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# Synthesis and Crystal Structures of New Trinuclear Cobalt(II) and Nickel(II) Fluorocarboxylate Complexes

**D. S. Tereshchenko[a], T. Yu. Glazunova[a, *], M. E. Buzoverov[a],**
**E. Kh. Lermontova[b], and V. E. Goncharenko[a]**
[a] *Moscow State University, Moscow, Russia*
[b] *Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Moscow, 119992 Russia*
**e-mail: ctpayc@mail.ru*

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**Abstract**—Three new complexes from the family of 3*d*-metal fluorocarboxylatometallates are synthesized and studied. Isotypical complex compounds $K[Co_3(\mu_3\text{-}F)(CF_3COO)_6(CH_3COOH)_3](CH_3COOH)$ (**I**) and $K[Ni_3(\mu_3\text{-}F)(CF_3COO)_6(CH_3COOH)_3](CH_3COOH)_{0.6}(CF_3COOH)_{0.4}$ (**II**) are analogs of potassium fluorotrifluoroacetatometallates(II) in which axial ligands are replaced by acetic acid molecules. Complex $NH_4[Ni_3(\mu_3\text{-}F)(CH_3COO)_6(CH_3COOH)_3](CH_3COOH)_6$ (**III**) is the first example of fluorocarboxylate with acetate bridging ligands. The presence of acetic acid in the system results in an increase in the coordination number of alkaline metal and (due to the formation of a developed system of hydrogen bonds) in an increase in the dimensionality of the structure from the chain one in the earlier studied analogs to the layered structure. The structure of the complex fluorocarboxylate anion in compound **III** resembles those of fluorotrifluoroacetate analogs **I** and **II**, the character of interaction of the complex anion with the single-charge cation is retained, and the structure exists in the form of corrugated layers formed by chains linked via hydrogen bonds with the solvate molecules of acetic acid (CIF files CCDC nos. 2124887 (**I**), 2124888 (**II**), and 2127163 (**III**)).

**Keywords:** synthesis, crystal structure, trifluoroacetate complexes, acetate complexes, cobalt trifluoroacetate, nickel trifluoroacetate

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## INTRODUCTION

The present study is a continuation of the cycle of works devoted to studying and revealing criteria of existence of the fluorocarboxylatometallate complexes containing the trinuclear fragment $[M_3(\mu_3\text{-}F)(RCOO)_6(L)_3]$. In the previous works we reported the discovery of the new family of fluorotrifluoroacetate complexes, and the subsequent development of this trend resulted in the synthesis and structural characterization of more than 15 fluorotrifluoroacetate complexes of transition metals with the general formula $M'[M_3(\mu_3\text{-}F)(CF_3COO)_6(L)_3]$ (M' = Li–Cs, $NH_4$; M = Mn, Fe, Co, Ni, Zn; L = $CF_3COO^-$, $CF_3COOH$, $H_2O$) [1]. At the moment, these data represent the most systematic study of the structures and properties of this family of carboxylates. All complexes studied are formed by the single-charge anions $[M_3(\mu_3\text{-}F)(CF_3COO)_6(L)_3]^-$ in which three transition metal atoms localized at the vertices of an almost regular triangle coordinate the tridentate fluorine atom via the planar mode. Each pair of the 3*d*-metal atoms is linked with each other by two bidentate trifluoroacetate groups. The coordination environment of the 3*d*-metal atom is supplemented to the octahedral environment by the oxygen atoms of the axial ligands. We described a possibility of replacing the axial ligands and, correspondingly, changing the composition of the complexes by the variation of the synthesis conditions, which can lead to a change in the dimensionality of the structure [2]. Single-charge alkaline metal, ammonium, or nitrosonium cations are counterions to the complex anions [1, 3]. Depending on the complex anion composition and cation size, solvent molecules involved in structure formation can enter the compositions of the compounds.

The fluorocarboxylate complexes containing the $[M_3(\mu_3\text{-}F)(RCOO)_6(L)_3]$ trinuclear fragment are stable and serve as structural blocks for the formation of frameworks when using dibasic carboxylic acids. The examples are metal-organic frameworks (MOFs) based on the cadmium isonicotinate complexes $[Cd_3(\mu_3\text{-}F)(Ina)_4(4\text{-}Pic)_3]\cdot BF_4$, $[Cd_3(\mu_3\text{-}F)(Ina)_3\text{-}(4,4'\text{-}Bipy)_2\text{-}(4\text{-}Pic)_2]\cdot 2BF_4\cdot(4,4'\text{-}Bipy)\cdot 2H_2O$, and $[Cd_3(\mu_3\text{-}F)(Ina)_3(4,4'\text{-}Bipy)_3]\cdot 2BF_4\cdot(4,4'\text{-}Bipy)\cdot 2H_2O$, where Ina is isonicotinate, 4,4'-Bipy is 4,4'-bipyridine, and 4-Pic is 4-methylpyridine [4]; MOF $[H_{1.1}F_{0.5}Na_{0.3}K_{0.1}][Mn_3\text{-}$

$(\mu_3\text{-F})(\text{Tcpep})_2(\text{DMF})(\text{H}_2\text{O})_2]\cdot9\text{H}_2\text{O}\cdot2\text{DMF}$, where Tcpep is tris(*para*-carboxyphenylethynyl)phosphine ($\text{P}\{\text{C}\equiv\text{CC}_6\text{H}_5\text{-4-CO}_2\text{H}\}_3$) [5]; and MOFs based on the cobalt and nickel complexes with 4-(4,4'-bipyridinium)benzoic acid and classical framework-forming dibasic acids, such as terephthalic acid and its derivatives, biphenyldicarboxylic and stilbenedicarboxylic acids [6].

