, LiHSeO_3 (crystallization field *V*). The equilibrium between two solid phases and solutions with the compositions (w_i) of invariant points *A* (3.6 % Li_2SeO_3 ; 78.3 % H_2SeO_3 ; 18.1 % H_2O), *B* (28.4 % Li_2SeO_3 ; 37.8 % H_2SeO_3 ; 33.8 % H_2O), and *C* (33.1 % Li_2SeO_3 ; 31.3 % H_2SeO_3 ; 35.6 % H_2O) is described by fields *II*, *IV*, and *VI*.

In field *III*, at the liquid phase composition given by point *B*, a phase reaction occurs producing trihydrogen-bis(selenite)



Analogously, in field *V*, a phase reaction takes place at the liquid phase composition given by point *C*, with the formation of hydrogen selenite

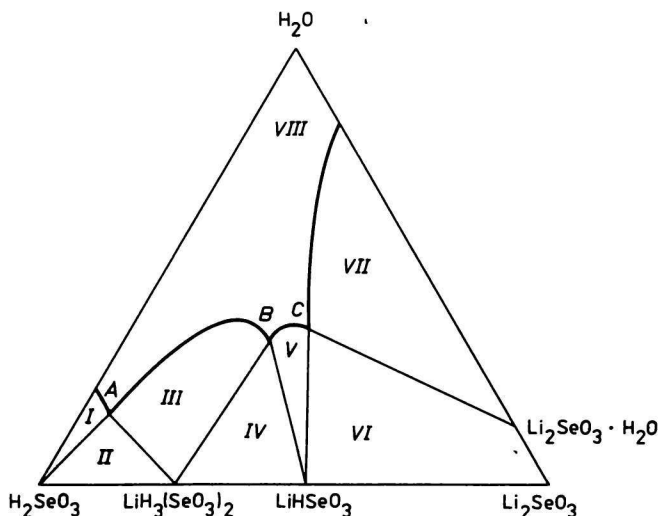
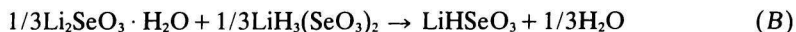


Fig. 1. Solubility diagram of the $\text{Li}_2\text{SeO}_3\text{—H}_2\text{SeO}_3\text{—H}_2\text{O}$ system at 298 K ($w_i/\%$).

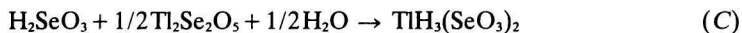
On the basis of the solubility study, the compounds $\text{LiH}_3(\text{SeO}_3)_2$ and LiHSeO_3 were prepared. The compounds formed by heterogeneous reactions were filtered off on an S2 frit, washed with chloroform and dried in the air at laboratory temperature. The isolated compounds are colourless, crystalline compounds. The results of the gravimetric analysis correspond to the calculated values.

For $\text{LiH}_3(\text{SeO}_3)_2$ ($M_r = 263.88$) $w_i(\text{found})$: 2.60 % Li, 59.73 % Se; $w_i(\text{calc.})$: 2.63 % Li, 59.84 % Se. For LiHSeO_3 ($M_r = 134.90$) $w_i(\text{found})$: 5.06 % Li, 58.40 % Se; $w_i(\text{calc.})$: 5.14 % Li, 58.53 % Se.

Solubility study in the Tl_2SeO_3 — H_2SeO_3 — H_2O system at 298 K

It follows from the phase diagram (Fig. 2) that, in addition to the initial substances — selenious acid (crystallization field I) and thallium(I) selenite (crystallization field VI), two substances are formed in the system, namely, thallium(I) trihydrogen-bis(selenite), $\text{TlH}_3(\text{SeO}_3)_2$ (crystallization field II) and thallium(I) diselenite, $\text{Tl}_2\text{Se}_2\text{O}_5$ (crystallization field IV). The equilibrium between two solid phases and solutions with the compositions (w_i) of invariant points C (63.0 % Tl_2SeO_3 ; 31.4 % H_2SeO_3 ; 5.6 % H_2O) and D (30.5 % Tl_2SeO_3 ; 9.0 % H_2SeO_3 ; 60.5 % H_2O) is described by fields III and V.

