

Diprotonation of taurine: 2-[dihydroxy(oxo)sulfanyliumyl]ethanaminium bis[hexafluoroarsenate(V)]

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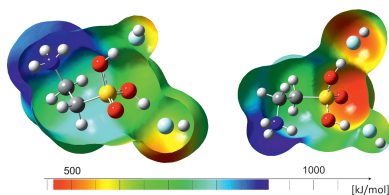
Taurine is part of the cysteine cycle and is one of the few naturally occurring organosulfur-based molecules in the human body. As implied by modern studies, protonated taurine is of biological impact. The first attempts to isolate its protonated species in the binary superacidic system HF/SbF₅ were performed by Hopfinger, resulting in the isolation of monoprotonated taurine. Since the chosen conditions seemed rather harsh, investigations in less acidic systems were performed at room temperature to explore the involved protonated species. Herein, we present the structure of 2-[dihydroxy(oxo)sulfanyliumyl]ethanaminium bis[hexafluoroarsenate(V)], [H₂O₃SC₂H₄NH₃][AsF₆]₂, the diprotonated form of 2-aminoethanesulfonic acid (taurine). It was synthesized in the binary superacidic system HF/AsF₅ and crystallizes as colourless needles. Diprotonated taurine was structurally characterized by single-crystal X-ray diffraction analysis, low-temperature vibrational spectroscopy and NMR spectroscopy.

1. Introduction

Taurine represents the smallest naturally occurring aminoalkylsulfonic acid. It was discovered in 1827 by Gmelin and Tiedemann, and its crystal structure was investigated in 1963 for the first time (Sutherland & Young, 1963). Its existence in the form of a zwitterion was proven by Okaya (1966). Being a part of the cysteine metabolism cycle, taurine appears naturally in animal and human bodies as a product of enzymatic catalysis *via* oxidation, decarboxylation and further oxidation under energy consumption. Depending on physiology, it is mainly stored in muscle cells. New studies have revealed the biological impact of protonated taurine by inhibition of connexin 26-containing channels (Tao & Harris, 2004). By spatial separation, strong acidic conditions can prevail in compartments, which might lead to the protonation of taurine. Limited by the levelling effect, it might only exist as a short-lived species in enzymatic catalysis in such compartments.

The first protonated structure of taurine was reported for 2-sulfoethylammonium hexafluoroantimonate(V), [HO₃S-C₂H₄NH₃][SbF₆], together with its spectroscopic data (Hopfinger *et al.*, 2011; Hopfinger, 2012). Since this first protonation of taurine, which was achieved at −50 °C, the question arises whether physiological conditions, especially room temperature, could lead to higher states of protonation. Although sulfonic acid moieties (HO₃S–R) are known to be strong acids, for example, chlorosulfonic acid, which already belongs to the class superacids, they can be protonated with the formation of their corresponding sulfonium cations. Furthermore, diprotonation of sulfonic acid moieties ([H₃O₃S–R]²⁺) has not been observed so far.

Regarding other known structures containing sulfonium moieties ([H₂O₃S–R]⁺) with more acidic side chains (Soltner *et*



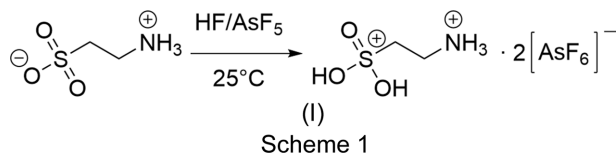
al., 2011; Seelbinder *et al.*, 2010), it is also possible that a weaker acidic system might succeed in protonating taurine or even 2-sulfoethylammonium. Therefore, we investigated the protonation of taurine in the binary superacidic system HF/AsF₅ at room temperature.

2. Experimental

Caution! Note that any contact with the described compounds should be avoided. Hydrolysis of AsF₅ and the synthesized salts forms HF which burns skin and causes irreparable damage. Safety precautions should be taken while handling these compounds. All reactions were carried out by employing standard Schlenk techniques on a stainless steel vacuum line. The syntheses of the salts were performed using FEP/PFA reactors with stainless steel valves.

2.1. Synthesis and crystallization

Anhydrous hydrogen fluoride (80.04 mg, 4.0 mmol) and arsenic pentafluoride (339.82 mg, 2.0 mmol) were condensed into a FEP reactor under liquid nitrogen cooling. The solution was warmed to −78 °C and thoroughly mixed for 5 min. Taurine (125.14 mg, 1.0 mmol) was added to the superacid after freezing it at liquid nitrogen temperature and the solution was warmed to room temperature again and thoroughly mixed for 5 min. The volatile components were removed over 12 h *in vacuo* at −78 °C. The product, [H₂O₃SC₂H₄NH₃][AsF₆]₂, (I) (Scheme 1), was obtained in the form of colourless needles in quantitative yield.



2.2. Crystal structure refinement

Basic crystallographic data, details on data collection, and structure refinement are summarized in Table 1. The positions of the H atoms in the structure were localized in a difference Fourier map and refined without any restrictions. All atoms occupy the general position 4*a* since no special positions exist in *P*2₁2₁2₁.

2.3. Analysis

The product, (I), was characterized by single-crystal X-ray diffraction, low-temperature vibrational spectroscopy and NMR spectroscopy.

Low-temperature vibrational spectroscopy measurements were performed to confirm the conformation and protonation state of taurine. IR spectroscopic investigations were carried out with a Bruker VERTEX 80V FT-IR spectrometer using a cooled cell with a single-crystal CsBr plate on which small amounts of the sample were placed (Bayersdorfer *et al.*, 1972). For Raman measurements, a Bruker MultiRam FT-Raman spectrometer with Nd:YAG laser excitation ($\lambda = 1064$ nm) was

Table 1

Experimental details.

