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Thermal properties of fibrillar forms of Co(II), Ni(II), Zn(II) and Cu(II) isopolytrimolybdates hydrates

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Abstract

Stoichiometry and the mechanism of the thermal decomposition of fibrillar isopolytrimolybdates Co(II), Ni(II), Zn(II) and Cu(II) of the following general formulae: $CoMo_3O_{10}{\cdot}5H_2O$, $NiMo_3O_{10}{\cdot}5H_2O$, $ZnMo_3O_{10}{\cdot}5H_2O$, $ZnMo_3O_{10}{\cdot}3.75\,H_2O$ and $CuMo_3O_{10}{\cdot}5H_2O$ have been investigated. Water was found to be essential to the structure of these compounds, and with its loss on heating, the compounds became amorphous and (above 300°C) decomposed, forming $MMoO_4$ and MoO_3 where M=Co(II), Ni(II), Zn(II) and Cu(II). The change in enthalpy of each process ($\Delta_{deh}H$ and $\Delta_{dec}H$) has been determined. © 1998 Elsevier Science B.V.

Keywords: Decomposition; Fibrillar isopolytrimolybdates with transition metals

1. Introduction

The first reports on trimolybdates with cations of transition metals date back to the 1860s. Ullik [1] described the preparation of cobaltous(II)trimolybdate of the formula $CoO{\cdot}3MoO_3{\cdot}10H_2O$ obtained as a result of boiling a solution containing excess molybdic acid and cobalt carbonate. The crystals obtained were fibre-shaped. Marckwald, in turn, obtained nickel(II)-trimolybdate of the formula $NiO{\cdot}3MoO_3{\cdot}18H_2O$ as a result of evaporating the solution containing equivalent quantities of nickel chloride and sodium paramolybdate [1]. Further investigations led to the preparations of fibrillar trimolybdates of Co(II) and Ni(II) with the following soichiometric formulae: $CoMo_3O_{10}{\cdot}4.6H_2O$ oraz $NiMo_3O_{10}{\cdot}9H_2O$ [2]. The thermal characteristic and X-ray diffraction data were also determined. Ullik [1] also mentioned zinc(II)trimolybdate decahydrate which was prepared by addition of molybdenum trioxide to a boiling zinc carbonate solution. Carriere et al. [3], in turn, obtained zinc(II)trimolybdate whose hydration was not determined through mixing the solution of zinc(II)chloride with a boiling solution of sodium monomolybdate acidified with hydrochloric acid to pH=3. The required product was precipitated by adding ethanol. Meullemeestre and Penigault reported the preparation of fibrillar zinc(II)trimolybdate, whose fibers were 1–2 cm in length, with 3.75 or 5 molecules of water, depending on the method of drying the samples [4]. Further investigations on zinc(II)trimolybdates showed that under well-defined conditions it can occur as an anhydrous phase, and with 5 and 3.75 molecules of water [5]. The lattice parameters of the individual phase were determined. The only report on copper-

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(II)trimolybdate is that of Ref. [6]. Ullik described the preparation of $CuO{\cdot}3MoO_3{\cdot}9H_2O$ as a result of boiling solutions containing 1 M of copper carbonate and 4 M of molybdic acid. Light-blue fibrous obtained. When the solution was not spontaneously evaporated but left to stand on a glass plate, Ullik obtained greenish-blue gummy mass of formula $CuO{\cdot}3MoO_3{\cdot}6.5H_2O$. As there is a much of controversy over which hydrated forms of the individual trimolybdates is present under each set of conditions and what is the mechanism of their thermal decomposition, an investigation on a group of these compounds as catalysts has been undertaken.

2. Experimental

Molybdene(VI)trioxide pure (POCh Gliwice) was added in small portions to a boiling solution of basic cobaltous carbonate (nickel, zinc, copper) (p.a. POCh Gliwice) until saturation has been reached. Initially, the reactions were vigorous with the evolution of gas bubbles and then it ceased to proceed so that successive portions of MoO_3 did not dissolve any more. The solutions were then filtered through a Buchner funnel, decanted into a flask with stopper and left to cool in order to crystallize out unreacted MoO_3. The operation was repeated twice. After few days, a fibrillar precipitate fell out. The precipitates were filtered off, washed repeatedly with water and dried (for at least two weeks) in the air or over silica gel. The Mo content was assayed gravimetrically by the modified Busiev method [7], the cations of transition metals content were determined by titration with EDTA [8], and water content was determined by drying the compounds at above 300°C. The results of the chemical analysis are given in Table 1.

