

# Ammonium selenites

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The solubility diagrams of the  $(\text{NH}_4)_2\text{SeO}_3$ — $\text{H}_2\text{SeO}_3$ — $\text{H}_2\text{O}$  system at 298 K and 303 K were studied for the first time. The effect of temperature on the character of the studied system considering the formation of diselenite from hydrogen selenite was examined. The results of the solubility studies were employed to prepare ammonium hydrogen selenite,  $\text{NH}_4\text{HSeO}_3$ , ammonium trihydrogen-bis(selenite),  $\text{NH}_4\text{H}_3(\text{SeO}_3)_2$ , and ammonium diselenite  $(\text{NH}_4)_2\text{Se}_2\text{O}_5$ . The thermoanalytical properties of the selenites  $(\text{NH}_4)_2\text{SeO}_3$  and  $(\text{NH}_4)_2\text{SeO}_3 \cdot \text{H}_2\text{O}$  were studied and mechanisms were proposed for the thermal decomposition. The force constants of the selenium-oxygen bonds were found on the basis of a study of the infrared molecular spectra.

Впервые изучены диаграммы растворимости системы  $(\text{NH}_4)_2\text{SeO}_3$ — $\text{H}_2\text{SeO}_3$ — $\text{H}_2\text{O}$  при 298 К и 303 К. Изучено влияние температуры на характер изучаемой системы с точки зрения образования диселенита из гидроселенита. Результаты изучения растворимости были использованы при получении гидроселенита аммония  $\text{NH}_4\text{HSeO}_3$ , тригидро-бис(селенита) аммония  $\text{NH}_4\text{H}_3(\text{SeO}_3)_2$  и диселенита аммония  $(\text{NH}_4)_2\text{Se}_2\text{O}_5$ . Были изучены термоаналитические свойства селенитов  $(\text{NH}_4)_2\text{SeO}_3$  и  $(\text{NH}_4)_2\text{SeO}_3 \cdot \text{H}_2\text{O}$  и предложены механизмы их термического разложения. На основе изучения инфракрасных молекулярных спектров найдены силовые константы связей селен—кислород.

*Berzelius* [1, 2], *Nilson* [3], *Divers* [4, 5], *Miolatti* [6], *Muspratt* [7, 8], and *Cornec* [9] studied methods for the preparation of ammonium selenites and described compounds with the compositions  $(\text{NH}_4)_2\text{SeO}_3$ ,  $(\text{NH}_4)_2\text{SeO}_3 \cdot \text{H}_2\text{O}$ , and  $(\text{NH}_4)\text{H}_3(\text{SeO}_3)_2$ . They also found the compounds  $(\text{NH}_4)\text{HSeO}_3$ ,  $(\text{NH}_4)_2\text{SeO}_3 \cdot \text{NH}_3$ , and  $2(\text{NH}_4)_2\text{SeO}_3 \cdot \text{H}_2\text{SeO}_3$ ; *Janickis* [10, 11] has stated that these compounds do not exist. The latter author studied the behaviour of aqueous solutions of ammonium selenites and prepared the diselenites  $(\text{NH}_4)_2\text{Se}_2\text{O}_5$  and  $(\text{NH}_4)_2\text{Se}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$ .

*Shuvalov* [12] described the crystal structure of the compound  $(\text{NH}_4)\text{H}_3(\text{SeO}_3)_2$  on the basis of an X-ray structure study; this structure was refined by *Tellgren* [13]

using the neutron diffraction method. *Chomnilpan* [14] carried out X-ray structural analysis of the diselenite  $(\text{NH}_4)_2\text{Se}_2\text{O}_5$ .

The dielectric behaviour of the compound  $(\text{NH}_4)\text{H}_3(\text{SeO}_3)_2$  was clarified using the PMR method [15], by studying the optical properties [16, 17], by measuring the Raman spectra [18, 19] and by finding the temperatures of structural transitions [20].

