

The Hydrates of Double Selenates

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This study deals with the hydrates of double selenates of the type $M_2M^{II}(SeO_4)_2 \cdot xH_2O$ ($x = 2$ or 6) from the point of view of the effect of the M^I ($M^I = K, Rb, Cs, Tl, NH_4$) and M^{II} ($M^{II} = Mg, Zn, Cd, Mn, Co, Ni, Cu$) cations on the water molecules in the coordination sphere of the bivalent metal. The bonds of the water molecules were studied on the basis of the bands of the "wagging" libration modes of the water molecules, and the bands of the stretching vibrations in the infrared molecular spectrum, and using thermal analysis. According to the study of "wagging" libration modes the deformation of the coordination sphere of the hexaaqua cations $[M^{II}(H_2O)_6]^{2+}$ increases with the decreasing radius of cation M^+ and with the increasing radius of cation M^{2+} , and thus the tendency to form dihydrates of the studied double selenates also increases. This dependence corresponds with the thermal decomposition of the hexahydrates to dihydrates. Thermal decomposition of dihydrates to the anhydrous salts is determined primarily by the strength of the hydrogen bonds between the test anions and the water molecules, once again affected by the two types of cations. The NH_4^+ , Tl^+ , Cu^{2+} , and Ni^{2+} cations specifically affect the thermal decomposition of the hydrates of the double selenates.

The hydrates of double selenates belong to the group of ionic salts the formation of which is dependent on electrostatic interactions between the cations, on the one hand, and the anions and water molecules, on the other hand. *Balarev* [1–3] discussed ionic crystal hydrates and came to a number of general conclusions on their formation and behaviour. He states that the properties of the cationic hydration spheres in crystal hydrates are determined by the Pauling rules, strength of the bond $M-OH_2$, action of cations outside the spheres, stabilization of the crystal field energy, the Jahn–Teller effect, hydrogen bonds and metal–metal bonds. Here, we studied the crystal hydrates of double selenates of the type $M_2M^{II}(SeO_4)_2 \cdot xH_2O$ (M^I — monovalent metal, M^{II} — bivalent metal, $x = 2$ or 6), as these substances have been studied only rarely and briefly. We decided to complete systematic data in this field and we have already studied a number of systems [4–10] to determine the conditions for their formation. This work describes the behaviour of the crystal hydrates of double selenates in the solid state from the point of view of the type of bonding of the water molecules in the hydration sphere of the M^{2+} cation. The M^+ cations were selected as K^+ , Rb^+ , Cs^+ , Tl^+ , and NH_4^+ and the M^{2+} cations as transition metal cations, Co^{2+} , Ni^{2+} or Cu^{2+} , or cations with zero stabilization energy, Mg^{2+} , Mn^{2+} , Zn^{2+} or Cd^{2+} , which, according to *Balarev* [1], are especially suitable for the formation of crystal hydrates of double salts. The study was carried out using the well-defined bands of the libration modes of the water molecule of the "wagging" type [11–29] and the bands of the stretching vibrations of the water molecule in the infrared spectra, X-ray diffraction analysis and thermal analysis [30–35].

EXPERIMENTAL

The selenates M_2SeO_4 , $M^{II}SeO_4 \cdot xH_2O$, and $M_2M^{II}(SeO_4)_2 \cdot xH_2O$ were prepared by previously described methods [4–10, 36]. All the selenates prepared were repeatedly recrystallized from water and their composition was confirmed by analysis of Se and metals using standard methods [37–40]. Deuterated salts were prepared by multiple recrystallization from D_2O and their composition was confirmed by analysis as described above. The deuterated and undeuterated salts were characterized using powder X-ray diffraction patterns indicating that they are isostructural.

Infrared spectra in the $\tilde{\nu}$ region $350-4000\text{ cm}^{-1}$ were measured on UR-20 (Zeiss, Jena) and Perkin–Elmer 225 instruments using the nujol suspension, triprene suspension, and KE1-F suspension methods and KBr cuvettes at laboratory temperature. The thermal stability was studied on the derivatograph (MOM, Budapest), in the temperature region $25-600\text{ }^\circ\text{C}$ at a heating rate of $5\text{ }^\circ\text{C min}^{-1}$ and in the region $25-300\text{ }^\circ\text{C}$ at a heating rate of $2.5\text{ }^\circ\text{C min}^{-1}$. In connection with the preparation of the double selenates, a study was also carried out of the thermal decomposition on heating for 24 h at a preselected temperature in the interval $5-7\text{ }^\circ\text{C}$ in the temperature range $25-430\text{ }^\circ\text{C}$.

