CRYSTAL STRUCTURE, THERMOANALYTICAL PROPERTIES AND INFRARED SPECTRA OF DOUBLE MAGNESIUM SELENATES

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Dedicated to Professor Jaroslav Podlaha on the occasion of his 60th birthday.

Magnesium selenates double salts $K_2Mg(SeO_4)_2 \cdot 6\,H_2O$, $Rb_2Mg(SeO_4)_2 \cdot 6\,H_2O$, $Cs_2Mg(SeO_4)_2 \cdot 6\,H_2O$, and $(NH_4)_2Mg(SeO_4)_2 \cdot 6\,H_2O$ have been studied by means of X-ray diffraction methods, thermoanalytical methods, and infrared spectroscopy. The basic building units of these compounds are slightly deformed tetrahedra of selenate anions and octahedra of hexaaquamagnesium(II) cations interconnected by a system of hydrogen bonds. The investigation of IR spectra has been used in the discussion of X-ray diffraction results in the field of description of the hydrogen bond system and deformation of the basic polyhedra of selenate anion and hexaaquamagnesium cation. The thermoanalytical studies are used in evaluating the effects of hydrogen bonds and polarization influence of M^+ cations on thermal stability of the compounds studied.

Key words: Double magnesium selenates with potassium, rubidium, caesium, and ammonium; X-Ray diffraction analysis; Infrared spectra; Thermoanalytical properties.

The so far described structures of double selenates of the type of Tutton's salts of general formula $M^I_2M^{II}(XO_4)_2 \cdot 6\,H_2O$, where X = S or Se, M^I = NH_4, and M^{II} = Cu (ref.[1]), M^I = NH_4 and M^{II} = Ni (ref.[2]), M^I = K and M^{II} = Cu (ref.[3]) proved that these compounds crystallize in the monoclinic system (space group $P2_1/c$). The structure is formed by a slightly deformed selenate tetrahedron and the M^{2+} cation surrounded by an octahedron of water molecules.

Molecular spectroscopy of selenates and double selenates was dealt with by a number of authors, who from the character of fundamental vibration came to the conclusion of deformed tetrahedral arrangement of the anions. The attention was also focused on evaluation of the way of bonding of the water molecules[4–11].

Thermal decomposition of simple selenates was studied in detail by Selivanova[12], Malard[13–15] and Vojtisek[8–11] using the TG and DTA methods. The selenate hydrates undergo dehydration (in several steps) at first, whereupon the anhydrous selenate is reduced to selenite (up to 600 °C) or, as the case may be, the oxide of the respective metal is formed (up to 700 °C).

The present paper deals with double selenates $M^I_2Mg(SeO_4)_2 . 6 H_2O$, where M^I = K, Rb, Cs or NH_4 and forms a part of a systematic research project concerning selenates and hydrogenselenates. These compounds are interesting as potential ferroelectrics[16].

EXPERIMENTAL

Crystallography

To obtain the single crystal data we used a four-circle diffractometer CAD4-MACH III of Enraf-Nonius Comp. (graphite monochromator, molybdene radiation (λMoKα = 7.093 . 10^{-1} Å)). The basic crystallographic data along with selected measurement parameters are given in Table I. The crystal structures were solved by the method of heavy atom (SHELXS86, ref.[17]) and further refined by the least squares treatment with complete matrix (SHELX93, ref.[18]) and with minimized $\Sigma w(F_o^2 - F_c^2)$ function. The nonhydrogen atoms were specified by anisotropic thermal vibrations, the hydrogen atoms found in the difference map of electron densities were specified isotropically. No correction

