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Thermal dehydration of cobalt selenate hydrates

Violeta Koleva*, Donka Stoilova

Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria

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Abstract

The dehydration of $CoSeO_4{\cdot}6H_2O$, $CoSeO_4{\cdot}5H_2O$ $CoSeO_4{\cdot}4H_2O$ and $CoSeO_4{\cdot}H_2O$ has been studied by TG and DTA and DSC. The dehydration of $CoSeO_4{\cdot}6H_2O$ occurs in steps and intermediate hydrates $CoSeO_4{\cdot}5H_2O$, $CoSeO_4{\cdot}4H_2O$, $CoSeO_4{\cdot}2H_2O$ and $CoSeO_4{\cdot}H_2O$ are formed. The enthalpies of dehydration of the observed dehydration processes have been determined. The enthalpies of formation of $CoSeO_4{\cdot}6H_2O$; $CoSeO_4{\cdot}5H_2O$; $CoSeO_4{\cdot}4H_2O$ and $CoSeO_4{\cdot}H_2O$ (amorphous and crystalline) as well as the enthalpy of transformation of amorphous $CoSeO_4{\cdot}H_2O$ into crystalline $CoSeO_4{\cdot}H_2O$ have been calculated from DSC data. The lattice parameters of $CoSeO_4{\cdot}4H_2O$ have been calculated. It crystallizes in a monoclinic system with lattice constants: a=6.001(2) Å; b=13.836(3) Å; c=8.059(3) Å; β=90.91(4)°; V=669.2(3) Å; SG $P2_1/n$. © 1997 Elsevier Science B.V.

Keywords: Cobalt selenate hydrates; Dehydration; DSC; DTA; Heat of dehydration; Heat of formation; Lattice parameters

1. Introduction

The present paper continues our previous studies on the dehydration of metal (II) selenate hydrates–$ZnSeO_4{\cdot}nH_2O$ [1], $MgSeSO_4{\cdot}nH_2O$ [2,3] and $NiSeO_4{\cdot}nH_2O$ [4]. The literature data on the thermal dehydration of cobalt selenate hydrates are scanty. Using a thermobalance and an X-ray method, Malard [5] has shown that $CoSeO_4{\cdot}5H_2O$, $CoSeO_4{\cdot}H_2O$ and $CoSeO_4$ are formed as a result of the dehydration of cobalt selenate hexahydrate. Based on the results obtained from TG, DTG and DTA measurements Nabar and Paralkar [6] proposed the following scheme of the dehydration and decomposition of $CoSeO_4{\cdot}4H_2O$:

$$CoSeO_4 \cdot 4H_2O \overset{170^\circ C}{\longrightarrow} CoSeO_4 \cdot 2H_2O$$

$$\overset{345^\circ C}{\longrightarrow} CoSeO_4 \overset{625^\circ C}{\longrightarrow} Co_3O_4 + CoO$$

The purpose of the present paper is to study the thermal dehydration of $CoSeO_4{\cdot}6H_2O$; $CoSeO_4{\cdot}5H_2O$; $CoSeO_4{\cdot}4H_2O$ and $CoSeO_4{\cdot}H_2O$ using TG and DTA methods as well as to determine the ΔH of dehydration ($\Delta_{deh}H$) and ΔH of formation ($\Delta_f H^0$) of cobalt selenate hydrates on the basis of DSC measurements.

2. Experimental

Cobalt selenate hexahydrate was prepared by neutralization of cobalt hydroxide carbonate with an aqueous solution of selenic acid at 60 to 70°C. Crystals of $CoSeO_4{\cdot}6H_2O$ were obtained by evaporation of the solution at room temperature, then recrystallized

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*Corresponding author.

