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Preparation, Thermal Behaviour, and Structure of Calcium Trifluoroacetate Monohydrate

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Summary. Calcium trifluoroacetate was prepared as its monohydrate $Ca(CF_3COO)_2 \cdot H_2O$ by reaction of $CaCO_3$ with an aqueous solution of CF_3COOH. It has been established by thermogravimetry and differential thermal analysis that this salt possesses a low thermal stability. When heated in air, decomposition starts already at 106°C, yielding the final product CaF_2. Single crystals of $Ca(CF_3COO)_2 \cdot H_2O$ were obtained and found to be monoclinic (space group $P2_1/n$); unit cell parameters: $a = 9.465(2)$, $b = 9.360(3)$, $c = 16.565(7)$ Å.

Keywords. Calcium trifluoroacetate; Preparation; Structure; Thermal behaviour.

Herstellung, thermisches Verhalten und Struktur von Calciumtrifluoracetat-Hydrat

Zusammenfassung. Calciumtrifluoracetat wurde durch Reaktion von $CaCO_3$ mit einer wäßrigen Lösung von CF_3COOH als sein Monohydrat $Ca(CF_3COO)_2 \cdot H_2O$ erhalten. Thermogravimetrische und differentialthermoanalytische Untersuchungen zeigen, daß dieses Salz eine geringe thermische Beständigkeit besitzt. Bei Erhitzen in Gegenwart von Luft beginnt die Zersetzung des Salzes bereits bei 106°C, wobei das Endprodukt CaF_2 entsteht. Einkristalle von $Ca(CF_3COO)_2 \cdot H_2O$ wurden hergestellt; sie sind monoklin (Raumgruppe $P2_1/n$). Parameter der Elementarzelle: $a = 9.465(2)$, $b = 9.360(3)$, $c = 16.565(7)$ Å.

Introduction

Among the salts of carboxylic acids, metal trifluoroacetates belong to those which have been relatively less studied. *Swarts* [1] has first reported data on the synthesis and some properties of the trifluoroacetates of Cu, Ag, Hg, Ba, and Pb. More recently, such data have been published on the salts of the trifluoroacetic acid with alkali metals [2–4], metals of groups IIA [3, 5–7], IVA and IVB [8, 9], VIA [10, 11], and VIIIA [6, 10, 12, 13] as well as with yttrium, lanthanum and some

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lanthanides [14–18], manganese [10], zinc [6, 10], aluminum [5], and bismuth [19].

There are not data on the crystal structures of metal trifluoroacetates, and data concerning their thermal behaviour are available only for a restricted number [4, 10, 17, 18]. However, these data are very important due to the application of trifluoroacetates as precursors for the preparation of thin layers of complex oxides and, in particular, of thin films of high-temperature superconductors obtained by chemical methods [14]. The method most frequently used is the pyrolysis of unsubstituted metal carboxylates deposited on a substrate by spray-, dip-, or spin-coating. In this case, the pyrolysis results in the formation of films with a rather broad transition to the superconducting state due to the reactivity of the intermediate alkaline earth oxides participating in the composition of all high-temperature oxide superconductors and to carbon contamination during the decomposition of these carboxylates. On the other hand, it has been shown that fluorine gas treatment prevents atmospheric degradation and improves the properties of oxide superconductors [20]. On this basis it can be assumed that better pyrolytic films might be obtained from precursors yielding the corresponding metal fluorides upon decomposition. As has been shown by *Gupta et al.*, the salts of trifluoracetic acid can be used as precursors of that kind [21].

The present work reports data on the synthesis of the crystalline hydrate of $Ca(CF_3COO)_2$, its composition, behaviour during heating, and structure.

Results and Discussion

Chemical and thermal analyses

The scarce data available present no definite opinion on the composition of the hydrate of calcium trifluoroacetate which crystallizes from aqueous solutions. According to Ref. [3], it has the formula $Ca(CF_3COO)_2 \cdot 4H_2O$, whereas others [7] are of the opinion that the dihydrate $Ca(CF_3COO)_2 \cdot 2H_2O$ is obtained after recrystallization from an acid aqueous solution. This discrepancy may be due both to differences in the synthetic methods and to the considerable hygroscopicity of the salt.

