

Cadmium(II) and mercury(II) selenites

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The solubility diagrams in the $\text{CdSeO}_3\text{—SeO}_2\text{—H}_2\text{O}$ and $\text{HgSeO}_3\text{—SeO}_2\text{—H}_2\text{O}$ systems at 298 K were studied for the first time. Two modifications of CdSeO_3 , cadmium(II) diselenite CdSe_2O_5 and cadmium(II) dihydrogen-tetrakis(selenite) $\text{Cd}_3\text{H}_2(\text{SeO}_3)_4$, and mercury(II) dihydrogen-tetrakis(selenite) $\text{Hg}_3\text{H}_2(\text{SeO}_3)_4$ were prepared. The thermal stability and infrared molecular spectra of these compounds were studied and used to determine the force constants of the selenium—oxygen bonds and to characterize the hydrogen bonds present. Modifications of cadmium(II) selenite were studied by X-ray powder analysis.

Впервые изучены диаграммы растворимости в системах $\text{CdSeO}_3\text{—SeO}_2\text{—H}_2\text{O}$ и $\text{HgSeO}_3\text{—SeO}_2\text{—H}_2\text{O}$ при 298 К. Получены две модификации CdSeO_3 , диселенит кадмия(II) CdSe_2O_5 и его дигидротетракис(селенит) $\text{Cd}_3\text{H}_2(\text{SeO}_3)_4$, а также дигидротетракис(селенит) ртути(II) $\text{Hg}_3\text{H}_2(\text{SeO}_3)_4$. Исследованы термическая устойчивость и инфракрасные молекулярные спектры этих соединений, и результаты были использованы для определения силовых постоянных связей селен—кислород и для характеристики имеющихся водородных связей. Модификации селенита кадмия(II) были исследованы методом рентгеноструктурного анализа порошка образца.

Nilson [1] and *Boutzoureano* [2] described the preparation of cadmium(II) selenites and obtained substances with compositions CdSeO_3 , $2\text{CdSeO}_3 \cdot 3\text{H}_2\text{O}$, $2\text{CdSeO}_3 \cdot \text{H}_2\text{SeO}_3$, $2\text{CdSeO}_3 \cdot \text{H}_2\text{SeO}_3 \cdot \text{H}_2\text{O}$, $3\text{CdSeO}_3 \cdot \text{H}_2\text{SeO}_3$, and CdSe_2O_5 . *Markovskii* and *Sapozhnikov* [3] described the preparation and course of the thermal decomposition of two modifications of compound CdSeO_3 (*I* and *II*) and also of substances $3\text{CdSeO}_3 \cdot \text{H}_2\text{SeO}_3$ and $3\text{CdSeO}_3 \cdot \text{SeO}_2$.

Of the mercury selenites, substances with compositions HgSeO_3 [2, 4], $3\text{HgO} \cdot 4\text{HgSeO}_3$ [5], $4\text{HgSeO}_3 \cdot \text{H}_2\text{SeO}_3 \cdot 2\text{H}_2\text{O}$ [4], $\text{Hg}(\text{HSeO}_3)_2$ [4], and $\text{Na}_2\text{Hg}(\text{SeO}_3)_2$ [6] have been described.

Chukhlantsev [7], *Harvey* [8], *Vericeanu* [9], and *Erdenbaeva* [10] studied the solubility products of cadmium(II) and mercury(II) selenites; the latter obtained a value of 9.33×10^{-10} for CdSeO_3 and 1.75×10^{-14} for HgSeO_3 .

Sathianandan [11] studied the infrared spectra of CdSeO_3 . *Paetzold* and *Simon* [12–14] determined the constitution and symmetry of the selenite, hydrogen-selenite, and diselenite anions on the basis of study of infrared spectra.

In the framework of a systematic study of selenites as potential ferroelectric substances, this study was centred on determining all the selenites present in the $\text{CdSeO}_3\text{—SeO}_2\text{—H}_2\text{O}$ system and the $\text{HgSeO}_3\text{—SeO}_2\text{—H}_2\text{O}$ system at 298 K. Simultaneously, the physicochemical properties of these compounds were studied, with special attention to the hydrogen bonds in the acid selenites.

