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Research paper

Two novel mixed-ligand Ni(II) and Co(II) complexes with 1,10-phenanthroline: Synthesis, structural characterization, and thermal stability

Nicolay N. Golovnev[a], Maxim S. Molokeev[b,a,c,*], Irina V. Sterkhova[d], Maxim K. Lesnikov[a]

[a] Siberian Federal University, 79 Svobodny Ave., Krasnoyarsk 660041, Russia
[b] Laboratory of Crystal Physics, Kirensky Institute of Physics, Federal Research Center KSC SB RAS, bld. 38 Akademgorodok 50, Krasnoyarsk 660036, Russia
[c] Department of Physics, Far Eastern State Transport University, 47 Seryshev Str., Khabarovsk 680021, Russia
[d] Favorsky Institute of Chemistry, Siberian Branch, Russian Academy of Sciences, 1 Favorsky, Irkutsk 664033, Russia

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ABSTRACT

Two nickel(II) and cobalt(II) complexes with phenanthroline, $[Ni(Phen)(H_2O)_3Br]Br$ (**1**) and $[Co(Phen)_2(H_2O)_2](Hba)_2{\cdot}2H_2O$ (**2**), Phen = 1,10-phenanthroline and Hba^- = barbiturate anion, were synthesized and characterized by powder XRD, TGA and FT-IR. Their structures were determined by single crystal X-ray diffraction techniques. The Ni^{2+} ion is coordinated by two N atoms of Phen molecule, Br^- ion and three H_2O molecules forming an octahedron. Uncoordinated and coordinated Br^- ions are connected with water molecules by O—H···Br intermolecular hydrogen bonds with the formation of a 2D plane network which is extended into a 3D network by π–π stacking interactions. The $[Co(Phen)_2(H_2O)_2]^{2+}$ cation contains a six-coordinated cobalt atom chelated by two Phen ligands and two aqua ligands in the *cis* arrangement. N—H···O, O—H···O and C—H···O intermolecular hydrogen bonds form a 3D net. N—H···O hydrogen bonds form the infinite chains of Hba^-. In addition, coordinated Phen molecules and lattice water molecules are linked *via* C—H···OW hydrogen bonds to form infinite zigzag chains. These different chains are connected by OW—H···O hydrogen bonds. π–π interaction plays an important role in the stabilization of structures **1**–**2**. FT-IR, TGA, the diffuse reflectance, and UV–Vis spectra were also used to characterize these compounds.

1. Introduction

Mixed-ligand metal complexes are used because of their unique physical and chemical properties [1,2], for example, complexes containing 1,10-phenanthroline (Phen) play an important role in analytical chemistry [3], catalysis [4], and magnetochemistry [5]. Phen used as an auxiliary ligand is an excellent candidate for the construction of novel mixed-ligand complexes, since it can form strong bonds with metal ions, and act as a hydrogen bond donor and acceptor, and the pyridine rings can interact to each other or other molecules with π–π stacking interactions [6]. Like hydrogen bonding, the π–π interaction plays an important role in molecular recognition and self-assembly processes in the solid state and significantly influences the properties of many materials. Cationic complexes of transition metals containing 1,10-phenanthroline and other π-conjugated ligands of special interest because they can be formed solid-state structures with abundant supramolecular architecture and with potentially useful properties, for example, the metal complex $[Co(Phen)_2(H_2O)_2]^{2+}$ has high catalytic activity in the hydroxylation of phenols [7]. We describe here the synthesis and structures of two new mixed-ligand complexes, $[Ni(Phen)(H_2O)_3Br]Br$ (**1**) and $[Co(Phen)_2(H_2O)_2](Hba)_2{\cdot}2H_2O$ (**2**), where, Hba^- = barbiturate anion. Barbituric acid (H_2ba) and their derivatives are important groups of sedative/hypnotic drugs. On the other hand, the non-covalent interactions, such as hydrogen bonding and π–π stacking, are of great importance in the chemistry of barbiturate compounds [8].