In field III, at the liquid phase composition given by point C, a phase reaction takes place giving rise to trihydrogen-bis(selenite)



and in field V, at the liquid phase composition given by point D, a phase reaction leads to the formation of diselenite

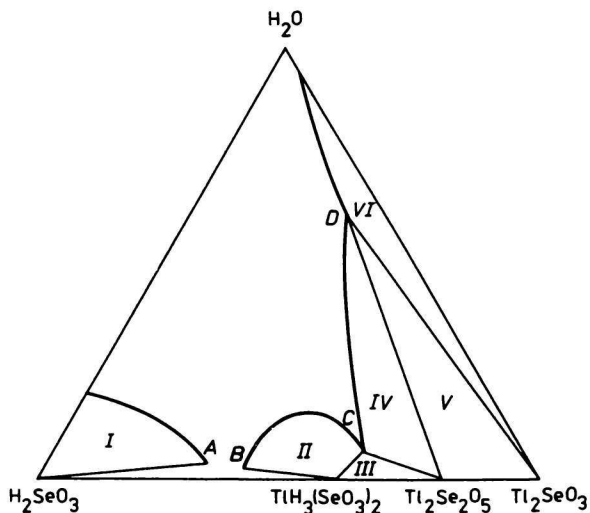
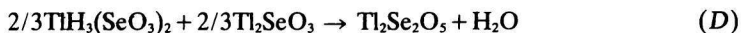


Fig. 2. Solubility diagram of the Tl_2SeO_3 — H_2SeO_3 — H_2O system at 298 K ($w_i/\%$).

In the study of the solubility diagram the compounds $\text{Tl}_2\text{Se}_2\text{O}_5$ and $\text{TlH}_3(\text{SeO}_3)_2$ were isolated. The substances were filtered off on an S2 frit, residues of H_2SeO_3 were removed, the substances were washed with ethanol and dried in the air at laboratory temperature. Both the compounds are white, finely crystalline substances, readily soluble in water. The results of the analysis for selenium and thallium are in agreement with the theoretical values.

For $\text{Tl}_2\text{Se}_2\text{O}_5$ ($M_r = 646.60$) $w_i(\text{found})$: 63.14 % Tl, 24.27 % Se; $w_i(\text{calc.})$: 63.21 % Tl, 24.42 % Se. For $\text{TlH}_3(\text{SeO}_3)_2$ ($M_r = 461.31$) $w_i(\text{found})$: 44.33 % Tl, 16.79 % Se; $w_i(\text{calc.})$: 44.30 % Tl, 17.12 % Se.

Thermoanalytical properties and infrared spectra

The results of the study of the thermoanalytical properties of the investigated compounds are given in Tables 1 to 4. The intermediates and the final products were studied analytically and by IR spectroscopy.