Experimental

Chemicals and methods

Anhydrous cadmium(II) selenite CdSeO_3 was prepared by precipitation of an aqueous solution of cadmium(II) sulfate (Lachema, Brno, pure) [$c(1/2\text{CdSeO}_3) = 3 \text{ mol dm}^{-3}$] by a sodium selenite solution (Lachema, Brno, anal. grade) of the same concentration at 333 K. According to the literature [3] the compound obtained corresponds to modification CdSeO_3 (I). Anhydrous mercury(II) selenite HgSeO_3 was obtained by precipitation of an aqueous mercury(II) nitrate solution (the hemihydrate, Lachema, Brno, anal. grade) [$c(1/2(\text{Hg}(\text{NO}_3)_2) = 0.3 \text{ mol dm}^{-3}$] by a sodium selenite solution (Lachema, Brno, anal. grade) of the same concentration at 323 K. Deuterated analogous $\text{Cd}_3\text{D}_2(\text{SeO}_3)_4$ and $\text{Hg}_3\text{D}_2(\text{SeO}_3)_4$ for infrared spectroscopy were prepared according to the solubility diagram from compounds CdSeO_3 or HgSeO_3 , SeO_2 (Lachema, Brno, anal. grade) and D_2O .

The initial substances and products obtained were analyzed gravimetrically. Selenium was determined by a modified *Bode* [15] method, cadmium after precipitation of the solution with ammonium phosphate and ignition as $\text{Cd}_2\text{P}_2\text{O}_7$ [16] and mercury after prior separation of selenium as mercury(II) sulfide [16]. Solubility was studied by titration analysis. Selenium(IV) was determined iodometrically [17], and cadmium was titrated in a Schwarzenbach buffer medium complexometrically using Eriochrome Black T indicator [18]. In the determination of mercury, an excess of magnesium EDTA was added to the solution; after pH adjustment and addition of Schwarzenbach buffer, the solution was titrated complexometrically using Eriochrome Black T indicator [18]. The mercury content was also determined by atomic absorption spectrometry on a Varian Techtron 1200 instrument at a wavelength of 253.7 nm using an acetylene—air flame.

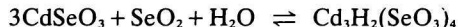
The infrared spectra were measured on an UR-20 instrument (Zeiss, Jena) in the region $\tilde{\nu} = 700\text{—}4000 \text{ cm}^{-1}$. The samples were measured in a nujol suspension using a potassium bromide cuvette. The region $\tilde{\nu} = 1600\text{—}4000 \text{ cm}^{-1}$ was also measured by the tripene suspension method.

The thermal stability of the compounds was studied thermogravimetrically and by differential thermal analysis. The measurements were carried out on a Derivatograph instrument (MOM, Budapest) in the temperature region 298—873 K at a linear temperature increase of 5 K min^{-1} .

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

Study of the solubility in the CdSeO₃—SeO₂—H₂O system at 298 K

The solubility in the CdSeO₃—SeO₂—H₂O system was studied by the Schreinemakers method. The time required for establishment of equilibrium in the individual samples varied from one to two months for the individual samples. The solubility diagram obtained is shown in Fig. 1. It follows from this diagram that the studied system contains the original substance (identified by the X-ray powder pattern) CdSeO₃, as the so far not described modification III (crystallization field I), selenious acid (crystallization field VII) and two incongruently soluble substances, cadmium(II) dihydrogen-tetrakis(selenite) Cd₃H₂(SeO₃)₄ (crystallization field III) and cadmium(II) diselenite CdSe₂O₅ (crystallization field V). Equilibrium between two solid phases and solutions with the compositions of the peritonic points P₂ and P₁ or eutonic point E corresponds to fields II, IV, and VI. Peritonic point P₂ corresponds to values w₁: 1.8 mass % CdSeO₃, 13.5 mass % SeO₂, and 84.7 mass % H₂O. Peritonic point P₁ corresponds to values w₁: 1.6 mass % CdSeO₃, 38.4 mass % SeO₂ and 60.0 mass % H₂O. The eutonic point corresponds to values w₁: 0.9 mass % CdSeO₃, 67.5 mass % SeO₂, and 31.6 mass % H₂O. In field II at a liquid phase composition corresponding to point P₂, the phase reaction occurs with formation of cadmium(II) dihydrogen-tetrakis(selenite) according to the equation



