UDC 546+54-386+543.42+543.57

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SYNTHESIS AND STUDY OF MIXED-LIGAND HETEROMETALLIC COMPLEXES OF COBALT AND NEODYMIUM SUCCINATES WITH PYRIDINE OR PHENANTHROLINE

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The paper reports the results of the study on the synthesis of new heterometallic complexes of Co(II) and Nd(III) with succinic acid in the presence of 1,10-phenanthroline or pyridine. The following hetero- and monocomplexes were synthesized: $[Co(C_4H_4O_4) \cdot 2Py] \cdot 2H_2O_4$ and $[Co(C_4H_4O_4)$ Phen] $2H_2O$; $[Nd_2(C_4H_4O_4)_3] 5H_2O$ and $[Nd_2(C_4H_4O_4)_3 2Phen] 2H_2O$; $[Co_2Nd_2(C_4H_4O_4)_5 \cdot 4Py] \cdot 4H_2O$ and $[Co_2Nd_2(C_4H_4O_4)_5 \cdot 2Phen] \cdot 4H_2O$ (Phen – phenanthroline, and Py – pyridine). The study of their composition, structure, thermal properties and determination of the ability of heterocomplexes to form complex oxides was carried out. The complexes were characterized by a number of physicochemical methods: elemental analysis, IR- and diffuse reflection spectroscopies, X-ray powder diffraction and differential thermal analysis. Based on the analysis of diffuse reflection spectra and IR spectra of heterocomplexes, it was shown that succinic acid and 1,10-phenanthroline are bidentately bound to metal atoms. The metals are connected by succinic acid, forming a chain. Oxide powders were obtained during thermolysis of heterocomplexes up to 800°C. The composition of the synthesized heterometallic compounds was controlled by X-ray powder diffraction. It was shown that a complex oxide of $NdCoO_3$ (cubic crystal system), without impurities, was formed, when the heterocomplex of phenanthroline $[Co_2Nd_2(C_4H_4O_4)_5 2Phen] \cdot 4H_2O$ was heated to 800°C. When heating the heterocomplex of pyridine $[Co_2Nd_2(C_4H_4O_4), 4Py] 4H_2O_3$, in addition to the complex oxide NdCoO₃, oxides Nd₂O₃ (hexagonal crystal system), Nd₂O₃ (cubic crystal system) and Co₃O₄ oxide (cubic crystal system) were formed. The heterocomplex $[Co_2Nd_2(C_4H_4O_4)_5 \cdot 2Phen] \cdot 4H_2O$ can be used as a precursor for the synthesis of cobaltate of neodymium with lower energy costs than in solid-phase synthesis.

Keywords: heterometallic complex, neodymium, cobalt, succinic acid, phenanthroline, pyridine, complex oxide.

DOI: 10.32434/0321-4095-2023-149-4-94-104

Introduction

Homo- and heterometallic coordination compounds, which include 3d- and 4f-metals, are among the most intensively studied ones. This is due to the possibility of synthesizing compounds with valuable properties of molecular magnets and luminescent, sorption, catalytic and biologically active characteristics. The study of the possibility of using such coordination compounds as precursors of functional oxide materials of various morphologies (polycrystalline samples, thin films, and nanoparticles) is an urgent task. Intensive research in the field of synthesis and characterization of heterometallic complexes with organic ligands made it possible to consider and use them as individual precursors of complex oxide materials. For the synthesis of complex oxides, the method of thermal destruction of heterometallic precursors is the most optimal, since this method makes allows obtaining materials with a high degree of homogeneity of the phase composition.

According to the literature data [1-7], the use

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of precursor methods for the synthesis of Lncontaining complex oxides has a number of advantages. When using the optimal precursor, the phase homogeneity of the resulting thermolysis product is achieved due to the mixing of heterometal ions at the molecular level of the precursor. It is possible to obtain polycrystalline products with a developed surface under conditions that are not harsh. In addition, control of the metal stoichiometry in the resulting oxide system is ensured at the stage of precursor synthesis.

It can be noted that in most works devoted to the synthesis of complex oxides with 3d-4f metals from the corresponding carboxylate precursors, there are no complete and correct data on the structure of these precursors. Many works that use the precursor synthesis of complex oxides are mostly of a technological nature [8,9]. Therefore, the search for and development of efficient methods for the synthesis of such heterometallic compounds is a very topical issue.

This work was aimed at determining the conditions for the synthesis of new heterometallic complexes Co(II) and Nd(III) with succinic acid in the presence of pyridine or phenanthroline, studying their composition, structure, thermal properties and ability to form complex oxides in «soft» conditions; and synthesizing Co(II) and Nd(III) succinates with phenanthroline or pyridine as starting coordination compounds for preparing heterometallic complexes.

Experimental

Materials

Neodymium nitrate Nd(NO₃)₃·6H₂O, cobalt nitrate Co(NO₃)₂·6H₂O, phenanthroline and pyridine used for the synthesis of mono- and heterometallic succinate complexes of cobalt and neodymium with phenanthroline or pyridine were of the grade chemically pure. Succinic acid was of the analytical grade. A solution of ammonium hydroxide (10%) NH₄OH was used. The solutions of the salts of required concentration were prepared using samples of reagents with exact weights.