Preliminary derivatographic investigations (TG, DTG, DTA curves) were taken using a MOM (Budapest) derivatograph. The sample weight was 0.4–1 g, the heating rate was 5°C/min from 20°C to 1000°C, the sensitivity was 200 or 500 mg in TG, 1/5 in DTA and DTG. Calcined Al_2O_3 was used as a reference material.

More thorough thermal investigations were under taken on Du Pont 1090 Thermal Analyzer equipped with a 951 Thermogravimetric Analyzer and 910 Differential Scanning Calorimeter. The measurenents were carried out in air at a heating rate of 5 K/min using Al crucibles in relation to an empty crucible. The calorimeter was calibrated with metalic pure indum.

Table 1
Analytical data for investigation compounds

Compound	Colour	M(II) (%)	Mo (%)	H_2O (%)
$CoMo_3O_{10}{\cdot}5H_2O$ (596.82)	Pink	9.72	47.69	15.90[a]
		(9.87)	(48.23)	15.09
$CoMo_3O_{10}$ (506.75)	Grey	11.63	56.27	—
		(11.63)	(56.80)	—
$NiMo_3O_{10}{\cdot}5H_2O$ (596.58)	Light-green	9.34	47.93	15.20[a]
		(9.84)	(48.24)	15.10
$NiMo_3O_{10}$ (506.50)	Grey yellow	11.43	56.38	—
		(11.59)	(56.82)	—
$ZnMo_3O_{10}{\cdot}5H_2O$ (603.28)	White	10.73	47.48	15.07[a]
		(10.84)	(47.71)	(14.94)
$ZnMo_3O_{10}{\cdot}3.75H_2O$ (580.76)	White	11.20	49.71	11.70[a]
		(11.26)	(49.56)	(11.63)
$ZnMo_3O_{10}$ (513.20)	Blue-grey	12.74	56.16	—
		(12.74)	(56.08)	—
$CuMo_3O_{10}{\cdot}5H_2O$ (601.44)	Blue-green	10.54	47.76	14.54[a]
		(10.57)	(47.85)	(14.98)
$CuMo_3O_{10}$ (511.44)	Bright-yellow	12.35	56.20	—
		(12.43)	(56.28)	—

[a] Result for the completly dehydrated (at >300°C) compound.

The XRD investigation were carried out on a DRON-2 (Russia) diffractometer connected to an IBM computer, stepwise, over the 2θ angle range of 4–65°.

Redistilled water was used throughout.

3. Results and discussion

3.1. Stoichiometry of thermal decomposition and structural investigation

Cobalt(II)isopolytrimolybdate forms well-defined fibrillar crystals only when they are in a crystallizing environment. When dried in air it forms a stable pentahydrous phase. As shown by TG measurements taken at 42°C and 105°C, this compound loses 2 molecules of water altogether, being made amorphous at the same time (Fig. 1). The rest of the water is removed within the range of 138–300°C (Table 2). This process involves a further amorphisation of the compound. The changes occurring here can be shown as follows:

$$\mathrm{CoMo_3O_{10}\cdot}n\mathrm{H_2O\,(c)}\xrightarrow{\text{air}}\mathrm{CoMo_3O_{10}\cdot 5H_2O\,(c)}$$

$$\mathrm{CoMo_3O_{10}\cdot 5H_2O\,(c)}\xrightarrow[\text{endo}]{22-67^\circ\mathrm{C}}\mathrm{CoMo_3O_{10}\cdot 4.5H_2O\,(sc)+0.5H_2O}$$

$$\mathrm{CoMo_3O_{10}\cdot 4.5H_2O}\xrightarrow[\text{endo}]{67-138^\circ\mathrm{C}}\mathrm{CoMo_3O_{10}\cdot 3H_2O\,(sc)+1.5H_2O}$$

$$\mathrm{CoMo_3O_{10}\cdot 3H_2O\,(sc)}\xrightarrow[\text{endo}]{138-390^\circ\mathrm{C}}\mathrm{CoMo_3O_{10}\,(a)+3H_2O}$$

Moreover, from DSC investigations [9,10] it has been concluded that above 300°C the following

