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Synthesis, crystal structure and thermal properties of $Na_2Ti(CF_3COO)_6(CF_3COOH)_2$

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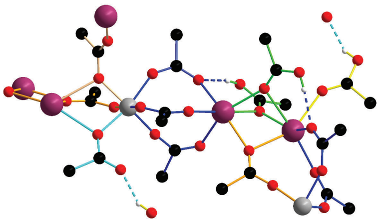
The compound $Na_2Ti(CF_3COO)_6(CF_3COOH)_2$ was synthesized as colorless crystals, extremely unstable in air, by the reaction of $TiCl_4$ with trifluoroacetic acid and sodium trifluoroacetate. Crystallographic studies have shown that this sodium trifluoroacetatotitanate is the first example of a tetravalent titanium carboxylate $[Ti(RCOO)_6]^{2-}$ containing titanium in an octahedral environment of oxygen atoms of carboxylate groups. Thermal decomposition of $Na_2Ti(CF_3COO)_6(CF_3COOH)_2$ in an argon atmosphere results in the complex fluoride Na_2TiF_6.



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In most cases, titanium(IV) compounds are stabilized due to the formation of oxo bridges. Titanyl TiO^{2+} salts are the best-known compounds with inorganic acid anions. In oxotitanium(IV) compounds containing carboxylic acid anions, the greatest diversity is observed among structures with titanium oxo clusters comprising up to 52 titanium atoms bound by μ_2-, μ_3- and μ_4-bridging oxygen atoms or their various combinations.[1]

Isolated titanium atoms are rarely found in the crystal structures of Ti^{IV} coordination compounds. Such atoms are generally typical of compounds with bulky chelating ligands, in which they have a coordination number of eight. Of interest in this respect are carbamate complexes of the general formula $Ti(O_2CNR_2)_4$, where titanium is in a pseudo-dodecahedral environment.[2–4] Separately, it is worth noting the mononuclear complex $Ti(pic)_4$ obtained by Fenton *et al.*[5] with the anion of picolinic acid (pyridine-2-carboxylic acid) as the N,O-ligand, in which titanium atoms are located in an almost perfect triangular dodecahedron. The titanium(IV) compound with citric acid, formed from the $[Ti(C_6H_{4.5}O_7)_2(C_6H_5O_7)]^{6-}$ complex ion, is also mononuclear.[6] Due to the large volume of citrate ligands, this compound contains only three anions, forming a distorted octahedral environment.

Mononuclear coordination compounds of titanium(IV) with monobasic carboxylic acids have not yet been known. It is interesting to note that, aside from titanium(IV) trifluoroacetate, titanium oxo clusters with trifluoroacetate groups are also unknown, except for a number of clusters doped with transition metals. Their cores are composed of $M_2Ti(\mu_3\text{-}O)$ or $MTi_2(\mu_3\text{-}O)$ moieties, sometimes linked into oligomers by bridging oxo or hydroxo groups. Clusters of this type are known for M = Mg,[7,8] Mn,[9,10] Co,[11,12] Zn,[13] Fe,[14] Cd[15,16] and Pb.[17]

In this communication, we describe the synthesis and crystal structure of sodium trifluoroacetatotitanate $Na_2Ti(CF_3COO)_6(CF_3COOH)_2$, in which titanium atoms are in the octahedral environment of oxygen atoms of trifluoroacetate groups. It is a new compound in the coordination chemistry of titanium(IV) carboxylates. Its preparation opens up great opportunities for the synthesis of similar carboxylate titanates, which can be used as precursors for materials containing fluoride, oxide or both, as well as for the preparation of TiO_2 phases of various dimensionalities with grafted active centers.