Methods

The content of metals in the complexes was determined by the method of absorption spectroscopy using a Perkin Elmer-200 atomic absorption spectrophotometer. The content of carbon and nitrogen was determined by the method of elemental microanalysis using a C, H, N Perkin Elmer-2400 analyzer.

The composition of the phases in the obtained compounds during the thermolysis of the heterometallic precursor was established by means of X-ray powder diffraction (XRD) method. X-ray powder diffraction patterns of the samples were recorder using X-ray diffractometer DRON-3M. The experiment was carried out under normal conditions using CuK_a-radiation (λ =1.54187 Å) with computer recording of the output signal. The beams were focused according to the scheme of Bragga-Brentano in the range of angles of $20^{\circ} \le 20^{\circ} \le 90^{\circ}$ with a scanning step of 0.05° and with exposure time of 5 s. The measurement error was 0.01%. The diffraction patterns were processed using Match! Crystal Impact¹ with COD (Crystallography Open Database) and ICDD PDF databases for identifying the composition phases of the final products. The crystal cells parameters were calculated using the «Unit Cell» program. This software allows installing the unit cell parameters from powder diffraction data using the least non-linear squares method, which allows refining the data actually obtained. The method and its implementation are detailed elsewhere [10].

X-ray diffraction analysis of the complexes were carried out using a Bruker SMART APEX 2 singlecrystal diffractometer (MoK_{α}-radiation, λ =0.71073 Å, with graphite monochromator) with a CCD array detector in a nitrogen flow at 100 K by ω - and ϕ -scanning.

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

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

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

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

Synthesis

The synthesis of $[Co(C_4H_4O_4)\cdot 2Py]\cdot 2H_2O$ and $[Co(C_4H_4O_4)\cdot Phen]\cdot 2H_2O$ was carried out by mixing equimolar warm solutions of cobalt nitrate and sodium succinate in the presence of pyridine or phenanthroline at pH 5.5. The solutions were kept in a water bath at the temperature of 60°C for 45 minutes. The formed brick-red precipitates for

¹ 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.

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 $[Co(C_4H_4O_4)\cdot 2Py]\cdot 2H_2O$ and bright-orange precipitates for $[Co(C_4H_4O_4)\cdot Phen]\cdot 2H_2O$, which precipitated, were left for a day, filtered and dried to a constant weight at room temperature. The yields were as follows: 44 wt.% and 57 wt.% for $[Co(C_4H_4O_4)\cdot 2Py]\cdot 2H_2O$ and $[Co(C_4H_4O_4)\cdot Phen]\cdot 2H_2O$, respectively.

Synthesis of $[Nd_2(C_4H_4O_4)_3] \cdot 5H_2O$ and $[Nd_2(C_4H_4O_4)_3 \cdot 2Phen] \cdot 2H_2O$

An aqueous solution of sodium succinate was added to a warm aqueous solution of neodymium nitrate in the presence of solutions of pyridine or phenanthroline (pH ~5). Both salts were taken in equimolar ratios. The resulting solution was kept in a water bath at 60°C for one hour. The pale pink precipitates that formed, were left for a day, filtered, and dried to a constant weight at room temperature. The product yields were as follows: 63 wt.% and 54 wt.% for $[Nd_2(C_4H_4O_4)_3] \cdot 5H_2O$ and $[Nd_2(C_4H_4O_4)_3 \cdot 2Phen] \cdot 2H_2O$, respectively.

Synthesis of $[Co_2Nd_2(C_4H_4O_4)_5 \cdot 4Py] \cdot 4H_2O$

To 10 ml of the warm (t=50°C) solutions of $Co(NO_3)_2 \cdot 6H_2O$ and $Nd(NO_3)_3 \cdot 6H_2O$ with a concentration of 0.15 mol/l each, was added to 20 ml of the ethanolic solution of pyridine (0.15 mol/l), and 10 ml of the 10% solution of succinic acid was further added at stirring. The pH of the solution was controlled (pH ~5) by adding a solution of NH₄OH. The resulting pale orange precipitate was left for a day, and then it was filtered, and dried to a constant weight at room temperature. The yield was 43 wt.%.

Synthesis of $[Co_2Nd_2(C_4H_4O_4)_5 \cdot 2Phen] \cdot 4H_2O$

20 ml of the ethanolic solution of phenanthroline (C=0.15 mol/l) was added to 10 ml of the warm (t=50°C) solutions of $Co(NO_3)_2$ ·6H₂O and Nd(NO₃)₃·6H₂O with a concentration of 0.15 mol/l each, and then 10 ml of the 10% solution of succinic acid was added at stirring. The pH of the solution was controlled (pH ~5) by adding a solution

of NH_4OH . The resulting bright orange precipitate was left for a day, and then it was filtered, dried to a constant weight at room temperature. The yield was 50 wt.%.

Results and discussion

The results of chemical analysis of hetero- and monocomplexes of Co(II) and Nd(III) with succinic acid and phenanthroline or pyridine are given below. Found (calculated) (%):

1. Co 15.94 (15.96), C 45.52 (45.54), H 4.85 (4.87), N 7.56 (7.59) for $[Co(C_4H_4O_4)\cdot 2Py]\cdot 2H_2O(C_{14}CoH_{18}N_2O_6)$ (368.90 g/mol).