2. Experimental section

2.1. Reagents and synthesis

1,10-phenanthroline monohydrate (CAS number: 5144-89-8) and barbituric acid (CAS number: 67-52-7) with a purity of ≥98% were commercially available from Sigma-Aldrich. $CoCO_3$

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* Corresponding author at: Laboratory of Crystal Physics, Kirensky Institute of Physics, Federal Research Center KSC SB RAS, bld. 38 Akademgorodok 50, Krasnoyarsk 660036, Russia.

E-mail address: msmolokeev@gmail.com (M.S. Molokeev).

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and $NiCl_2·6H_2O$ were obtained as a reagent analytical grade (Acros) and they were used without additional purification also. 2.5 mmol (0.59 g) $NiCl_2·6H_2O$ was dissolved in 5 M LiBr (5 cm^3), then a solid Phen·H_2O (0.5 mmol, 0.099 g) was added to the resulting solution. The mixture was kept at 90 °C for 15 min in a water bath and, then, it was filtered. The resulting filtrate was left at room temperature for slow evaporation of water. The solution pH was equal to 6 (a multitest IPL-103 pH meter, Semico, Russia). Two days later, the green crystals of **1** were precipitated from the volume of the solution ≈4.5 ml, which were filtered off and dried in air to a constant mass. The yield was 24% (0.054 g) on based Phen. A single crystal for the X-ray diffraction analysis was taken directly from the total mass of the product. The elemental analysis for $C_{12}H_{14}Br_2N_2NiO_3$ (**1**): Calc.: C, 31.8%; H, 3.12%; N, 6.19%. Found: C, 31.4%; H, 3.38%; N, 6.07%. The attempts to obtain single crystals of barbiturate Ni(II) complex containing coordinated phenanthroline molecules were failed. Compound **2** was prepared by the neutralization of the barbituric acid with the cobalt(II) carbonate in an aqueous solution with the subsequent addition of phenanthroline monohydrate. 0.78 mmol (0.10 g) barbituric acid was mixed with 0.39 mmol (0.046 g) $CoCO_3$ in water (5 cm^3) and stirred for 3 h at 90 °C, then a solid Phen·H_2O (0.78 mmol, 0.155 g) was added to the resulting mixture under stirring. Light orange solution (pH 6) was slowly cooled and allowed to evaporate at room temperature. A one day later, light orange crystals of a cubic shape were precipitated. The crystalline product was filtered off and dried between sheets of filter paper in the air at room temperature. The yield was 28% (0.082 g) based on Phen. A single crystal for the X-ray diffraction analysis was directly selected from the total mass of the precipitate. The elemental analysis for $C_{32}H_{30}CoN_8O_{10}$ (**2**): Calc.: C, 51.6%; H, 4.06%; N, 15.0%. Found: C, 51.1%; H, 4.20%; N, 14.7%.

2.2. X-ray diffraction analysis

The intensity patterns were collected from single crystals **1** and **2** at 100 K using a D8 Venture X-ray single crystal diffractometer (Bruker AXS) equipped with a CCD-detector, graphite monochromator and a Mo Kα radiation source. The absorption corrections were applied using the SADABS program. The structures were solved by the direct methods using package SHELXS and refined in the anisotropic approach for non-hydrogen atoms using the SHELXL program [9]. All hydrogen atoms were found *via* Fourier difference maps. Then, the hydrogen atoms, which are linked with C, N atoms in the Hba^-, $PhenH^+$ ions, were positioned geometrically as riding on their parent atoms with d(C—H) = 0.93–0.98 Å, d(N—H) = 0.86–0.89 Å depending on geometry and $U_{iso}(H) = 1.2U_{eq}(C, N)$. All hydrogen atoms of the H_2O molecules were refined with bond length restraint d(O—H) = 0.9 Å and $U_{iso}(H) = 1.2U_{eq}(O)$. The structural test for the presence of missing symmetry elements and possible voids was produced using the PLATON program [10]. The DIAMOND program is used for the crystal structure plotting [11].

The powder X-ray diffraction data of **1** and **2** were obtained at room temperature using a diffractometer D8 ADVANCE (Bruker) equipped by a VANTEC detector with a Ni filter. The measurements were made using Cu Kα radiation. The cell parameters defined by a single crystal analysis were used as a base in powder pattern Le Bail fitting but obtained final parameters were slightly bigger (Table 1S) due to different temperatures of single crystal experiment (100 K) and powder diffraction experiment (300 K). The refinement was produced using program TOPAS 4.2 [12]. The low *R*-factors and the good refinement results shown in (Fig. 1S, Table 1S) indicate the crystal structures of the powder samples to be representative ones of the (**1, 2**) bulk structure, respectively.