Fluorocarboxylate complexes containing the $[\text{M}_3(\mu_3\text{-F})(\text{RCOO})_6(\text{L})_3]$ trinuclear fragment can be formed by both *p*-metals, for example, in the trinuclear magnesium trifluoroacetate complex $[\text{Mg}_3(\mu_3\text{-F})(\text{TFA})_6(\text{OCH}_3)_2(\text{Py})]\cdot4(\text{PyH})\cdot\text{OMe}$ [7], and various metal atoms and in the heterometallic pivalate complexes $[\text{Ni}_2\text{Cr}(\mu_3\text{-F})(\text{Piv})_6(\text{HPiv})_3]$, $[\text{Ni}_2\text{Cr}(\mu_3\text{-F})(\text{Piv})_6(\text{Py})_3]$, and $[\text{Ni}_2\text{Cr}(\mu_3\text{-F})(\text{Piv})_6(4\text{-CH}_3\text{-Py})_3]$ [8]. These compounds are popular objects for investigation due to their magnetic properties.

In this work, we continue the systematic study of the family of 3*d*-metal fluorocarboxylatometallates on the basis of elucidation of criteria for the existence of these compounds. The main attention is given to a possibility of synthesizing representatives of this family of compounds when acetic acid is used and to the formation of complexes in a mixture of acetic and trifluoroacetic acids. The $\text{K}[\text{Co}_3(\mu_3\text{-F})(\text{CF}_3\text{COO})_6(\text{CH}_3\text{COOH})_3](\text{CH}_3\text{COOH})$ (**I**), $\text{K}[\text{Ni}_3(\mu_3\text{-F})\text{-}(\text{CF}_3\text{COO})_6(\text{CH}_3\text{COOH})_3](\text{CH}_3\text{COOH})_{0.6}(\text{CF}_3\text{COOH})_{0.4}$ (**II**), and $\text{NH}_4[\text{Ni}_3(\mu_3\text{-F})(\text{CH}_3\text{COO})_6\text{-}(\text{CH}_3\text{COOH})_3](\text{CH}_3\text{COOH})_6$ (**III**) complexes synthesized for the first time are described. The structures of the triangular trinuclear anions, the coordination environment of the alkaline metal cations, and specific features of the anion and cation packing in these structures are discussed.

## EXPERIMENTAL

The following starting reagents were used: $\text{CoCO}_3\cdot n\text{Co(OH)}_2\cdot m\text{H}_2\text{O}$ (high-purity grade), $\text{NiCO}_3$ (analytical grade), $\text{KHF}_2$ (special purity grade), $\text{NH}_4\text{F}$ (analytical grade), $\text{CH}_3\text{COOH}$ (glacial, high-purity grade), and $\text{CF}_3\text{COOH}$ (99.9%, high-purity grade).

For the synthesis of compounds **I–III**, solutions of the starting compounds in glacial acetic acid were prepared and left for concentrating at room temperature in an desiccator over $\text{P}_4\text{O}_{10}$. Cobalt and nickel trifluoroacetates tetrahydrates $\text{M}(\text{CF}_3\text{COO})_2(\text{H}_2\text{O})_4$ (M = Co, Ni) used in the synthesis were prepared using a known procedure [1]. In all cases, the compounds unstable in air began to crystallize in 7–9 days. Platy single crystals of compounds **I–III** suitable for X-ray diffraction analysis (XRD) were taken from the mother liquor of the corresponding compounds. In two weeks, polycrystalline compounds **I–III** were filtered off from the mother liquor and dried in an argon flow. The single-phase character of all the synthesized compounds was confirmed by XRD (Huber G670 Guinier camera, Ge (111) monochromator, Cu$K_{\alpha1}$).

**Synthesis of $\text{K}[\text{Co}_3(\mu_3\text{-F})(\text{CF}_3\text{COO})_6\text{-}(\text{CH}_3\text{COOH})_3](\text{CH}_3\text{COOH})$ (I).** A weighed sample of $\text{KHF}_2$ (0.260 g, 3.3 mmol) was added to a solution of $\text{Co(TFA)}_2(\text{H}_2\text{O})_4$ (3.570 g, 10 mmol) in glacial acetic acid (15 mL). The yield of complex **I** was 64%.

**Synthesis of $\text{K}[\text{Ni}_3(\mu_3\text{-F})(\text{CF}_3\text{COO})_6\text{-}(\text{CH}_3\text{COOH})_3](\text{CH}_3\text{COOH})_{0.6}(\text{CF}_3\text{COOH})_{0.4}$ (II).** A weighed sample of $\text{KHF}_2$ (0.260 g, 3.3 mmol) was added to a solution of $\text{Ni(TFA)}_2(\text{H}_2\text{O})_4$ (3.570 g, 10 mmol) in 99% acetic acid (15 mL). The yield of complex **II** was 76%.

**Synthesis of $\text{NH}_4[\text{Ni}_3(\mu_3\text{-F})(\text{CH}_3\text{COO})_6(\text{CH}_3\text{COOH})_3]\text{-}(\text{CH}_3\text{COOH})_6$ (III).** A weighed sample of $\text{NH}_4\text{F}$ (0.122 g, 3.3 mmol) was added to a solution of $\text{Ni(OAc)}_2(\text{H}_2\text{O})_4$ (2.488 g, 10 mmol) in glacial acetic acid (25 mL). The yield of complex **III** was 58%.