2. Co 15.08 (15.06), C 49.13 (49.12), H 2.84 (2.81), N 7.15 (7.16) for $[Co(C_4H_4O_4) \cdot Phen] \cdot 2H_2O(C_{16}CoH_{16}N_2O_6)$ (390.90 g/mol).

3. Nd 39.69 (39.66), C 19.85 (19.83), H 3.05 (3.03) for $[Nd_2(C_4H_4O_4)_3] \cdot 5H_2O$ ($C_{12}H_{22}Nd_2O_{17}$) (726.00 g/mol).

4. Nd 27.92 (27.91), C 13.94 (13.95), H 3.13 (3.10), N 5.43 (5.42) for $[Nd_2(C_4H_4O_4)_3 \cdot 2Phen] \cdot 2H_2O$ ($C_{36}H_{32}Nd_2N_4O_{14}$) (1032.00 g/mol).

5. Nd 21.09 (20.96), Co 8.50 (8.57), C 34.85 (34.94), H 3.43 (3.49), N 3.98 (4.07) for $[Co_2Nd_2(C_4H_4O_4)_5 \cdot 4Py] \cdot 4H_2O (C_{40}Co_2H_{48}Nd_2N_4O_{24})$ (1373.80 g/mol).

6. Nd 21.29 (20.31), Co 8.20 (8.30), C 37.25 (37.24), H 3.13 (3.10), N 3.93 (3.95) for [C o $_2$ N d $_2$ (C $_4$ H $_4$ O $_4$) $_5 \cdot 2$ P h e n] $\cdot 4$ H $_2$ O (C₄₄Co₂H₄₄Nd₂N₄O₂₄) (1417.80 g/mol).

In order to obtain data on the composition, structure, and thermal properties of the synthesized mono- and heterometallic complexes of cobalt and neodymium with succinic acid and pyridine or phenanthroline, IR spectra and diffuse reflection spectra were recorded and the elemental analysis, X-ray powder diffraction, differential thermal analysis were carried out.

The structure of the complexes $[Co(C_4H_4O_4)\cdot 2Py]\cdot 2H_2O$ was established by the



Fig. 1. Fragment of the molecular structure of the compound $[Co(C_4H_4O_4)\cdot 2Py]\cdot 2H_2O$ (a), and packing of the structural units of the crystals of the compound $[Co(C_4H_4O_4)\cdot 2Py]\cdot 2H_2O$ in projection along the c axis (b). H atoms have been omitted for clarity

method of X-ray structure analysis of single crystals. The unit cell of the complex is shown in Fig. 1.

It is seen that the complex has a chain structure with a cell $[Co(C_4H_4O_4) \cdot 2Py \cdot 2H_2O]$. The monodentate coordination of the carboxyl group to the metal atom is realized in the complex.

The IR spectra of the synthesized coordination compounds were compared with the IR spectra of succinic acid, pyridine and phenanthroline (Table 1). The IR spectrum of $[Co_2Nd_2(C_4H_4O_4)_52Phen]\cdot4H_2O$ is shown in Fig. 2. The assignment of vibration frequencies for all synthesized compounds is given in Table 1.



Fig. 2. IR spectrum of succinate heterocomplex $[Co_2Nd_2(C_4H_4O_4)_5 \cdot 2Phen] \cdot 4H_2O$

The assignment of the most important absorption bands in the IR spectra was carried out in accordance with the literature data for Co(II) and Nd(III) complexes with carboxylic acids [3–7,9,11]. Succinic acid in the complexes is in the ionized form, which is confirmed by the presence of vibration bands, the frequencies of which are assigned to asymmetric and symmetric vibrations of the deprotonated carboxyl group in the regions of 1610–1530 cm⁻¹ and 1440–1390 cm⁻¹, respectively.

It is known that the difference between $v_{as}(C-OO)$ and $v_s(C-OO)$ (v(C-OO)) of the carboxyl group COO⁻ in an ionized state can serve to determine the method of its coordination with the metal complexing agent [11]. The difference in the positions of the $v_{as}COO^-$ and v_sCOO^- bands is 229 cm⁻¹ and indicates monodentately coordinated COO⁻ groups of succinic acid, which is confirmed by the results of X-ray structure analysis of single crystals for the [Co(C₄H₄O₄)·2Py]·2H₂O (Table 1).

In the IR spectrum of $[Nd_2(C_4H_4O_4)_3] \cdot 5H_2O$, in the regions of $1610-1520 \text{ cm}^{-1}$ and $1465-1344 \text{ cm}^{-1}$, the bands of deprotonated carboxyl groups appear as doublet and triplet bands, which may indicate different ways of their coordination in the complex. For lanthanides, monodentate coordination is not typical; most often a bidentate mode of coordination is observed, which is realized in the case of neodymium succinate.

