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THERMAL PROPERTIES OF $[M^{II}(phen)_3]_2V_4O_{12}\cdot phen\cdot 22H_2O$ (M^{II}=Co, Ni, Cu, *phen*=1,10-PHENANTHROLINE)

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Abstract

Thermal decomposition of three tetravanadates, $[M^{II}(phen)_3]_2V_4O_{12}\cdot phen\cdot 22H_2O$, where M^{II} is Co (**1**), Ni (**2**), Cu (**3**) and *phen* is 1,10-phenanthroline, was studied by dynamic method (for **1** and **2**) or isothermally (for **3**). The thermal decomposition of the studied compounds is a multi-step process which involve: discontinuous dehydration, release of uncoordinated, and of coordinated phenanthroline molecules. In course of the latter process, a phase transition of the cyclo-tetravanadates to polymeric metavanadates occurred. Metavanadates with chain structure of the anion were the final decomposition products of all tetravanadates studied.

Keywords: cobalt, copper, inorganic-organic hybrid tetravanadate, nickel, phenanthroline

Introduction

In the last years, an increased attention is paid to inorganic-organic hybrid compounds based on polyoxovanadates [1–10]. Their structural diversity and interesting physical and chemical properties, e.g. catalytic activity, electrical conductivity, magnetism and photochemical properties, give rise to the application and utilization in different fields of praxis [4].

The recently prepared inorganic-organic hybrid tetravanadates represent one type of such compounds [3, 4, 7, 8, 11–13]. In tetravanadates, the cyclic $V_4O_{12}^{4-}$ anion may form: isolated structural units [7, 11], bridges between two coordination centers [4, 12] or layers [8, 10]. Tetravanadates with chain structure are rare [14]. Among the physical properties of interest, the spectral, magnetic, sorption and thermal properties of the inorganic-organic hybrid polyoxovanadates have been investigated [2–4, 8, 9, 14].

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We report here the study of thermal properties of three tetravanadates, $[M^{II}(phen)_3]_2V_4O_{12}\cdot phen\cdot 22H_2O$ [M^{II}=Co (**1**), Ni (**2**), Cu (**3**), *phen*=1,10-phenanthroline], with crystal structures built up of two types of layers: cationic, consisting of $[M^{II}(phen)_3]^{2+}$ chelates and phenanthroline solvate molecules in the interstices, and anionic one formed by cyclic $V_4O_{12}^{4-}$ anions and water molecules localized between the anions [13].

Experimental

Syntheses

$[Co(phen)_3]_2V_4O_{12}\cdot phen\cdot 22H_2O$ (**1**), $[Ni(phen)_3]_2V_4O_{12}\cdot phen\cdot 22H_2O$ (**2**) and $[Cu(phen)_3]_2V_4O_{12}\cdot phen\cdot 22H_2O$ (**3**) were synthesized as described in [13, 15].

All chemicals used were of analytical grade. The elemental analysis was performed on a CHN analyzer 1106 (Carlo Erba). Vanadium(V) was determined in samples which were previously annealed in a Pt crucible to $M(VO_3)_2$ (*M*=Ni, Co, Cu) by titration with 0.1 M $FeSO_4$ solution in the presence of H_3PO_4 and diphenylamine as indicator [16]. The IR spectra in Nujol mulls were recorded in the 400–1800 cm^{-1} region on a FT IR Nicolet Magna 750 spectrometer. The X-ray powder diffraction patterns were obtained on a Philips PW 1050 diffractometer using CuK_α radiation. The thermal analysis was performed on a STD 2960 (T.A. Instruments) enabling a simultaneous collection of TG, DTG and DTA curves. Topical experimental parameters: air atmosphere, sample mass 20 mg, heating rate 5°C min^{-1}, Pt crucible, Al_2O_3 as reference material. The temperature intervals were: 20–700°C (for **1** and **2**), and 20–350°C (for **3**). KNO_3, $KClO_4$ and K_2SO_4 (Chemcomex) were used as reference standards for the temperature calibration of DTA. The interrupted thermal treatment was accomplished on a Derivatograph Q1500 D (MOM, Hungary). The experimental parameters: as formerly, with the exception of sample mass – 100 mg.

Results and discussion

Thermal decomposition

The thermal decomposition of the studied compounds (Fig. 1) is a multi-step process. To understand better the individual steps, the thermal analysis was interrupted at: 120, 300 and 450°C for **1**, and 100, 265 and 470°C for **2**. The intermediate products obtained at these temperatures were cooled down to room temperature and identified by chemical analysis, IR spectroscopy and X-ray phase analysis.