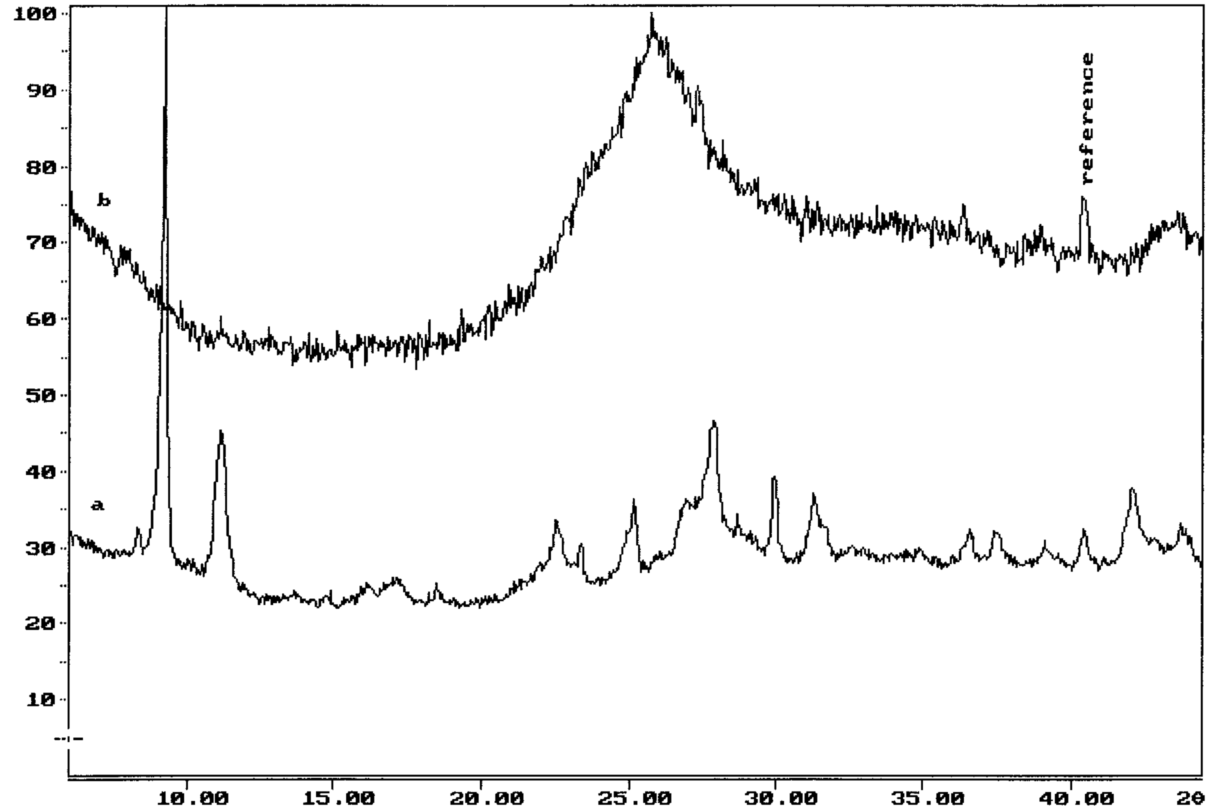

Fig. 1. Diffractograms obtained for (a) $\mathrm{CoMo_3O_{10}\cdot 5H_2O}$; (b) $\mathrm{CoMo_3O_{10}}$.

Table 2
Thermal analysis results for investigation fibrillar isopolytrimolybdates