In field IV at a liquid phase composition corresponding to point P₁, the phase reaction occurs with formation of diselenite according to the equation

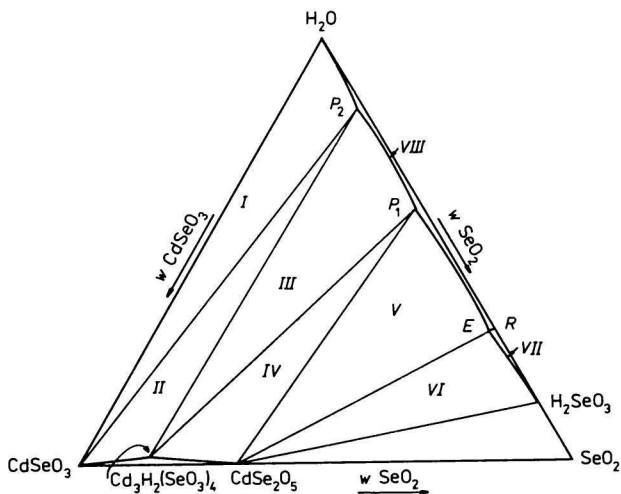
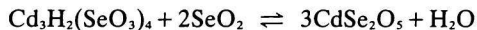


Fig. 1. Solubility diagram in the CdSeO₃—SeO₂—H₂O system at 298 K.



The compounds cadmium(II) dihydrogen-tetrakis(selenite) and cadmium(II) diselenite were prepared on the basis of this solubility diagram. To remove traces of selenious acid, both substances were shaken for several hours with chloroform, collected on an S3 frit under vacuum, washed with chloroform and dried at laboratory temperature. The isolated compounds are white, fine crystalline powders that can be dissolved in dilute acids. The results of the analyses of cadmium and selenium correspond to the calculated data. For $\text{Cd}_3\text{H}_2(\text{SeO}_3)_4$, was found $w(\text{Cd}) = 39.98$ mass % and $w(\text{Se}) = 37.0$ mass % and calculated $w(\text{Cd}) = 39.81$ mass % and $w(\text{Se}) = 37.29$ mass %. For CdSe_2O_5 was found $w(\text{Cd}) = 31.51$ mass % and $w(\text{Se}) = 44.84$ mass % and calculated $w(\text{Cd}) = 32.08$ mass % and $w(\text{Se}) = 45.07$ mass %.

Study of the solubility in the HgSeO_3 — SeO_2 — H_2O system at 298 K

The solubility diagram is shown in Fig. 2. In addition to the starting substances, HgSeO_3 (crystallization field I) and selenious acid H_2SeO_3 (crystallization field V), the system contains the new incongruently soluble substance mercury(II) dihydrogen-tetrakis(selenite), $\text{Hg}_3\text{H}_2(\text{SeO}_3)_4$ (crystallization field III). Fields II and IV describe equilibrium between two solid phases and a solution with the composition of the peritonic point P or eutonic point E. Peritonic point P corresponds to values w_i : 0.20 mass % HgSeO_3 , 31.4 mass % SeO_2 , and 68.4 mass % H_2O . Eutonic point E corresponds to values w_i : 0.30 mass % HgSeO_3 , 69.8 mass % SeO_2 , and 29.9 mass % H_2O . In field II at a composition of the liquid phase

