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THE THERMAL TRANSFORMATIONS OF AQUAAMMINE COBALT(II)-ZINC PHOSPHATES

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The mixed-cation complex aquaammine phosphates of general formula $Co_xZn_{3-x}(PO_4)_2 \cdot nNH_3 \cdot mH_2O$ were prepared by exposing of solid $M_3(PO_4)_2 \cdot nH_2O$ ($M=Co^{2+}$, Zn^{2+}) to a saturated atmosphere of ammonia in a dessicator. The thermal transformations of this series were studied in the range 20...660°C.

Introduction. $Co_xZn_{3-x}(PO_4)_2 \cdot nNH_3 \cdot mH_2O$ is a member of a large family of aquaammine phosphates [1, 2], isolated of "wet" (from ammonia solution) or "gaseous-solid" (by saturating of solid powder mix of neutral phosphates in ammonia atmosphere) ways. Determining nature of coordinate arrangement and strength of bonding it was made the wide studies of thermal transformations of the described phosphates.

Experimental. Aquaammine Cobalt(II)-Zinc phosphates were synthesized of $Co_3(PO_4)_2 \cdot 8H_2O$ and $Zn_3(PO_4)_2 \cdot 4H_2O$ solid powder mixture by saturation with gaseous ammonia, in the hermetic ally packed dessicator during 30 days [3]. The molar of ratio $Co^{2+}:Zn^{2+}$ in mixtures is taken from 1.5:0.5 till 2.5:1.5. The products are microcrystalline pink or dark-pink powder. General formula of compounds is $Co_xZn_{3-x}(PO_4)_2 \cdot nNH_3 \cdot mH_2O$, where x=1.5÷2.5; n=3.4÷4.3; m=5.2÷7.7. Table 1 shows chemical composition of isolated compounds.

It was studied the thermal transformations of Aquaammine Cobalt(II)-Zinc phosphates of noted above compositions. Thermolysis of $Co_{2.0}Zn_{1.0}(PO_4)_2 \cdot 3.8NH_3 \cdot 6.7H_2O$ is analyzed in details.

Thermal transformations of compounds were studied by complex thermal analysis (DTA+TG+DTG) using a Q-1500D derivatograph. The samples were heated in air. In experiments with a constant heating rate of 5°C/min, the samples (0.5 g) were placed in covered cylindrical platinum crucibles.

Order of thermal transformations was estimated by using data of chemical analysis

Table 1. Chemical composition of Aquaammine Cobalt(II)-Zinc phosphates

Index of compounds	Product composition				
	CoO	ZnO	P_2O_5	NH_3	H_2O
Found, wt %:					
sample 1	33.08	7.16	24.96	10.04	24.41
sample 2	26.82	14.64	25.28	11.45	21.45
sample 3	20.50	22.42	26.06	13.51	17.14
Calculated, wt %:					
for $Co_{2.5}Zn_{0.5}(PO_4)_2 \cdot 3.4NH_3 \cdot 7.7H_2O$	33.10	7.19	25.08	10.09	24.52
for $Co_{2.0}Zn_{1.0}(PO_4)_2 \cdot 3.8NH_3 \cdot 6.7H_2O$	26.82	14.64	25.28	11.45	21.45
for $Co_{1.5}Zn_{1.5}(PO_4)_2 \cdot 4.3NH_3 \cdot 5.2H_2O$	20.68	22.46	26.12	13.54	17.18

of calcinated products and quantitative paper chromatography [4, 5]. Chemical composition of starting reagents and synthesized compounds was determined using photometry (Co^{2+}) [6], inverse chronopotentiometry (Zn^{2+}) [7], gravimetry (P_2O_5) [8] and modified distillation in a Seren'ev apparatus (NH_3) [9–11]. The water content was analyzed as the difference between the weight loss during calcination at 750˚C for 2 h and the NH_3 content.

IR spectra were measured on a Specord 75-IR spectrophotometer using samples prepared as pellets with KBr where the analyte concentration was 0.2–0.3 wt % [12].