Table 1

Thermal analysis of lithium selenites using the TG and DTA methods

T/K	TG	DTA	Assignment
$\text{Li}_2\text{SeO}_3 \cdot \text{H}_2\text{O}$			
298—370	plateau		$\text{Li}_2\text{SeO}_3 \cdot \text{H}_2\text{O}$
370—435	8.75 % loss	endo	decomp. to $\text{Li}_2\text{SeO}_3 \cdot 0.25\text{H}_2\text{O}$ and H_2O
435—515	plateau		$\text{Li}_2\text{SeO}_3 \cdot 0.25\text{H}_2\text{O}$
515—675	11.65 % loss	endo	decomp. to Li_2SeO_3 and H_2O
675—875	plateau	endo	fusion of Li_2SeO_3
LiHSeO_3			
298—375	plateau		LiHSeO_3
375—435	6.95 % loss	endo	decomp. to $\text{Li}_2\text{Se}_2\text{O}_5$ and H_2O
435—675	plateau	endo	fusion of $\text{Li}_2\text{Se}_2\text{O}_5$
675—700	16.6 % loss	endo	partial decomp. to SeO_2 and Li_2SeO_3
700—720	plateau		
720—730	26.3 % loss	endo	
730—780	plateau		
780—825	47.2 % loss	endo	complete decomp. to SeO_2 and Li_2SeO_3
$\text{LiH}_3(\text{SeO}_3)_2$			
298—365	plateau		$\text{LiH}_3(\text{SeO}_3)_2$
365—400	0.25 % loss	endo	incongruent fusion and liberation of part of H_2O
400—475	10.55 % loss	endo	evapor. of H_2O with formation of $\text{Li}_2\text{Se}_2\text{O}_5(\text{s})$ and $\text{SeO}_2(\text{s})$
475—505	plateau		
505—525	73.25 % loss	endo	SeO_2 sublimation and decomp. to Li_2SeO_3 and SeO_2
775—835		endo	

Table 2

Thermal analysis of lithium selenites by the method of gradual temperature increase

T/K	Mass loss/%	Assignment
$\text{Li}_2\text{SeO}_3 \cdot \text{H}_2\text{O}$		
298—365		$\text{Li}_2\text{SeO}_3 \cdot \text{H}_2\text{O}$
365—400	8.95	decomp. to $\text{Li}_2\text{SeO}_3 \cdot 0.25\text{H}_2\text{O}$ and H_2O
400—455		$\text{Li}_2\text{SeO}_3 \cdot 0.25\text{H}_2\text{O}$
455—515	11.8	decomp. to Li_2SeO_3 and H_2O
515—725		Li_2SeO_3
LiHSeO_3		
298—365		LiHSeO_3
365—405	6.85	decomp. to $\text{Li}_2\text{Se}_2\text{O}_5$ and H_2O
405—515		$\text{Li}_2\text{Se}_2\text{O}_5$
515—555	26.5	partial decomp. to Li_2SeO_3 and SeO_2
555—615		
615—675	46.5	complete decomp. to Li_2SeO_3 and SeO_2
$\text{LiH}_3(\text{SeO}_3)_2$		
298—365		$\text{LiH}_3(\text{SeO}_3)_2$
365—435	10.15	decomp. to $\text{Li}_2\text{Se}_2\text{O}_5$, SeO_2 , and H_2O
385—585	51.95	SeO_2 sublimation
585—615		$\text{Li}_2\text{Se}_2\text{O}_5$
615—725	69.10	decomp. to Li_2SeO_3 and SeO_2

Table 3

Thermal analysis of thallium(I) selenites by the TG and DTA methods

T/K	TG	DTA	Assignment
Tl_2SeO_3			
298—405	plateau		Tl_2SeO_3
	0.2 % loss	endo	partial decomp.
405—715		endo (626 K)	fusion of Tl_2SeO_3
715—875	3.0 % loss	endo	Tl_2SeO_3 decomp. with liberation of SeO_2
$\text{Tl}_2\text{Se}_2\text{O}_5$			
298—415	plateau		$\text{Tl}_2\text{Se}_2\text{O}_5$
415—615	0.5 % loss	endo	fusion and partial decomp.
615—775	15.9 % loss	endo	decomp. to Tl_2SeO_3 and SeO_2
775—835	plateau		Tl_2SeO_3
835—875	21.2 % loss	endo	Tl_2SeO_3 decomp.
$\text{TlH}_3(\text{SeO}_3)_2$			
298—320	plateau	endo	fusion of $\text{TlH}_3(\text{SeO}_3)_2$
320—475	6.2 % loss	endo	decomp. to $\text{Tl}_2\text{Se}_2\text{O}_5$ and SeO_2
445—875	41.5 % loss	endo	sublimation of SeO_2 , fusion and decomp. of $\text{Tl}_2\text{Se}_2\text{O}_5$ to yield Tl_2SeO_3

