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*L.I. Sliusarchuk, L.I. Zhelezнова, S.V. Kuleshov, O.K. Trunova***MONO- AND HETEROCOMPLEXES OF Co(II), Nd(III) WITH OXALIC ACID AND PHENANTHROLINE: SYNTHESIS, STRUCTURE AND THERMAL DECOMPOSITION****V.I. Vernadsky Institute of General and Inorganic Chemistry of the National Academy of Sciences of Ukraine, Kyiv, Ukraine**

This work presents the results of studies aimed at determining the conditions for the synthesis of a new heterometallic complex of Co(II) and Nd(III) with oxalic acid in the presence of 1,10-phenanthroline, studying its composition, structure, thermal properties and its ability to form complex oxides. The hetero- and monocomplexes $[\text{Co}(\text{C}_2\text{O}_4)\cdot\text{Phen}]_2\cdot 4\text{H}_2\text{O}$, $[\text{Nd}_2(\text{C}_2\text{O}_4)_3\cdot 2\text{Phen}]$, $[\text{Co}_2\text{Nd}_2(\text{C}_2\text{O}_4)_5\cdot 2\text{Phen}]\cdot 4\text{H}_2\text{O}$ (Phen – phenanthroline) were synthesized. The complexes were investigated by the following physicochemical research methods: elemental analysis, differential thermal analysis, IR- and diffuse reflection electronic spectroscopies, and X-ray powder diffraction. Based on the analysis of electronic and IR spectra, it was shown that ions of metals bind bidentately with ions of oxalates and with molecules of 1,10-phenanthroline. The structures of the ion of cobalt and ion of neodymium correspond to the distorted octahedron. The ions of metals are bound together by oxalate ligands. The powders of oxides were prepared by thermolysis of the heterocomplex up to 800°C and 1000°C. The composition of the obtained oxide powders was controlled by X-ray powder diffraction. When the heterocomplex is heated to 800°C, in addition to the complex oxide NdCoO_3 , we obtained the following oxides: Nd_2O_3 (hexagonal crystal system), Nd_2O_3 (cubic crystal system) and Co_3O_4 (cubic crystal system). After heating to 1000°C, a more pure complex oxide NdCoO_3 was obtained. Neodymium cobaltate NdCoO_3 crystallizes in the cubic crystal system, the unit cell parameter is $a=3.770 \text{ \AA}$, the cell volume is 53.568 \AA^3 . The average crystallite size was calculated using the Scherrer formula, and it is equal to $\sim 35 \text{ nm}$. The synthesized heterometallic complex $[\text{Co}_2\text{Nd}_2(\text{C}_2\text{O}_4)_5\cdot 2\text{Phen}]\cdot 4\text{H}_2\text{O}$ can be used as a precursor for the preparation of cobaltate of neodymium with lower energy consumption than in solid-phase synthesis.

Keywords: complexes, neodymium, cobalt, carboxylic acid, phenanthroline, synthesis, complex oxides.

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Introduction

The preparation of heterometallic complexes of 3d - and 4f- metals with carboxylic acids and study of their physicochemical properties are of great interest, since these compounds as well as their thermolysis products are widely used in various fields of science and technology. The works on the synthesis of heteronuclear complexes with organic ligands, such as carboxylic acids, have been carried out for a long time [1], but their use for the preparation of complex

oxides has begun in recent decades [2,3]. The proposed method for obtaining oxides makes it possible to control the composition and structure of compounds by changing their properties. Oxides of rare earth elements and d-elements with a perovskite or spinel structure have a combination of semiconductor and magnetic properties [1,3,4], which allows them to be used in microwave technology and computer storage devices. They are also used as catalysts in the oxidative catalysis of

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saturated hydrocarbons and nitrogen oxides. Previously, complex oxides were obtained mainly by solid-phase synthesis at temperatures above 1000°C, and the use of precursors of heteronuclear compounds allows reducing energy consumption during their obtaining [4]. A huge number of works of a preparative nature are devoted to the study, isolation, and research of the physicochemical properties of compounds of rare earth elements with various carboxylic acids in solutions [5,6]. Due to the wide use in the chemical industry for the purification and separation of rare earth elements, oxalates are the most studied, the structure and composition of which being described elsewhere [7].

Eight types of ligand coordination are possible in the complexes of transition elements with monocarboxylic acids [8]. In the case of dicarboxylic acids which include oxalic acid, there are already more than 15 ways of metal addition to oxalato and bioxalato groups [9]. The number of the ways to coordinate ligands increases significantly if two or more different metals are involved in the complex formation, since one COO group can participate in the formation of bonds with 2–4 metal ions. In reality, when the complexes are isolated, a mixture of compounds is formed in which several types of coordination are carried out. Since products with different structures are obtained from the same initial complexes, depending on the synthesis conditions, this creates certain problems in the synthesis of carboxylates.

The determination of the identity of isolated compounds is the most controversial question of heteronuclear complexation. The comparison of its properties with the properties of the corresponding homometallic compounds can be evidence of the formation of an individual heterometallic compound.

This work was aimed at determining the conditions for the synthesis of a new heterometallic complex of Co(II) and Nd(III) with oxalic acid in the presence of phenanthroline and studying its composition, structure, thermal properties and the ability to form complex oxides under the «soft» conditions.