The compound **3** could be studied dynamically only up to 350°C, because at higher temperatures an explosive decomposition occurred. The thermal properties of **3** were also studied under isothermal conditions: the sample was heated to constant mass at 71, 115, 160 and 550°C, and the products formed were cooled down to ambient temperature and identified.

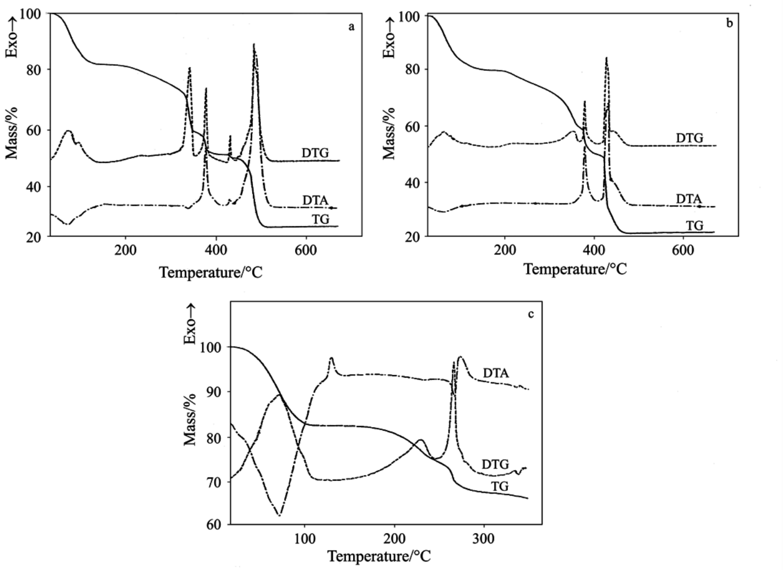

Fig. 1 Thermoanalytical curves of a – **1**; b – **2** and c – **3**

$[Co(phen)_3]_2V_4O_{12}\cdot phen\cdot 22H_2O$ (1)

The red crystalline $[Co(phen)_3]_2V_4O_{12}\cdot phen$ formed as the intermediate at 120°C (Table 1). The endothermic processes in the temperature interval 20–120°C (Fig. 1a) correspond to the release of $22H_2O$ accompanied by mass loss Δm=18.03% (Δm_{calcd}=18.26%), and colour change of the parent compound from yellow to red. In the temperature interval 120–300°C, no endo- or exo-effect on the DTA curve (Fig. 1a), but a mass loss, Δm=8.88% (Δm_{calcd}=8.29%), was observed. The mass loss and the results of chemical analysis of the decomposition product obtained at 300°C (Table 1) confirm the release of uncoordinated phenanthroline molecules and formation of $[Co(phen)_3]_2V_4O_{12}$. The crystal structure determination of **1** showed that uncoordinated phenanthroline molecules occupy the interstices in the cationic layers [13]. It means that only weak van der Waals' forces between the uncoordinated phenanthroline molecules and complex cations exist. The DTA curve shows that in the temperature interval 300–670°C, the mass loss observed on the TG curve corresponds to a four-step process: a small endo-effect with minimum at 330°C, and three exo-effects with maxima at 380, 425 and 490°C. The intermediate formed at 450°C is a black, X-ray amorphous and analytically unidentified product, however, the IR spectrum (Fig. 2a) and TG curve (Fig. 1a) prove the presence of phenanthroline.

$Co(VO_3)_2$ is the end-product of thermal decomposition of **1** (Table 1, Figs 2a and 3a), as confirmed by the corresponding mass loss, Δm=76.62% (Δm_{calcd}=76.35%). In course of heating in this temperature interval, the coordinated phenanthroline molecules were subsequently released, the structure of $[Co(phen)_3]_2V_4O_{12}$ collapsed, and $Co(VO_3)_2$ was formed.

