Supporting Information

Structural Investigation of the Protonation States of Sulfamic Acid

Valentin Bockmair,*[a] Andreas Klöck,[a] Lukas Stanzel,[a] Sven Ringelband,[b] Frank Tambornino[b] and Andreas J. Kornath [a]†

* Corresponding author; † deceased

[a] Department Chemie, LMU München, Butenandtstraße 5-13(D), D-81377 München, Germany

[b] Fachbereich Chemie, Philipps-Universität Marburg, Hans-Meerwein-Straße 4, D-35043 Marburg, Germany

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1 Experimental Details

Caution! Note that any contact with the described compounds should be avoided. Hydrolysis of AsF_5, SbF_5, BF_3, GeF_4, and the synthesized salts forms HF which burns skin and causes irreparable damage. Safety precautions should be taken while handling these compounds.

1.1 Apparatus and Materials

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. Before each reaction or NMR measurement, the stainless steel vacuum line and the reactors were dried with fluorine.

For Raman measurements a Bruker MultiRam FT-Raman spectrometer with Nd:YAG laser excitation (λ = 1064 nm) was used. The measurement was performed after transferring the sample into a cooled (−196 °C) glass cell under nitrogen atmosphere and subsequent evacuation of the glass cell.

Low temperature IR-spectroscopic investigations were carried out with a Bruker Vertex-80V FTIR spectrometer using a cooled cell with a single-crystal CsBr plate on which small amounts of the samples were placed.[1]

The single crystal X-Ray diffraction studies were performed with an Oxford XCalibur3 diffractometer equipped with a Spellman generator (voltage 50 kV, current 40 mA) and a KappaCCD detector, operating with Mo-Kα radiation (λ = 0.7107 Å) The measurements were performed at 173 K. The program CrysAlisPro 1.171.39.46e (Rigaku Oxford Diffraction, 2018) was employed for the data collection and reduction.[2] The structures were solved utilizing SHELXT[3] and SHELXL-2018/3[4] of the WINGX software package.[5] The structures were checked using the software PLATON.[6] The absorption correction was performed using the SCALE3 ABSPACK multiscan method.[7] Visualization was done with the software Mercury.[8] Hirshfeld surface analysis was conducted with the CrystalExplorer software.[9]

1.2 Computational Methods

Periodic quantum-chemical calculations were carried out for all discussed compounds with the PBE0 hybrid density functional theory method (DFT-PBE0).[10,11] All calculations were performed with the CRYSTAL17 program package.[12] Triple-ζ-valence + polarization (TZVP) level basis sets were applied for C, O, S, N, H, F, B, Ge, Sb and As. The basis sets have been previously derived from the Karlsruhe def2 basis sets and can be found elsewhere in literature.[13–17] Intermolecular van der Waals dispersion interactions were taken into account using Grimme's empirical D3 dispersion correction with zero damping, except for xk054.[18] Reciprocal space was sampled by Monkhorst−Pack-type k-point grids: 6 x 3 x 2 for xl001, 6 x 4 x 3 for xl002, 4 x 4 x 3 for xk052, 6 x 4 x 3 for xk054 and 3 x 6 x 2 for xk055,.[19] For the evaluation of the Coulomb and exchange integrals (TOLINTEG), tolerance factors of 8, 8, 8, 8, and 16 were used for xk052 and xk055, 6, 6, 6, 6 and 12 for xl001, 7, 7, 7, 7, 14 for xl002. Both the atomic positions and lattice parameters were fully optimized within the constraints imposed by the space group symmetry. Default DFT integration grids and optimization convergence thresholds were applied in all calculations. The harmonic vibrational frequencies and Raman and IR intensities were obtained through usage of the computational Scheme implemented in CRYSTAL17.[20–23] Raman and IR intensities were calculated for a polycrystalline powder sample (total isotropic intensity in arbitrary units). The Raman spectra were obtained by using a pseudo-Voigt band profile (50:50 Lorentzian:Gaussian) and a full width at half-maximum (fwhm) of 8 cm^{-1} and simulated considering the experimental setup (293.15 K; λ = 532 nm). Bands for the Raman and IR spectrum were assigned by visual inspection of the normal modes with the Jmol program package at http://crysplot.crystalsolutions.eu/.[24,25]

Quantum chemical calculations were carried out using the software packages Gaussian09 and Gaussian16.[26] For visualization and illustration of the calculated structures and mapped MEP surfaces the software GaussView 6 was used.[27] If not stated otherwise, all calculations were carried out on the MP2/aug-cc-pVTZ level of theory.

1.3 Experimental Procedures

[ASA]
Amido sulfuric acid was synthesized according to the common literature procedure, from starting from urea and oleum as described by *Söderlund*.

[ASA+1H][BF_4]·ASA
ASA (97.1 mg, 1.00 mmol, 1.0 eq) was filled into an FEP reactor, *a*HF (50.0 mg, 2.50 mmol, 2.5 eq) and BF_3 (136 mg, 2.00 mmol, 2.0 eq) were condensed into the vessel. The reactants were warmed to room temperature and thoroughly mixed for 3 min. A colorless precipitant was formed. The excess solvent was removed *in vacuo* at −78 °C. The product $[ASA+1H]^+[BF_4]^-$·ASA was obtained as a colorless solid in quantitative yield.

[ASA+1H][GeF_5]
ASA (97.1 mg, 1.00 mmol, 1.0 eq) was filled into an FEP reactor, *a*HF (100 mg, 5.00 mmol, 5.0 eq) and GeF_4 (594 mg, 4.00 mmol, 4.0 eq) were condensed into the vessel. The reactants were warmed to room temperature and thoroughly mixed for 3 min. A colorless precipitant was formed. The excess solvent was removed *in vacuo* at −78 °C. The product was $[ASA+1H]^+[GeF_5]^-$ obtained as a colorless solid in quantitative yield.

[ASA+1H][AsF_6]
ASA (97.1 mg, 1.00 mmol, 1.0 eq) was filled into an FEP reactor, *a*HF (60.03 mg, 3.0 mmol, 3.0 eq) and AsF_5 (340 mg, 2.00 mmol, 2.0 eq) were condensed into the vessel. The reactants were warmed to room temperature and thoroughly mixed for 3 min. A colorless precipitant was formed. The excess solvent was removed *in vacuo* at −78 °C. The product $[ASA+1H]^+[AsF_6]^-$ was obtained as a colorless solid in quantitative yield.

[ASA+1H][SbF_6]
SbF_5 (280 mg, 1.29 mmol, 2.0 eq) was condensed into an FEP and dissolved in *a*HF (60.03 mg, 3.0 mmol, 3.0 eq). ASA (62.6 mg, 0.645 mmol, 1.0 eq) was filled into the vessel. The reactants were warmed to room temperature and thoroughly mixed for 3 min. A colorless precipitant was formed out of a turquoise solution. The excess solvent was removed *in vacuo* at −78 °C. The product $[ASA+1H]^+[SbF_6]^-$ was obtained as a colorless solid in quantitative yield.

2 Crystallographic Data

Table S1. Crystal data and structure refinement of ASA (**1**), [ASA+1H][BF_4]·ASA (**2**) and [ASA+1H][GeF_5] (**3**).

