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*O.K. Trunova, L.I. Zheleznova, V.V. Dyakonenko, L.I. Sliusarchuk***CRYSTAL STRUCTURE OF THE HETEROMETALLIC COMPLEX OF Co(II) AND Nd(III) WITH PHENANTHROLINE****V.I. Vernadsky Institute of General and Inorganic Chemistry of the NAS of Ukraine, Kyiv, Ukraine**

A new heterometallic complex of Co<sup>II</sup> and Nd<sup>III</sup> with phenanthroline [Co(Phen)<sub>3</sub>][Nd(NO<sub>3</sub>)<sub>5</sub>(H<sub>2</sub>O)][Nd(NO<sub>3</sub>)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>] $\cdot$ H<sub>2</sub>O was synthesized for the first time by the self-assembly method. The crystal structure of the complex was determined by X-ray crystallography. The compound is an anion-cation complex and crystallizes in the monoclinic space group P2<sub>1</sub>/n with unit cell parameters a=12.4251(4) Å, b=11.7206(3) Å, c=36.5374(12) Å.  $\alpha=\gamma=90^\circ$ ,  $\beta=90.581(3)^\circ$ . In the crystalline phase, the complex is in the form of a crystal hydrate with a composition of 1:1. The anionic part of the complex consists of two nitrate hydrated Nd<sup>III</sup> complexes: [Nd(NO<sub>3</sub>)<sub>5</sub>(H<sub>2</sub>O)]<sup>2-</sup> and [Nd(NO<sub>3</sub>)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>-</sup>, in which the coordination number of neodymium is 11 and 10, respectively. The [Co(Phen)<sub>3</sub>]<sup>3+</sup> ion is a cationic part of the complex in which the Co<sup>II</sup> atom has a distorted CoN<sub>6</sub> octahedral environment, bidentately coordinating three phenanthroline molecules. Due to intermolecular hydrogen bonds (N–H $\cdots$ O, O–H $\cdots$ O), a three-dimensional supramolecular architecture is formed in the crystal, in which the polymer layers are packed parallel along the crystallographic axis a.

**Keywords:** heterometallic complexes, cobalt, neodymium, phenanthroline, crystal structure.**DOI:** 10.32434/0321-4095-2024-156-5-104-110**Introduction**

Analysis of the scientific literature devoted to the problems of modern coordination chemistry shows that the attention of researchers has shifted from classic monomeric to heteronuclear complexes (HMC), which is mainly due to intensive searches for new functional materials: optical and magnetic, biologically active substances, chemical sensors, catalysts of technological and biochemical processes [1–4]. Due to the combination in HMC of metals of different nature (3d-4f- or 4f-4f) with various organic ligands, the final characteristics of the synthesized materials are significantly improved through the synergistic effect. By changing the qualitative and quantitative composition of metals and donor ligands, it is possible to produce a large number of new compounds with a set of certain functional properties.

Among the large number of heterometallic complexes, the most studied are 3d-3d and 3d-4f complexes. For example, Yin and Sun [5] studied

the phenanthroline tetranuclear HMCs of Tb<sup>III</sup> and Zn<sup>II</sup> with benzophenone (Bzo, L<sup>1</sup>) and the 3-thiophene carboxylate (TPA, L<sup>2</sup>) composition [Tb<sub>2</sub>Zn<sub>2</sub>(L<sup>1,2</sup>)<sub>10</sub>(Phen)<sub>2</sub>]. The Zn atoms in complexes are coordinated by two nitrogen atoms from one Phen ligand, four oxygen atoms from two bidentate bridging and a tridentate chelating-bridging carboxylate group. However, the coordination spheres around the Tb atoms are different. Each Tb atom in the benzoate complex is eight-coordinate and it is bonded to four oxygen atoms of three tridentate Bzo chelate bridging groups, two oxygen atoms of two bidentate Bzo bridging groups, and two O atoms of one bidentate Bzo chelate group. In the complex with TPA, each Tb atom is seven-coordinated and bound to two oxygen atoms of the TPA chelate group, four oxygen atoms from four bridging TPA molecules, and one oxygen atom from one tridentate chelate bridging TPA group. Both complexes exhibit a green emission when irradiated with UV light. Compared to binary terbium benzoate,

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the introduction of  $Zn^{2+}$  and Phen ions sharply increases the luminescence intensity.