TABLE I
Basic crystallographical data and selected parameters of measurement

Parameter	$K_2Mg(SeO_4)_2 . 6 H_2O$	$Rb_2Mg(SeO_4)_2 . 6 H_2O$	$Cs_2Mg(SeO_4)_2 . 6 H_2O$	$(NH_4)_2Mg(SeO_4)_2 . 6 H_2O$
M_r	496.51	589.25	684.12	454.39
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
Lattice parameters Å, °	a = 6.2502(5) b = 12.4202(8) c = 9.2641(8) β = 104.303(7)	a = 6.338(3) b = 12.651(1) c = 9.399(1) β = 105.253(4)	a = 6.4725(3) b = 13.036(2) c = 9.510(1) β = 106.246(7)	a = 6.3309(2) b = 12.7521(4) c = 9.4602(4) β = 106.491(3)
V, Å^3	696.87(9)	727.08(7)	770.34(9)	732.33(8)
Z	2	2	2	2
D_{calc}, kg m^{-3}	2 365(8)	2 691(1)	2 948(8)	2 060(3)
No. of reflections measured	2 739	2 848	3 012	2 867
No. of reflections used	1 368	1 423	1 506	1 432
$F(000)$	484	556	628	452
μ, mm^{-1}	6.40	12.62	10.00	5.55
R_r	0.0434	0.0290	0.0468	0.0280
R_w	0.1156	0.0746	0.1279	0.0831
Δ/σ_{MHX}	0.001	0.001	0.033	0.015
$\Delta\rho$	1.01; –1.90	1.27; –0.81	2.13; –3.36	1.47; –0.99

for absorption was carried out because the greatest dimension of the crystal measured was 0.15 mm, which gives a relatively low μ*R* value.

Powder X-Ray Diffractograms

The powder X-ray diffractograms were obtained on a URD-6 apparatus (Freiberg, Germany), using the radiation of copper lamp with nickel filter (λCuKα = 1.5418 Å). The recordings were obtained in the interval of 20–40° 2θ. The theoretical powder X-ray diffractograms were calculated with the use of the Lazy Pulverics program[19] on the basis of known structures.

Infrared Spectra

The infrared spectra were measured with a Genesis FTIR spectrometer of Mattson Comp. in the region of 400–4 000 cm^{-1} in Nujol suspension or KBr cells at room temperature.

Thermal Decomposition

The thermal decomposition by the TG method was carried out with a Stanton Redcraft apparatus. The decomposition parameters: temperature increase 5 °C min^{-1}; temperature interval 20–650 °C. The thermal decomposition by the DTA method was carried out on an apparatus constructed in the Laboratory of Thermal Analysis, Central Laboratories, Prague Institute of Chemical Technology. Decomposition parameters: temperature increase 5 °C min^{-1}; temperature interval 20–650 °C.

Analytical Methods

The selenium content was determined by potentiometric titration of released bromine using hydrazinium sulfate standard solution[20]. The content of magnesium was determined by means of chelatometry[21], that of nitrogen by the distillation method[8]. Potassium, rubidium and caesium were determined by means of the AAS method using a Varian Spectra AA300 apparatus.

Chemicals

The double selenates were prepared from magnesium selenate and potassium (or rubidium, or caesium, or ammonium) selenate by dissolving the calculated amounts corresponding to the stoichiometric ratios and subsequent crystallization[8]. The starting selenates were prepared by neutralization of potassium (or rubidium, or caesium, or magnesium) carbonate with selenic acid. Ammonium selenate was prepared by neutralization of selenic acid with dilute ammonia solution.

RESULTS AND DISCUSSION

X-Ray Diffraction Analysis

The basic crystallographical data of the compounds studied are presented in Table I and the resulting fractional coordinates of their nonhydrogen atoms with temperature factors U_{eq} are given in Table II. The X-ray diffraction analysis of the double selenates $K_2Mg(SeO_4)_2 \cdot 6\,H_2O$, $Rb_2Mg(SeO_4)_2 \cdot 6\,H_2O$, $Cs_2Mg(SeO_4)_2 \cdot 6\,H_2O$ and $(NH_4)_2Mg(SeO_4)_2 \cdot 6\,H_2O$ proved that the four compounds are isostructural; they crystallize in monoclinic system, space group *P*2$_1$/*c*, the number of formula units in a basic cell being 2. The basic

TABLE II
Fractional coordinates of atoms and their temperature parameters. $U_{eq} = \{U_{22} + (U_{11} + U_{33} + 2\ U_{13} \sin^2 \beta) / \sin^2 \beta\}/3$