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in water and dried in air. The reagents used were p.a. grade (Merck). The lower crystal hydrates of cobalt selenate were prepared by crystallization from solutions at different temperatures according to the solubility data in the binary system $CoSeO_4$–H_2O. Four hydrates ($CoSeO_4 \cdot 7H_2O$; $CoSeO_4 \cdot 6H_2O$; $CoSeO_4 \cdot 4H_2O$ and $CoSeO_4 \cdot H_2O$) crystallize in the temperature interval from −6.4 to 100°C (Klein [7]). $CoSeO_4 \cdot 4H_2O$, which is stable in the temperature interval from 33.5 to 73.5°C, was prepared at 70°C using two methods - isothermal decrease of supersaturation and isothermal evaporation of solutions. Our experiments, however, showed that in the temperature interval from 40 to 55°C $CoSeO_4 \cdot 5H_2O$ crystallizes from the binary system, irrespective of the method used. Crystalline $CoSeO_4 \cdot H_2O$ was prepared either by crystallization from solutions at 80°C or by heating of $CoSeO_4 \cdot 6H_2O$ crystals at 180°C for about 5 to 6 h. In the case of heating time of 1 h an amorphous $CoSeO_4 \cdot H_2O$ was obtained.

The salts obtained were identified by chemical analysis (Co ion concentrations were determined complexometrically), X-ray powder diffraction analysis (DRON-3 powder diffractometer, using CuKα radiation) and IR spectroscopy (Burker model IFS 25 Fourier transform interferometer using KBr discs as matrices). The pattern of $CoSeO_4 \cdot 4H_2O$ was obtained at a scanning speed of 1° min^{-1} in the 2θ range from 5 to 50°. α-SiO_2 was used as a standard. The lattice parameters of $CoSeO_4 \cdot 4H_2O$ were calculated on the basis of 23 diffraction peaks using ITO and LSUCR programs. The thermal dehydration processes were studied in an atmosphere of air using a derivatograph (Paulik–Paulik–Erdey MOM OD-102) in a temperature range up to 500°C at a heating rate of 5°C min^{-1} using α-alumina as a reference material. The DSC-measurements were recorded on Perkin-Elmer DSC-4 instrument in a flowing air atmosphere up to 400°C at a heating rate of 5°C min^{-1} using standard Al-pans (with pin holes) and volatile sample pans (aluminium capsules, which have an effective volume of 20 µl and can withstand internal pressure up to 3 bar). Sample masses were from 2 to 5 mg. Temperature, heat and sensitivity were carefully calibrated before the experiments using indium (purity >99.9%) as a standard substance. The experimental error $\Delta_{deh}H$ is about 2–2.5%. The enthalpy values were obtained as mean values from three measurements.

3. Results and discussion

TG, DTG and DTA curves of $CoSeO_4 \cdot 6H_2O$, $CoSeO_4 \cdot 5H_2O$ and $CoSeO_4 \cdot 4H_2O$ are shown in Fig. 1. It is seen from Fig. 1(a) that $CoSeO_4 \cdot 6H_2O$ begins to dehydrate at 50°C and the dehydration occurs in three steps. The first endothermic peak at 80°C corresponds to the separation of one water molecule thus producing $CoSeO_4 \cdot 5H_2O$ ($\Delta m_{exp}=6.0\%$; $\Delta m_{th}=5.8\%$). The pentahydrate obtained immediately loses four water molecules and transforms into $CoSeO_4 \cdot H_2O$ ($\Delta m_{exp}=28.5\%$; $=m_{th}=29.0\%$). The formation of $CoSeO_4 \cdot H_2O$ is registered on the DTA curve with a strong endothermic peak with a maximum at 115°C. The last water molecule separates at 315°C thus forming an anhydrous cobalt selenate. On the basis of the experimental results the following scheme of the dehydration of $CoSeO_4 \cdot 6H_2O$ could be proposed:

$$\mathrm{CoSeO_4 \cdot 6H_2O} \xrightarrow{80^\circ C} \mathrm{CoSeO_4 \cdot 5H_2O}$$

$$\xrightarrow{115^\circ C} \mathrm{CoSeO_4 \cdot H_2O} \xrightarrow{315^\circ C} \mathrm{CoSeO_4}$$