X-ray diffraction (XRD) studies were carried out with a DRON-UM1 diffractometer (CuK_α radiation, 2Θ 4-80˚, scan step of 0.05˚, counting time of 9 s per data point) with a graphite-crystal monochromator mounted on the diffracted beam line. The measured diffraction peaks were fit by the pseudo-Voigt function with the isolation of the Kα1 component. 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 [13].

Results and discussion. Thermolysis of $Co_2.0Zn1.0(PO_4)_2 \cdot 3.8NH_3 \cdot 6.7H_2O$ was studied in the temperature range 21-650˚C (Fig. 1). According to DTA and DTG data, the thermal transformations were accompanied by a few endothermic effects: weak defined with minimum at 80 ˚C and several powerful endoeffects with minima at 127, 160, 220˚C. Several consistent series of effects were observed. Endothermic effects had superimposed into exothermal ones at 250–300˚C and at 350–500˚C powerful exoeffects are shown at DTA curve with maxima at 396 and 402˚C, processes accompanied weight loss of sample at TG curve.

All calcinated products in the range 21...101 ˚C are crystalline (Fig. 2, curve 1), iso-structural to initial $Co_{2.0}Zn_{1.0}(PO_4)_2 \cdot 3.8NH_3 \cdot 6.7H_2O$ and to $Co_3(PO_4)_2 \cdot 8H_2O$ [14]. At 144–295˚C the

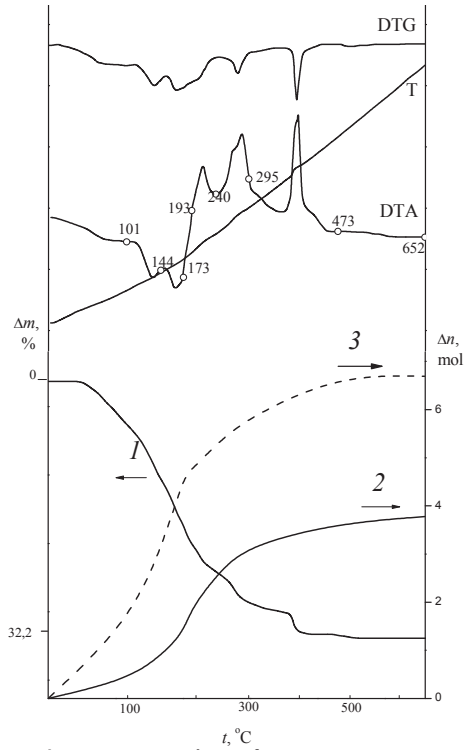

Fig. 1. Heating curves DTA and DTG of $Co_{2.0}Zn_{1.0}(PO_4)_2 \cdot 3.8NH_3 \cdot 6.7H_2O$: Δm – mass lose (% wt), Δn –change of substance amount (mol), T – temperature; ○ – points of sampling, corresponding values of 1 – weight lose TG; 2 – loses of NH_3; 3 – loses of H_2O of dynamic heating at a rate of 2.5 ˚C/min.

total amorphization was observed (Fig. 2, curve 2). Products of heating after 473 are crystalline (Fig. 2, curve 3, 4).

IR spectra of sample preparation are given at Fig. 3. Identification of absorption bands was done on the basis of comparative analysis of IR spectra for the series of monophosphates and diphosphates [15] and ammine complexes of the transition metals [16, 17]. It was determined, that IR spectra of products of heating till 473˚C include band around 1450 cm^{-1}. This band arises from the bending mode of an NH_3 molecule coordinated to a metal ion. Noted band disappeared only after complete evaporation of ammonia. All spectra included bands corresponded to antisymmetric and symmetric