The calcium content in the salt obtained in this study was determined gravimetrically by a method employing precipitation of the calcium as oxalate ($CaC_2O_4 \cdot H_2O$) from a hydrochloric acid solution followed by calcination of the precipitate and weighing as CaO [22]. The results from the determinations showed a 14.11% (w/w) mean calcium content in the product. This agrees exactly with the theoretical calcium content in calcium trifluoroacetate monohydrate, $Ca(CF_3COO)_2 \cdot H_2O$.

The *Karl Fischer* method [23] has been used to determine the total amount of water in the salt. The value obtained (7.6%) exceeds the theoretical amount of constitution water in the monohydrate (6.34%), but is close to it. The theoretical water content, say, for a dihydrate, should be 11.92%, and for a tetrahydrate 21.31%. The enhanced water content with respect to the theoretical one for a monohydrate is probably due to some water absorbed by the hygroscopic product during the preparation for analysis.

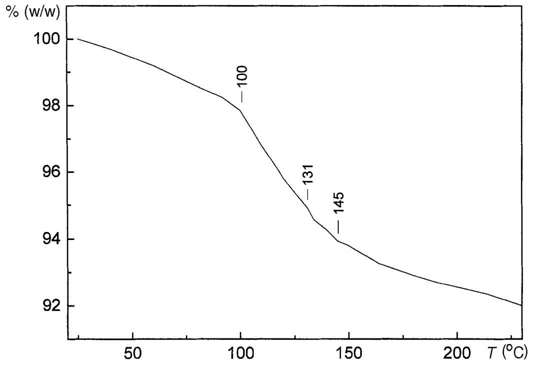

Fig. 1. TG curve of $Ca(CF_3COO)_2 \cdot H_2O$ obtained with a heating rate of 2°C/min up to a temperature of 230°C

The behaviour of the calcium trifluoroacetate during heating was determined by thermogravimetry (TG) and differential thermal analysis (DTA). With respect to a more detailed study of the dehydration process of $Ca(CF_3COO)_2 \cdot H_2O$, its TG curve was registered up to 230°C at a heating rate of 2°C/min (Fig. 1). Weight loss starts at relatively low temperatures. This is probably associated with the desorption of physically absorbed moisture. An evidence in this respect is the endothermic effect at 106°C on the DTA curve (Fig. 2). The smooth shape of the TG curve indicates that the crystallization water evolves in a single stage, in contrast to the case of some rare earth trifluoroacetates. Obviously, at a low heating rate the dehydration process, which, according to the weight loss should have ended at about 145°C, passes quickly to a decomposition process of the salt as indicated by the absence of a characteristic plateau on the TG curve. This plateau is formed when the heating proceeds at a higher rate (*e.g.* 5°C/min), as is demonstrated by the TG curve in Fig. 2 registered up to a maximum temperature of 1000°C. This curve and the DTA curve in Fig. 2 demonstrate that the major part of the anhydrous salt decomposes at 266–305°C.

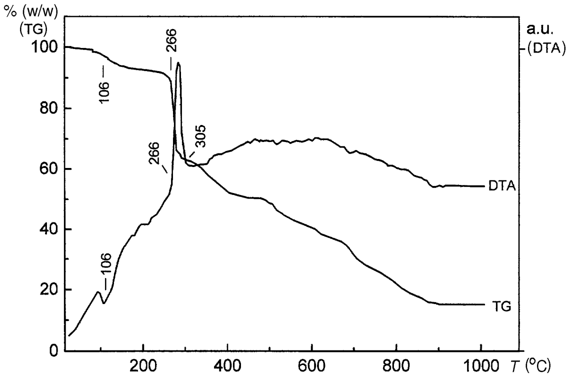

Fig. 2. DTA and TG curves of $Ca(CF_3COO)_2 \cdot H_2O$ obtained with a heating rate of 5°C/min up to a temperature of 1000°C

The final decomposition product of calcium trifluoroacetate is CaF_2. This is established from the X-ray data on the products in all cases of prolonged isothermal heating of $Ca(CF_3COO)_2 \cdot H_2O$ up to a temperature of 1000°C.

