Cobalt(II) selenites

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Dedicated to Professor Dr. Ing. J. Klikorka, in honour of his 60th birthday

The solubility diagram of $CoSeO_3$—SeO_2—H_2O at 298 K was studied for the first time; on the basis of this diagram, the dihydrate of cobalt(II) hydrogenselenite, $Co(HSeO_3)_2 \cdot 2H_2O$, was prepared. The $CoSeO_3 \cdot 2H_2O$ and $Co(HSeO_3)_2 \cdot 2H_2O$ selenites were studied by the powder X-ray technique and by infrared molecular and electronic reflectance spectroscopy and their magnetic properties were determined. The force constants of the bonds between selenium and oxygen were found from the infrared spectra: 454 N m^{-1} for $CoSeO_3 \cdot 2H_2O$, 541 N m^{-1} in the SeO_2 group, and 307 N m^{-1} in the SeOH group for $Co(HSeO_3)_2 \cdot 2H_2O$. Weak to strong hydrogen bonds between the water molecules and the anions, between water molecules, and between anions are present in both selenites. Study of the electronic reflectance spectra and of the magnetic properties indicated octahedral arrangement of the coordination sphere of the cobalt(II) cation, yielding a weak crystal field with a high-spin arrangement.

Впервые была изучена диаграмма растворимости системы $CoSeO_3$—SeO_2—H_2O при 298 K. На основании этой диаграммы был приготовлен дигидрат гидрогенселенита кобальта(II) $Co(HSeO_3)_2 \cdot 2H_2O$. Селениты $CoSeO_3 \cdot 2H_2O$ и $Co(HSeO_3)_2 \cdot 2H_2O$ были изучены методами порошковой рентгенографии, инфракрасной спектроскопии, спектров электронного отражения и были определены их магнитные свойства. Силовые константы связей между селеном и кислородом были определены по ИК спектрам: 454 Н $м^{-1}$ для $CoSeO_3 \cdot 2H_2O$, 541 Н $м^{-1}$ для группы SeO_2 и 307 Н $м^{-1}$ для SeOH в $Co(HSeO_3)_2 \cdot 2H_2O$. В обоих селенитах присутствуют от слабых до сильных водородные связи между водой и анионами, между молекулами воды и между анионами. Изучение электронных спектров отражения и магнитных свойств приводит к заключению о октаэдрической координационной сфере катиона кобальта(II) со слабым кристаллическим полем и высокоспиновой электронной застройкой.

Espil [1], *Boutzoureano* [2], *Gattow* [3], *Makatun* [4], and *Nilson* [5] have discussed the preparation of cobalt(II) selenites and have described anhydrous cobalt(II) selenite and compounds with the composition $CoSeO_3 \cdot nH_2O$ ($n = 1/3$, 1, 2). *Kohn* [6, 7] and *Chukhlantsev* [8] studied the crystal structure, magnetic properties, and solubility products of $CoSeO_3$. *Makatun* [4], *Pechkovskii* [9], *Selivanova* [10], and *Lieder* [11] studied the thermal decomposition of $CoSeO_3 \cdot 2H_2O$ and the latter also carried out a preliminary determination of the structure of cobalt(II) selenites; hydration was studied by *Melinkova* [12] and *Makatun* [13].

Boutzoureano [2] and *Nilson* [5] studied salts with a cobalt to selenium ratio other than 1 : 1 and prepared substances with the composition $CoO \cdot 2SeO_2 \cdot 3H_2O$, $CoO \cdot 2SeO_2$, and $CoSeO_3 \cdot 2SeO_2 \cdot H_2O$. Cobalt(II) diselenite trihydrate and its crystallographic parameters were studied by *Lieder* [14].

Paetzold and *Simon* [15—17] determined the constitution and symmetry of the selenite, hydrogenselenite, and diselenite anions on the basis of the infrared spectra. *Khanna* [18], *Torrie* [19], and *Cody* [20] carried out similar studies of the stretching vibration region of the SeO_3, SeO_2, and SeOH groups.