Prior et al. [6] synthesized complex  $[Ni(Phen)_2(H_2O)_2](NO_3)_2$  with a rather complex architecture. A huge asymmetric block containing six discrete  $[Ni(Phen)_2(H_2O)_2]^{2+}$  cation ensembles and 12 nitrate anions was found in its crystal structure. Due to O–H...O and CH...O bonds between metal complexes and nitrate, a bent 2-D chain structure is formed. It was found that the crystal structure is preserved at room temperature (291 K), but heating the sample to 308 K leads to a simplification of the structure associated with the elimination of nitrate ordering due to differences in the location of hydrogen bonds, while the coordination of the metal remains unchanged.

Similar nickel phenanthroline complexes with other acid anions ( $[Ni(Phen)_2(H_2O)_2](ClO_4)_2 \cdot 4H_2O$ ,  $[Ni(Phen)_2(H_2O)_2](SO_4) \cdot 5.6H_2O$ ) were obtained [7,8], although these structures have simpler asymmetric links, which consist of either half or one cationic cluster with counter anions of tetrahedral geometry (in contrast to the triangular planar nitrate anion).

New heterometallic nitrate complexes,  $[Ni(bipy)_3][Yb(NO_3)_5] \cdot 0.58MeOH$  (I),  $[Ni(phen)_3][Yb(NO_3)_5]$  (II) and  $[Ni(phen)_3][Yb(NO_3)_5] \cdot MeOH$  (II·MeOH), were prepared and studied [9]. Anions  $[Yb(NO_3)_5]^{2-}$  in these complexes are the first examples of homoleptic ten-coordinated Yb complexes. The magnetic behavior of single-phase complexes I and II was studied in static and dynamic modes. A field-induced slowdown of magnetic relaxation, i.e., properties of single-ion magnets (SIMs), was revealed for I and II [9].

Direct self-assembly reaction of the neutral dicyano-bis(1,10-phenanthroline) iron(II) complex ( $[Fe(Phen)_2(CN)_2]$ ) as a ligand with lanthanide nitrates and triflates  $Ln(CF_3SO_3)_3 \cdot nH_2O$  ( $Ln=Eu^{III}$ ,  $Gd^{III}$ ,  $Er^{III}$ ) leads to the formation of two different classes of 3d-4f heterometallic compounds with cyano-bridging architecture [10]. The bidentate nitrate anion results in the formation of tetranuclear structures with a  $Fe_2Ln_2$  core of square topology and only one water molecule in the lanthanide coordination sphere. The more sterically demanding triflate acts as an O-monodentate ligand to the lanthanide ion, thus leaving several coordination positions open for the coordination of water molecules, which in turn participate in an extensive network of hydrogen bonds, resulting in the formation of an unusual 1D coordination polymer. The different structural motifs have important consequences for the thermal stability of the compounds when the polymer assembly begins to degrade at much higher temperatures than the oligomer.

For both classes of heterometallic compounds, noticeable negative optical chromism is observed for the iron(II) metal ligand, accompanied by a pronounced color change from dark purple to red, both in acetonitrile solution and in the solid state. It was suggested [10] that this is due to the geometry of the CN–Ln bridge, which deviates significantly from linearity in the polymer assembly. The results obtained open up new prospects for the architectural construction of 3d-4f heterometallic compounds, which are of current interest for the development of mono- and multifunctional magnetic/optical materials, including single-molecule magnets and chemical sensors. In such systems, replacement of coordinated water molecules with suitable chelating agents/organic ligands also represents an excellent opportunity to expand and improve their functionality and application potential [10].

In continuation of studies of heterometallic 3d-4f complexes with O,N-donor ligands [11], this work presents a study of the crystal structure of a new heterometallic complex of  $Co^{II}$  and  $Nd^{III}$  with phenanthroline, which can subsequently serve as a precursor for the production of a complex oxide such as  $LnMO_3$  as a catalyst in the decomposition process peroxide compounds.

### Experimental

#### Materials and methods

Neodymium nitrates  $Nd(NO_3)_3 \cdot 6H_2O$  and cobalt  $Co(NO_3)_2 \cdot 6H_2O$  were used as starting salts for the synthesis of the heterometallic complex. Phenanthroline (Phen) was purchased from Sigma-Aldrich. All chemicals were of analytical purity and were used without further purification. The solutions of the salts of required concentration were prepared using samples of reagents with exact weights. The required pH value was set with a 10% solution of ammonium hydroxide  $NH_4OH$ . The pH value was recorded on a Mettler Toledo Seven Easy pH meter (with accuracy of  $\pm 0.05$ ) at a temperature of  $20 \pm 3^\circ C$ .

