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Synthesis and Crystal Structures of New Potassium Fluorotrifluoroacetatometallates: $K_n[M_3(\mu_3\text{-}F)(CF_3COO)_6L_3]L'$ (M = Co, Ni; L = CF_3COO^-, CF_3COOH, H_2O; L' = CF_3COOH, H_2O; n = 1, 2)

T. Yu. Glazunova[a], *, D. S. Tereshchenko[a], M. E. Buzoverov[a], E. V. Karpova[a], and E. Kh. Lermontova[b]
[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—Four new representatives of potassium fluorotrifluoroacetatometallates are synthesized and crystallographically studied: $K_2[Co_3(\mu_3\text{-}F)(CF_3COO)_6(CF_3COO)(CF_3COOH)_2]\cdot CF_3COOH$ (**I**), $K[Co_3(\mu_3\text{-}F)(CF_3COO)_6(H_2O)_3]\cdot H_2O\cdot 2CF_3COOH$ (**II**), $K[Ni_3(\mu_3\text{-}F)(CF_3COO)_6(H_2O)_3]\cdot H_2O\cdot 2CF_3COOH$ (**III**), and $K_2[Ni_3(\mu_3\text{-}F)(CF_3COO)_6(CF_3COOH)_3][Ni_3(\mu_3\text{-}F)(CF_3COO)_6(CF_3COOH)_2(H_2O)]\cdot CF_3COOH$ (**IV**). All complexes under study contain trinuclear triangular complex anions $[M_3(\mu_3\text{-}F)(CF_3COO)_6(L)_3]^{n-}$ (M = Ni, Co; L = CF_3COO^-, CF_3COOH, H_2O; n = 1, 2) resembling in structure the earlier studied fluorotrifluoroacetatometallates of alkaline metals and ammonium. The μ_3-bridging F atom is localized at the center of the triangle of the Ni(II) or Co(II) atoms. Six bridging trifluoroacetate groups arranged above and under the plane of the $[M_3F]$ triangle pairwise bind the metal atoms. The oxygen atoms of ligands L supplement the coordination environment of the M atoms to the octahedral environment. The possibility of the charge –2 on the complex anion $[M_3(\mu_3\text{-}F)(CF_3COO)_6L_3]$ is shown. The consecutive replacement of the axial molecules of trifluoroacetic acid by water changes the type of the structure from the chain (**IV**) to layered (**II**, **III**) structure and then to the volume network (**I**). The molecular structures of complexes **I**–**IV** are determined by X-ray structure analysis (CIF files CCDC nos. 2010760 (**I**), 2010761 (**II**), 2010762 (**III**), and 2010763(**IV**)).

Keywords: synthesis, crystal structure, fluorotrifluoroacetatometallates, trifluoroacetate complexes, cobalt trifluoroacetate, nickel trifluoroacetate

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INTRODUCTION

At present, one of the urgent aspects of the development of inorganic chemistry is the targeted synthesis of substances and materials with specified properties, in particular, design of crystal structures of complexes. The solution of this problem provides a possibility for the purposeful development of new materials by modeling the crystal structure in order to finely tune the physical properties of matter at the nanolevel.

Coordination compounds based on trifluoroacetates of *d* elements containing infinite chains or layers with the triangular motif of the metal cation arrangement represent a new platform for studying low-dimensional magnetism [1], and the polynuclear Co(II) and Ni(II) carboxylate complexes can be interesting objects for the study of spin–spin exchange interactions between paramagnetic ions [2].

Low-dimensional and frustrated magnetic systems in which the long-range magnetic order cannot be found because of geometric features of the exchange interactions are presently among the most discussed and promising objects of the chemistry and physics of condensed state [3].

This work continues the studies in the area of fluorotrifluoroacetatometallates of transition metals, where only 15 compounds [4–6] of the general formula $[M_3(\mu_3\text{-}F)(CF_3COO)_6(CF_3COOH)_3]^-$ (M = Mn–Ni) were described before the publication of the present work and the single example of the $Na[Zn_3(\mu_3\text{-}F)(CF_3COO)_6(H_2O)_3](H_2O)_{4.34}$ complex of different composition containing water molecules as axial ligands was presented [6].

The single crystallographic systematization of a number of fluorotrifluoroacetatometallates of alkaline metals, ammonium, and nitrosonium of the general formula $M'[M_3(\mu_3\text{-}F)(CF_3COO)_6(L)_3]$ (where M' = Li–Cs, NH_4, and NO; M = Mn, Fe, Co, Ni, and Zn;

$L = CF_3COO^-$, CF_3COOH, and H_2O) is presented in the review [6].

Fluorotrifluoroacetatometallates of *p* elements are presented by the single example: $(PyH)_4[Mg_3(\mu_3\text{-}F)(CF_3COO)_6(OCH_3)_2(Py)](OCH_3)$ [7].

The structural fragment $M_3(\mu_3\text{-}F)$ in the crystal structures of other carboxylates is presented by a few examples. The heterometallic complexes $[Ni_2Cr(\mu_3\text{-}F)(O_2CtBu)_6L_3]$ (L = HO_2CBut, C_5H_5N, and (4-CH_3)-C_5H_4N)) [8] and the Cd complexes [9] and Co and Ni complexes [10] classified as metal-organic frameworks (MOF) were described.

