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Short communication

A one-dimensional coordination polymer formed by a 2:1 adduct of trifluoroacetic acid and its sodium salt

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ABSTRACT

The crystal structure of the 2:1 adduct of trifluoroacetic acid and its sodium salt has been determined and its bond situation is compared to earlier descriptions based on IR spectroscopy and dissociation pressure measurements.

1. Introduction

Trifluoroacetic acid is a reagent frequently used in organic synthesis because of a combination of convenient properties: volatility, solubility in organic solvents, and its acidity. Moreover it is widely used as a solvent for proteins in biotechnology [1]. The treatment and disposal of such solutions can be an issue under environmental aspects. Apart from distillation to recycle the acid, neutralization with bases – usually basic alkali metal salts – is the frequent procedure. Surprisingly, the knowledge concerning these salts is limited especially with respect to structural aspects. Crystal structures of simple binary alkali metal trifluoroacetates are only known for potassium, rubidium and cesium [2,3]. For all these structures one-dimensional coordination polymers are found which are formed by attractive interaction between the metal cations and the oxygen atoms of the acetate units. However, similar structures involving sodium have not been described so far. By contrast, adducts of trifluoroacetic acid (TFA) and its corresponding sodium salt have already been proposed in 1954 by Klemperer and Pimentel based on IR spectroscopy and dissociation pressure measurements [4]. Although sodium trifluoroacetate is widely used in trifluoromethylation reactions in organic synthesis, no further evidence for this adduct has been established so far [5,6]. Our own interest concerning sodium trifluoroacetate and its solutions in trifluoroacetic acid has been triggered by the advantageous properties of such solutions to effect condensation reactions of suitable silanols to silsesquioxanes [7]. The 2:1 adduct of trifluoroacetic acid with sodium trifluoroacetate **1** was been frequently obtained in our investigations when mixtures with TFA where neutralized in the presence of sodium cations.

2. Results and discussion

By reacting sodium hydride and anhydrous trifluoroacetic acid in the absence of organic solvents, we were able to selectively prepare the title compound (**1**). The exothermic character of the reaction requires efficient cooling with ice during the addition of NaH. We have been able to isolate crystals of **1** which were suitable for X-ray purposes (Table 1). The crystal structure proved the composition as the 2:1 adduct of trifluoroacetic acid and sodium trifluoroacetate. The asymmetric unit contains two molecules of TFA which are connected to the trifluoroacetate anion via hydrogen bonds. Furthermore, the sodium cation coordinates to one oxygen atom of the anion as well as to the carbonyl oxygen of an acid molecule. The bond lengths of the C–O distances reflect the increase of the bond order in the sequence C–OH [1.283(4)Å, 1.291(4)Å], COO^-[1.241(4)Å, 1.246(4)Å], and C=O [1.213(4)Å, 1.214(4)Å], respectively. Regarding the packing within the tetragonal crystals two rows parallel to the *c*-axis are present with sodium ions winding around the fourfold 4_1 screw axis (Na–Na′ 4.003(2)Å, Na–Na′–Na″ 173.20(4)°). In the structure trifluoroacetic acid and its corresponding anion are helically wound around columns of the sodium cations resulting in the formation of a one-dimensional coordination polymer along the *c*-axis (Figs. 1 and 2). Helices of opposite chirality are connected by an inversion center resulting in total in an achiral assembly. In each formula unit two coordinative bonds of the

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Table 1
Summary for the crystal structure determination of **1**.