The derivatograms of $CoSeO_4 \cdot 5H_2O$ and $CoSeO_4 \cdot 4H_2O$ are shown in Fig. 1(b) and (c). Two strong endothermic peaks are registered on the DTA and DTG curves of both hydrates i.e. their dehydration occurs in two steps. The mass losses calculated from the TG curves show that the following dehydration processes occur:

$$\mathrm{CoSeO_4 \cdot 5H_2O} \xrightarrow[\substack{\Delta m_{exp} = 22.2\% \\ \Delta m_{th} = 21.9\%}]{T_{max}=120^\circ C} \mathrm{CoSeO_4 \cdot H_2O} \xrightarrow[\substack{\Delta m_{exp} = 31.4\% \\ \Delta m_{th} = 30.8\%}]{T_{max}=345^\circ C} \mathrm{CoSeO_4}$$

$$\mathrm{CoSeO_4 \cdot 4H_2O} \xrightarrow[\substack{\Delta m_{exp} = 19.2\% \\ \Delta m_{th} = 19.7\%}]{T_{max}=120^\circ C} \mathrm{CoSeO_4 \cdot H_2O} \xrightarrow[\substack{\Delta m_{exp} = 26.7\% \\ \Delta m_{th} = 26.3\%}]{T_{max}=335^\circ C} \mathrm{CoSeO_4}$$

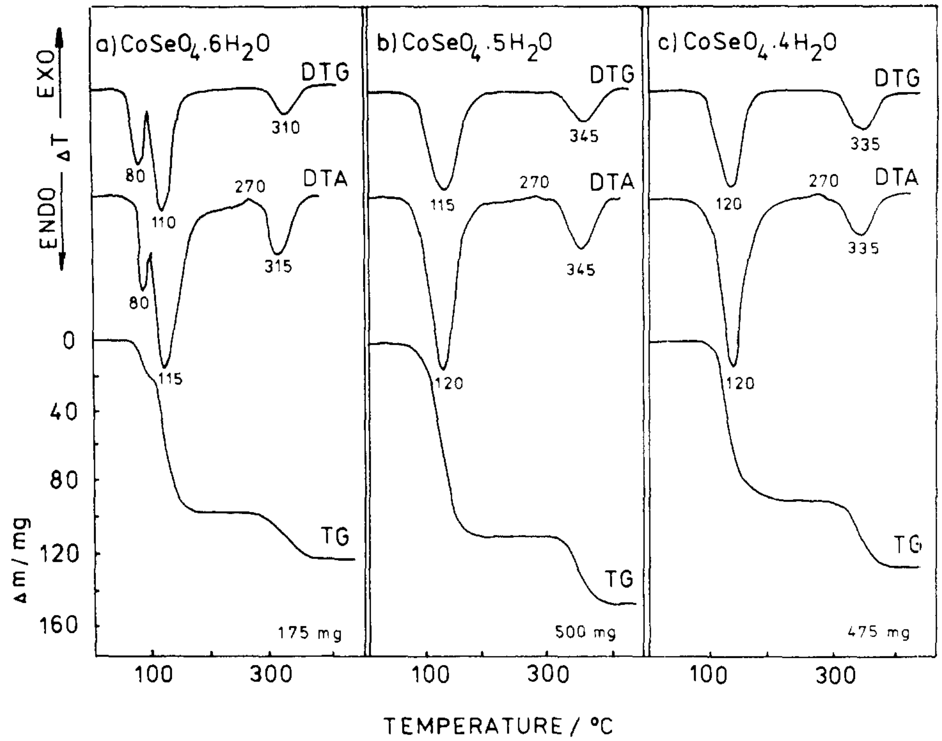

Fig. 1. TG, DTG and DTA curves of $CoSeO_4{\cdot}6H_2O$ (a); $CoSeO_4{\cdot}5H_2O$ (b) and $CoSeO_4{\cdot}4H_2O$ (c).