Table 1 Chemical analysis of **1**, **2** and **3**, and of the thermal decomposition products

Compounds Thermal decomposition products		C/%	H/%	N/%	V/%
$[Co(phen)_3]_2V_4O_{12}{\cdot}phen{\cdot}22H_2O$ (**1**)	exp.	46.64	4.42	8.71	9.42
	calcd.	46.46	4.64	9.03	9.38
120°C: $[Co(phen)_3]_2V_4O_{12}{\cdot}phen$	exp.	57.07	3.11	11.09	11.52
	calcd.	56.84	3.18	11.04	11.47
300°C: $[Co(phen)_3]_2V_4O_{12}$	exp.	55.70	2.91	10.60	12.64
	calcd.	54.22	3.03	10.54	12.77
670°C: $Co(VO_3)_2$	exp.	–	–	–	39.08
	calcd.	–	–	–	39.67
$[Ni(phen)_3]_2V_4O_{12}{\cdot}phen{\cdot}22H_2O$ (**2**)	exp.	46.38	4.53	8.93	9.71
	calcd.	46.47	4.64	9.03	9.38
100°C: $[Ni(phen)_3]_2V_4O_{12}{\cdot}phen$	exp.	57.14	3.06	11.12	10.93
	calcd.	56.85	3.18	11.05	11.48
265°C: $[Ni(phen)_3]_2V_4O_{12}$	exp.	53.88	2.95	10.30	12.45
	calcd.	54.24	3.03	10.54	12.78
670°C: $Ni(VO_3)_2$	exp.	–	–	–	39.16
	calcd.	–	–	–	39.70
$[Cu(phen)_3]_2V_4O_{12}{\cdot}phen{\cdot}22H_2O$ (**3**)	exp.	46.70	46.65	8.80	8.80
	calcd.	46.26	46.62	8.90	9.30
70°C: $[Cu(phen)_3]_2V_4O_{12}{\cdot}phen{\cdot}3H_2O$	exp.	54.29	3.06	10.61	10.82
	calcd.	54.88	3.39	10.66	11.08
115°C: $[Cu(phen)_3]_2V_4O_{12}{\cdot}phen$	exp.	55.75	2.90	10.51	10.97
	calcd.	56.54	3.16	10.99	11.42
160°C: $[Cu(phen)_3]_2V_4O_{12}$	exp.	53.06	2.84	10.11	11.95
	calcd.	53.91	3.02	10.47	12.70
550°C: $Cu(VO_3)_2$	exp.	–	–	–	37.07
	calcd.	–	–	–	37.27

$[Ni(phen)_3]_2V_4O_{12}{\cdot}phen{\cdot}22H_2O$ (2)

The thermal decomposition of **2** (Fig. 1b) is characterized by three main endo- and exo-effects observed on the DTA curve. The first one, in the temperature interval 20–100°C, is the endo-effect connected with release of $22H_2O$ and mass loss Δm=18.11% (Δm_{calcd}=18.26%). The chemical analysis confirmed that the product obtained at 100°C is the anhydrous compound (Table 1). Unlike for **1**, the colour of **2** did not change in the first step of thermal decomposition. The DTA curve of **2** exhibits a plateau between 100 and 265°C (Fig. 1b), but the chemical analysis of the intermediate obtained at 265°C (Table 1), and the corresponding mass loss, Δm=8.38%