The title compound was synthesized from titanium tetrachloride and trifluoroacetic acid as starting compounds in an argon atmosphere in the presence of trifluoroacetic anhydride to prevent possible hydrolysis and clustering processes (for details, see Online Supplementary Materials). The crystalline reaction product can be isolated by adding sodium cations as sodium trifluoroacetate to the system. The composition of the compound, determined by single crystal X-ray diffraction analysis, corresponds to the formula $Na_2Ti(CF_3COO)_6(CF_3COOH)_2$.[†] Titanium(IV) trifluoroacetate ‘$Ti(CF_3COO)_4$’, formed at the intermediate stage, is a

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[†] *Crystal data for* $Na_2Ti(CF_3COO)_6(CF_3COOH)_2$. $C_{48}H_6F_{72}Na_6O_{48}Ti_3$ (M = 3000.17), T = 100 K, triclinic, space group $P\bar{1}$, a = 8.5999(4), b = 12.4742(6) and c = 24.1371(11) Å, α = 101.057(2)°, β = 92.957(2)°, γ = 109.916(2)°, V = 2370.04(19) Å^3, Z = 1, d_{calc} = 2.102 g cm^{-3}, μ(MoKα) = 0.511 mm^{-1}, $F(000)$ = 1458. The intensities of 33712 reflections (11437 independent reflections, R_{int} = 0.0348) were measured by ω-scanning in the range of $2.15° < \theta < 28.00°$ ($-11 \leqslant h \leqslant 11$, $-16 \leqslant k \leqslant 16$, $-31 \leqslant l \leqslant 31$).

A single crystal with dimensions of 0.10×0.17×0.18 mm was subjected to X-ray diffraction analysis on a Bruker SMART APEX II CCD automatic diffractometer using graphite-monochromated MoKα radiation (λ = 0.71073 Å) under a stream of cooled nitrogen. The absorption correction was based on measurements of the intensities of equivalent reflections.[19] Data reduction was performed using the SAINT program.[20] The structure was solved by direct methods and refined on F^2 by the full-matrix least-squares method in the anisotropic approximation for non-hydrogen atoms using the SHELXTL-Plus software.[21] The positions of hydrogen atoms were calculated and refined using the ‘riding’ model. A summary of crystallographic data and structure determination parameters is provided in Online Supplementary Materials.

CCDC 2108171 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

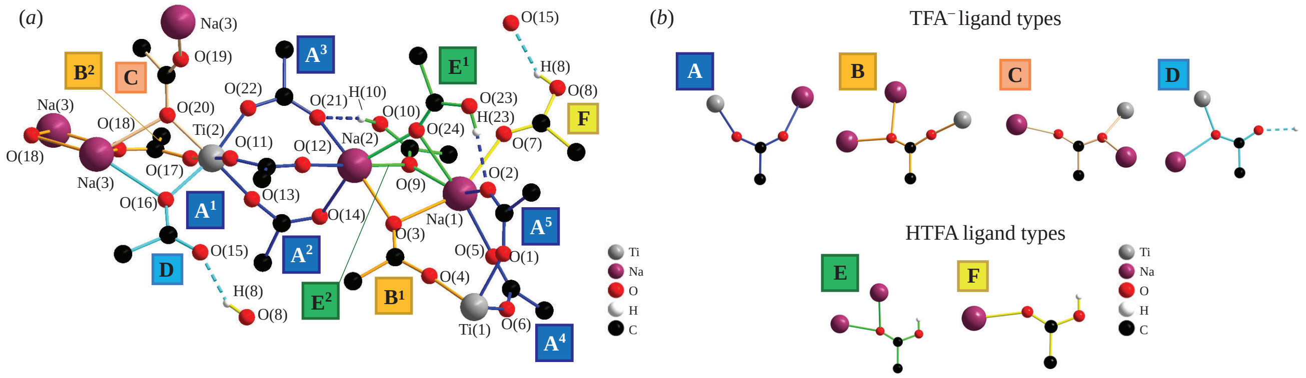

Figure 1 (*a*) A crystallographically independent fragment of the $Na_3Ti_{1.5}(TFA)_9(HTFA)_3$ chain in $Na_2Ti(CF_3COO)_6(CF_3COOH)_2$. (*b*) Structural functions of carboxylate ligands in $Na_2Ti(CF_3COO)_6(CF_3COOH)_2$. Fluorine atoms of trifluoromethyl groups are not shown.

yellow liquid under standard conditions. It probably has a molecular structure similar to $Ti(NO_3)_4$ previously reported.[18]

