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# Synthesis, thermal and calorimetric investigations of $CuH_3IO_6\cdot 2H_2O$ and $Ag_2H_3IO_6\cdot H_2O$☆

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## Abstract

Two new hydrogen periodate hydrates, $CuH_3IO_6\cdot 2H_2O$ and $Ag_2H_3IO_6\cdot H_2O$, were synthesized and identified by quantitative analysis, DTA, TG, DSC and IR spectra. Based upon data from DTA and DSC curves, a thermal decomposition scheme has been proposed. The lattice parameters of $CuH_3IO_6\cdot 2H_2O$ were obtained.

*Keywords:* Hydrogen periodate hydrates; $CuH_3IO_6\cdot 2H_2O$; $Ag_2H_3IO_6\cdot H_2O$; Thermal decomposition; IR spectra

## 1. Introduction

This paper continues our investigations on the synthesis and characterization of normal and hydrogen periodates (anhydrous and hydrates). Our interest in the metal periodates is determined by their interesting electrical properties. One type of these compounds contains in their crystal structure $H_3IO_6{}^{2-}$ ion. In the literature, only $Li_2H_3IO_6$ [1], $Na_2H_3IO_6$ [2], $(NH_4)_2H_3IO_6$ [3], $NiH_3IO_6\cdot 6H_2O$ [4], $BaH_3IO_6$ [5], $CdH_3IO_6\cdot 3H_2O$ [6] and $MgH_3IO_6\cdot 6H_2O$ [7] are known. It is of interest to give information on other compounds of this type. The aim of the present investigation is to study the synthesis conditions of hydrogen periodate hydrates of $Cu^{2+}$ and $Ag^{+}$ and their thermal behavior. There are some data on the crystal structure of anhydrous $Ag_2H_3IO_6$ [8].

## 2. Experimental

Crystals of $CuH_3IO_6\cdot 2H_2O$ were obtained by adding solid $CuCO_3\cdot Cu(OH)_2$ (Merck, p.a.) to a water solution of $H_5IO_6$ and stirring. The solution, $pH > 1$, was filtered and the solid phase crystallized at room temperature. The green, well-shaped crystals were dried in a desiccator over silica gel to constant weight. $Ag_2H_3IO_6\cdot H_2O$ was obtained by precipitation of 30% solution of $AgNO_3$ (Merck, p.a.) with stoichiometric quantity of 30% solution of $H_5IO_6$ (Fluka, p.a.). The yellow precipitate was filtered and dried in a desiccator over silica gel to constant weight.

The compounds were identified as $Cu^{2+}$, complexometrically [9]; iodine, iodometrically [10]; $H_2O$, thermogravimetrically; and $Ag^{+}$, by gravimetric analysis [11].

IR spectra were taken in the region 4000–200 $cm^{-1}$ in CsI tablets on a PU 9700 Philips apparatus at 250°C. DTA curves were obtained on a MOM-OD-102 Paulik–Paulik–Erdey derivatograph at a heating rate of 10°C $min^{-1}$ to 600°C, with a sample mass of 150 mg

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☆ Dedicated to Professor Dr. H.D. Lutz on the occasion of his 65th birthday.

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for $Cu^{2+}$ and 250 mg for $Ag^{+}$. DSC curves were obtained using a DSC-4 Perkin–Elmer apparatus in the temperature region 40–500°C at a heating rate of 10° $min^{-1}$. The obtained single crystals were studied rentgenographically. The lattice parameters of $CuH_3IO_6{\cdot}2H_2O$ were calculated on the base of 44 reflections, using SHELXL program [12].

## 3. Results and discussion

Quantitative analysis of the synthesized compounds coincided most satisfactorily with that calculated for $CuH_3IO_6{\cdot}2H_2O$:

| | Cu (%) | I (%) | $H_2O$ (%) |
|---|---|---|---|
| Theoretical | 19.48 | 38.96 | 11.04 |
| Experimental | 19.32 | 39.23 | 11.00 |

For $Ag_2H_3IO_6{\cdot}H_2O$:

| | Ag (%) | I (%) | $H_2O$ (%) |
|---|---|---|---|
| Theoretical | 46.90 | 27.61 | 3.91 |
| Experimental | 47.50 | 28.23 | 3.91 |

$CuH_3IO_6{\cdot}2H_2O$ crystallizes in monoclinic system with the lattice constants a = 10.199 Å, b = 31.794 Å, c = 9.790 Å, $\alpha = \gamma = 90°$ and $\beta = 106.726°$.

