*Journal of Thermal Analysis and Calorimetry, Vol. 84 (2006) 2, 401–403*

# SYNTHESIS, THERMAL AND CALORIMETRIC INVESTIGATIONS OF COBALT(II) TRIHYDROGEN HEXAOXOPERIODATE TETRAHYDRATE

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A new cobalt(II) trihydrogen hexaoxoperiodate tetrahydrate has been synthesized: $CoH_3IO_6{\cdot}4H_2O$ and has been characterized by quantitative analysis, TG, DTA, DSC and IR spectroscopy. Based on DTA and DSC data, a thermal decomposition scheme has been proposed for this complex.

***Keywords:*** *cobalt(II) trihydrogen hexaoxoperiodate tetrahydrate,* $CoH_3IO_6{\cdot}4H_2O$*, thermal decomposition*

## Introduction

The present paper continues our investigations on hydrogen orthoperiodate complexes of Ni, Ag and Cu. Information on the kinetics of thermal dehydration and decomposition of $NiH_3IO_6{\cdot}6H_2O$ is reported in [1] and its crystal structure is given in [2].

The thermal and calorimetric studies of $Ni(H_4IO_6)_2{\cdot}4H_2O$ are presented in [3], and the thermal behaviour of $CuH_3IO_6{\cdot}2H_2O$, $Ag_2H_3IO_6{\cdot}H_2O$ in [4].

There are other compounds containing $H_3IO_6^{2-}$ ion in their crystal structure: $Li_2H_3IO_6$ [5], $Na_2H_3IO_6$ [6], $(NH_4)_2H_3IO_6$ [7], $BaH_3IO_6$ [8], $CdH_3IO_6{\cdot}3H_2O$ [9] and $MgH_3IO_6{\cdot}6H_2O$ [10], $Rb_2H_3IO_6$ [11].

There are many data on complex periodates of cobalt in the literature: $[Co(NH_3)_6]{\cdot}[H_4IO_6]_3$ [12]; $[Li(H_2O)_4]_2H[Co_4H_{12}I_3O_{24}]{\cdot}3H_2O$ [13, 14]; $Na_5H_2Co(IO_6)_2{\cdot}10H_2O$ [15, 16]; $Na_5H_2Co(IO_6)_2{\cdot}8H_2O$ [17]; $LiMCoIO_6$ ($M$=K, Rb, Cs) [18], however there are no data on primary hydrogen orthoperiodates of cobalt.

The purpose of this paper is to report the synthesis of the primary hydrogen orthoperiodate hydrate of cobalt and to study its thermal dehydration by TG, DTA and DSC techniques and to enrich the orthoperiodate complexes data, because they possess valuable characteristics.

## Experimental

$CoH_3IO_6{\cdot}4H_2O$ was prepared by adding solid $H_5IO_6$ (Merck, p.a.) to an aqueous solution of $Co(NO_3)_2{\cdot}6H_2O$ (Merck, p.a.) and stirring at ambient temperature. The resulting solution (pH∼1) was filtered. Crystals of $CoH_3IO_6{\cdot}4H_2O$ were obtained by evaporation of the solution at ambient temperature and dried in air.

The compound was characterized by quantitative analysis: $Co^{2+}$ complexometrically [19] and iodine iodometrically [20].

The 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°C $min^{-1}$ in a temperature range up to 1273 K with a sample mass of 100 mg.

The DSC measurements were recorded on PerkinElmer 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

The chemical analysis data of the synthesized compound coincided with that calculated for $CoH_3IO_6{\cdot}4H_2O$.

| | Co/% | I/% | $H_2O$/% |
|---|---|---|---|
| Theoretical | 16.50 | 35.56 | 20.18 |
| Experimental | 16.62 | 35.64 | 20.17 |

The compound was also characterized by IR spectroscopy (Fig. 1a). The characteristic absorption bands corresponding to the deformation vibration of the I–OH group at 1070 and 1150 $cm^{-1}$ are evidence of the acidic character of the compound in accordance with [21].