Table 4

Thermal analysis of thallium(I) selenites by the method of gradual temperature increase

T/K	Mass loss/%	Assignment
298—685	Tl ₂ SeO ₃ 0.6	partial decomp.
298—575	Tl ₂ Se ₂ O ₅	Tl ₂ Se ₂ O ₅
575—685	7.7	decomp. to Tl ₂ SeO ₃ and SeO ₂
298—315	TlH ₃ (SeO ₃) ₂	TlH ₃ (SeO ₃) ₂
315—460	6.0	decomp. to Tl ₂ Se ₂ O ₅ (s), SeO ₂ (s) and liberation of H ₂ O
460—605	25.7	SeO ₂ sublimation
605—685	33.0	Tl ₂ Se ₂ O ₅ decomp. to yield Tl ₂ SeO ₃ and SeO ₂

The IR spectra of the studied compounds are summarized in Tables 5 to 10. The individual bands were assigned on the basis of the literature [17—20, 28—30]. Common abbreviations are used in the tables, X denoting a hydrogen or deuterium atom.

Table 5

IR spectra of Li₂SeO₃, Li₂SeO₃ · H₂O, and Li₂SeO₃ · D₂O

Li ₂ SeO ₃ $\tilde{\nu}/\text{cm}^{-1}$	Li ₂ SeO ₃ · H ₂ O $\tilde{\nu}(\text{I})/\text{cm}^{-1}$	Li ₂ SeO ₃ · D ₂ O $\tilde{\nu}(\text{II})/\text{cm}^{-1}$	$\tilde{\nu}(\text{I})/\tilde{\nu}(\text{II})$	Assignment
435 m	427 m	427 m	1.00	$\delta_s(\text{SeO}_3)$
	493 m			$\rho(\text{X}_2\text{O})$
528 m	535 sh	536 sh		$\rho(\text{X}_2\text{O})$
	630 m			$\nu_{\text{as}}(\text{SeO})(\text{SeO}_3)$
753 s	740 s	734 s	1.01	$\nu_s(\text{SeO})(\text{SeO}_3)$
	760 s	758 s	1.00	
790 s	805 m	805 m	1.00	
	830 m	830 m	1.00	$\delta(\text{X}_2\text{O})$
841 m	850 sh	855 sh	0.99	
	1618 vw	1185 vw	1.37	
	1669 w	1224 vw	1.39	$\nu(\text{OX})(\text{X}_2\text{O})$
	3340 m	2480 m	1.35	
	3490 m	2540 m	1.37	
	3520 sh	2650 sh	1.33	

Table 6
IR spectrum of Tl_2SeO_3

$\tilde{\nu}/\text{cm}^{-1}$	Assignment
420 m } 435 w, sh } 675 s } 755 s } 783 m }	$\sigma(\text{SeO}_3)$ $\nu_{\text{as}}(\text{SeO})(\text{SeO}_3)$ $\nu_s(\text{SeO})(\text{SeO}_3)$

Table 7
IR spectra of LiHSeO_3 and LiDSeO_3

LiHSeO_3 $\tilde{\nu}(\text{I})/\text{cm}^{-1}$	LiDSeO_3 $\tilde{\nu}(\text{II})/\text{cm}^{-1}$	$\tilde{\nu}(\text{I})/\tilde{\nu}(\text{II})$	Assignment
423 m } 462 s } 487 sh } 627 s } 803 s } 845 s } 870 s } 960 sh } 1319 s } 1545—1565 w } 2200—2600 m, b } (max. 2450) } 2600—3200 s, b } (max. 2750) }	415 m } 462 s } 487 sh } 620 s } 594 m } 810 s } 835 s } 870 s } 970 s } 1160—1700 w } 1800—1950 m, b } (max. 1900) } 1950—2300 s, b } (max. 2100) }	1.02 } 1.00 } 1.00 } 1.01 } 0.99 } 1.01 } 1.00 } 1.36 } 1.33 } 1.30 } 1.31 }	$\delta(\text{SeO}_2), \nu(\text{LiO})$ $\nu(\text{SeO})(\text{SeOX})$ $\nu_{\text{as}}(\text{SeO})(\text{SeO}_2)$ $\nu_s(\text{SeO})(\text{SeO}_2)$ $\gamma(\text{OX})(\text{SeOX})$ $\delta(\text{OX})(\text{SeOX})$ $\nu(\text{OX})(\text{SeOX})$

