

CRYSTALLIZATION IN THE THREE-COMPONENT SYSTEMS $\text{Rb}_2\text{SeO}_4 - \text{MeSeO}_4 - \text{H}_2\text{O}$ (Me = Mg, Ni, Cu) at 25°C

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ABSTRACT

The solubility in the three-component systems $\text{Rb}_2\text{SeO}_4\text{-MeSeO}_4\text{-H}_2\text{O}$ (Me = Mg, Ni, Cu) is studied at 25°C by the method of isothermal decrease of supersaturation. It has been established that double compounds, $\text{Rb}_2\text{Me}(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$ (Me = Mg, Ni, Cu), crystallize from the ternary solutions within wide concentration ranges. The X-ray diffraction data reveal that the title compounds crystallize in the monoclinic space group $\text{P}2_1/c$ (C_{2h}^5) with lattice parameters: $\text{Rb}_2\text{Mg}(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$ – $a = 6.353(3) \text{ \AA}$, $b = 12.674(5) \text{ \AA}$, $c = 9.412(3) \text{ \AA}$, $\beta = 105.22(2)^\circ$, $V = 731.2(3) \text{ \AA}^3$; $\text{Rb}_2\text{Ni}(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$ – $a = 6.349(1) \text{ \AA}$, $b = 9.324(2) \text{ \AA}$, $c = 12.617(2) \text{ \AA}$, $\beta = 105.35(1)^\circ$, $V = 720.3(1) \text{ \AA}^3$; $\text{Rb}_2\text{Cu}(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$ – $a = 6.361(1) \text{ \AA}$, $b = 12.569(2) \text{ \AA}$, $c = 9.414(2) \text{ \AA}$, $\beta = 104.68(1)^\circ$, $V = 728.1(2) \text{ \AA}^3$. The infrared spectra are discussed with respect to the normal vibrations of the selenate ions and water molecules. The unit-cell group theoretical treatment of the double salts is presented. Infrared spectroscopy experiments show that the effective spectroscopic symmetry of the selenate ions is close to C_{3v} . Comparatively strong hydrogen bonds are formed in the rubidium Tutton selenates as deduced from both the wavenumbers of the stretching modes of the water molecules and the water librations due to the strong proton acceptor strength of the selenate ions.

Keywords: rubidium magnesium selenate hexahydrate, rubidium nickel selenate hexahydrate, rubidium copper selenate hexahydrate, solubility diagrams, X-ray powder diffraction, infrared spectra.

INTRODUCTION

The rubidium double selenates belong to a large number of isomorphous compounds with a general formula $\text{Me}_2^+\text{Me}^{2+}(\text{XO}_4)_2 \cdot 6\text{H}_2\text{O}$ (Me⁺ = K, NH₄⁺, Rb, Cs; Me²⁺ = Mg, Mn, Co, Ni, Cu, Zn; X = S, Se) known as Tutton salts. They crystallize in the monoclinic space group $\text{P}2_1/c$ (C_{2h}^5) with two formula units in the unit-cell. The crystal structures of these compounds are built up from isolated octahedra, $[\text{Me}^{2+}(\text{H}_2\text{O})_6]$, (three crystallographically different water molecules are coordinated to the Me²⁺ ions) and tetrahedra XO_4 . The polyhedra are linked by hydrogen bonds. All atoms, except the divalent metal ions, which lie at centre of inversion C_i , are located at general positions C_1 . Recently, the crystal structures of some rubidium Tutton compounds have been reported in [1-3]. As an example the crystal

structures of $\text{Rb}_2\text{Co}(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$ is presented in Fig. 1.

In this paper we present the results on the study of the solubility in the three-component systems $\text{Rb}_2\text{SeO}_4\text{-MeSeO}_4\text{-H}_2\text{O}$ (Me = Mg, Ni, Cu) at 25 °C. There are no available data in the literature about the phase diagrams of the above systems. The solubility data for the systems $\text{Rb}_2\text{SeO}_4\text{-MeSeO}_4\text{-H}_2\text{O}$ (Me = Co, Zn) are reported only in the literature [4, 5]. The Tutton salts are characterized by means of both the infrared spectroscopy and the X-ray powder diffraction methods. For comparison the infrared spectra of $\text{Rb}_2\text{Co}(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Rb}_2\text{Zn}(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$ are also presented and discussed. A practical point of studying is that the Tutton compounds could be considered as proton conductors due to the existence of comparatively strong hydrogen bonds determined by the strong proton acceptor capabilities of the selenate ions.

