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Trifluoroacetate Complexes of 3*d* Elements: Specific Features of Syntheses and Structures

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Abstract—Data on the syntheses and structures of trifluoroacetates of 3*d* elements mainly based on our results are reviewed. Specific features of the coordination chemistry of mono-, oligo-, and polynuclear trifluoroacetate complexes are successively considered. Special attention is given to oxo- and fluorotrifluoroacetates containing the trinuclear triangular fragment as a structural unit. Structural features of trifluoroacetates compared to other carboxylates are discussed.

Keywords: 3*d* elements, crystal structures, syntheses, trifluoroacetates, trinuclear and chain trifluoroacetate complexes

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INTRODUCTION

Trifluoroacetic acid CF_3COOH (HTFA) is a strong acid due to the influence of the trifluoromethyl group on the carboxyl group (the dissociation constant of HTFA is 0.69 [1]). The bond between the trifluoroacetate anion and the complexing atom is more ionic and weaker than coordination bonds in the most part of carboxylates. As a consequence, special approaches inappropriate for salts of other carboxylic acids (for example, synthesis from solutions containing anhydrous nitric acid) can be used for the synthesis of trifluoroacetates. When using these approaches, products with compositions and structures differed from those of other carboxylates are formed in some cases.

A variety of trifluoroacetate structures are determined, to a high extent, by different coordination modes of the trifluoroacetate anion, which are also characteristic of other carboxylate anions (terminal mono- and binuclear, as well as bridging, bridging-chelate, and other anions) [2–4]. At the same time, an additional coordination mode involving the fluorine atom appears [4].

A special interest in trifluoroacetates is mainly related to the possibility of obtaining simple and complex fluorides by their thermal decomposition [4–7]. They can be obtained as nanoparticles, fluoride solid solutions with valuable functions [8], and fluoride glasses of various compositions [9–11]. Another important property of many trifluoroacetates is the capability of subliming under reduced pressure [12, 13]. This property is used for the synthesis of fluoride and oxide films using the CVD method [14]. Trifluoroacetates of a series of metals are applied to carry out trifluoromethylation reactions. In particular, the trifluoromethylating activity of silver(I), copper(II), palladium(II), and chromium(II) trifluoroacetates with respect to fullerenes was demonstrated [15, 16].

Specific features of the coordination chemistry of trifluoroacetates of 3*d* elements, including those of the synthesis of these compounds, based on our earlier results are briefly considered in this review.

MONONUCLEAR TETRAAQUA COMPLEXES

Since HTFA is fairly strong, it can form trifluoroacetates (TFA) due to the reactions with metals, oxides, and hydroxides and also with many salts by displacing weaker acids. The reaction in the presence of a solvent with more pronounced donor properties, as a rule, affords predominantly mononuclear complexes in which the coordination environment of the metal cation is supplemented to the octahedral one by solvent molecules, for example, water. An example is a large series of the same-type compounds of 3*d* elements with the general formula $M(TFA)_2 \cdot 4H_2O$ (M = Mn, Fe, Co, Ni, Cu, and Zn) containing the M atom in the oxidation state +2 and formed by isolated molecular complexes $[M(TFA)_2(H_2O)_4]$ (Table 1; Figs. 1a, 1b). A specific feature of the synthesis of iron(II) and manganese(II) tetraaquatrifluoroacetates is the necessity to form a reductive atmosphere, for instance, by the direct interaction of a metal excess with HTFA or using electrochemical synthesis.

Table 1. Lengths of M–O and M–N bonds in complex molecules of trifluoroacetates $M(TFA)_2L_4$ (M is 3*d* element; L is H_2O or Py) and $Cu(TFA)_2(En)_2$ and intramolecular hydrogen O–H···O bond lengths in molecules $M(TFA)_2(H_2O)_4$

Compound	M–O (M–N), Å		O–H···O, Å	References; code CCSD/ CCDC
	$M–O_{H_2O}$	$M–O_{TFA}$		
$Mg(TFA)_2(H_2O)_4$	2.026, 2.037, 2.068, 2.079	2.098, 2.091	2.743, 2.711	
$Fe(TFA)_2(H_2O)_4$	2.099, 2.101, 2.108, 2.112	2.172, 2.179	2.732, 2.763	[17]
$Co(TFA)_2(H_2O)_4$	2.087, 2.093, 2.118, 2.130	2.137, 2.143	2.745, 2.761	[17]
$Ni(TFA)_2(H_2O)_4$	2.037, 2.046, 2.072, 2.080	2.084, 2.091	2.697, 2.735	
$Cu(TFA)_2(H_2O)_4$	1.931, 1.943, 2.436, 2.459	1.967, 2.003	2.640, 2.667	[18]; JUQNEO
$Zn(TFA)_2(H_2O)_4$	2.025, 2.066, 2.112, 2.112	2.124, 2.124	2.705, 2.705	
$[Al(TFA)_2(H_2O)_4]^+$ *	1.898, 1.925, 1.871	1.856	2.60	[17]
$Cu(TFA)_2(Py)_4$	Cu–N 2.037, 2.039, 2.047, 2.052	2.351, 2.362		[19]; TFAPCU
$Co(TFA)_2(Py)_4$	Co–N 2.100, 2.172, 2.176, 2.180	2.099, 2.060		[17]
$Cu(TFA)_2(En)_2$	Cu–N 1.985	2.579		[20]; XEYVAZ

* The Al–O bond lengths in cation $[Al(TFA)_2(H_2O)_4]^+$ of aluminum trifluoroacetate pentahydrate $[Al(H_2O)_6][Al(TFA)_2(H_2O)_4](TFA)_4$ are given.

Note that the octahedral cation of the sample composition $[Al(TFA)_2(H_2O)_4]^+$ is observed in the $Al(TFA)_3 \cdot 5H_2O$ structure. This compound can be synthesized by the interaction of metallic aluminum or freshly precipitated aluminum hydroxide with an aqueous solution of HTFA. The compound has the crystal chemical formula $[Al(H_2O)_6][Al(TFA)_2(H_2O)_4](TFA)_4$ and is a single example for neutral aluminum carboxylate, whereas with other weaker carboxylic acids aluminum forms trinuclear oxocarboxylates typical of three-charged cations.

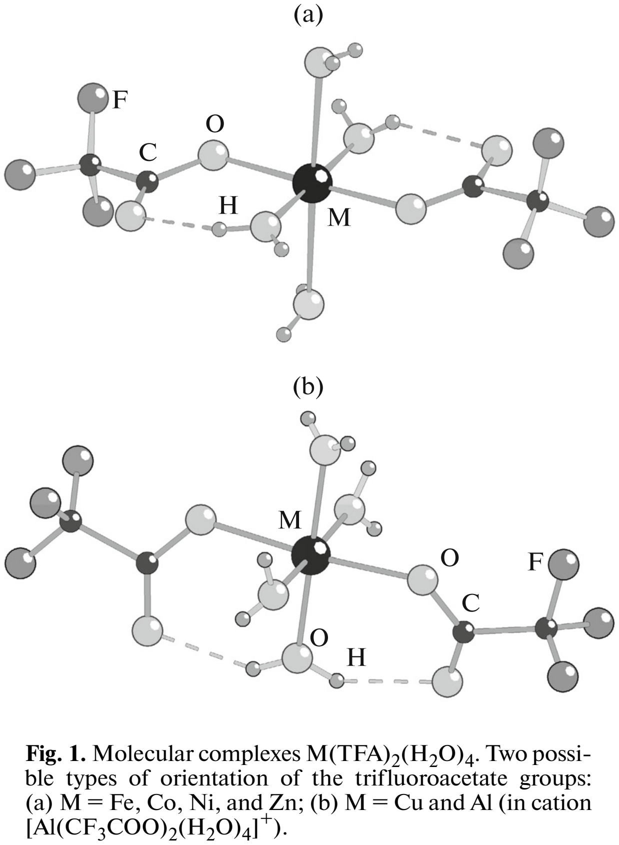

Fig. 1. Molecular complexes $M(TFA)_2(H_2O)_4$. Two possible types of orientation of the trifluoroacetate groups: (a) M = Fe, Co, Ni, and Zn; (b) M = Cu and Al (in cation $[Al(CF_3COO)_2(H_2O)_4]^+$).

A comparison of the M–O distances in the $[MO_6]$ octahedron makes it possible to reveal the following regularities (Table 1): (1) water molecules are coordinated at shorted distances and (2) the shortest M–O distance corresponds to the oxygen atom of the water molecule involved in the formation of an intramolecular hydrogen bond. Complex molecules $[M(TFA)_2(H_2O)_4]$ are linked to each other by intermolecular hydrogen bonds to form a three-dimensional framework [18].

