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RESEARCH ARTICLE

A novel calcium trifluoroacetate structure

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Abstract

Objectives. *The study was devoted to considering the features of the synthesis and crystal structure of calcium trifluoroacetate $Ca_2(CF_3COO)_4 \cdot 8CF_3COOH$ and investigating the products of its thermal behavior.*

Methods. *The compositions of the proposed structural form were characterized by various physicochemical methods (X-ray diffraction, IR spectroscopy), and the products of thermal decomposition were determined under dynamic vacuum conditions.*

Results. *The reaction between calcium carbonate and 99% trifluoroacetic acid yielded a new structural type of calcium trifluoroacetate $Ca_2(CF_3COO)_4 \cdot 8CF_3COOH$ (I) in the form of colorless prismatic crystals unstable air. X-ray diffraction results confirmed the composition **I**: space group $P2_1$, with unit cell parameters: a = 10.0193(5) Å, b = 15.2612(7) Å, c = 16.3342(8) Å, β = 106.106(2)°, V = 2399.6(2) Å^3, Z = 2. The structure is molecular, constructed from $Ca_2(CF_3COO)4 \cdot 8CF_3COOH$ dimers. The end molecules of the trifluoroacetic acid were involved in the formation of intramolecular hydrogen bonds with oxygen atoms of the bidentate bridging anions CF_3COO^-. There were strongly pronouncedsymmetric and asymmetric absorption bands of COO and CF_3-groups in the IR spectrum of the resulting compound in the range of 1200–1800 cm^{-1}. The definite peak of the oscillation of the OH-group at 3683 cm^{-1} corresponds to the trifluoroacetic acid molecules present in the structure. The broadpeak of the valence oscillations in the range of 3300–3500 cm^{-1} is caused by the presence of intramolecular hydrogen bonds. Decomposition began at 250°C and 10^{-2} mm Hg with calcium fluoride CaF_2 as the final decomposition product.*

Conclusions. *We obtained a previously undescribed calcium–trifluoroacetic acid complex whose composition can be represented by $Ca_2(CF_3COO)_4 \cdot 8CF_3COOH$. The crystal island structure is a dimeric molecule where the calcium atoms are bound into dimers by four trifluoroacetate groups. The complex was deposited in the Cambridge Structural Data Bank with a deposit number CCDC 2081186. Although the compound has a molecular structure, thermal decomposition leads to the formation of calcium fluoride characterized by a small particle size, which may further determine its applications.*

Keywords: *trifluoroacetate complexes, alkaline earth metals, crystal structure, IR spectroscopy, thermal properties, calcium fluoride*

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НАУЧНАЯ СТАТЬЯ

Трифторацетат кальция: новый структурный тип

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Аннотация

Цели. *Работа посвящена рассмотрению особенностей синтеза и кристаллического строения трифторацетата кальция $Ca_2(CF_3COO)_4 \cdot 8CF_3COOH$, а также изучению продуктов его термического поведения.*

Методы. *Соединение охарактеризовано различными физико-химическими методами (рентгеноструктурный анализ, ИК-спектроскопия), установлены продукты термического разложения в условиях динамического вакуума.*

Результаты. *Взаимодействием карбоната кальция с 99% трифторуксусной кислотой синтезирован новый структурный тип трифторацетата кальция $Ca_2(CF_3COO)_4 \cdot 8CF_3COOH$ (I) в виде неустойчивых на воздухе бесцветных призматических кристаллов. Строение **I** установлено по результатам рентгеноструктурного анализа: пространственная группа $P2_1$, параметры элементарной ячейки: a = 10.0193(5) Å, b = 15.2612(7) Å, c = 16.3342(8) Å, β = 106.106(2)°, V = 2399.6(2) Å^3, Z = 2. Структура молекулярная, построена из димеров $Ca_2(CF_3COO)_4 \cdot 8CF_3COOH$. Торцевые молекулы трифторуксусной кислоты участвуют в образовании внутримолекулярных водородных связей с атомами кислорода бидентатных мостиковых анионов CF_3COO^-. На ИК-спектре полученного соединения в диапазоне 1200–1800 см$^{-1}$ присутствуют ярко выраженные симметричные и асимметричные полосы поглощения COO и CF_3-групп. Четкий пик колебания OH-группы на 3683 см$^{-1}$ соответствует присутствующим в структуре молекулам трифторуксусной кислоты. Широкий пик валентных колебаний в области 3300–3500 см$^{-1}$ обусловлен наличием внутримолекулярных водородных связей. При давлении 10^{-2} мм рт.ст. разложение начинается при 250 °C, конечным продуктом разложения является фторид кальция CaF_2.*