In this work, the synthetic approach developed previously for the synthesis of transition metal fluorotrifluoroacetatometallates [4–6] was modified for the preparation of new compounds. A possibility of changing the compositions and, as a consequence, the crystal structures of the complexes due to the variation of the synthesis conditions was shown. The structures of the triangular trinuclear anions, the coordination environments of the alkaline metal cations, and specific features of packing of the anions and cations in these structures are discussed.

EXPERIMENTAL

The following initial reagents synthesized by a described procedure [6] were used: KHF_2, P_4O_{10}, CF_3COOH (all reagent grade), $Co(CF_3COO)_2 \cdot 4H_2O$, and $Ni(CF_3COO)_2 \cdot 4H_2O$.

The synthesis of complexes **I–IV** is based on the thoroughly elaborated procedure of synthesis of alkaline metal fluorotrifluoroacetatometallates. Hot saturated solutions of cobalt or nickel trifluoroacetate tetrahydrate and alkaline metal fluoride in trifluoroacetic acid (molar ratio 3 : 1) were poured together, and the resulting mixtures were left for crystallization in a vacuum desiccator over P_4O_{10}. An amorphous precipitate, probably, of 3*d* metal fluoride formed immediately after pouring together the solutions was recrystallized for a week to obtain well formed crystals of alkaline metal fluorotrifluoroacetatometallates [6].

Synthesis of $K_2[Co_3(\mu_3\text{-}F)(CF_3COO)_6(CF_3COO)(CF_3COOH)_2] \cdot CF_3COOH$ (I). A solution of KHF_2 (0.073 g 0.94 mmol) in CF_3COOH (5 mL) was added to a solution of $Co(CF_3COO)_2 \cdot 4H_2O$ (1.000 g, 2.81 mmol) in CF_3COOH (10 mL) with stirring. The formed precipitate was filtered through a paper “blue ribbon” filter. The mother liquor was left for crystallization in a vacuum desiccator over phosphorus anhydride P_4O_{10} at room temperature, and the desiccator was evacuated approximately once three days. Unstable in air well formed red crystals were obtained after the complete removal of the liquid phase for 10–15 days.

The counter synthesis (KHF_2 (0.146 g, 1.87 mmol), $Co(CF_3COO)_2 \cdot 4H_2O$ (1.000 g, 2.81 mmol), and CF_3COOH (20 mL)) makes it possible to isolate compound **I** as the single reaction product.

Synthesis of $K[Co_3(\mu_3\text{-}F)(CF_3COO)_6(H_2O)_3] \cdot H_2O \cdot 2CF_3COOH$ (II), $K[Ni_3(\mu_3\text{-}F)(CF_3COO)_6(H_2O)_3] \cdot H_2O \cdot 2CF_3COOH$ (III), and $K_2[Ni_3(\mu_3\text{-}F)(CF_3COO)_6(CF_3COOH)_3][Ni_3(\mu_3\text{-}F)(CF_3COO)_6(CF_3COOH)_2(H_2O)] \cdot CF_3COOH$ (IV). A solution of KHF_2 (0.073 g, 0.94 mmol) in CF_3COOH (5 mL) was added to a solution of $Co(CF_3COO)_2 \cdot 4H_2O$ or $Ni(CF_3COO)_2 \cdot 4H_2O$ (1.000 g, 2.81 mmol) in CF_3COOH (10 mL) on heating to 80°C. To obtain compounds **II** and **III**, the reaction mixture was kept at 80°C for 2 h. Then, in all cases (**II–IV**), the solution was left to crystallize in a vacuum desiccator over P_4O_{10} at room temperature, and the desiccator was evacuated approximately once a day. In all cases, the crystallization of the unstable in air compounds was observed for 24–48 h. The liquid phase was removed completely within 5–10 days.

X-ray diffraction analysis was carried out on a DRON3-M diffractometer ($CuK_{\alpha 1}$ radiation, Ge monochromator). Since the synthesized compounds are unstable in air, the samples were prepared in a sealed box in a dry nitrogen atmosphere and placed under a polystyrene film. The diffraction patterns were processed and the peaks obtained by integration were indexed using the STOE WinXPOW program. The phases were identified using the PC PDF database [11].

Hygroscopic crystals were selected under a Nujol layer using a polarization microscope and were rapidly (less than within 1 min) transferred to a diffractometer, where they were cooled with a flow of dry gaseous nitrogen.

X-ray structure analysis. X-ray diffraction data for crystals were collected on a Bruker SMART APEX II automated diffractometer at 150 K (for **II** and **IV**) and 100 K (for **III**) and on an Enraf-Nonius CAD4 diffractometer at 123 K (for **I**) using MoK_α radiation (λ = 0.71073 Å, graphite monochromator). An absorption correction was applied by measurements of equivalent reflection intensities [12]. The structures were solved by a direct method and refined by full-matrix anisotropic least squares for F^2 for all non-hydrogen atoms (SHELXTL-Plus [13]). Hydrogen atoms were placed in the calculated positions and refined by the riding model. In the case of complex **IV**, the solvent molecules were disordered and cannot adequately be modeled and, hence, the SQUEESE procedure implemented into the PLATON program was used to solve the structure [14]. The crystallographic data and experimental and structure refinement details for compounds **I–IV** are presented in Table 1.