It should be mentioned that other carboxylates can also crystallize from aqueous solutions as tetraaqua complexes [21–24]. However, zinc and copper acetate hydrates have other compositions and structures, which can be due to an increase in the strength of the coordination bond and the enhancement of the tendency of the acetate anion to the bidentate or bridging coordination mode compared to the TFA^- anion. For example, in the molecular structure of dihydrate $[Zn(CH_3COO)_2(H_2O)_2]$ [25], the Zn atoms coordinate two bidentate acetate anions and two water molecules to form a strongly distorted octahedral polyhedron (Fig. 2a). Copper(II) acetate monohydrate $[Cu(CH_3COO)_2(H_2O)]_2$ has the dimeric structure

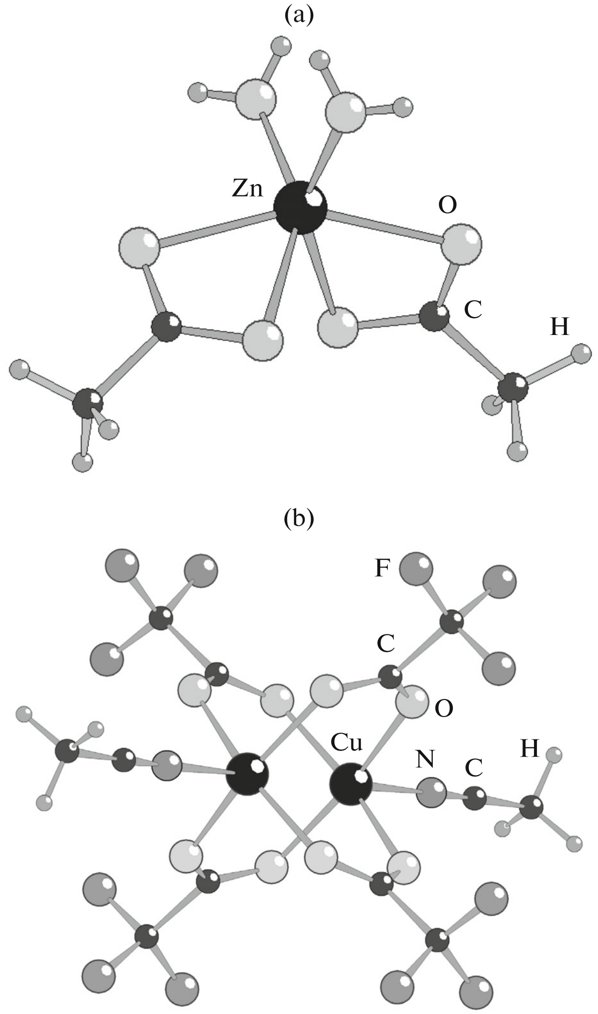

Fig. 2. Structures of (a) complex molecules $Zn(CH_3COO)_2(H_2O)_2$ and (b) molecular dimer $[Cu(CF_3COO)_2(CH_3CN)]_2$ in the composition of the structures of the same name.

(similar to that presented in Fig. 2b) named the “Chinese lantern” or “paddle-wheel” in which two copper atoms are linked by four bridging acetate anions, and water molecules occupy the apical positions [26].

A donor solvent also affects the composition and geometry of the formed structural fragment. For example, if ethylenediamine is used as a solvent, two types of copper(II) salts can be obtained: $Cu(TFA)_2(En)_2$ [20] and $[Cu(En)_3](TFA)_2$ [27]. A significant remoteness of the TFA^- anion (2 × 2.579 Å) corresponds to the situation where this anion is a less favorable ligand compared to ethylenediamine. In $[Cu(En)_3](TFA)_2$, the TFA^- anions are completely displaced from the coordination environment of copper(II) by ethylenediamine molecules.

In structure $Cu(TFA)_2(Py)_4$, as well as in $Cu(TFA)_2(En)_2$, the Cu(II) atom forms a coordination polyhedron of the 4N + 2O type in which the O atoms of the TFA groups are remote at a considerably longer distance than the N atoms of the pyridine molecules. In the cobalt compound of the same composition, viz., $[Co(TFA)_2(Py)_4]$, the mutual arrangement of the ligands is retained, and the distortion of the octahedral polyhedron is significantly lower (Fig. 3, Table 1).

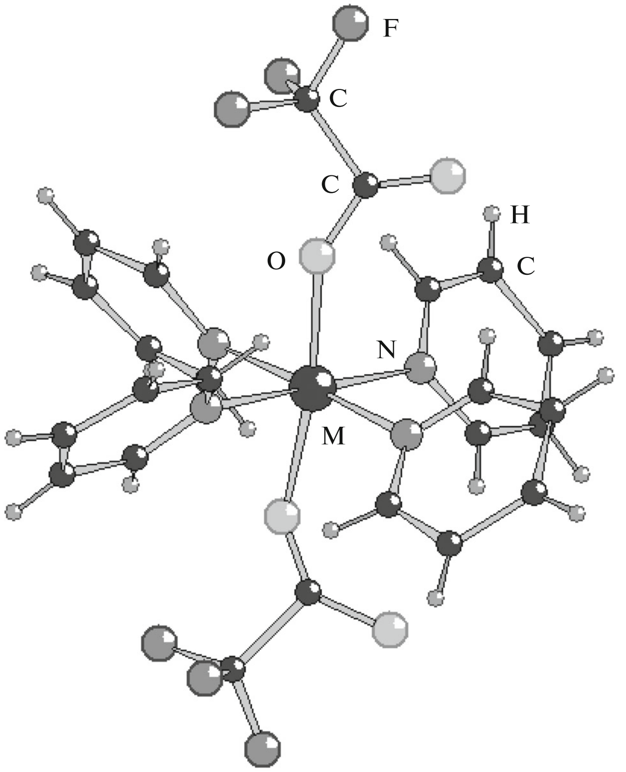

Fig. 3. Structure of complex molecules $M(TFA)_2(Py)_4$ (M = Co and Cu).

The crystallization of copper(II) trifluoroacetate from acetonitrile, which is the ligand of a weaker field than En, Py, and H_2O molecules, gives dimer $[Cu(TFA)_2(CH_3CN)]_2$, being a “Chinese lantern” similar in structure to copper(II) acetate monohydrate (Fig. 3) [28]. The coordination polyhedron of the copper atom is a square pyramid, the base of which contains the O atoms of the bridging TFA groups (Cu–O 1.964–1.972 Å), and the N atom of the CH_3CN molecule is coordinated in the vertex at a noticeably longer distance (Cu–N 2.114 Å). The Cu atoms are somewhat shifted from the pyramid base toward the vertex (Cu···Cu 2.77 Å). Thus, the trifluoroacetate anion manifests the bridging function in the cases where the system contains no ligands of a stronger field with pronounced donor properties.

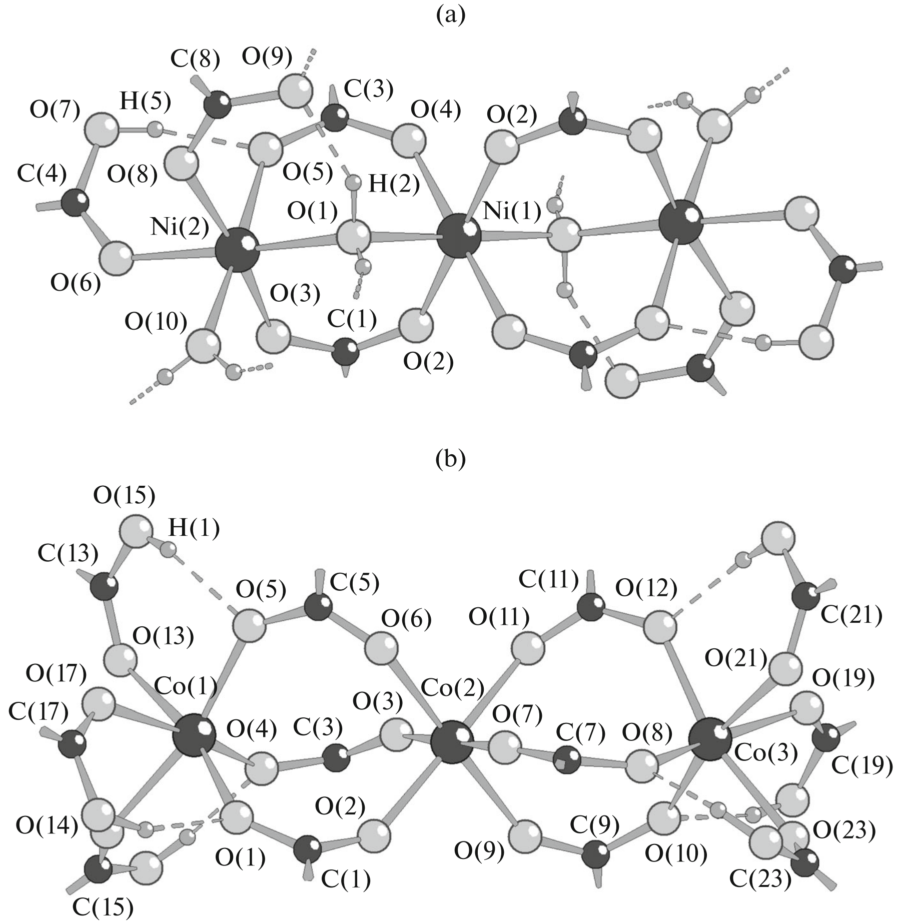

Fig. 4. Trinuclear molecular complexes in structures (a) **2** and (b) **3**. The CF_3 groups are omitted.