The synthesized complex was identified by the methods of elemental analysis and IR spectroscopy. The content of C, H, and N was determined on a Perkin-Elmer CHN 2400 analyzer. The metal content was determined by atomic absorption using a Philips Pye Unicam 8000 atomic absorption spectrophotometer. IR spectra were recorded on a Specord-M 80 spectrometer in the spectral range of  $4000-400\text{ cm}^{-1}$  in the form of tablets with KBr. KBr was previously calcined to remove water of crystal hydrate.

#### Synthesis

The heterometallic complex  $[Co(Phen)_3][Nd(NO_3)_5(H_2O)][Nd(NO_3)_4(H_2O)_2] \cdot H_2O$

was synthesized via self-assembly using the following method. Up to 10 ml of a warm (50°C) aqueous solution, which contained a mixture of cobalt nitrates and neodymium with a concentration of 0.15 mol/l of each salt, was added to 20 ml of an ethanolic solution of phenathroline (C=0.15 mol/l). The solution was intensively stirred for 30 min at a constant pH (approximately 5.5), which was controlled by adding 10% NH<sub>4</sub>OH solution. The resulting solution was left in a closed flask at room temperature (20±3°C) in the dark. After 4 days, bright pink crystals (with a yield of 50%) of the composition C<sub>36</sub>H<sub>32</sub>CoN<sub>15</sub>Nd<sub>2</sub>O<sub>31</sub> (according to the X-ray structural analysis) was precipitated from the solution.

For C<sub>36</sub>H<sub>32</sub>CoN<sub>15</sub>Nd<sub>2</sub>O<sub>31</sub> (M=1518.17): anal. calc. (%): C 28.45; H 2.11; N 13.83; Co 3.89; Nd 18.97. Found (%): C 28.52; H 2.18; N 13.96; Co 4.03; Nd 19.02. FT-IR (KBr, cm<sup>-1</sup>): 3243, 3427 (ν(H<sub>2</sub>O)); 3030, 2950, 2875 (ν(N-H)); 1415, 1386 (ν<sub>as</sub>(NO)); 1068, 1038, 1008 (δ(OH)<sub>coord.</sub>); 852, 840, 796, 720 (δ(NO)); 516, 531, 575, 638 (n(MO)); 443, 465, 482 (ν(MN)).

#### X-ray structural study

X-ray diffraction data of compound [Co(Phen)<sub>3</sub>][Nd(NO<sub>3</sub>)<sub>5</sub>(H<sub>2</sub>O)][Nd(NO<sub>3</sub>)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>·H<sub>2</sub>O (I) were collected on a Bruker APEX-II CCD diffractometer (graphite monochromated MoK<sub>α</sub> radiation, ω-scanning). The structure was solved using SHELXT [12] and refined using SHELXL [13] programs implemented in Olex2 software [14]. Full-matrix least-squares refinement against F<sup>2</sup> in anisotropic approximation was used for the non-hydrogen atoms. Positions of the hydrogen atoms were located from electron density difference maps and refined by the «riding» model with U<sub>iso</sub>=n U<sub>eq</sub> of the carrier atom (n=1.5 for water and n=1.2 for

other hydrogen atoms).

The structure of [Co(phen)<sub>3</sub>][Nd(NO<sub>3</sub>)<sub>5</sub>(H<sub>2</sub>O)][Nd(NO<sub>3</sub>)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>·H<sub>2</sub>O (Table 1) contains disorder of the two (NO<sub>3</sub>)<sup>-</sup> ions of the [Nd(NO<sub>3</sub>)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>-</sup> anion at two positions. All N–O bond distances were restrained to be similar to each other (within a standard deviation of 0.002 Å) and with a target value of 1.25 Å. The U<sub>ij</sub> values of the disordered O and N atoms were restrained to be similar to each other (within a standard deviation of 0.02 Å<sup>2</sup>). The disorder ratio was 50:50%.