Analyzing the IR spectrum of

Table 1

Vibrational frequencies and their assignments in the IR spectra of the complexes of cobalt and neodymium succinates with phenanthroline or pyridine

	Assignments/frequencies, cm ⁻¹							
Compound	ν(М–О)	ν _{as} (C–OO), ν(H ₂ O)	v _s (C–OO)	ν(M–N)	δ(С–Н)	ν(H ₂ O), ν(C–H)		
$[Co(C_4H_4O_4)\cdot 2Py]\cdot 2H_2O$	434, 551, 645	1565, 1696	1467	724, 773	1153, 1231	3440		
$[Nd_2(C_4H_4O_4)_3]\cdot 5H_2O$	484, 596, 657, 695	1516, 1560	1410, 1430	-	1184, 1230	3450		
$[Co_2Nd_2(C_4H_4O_4)_5 \cdot 4Py] \cdot 4H_2O$	482, 517, 584, 620, 643, 675	1528, 1570	1383, 1430	740, 758	1168, 1260	3360		
$H_6C_4O_4$	—	1694	1400	_	1170	3400		
Ру	-				1100, 1220, 1590, 1618	3060		
$[Co(C_4H_4O_4)\cdot Phen]\cdot 2H_2O$	434, 551, 642	1565, 1696 sh.	1467	732	1153, 1230	2980, 3440		
$[\mathrm{Nd}_2(\mathrm{C}_4\mathrm{H}_4\mathrm{O}_4)_3{\cdot}2\mathrm{Phen}]{\cdot}2\mathrm{H}_2\mathrm{O}$	448, 528, 579, 648	1511, 1561, 1633 sh.	1424	730	1145, 1203	2920, 3405		
$[Co_2Nd_2(C_4H_4O_4)_5 \cdot 2Phen] \cdot 4H_2O$	430,521, 582, 639	1510, 1566, 1651 sh., 1680 sh.	1397	711	1185, 1305	2975, 3433		
Phen	—	-	-	-	1090, 1138, 1216	3060		

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 $[Co_2Nd_2(C_4H_4O_4)_5 \cdot 4Py] \cdot 4H_2O$, it can be seen that the difference in the position of the $v_{as}COO^-$ and v_sCOO^- bands is 140 cm⁻¹-145 cm⁻¹, i.e., the carboxyl groups are coordinated bidentately in the complex. A similar difference is observed for the phenanthroline heterocomplex

 $[Co_2Nd_2(C_4H_4O_4)_5 \cdot 2Phen] \cdot 4H_2O.$

Bands of metal-oxygen stretching vibrations are observed for all complexes in the spectra in the region of 400–650 cm⁻¹, and when comparing the spectra of monocomplexes with the spectrum of heterocomplexes, their slight shift is noted, which may be due to a slight distortion in the coordination environment of cobalt and neodymium.

In the region of 1000–1300 cm⁻¹, the bands of C–H bending vibrations assigned to δ (C–H) of succinic acid and δ (C–H) in the rings of pyridine or phenanthroline are observed.

In the region of $3400-3300 \text{ cm}^{-1}$, broad bands assigned to the vibrations of the O–H groups of water molecules are observed for all coordination compounds.

The diffuse reflection spectra of mono- and heterocomplexes were recorded to assess the geometry of the coordination environment of cobalt and neodymium in the studied complexes. Diffuse reflection spectra of samples of coordination compounds of cobalt (II) and neodymium (III) with succinic acid and phenanthroline in the near ultraviolet region (200–400 nm) are presented in Fig. 3. The bands corresponding to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions from the ground state (S₀) to the excited state (S₁) of ligand molecules are observed for all coordination compounds in this region.

In all cases, this band is extended and split into two components. Considering that pure phenanthroline is also characterized by the presence of bands of transition in the low-energy region, this may be due to the presence of two ligands in the composition of the complexes (succinic acid and phenanthroline) and is associated with the superposition of $\pi \rightarrow \pi^*$ bands of transition and bands of charge transfer from the ligand to the metal. A significant bathochromic shift and broadening of this band is observed in the spectrum of $[Co_2Nd_2(C_4H_4O_4)_5 \cdot 2Phen] \cdot 4H_2O$, which can indirectly confirm the formation of a heterometallic complex.

Let us consider the diffuse reflection spectra in the visible region for each complex separately in detail. Figure 4 shows the diffuse reflection spectrum of $[Co(C_4H_4O_4)\cdot Phen]\cdot 2H_2O$ in the range of 400– 800 nm, where one broad band is observed with a transition maximum at 19380 cm⁻¹, which is in the region characteristic of transitions for ion cobalt: ${}^{4}T_{1g}({}^{4}F) \rightarrow {}^{4}A_{2g}({}^{4}F)$, and ${}^{4}T_{1g}({}^{4}F) \rightarrow {}^{4}T_{1g}({}^{4}P)$ (18200– 23550 cm⁻¹). Based on the shape, intensity of the reflection spectrum, and the position of the single transition band for $[Co(C_4H_4O_4)\cdot Phen]\cdot 2H_2O$, we can assume that cobalt is in a curved octahedral environment.

