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Syntheses and Structural Studies of the Nickel(II) Octahedral Complexes $Ni(N\cap N)_xL_2$ with Nitrogen-Containing and Carboxylate Ligands

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Abstract—A series of new mononuclear octahedral nickel(II) complexes with the $Ni(N\cap N)_xL_2$ framework ($x = 2$ or 3, $N\cap N$ = Phen (1,10-phenanthroline), AMPy (2-(aminomethyl)pyridine), L is H_2O, anions of carboxylic acids ($CF_3CO_2^-$, $CCl_3CO_2^-$, HCO_2^-), chloride ion, and water) is synthesized and described by IR spectroscopy, mass spectrometry, elemental analysis, and X-ray diffraction analysis: $[Ni(Phen)_2(OH_2)Cl]Cl \cdot 2H_2O$ (**I**), $[Ni(Phen)_2(OH_2)(O_2CCF_3)](O_2CCF_3)$ (**II**, **IIa**), $[Ni(Phen)_2(HCOO)_{1.618}(H_2O)_{0.382}](HCOO)_{0.382} \cdot 4.618H_2O$ (**III**), $([Ni(Phen)_2(OH_2)_2](O_2CCCl_3)_2 \cdot 6.2H_2O$ (**IV**), $[Ni(AMPy)_2(OH_2)_2](HCO_2)_2 \cdot 6H_2O$ (**V**), and $[Ni(Phen)_3](CCl_3COO)_2 \cdot 7H_2O$ (**VI**). The subunit containing two formate ligands in the inner sphere of the $[Ni(Phen)_2(HCO_2)_2]$ complex prevails in the crystal structure of complex **III**, which is not characteristic of the nickel carboxylate complexes of this type. In aqueous solutions complex **IV** undergoes decarboxylation to form $[Ni(Phen)_2(CO_3)] \cdot 7H_2O$. A change in the nature of the N-donor ligands in $Ni(N\cap N)_2L_2$ leads to the change (*cis* or *trans*) in the configuration of the whole complex (CIF files CCDC no. 880414 (**I**), 842336 (**II**), 1430414 (**IIa**), 1478111 (**III**), 1430430 (**IV**), 1443133 (**V**), and 1430415 (**VI**)).

Keywords: nickel(II) complexes, carboxylate complexes, structure, isomerism

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INTRODUCTION

The nickel(II) carboxylate complexes are interesting from the viewpoint of coordination chemistry or bioinorganic chemistry [1] as analogues of the biologically active platinum and palladium compounds or as models of the nickel-containing enzymes [2] and also in respect of their application, for example, as the starting substances for the production of new materials by the metal-organic chemical vapor deposition (MOVCD) method [3, 4] or as a basis of “single-molecule magnets” (SMM) [5]. In addition, the study of the influence of the acidoligand and synthesis conditions on the formation of an inner coordination sphere and self-organization processes of the complexes to form supramolecular structures via a system of hydrogen bonds and/or π–π-stacking interactions between the aromatic segments of the ligands are also of certain interest [6, 7].

This work is devoted to the study of the influence of the nature of radical R of the carboxylate ligands RCO_2^- on the formation of molecular and crystal structures of the nickel(II) complexes with the aminate ligands $[Ni(N\cap N)_x(L)_2]$ and their behavior in solutions.

EXPERIMENTAL

All compounds used in the syntheses, except for those described below, were procured from commercial sources and used as received. Silver trifluoroacetate was synthesized by the dissolving of freshly precipitated silver(I) oxide in an excess of CF_3COOH followed by evaporation to obtain the dry salt. Nickel(II) trichloroacetate was obtained using a described procedure [8]. According to the elemental analyses data, the composition of the latter corresponds to the formula $Ni(O_2CCCl_3)_2 \cdot 3.5H_2O$.

The analysis of the synthesized compounds to nickel was carried out gravimetrically by the calcination of the samples in a dried hydrogen flow. The C, H, and N elemental analyses were carried out using a LECO CHNS(O)-932. FTIR spectra were recorded

Table 1. Crystallographic data and the experimental and refinement parameters for the structures of complexes **I–III**

Parameter	Value		
	I	**II**	**III**
FW	544.07	663.17	599.23
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a, Å	9.5857(8)	7.7232(11)	10.9968(6)
b, Å	11.3168(10)	13.1750(19)	27.0316(14)
c, Å	12.8425(11)	14.417(2)	9.2432(5)
α, deg	64.228(2)	69.722(3)	90
β, deg	94.599(4)	85.551(3)	107.7290(10)
γ, deg	78.464(2)	76.132(3)	90
V, Å^3	1228.87(18)	1335.9(3)	2617.2(2)
Z; ρ_{calcd}, g/cm^3	2, 1.470	2, 1.649	4, 1.521
$F(000)$	560	672	1248
μ, mm^{-1}	1.040	0.816	0.804
Ranges of indices	$-12 \le h \le 10$, $-14 \le k \le 14$, $-16 \le l \le 16$	$-9 \le h \le 9$, $-15 \le k \le 15$, $-16 \le l \le 17$	$-15 \le h \le 15$, $-35 \le k \le 38$, $-8 \le l \le 13$
$2\theta_{\text{max}}$, deg	55	50	61.10
Number of measured/independent reflections	5642/4393	4685/3075	7604/4852
R_{int}	0.0762	0.0363	0.0366
Number of parameters	302	448	404
GOOF	1.088	0.9	1.000
R_1, wR_2 ($I > 2\sigma(I)$)	0.0659, 0.2004	0.0383, 0.0806	0.0514, 0.1403
R_1, wR_2 (all data)	0.0784, 0.2113	0.0664, 0.0868	0.0827, 0.1521
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$, e Å^{-3}	3.134, –1.334	0.237, –0.177	1.252, –0.653

in a range of 400–4000 cm^{-1} with a Shimadzu IRAffinity-1 in pellets with KBr.