*Paetzold* and *Simon* [21–23] found the constitution and symmetry of the selenite, hydrogen selenite, and diselenite anions on the basis of a study of the infrared molecular spectra of these substances.

In the framework of a systematic study of selenites as potential ferroelectric substances, this work deals with ammonium selenites. All the compounds formed in the  $(\text{NH}_4)_2\text{SeO}_3\text{—H}_2\text{SeO}_3\text{—H}_2\text{O}$  system at 298 K and 303 K were isolated and their physicochemical properties were studied, primarily the thermoanalysis curves, which contributed to clarification of the mechanisms of thermal decomposition. Attention was also paid to the effect of temperature on the character of the studied system, especially considering the transition between hydrogen selenite and diselenite.

## Experimental

### *Chemicals and methods*

The solubility diagrams were studied using anhydrous ammonium selenite, obtained by dehydration of the monohydrate [10]. Ammonium selenite monohydrate was prepared by introduction of gaseous ammonia into a solution of selenious acid with simultaneous cooling of the reaction mixture. Addition of an acetone—methanol mixture (volume ratio = 3 : 1) yielded a white crystalline substance at 260 K.

Selenium in the starting substances and products was determined gravimetrically by the *Koreman* method [24]; in the solubility studies it was determined by iodometric titration [25]. Ammonia was determined by the *Parnas—Wagner* [26] and *Conway* [26] methods.

Infrared spectra were measured on a PE 684 (Perkin—Elmer) instrument with a PE 3600 data processor in the wavenumber region  $\bar{\nu} = 350\text{—}4000\text{ cm}^{-1}$ . Samples were measured by the Nujol suspension method using a potassium bromide cell. The tripene suspension method was also used for measurements in the  $\bar{\nu}$  region  $1200\text{—}1500\text{ cm}^{-1}$  and  $2000\text{—}4000\text{ cm}^{-1}$ .

The thermoanalytical properties of the compounds were studied by the thermogravimetric method and by differential thermal analysis. The measurements were carried out on a Derivatograph instrument (MOM, Budapest) in the region 298—573 K with a linear temperature increase of  $2.5\text{ K min}^{-1}$ .

Powder X-ray patterns were measured using a Mikrometa 2 instrument (Chirana, Prague) using a chamber with a radius of 57.3 mm. The radiation of a copper anode and a nickel filter were used. The exposure time was 90 min at a voltage of 35 kV and a current of 20 mA.

*Study of the solubility of the  $(\text{NH}_4)_2\text{SeO}_3\text{—H}_2\text{SeO}_3\text{—H}_2\text{O}$  system  
at 298 K*

The Schreinemakers method was used to study the solubility in the  $(\text{NH}_4)_2\text{SeO}_3\text{—H}_2\text{SeO}_3\text{—H}_2\text{O}$  system. The period required for establishment of equilibrium at 298 K varied from 1 to 2 months. The solubility diagram obtained and plotted by the Roozeboom method is in Fig. 1. It follows from the diagram that in addition to the initial

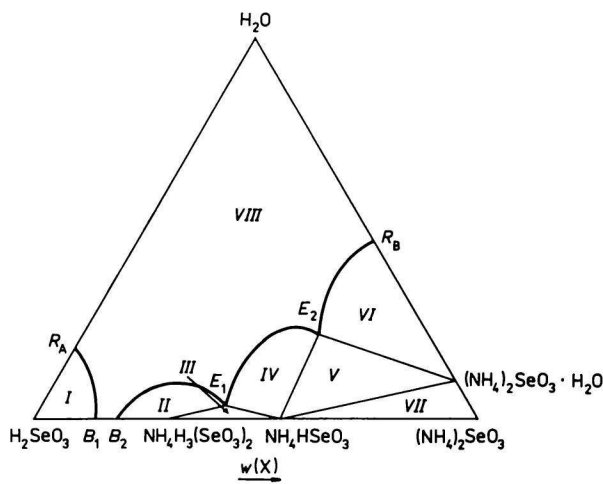


Fig. 1. Solubility diagram in the  $(\text{NH}_4)_2\text{SeO}_3\text{—H}_2\text{SeO}_3\text{—H}_2\text{O}$  system at 298 K.