	ASA (**1**)	[ASA+1H][BF_4]·ASA (**2**)	[ASA+1H][GeF_5] (**3**)
Molecular Formula	H_3NSO_3	$BF_4H_7N_2O_6S_2$	$F_{10}Ge_2H_8N_2O_6S_2$
M_r [g·mol^{-1}]	97.09	282.01	531.38
Crystal size [mm^3]	0.604 × 0.429 × 0.090	0.402 × 0.232 ×0.113	0.192 × 0.135 × 0.103
Crystal system	orthorhombic	monoclinic	orthorhombic
Space group	*Pbca*	$P2_1/n$	$P2_12_12_1$
a [Å]	7.964(3)	12.5176(12)	4.7928(2)
b [Å]	7.998(2)	4.8386(4)	8.6658(3)
c [Å]	9.181(3)	15.5064(13)	14.9064(6)
α [°]	90	90	90
β [°]	90	99.877(9)	90
γ [°]	90	90	90
V [Å^3]	584.8(3)	925.27(14)	619.11(4)
Z	8	4	2
ρ_{calc} [g·cm^{-3}]	2.206	2.024	2.850
μ [mm^{-1}]	0.891	0.655	5.355
$\lambda_{MoK\alpha}$ [Å]	0.71073	0.71073	0.71073
F(000)	400	568	512
T [K]	105	112	112
h, k, l range	–11:5,–11:11,–6:13	–16:17,–6:6,–21:17	–6:6,–12:12,–20:21
Measured reflexes	3022	4637	6220
Unique reflexes	894	2494	1889
R_{int}	0.0295	0.0227	0.0345
Parameters	58	142	105
R(F)/wR(F^2)[a] (all data)	0.0323/0.0823	0.0523/0.0955	0.0283/0.0425
Weighting scheme[b]	0.0423/0.2743	0.0431/0.4368	0.0158
S (GooF)[c]	1.135	1.045	1.000
Flack parameter			–0.005(9)
Residual density [e·Å^{-3}]	0.419/–0.455	0.493/–0.484	0.347/–0.423
Device	Oxford XCalibur	Oxford XCalibur	Oxford XCalibur
CCDC	2418182	2418186	2418188

[a] $R_1 = \Sigma||F_0|-|F_c||/\Sigma|F_0|$.

[b] $wR_2 = [\Sigma[w(F_0^2-F_c^2)^2]/\Sigma[w(F_0)^2]]^{1/2}$; $w = [\sigma_c^2(F_0^2)+(xP)^2+yP]-1$; $P = (F_0^2+2F_c^2)/3$.

[c] GooF = $\{\Sigma[w(F_o^2-F_c^2)^2]/(n-p)\}^{1/2}$ (n = number of reflections; p = total number of parameters).

Table S2. Crystal data and structure refinement of [ASA+1H][AsF_6] (**4**), [ASA+1H][SbF_6] (**5**) and $(NH_4)_2[Cu(H_2O)_6](SO_4)_2$ (**6**).

	[ASA+1H][AsF_6] (**4**)	[ASA+1H][SbF_6] (**5**)	$(NH_4)_2[Cu(H_2O)_6](SO_4)_2$ (**6**)
Molecular Formula	$AsF_6H_4NO_3S$	$F_6H_4NO_3SSb$	$CuH_{20}N_2O_{14}S_2$
M_r [g·mol^{-1}]	287.02	333.85	399.84
Crystal size [mm^3]	0.165 × 0.068 x 0.038	0.392 × 0.056 × 0.045	0.506 × 0.228 × 0.112
Crystal system	triclinic	triclinic	monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a [Å]	4.8458(3)	4.92150(10)	6.3541(7)
b [Å]	7.4477(5)	7.5792(2)	12.2553(11)
c [Å]	9.3459(7)	9.3947(2)	9.1331(11)
α [°]	86.310(6)	86.173(2)	90
β [°]	79.633(6)	80.961(2)	106.261(12)
γ [°]	89.731(6)	89.675(2)	90
V [Å^3]	331.09(4)	345.304(14)	682.76(13)
Z	2	2	2
ρ_{calc} [g·cm^{-3}]	2.879	3.211	1.945
μ [mm^{-1}]	5.546	4.391	1.977
$\lambda_{MoK\alpha}$ [Å]	0.71073	0.71073	0.71073
F(000)	276	312	414
T [K]	112	112	115
h, k, l range	–6:6,–9:9:–12:12	–7:7,–10:10,–13:13	–8:8,–14:15,–11:7
Measured reflexes	5165	6646	3064
Unique reflexes	1518	2097	1506
R_{int}	0.0590	0.0362	0.0499
Parameters	118	112	119
R(F)/wR(F^2)[a] (all data)	0.0568/0.0741	0.0290/0.0620	0.0655/0.1217
Weighting scheme[b]	0.0189/0.0000	0.0237/0.6660	0.0551
S (GooF)[c]	1.125	1.146	1.020
Flack parameter			
Residual density [e·Å^{-3}]	0.597/–0.710	1.790/–1.027	0.827/–1.333
Device	Oxford XCalibur	Oxford XCalibur	Oxford XCalibur
CCDC	2418183	2418190	2418192

[a] $R_1 = \Sigma||F_0|-|F_c||/\Sigma|F_0|$.

[b] $wR_2 = [\Sigma[w(F_0^2-F_c^2)^2]/\Sigma[w(F_0)^2]]^{1/2}$; $w = [\sigma_c^2(F_0^2)+(xP)^2+yP]-1$; $P = (F_0^2+2F_c^2)/3$.

[c] GooF = $\{\Sigma[w(F_o^2-F_c^2)^2]/(n-p)\}^{1/2}$ (n = number of reflections; p = total number of parameters).

2.1 ASA

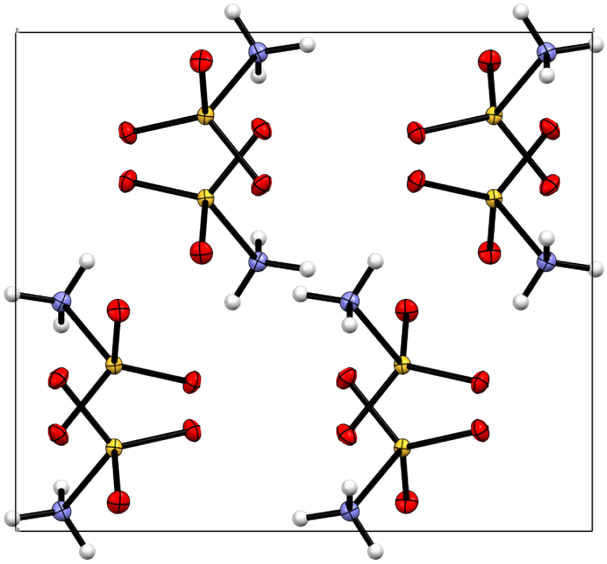

Figure S1. View along the *b*-axis in the crystal packing of (**1**) (thermal ellipsoids with 50% probability). Atom label: S (yellow), O (red), N (blue) and H (white).

Table S3. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2) for ASA (**1**).

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	0.66678 (5)	0.40712 (4)	0.67060 (4)	0.00679 (14)
O3	0.55815 (16)	0.54980 (14)	0.67819 (11)	0.0111 (3)
O2	0.80642 (15)	0.42583 (14)	0.57381 (12)	0.0114 (2)
O1	0.70165 (16)	0.32524 (15)	0.80559 (11)	0.0112 (2)
N1	0.54030 (18)	0.26037 (16)	0.57927 (14)	0.0089 (3)
H1	0.459 (3)	0.256 (3)	0.624 (3)	0.025 (6)*
H2	0.525 (3)	0.298 (3)	0.494 (3)	0.024 (6)*
H3	0.587 (4)	0.163 (3)	0.579 (3)	0.035 (7)*

Table S4. Atomic displacement parameters (Å^2) for ASA (**1**).

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0088 (2)	0.0046 (2)	0.0070 (2)	–0.00042 (12)	0.00018 (11)	–0.00032 (11)
O3	0.0139 (6)	0.0063 (5)	0.0132 (5)	0.0030 (4)	0.0006 (4)	–0.0012 (4)
O2	0.0120 (5)	0.0107 (5)	0.0116 (5)	–0.0027 (4)	0.0034 (4)	–0.0004 (4)
O1	0.0136 (6)	0.0111 (5)	0.0089 (5)	–0.0002 (4)	–0.0020 (4)	0.0020 (4)
N1	0.0103 (6)	0.0070 (6)	0.0093 (6)	–0.0003 (5)	–0.0006 (4)	–0.0001 (5)

Table S5. Geometric parameters (Å, º) for ASA (**1**).