Single crystal analysis

The analysis revealed that the structure of $Ca(CF_3COO)_2 \cdot H_2O$ consists of layers parallel to the (101) diagonal, in which the cations are perfectly coplanar (Fig. 3) and are bonded by the carboxyl groups of the trifluoroacetate (*TFA*) anions which are directed inwards. The trifluoromethyl groups are directed outwards and establish *Van der Waals* contacts only with the next layer. Within the layer, the cations are bonded in centrosymmetric trimers through two bridging O atoms from the two *TFA*1 anions and four bridging carboxyl groups from two *TFA*2 and two *TFA*3 anions (Fig. 4). The trimers are further bonded by the second O atom from the *TFA*1 anions to the terminal Ca atoms from neighbouring trimers. The central Ca1 atom is coordinated to six carboxyl O atoms from six *TFA* anions, and the terminal Ca2 atom is bonded to four carboxyl O atoms and two water O atoms. The coordination bonds to the central Ca atom are slightly shorter than those to the terminal cations (Table 1).

The bridging O12 atom from the *TFA*1 ion forms the longest bonds (2.421(4) and 2.463(4) Å) to the Ca1 and Ca2 atoms, respectively. Both

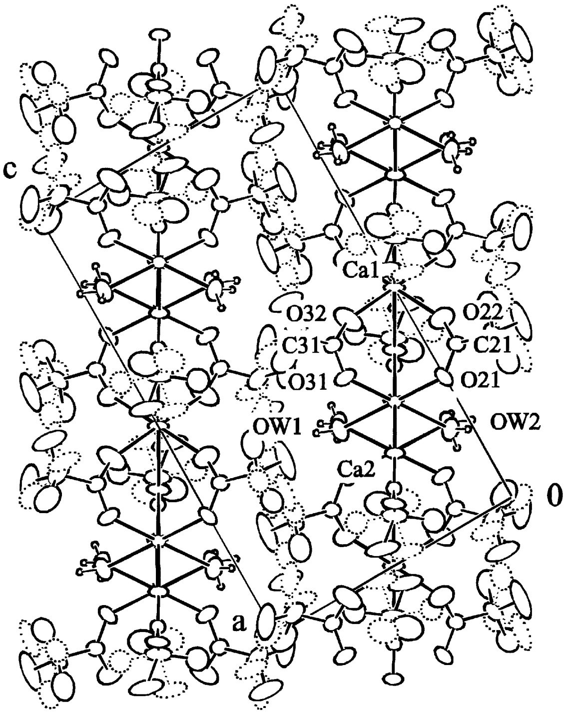

Fig. 3. Projection of the structure of $Ca(CF_3COO)_2 \cdot H_2O$ along the *b*-axis including the atom numbering scheme; 30% probability thermal displacement ellipsoids; H atoms are arbitrarily reduced; the fluorine positions of less occupation levels are shown by dotted lines

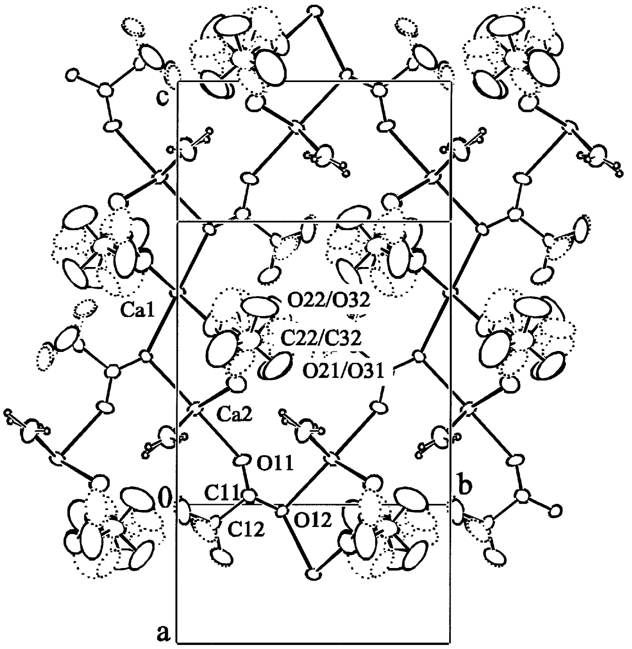

Fig. 4. A view of the layer in the structure of $Ca(CF_3COO)_2 \cdot H_2O$; 30% probability thermal displacement ellipsoids; H atoms are arbitrarily reduced; the fluorine positions of less occupation levels are shown by dotted lines