selenious acid, corresponding to crystallization field I, ammonium trihydrogen-bis(selenite)  $(\text{NH}_4)_3(\text{SeO}_3)_2$  (crystallization field II), ammonium hydrogen selenite  $(\text{NH}_4)\text{HSeO}_3$  (crystallization field IV), and ammonium selenite monohydrate  $(\text{NH}_4)_2\text{SeO}_3 \cdot \text{H}_2\text{O}$  (crystallization field VI) are also formed in the system. All the compounds formed in the system are congruently soluble. Fields III and V correspond to equilibrium between two solid phases and solutions with compositions corresponding to eutonic points  $E_1$  and  $E_2$ , respectively. Eutonic point  $E_1$  corresponds to the mass fractions 41.8 %  $(\text{NH}_4)_2\text{SeO}_3$ , 54.5 %  $\text{H}_2\text{SeO}_3$ , and 3.7 %  $\text{H}_2\text{O}$  and eutonic point  $E_2$  to the composition 55.3 %  $(\text{NH}_4)_2\text{SeO}_3$ , 29.9 %  $\text{H}_2\text{SeO}_3$ , and 21.8 %  $\text{H}_2\text{O}$ . Points  $B_1$  (14.4 %  $(\text{NH}_4)_2\text{SeO}_3$ , 85.6 %  $\text{H}_2\text{SeO}_3$ ) and  $B_2$  (19.5 %  $(\text{NH}_4)_2\text{SeO}_3$ , 80.5 %  $\text{H}_2\text{SeO}_3$ ) delimit the fusion region. In field V and with the composition of the liquid phase corresponding to point  $E_2$ , a phase reaction occurs with formation of hydrogen selenite



In field III with the composition of the liquid phase given by point  $E_1$ , a phase reaction occurs with formation of trihydrogen-bis(selenite)



The compounds, ammonium trihydrogen-bis(selenite) and ammonium hydrogen selenite, were prepared on the basis of study of this solubility diagram. The crystals of both substances were collected on an  $S_2$  frit under vacuum and dried in a desiccator over potassium hydroxide at laboratory temperature. The compounds obtained are colourless crystalline substances;  $(NH_4)H_3(SeO_3)_2$  is unstable in the air. The results of analyses for selenium and ammonia correspond to the calculated data. For  $(NH_4)H_3(SeO_3)_2$   $w_i(\text{calc.})$ : 57.4 % Se, 6.95 %  $NH_3$ ;  $w_i(\text{found})$ : 57.3 % Se, 7.3 %  $NH_3$ . For  $(NH_4)HSeO_3$   $w_i(\text{calc.})$ : 54.5 % Se, 11.7 %  $NH_3$ ;  $w_i(\text{found})$ : 54.2 % Se, 11.5 %  $NH_3$ .

### Study of solubility in the $(NH_4)_2SeO_3$ — $H_2SeO_3$ — $H_2O$ system at 303 K

The solubility diagram obtained is depicted in Fig. 2. It is apparent from the diagram that, in addition to the initial substances (crystallization fields *I* and *V*), ammonium trihydrogen-bis(selenite) (crystallization field *II*) and ammonium diselenite (crystallization field *III*) are formed in the system. Both substances are congruently soluble. Field *IV* describes equilibrium between two solid phases and a solution with a composition corresponding to the eutonic point *E* (58.7 %  $(NH_4)_2SeO_3$ , 30.5 %  $SeO_2$ , and 10.8 %  $H_2O$ ). Points obtained by extrapolation to the solubility curves,  $B_1$  (16.0 %  $(NH_4)_2SeO_3$ , 72.3 %  $SeO_2$ , 11.7 %  $H_2O$ ) and  $B_2$  (23.9 %  $(NH_4)_2SeO_3$ , 65.2 %  $SeO_2$ , 10.9 %  $H_2O$ ) and  $C_1$  (37.4 %  $(NH_4)_2SeO_3$ , 54.1 %  $SeO_2$ , 8.5 %  $H_2O$ ) and  $C_2$  (45.5 %  $(NH_4)_2SeO_3$ , 47.0 %  $SeO_2$ , 7.5 %  $H_2O$ ) delimit the melting region. A phase reaction occurs in field *IV* at a composition of the liquid phase corresponding to point *E*, with formation of diselenite