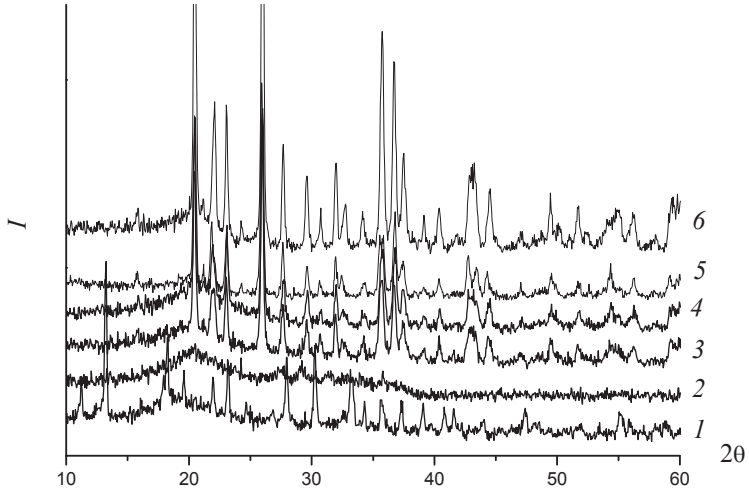

Fig. 2. X-ray patterns of: $Co_{2.0}Zn_{1.0}(PO_4)_2 \cdot 3.4NH_3 \cdot 5.2H_2O$ (1), $Co_{2.0}Zn_{1.0}(PO_4)_2 \cdot 0.6NH_3 \cdot 0.9H_2O$ (2), $Co_{2.0}Zn_{1.0}(PO_4)_2 \cdot 0.1NH_3$ (3), $Co_{2.0}Zn_{1.0}(PO_4)_2$ (4), $Co_{2,5}Zn_{0,5}(PO_4)_2$ (5), $Co_{1,5}Zn_{1,5}(PO^4)^2$ (6).

vibrations of PO_4^{3-} group (1050–710 cm^{-1}) and bonds Me–O (near 500 cm^{-1}).

Process of weight loss was studied in the range 80–550°C and is observed at TG curve (Fig. 1). Crystalline compound sampled at 101°C lost 0.4 mol of ammonia and more than 1 H_2O mol, according to the chemical analysis data (Table 1):

$$[Co_{2.0}Zn_{1.0}(NH_3)_{3.8}(H_2O)_{6.7}(PO4)_2] \xrightarrow{101\,^oC} 0.4NH_3 + 1.5H_2O + \\ +[Co_{2.0}Zn_{1.0}(NH_3)_{3.4}(H_2O)_{5.2}(PO_4)_2].$$

During subsequent temperature increasing 0.5 NH_3 mole and about half of all quantity of water are lost. This process accompanies by endothermic effect and amorphization of the product:

$$[Co_{2.0}Zn_{1.0}(NH_3)_{3.4}(H_2O)_{5.2}(PO_4)_2] \xrightarrow{144\,^oC} 0.5NH_3 + 1.6H_2O + \\ +[Co_{2.0}Zn_{1.0}(NH_3)_{2.9}(H_2O)_{3.6}(PO_4)_2].$$

Next phase are attended by the second powerful endothermic effect. This step can be represented by the scheme:

$$[Co_{2.0}Zn_{1.0}(NH_3)_{2.9}(H_2O)_{3.6}(PO_4)_2] \xrightarrow{173^oC} 0.5NH_3 + 1.5H_2O + \\ +[Co_{2.0}Zn_{1.0}(NH_3)_{2.4}(H_2O)_{2.1}(PO_4)_2].$$

During temperature increasing for the next 20°C 50% of all quantity of ammonia is lost:

$$[Co_{2.0}Zn_{1.0}(NH_3)_{2.4}(H_2O)_{2.1}(PO_4)_2] \xrightarrow{193^oC} 0.5NH_3 + 0.2H_2O + \\ +[Co_{2.0}Zn_{1.0}(NH_3)_{1.9}(H_2O)_{1.9}(PO_4)_2].$$