Measurements of the complexes by high resolution mass spectrometry (HR-MS) were carried out on an ESI-TOF mass spectrometer (microTOF, Bruker) in a methanol solution in the mass range 50–3000 *m/z* in positive ion detection mode. The experimental conditions were optimized to obtain the maximum peak intensity of the nickel(II) complexes (the voltage on the tip of the ion source was +4500 V, the temperature was 180°C, and the flow rate of nitrogen was 4 L/min).

X-ray diffraction analyses of the complexes were carried out on Bruker Kappa APEX II DUO at 100 K (**I** and **III**), Bruker Smart APEX II at 210 K (**II**), and Rigaku Oxford Diffraction Excalibur Eos at 100 K (**IIa**, **IV**, **V**, **VI**) diffractometers (MoK_α radiation, λ = 0.71073 Å, graphite monochromator). The structures of the compounds were solved by direct methods and refined using the SHELX program [9] integrated in the OLEX2 complex [10]. The final models included the coordinates and anisotropic thermal parameters for all non-hydrogen atoms. The positions of the hydrogen atoms of the organic fragments in the complexes were calculated using the algorithm incorporated in the SHELX program. The positions of the hydrogen atoms of the water molecules were localized from the difference Fourier synthesis and fixed in the refinement. The crystallographic data and the experimental and refinement parameters for the structures of complexes **I–VI** are presented in Tables 1 and 2. Selected bond lengths and bond angles of complexes **I–V** are listed in Table 3.

X-ray and mass spectrometric studies were carried out at the resource centers "Center of X-ray diffraction studies" and "Chemical Analysis and Materials Research Centre" at the St. Petersburg State University. The crystals of the complexes suitable for X-ray diffraction analysis were obtained directly from the reaction mixtures.

Table 2. Crystallographic data and the experimental and refinement parameters for the structures of complexes **IV–VI**

Parameter	Value		
	IV	**V**	**VI**
Empirical formula	$C_{28}H_{32.40}Cl_6N_4NiO_{12.20}$	$C_{14}H_{34}N_4NiO_{12}$	$C_{40}H_{38}Cl_6N_6NiO_{11}$
FW	891.59	509.16	1050.17
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$	*Cc*
a, Å	10.1520(5)	13.5417(3)	23.3371(10)
b, Å	12.4154(6)	6.83220(15)	11.3994(2)
c, Å	16.3585(7)	12.7917(3)	18.7463(6)
α, deg	74.158(4)	90	90
β, deg	87.142(4)	92.261(2)	114.855(3)
γ, deg	66.655(5)	90	90
V, Å^3	1817.19(16)	1182.56(5)	4525.13
Z; ρ_{calcd}, g/cm^3	2, 1.629	2, 1.430	4, 1.541
F(000)	912	540	2152
μ, mm^{-1}	1.041	0.883	0.848
Ranges of indices	$-12 \le h \le 12$, $-15 \le k \le 15$, $-20 \le l \le 20$	$-17 \le h \le 17$, $-8 \le k \le 8$, $-16 \le l \le 16$	$-30 \le h \le 30$, $-14 \le k \le 14$, $-24 \le l \le 24$
$2\theta_{max}$, deg	52.988	55	55
Number of measured/independent reflections	7373/5022	2665/2206	10230/9092
R_{int}	0.0585	0.0237	0.0455
Number of parameters	492	175	614
GOOF	1.044	1.040	1.039
R_1, wR_2 ($I > 2\sigma(I)$)	0.0622, 0.1544	0.0290, 0.0381	0.0411, 0.0813
R_1, wR_2 (all data)	0.0991, 0.1887	0.0707, 0.0763	0.0511, 0.0870
$\Delta\rho_{max}$, $\Delta\rho_{min}$, e Å^{-3}	2.324, –1.880	0.272, –0.294	1.086, –0.671

Table 3. Selected bond lengths and bond angles of complexes **I–V**

Complex	**I**	**II**	**IIa**	**III**	**IV**	**V**
Bond length (*d*), Å	Ni–O (*w*, H_2O) 2.088	Ni–O (*w*, H_2O) 2.066	Ni–O (*w*, H_2O) 2.070	Ni–O (*w* H_2O and O_2CH) 2.058	Ni–O (*w*, H_2O) 2.054	Ni–O (*w*, H_2O) 2.099
Bond length (*d*), Å	Ni–Cl 2.380	Ni–O (O_2CCF_3) 2.068	Ni–O (O_2CCF_3) 2.081	Ni–O (O_2CH) 2.066	Ni–O (*w*, H_2O) 2.059	Ni–O (*w*, H_2O) 2.099
Bond angle (ω), deg	ONiCl 89.02	ONiO 93.25	ONiO 93.44	ONiO 89.89	ONiO 83.29	ONiO 180.00

The crystallographic data for complexes **I–VI** were transfered to the Cambridge Crystallographic Data Centre (CIF files CCDC no. 880414 (**I**), 842336 and 1430414 (**II**, **IIa**), 1478111 (**III**), 1430430 (**IV**), 1443133 (**V**), and 1430415 (**VI**); deposit@ccdc.cam.ac.uk or https://summary.ccdc.cam.ac.uk/structure-summary-form).