RESULTS AND DISCUSSION

Infrared Molecular Spectra

Table 1 gives the wavenumbers of the bands of the "wagging" type libration modes of the water

molecule, $\tilde{\nu}_w^1$ and $\tilde{\nu}_w^2$, in the test hexahydrates of the double selenates and their difference $\Delta\tilde{\nu}_w$. These bands were assigned on the basis of the results in a number of publications [11–29], from which it also followed that this libration mode can be used to study the octahedral coordination sphere of the M^{2+} cation. The splitting of the band of this libration mode indicates deformation of the octahedral hydrate sphere $[M^{II}(H_2O)_6]^{2+}$, as has also been confirmed by the X-ray study of some crystal structures [19–21]. It follows from analysis of these structures that the octahedral coordination sphere is subject to orthorhombic distortion for the cations of the bivalent metals with shorter distance of the water molecule from the central cation in the polar position compared to the equatorial position. Thus, the splitting of the “wagging” type libration mode can be employed to study the state of the hydration sphere of the cations of bivalent metals under the influence of the cation of a monovalent and bivalent metal, and thus also the strength of the bonds between the molecules of water and the central cation. It follows from Table 1 that the value of the difference $\Delta\tilde{\nu}_w$ and thus also the corresponding deformation of the hydration sphere increases with decreasing radius of cation M^+ and thus also with increasing contrapolarization effect [1]. The exceptional position of the NH_4^+ cation is a consequence of the directional character of its bonding interactions based on hydrogen bonds [19–21]. The stronger action of the Tl^+ cation on the hydration sphere compared with the rubidium cation, which is

of similar size, is a result of its electron structure, which is different from the rare gas structure. The difference $\Delta\tilde{\nu}_w$ also depends on the nature of cation M^{2+} , where the cation size and the stabilization energy are important for transition metal cations. The copper cation is an exception, and the $\Delta\tilde{\nu}_w$ values in the case of the double selenates are primarily a consequence of the Jahn–Teller effect. In conclusion, the $\Delta\tilde{\nu}_w$ values are suitable parameters for characterizing the deformation of the octahedral hydration spheres of the M^{2+} cation and thus also the tendency of the hexahydrate to undergo thermal decomposition.

Thermal Analysis

The values for the thermal decomposition of the test hydrates given in Tables 2 and 3 were determined on the basis of differential thermal analysis (DTA) and thermogravimetric analysis (TGA). Thermal decomposition of the hexahydrates usually occurs in two stages, through the dihydrate, and sometimes directly to the anhydrous salt. It follows from the temperatures of the decomposition of the hexahydrates to the dihydrates for magnesium, cobalt, and copper that these values increase with increasing size of cation M^+ and thus with decreasing contrapolarization action. The higher temperature for the ammonium salt is a consequence of stabilization of the structure based on the hydrogen bond system between the ammonium cation and molecules of coordinated water. The lower temperature for salts containing the Tl^+ cation is a consequence of its electronic structure, which is different from the rare gas structure. Thermal decomposition directly to the anhydrous salt has been ob-

Table 1. Wavenumbers of the Split Bands of the Libration Modes of the Water Molecules of the “Wagging” Type for the Studied Selenates $\tilde{\nu}_w^1$, $\tilde{\nu}_w^2$ and the Differences in the Wavenumbers of these Bands $\Delta\tilde{\nu}_w$

