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SYNTHESIS, SPECTROSCOPIC AND THERMAL CHARACTERIZATION OF Co(II) TETRAHYDROGEN HEXAOXOIODATE TETRAHYDRATE

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A new cobalt(II) tetrahydrogen hexaoxoiodate tetrahydrate $Co(H_4IO_6)_2 \cdot 4H_2O$ is prepared by crystallization from an acidic aqueous solution. This compound is identified by quantitative analysis, TG, DTA, DSC and IR spectra. A thermal decomposition scheme is proposed. Some phase transitions are identified and the corresponding enthalpy changes are determined.

Keywords: *cobalt(II) tetrahydrogen hexaoxoiodate tetrahydrate, $Co(H_4IO_6)_2 \cdot 4H_2O$, IR spectra, thermal analysis*

Introduction

The studies described in the present paper are a part of our continuing investigations of the chemistry of periodates. The interest in acid salts of hexaoxoiodic acid has been provoked by their useful properties like the high proton conductivity and some other electric characteristics. Nevertheless, these have found surprisingly weak attention in the literature up to the present time. There are scarce data about the synthesis, structure and the properties of these compounds. Some data that are a result from the thermal and calorimetric investigations of $Ni(H_4IO_6)_2 \cdot 4H_2O$ are presented in [1] and those of $CoH_3IO_6 \cdot 4H_2O$ in [2]. The compounds $LiH_4IO_6 \cdot H_2O$, $NaH_4IO_6 \cdot H_2O$, $[Al(H_2O)_6(H_4IO_6)_3]$ and $[Co(NH_3)_6(H_4IO_6)_3]$ have been characterized by IR and Raman spectroscopy [3]. $Be(H_4IO_6)_2 \cdot 4H_2O$ has been prepared, analyzed by vibrational spectroscopy and structurally characterized using single crystals [4, 5]. There are also many data in the literature on some complex periodates of cobalt of different types $[Li(H_2O)_4]_2H[Co_4H_{12}I_3O_{24}] \cdot 3H_2O$ [6, 7], $Na_5H_2Co(IO_6)_2 \cdot 10H_2O$ [8, 9], $Na_5H_2Co(IO_6)_2 \cdot 8H_2O$ [10], $LiMCoIO_6$ (M=K, Rb, Cs) [11]. Crystal structure, IR, Raman spectra and thermal analysis of $Sr(H_4IO_6)_2 \cdot 3H_2O$ are reported in [12].

The purpose of this paper is to enrich the existing data about the synthesis and thermal behaviour of acid salts of the hexaoxoiodic acid containing the anion $H_4IO_6^-$.

Experimental

Polycrystalline samples of $Co(H_4IO_6)_2 \cdot 4H_2O$ were prepared by adding 0.5 g $Co(NO_3)_2 \cdot 6H_2O$ to a solution of 5 g H_5IO_6 in 20 cm^3 distilled water in stirring at ambient temperature for an hour. The resulting solution (pH~1) was filtered. Crystals of $Co(H_4IO_6)_2 \cdot 4H_2O$ were obtained by evaporation of the solution at ambient temperature and dried in air. All reagents used were Merck p.a. grade.

The compound was characterised by quantitative analysis: Co^{2+} complexometrically [13], iodine iodometrically [14] and the water of crystallization by Fisher's method [15].

IR spectra were obtained in the region 4000–200 cm^{-1} using KBr tablets and a PU 9700 Philips apparatus. The thermal dehydration process was studied in an atmosphere of air using a derivatograph: Paulik–Paulik–Erdey MOM OD-102 at a heating rate of 10 K min^{-1} in a temperature range up to 1273 K with a sample mass of 110 mg. DSC measurements were recorded on Perkin-Elmer DSC-4 instrument at a heating rate of 5°C min^{-1} up to 773 K. The sample mass was 2 mg.

The intermediate products were characterized by X-ray diffraction using a Zeiss TUR-M-62 apparatus with CuK$_\alpha$ radiation.