Crystal data	
Chemical formula	(C ₂ H ₉ NO ₃ S)[AsF ₆] ₂
<i>M</i> _r	505.00
Crystal system, space group	Orthorhombic, <i>P</i> 2 ₁ 2 ₁ 2 ₁
Temperature (K)	112
<i>a</i> , <i>b</i> , <i>c</i> (Å)	9.7110 (5), 9.7629 (4), 13.5461 (6)
<i>V</i> (Å ³)	1284.27 (10)
<i>Z</i>	4
Radiation type	Mo <i>K</i> α
μ (mm ^{−1})	5.52
Crystal size (mm)	0.45 × 0.10 × 0.06
Data collection	
Diffractometer	Rigaku OD Xcalibur with a Sapphire3 detector
Absorption correction	Multi-scan (<i>CrysAlis PRO</i> ; Rigaku OD, 2020)
<i>T</i> _{min} , <i>T</i> _{max}	0.281, 1.000
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	13161, 3910, 3424
<i>R</i> _{int}	0.044
(sin θ/λ) _{max} (Å ^{−1})	0.714
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.034, 0.062, 1.01
No. of reflections	3910
No. of parameters	199
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ^{−3})	0.76, −0.61
Absolute structure	Flack <i>x</i> determined using 1283 quotients [(<i>I</i> ⁺) − (<i>I</i> [−])]/[(<i>I</i> ⁺) + (<i>I</i> [−])] (Parsons <i>et al.</i> , 2013)
Absolute structure parameter	0.005 (7)

Computer programs: *CrysAlis PRO* (Rigaku OD, 2020), *SHELXT* (Sheldrick, 2015a), *SHELXL2019* (Sheldrick, 2015b), *ORTEP-3 for Windows* (Farrugia, 2012) and *PLATON* (Spek, 2020).

used. The measurement was performed after transferring the sample into a cooled (−196 °C) glass cell under a nitrogen atmosphere and subsequent evacuation of the glass cell. The low-temperature spectra are depicted in the supporting information (Fig. S1).

Single crystals of [H₂O₃SC₂H₄NH₃][AsF₆]₂, (I), suitable for single-crystal diffraction analysis were selected under a stereo microscope in a cooled nitrogen stream. The single crystal was prepared on a stainless steel polyamide micromount and data collection was performed at 112 K on an Xcalibur diffractometer system (Rigaku Oxford Diffraction). For the diffraction pattern of (I) and an image of the single crystal on the polyamide loop of the micromount, see Fig. S2 of the supporting information.

NMR measurements were performed on a Bruker AV400 TR spectrometer at various temperatures. NMR samples were measured in FEP tubes inlaid with anhydrous HF as solvent, and acetone-*d*₆ was used as an external reference. The NMR spectra are depicted in the supporting information (Figs. S3–S13).

2.4. Quantum chemical calculations

Quantum chemical calculation were based on the single-crystal structure of diprotonated taurine using the DFT

Table 2Vibration assignment (frequencies in cm^{-1}) for diprotonated taurine [see Note 2].

Raman	IR ^a	Calculated IR/Raman ^b	Assignment
3325 (1)	shoulder	3326 (121/24)	$\nu(\text{NH}_3)$
3304 (2)	shoulder	3320 (172/22)	$\nu(\text{NH}_3)$
3251 (3)	3252 (<i>vs</i> , <i>br</i>)	3257 (57/96)	$\nu(\text{NH}_3)$
3051 (6)	3068 (<i>vs</i> , <i>br</i>)	3038 (9/34)	$\nu(\text{C}_2\text{H}_2)$
3016 (11)	shoulder	3005 (20/44)	$\nu(\text{C}_1\text{H}_2)$
3005 (12)	shoulder	2987 (2/104)	$\nu(\text{C}_2\text{H}_2)$
2960 (18)	shoulder	2957 (15/104)	$\nu(\text{C}_1\text{H}_2)$
2906 (2)	2852	2886 (2267/162)	$\nu(\text{O}_1\text{H}) + (\text{O}_2\text{H})$
2789 (3)	shoulder	2818 (2303/108)	$\nu(\text{O}_1\text{H}) + (\text{O}_2\text{H})$
1611 (7)	1632 (<i>w</i>)	1611 (35/3)	$\delta(\text{NH}_3)$
1585 (8)	1587 (<i>w</i>)	1607 (40/5)	$\delta(\text{NH}_3)$
1509 (6)	1491 (<i>w</i>)	1490 (147/1)	$\gamma(\text{NH}_3)$
1461 (15)	1454 (<i>w</i>)	1446 (25/5)	$\delta(\text{C}_2\text{H}_2)$
1404 (6)		1392 (13/4)	$\delta(\text{C}_1\text{H}_2)$
1394 (11)		1389 (23/1)	$\omega(\text{C}_2\text{H}_2)$
1361 (9)	shoulder	1351 (109/7)	$\nu(\text{S}=\text{O})$
1342 (17)	shoulder	1323 (55/5)	$\tau(\text{C}_2\text{H}_2)$
1304 (5)	shoulder	1279 (26/5)	$\omega(\text{C}_1\text{H}_2)$
1236 (10)	1253 (<i>m</i> , <i>br</i>)	1225 (50/2)	$\tau(\text{C}_1\text{H}_2)$
1197 (3)	1213 (<i>m</i>)	1216 (50/1)	$\delta(\text{O}_1\text{H})$
1115 (6)	1118 (<i>w</i>)	1203 (25/2)	$\delta(\text{O}_2\text{H})$
1038 (8)	1090 (<i>w</i>)	1085 (31/1)	$\tau(\text{C}_1\text{H}_2) + \rho(\text{NH}_3)$
1008 (4)	1041 (<i>w</i>)	1068 (21/1)	$\tau(\text{C}_2\text{H}_2) + \rho(\text{NH}_3)$
975 (21)	968 (<i>w</i>)	976 (92/2)	$\nu(\text{C}-\text{C}) + \nu(\text{C}-\text{N})$
928 (8)	919 (<i>w</i>)	935 (173/2)	$\nu(\text{S}-\text{O})$
877 (8)	867 (<i>w</i>)	889 (102/12)	$\nu(\text{S}-\text{O}) + \rho(\text{C}_1\text{H}_2)$
		877 (39/1)	$\rho(\text{NH}_3) + \rho(\text{C}_2\text{H}_2) + \rho(\text{C}_1\text{H}_2)$
832 (23)	825 (<i>w</i>)	829 (34/2)	$\tau(\text{NH}_3) + \rho(\text{C}_2\text{H}_2) + \omega(\text{C}_1\text{H}_2)$
		787 (42/2)	$\nu(\text{C}_2-\text{N}) + \rho(\text{C}_2\text{H}_2)$
		777 (76/2)	$\rho(\text{C}_1\text{H}_2) + \delta(\text{O}_1\text{H}_1) + \delta(\text{O}_2\text{H}_2)$
		752 (65/0)	$\delta(\text{O}_1\text{H}_1)$
		637 (39/17)	$\nu(\text{C}-\text{S}) + \rho(\text{C}_2\text{H}_2)$
671 (26)	675 (<i>s</i>)		
626 (12)	615 (<i>s</i>)		
610 (8)			
554 (11)	541 (<i>w</i>)		
523 (6)	519 (<i>w</i>)	514 (6/2)	$\gamma(\text{SO}_3)$
485 (18)	463 (<i>w</i>)	445 (23/2)	$\delta(\text{SO}_3)$
473 (16)		430 (4/4)	$\omega(\text{SO}_3)$
438 (9)			
403 (9)	390 (<i>m</i>)	404 (47/2)	$\rho(\text{C}_1\text{H}_2)$
300 (9)		309 (16/1)	$\rho(\text{C}_1\text{H}_2) + \rho(\text{C}_2\text{H}_2) + \rho(\text{NH}_3)$
282 (6)		291 (32/3)	
267 (6)		244 (9/0)	
247 (6)		224 (2/0)	$\tau(\text{NH}_3)$
		157 (8/0)	$\rho(\text{C}_2\text{H}_2) + \rho(\text{NH}_3)$

