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In situ crystallization of the tetrahydrate of pentafluoro-benzenesulfonic acid, featuring the *Eigen* ion $(H_9O_4)^+$

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Abstract: The tetra-hydrate of pentafluorobenzene sulfonic acid has been crystallized using an *in situ* technique on a single crystal diffractometer ($P\bar{1}$, $Z = 2$, $a = 705.65(3)$ pm, $b = 761.62(3)$ pm, $c = 1{,}132.34(4)$ pm, $\alpha = 91.492(2)°$, $\beta = 102.974(2)°$, $\gamma = 90.718(2)°$). It turns out that the compound has to be described according to $(H_9O_4)[C_6F_5SO_3]$. It contains the so-called *Eigen* ion which is a combination of a central H_3O^+ and three H_2O molecules attached by hydrogen bonds.

Keywords: fluorobenzene sulfonic acid; *in situ* crystallization; *Eigen* cation; crystal structure; hydrogen bonding

1 Introduction

Benzenesulfonic acid is a well-known derivative of both, benzene and sulfuric acid. Its preparation by aromatic sulfonation represents one of the classical electrophilic substitution reactions and is of considerable importance in industrial chemistry, where sulfonic acids and their salts serve as intermediates for detergents, dyes, and ion exchange resins.[1–4] Further sulfonation to form polysulfonic acids is possible but more difficult because the $[SO_3H]$ group is an electron-withdrawing substituent, exerting both inductive (–I) and mesomeric (–M) effects that reduce the electron density of the aromatic ring. As we have shown, various benzene polysulfuric acids can nevertheless be prepared, but preferably not by electrophilic substitution at the phenyl ring.[5] Similarly, the sulfonation of pentafluorobenzene, C_6F_5H, is hindered by the electron withdrawing presence of the fluorine atoms. According to the early literature, sulfonation of C_6F_5H is possible within 48 hours using oleum containing 20 % of SO_3.[6] Later, *Sartori* et al. described a faster synthesis applying neat SO_3 at a temperature of 100 °C.[7] This group also conducted experiments to determine the acidity of the acid.[8] To date, neither pentfluorobenzenesulfonic acid, $C_6H_5(SO_3H)$, nor any of its hydrates have been structurally described. For the monohydrate, $C_6H_5(SO_3H)\cdot H_2O$, a melting point of 101 °C has been reported, making it likely that the compound is an oxonium salt according to $(H_3O)[C_6F_5(SO_3)]$.[7] The acid and some of its salts have been used occasionally in catalytic reactions,[9] and the lithium salt was considered as an electrolyte.[10] Moreover, the $[C_6H_5(SO_3)]^-$ anion has been used as a weakly coordination anion, similarly to the well-known triflate anion, $CF_3SO_3^-$.[11] Structurally, only a handful of pentafluorobenzenesulfonates are known.[9,12,13] In course of our investigations on sulfonic acids we became also interested in fluorinated sulfonates.[14,15] The absence of any C–H bonds makes this anion a particularly attractive ligand for the synthesis of lanthanide complexes. This is helpful to suppress quenching effects in the luminescence of such complexes. Pentafluorobenzenesulfonates, in particular the sodium salt, are commercially available but unreasonable expensive compounds. Thus, we decided to prepare the acid ourselves from C_6F_5H and oleum (20 % SO_3). After work-up, a light brown oily liquid was obtained, probably a higher hydrate of the acid compared to the above-mentioned solid mono-hydrate. Based on our experience with *in situ* crystallization using an optical heating and crystallization device (OHCD),[16,17] we were able to grow single crystals from the brown oil. It turned out that the compound is a tetrahydrate of the acid according to the formulation $(H_9O_4)[C_6F_5SO_3]$, containing the so-called Eigen ion $(H_9O_4)^+$ which is rarely described so far. It consists of a central $(H_3O)^+$ ion surrounded by three H_2O molecules according to $[(H_3O)(H_2O)_3]^+$ leading to the star-shaped structure of the ion. Interestingly, there is another structural motif for the $(H_9O_4)^+$ known, which has a chain-like arrangement an can be seen as the dihydrate of the Zundel cation, $(H_5O_2)^+$, according to $[(H_5O_2)(H_2O)_2]^+$.[18]