Atom	x	y	z	$U_{eq} \cdot 10^2$
$K_2Mg(SeO_4)_2 \cdot 6\ H_2O$				
Se	0.77358(6)	0.13536(3)	0.58735(4)	1.91(3)
Mg	0.5	0	0	1.79(4)
K	0.1632(2)	0.1599(1)	0.3641(1)	3.32(3)
O1	0.5340(5)	0.1771(3)	0.6080(4)	3.02(7)
O2	0.8879(5)	0.0517(3)	0.7211(3)	2.59(7)
O3	0.9402(5)	0.2377(3)	0.5948(4)	3.64(8)
O4	0.7444(6)	0.0743(4)	0.4290(4)	4.7(1)
O5	0.6658(6)	–0.1058(3)	0.1662(4)	2.65(8)
O6	0.4682(6)	0.1116(3)	0.1637(4)	2.50(7)
O7	0.7905(5)	0.0677(3)	–0.0090(4)	2.46(7)
$Rb_2Mg(SeO_4)_2 \cdot 6\ H_2O$				
Rb	0.15895(7)	0.15477(3)	0.36779(4)	3.09(2)
Se	0.76808(6)	0.13873(3)	0.59467(4)	1.84(2)
Mg	0.5	0	0	1.72(4)
O6	0.4771(5)	0.1087(3)	0.1636(3)	2.57(7)
O7	0.7894(4)	0.0658(2)	–0.0061(3)	2.49(6)
O5	0.6626(5)	–0.1063(3)	0.1618(3)	2.57(6)
O2	0.8690(4)	0.0615(2)	0.7293(3)	2.49(6)
O4	0.7207(5)	0.0717(3)	0.4419(3)	4.27(8)
O1	0.5392(4)	0.1813(2)	0.6247(3)	2.80(6)
O3	0.9274(4)	0.2387(2)	0.5881(3)	3.21(7)
$Cs_2Mg(SeO_4)_2 \cdot 6\ H_2O$				
Cs	0.14929(7)	0.14806(4)	0.36814(5)	2.99(3)
Mg	0.5	0	0	1.82(6)
Se	0.7579(1)	0.14554(5)	0.60074(6)	1.87(3)
O7	0.7860(7)	0.0629(4)	–0.0082(5)	2.3(1)
O5	0.6619(8)	–0.1040(4)	0.1596(5)	2.7(1)
O6	0.4893(8)	0.1055(4)	0.1640(5)	2.7(1)
O1	0.5398(8)	0.1868(4)	0.6393(6)	2.8(1)
O2	0.9005(7)	0.0758(4)	0.7353(5)	2.6(1)
O3	0.9061(8)	0.2432(4)	0.5812(5)	3.2(1)
O4	0.6962(9)	0.0761(5)	0.4523(5)	3.6(1)

TABLE II
(*Continued*)

Atom	*x*	*y*	*z*	U_{eq} . 10^2
		$(NH_4)_2Mg(SeO_4)_2$. 6 H_2O		
Se	0.75540(4)	0.13589(2)	0.58984(3)	2.19(2)
Mg	0.5	0	0	1.86(3)
N	0.1390(6)	0.1555(3)	0.3619(4)	3.26(6)
O1	0.5253(3)	0.1802(2)	0.6144(2)	3.31(5)
O2	0.8810(3)	0.0576(1)	0.7252(2)	2.89(5)
O3	0.9216(3)	0.2337(2)	0.5875(3)	3.58(5)
O4	0.7084(5)	0.0715(2)	0.4360(3)	5.03(7)
O5	0.6686(4)	–0.1014(2)	0.1678(3)	2.93(5)
O6	0.4667(4)	0.1089(2)	0.1552(3)	2.81(5)
O7	0.7907(3)	0.0675(2)	–0.0051(2)	2.71(5)

structural formations of the compounds studied are selenate anions in tetrahedral arrangement and magnesium(II) cation with water molecules in octahedral arrangement as it can be seen e.g. for the potassium salt (Fig. 1). The basic structural formations are interconnected by hydrogen bonds whose parameters, together with bond lengths and angles of selenate anion and hexaaquomagnesium(II) cation, are summarized in Table III.