Experimental

Materials

Neodymium nitrate $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, cobalt nitrate $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and phenanthroline used for the synthesis of mono- and heterometallic oxalate complexes of cobalt and neodymium with phenanthroline were of chemically pure grade. Oxalic

acid was of analytical grade. Solution of ammonium hydroxide (10%) NH_4OH was used in the work. The solutions of salts with the required concentration were prepared using the exactly weighed samples.

Methods

The elemental analysis, X-ray powder diffraction and differential thermal analysis were used to study the composition and structure of the obtained products. Electronic diffuse reflection spectra and IR spectra were also registered.

The content of metals in the complexes was determined using of Perkin Elmer-200 atomic absorption spectrophotometer. The contents of carbon, hydrogen and nitrogen were determined by elemental microanalysis on a C, H, N Perkin Elmer model 2400 Analyzer.

The composition of the phases of compounds obtained during the thermolysis of the heterometallic precursor was determined using X-ray powder diffraction method. X-ray powder diffraction was performed by X-ray diffractometer DRON-3M. The experiment was conducted under normal conditions using CuK_α -radiation, $\lambda=1.54187 \text{ \AA}$, with computer registration of the output signal. Spectra were recorded in the range of angles $10^\circ < 2\theta < 80^\circ$, with a scanning step of 0.04° and with an exposure time of $\tau=1 \text{ s}$. To identify the composition of the phases of the final products, diffraction patterns were studied using the Match! Crystal Impact¹ with COD (Crystallography Open Database) and ICDD PDF databases. The crystal cells parameters were calculated by using the «Unit Cell» program. This software allows installing the unit cell parameters from powder diffraction data using the least non-linear squares method to refine the actual data. The method and its implementation are described in detail elsewhere [10].

The infrared spectra were recorded in a KBr matrix on a spectrophotometer Specord M-80, in a range of $4000\text{--}400 \text{ cm}^{-1}$.

The diffuse reflection electronic spectra were recorded on a UV-2450-Shimadzu spectrophotometer with an ISR-240A attachment in the range of $190\text{--}900 \text{ nm}$.

The thermogravimetric study was performed using a Q-1500D Paulik-Paulik Erdey system derivatograph in open ceramic microcrucibles in the temperature range of $20\text{--}800^\circ\text{C}$ at the heating rate of $5^\circ\text{C}\cdot\text{min}^{-1}$.

The pH was measured on a pH meter «150-MA», the accuracy being ± 0.05 .

¹ 10. Match! – Phase identification from powder diffraction. Crystal impact, version 3: manual. – Dr.H. Putz and Dr.K. Brandenburg GbR, Kreuzherrenstr. 102, 53227 Bonn, Germany, 2020. 143 p. <http://www.crystalimpact.com/match>.

Synthesis

The coordination compounds were synthesized from the water-alcohol solutions.

Synthesis of $[\text{Co}(\text{C}_2\text{O}_4)\cdot\text{Phen}]_2\cdot 4\text{H}_2\text{O}$

To 10 ml of the warm ($t=50^\circ\text{C}$) solution of $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ ($c=0.15$ mol/l) was added 10 ml of the ethanolic solution of phenanthroline ($c=0.15$ mol/l) and 5 ml of the 10% solution of oxalic acid with stirring. The pH of the solution was adjusted by adding dropwise a solution of NH_4OH (pH ~ 5). The formed brick-orange precipitate was left for a day, then it was filtered and dried to constant weight at the room temperature. The yield was 60%.

Synthesis of $[\text{Nd}_2(\text{C}_2\text{O}_4)_3\cdot 2\text{Phen}]$

To 10 ml of the warm ($t=50^\circ\text{C}$) solution of $\text{Nd}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$ ($c=0.15$ mol/l) was added 10 ml of the ethanolic solution of phenanthroline ($c=0.15$ mol/l) and 5 ml of the 10% solution of oxalic acid with stirring. To prevent the formation of lanthanide hydroxocomplexes, pH during synthesis should not exceed ~ 6.5 . The pH of solution was controlled (pH ~ 5) by adding NH_4OH . The resulting white precipitate was left for a day, then it was filtered and dried to constant weight at the room temperature. The yield was 47%.

Synthesis of $[\text{Co}_2\text{Nd}_2(\text{C}_2\text{O}_4)_5\cdot 2\text{Phen}]\cdot 4\text{H}_2\text{O}$

To 10 ml of the warm ($t=50^\circ\text{C}$) solutions of $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ and $\text{Nd}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$ with a concentration of 0.15 mol/l each, was added 20 ml of the ethanolic solution of phenanthroline ($c=0.15$ mol/l) and was added 10 ml of the 10% solution of oxalic acid with stirring. The pH of the solution was controlled (pH ~ 5) by adding a solution of NH_4OH . The resulting brick-orange precipitate was left for a day, then it was filtered and dried to constant weight at the room temperature. The yield was 40%.

The results of the chemical analysis of hetero- and monocomplexes of Co(II) and Nd(III) with oxalic acid and phenanthroline are presented below.

Found (calculated) (%):

1. Co 16.20 (16.25), C 46.30 (46.28), H 3.27 (3.31), and N 7.73 (7.71) for $\text{C}_{28}\text{Co}_2\text{H}_{24}\text{N}_4\text{O}_{12}$.