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2 Experimental

2.1 Synthesis

Pentafluorobenzenesulfonic acid (PFBSA) was prepared from pentafluorobenzene, C_6F_5H, and oleum similarly to the procedure given in Ref. 2. Therefore, 2.00 g of C_6F_5H (11.9 mmol, 1.00 eq) and 25 mL of oleum containing 20 % SO_3 were added to a round bottom flask in a water bath and the mixture was stirred for four days at room temperature. The mixture was poured on ice (100 g), extracted with ethyl acetate (150 mL) and diethyl ether (2 × 150 mL), the combined organic phases were dried over $MgSO_4$ and the solvent was removed *in vacuo*. The desired product was obtained as a brown oil in yield of 2.28 g (9.2 mmol, 77 %). ^{19}F NMR (282 MHz, D_2O, r.t.) δ [ppm] = –139.96 to –140.14 (m, 2F), –150.53 (tt, J = 20.9, 5.3 Hz, 1F), –160.81 to –161.04 (m, 2F).

2.2 *In situ* crystallization of $(H_9O_4)[C_6F_5SO_3]$

For the crystallization of $(H_9O_4)[C_6F_5SO_3]$, the compound was placed in glass capillary which was sealed and fixed onto the goniometer of a Bruker D8 Venture Kappa single crystal diffractometer. The sample was cooled to a temperature of 230 K upon which the acid solidified. Subsequently the CO_2 LASER of the OHCD (*optical heating crystallization device*) is used to heat the shock frozen acid in the capillary in order to provoke zone melting and crystallite formation. Repeated heating and cooling finally leads to the formation of a single crystal. This can be nicely seen from the diffraction pattern which shows the typical Debye rings of a polycrystalline powder in the beginning and then changes to the diffraction pattern of a single crystal (Figure 1). From the collected data the crystal structure could be elucidated.

2.3 Structure determination $(H_9O_4)[C_6F_5SO_3]$

The collected diffraction data were processed with the software of the diffractometer,[19,20] and the structure determination and refinement was done with SHELX suite (Table 1).[21,22] Anisotropic displacement parameters have been introduced for all of the non-hydrogen atoms. It turned out that one of the oxygen atoms (O4) shows a quite unsymmetrical displacement ellipsoid. Significant improvement was achieved by splitting of the atom site. Refinement of the site occupation factors gave an 70 %/30 % ratio for the atoms with a distance of 64 pm. The hydrogen atoms could be detected in difference Fourier maps but an unstrained refinement was not possible for all of the hydrogen atoms. However, for the hydrogen atoms of the H_3O^+ ion in the centre of the $(H_9O_4)^+$ the hydrogen atom were refined without restrictions leading to reasonable bond distances. The remaining H atoms were refined on fixed positions with isotropic displacement parameters 1.5 time higher than those of the respective donor oxygen atoms (“riding model”).

3 Results and discussion

The crystal structure $(H_9O_4)[C_6F_5SO_3]$ is triclinic with space group $P\bar{1}$ and contains two formula units in the cell (Table 1). Crystallographically, there is one independent $[C_6F_5SO_3]^-$ anion and one $(H_9O_4)^+$ cation. The pentafluorobenzenesulfonate anion displays almost C_s symmetry with the mirror plane located in the plane of the phenyl ring. The bond distances S–O within the $[SO_3]$ moiety of the anion range from 143.6(1) to 145.1(1) pm (Table 2). The longest distance occurs to the oxygen atom (O12) with strong participation in hydrogen bonds to the $(H_9O_4)^+$ cation. The S–C bond length is 179.1(2) pm and in line with previous findings.[12,13] The most interesting feature of the