Notes: (a) abbreviations for IR intensities: ν = very, s = strong, m = medium and w = weak. IR intensities in kJ mol^{-1} and Raman intensities in $\text{\AA}^4 \text{u}^{-1}$. Experimental Raman activities are relative to a scale of 1 to 100. (b) Calculated at the B3LYP/aug-cc-pVTZ level of theory (scaling factor of 0.968), displaying the relative activity of IR and Raman vibrations.

(B3LYP) and MP2 methods at the cc-pVTZ-aug level of theory with *Gaussview/GAUSSIAN16* software (Dennington *et al.*, 2016; Frisch *et al.*, 2016).

For calculations, the hydrogen bonds were simulated by adding two additional HF molecules to the cation in the gas phase (Fig. 1), resulting in more suitable calculated vibrational frequencies, in particular with regard to the vibrations of the hydroxy groups. This method is already established in the literature in order to simulate gas phase basicity (Soltner *et al.*, 2011).

The structure of the cation and simulated contacts was optimized with DFT methods and vibration frequencies were calculated as reported in Table 2. For the calculation of more

Table 3Vibrational frequencies (cm^{-1}) of the $[\text{AsF}_6]^-$ anion (C_{4v}).

Raman	IR	Raman (literature)	IR (literature)
726 (27)		730 (30)	
717 (27)	698 (<i>s</i>)	709 (10)	700
690 (100)		680 (100)	
589 (9)		587 (11)	
573 (17)		563 (10)	
403 (9)		400 (15)	400
	390 (<i>m</i>)	390 (20)	
373 (39)	374 (<i>w</i>)	381 (25)	
	365 (<i>w</i>)	363 (25)	

accurate energy values of the mapped electrostatic potential, MP2 methods were used based on the optimized structure.

As visualized by the mapped electrostatic potential of diprotonated taurine, the positive charge on the S atom is partially shifted along the carbon backbone. The positive potential of the ammonium group represents the maximum of the positive potential (blue), which is in good agreement with its cationic state. The minimum of the positive potential is located on the sulfuryl O atom (red).

3. Results and discussion

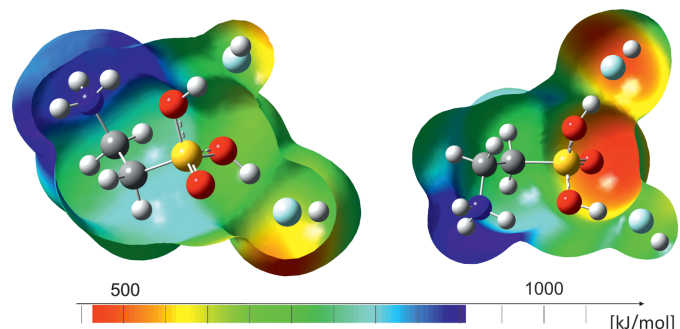
3.1. Vibrational spectroscopy

The observed experimental vibration frequencies for diprotonated taurine were assigned to the anion and cation (Tables 2 and 3) in accordance with quantum chemical calculations (DFT-B3LYP/aug-cc-pVTZ) and compared to the vibrational spectroscopic data for the monoprotated species (Hopfinger, 2012).