In the range 193–240°C thermolysis intensifies without changes in anionic component. This stage is accompanied by the loss of near 70% NH_3 and 80% H_2O of their total quantity:

$$[Co_{2.0}Zn_{1.0}(NH_3)_{1.9}(H_2O)_{1.9}(PO_4)_2] \xrightarrow{240\,^oC} 0.6NH_3 + 0.5H_2O + \\ [Co_{2.0}Zn_{1.0}(NH_3)_{1.3}(H_2O)_{1.4}(PO_4)_2].$$

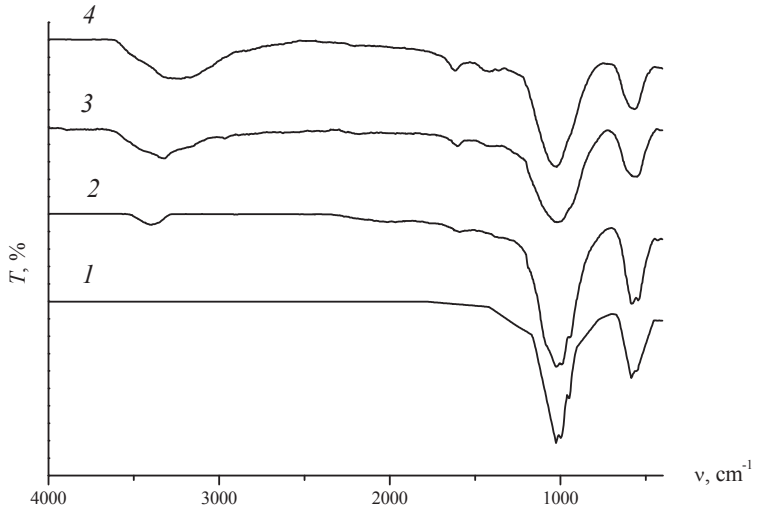

Fig. 3. IR spectra of heated samples taken at: 652 (1), 473 (2), 295 (3), 240 (4) ˚C.

Table 2. Changes in the anion and chemical composition of $Co_{2.0}Zn_{1.0}(PO_4)_2 \cdot 3.8NH_3 \cdot 6.7H_2O$ during dynamic heating

Sampling temperature, °C	Chemical analysis data	Anion composition (P_2O_5), % wt		Number of molecules lost per formula unit, mol	
		PO_4^{3-}	$P_2O_7^{4-}$	NH_3	H_2O
21	$2.0CoO \cdot 1.0ZnO \cdot P_2O_5 \cdot 3.8NH_3 \cdot 6.7H_2O$	100.00	–	0	0
101	$2.0CoO \cdot 1.0ZnO \cdot P_2O_5 \cdot 3.4NH_3 \cdot 5.2H_2O$	100.00	–	0.4	1.5
144	$2.0CoO \cdot 1.0ZnO \cdot P_2O_5 \cdot 2.9NH_3 \cdot 3.6H_2O$	100.00	–	0.9	3.1
173	$2.0CoO \cdot 1.0ZnO \cdot P_2O_5 \cdot 2.4NH_3 \cdot 2.1H_2O$	100.00	–	1.4	4.6
193	$2.0CoO \cdot 1.0ZnO \cdot P_2O_5 \cdot 1.9NH_3 \cdot 1.9H_2O$	100.00	–	1.9	4.8
240	$2.0CoO \cdot 1.0ZnO \cdot P_2O_5 \cdot 1.3NH_3 \cdot 1.4H_2O$	100.00	–	2.5	5.3
295	$2.0CoO \cdot 1.0ZnO \cdot P_2O_5 \cdot 0.6NH_3 \cdot 0.9H_2O$	97.04	2.96	3.2	5.8
473	$2.0CoO \cdot 1.0ZnO \cdot P_2O_5 \cdot 0.14NH_3$	100.0	trace	3.6	6.7
652	$2.0CoO \cdot 1.0ZnO \cdot P_2O_5$	100.00	–	3.8	-