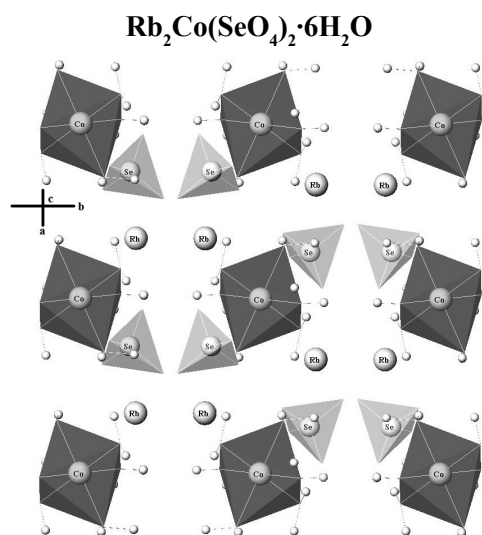


Fig. 1. Crystal structure of Rb₂Co(SeO₄)₂·6H₂O (structural data according to [1]; plane ba).

EXPERIMENTAL

Rb₂SeO₄, MeSeO₄·6H₂O (Me = Mg, Co, Ni, Zn) and CuSeO₄·5H₂O were prepared by neutralization of the respective carbonate and hydroxide carbonates with dilute selenic acid solutions at 60-70°C. Then the solutions were filtered, concentrated at 50-60°C, and cooled to room temperature. The crystals were filtered, washed with alcohol and dried in air. The solubility in the three-component systems was studied by the method of isothermal decrease of supersaturation. The equilibrium between the liquid and solid phases was reached in about 20 hours.

About 3-4 g from the liquid and wet solid phases were taken from the systems and analyzed as follows: the metal ion contents were determined complexometrically at pH 9.5-10 using eriochrome black as indicator (magnesium ions) and at pH 5.5-6 using xylenol orange as indicator (copper and nickel ions); the sum of the selenate ions was determined after precipitation with Pb(NO₃)₂ solutions and the concentration of the excess Pb²⁺ ions was determined complexometrically using xylenol orange as indicator; the content of the rubidium selenate was calculated by difference [G. Schwarzenbach, H. Flaschka, Die komplexometrische Titration, Ferdinand Enke Verlag, Stuttgart, 1965]. The composition of the solid phases was identified by means



Fig. 2. Solubility diagrams of the three-component systems Rb₂SeO₄ - MeSeO₄ - H₂O (Me = Mg, Ni, Cu) at 25°C.

of X-ray diffraction and infrared spectroscopy methods as well. The cobalt and zinc analogues are prepared according to [4, 5]. All reagents used were of reagent grade quality (Merck).

The infrared spectra were recorded on a Bruker model

IFS 25 Fourier transform interferometer (resolution < 2 cm⁻¹) at ambient temperature using KBr discs as matrices. Ion exchange or other reactions with KBr have not been observed.

The X-ray powder diffraction spectra were collected within the range from 10° to 50° 2θ with a step 0.02° 2θ and counting time 35 s/step on Bruker D8 Advance diffractometer with Cu Kα radiation and LynxEye detector. The lattice parameters of the double salts were calculated using the program ITO and refined with the program LSUCR.

RESULTS AND DISCUSSION

Solubility diagrams of the three-component systems Rb₂SeO₄-MeSeO₄-H₂O (Me = Mg, Ni, Cu) at 25°C

The solubility diagrams of the above systems are presented in Fig. 2 (the respective experimental data are summarized in Tables 1-3). It is seen from Fig. 2 that the simple salts Rb₂SeO₄, MgSeO₄·6H₂O, NiSeO₄·6H₂O and CuSeO₄·5H₂O crystallize within very narrow concentration ranges, whereas the rubidium double selenates crystallize within wide concentration ranges, thus indicating that strong complex formation processes occur in the ternary solutions. For example, the magnesium compound crystallizes from solutions containing 1.01 mass% magnesium selenate and 60.94 mass% rubidium selenate up to solutions containing 32.21 mass% mag-

