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THERMAL BEHAVIOR OF THE SYNTHESIZED NICKEL(II) AQUA AMMINE ORTHOPHOSPHATE

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Nickel(II) aqua ammine orthophosphate was prepared by homogeneous synthesis. According to the results of the X-ray phase analysis, it is a compound with an individual type of crystal system. Thermal transformations of the substance was studied in the range of 16-850 °C. The results showed that thermolysis of $Ni_3(PO_4)_2·3.5NH_3·8.9H_2O$ are different to those $Ni_3(PO_4)_2·8H_2O$ and $Co_3(PO_4)_2·8H_2O$ reported in literature previously.

Introduction. Phosphate materials have received a lot of research attention in recent years. They can serve as attractive biomedical materials, highly effective phosphors, food additives, detergents, chemical fertilizers, ceramic, pigments, catalysts, etc. [1, 2, 3, 4, 5]. As a result, divalent cation phosphates has been extensively studied due to their potential applications in various industries and their ability to transform into various phosphate forms at elevated temperature via dehydratation and ammonia loss as well as polycondensation processes.

Experimental. Nickel(II) aqua ammine orthophosphate was prepared by homogeneous synthesis [6]. It was salted out from an ammonia solution with an organic solvent. $Ni_3(PO_4)_2·8H_2O$ was synthesized as described previously [7] and used as a starting reagent. This compound was dissolved in concentrated aqueous ammonia, and the obtained solution was poured into acetone. The mother liquor was separated, and the bottom phase – an intensely blue liquid – was kept on air at 15–25 °C to crystallization and constant weight.

The chemical composition of the synthesized compound is given in the Table 1.

The content of Ni^{2+} was determined complexometrically [8]; the phosphorus content – gravimetrically by the quinolone-molybdenum method [9]; the ammonia content – by distillation in a vacuum on Seren'ev's apparatus [10, 11, 12]; and total water and ammonia content – by the weight loss on heating for 2 h at 750 °C. The anionic composition of the calcined products was determined by quantitative paper chroma-

Table 1. Composition of Nickel(II) aqua ammine orthophosphate

Compound	Found, % / Calculated, %				
	NiO	CoO	P_2O_5	NH_3	H_2O
$Ni_3(PO_4)_2·3.5NH_3·8.9H_2O$	38.4/38.1	-	24.2/24.1	10.3/10.1	27.3/27.6

tography [13]. The IR spectra were determined by a Specord 75-IR spectrophotometer at room temperature. Samples of the analyzed compounds were prepared in the form of KBr pellets in which the concentration of a studied substance was 0,2–0.3 wt. % [14]. The X-ray phase analysis was carried out on a DRON-UM1 diffractometer (CuKα radiation). A single crystal of graphite placed in a diffracted beam was used as a monochromator. The diffraction patterns were taken by the method of step scanning in the range of angles 2Θ 4–80°. The scanning step was 0.05°, and the exposure time in a point 3–9 s. The measured diffraction maxima were approximated by the pseudo-Voight function, with the $K\alpha_1$ component being separated out. The indexing of X-ray absorption peaks and the refinement of unit cell periods were done according to the Ritveld method using the PowderCell 2.4 software [15]. Thermal transformations of the substance was studied on a Q-1500D derivatograph. Sample was heated on air up to termination of weight loss in the range of 16–850 °C. The experiment with the dynamic heating mode was carried out using cylindrical platinum crucibles with lids. The weighted portion of the compound was 0.450 g. The final and all intermediate decomposition products were obtained at a heating rate of the samples of the 5 deg min^{-1}.

Results and discussion. Identification of absorption bands was done on the basis of comparative analysis of IR spectra for the series of monophosphates and diphosphates [16] and ammine complexes of the transition metals [17, 18]. The IR spectra of the synthesized aqua ammine orthophosphate and its calcined products (Fig. 1, curves 1–5) contain a strong absorption bands at 3445–2230 cm^{-1} characteristic for stretching vibrations of water and coordinated ammonia molecules. It is similar to those reported in literature [19], where bands at 3400 and 3200–3000 cm^{-1} were attributed to stretching vibrations of water. The band intensity was decreasing with the temperature rise and the loss of water and ammonia. In the IR spectra of calcined product at 662 °C (Fig. 1, curve 6) bands were expressed very weakly and they were absent in final calcined orthophosphate (Fig. 1, curve 7), same as in calcined products of $Ni_3(PO_4)_2{\cdot}8H_2O$ and $Co_3(PO_4)_2{\cdot}8H_2O$ [21]. Bands corresponding to bending vibrations of water and ammonia molecules are observed at 1600-1560 cm^{-1}. At the range of 1490–1365 cm^{-1} is the absorption band corresponding to bending vibrations of metal-coordinated ammonia molecules, which form stable hydrogen bonds with the anion [20]. This band is absent in the IR spectra of the synthesized aqua orthophosphates and their calcined products as described previously [21].