C_1 symmetry was assigned to the diprotonated species of taurine with 42 fundamental vibrations, which are compiled in Table 2.

While the vibrations along the ethylammonium chain only differ weakly compared to monoprotection, the vibrations of the sulfonium moiety show a split of the SO_3 vibrations and coupled C—S stretching vibrations.

For the $[\text{AsF}_6]^-$ anions, more vibrations were observed than expected, due to solid-state effects leading to a lowered

**Figure 1**

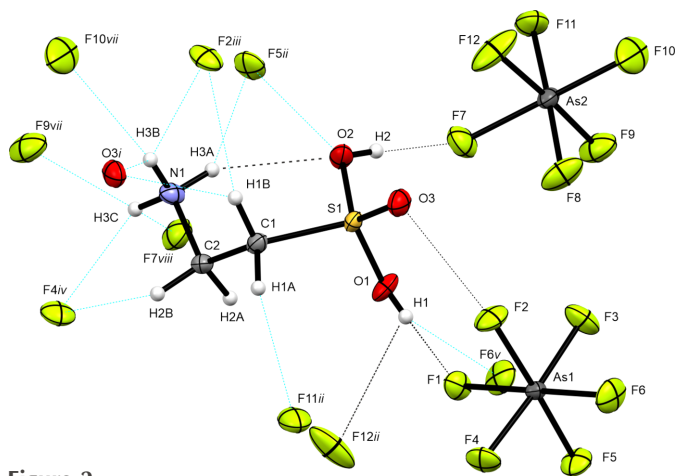
Calculated electrostatic potential mapped onto an electron-density isosurface value of 0.0004 bohr^{-3} with the colour scale ranging from 464.714 (red) to 905.798 kJ mol^{-1} (blue) of $[\text{H}_2\text{O}_3\text{SC}_2\text{H}_4\text{NH}_3][\text{AsF}_6]_2$ for two different orientations.

Table 4

Hydrogen-bond interactions (distances are Å) in the crystal structure of $[\text{H}_2\text{O}_3\text{SC}_2\text{H}_4\text{NH}_3][\text{AsF}_6]_2$.

Contact	Distance	Contact	Distance
O1—H1...F1	2.522 (5)	C2—H2B...F4 ^{iv}	3.075 (6)
O1—H1...F6 ^v	2.776 (5)	N1—H3B...F2 ⁱⁱⁱ	2.853 (5)
O1—H1...F12 ⁱⁱ	2.904 (6)	N1—H3A...F5 ⁱⁱ	2.922 (5)
O2—H2...F7	2.607 (5)	N1—H3C...F4 ^{iv}	2.964 (5)
O2—H2...F5 ⁱⁱ	2.847 (5)	N1—H3C...F7 ^{viii}	3.023 (6)
O3 ⁱ ...H1B—C1	2.972 (6)	N1—H3C...F9 ^{vii}	3.161 (6)
O3 ⁱ ...H3B—N1	3.240 (6)	N1—H3B...F10 ^{vii}	3.026 (6)
C1—H1A...F11 ⁱⁱ	3.136 (5)	N1—H3A...O2	2.998 (6)

Symmetry codes: (i) $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$; (ii) $-x + \frac{3}{2}, -y + 1, z - \frac{1}{2}$; (iii) $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$; (iv) $x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1$; (v) $x + \frac{1}{2}, -y + \frac{3}{2}, -z + 1$; (vi) $x, y - 1, z$; (vii) $x, y - 1, z$; (viii) $-x + 2, y - \frac{1}{2}, -z + \frac{1}{2}$.

**Figure 2**

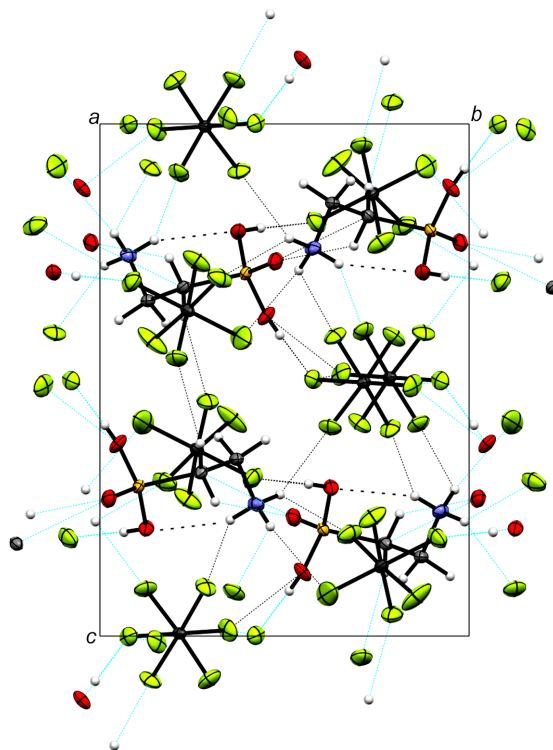
The asymmetric unit of $[\text{H}_2\text{O}_3\text{SC}_2\text{H}_4\text{NH}_3][\text{AsF}_6]_2$. Displacement ellipsoids are drawn at the 50% probability level.

symmetry compared to an ideal octahedral coordination (Table 3).

3.2. Crystal structure

As implied by the two $[\text{AsF}_6]^-$ anions in the asymmetric unit (Fig. 2), taurine forms a dication with protonation to the sulfonate moiety. The crystal structure of diprotonated taurine (Fig. 3) is built up on a three-dimensional network of many interactions, especially hydrogen bonds (Table 4).