Next sample was taken at 295°C after strong exothermal effect that is observed in the DTG curve (Fig. 1). It is realized two processes simultaneously the first is hydrolysis a part of monophosphate, the second one – condensation of hydrogen monophosphate to diphosphate. This step could be represented by the schemes according to chromatography results (Table 2):

$$[Co_{2,0}Zn_{1,0}(NH_3)_{1,3}(H_2O)_{1,4}(PO_4)_2] \xrightarrow{295^oC} 0{,}7NH_3 + 0{,}5H_2O + \\ +[Co_{2,0}Zn_{1,0}(NH_3)_{0,6}(H_2O)_{0,9}(PO_4)_{1,94}(P_2O_7)_{0,03}].$$

$$[Me \leftarrow OH_2 \cdots (PO_4)] \xrightarrow{240\text{-}295\ ^oC} MeOH^+ + HPO_4^{2-};$$

$$2\,HPO_4^{2-} \longrightarrow P_2O_7^{4-} + H_2O$$

The strongest exothermal effect is observed in the range 295–473°C. All amount of water and most ammonia has been lost. The pre-final product of thermolysis is crystalline according to X-ray data. Table 3 shows parameters of cells. This structure is isostructural to anhydrous $Co_2Zn1(PO_4)_2$ and $Co_3(PO_4)_2$ [18, 19]. Crystal phase include trash quantity of diphosphate-anion (Table 3). Scheme of this stage is:

$$[Co_{2,0}Zn_{1,0}(NH_3)_{0,6}(H_2O)_{0,9}(PO_4)_{1,94}(P_2O_7)_{0,03}] \xrightarrow{473^oC} 0{,}5NH_3 + 0{,}9H_2O + \\ +[Co_{2,0}Zn_{1,0}(NH_3)_{0,1}(PO_4)_2].$$

Sample lost all NH_3 at the final stage of thermal transformation, product is crystalline (Table 3) and isostructural to $Co_2Zn(PO_4)_2$ [16]:

$$[Co_{2,0}Zn_{1,0}(NH_3)_{0,14}(PO_4)_2] \xrightarrow{652^oC} 0{,}14NH_3 + Co_{2,0}Zn_{1,0}(PO_4)_2.$$

Cobalt(II)-Zinc aqua amino orthophosphates with another ratio between cations were studied by thermal analysis, DTA curves are shown at Fig. 4. Curves

Table 3. X-ray data of thermolysis products

Chemical analysis data	Parameters of cell				Cell volume, nm^3	Structure
	a, nm	*b*, nm	*c*, nm	γ, gr.		
$2.0CoO \cdot 1.0ZnO \cdot P_2O_5 \cdot 3.4NH_3 \cdot 5.2H_2O$	1.001(6)	1.331(6)	0.467(2)	104.82	0.60242(6)	monoclinic
$2.0CoO \cdot 1.0ZnO \cdot P_2O_5 \cdot 2.9NH_3 \cdot 3.6H_2O$	–	–	–	–	–	amorphous
$2.0CoO \cdot 1.0ZnO \cdot P_2O_5 \cdot 2.4NH_3 \cdot 2.1H_2O$	–	–	–	–	–	amorphous
$2.0CoO \cdot 1.0ZnO \cdot P_2O_5 \cdot 1.9NH_3 \cdot 1.9H_2O$	–	–	–	–	–	amorphous
$2.0CoO \cdot 1.0ZnO \cdot P_2O_5 \cdot 1.3NH_3 \cdot 1.4H_2O$	–	–	–	–	–	amorphous
$2.0CoO \cdot 1.0ZnO \cdot P_2O_5 \cdot 0.6NH_3 \cdot 0.9H_2O$	–	–	–	–	–	amorphous
$2.0CoO \cdot 1.0ZnO \cdot P_2O_5 \cdot 0.14NH_3$	0.754(5)	0.839(9)	0.506(2)	94.38	0.31984(3)	monoclinic
$2.0CoO \cdot 1.0ZnO \cdot P_2O_5$	0.755(4)	0.839(0)	0.507(0)	94.28	0.30245(7)	monoclinic