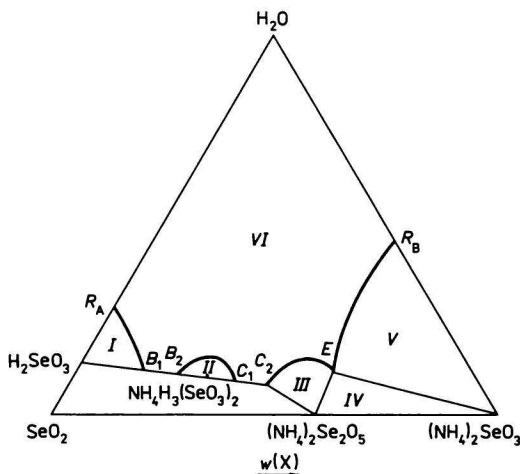


Fig. 2. Solubility diagram in the  $(NH_4)_2SeO_3$ — $H_2SeO_3$ — $H_2O$  system at 303 K.

Ammonium diselenite  $(\text{NH}_4)_2\text{Se}_2\text{O}_5$ , obtained on the basis of the solubility study, is a colourless crystalline substance that is stable in the air. The results of analyses for selenium and ammonia correspond to the calculated data ( $w_i(\text{calc.})$ ): 57.6 % Se, 12.4 %  $\text{NH}_3$ ;  $w_i(\text{found})$ : 57.5 % Se, 12.5 %  $\text{NH}_3$ ).

### *Thermoanalytical properties and infrared molecular spectra*

Table 1 lists the results of study of the thermoanalytical properties of the compounds considered. The intermediates and the final products of the thermal decomposition were studied analytically, by X-ray analysis and by the infrared molecular spectroscopic method.

Table 1

#### Thermal decomposition of ammonium selenites

T/K	TG	DTA	Assignment
$(\text{NH}_4)_2\text{SeO}_3$			
273—305	pause		
305—355	decrease 15.0 %	endo	loss of $\text{H}_2\text{O}$ and $\text{NH}_3$ with formation of
$(\text{NH}_4)_2\text{Se}_2\text{O}_5$			
355—360	pause		
360—420	decrease 22.0 %	endo	loss of $\text{NH}_3$ with formation of $(\text{NH}_4)\text{HSe}_2\text{O}_5$
420—505	decrease 73.7 %	endo	complete decomp. with reduction to Se and melting
505—575	decrease 80 %	endo	vaporization of Se
$(\text{NH}_4)_2\text{SeO}_3 \cdot \text{H}_2\text{O}$			
273—310	pause		
310—355	decrease 18.1 %	endo	loss of $\text{H}_2\text{O}$ and $\text{NH}_3$ with formation of
$(\text{NH}_4)_2\text{Se}_2\text{O}_5$			
355—400	decrease 27.9 %	endo	loss of $\text{NH}_3$ with formation of $(\text{NH}_4)\text{HSe}_2\text{O}_5$
400—405	pause		
405—500	decrease 76.6 %	endo	complete decomp. with reduction to Se and melting
500—575	decrease 83.5 %	endo	vaporization of Se
$(\text{NH}_4)\text{HSeO}_3$			
273—300	pause		
300—315	decrease 7.5 %	endo	loss of $\text{H}_2\text{O}$ with formation of
$(\text{NH}_4)_2\text{Se}_2\text{O}_5$			
315—355	pause		
355—425	decrease 11.9 %	endo	loss of $\text{H}_2\text{O}$ and $\text{NH}_3$ with formation of
$(\text{NH}_4)\text{HSe}_2\text{O}_5$			
425—495	decrease 68.0 %	endo	complete decomp. with reduction to Se and melting
495—575	decrease 76.5 %	endo	vaporization of Se