Asymmetric and symmetric stretching vibrations of the PO_4^{3-} group are observed in the range of 1065–745 cm^{-1}. The absorption bands at 650–545 cm^{-1} correspond to the vibrations of P–O–P and P–O–P groups, as described previously [21, 21]. In the IR spectra of the calcined products taken at 662 and 780 °C (Fig. 1, curves 6–7) at wavelength lower than 545 cm^{-1}, there are strong absorption bands assigned to bending vibrations of phosphate's tetrahedron and stretching vibrations of valence bonds Ni–N and Ni–O.

According to the results of the X-ray phase analysis, $Ni_3(PO_4)_2{\cdot}3.5NH_3{\cdot}8.9H_2O$ is a compound with an individual type of crystal system. The unit cell parameters are listed in the Table 2.

According to the obtained data (Fig. 2), thermolysis of the Nickel(II) aqua ammine orthophosphate occurs in the range of 60–780 °C. This process is accompanied by three endothermic effects in the DTA curve with minima at 58, 110, and 295 °C. At 620 and 758 °C, we observed two maxima of exothermic effects, which superimpose on endothermic effects and are accompanied by steps of the sample weight loss in the DTG and TG curves.

Table 2. Lattice parameters and average crystalline sizes of the synthesized Nickel(II) aqua ammine orthophosphate and its calcined products

Temperature, °C	Compound	Unit cell parameters				Unit cell volume, nm^3	Structure
		a, nm	b, nm	c, nm	γ, deg		
21	$Ni_3(PO_4)_2·3.5NH_3·8.9H_2O$	0.737(2)	0.823(5)	1.501(8)	96.41	90.609	Monoclinic
60	$Ni_3(PO_4)_2·3.5NH_3·8.3H_2O$	-	-	-	-	-	Amorphous
223	$Ni_3(PO_4)_2·1.6NH_3·1.5H_2O$	-	-	-	-	-	Amorphous
319	$Ni_3(PO_4)_2·1.3NH_3·1.0H_2O$	-	-	-	-	-	Amorphous
543	$Ni_3(PO_4)_2·0.6NH_3·0.3H_2O$	-	-	-	-	-	Amorphous
662	$Ni_3(PO_4)_2·0.1NH_3$	5,828	4,696	10,099	91,01	276,35	Monoclinic
780	$Ni_3(PO_4)_2$	5,828	4,698	10,103	91,03	276,56	Monoclinic

The chemical composition of the thermolysis products exhibits (Fig. 3) starting reaction at room temperature until 60 °C. The total loss was 0.7 mol of outer sphere crystallization H_2O and could be described as follows:

$$[Ni_3(NH_3)_{3.5}(H_2O)_{8.2}(PO_4)_2]·0.7H_2O_{(s)} \xrightarrow{\theta\ ^{o}C} 0.7H_2O_{(g)} + Ni_3(NH_3)_{3.50}(H_2O)_{8.2}(PO_4)_{2(s)} \quad (1)$$

At the range of 60 – 223 °C, the total mass loss was ≈ 83 % of NH_3 and H_2O, which was accompanied by amorphization of calcined products. We suggest the following thermal decomposition reaction:

$$Ni_3(NH_3)_{3.5}(H_2O)_{8.2}(PO_4)_{2(s)} \xrightarrow{223\,^{o}C} 1.9NH_{3(g)} + 7.4H_2O_{(g)} + + Ni_3(NH_3)_{1.6}(H_2O)_{1.5}(PO_4)_{2(s).} \quad (2)$$

Table 3. Comparison between the chemical composition of calcined products and values of total loss of H

T, °C	Composition	Anionic composition, rel. % P_2O_5		Total loss of H_2O and NH_3, mol	
		PO_4^{3-}	$P_2O_7^{4-}$	NH_3	H_2O
21	$Ni_3(PO_4)_2·3.5NH_3·8.9H_2O$	100	-	0	0
60	$Ni_3(PO_4)_2·3.5NH_3·8.3H_2O$	100	-	0	0.7
223	$Ni_3(PO_4)_2·1.6NH_3·1.5H_2O$	100	-	1.9	7.4
319	$Ni_3(PO_4)_2·1.3NH_3·1.0H_2O$	66.67	33.33	2.3	7.9
543	$Ni_3(PO_4)_2·0.6NH_3·0.3H_2O$	69.71	30.29	2.9	8.6
662	$Ni_3(PO_4)_2·0.1NH_3$	75.20	24.80	3.4	8.9
780	$Ni_3(PO_4)_2$	100	-	3.5	8.9