Salt	$\tilde{\nu}_w^1/\text{cm}^{-1}$	$\tilde{\nu}_w^2/\text{cm}^{-1}$	$\Delta\tilde{\nu}_w/\text{cm}^{-1}$
$K_2Mg(SeO_4)_2 \cdot 6H_2O$	625	585	40
$Rb_2Mg(SeO_4)_2 \cdot 6H_2O$	623	600	23
$Cs_2Mg(SeO_4)_2 \cdot 6H_2O$	625	610	15
$Tl_2Mg(SeO_4)_2 \cdot 6H_2O$	608	575	33
$(NH_4)_2Mg(SeO_4)_2 \cdot 6H_2O$	600	555	45
$K_2Co(SeO_4)_2 \cdot 6H_2O$	625	565	60
$Rb_2Co(SeO_4)_2 \cdot 6H_2O$	620	585	35
$Cs_2Co(SeO_4)_2 \cdot 6H_2O$	620	605	15
$(NH_4)_2Co(SeO_4)_2 \cdot 6H_2O$	600	535	65
$K_2Ni(SeO_4)_2 \cdot 6H_2O$	622	568	54
$Rb_2Ni(SeO_4)_2 \cdot 6H_2O$	626	589	37
$(NH_4)_2Ni(SeO_4)_2 \cdot 6H_2O$	596	538	58
$K_2Cu(SeO_4)_2 \cdot 6H_2O$	640	525	115
$Rb_2Cu(SeO_4)_2 \cdot 6H_2O$	615	570	45
$Cs_2Cu(SeO_4)_2 \cdot 6H_2O$	600	560	40
$(NH_4)_2Cu(SeO_4)_2 \cdot 6H_2O$	615	450	165
$K_2Zn(SeO_4)_2 \cdot 6H_2O$	620	565	55
$(NH_4)_2Zn(SeO_4)_2 \cdot 6H_2O$	605	535	70
$Rb_2Mn(SeO_4)_2 \cdot 6H_2O$	631	583	48
$(NH_4)_2Mn(SeO_4)_2 \cdot 6H_2O$	602	546	56
$Rb_2Zn(SeO_4)_2 \cdot 6H_2O$	623	586	37

Table 2. Temperature of Thermal Decomposition of the Hexahydrate to the Dihydrate Determined by Differential Thermal Analysis (DTA) and Thermogravimetric Analysis (TGA)

Salt	Decomposition temperature/°C	
	DTA	TGA
$K_2Mg(SeO_4)_2 \cdot 6H_2O$	80	90
$Rb_2Mg(SeO_4)_2 \cdot 6H_2O$	125	145
$Cs_2Mg(SeO_4)_2 \cdot 6H_2O$	135	–
$(NH_4)_2Mg(SeO_4)_2 \cdot 6H_2O$	140	150
$Tl_2Mg(SeO_4)_2 \cdot 6H_2O$	115	140
$K_2Co(SeO_4)_2 \cdot 6H_2O$	75	80
$Rb_2Co(SeO_4)_2 \cdot 6H_2O$	105	120
$Cs_2Co(SeO_4)_2 \cdot 6H_2O$	115	125
$(NH_4)_2Co(SeO_4)_2 \cdot 6H_2O$	125	130
$K_2Cu(SeO_4)_2 \cdot 6H_2O$	65	75
$Rb_2Cu(SeO_4)_2 \cdot 6H_2O$	90	100
$(NH_4)_2Cu(SeO_4)_2 \cdot 6H_2O$	115	120
$K_2Ni(SeO_4)_2 \cdot 6H_2O$	115	130
$K_2Zn(SeO_4)_2 \cdot 6H_2O$	90	90
$Rb_2Mn(SeO_4)_2 \cdot 6H_2O$	45	60
$(NH_4)_2Mn(SeO_4)_2 \cdot 6H_2O$	50	70

Table 3. Temperature of Thermal Decomposition of the Dihydrate to the Anhydrous Salt Determined by Differential Thermal Analysis (DTA) and Thermogravimetric Analysis (TGA)