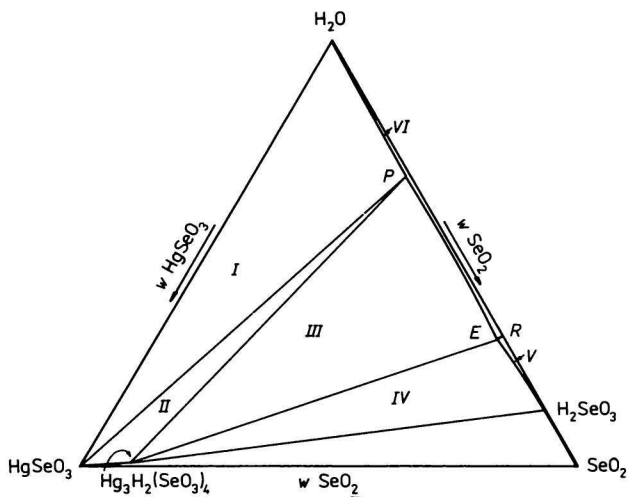


Fig. 2. Solubility diagram in the HgSeO_3 — SeO_2 — H_2O system at 298 K.

given by point *P*, the phase reaction occurs with formation of mercury(II) dihydrogen-tetrakis(selenite) according to the equation



Mercury(II) dihydrogen-tetrakis(selenite) was prepared on the basis of the solubility diagram. Traces of selenious acid were removed by shaking the isolated substance for several hours with chloroform, collection under vacuum on an *S4* frit, washing with chloroform and drying at laboratory temperature. The substance obtained is a white, fine crystalline powder that is readily soluble in dilute acids. The results of analysis of mercury and selenium correspond to the calculated data. For $\text{Hg}_3\text{H}_2(\text{SeO}_3)_4$, was found $w(\text{Hg}) = 54.12$ mass % and $w(\text{Se}) = 27.88$ mass % and calculated $w(\text{Hg}) = 54.14$ mass % and $w(\text{Se}) = 28.41$ mass %.

X-ray powder patterns, thermal stability, and infrared molecular spectra

The newly obtained modification of CdSeO_3 (*III*) and modification of CdSeO_3 (*I*) were characterized by the X-ray powder patterns. The table lists the numerical values of the interplanar distances in pm; the visually evaluated line intensity is given in brackets on a relative scale of 1—10:

CdSeO_3 (*I*): 396(6), 363(6), 356(7), 335(8), 307(8), 299(6), 273(10), 267(1), 256(1), 244(2), 236(2), 218(2), 209(4), 199(6), 194(2), 183(3), 178(5), 173(2), 170(4), 165(2), 159(1), 154(5), 150(6), 132(1), 125(2), 112(3), 108(1), 106(1).

CdSeO_3 : (*III*): 403(2), 361(1), 313(4), 285(10), 263(3), 243(1), 232(1), 221(1), 201(6), 194(1), 189(1), 180(1), 174(6), 169(4), 160(3), 156(6), 145(1), 143(5), 140(1), 135(2), 132(1), 128(6), 124(2), 122(2), 121(1), 117(3), 112(3), 111(4), 105(3), 104(3), 102(1), 101(4), 99(2), 98(1), 97(1), 96(1), 95(2), 94(1), 93(1), 92(2), 91(6), 88(1), 87(2), 86(2), 85(2).

Tables 1 and 2 list the results of study of the thermal stabilities of the studied compounds. The intermediates and final products of thermal decomposition were studied analytically, by X-ray analysis and by the infrared molecular spectroscopic method.

The infrared molecular spectra of the studied compounds are given in Tables 3—6. The absorption bands were assigned according to the work of *Paetzold* and *Simon* [12—14]. The following abbreviations were employed in the tables: vs — very strong, s — strong, m — medium, w — weak, vw — very weak, b — broad, sh — shoulder, ν_s — symmetric stretching, ν_{as} — antisymmetric stretching, δ — deformation, $\tilde{\nu}$ — wavenumber of the absorption band, X = H or D.