Empirical formula	$C_6H_2F_9NaO_6$
Formula weight	364.07
Crystal description	block, colourless
Crystal size [mm]	0.40 × 0.20 × 0.20
Temperature [K]	95(2)
Wavelength [Å]	Mo Kα, 0.71069
Monochromator	Graphite
Diffractometer	Stoe
Crystal system, space group	Tetragonal, $I\,4_1/a$
Unit cell dimensions	
$A = b$ [Å]	17.400(3)
C [Å]	15.957(3)
$\alpha = \beta = \gamma$ [deg]	90
Volume [$Å^3$]	4831.1(15)
Z	16
Calculated density [mg/m^3]	2.002
$F(0\,0\,0)$	2848
Linear absorption coefficient μ [mm^{-1}]	0.280
Theta range for data collection [°]	2.34–26.00
Index ranges	$0 \le h \le 21$, $-1 \le k \le 21$, $-1 \le l \le 19$
Reflections collected/unique	2967/2368
Significant unique reflections	1870 with $I > 2\sigma(I)$
R(int), R(sigma)	0.0301, 0.0504
Completeness to theta	100%
Refinement method	Full-matrix least-squares on F^2
Data/parameter/restraints	2368/203/0
Goodness-of-fit on F^2	1.053
Absorption correction	Empirical
Final R indices [$I > 2\text{sigma}(I)$]	$R1 = 0.0622$, $wR2 = 0.1467$
R indices (all data)	$R1 = 0.0787$, $wR2 = 0.1585$
Largest diff. peak and hole [$e/Å^3$]	0.710 and −0.505 $e/Å^3$

Table 2
IR data of **1** (KBr pellets). Values are given in cm^{-1}.

Assignment	(**1**)	Ref. [3]
$\nu_{(O–H)}$	2850 (w)	2910
$\nu_{(O–H)}$	2733 (ms)	2760
$\nu_{(O–H)}$	2588 (ms),	2430
$\nu_{(O–H)}$	1980 (w, b)	1900
$\nu_{(C=O)\ \text{acid}}$	1776 (s),	1780
$\nu_{(C=O)\ \text{acetate}}$	1686 (s),	1625

trifluoroacetic acid and its corresponding anion are provided towards the sodium ions resulting in an effective coordination number of six for the sodium (Na^+–O of 2.400(3) Å and 2.421(3) Å to the anions and 2.487(3) Å to 2.582(3) Å to the O atoms of the C=O groups of the acid molecules). The hydrogen bonding in this adduct has been described earlier based on infrared spectroscopy. The absence of OH stretching frequencies at about 3500 cm^{-1} led the authors to the assumption that the OH-group of the acid group is interacting through hydrogen bonding with the acetate carbonyl functionality, which is now confirmed by us based on structural data. Furthermore the presence of two C=O stretching modes with frequencies at 1780 and 1625 cm^{-1} is consistent with the proposed structure. Our own IR measurements (see Table 2) of crystalline **1** are in good agreement with the data in the literature, although there are slight deviations which may originate from different sample handling. Based on the structural parameters, i.e. the D···A distances of 2.575(3) and 2.549(3) Å and the DHA angles of 173.9° and 178.0°, these hydrogen bonds qualify for a classification just at the border between strong and medium strong hydrogen bonds [8]. On the other hand, the bathochromic shift of the OH-stretching vibration to about 2500 cm^{-1} in the adduct compared to 3500 cm^{-1} for "free" trifluoroacetic acid in the gas phase clearly indicates the presence of strong hydrogen bonds according to the categories established by Steiner [8].

It seems unlikely that the structure observed for the solid state is retained in solution. In agreement with this assumption the ^{19}F-NMR spectra show only a single signal at −65 ppm in chloroform solution at room temperature. The equivalence of trifluoroacetic acid with its conjugated base is due to proton exchange, which is fast on the NMR timescale under these conditions.