Synthesis of nickel(II) *cis*-aquachloridobis(1,10-phenanthroline) chloride dihydrate (*cis*-[Ni(Phen)$_2$(OH$_2$)Cl]Cl · 2H$_2$O) (I). The complex was synthesized by the reaction of $NiCl_2 \cdot 6H_2O$ (0.7980 g, 3.3821 mmol) and Phen (1.2180 g, 6.7643 mmol) in ethanol. Blue orthorhombic crystals precipitated on slow cooling of the solution were filtered off and washed with cooled ethanol. The yield was ~40%.

For $C_{24}H_{22}N_4O_3Cl_2Ni$

anal. calcd., %: C, 52.58; H, 3.62; N, 10.11; Ni, 10.79.
Found, %: C, 52.81; H, 3.89; N, 10.22; Ni, 10.61.

IR (KBr), ν, cm^{-1}: 3055 m, 1648 m, 1623 s, 1604 m, 1587 s, 1580 s, 1516 vs, 1495 m, 1425 vs, 1343 m, 1320 w, 1308 w, 1257 w, 1225 m, 1208 m, 1199 w, 1142 m, 1103 m, 1150 w, 870 s, 855 vs, 776 m, 727 vs, 643 m, 507 w.

Synthesis of nickel(II) *cis*-aquatrifluoroacetatobis(1,10-phenanthroline) trifluoroacetate (*cis*-$[Ni(Phen)_2(OH_2)(O_2CCF_3)]O_2CCF_3$) (II, IIa). Silver salt CF_3COOAg (0.8240 g, 3.7472 mmol) dissolved in a minimum amount of water was added to an aqueous solution (50 mL) of compound **I** (1.0156 g, 1.8736 mmol). After silver chloride was separated, the supernatant was left to crystallize. Violet orthorhombic crystals precipitated from the solution in ~1.5 weeks on slow evaporating in air. The yield was 70%.

For $C_{28}H_{18}F_6N_4O_5Ni$

anal. calcd., %: C, 50.40; H, 2.74; N, 8.28; Ni, 8.85.
Found, %: C, 50.59; H, 1.99; N, 8.40; Ni, 8.65.

IR (KBr), ν, cm^{-1}: 3419 m br, 3063 w br, 1678 vs, 1627 sh, 1583 w, 1519 m, 1427 s, 1411 sh, 1346 w, 1201 vs, 1176 s, 1136 s, 1120 s, 869 w, 850 m, 798 m, 729 s, 717 sh, 644 w, 426 vw.

Synthesis of *cis*-$[Ni(Phen)_2(HCOO)_{1.618}(H_2O)_{0.382}](HCOO)_{0.382} \cdot 4.618H_2O$ (III) was carried out similarly to the synthesis of complex **V**. The crystals suitable for X-ray diffraction analysis were obtained by slow crystallization from the concentrated aqueous–methanol mother liquor. The mother liquors tend to oversaturation. The yield was ~80%.

For $C_{26}H_{28}N_4NiO_9$

anal. calcd., %: C, 52.11; H, 4.71; N, 9.30; Ni, 9.80.
Found, %: C, 51.85; H, 4.50; N, 9.46; Ni, 9.93.

IR (KBr pellets), ν, cm^{-1}: 3227 vs br, 2871 s, 2819 s, 2726 m, 1980 w, 1928 w, 1816 vw, 1694 s, 1623 vs, 1515 s, 1493 m, 1426 s, 1381 s, 1374 s, 1355 s, 1343 s, 1321 m, 1226 m, 1145 w, 1139 m, 1104 m, 1090 w, 867 m, 848 s, 794 s, 780 s, 727 vs, 668 s, 642 vs, 508 w.

Synthesis of nickel(II) *cis*-diaquabis(1,10-phenanthroline) trichloroacetate–water (1/6.2) (*cis*-$[Ni(Phen)_2(OH_2)_2](O_2CCCl_3)_2 \cdot 6.2H_2O$) (IV) was carried out similarly to the synthesis of complex **III** but with the ratio Ni : Phen = 1 : 2. The yield was ~60%.

For $C_{28}H_{32.40}N_4O_{12.20}Cl_6Ni$

anal. calcd., %: C, 37.51; H, 3.88; N, 6.12; Ni, 6.42.
Found, %: C, 37.72; H, 3.63; N, 6.28; Ni, 6.58.