This work was carried out in order to prepare all the selenites in the $CoSeO_3$—SeO_2—H_2O system at 298 K, to find optimal conditions for their preparation and to study their bonding conditions.

Experimental

Chemicals and methods

Cobalt(II) selenite dihydrate $CoSeO_3 \cdot 2H_2O$ was prepared by precipitating a 0.05 M aqueous solution of cobalt(II) nitrate (Lachema, Brno; anal. grade) with a 0.05 M aqueous solution of sodium selenite (Lachema, Brno; anal. grade) at 323 K. The deuterated analogue $CoSeO_3 \cdot 2D_2O$ for infrared spectroscopy was prepared in a similar manner using D_2O. The deuterated analogue $Co(DSeO_3)_2 \cdot 2D_2O$ for infrared spectroscopy was prepared from $CoSeO_3 \cdot 2D_2O$, SeO_2 (Lachema, Brno; anal. grade), and D_2O using the solubility diagram.

The initial substances and final products were analyzed gravimetrically. Selenium was determined by a modified method as described by *Bode* [21] and cobalt was found electrogravimetrically after separation of selenium [22]. Titration analysis was used in the solubility study. Selenium(IV) was determined iodometrically by the *Ganitskii* method [23]; after preliminary adjustment of the solution pH with ammonia, cobalt was titrated complexometrically using murexide indicator [24].

Powder X-ray patterns were measured on a Mikrometa 2 instrument (Chirana, Czechoslovakia) using cells with a diameter of 57.3 mm and an iron filter with an exposure of 100—120 min, voltage of 35 kV and current of 20 mA.

The infrared spectra were measured on a UR-20 instrument (Zeiss, Jena) in the region of 400—4000 cm^{-1}. The spectra were recorded using the nujol mull method with potassium bromide cells. The region of the hydroxyl group stretching vibrations was also measured by the tripene suspension method.

The electronic reflectance spectra in the region of 10 000—50 000 cm^{-1} were measured on a VSU-1 instrument (Zeiss, Jena). Samples were diluted in a ratio of 1:1 or 1:2 with magnesium oxide, which was simultaneously used as a reference. In the region of 5000—12 000 cm^{-1}, the spectra were measured on a Unicam S.P. 700 instrument in a nujol mull applied to filter paper.

The magnetic susceptibility was measured on a magnetic balance by the Gouy method [25] at 298 K using $Co[Hg(SCN)_4]$ as a standard.

Study of solubility in the $CoSeO_3$—SeO_2—H_2O *system at 298 K*

The Schreinemakers method was used to study solubility in the $CoSeO_3$—SeO_2—H_2O system. The time required for equilibration in the individual samples was from 1 to 2 months. The solubility diagram obtained, constructed by the Gibbs—Roozeboom method, is shown in Fig. 1. It follows that, in addition to the original substances, corresponding to crystallization fields *I* and *V*, cobalt(II) hydrogenselenite dihydrate $Co(HSeO_3)_2 \cdot 2H_2O$ is formed in the system, corresponding to crystallization field *III*. Equilibration between two solid phases and a solution with the composition of the peritonic point *P* or the eutonic point

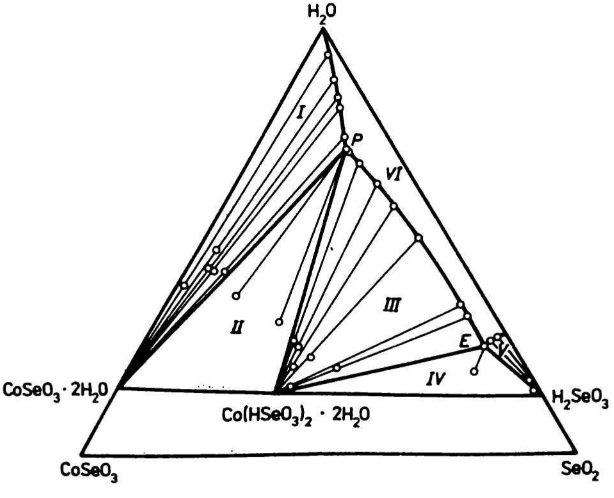

Fig. 1. Solubility diagram of the $CoSeO_3$—SeO_2—H_2O system.