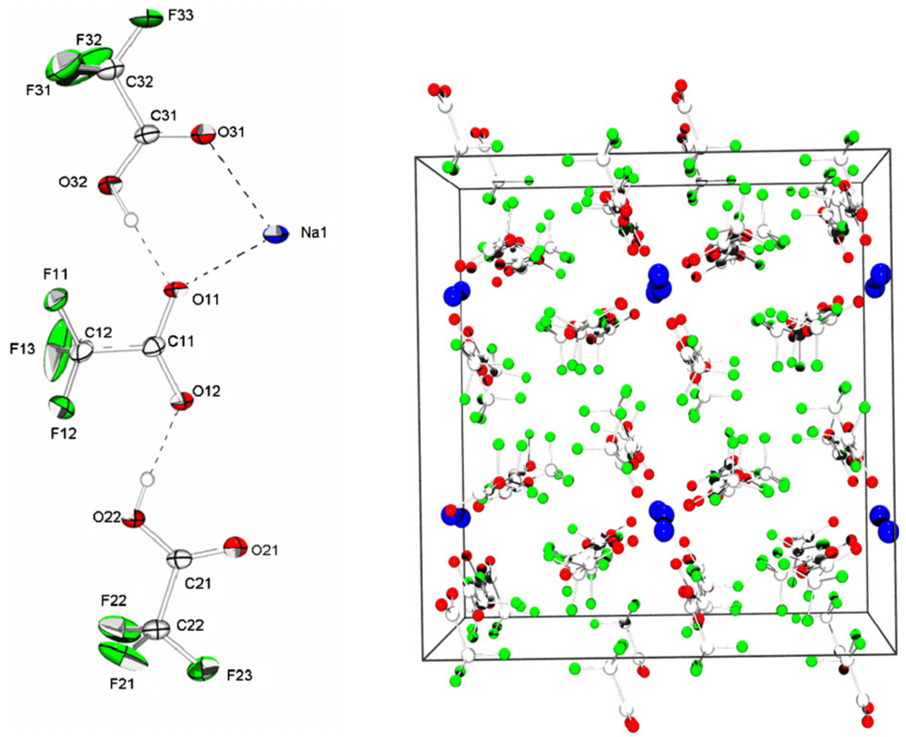

Fig. 1. Left: ORTEP plot of the asymmetric unit of **1** showing the atomic numbering scheme. The probability ellipsoids are drawn at 50% probability level. The hydrogen bonds and the coordinative bonds towards the Na^+ cation are drawn with dotted lines. Right: ORTEP plot of the packing of **1** viewed along the c-axis. The atoms are drawn with arbitrary radii.