IR (KBr), ν, cm^{-1}: 3384 m, 3215 m, 3062 m, 1675 vs, 1607 m, 1585 m, 1518 s, 1496 w, 1427 s, 1334 vs, 1223 w, 1145 w, 1106 w, 870 m, 847 s, 830 s, 745 m, 727 s, 679 s, 643 w, 501 vw, 426 w.

Synthesis of nickel(II) *trans*-diaquabis(2-(aminomethyl)pyridine) formate hexahydrate (*trans*-$[Ni(AMPy)_2(OH_2)_2](HCO_2)_2 \cdot 6H_2O$) (V). The complex was obtained by the reaction of an aqueous suspension of nickel(II) formate dihydrate (0.9198 g, 5 mmol) in water (30 mL) acidified with a 70% solution of formic acid (0.5 mL) and AMPy (1.0807 g, 10 mmol) at ~80°C with stirring for 1.5 h. The crystals suitable for X-ray diffraction analysis were obtained on slow cooling of the solution followed by concentrating. The yield was ~80%.

For $C_{14}H_{34}N_4O_{12}Ni$

anal. calcd., %: C, 33.06; H, 6.74; N, 11.02; Ni, 11.40.
Found, %: C, 33.23; H, 6.21; N, 11.10; Ni, 11.53.

IR (KBr), ν, cm^{-1}: 3335 s, 3260 s, 3154 s, 3074 m, 2821 w, 2800 w, 1630 s, 1590 vs, 1567 vs, 1487 m, 1435 m, 1393 m, 1383 m, 1344 s, 1286 w, 1251 w, 1195 w, 1139 m, 1120 m, 1100 m, 1032 s, 936 w, 770 vs, 730 m, 670 m.

Synthesis of nickel(II) tris(1,10-phenanthroline) trichloroacetate heptahydrate ($[Ni(Phen)_3](CCl_3COO)_2 \cdot 7H_2O$) (VI). An ethanol solution (30 mL) of Phen (0.8103 g, 4.500 mmol) was added to an aqueous-ethanol (30 : 70 vol/vol) solution (30 mL) of "nickel(II) trichloroacetate" (0.5696 g, 1.500 mmol). The solution was evaporated to ~30 mL, cooled, and filtered. Red needle-like crystals of the complex were separated from the solution for several days. The yield was ~90%.

For $C_{40}H_{38}N_6O_{11}Cl_6Ni$

anal. calcd., %: C, 45.82; H, 3.39; N, 8.12; Ni, 5.45.
Found, %: C, 45.75; H, 3.65; N, 8.00; Ni, 5.59.

IR (KBr), ν, cm^{-1}: 3413 m, 1694 vs, 1627 m, 1586 w, 1515 s, 1428 vs, 1344 m, 1307 s, 1287 m, 1223 w, 1143 w, 1105 w, 854 s, 845 s, 776 m, 721 vs, 663 m.

RESULTS AND DISCUSSION

Complex **I** is formed by the reaction of nickel(II) chloride with Phen (2 equiv.). Many solvate isomers of this complex are known [11–13], but all of them con-

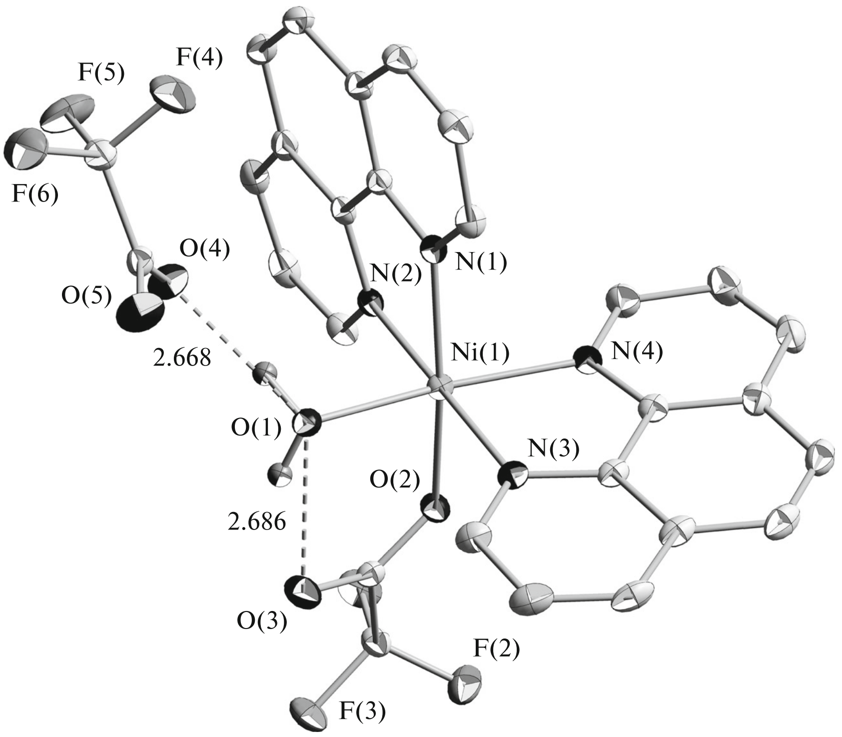


Fig. 1. Molecular structure of complex **IIa**. Thermal vibration ellipsoids are shown at the 50% probability level. The hydrogen atoms of the Phen ligands are omitted.

tain molecules of the organic solvent in the outer sphere of the complex. Complexes **II–VI** are formed by the reactions of the corresponding nickel carboxylates with Phen. Complex **II** can also be obtained by the exchange reaction of complex **I** with silver trifluoroacetate.