Table 1 (Continued)

T/K	TG	DTA	Assignment
$(\text{NH}_4)_2\text{Se}_2\text{O}_5$			
275—360	pause		
360—390	decrease 6.2 %	endo	loss of $\text{NH}_3$ with formation of $(\text{NH}_4)\text{HSe}_2\text{O}_5$
450—500	decrease 64.6 %	endo	complete decomp. with reduction to Se and melting
505—575	decrease 72.8 %	endo	vaporization of Se
$(\text{NH}_4)\text{H}_3(\text{SeO}_3)_2$			
275—310	pause	endo	incongruent melting
315—425	decrease 6.8 %	endo	loss of $\text{H}_2\text{O}$ with formation of $(\text{NH}_4)\text{HSe}_2\text{O}_5$
430—510	decrease 61.2 %	endo	complete decomp. with reduction to Se and melting
510—575	decrease 69.0 %	endo	vaporization of Se

The infrared molecular spectra of the studied compounds are listed in Tables 2—6. The absorption bands were assigned according to the work by Paetzold and Simon [21—23]. The usual abbreviations were employed in the tables.

Table 2  
Infrared spectra of  $(\text{NH}_4)_2\text{SeO}_3$  and  $(\text{NH}_4)_2\text{SeO}_3 \cdot \text{H}_2\text{O}$

$(\text{NH}_4)_2\text{SeO}_3$ $\bar{\nu}/\text{cm}^{-1}$	$(\text{NH}_4)_2\text{SeO}_3 \cdot \text{H}_2\text{O}$ $\bar{\nu}/\text{cm}^{-1}$	Assignment
382 s	383 s	$\delta_{\text{as}}(\text{SeO}_3)$
441 s	434 s	$\delta_{\text{s}}(\text{SeO}_3)$
	570 vw	$\rho(\text{H}_2\text{O})$
678 vs, b	720 vs, b } }	$\nu_{\text{as}}(\text{SeO}_3)$
722 vs		
795 s	800 s	$\nu_{\text{s}}(\text{SeO}_3)$
1421 vs	1407 vs } }	$\delta_{\text{as}}(\text{NH}_4^+)$
1454 vs	1448 s } }	
1608 w	1645 sh } }	$\delta(\text{H}_2\text{O})$ and bands of combined vibrations
1684 w	1674 s } }	
1718 vw	1707 sh } }	
1897 m, b	1920 s, b	band of combined vibration
2200 w, b	2180 m, b	
2400—3300 vs, vb (max. 2780, 3050, 3230)	2300—3700 vs, vb (max. 2990, 3060, 3150)	$\nu_{\text{s, as}}(\text{NH}_4^+)$ and $\nu_{\text{s, as}}(\text{H}_2\text{O})$

Table 3

Infrared spectrum of  $(\text{NH}_4)\text{HSeO}_3$ 

$\tilde{\nu}/\text{cm}^{-1}$	Assignment
396 m } 410 m }	$\delta(\text{SeO}_2)$
613 s, b	$\nu(\text{SeO})$ (SeOH)
804 vs, b	$\nu_{\text{as}}(\text{SeO}_2)$
838 sh	$\nu_s(\text{SeO}_2)$
1160 m	$\delta(\text{OH})$ (SeOH)
1409 vs, 1446 sh, 1462 sh	$\delta_{\text{as}}(\text{NH}_4^+)$
1645 sh, 1667 m, 1690 sh, 1852 w	bands of combined vibrations
2165 sh, 2430 sh 2600—3600 vs, vb (max. 2830, 3035, 3160) }	$\nu_{s, \text{as}}(\text{NH}_4^+)$ and $\nu(\text{OH})$ (SeOH)