ACIDIC TRIFLUOROACETATES

When trifluoroacetates crystallize in a medium of 100% HTFA or in an HTFA–trifluoroacetic anhydride mixture, the absence of other donor molecules in this system results in the manifestation of the bridging function of the trifluoroacetate anion and the formation of trinuclear or polynuclear extended structures (Table 2). The recrystallization of $M(TFA)_2 \cdot 4H_2O$ (M = Co and Ni) from an excess of 99% HTFA gives unstable in air dark crimson (Co) and emerald-green (Ni) crystals, being trinuclear acidic trifluoroacetates $[M_3(TFA)_6(HTFA)_2(H_2O)_4](HTFA)_2$ (M = Co (**1**) and Ni (**2**)). Compounds **1** and **2** are isostructural (Fig. 4a, Table 2). They contain solvate HTFA molecules and linear centrosymmetric trinuclear molecules $[M_3(TFA)_6(HTFA)_2(H_2O)_4]$ (M = Co, Ni) in which two terminal crystallographically equivalent M atoms are linked to the central atom by two bidentate TFA groups and the bridging water molecule. Thus, a weakly distorted oxygen octahedral polyhedron is formed around the central M atom, and the octahedral coordination mode of the terminal M atoms is supplemented by the terminal monodentate molecules H_2O and HTFA and anion TFA^-. Four intramolecular hydrogen bonds O–H···O (O···O 2.64–2.68 Å) formed due to the interaction of the terminal and bridging ligands enforce the trinuclear molecules, and the complex molecules are joined into layers due to the hydrogen bonds involving outer-sphere HTFA molecules.

If in the initial reaction mixture HTFA is replaced by trifluoroacetic anhydride, the initial compounds are completely dehydrated. In this case, the reaction products are structurally relative trinuclear linear trifluoroacetates $[M_3(TFA)_6(HTFA)_6](HTFA)$ (M = Co (**3**) and Ni (**4**)) in which, as compared to **1** and **2**, the bridging water molecules are replaced by trifluoroacetate anions and the terminal anions are replaced by HTFA molecules (Fig. 4). Thus, the octahedral polyhedron of the central M atom is formed by six bridging anions TFA^-, and the coordination environment of the terminal M atoms contains three bridging TFA^- anions and three HTFA molecules. The oxygen atoms of the trifluoroacetate groups and the hydrogen atoms of the HTFA molecules form intramolecular hydrogen bonds (O···O 2.60–2.65 Å), and the solvate HTFA molecules are bound into dimers by intermolecular

Table 2. Bond lengths in molecules of linear trimers $[M_3(TFA)_6(HTFA)_2(H_2O)_4](HTFA)_2$ (M is Co (**1**) and Ni (**2**)), $[M_3(TFA)_6(HTFA)_6](HTFA)$ (M is Co (**3**) and Ni (**4**)) and in chain structures $M_2(TFA)_4(TFAH)_4$ (M is Fe (**5**) and Mg (**6**)), $Zn_2(TFA)_4(HTFA)_2$ (**7**), and $Cu(TFA)_2$ (**8**) (the numeration of atoms in isostructural compounds **1** and **2** as well as in **5** and **6** coincide)

Structure	Environment of central atom (M_c)			Environment of terminal atoms (M_{t1} and M_{t2}) ***				References
	M_c	bridging bonds		terminal bonds			M_{t1}, M_{t2}	
		Ligand*	M_c–O**	M_t–O**	Ligand*	M_t–O**		
1	Co(1)	TFA3	2.036(6) (O(4))	2.074(6) (O(5))	HTFA5	2.158(6) (O(6))	Co(2)	[29]
		TFA1	2.042(6) (O(2))	2.055(6) (O(3))	TFA7	2.048(6) (O(8))		
		H_2O	2.126(6) (O(1))	2.201(6) (O(1))	H_2O	2.004 (O(10))		
2	Ni(1)	TFA3	2.022 (O(4))	2.057 (O(5))	HTFA4	2.089 (O(6))	Ni(2)	[29]
		TFA1	2.014 (O(2))	2.043 (O(3))	TFA8	2.037 (O(8))		
		H_2O	2.105 (O(1))	2.108 (O(1))	H_2O	2.010 (O(10))		
3	Co(2)	TFA1	2.070(3) (O(2))	2.052(2) (O(1))	HTFA13	2.154(2) (O(13))	Co(1)	[29]
		TFA3	2.073(3) (O(3))	2.053(3) (O(4))	HTFA15	2.152(3) (O(14))		
		TFA5	2.057(3) (O(6))	2.053(3) (O(5))	HTFA17	2.144(3) (O(17))		
		TFA7	2.059(3) (O(7))	2.046(3) (O(8))	HTFA19	2.144(3) (O(19))	Co(3)	
		TFA9	2.059(3) (O(9))	2.045(3) (O(10))	HTFA21	2.137(3) (O(21))		
		TFA11	2.062(3) (O(11))	2.045(3) (O(12))	HTFA23	2.153(3) (O(23))		
4	Ni(2)	TFA1	2.024(6) (O(2))	2.009(7) (O(1))	HTFA5	2.090(7) (O(5))	Ni(1)	[29]
		TFA3	2.025(6) (O(3))	2.016(5) (O(4))	HTFA7	2.089(6) (O(7))	Ni(3)	
5	Fe	TFA1	2.099(2) (O(1))	2.062(3) (O(2))	HTFA3	2.183(3) (O(3))	Fe	
		TFA1'	2.062(3) (O(2))	2.099(2) (O(1))				
		HTFA'	2.183(3) (O(3))					
6	Mg	TFA1	2.097(2) (O(1))	1.987(2) (O(2))	HTFA3	2.111(2) (O(3))	Mg	
		TFA1'	1.987(2) (O(2))	2.097(2) (O(1))				
		HTFA'	2.111(2) (O(3))					
7	Zn(2)	TFA1	1.939(4) (O(2))	2.017(3) (O(1))	HTFA9	2.157(4) ((O9))	Zn(1)	
		TFA3	1.949(4) (O(4))	2.083(3) (O(3))	HTFA11	2.157(3) (O(11))		
		TFA5	1.967(4) (O(6))	2.125(3) (O(5))				
		TFA7	1.972(3) (O(8))	2.094(3) (O(7))				
8	Cu(1)	TFA1	2.058(2) (O(1))					[30]
		TFA1'	1.917(2) (O(2))					
		TFA1''	2.441(3) (O(1'))					
		TFA3	1.967(2) (O(3))					
		TFA3'	1.909(2) (O(4))					

* The number of the carboxylic carbon atom in a given TFA anion is indicated.

** The oxygen atom coordinated by a given metal cation is indicated in parentheses.

*** In chain structures **5**–**7**, the adjacent metal in the same chain is considered instead of the terminal M_t atom.

hydrogen bonds with the O···O distance equal to 2.63 Å, which is comparable with the corresponding distance in the structure of crystalline HTFA (2.65 Å) [31]. Unlike layered compounds **1** and **2**, structures **3** and **4** are isle. Evidently, this difference in crystal packing is related to the presence of water molecules in structures **1** and **2**, resulting in an increase in the number of intra- and intermolecular hydrogen bonds [29].

The manganese(II) complex $Mn_3(TFA)_6(C_6H_5CN)_6$ similar in structure with complex **4** was described [32]. In this complex, as in compounds **1–4**, all bridging TFA groups are bidentate (the overall dentate mode of the ligand is implied). However, these examples are rare. Trinuclear linear carboxylates more frequently contain chelate-bridging ligands along with the bridging ones, due to which the number of ligands in trimers is reduced with the retention of the octahedral coordination of the complexing atom: $Fe_3(C_6H_5COO)_6(C_5H_5N)_4 \cdot 2CH_3CN$ [33], $Co_3(CH_3COO)_6(2,2'\text{-Bipy})_2$ [34], $Mn_3(CH_3COO)_6(2,2'\text{-Bipy})_2$ [35], and $Mn_3(CH_3COO)_6(1,10\text{-Phen})_2$ [36]. This difference in structures of the acetate and trifluoroacetate complexes can be due to the fact that the TFA group is less prone to manifesting the chelating function.

Unlike compounds **1–4**, in the case of M(II) = Fe, Zn, and Mg, the association of the mononuclear trifluoroacetate fragments is not restricted by trinuclear molecules but results in the formation of infinite chains $[M(TFA)_2(HTFA)_2]_n$ (M = Fe (**5**) and Mg (**6**)) and $[Zn_2(TFA)_4(HTFA)_2]_n$ (**7**). Complex **7** was synthesized similarly to complexes **3** and **4**, and the procedure for compound **5** was modified to avoid the oxidation of Fe^{2+}. Isostructural magnesium trifluoroacetate **6** was synthesized by the reaction of $Mg(NO_3)_2 \cdot 6H_2O$ with HTFA in a vacuum desiccator over P_4O_{10} in the presence of fuming HNO_3.