S1—O1	1.4289 (11)	S1—O3	1.4338 (13)
S1—O2	1.4313 (12)	S1—N1	1.7594 (14)
O1—S1—O2	115.81 (8)	O1—S1—N1	102.64 (7)
O1—S1—O3	116.10 (7)	O2—S1—N1	102.64 (7)
O2—S1—O3	114.57 (7)	O3—S1—N1	102.05 (7)

2.2 [ASA+1H][BF_4]·ASA

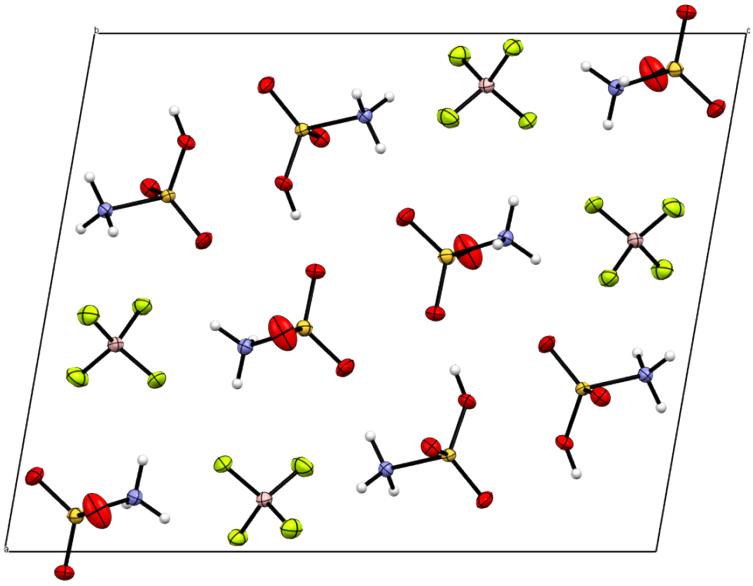

Figure S2. View along the *b*-axis in the crystal packing of (**2**) (thermal ellipsoids with 50% probability). Atom label: S (yellow), F (green), O (red), N (blue), B (grey) and H (white).

Table S6. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2) for [ASA+1H][BF_4]·ASA (**2**).

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	0.18594 (4)	0.64823 (10)	0.34420 (3)	0.01312 (13)
S2	0.56902 (4)	0.65463 (11)	0.39991 (3)	0.01704 (14)
F4	0.02719 (10)	–0.1323 (3)	0.64566 (9)	0.0229 (3)
F3	0.16877 (11)	0.1625 (3)	0.68799 (9)	0.0266 (3)
F1	0.04399 (11)	0.2568 (3)	0.56588 (9)	0.0270 (3)
F2	0.16338 (11)	–0.0968 (3)	0.56532 (10)	0.0310 (3)
O1	0.28978 (12)	0.5115 (3)	0.33023 (10)	0.0191 (3)
O2	0.20115 (13)	0.9239 (3)	0.37329 (10)	0.0206 (3)
O3	0.09988 (13)	0.5712 (4)	0.27698 (10)	0.0240 (4)
O4	0.45934 (12)	0.7455 (4)	0.40245 (10)	0.0249 (4)
O6	0.64539 (14)	0.7405 (4)	0.47391 (11)	0.0322 (4)
N2	0.60478 (14)	0.8582 (4)	0.31474 (11)	0.0165 (4)
H2A	0.676236	0.832884	0.312296	0.025*
H2B	0.592561	1.039537	0.325153	0.025*
H2C	0.563973	0.806973	0.262878	0.025*
N1	0.15874 (14)	0.4654 (4)	0.43642 (11)	0.0147 (3)
H1A	0.222278	0.409272	0.469379	0.022*
H1B	0.117043	0.315211	0.418501	0.022*
H1C	0.122858	0.577442	0.468975	0.022*
O5	0.5785 (2)	0.3826 (4)	0.36870 (15)	0.0463 (6)
B1	0.10058 (19)	0.0480 (5)	0.61520 (15)	0.0159 (4)
H1	0.350 (3)	0.586 (7)	0.357 (2)	0.062 (11)*

Table S7. Atomic displacement parameters (Å^2) for [ASA+1H][BF_4]·ASA (**2**).

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}

S1	0.0107 (2)	0.0162 (2)	0.0121 (2)	–0.00141 (18)	0.00083 (18)	0.00028 (18)
S2	0.0148 (2)	0.0182 (3)	0.0181 (3)	0.00071 (19)	0.0027 (2)	0.0022 (2)
F4	0.0182 (6)	0.0263 (7)	0.0234 (7)	–0.0052 (5)	0.0014 (5)	0.0068 (5)
F3	0.0175 (6)	0.0421 (8)	0.0191 (7)	–0.0064 (6)	–0.0001 (5)	–0.0063 (6)
F1	0.0237 (7)	0.0277 (7)	0.0290 (7)	0.0011 (6)	0.0027 (6)	0.0107 (6)
F2	0.0236 (7)	0.0381 (8)	0.0334 (8)	0.0003 (6)	0.0109 (6)	–0.0121 (6)
O1	0.0147 (7)	0.0246 (8)	0.0192 (7)	0.0034 (6)	0.0061 (6)	–0.0007 (6)
O2	0.0223 (8)	0.0161 (7)	0.0244 (8)	–0.0008 (6)	0.0069 (7)	0.0001 (6)
O3	0.0187 (8)	0.0358 (9)	0.0155 (7)	–0.0090 (7)	–0.0030 (6)	0.0033 (7)
O4	0.0129 (7)	0.0391 (9)	0.0228 (8)	–0.0006 (7)	0.0034 (6)	0.0010 (7)
O6	0.0195 (8)	0.0554 (11)	0.0193 (8)	–0.0021 (8)	–0.0037 (7)	0.0110 (8)
N2	0.0156 (8)	0.0185 (8)	0.0152 (8)	0.0007 (7)	0.0026 (7)	0.0014 (7)
N1	0.0135 (8)	0.0167 (8)	0.0141 (8)	0.0003 (7)	0.0031 (6)	0.0009 (7)
O5	0.0742 (16)	0.0172 (9)	0.0555 (13)	0.0018 (9)	0.0337 (12)	0.0010 (8)
B1	0.0134 (10)	0.0196 (11)	0.0146 (10)	–0.0015 (9)	0.0017 (8)	0.0012 (9)

Table S8. Geometric parameters (Å, º) for [ASA+1H][BF_4]·ASA (**2**).

S1—O2	1.4106 (16)	S2—O4	1.4487 (16)
S1—O3	1.4145 (15)	S2—N2	1.7655 (18)
S1—O1	1.5069 (15)	F4—B1	1.406 (3)
S1—N1	1.7637 (17)	F3—B1	1.407 (3)
S2—O5	1.4146 (18)	F1—B1	1.386 (3)
S2—O6	1.4236 (17)	F2—B1	1.384 (3)
O2—S1—O3	121.93 (10)	O5—S2—N2	102.49 (11)
O2—S1—O1	112.88 (9)	O6—S2—N2	102.64 (10)
O3—S1—O1	110.18 (10)	O4—S2—N2	102.36 (9)
O2—S1—N1	104.43 (9)	F2—B1—F1	110.25 (18)
O3—S1—N1	103.69 (9)	F2—B1—F4	109.86 (19)
O1—S1—N1	100.81 (8)	F1—B1—F4	109.64 (18)
O5—S2—O6	117.59 (13)	F2—B1—F3	108.85 (18)
O5—S2—O4	115.30 (12)	F1—B1—F3	109.76 (19)
O6—S2—O4	113.45 (11)	F4—B1—F3	108.45 (17)

2.3 [ASA+1H][GeF_5]