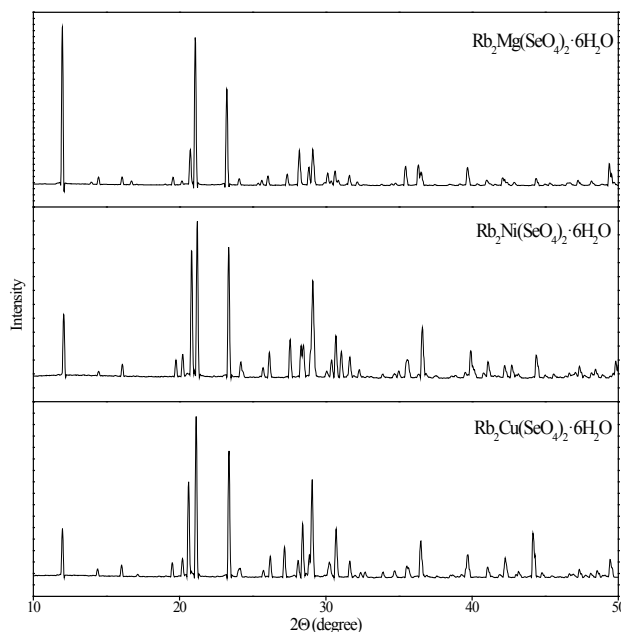


Fig. 3. X-ray powder diffraction patterns of Rb₂Me(SeO₄)₂·6H₂O (Me = Mg, Ni, Cu).

nesium selenate and 5.28 mass % rubidium selenate; the copper compound - from solutions containing 1.43 mass % copper selenate and 61.02 mass % rubidium selenate up to solutions containing 18.80 mass % copper selenate and 10.56 mass % rubidium selenate; the nickel compound - from solutions containing 1.06 mass % nickel selenate and 60.74 mass % rubidium selenate up to solutions containing 27.54 mass % nickel selenate and 6.94 mass % rubidium selenate.

Table 1. Solubility in the Rb₂SeO₄ - MgSeO₄ - H₂O system at 25°C.

Liquid phase mass%		Wet solid phase mass%		Composition of the solid phases
Rb ₂ SeO ₄	MgSeO ₄	Rb ₂ SeO ₄	MgSeO ₄	
62.02	-	-		Rb ₂ SeO ₄
60.94	1.01	71.58	10.36	Rb ₂ SeO ₄ +Rb ₂ Mg(SeO ₄) ₂ ·6H ₂ O
54.96	1.47	53.66	23.87	Rb ₂ Mg(SeO ₄) ₂ ·6H ₂ O
44.81	1.66	51.42	21.96	“ - “
37.47	2.24	50.94	23.59	“ - “
29.06	4.47	49.06	23.84	“ - “
21.51	8.02	49.83	25.71	“ - “
9.49	15.23	46.17	26.74	“ - “
6.50	25.02	47.25	28.04	“ - “
6.28	32.21	23.44	42.10	MgSeO ₄ +Rb ₂ Mg(SeO ₄) ₂ ·6H ₂ O
-	35.43			MgSeO ₄ ·6H ₂ O

Table 2. Solubility in the Rb_2SeO_4 - NiSeO_4 - H_2O system at 25°C.

Liquid phase mass%		Wet solid phase mass%		Composition of the solid phases
Rb_2SeO_4	NiSeO_4	Rb_2SeO_4	NiSeO_4	
62.02	-			Rb_2SeO_4
60.74	1.06	69.17	16.42	$\text{Rb}_2\text{SeO}_4 + \text{Rb}_2\text{Ni}(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$
55.83	0.92	51.45	24.08	$\text{Rb}_2\text{Ni}(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$
47.65	1.58	50.19	28.85	“ - “
39.17	1.63	48.76	27.69	“ - “
29.31	0.84	45.58	25.27	“ - “
22.90	2.07	45.72	28.93	“ - “
13.36	5.64	42.07	27.45	“ - “
8.67	13.79	42.93	29.24	“ - “
7.21	20.30	39.62	29.78	“ - “
6.97	27.54	28.55	44.69	$\text{NiSeO}_4 + \text{Rb}_2\text{Ni}(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$
	26.47			$\text{NiSeO}_4 \cdot 6\text{H}_2\text{O}$

Table 3. Solubility in the Rb_2SeO_4 - CuSeO_4 - H_2O system at 25°C.