2. Nd 31.58 (31.57), C 39.50 (39.47), H 1.78 (1.75), and N 6.16 (6.14) for $\text{C}_{30}\text{H}_{16}\text{Nd}_2\text{N}_4\text{O}_{12}$.

3. Nd 22.56 (22.53), Co 9.20 (9.23), C 31.95 (31.92), H 1.88 (1.87), and N 4.34 (4.38) for $\text{C}_{34}\text{Co}_2\text{H}_{24}\text{Nd}_2\text{N}_4\text{O}_{24}$.

Results and discussion

A comparative analysis of the IR spectrum of the synthesized heterometallic complex and the IR spectra of homonuclear complexes was carried out to confirm the individuality of the heterometallic oxalate complex of Co(II) and Nd(III) (Fig. 1).

The assignment of the most important absorption bands in the IR spectra was carried out in accordance with the literature data on Co(II) and Nd(III) complexes with oxalic acid and phenanthroline [11]. The IR spectra of carboxylate complexes are shown in Fig. 1 and their assignments are given in Table 1.

Several vibrational regions can be identified in the IR spectra of the synthesized mono- and heterocomplexes. In the IR spectrum of oxalic acid, the C=O stretching vibrations are in the region of $1690\text{--}1700\text{ cm}^{-1}$. The presence of these absorption bands indicates the deprotonization of the carboxyl groups of the acid involved in the complexation. If all carboxyl groups are bound by a metal, then the band of the carbonyl group disappears and the bands of asymmetric stretching vibrations of the carboxyl ion appear in the frequency range of $1510\text{--}1650\text{ cm}^{-1}$, this being observed in the spectra of all synthesized complexes.

The position of the maximum of this absorption band corresponds to the frequency of 1623 cm^{-1} , 1609 cm^{-1} , and 1602 cm^{-1} for the cobalt monocomplex, the neodymium monocomplex, and the heterocomplex, respectively. All bands are expanded, the maximum expansion being observed

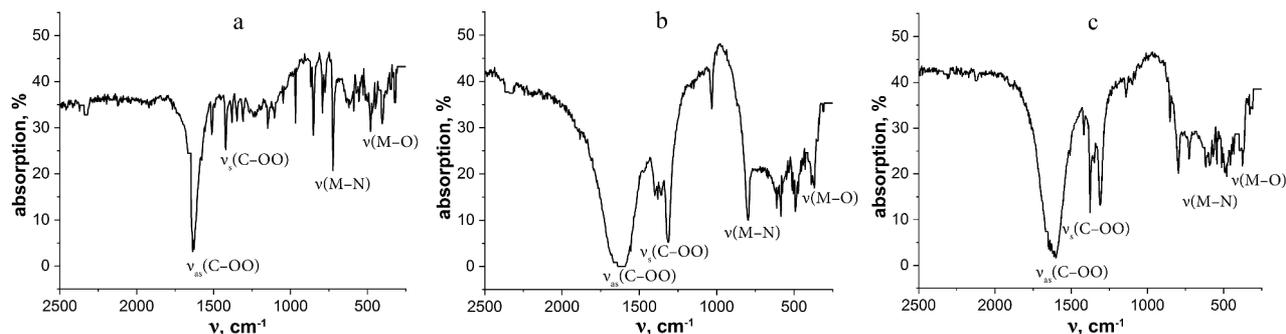


Fig. 1. IR spectra of carboxylate complexes $[\text{Co}(\text{C}_2\text{O}_4)\cdot\text{Phen}]_2\cdot 4\text{H}_2\text{O}$ (a), $[\text{Nd}_2(\text{C}_2\text{O}_4)_3\cdot 2\text{Phen}]$ (b), and $[\text{Co}_2\text{Nd}_2(\text{C}_2\text{O}_4)_5\cdot 2\text{Phen}]\cdot 4\text{H}_2\text{O}$ (c)

Table 1

Vibrational frequencies and their assignments in the IR spectra of complexes of cobalt and neodymium oxalates with phenanthroline

Frequency, cm ⁻¹					Assignments
[Co(C ₂ O ₄)·Phen] ₂ ·4H ₂ O	[Nd ₂ (C ₂ O ₄) ₃ ·2Phen]	[Co ₂ Nd ₂ (C ₂ O ₄) ₅ ·2Phen]·4H ₂ O	oxalic acid (H ₂ C ₂ O ₄)	phenanthroline (Phen)	
478, 548	478, 590	429, 450, 478, 562		408	ν(M–O)
611, 716	610	604		620	δ _{ring}
785	792	723		737	ν(M–N)
848, 967	810	799	808	853, 988	γ(CH)
	1029			1090	δ _{ring}
1148, 1239		1134, 1288	1250	1138, 1216	δ(CH)
1309, 1351	1309, 1351, 1376	1309, 1322		–	ν _s (C–OO) [–]
1379		1379			
1413	1410	1421		1423	ν(C–N)
1504	1470	1504	1510		ν _s (C–OO)
					δ _{ring}
1623	1609	1602	1625		ν _{as} (C–OO)
			1700		ν(C=O)

for the neodymium complex. Such complex nature of the spectrum in this region indicates that the oxalate groups that can participate in the metal-oxygen bond are added in various ways: monodentate, bidentate and chelate-bridging. Analysis of the obtained spectra confirms the presence of coordinated phenanthroline molecules in the composition of the complexes, although it is difficult to assign the frequencies of the absorption bands due to the overlap of the bands between different vibrational frequencies. In the region of 1300–1650 cm⁻¹, there is a series of the bands of skeletal stretching vibrations of the heterocycle of phenanthroline. In the region of 1000–1300 cm⁻¹, the bands are observed that can be assigned to the planar deformation vibrations of C–H and stretching vibrations of the phenanthroline ring. In the region below 1000 cm⁻¹, there are bands assigned to non-planar deformation vibrations of C–H and to planar and non-planar deformation vibrations of phenanthroline rings.