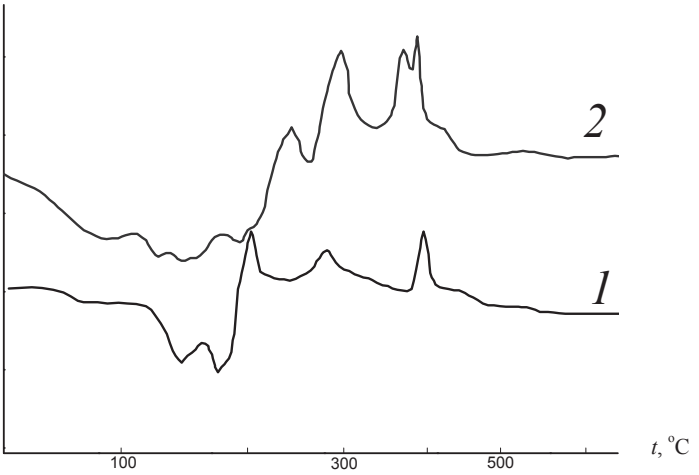

Fig. 4. Curves DTA $Co_{1,5}Zn_{1,5}(PO_4)_2 \cdot 4,3NH_3 \cdot 5,2H_2O$ (1), $Co_{2,5}Zn_{0,5}(PO_4)_2 \cdot 3,4NH_3 \cdot 7,7H_2O$ (2)

DTG registered that thermolysis of $Co_{1.5}Zn_{1.5}(PO_4)_2 \cdot 4.3NH_3 \cdot 5.2H_2O$ (Fig. 4, curve 1) is similar to the previous one, only the intensity of effects at the DTA has changed. From X-ray diffraction data was found (Fig. 2) that the final product of thermolysis $Co_{1.5}Zn_{1.5}(PO_4)_2 \cdot 4.3NH_3 \cdot 5.2H_2O$ is crystalline and iso-structural to $Co_2Zn(PO_4)_2$ and $Co_3(PO_4)_2$ [18, 19].

$Co_{2.5}Zn_{0.5}(PO_4)_2 \cdot 3.4NH_3 \cdot 7.7H_2O$ thermal transformations are different from two previous objects, DTA curves testify to this fact. Near 5 endothermic effects are observed in the range 80–200°C (Fig. 4, curve 2). Two first effects are displaced at more then 200°C to higher temperature side. Final product of heating is iso-structural to $Co_3(PO_4)_2$ and $Co_2Zn(PO_4)_2$ [18, 19].

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АНОТАЦІЯ

Прокопчук Н.М., Копілевич В.А., Войтенко Л.В., Савченко Д.А. *Термічні перетворення акваамінофосфатів кобальту(II)-цинку // Біоресурси і природокористування. – 2014. – **6**, №5–6. – С.50 –56.*

Шляхом витримування суміші твердих фосфатів $M_3(PO_4)_2 \cdot nH_2O$ (де $M=Co^{2+}$, Zn^{2+}) у насиченій аміачній атмосфері в ексикаторі було одержано змішано-катіонні комплексні акваамінофосфати загальної формули $Co_xZn_{3-x}(PO_4)_2 \cdot nNH_3 \cdot mH_2O$. Вивчено їхні термічні перетворення в температурних межах 20…660°С.

АННОТАЦИЯ

Прокопчук Н.Н., Копилевич В.А., Войтенко Л.В., Савченко Д.А. *Термические превращения акфаамминофосфатов кобальта(II)-цинка // Биоресурсы и природопользование. – 2014. – **6**, №5–6. – С.50 –56.*

Путем выдерживания смеси твердых фосфатов $M_3(PO_4)_2 \cdot nH_2O$ (где $M=Co^{2+}$, Zn^{2+}) в насыщенной аммиачной атмосфере в эксикаторе получены смешанно-катионные комплексные акваамминофосфаты общей формулы $Co_xZn_{3-x}(PO_4)_2 \cdot nNH_3 \cdot mH_2O$. Изучены их термические превращения в температурном интервале 20…660°С.