Table 8
IR spectra of $\text{Li}_2\text{Se}_2\text{O}_5$ and $\text{Tl}_2\text{Se}_2\text{O}_5$

$\text{Tl}_2\text{Se}_2\text{O}_5$ $\tilde{\nu}/\text{cm}^{-1}$	$\text{Li}_2\text{Se}_2\text{O}_5$ $\tilde{\nu}/\text{cm}^{-1}$	Assignment
443 m } 530 s } 800 vs } 835 s } 860 sh }	412 m } 468 s } 490 sh } 568 s } 843 s } 860 s } 884 s }	$\delta(\text{SeO}_2), \nu(\text{LiO})$ $\nu_s(\text{SeO})(\text{SeOSe}), \nu(\text{LiO})$ $\nu_{\text{as}}(\text{SeO})(\text{SeOSe})$ $\nu_{\text{as}}(\text{SeO})(\text{SeO}_2)$ $\nu_s(\text{SeO})(\text{SeO}_2)$

Table 9

IR spectra of $\text{LiH}_3(\text{SeO}_3)_2$ and $\text{LiD}_3(\text{SeO}_3)_2$

$\text{LiH}_3(\text{SeO}_3)_2$ $\tilde{\nu}(\text{I})/\text{cm}^{-1}$	$\text{LiD}_3(\text{SeO}_3)_2$ $\tilde{\nu}(\text{II})/\text{cm}^{-1}$	$\tilde{\nu}(\text{I})/\tilde{\nu}(\text{II})$	Assignment
450 s	440 s	1.02	$\delta_s(\text{SeO}_2)(\text{X}_2\text{SeO}_3)$
655 s	632 s	1.03	$\nu(\text{SeOX})(\text{XSeO}_3^-)$
730 s	730 s	1.00	$\nu_s(\text{SeO}_2)(\text{X}_2\text{SeO}_3),$ $\nu_{as}(\text{SeO}_2)(\text{XSeO}_3^-)$
770 s	810 s		
835 sh	845 s	0.99	$\nu_s(\text{SeO})(\text{X}_2\text{SeO}_3)$ $\nu_s(\text{SeO}_2)(\text{XSeO}_3^-)$
1030 w			
1170 m	903 m	1.30	$\delta(\text{OX})(\text{SeOX})$
1260 w	970 sh	1.33	
1640 w, b	1180 w, b	1.35	$\nu(\text{OX})(\text{SeOX})$
2050—2500 s, b (max. 2350)	1650—1800 s, b (max. 1750)	1.34	
2600—3300 s, b (max. 2800)	1950—2450 s, b (max. 2100)	1.33	