The compounds were identified by their IR spectra (Fig. 1). The characteristic absorption bands – deformation vibration of the I-OH group at 1180 $cm^{-1}$ of $Ag_2H_3IO_6{\cdot}H_2O$ resp. at 1230 $cm^{-1}$, 1180 $cm^{-1}$ of $CuH_3IO_6{\cdot}2H_2O$, according to [13], is a proof of the acidic character of the compounds. The presence of $H_3IO_6^{2-}$ can be proved by the observed absorption bands at 830, 760, 660, 550, 430 and 360 $cm^{-1}$, due to stretching vibrations of I-O, whereas the same absorption bands of $IO^{4-}$ lie at higher frequencies [14]. DTA and TG curves of $CuH_3IO_6{\cdot}2H_2O$ are shown in Fig. 2, and the DSC curves are shown in Fig. 3. The information on the thermal decomposition of $CuH_3IO_6{\cdot}2H_2O$ is presented in Table 1.

From the derivatogram (Fig. 2, Table 1), it is seen that the compound is thermal stable up to $T = 100°C$. The first endothermic peak with $T_{max} = 125°C$ corresponds to a mass loss of 11.2%, according to TG curve. This value is in very good agreement with the

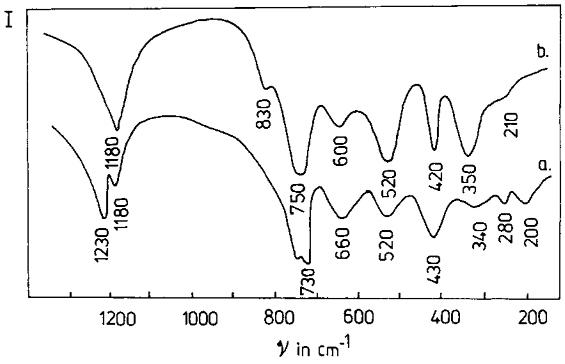

Fig. 1. IR spectra of $CuH_3IO_6{\cdot}2H_2O$ (a) and $Ag_2H_3IO_6{\cdot}H_2O$ (b) in CsI tablets, in the region 1400–200 $cm^{-1}$.

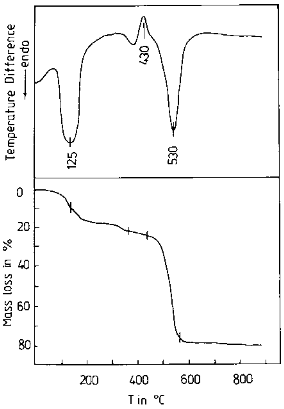

Fig. 2. DTA- and TG-curves of $CuH_3IO_6{\cdot}2H_2O$.

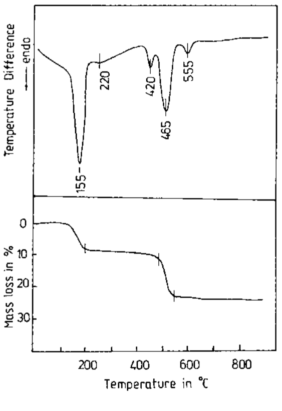

Fig. 3. DTA- and TG-curves of $Ag_2H_3IO_6{\cdot}H_2O$.

Table 1
DTA, TG and DSC data of $CuH_3IO_6{\cdot}2H_2O$

| Phase transition | DTA, TG | | | DSC | |
|---|---|---|---|---|---|
| | $T$ (°C) | $\Delta m_{theor}$ (%) | $\Delta m_{exp}$ (%) | $T$ (°C) | $\Delta H_{ph.tr.}$ (kJ $mol^{-1}$) |
| $2CuH_3IO_6{\cdot}2H_2O \rightarrow 2CuH_3IO_6 + 4H_2O$ | 125 | 11.0 | 11.2 | 127 | 114.47 |
| $2CuH_3IO_6 \rightarrow 2CuHIO_5 + 2H_2O$ | 410 | 16.6 | 17.2 | – | – |
| $2CuHIO_5 \rightarrow CuO + H_2O + O_2 + Cu(IO_3)_2$ | 430 | 18.8 | 19.8 | 410.5 | −11.56 |
| $Cu(IO_3)_2 \rightarrow CuO + I_2 + 2{,}5O_2$ | 530 | 75.5 | 76.1 | – | – |

calculated ($\Delta m = 11.0\%$) for the separation of two water molecules, thus forming $CuH_3IO_6$. An analogical endothermic peak, with $T_{max} = 127°C$ and $\Delta H_{ph.tr.} = 144.47$ kJ $mol^{-1}$, is observed in DSC curve (Fig. 3). The obtained anhydrous $CuH_3IO_6$ decomposes with mass decrease, as shown by the TG curve.

A weak and wide exothermic effect, which passes over in endothermic peak with $T_{max} = 410°C$, is observed in the beginning of the DTA curve in the temperature interval considered. $\Delta m = 17.5\%$ corresponds to these changes in the DTA curve. If we assume that $CuHIO_5$ is obtained, the mass loss will be $\Delta m = 16.6\%$. It is of interest to investigate an intermediate sample at 380°C. The data from its IR spectra (Fig. 4a) show strong absorption bands at 750 $cm^{-1}$, which, according to [15], is due to $IO_5^{3-}$. A weak exothermic effect, with $T_{max} = 410.5°C$ ( $\Delta H_{ph.tr.} = -11.95$ kJ $mol^{-1}$), can be observed in the DSC curve.