In the diprotonated taurine species, the S1—C1—C2—N1 torsion angle of $-79.7(5)^\circ$ is enlarged [$\Delta(\text{torsion}) = 6.2^\circ$] compared to the monoprotonated species, allowing more interactions with the isolated $[\text{AsF}_6]^-$ anions. This conformation leads to a weakening of the intramolecular hydrogen bond to 2.998 Å [$\Delta(\text{N—H} \cdots \text{O}) = 0.091 \text{ Å}$], but increases the

**Figure 3**

The crystal structure of $[\text{H}_2\text{O}_3\text{SC}_2\text{H}_4\text{NH}_3][\text{AsF}_6]_2$, viewed along the *a* axis. Displacement ellipsoids are drawn at the 50% probability level.

number of fluorine acceptors for the intermolecular hydrogen bonds.

The sulfonium moiety shows two S—O bonds of similar length for the hydroxy O atoms [S1—O1 = 1.511 (4) Å and S1—O2 = 1.513 (4) Å], which appear to be slightly shortened in comparison with the monoprotonated species [$\Delta(\text{S—O}) = -0.036 \text{ Å}$]. The bond length in the sulfonyl group is significantly shortened [S1—O3 = 1.410 (4) Å] compared with monoprotonation [1.437 (2) Å] [$\Delta(\text{S=O}) = -0.027 \text{ Å}$]. The bond lengths of the sulfonium moiety are nearly equal to the values reported by Soltner for the trifluoromethanesulfonium ion (Soltner *et al.*, 2011).

The C1—S1, C1—C2 and C1—N1 bond lengths differ only marginally considering the influence of protonation, which can be justified by the orbital situation as the S atom does not participate in hyperconjugation along the ammoniumalkyl chain. Therefore, substituent effects on the chain cause larger changes of the bond lengths in the chain (Soltner *et al.*, 2011). For comparison with calculated data and related structures, see Table 5.

Table 5

Bond-length (Å) comparison of $[\text{H}_2\text{O}_3\text{SC}_2\text{H}_4\text{NH}_3]^{2+}$ (observed/calculated) with $[\text{HO}_3\text{SC}_2\text{H}_4\text{NH}_3]^+$ and $[\text{H}_2\text{O}_3\text{SCF}_3]^+$.

$[\text{H}_2\text{O}_3\text{SC}_2\text{H}_4\text{NH}_3]^{2+}$	Observed	Calculated	$[\text{HO}_3\text{SC}_2\text{H}_4\text{NH}_3]^+$	$[\text{H}_2\text{O}_3\text{SCF}_3]^+$
S1—O1	1.511 (4)	1.562	S1—O1	1.437 (2)
S1—O2	1.513 (4)	1.547	S1—O2	1.427 (2)
S1—O3	1.410 (4)	1.423	S1—O3	1.548 (2)
S1—C1	1.754 (5)	1.801	S1—C1	1.765 (3)
C1—C2	1.516 (7)	1.526	C1—C2	1.511 (4)
C2—N1	1.496 (6)	1.517	C2—N1	1.496 (4)
			S1—O1	1.505 (2)
			S1—O2	1.483 (2)
			S1—O3	1.405 (2)
			S1—C1	1.855 (2)

Table 6

Coordination environment (bond lengths in Å) of $[\text{AsF}_6]^-$ units in diprotonated taurine.

$[\text{As1F}_6]^-$		$[\text{As2F}_6]^-$		$\text{Na}[\text{AsF}_6]$	
As1—F1	1.760 (3)	As2—F7	1.750 (3)	As1—F1	1.702
As1—F2	1.718 (3)	As2—F8	1.710 (3)		
As1—F3	1.708 (3)	As2—F9	1.704 (3)		
As1—F4	1.710 (3)	As2—F10	1.688 (3)		
As1—F5	1.711 (3)	As2—F11	1.708 (3)		
As1—F6	1.693 (3)	As2—F12	1.711 (3)		

In the crystal structure, the diprotonated taurine is surrounded by eight $[\text{AsF}_6]^-$ anions and two cations. The cations are arranged in antiparallel zigzag chains along the *b* axis (Fig. 4). Two very strong hydrogen bonds are formed, *i.e.* $\text{O1—H1}\cdots\text{F1}$ [2.522 (5) Å] and $\text{O2—H2}\cdots\text{F7}$ [2.607 (5) Å]. Medium–strong hydrogen bonds are found in the range 2.776 (5)–3.161 (6) Å (Table 4). In accordance with the criteria given by Jeffrey, the assignment of weak/strong hydrogen bonds shows short and directed contacts for strong hydrogen bonds, and longer and nondirectional contacts for weaker hydrogen bonds (Jeffrey, 1997).

Atom As1 is surrounded by atoms F1–F6 and As2 by F7–F12, with As–F bond lengths in the range 1.688 (3)–1.759 Å. The $[\text{AsF}_6]^-$ octahedra are slightly distorted compared with idealized O_h symmetry in $[\text{AsF}_6]^-$ (Biswal *et al.*, 2012), through elongation of the As–F bond along the strongest hydrogen bonds in the crystal structure (Table 6).