Выводы. *Нами получен ранее не описанный комплекс кальция с трифторуксусной кислотой, состав которого может быть представлен формулой $Ca_2(CF_3COO)_4 \cdot 8CF_3COOH$, кристаллическая островная структура которого представляет собой димерную молекулу, а атомы кальция связаны в димеры четырьмя трифторацетатными группами. Комплекс задепонирован в Кембриджском банке структурных данных, номер депонирования – CCDC 2081186. Соединение имеет молекулярное строение, термическое разложение приводит к образованию фторида кальция, характеризующегося небольшим размером частиц, что может в дальнейшем обусловить его применение.*

Ключевые слова: *трифторацетатные комплексы, щелочноземельные металлы, кристаллическая структура, ИК-спектроскопия, термические свойства, фторид кальция*

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INTRODUCTION

Trifluoroacetic acid CF_3COOH (dissociation constant 0.69 [1]) is considered a strong acid due to the influence of the trifluoromethyl group on the carboxyl group. The bond between the trifluoroacetate anion and the complexing atom exhibits a more ionic character and is weaker than the coordination bond in most carboxylates. As a consequence, the coordination chemistry of trifluoroacetate complexes often differs from most carboxylates. At the same time, trifluoroacetic acid performs various structural functions depending on the conditions of the synthesis, leading to the appearance of certain characteristic features in the composition and structure of the resulting trifluoroacetate metal complexes. A review of trifluoroacetate complexes of 3d metals was provided in [2].

Interest in the study of trifluoroacetate complexes of various metals is primarily associated with the possibility of obtaining simple and complex fluorides during their thermal decomposition [3–6] in the form of nanoparticles, solid fluoride solutions [7], and fluoride glasses of various compositions [8–10].

The study aims at synthesizing a calcium trifluoroacetate complex not previously described, investigate its crystal structure by X-ray diffraction and IR spectroscopy, compare the features of the crystal structure of trifluoroacetate complexes of various alkaline-earth metals based on their synthesis conditions, and analyze the product of thermal decomposition of the resulting compound.

MATERIALS AND METHODS

The starting materials for the synthesis were calcium carbonate, $CaCO_3$ (analytical grade, *Vecton*, Russia), and trifluoroacetic acid, CF_3COOH (99% chemically pure, *Argentum 107*, Russia).

*Synthesis of $Ca_2(CF_3COO)_4 \cdot 8CF_3COOH$ (complex **I**):*

A sample of 90.0 mg of $CaCO_3$ (1.0714 mmol) was dissolved by heating in 5.0 mL of 99% CF_3COOH. Concentrating the resulting solution in a desiccator over phosphorus pentoxide (P_2O_5, pure, *Vecton*, Russia) produced isolated colorless and air-unstable crystals, filtered and dried in an argon atmosphere with the yield of 630 mg (81%). Complex **I** is soluble in concentrated trifluoroacetic acid but decomposes in moist air and aqueous solutions with the formation of calcium trifluoroacetate hydrate.

Compound **I** was characterized by IR spectroscopy and X-ray diffraction. IR spectra were recorded on the FTIR Spectrum using One Perkin-Elmer spectrometer (*SpectraLab Scientific Incorporation*, Canada) in KBr tablets in the region of 400–4000 cm^{-1} with a resolution of 0.5 cm^{-1}. The assignment of bands in the IR absorption spectrum of the complex is given in Table 1. The observed spectrum is shown in Fig. 1.

The shift in the absorption bands of the COO groups of compound **I** relative to similar data for the calcium trifluoroacetate complex described in [11] indicated an attenuation of the interaction and an increase in the Ca–O bond length, consistent with an increase in the coordination number of the calcium atom to 8 in compound **I**.