coordination octahedra around the Ca1 and Ca2 atoms are significantly distorted, with O-Ca-O angular variations of 78.7(2) – 101.3(2) and 78.2(2) – 110.2(2)°, respectively. The two water molecules are *cis*-positioned at 2.335(4) and 2.375(5) Å. The bond lengths and angles in the *TFA* anions have typical values which have been found earlier in potassium and cesium hydrogen ditrifluoroacetate [24], ammonium trifluoroacetate [25], and carboxylate anions [26]. The trifluoromethyl groups in all anions are positionally disordered and occupy two positions with different occupancy factors. The two positions for the *TFA*1 group are located at 0.464 and 0.536 levels, those for the *TFA*2 group at 0.685 and 0.315 levels, and those for the *TFA*3 group at 0.698 and 0.302 levels. The observed disorder results from the outward disposition of the trifluoromethyl groups with respect to the layers and the weak interactions they are involved in. The water hydrogen atoms take part in intra- and interlayer H-bonding to carboxyl oxygen and fluorine atoms. The candidates for such H-bonds are summarized in Table 2.

Experimental

Calcium trifluoroacetate synthesis and single crystal preparation

The educts used were $CaCO_3$ (Merck, 99%) and CF_3COOH (Aldrich, 99%). The salt was prepared by adding an excess of $CaCO_3$ to a 50% aqueous solution of CF_3COOH, followed by heating to the boiling point, standing for 2 h, and filtering off the excess of carbonate. After slow evaporation on a water bath, upon cooling and standing, the solution gave crystals of calcium trifluoroacetate. The crystals were separated by filtration and dried first in air at room temperature and then at 100–105°C

Table 1. Selected interatomic distances (Å) and angles (°); estimated standard deviations in parentheses

CaO$_6$ groups			
Ca1–O12	2.421(4)×2	Ca2–OW1	2.335(3)
Ca1–O22	2.293(6)×2	Ca2–OW2	2.335(4)
Ca1–O32	2.277(6)×2	Ca2–O11	2.377(4)
		Ca2–O12	2.463(4)^{1}
		Ca2–O21	2.378(5)
		Ca2–O31	2.375(5)
O32^{11}–Ca1–O22^{11}	90.5(2)	OW2–Ca2–OW1	110.20(15)
O32–Ca1–O22^{11}	89.5(2)	OW2–Ca2–O31	167.02(16)
O32^{11}–Ca1–O22	89.5(2)	OW1–Ca2–O31	78.17(16)
O32–Ca1–O22	90.5(2)	OW2–Ca2–O11	88.34(15)
O32^{11}–Ca1–O12^{111}	78.72(19)	OW1–Ca2–O11	88.16(15)
O32–Ca1–O12^{111}	101.28(19)	O31–Ca2–O11	81.90(18)
O22^{11}–Ca1–O12^{111}	79.23(18)	OW2–Ca2–O21	78.07(15)
O22–Ca1–O12^{111}	100.77(18)	OW1–Ca2–O21	166.95(16)
O32^{11}–Ca1–O12^{1}	101.28(19)	O31–Ca2–O21	92.02(18)
O32–Ca1–O12^{1}	78.72(19)	O11–Ca2–O21	81.89(18)
O22^{11}–Ca1–O12^{1}	100.77(18)	OW2–Ca2–O12^{1}	91.28(15)
O22–Ca1–O12^{1}	79.23(18)	OW1–Ca2–O12^{1}	91.09(15)
		O31–Ca2–O12^{1}	98.61(17)
		O11–Ca2–O12^{1}	178.99(15)
		O21–Ca2–O12^{1}	98.95(17)
Trifluoroacetate anions			
O11–C11	1.235(7)	O11–C11–O12	126.1(6)
O12–C11	1.243(7)	O11–C11–C12	116.9(6)
O21–C21	1.242(7)	O12–C11–O12	116.9(6)
O22–C21	1.207(8)	O22–C21–C21	128.1(7)
O31–C31	1.221(7)	O22–C21–C22	115.5(7)
O32–C31	1.205(8)	O21–C21–O22	116.4(7)
C11–C12	1.517(9)	O32–C31–C31	127.2(8)
C21–C22	1.511(11)	O32–C31–C32	115.7(8)
C31–C32	1.504(13)	O31–C31–C32	117.2(8)
C12–F11	1.23(2)	C12–F11′	1.298(18)
C12–F12	1.25(3)	C12–F12′	1.332(19)
C12–F13	1.404(14)	C12–F13′	1.382(13)
C22–F21	1.361(14)	C22–F21′	1.18(3)
C22–F22	1.272(13)	C22–F22′	1.32(3)
C22–F23	1.357(13)	C22–F23′	1.27(2)
C32–F31	1.355(14)	C32–F31′	1.18(3)
C32–F32	1.346(15)	C32–F32′	1.42(3)
C32–F33	1.234(13)	C32–F33′	1.32(3)