2.3. Physical measurements

TGA was carried out on the simultaneous SDT-Q600 thermal analyzer (TA Instruments, USA) under the dynamic air atmosphere (50 ml/min flow rate) within 25–850 °C at the scan rate of 10 °C/min. The qualitative composition of the evolved gases was determined by FT-IR spectrometer Nicolet380 (Thermo Scientific, USA) combined with a thermal analyzer and with the TGA/FT-IR

Table 1
Crystallographic data and structure refinement parameters.

Single crystal	$[Ni(Phen)(H_2O)_3Br]Br$ (**1**)	$[Co(Phen)_2(H_2O)_2](Hba)_2·2H_2O$ (**2**)
Moiety formula	$C_{12}H_{14}Br_2N_2NiO_3$	$C_{32}H_{30}CoN_8O_{10}$
Dimension (mm)	0.34 × 0.25 × 0.22	0.37 × 0.23 × 0.16
Color	green	pink
Molecular weight	452.78	745.57
Temperature (K)	100	100
Space group, *Z*	$P2_1/c$, 2	$C2/c$, 4
a (Å)	12.0233 (4)	16.716 (2)
b (Å)	9.2344 (3)	12.4771 (16)
c (Å)	13.8857 (4)	14.961 (2)
β (°)	107.379 (1)	92.022 (4)
V ($Å^3$)	1471.56 (8)	3118.3 (7)
ρ_{calc} (g/cm^3)	2.044	1.588
μ (mm^{-1})	6.756	0.626
Reflections measured	40,327	24,226
Reflections independent	4342	4597
Reflections with $F > 4\sigma(F)$	3918	2934
$2\theta_{max}$ (°)	60.34	60.29
h, *k*, *l* – limits	$-16 \le h \le 17$; $-13 \le k \le 13$; $-19 \le l \le 19$	$-23 \le h \le 23$; $-17 \le k \le 17$; $-21 \le l \le 20$
R_{int}	0.0501	0.0891
The weighed refinement of F^2	$w = 1/[\sigma^2(F_o^2) + (0.0374P)^2 + 1.3299P]$	$w = 1/[\sigma^2(F_o^2) + (0.0545P)^2 + 9.9068P]$
Number of refinement parameters	199	243
$R1$ $[F_o > 4\sigma(F_o)]$	0.0279	0.0605
$wR2$	0.0696	0.1505
Goof	1.068	1.015
$\Delta\rho_{max}$ ($e/Å^3$)	0.508	0.991
$\Delta\rho_{min}$ ($e/Å^3$)	−1.529	−0.666
$(\Delta/\sigma)_{max}$	0.001	0.001

interface (attachment for the gas phase analysis). This set up allows simultaneous accumulation of the DTA/TG data and the released gas composition. The compound weight was 13.168 mg for **1** and 8.646 mg for **2**. Platinum crucibles with perforated lids were used as the containers. The IR absorption spectra of the compounds inserted into the KBr tablets were recorded over the range of 400–4000 cm^{-1} at room temperature on an FT-IR spectrometer Nicolet 6700 (Thermo Scientific, USA, SFU CEJU). UV–Vis spectra were recorded on an Evolution 300 spectrophotometer (Thermo Scientific, UK). The diffuse reflectance spectrum (DRS) of **1**–**2** in the region of 380–720 nm was recorded using a Pulsar spectrocolorimeter (NPO Khimavtomatica, Russia). All the excitation and emission spectra were measured with a PerkinElmer LS 55 Fluorescence spectrometer with a xenon pulsed lamp as the excitation light source for the solid-state samples. The chemical analysis was carried out with an HCNS-0 EA 1112 Flash Elemental Analyser.