Discussion

The CdSeO_3 — SeO_2 — H_2O system at 298 K was found to contain incongruently soluble selenites with composition $n(\text{Cd}):n(\text{Se}):n(\text{H}_2\text{O}) = 1:2:0$ and $3:4:1$. Analysis of the infrared spectra and thermoanalytical curves confirmed that the compounds formed in the system are cadmium(II) diselenite CdSe_2O_5 and cadmium(II) dihydrogen-tetrakis(selenite) $\text{Cd}_3\text{H}_2(\text{SeO}_3)_4$. Compounds with these

Table 1

Thermal decomposition of cadmium(II) selenites

T/K	TGA	DTA	Assignment
298—855	CdSeO ₃ (I) plateau		CdSeO ₃ (I)
298—435	CdSeO ₃ (III) plateau		CdSeO ₃ (III)
435—690	decrease, 1.3 mass %		partial decomposition
690—725	plateau	endo (705 K)	change in modification (III→I)
725—870	decrease, 1.7 mass % CdSe ₂ O ₅		partial decomposition
298—565	plateau		CdSe ₂ O ₅
565—665	decrease, 31.5 mass %	endo (575 K)	decomposition, loss of SeO ₂
665—875	plateau Cd ₃ H ₂ (SeO ₃) ₄		CdSeO ₃ (I)
298—485	plateau		Cd ₃ H ₂ (SeO ₃) ₄
485—555	decrease, 2.7 mass %	endo (485 K)	loss of water, formation of Cd ₃ Se ₄ O ₁₁
555—645	decrease, 15.8 mass %	endo (555 K)	decomposition, loss of SeO ₂
645—875	plateau		CdSeO ₃ (I)

Table 2

Thermal decomposition of mercury(II) selenites

T/K	TGA	DTA	Assignment
298—405	HgSeO ₃ plateau		HgSeO ₃
405—595	decrease, 1.1 mass %		partial decomposition
595—815	decrease, 99.9 mass %	endo (T/K: 605, 645, 670, 755)	complete decomposition and loss of SeO ₂ , O ₂ , Hg
298—420	Hg ₃ H ₂ (SeO ₃) ₄ plateau		Hg ₃ H ₂ (SeO ₃) ₄
420—480	decrease, 1.7 mass %	endo (435 K)	loss of water, formation of Hg ₃ Se ₄ O ₁₁
480—590	decrease, 11.7 mass %	endo (515 K)	loss of SeO ₂ , formation of HgSeO ₃
590—815	decrease, 99.8 mass %	endo (T/K: 595, 650, 750)	complete decomposition and loss of SeO ₂ , O ₂ , Hg

Table 3

Infrared spectra of CdSeO₃ (I), CdSeO₃ (III), and HgSeO₃

CdSeO ₃ (I) $\tilde{\nu}/\text{cm}^{-1}$	CdSeO ₃ (III) $\tilde{\nu}/\text{cm}^{-1}$	HgSeO ₃ $\tilde{\nu}/\text{cm}^{-1}$	Assignment
443 w	452 sh	400 vw	} $\delta(\text{SeO}_3)$
475 m	485 s	424 vw	
508 m		498 m	
725 vs	718 vs	680 vs	} $\nu_{\text{as}}(\text{SeO}_3)$
740 sh		723 vs	
760 s	788 s	820 w	} $\nu_s(\text{SeO}_3)$
		831 m	

Table 4

Infrared spectrum of CdSe₂O₅

$\tilde{\nu}/\text{cm}^{-1}$	Assignment
448 s	$\delta(\text{SeO}_2)$
625 s	$\nu(\text{SeOSe})$
791 vs	$\nu_{\text{as}}(\text{SeO}_2)$
860 s	} $\nu_s(\text{SeO}_2)$
885 vs	

compositions have been described by Nilson [1] and Boutzoureano [2] without closer description of their nature. The mole ratio of the initial compounds $n(\text{CdSeO}_3):n(\text{H}_2\text{SeO}_3):n(\text{H}_2\text{O})$ yielding optimum amounts of these substances was found from the solubility diagram: for preparation of CdSe₂O₅, a ratio of 1.0:3.9:12.2 and for preparation of Cd₃H₂(SeO₃)₄ a ratio of 1.0:1.3:17.1.