The unit cells of complexes **I**, **II**, and **IV** contain two formula units of the complexes bound by the symmetry center. This fact along with the idealized symmetry C_1 of the cations makes it possible to consider complexes **I** and **II** as racemates as it is shown for complexes **II** and **IIa** taken as examples.

In the molecular structures of the complexes, the nickel ions exist in the distorted octahedral environments NiN_4O_2 (**II**) or NiN_4OCl (**I**) formed by the nitrogen atoms of two Phen molecules coordinated through the bidentate mode, the oxygen atoms of the water molecules, and the oxygen atom of the trifluoroacetate (**II**, **IIa**) (Fig. 1) ion or chloride ligand (**I**).

Selected bond lengths and bond angles for complexes **I**, **II**, **IIa**, and **III–V** are given in Table 3. The Ni–O(*w*, H_2O) bond lengths are 2.066 (**I**), 2.066 (**II**), 2.070 (**IIa**), and 2.054 Å (**IV**), which is close to the corresponding values in crystalline nickel acetate $Ni(O_2CCH_3)_2 \cdot 4H_2O$ (2.11, 2.06 Å [14]) or related complexes ($Ni(Phen)(O_2CCH_3)(H_2O)_2$) containing phenanthroline ligands [6]. The Ni–N(Phen) distances of the next described complexes are 2.076–2.099, 2.079–2.098, 2.074–2.116, and 2.065–2.088 Å for compounds **I–IV**, respectively. The Ni–N(Phen) bonds located in the *trans* position to the acido ligands are slightly elongated (~0.02 Å in the case of complexes **I**, **II**, and **IV** and 0.042 Å for **III**). The Ni–N distances in complex **V** differ insignificantly in the case of the aromatic and aliphatic nitrogen atoms of AMPy: Ni(1)–N(1) (NH_2–) 2.098 Å, Ni(1)–N(2) (Py) 2.082 Å.

The oxygen and fluorine atoms of the outer-sphere trifluoroacetate ion of complex **II** are disordered over two crystallographically independent positions with a general occupancy of 1.0 au. The inner-sphere water molecule in the structures of complexes **II** and **IIa** participates in the formation of two hydrogen bonds: the intramolecular bond with the coordinated trifluoroacetate ion (O(1)···O(3)) 2.686 Å for **IIa** (O(2)···O(3)) 2.683 Å for **II**) (Fig. 1) and the intermolecular bond with the outer-sphere trifluoroacetate ion (O(1)···O(4)) 2.668 Å (O(3)···O(4*A*)) 2.595 Å for **II**).

All fragments in the crystal structures of complexes **I** and **IV** are joined by intermolecular hydrogen bonds into infinite chains along the direction $[01\bar{1}]$. The coordinated and outer-sphere water molecules and chloride ions (in **I**) or trichloroacetate ions (in **IV**) are involved in the formation of these hydrogen bonds.

The Ni–N bond lengths in complex **VI** are ~2.090 Å, which is characteristic of similar complexes

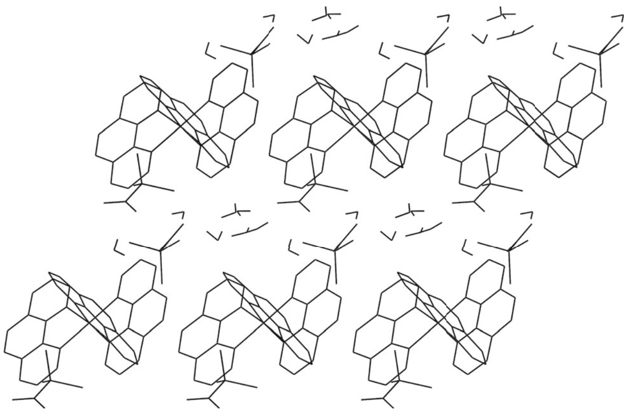


Fig. 2. Crystal structure of complex **VI**. The hydrogen atoms of the Phen ligands are omitted.

[15]. The cationic fragments $\mathrm{Ni(Phen)_3^{2+}}$, which form infinite 2D supramolecular structures parallel to the (100) plane (Fig. 2), are stabilized by the π–π-stacking interactions of the aromatic Phen ligands with average interligand distances of ~3.2 Å [6, 7]. The average interplanar distances between the 2D layers $\{\mathrm{Ni(Phen)_3^{2+}}\}_\infty$ are ~11.5 Å. The outer-sphere trichloroacerate ions and crystallization water molecules are arranged in the interplanar spaces with a width of ~6.5 Å (Fig. 2) and bounded via hydrogen bonds. The trichloroacetate ions are bound in pairs through the water molecule and form the $\mathrm{CCl_3CO_2\cdots OH_2\cdots O_2CCCl_3}$ fragment (the average length of the O···O hydrogen bond is ~2.7 Å).