3. Results and discussion

3.1. Crystal structures of **1**

The unit cells of [Ni(Phen)(H_2O)$_3$Br]Br (**1**) correspond to monoclinic symmetry. Space group $P2_1/c$ was determined from the statistical analysis of the reflection intensities. The main crystal data are shown in Table 1. The asymmetric unit of complex **1** contains one Ni^{2+} ion, one Phen molecule, three H_2O molecules and two Br^- ions (Fig. 1a). The Ni^{2+} ion is coordinated by two N atoms of one Phen molecule, one Br^- ion and three H_2O molecules forming an octahedron. So far, the structure of 27 complexes, containing [Ni(Phen)(H_2O)$_3$X] unit, where, X = H_2O or other O-, N- and S-donor ligands, has been determined. As in **1** and **2**, in these compounds, 1,10-phenanthroline coordinates with metal atoms in chelating modes *via* two N atoms [13]. In **1**, the Ni—O1 and Ni—O3 bond lengths are 2.054(2) and 2.055(2) Å, while the Ni—O2 distance bond that is *trans* to the Br atom is slightly longer than other (2.097(2) Å). The Ni—N distances are 2.061(2) and 2.063(2) Å, with a chelating N1—Ni—N2 bond angle of 81.02(7)°. These bond lengths and angles fall within the ranges observed in complexes containing [Ni(Phen)(H_2O)$_3$X] units, the length of the Ni—Br bond is 2.5759 (3) Å, that is, it also has the usual value [13]. The main bond lengths C—N, C—C, C—O (Table S2) and the angles are in a good agreement with other related compounds of Phen (CSD refcodes HICYOI, KEBFEC, IYULET) [13–16].

There are six OW—H···Br intermolecular hydrogen bonds in the structure (Table S3), and all H atoms of all H_2O molecules are involved in them. As a result, OW—H···Br2 hydrogen bonds are bound the outer sphere Br^- ion with four water molecules from different [Ni(Phen)(H_2O)$_3$Br]$^+$ cations and this above-mentioned cation is connected with six outer spheres Br^- ions.

The coordinated Br^- ion forms two weak OW—H···Br1 hydrogen bonds. The hydrogen bonds form a 2D plane network in *bc* plane with the shortest ring motifs $R_4^2(8)$, $R_3^2(10)$, $R_4^2(10)$ (Fig. 2a). The Phen molecules are not involved in hydrogen bonding. However, they combine [Ni(Phen)(H_2O)$_3$Br]$^+$ cations into pairs by π-π interactions (the head-to-tail type) between neighboring Phen rings (Table 4 S, Fig. 2Sa) in resulting the 2D layers are extended into a 3D supramolecular network. Topological analysis of the net [17], using simplification that [Ni(Phen)(H_2O)$_3$Br]$^+$ is first node and another Br atom is second node, revealed that this is 2-nodal (4-c)(8-c) net with point symbol $(3^3.4^3)(3^6.4^{13}.5^6.6^3)$ and 4,8L38 label which was previously observed in four metal-organic compounds with refcodes: AFAYEL; KEBFAY; PARKOK; WEVNAN [13]. It should be noted that AFAYEL (Triaqua-(2,2′-bipyridine)-(nitrato)-manganese(II) nitrate) has similar local structure, but phenanthroline molecule should be replaced by bipyridine and Br^- ion should be replaced by NO_3^- ion. In addition, **1** and AFAYEL ($P2_1/c$, *a* = 11.5797 (5), *b* = 9.5007 (4), *c* = 14.8683 (6) Å, β = 107.899 (1)°) have similar cell parameters and the same space group, proving their similarities. The KEBFAY compound isostructural to AFAYEL, but Mn^{2+} ion was replaced by Ni^{2+}.