Salt	Decomposition temperature/°C	
	DTA	TGA
$K_2Mg(SeO_4)_2 \cdot 2H_2O$	240	255
$Rb_2Mg(SeO_4)_2 \cdot 2H_2O$	190	210
$Cs_2Mg(SeO_4)_2 \cdot 2H_2O$	140	–
$(NH_4)_2Mg(SeO_4)_2 \cdot 2H_2O$	205	215
$Tl_2Mg(SeO_4)_2 \cdot 2H_2O$	220	245
$K_2Co(SeO_4)_2 \cdot 2H_2O$	205	220
$Rb_2Co(SeO_4)_2 \cdot 2H_2O$	195	210
$Cs_2Co(SeO_4)_2 \cdot 2H_2O$	140	170
$(NH_4)_2Co(SeO_4)_2 \cdot 2H_2O$	195	200
$K_2Cu(SeO_4)_2 \cdot 2H_2O$	135	140
$Rb_2Cu(SeO_4)_2 \cdot 2H_2O$	150	160
$(NH_4)_2Cu(SeO_4)_2 \cdot 2H_2O$	145	160
$K_2Mn(SeO_4)_2 \cdot 2H_2O$	180	190
$Rb_2Mn(SeO_4)_2 \cdot 2H_2O$	120	130
$(NH_4)_2Mn(SeO_4)_2 \cdot 2H_2O$	110	120
$K_2Cd(SeO_4)_2 \cdot 2H_2O$	155	165
$Rb_2Cd(SeO_4)_2 \cdot 2H_2O$	110	115
$(NH_4)_2Cd(SeO_4)_2 \cdot 2H_2O$	160	170
$K_2Ni(SeO_4)_2 \cdot 2H_2O$	255	270
$K_2Zn(SeO_4)_2 \cdot 2H_2O$	160	175

served for the hexahydrates $Cs_2Cu(SeO_4)_2 \cdot 6H_2O$, $Rb_2Ni(SeO_4)_2 \cdot 6H_2O$, $(NH_4)_2Ni(SeO_4)_2 \cdot 6H_2O$, $Rb_2Zn(SeO_4)_2 \cdot 6H_2O$, and $(NH_4)_2Zn(SeO_4)_2 \cdot 6H_2O$. The comparison of the decomposition temperature of the hexahydrates of the various bivalent metals reveals an unusually low temperature for manganese and copper salts. For the manganese(II) salts, this is apparently a consequence of the large radius of the Mn^{2+} cations and, for the copper(II) salts, of the large deformation of the hydrate coordination sphere $[Cu(H_2O)_6]^{2+}$, produced by the Jahn–Teller effect. The highest thermal decomposition temperature for the potassium salts was found for the hexahydrate $K_2Ni(SeO_4)_2 \cdot 6H_2O$, where the large stabilization energy of the coordination sphere of $[Ni(H_2O)_6]^{2+}$ is important.

The dihydrate was not found in the decomposition of the hexahydrate $Cs_2Mg(SeO_4)_2 \cdot 6H_2O$ on the basis of gravimetric analysis, which is less sensitive than DTA.

The dependence of the decomposition temperature on the cation M^+ for the dihydrate of double selenates with heterogeneous octahedral coordination sphere of the bivalent metal with two water molecules and four selenate anions [41, 42] has a different course than for the hexahydrates. Apparently, other factor than deformation of the octahedral coordination sphere of the cation M^{2+} is decisive for the thermal decomposition of the dihydrates. This could be a consequence of the stability of the hydrogen bonds between the water molecules and the selenate anions in the coordination sphere of the M^{2+} cation, confirmed by the structures $Na_2Cu(SeO_4)_2 \cdot 2H_2O$ and $K_2Cd(SeO_4)_2 \cdot 2H_2O$ [41, 42] and the infrared molecular spectra of the dihydrates (Table 4). Here the stability of the hydrogen bonds is a consequence of the contrapolarization effect of the extra-spherical M^+ cation and the polarization effect of the central M^{2+} cation. The stability of the hydrogen bonds in the double selenates of Mg^{2+} , Co^{2+} , Mn^{2+} , and Cd^{2+} cations decreases with increasing size of the M^+ cation. The M^+ cation increases the strength of the hydrogen bonds, decreasing the electron density between the oxygen and hydrogen atoms in the water molecule as a proton donor in hydrogen bonds. Thus, potassium salts are the most stable and cesium salts are the least stable among the dihydrates of the double selenates of magnesium(II) and cobalt(II), while the rubidium salts of the dihydrates of the double selenates of Mn^{2+} and Cd^{2+} cations are less stable than the potassium salts. The higher decomposition temperature of $Tl_2Mg(SeO_4)_2 \cdot 2H_2O$ among magnesium(II) double selenates is a consequence of the electron structure of the thallium(I) ion, which differs from the rare gas structure. As a consequence of the Jahn–Teller effect, the coordination sphere in the double selenates of Cu^{2+} cations is so strongly deformed that the polarization effect of the Cu^{2+} cation on the oxygen atoms in the selenate anions becomes decisive, where these anions act as proton acceptors, their electron densities are decreased and thus the stability of the hydrogen bonds between the selenate anions and water molecules also