The study of the thermal behavior of the sample $Ca_2(CF_3COO)_4 \cdot 8CF_3COOH$ under dynamic vacuum conditions was carried out by heating the sample in a glass ampoule using a tubular furnace. Under dynamic vacuum conditions (at 10^{-2} mm Hg), compound **I** was stable up to a temperature of 250°C, after which it began to decompose, resulting in a sharp decrease in pressure up to 10^{-1} mm Hg. However, as the temperature increased to 270°C, the pressure became stabilized at 10^{-2} mm Hg.

Experimental and theoretical values of mass loss are given in Table 2.

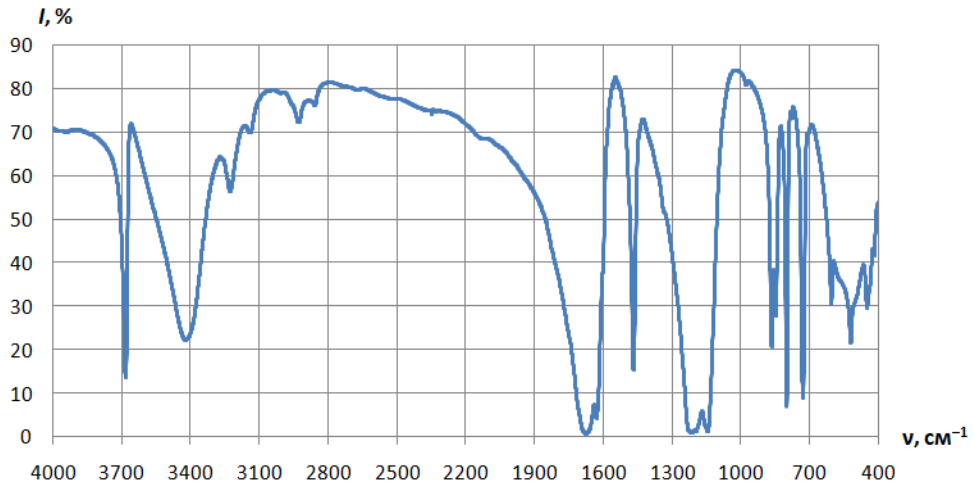

Fig. 1. IR absorption spectrum of the compound **I** $Ca_2(CF_3COO)_4 \cdot 8CF_3COOH$.

Table 1. Assignment of the peaks of the IR spectrum of the compound **I** $Ca_2(CF_3COO)_4 \cdot 8CF_3COOH$

Wavenumber, cm^{-1}	Assignment	Notes/references
3683	υ(OH)	–
3419.5	υ(O–H…O)	3431 [12]
3226.3	υ(O–H…O)	–
1677.7	$υ_{as}$(COO)	1660 [11]
1469.3	$υ_s$(COO)	1444 [11]
1215.2	$υ_s(CF_3)$	1210 [11]
1145.9	$υ_{as}(CF_3)$	1142 [11]
867.33	υ(C–C) υ(C–O)	850 [11]
801.35	CF_3 symmetric stretch	800 [11]
729.95	δ(COO) (C–CO_2 in-planebend)	728 [11]
606.41	$δ_s(CF_3)$	605 [11]
522.09	$δ_{as}(CF_3)$	520 [11]
450.08	δ(CCF_3) (C–CF_3 planerock)	υ(Ca–O), 430 [12]

Table 2. Experimental and theoretical mass loss values for the formation of CaF_2 from compound **I** $Ca_2(CF_3COO)_4 \cdot 8CF_3COOH$

Compound	$\Delta m_{exper.}$, %	$\Delta m_{theor.}$, %
$Ca_2(CF_3COO)_4 \cdot 8CF_3COOH$	89.26	89.20
CaF_2		

X-ray phase analysis of the decomposition products of the sample $Ca_2(CF_3COO)_4 \cdot 8CF_3COOH$ was performed on the STOE STADI IP device (*Stoe*, Germany) (Ge (111) monochromator, Cu Ka1). In addition, measurement and indexing of radiographs were carried out by the STOE WinXPow and Powder2 software package[1].

[1] STOE WinXPow, Jana, 2006; Powder2, Laboratory of Inorganic Crystallochemistry, MSU by Oleynikov Peter, 1998.

The product of thermal decomposition is a cubic modification of calcium fluoride CaF_2 (a = 5.4626 Å, Z = 4, space group $Fm3m$). The X-ray diffraction pattern is shown in Fig. 2, where the peaks were indicated according to the data of the powder data bank[2] [00-077-2093], with the results of indexing presented in Table 3.