The coordination environments of the nickel(II) atoms in complexes **II** and **III** are similar, but the molecular structure of complex **III** is presented by two different subunits: *cis*-$\mathrm{[Ni(Phen)_2(OH_2)(O_2CH)]^+}$ and *cis*-$\mathrm{[Ni(Phen)_2(O_2CH)_2]}$. In the molecular structures of both subunits, the nickel ion exists in the distorted octahedral environment $\mathrm{NiN_4O_2}$ formed by four nitrogen atoms of two phenanthroline molecules coordinated through the bidentate mode in the perpendicular planes and by two oxygen atoms O(1) and O(3) (Fig. 3), whose site occupancy is equal to 1. The O(1) atom is attributed to the outer-sphere formate ion, and O(3) refers to the coordinated water molecule in the case of the first subunit (the site occupancy of H(3*A*) and H(3*B*) is 0.38) and to the inner-sphere formate ion in the case of the second subunit (the site occupancies of O(4), C(26), and H(26) are 0.62). The outer-sphere formate ions and molecules of water of crystallization are located in the structural channels (similarly to complex **VI**) oriented along the crystallographic *z* axis (Fig. 4) and formed by the π–π-stacking interactions of the subunits of the complex.

In the crystal structures of complexes **I–IV**, the $\mathrm{[Ni(Phen)_2(OH_2)L]^+}$ (L = Cl (**I**), $\mathrm{CF_3CO_2}$ (**II**, **IIa**), $\mathrm{HCO_2/OH_2}$ (**III**), and $\mathrm{OH_2}$ (**IV**)) cations are joined in pairs by the π–π-stacking interactions between the Phen fragments of the adjacent complexes with interplanar distances of 3.41 (**I**), 3.95 (**II**, **IIa**), 3.36–3.58 (**III**), and 3.38 Å (**IV**), which is characteristic of a similar type of interactions [7].

The nickel(II) atom in the structure of complex **V** occupies the partial position at the inversion center and is bound to four nitrogen atoms of the *trans*-AMPy ligands coordinated through the bidentate mode. The axial positions of the $\mathrm{NiN_4O_2}$ octahedron are occupied by two oxygen atoms of the coordination water molecules. The outer-sphere formate ions compensate the charge and participate in the formation of a system of hydrogen bonds with the coordination

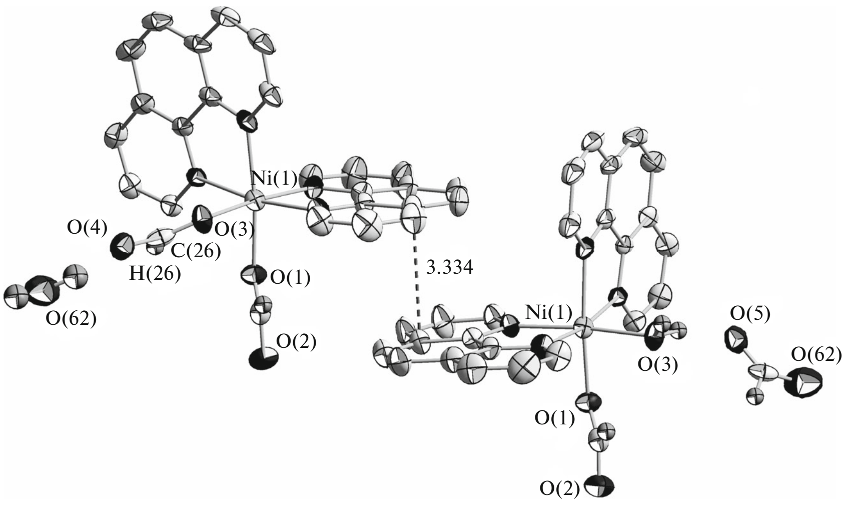


Fig. 3. Molecular structure of two subunits of complex **III**. Thermal vibration ellipsoids are shown at the 50% probability level. The hydrogen atoms of the Phen ligands are omitted.

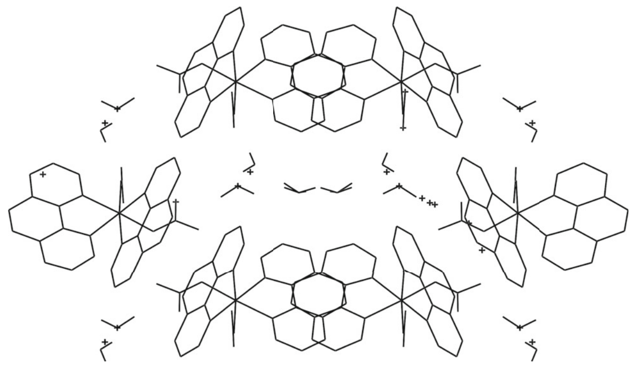
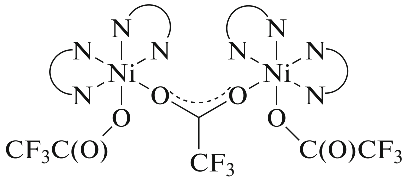


Fig. 4. Crystal structure of complex **III**. Arrangement of the formate ligands and water molecules in the structural channels (view along the z axis). The hydrogen atoms of the Phen ligands are omitted.

water molecules and amino groups of the AMPy ligands (Fig. 5).