Results and discussion

Quantitative analysis data of synthesized compound coincided with that calculated for $Co(H_4IO_6)_2 \cdot 4H_2O$:

	Co/%	I/%	H_2O/%
Experimental	10.15	43.61	12.19
Calculated	10.07	43.40	12.31

The compound was also identified by IR spectroscopy. The presence of H_4IO_6 groups can be proven by absorption bands δ_{I-OH} at 1010 cm^{-1} (w) [3, 16]. Absorption bands at 770 cm^{-1} (m), 750 cm^{-1} (sh) and

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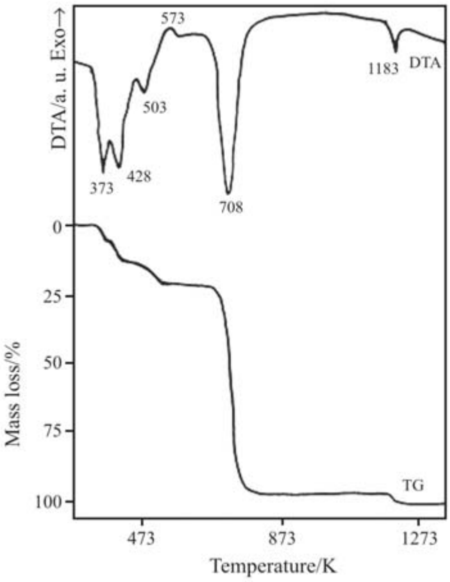

Fig. 1 TG and DTA curves of $Co(H_4IO_6)_2{\cdot}4H_2O$

620 cm^{-1} (m) are due to the unsymmetrical stretching vibration (ν_3) of I–O and I=O [16, 17]. Unsymmetrical deformation vibration ν_4 of the periodate group is observed at 330 cm^{-1}.

The presence of the water of crystallization is proven by band at 3362 cm^{-1} due to the stretching vibration of OH group (ν_{OH}) and at 1620 cm^{-1} deformation vibration of water (δ_{H_2O}).

The thermal parameters of newly synthesized compound are measured by DTA at a heating rate of 10°C min^{-1}. The data observed in the DTA are presented in Fig. 1, Table 1. A large endothermic process is observed at temperature interval 353–473 K with shoulders at 373 and 428 K. This fact shows that the dehydration process in this temperature interval occurred in two steps. The first step could be described as follows:

$$Co(H_4IO_6)_2{\cdot}4H_2O \rightarrow Co(H_4IO_6)_2{\cdot}2H_2O+2H_2O$$

The mass loss at 373 K by TG is 6.3% (calculated 6.1%).

The second step is described by the following reaction:

$$Co(H_4IO_6)_2{\cdot}2H_2O \rightarrow Co(H_4IO_6)_2+2H_2O$$

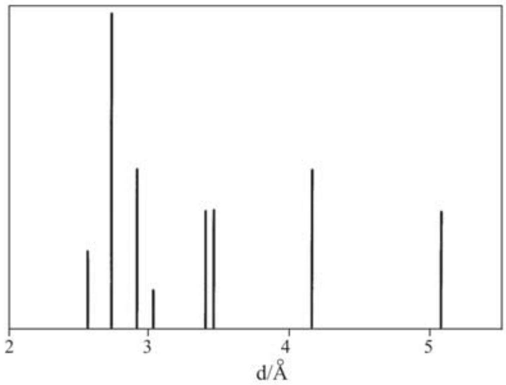

Fig. 2 Schematic diagram of the X-ray diffraction lines for $Co(IO_3)_2{\cdot}4H_2O$

The mass loss derived from the TG curve is 12.3% that corresponds to the loss of two moles H_2O (calculated 11.7%).

The next endothermic process with T_{max}=503 K is due to decomposition of $Co(H_4IO_6)_2$ to $Co(IO_3)_2{\cdot}4H_2O$. The decrease in sample mass is 16.9% which corresponds to the theoretical calculations – 17.7%.

The presence of the low exothermic peak with T_{max}=573 K is due to the process of crystallization of the amorphous $Co(IO_3)_2{\cdot}4H_2O$. According to X-ray diffraction patterns the intermediate phase isolated at 603 K shows crystallinity (Fig. 2).

The interplanar distances coincide most satisfactorily with the data reported in [18]. A broad exothermic process with T_{max}=708 K is due to the decomposition of $Co(IO_3)_2{\cdot}4H_2O$ to $Co(IO_3)_2$ according to [19]. $Co(IO_3)_2$ obtained decomposes itself to Co_3O_4, I_2, O_2 immediately. Distinction between the two processes by DTA is impossible because they are merged into a common endothermic peak. The decrease in sample mass during the whole process of dehydration and decomposition is 85.7%, which is an agreement with the value calculated – 86.3%.

The last endothermic peak observed in DTA curves at T_{max}=1183 K corresponds to the decomposition of Co_3O_4 to CoO, which fact is in accordance with [20].

The decrease in sample mass during the whole process of thermal dehydration and decomposition is 86.1% which corresponds to the theoretical calculations – 87.2%.