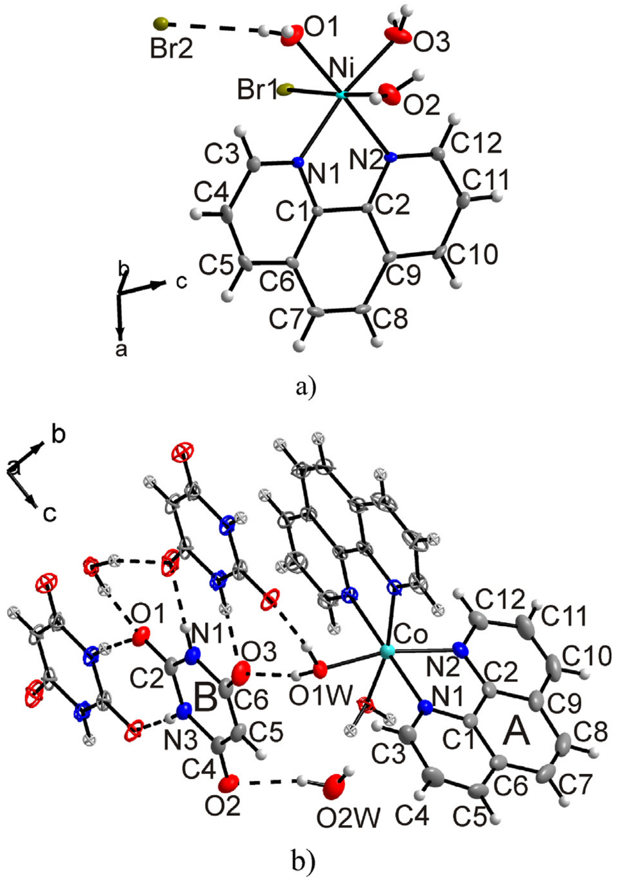
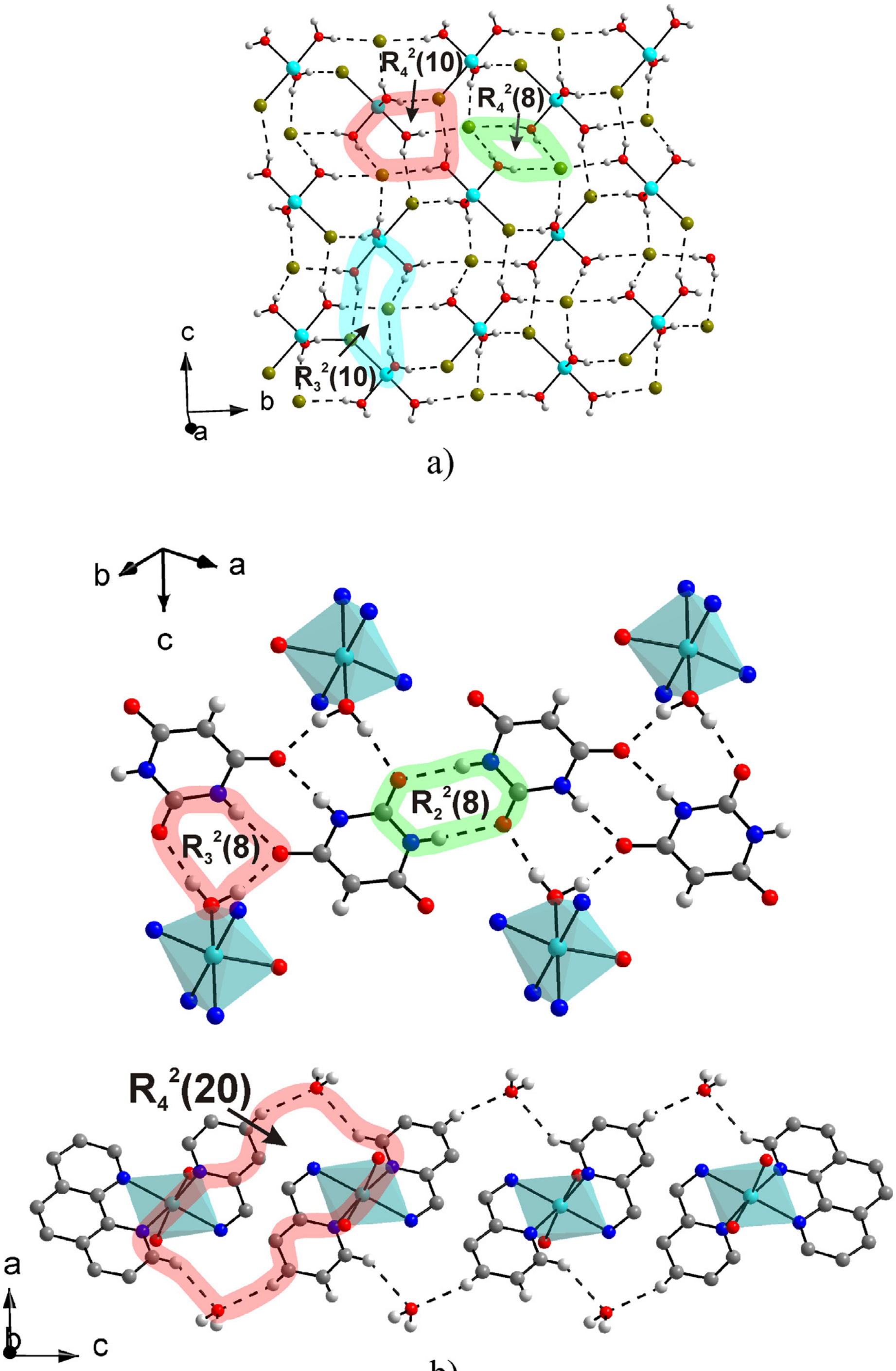