The chemical analysis of product calcined at 319 °C (Table 3) showed the partial conversion of orthophosphate into pyrophosphate anion. The chemical reaction process is proposed in Eq. (3).

$$Ni_3(NH_3)_{1.6}(H_2O)_{1.5}(PO_4)_{2(s)} \xrightarrow{319\,^oC} 0.4NH_{3(g)} + 0.5H_2O_{(g)} + \\ + Ni_3(NH_3)_{1.3}(H_2O)_{0.9}(PO_4)_{1.33}(P_2O_7)_{0.38(s)} \quad (3)$$

When the calcination temperature reached 543 °C, phase transition from amorphous to low crystallinity took place (Fig. 3). This stage of thermal decomposition is proposed in the following reaction:

$$Ni_3(NH_3)_{1.26}(H_2O)_{0.94}(PO_4)_{1.33}(P_2O_7)_{0.38(s)} \xrightarrow{319\text{–}543\,^oC} 0.68NH_{3(g)} \\ + 0.69H_2O_{(g)} + Ni_3(NH_3)_{0..58}(H_2O)_{0..25}(PO_4)_{1.39}(P_2O_7)_{0.30(s)} \quad (4)$$

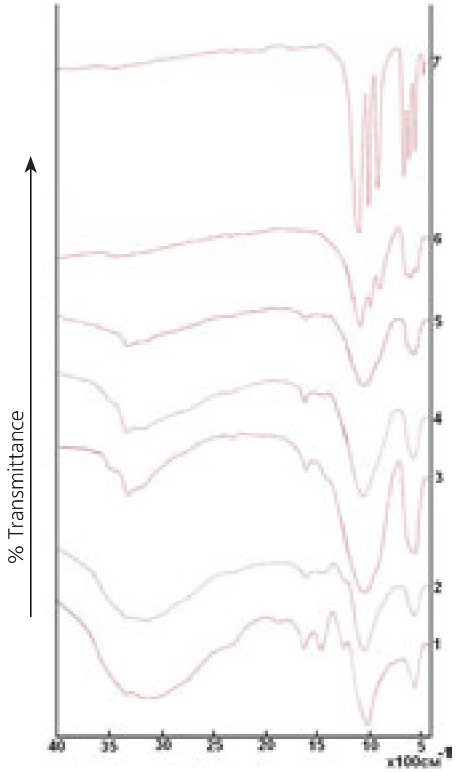

Fig. 1. IR spectra of $Ni_3(PO_4)_2$•3,5NH_3•8,9H_2O (I) and calcined products at: 60 °C (2), 223 °C (3), 319 °C (4), 543 °C (5), 662 °C (6), 780 °C (7)

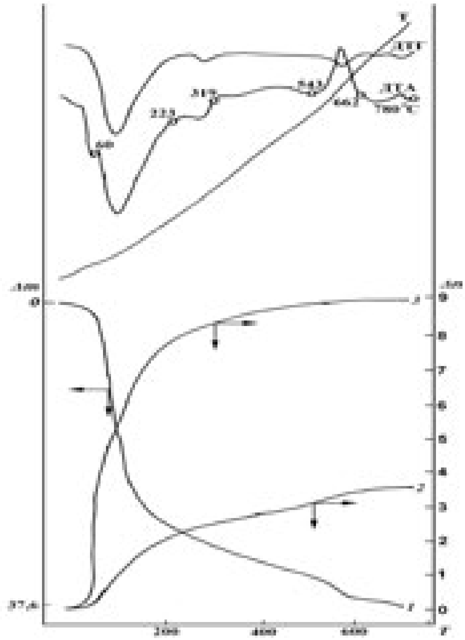

Fig. 2. TG/DTG/DTA curves of $Ni_3(PO_4)_2$•3.5NH_3•8.9H_2O, where Δm – weight loss of gaseous compounds (%),Δn –weight loss of gaseous compounds (mol), T – temperature (°C), ○ – sampling points, 1 – total weight loss at heating rate of the samples of the 5 deg min^{-1}; 2 – weight loss of NH_3; 3 weight loss of H_2O