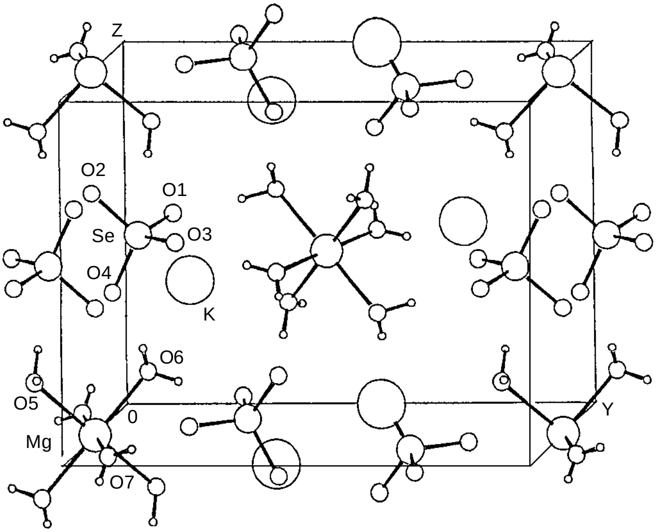

FIG. 1
Arrangement of atoms in basic cell of $K_2Mg(SeO_4)_2$. 6 H_2O

In the case of ammonium magnesium selenate, additional hydrogen bonds are present between the ammonium cation and selenate anion.

A comparison of bond lengths in the anions shows that the selenate tetrahedron is slightly deformed; the largest range of O–Se bond lengths can be observed in $Cs_2Mg(SeO_4)_2 . 6 H_2O$ and the smallest one in $Rb_2Mg(SeO_4)_2 . 6 H_2O$. The deformation of selenate anion is in accordance with the data published about the X-ray diffraction of ammonium nickel(II) selenate hexahydrate[22] and hexahydrates of sulfates of divalent metals[22–27]. The deformation of $[Mg(H_2O)_6]^{2+}$ octahedron reveals an opposite trend: the

TABLE III
Bond lengths (Å) and angles (°) of double magnesium selenates

Atoms	K	Rb	Cs	NH_4
		Bond distances		
Se–O1	1.640(3)	1.641(3)	1.647(5)	1.640(2)
Se–O2	1.640(3)	1.637(3)	1.633(4)	1.640(2)
Se–O3	1.634(3)	1.630(3)	1.635(5)	1.636(2)
Se–O4	1.622(3)	1.628(3)	1.625(5)	1.624(2)
Mg–O5	2.094(3)	2.088(3)	2.083(5)	2.090(2)
Mg–O6	2.100(3)	2.100(3)	2.096(5)	2.075(2)
Mg–O7	2.021(3)	2.030(3)	2.050(5)	2.044(2)
O5–O2	2.806(5)	2.772(4)	2.757(6)	2.799(3)
H1–O2	2.20(5)	2.03(4)	1.82(4)	2.07(4)
O7–O3	2.682(5)	2.695(4)	2.711(6)	2.736(3)
H5–O3	1.94(8)	1.63(6)	1.79(5)	1.93(4)
O6–O1	2.727(5)	2.725(4)	2.748(7)	2.755(3)
H4–O1	1.81(8)	1.88(6)	1.89(5)	1.95(4)
O5–O1	2.831(5)	2.813(4)	2.815(8)	2.862(3)
H2–O1	1.97(8)	2.03(5)	1.94(6)	2.16(4)
O6–O4	2.670(5)	2.705(4)	2.725(6)	2.707(3)
H3–O4	1.94(6)	2.07(5)	1.82(5)	2.03(4)
N–O1				2.911(4)
H9–O1				2.18(4)
N–O2				2.833(4)
H10–O2				2.02(6)
N–O3				3.019(4)
H7–O3				2.36(4)

TABLE III
(*Continued*)