The relatively large half-width of the peaks on the radiograph indirectly indicated the formation of calcium fluoride, characterized by small particle size.

For the X-ray analysis, $Ca_2(CF_3COO)_4 \cdot 8CF_3COOH$ crystals were selected under a layer of vaseline oil in a Meiji Techno EMZ-8TRD polarization microscope (Japan) and were quickly (in less than 1 min) transferred to a diffractometer, where a stream of dry nitrogen gas was used to cool them. The analysis was carried out in an automatic diffractometer, Bruker SMART APEX II, *Bruker AXS GmbH* (Germany) at a temperature of 100K using MoKα radiation (λ = 0.71073 Å, graphite monochromator). Absorption was calculated by measuring the intensities of equivalent reflections [13]. The structures were solved by the direct method and refined by the full-matrix anisotropic least-squares method in F^2 for all non-hydrogen atoms (SHELXTL-Plus [14]). The hydrogen atoms were placed in the calculated positions and refined using the "riding" scheme. The crystallographic data, the experimental details, and the $Ca_2(CF_3COO)_4 \cdot 8CF_3COOH$ structure refinement data are given in Table 4. Tables of atomic coordinates, bond lengths, valence and torsion angles, and anisotropic temperature parameters for the compound **I** are available in the Cambridge Structural Data Bank,[3] with the deposit number CCDC 2081186.

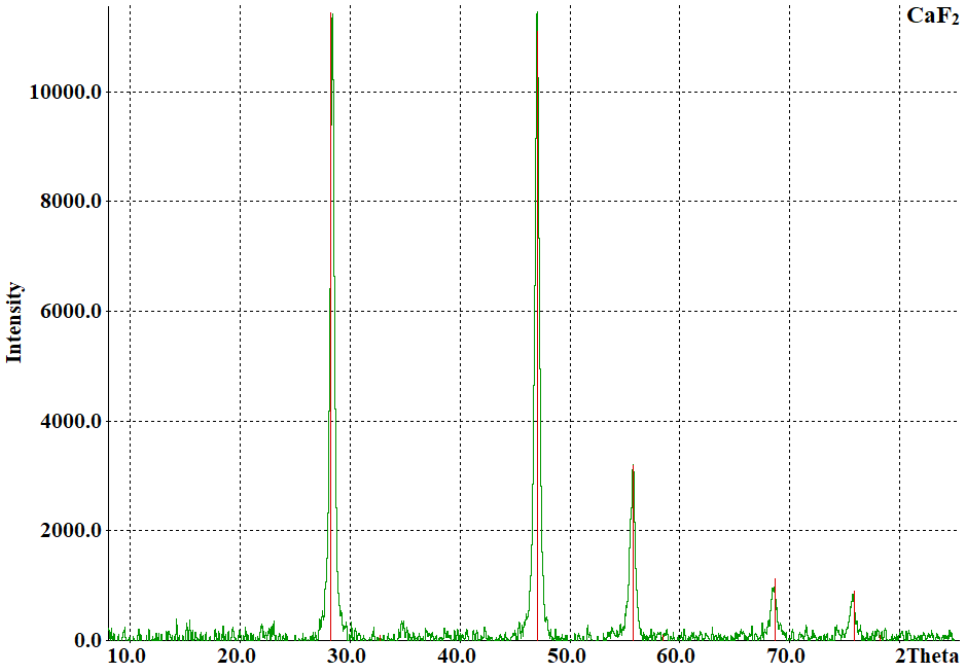

Fig. 2. Radiograph of the decomposition product of compound **I** $Ca_2(CF_3COO)_4 \cdot 8CF_3COOH$. The assignment was made with the powder database [00-077-2093].