Starting compound	Interval (°C)	DTG T_p (°C)	TG weight loss (%)		Resulting intermediate
			Found	Calcd.	
$CoMo_3O_{10}\cdot 5H_2O$	22–67	42	1.51	1.51	$CoMo_3O_{10}\cdot 4.5H_2O$
	67–137.5	104	5.23	4.53	$CoMo_3O_{10}\cdot 3H_2O$
	137.5–390	179	9.32	9.06	$CoMo_3O_{10}$
$NiMo_3O_{10}\cdot 5H_2O$	25–145	118	4.92	4.53	$NiMo_3O_{10}\cdot 3.5H_2O$
	145–400	203	10.08	10.57	$NiMo_3O_{10}$
$ZnMo_3O_{10}\cdot 5H_2O$	25–105	70	4.96	4.48	$ZnMo_3O_{10}\cdot 3.5H_2O$
	105–198	173	6.61	672	$ZnMo_3O_{10}\cdot 1.25H_2O$
	198–390	225	3.64	3.73	$ZnMo_3O_{10}$
$ZnMo_3O_{10}\cdot 3.75H_2O$	18–100	—	1.33	1.55	$ZnMo_3O_{10}\cdot 3.25H_2O$
	100–150	150	1.47	1.55	$ZnMo_3O_{10}\cdot 2.75H_2O$
	150–210	173	5.41	5.43	$ZnH_2O_3O_{10}\cdot H_2O$
	210–380	228	3.40	3.10	$ZnMo_3O_{10}$
$CuMo_3O_{10}\cdot 5H_2O$	15–84	57.5	4.11	3.74	$CuMo_3O_{10}\cdot 3.75H_2O$
	84–127.5	100	3.02	2.99	$CuMo_3O_{10}\cdot 2.75H_2O$
	127.5–400	175	8.03	8.24	$CuMo_3O_{10}$

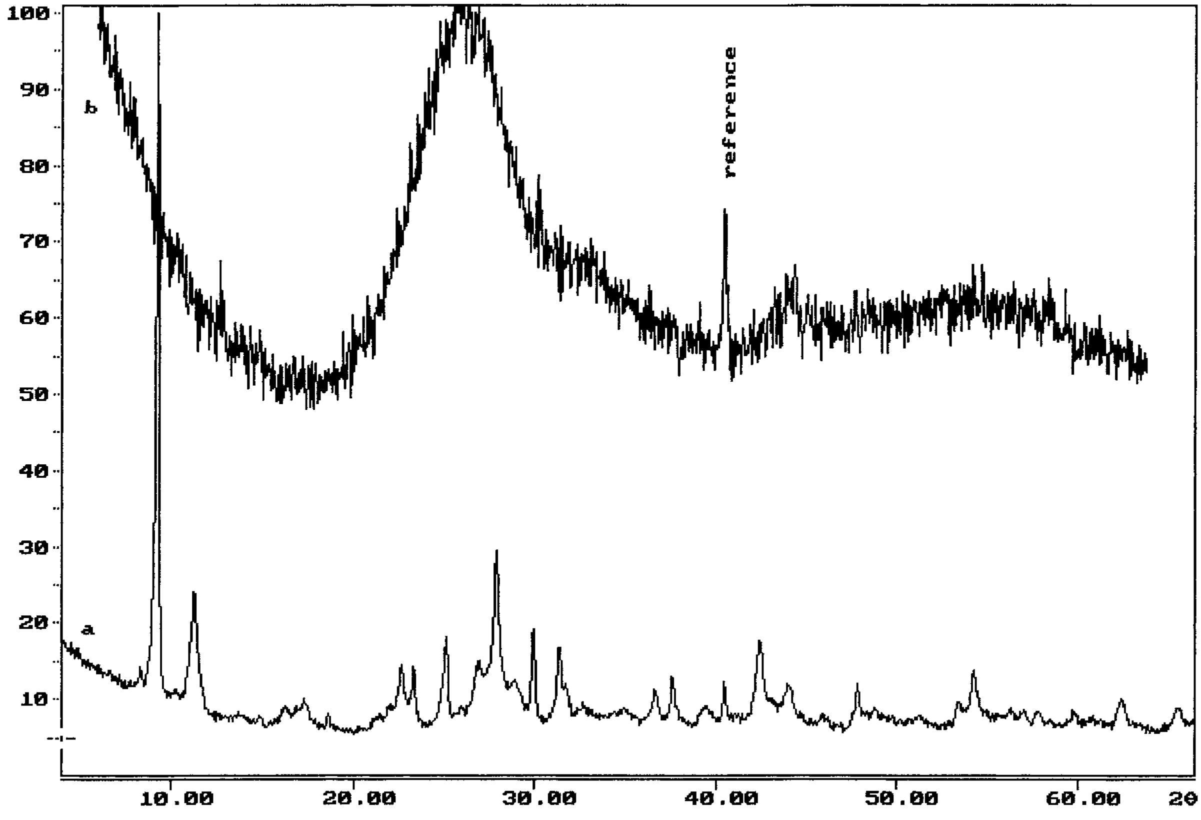

Fig. 2. Diffractograms obtained for (a) $NiMo_3O_{10}\cdot 5H_2O$; (b) $NiMo_3O_{10}$.