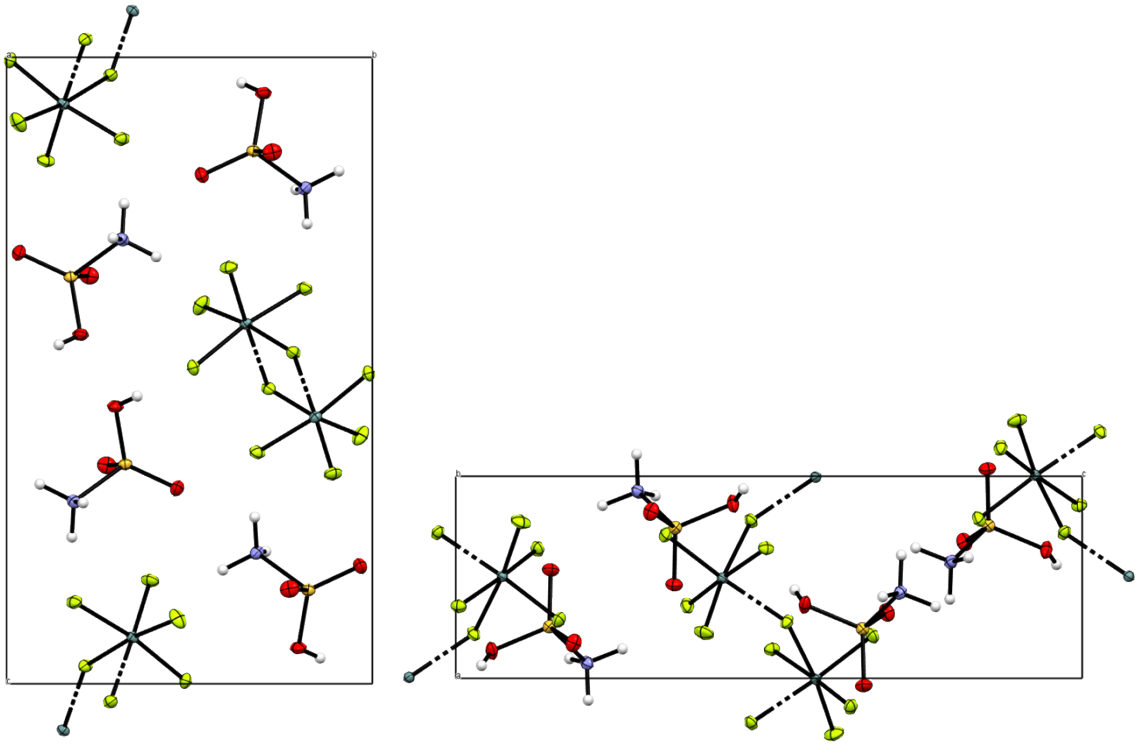

Figure S3. View on the unit cell of [ASA+1H][GeF_5] (**3**) view along the *a*-axis (left) and *b*-axis (right) (thermal ellipsoids with 50% probability). Atom label: Ge (grey), S (yellow), F (green), O (red), N (blue) and H (white).

Table S9. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2) for [ASA+1H][GeF_5] (**3**).

	x	*y*	*z*	U_{iso}*/U_{eq}
Ge1	0.50472 (8)	0.65512 (3)	0.42560 (2)	0.00798 (8)
S1	0.75549 (18)	0.32445 (9)	0.64939 (5)	0.00990 (16)
F1	0.3562 (4)	0.5105 (2)	0.49532 (13)	0.0114 (4)
F3	0.2888 (4)	0.6075 (2)	0.33522 (13)	0.0143 (4)
F4	0.6406 (4)	0.8145 (2)	0.36950 (13)	0.0131 (4)
F5	0.2206 (4)	0.7840 (2)	0.47142 (12)	0.0112 (4)
F2	0.7744 (4)	0.5323 (2)	0.39616 (13)	0.0172 (5)
O2	1.0364 (5)	0.2739 (3)	0.65140 (16)	0.0159 (5)
O3	0.6746 (5)	0.4663 (3)	0.68799 (16)	0.0147 (5)
O1	0.6357 (6)	0.2977 (3)	0.55735 (17)	0.0143 (6)
N1	0.5759 (6)	0.1841 (3)	0.70913 (18)	0.0109 (6)
H1A	0.645105	0.178488	0.765883	0.016*
H1B	0.596754	0.091152	0.681511	0.016*
H1C	0.391548	0.209029	0.711326	0.016*
H1	0.563 (11)	0.357 (6)	0.541 (4)	0.052 (19)*

Table S10. Atomic displacement parameters (Å^2) for [ASA+1H][GeF_5] (**3**).

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ge1	0.00694 (14)	0.00889 (13)	0.00812 (14)	–0.00016 (17)	0.00075 (16)	–0.00109 (12)
S1	0.0094 (4)	0.0110 (4)	0.0093 (3)	0.0000 (3)	0.0004 (3)	–0.0002 (3)
F1	0.0105 (10)	0.0098 (9)	0.0138 (10)	–0.0012 (8)	0.0006 (8)	0.0015 (8)

F3	0.0144 (11)	0.0183 (10)	0.0102 (10)	–0.0033 (9)	–0.0021 (9)	–0.0024 (8)
F4	0.0144 (10)	0.0147 (10)	0.0101 (9)	–0.0044 (9)	0.0012 (8)	0.0011 (8)
F5	0.0115 (10)	0.0120 (9)	0.0102 (9)	0.0035 (8)	0.0024 (8)	0.0014 (7)
F2	0.0121 (11)	0.0170 (10)	0.0225 (11)	0.0023 (9)	0.0047 (9)	–0.0065 (9)
O2	0.0095 (13)	0.0210 (12)	0.0171 (12)	0.0022 (11)	–0.0004 (11)	0.0010 (10)
O3	0.0189 (14)	0.0103 (12)	0.0150 (13)	0.0009 (10)	0.0019 (10)	–0.0019 (10)
O1	0.0188 (14)	0.0156 (13)	0.0084 (13)	0.0059 (11)	–0.0022 (10)	0.0002 (10)
N1	0.0108 (15)	0.0110 (13)	0.0110 (14)	–0.0015 (10)	–0.0015 (10)	0.0022 (11)

Table S11. Geometric parameters (Å, º) for [ASA+1H][GeF_5] (**3**).

Ge1—F2	1.731 (2)	Ge1—F5^{i}	1.9249 (19)
Ge1—F4	1.7407 (18)	S1—O3	1.412 (2)
Ge1—F3	1.748 (2)	S1—O2	1.416 (3)
Ge1—F1	1.7768 (19)	S1—O1	1.505 (3)
Ge1—F5	1.8888 (19)	S1—N1	1.736 (3)
F2—Ge1—F4	94.97 (10)	F4—Ge1—F5^{i}	87.97 (8)
F2—Ge1—F3	95.83 (10)	F3—Ge1—F5^{i}	175.88 (9)
F4—Ge1—F3	92.19 (9)	F1—Ge1—F5^{i}	86.69 (8)
F2—Ge1—F1	90.79 (9)	F5—Ge1—F5^{i}	86.39 (3)
F4—Ge1—F1	172.02 (9)	O3—S1—O2	121.45 (15)
F3—Ge1—F1	92.71 (9)	O3—S1—O1	113.64 (15)
F2—Ge1—F5	173.49 (9)	O2—S1—O1	109.53 (15)
F4—Ge1—F5	88.54 (8)	O3—S1—N1	105.36 (14)
F3—Ge1—F5	89.50 (9)	O2—S1—N1	104.12 (14)
F1—Ge1—F5	85.22 (9)	O1—S1—N1	99.82 (15)
F2—Ge1—F5^{i}	88.26 (9)	Ge1—F5—Ge1^{ii}	146.93 (10)
F4—Ge1—F5—Ge1^{ii}	-135.3 (2)	F1—Ge1—F5—Ge1^{ii}	39.7 (2)
F3—Ge1—F5—Ge1^{ii}	132.5 (2)	F5^{i}—Ge1—F5—Ge1^{ii}	-47.3 (2)

Symmetry codes: (*i*) = *x*+1/2, –*y*+3/2, –*z*+1; (*ii*) = *x*–1/2, –*y*+3/2, –*z*+1.

2.4 [ASA+1H][AsF_6]

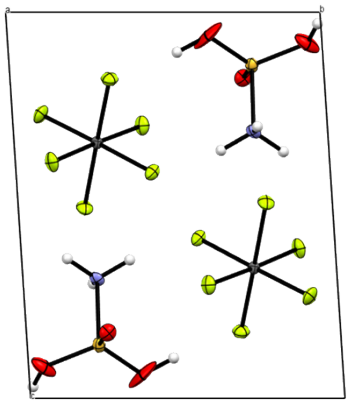

Figure S4. View on the unit cell of [ASA+1H][AsF_6] (**4**), view along the *a*-axis (thermal ellipsoids with 50% probability). Atom label: As (grey), S (yellow), F (green), O (red), N (blue) and H (white).

Table S12. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2) for [ASA+1H][AsF_6] (**4**).