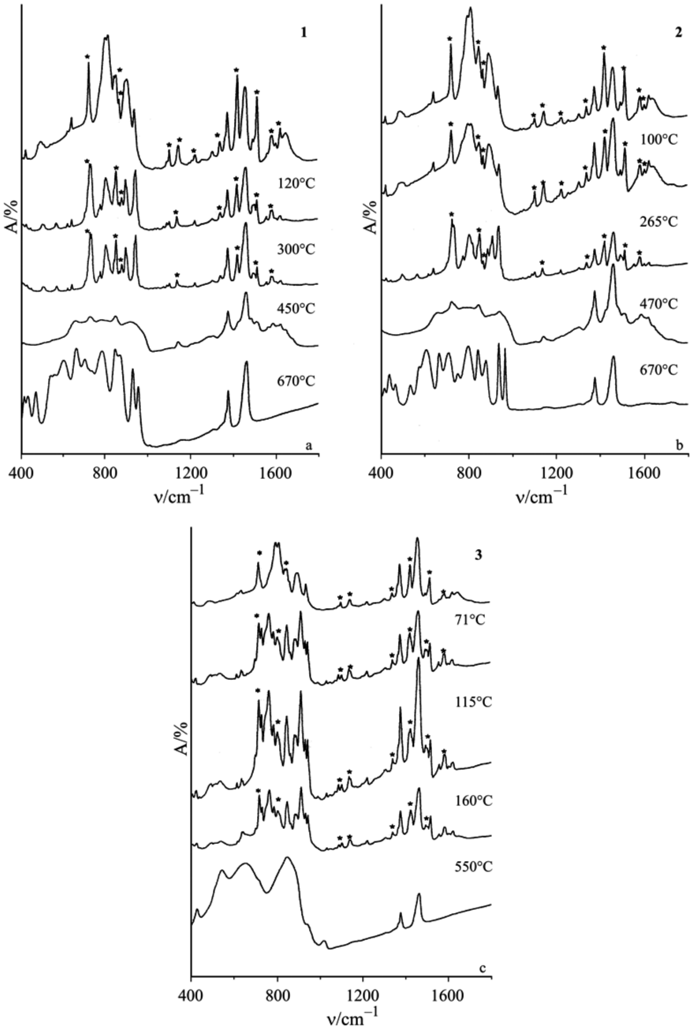

Fig. 2 IR spectra of the parent compounds and their thermal decomposition products: a – **1**; b – **2** and c – **3** (∗ – phenanthroline bands)

(Δm_{calcd}=8.30%) indicate the formation of $[Ni(phen)_3]_2V_4O_{12}$. As follows from the comparison of X-ray diffraction patterns of the red $[Ni(phen)_3]_2V_4O_{12}\cdot$phen and green $[Ni(phen)_3]_2V_4O_{12}$, the crystal structure has changed in course of the heating (Fig. 3b). It means that the uncoordinated phenanthroline molecules play in **2** a more significant role in structure stabilization than in **1**. In the temperature interval 100–265°C, the release of uncoordinated phenanthroline molecules, colour change from red to green, and the recrystallization occurred. In this temperature interval, probably a superposition of all exo- and endothermic processes connected with the above mentioned changes must

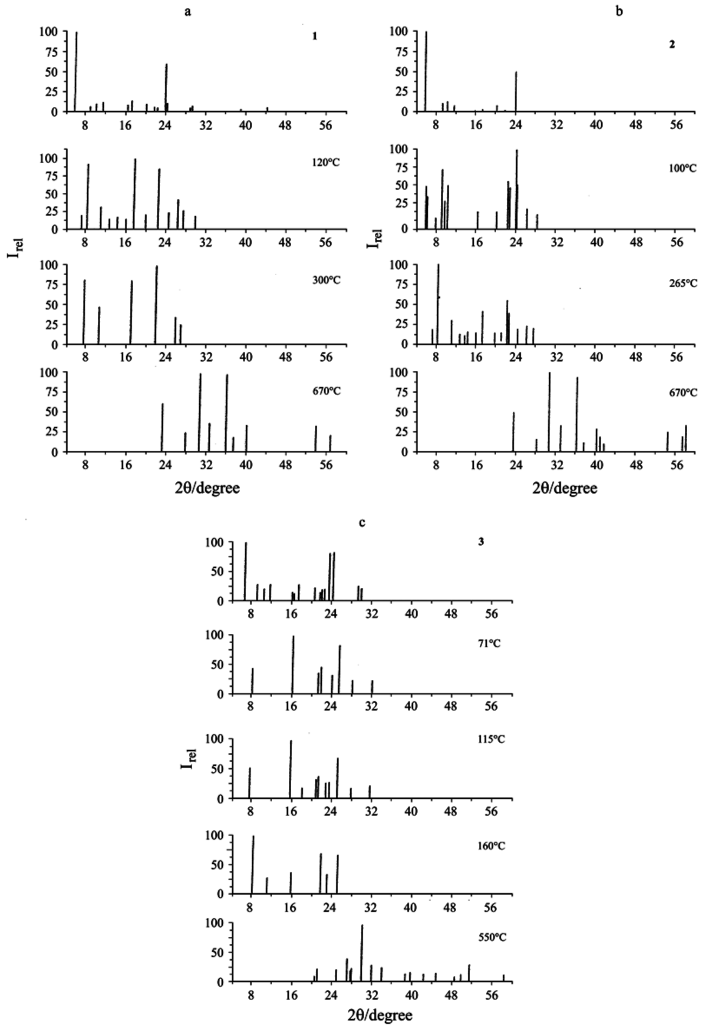

Fig. 3 X-ray powder diffraction patterns of the parent compounds and their thermal decomposition products: a – **1**; b – **2** and c – **3**

occur. This could be the reason why no endo- or exo-effects on the DTA curve could be observed. In the temperature interval 265–670°C, two exothermic peaks with maxima at 390 and 440°C were observed on the DTA curve. However, the latter one is a superposition of at least two exothermic processes. The intermediate obtained at 470°C is a black, X-ray amorphous and analytically unidentified product, still containing phenathroline, as confirmed by the IR spectrum (Fig. 2b) and thermoanalytical curves (Fig. 1b). A four-step mass loss connected with a gradual release of coordinated phenanthroline molecules was observed in this temperature interval.

