



Accepted Article

Title: The Influence of the Counterions [AsF6]⁻ and [GeF6]2⁻ on the Structure of the [CISO2NH3]⁺ Cation

Authors: Dominik Leitz, Karin Stierstorfer, Yvonne Morgenstern, Florian Zischka, and Andreas J. Kornath

This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: Z. anorg. allg. Chem. 10.1002/zaac.201800067

Link to VoR: http://dx.doi.org/10.1002/zaac.201800067

WILEY-VCH

www.zaac.wiley-vch.de

FULL PAPER

WILEY-VCH

The Influence of the Counterions $[AsF_6]^-$ and $[GeF_6]^{2-}$ on the Structure of the $[CISO_2NH_3]^+$ Cation

Dominik Leitz,^[a] Karin Stierstorfer,^[a] Yvonne Morgenstern,^[a] Florian Zischka^[a] and Andreas J. Kornath^{[a]*}

Abstract: Chlorosulfonamide reacts in the superacidic solutions HF/GeF_4 and HF/AsF_5 under the formation of $([CISO_2NH_3]^*)_2[GeF_6]^{2^-}$ and $[CISO_2NH_3]^*[AsF_6]^-$, respectively. The chlorosulfonamonium salts were characterized by X-ray single crystal structure analysis as well as vibrational spectroscopy and discussed together with quantum chemical calculations. $([CISO_2NH_3]^*)_2[GeF_6]^{2^-}$ crystallizes in the triclinic space group P-1 with one formula unit in the unit cell. $[CISO_2NH_3]^*[AsF_6]^-$ crystallizes in the monoclinic space group $P_{2_1/n}$ with four formula units in the unit cell. Dependent on the counterion, $[AsF_6]^-$ or $[GeF_6]^{2^-}$, considerable structural differences of the $[CISO_2NH_3]^+$ cation are observed. Furthermore, the hitherto unknown X-ray single crystal structure of chlorosulfonamide is determined in the course of this study. Chlorosulfonamide crystallizes in the orthorhombic space group Pmc2 with four formula units per unit cell.

Introduction

Chlorosulfonamide is one of the simplest representatives of sulfonamides and was synthesized by Graf for the first time.^[1] The title compound is well characterized by vibrational^[2-3] and theoretical studies.^[4] However, surprisingly a single crystal X-ray diffraction study has not been reported so far. Despite the numerous studies on sulfonamide derivatives investigations of its protonation sites are rarely described in literature^[5-7] In these studies protonations at the nitrogen site are indicated which is in agreement with a theoretical study where it was confirmed that the nitrogen site is favorable to the protonation.^[8] In a previous study methanesulfonamide was investigated in the superacidic systems HF/MF₅ (M=As, Sb).^[9] It was found that the protonation takes place selectively at the nitrogen atom. Herein we present a study of chlorosulfonamide in the superacidic solutions HF/GeF4 and HF/AsF₅. While the superacidic system HF/AsF₅ is well established the superacidic system HF/GeF₄ is rarely described in literature. However, it showed an acidity beyond sulfuric acid and demonstrated an interesting structural versatility of the formed fluoridogermanate anions.^[10-11] We present the structural investigations of ([CISO₂NH₃]⁺)₂[GeF₆]²⁻ and [CISO₂NH₃]⁺[AsF₆]⁻ by vibrational spectroscopy and single-crystal X-ray structure analyses. Furthermore the structural influence of the counterions

*	Prof. Dr. A. Kornath
	*E-mail: andreas.kornath@cup.uni-muenchen.de
[a]	Department Chemie
	Ludwig-Maximilians-Universität München
	Butenandtstr. 5–13,
	81377 Munich, Germany

 $[AsF_6]^-$ and $[GeF_6]^{2^-}$ is discussed together with quantum chemical calculations.

Results and Discussion

Synthesis and Properties of $([CISO_2NH_3]^+)_2[GeF_6]^{2-}(I)$ and $[CISO_2NH_3]^+[AsF_6]^-(II)$. The salts (I) and (II) were obtained quantitatively according to Equation (1) and (2).

$$2 \operatorname{CISO}_2\operatorname{NH}_2 + \operatorname{GeF}_4 \xrightarrow{\operatorname{HF}} ([\operatorname{CISO}_2\operatorname{NH}_3]^+)_2[\operatorname{GeF}_6]^{2-1}$$

$$CISO_2NH_2 + AsF_5 \xrightarrow{HF} [CISO_2NH_3]^+ [AsF_6]^-$$

In the first step CISO₂NH₂ was synthesized in situ in an FEP reaction vessel. The synthesis was carried out by the reaction of chlorosulfuryl isocyanate and formic acid as described in a previous study.^[12] Then an excess of anhydrous HF (aHF), which serves as reagent as well as solvent, was condensed into the reaction vessel followed by three equivalents of GeF₄ or AsF₅, respectively. The reaction mixtures were allowed to warm up to -40° C and stored for 72 hours. Colorless crystals were obtained and characterized by single-crystal X-ray structure analyses and vibrational spectroscopy.