According to the X-ray diffraction results, each metal atom in structures **5** and **6** is bound to two adjacent atoms by a pair of bridging TFA groups, and two terminal HTFA molecules supplement the environment of M(II) to the octahedral one (Fig. 5a, Table 2). The hydrogen atoms of the HTFA molecules participate in hydrogen bonding with the O(1) atoms of the bridging trifluoroacetate groups (O···O 2.655(4) and 2.626(3) Å in structures **5** and **6**, respectively). The uncharged chains in crystal structures **5** and **6** are directed along the *x* axis and linked to each other by forces of van der Waals interactions.

Compound **7** contains two crystallographically independent zinc atoms. The coordination environment of Zn(1) is octahedral, whereas that of Zn(2) is a tetrahedron formed by the O atoms of four bridging trifluoroacetate groups (Fig. 5b, Table 2). The possibility for zinc ions to combine octahedral and tetrahedral polyhedra in the same structure can be explained by the absence of the effect of stabilization by the crystal field for the Zn^{2+} cation with the completely filled *d* sublevel.

The comparison of the M–O distances in the studied acidic trifluoroacetates shows that for the same complexing atom the bond length decreases in the series HTFA > H_2O_{br} > TFA^{-1} > H_2O_t. Evidently, the strength of the corresponding bonds increases in the same series. The shortening of the $M–O_{TFA}$ distances for the M atoms in the series Fe > Zn > Co > Ni > Mg correlates well with a decrease in the effective ionic radii of the octahedrally coordinated M^{2+} cations in the same series [37].

ANHYDROUS COPPER AND SILVER TRIFLUOROACETATES

Unlike trifluoroacetates of many transition metals, neutral salt $Cu(CF_3COO)_2$ (**8**, Table 2) is formed due to the crystallization of copper(II) trifluoroacetate from an HTFA–trifluoroacetic anhydride mixture (with a substantial excess of the anhydride) [30]. Crystal structure **8** is built of infinite chains of unusual structure consisting of mutually bound dimers $Cu_2(TFA)_4$ (Fig. 6) [30, 38]. All Cu atoms in the chain are equivalent. The coordination sphere of the copper atom contains five O atoms of the trifluoroacetate groups forming a coordination polyhedron in the form of a distorted trigonal bipyramid with the shortened axial O(2)–Cu–O(4) axis and elongated Cu–O(1)' distance (2.44 Å) in the pyramid base [30]. An alternative description of this coordination mode of the copper atom is a strongly distorted square pyramid [38]. The $[CuO_5]$ polyhedra are bound into dimers due to four bridging TFA groups. The Cu···Cu distance in the dimer is 3.10 Å, which is substantially longer than the Cu···Cu distance characteristic of "Chinese lantern" (for example, 2.77 Å in $[Cu(TFA)_2(CH_3CN)]_2$ (Fig. 3)). Owing to the bridging trifluoroacetate groups, each copper atom from one dimer is linked to three Cu atoms of two adjacent dimers at distances of 3.53 and 2 × 5.14 Å. It should be mentioned that structure **8** differs substantially from the most part of chain structures of other anhydrous copper(II) carboxylates by a strong distortion of the dimeric fragment, and the Cu···Cu distance inside the dimer is substantially elongated, whereas this distance between the copper atoms of the adjacent dimers is shortened [30, 38]. Rare examples for a similar distortion of the dimeric fragment are observed in the structures of copper(II) trichloroacetate $[Cu(CCl_3COO)_2(C_7H_9N)]_2$ [39] and triphenylacetate $[Cu(Ph_3CCOO)_2(C_5H_4N)]_2$ [40]. The structural strain of compound **8** appears as a high reactivity of the compound in the addition reactions of donor ligands, for example, water molecules.

The structures of nonsolvated univalent copper and silver trifluoroacetates are also very unusual. The synthesis of CuTFA and the study of its unique structure were performed in [38]. We studied silver trifluoroacetate. Unlike trifluoroacetates of bi- and trivalent *d* elements, anhydrous salt $[AgTFA]_2$ directly crystal-

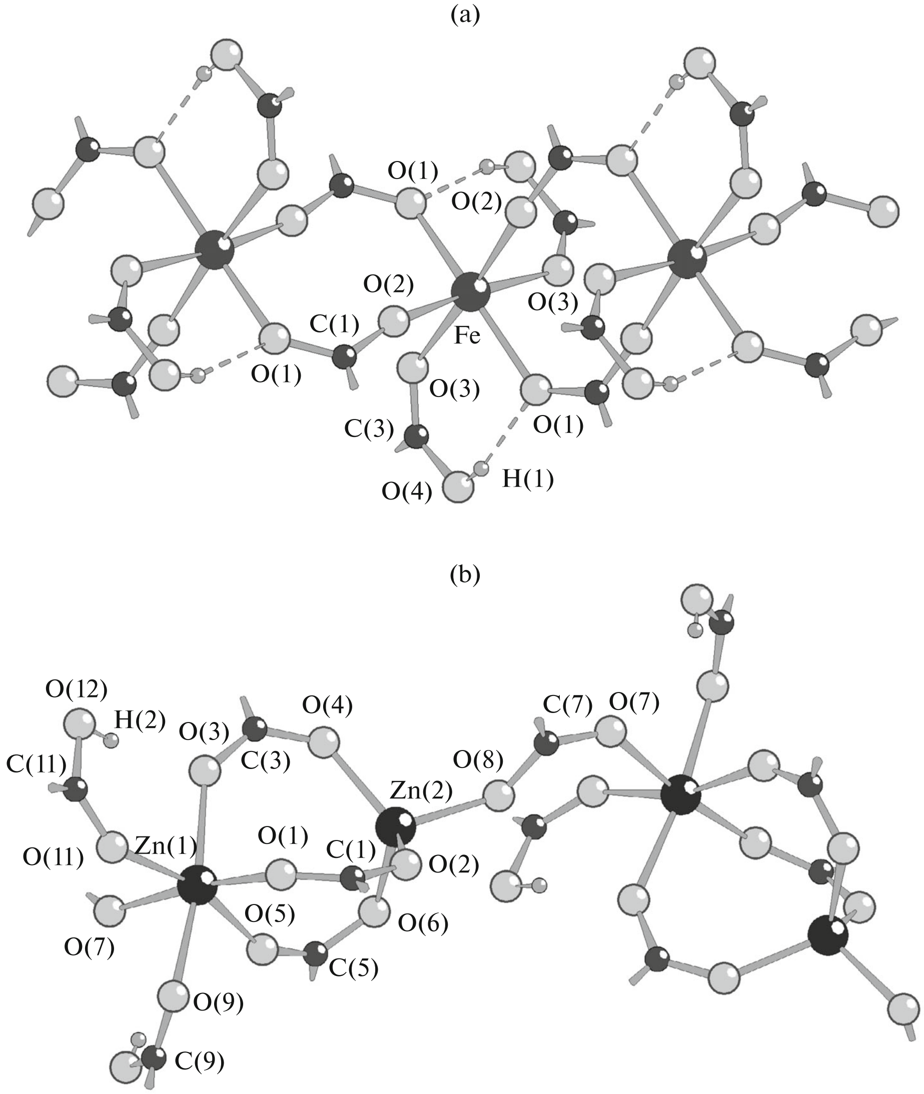

Fig. 5. Fragment of the chain in crystal structures (a) $[Fe(TFA)_2(HTFA)_2]_n$ and (b) $[Zn_2(TFA)_4(HTFA)_2]_n$. The CF_3 groups are omitted.

lizes from aqueous solutions [41]. As in the majority of nonsolvated silver carboxylates, the structure of AgTFA is based on dimers $[AgTFA]_2$. Infinite ribbons are usually formed due to the bond between the Ag and O atoms of the adjacent dimers (Fig. 7a) [42]. In the case of silver trifluoroacetate, the coordination number of the Ag^+ cation increases from three to four. As a result, the Ag^+ cation of one dimer forms bonds with two other dimers to form a three-dimensional openwork structure (Fig. 7b). The transition of silver to the coordination number 4 is also accompanied by the distortion of a usually planar ring of the $[AgTFA]_2$ dimer. Two shorter Ag–O distances (of four distances) characterize the bonds inside the dimer (2.235 and 2.246 Å), and two other distances to the O atoms of the adjacent dimers are much longer (2.582 and 2.681 Å).

Crystallization from acetonitrile gives compound $(Ag(CH_3CN)_2)(Ag_2(CF_3COO)_3)$ [43] in which the dimeric fragments characteristic of carboxylates and joined into pairs can be distinguished. The pairs of dimers are bound into infinite ribbons by the bridging trifluoroacetate groups and silver cations $Ag(3)^+$ coordinating two acetonitrile molecules and two O atoms of the adjacent pairs of dimers (Fig. 8). The silver atoms Ag(1) and Ag(2) forming dimers coordinate four oxygen atoms each, and the Ag–O distances are rather close to those in the dimers of the AgTFA structure.