A single incongruently soluble compound with composition $n(\text{Cd}):n(\text{Se}):n(\text{H}_2\text{O})=3:4:1$ was found in the HgSeO₃—SeO₂—H₂O system at 298 K. Study of the infrared spectra and thermal decomposition confirmed that this so far undescribed compound is mercury(II) dihydrogen-tetrakis(selenite), Hg₃H₂(SeO₃)₄. The mole ratio of the starting compounds $n(\text{HgSeO}_3):n(\text{H}_2\text{SeO}_3):n(\text{H}_2\text{O})$ leading to optimum yield of this acid salt is 1.0:3.2:13.6.

The above systems can be compared with the systems of the selenites of the other divalent metals on the basis of the types of salts formed. Under similar conditions, the formation of acid salts of the type M^{II}(HSeO₃)₂ · xH₂O was observed in systems containing the selenites of magnesium [19], calcium [20], strontium [21], cobalt

Table 5

Infrared spectra of $\text{Cd}_3\text{H}_2(\text{SeO}_3)_4$ and $\text{Cd}_3\text{D}_2(\text{SeO}_3)_4$

$\text{Cd}_3\text{H}_2(\text{SeO}_3)_4$ $\tilde{\nu}/\text{cm}^{-1}$	$\text{Cd}_3\text{D}_2(\text{SeO}_3)_4$ $\tilde{\nu}/\text{cm}^{-1}$	$\frac{\tilde{\nu}(\text{Cd}_3\text{H}_2(\text{SeO}_3)_4)}{\tilde{\nu}(\text{Cd}_3\text{D}_2(\text{SeO}_3)_4)}$	Assignment
401 m	400 w	1.00	} $\delta(\text{SeO}_2, \text{SeO}_3)$
462 m	460 m	1.00	
487 m	485 m	1.00	
509 m	510 m	1.00	
663 s	653 m	1.02	} $\nu(\text{SeO})(\text{SeOX})$
680 sh	680 m	1.00	
708 s	704 m	1.01	} $\nu_{\text{as}}(\text{SeO}_2, \text{SeO}_3)$
739 vs	735 s	1.01	
	794 m		
809 sh	807 m	1.01	} $\nu_s(\text{SeO}_2, \text{SeO}_3)$
828 s	828 s	1.00	
	860 w		
885 sh	883 w	1.00	} $\delta(\text{OX})(\text{SeOX})$
1250 m	925 m	1.35	
2200—2600 mb (max. 2450)	1700—2000 mb (max. 1840)	1.33	} $\nu(\text{OX})(\text{SeOX})$
2750—3500 mb (max. 2950)	2050—2350 mb (max. 2200)	1.33	

Table 6

Infrared spectra of $\text{Hg}_3\text{H}_2(\text{SeO}_3)_4$ and $\text{Hg}_3\text{D}_2(\text{SeO}_3)_4$

$\text{Hg}_3\text{H}_2(\text{SeO}_3)_4$ $\tilde{\nu}/\text{cm}^{-1}$	$\text{Hg}_3\text{D}_2(\text{SeO}_3)_4$ $\tilde{\nu}/\text{cm}^{-1}$	$\frac{\tilde{\nu}(\text{Hg}_3\text{H}_2(\text{SeO}_3)_4)}{\tilde{\nu}(\text{Hg}_3\text{D}_2(\text{SeO}_3)_4)}$	Assignment
400 vw	400 vw	1.00	} $\delta(\text{SeO}_2, \text{SeO}_3)$
446 w	444 w	1.00	
516 w	516 w	1.00	
647 m	636 m	1.02	} $\nu(\text{SeO})(\text{SeOX})$
705 m	701 m	1.01	
	720 sh		} $\nu_{\text{as}}(\text{SeO}_2, \text{SeO}_3)$
800 sh	800 sh	1.00	
825 m	822 m	1.00	
1235 w	915 w	1.35	} $\delta(\text{OX})(\text{SeOX})$
2250—2600 wb (max. 2440)	1650—2000 wb (max. 1810)	1.35	
2650—3200 mb (max. 2900)	2100—2400 mb (max. 2240)	1.30	} $\nu(\text{OX})(\text{SeOX})$