Table 3. CaF_2 indexing results

Cubic F-centered cell parameters: a = 5.471(2), Volume = 163.8(2), $F(5)$ = 17.1(0.0488, 6) $M(5)$ = 114.6(4.62, 6)									
No.	**2θ(obs)**	***D*(obs)**	***Q*(obs)**	***I*/*I*o**	***h***	***k***	***l***	***Q*(calc)**	**Δ*Q***
1	28.364	3.1440	1011.66	100	1	1	1	1002.25	9.41
2	46.998	1.9319	2679.36	98	2	2	0	2672.68	6.68
3	55.685	1.6493	3676.21	27	3	1	1	3674.93	1.28
4	68.524	1.3683	5341.18	8	4	0	0	5345.35	−4.17
5	75.708	1.2553	6346.07	6	3	3	1	6347.60	−1.53

[2] ICDD PDF-2 (Database), International Centre for Diffraction Data, Newtown Square, PA, USA. № 00-077-2093.
[3] The Cambridge Crystallographic Data Center, www.ccdc.cam.ac.ukn. Accessed April 30, 2021.

Table 4. Crystallographic data for $Ca_2(CF_3COO)_4 \cdot 8CF_3COOH$

Parameter	Value
Empirical formula	$C_{24}H_8Ca_2F_{36}O_{24}$
Formula weight	1444.46
Crystal size, mm	0.30 × 0.25 × 0.21
Syngonia	Monoclinic
Space group	$P2_1$
a, Å	10.0193(5)
b, Å	15.2612(7)
c, Å	16.3342(8)
α, °	90
β, °	106.106(2)
γ, °	90
V, Å^3	2399.6(2)
Z	2
ρ_{calc}, g/cm^3	1.999
μ(MoKα), mm^{-1}	0.458
F(000)	1416
Interval of θ, °	2.533–25.717
Intervals of indexes	$-12 \le h \le 12$ $-19 \le k \le 17$ $-20 \le l \le 17$
Total reflections	17553
Independent reflections	8795 (R_{int} = 0.1084)
Number of parameters	783
R_1 for $I > 2\sigma(I)$	0.0607
wR_2 (all data)	0.0862
Q factor according to F^2 (GOF)	1.045
$\Delta\rho_{min}/\Delta\rho_{max}$, e/Å^3	−0.500/0.608

RESULTS AND DISCUSSION

The reviewed literature allowed us to establish the relationship between the synthesis conditions (the ratio of solvent and trifluoroacetic acid) and the cation size on the structure of the resulting trifluoroacetate complexes of alkaline-earth metals.

With an excess of a donor solvent, such as water, mononuclear tetraaquacomplexes were formed. Thus, for magnesium, island structures $Mg(CF_3COO)_2 \cdot (H_2O)_4$ were previously obtained, in which the trifluoroacetate anion is a monodentate ligand with a magnesium coordination number (c.n.) of 6 [2].

In the absence of a donor solvent, trifluoroacetic acid exhibited a bridging function. For example, in the presence of tetrahydrofuran (THF), the formation of chain-bounded $Ca_2(CF_3COO)_4 \cdot (THF)_4$ dimers with the help of trifluoroacetate groups (c.n. Ca = 6) [12].

In the absence of trifluoroacetic acid, the trifluoroacetate anion was either a tri- or tetradentate. CF_3-group fluorine atoms can complete the metal environment, shown by the example of crystal structures of polymer trifluoroacetate obtained from calcium ($Ca_3(CF_3COO)_6 \cdot (H_2O)_4$, c.n. Ca = 6) [15] and strontium ($Sr_3(CF_3COO)_6 \cdot (THF)$, c.n. Sr = 8–9) [16].

In the complete absence of a donor solvent, the synthesis between a trifluoroacetic acid and excess alkaline-earth metal carbonates as precursors lead to the formation of strontium trifluoroacetate $Sr(CF_3COO)_2$ and barium $Ba(CF_3COO)_2$, in which the trifluoroacetic acid anion was bridged and tridentate [17].

The synthesis in excess trifluoroacetic acid also lead to the manifestation of bridge functions by the trifluoroacetate anion. The primary factor responsible for forming the crystal structure is the size of the metal ion—the complexing agent. For small-sized ions such as magnesium, infinite chains were obtained $[Md(CF_3COO)_2(CF_3COOH)_2]_n$ [2], c.n. Mg = 6.

In this work, the synthesis was carried out in a trifluoroacetic acid medium that acted as the reagent and solvent, making it possible to stabilize a new structural type of acidic calcium trifluoroacetate $Ca_2(CF_3COO)_4 \cdot 8CF_3COOH$ (c.n. Ca = 8). Dimeric molecules formed the resulting structure, which is island and coordination saturated (c.n. Ca = 8).