The structural data of the synthesized complexes were deposited with the Cambridge Crystallographic Data Centre (CIF files CCDC nos. 2010760 (**I**),

Table 1. Crystallographic data and structure refinement parameters for complexes **I**–**IV**

Parameter	Value			
	I	**II**	**III**	**IV**
Empirical formula	$C_{20}H_3O_{20}F_{31}K_2Co_3$	$C_{16}H_{10}O_{20}F_{25}KCo_3$	$C_{16}H_{10}O_{20}F_{25}KNi_3$	$C_{36}H_8O_{37}F_{56}K_2Ni_6$ (+solvent)
FW	1407.21	1213.13	1212.47	2526.88
Crystal size, mm	0.25 × 0.20 × 0.15	0.24 × 0.15 × 0.08	0.10 × 0.08 × 0.06	0.18 × 0.11 × 0.06
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P\bar{1}$
Cell parameters:				
a, Å	15.196(2)	13.1069(3)	13.0239(6)	13.9177(8)
b, Å	17.942(2)	13.9789(2)	13.9153(6)	17.1389(9)
c, Å	16.492(2)	20.9794(3)	20.8055(8)	18.7737(10)
α, deg	90	90	90	78.246(2)
β, deg	99.53(2)	100.5980(10)	100.423(2)	86.370(2)
γ, deg	90	90	90	80.643(2)
V, Å^3	4434.3(10)	3778.28(12)	3708.4(3)	4323.8(4)
Z	4	4	4	2
ρ_{calc}, g/cm^3	2.108	2.133	2.172	1.941
$\mu(MoK_\alpha)$, mm^{-1}	1.498	1.610	1.822	1.574
F(000)	2724	2364	2376	2460
Range of θ, deg	1.135–24.990	2.241–29.753	2.161–26.595	2.217–29.649
Ranges of indices	$-3 \leq h \leq 18$, $-1 \leq k \leq 21$, $-19 \leq l \leq 19$	$-17 \leq h \leq 17$, $-18 \leq k \leq 18$, $-27 \leq l \leq 27$	$-16 \leq h \leq 16$, $-17 \leq k \leq 17$, $-25 \leq l \leq 26$	$-17 \leq h \leq 17$, $-21 \leq k \leq 21$, $-23 \leq l \leq 23$
Total number of reflections	16286	46384	42931	64982
Independent reflections (R_{int})	7791 (0.0539)	9118 (0.0517)	8092 (0.0967)	16952 (0.1472)
Number of refined parameters	718	689	653	1370
R_1 for $I > 2\sigma(I)$	0.0752	0.0507	0.0688	0.0818
wR_2 (all data)	0.1960	0.0890	0.1230	0.1958
GOOF	1.067	1.099	1.061	0.935
$\Delta\rho_{min}/\Delta\rho_{max}$, e/Å^3	−1.371/1.923	−0.810/0.972	−1.145/0.932	−1.043/0.901

2010761 (**II**), 2010762 (**III**), and 2010763 (**IV**); deposit@ccdc.cam.ac.uk; http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

The synthesis of fluorotrifluoroacetatometallates of the general formula M'[$M_3(\mu_3$-F)$(CF_3COO)_6(L)_3$] (M' = Li–Cs and NH_4; M = Mn, Fe, Co, Ni, and Zn; L = CF_3COO, CF_3COOH, and H_2O) was described [4–6]. The first trinuclear nitrosonium fluorotrifluoroacetatometallates NO[$Ni_3(\mu_3$-F)$(CF_3COO)_6$-$(CF_3COOH)_3$] and NO[$Co_3(\mu_3$-F)$(CF_3COO)_6$-$(CF_3COOH)_3$] were obtained randomly without addition of alkaline metal fluorides using trifluoroacetic acid containing ~0.05 wt % HF as an impurity [4]. Later we synthesized and structurally studied more than 15 representatives of the fluorotrifluoroacetatometallate family [6].

The influence of the alkaline metal on structure formation was shown when considering a series of the closest structural analogues of fluorotrifluoroacetatometallates of the alkaline metal series. The longer the radius of the cation, the more possibilities for the formation of hydrogen bonds in the structure due to the inclusion of solvate solvent molecules, which was shown for Cs^+ cations that can form compounds of various structures depending on the synthesis conditions [5, 6].

The shorter the radius of the cation, the higher the contribution of σ bonds. Thus, the compounds containing Na and the more so Li form the structure in which each cation coordinates three oxygen atoms of adjacent complex anions to form 1D polymeric structures [6]. The elongation of the cation radius on going to K results in the situation where the environment of the alkaline metal is formed by the oxygen and fluorine atoms of the complex cations and the oxygen atoms of the solvate ligands. In this case (as will be shown below), different structural types are formed by the system of hydrogen bonds that takes place in each case due to the introduction of various ligands that do not change the nature of the compound. Each compound can be synthesized if the synthesis conditions are strictly fulfilled.

In this work, we synthesized for the first time and structurally studied complex **I**, the charge of the complex anion of which is –2. The external sphere of the complex contains two potassium atoms. The possibility of the double-charge complex anion [$M_3(\mu_3$-F)$(CF_3COO)_6L_3]^{2-}$ to exist was shown for the first time and additionally indicates the stability of the trinuclear fluorocarboxylate structural fragment.