**XRD.** Data for compounds **I** and **II** were collected using a Bruker D8 Quest diffractometer with a Photon III detector (Mo$K_\alpha$ radiation, $\lambda = 0.71073$ Å) at 100(2) K in the $\varphi$ and $\omega$ scan modes. Experimental data for compound **III** were collected on a Bruker SMART APEX II automated diffractometer (Mo$K_\alpha$ radiation, $\lambda = 0.71073$ Å, graphite monochromator) at 150 K in the $\omega$ scan mode. An absorption correction was applied by measuring equivalent reflection intensities [9]. The structures were solved by direct methods and refined by full-matrix least squares for $F^2$ using the SHELXTL and Olex2 program packages [10–12]. Hydrogen atoms were placed in the calculated positions and refined by the riding model. Populations of disordered $\text{CF}_3$ groups were refined using free variables. The crystallographic data and experimental structure refinement parameters are given in Table 1.

The coordinates of atoms, bond lengths, bond angles, and thermal shift parameters were deposited with the Cambridge Crystallographic Data Centre (CIF files CCDC nos. 2124887 (**I**), 2124888 (**II**), and 2127163 (**III**)).

## RESULTS AND DICUSSION

Compounds $\text{K}[\text{Co}_3(\mu_3\text{-F})(\text{CF}_3\text{COO})_6\text{-}(\text{CH}_3\text{COOH})_3](\text{CH}_3\text{COOH})$ (**I**) and $\text{K}[\text{Ni}_3(\mu_3\text{-F})(\text{CF}_3\text{COO})_6(\text{CH}_3\text{COOH})_3](\text{CH}_3\text{COOH})_{0.6}(\text{CF}_3\text{COOH})_{0.4}$ (**II**) were synthesized by the reactions of nickel or cobalt trifluoroacetate tetrahydrate with an excess of concentrated acetic acid in the presence of acidic potassium fluoride. Weaker acetic acid existed in the system predominantly in the nondissociated form and entered the crystal structure of the complex as a neutral ligand.

Ammonium fluoroacetatonickelate(II) $\text{NH}_4[\text{Ni}_3(\mu_3\text{-F})(\text{CH}_3\text{COO})_6(\text{CH}_3\text{COOH})_3](\text{CH}_3\text{COOH})_6$ (**III**) was synthesized for the first time using nickel acetate as the starting compound. Compounds **I–III** are built of trinuclear complex anions of the general formula

**Table 1.** Crystallographic data and experimental structure refinement parameters for compounds **I–III**

| Parameter | Value | | |
|---|---|---|---|
| | **I** | **II** | **III** |
| Empirical formula | $C_{20}H_{16}F_{19}O_{20}KCo_3$ | $C_{20}H_{16}F_{19}O_{20}KNi_3$ | $C_{30}H_{58}FNO_{30}Ni_3$ |
| *FW* | 1153.22 | 1174.15 | 1107.90 |
| Temperature, K | 100(2) | 100(2) | 150(2) |
| Crystal size, mm | 0.133 × 0.129 × 0.038 | 0.154 × 0.133 × 0.046 | 0.600 × 0.300 × 0.080 |
| Crystal system | Monoclinic | Monoclinic | Monoclinic |
| Space group | $P2_1/c$ | $P2_1/c$ | $P2_1/n$ |
| $a$, Å | 10.2799(4) | 10.3517(9) | 13.0632(2) |
| $b$, Å | 22.9727(7) | 22.7966(18) | 14.2954(2) |
| $c$, Å | 17.0025(6) | 16.9531(15) | 26.9907(4) |
| $\beta$, deg | 96.993(2) | 97.464(3) | 101.8180(10) |
| $V$, Å$^3$ | 3985.4(2) | 3966.8(6) | 4933.50(13) |
| $Z$ | 4 | 4 | 4 |
| $\rho_{calc}$, g/cm$^3$ | 1.922 | 1.966 | 1.492 |
| $\mu$, mm$^{-1}$ | 1.500 | 1.683 | 1.227 |
| $F(000)$ | 2268 | 2318 | 2312 |
| Range of $\theta$, deg | 2.15–26.00 | 1.98–26.00 | 2.099–27.00 |
| Range of indices | $-12 \le h \le 12$,<br>$-23 \le k \le 28$,<br>$-20 \le l \le 20$ | $-12 \le h \le 12$,<br>$-27 \le k \le 28$,<br>$-20 \le l \le 20$ | $-16 \le h \le 16$,<br>$-18 \le k \le 18$,<br>$-34 \le l \le 34$ |
| Total number of reflections | 30671 | 30268 | 56898 |
| Independent reflections ($R_{int}$) | 7820 (0.0659) | 7790 (0.0763) | 10764 (0.0424) |
| Data completeness for $\theta$, % | 99.9 | 100 | 99.9 |
| Number of parameters/restraints | 555/45 | 589/94 | 647/37 |
| GOOF | 1.035 | 1.040 | 1.011 |
| $R_1$ ($I > 2\sigma(I)$) | 0.0693 | 0.0668 | 0.0346 |
| $wR_2$ (for all data) | 0.1817 | 0.1728 | 0.0828 |
| $\Delta\rho_{max}/\Delta\rho_{min}$, e/Å$^3$ | 1.980/–1.356 | 1.751/–1.698 | 0.523/–0.574 |

$[M_3(\mu_3\text{-}F)(RCOO)_6(CH_3COOH)_3]^-$ (R = $CF_3$ (**I**, **II**) or $CH_3$ (**III**)) and potassium (**I**, **II**) or ammonium (**III**) cations. The *d*-metal atoms forming the complex anion are arranged at the vertices of an almost regular triangle, the tridentate fluorine atom is localized in the triangle plane, and each pair of metal atoms is bound to each other by two carboxylate groups (trifluoroacetate in **I** and **II** or acetate in **III**). The coordination environment of the metal atom is supplemented to the octahedral environment by the oxygen atom of the acetic acid molecule acting as a neutral ligand.