Table 1 TG, DTA data for $Co(H_4IO_6)_2{\cdot}4H_2O$

Phase transition	T_{max}/K	Δm_{th}/%	Δm_{exp}/%
$Co(H_4IO_6)_2{\cdot}4H_2O \rightarrow Co(H_4IO_6)_2{\cdot}2H_2O+2H_2O$	373	6.1	6.3
$Co(H_4IO_6)_2{\cdot}2H_2O \rightarrow Co(H_4IO_6)_2+2H_2O$	428	12.3	11.7
$Co(H_4IO_6)_2 \rightarrow Co(IO_3)_2{\cdot}4H_2O+O_2$	503	17.7	16.9
$Co(IO_3)_2{\cdot}4H_2O_{am} \rightarrow Co(IO_3)_2{\cdot}4H_2O_{cr}$	573	–	–
$Co(IO_3)_2{\cdot}4H_2O \rightarrow 1/3Co_3O_4+I_2+7/3O_2+4H_2O$	708	86.3	85.7
$1/3Co_3O_4 \rightarrow CoO+1/6O_2$	1183	87.2	86.1

Table 2 DSC data for $Co(H_4IO_6)_2{\cdot}4H_2O$

Phase transition	T_{max}/K	$\Delta H_{ph.\ tr.}$/kJ mol^{-1}
$Co(H_4IO_6)_2{\cdot}4H_2O \rightarrow Co(IO_3)_2{\cdot}4H_2O+O_2+4H_2O$	375	330.04
$Co(IO_3)_2{\cdot}4H_2O_{am} \rightarrow Co(IO_3)_2{\cdot}4H_2O_{cr}$	575	41.23
$Co(IO_3)_2{\cdot}4H_2O \rightarrow 1/3Co_3O_4+I_2+7/3O_2+4H_2O$	695	128.73

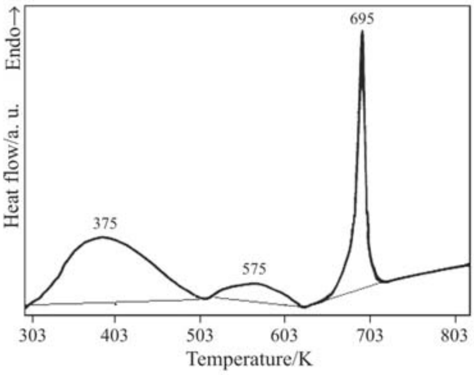

Fig. 3 DSC curves of $Co(H_4IO_6)_2{\cdot}4H_2O$

The thermal properties of $Co(H_4IO_6)_2{\cdot}4H_2O$ are also measured by DSC at a heating rate of 10°C min^{-1} (Fig. 3, Table 2). An endothermic process is observed in the range of 300–503 K. It corresponds to the dehydration and decomposition of $Co(H_4IO_6)_2{\cdot}4H_2O$ with production of $Co(IO_3)_2{\cdot}4H_2O$ and $\Delta H_{ph.\ tr.}$=330.04 kJ mol^{-1}.

The second endothermic peak in the range of 507–623 K is due to the process of crystallization of the primary amorphous $Co(IO_3)_2{\cdot}4H_2O$ with $\Delta H_{ph.\ tr.}$=41.23 kJ mol^{-1}. The process of dehydration of $Co(IO_3)_2{\cdot}4H_2O$ and decomposition of $Co(IO_3)_2$ obtained is observed in the range of 651–718 K. The value of $\Delta H_{ph.\ tr.}$ of the entire process of thermal dehydration and decomposition is 128.73 kJ mol^{-1}.

Conclusions

A new acid salt of hexaoxoiodic acid, $Co(H_4IO_6)_2{\cdot}2H_2O$ is prepared. It is characterized by quantitative analysis and IR spectroscopy. DTA and DSC measurements are carried out and from their data the thermal behavior of $Co(H_4IO_6)_2{\cdot}4H_2O$ could be observed. The process of thermal dehydration proceeds in two stages: at the first stage by DTA, $Co(H_4IO_6)_2{\cdot}2H_2O$ is obtained at T_{max}=373 K, and anhydrous $Co(H_4IO_6)_2$ is obtained at T_{max}=428 K. The process of thermal decomposition of $Co(H_4IO_6)_2$ leads to the formation of amorphous $Co(IO_3)_2{\cdot}4H_2O$ which after the crystallization decomposes to CoO and O_2. From the DSC measurements the enthalpy changes of the main phase transitions are defined.

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