Table 2. Proposed hydrogen bonding geometry

D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (°)
OW1–HW11···F22$^{\mathrm{IV}}$	0.87	2.28	3.009(10)	140.9
OW1–HW11···F32$^{\mathrm{V}}$	0.87	2.61	3.06(2)	113.2
OW1–HW12···O21$^{\mathrm{I}}$	0.73	2.10	2.815(6)	163.6
OW2–HW21···F33$^{\mathrm{VI}}$	0.82	2.52	3.326(11)	170.2
OW2–HW22···O31$^{\mathrm{I}}$	1.02	1.91	2.846(6)	151.3
OW2–HW22···F31$^{\mathrm{I}}$	1.02	2.29	3.045(9)	130.3

Table 3. Crystal data and experimental parameters

Chemical formula	$C_{12}H_8Ca_3F_{18}O_{16}$
Formula weight	870.39
Crystal system	Monoclinic
Space group	$P2_1/n$
Z	2
a (Å)	9.465(2)
b (Å)	9.360(3)
c (Å)	16.565(7)
β (°)	90.79(3)
V (Å^3)	1467.4(8)
Temperature (K)	292
F(000)	430
Calculated density (g · cm^{-3})	1.970
Dimensions (mm)	0.40×0.20×0.13
Absorption coefficient (cm^{-1})	0.744
MoKα wavelength (Å)	0.71073
Monochromator	Graphite
Scan mode	ω scan
Scan width (°)	$0.80+0.40\tan\theta$
Number/frequency of standards	3/120
Data collection limits (°)	$0<\theta<28$, h, $\pm k$, $\pm l$ (12, 12, 21)
Total number of reflections	7433
Independent reflections	2627
$I>2\sigma(I)$	1042
Refinement	F_o^2
Weighting scheme	$1/(\sigma^2(F_o^2) + (0.0558P)^2), P = (F_o^2 + 2F_c^2)/3$
Hydrogen treatment	Located and refined with fixed $U=0.05$ Å^2
Extinction expression	$F_{c,corr} = kF_c(1 + 0.001 \times F_c^2 \backslash \lambda^3/\sin(2\theta))^{-1/4}$
Extinction coefficient	0.0001(10)
Least-squares parameters	254
R	0.0605
R_W	0.1311
Goodness of fit	0.873
Δ/ρ	0.002
$\Delta\rho_{max}$ (e · Å^{-3})	0.409

for 4 h. The dried hygroscopic, salt was transferred to a desiccator over freshly dried silicagel immediately after drying.

In order to determine the structure of $Ca(CF_3COO)_2 \cdot H_2O$, experiments aimed at obtaining appropriate single crystals by spontaneous crystallization from saturated solutions in water, methanol, and a 1:1 water-methanol mixture were performed at 25°C. It was established that crystals with appropriate sizes can be obtained from a water/methanol mixture only.