Final atomic coordinates, geometrical parameters and crystallographic data have been deposited to the Cambridge Crystallographic Data Centre, 11 Union Road, Cambridge, CB2 1EZ, UK (<https://www.ccdc.cam.ac.uk/structures/>) and are available on request quoting the deposition number CCDC 2363478.

#### Results and discussion

According to the results of X-ray diffraction study, the compound [Co(Phen)<sub>3</sub>][Nd(NO<sub>3</sub>)<sub>5</sub>(H<sub>2</sub>O)][Nd(NO<sub>3</sub>)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>·H<sub>2</sub>O is an anion-cation complex compound with two different complexes [Nd(NO<sub>3</sub>)<sub>5</sub>(H<sub>2</sub>O)]<sup>2-</sup> and [Nd(NO<sub>3</sub>)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>-</sup> as anions and [Co(Phen)<sub>3</sub>]<sup>3+</sup> as cation. In the crystal phase, the complex (I) exists in a crystal hydrate of the composition 1:1. The complex crystallizes in the monoclinic space group P2<sub>1</sub>/n with unit cell parameters a=12.4251(4) Å, b=11.7206(3) Å, c=36.5374(12) Å, α=γ=90°, β=90.581(3)° (Table 1).

This structure contains three crystallographically distinct metal cations Nd1, Nd2 and Co1. The anions of the complex, consisting of hydrated Nd<sup>III</sup> nitrates, have different structures. In the [Nd(NO<sub>3</sub>)<sub>5</sub>(H<sub>2</sub>O)]<sup>2-</sup> anion, the Nd1 atom is bidentately bonded to the

Table 1

Crystal data and structure refinement for the complex C<sub>36</sub>H<sub>32</sub>CoN<sub>15</sub>Nd<sub>2</sub>O<sub>31</sub>

| Empirical formula                      | C <sub>36</sub> H <sub>32</sub> CoN <sub>15</sub> Nd <sub>2</sub> O <sub>31</sub> | Z                          | 4      |
|--|---|----------------------------|--------|
| D <sub>calc.</sub> , g/cm <sup>3</sup> | 1.895   | Measured refl.             | 35273  |
| μ, mm <sup>-1</sup>                    | 2.341   | Independent refl.          | 10451  |
| Formula weight                         | 1518.17   | Refl. I≥2 σ(I)             | 6088   |
| T, K                                   | 296.15  | R <sub>int</sub>           | 0.0981 |
| Crystal system                         | monoclinic  | Parameters                 | 843    |
| Space group                            | P2 <sub>1</sub> /n  | Restraints                 | 163    |
| a, Å                                   | 12.4251(4)  | Largest peak               | 1.140  |
| b, Å                                   | 11.7206(3)  | Deepest hole               | -1.019 |
| c, Å                                   | 36.5374(12)   | GooF                       | 0.919  |
| α, °                                   | 90  | wR <sub>2</sub> (all data) | 0.1149 |
| β, °                                   | 90.581(3)   | wR <sub>2</sub>            | 0.1018 |
| γ, °                                   | 90  | R <sub>1</sub> (all data)  | 0.1127 |
| V, Å <sup>3</sup>                      | 5320.7(3)   | R <sub>1</sub>             | 0.0529 |

oxygen atoms of 5  $\text{NO}_3^-$  ions (O1–O2, O4–O5, O7–O8, O10–O11, and O13–O14) and monodentately to the oxygen O16 of one water molecule. The Nd1 atom has a coordination number of 11 (Fig. 1a) with a maximum deviation from  $180^\circ$  of the diagonal bond angles O2–Nd1–O11= $175.47(17)^\circ$ , O4–Nd1–O13= $172.80(19)^\circ$  and O2–Nd1–O10= $151.5(2)^\circ$ . In this case, four nitrate ions are located in the equatorial plane of the polyhedron, and the fifth anion  $\text{NO}_3^-$  occupies an axial position with the vertex angle O7–Nd1–O8= $48.58(18)^\circ$ . The water molecule occupies an axial position (O16–Nd1–O7= $172.3(2)^\circ$ , and O16–Nd1–O8= $128.3(2)^\circ$  (Table 2).