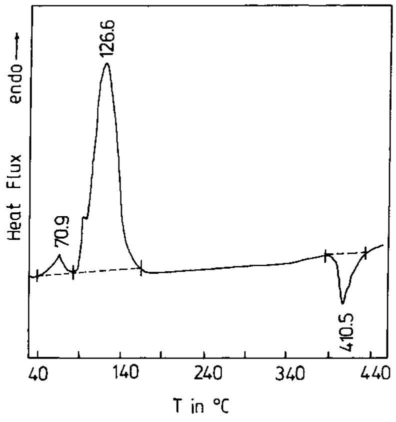

Fig. 4. DSC curves of $Ag_2H_3IO_6{\cdot}H_2O$.

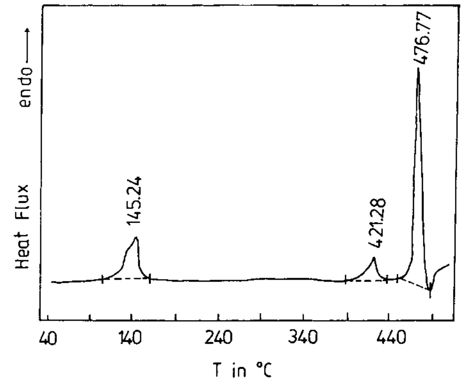

Fig. 5. DSC curves of $CuH_3IO_6{\cdot}2H_2O$.

The strong endothermic effect, with $T_{max} = 530°C$, is due to the decomposition of Cu $(IO_3)_2$ to CuO, with $\Delta m = 76.0\%$, by TG curve ($\Delta m_{calc.} = 75.5\%$). The obtained CuO is proved by quantitative analysis.

The DTA and DSC curves of $Ag_2H_3IO_6{\cdot}H_2O$ are shown in Fig. 5 and Fig. 6. The information about its thermal behavior is presented in Table 2.

The endothermic effect, with $T_{max} = 155°C$, in the DTA curve (analogical peak in DSC-$T_{max} = 145.24°C$) is due to the separation of crystal-

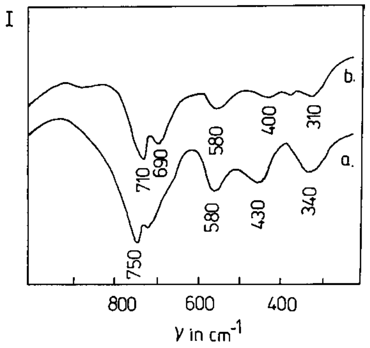

Fig. 6. IR spectra of sample isolated at 380°C $CuH_3IO_6{\cdot}2H_2O$ (a) and $Ag_2H_3IO_6{\cdot}H_2O$ (b).

Table 2
DTA, TG and DSC data of $Ag_2H_3IO_6{\cdot}H_2O$

| Phase transition | DTA, TG | | | DSC | |
|---|---|---|---|---|---|
| | $T$ (°C) | $\Delta m_{theor}$ (%) | $\Delta m_{exp}$ (%) | $T$ (°C) | $\Delta H_{ph.tr.}$ (kJ mol$^{-1}$) |
| $2Ag_2H_3IO_6{\cdot}H_2O \rightarrow 2Ag_2HIO_5 + 4H_2O$ | 155 | 7.82 | 8.00 | 145 | 67.86 |
| $2Ag_2HIO_5 \rightarrow 2AgIO_4 + Ag_2O + H_2O$ | 420 | – | – | 421 | 20.99 |
| $2AgIO_4 + Ag_2O \rightarrow 2AgI + 2Ag + 4{,}5O_2$ | 465 | 24.90 | 25.10 | 475 | – |

lization water as well as a part of constitution water, thus producing $Ag_2HIO_5$ (Table 2). The mass decrease by the TG curve is $\Delta m = 8.0\%$. This value is in very good agreement with the calculated—$\Delta m_{calc.}$ 7.82%. It is of interest to identify the intermediate phase—$Ag_2HIO_5$. It is isolated and determined by methods of quantitative analysis and IR spectroscopy. The data from IR spectra of this intermediate phase show intensive absorption bands at 750 cm$^{-1}$, which, according to [15], prove the presence of $HIO_5{}^{2-}$. The weak endothermic effect, with $T_{max} = 420°C$, observed in the DTA curve, corresponds to the decomposition of $Ag_2HIO_5$ to mixture of $AgIO_4$, $Ag_2O$ and $H_2O$ (Table 2). The same effect in DSC, with $T_{max} = 465°C$, corresponds to the decomposition of $AgIO_4$ to AgI and $O_2$, as well as of $Ag_2O$ to Ag and $O_2$. The presence of AgI and Ag as final products is established by quantitative determination of iodine, taking into account the ratio between AgI and Ag in the sample investigated. A weak endothermic effect, with $T_{max} = 555°C$, is due to the melting of AgI, which is known, $T_{max} = 552°C$, according to [15].

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