In Table 1 are listed the X-ray powder diffraction data for $CoSeO_4{\cdot}4H_2O$. It crystallizes in a monoclinic system with lattice parameters: a=6.001(2) Å; b= 13.836(3) Å; c=8.059(3) Å; β=90.91(4)°; V= 669.2(3)Å^3; SG P2$_1$/n and is isomorphous with $CoSO_4{\cdot}4H_2O$ [8], $MgSeO_4{\cdot}4H_2O$ [3], $MnSO_4{\cdot}4H_2O$ [9]. The calculated lattice constants do not differ considerably to those reported by Nabar and Paralkar [10].

The DSC curves of cobalt selenate hydrates are shown in Fig. 2. The measured enthalpies of the observed processes are given in Table 2.

In Fig. 2(a) and (b) are shown the DSC curves of $CoSeO_4{\cdot}6H_2O$ recorded in a standard Al pan and in a volatile sample pan, respectively. It is easily seen that the second DSC curve is more complicated in the temperature interval from 40 to 150°C which is an evidence that more dehydration stages could be distinguished under conditions of an increased water vapor pressure. The comparison of the DSC curves from Fig. 2 shows that the first endothermic effect for $CoSeO_4{\cdot}6H_2O$ is due to separation of one water molecule thus producing $CoSeO_4{\cdot}5H_2O$. In all cases at 150°C $CoSeO_4{\cdot}H_2O$ is formed irrespective of the initial hydrate investigated. While the formation of $CoSeO_4{\cdot}H_2O$ occurs as a result of only two dehydration stages (Fig. 2(a)), in all other cases the formation of $CoSeO_4{\cdot}H_2O$ occurs in more steps thus forming the intermediate hydrates $CoSeO_4{\cdot}4H_2O$ and probably $CoSeO_4{\cdot}2H_2O$ (Fig. 2(b),(c),(d) and Table 2). Our assumption for the formation of $CoSeO_4{\cdot}2H_2O$ is based on the data on the existence of cobalt selenate dihydrate reported by Mayer et al. [11] and Nabar and Paralkar [6]. However, these processes occur continuously and for this reason total values of ΔH of dehydration would be measured (Table 2).

A small exothermic peak is observed on both DTA and DSC curves at 270 and 250°C, respectively. In the case of a crystalline monohydrate, however, this peak disappears in the DSC curve. On the other hand, the X-ray powder diffraction method shows that an amorphous cobalt selenate monohydrate is obtained in the temperature interval from 200 to 250°C and a longer

Table 1
X-ray powder diffraction data for $CoSeO_4 \cdot 4H_2O$

d_{calc} Å	d_{exp} Å	*hkl*	I/I_0
6.96	6.96	011	10
5.51	5.51	$\bar{1}10$	15
4.85	4.85	$\bar{1}01$	10
4.53	4.53	120	35
4.03	4.03	002	100
3.87	3.86	012	7
3.66	3.65	$\bar{1}30$	7
3.48	3.48	022	15
3.46	3.46	040	20
3.34	3.34	$\bar{1}31$	10
3.23	3.23	112	22
3.03	3.03	032	17
2.997	2.996	140	17
2.994		122	
2.932	2.932	210	8
2.816	2.817	$\bar{1}41$	10
2.617	2.618	051;$\bar{2}21$	17
2.437	2.438	103	25
2.438	2.429	$\bar{1}13$	22
2.392	2.391	231	9
2.389		$\bar{2}12$	
2.321	2.319	033	10
2.306	2.306	060	12
2.122		043	12
2.121	2.121	232	
2.001	2.002	062	12

heating time is needed for the transformation of the amorphous to crystalline monohydrate form. Consequently, the results from DTA and DSC measurements show that the exothermic effect is due to the recrystallization of the amorphous $CoSeO_4 \cdot H_2O$ initially obtained. The ΔH of the recrystallization is given in Table 2.