The assignments of the characteristic bands of transitions for the mixed-ligand and heterometallic



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Table 2	2
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Transitions	Nd _{aq} ³⁺	[Nd ₂ (C ₄ H ₄ O ₄) ₃ ·2Phen]·2H ₂ O	$v_{\text{NdL}} - v_{\text{Ndaq}}, \text{ cm}^{-1}$	$[Co_2Nd_2(C_4H_4O_4)_5 \cdot 2Phen] \cdot 4H_2O$	$v_{hetero} - v_{NdL}, cm^{-1}$
${}^{4}I_{9/2} \rightarrow {}^{2}P_{1/2}$	23400	23245	-155	—	
${}^{4}I_{9/2} \rightarrow {}^{4}G_{9/2,11/2}$	21467	21623	156	—	-
${}^{4}I_{9/2} \rightarrow {}^{2}D_{3/2}, {}^{2}P_{3/2}$		20973		21132	159
${}^{4}I_{9/2} \rightarrow {}^{2}G_{9/2}, {}^{4}G_{7/2}$	19560, 19160	19504, 19054	-56, -106	19141	87
${}^{4}I_{9/2} \rightarrow {}^{2}G_{7/2} {}^{4}G_{5/2}$	17360	17285	-75	17231	-54
$^{4}I_{9/2} \rightarrow ^{2}H_{11/2}$		15949		—	-
${}^{4}I_{9/2} \rightarrow {}^{4}F_{9/2}$	14720	14681	-39	14845	164
${}^{4}I_{9/2} \rightarrow {}^{4}S_{3/2}, {}^{4}F_{7/2}$	13480	13441	-39	13618	177
${}^{4}I_{9/2} \rightarrow {}^{4}F_{5/2}, {}^{2}H_{9/2}$	12560, 12484	12537, 12415	-23, -69	12543	6
${}^{4}I_{9/2} \rightarrow {}^{4}F_{3/2}$	11561	11510	-51	_	—

Transition energies (cm⁻¹) in the diffuse reflection spectra of complexes $[Nd_2(C_4H_4O_4)_3\cdot 2Phen]\cdot 2H_2O$ and $[Co_2Nd_2(C_4H_4O_4)_5\cdot 2Phen]\cdot 4H_2O$

complexes of neodymium are given in Table 2.

The diffuse reflection spectrum of the mixedligand neodymium complex with succinic acid and phenanthroline, taken at room temperature for fine crystal samples, is presented in Fig. 5. It is known that lanthanides are characterized by narrow-line spectra, which are due to the weaker interaction of 4f-orbitals of lanthanides with electronic shells of ligands compared, for example, with 3d-metals. The study and analysis of the diffuse reflection spectra of lanthanides allows obtaining information about the structure and symmetry of the nearest coordination environment of the ion, since there is a shift and splitting of the characteristic transition bands during complexation.

The bands corresponding to the f-f transitions of the neodymium ion from the ground state are



 $[Nd_2(C_4H_4O_4)_3 \cdot 2Phen] \cdot 2H_2O$

present in the visible region of the spectrum for $[Nd_2(C_4H_4O_4)_3 \cdot 2Phen] \cdot 2H_2O$. The so-called «ultrasensitive» transition bands are usually chosen to consider the effect of the ligand field in the complexes. The most informative in the spectrum of neodymium complexes is the transition ${}^{4}I_{9/2} \rightarrow {}^{2}P_{1/2}$, due to the fact that the upper levels of this transition are not split in the fields of any symmetry. It is known that the value of the relative displacement of the transition bands depends on the nature of the lanthanide-ligand bond and can characterize deviations from the ionic type of bond. Comparing the presented spectrum with the spectrum of the aqua-ion of neodymium and calculating the value of the nepheloauxetic shift for the transition ${}^{4}I_{9/2} \rightarrow {}^{2}P_{1/2}$, the following can be concluded.

The presence of one unsplit band at 23245 cm⁻¹ indicates that only one type of compound (one absorption center) is present in the investigated complex. The long-wavelength shift of this band compared to the spectrum of the aqua-ion $(\Delta = 155 \text{ cm}^{-1})$ can be a confirmation of the increase in the covalency of the bond. Sinha's parameters are as follows: β =0.9934 and δ =0.66% [12]. They were calculated based on the position of the transition ${}^{4}I_{9/2} \rightarrow {}^{2}P_{1/2}$. The β value is close to 1, which may be an indication of the high ionicity of the Nd–O bond. At the same time, since the absolute value of δ is significantly less than 1.5%, the presence of a minor covalent component in the metal-ligand bond can be assumed. In addition, it is known that each type of connection corresponds to a certain value of the nepheloauxetic effect. For example, as a result of the addition of a dissociated carboxyl group, this band is shifted by 25 cm^{-1} [13]. In the case of simultaneous joining of several groups, the total

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displacement is approximately equal to the sum of all displacements that are characteristic of each individual group. The obtained value of the nepheloauxetic shift correlates well with the proposed structure of the complex $[Nd_2(C_4H_4O_4)_3 \cdot 2Phen] \cdot 2H_2O$, in which the central atom attaches three $-COO^-$ groups and two nitrogen atoms of phenathroline.

It is also possible to talk about the symmetry of the coordination environment of the central ion based on the shape and position of the bands of hypersensitive transitions in the region of 570– 620 nm. Thus, in the presented spectrum of $[Nd_2(C_4H_4O_4)_3\cdot 2Phen]\cdot 2H_2O$, the half-width of the «ultrasensitive» transition bands ${}^{4}I_{9/2} \rightarrow {}^{4}G_{5/2}$, ${}^{2}G_{7/2}$ is -169 cm^{-1} and $+287 \text{ cm}^{-1}$, which is characteristic for complexes with sufficiently high symmetry. At the same time, a slight long-wavelength shift (Δ =75 cm⁻¹) is observed with respect to the aqua-ion.