Liquid phase mass%		Wet solid phase mass%		Composition of the solid phases
Rb_2SeO_4	CuSeO_4	Rb_2SeO_4	CuSeO_4	
62.02				Rb_2SeO_4
61.02	1.43	62.17	20.76	$\text{Rb}_2\text{SeO}_4 + \text{Rb}_2\text{Cu}(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$
58.10	0.55	54.63	21.74	$\text{Rb}_2\text{Cu}(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$
52.04	0.96	52.41	20.08	“ - “
49.79	0.98	51.78	21.93	“ - “
41.09	2.14	49.21	19.57	“ - “
33.92	2.24	46.89	19.86	“ - “
28.24	4.48	46.05	21.71	“ - “
17.07	8.58	46.76	24.68	“ - “
11.14	14.24	43.41	25.19	“ - “
10.56	18.80	18.73	46.57	$\text{CuSeO}_4 + \text{Rb}_2\text{Cu}(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$
6.34	17.45	1.34	61.37	$\text{CuSeO}_4 \cdot 5\text{H}_2\text{O}$
	15.72			“ - “

X-ray powder diffraction data of the rubidium Tutton compounds

The X-ray powder diffraction patterns of the rubidium Tutton compounds are shown in Fig. 3 (d-spacing, hkl and relative intensities are given in Table 4). The double salts form monoclinic crystals (SG $\text{P2}_1/\text{a}$ ($\text{C}_{2\text{h}}^5$)). The calculated unit-cell parameters have values of: $\text{Rb}_2\text{Mg}(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$ – $a = 6.353(3)$ Å, $b = 12.674(5)$ Å, $c = 9.412(3)$ Å, $\beta = 105.22(2)^\circ$, $V = 731.2(3)$ Å³; $\text{Rb}_2\text{Ni}(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$ – $a = 6.349(1)$ Å, $b = 12.617(2)$ Å, $c = 9.324(2)$ Å, $\beta = 105.35(1)^\circ$, $V = 720.3(1)$ Å³; $\text{Rb}_2\text{Cu}(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$ – $a = 6.361(1)$ Å,

$b = 12.569(2)$ Å, $c = 9.414(2)$ Å, $\beta = 104.68(1)^\circ$, $V = 728.1(2)$ Å³. Our results coincide well with those determined from single crystal X-ray diffraction data [1, 2].

Infrared spectra of rubidium Tutton compounds

The free tetrahedral ions (XO_4^{n-}) under perfect T_d symmetry exhibit four internal vibrations: $\nu_1(A_1)$, the symmetric X–O stretching modes, $\nu_2(E)$, the symmetric XO_4 bending modes, $\nu_3(F_2)$ and $\nu_4(F_2)$, the asymmetric stretching and bending modes, respectively. The normal vibrations of the free tetrahedral ions in aqueous solutions are reported to appear, as follows: for the selenate

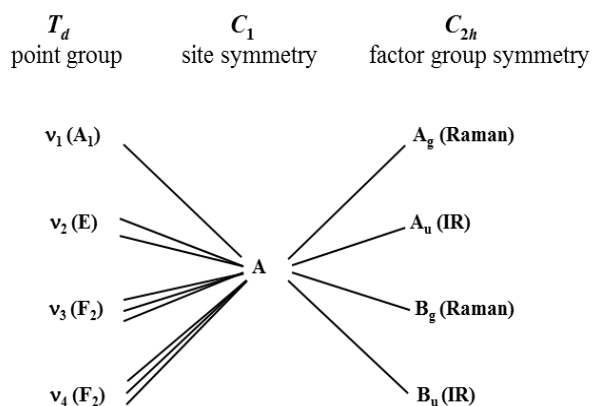


Fig. 4. Correlation diagram between T_d point symmetry, C_1 site symmetry and C_{2h} factor group symmetry (SeO_4^{2-} ions).

ions – $\nu_1 = 833 \text{ cm}^{-1}$, $\nu_2 = 335 \text{ cm}^{-1}$, $\nu_3 = 875 \text{ cm}^{-1}$, $\nu_4 = 432 \text{ cm}^{-1}$ [6]. On going into solid state, the normal modes of the XO_4^{n-} ions are expected to shift to higher or lower frequencies.

The static field (related to the symmetry of the site on which the XO_4^{n-} ions are situated) will cause a removal of both the doubly degenerate ν_2 modes and the triply degenerate ν_3 and ν_4 modes. Since the tetrahedral ions in the structures of Tutton compounds occupy site symmetry C_1 , two bands for ν_2 (2A) and three bands for ν_3 and ν_4 (3A), respectively, are expected to appear in the vibrational spectra as predicted from the site group

Table 4. X-ray powder diffraction data of $\text{Rb}_2\text{Me}(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$ (Me-Mg, Ni, Cu).