It is known that the difference between ν_{as}(C–OO) and ν_s(C–OO), (ν(C–OO)) can be a characteristic of the bond formed in the metal-ligand complex [11]. For monodentate coordination of the carboxyl group to the metal, ν(C–OO) is greater than 200 cm⁻¹, whereas ν(C–OO) is less than 200 cm⁻¹ for bidentate coordination of the carboxyl group to the metal. In our case, analysis of the IR spectra data allowed us to conclude that the carboxyl groups of the acid are involved in the complexation with the metal, and they are mainly characterized by the bidentate mode of coordination.

A slight shift of the bands is noted, and an

overlap of bands in the IR spectrum of the heterocomplex can be observed, when comparing the spectra of the monocomplexes with the spectrum of the heterocomplex. Based on this, it can assume the formation of a heterocomplex with a chain structure of the Nd–L–Co–L-type.

For a qualitative assessment of the geometry of the coordination environment of cobalt and neodymium in the studied complexes, the diffuse reflection spectra of mono- and heterocomplexes were recorded and analyzed.

The bands corresponding to f–f transitions of the Nd³⁺ ion from the ground state ⁴I_{9/2} to multiplets of excited levels (Table 2) and bands corresponding to d–d transitions of the cobalt ion (Table 3) are observed in the diffuse reflection spectra of the synthesized complexes [Co(C₂O₄)·Phen]₂·4H₂O, [Nd₂(C₂O₄)₃·2Phen] and [Co₂Nd₂(C₂O₄)₅·2Phen]·4H₂O (Fig. 2).

The bands due to transitions from the ground d–d level of the Co²⁺ ion ⁴T_{1g}(⁴F) (⁴F) to the excited levels ⁴T_{2g}(⁴F), ⁴A_{2g}(⁴F) and ⁴T_{1g}(⁴P) are fixed in the spectra of cobalt complexes. Cobalt ion (Co²⁺) is in the octahedral configuration.

Two regions of bands are observed in the spectrum of the [Co(C₂O₄)·Phen]₂·4H₂O complex: the first region is a wide band of the ⁴T_{1g}(⁴F)→⁴T_{2g}(⁴F) transition at ~9000 cm⁻¹, which is not fully manifested due to instrumental limitations spectral range, and the second region of transitions is ⁴T_{1g}(⁴F)→⁴A_{2g}(⁴F) and ⁴T_{1g}(⁴F)→⁴T_{1g}(⁴P) at 18200–23550 cm⁻¹. Table 3 shows the values of the bands of transition for [Co(C₂O₄)·Phen]₂·4H₂O as a

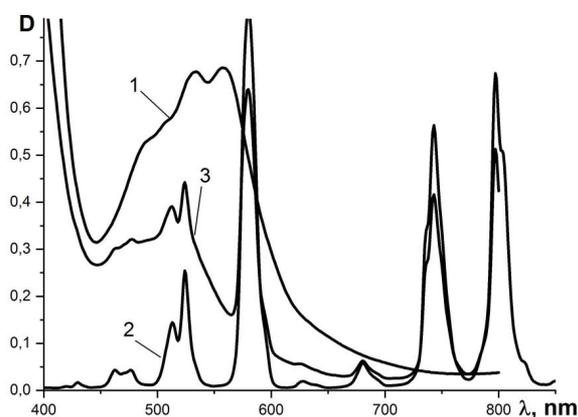
Table 2

Transition energies in the diffuse reflection spectra of complexes $[\text{Nd}_2(\text{C}_2\text{O}_4)_3 \cdot 2\text{Phen}]$ and $[\text{Co}_2\text{Nd}_2(\text{C}_2\text{O}_4)_5 \cdot 2\text{Phen}] \cdot 4\text{H}_2\text{O}$