The value of $\Delta_{deh}H$ for the following dehydration processes have been calculated as a difference in $\Delta_{deh}H$ of hexa-, penta-, and tetrahydrates, respectively, to anhydrous salt.

$$CoSeO_4 \cdot 6H_2O \rightarrow CoSeO_4 \cdot 5H_2O + H_2O$$
$$\Delta_{deh}H = 51.3\,\mathrm{kJ\,mol^{-1}}$$
$$CoSeO_4 \cdot 6H_2O \rightarrow CoSeO_4 \cdot 4H_2O + 2H_2O$$
$$\Delta_{deh}H = 129.7\,\mathrm{kJ\,mol^{-1}}$$
$$CoSeO_4 \cdot 5H_2O \rightarrow CoSeO_4 \cdot 4H_2O + H_2O$$
$$\Delta_{deh}H = 78.4\,\mathrm{kJ\,mol^{-1}}$$

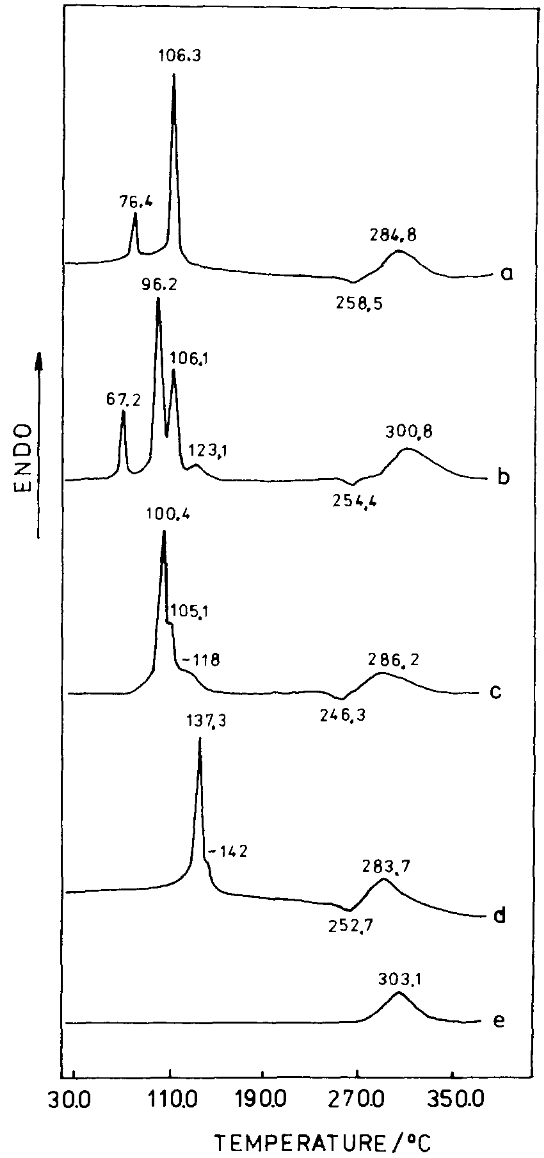

Fig. 2. DSC curves of (a) $CoSeO_4 \cdot 6H_2O$ (standard pan); (b) $CoSeO_4 \cdot 6H_2O$ (volatile sample pan); (c) $CoSeO \cdot 5H_2O$ (standard pan); (d) $CoSeO_4 \cdot 4H_2O$ (standard pan); (e) crystalline $CoSeO_4 \cdot H_2O$ (standard pan).

Using the $\Delta_{deh}H$ data obtained from DSC measurements in standard pans, as well as the $\Delta_f H^0$ of $CoSeO_4$ [12], the enthalpies of formation of the cobalt selenate hydrates have been calculated:

$$\Delta_f H^0 \text{ of } CoSeO_4 \cdot 6H_2O$$
$$= -2369.8\,\mathrm{kJ\,mol^{-1}}(-2384.0\,\mathrm{kJ\,mol^{-1}})$$