Table 4. Wavenumbers of the Bands of the Stretching Vibrations of the Water Molecules in the Dihydrates of the Double Selenates $\tilde{\nu}_H$ and Their Deuterates $\tilde{\nu}_D$ and the Corresponding Isotopic Ratios $\tilde{\nu}_H/\tilde{\nu}_D$

Salt	$\tilde{\nu}_H/cm^{-1}$	$\tilde{\nu}_D/cm^{-1}$	$\tilde{\nu}_H/\tilde{\nu}_D$
$K_2Mg(SeO_4)_2 \cdot 2H_2O$	3190, 3300, 3410	2380, 2450, 2540	1.34; 1.35; 1.34
$K_2Co(SeO_4)_2 \cdot 2H_2O$	3290, 3400	2430, 2515	1.35; 1.35
$K_2Ni(SeO_4)_2 \cdot 2H_2O$	3160, 3390	2410, 2520	1.31; 1.35
$K_2Cu(SeO_4)_2 \cdot 2H_2O$	3160, 3230	2380, 2445	1.33; 1.32
$Rb_2Cu(SeO_4)_2 \cdot 2H_2O$	3010, 3200	2290, 2440	1.31; 1.31
$K_2Zn(SeO_4)_2 \cdot 2H_2O$	3250, 3380	2410, 2510	1.35; 1.35
$K_2Cd(SeO_4)_2 \cdot 2H_2O$	3140, 3350, 3400	2335, 2500, 2520	1.34; 1.34 1.35

Table 5. Survey of the Hydrates of Double Selenates with Cations M^+ and M^{2+}

M^{2+}	$M^+ = Na^+$	K^+	NH_4^+	Rb^+	Tl^+	Cs^+
Mg^{2+}	DH ^{a,b}	HH DH	HH DH	HH	HH	HH
Ni^{2+}	DH ^a	HH DH	HH	HH ^c	HH ^d	HH ^c
Co^{2+}	DH ^a	HH DH	HH DH	HH	HH ^d	HH
Fe^{2+}	DH ^a	HH DH ^e	HH ^e	HH ^e	—	HH ^e
Cu^{2+}	DH ^a	HH DH	HH DH	HH DH	—	HH
Zn^{2+}	DH ^a	HH DH	HH	HH ^d	HH ^d	HH ^d
Mn^{2+}	DH ^a	DH	HH DH ^d	HH DH ^d	HH ^d DH ^d	HH ^d
Cd^{2+}	DH ^a	DH	DH	HH ^f DH ^e	—	HH ^e DH ^e

DH — dihydrate, HH — hexahydrate. a) Ref. [43], b) Ref. [44], c) Ref. [30], d) Ref. [35], e) Ref. [45], f) Ref. [46].

decreases. Consequently, the thermal stabilities of the dihydrates of the potassium—copper double selenates are minimal compared with the double selenates of the other bivalent metals. In contrast, the dihydrate of the potassium—nickel selenate is the most stable one as a consequence of the maximal crystal field stabilization energy. It follows evidently from the comparison of the potassium and rubidium salts of the dihydrates of double selenates of Cu^{2+} cations that the contrapolarization effect of the Rb^+ cation on the water molecule as a proton donor predominates over the polarization action of the Cu^{2+} cation on the selenate anions as proton acceptors and the rubidium salt is thus more stable than the potassium salt. The low temperature of thermal decomposition of the manganese(II) and cadmium(II) dihydrates of double selenates with rubidium and ammonium cations is apparently a consequence of the larger radii of the Cd^{2+} and Mn^{2+} cations, or of their polarization effect on the oxygen atoms of the selenate anions as proton acceptors, connected with weakening of the hydrogen bonds.