The HR-MS spectra of compounds **II** and **III** exhibit no signal corresponding to the molecular ion but contain intense peaks with m/z = 531.0590 and 463.0686 characteristic of the $[M-CF_3COO]^+$ and $[M-HCOO]^+$ ions. In the case of complex **II**, the peak with m/z = 1175.0999 is observed and assigned to the hypermolecular ion $[(Phen)_2(O_2CCF_3)Ni](\mu\text{-}O_2CCF_3)[Ni(O_2CCF_3)(Phen)_2]^+$.



It can be mentioned that similar associates were found [16] in aqueous-methanol solutions of trinuclear chromium(III) carboxylates using ESI FT-ICR mass spectrometry. The trinuclear chromium complexes $[Cr^{III}_3(\mu_3\text{-}O)(\mu\text{-}O_2CC_6H_5)_6L_2(H_2O)](ClO_4)$ were concluded [16] to tend to "supramolecular organization" with the formation of ensembles $\{(ClO_4)[Cr^{III}_3(\mu_3\text{-}O)(\mu\text{-}O_2CC_6H_5)_6L_2(H_2O)]_n\}^{Z+}$ (where L is the monodentate terminal ligand, $1 \le n \le 3$, $z = n - 1$) due to hydrogen bonds.

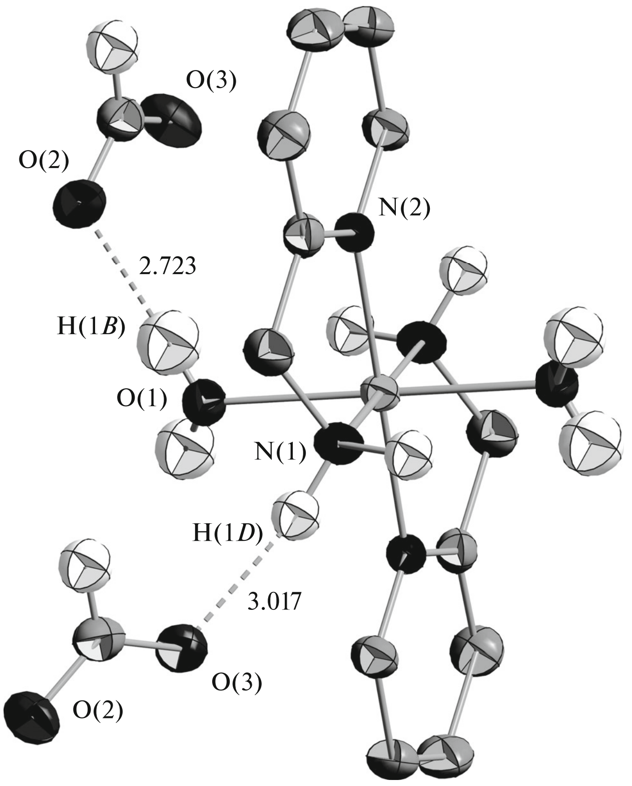


Fig. 5. Molecular structure of complex **V**. Thermal vibration ellipsoids are shown at the 50% probability level. Some hydrogen atoms of the AMPy ligands are omitted.

All complexes studied are characterized by the formation of similar species. In the case of complex **III**, there is a series of signals with m/z exceeding the value for the molecular ion, for example, the peak with m/z = 610.9977, which can be assigned to $[Ni_2(Phen)_2(HCO_2)_3]^+$. In the case of complex **V**, an ion similar to those existing in solutions of complexes **II** and **III** and being $[Ni(AMPy)_2(HCOO)]^+$ (m/z = 319.0691) rather than $[Ni(AMPy)_2-H]^+$ (m/z = 273.0632) predominates in a methanol solution. Its formation is probably related to a high lability of the inner-sphere water molecules and their substitution by the acido ligand on transiting to non-aqueous systems. As in the case of the previous complexes, the HR-MS spectrum of complex **V** exhibits signals with high m/z, and one of the signals was assigned to $[Ni_2(AMPy)_2(HCO_2)_3]^+$ (m/z = 467.0005).

An attempt to obtain a trichloroacetate analog of complexes **I**–**III** with the intramolecular acidoligand, namely, $[Ni(Phen)_2(OH_2)(O_2CCCl_3)]^+$, was unsuccessful. All attempts of the synthesis from the aqueous systems gave the blue-green carbonate complex $[Ni(Phen)_2(CO_3)] \cdot 7H_2O$ (X-ray diffraction analysis data: space group $P2_1/c$; a = 9.8284(5), b = 26.2057(12), c = 0.4842(6) Å; β = 105.707(6)°, V = 2599.47 Å^3, Z = 4) described previously [17]. Probably, the $R-CO_2^-$, bond is polarized due to the unusual electronic properties of the trichloroacetate ion [18] transiting to the inner sphere of the complex, which results in the intramolecular decarboxylation of the trichloroacetate ligand via the earlier described mechanism [19]

$$[Ni(Phen)_2(OH_2)_2](CCl_3CO_2)_2$$
$$\rightarrow [Ni(Phen)_2(OH_2)(CCl_3CO_2)](CCl_3CO_2)_2 + H_2O,$$