Table 10

IR spectra of $\text{TlH}_3(\text{SeO}_3)_2$ and $\text{TlD}_3(\text{SeO}_3)_2$

$\text{TlH}_3(\text{SeO}_3)_2$ $\tilde{\nu}(\text{I})/\text{cm}^{-1}$	$\text{TlD}_3(\text{SeO}_3)_2$ $\tilde{\nu}(\text{II})/\text{cm}^{-1}$	$\tilde{\nu}(\text{I})/\tilde{\nu}(\text{II})$	Assignment
415 m, sh } 435 w, sh }			$\delta_s(\text{SeO}_3)$
655 s	650 s	1.01	$\nu(\text{SeOX})(\text{XSeO}_3^-)$
683 s, sh	675 s, sh	1.01	$\nu_{as}(\text{SeO}_2)(\text{X}_2\text{SeO}_3)$
720 m, sh	720 s, sh	1.00	$\nu_s(\text{SeO}_2)(\text{XSeO}_3^-)$
745 s	740 s	1.01	$\nu_{as}(\text{SeO}_2)(\text{XSeO}_3^-)$
825 m	810 s	1.02	$\nu_s(\text{SeO})(\text{X}_2\text{SeO}_3)$
855 m, sh	855 s, sh	1.00	$\nu_s(\text{SeO}_2)(\text{XSeO}_3^-)$
1230 m	960 m	1.28	$\delta(\text{OX})(\text{SeOX})$
1650 w, b	1180 w, b	1.34	$\nu(\text{OX})(\text{SeOX})$
2000—2500 s, b (max. 2380)	1600—2000 s, b (max. 1750)	1.34	
2600—3200 s, b (max. 2760)	1950—2350 (max. 2100)	1.32	

Discussion

In the $\text{Li}_2\text{SeO}_3\text{—H}_2\text{SeO}_3\text{—H}_2\text{O}$ system at 298 K, congruently soluble selenites have been found with $n(\text{Li}):n(\text{Se}):n(\text{H}_2\text{O})$ compositions of 2:2:1 and 2:4:3. The analysis of the IR spectra and the thermoanalytical curves has confirmed that the compounds formed are the substances described in the literature [1—6], lithium hydrogen selenite, LiHSeO_3 and lithium trihydrogen-bis(selenite), $\text{LiH}_3(\text{SeO}_3)_2$. The mole ratios of the initial compounds, $n(\text{Li}_2\text{SeO}_3):n(\text{H}_2\text{SeO}_3):n(\text{H}_2\text{O})$, leading to the optimal yields of the studied substances were found: a ratio of 1:1.1:7.5 for LiHSeO_3 and 1:2.8:12.5 for $\text{LiH}_3(\text{SeO}_3)_2$.

The study of the $\text{Tl}_2\text{SeO}_3\text{—H}_2\text{SeO}_3\text{—H}_2\text{O}$ system at 298 K has shown that heterogeneous reactions lead to the formation of congruently soluble compounds with the compositions $n(\text{Tl}):n(\text{Se}):n(\text{H}_2\text{O}) = 1:1:0$ and 2:4:3. It follows from the physicochemical study that the former substance is thallium(I) diselenite that has not yet been described in the literature. The other compound, thallium(I) trihydrogen-bis(selenite), $\text{TlH}_3(\text{SeO}_3)_2$ is known from the literature [7, 8]. The optimal yields in the preparation of $\text{Tl}_2\text{Se}_2\text{O}_5$ and $\text{TlH}_3(\text{SeO}_3)_2$ are attained at mole ratios of the initial compounds of $n(\text{Tl}_2\text{SeO}_3):n(\text{H}_2\text{SeO}_3):n(\text{H}_2\text{O}) = 1:1.4:29$ and 1:3.5:7.0, respectively.

According to the type of the salts formed, the above systems can be compared with the systems of selenites of other univalent metals and of the ammonium cation. Similar to lithium, acid salts of the MHSeO_3 and $\text{MH}_3(\text{SeO}_3)_2$ types have been found at 298 K for all the other alkali metals [31]. The formation of diselenites analogous to $\text{Tl}_2\text{Se}_2\text{O}_5$ has been observed for potassium [32] and ammonium [33] selenites, but at higher temperatures. The existence of an acid salt and a diselenite simultaneously at a single temperature, analogous to thallium(I) selenites, has only been observed with ammonium selenites at 303 K [33] and cadmium selenites at 298 K [34].