Transition	Transition energy, cm^{-1}/nm	
	$[\text{Nd}_2(\text{C}_2\text{O}_4)_3 \cdot 2\text{Phen}]$	$[\text{Co}_2\text{Nd}_2(\text{C}_2\text{O}_4)_5 \cdot 2\text{Phen}] \cdot 4\text{H}_2\text{O}$
${}^4\text{I}_{9/2} \rightarrow {}^2\text{P}_{1/2}$	23274/429.7	–
${}^4\text{I}_{9/2} \rightarrow {}^2\text{G}_{9/2,11/2}$	21607/462.8	21547/464.1
${}^4\text{I}_{9/2} \rightarrow {}^2\text{D}_{3/2}, {}^2\text{P}_{3/2}$	20980/476.6	20964/477.0
${}^4\text{I}_{9/2} \rightarrow {}^4\text{G}_{9/2}$	19500/512.8	19531/512.0
${}^4\text{I}_{9/2} \rightarrow {}^4\text{G}_{7/2}$	19064/524.5	19084/524.0
${}^4\text{I}_{9/2} \rightarrow {}^4\text{G}_{5/2}, {}^2\text{G}_{7/2}$	17242/579.9	17271/579.0
${}^4\text{I}_{9/2} \rightarrow {}^2\text{H}_{11/2}$	15927/627.8	15931/627.7
${}^4\text{I}_{9/2} \rightarrow {}^4\text{F}_{9/2}$	14680/681.2	14691/680.7
${}^4\text{I}_{9/2} \rightarrow {}^4\text{F}_{7/2}$	13458/743.1	13464/742.7
${}^4\text{I}_{9/2} \rightarrow {}^4\text{H}_{9/2}$	12542/797.3	12547/797.0

Table 3
Transition energies in the diffuse reflection spectra of complex $[\text{Co}(\text{C}_2\text{O}_4) \cdot \text{Phen}]_2 \cdot 4\text{H}_2\text{O}$

Transition	Transition energy, cm^{-1}/nm
${}^4\text{T}_{1g}({}^4\text{F}) \rightarrow {}^4\text{T}_{2g}({}^4\text{F})$	~9000/1111
${}^4\text{T}_{1g}({}^4\text{F}) \rightarrow {}^4\text{A}_{2g}({}^4\text{F})$	21413/467
${}^4\text{T}_{1g}({}^4\text{F}) \rightarrow {}^4\text{T}_{1g}({}^4\text{P})$	18416/543

Fig. 2. The diffuse reflection spectra of $[\text{Co}(\text{C}_2\text{O}_4) \cdot \text{Phen}]_2 \cdot 4\text{H}_2\text{O}$ (1), $[\text{Nd}_2(\text{C}_2\text{O}_4)_3 \cdot 2\text{Phen}]$ (2), and $[\text{Co}_2\text{Nd}_2(\text{C}_2\text{O}_4)_5 \cdot 2\text{Phen}] \cdot 4\text{H}_2\text{O}$ (3)

consequence of the decomposition into Gaussian components of the spectrum bands. Based on the results obtained in the analysis of the diffuse reflection spectrum of $[\text{Co}(\text{C}_2\text{O}_4) \cdot \text{Phen}]_2 \cdot 4\text{H}_2\text{O}$ as well as its shape and region of transition, it can be concluded that cobalt is in a distorted octahedral environment.

It is impossible to distinguish the bands of transitions belonging to the ion of cobalt in the diffuse reflection spectrum of the heterocomplex, since they are completely overlapped by the bands of transitions

of the ion of neodymium. The widening of the ${}^4\text{I}_{9/2} \rightarrow {}^2\text{D}_{3/2}, {}^2\text{P}_{3/2}$ and ${}^4\text{I}_{9/2} \rightarrow {}^4\text{G}_{9/2}$ bands of the ion of neodymium due to the superposition of bands of absorption in this region related to the d–d transitions of the ion of cobalt is observed in the spectrum of heterocomplex. A slight shift of the bands of transitions to both high and low energies is observed when comparing the spectra of mono- and heterocomplexes of neodymium. It can be noted that the positions of the absorption band maxima in the diffuse reflection spectra of the heterometallic and mononeodymium complexes have close values, which is a consequence of the absence of significant structural changes in the immediate environment during the formation of the heterometallic complex. In the spectral region $16666\text{--}20000\text{ cm}^{-1}$, the positions of the bands of the transitions ${}^4\text{I}_{9/2} \rightarrow {}^4\text{G}_{9/2}$, ${}^4\text{I}_{9/2} \rightarrow {}^4\text{G}_{7/2}$, and ${}^4\text{I}_{9/2} \rightarrow {}^4\text{G}_{5/2}, {}^2\text{G}_{7/2}$ and the ratio of their intensities are similar to those in the spectra of neodymium complexes with coordination number 8 [12,13]. This confirms the composition of the $[\text{Nd}_2(\text{C}_2\text{O}_4)_3 \cdot 2\text{Phen}]$ complex, in which neodymium ions are bound to bidentate coordinated oxalate ligands and 1,10-phenanthroline. The coordination of this type is also confirmed by IR spectroscopy data. Probably, the structure of the heterocomplex can be represented as a chain with alternating structural elements consisting of neodymium and cobalt ions bound by oxalate ligands.

The differential thermal analysis and X-ray powder diffraction were carried out in order to determine the final products of the decomposition of the synthesized complexes and the direction of thermal decomposition. The thermal decomposition of the complexes was studied by thermogravimetry in air. The derivatograms of mono- and heterocomplexes are shown in Fig. 3. As can be