OXOTRIFLUOROACETATES

As shown in the previous section, the synthesis of trifluoroacetates in concentrated or anhydrous HTFA favors the manifestation of the bridging function by

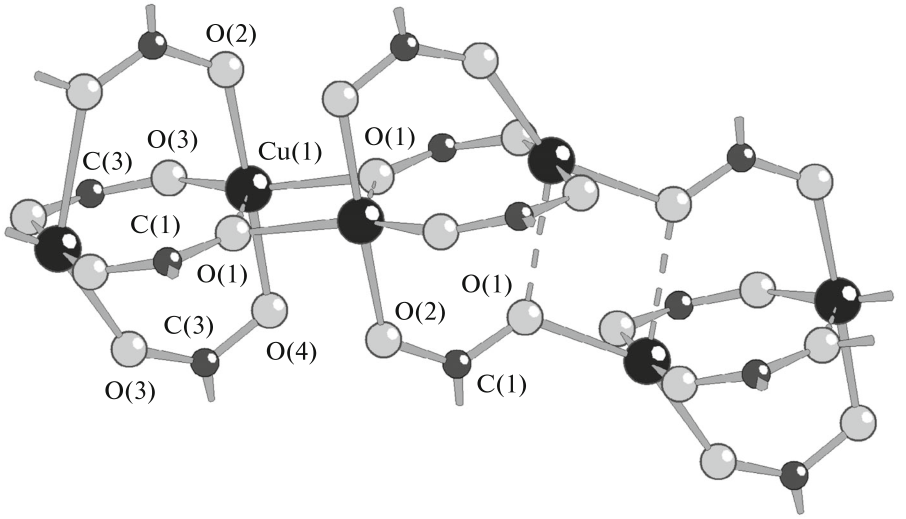

Fig. 6. Fragment of the infinite chain in structure $Cu(CF_3COO)_2$. The CF_3 groups are omitted.

the TFA^- anion and the acid can act as a neutral ligand. In the case of bivalent cations, this results in the formation of compounds with unusual structures.

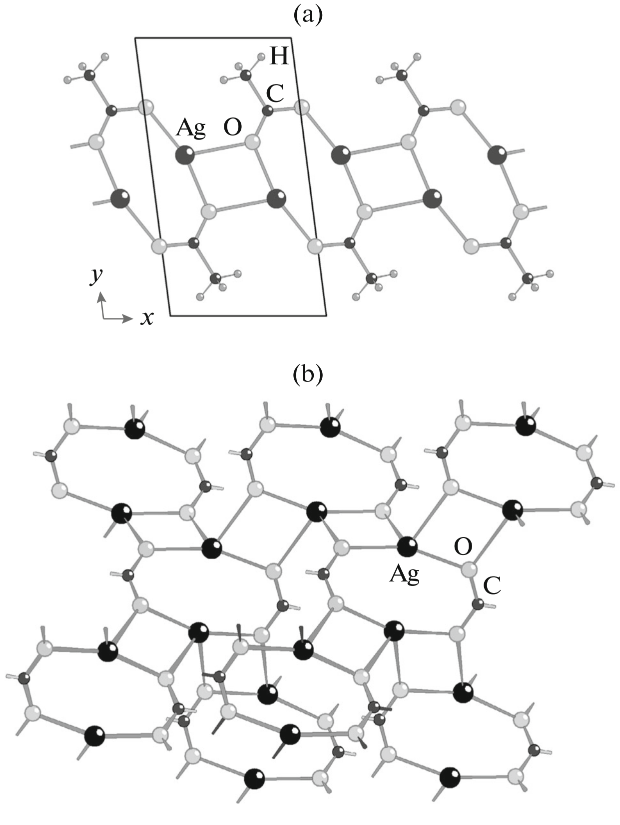

Fig. 7. Fragment of crystal structures (a) $[Ag(CH_3COO)]_2$ [29] and (b) $[AgTFA]_2$ (the CF_3 groups are omitted).

The application of this approach also turned out to be productive for trivalent aluminum: unique pentahydrate, whose structure is considered in the section devoted to mononuclear tetraaqua complexes, was obtained. However, the crystallization of trifluoroacetates of trivalent d elements, namely, chromium and iron, from acidic solutions provides compounds of the known family of trinuclear triangular oxocarboxylates $M_3(\mu_3\text{-}O)(RCOO)_6L_3$. This allowed us to produce complexes in which all the three metal atoms are in the oxidation state +3 and also heterovalent compounds simultaneously containing cations in the oxidation states +3 and +2.

Dark green hexagonally prismatic crystals of $[Cr_3(\mu_3\text{-}O)(TFA)_6(H_2O)_3](H_2O)(NO_3)$ (**9**) were grown from a solution obtained by the reaction of chromium nitrate nonahydrate with 99% HTFA taken in a twofold excess. To obtain complex $[Cr_3(\mu_3\text{-}O)(TFA)_6(TFA)(H_2O)_2](HTFA)$ (**10**) [44], metallic chromium was dissolved in 50% HTFA with the addition of a 50% solution of hydrogen peroxide.

For the preparation of the Cr(II) derivatives, compounds **11** and **12** were synthesized using the anodic dissolution of chromium in an electrolytic cell isolated from air moisture in a solution of HTFA in THF or acetonitrile. Crystallization from an HTFA–CH_3CN system gave stable in air green plate-like crystals of $Cr_3(\mu_3\text{-}O)(TFA)_6(CH_3COOH)_2(TFA)$ (**11**) [45], and crystallization from an HTFA–THF (volume ratio 1 : 1) mixture gave stable in air red-brown prismatic crystals of heterovalent complex $Cr_3(\mu_3\text{-}O)(TFA)_6(CH_3COOH)_2(THF)$ (**12**) [45].

All synthesized compounds contain complex molecules of cations $[Cr_3(\mu_3\text{-}O)(TFA)_6(L)_3]$ belonging to the well known family of trinuclear triangular oxocarboxylates. They are similar in structure and differ by a

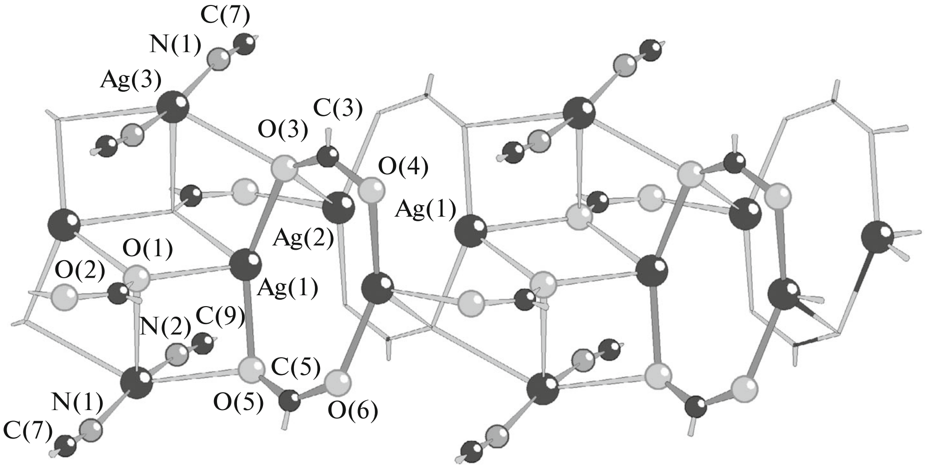

Fig. 8. Fragment of structure $(Ag(CH_3CN)_2)(Ag_2(CF_3COO)_3)$. The CF_3 and CH_3 groups are omitted.

set of ligands L, which can be molecules CH_3COOH, H_2O, and THF or TFA^- anions (Fig. 9a). In these complex particles, the chromium atoms occupy positions in vertices of the triangle (Cr···Cr 3.312(4)–3.387(5) Å) simultaneously coordinating the μ_3-O atom at the center of the triangle.

Let us consider briefly structural features of trinuclear chromium oxotrifluoroacetates. The trinuclear cation $[Cr_3(\mu_3\text{-}O)(TFA)_6(H_2O)_3]^+$ in structure **9** is highly symmetric, and the point group of symmetry C_{3h} with the 3-fold rotary axis passing through the μ_3-O atom perpendicularly to the triangle plane corresponds to this cation. Structure **9** also contains outer-sphere NO_3^- anions and H_2O molecules. A three-dimensional framework is formed due to the attraction of the trinuclear cations and anions NO_3^- and due to the hydrogen bonds involving water molecules and NO_3^- and TFA^- anions.

Other trinuclear oxotrifluoroacetates are less symmetric, and each of them contains three crystallographically independent Cr atoms. Nevertheless, a comparison of the Cr–O distances in the coordination environment of each atom shows (Table 3) that the bond involving the central O atom is the shortest, whereas the distance to the O_L atom occupying the opposite axial vertex is most elongated. The lengths of the $Cr–O_{TFA}$ bonds involving the oxygen atoms of four bridging TFA groups lying in the equatorial plane are intermediate, and the Cr atom is somewhat shifted from this plane toward the μ_3-O atom. This distortion of the octahedral polyhedra $[MO_6]$ is characteristic of triangular trinuclear oxocarboxylates [3].