Fig. 1. The asymmetric unit of the [Ni(Phen)(H_2O)$_3$Br]Br (a), [Co(Phen)$_2$(H_2O)$_2$](Hba)$_2$·2H_2O (b) unit cell. Symmetry independent, different molecules are marked by A, B labels. All atoms in the asymmetric unit are labeled. The neighboring symmetry-generated atoms are represented by principal ellipses with an individual color. The intermolecular hydrogen bonds are represented by dashed lines. The ellipsoids are drawn at the 50% probability level, except for the hydrogen atoms represented by spheres.

3.2. Crystal structures of (**2**)

Complex [Co(Phen)$_2$(H_2O)$_2$](Hba)$_2$·2H_2O (**2**) crystallizes in the $C2/c$ space group and the asymmetric unit contains half Co^{2+} ion, one Phen molecule, one Hba^- ion, one coordinated water and one crystallized water molecule (Fig. 1b). The main crystal data are shown in Table 1. In [Co(Phen)$_2$(H_2O)$_2$]$^{2+}$ cation, the Co^{2+} ion is coordinated by four N atoms from two Phen molecules, and two H_2O molecules forming the octahedron. The barbiturate ions do not coordinate to the metal ion. As in all compounds containing [Co(Phen)$_2$(H_2O)$_2$]$^{2+}$ cation, two coordinated water molecules are situated in a *cis* position with an O1W—Co—O1W^i angle of 87.00 (11)° and the coordination around the Co atom is a distorted octahedron, expected because of the presence of two rigid Phen ligands [18–20]. A dihedral angle between Phen molecules coordinated to one Co atom is 71.05(3)°. The Co—OW bond lengths are 2.106 (2) Å, while the Co—N bond distances are of 2.130(2) and 2.121 (2) Å, with a chelating N1—Co—N2 bond angle of 78.22 (9)°. The Co—N bond distances are similar to the Co—N bond lengths in high-spin Co(II) complexes. The low-spin complexes contain shorter



a)

b)

Fig. 2. Hydrogen bonding in 1 (a) and 2 (b). The H-bonds are marked by dashed lines, the H-bond motifs are marked by circles. The Phen molecules in (a), which are not involved in hydrogen bonding, were deleted to clarify the figure. Some H and C atoms were deleted to simplify the figure (b).

Co—N distances of about 1.97(4) Å [21]. In $[Co^{III}(Phen)_2(H_2O)_2](NO_3)_3 \cdot 2H_2O$ the Co—N bond distances even shorter are of 1.933 and 1.935 Å [18]. The main C—O, C—N, C—C bond lengths and the angles in **2** (Table S2) coincide with those found earlier in other related compounds containing Phen molecules [19,20] and uncoordinated Hba^- ions [22–24].