The ratio of the intensities of the «ultrasensitive» transition bands in the spectrum of a solid sample of a succinate of neodymium with phenanthroline at ${}^{4}I_{9/2} \rightarrow {}^{4}F_{5/2}, {}^{2}H_{9/2}$ and $I_{9/2} \rightarrow {}^{4}G_{5/2}, {}^{2}G_{7/2}$ is 0.94 (for neodymium nitrate -1.07), which may indicate a similar symmetry of the studied complex compared to the original lanthanide salt. Based on the received research data, it can be assumed that the coordination environment of neodymium is not cubic, but of lower symmetry.

Figure 6 shows the diffuse reflection spectrum of the heterometallic complex $[Co_2Nd_2(C_4H_4O_4)_5 \cdot 2Phen] \cdot 4H_2O$. There is an overlap of the transition bands that are present in the diffuse reflection spectra of monometallic complexes in the region of 400–550 nm discussed above. It is impossible to assign transition bands in this region.

The bands characteristic of the f-f transitions of the neodymium(III) ion $({}^{4}I_{9/2} \rightarrow {}^{2}G_{7/2}, {}^{4}G_{5/2};$ ${}^{4}I_{9/2} \rightarrow {}^{4}F_{9/2}; {}^{4}I_{9/2} \rightarrow {}^{4}F_{7/2};$ and ${}^{4}I_{9/2} \rightarrow {}^{2}H_{9/2})$ are clearly manifested in the region of higher energies, at the same time, they slightly shift (Δ =30-200 cm⁻¹) in comparison with the spectrum of



 $[Co_2Nd_2(C_4H_4O_4)_5 \cdot 2Phen] \cdot 4H_2O$

 $[Nd_2(C_4H_4O_4)_3 \cdot 2Phen] \cdot 2H_2O$ both in the region of low and high energies.

In addition, a significant increase in the intensities of the transition bands occurs, which may indirectly indicate the formation of heterometallic complexes. Based on the results of a comparison of the diffuse reflection spectra of mono- and heterometallic complexes, it can be concluded that significant changes in the coordination environment of the neodymium ion do not occur during the synthesis of heterometallic complexes, and slight shifts in the characteristic absorption bands can be explained by the distortion of the geometry of the coordination node during the formation of the heterometallic compound.

X-ray powder diffraction and differential thermal analysis were carried out in order to determine the final decomposition products of the synthesized heterometallic complex compounds. The thermal decomposition of the synthesized heterocomplexes is gradual and has a multistage character (Tables 3 and 4).

Complex oxides are formed after heating

Table 3

Thermal stability of the complexes $[Co(C_4H_4O_4)\cdot 2Py]\cdot 2H_2O$, $[Nd_2(C_4H_4O_4)_3]\cdot 5H_2O$ and $[Co_2Nd_2(C_4H_4O_4)_5\cdot 4Py]\cdot 4H_2O$

Compounds	Process and temperature region								
			decomposition						
	H ₂ O			Ру				found	
	t, ⁰ C	found,	calculated,	t ⁰ C	found,	calculated,	t, ⁰ C	10ulla,	
		%	%	ι, υ	%	%		/0	
$[Co(C_4H_4O_4)\cdot 2Py]\cdot 2H_2O$	145-230	10.0	9.7	230-400	42.9	42.8	400-520-800	22.0	
$[\mathrm{Nd}_2(\mathrm{C}_4\mathrm{H}_4\mathrm{O}_4)_3]\cdot 5\mathrm{H}_2\mathrm{O}$	100-260	12.8	12.4	300-400	_	_	440-750	41.8	
$\overline{[Co_2Nd_2(C_4H_4O_4)_5\cdot 4Py]\cdot 4H_2O}$	100-220	5.1	5.5	200-310	24.6	24.0	330-700	46.8	

Table 4

Compounds	Process and temperature region								
			Decomposition						
	H ₂ O			Ру					
	t, ⁰ C	found,	calculated,	+ ⁰ C	found, calculated,		t, ⁰ C	found, %	
		%	%	ι, υ	%	%			
$[Co(C_4H_4O_4)\cdot Phen]\cdot 2H_2O$	90–155	9.0	9.2	155-400	41.9	46.0	400-590-800	13.2	
$[Nd_2(C_4H_4O_4)_3 \cdot 2Phen] \cdot 2H_2O$	100-150	3.3	3.48	150-330	33.5	34.8	350-750	16.5	
$[Co_2Nd_2(C_4H_4O_4)_5 \cdot 2Phen] \cdot 4H_2O$	100-185	5.5	5.10	185-260	26.56	25.39	260-600	41.6	

Thermal stability of the complexes $[Co(C_4H_4O_4)\cdot Phen]\cdot 2H_2O$, $[Nd_2(C_4H_4O_4)_3\cdot 2Phen]\cdot 2H_2O$ and $[Co_2Nd_2(C_4H_4O_4)_5\cdot 2Phen]\cdot 4H_2O$

succinates without the formation of carbonates as intermediate products. This nature of decomposition is comparable to the process of thermolysis of succinic acid, which decomposes with the formation of succinic anhydride and water. The process of loss of water molecules, which is accompanied by an endothermic effect, is observed first for the complex $[Co(C_4H_4O_4)\cdot 2Py]\cdot 2H_2O$. The weight loss is 10%, which corresponds to 2 mol of coordinated water (theoretically 9.7%). Further weight loss is associated with the removal of molecules of pyridine, after which intense decomposition of cobalt succinate begins at temperatures above 400°C.