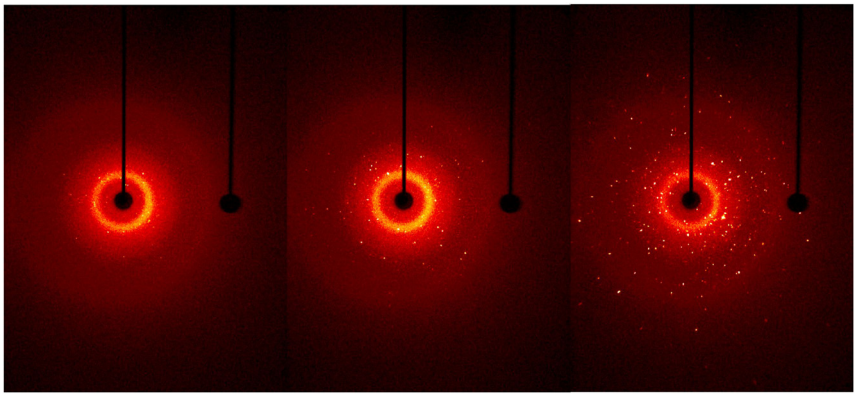

Figure 1: Diffraction patterns of $(H_9O_4)[C_6F_5SO_3]$ during CO_2 laser heating as seen by the detector of the single crystal diffractometer. The left image shows that the solidified acid is highly polycrystalline, almost a powder. Repeated treatment with the laser leads to the growth of a single crystal with the defined diffraction pattern shown in the right-hand picture.

Table 1: Crystallographic data and refinement parameters for $(H_9O_4)[C_6F_5SO_3]$

Crystal system	*Triclinic*
Space group	$P\bar{1}$
a [pm]	705.65(3)
b [pm]	761.62(3)
c [pm]	1132.34(4)
α [°]	91.492(2)
β [°]	102.974(2)
γ [°]	90.718(2)
V [Å^3]	592.72(4)
Z	2
F(000)	324
Density	1.794
Radiation, wavelength [Å]	Mo K_α, 0.7107
Temperature [K]	230
Ranges of *h, k, l*	$-8 \le h \le 8$
	$-9 \le h \le 9$
	$-13 \le h \le 13$
Number of reflections	8,587
Number of unique reflections	2,177
R_{int}/R_{sigma}	0.0363/0.0307
R_1/wR_2 (F >2σ(F))	0.0399/0.1101
R_1/wR_2 (all data)	0.0476/0.1165
Goof	1.084
CSD deposition number	2471369

crystal structure of $(H_9O_4)[C_6F_5SO_3]$ is the $(H_9O_4)^+$ cation which is composed of a central $(H_3O)^+$ ion coordinated by three H_2O molecules. Meanwhile this ion is referred to as *Eigen* ion, in appreciation of *Manfred Eigen´*s groundbreaking work on proton transport in aqueous media (occasionally also the H_3O^+ is named *Eigen* ion, while its monohydrate, $(H_5O_2)^+$, is called *Zundel* ion).[23] The $(H_9O_4)^+$ has been investigates by several methods, including mass spectrometry, spectroscopy, and theoretical calculations.[24–28] Contrastingly, structural investigations in the solid state are scarce, especially compared to numerous reports on the $(H_3O)^+$ and the $(H_5O_2)^+$ ion, respectively.[29–31] In the structure of $(H_9O_4)^+$ a central $(H_3O)^+$ ion is coordinated by three H_2O molecules via hydrogen bonds. With respect to the limitations of hydrogen atom localization by means of X-ray diffraction, the distance of the respective donor (D) and acceptor (A) oxygen atoms is a key parameter to estimate the strength of a hydrogen bond: Shorter D–A hint at stronger hydrogen bonds.[32,33] To some extent a validation of this assumption has been made additional methods, for example neutron diffraction (which gives accurate H-atom positions) and IR as well as NMR measurements. Thus, for strong hydrogen bonds the distance between donor and acceptor atom should be significantly shorter than the sum of their *van der Waals* radii, and the angle D–H···A should be almost 180°. For hydrogen bonds with oxygen as donor and acceptor atoms, very strong hydrogen bonds show D–A distances of 250 pm or even shorter.