The distinction of the composition of compound **I** from the nominal composition is explained by a change in the composition of the reaction mixture during the synthesis. Potassium hydrodifluoride KHF_2 was used as the initial compound. The concentration of F^- ions in the reaction mixture exceeded the concentration of K^+ by two times, and the ratio K : Co : F = 1 : 3 : 2 was maintained. The removal from the reaction mixture of a finely dispersed precipitate of CoF_2, which precipitated at the first stage of the synthesis, resulted in an increase in the K : Co ratio and, as a consequence, in the formation of compound **I** in which two alkaline metal cations fall onto one complex anion. This assumption is confirmed by the counter synthesis that makes it possible to isolate compound **I** with the ratio K : Co : F = 2 : 3 : 1 from the solution.

Compounds **II** and **III** were obtained from the solution, which were concentrated not only in a desiccator over P_2O_5 but also by preliminary partial evaporation at 80°C. The conditions leading to the depletion of the reaction mixture primarily in trifluoroacetic acid and then to the removal of water from the reaction mixture were created. Only concentrating of solutions in a desiccator over P_2O_5 was used in the previously described experimental procedures for the synthesis of alkaline metal fluorotrifluoroacetates [5, 6], which allowed the isolation of compounds of the general formula K[$M_3(\mu_3$-F)$(CF_3COO)_6(CF_3COOH)_3$] containing no water molecules [5]. The change in both the synthesis and crystallization conditions results in the formation of isostructural compounds **II** and **III**. The principal possibility of the replacement of the axial ligands in the complex anions [$M_3(\mu_3$-F)$(CF_3COO)_6$-$(CF_3COOH)_3$] ↔ [$M_3(\mu_3$-F)$(CF_3COO)_6(H_2O)_3$] was shown for the first time, which additionally indicates the stability of the [$M_3(\mu_3$-F)] framework.

An additional confirmation of the stability of the trinuclear framework [$M_3(\mu_3$-F)$(CF_3COO)_6L_3$] is compound **IV** in which the complex anions [$Ni_3(\mu_3$-F)-$(CF_3COO)_6(CF_3COOH)_3]^-$ and [$Ni_3(\mu_3$-F)-$(CF_3COO)_6$-$(CF_3COOH)_2(H_2O)]^-$ coexist and the axial positions of the 3*d*-metal atoms are occupied by both trifluoroacetic acid and water molecules. The fact of the existence of compound **IV** shows the permanent equilibrium [$M_3(\mu_3$-F)$(CF_3COO)_6(CF_3COOH)_3]^-$ ↔ [$M_3(\mu_3$-F)$(CF_3COO)_6$-$(CF_3COOH)_{3-n}(H_2O)_n]^-$ in the reaction medium and favors the isolation of each equilibrium product depending on the synthesis conditions.

The crystal structures of complexes **I**–**IV** are formed by the potassium cations and complex trinuclear anions [$Co_3(\mu_3$-F)$(CF_3COO)_6(CF_3COO)$-$(CF_3COOH)_2]^{2-}$ in the case of compound **I**, [$M_3(\mu_3$-F)$(CF_3COO)_6(H_2O)_3]^-$ (M = Co and Ni) for compounds **II** and **III**, and [$Ni_3(\mu_3$-F)-$(CF_3COO)_6$-$(CF_3COOH)_2L]^-$ (L = CF_3COOH and H_2O) for complex **IV**. The latter resemble in structure the earlier described fluorotrifluoroacetatometallate anions [4–6]. The fluorine atom coordinates via the planar mode three 3*d*-metal atoms occupying the vertices of the distorted (**I**) or nearly regular (**II** and **III**) triangle. The

M–F distances range from 2.004 to 2.040 Å (average 2.023 Å) for the structure of complex **I**. The difference in the M–F bond lengths in compounds **II** and **III** is significantly lower, and they range from 2.0184(18) to 2.0298(17) Å (average 2.025 Å) for complex **II** and from 1.991(3) to 2.007(3) Å (average 1.996 Å) for complex **III**, which is related to the same coordination environment. In the structure of compound **IV**, the M–F distances range from 1.979(8) to 1.991(8) Å (average 1.986 Å) for the $[Ni_3(\mu_3\text{-}F)(CF_3COO)_6(CF_3COOH)_3]^-$ anion and from 1.973(7) to 2.002(8) Å (average 1.989 Å) for the $[Ni_3(\mu_3\text{-}F)(CF_3COO)_6(CF_3COOH)_2(H_2O)]^-$ anion. In this case, the range of M–F distances increases upon the replacement of one axial molecule of trifluoroacetic acid by a water molecule. In all compounds **I**–**IV**, three bridging trifluoroacetate groups binding pairwise the 3*d*-metal atoms are arranged at both sides of the triangle plane.

In the structure of complex **I** (Fig. 1a), the coordination environment of the Co(1) and Co(2) atoms is supplemented to a distorted octahedron by the carbonyl oxygen atoms of the trifluoroacetic acid molecules. In the case of the Co(3) atom, the trifluoroacetate ion acts as an axial ligand. The structural characteristics additionally confirm that the carboxyl oxygen atom of the trifluoroacetic acid anion exists in the axial position to the Co(3) atom. The $Co–O_{ax}$ bond length for Co(3) is minimum, and the Co–F bond length, on the contrary, takes the maximum value. The Co(1)F(1)Co(3) and Co(2)F(1)Co(3) angles are equal to each other being 121.9°, whereas the Co(1)F(1)Co(2) angle is equal to 116.2°. The carboxyl groups in the axial positions of the Co(1) and Co(2) atoms are arranged at one side from the plane of the Co(1)...Co(2)...Co(3) triangle and, correspondingly, are turned toward the oxygen atoms O(1) and O(20) of the bridging trifluoroacetate groups, which are involved in the formation of hydrogen bonds (the O(10*A*)...O(1), O(10*B*)...O(1), O(12*A*)...O(20), and O(12*B*)...O(20) distances are 2.65(2), 2.64(2), 2.588(15), and 2.577(12) Å, respectively). The carboxylate group in the axial position of the Co(3) atom lies at another side of the Co(1)...Co(2)...Co(3) triangle and is turned toward the K(2) atom (the O(18)...K(2) distance is 2.662(6) Å, and the distance from O(18) to the nearest oxygen atom of the bridging trifluoroacetate group is longer than 3.5 Å).