$\text{Rb}_2\text{Mg}(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$			$\text{Rb}_2\text{Ni}(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$			$\text{Rb}_2\text{Cu}(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$		
$d_{\text{obs}}, \text{\AA}$	hkl	I/I ₀	$d_{\text{obs}}, \text{\AA}$	hkl	I/I ₀	$d_{\text{obs}}, \text{\AA}$	hkl	I/I ₀
7.380	011	100	7.320	011	42	7.376	011	31
6.340	020	<5	6.125	100	<5	6.153	100	6
6.131	100	5	5.513	110	9	5.527	110	8
5.524	110	5	4.495	002	12	5.172	021	<5
5.305	-111	<5	4.395	120	14	4.553	002	10
4.543	002	5	4.264	111	82	4.397	120	13
4.403	-120	<5	4.193	-102	100	4.309	111	63
4.288	111	21	3.811	031	83	4.205	-102	100
4.216	-102	89	3.679	121	9	3.806	031	79
3.830	031	58	3.663	022	<5	3.687	022	7
3.696	121	<5	3.466	130	5	3.463	130	<5
3.479	-130	<5	3.411	-131	16	3.402	-131	14
3.424	-131	5	3.238	102	23	3.284	102	19
3.261	102	7	3.155	040	21	3.177	112	13
3.169	040	20	3.137	112	21	3.142	040	35
3.097	131	11	3.070	032	60	3.094	131	15
3.070	-211	20	2.9758	041	<5	3.072	-211	61
2.9673	-113	<5	2.9447	-113	12	2.9507	013	10
2.9444	013	7	2.9154	013	26	2.9105	122	29
2.9209	-202	9	2.8810	122	16	2.8292	-221	10
2.9004	122	<5	2.8292	-221	13	2.7660	-141	<5
2.8318	-221	6	2.7745	-141	<5	2.6443	-222	<5
2.7852	-141	<5	2.5659	132	<5	2.5862	042	<5
2.5326	-142	11	2.5288	-231	10	2.5272	-231	8
2.4741	-133	12	2.5204	-142	13	2.5171	-142	8
2.4603	-213	8	2.4560	-133	32	2.4636	-133	22
2.2710	004	11	2.2592	142	19	2.2777	231	7
2.2030	-240	<5	2.1968	240	10	2.2703	142	15
2.1476	-242	5	2.1401	-242	9	2.1984	240	7
2.0409	300	<5	2.1172	024	9	2.1901	-124	<5
1.9246	-313	<5	2.0410	300	16	2.1370	-242	11
1.8449	044	14	2.0356	-134	9	2.1025	-204	<5
1.8407	330	8	1.9200	-313	8	2.0948	060	<5
			1.8787	-162	5	2.0499	-312	29
			1.8298	044	12	2.0243	310	15
						1.9467	250	<5
						1.9204	-313	7
						1.8750	-162	7

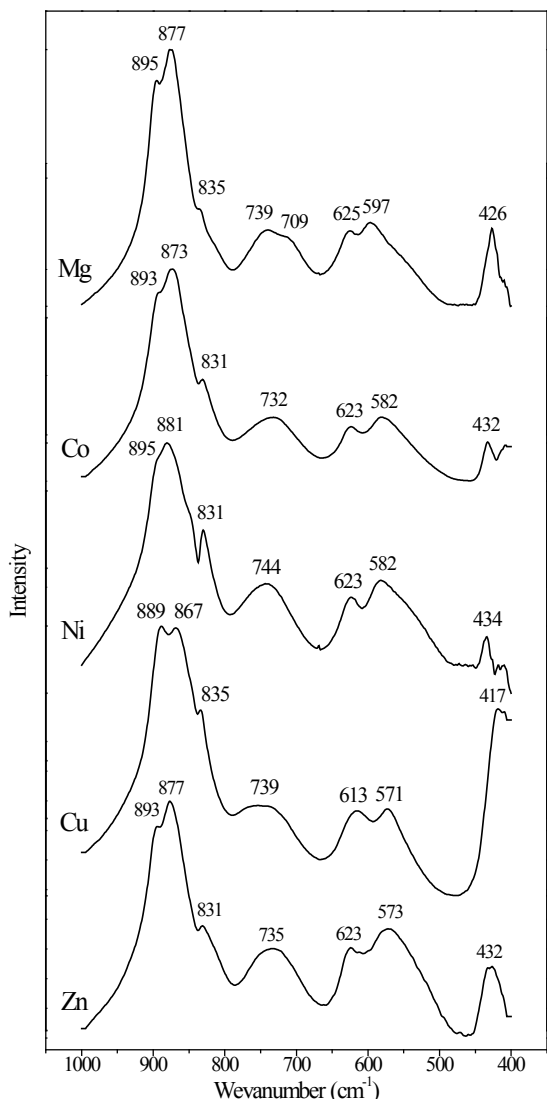


Fig. 5. Infrared spectra of $\text{Rb}_2\text{Me}(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$ (Me = Mg, Ni, Cu) in the region of $1100\text{--}350\text{ cm}^{-1}$ (normal vibrations of the SeO_4^{2-} ions and water librations).