In the  $[\text{Nd}(\text{NO}_3)_4(\text{H}_2\text{O})_2]^-$  anion, the Nd2 atom has a coordination number of 10 due to the coordination of eight oxygen atoms (O17, O18, O20, O21, O23A, O23B, O26A, and O26B) of four  $\text{NO}_3^-$  ions and two oxygen atoms (O28 and O29) of two water molecules (Fig. 1b). The Nd2 coordination polyhedron corresponds to a distorted double-capped square antiprism, in which the oxygen atoms of nitrate anions are located at the vertices of the distorted square antiprism, and the O atoms of two water molecules occupy a place above the square faces of the antiprism. The phenanthroline complex of cerium  $[\text{CePhen}_4(\text{MeCN})_2]$  has a similar structure [15]. The values of Nd–O bond lengths in the coordination polyhedra vary in the range 2.452(5)–2.639(7) Å (Table 2). It should be noted that the lengths of the Nd1 bonds with nitrate oxygen atoms located in the equatorial plane differ only slightly from each other, but the length of the Nd1–O<sub>water</sub> bond is slightly

shorter than the lengths of the Nd1–O<sub>nitrate</sub> bonds, which is apparently due to the axial distortion of the neodymium coordination polyhedron. In the  $[\text{Nd}(\text{NO}_3)_4(\text{H}_2\text{O})_2]^-$  anion, the average Nd–O<sub>nitrate</sub> bond distance (2.565 Å) is less than the corresponding value for the  $[\text{Nd}(\text{NO}_3)_5(\text{H}_2\text{O})]^{2-}$  anion (2.572 Å), which is due to different geometry of the lanthanide coordination sphere.

In the  $[\text{Co}(\text{Phen})_3]^{3+}$  cation, the Co1 atom is located in the octahedral  $\text{CoN}_6$  environment, bidentately coordinating three phenanthroline molecules (Fig. 1c). Phenanthroline ligands adopt the expected chelate coordination mode with chelation angles N1–Co1–N2, N1–Co1–N3, N2–Co1–N6, N3–Co1–N4, N4–Co1–N5, and N5–Co1–N6 in the range of  $84.2(2)$ – $89.9(2)^\circ$ . At the same time, the values of the N–Co–N bond angles have minimal deviations from  $90^\circ$ , which indicates a slight distortion of the octahedral cobalt polyhedron. The Co–N bond lengths are close to each other and varies within 1.932(5)–1.959(5) Å with an average value of 1.940 Å and a standard deviation of 0.007 Å (Table 1).

In the crystal structure of the complex, intramolecular (O–H...O) and intermolecular (N–H...O) hydrogen bonds are observed, the lengths of which are in the range of 1.88–2.06 Å and 2.675(9)–2.856(8) Å, respectively (Table 3).

Due to hydrogen bonds, anions, cations and water molecules in the crystal are combined into a three-dimensional supramolecular architecture, in which the polymer layers are packed parallel along the crystallographic *a*-axis (Fig. 2). It should also be

Table 2

Selected bond distances (d) and angles (θ) for the complex  $\text{C}_{36}\text{H}_{32}\text{CoN}_{15}\text{Nd}_2\text{O}_{31}$ 

| Bond    | d, Å     | Bond     | d, Å      | Angles     | θ, °       |
|---------|----------|----------|-----------|------------|------------|
| Co1–N1  | 1.944(5) | Nd1–O16  | 2.512(5)  | N2–Co1–N1  | 84.5(2)    |
| Co1–N2  | 1.937(5) | Nd2–O17  | 2.596(5)  | N2–Co1–N5  | 93.3(2)    |
| Co1–N3  | 1.934(6) | Nd2–O18  | 2.568(5)  | N3–Co1–N1  | 89.2(2)    |
| Co1–N4  | 1.932(5) | Nd2–O20  | 2.558(5)  | N3–Co1–N2  | 93.0(2)    |
| Co1–N5  | 1.959(5) | Nd2–O21  | 2.629(7)  | N3–Co1–N5  | 93.1(2)    |
| Co1–N6  | 1.936(5) | Nd2–O22A | 2.639(11) | N4–Co1–N1  | 92.6(2)    |
| Nd1–O1  | 2.568(6) | Nd2–O22B | 2.549(13) | N4–Co1–N3  | 84.3(2)    |
| Nd1–O2  | 2.615(5) | Nd2–O23A | 2.574(11) | N4–Co1–N5  | 89.8(2)    |
| Nd1–O4  | 2.644(5) | Nd2–O23B | 2.598(13) | N4–Co1–N6  | 93.0(2)    |
| Nd1–O5  | 2.535(5) | Nd2–O25A | 2.518(2)  | N6–Co1–N1  | 94.2(2)    |
| Nd1–O7  | 2.545(5) | Nd2–O25B | 2.519(2)  | N6–Co1–N2  | 89.9(2)    |
| Nd1–O8  | 2.553(6) | Nd2–O26A | 2.518(2)  | N6–Co1–N5  | 83.6(2)    |
| Nd1–O10 | 2.540(6) | Nd2–O26B | 2.519(2)  | O2–Nd1–O11 | 175.47(17) |
| Nd1–O11 | 2.577(5) | Nd2–O28  | 2.490(5)  | O4–Nd1–O13 | 172.80(19) |
| Nd1–O13 | 2.607(6) | Nd2–O29  | 2.452(5)  | O2–Nd1–O10 | 151.5(2)   |
| Nd1–O14 | 2.535(5) | Nd1–N9   | 2.977(7)  | O16–Nd1–O8 | 128.3(2)   |