The complex anions in the structure of compound **I** are joined into dimers due to the interaction of the oxygen atoms O(5), O(6), and O(9) of the bridging trifluoroacetate groups and the O(18) oxygen atoms of the axial trifluoroacetate groups with the K(2) potassium atoms (Fig. 1b). The environment of K(2) also contains the carbonyl oxygen atom O(31) of the disordered trifluoroacetic acid molecule and the hydroxyl oxygen atom O(32) involved in the formation of the

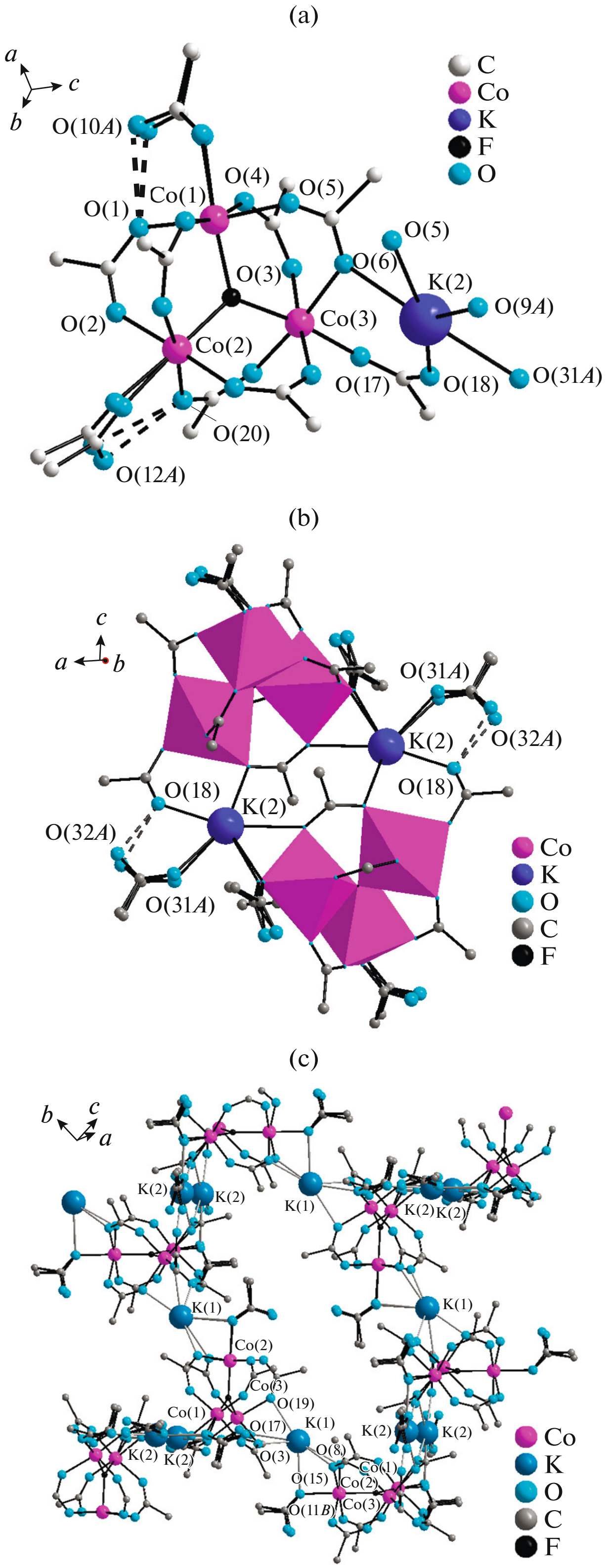

Fig. 1. Fragments of the crystal structure of complex **I**: (a) the complex anion $[Co_3(\mu_3\text{-}F)(CF_3COO)_6(CF_3COO)(CF_3COOH)_2]^{2-}$, (b) joining into dimers, and (c) layers arranged parallel to the {–1, 0, 0} plane. The fluorine atoms of the trifluoroacetate groups are omitted.

hydrogen bond with the O(18) atom of the axial trifluoroacetate group.

The dimers in compound **I** are joined into layers arranged parallel to the {–1, 0, 0} plane by the K(1) potassium atom, which coordinates the oxygen atoms O(3), O(8), O(15), and O(19) of the bridging trifluoroacetate groups, the carbonyl oxygen atoms O(11) of the axial trifluoroacetic acid molecule, and O(17) of the axial trifluoroacetate group (Fig. 1c).

In the structures of compounds **II** and **III**, the system of hydrogen bonds formed by the solvate molecules of water and trifluoroacetic acid results in the formation of layers, and no chains are formed due to the coordination of the potassium atoms with the oxygen atoms of the adjacent triangular complex anions.