Atoms	K	Rb	Cs	NH_4
		Bond angles		
O1–Se–O2	110.6(2)	110.1(2)	109.7(3)	110.6(1)
O1–Se–O3	109.9(2)	109.7(2)	109.9(3)	109.9(1)
O1–Se–O4	110.6(2)	111.0(2)	110.8(3)	110.9(1)
O2–Se–O3	107.9(2)	107.9(1)	107.9(2)	107.7(1)
O2–Se–O4	108.6(2)	108.1(2)	108.4(2)	108.5(1)
O3–Se–O4	109.3(2)	110.1(2)	110.1(3)	109.2(1)
O5–Mg–O5′	180.00(0)	180.00(0)	180.00(0)	180.00(0)
O5–Mg–O6	90.1(1)	90.2(1)	90.1(2)	90.5(1)
O5–Mg–O6′	89.9(1)	89.8(1)	89.9(2)	89.5(1)
O5–Mg–O7	90.3(2)	90.5(1)	90.7(2)	90.5(1)
O5–Mg–O7′	89.7(2)	89.5(1)	89.3(2)	89.5(1)
O6–Mg–O6′	180.00(0)	180.00(0)	179.97(O)	180.00(0)
O6–Mg–O7	90.1(1)	89.4(1)	89.2(2)	90.4(9)
O6–Mg–O7′	89.9(1)	90.6(1)	90.8(2)	89.6(9)
O7–Mg–O7′	180.00(0)	180.00(0)	180.00(0)	180.00(0)
O5–H1–O2	169(9)	173(5)	163(3)	176(3)
O7–H5–O3	179(8)	172(5)	172(3)	170(4)
O6–H4–O1	174(5)	166(5)	167(4)	170(3)
O5–H2–O1	179(7)	168(5)	164(3)	171(4)
O6–H3–O4	165(4)	173(6)	154(4)	176(5)

highest and the lowest ranges of bond lengths were found with $K_2Mg(SeO_4)_2 . 6 H_2O$ and $Cs_2Mg(SeO_4)_2 . 6 H_2O$, respectively.

The parameters of powder diffractograms (*d*, *I*) calculated from the structures determined with the help of the Lazy Pulverix program[19] agree well with the results of investigation of the powder X-ray diffractograms.

Infrared Spectra

The spectral data of the compounds studied are presented in Table IV. When evaluating the way of bonding of water molecules, we focused attention on the behaviour of the hydrogen bonds connecting the water molecules in the compounds studied with the oxygen atoms of tetrahedra of selenate anions.

Characterization of hydrogen bonds often makes use of a number of correlations between wavenumbers of valence vibrations of OH groups and the bond length or energy[28–31]. Using the said correlations, we can assign the bands in the region of 3 100–3 400 cm^{-1} to the hydrogen bonds found by the X-ray diffraction analysis in the length range of 2.682–2.862 Å. In this region we also found broad bands; the wavenumbers of their maxima form the sequence: $Rb^+ < K^+ < Cs^+ < NH_4^+$. This order, however, does not correspond to the X-ray diffraction data which indicate the strongest hydrogen bond for the potassium salt. In addition, these bands completely lack any fine structure which would correspond to hydrogen bonds of various lengths. The above-given comparison of results of spectral and X-ray diffraction studies indicates that the correlation methods of study of hydrogen bonds can only be used for very rough estimates. In the present case another possible explanation appears useful: that described by Schmidt and Vehling[32] studying the hydrogen bonds of hydrogen salts. They consider a slow extra-bond tunnelling effect which leads to a practically identical character of bands in the region of valence vibrations irrespective of the number and length of the hydrogen bonds present.

The information about the way of bonding of water molecules in the polyhedron around the magnesium atom can be obtained by analyzing the vibrational modes of

Table IV
Infrared spectra (cm^{-1}) of hexahydrates of double magnesium selenates