The presence of $H_3IO_6^{2-}$ is verified by the observed absorption bands at 360, 620, 660, 760 $cm^{-1}$ due to stretching vibrations of I–O. The same absorption

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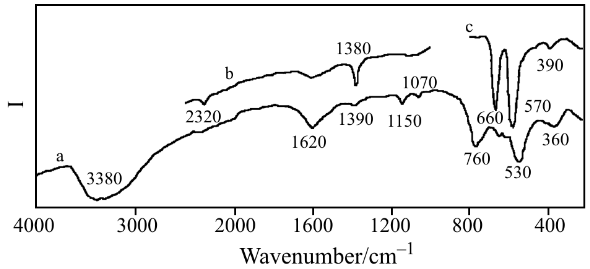

**Fig. 1** IR spectra of a – $CoH_3IO_6{\cdot}4H_2O$, b – partly deuterated compound and c – sample isolated at 1073 K

band of the $IO_4^-$ group is at higher frequencies [22]. The absorption band at 530 cm$^{-1}$ is due to deformation vibration of I–O–I [23]. The presence of the water of crystallization is proved by a wide absorption band at 3380 cm$^{-1}$ due to the stretching vibration of OH-group and by an absorption band at 1620 cm$^{-1}$, due to a deformation vibration of water. The data from IR spectra (Fig. 1b) of partly deuterated compound are in good agreement with the conclusion for the presence of constitutional water. The peaks at 2320 cm$^{-1}$ are due to the stretching vibration of the OD group and that at 1380 cm$^{-1}$ is due to deformation vibration of the HDO group. These data show that the salt was primarily the orthoperiodate hydrate $CoH_3IO_6{\cdot}4H_2O$.

TG and DTA curves of $CoH_3IO_6{\cdot}4H_2O$ are shown in Fig. 2 and the phase transitions are given in Table 1. On the basis of these thermal data, the following scheme for the thermal decomposition of $CoH_3IO_6{\cdot}4H_2O$ is proposed:

$$CoH_3IO_6{\cdot}4H_2O \rightarrow CoH_3IO_6 \rightarrow Co(IO_3)_2 \rightarrow Co_3O_4 \rightarrow CoO$$

It is seen from Fig. 2 that $CoH_3IO_6{\cdot}4H_2O$ begins to dehydrate at 323 K: a large endothermic peak is observed in DTA curve in the temperature range of 323–653 K with $T_{max}$=368 K. It is easily seen that the steps of dehydration in this temperature range are not separated. This endothermic peak corresponds to a mass loss of 19.5% according to TG curve. This value is in good agreement with the calculated 20.0% for the separation of four water molecules, thus forming $CoH_3IO_6$. The isolated intermediate phase at 623 K is proved by quantitative analysis: $Co^{2+}$ complexometrically and iodine iodometrically. Its IR spectra shows the presence of $H_3IO_6^{2-}$ only, absorption band of the crystallization water is absent.

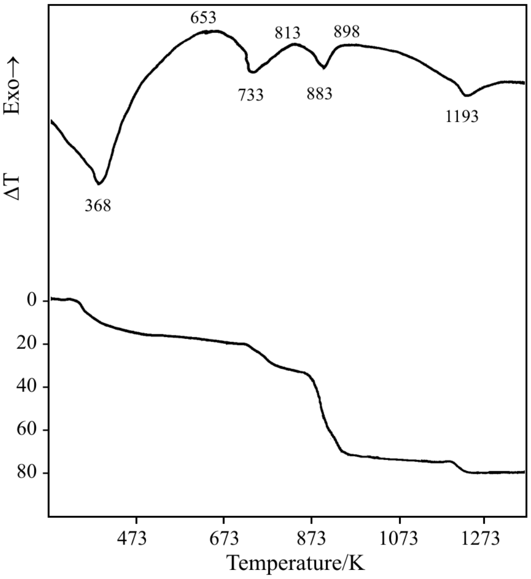

**Fig. 2** TG and DTA curves of $CoH_3IO_6{\cdot}4H_2O$

The subsequent endothermic peak in the temperature range of 653–813 K with $T_{max}$=733 K corresponds to decomposition of $CoH_3IO_6$ to $Co(IO_3)_2$ and $Co_3O_4$. The intermediate phase isolated at 753 K is proved by X-ray diffraction data shown in Fig. 3.

It can be seen in this figure that the intermediate phase is a mixture of $Co(IO_3)_2$ and $Co_3O_4$, because of the presence of peaks characteristic both for $Co(IO_3)_2$ and for $Co_3O_4$ [24, 25].

The next stage of the thermal decomposition of $Co(IO_3)_2$ in the temperature range of 813–898 K (Fig. 2) corresponds to the formation of $Co_3O_4$, $I_2$ and $O_2$ with $\Delta m$=77.8% by TG. The change in the sample mass dur-

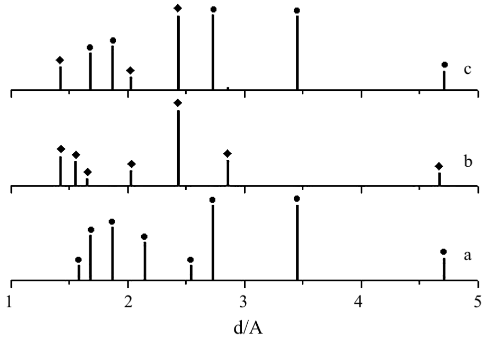

**Fig. 3** Schematic diagram of the X-ray diffraction lines for a – $Co(IO_3)_2$, b – $Co_3O_4$ and c – $nCo(IO_3)_2+mCo_3O_4$