[22], and nickel [23]. For zinc [24] and barium [21] at 298 K, only the corresponding diselenite was found. The systems of cadmium(II) and mercury(II) selenites are located, according to their behaviour, between the systems of zinc(II) and barium(II) selenites and the systems of the other divalent metals. With Cd(II) and Hg(II), an acid salt with a $n(\text{M}^{\text{II}}):n(\text{Se})$ ratio greater than 1:2 is formed and, in addition, a condensed salt of Cd(II) — a diselenite. The formation of acid salts with a ratio of $n(\text{M}^{\text{II}}):n(\text{Se}) = 1:2$, found for a number of other divalent metals, can be assumed at lower temperatures. For zinc, this has been confirmed in the formation of $\text{Zn}(\text{HSeO}_3)_2 \cdot 2\text{H}_2\text{O}$ in the study of the $\text{ZnSeO}_3\text{—SeO}_2\text{—H}_2\text{O}$ system at 273 K [24]. So far, the $\text{CdSeO}_3\text{—SeO}_2\text{—H}_2\text{O}$ system is the only system containing selenites known that contains diselenite and an acid salt simultaneously at a single temperature.

Study of the powder patterns has indicated that modification CdSeO_3 (I) is formed in fast processes (precipitation of a cadmium(II) sulfate solution by sodium selenite, thermal decomposition), while modification CdSeO_3 (III) can be prepared when the crystal formation occurs more slowly (recrystallization in a heterogeneous mixture of the phase diagram). Formation of modification CdSeO_3 (II), obtained by *Markovskii* and *Sapozhnikov* [3] in the reaction of CdCO_3 with excess Na_2SeO_3 , was not observed in this study.

Study of the thermoanalytical curves of cadmium(II) selenites has indicated that modification CdSeO_3 (III) is converted to modification CdSeO_3 (I) at 705 K. Only partial decomposition of CdSeO_3 (III) occurs in the temperature range 298—870 K, accompanied by a small mass loss (1.7%). Similar partial decomposition has been observed for a number of other selenites [25]. In the temperature range 405—595 K, mercury(II) selenite decomposes only partly, followed by complete decomposition of the substance, accompanied by formation of volatile products (mass decrease of 99.9%).

Decomposition of compounds $\text{Cd}_3\text{H}_2(\text{SeO}_3)_4$ and $\text{Hg}_3\text{H}_2(\text{SeO}_3)_2$ in the temperature range 485—555 K and 420—480 K, respectively, leads to formation of the corresponding tetraselenites, $\text{M}_3^{\text{II}}\text{Se}_4\text{O}_{11}$ and water. The mass decrease in this decomposition is greater than predicted by theoretical calculations in both cases, as the loss of water is connected with partial decomposition of the compound and loss of part of the SeO_2 . This fact was also confirmed by analysis of the tetraselenite obtained, with a lower selenium content. Pure tetraselenite $\text{Cd}_3\text{Se}_4\text{O}_{11}$ and $\text{Hg}_3\text{Se}_4\text{O}_{11}$ cannot be prepared by thermal decomposition of the acid salts for this reason. The intermediates $\text{Cd}_3\text{Se}_4\text{O}_{11}$ and $\text{Hg}_3\text{Se}_4\text{O}_{11}$ decompose further to selenites with loss of selenium(IV) oxide. The CdSeO_3 (I) modification is formed from the cadmium compound. Cadmium(II) diselenite decomposes similarly with formation of the CdSeO_3 (I) modification and loss of selenium(IV) oxide.