Crystal Structure of ([CISO₂NH₃]⁺)₂**[GeF₆]**^{2–}(**I**). In Table 1 bond lengths and bond angles are summarized. (**I**) crystallizes in the triclinic space group P–1 with one formula unit in the unit cell. Figure 1 depicts the formula unit of (**I**).



Figure 1. Formula unit of ([CISO₂NH₃]⁺)₂[GeF₆]^{2–}. (50% probability displacement ellipsoids). Symmetry code:.i = -x, 1-y,-z.

The coordination sphere of the sulfur atom can be described as a strong distorted tetrahedron. Compared to the neutral compound

FULL PAPER

the bond angles O1–S1–O2 [122.7(2)°] and Cl1–S1–O1 [108.6(1)°] are increased by approximately 2° and the bond angles Cl1–S1–N1 [99.6(1)°] and N1–S1–O1 [107.2(2)°] are decreased by 7.2° and 1.8°, respectively. The S–Cl bond length of 1.956(1) Å is slightly shorter than the S–Cl bond in SO₂Cl₂ (1.980 Å).^[13] With 1.725(3) Å the S–N bond length is significantly elongated with respect to the starting material [1.571(4)/1.583(4) Å] and slightly shorter than the S–N bond in the CH₃SO₂NCl₂⁺ cation.^[14] The S–O bond lengths of 1.417(3) Å are comparable to the S–O bonds in SO₂Cl₂ (1.418 Å)^[13] In terms of the approximately octahedral [GeF₆]^{2–} anion the Ge–F bond lengths are in the range from 1.783(2) Å to 1.789(2) Å which is in accordance to a previous studies describing [GeF₆]^{2–}.^[10]

Crystal Structure of $[CISO_2NH_3]^+[AsF_6]^-$ (II). Bond lengths and bond angles are summarized in Table 1. (II) crystallizes in the monoclinic space group $P2_1/n$ with four formula units in the unit cell (Figure 2).



Figure 2. Asymmetric unit of $[CISO_2NH_3]^+[AsF_6]^-$. (50% probability displacement ellipsoids).

In comparison to (I) the distorted tetrahedral coordination of the sulfur atom is slightly different. The S–O bond lengths are slightly shorter whereas the S–N bond of 1.765(3) Å is significantly longer than in (I). Each cation is connected with two [AsF₆]⁻ anions by strong hydrogen bonds with N(–H)…F donor-acceptor distances of 2.894 Å and 2.953 Å, respectively. The cations are connected by N(–H)…O hydrogen bonds of donor-acceptor distances of 3.139(3) Å forming zig-zag chains.

Table 1. Selected bond lengths and bond angles of ([CISO_2NH_3]^+)_2[GeF_6]^{2-} and [CISO_2NH_3]^+[AsF_6]^-.

	[CISO ₂ NH ₃] ⁺		[CISO ₂ NH ₃] ⁺ ·	[CISO ₂ NH ₃] ⁺		
	[GeF ₆] ²⁻	[AsF ₆]⁻	HF			
	obsd.	obsd.	calcd. ^[a]	calcd. ^[a]		
Bond lengths	[Å]	1				
S1–O1	1.417(3)	1.406(2)	1.405	1.404		
S1-N1	1.725(3)	1.765(3)	1.820	1.854		
S1-CI1	1.956(1)	1.945(1)	1.964	1.959		
Bond angles [°]						
01-S1-02	122.7(2)	123.6(1)	126.3	126.3		

N1-S1-Cl1	99.6 (1)	100.3(1)	98.0	98.4	
01-S1-CI1	108.6(2)	111.0(1)	110.9	110.9	
01-S1-N1	107.2(2)	104.9(1)	102.6	102.8	

[a] Calculated at the PBE1PBE 6-311G++(3pd,3df) level of theory.