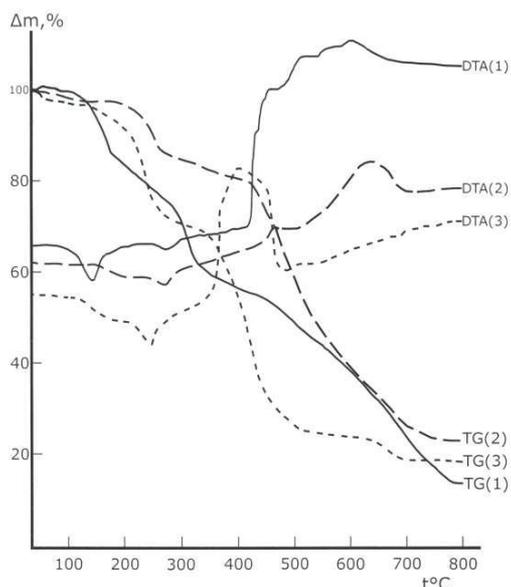


Fig. 3. Derivatograms of $[\text{Co}(\text{C}_2\text{O}_4)\cdot\text{Phen}]_2\cdot 4\text{H}_2\text{O}$ (1), $[\text{Nd}_2(\text{C}_2\text{O}_4)_3\cdot 2\text{Phen}]$ (2), and $[\text{Co}_2\text{Nd}_2(\text{C}_2\text{O}_4)_5\cdot 2\text{Phen}]\cdot 4\text{H}_2\text{O}$ (3) seen from the figure, the thermal decomposition of oxalates occurs in stages and has a multistage character (Table 4).

The removal of the water of crystallization is the first stage in the decomposition of the $[\text{Co}(\text{C}_2\text{O}_4)\cdot\text{Phen}]_2\cdot 4\text{H}_2\text{O}$ and $[\text{Co}_2\text{Nd}_2(\text{C}_2\text{O}_4)_5\cdot 2\text{Phen}]\cdot 4\text{H}_2\text{O}$ complexes, which corresponds to the first weak endo-

effects on the curves DTG and is accompanied by an insignificant weight loss. Probably, the water in these complexes is adsorbed. The second stage of decomposition corresponds to the loss of the molecule of phenanthroline. The resulting oxalates are stable over a wide temperature range: up to 240–340°C for the cobalt complex, up to 250–440°C for the neodymium complex, and up to 250–340°C for the heterocomplex. Subsequent heating leads to the decomposition. This process also proceeds stepwise, although it is difficult to clearly separate the stages. First, metal carbonates are formed then metal oxides are formed as a result of the increase in temperature.

The decomposition of the complexes ends at a temperature of $700\pm 20^\circ\text{C}$ and no subsequent weight loss is observed. The final products of the thermolysis of the complexes are the corresponding oxides.

The control of the composition phase of the obtained oxide powders was carried out using X-ray powder diffraction. Figure 4 shows the X-ray powder diffraction patterns of oxide powders obtained by heating of complexes $[\text{Co}_2\text{Nd}_2(\text{C}_2\text{O}_4)_5\cdot 2\text{Phen}]\cdot 4\text{H}_2\text{O}$ and $[\text{Nd}_2(\text{C}_2\text{O}_4)_3\cdot 2\text{Phen}]$.

It was established that the X-ray powder diffraction patterns (Fig. 4,a) of the products obtained by thermolysis of heterocomplex $[\text{Co}_2\text{Nd}_2(\text{C}_2\text{O}_4)_5\cdot 2\text{Phen}]\cdot 4\text{H}_2\text{O}$ to 1000°C exhibits peaks at $2\theta=23.40, 33.74, 41.00, 48.32, 54.52, 59.94,$ and 70.58° . This corresponds to card No. 00-025-1064 («ICDD PDF-2») –

Table 4
Thermal stability of complexes $[\text{Co}(\text{C}_2\text{O}_4)\cdot\text{Phen}]_2\cdot 4\text{H}_2\text{O}$, $[\text{Nd}_2(\text{C}_2\text{O}_4)_3\cdot 2\text{Phen}]$, and $[\text{Co}_2\text{Nd}_2(\text{C}_2\text{O}_4)_5\cdot 2\text{Phen}]\cdot 4\text{H}_2\text{O}$

Compound	Temperature, $^\circ\text{C}$			
	dehydration	removal of phenanthroline	intramolecular rearrangement	decomposition
$[\text{Co}(\text{C}_2\text{O}_4)\cdot\text{Phen}]_2\cdot 4\text{H}_2\text{O}$	95–150	220–244	240–340	380–720
$[\text{Nd}_2(\text{C}_2\text{O}_4)_3\cdot 2\text{Phen}]$	–	150–250	250–440	470–720
$[\text{Co}_2\text{Nd}_2(\text{C}_2\text{O}_4)_5\cdot 2\text{Phen}]\cdot 4\text{H}_2\text{O}$	90	182–250	250–340	415–720