A comparison of the complex anions in structures **I** and **II** shows a decrease in the bond lengths in the coordination environment of the transition metal atoms on going from Co to Ni due to a decrease in the ion radius of the complexing atom. As can be seen from Table 2, the $M–O_{equiv}$ bonds with the oxygen atoms of the bridging trifluoroacetate groups are most sensitive to a change in the ion radius, whereas the change in the M–F and $M–O_{axial}$ bond lengths is not so significant. On going from Co to Ni, the change in the average $M–O_{equiv}$ bond lengths is 0.044 Å, which is somewhat lower than the difference in the ion radii of $Co^{2+}$ and $Ni^{2+}$ with the coordination number 6 and amounts to 0.055 Å [13]. The M $M–O_{equiv}$ F and M $M–O_{equiv}$ $O_{axial}$ bonds shorten by 0.027 Å only (on the average). A decrease in the bond lengths in the coordination environment of the transition metal leads to a decrease in the size of the complex anion as a whole. The average M...M distances in compounds **I** and **II** are 3.51 and 3.46 Å, respectively.

**Table 2.** Distances (Å) and angles (deg) in the coordination environment of the metal atoms in the structures of complexes **I**–**III**

| Bond | *d*, Å | | | Angle | ω, deg | | |
|---|---|---|---|---|---|---|---|
| | **I** | **II** | **III** | | **I** | **II** | **III** |
| M(1)–F(1) | 2.032(3) | 2.008(3) | 1.9696(11) | F(1)M(1)O(2) | 92.5(1) | 92.9(1) | 95.38(5) |
| M(1)–O(2) | 2.103(4) | 2.050(4) | 2.0555(15) | F(1)M(1)O(4) | 90.3(1) | 91.1(1) | 92.46(6) |
| M(1)–O(4) | 2.081(4) | 2.042(4) | 2.0369(15) | F(1)M(1)O(7) | 93.5(1) | 93.6(1) | 92.62(6) |
| M(1)–O(7) | 2.065(4) | 2.017(4) | 2.0250(16) | F(1)M(1)O(9) | 89.2(1) | 90.9(1) | 93.59(5) |
| M(1)–O(9) | 2.084(4) | 2.025(4) | 2.0439(15) | F(1)M(1)O(5) | 174.5(1) | 176.3(1) | 178.08(6) |
| M(1)–O(5) | 2.078(4) | 2.060(4) | 2.0880(15) | O(4)M(1)O(2) | 87.9(2) | 88.7(2) | 90.59(7) |
| | | | | O(7)M(1)O(4) | 90.3(2) | 88.6(2) | 89.27(7) |
| | | | | O(7)M(1)O(9) | 92.6(2) | 93.8(2) | 91.06(7) |
| | | | | O(9)M(1)O(2) | 89.2(2) | 88.8(2) | 88.24(6) |
| M(2)–F(1) | 2.014(3) | 1.990(3) | 1.9734(12) | F(1)M(2)O(1) | 96.5(1) | 96.3(1) | 90.90(6) |
| M(2)–O(1) | 2.076(4) | 2.037(4) | 2.0674(15) | F(1)M(2)O(3) | 88.7(1) | 89.8(1) | 94.23(6) |
| M(2)–O(3) | 2.099(4) | 2.057(4) | 2.0384(15) | F(1)M(2)O(14) | 92.6(1) | 93.0(1) | 91.56(6) |
| M(2)–O(14) | 2.084(4) | 2.036(4) | 2.0139(15) | F(1)M(2)O(16) | 95.7(1) | 96.1(1) | 94.82(6) |
| M(2)–O(16) | 2.049(4) | 2.017(4) | 2.0303(15) | F(1)M(2)O(17) | 178.0(1) | 178.6(1) | 178.38(6) |
| M(2)–O(17) | 2.105(4) | 2.084(4) | 2.1179(16) | O(1)M(2)O(3) | 89.9(2) | 89.9(2) | 90.68(6) |
| | | | | O(1)M(2)O(14) | 86.1(2) | 86.5(2) | 89.55(6) |
| | | | | O(16)M(2)O(3) | 91.4(2) | 90.8(2) | 86.12(6) |
| | | | | O(16)M(2)O(14) | 92.4(2) | 92.3(2) | 93.08(6) |
| M(3)–F(1) | 2.033(3) | 1.998(3) | 1.9792(12) | F(1)M(3)O(8) | 93.7(1) | 93.6(1) | 89.40(6) |
| M(3)–O(8) | 2.055(4) | 2.014(4) | 2.0565(15) | F(1)M(3)O(10) | 92.8(1) | 93.5(1) | 93.88(5) |
| M(3)–O(10) | 2.089(4) | 2.041(4) | 2.0720(16) | F(1)M(3)O(13) | 91.1(1) | 91.2(1) | 89.86(5) |
| M(3)–O(13) | 2.049(4) | 2.022(4) | 2.0387(15) | F(1)M(3)O(15) | 95.5(1) | 95.3(1) | 98.13(6) |
| M(3)–O(15) | 2.072(4) | 2.030(4) | 2.0172(15) | F(1)M(3)O(11) | 177.2(1) | 176.4(1) | 178.68(6) |
| M(3)–O(11) | 2.099(4) | 2.058(4) | 2.0908(15) | O(8)M(3)O(10) | 90.7(2) | 91.6(2) | 89.59(6) |
| | | | | O(8)M(3)O(15) | 87.9(2) | 87.9(2) | 88.78(6) |
| | | | | O(13)M(3)O(10) | 85.7(2) | 85.8(2) | 89.82(6) |
| | | | | O(13)M(3)O(15) | 94.9(2) | 94.0(2) | 91.96(6) |
| M–F* | 2.026 | 1.999 | 1.974 | M(1)F(1)M(3) | 119.9(1) | 119.4(2) | 120.65(6) |
| M–$O_{equiv}$** | 2.076 | 2.032 | 2.041 | M(2)F(1)M(3) | 117.7(1) | 118.6(2) | 117.96(6) |
| M–$O_{axial}$*** | 2.094 | 2.067 | 2.099 | M(2)F(1)M(1) | 122.3(1) | 122.0(2) | 121.30(6) |