Study of the infrared spectra has demonstrated that the modifications CdSeO_3 (I) and (III) found differ in the region of deformation vibrations of the SeO_3 group

in the number and positions of the bands, while they differ only in a change in the band positions in the region of the stretching vibrations of the SeO group. For cadmium(II) diselenite or the acid salt, $\text{Cd}_3\text{H}_2(\text{SeO}_3)_4$ and $\text{Hg}_3\text{H}_2(\text{SeO}_3)_4$, the infrared spectra completely confirmed the presence of bridging groups Se—O—Se or of groups OH(Se) and SeO(H), appearing as the corresponding bands in the region of stretching and deformation vibrations. For the acid salts, spectral interpretation required consideration of the presence of the SeO_3 group because of the lower number of hydrogen atoms in the molecule (2 hydrogen atoms per 4 selenite anions); this group has bands that partially overlap with the bands of the SeO_2 group.

The force constants of the Se—O bonds were calculated from the wavenumbers of the bands of the stretching vibrations of the SeO_3 , SeO_2 , SeOH , and SeOSe groups using the *Lehmann* relationship [26], in the manner described for magnesium(II) selenite [19]. The values obtained are listed in Table 7 and indicate that the strength of the Se—O bond decreases in the studied compounds in the order of the groups: SeO_2 ($\text{Se}_2\text{O}_5^{2-}$), SeO_2 ($\text{H}_2(\text{SeO}_3)_4^{6-}$), SeO_3 , SeOH , Se—O—Se. Similar conditions were found for the force constants for a number of other selenites [19—25].

It follows from comparison of the force constants for Se—O in the SeOH group with acid zinc(II) selenite, $\text{Zn}(\text{HSeO}_3)_2 \cdot 2\text{H}_2\text{O}$ [24], that the strength of this bond decreases in acid cadmium(II) and mercury(II) selenites, causing a less marked weakening of the O—H bond, appearing for zinc in its easy breakage with formation of diselenite group and freed water. Thus, acid salts are found at a temperature of 298 K in heterogeneous systems of this metal, while the acid zinc salt is formed only at lower temperatures. The discussed bonding conditions are further reflected in the marked increase in the decomposition temperatures of the compounds $\text{Cd}_3\text{H}_2(\text{SeO}_3)_4$ and $\text{Hg}_3\text{H}_2(\text{SeO}_3)_4$ connected with breakage of the system of hydrogen bonds. While decomposition of $\text{Zn}(\text{HSeO}_3)_2 \cdot 2\text{H}_2\text{O}$ is complete

Table 7

Force constants of the selenium—oxygen bonds in the studied compounds

Compound	Group	$K_{\text{Se-O}}/\text{N m}^{-1}$
CdSeO_3 (I)	SeO_3	426
CdSe_2O_5	SeO_2	544
	SeOSe	307
	$\text{SeO}_2(\text{SeO}_3)$	474(453)
$\text{Cd}_3\text{H}_2(\text{SeO}_3)_4$	SeOH	345
	SeO_3	433
HgSeO_3	SeO_3	433
	$\text{SeO}_2(\text{SeO}_3)$	462(438)
$\text{Hg}_3\text{H}_2(\text{SeO}_3)_4$	$\text{SeO}_2(\text{SeO}_3)$	462(438)
	SeOH	328

at 365 K, this decomposition of acid cadmium(II) and mercury(II) salts brings at 480 K and 420 K, respectively.

Assuming that no interbond tunnel effect is present in the compounds $\text{Cd}_3\text{H}_2(\text{SeO}_3)_4$ and $\text{Hg}_3\text{H}_2(\text{SeO}_3)_4$ [27], found for the acid selenites of the alkali metals, the hydrogen bonds present can be characterized on the basis of the wavenumber of the stretching vibrations of the hydroxyl group. The lengths of these bonds were found from the correlation diagrams [28—32] $\nu_{\text{OH}}-R_{\text{O}\cdots\text{O}}$ and lie in the ranges 255—260 pm and 264—269 pm for the cadmium(II) and mercury(II) salts, respectively. These are all hydrogen bonds of the anion—anion type, that the observed lengths indicate to be between strong and medium strong. The determined lengths of the hydrogen bonds are comparable with hydrogen bonds in other known selenites of divalent metals [19—24, 33].

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