The 3*d*-metal atoms in the complex anions of isostructural compounds **II** and **III** are characterized by the same coordination environment. The octahedral environment consists of the tridentate fluorine atom, four oxygen atoms of the bidentate trifluoroacetate groups, and the oxygen atom of the water molecule. The difference in bond lengths of the M atoms with the oxygen and fluorine atoms of the nearest environment is caused only by the formation of hydrogen bonds in the structures and by the potassium cation.

The presence of water molecules in the axial positions of the metal atoms of the trinuclear complex anion in compounds **II** and **III** provides a wide set of diverse types of hydrogen atoms in these structures (Fig. 2a). First, the axial water molecules participate in the formation of the system of hydrogen bonds with the adjacent complex anions. For example, H(21*A*) and H(21*B*) of the axial water molecule of the coordination environment of M(1) take part in the formation of two hydrogen bonds with the O(2) and O(4) oxygen atoms of the bidentate trifluoroacetate groups of the coordination environment of M(3) of the adjacent trinuclear anion. The H(22*A*) and H(22*B*) hydrogen atoms of the axial water molecule of the environment of M(2) form hydrogen bonds with the O(10) and O(7) oxygen atoms of the bidentate trifluoroacetate groups of the coordination environment of M(2) of another trinuclear anion.

In addition, the uncoordinated molecules of water and trifluoroacetic acid are involved in the formation of hydrogen bonds in the structures of compounds **II** and **III**. The O(22) oxygen atom of the axial water molecule from the coordination of M(2) forms the O(22)...H(16)–O(16) hydrogen bond with the hydroxyl hydrogen atom of the solvate molecule of trifluoroacetic acid. The O(5) oxygen atom of the bidentate trifluoroacetate group from the environment of M(1) forms the O(5)...H(24*B*)–O(24) hydrogen bond with the solvate water molecule, the oxygen atom of which, in turn, forms the O(24)...H(14*A*)–O(14) hydrogen bond with the second solvate molecule of trifluoroacetic acid.

In the structures of complexes **II** and **III**, the trinuclear anion is bonded to three adjacent anions, leading to the formation of negatively charged layers parallel to the {101} plane.

The K atoms are localized between the negatively charged layers and thus bind the layers into a three-dimensional structure. The coordination environment of the K(1) atoms contains the O(6) and O(8) oxygen atoms of the bidentate trifluoroacetate groups (from the octahedron of M(3)), the O(23) oxygen atom of the axial water molecule (M(3)), the carbonyl O(13) and O(15) oxygen atoms of the solvate molecules of trifluoroacetic acid, and two fluorine atoms of the trifluoromethyl groups to form a one-capped trigonal prism (Fig. 2b).

Compound **IV** exhibits a layered structure, which is intermediate between the classical chain structures described for compounds M'[$M_3(\mu_3\text{-F})(CF_3COO)_6(CF_3COOH)_3$] [4–6] containing no water molecules and three-dimensional complexes **II** and **III**.

In the structure of complex **IV**, the coordination environment of the Ni atoms is supplemented to a distorted octahedron by the carbonyl oxygen atoms of the axial trifluoroacetic acid molecules and the oxygen atom of the water molecule. In the $[Ni_3(\mu_3\text{-F})(CF_3COO)_6(CF_3COOH)_3]^-$ anion, the trifluoroacetic acid molecules are arranged at different sides from the plane of the {Ni_3} triangle, and one of the molecules is disordered. The hydroxyl oxygen atoms of all the three molecules of trifluoroacetic acid are involved in the formation of hydrogen bonds with the oxygen atoms of the bidentate trifluoroacetate groups of this complex anion. In the $[Ni_3(\mu_3\text{-F})(CF_3COO)_6(CF_3COOH)_2(H_2O)]^-$ anion, two disordered molecules of trifluoroacetic acid arranged at one side of the {Ni_3} triangle participate in the formation of intramolecular hydrogen bonds.

The alternating complex anions form chains due to the interaction, in one case, of the oxygen atoms O(10), O(13), O(20), and O(23) of the bridging trifluoroacetate groups, the carbonyl oxygen atom O(25) of the axial molecule of trifluoroacetic acid, and the O(40) oxygen atom of the axial water molecule with the K(1) potassium atoms similarly to the situation observed in compounds **II** and **III**. In the second case, the chains are formed due to the interaction of the oxygen atoms O(6), O(11), O(15), and O(28) of the bridging trifluoroacetate groups and the carbonyl oxygen atoms O(17) and O(33) of the axial trifluoroacetic acid molecules with the K(2) potassium atoms similarly to the fluorotrifluoroacetatometallates described