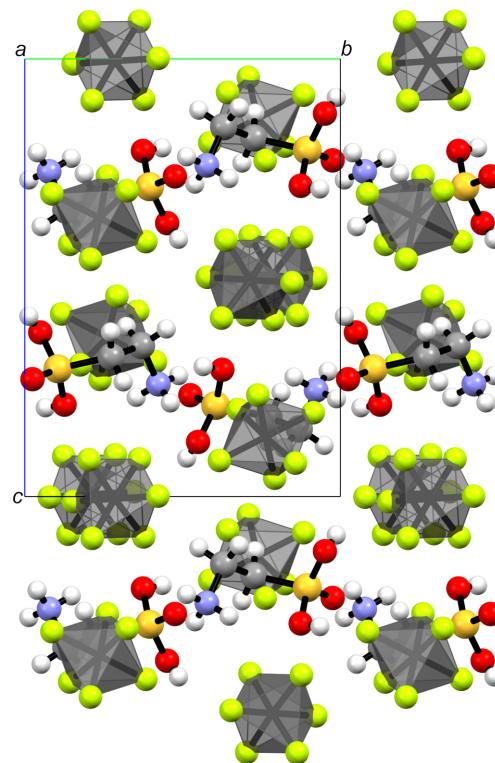
3.3. NMR spectroscopy

The ^1H , ^{13}C , ^{14}N and ^{19}F NMR spectra of taurine were measured in anhydrous hydrogen fluoride (aHF) and in the binary superacidic medium aHF/AsF₅.

The ^1H NMR spectrum (see Fig. S3 in the supporting information) shows three visible signals, apart from the solvent HF (7.75 ppm) and the external reference acetone (2.05 ppm), *i.e.* a triplet at 5.97 ppm (*t*, C1H₂, 2H) and two overlapping signals at about 3.42 (sextet, C2H₂, 2H) and 3.35 ppm (*t*, NH₃, 3H). Due to the fast proton exchange in HF, the sulfonic acid moiety might not be visible. In the ^{13}C NMR spectrum (Fig. S4), C1 (47.81 ppm) and C2 (36.75 ppm) were detected. In the ^{14}N NMR spectrum (Fig. S5), the NH₃⁺ moiety was detected at –352.18 ppm (*q*, NH₃⁺). In the ^{19}F NMR spectrum (Fig. S6), the only observed signal was assigned to the solvent (HF) at –198.21 ppm, therefore no decomposition was expected.

In order to test whether the protonation reaction in the binary superacidic system is temperature dependent, a second sample was prepared with two equivalents of AsF₅. Spectra were recorded at –50, –25 °C and room temperature. Because of the low solubility of the synthesized compound in HF at –50 °C and the fact that the spectra do not differ to that measured at –25 °C, only two sets of spectra are discussed.

Similar to the starting material, the ^1H spectrum (Fig. S7) shows two singlets at 9.35 (*s*, H[AsF₆], 1H) and 5.35 ppm (*s*, C1H₂, 2H), as well as a triplet at 3.39 ppm (*t*, NH₃, 2H) and a sextet at 3.42 ppm (*m*, C2H₂, 2H). The data of the ^1H spectra

**Figure 4**

Polyhedral illustration of the slicing in the crystal structure of $[\text{H}_2\text{O}_3\text{SC}_2\text{H}_4\text{NH}_3][\text{AsF}_6]_2$, viewed along the *a* axis.

suffer from bad shimming. In the ^{13}C NMR spectrum (Fig. S8), C1 (47.69 ppm) and C2 (34.86 ppm) were detected. No data were obtained from the ^{14}N spectrum, which might be caused by a change of symmetry in the NH₃ group. Besides the solvent at –142.85 ppm, unreacted H[AsF₆] was detected at –167.67 ppm in the ^{19}F NMR spectrum (Fig. S9).

In the ^1H spectrum (Fig. S10), a smaller singlet of H[AsF₆] occurs at 9.33 ppm, indicating a further protonation of taurine. In addition, a triplet at 5.43 ppm (*t*, C1H₂, 2H) and two signals of the CH₂ and NH₃⁺ moieties at about 3.46 (*t*, NH₃, 3H) and 3.10 ppm (sextet, C2H₂, 2H), respectively, were observed. In the ^{13}C NMR spectrum (Fig. S11), C1 (48.31 ppm) and C2 (35.13 ppm) were detected. The ^{14}N NMR spectrum (Fig. S12) shows the NH₃⁺ moiety at –354.94 ppm (*q*, NH₃, 3H). In the ^{19}F NMR spectrum (Fig. S13), the signals were assigned to the solvent at –144.72 ppm and to H[AsF₆] at –167.95 ppm, due to residues of AsF₅.

As monitored by NMR spectroscopy, we expect the protonation of taurine not to succeed in anhydrous hydrogen fluoride at room temperature, as no shift can be detected compared to the already known spectra of taurine (Lin *et al.*, 1988). In the binary superacidic system HF/AsF₅, monoprotation is observed at low temperature, with diprotonation observed in excess of Lewis acid at room temperature.

4. Conclusion

NMR spectroscopic investigations revealed that the protonation reaction in the binary superacidic systems HF/MF₅ (*M* =

As, Sb) is apparently temperature dependent. Thus, less acidic systems, such as HF/BF₃ or HF/GeF₄, might also be able to mono- or even diprotonate taurine at room temperature.

As diprotonation of taurine already occurs in less acidic systems, the question may be raised whether taurine can be triprotonated in the stronger acidic system HF/SbF₅ at room temperature or at even higher temperatures in excess SbF₅, supported by the formation of polyanions (*e.g.* [Sb₂F₁₁][−], [Sb₃F₁₆][−], *etc.*). As no protonation of sulfonium moieties has yet been observed, it is still unclear whether [H₃O₃S-R]²⁺ moieties might exist. Therefore, investigations of the protonation of alkylsulfonic acids, such as methanesulfonic acid, might give hints, due to a better stabilizing substituent effect, as shown by the mapped electrostatic potential.