**Table 1** TG, DTA data for $CoH_3IO_6{\cdot}4H_2O$

| Phase transition | $T$/°C | $T_{max}$/°C | $\Delta m_{th}$/% | $\Delta m_{exp}$/% |
|---|---|---|---|---|
| $2CoH_3IO_6{\cdot}4H_2O \rightarrow 2CoH_3IO_6+8H_2O$ | 323–653 | 368 | 20.0 | 19.5 |
| $2CoH_3IO_6 \rightarrow Co(IO_3)_2+1/3Co_3O_4+3H_2O+5/6O_2$ | 653–813 | 733 | 32.0 | 31.5 |
| $Co(IO_3)_2 \rightarrow 1/3Co_3O_4+I_2+7/3O_2$ | 813–898 | 883 | 78.3 | 77.8 |
| $2/3Co_3O_4 \rightarrow 2CoO+1/3O_2$ | 1173–1213 | 1193 | 79.0 | 79.6 |

**Table 2** DSC data for $CoH_3IO_6\cdot 4H_2O$

| Phase transition | $T$/°C | $T_{max}$ /°C | $\Delta H_{ph.tr}$ /kJ mol$^{-1}$ |
|---|---|---|---|
| $2CoH_3IO_6\cdot 4H_2O\rightarrow 2CoH_3IO_6\cdot H_2O+6H_2O$ | 303–453 | 375 | 65.2 |
| $2CoH_3IO_6\cdot H_2O\rightarrow Co(IO_3)_2+1/3Co_3O_4+5H_2O+5/6O_2$ | 453–773 | 745 | 66.5 |

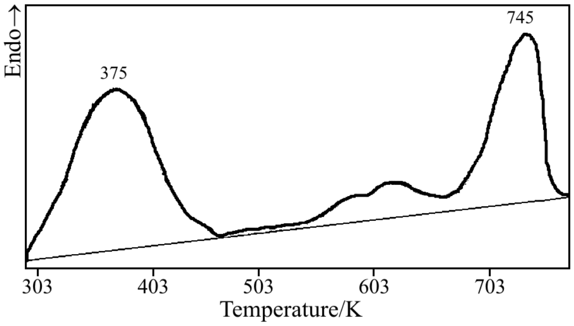

**Fig. 4** DSC curves of $CoH_3IO_6\cdot 4H_2O$

ing such transition corresponds to the theoretical values calculated for these products. The intermediate phase isolated at 1073 K is proved by the IR spectra (Fig. 1c). Absorption bands at 390, 570 and 660 cm are due to $Co_3O_4$ [26]. The last endothermic effect observed in DTA curves is in the temperature range of 1173–1213 K and corresponds to CoO formation [27]. The final product is characterized by quantitative analysis.

The first endothermic effect observed in DSC curves with $T_{max}$=375 K (Fig. 4, Table 2) is due to the separation of three water molecules of crystallization with $\Delta H_{ph.tr}$=65.2 kJ mol$^{-1}$.

The subsequent endothermic effect probably includes processes of decomposition which can not be differentiated. They merge in one common endothermic peak in the temperature range of 453–773 K with $T_{max}$=745 K and $\Delta H_{ph.tr}$=66.5 kJ mol$^{-1}$.

The composition of the intermediate product isolated at $T_{max}$=753 K is the same as that observed in Fig. 3.

## Conclusions

A new cobalt(II) hydrogen salt of hexaoxoperiodic acid is synthesized and characterized by quantitative analysis and IR-spectroscopy. The thermal behavior of $CoH_3IO_6\cdot 4H_2O$ is studied by DTA and DSC. The first phase of the thermal decomposition corresponds to the separation of four crystallization water molecules at $T_{max}$=368 K according to DTA. The subsequent endothermic peak corresponds to decomposition of $CoH_3IO_6$ to $Co(IO_3)_2$ and $Co_3O_4$ at $T_{max}$=733 K. The $Co(IO_3)_2$ obtained is decomposed to $Co_3O_4$, $I_2$ and $O_2$ at $T_{max}$=883 K. The last endothermic effect observed in DTA corresponds to CoO formation at $T_{max}$=1193 K. The enthalpy changes of the main phase transitions are calculated.

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Received: July 21, 2005
Accepted: December 8, 2005

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DOI: 10.1007/s10973-005-7235-1