Table 3
XRD data for trimolybdate pentahydrate

$CoMo_3O_{10}\cdot 5H_2O$		$NiMo_3O_{10}\cdot 5H_2O$		$ZnMo_3O_{10}\cdot 5H_2O$		$ZnMo_3O\cdot 5H_2O$ [12]		$CuMo_3O_{10}\cdot 5H_2O$	
d (Å)	*I* (%)	*d* (Å)	*I* (%)	*d* (Å)	*I* (%)	*d* (Å)	*I* (%)	*d* (Å)	*I* (%)
9.63	100	9.59	100	9.67	100	9.804	100	9.57	100
7.95	24	7.87	14	7.99	11	7.937	60	7.96	12
6.46	1	6.41	1	6.52	2	6.579	40	—	—
5.98	2	5.98	1	5.94	4	6.579	40	5.93	10
5.47	2	5.48	2	5.45	8	5.495	60	—	—
5.15	2	5.12	3	5.24	7	5.128	20	—	—
4.80	3	4.79	3	4.81	2	—	—	—	—
4.06	2	4.04	1	4.06	5	4.082	20	—	—
3.95	8	3.92	6	4.02	6	—	—	—	—
3.81	7	3.81	7	3.84	9	3.817	80	3.79	10
3.59	1	3.54	13	3.53	18	3.546	100	3.53	13
3.54	11	3.43	1	3.42	8	3.436	60	—	—
3.33	5	3.32	5	3.31	13	—	—	—	—
3.20	17	3.19	18	3.22	31	3.215	60	3.26	13
3.11	3	3.08	2	3.12	2	3.058	40	3.08	57
2.99	17	2.98	16	2.99	26	2.985	100	—	—
2.86	9	2.85	10	2.93	5	—	—	—	—
2.82	2	2.81	2	2.85	20	2.857	80	—	—
2.75	2	2.74	2	2.72	5	—	—	2.72	—
2.61	2	2.61	1	2.60	4	—	—	2.56	—
2.57	2	2.57	1	2.53	2	2.475	40	—	—
2.45	5	2.45	4	2.45	10	2.457	100	—	—
2.40	6	2.39	7	2.41	6	2.415	60	—	—
—	—	—	—	2.38	2	—	—	—	—
2.3	3	2.28	2	2.34	10	—	—	2.31	—
2.15	9	2.14	1	2.15	11	—	—	—	—
2.11	2	2.10	3	2.11	3	—	—	—	—
2.07	5	2.06	4	2.08	5	—	—	—	—
1.99	1	1.98	1	1.90	16	1.901	100	—	—

processes occur:

$$CoMo_3O_{10}\,(a) \overset{333-410^{\circ}C}{\underset{exo}{\rightarrow}} CoMoO_4\,(a) + 2MoO_3\,(c)$$

$$CoMoO_4\,(a) \overset{410-470^{\circ}C}{\underset{exo}{\rightarrow}} CoMoO_4\,(c)$$

where the letters ‘c’, ‘sc’ and ‘a’ in parenthesis denote crystal, semicrystal and amorphous, respectively. The final products were confirmed from their XRD patterns.

In a previous paper the stoichiometric formula $CoMo_3O_{10}\cdot 4.6H_2O$ was attributed to this compound [2]. Judging from the present studies a complete dehydration of this compound occurs at temperatures higher than thought previously because the water content of the compound had not been fully determined.

Nickel(II)isopolytrimolybdate exhibits structural similarity to the above cobalt derivative. The phase which is stable in time is a compound with the formula $NiMo_3O_{10}\cdot 5H_2O$. It can be obtained by drying for a large enough time $NiMo_3O_{10}\cdot nH_2O$ in air (about 1 month). Marckwald [1] attributes 18 molecules of water to its formula but as shown by the present investigations, the compound of such a hydration state can only exist in the presence of the mother liquor. On anything in air only, it loses the very weakly bound of water, giving diffraction patterns between the *n*-hydrous phase and the pentahydrous phase. A further loss of water occurs on heating but, unlike the cobalt derivative it occurs in two stages. As shown by TG in the range 25–145°C the compound loses 1.5 molecules of water and the rest of the water at 145–400°C. The remaining material is amorphous at the same time