* Averaged M–F bond lengths.
** Averaged M–O bond lengths involving bridging carboxylate groups.
*** Averaged M–O bond lengths involving axial $CH_3CO_2H$ molecules.

It seems reasonable to consider the influence of ligand replacement on a change in the geometry of the complex anion in the series $[Ni_3(\mu_3\text{-}F)(CF_3COO)_6(CF_3COOH)_3]^-$ [3], $[Ni_3(\mu_3\text{-}F)(CF_3COO)_6(AcOH)_3]^-$ (**II**), and $[Ni_3(\mu_3\text{-}F)(AcO)_6(AcOH)_3]^-$ (**III**). When acetic acid molecules are inserted as axial ligands instead of trifluoroacetic acid, the average M–$O_{axial}$ bond lengths decrease regularly (2.118 Å in [3] and 2.067 Å in **II**) due to an increase in the donor ability of the ligand. When trifluoroacetate groups are replaced by acetate groups acting as bridging ligands, an increase in the average M–$O_{axial}$ distances is observed (2.067 Å in **II** and 2.099 Å in **III**) instead of the expected decrease in the M–$O_{equiv}$ bond lengths, and the M–F distance decrease (1.999 Å in **II** and 1.976 Å in **III**) resulting in a stronger distortion of the octahedral environment of the nickel atoms (Table 2). The average Ni...Ni distances in the considered series are 3.44 [3], 3.46 (**II**), and 3.42 (**III**) Å, respectively.

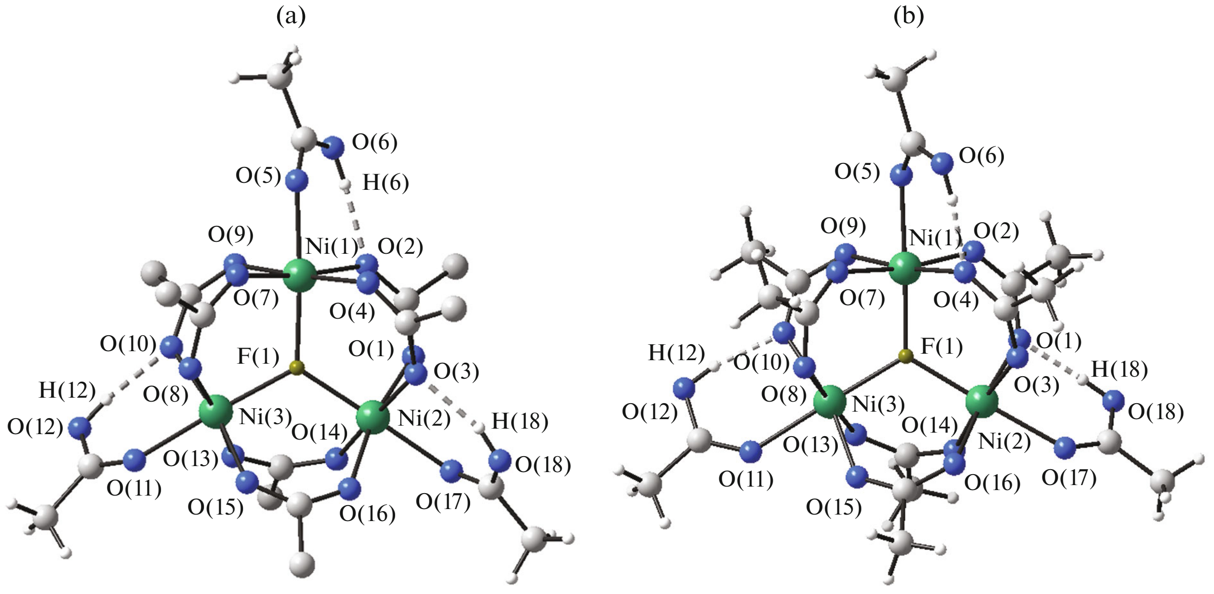

**Fig. 1.** Structures of complex anions in compounds (a) **II** and (b) **III**.

In structures **I**–**III**, the complex anions are bound into infinite chains due to the formation of contacts with the cations, and the chains are joined into layers of different structures by a system of hydrogen bonds involving solvate molecules of acetic acid.