E corresponds to fields *II* and *IV*. Peritonic point *P* corresponds to the composition 8.8% $CoSeO_3$, 18.9% SeO_2, and 72.3% H_2O and eutonic point *E* to the composition 4.8% $CoSeO_3$, 69.3% SeO_2, and 25.9% H_2O. In field *II* with a liquid phase composition corresponding to point *P*, a phase reaction occurs yielding the hydrogenselenite

$$CoSeO_3 + SeO_2 + 3H_2O \rightleftharpoons Co(HSeO_3)_2 \cdot 2H_2O$$

The dihydrate of cobalt(II) hydrogenselenite was obtained on the basis of the solubility diagram. The crystalline substance formed was collected on an *S3* frit, rinsed with chloroform and dried in the air at laboratory temperature. The isolated compound is a pink-purple crystalline powder which is stable in the air at laboratory temperature. The results of gravimetric analysis correspond to the calculated data (found: 16.75% Co, 45.22% Se; calculated: 16.79% Co, 45.0% Se).

Table 1

Infrared spectrum of $CoSeO_3 \cdot 2H_2O$ and of $CoSeO_3 \cdot 2D_2O$

$CoSeO_3 \cdot 2H_2O$ $\tilde{\nu}/cm^{-1}$	$CoSeO_3 \cdot 2D_2O$ $\tilde{\nu}/cm^{-1}$	$\frac{\tilde{\nu}CoSeO_3 \cdot 2H_2O}{\tilde{\nu}CoSeO_3 \cdot 2D_2O}$	Assignment
405 w	405 sh	1.00	$\nu(Co—O)$ $\delta(SeO_3)$
495 m	465 s	1.06	
505 m	470 s	1.07	
595 w	—	—	$\varrho(X_2O)$
705 sh	705 sh	1.00	$\nu_{as}(SeO_3)$
730 s	725 s	1.01	
—	755 m		
765 sh	575 w	1.33	$\varrho(X_2O)$
805 m	—	—	
820 s	820 s	1.00	$\nu_s(SeO_3)$
1625 w	1200 w	1.35	$\delta(OX)(X_2O)$
2210—2500 wb	—	—	?
2990 sb	2240 m	1.33	$\nu(OX)(X_2O)$
3180 sb	2400 m	1.33	
3250 s	2420 m	1.34	
3455 s	2570 m	1.34	

vs — very strong, s — strong, m — medium, w — weak, b — broad, sh — shoulder, ν_s — symmetric stretching, ν_{as} — antisymmetric stretching, δ — deformation, ϱ — rocking, $\tilde{\nu}$ — wavenumber of the absorption band, X = H, D.

Powder X-ray method, infrared molecular and electronic reflectance spectroscopy and magnetic susceptibility

The studied compounds were characterized by X-ray powder patterns. The interplanar distances are given in the further text in pm, and the numbers in brackets give a relative intensity of 1—5 found visually.

$CoSeO_3 \cdot 2H_2O$: 579(5), 453(2), 404(3), 378(4), 348(5), 321(2), 304(5), 272(3), 263(2), 256(1), 251(2), 238(4), 222(3), 214(1), 203(1), 199(1), 194(1), 188(1), 180(1), 174(4), 170(2), 166(2), 160(3), 152(2), 151(1), 150(2), 147(1), 146(3), 138(1), 136(1), 133(1), 130(1), 126(1), 117(1), 114(1), 110(1), 108(1), 98(1), 97(2), 95(1), 93(2), 92(1).