As results from the total mass loss, Δ*m*=77.78% (Δ*m*$_{\text{calcd}}$=76.64%), $Ni(VO_3)_2$ is the end-product of thermal decomposition of **2** at 670°C (Table 1). Thus, in the temperature interval 265–670°C, the coordinated phenanthroline molecules were released, the structure of $[Ni(phen)_3]_2V_4O_{12}$ collapsed, and $Ni(VO_3)_2$ crystallized.

$[Cu(phen)_3]_2V_4O_{12}\cdot phen\cdot 22H_2O$ (3)

The thermal decomposition of **3** under isothermal conditions starts with the dehydration: the trihydrate, $[Cu(phen)_3]_2V_4O_{12}\cdot phen\cdot 3H_2O$, is formed at 71°C, while at 115°C the anhydrous $[Cu(phen)_3]_2V_4O_{12}\cdot phen$ is observed (Table 1). The found mass loss, Δ*m*=17.64%, is connected with release of $22H_2O$ (Δ*m*$_{\text{calcd}}$=18.17%). The intermediates are green, i.e. the grey colour of **3** changed during the heating up to 71°C. The comparison of the IR spectra and X-ray diffraction patterns of the intermediates and of **3** showed that the structure of the cyclic $V_4O_{12}^{4-}$ anion did not significantly change (Fig. 2c), and that the crystal structures of the trihydrate and anhydrous compounds are very similar, but differ from that of **3** (Fig. 3c). Both the chemical analysis of the product obtained at 160°C (Table 1) and the mass loss, Δ*m*=26.85% (Δ*m*$_{\text{calcd}}$=26.43%), correspond to the release of uncoordinated phenanthroline molecules and formation of the green $[Cu(phen)_3]_2V_4O_{12}$ tetravanadate. The gradual release of the coordinated phenanthroline molecules started at 240°C. The product formed on heating to the constant mass at this temperature is an unhomogeneous brown substance. Under isothermal conditions, $Cu(VO_3)_2$ is the end-product of thermal decomposition of **3** at 550°C, as confirmed by chemical analysis and total mass loss, Δ*m*=74.93% (Δ*m*$_{\text{calcd}}$=74.92%), corresponding to the release of water and phenanthroline molecules.

The dynamic method showed that the endothermic process on the DTA curve, in the temperature interval 20–135°C with minimum at 70°C, corresponds to the release of 22 water molecules. As follows from the DTG curve, the dehydration is a discontinuous process (Fig. 1c). The thermoanalytical curves indicate that the release of uncoordinated phenanthroline molecules in the temperature interval 135–255°C is connected with an almost negligeable endothermic peak with minimum at 247°C. The release of coordinated phenanthroline molecules started at 260°C as manifested by the endothermic peak on the DTA curve. However, the explosive combustion of phenanthroline did not allow to study the decomposition of **3** at temperatures higher than 350°C.

IR spectroscopy and X-ray patterns

The crystal structure determination showed that **1**, **2** and **3** have a similar structure containing the cyclic $V_4O_{12}^{4-}$ anions [13, 15]. The IR spectroscopy, due to the rigidity of the structures of polyvanadate, just slightly influenced by the nature of the cation and hydrogen bonds formed, is a usefull method for identification of the type of polyvanadate ion present in the solids. From the above reason, all cyclo-tetravanadates have characteristic IR spectra in the region of the V–O vibrations (400–1000 cm^{-1}). The bands at 850–1000 cm^{-1} correspond to the stretching vibrations of the $[V(O_t)_2]$

groups, and the bands at 820–730 cm^{-1} and at about 650 cm^{-1} to ν_{as} and ν_s of the ($V–O_b–V$) groups (O_t and O_b are terminal resp. bridging oxygen atoms). The latter bands seem to be characteristic of the cyclic V_4O_{12} groups [15].