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
As1	0.53243 (10)	0.73690 (7)	0.66200 (5)	0.00770 (14)	
S1	0.7621 (2)	0.22799 (16)	0.86220 (13)	0.0111 (3)	
F6	0.8159 (5)	0.8836 (4)	0.6118 (3)	0.0150 (6)	
F2	0.7460 (5)	0.5666 (4)	0.5853 (3)	0.0129 (6)	
F5	0.4419 (5)	0.7891 (4)	0.4934 (3)	0.0143 (6)	
F1	0.6358 (5)	0.6831 (4)	0.8271 (3)	0.0146 (6)	
F3	0.2562 (5)	0.5894 (4)	0.7064 (3)	0.0147 (6)	
F4	0.3319 (5)	0.9093 (4)	0.7354 (3)	0.0158 (6)	
O3	0.4931 (7)	0.2584 (5)	0.8298 (4)	0.0150 (7)	
O2	0.8088 (8)	0.0476 (6)	0.9193 (4)	0.0264 (9)	
N1	0.9849 (7)	0.2358 (5)	0.6907 (4)	0.0110 (9)	
H1A	0.938471	0.145113	0.638519	0.017*	
H1B	1.166032	0.222827	0.703259	0.017*	
H1C	0.965312	0.343413	0.641858	0.017*	
O1	0.8831 (8)	0.3610 (7)	0.9389 (5)	0.0367 (12)	
H1	0.88 (3)	0.463 (9)	0.896 (15)	0.07 (6)*	0.5
H2	0.92 (3)	0.01 (3)	0.970 (19)	0.10 (7)*	0.5

Table S13. Atomic displacement parameters (Å^2) for [ASA+1H][AsF_6] (**4**).

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
As1	0.0068 (2)	0.0076 (3)	0.0091 (3)	0.00054 (18)	–0.00252 (17)	–0.00059 (17)
S1	0.0100 (6)	0.0091 (6)	0.0132 (7)	–0.0001 (5)	0.0007 (5)	–0.0003 (5)
F6	0.0101 (14)	0.0111 (16)	0.0228 (17)	–0.0050 (12)	–0.0013 (12)	0.0019 (12)
F2	0.0122 (14)	0.0136 (15)	0.0145 (15)	0.0036 (12)	–0.0054 (12)	–0.0046 (11)
F5	0.0164 (15)	0.0155 (15)	0.0131 (16)	0.0011 (12)	–0.0084 (12)	0.0007 (11)
F1	0.0166 (14)	0.0171 (16)	0.0111 (15)	0.0000 (12)	–0.0054 (11)	–0.0002 (11)
F3	0.0101 (14)	0.0128 (15)	0.0215 (16)	–0.0021 (12)	–0.0033 (12)	–0.0008 (12)
F4	0.0149 (14)	0.0138 (16)	0.0189 (16)	0.0057 (12)	–0.0016 (12)	–0.0068 (12)
O3	0.0095 (17)	0.0174 (19)	0.0177 (19)	0.0027 (14)	–0.0017 (14)	–0.0020 (14)
O2	0.019 (2)	0.033 (2)	0.023 (2)	0.0119 (18)	0.0004 (17)	0.0147 (18)

N1	0.008 (2)	0.012 (2)	0.011 (2)	–0.0009 (17)	0.0018 (17)	0.0016 (17)
O1	0.020 (2)	0.049 (3)	0.042 (3)	–0.014 (2)	0.006 (2)	–0.039 (3)

Table S14. Geometric parameters (Å, º) for [ASA+1H][AsF_6] (**4**).

As1—F4	1.710 (3)	As1—F2	1.741 (3)
As1—F3	1.711 (3)	S1—O3	1.404 (3)
As1—F1	1.729 (3)	S1—O1	1.445 (4)
As1—F5	1.730 (3)	S1—O2	1.445 (4)
As1—F6	1.737 (2)	S1—N1	1.761 (4)
F4—As1—F3	91.59 (13)	F3—As1—F2	90.37 (13)
F4—As1—F1	90.70 (13)	F1—As1—F2	89.39 (13)
F3—As1—F1	90.85 (13)	F5—As1—F2	88.87 (12)
F4—As1—F5	90.99 (13)	F6—As1—F2	88.25 (13)
F3—As1—F5	90.50 (13)	O3—S1—O1	118.6 (3)
F1—As1—F5	177.81 (14)	O3—S1—O2	114.9 (2)
F4—As1—F6	89.79 (13)	O1—S1—O2	111.4 (3)
F3—As1—F6	178.22 (13)	O3—S1—N1	104.42 (19)
F1—As1—F6	90.27 (13)	O1—S1—N1	103.2 (2)
F5—As1—F6	88.34 (13)	O2—S1—N1	101.7 (2)
F4—As1—F2	178.04 (13)		

2.5 [ASA+1H][SbF_6]

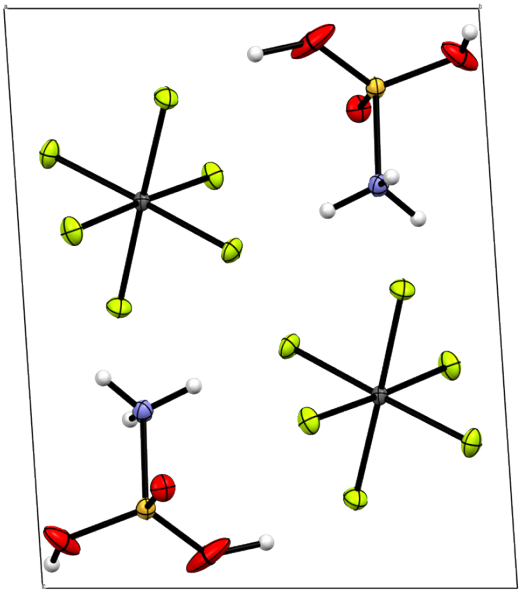

Figure S5. View on the unit cell of [ASA+1H][SbF_6], view along the *a*-axis (**5**) (thermal ellipsoids with 50% probability). Atom label: Sb (grey), S (yellow), F (green), O (red), N (blue) and H (white).

Table S15. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2) for [ASA+1H][SbF_6] (**5**).

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Sb1	0.52871 (4)	0.73674 (3)	0.66740 (2)	0.00847 (7)	
S1	0.77390 (16)	0.22826 (10)	0.86266 (9)	0.01148 (15)	
F6	0.2261 (4)	0.5841 (3)	0.7113 (2)	0.0146 (4)	
F5	0.3247 (4)	0.9239 (3)	0.7490 (2)	0.0167 (4)	
F4	0.4311 (4)	0.7996 (3)	0.4848 (2)	0.0159 (4)	
F3	0.8360 (4)	0.8884 (3)	0.6160 (2)	0.0166 (4)	
F2	0.7461 (4)	0.5537 (3)	0.5827 (2)	0.0144 (4)	
F1	0.6394 (4)	0.6711 (3)	0.8454 (2)	0.0161 (4)	
O3	0.5115 (5)	0.2670 (3)	0.8269 (3)	0.0155 (5)	
O2	0.8080 (6)	0.0470 (4)	0.9177 (3)	0.0295 (7)	
N1	0.9935 (6)	0.2359 (4)	0.6947 (3)	0.0131 (5)	
H1A	0.933752	0.157031	0.637452	0.020*	
H1B	1.167693	0.207834	0.708992	0.020*	
H1C	0.992382	0.346733	0.651180	0.020*	
O1	0.8995 (6)	0.3535 (5)	0.9430 (4)	0.0362 (8)	
H2	0.929300	0.022305	0.958700	0.02 (2)*	0.5
H1	0.972398	0.477098	0.921102	0.16 (10)*	0.5

Table S16. Atomic displacement parameters (Å^2) for [ASA+1H][SbF_6] (**5**).