The $(H_9O_4)^+$ cation in the crystal structure of $(H_9O_4)[C_6F_5SO_3]$ shows slight deviation from the ideal C_{3v} symmetry (Figure 2). The distances between the central oxygen atom of the H_3O^+ ion (O2) and the oxygen atoms of the surrounding H_2O molecules (O1, O3, O4) range from 249.7 to 253.0 pm, proving strong hydrogen bonding. The angles ∠ O–H···O are found between 171 and 177° and support the assumption of strong hydrogen bonds, even if it has to be mentioned that the hydrogen atom positions are not refined but calculated (Table 2). With respect to bond angles between the H_3O^+ oxygen atom and the H_2O oxygen atoms, which show values of 111.1°, 117.1°, and 110.3°, the cations are flattened with respect to a perfect tetrahedral arrangement. This is in line with the previous findings for this cation and it is also reasonable with respect to the high electronegativity of oxygen which makes the lone pair of the H_3O^+ ion less space filling. In the crystal structure of $(H_9O_4)[C_6F_5SO_3]$ the H_2O molecules of the $(H_9O_4)^+$ cation are involved in further hydrogen bonds with oxygen atoms of the $[SO_3]$ groups. These bonds are between 30 and 40 pm longer than observed within the $(H_9O_4)^+$ cation. Thus, they have to be classified as weak. Furthermore, there is a weak hydrogen bond between adjacent $(H_9O_4)^+$ cations, involving the oxygen atoms O1 and O4 (Figure 2). The respective hydrogen atom in this bond

Table 2: Selected bond lengths for $(H_9O_4)[C_6F_5SO_3]$

$[SO_3C]$ moiety			
Atoms	Bond/pm		Angle°
S1–O11	143.6(2)	O11–S1–O12	114.0(1)
S1–O12	145.1(2)	O12–S1–O13	112.4(1)
S1–O13	144.7(2)	O13–S1–O11	113.8(1)
S1–C1	179.4(2)	O11–S1–C1	106.0(1)
		O12–S1–C1	104.0(1)
		O13–S1–C1	105.5(1)

$[H_9O_4]^+$ cation				
D-H···A	D–H	H···A	D···A	∠D–H···A
O2–H2A···O4B	107(5)	147(4)	252.9(7)	166(5)
O2–H2B···O3	97(4)	154(4)	249.4(3)	165(5)
O2–H1C···O1	102(5)	152(5)	253.3(3)	173(6)
O1–H1A···O11	86	195	279.4(3)	167
O1–H1B···O12	86	194	279.1(2)	169
O3–H3A···O12	86	194	279.9(3)	175
O3–H3B···O13	86	203	287.3(3)	168
O4–H4B···O1	86	232	291.7(7)	147
O4–H4B···O11	86	238	294.3(6)	116
O4–H4A···O13	86	203	290.9(6)	173

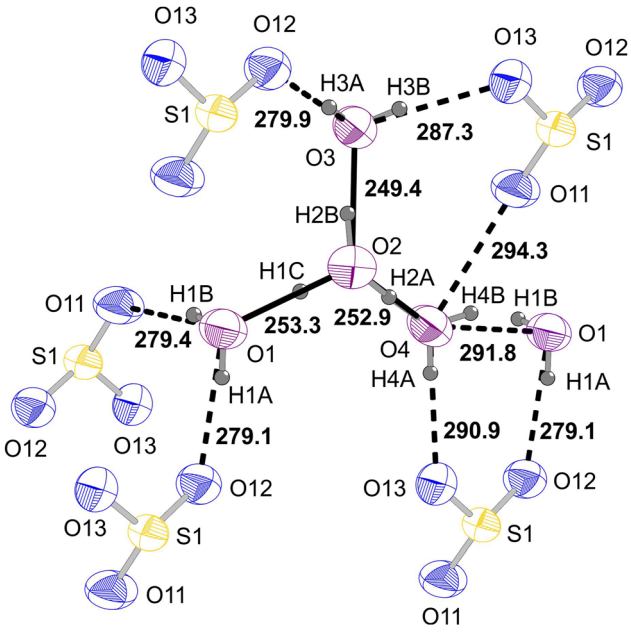

Figure 2: The $(H_9O_4)^+$ cation in the crystal structure of $(H_9O_4)[C_6F_5SO_3]$. The oxygen atoms of the cation are drawn in violet color. Short hydrogen bonds are drawn as black lines, long hydrogen bonds as hatched lines between the donor and acceptor oxygen atoms. The distances are given as bold type values in units of pm. The oxygen atom O4 shows a slight disorder over two positions with almost a 70/30 % ratio and only the major position is shown in the figure. The ellipsoids are set to 70 % probability (except H atoms).