Compound **12** is of special interest. Unlike three other complexes containing only Cr(III) atoms, trinuclear complex **12** is formed by two Cr(III) atoms and one Cr(II) atom. The comparison of the Cr–O distances in the coordination polyhedron of three Cr atoms in structure **12** (Table 3) shows that the oxidation state +2 cannot be ascribed to a specific chromium atom: the corresponding Cr–O distances are comparable and close (average Cr–O 2.02– 2.05 Å, Table 3) for all the three atoms. In other structures, the Cr–O bonds are shorter and comparable to each other (average 1.97–1.99 Å). The summation of average distances for all the three Cr atoms in structures **12** and **11** (for comparison, since structure **11** is closest to **12** in composition) shows that the sums differ by 0.14 Å, which can confirm that structure **12** formally contains one Cr(II) atom instead of Cr(III): according to [37], the effective ionic radii of the octahedrally coordinated Cr(III) and Cr(II) atoms differ by 0.185 and 0.115 Å in the case of the high- and low-spin states of Cr(II), respectively.

Interestingly, the Cr–O distances to the central O atom in structure **12** compared to structure **11** remained almost unchanged (and even decreased), whereas other Cr–O distances increased. It is most likely that this indicates the electron density redistribution in structure **12** and, in particular, an increase in the effective negative charge on the central O atom.

FLUOROTRIFLUOROACETATES

The formation of the trinuclear oxocarboxylate complexes is not characteristic of 3*d* metals tending to manifest the oxidation state +2 (for example, Co and Ni). In the known examples of trinuclear triangular carboxylates of bivalent 3*d* metals, the one-charged anion, for example, OH^-, instead of the two-charged anion $A = O^{2-}$ is located at the center of the triangular fragment $[M_3A]$ [46]. We synthesized and structurally studied the following representatives of the new family of the trinuclear triangular Co, Ni, Fe, Mn, and Zn complexes with the tricoordinated F^- atom (Table 4): $M'[M''_3(\mu_3\text{-}F)(TFA)_6(HTFA)_3]$, where M' is alkaline

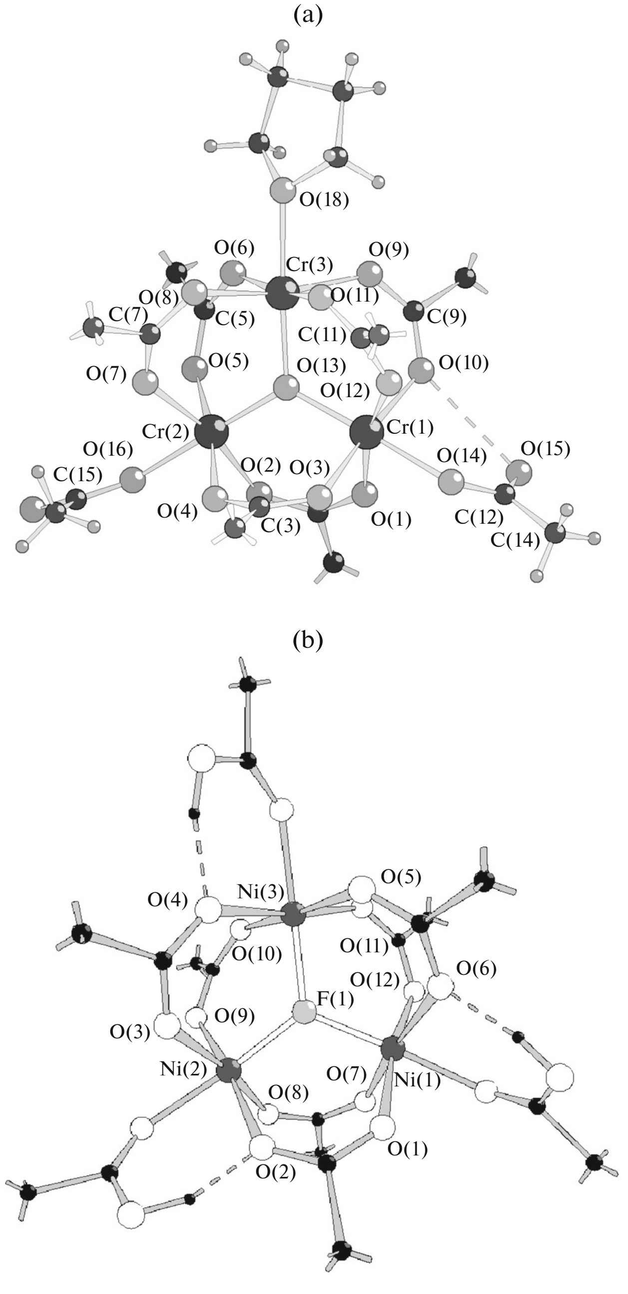

Fig. 9. Molecular structures of trinuclear complexes (a) $Cr_3(\mu_3\text{-}O)(TFA)_6(CH_3COOH)_2(THF)$ and (b) $Ni_3(\mu_3\text{-}F)(TFA)_6(CF_3COOH)_3$. The F atoms are omitted.

metal, NO, or NH_4; M" is Ni or Co (**13–22**); $Na[Zn_3(\mu_3\text{-}F)(TFA)_6(H_2O)_3] \cdot 4.34H_2O$ (**23**), $Na[Mn_3(\mu_3\text{-}F)(TFA)_6(TFA)(HTFA)_2] \cdot 2HTFA$ (**24**), and $Na[Fe_3(\mu_3\text{-}F)(TFA)_6(TFA)(HTFA)_2] \cdot 2HTFA$ (**25**). Two latter complexes simultaneously contain two M(II) atoms and one M(III) atom.

Fluorotrifluoroacetates $M'[M''_3(\mu_3\text{-}F)(TFA)_6(HTFA)_3]$ (**13–22**, except for **16** and **21**) were obtained by crystallization from solutions containing a stoichiometric mixture of cobalt or nickel nitrate hydrate with alkaline metal or ammonium fluoride in anhydrous HTFA with the addition of HNO_3 [47, 48]. A specific feature of this synthesis approach is the presence of nitric acid in the reaction mixture favoring the formation of coarse-crystalline samples. The first trinuclear nitrosonium fluorotrifluoroacetatometallates **16** and **21** were obtained occasionally without the addition of alkaline metal fluorides using HTFA containing ~0.05 wt % HF as an impurity [47].

Single-phase crystalline samples **23–25** were synthesized using a modified procedure: anhydrous nitric acid was not added to the system, and zinc or manganese trifluoroacetate tetrahydrates or metallic iron were used as the initial reactants. The components taken in stoichiometric amounts ($M(TFA)_2(H_2O)_4$: NaF = 3 : 1 or Fe : NaF = 3 : 1) were dissolved in concentrated HTFA and kept in a vacuum desiccator over phosphoric anhydride until the solvent was completely removed.

The crystals of the synthesized compounds are prisms or green (in the case of M" = Ni and Mn), red-pink (M" = Co), or dark blue (Fe) plates. The obtained compounds decompose in air and are highly soluble in water, but the initial compositions of the compounds are not retained upon recrystallization.

It should be mentioned that additional tests on the replacement of the central (μ_3) F atom by O were carried out for all structures at the final stage of refinement. The tests were accompanied by a slight increase in the *R* factors and a sharp decrease in the temperature of this atom. In addition to the charge balance determined by the composition of the compounds, this additionally indicated in favor of the presence of the F atom that centers the trinuclear fragments.

Crystal structures **13–25** are formed by cations of alkaline metals (Li–Cs), ammonium, or nitrosonium and complex trinuclear anions $[M''_3(\mu_3\text{-}F)(TFA)_6L_3]^-$, where M" = Ni (**13–20**), Co (**21**, **22**), Zn (**23**), Mn (**24**), and Fe (**25**). In almost all structures, HTFA molecules act as terminal ligands L. In **24** and **25**, one of three HTFA molecules is replaced by the TFA^- anion. Water molecules served as ligands L in structure **23**. In addition, structures **13**, **20**, **24**, and **25** contain HTFA molecules that are not observed in the composition of the trinuclear anions, whereas structure **23** contains such water molecules (Table 4).