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supporting information

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Diprotonation of taurine: 2-[dihydroxy(oxo)sulfanyliumyl]ethanaminium bis[hexafluoroarsenate(V)]

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Computing details

2-[Dihydroxy(oxo)sulfanyliumyl]ethanaminium bis[hexafluoroarsenate(V)]

Crystal data

(C₂H₉NO₃S)[AsF₆]₂
 $M_r = 505.00$
 Orthorhombic, $P2_12_12_1$
 $a = 9.7110$ (5) Å
 $b = 9.7629$ (4) Å
 $c = 13.5461$ (6) Å
 $V = 1284.27$ (10) Å³
 $Z = 4$
 $F(000) = 968$

$D_x = 2.612$ Mg m⁻³
 Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
 Cell parameters from 4191 reflections
 $\theta = 2.1\text{--}31.9^\circ$
 $\mu = 5.52$ mm⁻¹
 $T = 112$ K
 Needle, colourless
 $0.45 \times 0.10 \times 0.06$ mm

Data collection

Rigaku OD Xcalibur with a Sapphire3
 diffractometer
 Radiation source: Enhance (Mo) X-ray Source
 Graphite monochromator
 Detector resolution: 15.9809 pixels mm⁻¹
 ω scans
 Absorption correction: multi-scan
 (CrysAlis PRO; Rigaku OD, 2020)
 $T_{\min} = 0.281$, $T_{\max} = 1.000$

13161 measured reflections
 3910 independent reflections
 3424 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.044$
 $\theta_{\max} = 30.5^\circ$, $\theta_{\min} = 2.6^\circ$
 $h = -13 \rightarrow 13$
 $k = -13 \rightarrow 13$
 $l = -19 \rightarrow 19$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.034$
 $wR(F^2) = 0.062$
 $S = 1.01$
 3910 reflections
 199 parameters
 0 restraints
 Primary atom site location: structure-invariant
 direct methods
 Secondary atom site location: difference Fourier
 map

Hydrogen site location: mixed
 H atoms treated by a mixture of independent
 and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0258P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.76$ e Å⁻³
 $\Delta\rho_{\min} = -0.61$ e Å⁻³
 Absolute structure: Flack x determined using
 1283 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)
 Absolute structure parameter: 0.005 (7)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2 , conventional R-factors R are based on F, with F set to zero for negative F^2 . The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Reflections were merged by SHELXL according to the crystal class for the calculation of statistics and refinement.

_reflns_Friedel_fraction is defined as the number of unique Friedel pairs measured divided by the number that would be possible theoretically, ignoring centric projections and systematic absences.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\text{\AA}^2$)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.64337 (14)	0.39515 (11)	0.29191 (9)	0.0136 (2)
O3	0.5274 (4)	0.4756 (3)	0.2683 (3)	0.0224 (8)
O1	0.7304 (4)	0.4510 (4)	0.3751 (3)	0.0212 (8)
O2	0.7474 (4)	0.3742 (4)	0.2101 (3)	0.0200 (8)
C1	0.5956 (5)	0.2262 (5)	0.3196 (3)	0.0152 (9)
H1A	0.530488	0.228241	0.375836	0.018*
H1B	0.545674	0.188079	0.262136	0.018*
C2	0.7128 (5)	0.1300 (5)	0.3453 (4)	0.0167 (10)
H2A	0.778779	0.178859	0.388555	0.020*
H2B	0.675542	0.051510	0.383022	0.020*
N1	0.7883 (5)	0.0769 (4)	0.2570 (3)	0.0178 (9)
H3B	0.727203	0.038915	0.214066	0.027*
H3C	0.850270	0.012387	0.276398	0.027*
H3A	0.833325	0.147135	0.226845	0.027*
H1	0.687 (8)	0.487 (7)	0.412 (5)	0.04 (2)*
H2	0.792 (7)	0.435 (6)	0.203 (5)	0.03 (2)*
As1	0.46719 (5)	0.71523 (4)	0.50495 (3)	0.01210 (10)
F1	0.5842 (3)	0.5779 (3)	0.4988 (2)	0.0244 (6)
F5	0.5675 (3)	0.7864 (3)	0.5953 (2)	0.0275 (7)
F2	0.3720 (4)	0.6369 (3)	0.4141 (2)	0.0279 (8)
F4	0.3793 (3)	0.6234 (3)	0.5921 (2)	0.0279 (8)
F6	0.3537 (4)	0.8466 (3)	0.5113 (2)	0.0318 (7)
F3	0.5603 (4)	0.7965 (3)	0.4155 (2)	0.0324 (8)
As2	0.85105 (6)	0.73733 (5)	0.13631 (4)	0.01747 (12)
F11	0.9643 (4)	0.7082 (3)	0.0421 (2)	0.0355 (8)
F8	0.7390 (3)	0.7616 (4)	0.2321 (2)	0.0377 (9)
F12	0.7287 (4)	0.6424 (4)	0.0765 (3)	0.0491 (11)
F7	0.9089 (4)	0.5860 (3)	0.1917 (2)	0.0326 (9)
F9	0.9753 (4)	0.8244 (4)	0.1990 (2)	0.0373 (9)
F10	0.7959 (5)	0.8834 (4)	0.0826 (3)	0.0646 (15)