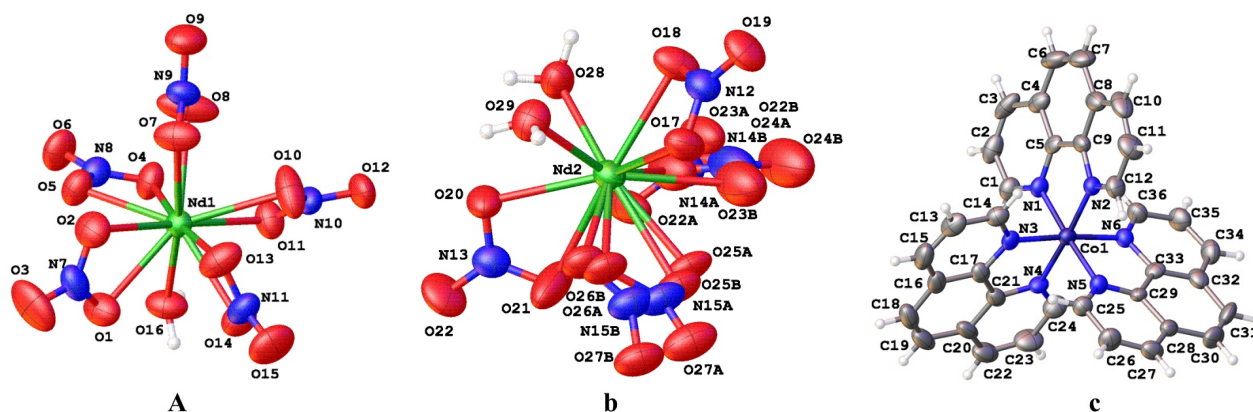


Fig. 1. The molecular structure of  $[\text{Nd}(\text{NO}_3)_5(\text{H}_2\text{O})]^{2-}$  (a) and  $[\text{Nd}(\text{NO}_3)_4(\text{H}_2\text{O})_2]^{-}$  (b) anions and  $[\text{Co}(\text{phen})_3]^{3+}$  cation (c) in compound  $[\text{Co}(\text{Phen})_3][\text{Nd}(\text{NO}_3)_5(\text{H}_2\text{O})][\text{Nd}(\text{NO}_3)_4(\text{H}_2\text{O})_2]\cdot\text{H}_2\text{O}$

Table 3  
Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ ) for compound  
 $\text{C}_{36}\text{H}_{32}\text{CoN}_{15}\text{Nd}_2\text{O}_{31}$

| D–H $\cdots$ A                     | H $\cdots$ A | D $\cdots$ A | D–H $\cdots$ A |
|------------------------------------|--------------|--------------|----------------|
| O28–H28A $\cdots$ O6 <sup>a</sup>  | 2.01         | 2.730(8)     | 134.4          |
| O29–H29A $\cdots$ O30              | 1.88         | 2.675(9)     | 148.9          |
| O29–H29B $\cdots$ O19 <sup>b</sup> | 2.00         | 2.856(8)     | 161.1          |
| O16–H16A $\cdots$ O3 <sup>c</sup>  | 2.06         | 2.823(8)     | 149.7          |

Notes: <sup>a</sup> – symmetry codes:  $x, y-1, z$ ; <sup>b</sup> – symmetry codes:  $-x+1, -y-1, -z+1$ ; <sup>c</sup> – symmetry codes:  $-x+1/2, y+1/2, -z+3/2$ .

noted that anions and water molecules are connected by a network of intermolecular hydrogen bonds N–H $\cdots$ O, which strengthen the three-dimensional polymer structure.