The study of the thermoanalytical curves and the products of the thermal decomposition of $\text{Li}_2\text{SeO}_3 \cdot \text{H}_2\text{O}$ has confirmed that the substance is dehydrated in two steps. In the first step, 3/4 of a molecule of the crystal water escapes and the complete dehydration occurs at a substantially higher temperature (515—675 K). The overall mass loss on dehydration fully confirms the above composition of the compound, for which a different formula has been given by some authors [2] ($\text{Li}_2\text{SeO}_3 \cdot 3/4\text{H}_2\text{O}$). Two types of water molecules in the structure of the crystallohydrate are also reflected in the splitting of the band of stretching vibration of water in the IR spectrum (at $\tilde{\nu} = 3300\text{—}3500\text{ cm}^{-1}$), which also indicates the presence of two different hydrogen bonds. No further degradation or oxidation of Li_2SeO_3 has been observed below 875 K, in agreement with the literature [5].

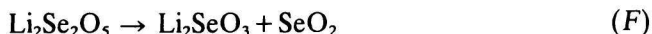
On heating Tl_2SeO_3 , a small mass loss of the substance occurs first, caused by

partial decomposition of the selenite anion to elemental selenium. An analogous partial decomposition has been observed with most alkali metal selenites [35]. The actual decomposition of Tl_2SeO_3 occurs at a temperature as high as 715 K and is preceded by melting of the compound.

Lithium hydrogen selenite is, analogous to the other alkali hydrogen selenites [31], decomposed to diselenite with liberation of water



A further increase in the temperature leads to fusion of lithium diselenite followed by stepwise decomposition with the liberation of selenium(IV) oxide and without formation of a stable intermediate. The final decomposition product is the selenite



Analogously, after fusion, $\text{Tl}_2\text{Se}_2\text{O}_5$ is decomposed to yield SeO_2 and Tl_2SeO_3 .

The initial process in the thermal degradation of the selenites, $\text{LiH}_3(\text{SeO}_3)_2$ and $\text{TlH}_3(\text{SeO}_3)_2$, can be expressed by the equation



This decomposition proceeds in steps. First, the studied compounds melt incongruently and the liberated water is evaporated at a higher temperature. A further increase in the temperature leads to the sublimation of selenium(IV) oxide, which strongly affects the further course of the thermoanalytical curves. As the sublimation is not terminated before the onset of the decomposition of $\text{Li}_2\text{Se}_2\text{O}_5$ and $\text{Tl}_2\text{Se}_2\text{O}_5$, no flat parts can be observed on the TG curves corresponding to the existence of these substances. However, this flat part has been found on the thermoanalytical curve of $\text{LiH}_3(\text{SeO}_3)_2$ when using the method of gradually increased temperature. Pure thallium(I) diselenite cannot, however, be prepared by thermal decomposition of $\text{TlH}_3(\text{SeO}_3)_2$, even when the above method is used.

The analysis of the IR spectra in the region of stretching vibrations of the SeO_3 group in the compounds $\text{Li}_2\text{SeO}_3 \cdot \text{H}_2\text{O}$ and $\text{Li}_2\text{SeO}_3 \cdot \text{D}_2\text{O}$ has indicated that the symmetry of the selenite anion, C_{3v} , is decreased by the presence of the molecules of crystal water which are manifested by appropriate vibrational modes. Moreover, a further absorption band is present in the spectra at $\tilde{\nu} = 500\text{--}550 \text{ cm}^{-1}$. In the literature [36], this band was assigned to asymmetric stretching vibration of the $\text{SeO}(\text{Se})$ group of diselenite anion in the anhydrous salt Li_2SeO_3 and the compound was formulated as $\text{Li}_2\text{O} \cdot \text{Li}_2\text{Se}_2\text{O}_5$. As a corresponding band of symmetric stretching vibration of the $\text{SeO}(\text{Se})$ group was not found in the spectra, the assignment and the formulation of the compound are problematic. Moreover, the presence of diselenite anions has not been observed with other alkali selenites.[31, 36]. On the contrary, it is probable that this absorption band corresponds to vibration of the $\text{Li}\text{--}\text{O}$ group, which appears in a region of $\tilde{\nu} = 400\text{--}550 \text{ cm}^{-1}$ [37, 38].