The structure is based on bent chains of titanium and sodium atoms linked to each other by trifluoroacetate anions and trifluoroacetic acid molecules. In the chain of the obtained compound, one can isolate the fragment $Na_3Ti_{1.5}(TFA)_9(HTFA)_3$ (HTFA = = CF_3COOH, TFA = CF_3COO^-), which is limited by inversion points located at both its edges, *i.e.*, on the Ti(1) atom and between two Na(3) atoms [Figure 1(*a*)]. The fragment contains 12 carboxylate ligands of six different types, which are atypical both for the chemistry of trifluoroacetates in general and for the chemistry of titanium(IV) carboxylate compounds in particular. Figure 1(*b*) shows various types of ligands we have proposed based on their structural functions. Figure 1(*a*) displays the $Na_3Ti_{1.5}(TFA)_9(HTFA)_3$ fragment, in which the roles of trifluoroacetate ligands are shown in different colors (for a representation of this fragment with thermal ellipsoids, see Online Supplementary Materials).

Most trifluoroacetate anions $\mathbf{A^1}$–$\mathbf{A^5}$ are bidentate bridging ligands that link sodium and titanium atoms. Ligands $\mathbf{A^3}$ and $\mathbf{A^5}$ participate in the formation of intra-chain hydrogen bonds with trifluoroacetic acid molecules $\mathbf{E^2}$ and $\mathbf{E^1}$, respectively. The tridentate trifluoroacetate anions $\mathbf{B^1}$ and $\mathbf{B^2}$ bind a pair of sodium atoms to one oxygen atom and a titanium atom to another. It is due to this type of ligands that bends of the infinite chain are formed. The tridentate trifluoroacetate anion **C** binds the sodium atom and the titanium atom of one chain to the sodium atom of the adjacent chain. Due to this ligand, the chains are linked into corrugated layers, as shown in Figure 2. Besides the monoatomic coordination of sodium atoms and titanium atoms, bidentate TFA⁻ anions **D** form hydrogen bonds, linking the layers into a three-dimensional framework.

There are two functionally different types of trifluoroacetic acid molecules in the structure. Molecules $\mathbf{E^1}$ and $\mathbf{E^2}$ of the first type perform a bridging function due to the bidentate carbonyl oxygen atom and participate in the formation of hydrogen bonds. Molecules **F** of the second type are coordinated by the sodium atom and participate in the formation of a hydrogen bond between the layers with anion **D** of the adjacent layer and are the only monodentate ligands in this structure. The wide variety of structural functions of ligands in $Na_2Ti(CF_3COO)_6(CF_3COOH)_2$ is associated with the need for CF_3COO^- and CF_3COOH to exhibit high denticity, which is usually atypical for weak ligands.

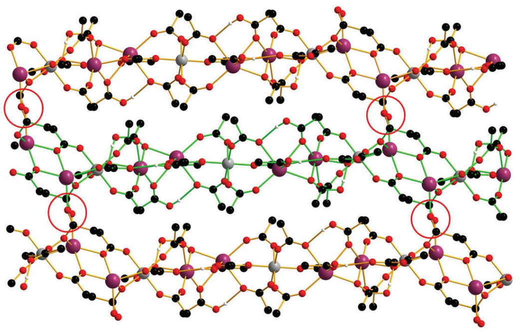

Figure 2 A corrugated layer formed from chains due to the binding role of ligand **C**. Fluorine atoms of trifluoromethyl groups are not shown.

The compound contains two crystallographically independent titanium atoms. The coordination environment of the Ti(1) atom is a rhombohedrally distorted octahedron. The bond lengths are given in Table S1, see Online Supplementary Material. The oxygen atoms of the trifluoroacetate groups coordinate to the Ti(2) atom, forming a distorted octahedral environment. The difference in the Ti–O bond lengths is determined by the structural functions of the trifluoroacetate anions. The longest distances are observed where the trifluoroacetate anion is involved in the formation of hydrogen bonds (ligands $\mathbf{A^3}$, $\mathbf{A^5}$ and **D**), as well as in the case of ligand $\mathbf{B^2}$, where the fluorine atoms of the trifluoromethyl group are involved in coordination with the sodium atom Na(3).