### Conclusions

A synthetically new heterometallic nitrate complex of  $\text{Co}^{\text{II}}$  and  $\text{Nd}^{\text{III}}$  with phenantroline  $[\text{Co}(\text{Phen})_3][\text{Nd}(\text{NO}_3)_5(\text{H}_2\text{O})][\text{Nd}(\text{NO}_3)_4(\text{H}_2\text{O})_2]\cdot\text{H}_2\text{O}$  was synthesized for the first time. Its crystal structure was determined by X-ray structural analysis. The complex is an anion-cation compound and consists of two nitrate hydrated  $\text{Nd}^{\text{III}}$  anion complexes:  $[\text{Nd}(\text{NO}_3)_5(\text{H}_2\text{O})]^{2-}$  (I) and  $[\text{Nd}(\text{NO}_3)_4(\text{H}_2\text{O})_2]^{-}$  (II) and a cation  $[\text{Co}(\text{Phen})_3]^{3+}$ . In anions,  $\text{Nd}^{\text{III}}$  atoms are bidentately bound to nitrate ions and monodentately to water molecules. The coordination number of  $\text{Nd}^{\text{III}}$  is 11 and 10 in anion (I) and (II), respectively. This is due to the different number of coordinated ligands. In the  $[\text{Co}(\text{Phen})_3]^{3+}$  cation, the  $\text{Co}^{\text{II}}$  atom is coordinated by three phenanthroline molecules. The coordination polyhedron of the Co atom is a distorted octahedron. The complex has a branched network of intra- and intermolecular hydrogen bonds that unite anions, cations and water molecules into a three-dimensional polymer. Thus,

the complex is a rare example of a 3d-4f coordination compound that has a discrete structure rather than a joint metal core.

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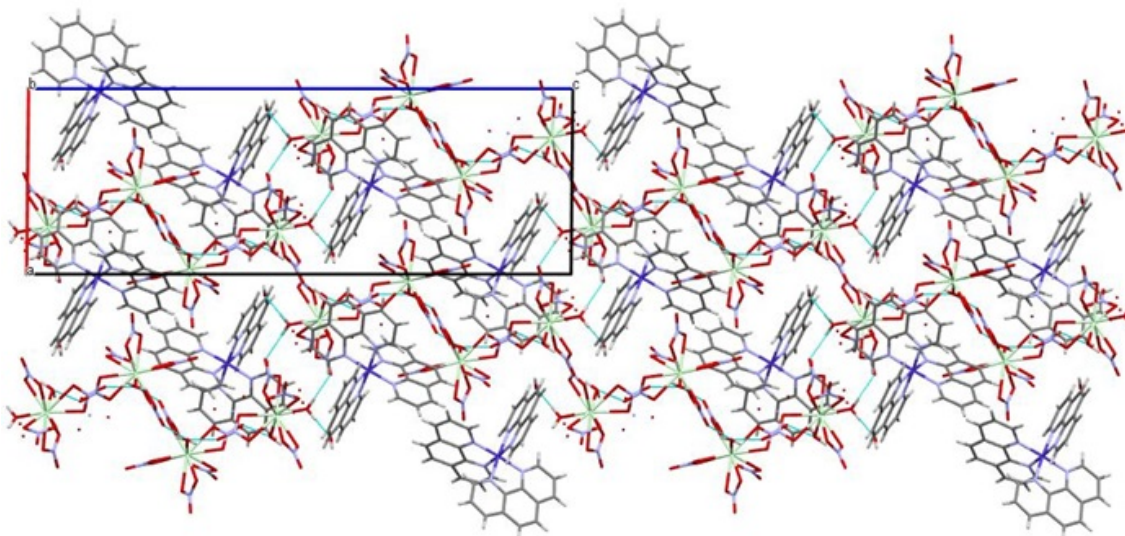


Fig. 2. Crystal packaging of complex  $[\text{Co}(\text{Phen})_3][\text{Nd}(\text{NO}_3)_5(\text{H}_2\text{O})][\text{Nd}(\text{NO}_3)_4(\text{H}_2\text{O})_2]\cdot\text{H}_2\text{O}$ .  
View along the crystallographic axis  $a$