Table 4

Infrared spectrum of  $(\text{NH}_4)_2\text{Se}_2\text{O}_5$ 

$\tilde{\nu}/\text{cm}^{-1}$	Assignment
347 s } 404 s }	$\delta(\text{SeO}_2)$
505 vs	$\nu_s(\text{SeOSe})$
562 vs	$\nu_{\text{as}}(\text{SeOSe})$
795 vs	$\nu_{\text{as}}(\text{SeO}_2)$
844 s } 863 s }	$\nu_s(\text{SeO}_2)$
1237 w, 1282 vw	
1407 vs, 1431 vs, 1445 sh, 1453 sh	$\delta_{\text{as}}(\text{NH}_4^+)$
1696 s, 1715 m	bands of combined vibrations
2130 m 2500—3200 vs, vb (max. 2830, 3040, 3160) }	$\nu_{s, \text{as}}(\text{NH}_4^+)$

Table 5

Infrared spectrum of  $(\text{NH}_4)\text{H}_2(\text{SeO}_3)_2$ 

$\bar{\nu}/\text{cm}^{-1}$	Assignment
376 sh } 415 m }	$\delta(\text{SeO}_2)$
579 sh } 629 m, b }	$\nu(\text{SeO})$ (SeOH)
724 m	$\nu_{\text{as}}(\text{SeO}_2)$
805 s } 841 sh }	$\nu_{\text{s}}(\text{SeO}_2)$
951 sh	
1158 m, 1235 w, 1306 w	$\delta(\text{OH})$ (SeOH)
1408 s, 1428 sh, 1442 sh } 1446 w, 1483 w }	$\delta_{\text{as}}(\text{NH}_4^+)$
1637 vw, 1669 w, 1800 sh	bands of combined vibrations
2250—2400 w, b } (max. 2330, 2370, 2390) } 2400—3550 vs, vb } (max. 2450, 2830, 3040, 3150) }	$\nu_{\text{as}}(\text{NH}_4^+)$ and $\nu(\text{OH})$ (SeOH)

Table 6

Infrared spectrum of  $(\text{NH}_4)\text{HSe}_2\text{O}_5$ 

$\bar{\nu}/\text{cm}^{-1}$	Assignment
403 m	$\delta(\text{SeO}_2)$
488 m } 573 m }	$\nu_{\text{s}}, \nu_{\text{as}}(\text{SeOSe})$
643 m	$\nu(\text{SeO})$ (SeOH)
813 s	$\nu_{\text{as}}(\text{SeO}_2)$
887 s	$\nu_{\text{s}}(\text{SeO}_2)$
1167 sh	$\delta(\text{OH})$ (SeOH)
1410 vw	$\delta_{\text{as}}(\text{NH}_4^+)$
1760 w, 1786 w, b	bands of combined vibrations
2155 m } 2450 m } 2600—3600 vs, vb } (max. 2710, 2990, 3160) }	$\nu_{\text{as}}(\text{NH}_4^+)$ and $\nu(\text{OH})$ (SeOH)



## Discussion

The  $(\text{NH}_4)_2\text{SeO}_3\text{—H}_2\text{SeO}_3\text{—H}_2\text{O}$  system at 298 K was found to contain congruently soluble selenites with compositions  $n(\text{NH}_4):n(\text{Se}):n(\text{H}_2\text{O}) = 2:2:1$  and  $2:4:3$ . Analysis of the infrared spectra and thermoanalytical curves confirmed that the compounds formed are ammonium hydrogen selenite  $(\text{NH}_4)\text{HSeO}_3$  and the compound, ammonium trihydrogen-bis(selenite),  $(\text{NH}_4)\text{H}_3(\text{SeO}_3)_2$ , described in the literature [2, 4]. The existence of the former compound has also been assumed [1—6]; however, conditions for its preparation were not yet found. The solubility diagram yielded the mole ratios of the initial compounds  $n((\text{NH}_4)_2\text{SeO}_3):n(\text{H}_2\text{SeO}_3):n(\text{H}_2\text{O})$  leading to optimal yields of the prepared substances: for  $(\text{NH}_4)\text{HSeO}_3$  a ratio of 1:0.9:3.2 and for  $(\text{NH}_4)\text{H}_3(\text{SeO}_3)_2$  a ratio of 1:2.5:1.8.