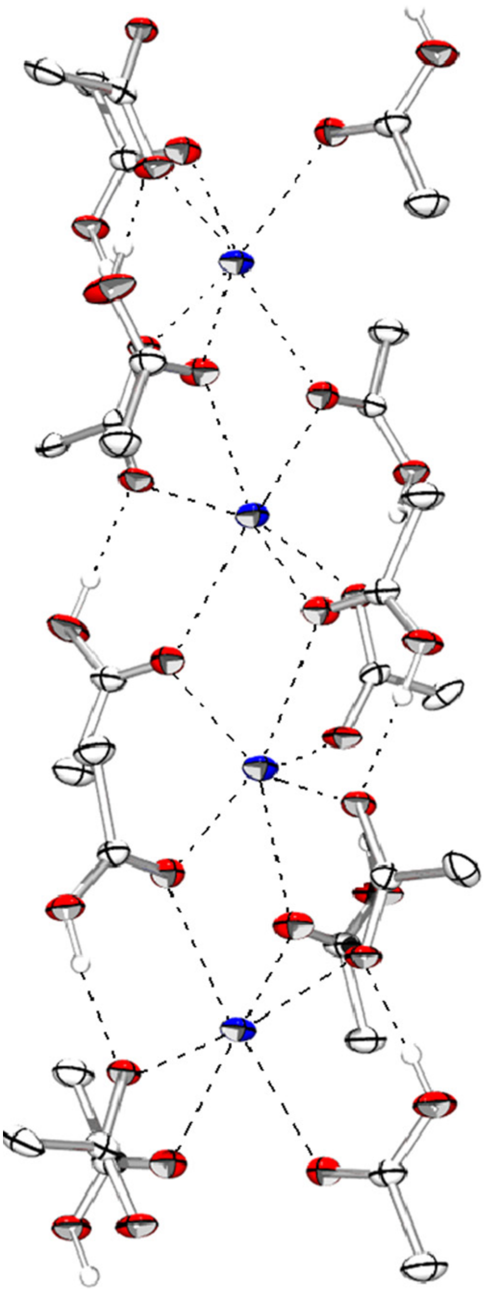

Fig. 2. ORTEP plot of the arrangement in which trifluoroacetic acid and trifluoroacetate wind around rows of Na^+ cations. The probability ellipsoids are drawn at 50% probability level. For clarity reasons all fluorine atoms are omitted.

In summary, we have been able to characterize the 2:1 adduct of trifluoroacetic acid and its sodium salt structurally by X-ray diffraction. The hydrogen bonding mode which had been proposed earlier based on IR measurements has been supported by our findings. Moreover, an unusual one-dimensional coordination polymer with an orientation along columns of sodium cations has been established based on X-ray crystallography. The title compound seems to play a promising yet unclear role in the transformation of silanetriols to silsesquioxanes [7].

3. Experimental section

3.1. General

Sodium hydride and trifluoroacetic acid were purchased from Fluka and used without further purification ^{19}F-NMR spectra are recorded on a Bruker 500 spectrometer at a frequency of 470.740 MHz. Chemical shift values are given in ppm and are referenced to external standards. IR-measurements were performed using KBr discs and values are given in cm^{-1}.

3.2. Preparation of **1**

In a dry argon atmosphere 0.201 g NaH (8.34 mmol) are treated slowly with an excess of anhydrous trifluoroacetic acid in the absence of any organic solvent under ice cooling. The resulting solution is allowed to stand for several days after which crystals of **1** precipitate. The crystals soften at 65 °C and decompose under evaporation of TFA at higher temperatures. ^{19}F-NMR($CDCl_3$): −65 (s). IR (KBr disc): 2850 (w), 2733 (w), 2588 (ms), 1980 (w, b), 1776 (s), 1686 (s), 1434 (w), 1202 (s), 1138 (s), 841 (w), 805 (w), 783 (w), 707 (w).

3.2.1. X-ray diffraction data of **1**

All the measurements were performed using graphite-monochromatized Mo Kα radiation at 95 K: $F_3C{-}COONa\cdot 2F_3C{-}COOH$, M_r 364.07, tetragonal, space group I $4_1/a$, $a = 17.400(3)$ Å, $c = 15.957(3)$ Å, $V = 4831.1(15)$ Å^3, $Z = 16$, $d_{calc} = 2.002$ g cm^{-3}, $\mu = 0.280$ mm^{-1}. A total of 2967 reflections were collected ($\Theta_{max} = 26.0°$), from which 2368 were unique ($R_{int} = 0.0301$), with 1870 having $I > 2\sigma(I)$. The structure was solved by direct methods (SHELXS-97) [9] and refined by full-matrix least-squares techniques against F^2 (SHELXL-97) [10]. The non-hydrogen atoms were refined with anisotropic displacement parameters without any constraints. The H atoms were refined with tetrahedral C–O–H angles, enabling rotation around the C–O bond, O–H distances of 0.84 Å, and with individual isotropic displacement parameters. Some of the fluorine atoms show unexpectedly large displacement parameters, but attempts of splitting the fluorine positions as suggested by the program SHELXL-97 did not improve the refinement. Absorption correction was done using XABS2 [11]. For 203 parameters final R indices of $R1 = 0.0622$ and $wR2 = 0.1585$ (GOF = 1.053) were obtained. The largest peak in a difference Fourier map was 0.710e Å^{-3}.

4. Supplementary information

Crystallographic data for the structure of **1** have been deposited with the Cambridge Crystallographic Data Centre. The CCDC reference number is 703478. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: int.code_(1223) 336-033 e-mail for inquiry: fileserv@ccdc.cam.ac.uk

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