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### КРИСТАЛІЧНА СТРУКТУРА ГЕТЕРОМЕТАЛІЧНОГО КОМПЛЕКСУ Co(II) ТА Nd(III) З ФЕНАНТРОЛІНОМ

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Методом самозбірки вперше синтезовано новий гетерометалічний комплекс  $\text{Co}^{\text{II}}$  та  $\text{Nd}^{\text{III}}$  з фенантроліном  $[\text{Co}(\text{Phen})_3][\text{Nd}(\text{NO}_3)_5(\text{H}_2\text{O})][\text{Nd}(\text{NO}_3)_4(\text{H}_2\text{O})_2]\cdot\text{H}_2\text{O}$ . Кристалічна структура комплексу визначена методом рентгенівської кристалографії. Сполука являє собою аніон-катионний комплекс і кристалізується в моноклінній просторовій групі  $\text{P}2_1/\text{n}$  з параметрами елементарної комірки  $a=12,4251(4)$  Å,  $b=11,7206(3)$  Å,  $c=36,5374(12)$  Å,  $\alpha=\gamma=90^\circ$ ,  $\beta=90,581(3)^\circ$ . У кристалічній фазі комплекс знаходиться у вигляді кристалогідрату складу 1:1. Аніонна частина комплексу складається з двох нітратних гідратованих комплексів  $\text{Nd}^{\text{III}}$ :  $[\text{Nd}(\text{NO}_3)_5(\text{H}_2\text{O})]^{2-}$  та  $[\text{Nd}(\text{NO}_3)_4(\text{H}_2\text{O})_2]^-$ , в яких координаційне число неодиму становить 11 і 10, відповідно. Іон  $[\text{Co}(\text{Phen})_3]^{3+}$  є катіонною частиною комплексу, в якому атом  $\text{Co}^{\text{II}}$  має викривлене октаедричне оточення  $\text{CoN}_6$ , бідентно координуючи три молекули фенантроліну. Завдяки міжмолекулярним водневим зв'язкам ( $\text{N}\cdots\text{H}\cdots\text{O}$ ,  $\text{O}\cdots\text{H}\cdots\text{O}$ ) в кристалі утворюється тривимірна супрамолекулярна архітектура, в якій полімерні шари упаковані паралельно вздовж кристалографічної осі  $a$ .

**Ключові слова:** гетерометалічні комплекси, кобальт, неодим, фенантролін, кристалічна структура.

**CRYSTAL STRUCTURE OF THE HETEROMETALLIC COMPLEX OF Co(II) AND Nd(III) WITH PHENANTHROLINE**

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A new heterometallic complex of Co<sup>II</sup> and Nd<sup>III</sup> with phenanthroline [Co(Phen)<sub>3</sub>][Nd(NO<sub>3</sub>)<sub>3</sub>(H<sub>2</sub>O)][Nd(NO<sub>3</sub>)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>].H<sub>2</sub>O was synthesized for the first time by the self-assembly method. The crystal structure of the complex was determined by X-ray crystallography. The compound is an anion-cation complex and crystallizes in the monoclinic space group P2<sub>1</sub>/n with unit cell parameters a=12.4251(4) Å, b=11.7206(3) Å, c=36.5374(12) Å, α=γ=90°, β=90.581(3)°. In the crystalline phase, the complex is in the form of a crystal hydrate with a composition of 1:1. The anionic part of the complex consists of two nitrate hydrated Nd<sup>III</sup> complexes: [Nd(NO<sub>3</sub>)<sub>3</sub>(H<sub>2</sub>O)]<sup>2-</sup> and [Nd(NO<sub>3</sub>)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>-</sup>, in which the coordination number of neodymium is 11 and 10, respectively. The [Co(Phen)<sub>3</sub>]<sup>3+</sup> ion is a cationic part of the complex in which the Co<sup>II</sup> atom has a distorted CoN<sub>6</sub> octahedral environment, bidentately coordinating three phenanthroline molecules. Due to intermolecular hydrogen bonds (N–H...O, O–H...O), a three-dimensional supramolecular architecture is formed in the crystal, in which the polymer layers are packed parallel along the crystallographic axis a.

**Keywords:** heterometallic complexes; cobalt; neodymium; phenanthroline; crystal structure.

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