The anions in all structures are similar and analogous to the structure of the trinuclear oxocarboxylates (section devoted to oxotrifluoroacetates). The central fluorine atom planarly coordinates three metal atoms occupying vertices of an almost planar triangle. Each metal atom in the axial position coordinates the O_L atom of the terminal ligand L (L = HTFA, TFA^-, and H_2O). Thus, the metal atoms exist in a weakly dis-

Table 3. Lengths of Cr–O bonds in the octahedral coordination polyhedra of the chromium atoms of the trinuclear complexes $[Cr_3(\mu_3\text{-}O)(TFA)_6(H_2O)_3](H_2O)(NO_3)$ (**9**), $[Cr_3(\mu_3\text{-}O)(TFA)_6(TFA)(H_2O)_2](HTFA)$ (**10**), $[Cr_3(\mu_3\text{-}O)(TFA)_6(CH_3COOH)_2(TFA)]$ (**11**), and $[Cr_3(\mu_3\text{-}O)(TFA)_6(CH_3COOH)_2(THF)]$ (**12**)

Structure	Atom	Distances, Å				References
		Cr–μ_3-O	Cr–O_{TFA}	Cr–O_L*	Cr–O**	
9	Cr	1.9118	1.964, 1.968	2.015 aq	1.97(3)	[44]
10	Cr(1)	1.942	1.980, 1.982, 1.992, 1.983	1.991 TFA	1.98(2)	[44]
	Cr(2)	1.918	1.965, 1.967, 1.9701, 1.985	2.051 aq	1.98(4)	
	Cr(3)	1.923	1.966, 1.976, 1.979, 1.982	2.007 aq	1.97(2)	
11	Cr(1)	1.900	1.991, 1.995, 2.001, 2.002	2.030 AA	1.99(4)	[45]
	Cr(2)	1.948	1.971, 1.980, 2.002, 2.002	1.985 AA	1.98(2)	
	Cr(3)	1.982	1.962, 1.982, 1.989, 2.017	2.005 TFA	1.99(1)	
12	Cr(1)	1.912	2.022, 2.039, 2.043, 2.094	2.055 AA	2.03(6)	[45]
	Cr(2)	1.897	2.03, 2.047, 2.049, 2.061	2.017 AA	2.02(6)	
	Cr(3)	1.971	2.04, 2.05, 2.067, 2.068	2.118 THF	2.05(5)	

* Axial ligands: AA is CH_3COOH, and aq is H_2O.
** Average Cr–O bond lengths.

torted octahedral coordination of one fluorine atom and five oxygen atoms (Fig. 9b, Table 4).

As compared to the bridging TFA groups, the HTFA molecules acting as terminal axial ligands are characterized by a significant asymmetry of the C–O bonds (see Table 3 in [47]). The hydroxyl groups of these molecules participate in the formation of intraionic hydrogen bonds with the oxygen atoms of the bridging TFA groups, due to which the axial HTFA molecules are arranged all at one side or two molecules are arranged at one side and the third molecule is located at another side of the triangle plane (Fig. 9b). The O–H···O hydrogen bond lengths in the anions of the synthesized compounds are 2.54–2.67 Å (average 2.59 Å).

The data in Table 4 and those in more detailed Table 2 in [48] show that the same-type anions $[M''_3(\mu_3\text{-}F)(TFA)_6(HTFA)_3]^-$ in structures **13–22** are similar in geometric characteristics. Some increase in the size of the octahedral polyhedron $[CoO_5F]$ compared to $[NiO_5F]$ is explained by a difference in effective ionic radii of Ni^{2+} and Co^{2+}. The average Ni–F distance is 1.99 Å (13–20), and the average Co–F bond length is somewhat greater (2.03 Å (**21** and **22**)), which is consistent with the values calculated using the ionic radii [37]: 1.99 Å (Ni–F) and 2.045 Å (Co–F). The average Ni–O_{TFA} distances involving four O atoms of the bridging TFA groups forming the equatorial plane of the $[NiO_5F]$ octahedron range from 2.02 to 2.06 Å, whereas the corresponding Co–O_{TFA} distances in structures **21** and **22** are somewhat longer (2.07–2.08 Å) (Table 4). The same tendency is observed when comparing the lengths of the Ni–O_L and Co–O_L bonds involving the oxygen atoms of the axial HTFA molecules: the Ni–O_L bonds are shorter (2.10–2.14 Å) than the Co–O_L bonds in structures **21** and **22** (2.17 Å) (Table 4).

As compared to the same-type trinuclear $[M''_3(\mu_3\text{-}F)(TFA)_6(HTFA)_3]^-$ anions (M' = Co(II) and Ni(II)) in structures **13–22**, a change in the synthesis conditions made it possible to obtain for the first time the trinuclear zinc fluorotrifluoroacetate complex (**23**) and the heterovalent manganese (**24**) and iron (**25**) complexes differed by the nature of the metal atom and also by the presence of other terminal ligands.

Unlike all fluorotrifluoroacetates considered above, compounds $Na[M_3(\mu_3\text{-}F)(TFA)_6(HTFA)_2TFA](HTFA)_2$ (M = Mn (**24**) and Fe (**25**)) include anions $[M_3(\mu_3\text{-}F)(TFA)_6(HTFA)_2TFA]^-$ containing simultaneously two M(II) atoms and one M(III) atom. This is manifested as both a change in the composition of the complexes (one of three neutral axial ligands L is replaced by the TFA^- anion) and a distortion of the triangular trinuclear anion due to a noticeable decrease in the sizes of the $[M^{III}FO_5]$ polyhedron compared to those of $[M^{II}FO_5]$.

For example, the presence in structure **24** of the TFA^- anion acting as an axial ligand and four HTFA molecules of which two molecules are axial ligands and two molecules are not in the coordination sphere of the trinuclear anion is confirmed by the differentiation of the corresponding C–O bond lengths and also by the presence of the corresponding hydroxylic oxygen atoms localized in structure refinement. The requirement of the electroneutral character of com-

Table 4. Bond lengths M μ_3-O and M μ_3-F in the octahedral coordination polyhedra of the M atoms in the trinuclear complexes $[M_3(\mu_3\text{-F})(TFA)_6L_3]$

Complex	Numeration		Average distance, Å					
	this article	[48]	Experiment				theory [37]	
			M–F		$M–O_{TFA}$	$M–O_L$*	M–F	M–O
$Li[Ni_3(\mu_3\text{-F})(TFA)_6(HTFA)_3](HTFA)_3$	**13**	**I**		1.99	2.04	2.10	1.99	2.04
$Na[Ni_3(\mu_3\text{-F})(TFA)_6(HTFA)_3]$	**14**	**II**		1.99	2.03	2.11		
$K[Ni_3(\mu_3\text{-F})(TFA)_6(HTFA)_3]$	**15**	**VIII**		1.99	2.04	2.12		
$NO[Ni_3(\mu_3\text{-F})(TFA)_6(HTFA)_3]$	**16**	**IX**		2.00	2.03	2.13		
$NH_4[Ni_3(\mu_3\text{-F})(TFA)_6(HTFA)_3]$	**17**	**IV**		1.99	2.02	2.12		
$Rb[Ni_3(\mu_3\text{-F})(TFA)_6(HTFA)_3]$	**18**	**V**		1.99	2.02	2.12		
$Cs[Ni_3(\mu_3\text{-F})(TFA)_6(HTFA)_3]$	**19**	**VI**		1.99	2.03	2.12		
$Cs[Ni_3(\mu_3\text{-F})(TFA)_6(HTFA)_3](HTFA)_{0.5}$	**20**	**VII**		2.01	2.06	2.13, 2.14		
$NO[Co_3(\mu_3\text{-F})(TFA)_6(HTFA)_3]$	**21**	**X**		2.03	2.076	2.17	2.045	2.095
$NH_4[Co_3(\mu_3\text{-F})(TFA)_6(HTFA)_3]$	**22**	**III**		2.03	2.07	2.17		
$Na[Zn_3(\mu_3\text{-F})(TFA)_6(H_2O)_3] \cdot 4.34H_2O$	**23**			2.03	2.09	2.10 (H_2O)	2.04	2.09
$Na[Mn_3^{II,II,III}(\mu_3\text{-F})(TFA)_6(TFA)(HTFA)_2](HTFA)_2$	**24**		Mn(II)	2.14	2.13	2.19	2.13	2.18
			Mn(III)	1.98	1.99	1.94 (TFA^-)	1.945	1.995
$Na[Fe_3^{II,II,III}(\mu_3\text{-F})(TFA)_6(TFA)(HTFA)_2](HTFA)_2$	**25**		Fe(II)**	2.11	2.10	2.16	2.08	2.13
			Fe(III)**	1.99	1.99	1.94 (TFA^-)	1.945	1.995

* Terminal ligands are indicated in parentheses. If is not indicated, then L = HTFA.