$Co(HSeO_3)_2 \cdot 2H_2O$: 491(3), 453(5), 407(1), 350(3), 333(2), 323(5), 312(1), 291(2), 281(3), 263(5), 230(2), 222(3), 214(1), 207(4), 195(3), 186(1), 177(1), 173(1), 171(4), 166(4), 162(3), 158(4), 153(4), 149(1), 144(2), 141(1), 139(2), 136(2), 132(3), 129(3),125(1),123(1), 121(1), 120(2), 116(1), 115(2), 113(1), 112(1), 110(1), 108(3), 105(3), 104(2), 103(2), 101(2), 99(1), 98(1), 97(1), 96(2), 95(3), 93(2).

The infrared spectra of cobalt(II) selenites and their deuterated analogues are given in Tables 1 and 2. Absorption band assignment was carried out according to the works of *Paetzold* [15—17] and *Cody* [20].

The results of the electronic reflectance spectra studies are listed in Table 3. Assignment of the individual absorption bands and calculation of the crystal field strength Δ and of the Racah parameters B were carried out by the *Reedijk* method [26]. Nephelauxetic parameter β was calculated from the relationship $\beta = B/B_0$ where B_0 is the Racah parameter B for isolated ions (for Co^{2+} 971 cm^{-1}).

Table 2

Infrared spectrum of $Co(HSeO_3)_2 \cdot 2H_2O$ and of $Co(DSeO_3)_2 \cdot 2D_2O$

$Co(HSeO_3)_2 \cdot 2H_2O$ $\tilde{\nu}/cm^{-1}$	$Co(DSeO_3)_2 \cdot 2D_2O$ $\tilde{\nu}/cm^{-1}$	$\frac{\tilde{\nu}Co(HSeO_3)_2 \cdot 2H_2O}{\tilde{\nu}Co(DSeO_3)_2 \cdot 2D_2O}$	Assignment
495 m	495 s	1.00	$\delta(SeO_2)$
555 m	420 m	1.32	$\varrho(X_2O)$
710 m	510 s	1.39	
625 s	615 m	1.02	$\nu(SeO)(SeOX)$
—	640 m	—	
810 s	810 s	1.00	$\nu_{as}(SeO_2)$
850 s	850 s	1.00	$\nu_s(SeO_2)$
1140 m	860 sh	1.33	$\delta(OX)(SeOX)$
1635 m	1210 w	1.35	$\delta(OX)(X_2O)$
2450 m	—	—	$\nu(OX)(SeOX)$
3100 sb	2320 sb	1.34	
3440 s	2550 s	1.35	$\nu(OX)(X_2O)$

Table 3

Electronic reflectance spectra of cobalt(II) selenites

Compound	$\tilde{\nu}/\text{cm}^{-1}$	Assignment	Δ/cm^{-1}	B/cm^{-1}	β
$CoSeO_3 \cdot 2H_2O$	7 700	${}^4T_{1g}(\vec{F}){}^4T_{2g}$	8390	810	0.834
	18 800	${}^4T_{1g}(\vec{F}){}^4T_{1g}(P)$			
$Co(HSeO_3)_2 \cdot 2H_2O$	7 600	${}^4T_{1g}(\vec{F}){}^4T_{2g}$	8270	830	0.855
	19 000	${}^4T_{1g}(\vec{F}){}^4T_{1g}(P)$			

$\tilde{\nu}$ — wavenumber of the absorption band, Δ – crystal field strength, B — Racah parameter, β — nephelauxetic parameter.

Table 4

Magnetic properties of cobalt(II) selenites

Compound	$\chi/\text{m}^3\ \text{kg}^{-1}$	$\chi'_M/\text{m}^3\ \text{kg}^{-1}$	μ_{eff}/B.M.
$CoSeO_3 \cdot 2H_2O$	50.10×10^{-9}	11.20×10^{-6}	5.19
$Co(HSeO_3)_2 \cdot 2H_2O$	31.45×10^{-9}	11.16×10^{-6}	5.18

Results of the magnetic susceptibility study are given in Table 4. The molar susceptibility values were found from the measured weight susceptibility values χ and were corrected for the diamagnetism of the cation, anion, and crystal water [27]. The corrected molar susceptibility values χ'_M were used to calculate the effective magnetic moments, μ_{eff}.