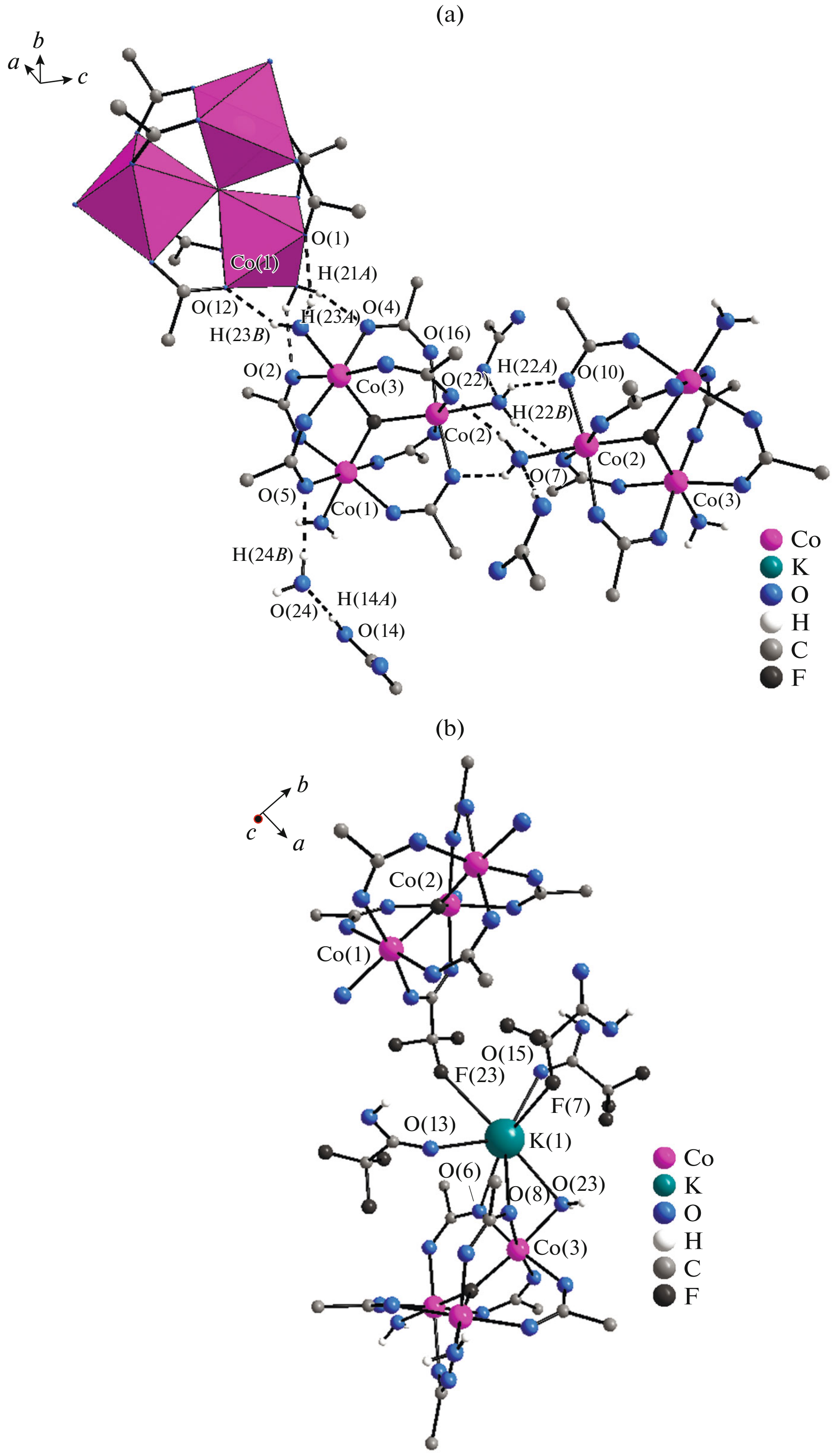

Fig. 2. Fragment of the crystal structure of complex **II**: (a) the system of hydrogen bonds leading to layer formation and (b) the coordination environment of the K atom. The fluorine atoms of the trifluoroacetate groups are omitted.

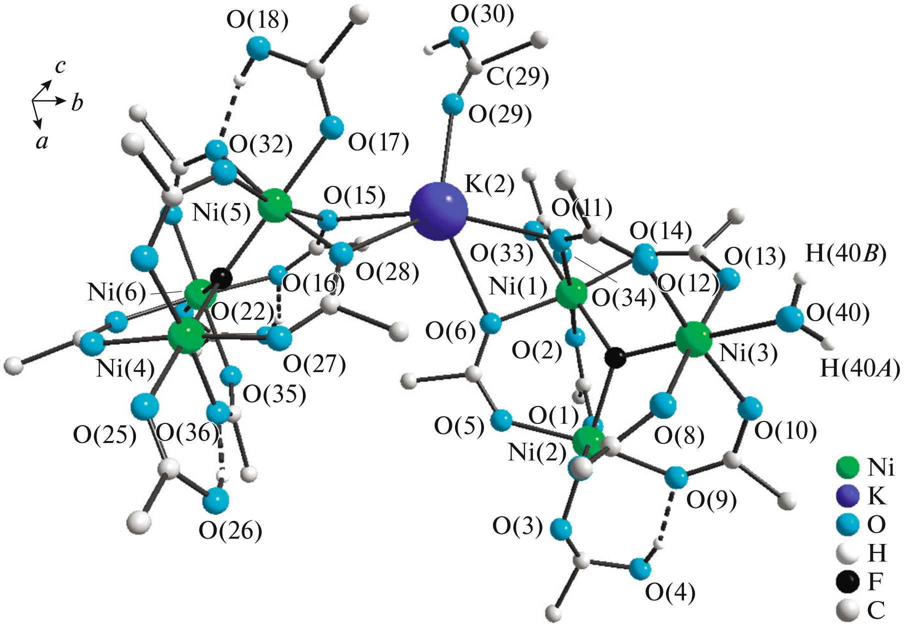

Fig. 3. Fragment of the crystal structure of complex **IV**. Formation of chains by the interaction of the K(2) atom with the oxygen atoms of the bidentate trifluoroacetate groups.

in detail [1]. The coordination environment of the K(2) atom also contains the carbonyl oxygen atom O(29) of the solvate molecule of trifluoroacetic acid (Figs. 3, 4).