The  $(\text{NH}_4)_2\text{SeO}_3\text{—H}_2\text{SeO}_3\text{—H}_2\text{O}$  system was found to contain  $(\text{NH}_4)\text{H}_3(\text{SeO}_3)_2$  as well as a congruently soluble compound with composition  $n(\text{NH}_4):n(\text{Se}) = 1:1$ . Physicochemical studies indicated that this compound is ammonium diselenite  $(\text{NH}_4)_2\text{Se}_2\text{O}_5$ . Optimal yields of this salt can be obtained at a ratio of the initial compounds of  $n((\text{NH}_4)_2\text{SeO}_3):n(\text{SeO}_2):n(\text{H}_2\text{O}) = 1:0.93:1.9$ .

Comparison of the studied diagrams indicates that the main differences are in the crystallization regions of  $(\text{NH}_4)\text{HSeO}_3$  and  $(\text{NH}_4)_2\text{Se}_2\text{O}_5$ . The transition temperature for the hydrogen selenite—diselenite transition (*i.e.* the temperature below which hydrogen selenite crystallizes from the given crystallization field and above which diselenite crystallizes) lies in the range 298—303 K for the studied system. The fact that the lower temperatures favour the formation of the acid salt — hydrogen selenite, and higher temperatures the condensed salt — diselenite — has already been observed for other metal cations [12, 27]: sodium (the transition temperature lies in the range 363—365 K), potassium (298—300 K), and zinc (273—298 K). For the other alkali metals [28], magnesium [29], calcium [30], strontium [31], cobalt [32], and nickel [33], the formation of the acid salt was found at 298 K; for barium [31], the diselenite is formed.

Study of the thermoanalytical curves and physicochemical properties of the decomposition products indicated that the anhydrous and hydrated ammonium selenites decompose to form water and ammonia in the temperature range 305—355 K and 310—355 K, respectively, to yield ammonium diselenite. Similarly, the first intermediate in the decomposition of ammonium hydrogen selenite is ammonium diselenite, formed in the temperature range 300—315 K with liberation of water. Further decomposition of diselenite occurs in the temperature range 355—425 K with formation of ammonia and yields the strongly hygroscopic, X-ray amorphous compound assigned the formula  $(\text{NH}_4)\text{HSe}_2\text{O}_5$  on the basis of analysis and study of the infrared molecular spectra (it can be seen from Table 6 that the vibrations of the  $\text{Se}(\text{OH})$  and  $\text{SeOSe}$  groups are present). A similar acid salt with

the diselenite anion was described for manganese selenites [34]. The formation of acid condensed anions has been observed for other ammonium salts, e.g. diphosphate [35] and diarsenate [36]. On a further increase in the temperature, the compound  $(\text{NH}_4)\text{HSe}_2\text{O}_5$  decomposes according to the reaction



The character of the TG and DTA curves corresponds to this decomposition connected with gradual formation of nitrogen, water, and selenium oxide. However, because of incomplete reduction, the overall mass loss in the reaction is greater (by an average of 5 %).