analysis (the non-degenerate ν_1 mode is activated). Additionally, the factor group analysis (C_{2h} factor group symmetry) predicts a splitting of each species of A

symmetry into $A_g + A_u + B_g + B_u$ (related to interactions of identical oscillators, correlation field effects). Consequently, 18 infrared bands ($9A_u + 9B_u$) and 18 Raman bands ($9A_g + 9B_g$) correspond to the normal vibrations of the tetrahedral ions. The correlation diagram between the T_d point symmetry, C_1 site symmetry of the selenate ions and C_{2h} factor group symmetry is presented in Fig. 4. Unit-cell theoretical treatment for the translational lattice modes (Rb , Me^{2+} , SeO_4^{2-} and H_2O) and librational lattice modes (SeO_4^{2-} and H_2O) yields: 69 modes of A_g , A_u , B_g and B_u symmetry and 48 modes of A_g , A_u , B_g and B_u symmetry for the translational and librational modes, respectively (see Table 5; the factor group analysis is made according to [7]).

Infrared spectroscopic investigations of the potassium Tutton sulfates and selenates are widely discussed in the literature [8-17 and Refs. therein], while those of the rubidium compounds are briefly commented [3].

Infrared spectra of $\text{Rb}_2\text{Me}(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$ (Me = Mg, Co, Ni, Cu, Zn) in the region of $4000\text{--}400\text{ cm}^{-1}$ are shown in Figs. 5-6. Some structural and spectroscopic data are summarized in Table 6 (for comparison the data for the respective potassium and ammonium Tutton selenates are presented; the data are taken from [25]). It is readily seen that the band positions and the shape of the spectra are similar owing to the isostructureness of the double salts. The eight infrared bands expected according to the factor group analysis for the stretching modes of the selenate ions coalesce into three bands for each compound: $\text{Rb}_2\text{Mg}(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$ – 895 and 877 cm^{-1} (ν_3) and 835 cm^{-1} (ν_1); $\text{Rb}_2\text{Co}(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$ – 893 and 873 cm^{-1} (ν_3) and 831 cm^{-1} (ν_1); $\text{Rb}_2\text{Ni}(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$ – 895 and 881 cm^{-1} (ν_3) and 831 cm^{-1} (ν_1); $\text{Rb}_2\text{Cu}(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$ – 889 and 867 cm^{-1} (ν_3) and 835 cm^{-1} (ν_1); $\text{Rb}_2\text{Zn}(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$ – 893 and 877 cm^{-1} (ν_3) and 831 cm^{-1} (ν_1).

Table 5. Unit-cell theoretical analysis of $\text{Rb}_2\text{Me}(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$ (Me = Mg, Ni, Cu).

Species	N	n_i SeO_4	n_i H_2O	n_T	n_R	n_T	Activity
A_g	45	9	6	18	12	0	R
A_u	45	9	6	18	12	0	R
B_g	45	9	6	17	12	1	IR
B_u	45	9	6	16	12	2	IR
Σ	180	36	24	69	48	3	

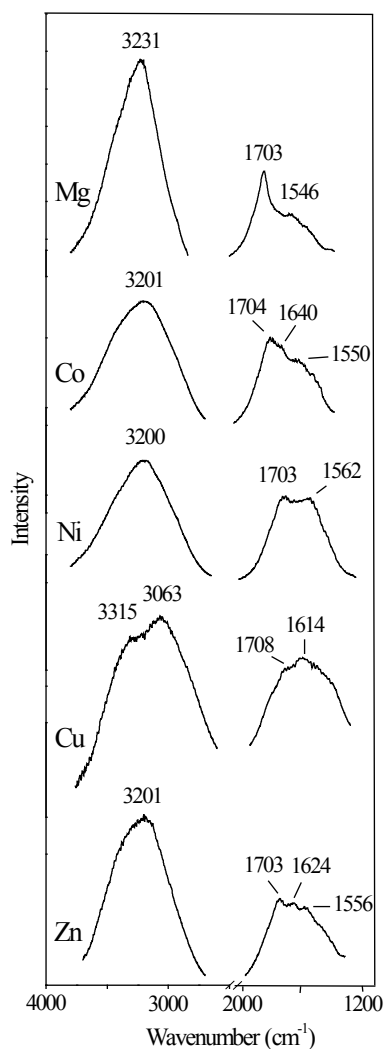


Fig. 6. Infrared spectra of $\text{Rb}_2\text{Me}(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$ ($\text{Me} = \text{Mg}, \text{Ni}, \text{Cu}$) in the region of the stretching and bending modes of the water molecules.