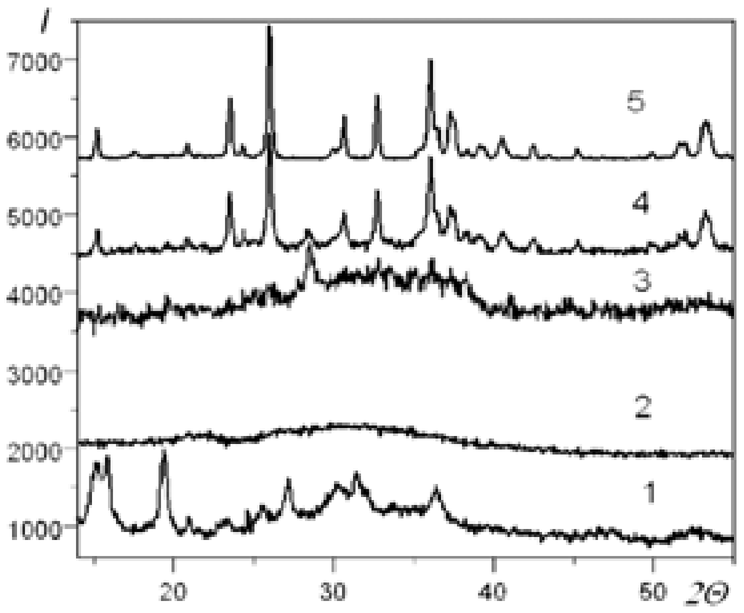

Fig. 3. The X–ray powder diffraction patterns of the synthesized $Ni_3(PO_4)_2{\cdot}3.5NH_3{\cdot}8.9H_2O$ (1), and its calcined products at 60 (2), 543 (3), 662 (4), 780 (5) °C

At the temperature range of 543–662 °C, the new crystal phase was formed (Fig. 3). This stage showed decrease of pyrophosphate content and full elimination of water, which was accompanied with the powerful exothermal effect (Fig. 2) .

$$Ni_3(NH_3)_{0.58}(H_2O)_{0.25}(PO_4)_{1.39}(P_2O_7)_{0.30(s)} \xrightarrow{662\,^oC} 0.53NH_{3(g)} + 0.25H_2O_{(g)} + \quad + Ni_3(NH_3)_{0.05}(PO_4)_{1.50}(P_2O_7)_{0.25(s)} \qquad (5)$$

With further heating to 780 °C, all ammonia and $P_2O_7^{4-}$ anions were totally eliminated and transformed into PO_4^{3-}. The X-ray pattern showed only a single phase of $Ni_3(PO_4)_2$ [22]. This phenomena is similar to those observed by [21] We suggest the following thermal decomposition reaction:

$$Ni_3(NH_3)_{0.05}(PO_4)_{1.65}(P_2O_7)_{0.27(s)} \xrightarrow{780\,^oC} 0.05NH_{3(g)} + Ni_3(PO_4)_{2(s)}. \qquad (6)$$

Conclusions. Thermal transformations of the Nickel(II) aqua ammine orthophosphate, $Ni_3(PO_4)_2{\cdot}3.5NH_3{\cdot}8.9H_2O$, studied at the range of 16–850 °C are different to those $Ni_3(PO_4)_2{\cdot}8H_2O$ and $Co_3(PO_4)_2{\cdot}8H_2O$ reported in literature previously [21]. The results of TG/DTG/DTA, X-ray phase analysis and IR spectra prove this fact. Final product of heating is iso-structural to $Ni_3(PO_4)_2$.

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АНОТАЦІЯ

Прокопчук Н.М., Копілевич В.А., Войтенко Л.В. *Термічна поведінка акваамінооротофосфату нікелю(II) // Біоресурси і природокористування. – 2015. – **7**, №3–4. – С. 22–27.*

Шляхом гомогенного синтезу було одержано акваамінооротофосфат нікелю(II). Згідно з даними рентгенофазового аналізу, ця сполука характеризується індивідуальним типом кристалічної структури. Вивчено її термічні перетворення в температурних межах від 16 до 850 °С. Результати показали, що термоліз $Ni_3(PO_4)_2 \bullet 3.5NH_3 \bullet 8.9H_2O$ *має низку особливостей порівняно з* $Ni_3(PO_4)_2 \bullet 8H_2O$ *та* $Co_3(PO_4)_2 \bullet 8H_2O$.

АННОТАЦИЯ

Прокопчук Н.М., Копилевич В.А., Войтенко Л.В. *Термическое поведение акваамминортофосфата никеля(II) // Биоресурсы и природопользование. – 2015. – **7**, №3–4. – С. 22 –27.*

Путем гомогенного синтеза был получен акваамминоортофосфат никеля (II). Согласно с данными рентгенофазового анализа это соединение характеризуется индивидуальным типом кристаллической структуры. Изучены его термические превращения в интервале температур от 16 до 850 °С. Результаты показали, что термолиз $Ni_3(PO_4)_2 \bullet 3.5NH_3 \bullet 8.9H_2O$ *имеет ряд особенностей относительно* $Ni_3(PO_4)_2 \bullet 8H_2O$ *та* $Co_3(PO_4)_2 \bullet 8H_2O$.