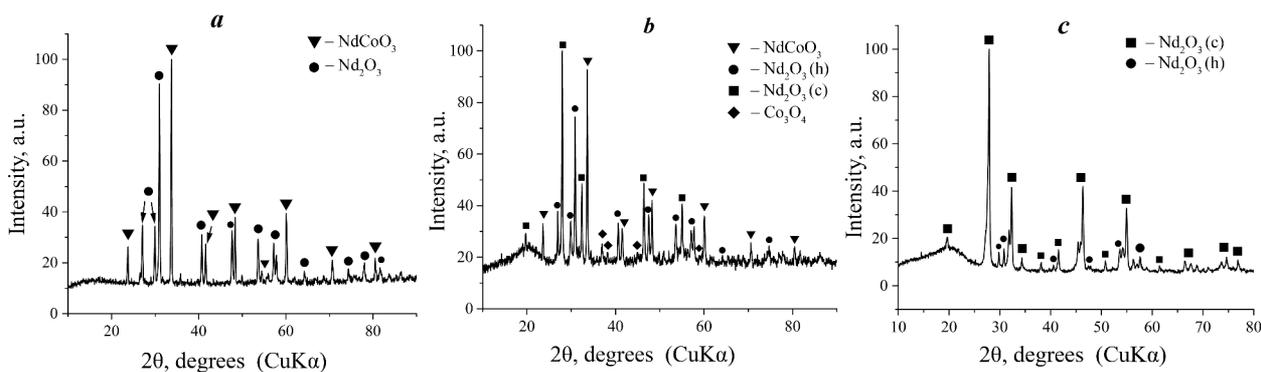


Fig. 4. X-ray powder diffraction patterns of samples obtained by thermolysis of $[\text{Co}_2\text{Nd}_2(\text{C}_2\text{O}_4)_5\cdot 2\text{Phen}]\cdot 4\text{H}_2\text{O}$ at 1000°C (a) and 800°C (b), and $[\text{Nd}_2(\text{C}_2\text{O}_4)_3\cdot 2\text{Phen}]$ at 800°C (c)

neodymium cobaltate NdCoO_3 . Neodymium cobaltate crystallizes in the cubic crystal system, the unit cell parameter is $a=3.770 \text{ \AA}$, the cell volume is $V=53.568 \text{ \AA}^3$.

The average crystallite size was calculated using the Scherrer formula and is equal to $d \sim 35 \text{ nm}$ [14]. In addition, the X-ray powder diffraction patterns exhibit the peaks at $2\theta=26.92, 29.75, 30.77, 40.54, 47.53, 53.63, \text{ and } 57.08^\circ$. The corresponding card in the database is No. 00-041-1089, neodymium oxide Nd_2O_3 , which crystallizes in the hexagonal crystal system, the unit cell parameters are as follows: $a=3.825 \text{ \AA}$, $c=5.990 \text{ \AA}$, and the cell volume is $V=75.875 \text{ \AA}^3$.

The X-ray powder diffraction patterns of the sample obtained by the heating of the heterocomplex to 800°C , in addition to the complex oxide NdCoO_3 and Nd_2O_3 oxide (hexagonal crystal system), demonstrate the peaks at $2\theta=27.98, 32.40, 46.41, \text{ and } 55.05^\circ$ (Fig. 4,b). This corresponds to the card in the database No. 00-021-0579 – neodymium oxide Nd_2O_3 , crystallizing in the cubic crystal system with a unit cell parameter $a=11.054 \text{ \AA}$, the cell volume is $V=1350.522 \text{ \AA}^3$. The peaks at $2\theta=19.03, 31.40, 36.98, 38.23, 44.96, 59.67, \text{ and } 65.36^\circ$ corresponding to the cubic crystal system Co_3O_4 were also recorded (card No. 00-042-1467). The unit cell parameter was calculated for it as follows: $a=8.067 \text{ \AA}$ and the cell volume is $V=525.013 \text{ \AA}^3$. Since the content of additional phases in the sample obtained after heating to 1000°C is significantly less than in the powder after heating to 800°C , it is advisable to heat the sample to higher temperatures to obtain pure complex oxide NdCoO_3 .

In case of the thermolysis of $[\text{Nd}_2(\text{C}_2\text{O}_4)_3 \cdot 2\text{Phen}]$, the X-ray powder diffraction pattern (Fig. 4,c) shows peaks of neodymium oxide crystallizing in the cubic crystal system (card No. 00-021-0579) and in the hexagonal crystal system (card No. 00-041-108). The unit cell parameters for cubic crystal system Nd_2O_3 are as follows: $a=11.059 \text{ \AA}$ and the cell volume is $V=1352.838 \text{ \AA}^3$. The unit cell parameters for hexagonal crystal system Nd_2O_3 are as follows: $a=3.840 \text{ \AA}$, $c=5.956 \text{ \AA}$ and the cell volume is $V=5.956 \text{ \AA}^3$.

Conclusions

A new heteronuclear complex $[\text{Co}_2\text{Nd}_2(\text{C}_2\text{O}_4)_5 \cdot 2\text{Phen}] \cdot 4\text{H}_2\text{O}$ and monocomplexes $[\text{Co}(\text{C}_2\text{O}_4) \cdot \text{Phen}]_2 \cdot 4\text{H}_2\text{O}$ and $[\text{Nd}_2(\text{C}_2\text{O}_4)_3 \cdot 2\text{Phen}]$ were synthesized and isolated in the crystalline state. The complexes were investigated by physicochemical research methods (elemental analysis, differential thermal analysis, IR- and diffuse reflection electronic

spectroscopies, and X-ray powder diffraction). It has been shown that ions of metals are bound to molecules of bidentately coordinated oxalate ligands and to molecules of 1,10-phenanthroline. The synthesized complexes decompose in the temperature range of $400\text{--}700^\circ\text{C}$. During the thermolysis of the synthesized heterocomplex, neodymium cobaltate was obtained. It was established that Co^{2+} and Nd^{3+} are in a distorted octahedral environment. The complex $[\text{Co}_2\text{Nd}_2(\text{C}_2\text{O}_4)_5 \cdot 2\text{Phen}] \cdot 4\text{H}_2\text{O}$ can be used as a precursor for the preparation of neodymium cobaltate with lower energy costs than in solid-phase synthesis.