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Sb1	0.00860 (10)	0.00701 (10)	0.01000 (10)	0.00026 (7)	–0.00208 (7)	–0.00056 (7)
S1	0.0113 (3)	0.0096 (3)	0.0131 (3)	–0.0002 (3)	–0.0003 (3)	–0.0007 (3)
F6	0.0108 (9)	0.0134 (9)	0.0196 (10)	–0.0033 (7)	–0.0037 (7)	0.0013 (8)
F5	0.0160 (10)	0.0123 (9)	0.0218 (10)	0.0040 (8)	–0.0013 (8)	–0.0050 (8)
F4	0.0201 (10)	0.0162 (10)	0.0125 (9)	0.0005 (8)	–0.0064 (7)	0.0005 (7)

F3	0.0128 (9)	0.0141 (10)	0.0222 (10)	–0.0050 (8)	–0.0019 (8)	0.0016 (8)
F2	0.0145 (9)	0.0122 (9)	0.0168 (9)	0.0046 (7)	–0.0017 (7)	–0.0048 (7)
F1	0.0207 (10)	0.0147 (10)	0.0140 (9)	–0.0008 (8)	–0.0068 (8)	0.0008 (8)
O3	0.0107 (11)	0.0165 (12)	0.0194 (12)	0.0028 (9)	–0.0029 (9)	–0.0010 (10)
O2	0.0263 (15)	0.0333 (16)	0.0238 (14)	0.0152 (12)	0.0040 (12)	0.0159 (12)
N1	0.0137 (13)	0.0107 (12)	0.0138 (13)	0.0006 (10)	0.0009 (10)	–0.0009 (10)
O1	0.0207 (14)	0.055 (2)	0.0336 (16)	–0.0159 (15)	0.0066 (12)	–0.0332 (16)

Table S17. Geometric parameters (Å, º) for [ASA+1H][SbF_6] (**5**).

Sb1—F6	1.8681 (19)	Sb1—F2	1.888 (2)
Sb1—F5	1.870 (2)	S1—O3	1.409 (2)
Sb1—F1	1.874 (2)	S1—O1	1.450 (3)
Sb1—F4	1.883 (2)	S1—O2	1.454 (3)
Sb1—F3	1.886 (2)	S1—N1	1.764 (3)
F6—Sb1—F5	91.63 (9)	F5—Sb1—F2	177.83 (9)
F6—Sb1—F1	90.73 (9)	F1—Sb1—F2	89.69 (9)
F5—Sb1—F1	90.46 (9)	F4—Sb1—F2	88.36 (9)
F6—Sb1—F4	90.46 (9)	F3—Sb1—F2	88.15 (9)
F5—Sb1—F4	91.44 (9)	O3—S1—O1	118.38 (19)
F1—Sb1—F4	177.73 (9)	O3—S1—O2	114.71 (17)
F6—Sb1—F3	177.90 (9)	O1—S1—O2	111.7 (2)
F5—Sb1—F3	89.69 (9)	O3—S1—N1	104.38 (15)
F1—Sb1—F3	90.90 (9)	O1—S1—N1	103.19 (16)
F4—Sb1—F3	87.88 (9)	O2—S1—N1	101.92 (16)
F6—Sb1—F2	90.53 (9)		

2.6 $(NH_4)_2[Cu(H_2O)_6](SO_4)_2$

The complex structure of $(NH_4)_2[Cu(H_2O)_6](SO_4)_2$ crystallizes in the monoclinic space group $P2_1/c$ with four formula units per unit cell. The structure was first described by Figgis *et al.* in 2000. The structure indicates a cleavage of the C–S bond upon deprotonation, as only isolated sulfate anions and ammonium tetrahedrons are found between *Jahn-Teller* distorted $[Cu(H_2O)_6]^{2+}$ octahedrons.

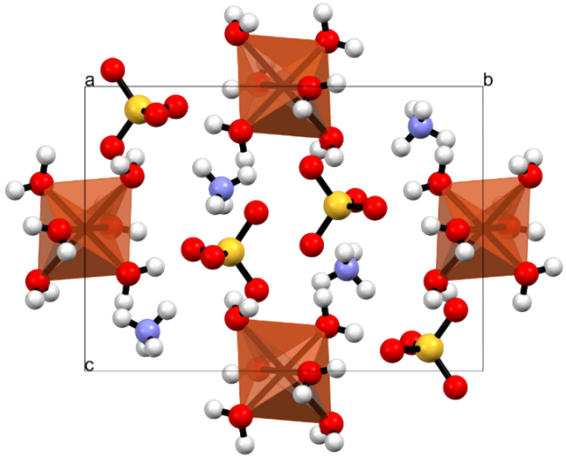

Figure S6. View on the unit cell of $(NH_4)_2[Cu(H_2O)_6](SO_4)_2$, view along the *a*-axis (**6**) (thermal ellipsoids with 50% probability). Atom label: Cu (orange), S (yellow), O (red), N (blue) and H (white).

Table S18. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²) for $(NH_4)_2[Cu(H_2O)_6](SO_4)_2$ (**6**).

	x	*y*	*z*	U_{iso}*/U_{eq}
Cu1	0.500000	0.500000	0.000000	0.0131 (2)
S1	0.75566 (16)	0.36446 (7)	0.58158 (11)	0.0140 (3)
O6	0.7816 (5)	0.4354 (2)	–0.0067 (3)	0.0158 (6)
O4	0.8671 (4)	0.4315 (2)	0.7152 (3)	0.0166 (6)
O5	0.4714 (5)	0.3911 (2)	0.1582 (3)	0.0175 (6)
O2	0.5471 (4)	0.3209 (2)	0.5999 (3)	0.0181 (6)
O3	0.9035 (5)	0.2717 (2)	0.5724 (3)	0.0198 (7)
O1	0.7158 (5)	0.4304 (2)	0.4431 (3)	0.0218 (7)
O7	0.6777 (6)	0.6187 (3)	0.1847 (4)	0.0188 (7)
N1	0.8582 (7)	0.6573 (3)	0.6397 (4)	0.0194 (8)
H5	0.562 (6)	0.402 (3)	0.258 (5)	0.003 (9)*
H6	0.497 (8)	0.324 (4)	0.134 (6)	0.026 (13)*
H9	0.795 (8)	0.588 (4)	0.223 (5)	0.012 (12)*
H10	0.619 (8)	0.626 (4)	0.249 (7)	0.028 (15)*
H7	0.808400	0.368402	0.010100	0.012 (11)*
H8	0.802000	0.453800	–0.081600	0.046 (18)*
H1	0.722 (3)	0.652 (3)	0.584 (4)	0.012 (11)*
H2	0.899 (9)	0.706 (3)	0.714 (5)	0.050 (18)*
H3	0.860703	0.593204	0.686800	0.038 (15)*
H4	0.933 (10)	0.673 (5)	0.583 (7)	0.052 (19)*

Table S19. Atomic displacement parameters (Å²) for $(NH_4)_2[Cu(H_2O)_6](SO_4)_2$ (**6**).

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0147 (4)	0.0138 (4)	0.0137 (4)	0.0010 (3)	0.0088 (3)	0.0006 (2)
S1	0.0156 (5)	0.0136 (5)	0.0149 (5)	–0.0007 (4)	0.0077 (4)	–0.0010 (4)
O6	0.0206 (15)	0.0131 (13)	0.0177 (15)	0.0027 (13)	0.0117 (12)	0.0019 (11)

O4	0.0183 (14)	0.0182 (13)	0.0151 (14)	–0.0013 (13)	0.0076 (12)	–0.0016 (11)
O5	0.0205 (16)	0.0170 (14)	0.0176 (15)	0.0026 (14)	0.0097 (13)	0.0002 (12)
O2	0.0132 (14)	0.0167 (13)	0.0265 (16)	–0.0027 (13)	0.0091 (12)	–0.0013 (12)
O3	0.0172 (14)	0.0165 (13)	0.0286 (17)	0.0002 (13)	0.0112 (13)	–0.0047 (12)
O1	0.0270 (17)	0.0219 (14)	0.0177 (15)	–0.0045 (14)	0.0081 (13)	0.0052 (12)
O7	0.0168 (16)	0.0240 (15)	0.0181 (15)	0.0009 (14)	0.0091 (14)	–0.0018 (13)
N1	0.020 (2)	0.0219 (18)	0.0184 (19)	–0.0010 (18)	0.0094 (17)	0.0009 (16)

Table S20. Geometric parameters (Å, º) for $(NH_4)_2[Cu(H_2O)_6](SO_4)_2$ (**6**).