In contrast to the literature [36], no bands corresponding to vibrations of the SeO(H) group were found in the spectrum of $\text{Li}_2\text{SeO}_3 \cdot \text{H}_2\text{O}$, which would confirm the formulation of the compound as $\text{Li}_2(\text{OH})(\text{HSeO}_3)$. In the region of the stretching vibrations of the OH(H_2O) group, the spectrum contains two absorption bands, from the wavenumbers of which the energies (E) were calculated according to Sokolov [39] and Yukhnevich [40], on the basis of correlation diagrams [41—45] were then determined the lengths ($R_{\text{O}\dots\text{O}}$) of the hydrogen bonds present (Table 11).

Table 11
Energies and lengths of the hydrogen bonds in $\text{Li}_2\text{SeO}_3 \cdot \text{H}_2\text{O}$

$\tilde{\nu}(\text{OH})/\text{cm}^{-1}$	$E/(\text{kJ mol}^{-1})$	$R_{\text{O}\dots\text{O}}/\text{pm}$
3490	17.4 ^a , 16.8 ^b	287
3340	29.9 ^a	280

a) Ref. [39]; b) Ref. [40].

It can be seen from the table that weak hydrogen bonds are present in the molecule, corresponding to the presence of two types of bound water molecules, which was also verified by the study of the thermoanalytical properties of the substance.

In the IR spectrum of Li_2SeO_3 , a band occurs at $\tilde{\nu} = 528 \text{ cm}^{-1}$, in addition to the bands characteristic of the selenite anion; this band apparently corresponds to the stretching vibration of the Li—O group, similar to the hydrated salt. On the other hand, in the Tl_2SeO_3 spectrum only the bands corresponding to vibrations of the SeO_3 group are found, the splitting of which, however, indicates a decrease in the anion symmetry.

The splitting of the stretching vibration bands of the SeO_2 groups in the spectra of lithium and thallium(I) diselenites demonstrates that the C_{2v} symmetry of the diselenite anion is decreased in these substances; this symmetry was derived by Simon [29] and verified by X-ray analysis [46]. Both the compounds further exhibit characteristic bands of stretching and bending vibrations of the SeO(Se) group, confirming the presence of the bridging Se—O—Se group.

In the study of the IR spectra of acid lithium and thallium(I) selenites attention has mainly been directed toward clarification of the behaviour of protons from the point of view of their ordering, as they decisively affect the dielectric properties of the substances [14—17]. The spectrum of lithium hydrogen selenite is marked by characteristic intense bands of stretching vibration of the SeO(H) group and

bending vibration of the OH(Se) group, corresponding to a hydrogen bond 261.6 pm long, found in the X-ray study [9]. The protons in this hydrogen bond are thus located asymmetrically in the ordered position, *i.e.* at the lowest discrete levels of the two-minimum asymmetrical potential function, with a virtually zero probability of tunnelling [15]. In the spectra of $\text{LiH}_3(\text{SeO}_3)_2$ and $\text{TlH}_3(\text{SeO}_3)_2$, absorption bands were found in the region of normal anion vibrations that suggest the presence of the HSeO_3^- and H_2SeO_3 groups in the structure. Hence at least two protons in these compounds are located in the hydrogen bonds analogously as in LiHSeO_3 , *i.e.* asymmetrically in ordered positions. This conclusion has also been verified for $\text{LiH}_3(\text{SeO}_3)_2$ by a study of the structure [10—13] and is manifested by the ferroelectric behaviour of the substance in the whole temperature existence region.

The spectra of all the studied acid salts are similar to those of other acid salts belonging among ferroelectrics of the potassium dihydrogen phosphate (KDP) type, as far as the number, position, and the shape of the absorption bands in the region of the stretching vibrations of the OH(Se) group are concerned [15]. The similar character of the spectra of the above substances that differ in the number and the lengths of the hydrogen bonds is caused by a slow interbonding tunnel effect [15, 47].

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