In complexes **I** and **II**, the oxygen atoms of the bridging trifluoroacetate groups (O(1), O(14)), carbonyl oxygen atom O(17) of the axial molecule of acetic acid, and fluorine atom F(15) of the trifluoromethyl group form contacts with the potassium atom, which, in turn, is bound to the adjacent trinuclear anion via contacts with the oxygen atoms O(8) and O(15) of the bridging trifluoroacetate groups, carbonyl oxygen atom O(11) of the axial acetic acid molecule, and fluorine atom F(10) (Fig. 1). In addition, the potassium atom forms a contact with the carbonyl oxygen atom O(19) of the solvate acetic acid molecule. It seems difficult to restrict correctly the coordination polyhedron of the potassium atom. The K...O distances range from 2.729(4) to 3.122(4) (average 2.85 Å) in structure **I** and from 2.728(4) to 3.128(5) Å (average 2.85 Å) in structure **II**. The K...F distances are 2.86(3)–3.119(19) Å (average 3.00 Å) in structure **I** and 2.842(16)–3.152(19) Å (average 2.97 Å) in structure **II**.

The trinuclear anions are bound by the potassium atoms to form infinite zigzag chains along the *c* axis. The solvate acetic acid molecule are joined into dimers by hydrogen bonds thus connecting the chains into layers parallel to the {*bc*} plane (Fig. 2). Interestingly, in structure **II** the solvate molecules of acetic acid are partially replaced randomly by trifluoroacetic acid molecules with populations of 0.6/0.4, respectively. The trifluoroacetic molecules are arranged in such a way that the hydrogen bond is formed with the O(17) oxygen atom belonging to the adjacent chain rather than with the solvate molecule of acetic acid. No similar disordering is observed in structure **I**. Thus, the chains in structure **II** are bound more weakly than those in structure **I**. The parameters of hydrogen bonds for structures **I** and **II** are given in Table 3.

In structure **III**, the anions are bound to each other to form spiral chains arranged along the *b* axis via the formation of hydrogen bonds with the ammonium cations: N(1)–H(1A)...O(2), N(1)–H(1B)...O(9), N(1)–H(1D)...O(3), and N(1)–H(1D)...O(16) (Fig. 3, Table 3). The chains are crosslinked between each other to form corrugated layers parallel to the {0, 0, 1} plane by a system of hydrogen bonds involving the ammonium cation, two solvate molecules of acetic acid, and O(8) oxygen atom of the bidentate acetate group. The hydrogen atom of the ammonium cation H(1C) forms the N(1)–H(1C)...O(25) hydrogen bond with the carbonyl oxygen atom of the solvate acetic acid molecule, the hydroxyl group of which forms the O(24)–H(24)...O(22) hydrogen bond with the carbonyl oxygen atom of the second solvate molecule of acetic acid, and the hydroxyl group of the latter is bound, in turn, by the O(23)–H(23)...O(8) hydrogen bond to the O(8) oxygen atom belonging to the adjacent chain.

The oxygen atoms from the coordination environment of the Ni(3) atom participate in the formation of another system of hydrogen bonds with three solvate molecules of acetic acid (Fig. 4). The O(11) and O(15) oxygen atoms form the forked hydrogen bond O(26)–H(26)...(O(11), O(15)) with the hydroxyl group of one solvate molecule of acetic acid. The O(13) oxygen atom forms the O(21)–H(21)...O(13) hydrogen bond