Thermogravimetry and differential thermal analysis

The thermal behaviour of the calcium trifluoroacetate was determined using a MOM Derivatograph (system Paulik-Paulik-Erdey). The measurements were performed in air on samples with an initial weight of about 160 mg.

Table 4. Fractional atomic coordinates and equivalent isotropic thermal displacement parameters for the non-hydrogen atoms

	x	y	z	U_{eq}
Ca1	0.0000	0.0000	0.5000	0.0408(6)
Ca2	0.20377(14)	0.06602(15)	0.29361(8)	0.0347(4)
O11	0.2947(5)	0.2381(5)	0.2025(3)	0.0433(12)
O12	0.3881(5)	0.3844(5)	0.1132(3)	0.0459(13)
O21	0.0026(5)	0.2180(5)	0.2863(3)	0.0545(14)
O22	−0.0962(7)	0.1267(6)	0.3943(3)	0.085(2)
O31	0.3177(6)	0.2165(6)	0.3898(3)	0.0619(16)
O32	0.2041(7)	0.1276(6)	0.4912(4)	0.100(2)
C11	0.3602(7)	0.2639(7)	0.1401(4)	0.0337(15)
C12	0.4066(11)	0.1366(9)	0.0904(5)	0.067(3)
F11	0.432(2)	0.024(2)	0.1259(17)	0.109(6)
F12	0.505(3)	0.164(3)	0.0430(11)	0.114(7)
F13	0.2926(14)	0.0970(15)	0.0402(8)	0.097(3)
F11′	0.3478(16)	0.0147(18)	0.1061(14)	0.109(6)
F12′	0.432(2)	0.163(3)	0.0130(9)	0.114(7)
F13′	0.5415(12)	0.1040(13)	0.1175(7)	0.097(3)
C21	−0.0964(7)	0.1974(8)	0.3333(4)	0.0427(18)
C22	−0.2346(9)	0.2700(12)	0.3123(6)	0.071(3)
F21	−0.2291(13)	0.3563(16)	0.2463(7)	0.129(5)
F22	−0.3428(10)	0.1901(12)	0.3056(11)	0.143(6)
F23	−0.2663(9)	0.3723(12)	0.3673(6)	0.114(4)
F21′	−0.223(3)	0.393(4)	0.2958(17)	0.129(5)
F22′	−0.286(2)	0.207(3)	0.247(2)	0.143(6)
F23′	−0.323(3)	0.252(3)	0.3679(14)	0.114(4)
C31	0.2987(8)	0.1948(8)	0.4615(4)	0.0451(19)
C32	0.4031(14)	0.2598(14)	0.5201(7)	0.095(4)
F31	0.4797(11)	0.3661(11)	0.4865(5)	0.129(4)
F32	0.5064(15)	0.1638(14)	0.5344(8)	0.157(5)
F33	0.3701(14)	0.3008(17)	0.5881(6)	0.174(6)
F31′	0.523(4)	0.234(4)	0.5082(17)	0.129(4)
F32′	0.354(3)	0.180(3)	0.5869(18)	0.157(5)
F33′	0.361(4)	0.392(3)	0.5351(12)	0.174(6)
OW1	0.4295(3)	−0.0342(4)	0.3013(2)	0.0629(16)
OW2	0.0762(3)	−0.0331(4)	0.1857(2)	0.0611(15)

Single crystal analysis

A prismatic colourless crystal of $Ca(CF_3COO)_2 \cdot H_2O$ was sealed in a thin glass capillary and mounted on an Enraf-Nonius CAD-4 single-crystal diffractometer [27, 28]. After cell parameters refinement using the diffractometer angles of 22 reflections at a θ range between 20 and 22°, intensity data were collected and processed in a standard manner. Crystal data and experimental details are summarized in Table 3. The data set was corrected for *Lorentz*, polarization, and extinction effects, but not for absorption because of the small dimensions of the measured crystal. The structure was solved by direct methods [29, 30] and difference *Fourier* synthesis[1]. Atomic fractional coordinates and isotropic thermal parameters with their estimated standard uncertainties are listed in Table 4, selected bond lengths and angles are given in Table 1. The atom numbering scheme is shown on Figures 3 and 4.

Acknowledgements

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