The distortion of the polyatomic ions at various lattice sites (as compared to the free ions in solution or gas) established by spectroscopic studies (infrared and Raman) is called an energetic distortion in order to distinguish it from the geometrical distortion revealed by structural data [18, 19]. Both the site group splitting of the asymmetric modes ($\Delta\nu_{\text{as}}$) and the value of $\Delta\nu_{\text{max}}$ (the difference between the highest and the lowest wavenumbered components of the stretching and bending modes, respectively) are an adequate measure for the degree of energetic distortion of the polyatomic ions, i.e. the strength of the electrostatic field at the lattice sites where these ions are located [19–21]. The small energetic distortions of the selenate ions ($\Delta\nu_3$ for the magnesium

compound has value of 18 cm^{-1} ; for the cobalt compound – 20 cm^{-1} ; for the nickel compound – 14 cm^{-1} ; for the copper compound – 22 cm^{-1} , and for the zinc compound – 16 cm^{-1}) are due to the small geometric distortion of the selenate ions (for the magnesium compound Δr has value of 0.014 \AA ; for the cobalt compound – 0.015 \AA ; for the nickel compound – 0.012 \AA ; for the copper compound – 0.024 \AA ; for the zinc compound – 0.013 \AA ; Δr is the distance between the longest and the shortest bond length in the selenate tetrahedra – calculations are made according to Refs. 1, 2). So, the infrared spectroscopic experiments show that effective spectroscopic symmetry of the selenate ions is closed to C_{3v} . The close values of $\Delta\nu_3$ and $\Delta\nu_{\text{max}}$ for potassium, ammonium and rubidium selenates reveal that the nature of the Me^+ and Me^{2+} ions do not influence on the energetic distortion of the SeO_4^{2-} ions since the latter are not coordinated to the divalent metal ions and form weak electrostatic bonds with Me^+ ions (see Table 6). The bending modes of the selenate ions appear in the spectral region below 400 cm^{-1} (only one band in the region of $417\text{--}434 \text{ cm}^{-1}$ is observed in the spectra, which is attributed to asymmetrical bending modes of the selenate ions).

The normal vibrations of the water molecules appear in the high frequency region of $3000\text{--}4500 \text{ cm}^{-1}$. The three crystallographically different water molecules (C_1 site symmetry) in the structures of the Tutton compounds are expected to display six infrared bands corresponding to the asymmetric and symmetric modes ν_3 and ν_1 , respectively. However, due to the strong interactions of identical oscillators O–H the different normal modes overlap and as a result one broad band centered at about 3200 cm^{-1} is observed in the spectra of the double Tutton salts (with exception of the copper compound). Three bands corresponding to ν_2 of three crystallographically different water molecules are observed in the spectra of cobalt and zinc compounds ($1704, 1640$ and 1550 cm^{-1} ; $1703, 1624$ and 1556 cm^{-1} for the cobalt and zinc salts, respectively). In the case of magnesium, nickel and copper compounds the three bands expected coalesce into two bands (1703 and 1546 cm^{-1} ; 1703 and 1562 cm^{-1} ; 1708 and 1614 cm^{-1} for the magnesium, nickel and copper compounds, respectively) (see Fig. 6). The

Table 6. Some structural and spectroscopic characteristics for the XO_4^{2-} ions in the neat Tutton salts (V/n , unit-cell volumes divided by the numbers of the XO_4^{2-} ions; $\overline{X-O}$, mean values of the X-O bond lengths; $\Delta r(\text{XO}_4)$, the difference between the longest and the shortest X-O bond lengths in the respective tetrahedra; Δv_{\max} , the difference between the highest and the lowest wavenumbered components of the stretches of the XO_4^{2-} ions; the structural data are taken from Refs. [1, 2, 25]).