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МОНО- І ГЕТЕРОКОМПЛЕКСИ Co(II), Nd(III) З ШАВЛЕВОЮ КИСЛОТОЮ І ФЕНАНТРОЛІНОМ: СИНТЕЗ, БУДОВА І ТЕРМОРОЗКЛАД

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В даній роботі наведені результати дослідження, метою яких було визначення умов синтезу нового гетерометалічного комплексу Co(II) і Nd(III) з шавлевою кислотою в присутності фенантроліну, вивчення його складу, будови та термічних властивостей і його здатності утворювати складні оксиди. Синтезовано гетеро- і монокомплекси $[Co(C_2O_4)_2 \cdot Phen]_2 \cdot 4H_2O$, $[Nd_2(C_2O_4)_3 \cdot 2Phen]$, $[Co_2Nd_2(C_2O_4)_5 \cdot 2Phen] \cdot 4H_2O$ (Phen – фенантролін). Комплекси охарактеризовано фізико-хімічними методами аналізу: елементним аналізом, ІЧ-спектроскопією і електронними спектрами дифузного відбиття, термогравіметричним методом і методом рентгенофазового аналізу. На підставі аналізу електронних та ІЧ-спектрів показано, що іони металів бідентатно зв'язуються з оксалат-іонами і молекулами 1,10-фенантроліну. Будова іону кобальту та іону неодиму відповідає викривленому октаедру. Іони металів з'єднані між собою оксалатними лігандами. При термолізі гетерокомплексу до 800°C і 1000°C отримано порошки оксидів. Контроль складу отриманих оксидних порошоків здійснювали за допомогою рентгенофазового аналізу. При нагріванні гетерокомплексу до 800°C, крім

складного оксиду $NdCoO_3$, одержано оксиди Nd_2O_3 (гексагональна сингонія), Nd_2O_3 (кубічна сингонія) та оксид Co_3O_4 (кубічна сингонія). Після нагрівання до 1000°C одержано чистіший складний оксид $NdCoO_3$. Складний оксид $NdCoO_3$ кристалізується в кубічній сингонії з параметром комірки $a=3,770 \text{ \AA}$, об'єм комірки $V=53,568 \text{ \AA}^3$. Розрахований за формулою Шерера середній розмір кристалітів становить ~35 нм. Синтезований гетерометалічний комплекс $[Co_2Nd_2(C_2O_4)_5 \cdot 2Phen] \cdot 4H_2O$ може використовуватися як прекурсор для отримання кобальтату неодиму з меншими енергетичними витратами, ніж у твердофазному синтезі.

Ключові слова: комплекси; неодим; кобальт; карбонова кислота; фенантролін; синтез; складні оксиди.

MONO- AND HETEROCOMPLEXES OF Co(II), Nd(III) WITH OXALIC ACID AND PHENANTHROLINE: SYNTHESIS, STRUCTURE AND THERMAL DECOMPOSITION

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This work presents the results of studies aimed at determining the conditions for the synthesis of a new heterometallic complex of Co(II) and Nd(III) with oxalic acid in the presence of 1,10-phenanthroline, studying its composition, structure, thermal properties and its ability to form complex oxides. The hetero- and monocomplexes $[Co(C_2O_4)_2 \cdot Phen]_2 \cdot 4H_2O$, $[Nd_2(C_2O_4)_3 \cdot 2Phen]$, $[Co_2Nd_2(C_2O_4)_5 \cdot 2Phen] \cdot 4H_2O$ (Phen – phenanthroline) were synthesized. The complexes were investigated by the following physicochemical research methods: elemental analysis, differential thermal analysis, IR- and diffuse reflection electronic spectroscopies, and X-ray powder diffraction. Based on the analysis of electronic and IR spectra, it was shown that ions of metals bind bidentately with ions of oxalates and with molecules of 1,10-phenanthroline. The structures of the ion of cobalt and ion of neodymium correspond to the distorted octahedron. The ions of metals are bound together by oxalate ligands. The powders of oxides were prepared by thermolysis of the heterocomplex up to 800°C and 1000°C. The composition of the obtained oxide powders was controlled by X-ray powder diffraction. When the heterocomplex is heated to 800°C, in addition to the complex oxide $NdCoO_3$, we obtained the following oxides: Nd_2O_3 (hexagonal crystal system), Nd_2O_3 (cubic crystal system) and Co_3O_4 (cubic crystal system). After heating to 1000°C, a more pure complex oxide $NdCoO_3$ was obtained. Neodymium cobaltate $NdCoO_3$ crystallizes in the cubic crystal system, the unit cell parameter is $a=3.770 \text{ \AA}$, the cell volume is 53.568 \AA^3 . The average crystallite size was calculated using the Scherrer formula, and it is equal to ~35 nm. The synthesized heterometallic complex $[Co_2Nd_2(C_2O_4)_5 \cdot 2Phen] \cdot 4H_2O$ can be used as a precursor for the preparation of cobaltate of neodymium with lower energy consumption than in solid-phase synthesis.

Keywords: complexes; neodymium; cobalt; carboxylic acid; phenanthroline; synthesis; complex oxides.

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