Heating of ammonium trihydrogen-bis(selenite) first leads to incongruent melting of the compound (m.p. =  $310 \pm 0.5$  K) and subsequent release of water (315—425 K) with formation of  $(\text{NH}_4)\text{HSe}_2\text{O}_5$ . Further decomposition of this intermediate proceeds in the same manner as for the other ammonium selenites. In contrast to the decomposition products of ammonium selenite found, the acid selenites of the alkali metals [28] always decompose to yield the corresponding diselenites, which further heating converts to selenites with partial oxidation to selenates. In contrast to ammonium selenites, the decomposition of the selenites of the alkali metals occurs directly without formation of diselenites as intermediates.

Analysis of the infrared spectra of ammonium selenite indicates a decrease in the assumed  $C_{3v}$  symmetry of the anions, appearing as splitting of the degenerate stretching vibration  $\nu_{\text{as}}(\text{SeO}_3)$ . The positions and numbers of absorption bands in the spectra of ammonium selenite and its monohydrate are almost identical. As a result of disappearance of the libration of water, the spectrum of  $(\text{NH}_4)_2\text{SeO}_3$  has better resolution of the bands of the stretching vibrations of the  $\text{SeO}_3$  group. In the hydrated salts, the bands of the vibrations of the  $\text{NH}_4^+$  cation overlap with the stretching vibration of the OH group and prevent more detailed characterization of the bonding of the water molecule by description of the hydrogen bonds present.

The spectrum of ammonium hydrogen selenite corresponds to  $C_s$  anion symmetry and is characterized by a typical intense band of the stretching vibration of the  $\text{Se}(\text{OH})$  group at  $\tilde{\nu} = 613 \text{ cm}^{-1}$  and a relatively strong band for the bending vibration of the  $\text{OH}(\text{Se})$  group at  $\tilde{\nu} = 1160 \text{ cm}^{-1}$ . It follows from analysis of the spectrum of the other acid salt, ammonium trihydrogen-bis(selenite), that this compound contains  $\text{HSeO}_3^-$  groups, while the  $\text{H}_2\text{SeO}_3$  group could not be found. A spectrum with similar character was found [28] for the compounds of the  $\text{MH}_3(\text{SeO}_3)_2$  type (where M is K, Rb or Cs), the structures of which are characterized by location of two protons in ordered positions. The third proton occupies a disordered position and the vibration corresponding to the  $\text{H}_2\text{SeO}_3$  group does not appear in the spectrum. This proton behaviour corresponds to the results published by Vinogradova [15]; earlier X-ray studies [13, 14] indicated rather a structure in which all three protons occupied ordered positions.

The spectra of diselenites contain bands corresponding to the stretching symmetric and antisymmetric vibrations of the SeO(Se) group in the  $\bar{\nu}$  region 500—560  $\text{cm}^{-1}$ . The character of the spectrum obtained completely corresponds to the presence of a bridging Se—O—Se group and the number of absorption bands for the  $\nu_s$  stretching vibration ( $\text{SeO}_2$ ) corresponds to a decrease in the assumed symmetry  $C_{2v}$  for the anion.

The force constants of the Se—O bonds were calculated from the wavelengths of the stretching vibrations of the  $\text{SeO}_3$ ,  $\text{SeO}_2$ , SeOH, and SeOSe groups by the method described for magnesium selenites [29] using the Lehmann relationship [37]. Values of 421  $\text{N m}^{-1}$ , 528  $\text{N m}^{-1}$ , 533  $\text{N m}^{-1}$ , 295  $\text{N m}^{-1}$ , and 200  $\text{N m}^{-1}$  were obtained for the  $\text{SeO}_3$ ,  $\text{SeO}_2(\text{HSeO}_3^-)$ ,  $\text{SeO}_2(\text{Se}_2\text{O}_5^{2-})$ , SeOH, and SeOSe groups. It follows from the values obtained that the strength of the Se—O bond decreases in the order  $\text{SeO}_2$ ,  $\text{SeO}_3$ , SeOH, and SeOSe. It simultaneously holds that the strength of the Se—O bond in the  $\text{SeO}_2$  group is greater for diselenites than for the acid salts. The order of bond strengths is in agreement with the results obtained so far for the selenites of other cations [27, 29—33].

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