Atomic displacement parameters ($\text{\AA}^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0161 (6)	0.0113 (5)	0.0133 (5)	0.0013 (5)	0.0003 (5)	−0.0030 (4)
O3	0.027 (2)	0.0173 (17)	0.023 (2)	0.0073 (16)	−0.0031 (17)	−0.0025 (14)
O1	0.020 (2)	0.0207 (18)	0.023 (2)	−0.0005 (14)	−0.0024 (17)	−0.0122 (16)
O2	0.024 (2)	0.0165 (18)	0.0191 (19)	−0.0024 (15)	0.0088 (16)	−0.0014 (15)
C1	0.017 (2)	0.014 (2)	0.014 (2)	−0.0017 (19)	0.0029 (17)	−0.0026 (18)
C2	0.024 (3)	0.015 (2)	0.011 (2)	0.0018 (18)	0.000 (2)	−0.0003 (18)
N1	0.019 (2)	0.021 (2)	0.014 (2)	0.0076 (17)	−0.0015 (17)	0.0015 (17)
As1	0.0119 (2)	0.0149 (2)	0.0096 (2)	0.00187 (17)	−0.0004 (2)	−0.00084 (18)
F1	0.0233 (16)	0.0247 (14)	0.0252 (16)	0.0107 (11)	0.0039 (15)	0.0016 (14)
F5	0.0281 (19)	0.0299 (17)	0.0245 (15)	−0.0018 (15)	−0.0129 (14)	−0.0070 (13)
F2	0.027 (2)	0.0350 (18)	0.0213 (16)	0.0007 (15)	−0.0105 (14)	−0.0098 (14)
F4	0.028 (2)	0.0369 (18)	0.0192 (16)	−0.0047 (15)	0.0092 (14)	0.0056 (13)
F6	0.0302 (18)	0.0285 (15)	0.0368 (19)	0.0189 (14)	−0.0024 (18)	−0.0072 (15)
F3	0.032 (2)	0.0380 (19)	0.0269 (16)	−0.0007 (16)	0.0062 (15)	0.0153 (15)
As2	0.0222 (3)	0.0159 (2)	0.0143 (2)	0.00355 (19)	−0.0041 (2)	−0.00337 (19)
F11	0.051 (2)	0.0346 (18)	0.0203 (15)	−0.0067 (17)	0.0128 (16)	−0.0026 (14)
F8	0.0229 (18)	0.054 (2)	0.0357 (19)	0.0034 (17)	0.0056 (15)	−0.0222 (17)
F12	0.028 (2)	0.065 (3)	0.054 (3)	0.0035 (18)	−0.0118 (19)	−0.041 (2)
F7	0.038 (2)	0.0279 (18)	0.0317 (19)	0.0101 (15)	0.0021 (16)	0.0100 (14)
F9	0.040 (2)	0.044 (2)	0.0282 (18)	−0.0186 (17)	0.0010 (17)	−0.0112 (15)
F10	0.114 (4)	0.037 (2)	0.043 (2)	0.040 (2)	−0.026 (3)	0.0001 (19)

Geometric parameters ($\text{\AA}$, $^\circ$)

S1—O3	1.410 (4)	N1—H3A	0.9100
S1—O1	1.511 (4)	As1—F6	1.693 (3)
S1—O2	1.513 (4)	As1—F3	1.708 (3)
S1—C1	1.754 (5)	As1—F4	1.710 (3)
O1—H1	0.75 (6)	As1—F5	1.711 (3)
O2—H2	0.74 (6)	As1—F2	1.718 (3)
C1—C2	1.516 (7)	As1—F1	1.760 (3)
C1—H1A	0.9900	As2—F10	1.688 (3)
C1—H1B	0.9900	As2—F9	1.704 (3)
C2—N1	1.496 (6)	As2—F11	1.708 (3)
C2—H2A	0.9900	As2—F8	1.710 (3)
C2—H2B	0.9900	As2—F12	1.711 (3)
N1—H3B	0.9100	As2—F7	1.750 (3)
N1—H3C	0.9100		
O3—S1—O1	114.5 (2)	F3—As1—F4	175.98 (16)
O3—S1—O2	116.2 (2)	F6—As1—F5	91.53 (16)
O1—S1—O2	102.8 (2)	F3—As1—F5	90.99 (15)
O3—S1—C1	111.2 (2)	F4—As1—F5	90.20 (16)
O1—S1—C1	109.1 (2)	F6—As1—F2	91.32 (15)
O2—S1—C1	101.9 (2)	F3—As1—F2	89.05 (17)

S1—O1—H1	111 (6)	F4—As1—F2	89.57 (15)
S1—O2—H2	112 (5)	F5—As1—F2	177.14 (16)
C2—C1—S1	115.6 (4)	F6—As1—F1	179.56 (16)
C2—C1—H1A	108.4	F3—As1—F1	88.74 (15)
S1—C1—H1A	108.4	F4—As1—F1	87.45 (15)
C2—C1—H1B	108.4	F5—As1—F1	88.61 (15)
S1—C1—H1B	108.4	F2—As1—F1	88.53 (15)
H1A—C1—H1B	107.4	F10—As2—F9	91.0 (2)
N1—C2—C1	113.5 (4)	F10—As2—F11	91.31 (19)
N1—C2—H2A	108.9	F9—As2—F11	89.97 (18)
C1—C2—H2A	108.9	F10—As2—F8	90.5 (2)
N1—C2—H2B	108.9	F9—As2—F8	90.17 (16)
C1—C2—H2B	108.9	F11—As2—F8	178.22 (17)
H2A—C2—H2B	107.7	F10—As2—F12	91.9 (2)
C2—N1—H3B	109.5	F9—As2—F12	177.1 (2)
C2—N1—H3C	109.5	F11—As2—F12	90.20 (17)
H3B—N1—H3C	109.5	F8—As2—F12	89.56 (18)
C2—N1—H3A	109.5	F10—As2—F7	179.7 (2)
H3B—N1—H3A	109.5	F9—As2—F7	88.86 (18)
H3C—N1—H3A	109.5	F11—As2—F7	88.46 (16)
F6—As1—F3	91.67 (16)	F8—As2—F7	89.78 (17)
F6—As1—F4	92.14 (16)	F12—As2—F7	88.21 (19)
O3—S1—C1—C2	179.5 (3)	O2—S1—C1—C2	55.0 (4)
O1—S1—C1—C2	−53.3 (4)	S1—C1—C2—N1	−79.7 (5)