The dehydration of neodymium(III) succinate for the $[Nd_2(C_4H_4O_4)_3]$ ·5H₂O complex occurs in two following stages: first, adsorbed water is removed, and then water molecules that enter the inner coordination sphere of the metal ion are split off. After the loss of water (100–260°C), anhydrous neodymium succinate is stable in a wide temperature range (300–440°C), then its decomposition begins.

Dehydration temperatures for heterometallic succinate $[Co_2Nd_2(C_4H_4O_4)_5 \cdot 4Py] \cdot 4H_2O$ are in the range of $100-220^{\circ}C$, and this process is superimposed on the process of removal of the pyridine molecule. The complete destruction of the heterometallic complex occurs at 260°C. The fact that the thermal characteristics corresponding to the processes of dehydration and complete destruction of mono- and heterocomplexes are significantly different can be an additional confirmation of the formation of individual compounds.

Control of the phase composition of the obtained oxide powders was carried out using X-ray powder diffraction. The X-ray powder diffraction pattern of the sample of $[Co_2Nd_2(C_4H_4O_4)_5$ ·2Phen]·4H₂O was given earlier [14], and it was shown that the product of thermolysis is a complex oxide NdCoO₃ of cubic crystal system without extraneous phase inclusions.

Figure 7 shows X-ray powder diffraction pattern

of sample obtained by heating the heterocomplex $[Co_2Nd_2(C_4H_4O_4)_5 \cdot 2Py] \cdot 4H_2O$ at 800°C for 1 hour. The analysis of the obtained results of the X-ray powder diffraction showed that the product of heating the pyridine heterocomplex is a complex oxide NdCoO₃ of cubic crystal system with diffraction peaks with the value of $2\theta=23.40^{\circ}$, 33.35° , 41.45° , 48.00° , 59.80° , 70.25° , and 80.25° correspond to ICDD PDF-2 card No. 00-025-1047. The unit cell parameter a is calculated which is 7.56(7) Å, and the unit cell volume V=433.31(9) Å³ (standard values for NdCoO₃ are 7.546 Å and 429.69 Å³, respectively). The calculated size of NdCoO₃ crystallites (coherent scattering blocks) is 20-35 nm.

The composition of the product also includes two phases Nd_2O_3 of cubic and hexagonal crystal systems, as evidenced by the presence of recorded reflexes that correspond to the data of cards No. 00-021-0579 (Nd_2O_3 cubic crystal system) and No. 00-041-1089 (Nd_2O_3 hexagonal crystal system). Peaks with low intensity are also recorded, which correspond to the data of card No. 00-002-0770 –



Fig. 7. X-ray powder diffraction pattern of sample obtained by thermolysis of $[Co_2Nd_2(C_4H_4O_4)_5 \cdot 2Py] \cdot 4H_2O$ at 800°C

Synthesis and study of mixed-ligand heterometallic complexes of cobalt and neodymium succinates with pyridine or phenanthroline

 Co_2O_3 hexagonal crystal system.

It can be concluded from the obtained results that for preparation of pure neodymium cobaltate by heating of $[Co_2Nd_2(C_4H_4O_4)_5 \cdot 2Phen] \cdot 4H_2O$, the temperature in the range of 700-800°C is sufficient, whereas it is necessary to decompose the heterocomplex at a higher temperature (1000°C) for preparation of neodymium cobaltate by heating of $[Co_2Nd_2(C_4H_4O_4)_5 \cdot 4Py] \cdot 4H_2O$.

Conclusions

New heterometallic complexes of Co(II) and Nd(III) with succinic acid were synthesized in the presence of phenanthroline and pyridine. The complexes were characterized by the methods of IR spectroscopy and electronic diffuse reflection spectra. Their thermal properties and ability to form complex oxides during thermal destruction were studied. The compounds $[Co_2Nd_2(C_2H_4O_4)_5$ ·2Phen]·4H₂O and $[Co_2Nd_2(C_4H_4O_4)_5$ ·4Py]·4H₂O can be used as precursors to obtain neodymium cobaltate with lower energy costs than in solid-phase synthesis.

Acknowledgments

The work was carried out with the financial support of the National Academy of Sciences of Ukraine within the state budget theme 322E «Creation of new hybrid, composite and polymer materials doped with coordination compounds of 3d- and 4f- metals based on β -diketonate and carboxylate acyclic ligands». The state registration number of the work is 0122U001299.