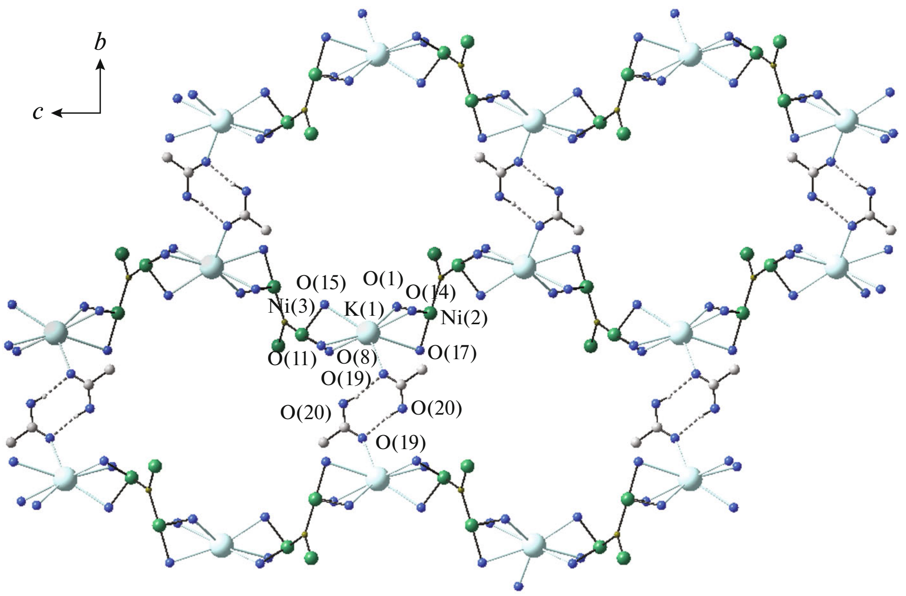

**Fig. 2.** Structure of the layer in compound **II**.

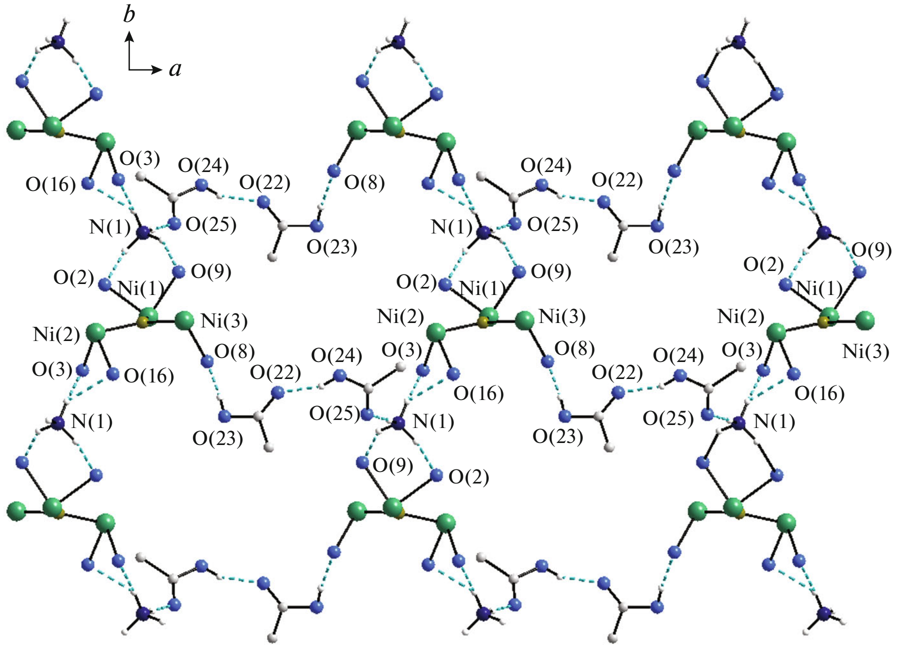

**Fig. 3.** Structure of the layer in compound **III**.

with the hydroxyl group of another acetic acid molecule, and the carbonyl atom of which forms, in turn, the O(29)–H(29)...O(20) hydrogen bond with the hydroxyl group of the third molecule of acetic acid. The structure also contains free dimers of acetic acid arranged between the layers and linked with the rest structure via van der Waals interactions.

To conclude, the synthesized for the first time complex $NH_4[Ni_3(\mu_3\text{-}F)(CH_3COO)_6(CH_3COOH)_3](CH_3COOH)_6$ (**III**) shows a principal possibility of existing trinuclear fluoroacetate complexes of transition metals. The synthesis of complexes $K[Co_3(\mu_3\text{-}F)(CF_3COO)_6(CH_3COOH)_3](CH_3COOH)$ (**I**) and $K[Ni_3(\mu_3\text{-}F)(CF_3COO)_6(CH_3COOH)_3](CH_3COOH)_{0.6}(CF_3COOH)_{0.4}$ (**II**) using in fact a mixture of acetic and trifluoroacetic acids as the starting compounds indicates the typical competitive reactions of ligand exchange that occur during the formation of a frame-

**Table 3.** Geometric parameters of hydrogen bonds for complexes **I–III**

| D–H···A | Distance, Å | | | Angle D–H···A, deg |
|---|---|---|---|---|
| | D–H | H···A | D···A | |
| **I** | | | | |
| O(6)–H(6)...O(2) | 0.840(5) | 1.853(5) | 2.695(6) | 163.1 |
| O(12)–H(12)...O(10) | 0.840(5) | 1.865(5) | 2.687(6) | 167.0 |
| O(18)–H(18)...O(3) | 0.839(5) | 1.804(5) | 2.636(6) | 165.5 |
| O(20)–H(20)...O(19) | 0.840(5) | 1.939(6) | 2.678(8) | 163.5 |
| **II** | | | | |
| O(6)–H(6)...O(2) | 0.840(5) | 1.881(5) | 2.670(7) | 163.4 |
| O(12)–H(12)...O(10) | 0.840(5) | 1.862(5) | 2.683(6) | 164.5 |
| O(18)–H(18)...O(3) | 0.841(5) | 1.815(4) | 2.617(7) | 162.2 |
| O(20)–H(20)...O(19) | 0.840(5) | 1.861(5) | 2.768(12) | 168.7 |
| O(21)–H(21)...O(17) | 0.840(5) | 2.263(5) | 2.888(15) | 144.5 |
| **III** | | | | |
| O(6)–H(6)...O(4) | 0.840(3) | 1.740(2) | 2.568(2) | 168.1 |
| O(12)–H(12)...O(10) | 0.840(2) | 1.723(2) | 2.549(2) | 167.2 |
| O(18)–H(18)...O(1) | 0.840(2) | 1.700(2) | 2.526(2) | 167.0 |
| O(24)–H(24)...O(22) | 0.840(3) | 1.801(3) | 2.605(3) | 159.4 |
| O(23)–H(23)...O(8) | 0.840(2) | 1.786(2) | 2.621(2) | 171.5 |
| O(21)–H(21)...O(13) | 0.840(2) | 1.785(2) | 2.603(2) | 164.1 |
| O(26)–H(26)...O(11) | 0.840(2) | 2.295(2) | 3.046(3) | 148.5 |
| O(26)–H(26)...O(15) | 0.840(2) | 2.241(2) | 2.888 | 134.0 |
| O(29)–H(29)...O(20) | 0.840(2) | 2.265(3) | 2.687(4) | 169.4 |
| O(30)–H(30)...O(31) | 0.840(2) | 2.265(3) | 2.653 | 175.7 |
| N(1)–H(1A)...O(2) | 0.958(2) | 2.141(2) | 2.883 | 133.4 |
| N(1)–H(1B)...O(9) | 0.969(2) | 1.953(2) | 2.823(3) | 148.2(17) |
| N(1)–H(1C)...O(25) | 0.959(2) | 2.416(2) | 2.802(3) | 174.0(18) |
| N(1)–H(1D)...O(3) | 0.959(2) | 2.443(2) | 3.028(3) | 147.4(16) |
| N(1)–H(1D)...O(16) | 0.959(2) | 1.955(2) | 2.816(3) | 125.5(15) |

work of the complex anion. The replacement of the ligands forming the complex anion changes the size of the complex anion.