$K_2Mg(SeO_4)_2$	$Rb_2Mg(SeO_4)_2$	$Cs_2Mg(SeO_4)_2$	$(NH_4)_2Mg(SeO_4)_2$	Assignment
412 s, 424 s	406 s, 424 s	402 s, 422 s	417 vs	$\nu_4(F_2)$ SeO_4^{2-}
578 m, 623 m	598 m, 626 sh	612 m, 632 m	523 m, 601 m	$w(H_2O)$
835 sh	764 sh	692 sh, 739 m	784 sh	$\rho(H_2O)$
	835 s	835 sh	833 sh	$\nu_1(A_1)$ SeO_4^{2-}
874 vs, 900 vs	873 vs, 889 vs	879 vs	859 vs, 902 vs	$\nu_3(F_2)$ SeO_4^{2-}
1 000–1 350 vw	1 000–1 350 vw	1 000–1 350 vw	1 000–1 350 vw	$\nu_2(H_2O)$?
			1 422 vs	$\nu_4(F_2)$ NH_4^+
1 698 w, 1 727 w	1 691 vw, 1 724 vw	1 700 w	1 676 s, 1 726 m	$\nu_2(H_2O)$ or $\nu_1(H_2O)$, $\nu_3(H_2O)$
2 320–2 730 vw, b	2 290–2 730 vw, b	2 280–2 750 w, b	2 250 w, b	$\nu_1(H_2O)$, $\nu_3(H_2O)$ or combined bands H_2O
3 210 vs, b	3 195 vs, b	3 210 vs, b	3 260 vs, b	$\nu_1(H_2O)$, $\nu_3(H_2O)$, or $\nu_3(F_2)$ NH_4^+

water molecules in the region of 500–850 cm^{-1} (refs[28,29,34–36]). This region involves beside the valence bands $\nu_3(F_2)$ SeO_4^{2-}, $\nu_4(F_2)$ SeO_4^{2-} other characteristic bands assignable to rocking and wagging vibrations of water molecules. In the compounds studied the water molecules can be divided into two types: that bound in axial position (one shorter interatomic O–Mg distance in each octahedron) and those bound in equatorial positions (two longer O–Mg distances). Although the splitting of the bands found is not always completely conclusive, it can be observed in most cases, the higher wavenumbers being always assignable to the vibrations corresponding to equatorial positions. If we compare the magnitude of band splitting $w(H_2O)$, we find the highest value with the potassium salt and the lowest with the caesium salt. This also agrees with the deformation of octahedra derivable from the differences in Mg–O interatomic distances obtained from the X-ray diffraction studies.

When evaluating the region of vibrations of selenate anion, we found bands belonging to the $\nu_1(A_1)$ SeO_4^{2-}, $\nu_3(F_2)$ SeO_4^{2-}, $\nu_4(F_2)$ SeO_4^{2-} vibrations. The band due to $\nu_2(E)$ SeO_4^{2-} vibration is found in the region below 400 cm^{-1}. With regard to the fact that we found the band of $\nu_1(A_1)$ SeO_4^{2-} vibration which should have been inactive, the attention was turned to the deformation of tetrahedral arrangement of the anions. The evaluation of degree of deformation of the arrangement of oxygen atoms around the selenium atom in the SeO_4^{2-} anions made use (in ref.[5]) of splitting of bands of valence vibrations in the region of 900–350 cm^{-1}. This splitting, which does not exceed the value of 42 cm^{-1}, is most convincing with the bands corresponding to the $\nu_3(F_2)$ SeO_4^{2-} vibrations. The splitting corresponds to an only slight deformation of tetrahedron and agrees with the X-ray diffraction results.

Thermoanalytical Properties

The evaluation of thermoanalytical curves of the compounds studied is given in Table V. The thermoanalytical curves of anhydrous selenates K_2SeO_4, Rb_2SeO_4, and Cs_2SeO_4 show no mass decreases up to the temperature of 650 °C. No endo effects in the region of 420–510 °C (which were assigned to polymorphous transitions in ref.[8]) are observed either. The thermoanalytical curve of ammonium selenate shows an endo effect at 150 °C, which is assigned to a polymorphous transition in accordance with literature[8], and subsequent total decomposition up to 420 °C whose several steps cannot easily be separated. The thermal decomposition of $MgSeO_4 . 6\,H_2O$ starts with a four-step dehydration in which it is possible to trace, in succession, three intermediates of the composition $MgSeO_4 . x\,H_2O$, x = 5, 2, 1. Stepwise dehydrations were also described in previous thermoanalytical studies[12–15]. A noteworthy fact is the high temperature of releasing of the last water molecule (up to 450 °C).