Cu1—O6	1.973 (3)	Cu1—O7	2.274 (3)
Cu1—O6^{i}	1.973 (3)	S1—O1	1.462 (3)
Cu1—O5^{i}	2.013 (3)	S1—O4	1.477 (3)
Cu1—O5	2.013 (3)	S1—O2	1.481 (3)
Cu1—O7^{i}	2.274 (3)	S1—O3	1.492 (3)
O6—Cu1—O6^{i}	180.0	O6^{i}—Cu1—O7	89.22 (12)
O6—Cu1—O5^{i}	88.80 (12)	O5^{i}—Cu1—O7	89.00 (12)
O6^{i}—Cu1—O5^{i}	91.20 (12)	O5—Cu1—O7	91.00 (12)
O6—Cu1—O5	91.20 (12)	O7^{i}—Cu1—O7	180.0
O6^{i}—Cu1—O5	88.80 (12)	O1—S1—O4	109.55 (16)
O5^{i}—Cu1—O5	180.0	O1—S1—O2	110.70 (17)
O6—Cu1—O7^{i}	89.22 (12)	O4—S1—O2	110.13 (17)
O6^{i}—Cu1—O7^{i}	90.78 (12)	O1—S1—O3	109.37 (18)
O5^{i}—Cu1—O7^{i}	90.99 (12)	O4—S1—O3	107.82 (16)
O5—Cu1—O7^{i}	89.00 (12)	O2—S1—O3	109.22 (16)
O6—Cu1—O7	90.78 (12)		

Symmetry code: (*i*) = –*x*+1, –*y*+1, –*z*.

3 Vibrational Data

Vibrational data files from the calculation are attached to the ESI.

3.1 ASA (1)

Table S21. Selected Observed Vibrational Frequencies [cm^{-1}] of ASA with Calculated Vibrational Frequencies [cm^{-1}] of ASA.

ASA			**1**
Ra	IR[a]	IR/Ra calc.	Assignment
3128(2)	3112(m, br)	3347	ν(N–H)
3105(2)		3293	ν(N–H)
3069(2)		3203	ν(N–H)
3040(3)	3051(m, sh)		
		1622	$\tau(NH_3)$
1534(3)	1538(w)	1592	$\delta(NH_3)$
1343(3)	1442(m)	1524	$\gamma(NH_3)$
1277(3)	1291(s)	1292	$\nu(SO_3)$
	1247(vs)	1230	$\nu(SO_3)$
		1071	$\rho(NH_3)$
1058(100)	1064(s)	1058	$\omega(NH_3)$
	1015(m)	1047	$\nu(SO_3)$
	1001(s)		
708(3)	682(vs, sh)	699	ν(N–S)
687(9)			
558(14)	581(w)	541	$\gamma(SO_3)$
538(16)	531(vs, sh)	531	$\delta(SO_3)$
		523	$\delta(SO_3)$

[a] Abbreviations for IR intensities: vs = very strong, s = strong, m = medium, w = weak, sh = shoulder, br = broad. Experimental Raman intensities are relative to a scale of 1 to 100. Calculated at the Triple-ζ-valence + polarization TZVP level of theory.

3.2 [ASA+1H][BF_4] ·ASA (2)

Table S22. Selected Observed Vibrational Frequencies [cm^{-1}] of $[ASA+1H]^+$salt (**2**) with Calculated Vibrational Frequencies [cm^{-1}] of $[ASA+1H]^+$.

[ASA+1H][BF4] ·ASA (**2**)			**2**	
Ra	IR[a]	IR/Ra calc.	Assignment	
3331(1)	3402(s)	3403	ν(N–H)	$[ASA+1H]^+$
3164(8)	3358(s)	3369	ν(N–H)	ASA
3132(12)		3337	ν(N–H)	$[ASA+1H]^+$
3085(6)	3257(s, sh)	3314	ν(N–H)	ASA
3049(5)	3063(m)	3180	ν(N–H)	ASA
3023(7)	2910(m)	3019	ν(N–H)	$[ASA+1H]^+$
2893(6)	2849(m)	2677	ν(O–H)	$[ASA+1H]^+$
		1638	δ(NH_3)	ASA
		1632	δ(NH_3)	$[ASA+1H]^+$
	1595(s, br)	1611	δ(NH_3)	ASA
1541(18)	1558(s)	1599	δ(NH_3)	ASA
1532(17)		1506	γ(NH_3)	$[ASA+1H]^+$
1467(9)	1464(m)	1495	γ(NH_3)	ASA
1435(49)	1375(m)	1450	ν(SO_2)+δ(SOH)	$[ASA+1H]^+$
1334(8,sh)	1315(m)	1355	ν(SO_2)+δ(SOH)	ASA+$[ASA+1H]^+$
		1328	ν(SO_2)+δ(SOH)	ASA+$[ASA+1H]^+$
	1283(m)	1313	ν(SO_2)+δ(SOH)	ASA+$[ASA+1H]^+$
1233(100, sh)	1238(m)	1205	ν(SO_3)	$[ASA+1H]^+$
	1151(m)	1128	$[BF_4]^-$	
	1097(m)	1104	$[BF_4]^-$	
1082(45, sh)		1079	τ(NH_3)	$[ASA+1H]^+$
		1071	τ(NH_3)	$[ASA+1H]^+$
		1061	τ(NH_3)	ASA
		1058	ρ(NH_3)	$[ASA+1H]^+$
1045(14, sh)	1028(m)	1048	ω(NH_3)	ASA
984(25)	987(s)	1029	ρ(NH_3)+$[BF_4]^-$	ASA
971(35)	953(m)	961	ν(S–O)	$[ASA+1H]^+$
956(33)	933(m)	876	δ(SOH)	$[ASA+1H]^+$
	777(m)	785	$[BF_4]^-$	
	712(w)	700	γ(SO_3)+ν(N–S)	$[ASA+1H]^+$
689(10)	625(m)	686	γ(SO_3)+ν(N–S)	ASA
	598(w)	576	δ(SO_2)	ASA
569(10)	554(w)	534	$[BF_4]^-$	
540(66)		529	$[BF_4]^-$	
		523	$[BF_4]^-$	
522(53)	519(w)	517	δ(SO_3)	$[ASA+1H]^+$
510(74)		512	γ(SO_3)+ν(N–S)	$[ASA+1H]^+$
503(71, sh)	486(w)	494	γ(SO_3)+ν(N–S)	ASA
	455(w)	490	δ(SOH)	$[ASA+1H]^+$
482(12)	426(w)	486	δ(SO_3)	$[ASA+1H]^+$

[a] Abbreviations for IR intensities: vs = very strong, s = strong, m = medium, w = weak, sh = shoulder, br = broad. Experimental Raman intensities are relative to a scale of 1 to 100. Calculated at the Triple-ζ-valence + polarization TZVP level of theory.

3.3 [ASA+1H][GeF_5] (3)

Table S23. Selected Observed Vibrational Frequencies [cm^{-1}] of [ASA+1H]$^+$salt (**3**) with Calculated Vibrational Frequencies [cm^{-1}] of [ASA+1H]$^+$.

[ASA+1H][GeF_5]			**3**
Ra	IR[a]	IR/Ra calc.	Assignment
	3375(w, br)	3336	ν(N–H)
3229(3)	3229(s)	3216	ν(N–H)
3153(14)	3182(m)	3147	ν(N–H)
2930(9)	2692(w, br)	2798	ν(O–H)
2869(9)			
	1712(w)	1685	δ(NH_3)
1569(9)	1608(w)	1589	τ(NH_3)
1553(11)	1554(w)	1583	δ(NH_3)
1529(15)	1483(w)		
1422(23)	1423(w)	1422	ν(SO_2)+δ(SOH)
	1350(w)	1326	δ(SOH)+ρ(NH_3)
	1315(w)		
1249(30)	1250(w)	1254	δ(SOH)
1217(26)	1226(w)	1223	ν(SO_3)
	1182(w)		
1072(38)	1095(w)	1090	ν(SO_3)+τ(NH_3)
1058(14)	1047(w)	1009	ν(SO_3)
995(72)	985(w)		
	929(w)	950	ν(S–O)
	878(w)	817	δ(SOH)+ρ(NH_3)
	796(w)		
735(100)	731(w)	723	ν(N–S)
691(27)	696(w)	664	[GeF_5]$^-$
649(8)	655(w)	646	[GeF_5]$^-$
619(9)	600(m)	590	[GeF_5]$^-$
543(35)	507(w)	510	δ(SO_3)
516(52)	500(w)	499	γ(SO_3)
502(16)	467(w)	479	δ(SO_3)
449(11)	438(w)	431	[GeF_5]$^-$
401(19)	401(w)	408	[GeF_5]$^-$

[a] Abbreviations for IR intensities: vs = very strong, s = strong, m = medium, w = weak, sh = shoulder, br = broad. Experimental Raman intensities are relative to a scale of 1 to 100. Calculated at the Triple-ζ-valence + polarization TZVP level of theory.