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Received 20.03.2023

СИНТЕЗ І ДОСЛІДЖЕННЯ РІЗНОЛІГАНДНИХ ГЕТЕРОМЕТАЛІЧНИХ КОМПЛЕКСІВ СУКЦИНАТІВ КОБАЛЬТУ ТА НЕОДИМУ З ПІРИДИНОМ АБО ФЕНАНТРОЛІНОМ

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У роботі надано результати дослідження синтезу нових гетерометалічних комплексів Co(II) та Nd(III) з янтарною кислотою у присутності 1,10-фенантроліну або піридину. Синтезовано моно- та гетерокомплекси: $[Co(C_4H_4O_4)\cdot 2Py]\cdot 2H_2O$ та $[Co(C_4H_4O_4)\cdot Phen]\cdot 2H_2O;$ $[Nd_2(C_4H_4O_4)_3] \cdot 5H_2O_i$ $[Nd_2(C_4H_4O_4)_3 \cdot 2Phen] \cdot 2H_2O;$ $[Co_2Nd_2(C_4H_4O_4)_5 \cdot 4Py] \cdot 4H_2O$ Ta $[Co_2Nd_2(C_4H_4O_4)_5 \cdot 2Phen] \cdot 4H_2O$ (Phen – фенантролін, Ру –піридин). Здійснено дослідження їх складу, структури, термічних властивостей і визначення здатності гетерокомплексів утворювати складні оксиди. Комплекси охарактеризовані фізико-хімічними методами аналізу: елементним аналізом, ІЧ- спектроскопією та спектроскопією дифузного відбиття, рентгеноструктурним та диференціальним термічним аналізом. На основі аналізу спектрів дифузного відбиття та ІЧ-спектрів гетерокомплексів показано, що янтарна кислота та 1,10-фенантролін зв'язані бідентатно з атомами металів. Метали з'єднуються бурштиновою кислотою, утворюючи ланцюг. Порошки оксидів одержано при нагріванні гетерокомплексів до 800⁰С. Склад синтезованих гетерометалічних сполук контролювався методом рентгеноструктурного аналізу. Показано, що при нагріванні гетерокомплексу з фенантроліном $[Co_2Nd_2(C_4H_4O_4)_5 \cdot 2Phen] \cdot 4H_2O_3 \cdot 2Phen] \cdot 4H_2O_3 \cdot 2Phen \cdot 2Phe$ до 800°С утворюється складний оксид NdCoO₃ (кубічна кристалічна сингонія), без домішок. При нагріванні гетерокомплексу з піридином $[Co_2Nd_2(C_4H_4O_4)_5 \cdot 4Py] \cdot 4H_2O$, крім складного оксиду NdCoO₃, одержують оксиди Nd₂O₃ (гексагональна кристалічна сингонія), Nd₂O₃ (кубічна кристалічна сингонія) та оксид Со₃О₄ (кубічна кристалічна сингонія). Гетерокомплекс $[Co_2Nd_2(C_4H_4O_4)_5 \cdot 2Phen] \cdot 4H_2O$ може бути використаний як прекурсор для синтезу кобальтату неодиму з меншими енергетичними витратами, ніж при твердофазному синтезі.

Ключові слова: гетерометалічний комплекс, неодим, кобальт, бурштинова кислота, фенантролін, піридин, складні оксиди.

SYNTHESIS AND STUDY OF MIXED-LIGAND HETEROMETALLIC COMPLEXES OF COBALT AND NEODYMIUM SUCCINATES WITH PYRIDINE OR PHENANTHROLINE

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The paper reports the results of the study on the synthesis of new heterometallic complexes of Co(II) and Nd(III) with succinic acid in the presence of 1,10-phenanthroline or pyridine. The following hetero- and monocomplexes were synthesized: $[Co(C_4H_4O_4)\cdot 2Py]\cdot 2H_2O$ and $[Co(C_4H_4O_4)\cdot Phen]\cdot 2H_2O;$ $[Nd_2(C_4H_4O_4)_3] \cdot 5H_2O$ and $[Nd_2(C_4H_4O_4)_3 \cdot 2Phen] \cdot 2H_2O$; $[Co_2Nd_2(C_4H_4O_4)_5 \cdot 4Py] \cdot 4H_2O$ and $[Co_2Nd_2(C_4H_4O_4)_5 \cdot 2Phen] \cdot 4H_2O$ (Phen – phenanthroline, and Py – pyridine). The study of their composition, structure, thermal properties and determination of the ability of heterocomplexes to form complex oxides was carried out. The complexes were characterized by a number of physicochemical methods: elemental analysis, IR- and diffuse reflection spectroscopies, X-ray powder diffraction and differential thermal analysis. Based on the analysis of diffuse reflection spectra and IR spectra of heterocomplexes, it was shown that succinic acid and 1,10-phenanthroline are bidentately bound to metal atoms. The metals are connected by succinic acid, forming a chain. Oxide powders were obtained during thermolysis of heterocomplexes up to 800°C. The composition of the synthesized heterometallic compounds was controlled by X-ray powder diffraction. It was shown that a complex oxide of NdCoO₃ (cubic crystal system), without impurities, was formed, when the heterocomplex of phenanthroline [Co₂Nd₂(C₄H₄O₄)₅·2Phen]·4H₂O was heated to 800°C. When heating the heterocomplex of pyridine $[Co_2Nd_2(C_4H_4O_4)_5 \cdot 4Py] \cdot 4H_2O$, in addition to the complex oxide NdCoO₃, oxides Nd₂O₃ (hexagonal crystal system), Nd₂O₃ (cubic crystal system) and Co_3O_4 oxide (cubic crystal system) were formed. The heterocomplex $[Co_2Nd_2(C_4H_4O_4)_5 \cdot 2Phen] \cdot 4H_2O$ can be used as a precursor for the synthesis of cobaltate of neodymium with lower energy costs than in solid-phase synthesis.

Keywords: heterometallic complex; neodymium; cobalt; succinic acid; phenanthroline; pyridine; complex oxide.

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