In agreement with that we assign the absorption bands at 940 and 905 cm^{-1} (for **1**), 941 and 899 cm^{-1} (for **2**), and 936 and 908 cm^{-1} (for **3**) to ν_s and $\nu_{as}[V(O_t)_2]$, whereas the bands at 819, 804 and 642 cm^{-1} (for **1**), 816, 801 and 645 cm^{-1} (for **2**), and 820, 799 and 642 cm^{-1} (for **3**) to ν_{as} and $\nu_s(V–O_b–V)$. The IR spectra of the intermediate products obtained (for **1**, **2** and **3**) indicate a certain deformation of the parent anion structure, however, without any essential change in arrangement of the cyclic $V_4O_{12}^{4-}$ anions (Fig. 2). The IR spectra exhibit all characteristic bands of the $V_4O_{12}^{4-}$ anions, besides the bands of phenanthroline.

Thus, all isolated intermediates are tetravanadates containing phenanthroline. The IR spectra and chemical analysis confirm that the first step of thermal decomposition of **1**, **2** and **3** is the dehydration, followed by release of uncoordinated phenanthroline molecules which result in formation of tetravanadates with $[M^{II}(phen)_3]^{2+}$ cations. The next process is the subsequent release of coordinated phenanthroline molecules which is accompanied by phase transition of the cyclo-tetravanadate to a metavanadate with chain structure. These thermal processes can be described by Eqs A, B and C:

$$[M^{II}(phen)_3]_2V_4O_{12}\cdot phen\cdot 22H_2O \xrightarrow{-22H_2O} [M^{II}(phen)_3]_2V_4O_{12}\cdot phen \quad (A)$$

$$[M^{II}(phen)_3]_2V_4O_{12}\cdot phen \xrightarrow{-phen} [M^{II}(phen)_3]_2V_4O_{12} \quad (B)$$

$$[M^{II}(phen)_3]_2V_4O_{12} \xrightarrow{-6\,phen} 2M^{II}(VO_3)_2 \quad (C)$$

The processes (A), (B) and (C) are obviously accompanied by reduction of vanadium(V) to vanadium(IV) and its reoxidation to vanadium(V) as we have described in [17, 18] and recently in [19].

A similar phase transition was already described: *tert*-butylammonium cyclotetravanadate was transformed in a very slow process proceeding several months at ambient temperature to the polymeric metavanadate [20].

As follows from the IR spectra, $M^{II}(VO_3)_2$ metavanadates with chain structure of the anion are the final products of thermal decomposition of **1**, **2** and **3**. This conclusion is based on the fact that all metavanadates with polymeric chain structure of the $V_nO_{3n}^{n-}$ anions formed by shared VO_4 tetrahedra [21, 22], have characteristic IR spectra in the region of V–O vibrations: with bands assigned to $\nu[V(O_t)_2]$ in the region 850–1000 cm^{-1}, and to $\nu(V–O_b–V)$ in the region 450–700 cm^{-1} [23, 24]. All these characteristic bands were also observed in the IR spectra of the end-products of thermal decomposition of **1**, **2** and **3** (Fig. 2).

The formation of metavanadates with chain structure as final products of the thermal decomposition was also confirmed by X-ray diffraction patterns. The most intensive diffractions for end-products of thermal decomposition of **2** and **3** are in good agreement with those published for $Ni(VO_3)_2$ and $Cu(VO_3)_2$, respectively [25]. The X-ray pattern of the final decomposition product of **1** differs from that published for α-$Co(VO_3)_2$ [25], but it is very similar to the pattern of the end-product of the decomposition of **2** (Figs 3a, b). This fact as well as the comparison of the IR-spectra (Figs 2a, b) allow to suppose that metavanadates, $M^{II}(VO_3)_2$ (M^{II}=Co, Ni), are the end-products of decomposition of **1** and **2**. The diffraction patterns of the intermediates of thermal decomposition of studied compounds indicate that certain change in crystal structure occurred during the dehydration and release of the uncoordinated phenanthroline molecules, however, the IR-spectra show that the structure of the cyclo-tetravanadate anions is maintained.

Conclusions

The thermal decomposition of the studied tetravanadates is a complicated multi-step process characterized by three major decomposition steps: discontinuous dehydration, release of uncoordinated phenathroline molecules, and release of coordinated phenanthroline molecules which result in formation of the corresponding metavanadates with chain structure of the anion. The metavanadates with composition $M^{II}(VO_3)_2$ were identified as the final products of the thermal decomposition of all three compounds studied.

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