## Short Communications

# STUDY OF THE THERMAL DEHYDRATION OF SOME FIBRILLAR ALKALI METAL TRIMOLYBDATES

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The dehydration process of the fibrillar potassium, rubidium and cesium isopolytrimolybdates was investigated by thermogravimetry and X-ray diffractometry. The dehydration took place in one step and the trimolybdates of general formula $X_2Mo_3O_{10}$ (where $X =$ K, Rb or Cs) were obtained.

In a previous paper, fibrillar crystals of potassium $K_2O \cdot 3\,MoO_3 \cdot 3\,H_2O$ [1] were described. Crystalline fractions of fibrillar crystals of rubidium and cesium isopolymolybdates were recently isolated in our laboratory. The results of chemical analyses correspond to the stoichiometric formula $Rb_2O \cdot 3\,MoO_3 \cdot H_2O$ and $Cs_2O \cdot 3\,MoO_3 \cdot H_2O$, respectively. The anions of the fibrillar trimolybdates have a chain structure [2] and contain one constitution water molecule bound directly to the central molybdenum atom [3]. Hence, it was interesting to study the structural changes of the above compounds in correlation with their dehydration process. In the present paper the results of thermogravimetric and X-ray powder diffraction investigations are described.

## Experimental

### *Preparation of the compounds*

The synthesis of fibrillar potassium trimolybdate was carried out using the method described in the previous paper [1]. The initial molybdenum concentration in the solution of normal potassium molybdate ($K_2MoO_4 \cdot 2\,H_2O$, p.a., POCh, Gliwice, Poland) was 0.250 *M* and the degree of acidity was $Z = 1.33$ ($Z$ is the number of $H^+$ g-ions per g-atom of molybdenum). Rubidium trimolybdate was obtained by adding portions of solid $MoO_3$ (POCh, Gliwice) to a boiling 0.5 *M* solution of RbOH (Fluka AG, Buchs SG) until saturation of the solution was reached. The resulting yellow-green solution was filtered and left to crystallize.

Cesium polytrimolybdate was obtained similarly, but the molybdenum trioxide was added to a boiling 0.5 *M* solution of cesium carbonate $Cs_2CO_3$ (International Enzymes Ltd., England).

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### Measurements

The thermogravimetric characteristics were obtained in air at normal pressure by means of a derivatograph (MOM, Budapest) up to 873 K. All samples were heated at a constant rate of 5° per min. In addition, static heatings (from 1 to 6 h) were performed at different temperatures up to 900 K.

X-ray studies were carried out on a Dron-2 (U.S.S.R.) diffractometer equipped with a high-temperature UWD-2000 camera. Copper $K_\alpha$ radiation, with a nickel filter, was used. The diffraction patterns were recorded in the temperature range 293 – 800 K. The measured samples were kept at the given temperature for about 20 min before the recording of the diffraction pattern.

The lattice parameters were calculated by least squares methods using 20 reflections. Calculations were carried out on the CDC CYBER computer.

## Results and conclusion

The X-ray diffraction data showed that all the investigated fibrillar trimolybdates crystallize in an orthorhombic system. In Table 1 the unit cell dimensions are listed. These parameters indicate that the above compounds are isostructural and they are true analogues of the other fibrillar trimolybdates [4].

The DTA curves were characterized by the appearance of endo peaks only. The minima of all the effects are listed in Table 2. For potassium trimolybdate

Table 1

Lattice parameters of the trimolybdates

| Compounds | Parameters | | | | Ref. |
|---|---|---|---|---|---|
| | $a$, Å | $b$, Å | $c$, Å | $\beta$, ° | |
| $K_2O \cdot 3\ MoO_3 \cdot 3\ H_2O$ | 13.72 | 7.66 | 12.00 | 90 | [4] |
| $K_2O \cdot 3\ MoO_3$ | 13.95 | 7.75 | 9.01 | 99.18 | [6] |
| | 13.90 | 7.91 | 8.84 | 98.84 | [7] |
| | 14.00 | 7.87 | 8.80 | 99.63 | this p. |
| $Rb_2O \cdot 3\ MoO_3 \cdot H_2O$ | 14.96 | 7.58 | 9.94 | 90 | this p. |
| $Rb_2O \cdot 3\ MoO_3$ | 14.19 | 8.12 | 9.23 | 99 | [7] |
| | 14.09 | 8.13 | 9.06 | 98.73 | this p. |
| $Cs_2O \cdot 3\ MoO_3 \cdot H_2O$ | 15.50 | 7.61 | 10.23 | 90 | this p. |
| $Cs_2O \cdot 3\ MoO_3$ | 14.55 | 8.43 | 9.52 | 99 | [7] |
| | 14.48 | 8.39 | 9.39 | 97.79 | this p. |