(Fig. 2), as follows:

$$\mathrm{NiMo_3O_{10}\cdot}n\mathrm{H_2O\,(c)}\xrightarrow{\text{air}}\mathrm{NiMo_3O_{10}\cdot 5H_2O\,(c)}$$

$$\mathrm{NiMo_3O_{10}\cdot 5H_2O\,(c)}\xrightarrow[\text{endor}]{25-148^{\circ}\mathrm{C}}\mathrm{NiMo_3O_{10}\cdot 3.5H_2O\,(sc)}+1.5\mathrm{H_2O}$$

$$\mathrm{NiMo_3O_{10}\cdot 3.5H_2O\,(sc)}\xrightarrow[\text{endo}]{145-400^{\circ}\mathrm{C}}\mathrm{NiMo_3O_{10}\,(a)}+3.5\mathrm{H_2O}$$

XRD investigations correlated with the DSC measurements showing that above 350°C the following changes were present [9,11]:

$$\mathrm{NiMo_3O_{10}\,(a)}\xrightarrow[\text{exo}]{370-477^{\circ}\mathrm{C}}\mathrm{NiMoO_4\,(a)}+2\mathrm{MoO_3\,(c)}$$

$$\mathrm{NiMoO_4\,(a)}\xrightarrow[\text{exo}]{447-480^{\circ}\mathrm{C}}\mathrm{NiMoO_4\,(c)}$$

Zinc(II)isopolytrimolybdate forms two hydrates which form stable crystalline phases with 5 and 3.75 molecules of water. The pentahydrous phase [4,5,12] is isostructural with the corresponding cobalt and nickel derivatives (Table 3). The structure of $\mathrm{ZnMo_3O_{10}\cdot 3.75H_2O}$, was determined by Meullemeestre et al. [4,13], and determined recently [14]. This compound is formed when the 5-hydrous phase is kept for a large period over silica gel. A higher hydration state of this molybdate (10 molecules of water has been attributed to it, as well as to the cobalt trimolybdate, by Ullik [1]) in the presence of the crystallizing environment. The TG investigations showed that the thermal decomposition of $\mathrm{ZnMo_3O_{10}\cdot 5H_2O}$ takes place in three stages, viz,

$$\mathrm{ZnMo_3O_{10}\cdot}n\mathrm{H_2O\,(c)}\xrightarrow{\text{air}}\mathrm{ZnMo_3O_{10}\cdot 5H_2O\,(c)}\xrightarrow{\text{silicagel}}\mathrm{ZnMo_3O_{10}\cdot 3.75H_2O\,(c)}$$

$$\mathrm{ZnMo_3O_{10}\cdot 5H_2O\,(c)}\xrightarrow[\text{endo}]{25-105^{\circ}\mathrm{C}}\mathrm{ZnMo_3O_{10}\cdot 3.5H_2O\,(c)}+1.5\mathrm{H_2O}$$

$$\mathrm{ZnMo_3O_{10}\cdot 3.5H_2O\,(c)}\xrightarrow[\text{endo}]{105-198^{\circ}\mathrm{C}}\mathrm{ZnMo_3O_{10}\cdot 1.25H_2O\,(a)}+2.25\mathrm{H_2O}$$

$$\mathrm{ZnMo_3O_{10}\cdot 1.25H_2O\,(a)}\xrightarrow[\text{endo}]{198-390^{\circ}\mathrm{C}}\mathrm{ZnMo_3O_{10}\,(a)}+1.25\mathrm{H_2O}$$

The dehydration of $\mathrm{ZnMo_3O_{10}\cdot 3.75H_2O}$ is different from that of the pentahydrous phase (Table 2), but the dehydration of the last molecule of water for both hydrates occur at high temperatures. At about 400°C, zinc(II)isopolytrimolybdate decomposes [15,9] according to

$$\mathrm{ZnMo_3O_{10}\,(a)}\xrightarrow[\text{exo}]{364-429^{\circ}\mathrm{C}}\mathrm{ZnMoO_4\,(c)}+2\mathrm{MoO_3\,(c)}$$