The investigation of thermoanalytical properties of double magnesium selenates was particularly focused on the field of dehydration of these compounds. Literature[36] describes the mechanism of this part of decomposition as a one- or two-step process. In

TABLE V
Thermal decomposition of magnesium selenates

T, °C	Mass decrease, wt.%		T, °C	DTA	Assignment
	exp.	theor.			
			$MgSeO_4 . 6 H_2O$[a]		
25– 75	–6.35	–6.52	65	*endo*	–1 H_2O
90–140	–25.60	–26.01	160	*endo*	–3 H_2O
230–285	–33.60	–32.74	245	*endo*	–1 H_2O
415–450	–38.50	–39.27			–1 H_2O
450–650	dwell			–	start of decomposition of anhydrous salt
			$K_2Mg(SeO_4)_2 . 6 H_2O$[b]		
55– 95	–19.05	–18.22	80	*endo*	–4 H_2O
95–140	–22.86	–21.84	135	*endo*	–2 H_2O
140–650	dwell		230	*endo*	?
			245	*endo*	
			435	*endo*	
			$Rb_2Mg(SeO_4)_2 . 6 H_2O$[c]		
75–185	–15.60	–15.59	163	*endo*	–5 H_2O
185–205	–18.10	–18.36	215	*endo*	–1 H_2O
			$Cs_2Mg(SeO_4)_2 . 6 H_2O$[d]		
100–165	–16.00	–15.79	160	*endo*	–6 H_2O
			$(NH_4)_2Mg(SeO_4)_2 . 6 H_2O$[e]		
105–170	–20.75	–19.89	165	*endo*	–5 H_2O
170–205	–24.5	–23.78			–1 H_2O
205–260	dwell		230	*endo*	
260–275	–34.75		265	*exo*	–(2 NH_3, H_2O,
			270	*endo*	SeO_3)
275–480	–62.70	–63.18	410	*endo*	$MgSeO_4$
480–650	dwell		575	*exo*	

Weighings: [a]TG 5.46 mg, DTA 30 mg; [b]TG 5.45, DTA 30 mg; [c]TG 5.38 mg, DTA 30; [d]TG 5.49 mg, DTA 30 mg; [e]TG 9.51 mg, DTA 30 mg.

some cases[13–15], formation of intermediates with the crystal water content $x = 0.25$, 0.5, 1.5, 3.5, and 4 was considered, too. The thermoanalytical examination of double magnesium selenates proved that the dehydration of $Cs_2Mg(SeO_4)_2 . 6\,H_2O$ proceeds in a single step and is finished at 165 °C by a complete loss of six water molecules. The dehydration of the double salts containing rubidium and potassium is a stepwise process involving monohydrate and dihydrate intermediates in the cases of the rubidium and potassium salts, respectively. In analogy to the rubidium salt, the dehydration of $(NH_4)_2Mg(SeO_4)_2 . 6\,H_2O$ is also a two-step process characterized by formation of the monohydrate intermediate. Further decomposition of the dehydrated salt ends in formation of magnesium(II) selenate.

The evaluation of course of dehydration of the double magnesium selenates studied must take into account a number of factors. The thermal stability of crystals predominantly reflects the polarization influence of cations, P_G ($K^+ = 56.5\ nm^{-2}$, $Rb^+ = 45\ nm^{-2}$, $Cs^+ = nm^{-2}$). The lowest temperature of dehydration start (55 °C) is then found with the potassium salt where the covalent contribution to the bond is most significant. On the other hand, the caesium salt with a distinctly more ionic character starts its dehydration only at 101 °C. Similarly, the decomposition of the ammonium salt starts at a higher temperature (103 °C). In this salt the compound is additionally stabilized by another type of hydrogen bonds: those between the nitrogen atom of NH_4^+ group and oxygen atoms of selenate tetrahedra.

The evaluation of length of hydrogen bonds also makes it possible to explain the individual steps of dehydration. The potassium salt contains two distinctly shorter hydrogen bonds (below 2.70 Å), which stands in accordance with the formation of dihydrate in the first decomposition step. Similarly, one shorter hydrogen bond in the rubidium compound corresponds to the decomposition in which it is possible to trace the monohydrate. In the caesium salt, all the hydrogen bonds are longer than 2.71 Å and the dehydration proceeds in a single step. The formation of monohydrate from the ammonium salt is most likely connected with the above-discussed complex system of hydrogen bonds.

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