Previously, such a method of metal atoms coordination and the type of crystal structure was not described for trifluoroacetate complexes. Of all the known carboxylates, such coordination was represented by a single example of a strontium salt of dimethylbutanoic acid and several rare-earth elements with dimethylbutanoic and pivalic acids [18].

Description of the crystal structure of $Ca_2(CF_3COO)_4 \cdot 8CF_3COOH$

The structure of compound **I** contains two independent crystallographic calcium atoms connected by four trifluoroacetate bidentate groups (Fig. 3). The coordination environment of each calcium atom is formed by four oxygen atoms of the bridge trifluoroacetate groups and four carbonyl oxygen atoms of trifluoroacetic acid molecules, producing a coordination polyhedron in the form of a quadrangular antiprism (Fig. 4). Thus, the structure of compound **I** is constructed from dimers

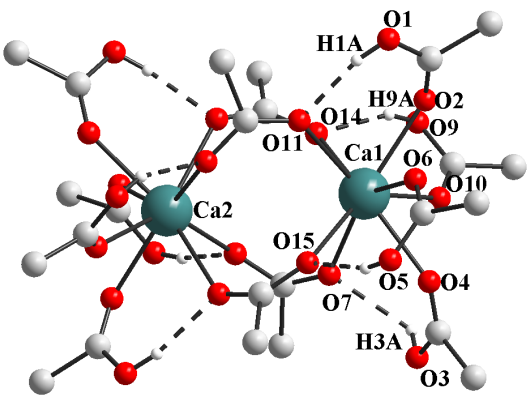

Fig. 3. Fragment of the crystal structure of $Ca_2(CF_3COO)_4 \cdot 8CF_3COOH$.

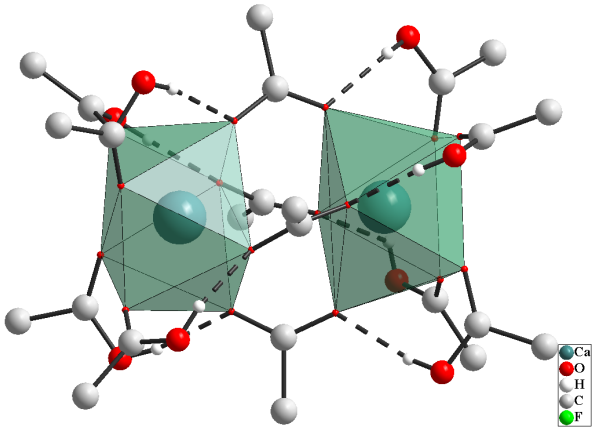

Fig. 4. The surrounding of calcium atoms in the crystal structure of $Ca_2(CF_3COO)_4 \cdot 8CF_3COOH$ is a quadrilateral antiprism.

$Ca_2(CF_3COO)_4 \cdot 8CF_3COOH$. Eight trifluoroacetic acid molecules formed eight intramolecular hydrogen bonds between the hydrogen atoms of the trifluoroacetic acids and the oxygen atoms of the bridged trifluoroacetate groups (Fig. 3).

The molecules in the structure are held together by Van der Waals interactions and are arranged in a staggered order (Fig. 5).

The Ca–O bond lengths and O–Ca–O angles are presented in Table 5. The distances between the calcium and the oxygen atoms of the bidentate trifluoroacetate groups (the average value: 2.456 Å) are less than between the calcium atoms and the carbonyl oxygen atoms of the trifluoroacetic acid molecules (2.462 Å). When the O atoms are oxygen