** Averaged for two structurally independent trinuclear anions.

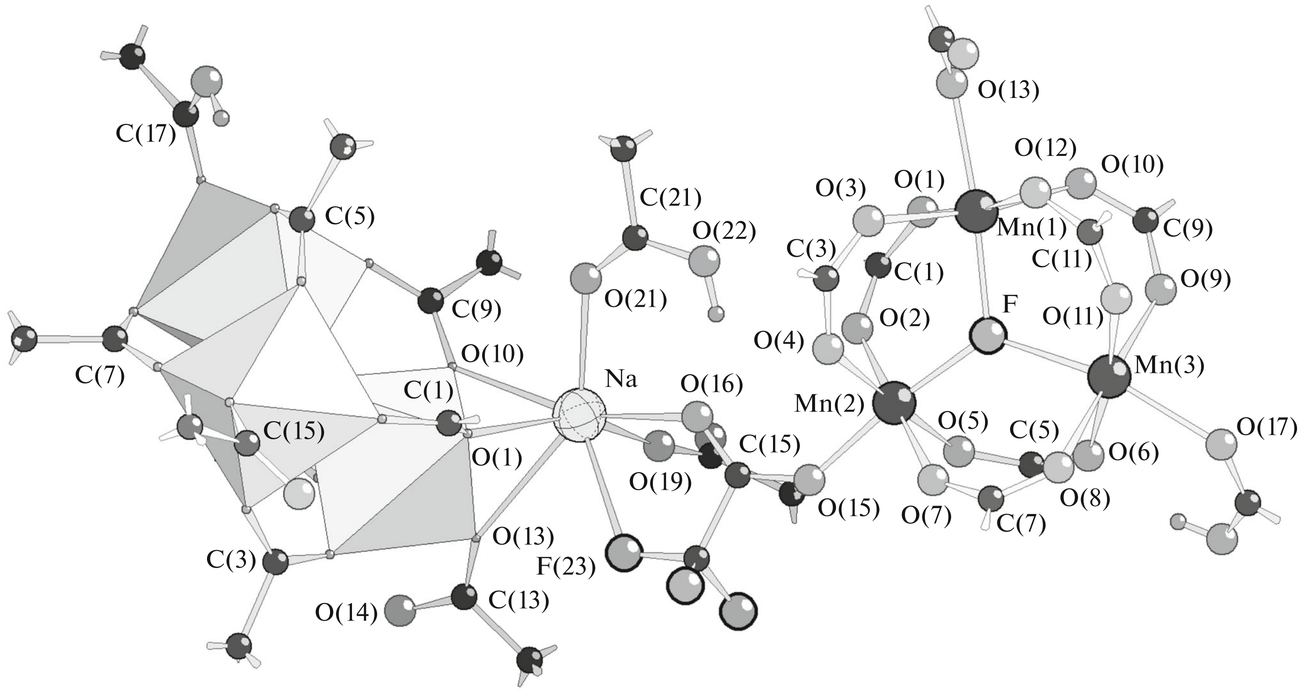

Fig. 10. Fragment of crystal structure $Na[Mn_3(\mu_3\text{-}F)(TFA)_6(TFA)(HTFA)_2](HTFA)_2$. The coordination environment of the Mn atoms of one of two trinuclear anions $[Mn_3(\mu_3\text{-}F)(TFA)_6(TFA)(HTFA)_2]^-$ is presented as octahedral polyhedra. Some CF_3 groups and F atoms are omitted.

pound $Na[M_3(\mu_3\text{-}F)(TFA)_6(HTFA)_2TFA](HTFA)_2$ results in an unambiguous conclusion about an increase in the oxidation state of one of three Mn atoms to +3.

The distribution of the oxidation states +2 and +3 between three Mn atoms is unambiguously revealed by the comparison of the sizes of the $[MnFO_5]$ polyhedra. It can easily be seen that the interatomic distances in the coordination environment of the Mn(2) atom are substantially shorter than the corresponding distances for the Mn(1) and Mn(3) atoms (Table 4). Thus, the oxidation state +3 should be ascribed to the Mn(2) atom. This conclusion is confirmed by a good correspondence of the Mn–F and Mn–O distances to those theoretically calculated using the tabulated ionic radii (Table 4).

The coordination of the terminal (axial) ligands by the Mn atoms occurs according to the determined distribution of their oxidation states: the TFA^- anion (O(15)) is coordinated by the trivalent Mn(2) ion, whereas the neutral HTFA molecules (O(13) and O(17)) are in the coordination environment of the bivalent Mn(1) and Mn(3) ions. The second oxygen atom of the TFA^- anion (O(16)) is coordinated by sodium, whereas the hydroxyl groups of the HTFA molecules form intramolecular hydrogen bonds with a length of 2.642(6) Å (O(14)···O(12)) and 2.652(5) Å (O(18)···O(6)).

The sodium cations in structure **24** coordinate six O atoms (Na–O 2.327(4)–2.769(4) Å) and also the F(23) atom of the CF_3 group in the same TFA^- anion (Na–F 2.638(4) Å) (Fig. 10). As a whole, the coordination mode of sodium can be described as a distorted pentagonal bipyramid. Interestingly, the bridging TFA^- anion bidentately binds the sodium atom due to the O and F atoms and simultaneously binds to the Mn(III) atom due to the second O atom thus demonstrating the specific coordination mode typical of the TFA^- anion.

Thus, zigzag cation-anionic chains directed along the *y* axis are formed in structure **24** due to the interaction of the sodium cations simultaneously with two trinuclear anions $[Mn_3(\mu_3\text{-}F)(TFA)_6(HTFA)_2TFA]$, and the Na···Na···Na angle is 117.5° (Fig. 10). On the whole, structure **25** containing Fe atoms instead of Mn is similar to structure **24** (Table 4).

The packing of one-charged M' cations and trinuclear anions considered for structure **24** is common for all studied structures **13–25** [46, 47]. In all cases, the oxygen (sometimes fluorine) atoms belonging to facets of two $[M''FO_5]$ octahedra of the adjacent trinuclear anions participate in the coordination mode of the alkaline metal cation (as well NH_4^+ and NO^+). In some structures, solvate molecules HTFA or H_2O can also be coordinated by the M' cation. As a result, infinite chains of alternating trinuclear anions and one-charged cations are formed. The single exception is the crystal structure of lithium fluorotrifluoroacetate **13** in which the Li atom coordinates the trinuclear anion only to form two Li–O bonds with it, and two positions in the tetrahedral environment of lithium are occupied by the carbonyl O atoms of two solvate HTFA molecules. Layers are formed in structure **13** due to the system of hydrogen bonds joining the Li^+ cations, trinuclear anions, and HTFA molecules.

To conclude the consideration of the trinuclear fluorotrifluoroacetate complexes, we can mention (Table 4) that the sizes of the octahedral polyhedra $[M^{II}FO_5]$ increase in the series $Ni^{+2} < Co^{+2} \approx Zn^{+2} < Fe^{+2} < Mn^{+2}$, which is well consistent with an increase in the effective ionic radii of the octahedrally coordinated cations in this series [37]. For the same M atoms, the $M–O_{TFA}$ and $M–O_{HTFA}$ bond lengths in the structures of triangular fluorotrifluoroacetates and in the linear trimers and chains (Table 2) vary in the same ranges. The sizes of the polyhedra formed by trivalent Mn^{+3} and Fe^{+3} cations almost coincide (Table 4) and are comparable with the $[Cr^{III}O_6]$ polyhedra in the Cr(III) oxotrifluoroacetates considered earlier ($r_{eff}(Mn^{3+}) = r_{eff}(Fe^{3+}) = 0.785$ Å, $r_{eff}(Cr^{3+}) = 0.755$ Å [37]).

It should also be noted that in the most part of the studied trinuclear fluorotrifluoroacetates, as well as in the oxocarboxylates, the length of the metal (M'')–central atom (F or O) bond is somewhat shorter and the $M''–O_L$ bond is noticeably longer than the $M''–O_{TFA}$ distances in the equatorial plane. This tendency is appreciably violated in the heterovalent fluorotrifluoroacetate anions in complexes **24** and **25**.

After our data on the synthesis of the first triangular fluorotrifluoroacetate complexes were published [47, 48], the syntheses and structural study of new representatives of trinuclear fluorocarboxylates $(PyH)_4[Mg_3(\mu_3\text{-}F)(TFA)_6(OCH_3)_2(Py)](OCH_3)$ [49] and three heteronuclear complexes $[Ni^{II}_2Cr^{III}(\mu_3\text{-}F)(O_2C^tBu)_6L_3]$ ($L = HO_2C^tB$, C_5H_5N, $(4\text{-}CH_3)C_5H_4N$)) [50] have been reported. Thus, the accumulated experimental information suggests that the triangular fragment $[M''_3(\mu_3\text{-}F)(RCOO)_6L_3]$ is a common rather stable structural element for the whole family of trinuclear carboxylate complexes.

To conclude, the crystal chemistry of trifluoroacetates of d elements is very diverse. Mono-, di-, and trinuclear complexes (both linear and triangular) and infinite chain and ribbon structures can be obtained by the variation of the synthesis conditions. Specific features of the trifluoroacetate ligand are determined, to a great extent, by its nature as a strong acid anion. As a result, the crystal chemical behavior of the trifluoroacetate anion resembles that of inorganic oxygen-containing acido ligands. In this sense, the trifluoroacetate anion occupies an intermediate position between anions of inorganic and organic acids, although on the whole it is undoubtedly close to the latter.

The most part of the synthesized and structurally studied trifluoroacetates, whose structure contains linear trimers or infinite trifluoroacetate chains, and the trinuclear complexes with the μ_3-O or μ_3-F atom were isolated from solutions of concentrated HTFA. This approach turned out to be rather productive. When considering the known structures of other carboxylates, one can conclude that compounds, in particular, heterometallic, with a similar or close structural motif can be derived from the carboxylates. However, suitable conditions that can substantially differ from the synthesis conditions for trifluoroacetates should be selected for their synthesis. One of the examples is the recent synthesis of the fluoropivalate triangular trinuclear complexes $[Ni_2Cr(\mu_3\text{-}F)(O_2CtBu)_6L_3]$ [50].

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