Discussion

An incongruently soluble selenite with composition $Co:Se:H_2O = 1:2:3$ was found in the $CoSeO_3$—SeO_2—H_2O system at 298 K. A mole ratio of the initial components leading to an optimal yield of this substance equal to $CoSeO_3:H_2SeO_3:H_2O = 1:1.5:5.7$ was found on the basis of study of the solubility diagram. A compound with this composition was described by *Boutzoureano* [2] who, however, did not give the bonding conditions differentiating between hydrated hydrogenselenite and diselenite. Under similar conditions, only acid salts are formed for the selenites of the alkali metals and of Mg, Ca, and Sr and only diselenites with the salts of Ba and Zn. It follows unambiguously from the infrared spectra that the new compound in the studied system is cobalt(II) hydrogenselenite dihydrate, $Co(HSeO_3)_2 \cdot 2H_2O$.

The force constants of the Se—O bonds were calculated from the wavenumbers of the stretching vibration bands of the SeO_3, SeO_2, and SeOH groups using the *Lehmann* relationship [28] by the method described with magnesium(II) selenites [30]. For groups SeO_3, SeO_2, and SeOH, the values 454, 541, and 307 $N\,m^{-1}$ have been obtained, respectively. The values obtained indicate that the force constant in the SeO_2 group of the hydrogenselenite anion is somewhat higher than in the SeO_3 group and that the force constant for the SeOH group is considerably lower than that for the SeO_3 group. Similar conditions were also observed for the selenites of the alkali metals [20, 29] and magnesium selenites [30]. The energies and lengths of the hydrogen bonds were found from the wavenumbers of the stretching vibration bands of the hydroxyl groups. The *Sokolov* relationship [31] modified for values in kJ was used for energy calculation

$$E = 246.3\,\frac{\tilde{\nu}_0 - \tilde{\nu}}{\tilde{\nu}_0}$$

where a value of 3750 was substituted for $\tilde{\nu}_0$, which is the wavenumber of the stretching vibration of the hydroxyl group of free water molecules and the wavenumber of the stretching vibration of the hydroxyl group in the hydrate was substituted for $\tilde{\nu}$.

The lengths of the hydrogen bonds were obtained from the ν_{OH}—$R_{O...O}$ correlation diagrams of *Naberukhin* [32], *Pirrene* [33], *Novak* [34], *Ratajczak* [35], and *Nakamoto* [36], were averaged and are given in Table 5. Weak to strong hydrogen bonds are present in $CoSeO_3 \cdot 2H_2O$ between the water molecules and anions and between the water molecules and in $Co(HSeO_3)_2 \cdot 2H_2O$ between water molecules and anions and between the anions. As the hydrogen bonds between the water molecules and the SeO_3^{2-} anions are stronger than between the water molecules, the anions can be classified as positively hydrated [37].

Table 5

Energies and lengths of the hydrogen bonds

Compound	Bond type	E/kJ mol^{-1}	O ... O Distance/pm
$CoSeO_3 \cdot 2H_2O$	w—w	19.4	286
	w—a	32.9	276
	w—a	37.5	273
	w—a	49.9	269
$Co(HSeO_3)_2 \cdot 2H_2O$	w—w	20.4	285
	w—a	42.7	271
	a—a	—	258

w — water, a — anion.

It has been demonstrated on the basis of the electronic reflectance spectra, magnetic properties, and known structure of the isomorphous dihydrate of zinc(II) selenite [38] that the coordination sphere of the cobalt(II) cation consists of an octahedron of donor oxygen atoms from the anions and water molecules, yielding a weak crystal field with a high-spin electron arrangement. The crystal field strength for selenite dihydrate is greater than that for hydrogenselenite dihydrate, corresponding to the conditions in the coordination sphere with phosphite and hydrogenphosphite anions [39].

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