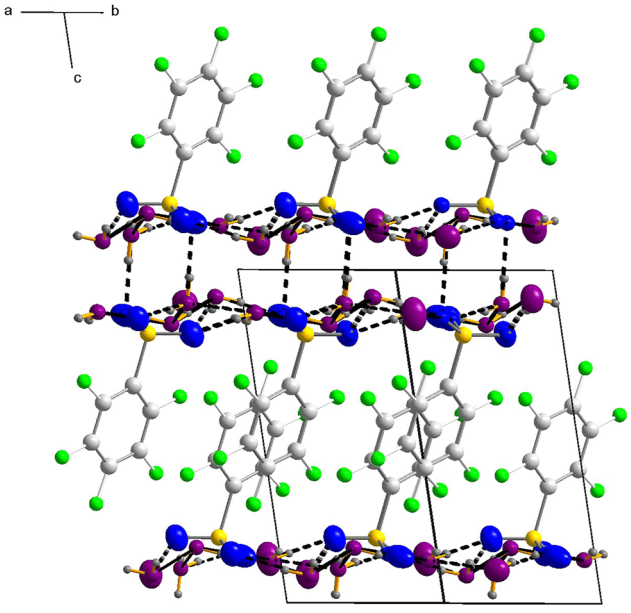

Figure 3: Crystal structure $(H_9O_4)[C_6F_5SO_3]$. The hydrogen bonds between the $(H_9O_4)^+$ ions (violet oxygen atoms) and the $[SO_3]$ moieties (blue oxygen atoms) of the anions are emphasized by black lines. The layers of the oxygen atoms alternate with layers of the fluorinated phenyl rings of the anions.

(H4B) is part of another hydrogen bond to the oxygen atom O11. In sum, this results in a so-called bifurcated hydrogen bond, with typical angles ∠O–H–O of 116 and 147°, respectively (Table 2).

The hydrogen bonding network between $(H_9O_4)^+$ cations and $[SO_3]$ groups lead to hydrophilic double layers which extend in the a–b plane of the unit cell (Figure 3). These layers are separated by the hydrophobic fluorinated phenyl rings of the anions. Within the hydrophobic layers the shortest distances between the aromatic rings are 328 pm, hinting at weak π–π interactions.[34]

4 Conclusions

With the help of *in situ* grown single crystals of $(H_9O_4)[C_6F_5SO_3]$ the first structure determination of a hydrate of the acid $C_6F_5SO_3H$ has been performed. The compound exhibits the rarely seen star-shaped *Eigen* ion, $(H_9O_4)^+$, which can be seen as the trihydrate of the $(H_3O)^+$ ion. The structure of the $(H_9O_4)^+$ cation is stamped by strong hydrogen bond. In the layered structure of $(H_9O_4)[C_6F_5SO_3]$ the cations are further connected to the sulfonate groups of the anions by weak hydrogen bonds.

Research ethics: Not applicable.
Informed consent: Not applicable.
Author contributions: Tobias Lapic has performed the experimental work. Rebecca Maier assisted in the experimental work during a practical study course. David van Gerven did the OHCD crystallization. Mathias Wickleder is the leader of the project. All authors have accepted responsibility for the entire content of this manuscript and approved its submission.
Use of Large Language Models, AI and Machine Learning Tools: None declared.
Conflict of interest: The authors state no conflict of interest.
Research funding: None declared.
Data availability: The crystallographic data have been deposited with the CCDC. The data can be downloaded by using the deposition number given in Table 1.

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