There are eight N—H···O, O—H···O, and C—H···O intermolecular hydrogen bonds, in the structure (Table S3) which form a 3D net. N—H···O hydrogen bonds form the infinite chains of Hba^- along the *a-b* direction based on the $R_2^2(8)$ pattern (Fig. 2b). $[Co(Phen)_2(H_2O)_2]^{2+}$ cation is bound to each of the two Hba^- ligands by OW—H···O hydrogen bond with the closure of the 8-membered ring ($R_3^2(8)$ motif). Crystallization water molecules combine $[Co(Phen)_2(H_2O)_2]^{2+}$ cations by hydrogen bonds C—H···OW into an infinite tape along the *c*-axis with the formation of the supramolecular $R_4^2(20)$ motif. At that, each of crystallization water molecules is connected with two molecules Phen belonging to nearby Co atoms. Tapes of alternating $[Co(Phen)_2(H_2O)_2]^{2+}$ cations and crystallization water molecules are associated with zig-zag chains of Hba^- ions by OW—H···O hydrogen bonds. Topological analysis using TopoPro program [17] showed that this 3D net is a 3-nodal (3-c)$_2$(7-c)$_2$(10-c) net with point symbol $(3^5.4^{10}.5^7.6^{19}.7^4)(3^5.4^6.5^3.6^7)_2(4^2.6)_2$ which is new. As in complex **1**, the cations are united into pairs by π–π interaction between neighboring Phen rings of a head-to-tail type (Table 4S, Fig. 2Sb). In addition, each of these Phen molecules is connected by π−π interaction with one Hba^- ion.

3.3. Spectroscopic study

The IR spectra of **1** and **2** are significantly different from the spectra of starting materials (Fig. 3S–4S) and this indicates the formation of new compounds. In the analysis of the IR spectra, the results of earlier studies were used for comparison [20,23–25]. In the IR spectrum of compound **1** (Fig. 3S, curve 2), a broad band centered at 3332 cm^{-1} is assigned to the ν(OH)) stretching vibrations of coordinated water molecules [26]. Vibration bands in IR spectra of **1** centered at 1622, 1583, 1515, 1426 and 1344 cm^{-1} indicate the presence of 1,10-phenanthroline. In the IR spectrum of compound **2** (Fig. 4S, curve 3), a band at 3626 cm^{-1} is assigned to the ν(OH) vibrations of water molecules and a medium broad band centered at 3160 cm^{-1} is assigned to the ν(NH) stretching vibrations of Hba^- ions. The band with a frequency 1655 cm^{-1} can be assigned to the stretching mode of CO in Hba^- ion [23,24]. Peaks at 426 cm^{-1} in the IR spectra of **1** and **2** were attributed to the M—N stretching vibrations [20].

The *d–d* spectra of aqueous solutions exhibit a broad band in the range 480–650 nm centered at *ca.* 560 nm for **1** and a broad band in the range 430–510 nm centered at *ca.* 460 nm for **2** (Fig. 5S), which are consistent with the presence of the Ni(II) and Co(II) chromophores with octahedral geometry. The response band at λ_{max} = 560 nm is assigned to d–d* transition of Ni(II) ion (d^8) [$^3A_{2g} \rightarrow {}^3T_{1g}(P)$]. The overlapped response band at λ_{max} = 460 nm is assigned to d–d* transitions of Co(II) ion (d^7) ($^4T_{1g}(F) \rightarrow {}^4A_{2g}$, $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$) [26,27]. The diffuse reflectance spectrum was plotted in the Gurevich-Kubelka-Munk coordinates (Fig. 6S). A broad band centered at 470 nm in spectrum **1** can be assigned to d–d* transitions of Ni(II) ion (d^8) [$^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$, $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$]. The DRS of **2** shows the overlapped response bands with the maxima at 610 and 640 nm. For the octahedral environment of Co(II) these bands can be attributed to *d-d* transitions $^4T_{1g}(F) \rightarrow {}^4A_{2g}$ and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ [26]. Free phenanthroline shows an emission maximum at 352 nm with a shoulder at 368 nm upon excitation with at 243 nm [28]. Complexes **1**–**2** practically did not luminesce, which can be explained by the bonding of phenanthroline to metal ions and the presence of water molecules in the coordination sphere of metals, which leads to nonradiative transitions [29].