Table 2

The temperatures of the DTA peaks

| Compounds | Temperature, K | Weight loss, % |
|---|---|---|
| $K_2O \cdot 3\,MoO_3 \cdot 3\,H_2O$ | 423 | 9.28; 9.31* |
| | 593 | — |
| | 843; 844** | — |
| $Rb_2O \cdot 3\,MoO_3 \cdot H_2O$ | 458 | 2.92; 2.82* |
| | 833; 836** | — |
| $Cs_2O \cdot 3\,MoO_3 \cdot H_2O$ | 433 | 2.60; 2.51* |
| | 571 | — |
| | 808; 818** | — |

* Calculated weight loss

** Temperatures of melting points of the anhydrous trimolybdates after Spicyn et al. [5]

the loss of water was observed in the temperature interval 353–513 K. This was associated with a minimum in the DTA curve at 423 K. For the rubidium compound, the weight loss began at 373 K and continued up to about 513 K (DTA minimum at 458 K). This weight decrease amounted to 2.92%, which corresponds to the splitting-off of one water molecule.

The thermal dehydration of the cesium salt started above 363 K. The dehydration rate became the highest at about 433 K and ceased at 493 K, with practically no appreciable change in weight up to 873 K.

The endothermic processes with minimum at 593 K for the potassium compound and 571 K for the cesium one are connected with structural transformations. This was also found in the diffraction patterns. In the temperature range from 773 to 873 K the anhydrous compounds melt. The temperatures of the DTA peaks (see Table 2) correspond to the melting-points of the trimolybdates $K_2Mo_3O_{10}$, $Rb_2Mo_3O_{10}$ and $Cs_2Mo_3O_{10}$, respectively [5]. This result is confirmed by the X-ray studies. In Table 1 the lattice parameters obtained by us for the anhydrous forms and those given in the literature [6, 7] for these trimolybdates are listed. The parameters for the anhydrous salts were calculated from samples obtained by heating the hydrated compounds at 773 K.

Based on the observations of this study, we conclude that:

1. Dehydration of fibrillar potassium, rubidium and cesium trimolybdates proceeds in one step. This character of the process for the potassium compound, which has three molecules of water, is caused by the previous change of the oxygen-hydrogen forms. According to NMR studies [8], in this compound an abrupt transition of the following type is observed:

$$K_2Mo_3O_{10-\alpha}(OH)_{2\alpha}(H_2O)_{1-\alpha} \cdot 2\,H_2O \quad \text{about} \quad 323\text{ K} \quad K_2Mo_3O_7(OH)_6$$

In the course of the dehydration process of fibrillar trimolybdates, no amorphous phases were observed. Hence, it can be assumed that the formation of the new crystal phases is a fast process.

2. The isostructural trimolybdates of the general formula $X_2Mo_3O_{10}$ (where $X$ = K, Rb or Cs) are the final products of heating. According to literature data [6, 7], these anhydrous compounds were obtained previously by direct synthesis.

3. In the course of calcination of the potassium and cesium salts, intermediate phases of unknown structure were observed. This is a problem for further consideration.

4. The anions of the initial fibrillar polytrimolybdates have a chain structure [4]. The zig-zag chains are formed by oxygen atoms in trans positions to each other. Every octahedron shares two apices with two $MoO_3$ groups. The anhydrous trimolybdates too have a chain structure. Infinite chains contain distorted $MoO_6$ octahedra and $MoO_5$ square pyramids [6, 7]. Thus, the dehydration processes described above are accompanied by the reconstruction of the trimolybdate chain links.

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