It follows from the study of the “wagging” libration modes of the water molecules in the hexahydrates and from the thermal decompositions of the hexa- and dihydrates of the double selenates of the studied metals that the stability of these structures is determined by the character of both the cations. In the hexahydrates, the cations affect the shape of the hydrate coordination sphere for the M^{2+} cation, while in the case of dihydrates the strength of the hydrogen bonds between the water molecules and the selenate anions is decisive. These relationships can also be studied on the basis of the survey of crystal hydrates of double selenates (Table 5). Lithium salts are not known.

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Phase Coexistence in the System $\text{Na}_2\text{O}-\text{P}_2\text{O}_5-\text{ZrO}_2$

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On the basis of the X-ray diffraction the phase compatibility of the system $\text{Na}_2\text{O}-\text{P}_2\text{O}_5-\text{ZrO}_2$ was determined at subsolidus temperatures (350–1200 °C). There are nine binary and three ternary phases present in the system. The phase compatibility diagram is presented.

The contribution presents basic study of the phase coexistence at subsolidus temperatures. The study relies on a knowledge of the phase coexistence in the binary subsystems: $\text{Na}_2\text{O}-\text{P}_2\text{O}_5$ [1, 2], $\text{Na}_2\text{O}-\text{ZrO}_2$ [3], and $\text{P}_2\text{O}_5-\text{ZrO}_2$ [4, 5], respectively. It is also based on the existence of ternary phases, which are present in the quasi-binary system $\text{N}_3\text{P}-\text{Z}_3\text{P}_2$ [6]. There are three compounds (NZ_4P_3 , NZP , $\text{N}_5\text{Z}_2\text{P}_3$) in this phase diagram. The first of them is the end member of the solid solution at which the quaternary "Nasicon" ($\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$) is constituted. The figurative points of solid solutions $\text{Na}_{5-4x}\text{Zr}_{1+x}\text{P}_3\text{O}_{12}$ ($\text{N}_5\text{Z}_2\text{P}_3$) ($0.04 < x < 0.11$) and of the phase ε [$\text{Na}_7\text{Zr}_{0.5}(\text{PO}_4)_3$] (N_7ZP_3) are located in this section, too.

EXPERIMENTAL

Following two ways of preparation of samples were used:

a) By the solid state reaction in which the homogenized mixtures of individual compounds in an agate mortar were used as starting powders. Following compounds were taken for preparation of powder mixtures: ZrO_2 , Na_2CO_3 , $\text{NH}_4\text{H}_2\text{PO}_4$, $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$.

b) By the sol/gel procedure in which the precursor gel was obtained from a mixed and tempered

solution. The solution with the desired ratio w_r of Na_2O , P_2O_5 , and ZrO_2 was prepared volumetrically using 0.169 M-zirconium acetate, 0.353 M- NaNO_3 , and 0.261 M- $\text{NH}_4\text{H}_2\text{PO}_4$.

All the chemicals used were of anal. grade.

Prepared powder mixtures were heated in the platinum crucible in an electric resistance furnace. The attainment of the phase equilibrium was checked by X-ray phase analysis. X-ray patterns were taken on the DRON-0.5, $\text{CuK}\alpha$ radiation. The interpretation of X-ray diffraction patterns was performed using the published data mainly [4, 5, 7–9].

RESULTS AND DISCUSSION

The results of the phase analysis of samples are presented in Table 1. In this table also the mole fractions of components and the heating schedules of samples are given.

The phase compatibility diagram was constructed using the obtained data (Fig. 1).

Only those ternary phases are present in the system, the figurative points of which lie on the tie line $\text{N}_3\text{P}-\text{Z}_3\text{P}_2$. All these compounds (as their structural formulae show) belong to orthophosphates.

On the orthophosphate join there exists also the phase ε the stoichiometry of which is close to

*The chemical composition of individual compounds is expressed in a notation at which: N = Na_2O , Z = ZrO_2 , S = SiO_2 , P = P_2O_5 . Then for example: $\text{NZ}_4\text{P}_3 = \text{Na}_2\text{O} \cdot 4\text{ZrO}_2 \cdot 3\text{P}_2\text{O}_5 = \text{Na}_4\text{Zr}_4\text{P}_6\text{O}_{24} = 2\text{NaZr}_2\text{P}_3\text{O}_{12}$.