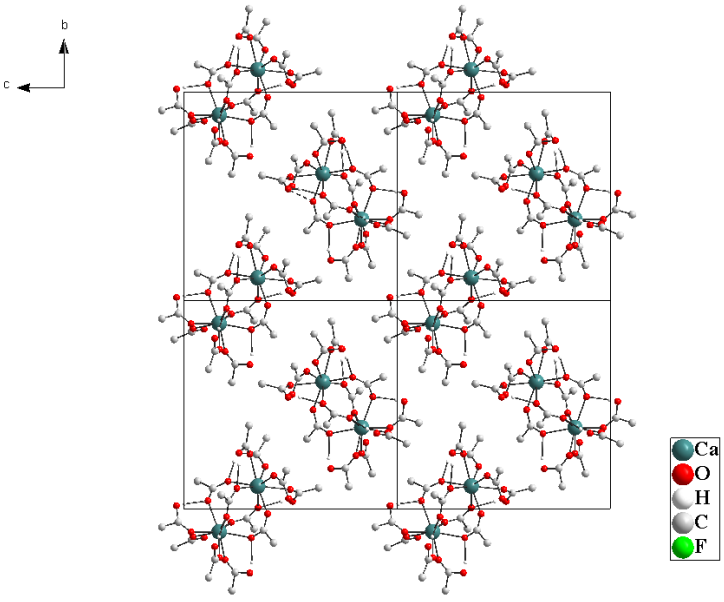

Fig. 5. The arrangement of molecules in the structure of $Ca_2(CF_3COO)_4 \cdot 8CF_3COOH$ along the *a*-axis.

Table 5. The lengths of the Ca–O bonds and O–Ca–O angles in the structure of $Ca_2(CF_3COO)_4 \cdot 8CF_3COOH$

Bond	Length of the bond, Å
$Ca–O14_{CF3COO}$	2.471 (5)
$Ca–O11_{CF3COO}$	2.434 (5)
$Ca–O15_{CF3COO}$	2.466 (5)
$Ca–O17_{CF3COO}$	2.454 (5)
$Ca–O4_{CF3COOH}$	2.448 (5)
$Ca–O6_{CF3COOH}$	2.473 (5)
$Ca–O10_{CF3COOH}$	2.481 (5)
$Ca–O2_{CF3COOH}$	2.447 (5)
Angle	**Value, °**
$O14_{CF3COO}–Ca–O11_{CF3COO}$	76.736 (2)
$O14_{CF3COO}–Ca–O15_{CF3COO}$	78.782 (2)
$O11_{CF3COO}–Ca–O15_{CF3COO}$	125.976 (2)
$O14_{CF3COO}–Ca–O17_{CF3COO}$	123.747 (2)
$O11_{CF3COO}–Ca–O17_{CF3COO}$	78.965 (2)
$O15_{CF3COO}–Ca–O17_{CF3COO}$	76.054 (2)
$O4_{CF3COOH}–Ca–O6_{CF3COOH}$	70.925 (2)
$O4_{CF3COOH}–Ca–O10_{CF3COOH}$	69.345 (2)
$O4_{CF3COOH}–Ca–O2_{CF3COOH}$	110.010 (2)
$O6_{CF3COOH}–Ca–O10_{CF3COOH}$	111.356 (2)
$O6_{CF3COOH}–Ca–O2_{CF3COOH}$	74.716 (2)
$O10_{CF3COOH}–Ca–O2_{CF3COOH}$	69.676 (2)

atoms of trifluoroacetic acid molecules, the O–Ca–O angles are smaller than in the case of oxygen atoms of bidentate trifluoroacetate groups.

Length relations of Ca–O of 0.1–0.2 Å exceeded the length relations of Ca–O in the previously described structures of $Ca_2(CF_3COO)_4 \cdot (TGF)_4$ [12] and $Ca_3(CF_3COO)_6 \cdot (H_2O)_4$ [15], which is associated with an increase in c.n. of calcium from 6 [12, 15] to 8 (compound **I**). This correlates with the interpretation of the absorption bands of the IR spectrum of compound **I**.

CONCLUSIONS

We have obtained a previously unknown calcium complex with trifluoroacetic acid whose composition can be represented as $Ca_2(CF_3COO)_4 \cdot 8CF_3COOH$. The crystal island structure is a dimeric molecule whose calcium atoms are linked in dimers by four trifluoroacetate groups. The complex was characterized by X-ray diffraction and IR spectroscopy. The crystallografic data of the complex was deposited in the Cambridge Structural Data Bank with deposit number CCDC 2081186. Although the compound has a molecular structure, thermal decomposition lead to calcium fluoride formation characterized by a small particle size, which may further determine its application.

Acknowledgments

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Authors' contribution

A.A. Vasilyeva – conducting synthesis, working with literary data, writing the text of the article;

T.Yu. Glazunova – conducting thermal analysis, working with literary data, writing the text of the article;

D.S. Tereshchenko – conducting physicochemical analyses;

E.Kh. Lermontova – X-ray diffraction analysis, solution of the structure.

The authors declare no conflicts of interest.

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