Table 2
DSC data for cobalt selenate hydrates

Phase transition	T_{max} °C	T_{onset} °C	ΔH kJ mol^{-1}
(a)			
$CoSeO_4 \cdot 6H_2O \rightarrow CoSeO_4 \cdot 5H_2O + H_2O$	76.4	73.3	268.6
$CoSeO_4 \cdot 5H_2O \rightarrow CoSeO_4 \cdot H_2O_{(am)} + 4H_2O$	106.3	104.1	
$CoSeO_4 \cdot H_2O_{(am)} \rightarrow CoSeO_4 \cdot H_2O_{(cr)}$	258.5	250.0	−2.8
$CoSeO_4 \cdot H_2O_{(cr)} \rightarrow CoSeO_4 + H_2O$	284.8	260.0	86.6
$CoSeO_4 \cdot 6H_2O \rightarrow CoSeO_4 + 6H_2O$			352.4
(b)			
$CoSeO_4 \cdot 6H_2O \rightarrow CoSeO_4 \cdot 5H_2O + H_2O$	67.2	64.2	
$CoSeO_4 \cdot 5H_2O \rightarrow CoSeO_4 \cdot 4H_2O + H_2O$	96.2	92.0	
$CoSeO_4 \cdot 4H_2O \rightarrow CoSeO_4 \cdot 2H_2O + 2H_2O$	106.1		244.2
$CoSeO_4 \cdot 2H_2O \rightarrow CoSeO_4 \cdot H_2O_{(am)} + H_2O$	123.1		
$CoSeO_4 \cdot H_2O_{(am)} \rightarrow CoSeO_4 \cdot H_2O_{(cr)}$	254.7	247.5	−2.7
$CoSeO_4 \cdot H_2O_{(cr)} \rightarrow CoSeO_4 + H_2O$	300.8	275.0	96.6
(a)			
$CoSeO_4 \cdot 5H_2O \rightarrow CoSeO_4 \cdot 4H_2O + H_2O$	100.4	98.2	
$CoSeO_4 \cdot 4H_2O \rightarrow CoSeO_4 \cdot 2H_2O + 2H_2O$	105.1		215.4
$CoSeO_4 \cdot 2H_2O \rightarrow CoSeO_4 \cdot H_2O_{(am)} + H_2O$	118 (shoulder)		
$CoSeO_4 \cdot H_2O_{(am)} \rightarrow CoSeO_4 \cdot H_2O_{(cr)}$	246.3	239.5	−2.9
$CoSeO_4 \cdot H_2O_{(cr)} \rightarrow CoSeO_4 + H_2O$	286.2	261.0	88.6
$CoSeO_4 \cdot 5H_2O \rightarrow CoSeO_4 + 5H_2O$			301.1
(a)			
$CoSeO_4 \cdot 4H_2O \rightarrow CoSeO_4 \cdot 2H_2O + 2H_2O$	137.3	135.3	147.8
$CoSeO_4 \cdot 2H_2O \rightarrow CoSeO_4 \cdot H_2O_{(am)} + H_2O$	142 (Shoulder)		
$CoSeO_4 \cdot H_2O_{(am)} \rightarrow CoSeO_4 \cdot H_2O_{(cr)}$	252.7	240.7	−2.7
$CoSeO_4 \cdot H_2O_{(cr)} \rightarrow CoSeO_4 + H_2O$	283.7	267.0	77.8
$CoSeO_4 \cdot 4H_2O \rightarrow CoSeO_4 + 4H_2O$			222.7
(a)			
$CoSeO_4 \cdot H_2O_{(cr)} \rightarrow CoSeO_4 + H_2O$	303.1	291.8	85.3

a: Data obtained in standard pan.
b: Data obtained in volatile sample pan; (am) amorphous product; (cr) crystalline product.

$$\Delta_f H^0 \text{ of } CoSeO_4 \cdot 5H_2O = -2076.7\,\text{kJmol}^{-1}$$

$$\Delta_f H^0 \text{ of } CoSeO_4 \cdot 4H_2O = -1756.5\,\text{kJ mol}^{-1}$$

$$\Delta_f H^0 \text{ of } CoSeO_4 \cdot H_2O(\text{crystalline}) = -893.6\,\text{kJ mol}^{-1}$$

$$\Delta_f H^0 \text{ of } CoSeO_4 \cdot H_2O(\text{amorphous}) = -890.2\,\text{kJ mol}^{-1}$$

For comparison, the data reported by Mayer et al. [11] are given in parentheses.

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