The structure includes three crystallographically independent sodium atoms. The coordination environment of Na(1) and Na(2) atoms consists of six oxygen atoms of molecules and anions of trifluoroacetic acid. The coordination number of the Na(3) atom is eight and is provided by five oxygen atoms and three fluorine atoms (for details, see Online Supplementary Materials). Naturally, the Na–O distances are longer if oxygen atoms belong to the trifluoroacetic acid molecules $\mathbf{E^1}$ and $\mathbf{E^2}$. As in the case of Ti–O bonds, the Na–O bond lengths are influenced by the denticity of the ligand and hydrogen bonds formed with the participation of trifluoroacetate anions $\mathbf{A^5}$, $\mathbf{B^2}$, **C** and **D**, which act as ligands and perform various structural functions. The Na–F distances are longer, about 2.7 Å on average.

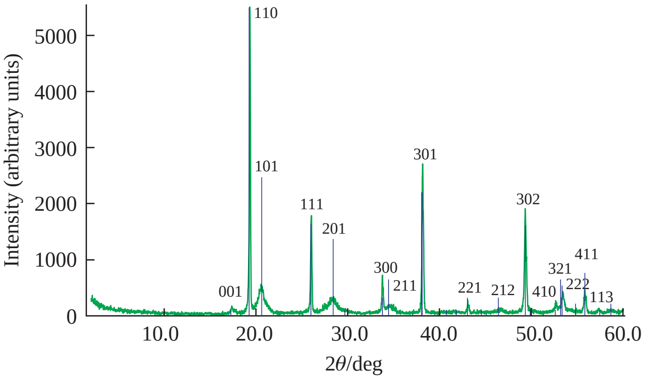

Figure 3 Powder XRD pattern of the decomposition product of the compound $Na_2Ti(CF_3COO)_6(CF_3COOH)_2$. The assignment is done using the powder XRD database [00-015-0581].

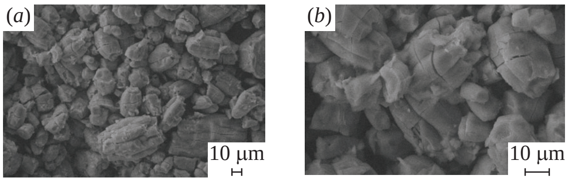

Figure 4 Photomicrographs of the decomposition product of the compound $Na_2Ti(CF_3COO)_6(CF_3COOH)_2$, taken with a magnification of (*a*) 1000$^\times$ and (*b*) 2500$^\times$.

There are two types of hydrogen bonds in the structure. A bond of the first type is formed within the chain and binds bidentate anions $\mathbf{A^3}$ and $\mathbf{A^5}$ with trifluoroacetic acid molecules $\mathbf{E^2}$ and $\mathbf{E^1}$, respectively. A hydrogen bond of the second type is formed with the participation of oxygen atoms O(8) and O(15) of ligands **D** and **F**, respectively.

Decomposition of the $Na_2Ti(CF_3COO)_6(CF_3COOH)_2$ complex in an argon atmosphere results in the complex fluoride Na_2TiF_6 (Figure 3). The noticeable difference in the peak half-widths in the X-ray diffraction (XRD) pattern is explained by the product texturing during decomposition. It leads to the formation of crystallites with irregular linear dimensions. The direction of crystallite growth is complex, and it was impossible to reveal the regularity from the XRD data. The decomposition product visually consists of ellipsoids formed by layers of curved thin plates (Figure 4).

In this work, sodium trifluoroacetatotitanate $Na_2Ti(CF_3COO)_6(CF_3COOH)_2$, a fundamentally new representative of titanium(IV) carboxylate complexes, was obtained. The composition of the compound was determined using single crystal X-ray diffraction analysis. The compound structure is built of corrugated layers bound to each other through a system of hydrogen bonds. Decomposition in an inert atmosphere gives the complex fluoride Na_2TiF_6. The complex compound $Na_2Ti(CF_3COO)_6(CF_3COOH)_2$ obtained for the first time may become the first representative of a series of similar compounds with other metal atoms instead of sodium, suitable for the synthesis of complex fluorides based on titanium tetrafluoride.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2022.03.019.

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