3.4. Thermal decomposition

Thermal decomposition of compounds **1** and **2** started with the release of water molecules. In compound **1**, an experimental weight loss (Δm) of 10.2% is observed between 75 and 150 °C (Fig. 7S), which corresponds to the release of the coordinated water molecules ($-3H_2O$, Δm_{theor} = 11.9%). The dehydration is accompanied by an endo effect at 119.2 °C. The water removal was confirmed by the IR spectroscopic analysis of released gases. According to the TG curve, a plateau is reached at approximately 150 °C (Fig. 7S). The weight of sample **1** remains unchanged up to ~450 °C, and there are no peaks in the DSC curve below this temperature. At *T* > 450 °C, the oxidative decomposition of [Ni(Phen)Br]Br most likely begins, accompanied by three exothermic effects, the strongest of which at 706.3 °C. According to the IR spectroscopic analysis of the gases evolved at T > 450 °C, CO_2, CO, and HBr are formed. At 800 °C, the final product consists mainly of nickel oxide NiO. The total experimental weight loss was found to be 85.9%, which is bigger than that calculated for the transformation of **1** to NiO (Δm_{theor} = 83.5%), the difference may be due to the impurities in the analyzed sample and thermolysis product.

The DSC and TG curves of $[Co(Phen)_2(H_2O)_2](Hba)_2\cdot 2H_2O$ (**2**) show two-step dehydration (Fig. 8S) which is accompanied by two endo effects at 98.0 °C and 180.7 °C. The first dehydration stage proceeded in the range of 70–140 °C which corresponds to the release of two lattice water molecules with Δm = 4.3% ($-2H_2O$, Δm_{theor} = 4.8). The second dehydration stage in the range of 150–200 °C showed Δm = 4.2 ($-2H_2O$, Δm_{theor} = 4.8%). It corresponds to the release of the coordinated water molecules. Two-step water removal was confirmed by IR spectroscopic analysis of the released gases. At 800 °C, the final product consists mainly of cobalt oxide Co_3O_4. The total Δm was found to be 87.3%, which is less than that calculated for the transformation of **1** to $1/3Co_3O_4$ (Δm_{theor} = 89.2%), the difference may be due to the impurities in the analyzed sample and thermolysis product. According to the IR spectroscopic analysis of the gases evolved at T > 270 °C, CO_2, NH_3 and NO are formed.

4. Conclusions

Two novel mixed-ligand Ni(II) and Co(II) complexes containing the 1,10-phenanthroline are synthesized and characterized by single-crystal X-ray diffraction analysis. The compounds **1** and **2** are mononuclear complexes which crystallize in the space groups $P2_1/c$ and $C2/c$, respectively. $[Ni(Phen)(H_2O)_3Br]Br$ (**1**) is the first of compounds containing $[Ni(Phen)(H_2O)_3Hal]^+$ cation, where Hal is a halogen atom. O—H···Br intermolecular hydrogen bonds (Table 3S, Fig. 2a) form a 2D plane network which is extended into a 3D network by π−π stacking interactions between Phen ligands (Fig. 2Sa). All hydrogen atoms of all H_2O molecules are involved in hydrogen bonding. Each outer sphere Br^- ion is bound with four water molecules from different $[Ni(H_2O)_3PhenBr]^+$ cations by O—H···Br2 hydrogen bonds. The coordinated Br^- ion forms two weak OW—H···Br1 intermolecular hydrogen bonds. The Phen molecules are not involved in hydrogen bonding. Numerous N—H···O, O—H···O, and C—H···O hydrogen bonds (Table 3S) form a 3D net in $[Co(Phen)_2(H_2O)_2](Hba)_2\cdot 2H_2O$ (**2**). The Hba^- ions form an infinite chain by N—H···O hydrogen bonds (based on the $R_2^2(8)$ pattern) (Fig. 2b). Lattice water molecules combine the $[Co(Phen)_2(H_2O)_2]^{2+}$ cations in an infinite tape by C_{Phen}—H···OW hydrogen bonds (based on the $R_4^2(20)$ motif). Similar to hydrogen bonding, the π−π interaction plays an important role in the stabilization of structures **1**–**2** (Table 4S, Fig. 2S). We used ToposPro program [15] for topological analysis to demonstrate that it was a new 3D network. The spectroscopic and thermal properties of compounds were analyzed.

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Appendix A. Supplementary material

The crystallographic data (excluding structure factors) for the structural analysis have been deposited with Cambridge Crystallographic Data Centre (1 CCDC 1829122; 2 CCDC 1829123). The information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44(1223)336-033, E-mail: deposit@ccdc.cam.ac.uk, or www: www.ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.cplett.2018.07.058.

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