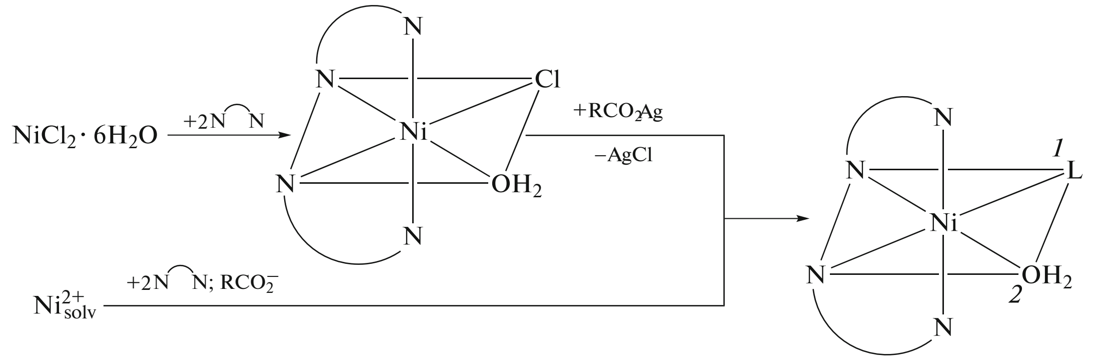
$$[Ni(Phen)_2(OH_2)(CCl_3CO_2)]^+ + H_2O$$

$$\rightarrow [\mathrm{Ni(Phen)_2(OH_2)(OH)}]^+ + \mathrm{CHCl_3} + \mathrm{CO_2}\ (\mathrm{H_2CO_3}),$$

$$[\mathrm{Ni(Phen)_2(OH_2)(OH)}]^+ + \mathrm{H_2CO_3}$$
$$\rightarrow [\mathrm{Ni(Phen)_2(CO_3)}] + 2\mathrm{H_2O} + \mathrm{H^+}.$$

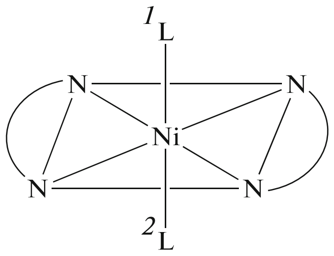
For similar parameters of the electron density distribution in the $\mathrm{CF_3CO_2^-}$ and $\mathrm{CCl_3CO_2^-}$ ions [18], intramolecular decarboxylation is observed only in the case of the trichloroacetate complexes.

Summating the obtained results and published data [20–22], we can assume that the *cis*-octahedral complexes with the common motif $[\mathrm{Ni(N{\cap}N)_2(OH_2)(L)}]$ ($\mathrm{N{\cap}N}$ are aromatic nitrogen-containing ligands (Phen, 2,2'-dipyridyl), $\mathrm{L} = \mathrm{RCO_2^-}$, $\mathrm{OH_2}$) are formed regardless of the synthesis procedure (one-pot synthesis, direct synthesis, or substitution of the halide ligands in the nickel(II) aminate complexes).



The rare exceptions are the *cis*-$[\mathrm{Ni(Bz)_2(Phen)_2}]$ complex (Bz is the diphenylhydroxyacetate ion) [23] and one of the subunits of complex **III**, where positions 1 and 2 are occupied by the carboxylate ligands coordinated through the monodentate mode. However, the obtained starting compounds probably containing water molecules were recrystallized [23] from a mixture of non-aqueous solvents, which could result in the preparation of a waterless complex. In the case of complex **V**, a similar regularity confirmed by the data of mass spectrometry is observed, where the water molecules were substituted by the outer-sphere acidoligands. It can be assumed that, in some cases, the absence of water in the reaction mixture exerts a noticeable effect on the formation of the inner sphere of the complex and results in a similar unusual (*cis*-$[\mathrm{Ni(Bz)_2(Phen)_2}]$ [23], complex **III**) coordination mode of the carboxylate ligands.

The coordination mode changes upon the replacement of the aromatic nitrogen-containing ligands (Phen, 2,2'-dipyridyl) by the bidentate ligands containing aliphatic donor nitrogen atoms (such as ethylenediamine (En), *N*,*N*,*N*',*N*'-tetramethylethylenediamine (Tmen), AMPy) in the nickel(II) octahedral complexes. In the structures of the most part of the described complexes, the aliphatic N-donor ligands are arranged in one plane to form *trans*-octahedral species.



The complexes containing both acido ligands in the inner sphere of the complex are formed if $\mathrm{N{\cap}N}$ is En or Tmen and L is the halide or pseudo-halide ion [24]. Both acido ligands [25–27] and water molecules [1, 28, 29] can be located in the inner sphere of the carboxylate complexes. The absolute majority of the $[\mathrm{Ni(N{\cap}N)_2(OH_2)_{\mathit{n}}(L)_{2-\mathit{n}}}]$ complexes with aliphatic amines crystallize in the *trans* configuration ($n = 2$), except for four known compounds with the *cis* configuration [30–32]. It should be mentioned that there are no mononuclear nickel(II) carboxylate complexes with two Tmen molecules in the inner sphere that were not studied by X-ray diffraction analysis.

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