The hydrogen atoms of the water molecule form two hydrogen bonds with the oxygen atoms of the bridging trifluoroacetate groups of the adjacent complex anion O(40)–(40*A*)...O(8) and O(40)–H(40*B*)...O(12) linking the structure-forming chains into layers (Fig. 4). The coordination environment of the K(1) atom contains the fluorine atoms of the trifluoromethyl group of the trifluoroacetate bidentate anion of the adjacent chain.

It should be mentioned that this example can be considered as intermediate between the described chain fluorotrifluoroacetatometallates [4–6] and three-dimensional structures of compounds **II** and **III** due to the formation of the layered structure in compound **IV**.

Evidently, hydrogen interactions exert the decisive effect on the structures of the synthesized fluorotrifluoroacetatometallates, and their role increases with an increase in the fraction of water molecules in the structure.

Thus, four new representatives of potassium fluorotrifluoroacetatometallates were synthesized and structurally studied. Compound $K_2[Co_3(\mu_3\text{-}F)(CF_3COO)_6(CF_3COO)(CF_3COOH)_2]\cdot CF_3COOH$ (**I**) is the first example of fluorotrifluoroacetatometallates in which the charge of the complex anion is –2. Fluorotrifluoroacetatometallate hydrates were synthesized and structurally studied for the first time: isostructural compounds $K[M_3(\mu_3\text{-}F)(CF_3COO)_6(H_2O)_3]\cdot H_2O\cdot 2CF_3COOH$ (M = Co (**II**) and Ni (**III**)). Compound $K_2[Ni_3(\mu_3\text{-}F)(CF_3COO)_6(CF_3COOH)_3][Ni_3(\mu_3\text{-}F)(CF_3COO)_6(CF_3COOH)_2(H_2O)]\cdot CF_3COOH$ (**IV**) combines in the composition the typical complex anion of alkaline metal fluorotrifluoroacetatometallate $[Ni_3(\mu_3\text{-}F)(CF_3COO)_6\text{-}(CF_3COOH)_3]^-$ and the complex anion $[Ni_3(\mu_3\text{-}F)\text{-}(CF_3COO)_6(CF_3COOH)_2\text{-}(H_2O)]^-$ in which one molecule of trifluoroacetic acid is replaced by the water molecule. It is shown that the introduction of water molecules into the composition of the complexes does not decompose the triangular framework $M_3(\mu_3\text{-}F)$ but makes it possible to model the structural type going from 1D to 2D and further to 3D structures.

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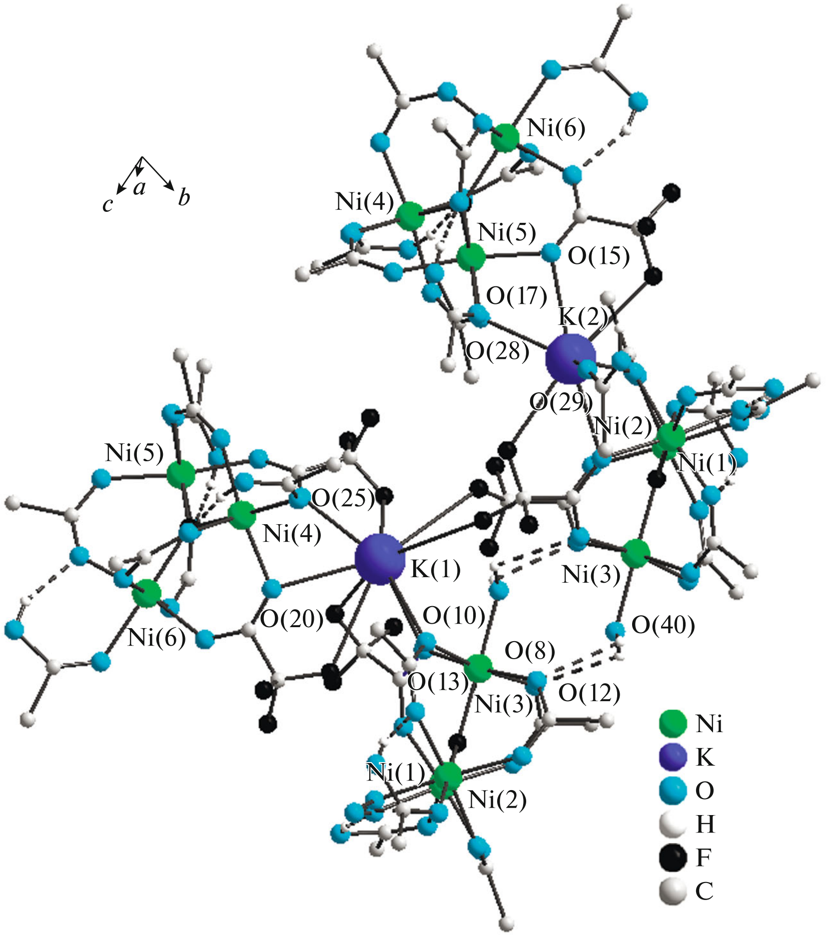

Fig. 4. Fragment of the crystal structure of complex **IV**. Joining of the chains into layers by the system of hydrogen bonds formed by the hydrogen atoms of the water molecules and the oxygen atoms of the bridging trifluoroacetate groups of the adjacent complex anion.

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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