Compounds	V/n \AA^3	$\overline{X-O}$ \AA	$\Delta r(\text{XO}_4)$ \AA	ν_3 cm^{-1}	$\overline{\nu_3}$ cm^{-1}	ν_1 cm^{-1}	$\Delta \nu_3$ cm^{-1}	Δv_{\max} cm^{-1}
$\text{K}_2\text{Mg}(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$	174	1.634	0.018	899, 877	888	835	22	64
$\text{Rb}_2\text{Mg}(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$	182	1.632	0.014	895, 877	886	835	18	60
$(\text{NH}_4)_2\text{Mg}(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$	183	1.635	0.016	901, 875	888	835	26	66
$\text{K}_2\text{Co}(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$	174	1.633	0.021	899, 877	888	831	22	68
$\text{Rb}_2\text{Co}(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$	181	1.638	0.020	893, 873	883	831	20	62
$(\text{NH}_4)_2\text{Co}(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$	182	1.638	0.017	899, 873	886	833	26	66
$\text{K}_2\text{Ni}(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$	172	1.633	0.015	896, 880	888	830	16	66
$\text{Rb}_2\text{Ni}(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$	179	1.637	0.019	895, 881	888	831	14	64
$(\text{NH}_4)_2\text{Ni}(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$	180	1.637	0.021	899, 873	886	831	26	68
$\text{K}_2\text{Cu}(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$	173	1.628	0.013	894, 881sh	888	837	13	57
$\text{Rb}_2\text{Cu}(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$	181	1.636	0.017	889, 867	878	835	22	54
$(\text{NH}_4)_2\text{Cu}(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$	181	1.628	0.030	893, 882sh, 877	884	835	16	58
$\text{K}_2\text{Zn}(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$	174	1.633	0.020	896, 879	888	833	17	63
$\text{Rb}_2\text{Zn}(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$	181	1.631	0.011	893, 877	885	831	16	62
$(\text{NH}_4)_2\text{Zn}(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$	182	1.639	0.017	898, 875	887	833	23	65

band positions of the stretching and bending modes indicate that comparatively strong hydrogen bonds are formed in the selenates and the hydrogen bond strengths do not depend on the Me^{2+} chemical nature (for the magnesium, cobalt, nickel and zinc salts). The appearance of a band at a lower frequency (3069 cm^{-1}) in the spectrum of the copper compound evidences that stronger hydrogen bonds are formed in this salt as compared to other rubidium ones. This spectroscopic finding is owing to the stronger synergetic effect of the Cu^{2+} ions, i.e. to the strong Cu-OH_2 interactions (increasing of the acidity of the water molecules). The formation of comparatively strong hydrogen bonds in the studied compounds is due to the strong proton acceptor capacity of the selenate ions [22-24].

The water librations (rocking, twisting and wagging) appear in the region below 1000 cm^{-1} and a strong overlapping with vibrations of other entities in the structure is expected. Two types of water librations for the Tutton sulfates are discussed briefly in the literature – rocking and wagging, the former observed

at higher frequencies [10]. Each type is characterized with two broad bands. The water molecules bonded to the Me^{2+} ions via shorter $\text{Me}^{2+}\text{-OH}_2$ bonds display water librations at higher frequencies as compared to those forming longer $\text{Me}^{2+}\text{-OH}_2$ bonds (equatorial water molecules). The former $\text{Me}^{2+}\text{-OH}_2$ bonds are much more polarized due to the stronger synergetic effect of the Me^{2+} ions (stronger metal-water interactions). The mean wavenumbers for the rocking librations are reported to have values of 855 and 740 cm^{-1} , and 770 and 680 cm^{-1} for the potassium and ammonium sulfates, respectively. The respective wagging modes have mean values of 570 and 441 cm^{-1} for the potassium compounds, and 544 and 425 cm^{-1} for the ammonium ones [10]. Thus, the broad bands in the spectral interval of $750\text{-}710 \text{ cm}^{-1}$ are attributed to the rocking modes of the water molecules and the two bands in the region of $630\text{-}570 \text{ cm}^{-1}$ to the wagging modes. The close wavenumbers of the water librations confirm the claim that hydrogen bonds of close strength are formed in the rubidium Tutton compounds.

CONCLUSIONS

Tutton compounds, $\text{Rb}_2\text{Me}(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$ (Me = Mg, Ni, Cu), have been obtained from the three-component systems $\text{Rb}_2\text{SeO}_4 - \text{MeSeO}_4 - \text{H}_2\text{O}$ (Me = Mg, Ni, Cu) at 25°C. The X-ray powder diffraction data reveal that the double salts are isostructural and have close lattice parameters. The analysis of the infrared spectra in the region of the normal vibrations of the selenate ions show that the effective spectroscopic symmetry of these ions is close to C_{3v} . Both the wavenumbers of the stretching modes of the water molecules and the water librations indicate that comparatively strong hydrogen bonds are formed in the rubidium Tutton selenates due to the strong proton acceptor capacity of the selenate ions.

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