Regardless of the nature of carboxylic acid involved in the formation of the complex anion, the alkaline metal and ammonium cations bind the complex cations into chains. An increase in the dimensionality of the structure due to the formation of many hydrogen bonds is achieved by the insertion of acetic acid into the compound.

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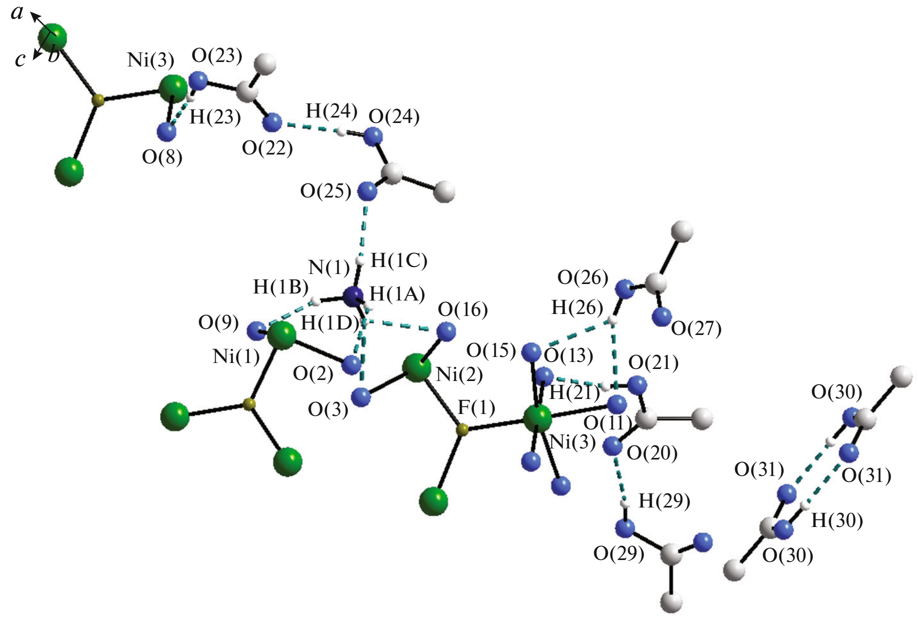

**Fig. 4.** System of hydrogen bonds in compound **III**.

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## CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

## REFERENCES

1. Morozov, I.V., Karpova, E.V., Glazunova, T.Y., et al., *Russ. J. Coord. Chem.*, 2016, vol. 42, p. 647. https://doi.org/10.1134/S107032841610002X
2. Glazunova, T.Y., Tereshchenko, D.S., Buzoverov, M.E., et al., *Russ. J. Coord. Chem.*, 2021, vol. 47, p. 347. https://doi.org/10.1134/S1070328421040023
3. Tereshchenko, D.S., Morozov, I.V., Boltalin, A.I., et al., *Russ. J. Inorg. Chem.*, 2004, vol. 49, no. 6, p. 836.
4. Zai-Lai Xie, Mei-Ling Feng, Bin Tan, and Xiao-Ying Huang, *Cryst. Eng. Commun.*, 2012, vol. 14, p. 4894. https://doi.org/10.1039/C2CE25169H
5. Reynolds III, J.E., Walsh, K.M., Li, B., et al., *Chem. Commun.*, 2018, vol. 54, p. 9937. https://doi.org/10.1039/C8CC05402A
6. Aulakh, D., Islamoglu, T., Bagundes, V.F., et al., *Chem. Mater.*, 2018, vol. 30, p. 8332. https://doi.org/10.1021/acs.chemmater.8b03885
7. Noack, J., Fritz, C., Flugel, C., et al., *Dalton Trans.*, 2013, vol. 42, p. 5706. https://doi.org/10.1039/C3DT32652G
8. Walsh, J.P.S., Meadows, S.B., Ghirri, A., et al., *Inorg. Chem.*, 2015, vol. 54, p. 12019. https://doi.org/10.1021/acs.inorgchem.5b01898
9. Sheldrick, G.M., *SADABS. Program for Scaling and Correction of Area Detector Data*, Göttingen: Univ. of Göttingen, 1997.
10. Sheldrick G.M., *Acta Crystallogr., Sect. A: Found. Adv.*, 2015, vol. 71, p. 3. https://doi.org/10.1107/S2053273314026370
11. Sheldrick G.M., *Acta Crystallogr., Sect. C: Struct. Chem.*, 2015, vol. 71, p. 3. https://doi.org/10.1107/S2053229614024218
12. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J., et al., *J. Appl. Crystallogr.*, 2009, vol. 42, p. 339. https://doi.org/10.1107/S0021889808042726
13. Shannon, R.D., *Acta Crystallogr., Sect. A: Cryst. Phys. Diffr., Theor. Gen. Crystallogr.*, 1976, vol. 32, p. 751. https://doi.org/10.1107/S0567739476001551

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