Copper(II)isopolytrimolybdate gave clear diffraction patterns when the crystals were in center with the crystallizing environment, with similar XRD patterns to the above-mentioned *n*-hydrous trimolybdates. The pentahydrous phase which was obtained by drying the *n*-hydrous phase in air, gave diffraction patterns which were much worse than other trimolybdates of the same hydration state here. Further dehydrations occur on heating in three stages:

$$\mathrm{CuMo_3O_{10}\cdot 5H_2O\,(sc)}\xrightarrow[\text{endo}]{15-84^{\circ}\mathrm{C}}\mathrm{CuMo_3O_{10}\cdot 3.75H_2O\,(a)}+1.25\mathrm{H_2O}$$

Table 4
DSC data of fibrillar isopolytrimolybdates

Compound	Temperature interval (°C)	DSC T_p (°C)	ΔH ($\mathrm{J\,g^{-1}}\pm1\%$)
$\mathrm{CoMo_3O_{10}\cdot 5H_2O}$	28–105	90	61.2
	105–170	148	184.0
	170–323	208	319.8
	333–410.5	381	−25.8
	410.5–470	452	−33.8
	470–518	475	−7.7
$\mathrm{NiMo_3O_{10}\cdot 5H_2O}$	82–182	159.5	179
	182–370	227	346
	370–447.5	423	−33.8
	447.5–480	476	−17.7
	480–545	525	−12.6
$\mathrm{ZnMo_3O_{10}\cdot 5H_2O}$	55–140	112	160
	140–274	207	303
	274–364	321	−9.52
	364–429	405	−35.9
$\mathrm{ZnMo_3O_{10}\cdot 3.75H_2O}$	119–279	208	289
	279–369	330	−9.43
	369–424	401.5	−34.2
$\mathrm{CuMo_3O_{10}\cdot 5H_2O}$	30–117.5	96	127
	117.5–160	137	115
	160–292.5	210	265
	292.5–405	330 345	−63.7