3.4 [ASA+1H][AsF_6] (4) and [ASA+1H][SbF_6] (5)

Table S24. Selected Observed Vibrational Frequencies [cm^{-1}] of [ASA+1H]$^+$salt (**3**) with Calculated Vibrational Frequencies [cm^{-1}] of [ASA+1H]$^+$.

[ASA+1H][AsF_6]		**4**	[ASA+1H][SbF_6]		**5**
Ra	IR/Ra calc.	Assignment	Ra	IR/Ra calc.	Assignment
3173(6)	3410	ν(N–H)		3300	ν(O–H)
3129(12)	3353	ν(N–H)		3288	ν(N–H)
3061(8)	3285	ν(N–H)+ν(O–H)	3039(1)	3280	ν(N–H)
2987(7)	3265	ν(O–H)		3202	ν(N–H)+ν(O–H)
1544(27)	1610	δ(NH_3)	1548(2)	1601	δ(NH_3)
1532(28)	1600	ρ(NH_3)	1534(2)	1589	ρ(NH_3)
1467(25)	1479	ω(NH_3)	1461(2)	1500	ω(NH_3)
1450(27)	1460	ν(SO_2)	1443(2)	1426	ν(SO_2)
1429(27)			1343(2)		
1376(26)			1305(2)		
1256(39)	1268	δ(SOH)+ν(S=O)	1257(2)	1246	ν(SO_3)
1172(25)			1158(2)	1206	δ(SOH)
1074(33)	1053	ρ(NH_3)+ν(S–O)	1072(2)	1092	τ(NH_3)
1038(29)	1025	ρ(NH_3)	1058(12)	1080	ω(NH_3)
1010(24)			1034(2)		
960(35)	926	ν(S–O)	1026(2)		
945(37)			963(2)	931	ν(S–O)
707(100)	716	δ(SOH)+ν(AsF6)	941(2)		
698(75)	684	ν(N–S)+[AsF_6]$^-$	709(3)	711	ν(N–S)
675(57)	670	ν(N–S)	691(3)	697	ν(N–S)
	635		686(4)	684	ν(SbF_6)
573(45)	547	[AsF_6]$^-$	673(100)	656	[Sb_2F_{11}; SbF_6]$^-$
559(43)	537	[AsF_6]$^-$	662(32)		
529(60)		[AsF_6]$^-$	649(4)	644	[Sb_2F_{11}; SbF_6]$^-$
520(74)	482		639(3)		
508(47)	477	δ(SO_3)	635(3)	629	[SbF_6]$^-$
479(42)	466	δ(SO_3)+ν(N–S)	621(6)		
412(38)	405	[AsF_6]$^-$	608(5)		[Sb_2F_{11}]$^-$
375(63)	388	[AsF_6]$^-$	585(5)	567	[Sb_2F_{11}; SbF_6]$^-$
	375		559(4)		
			540(4)	513	δ(SO_3)

Experimental Raman intensities are relative to a scale of 1 to 100. Calculated at the Triple-ζ-valence + polarization TZVP level of theory.

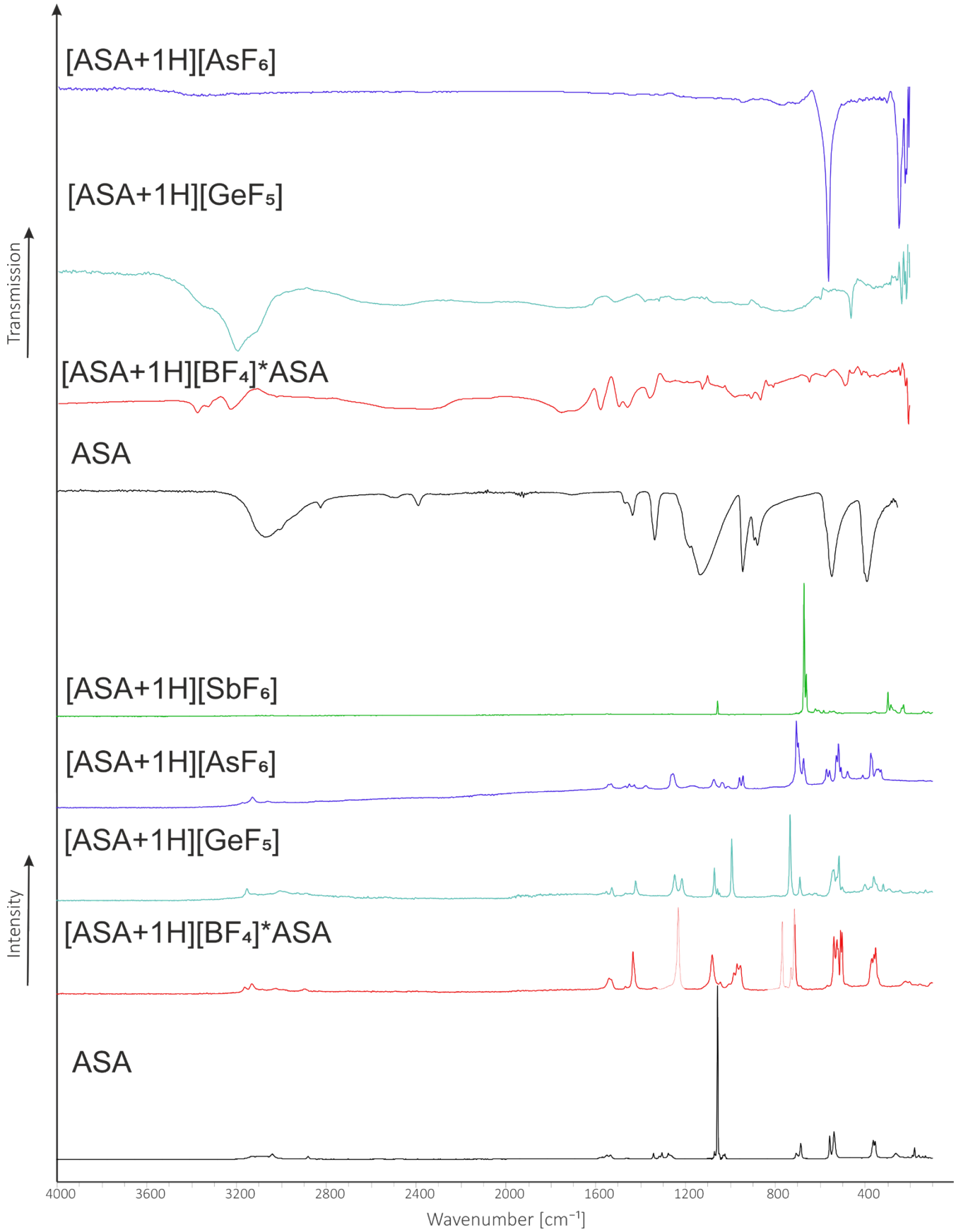

Figure S7. Low-temperature IR and Raman spectra ASA (**1**) and protonated species (**2–5**).

4 NPA charges

4.1 ASA

Atom	Charge
H6	0.434
H7	0.435
H8	0.433
N5	-0.910
S1	2.376
O2	-0.927
O3	-0.923
O4	-0.917

4.2 $[ASA+1H]^+$

Atom	Charge
H6	0.472
H7	0.465
H8	0.455
H9	0.564
N5	-0.902
S1	2.395
O2	-0.791
O3	-0.804
O4	-0.856

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