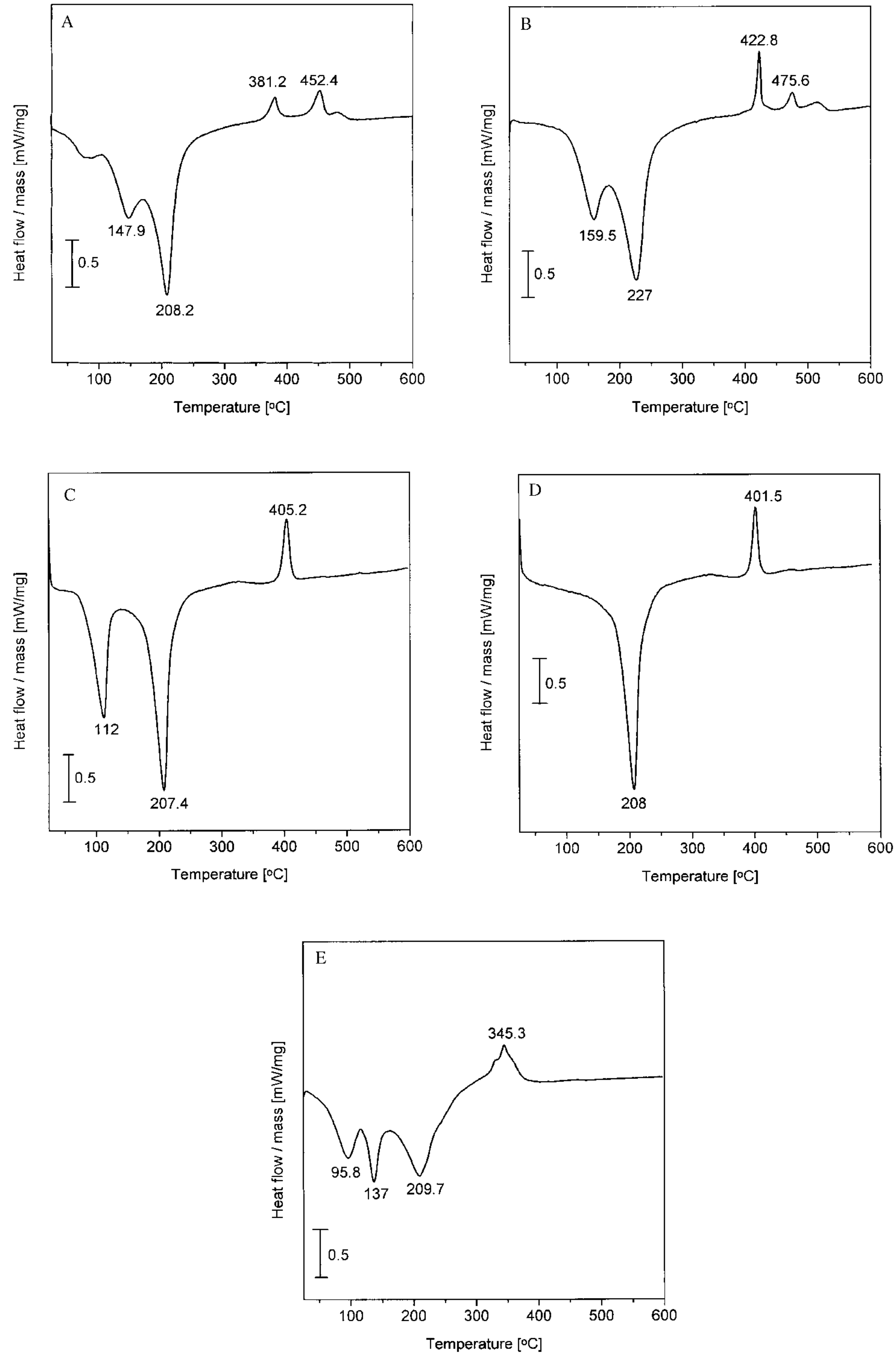

Fig. 3. DSC curve of $CoMo_3O_{10}{\cdot}5H_2O$; (b) DSC curve of $NiMo_3O_{10}{\cdot}5H_2O$; (c) DSC curve of $ZnMo_3O_{10}{\cdot}5H_2O$; (d) DSC curve of $ZnMo_3O_{10}{\cdot}3.75H_2O$; (e) DSC curve of $CuMo_3O_{10}{\cdot}5H_2O$.

$$CuMo_3O_{10} \cdot 3.75H_2O \xrightarrow[\text{endo}]{84-127^\circ C} CuMo_3O_{10} \cdot 2.75H_2O\,(a) + H_2O$$

$$CuMo_3O_{10} \cdot 2.75H_2O\,(a) \xrightarrow[\text{endo}]{127-400^\circ C} CuMo_3O_{10}\,(a) + 2.75H_2O$$

Further heating resulted in the trimolybdate decomposing [9,16] accordingly (DSC) we have

$$CuMo_3O_{10}\,(a) \xrightarrow[\text{exo}]{292-405^\circ C} CuMoO_4\,(a) + 2MoO_3\,(c)$$

$$CuMoO_4\,(a) \xrightarrow[\text{exo}]{292-405^\circ C} CuMoO_4\,(c)$$

3.2. Differential scanning calorimetry studies

The enthalpy change on complete dehydration of the isopolytrimolybdates of cobalt, nickel, zinc(I), zinc(II) and copper were 565, 525, 463, 289 and 507 J/g, respectively. However, the individual stages of dehydration are highly diversified within a given combination (Table 4, Fig. 3(a)–(e)). The loss of molecules of highly bounded water corresponds to the enthalpy changes of 300 J/g and, as a rule, involves a complete amorphization of the compound. The decomposition of trimolybdates occurs above 300°C as a result of two-stage exothermic changes. The first phase to appear is, as shown by the XRD investigations, crystalline MoO_3, and, then, normal molybdates of Co(II), Ni(II), Cu(II) are crystallized. The zinc derivative deviates from the rule as its change is single-staged.

4. Conclusions

The pentahydrous isopolytrimolybdates of Co(II), Ni(II), Zn(II) and Cu(II) obtained here are real analogues of $ZnMo_3O_{10} \cdot 5H_2O$ known before [4]. Water present in these compounds is essential in their structures, and its loss is followed by the compounds being made amorphous. The final dehydration is almost immediately followed by the polycondensate decomposition. In this respect polytrimolybdates with divalent cation of transition metals are considerably different from polytrimolybdates with cations of the I main group which can exist as crystalline anhydrous phases [17]. Unlike polytrimolybdates with alkali metals [18,19], they cannot be obtained by sintering adequate oxides, either. Phase of a higher hydration state exist in the crystallizing environment only, giving characteristic and sharp diffractograms. Reaserch on their complete crystal structure is in progress.

Acknowledgements

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