Crystal structure of CISO₂NH₂ (III). Single crystals of (III) were grown by slow evaporation of the solvent benzene in dynamic vacuum. The compound crystallizes in the orthorhombic space group Pmc2 with four formula units in the unit cell. Figure 3 shows a view of the two symmetrically independent molecules. Selected bond lengths and angles of (III) are summarized in Table 2.



Figure 3. Section of the crystal structure of CISO₂NH₂. (50% probability displacement ellipsoids). Symmetry codes: *i* : 1–x, y, z; *ii* : –x, y, z.

The S–Cl bond lengths of 2.018(1) and 2.014(3) Å, respectively, are in the range of regular S–Cl single bonds observed for SO₂Cl₂.^[13] The S–N bond distances of 1.571(4) Å and 1.583(4) Å, respectively, are in the region between regular S–N single and double bonds. The short S–N distance can be explained by $n_N \rightarrow \sigma^*_{(S-O)}$ and $n_N \rightarrow \sigma^*_{(S-N)}$ interactions where the molecule is predicted to provide 18 kJ/mol. This is in good agreement to a previous study where sulfamide was theoretically investigated.^[15] The S–O bonds of 1.424(2) Å and 1.425(2) Å are slightly longer than observed for the [CISO₂NH₃]⁺ cation.

Table 2. Selected bond lengths and bond angles of CISO ₂ NH ₂ .						
Bond lengths [Â]						
	obsd.	calcd. ^[a]				
S1_01 / S2_02	1 424(2) / 1 425(2)	1 4 1 6				
01 01/02 02	1.424(2) / 1.423(2)	1.410				
S1-N1 / S2-N2	1.571(4) / 1.583(4)	<mark>1.617</mark>				
S1-Cl1 / S2-Cl2	2.018(1) / 2.014(1)	<mark>2.052</mark>				

FULL PAPER

Bond angles [°]		
01-S1-01 / 02-S2-02	120.7(1) / 119.8(1)	<mark>123.8</mark>
01-S1-N1 / 01-S1-N1	109.0(1) / 108.9(1)	<mark>107.8</mark>
O1-S1-Cl1 / O2-S2-Cl2	105.3(1) / 105.8(1)	<mark>105.7</mark>
N1-S1-Cl1 / N2-S2-Cl2	106.8(1) / 106.9(1)	<mark>104.4</mark>

[a] Calculated at the PBE1PBE 6–311G++(3pd,3df) level of theory.

Figure 4 shows the crystal packing of CISO₂NH₂ molecules connected by strong donor-acceptor interactions (N(–H)…O) of 2.926(3) Å and 2.952(3) Å, respectively, forming 14-membered rings.



Figure 4. Crystal packing of $CISO_2NH_2$ (50% probability displacement ellipsoids). View along the b axis. Hydrogen bonds are represented by dashed lines.

Vibrational Spectroscopy of $([CISO_2NH_3]^+)_2[GeF_6]^{2^-}$ (I) and $[CISO_2NH_3]^+[AsF_6]^-$ (II). The Raman and infrared spectra of (I) and (II) are shown in Figure 5. In Table 3 the observed and quantum-chemically calculated frequencies are summarized. For $(CISO_2NH_3]^+$ with approximately C_s symmetry 18 fundamental vibrations are expected. The assignment of the vibrational frequencies is supported by quantum chemical calculations of $[CISO_2NH_3]^+$.HF. As expected, in case of the protonated species three NH stretching vibrations are observed which occur in the range from 3171 cm^{-1} to 2828 cm^{-1} and are significantly redshifted by approximately 200 cm^{-1} compared to the neutral compound. In the IR spectra of (I) and (II) at 1726 cm^{-1} a

combination band of v_5+v_8 is observed. At 1550 cm⁻¹ (I) a NH deformation mode is detected. The antisymmetric SO₂ stretching mode is observed at around 1450 cm⁻¹. the symmetric SO₂ stretching mode is splitted due to Fermi resonance and occurs at around 1215 cm⁻¹ and 1190 cm⁻¹, respectively. The SN stretching vibration occurs at around 485 cm⁻¹ and is red-shifted by 435 cm⁻¹ compared to the neutral compound. This remarkable shift can be explained by the significant elongation of the SN bond length. As expected for the almost ideal octahedral [GeF₆]²⁻ anion three Raman lines and two IR bands are observed. In case of the [AsF₆]⁻ more lines and bands than expected are detected which can be explained by the distortion of the octahedral structure according to the findings in the crystal structure.



Figure 4. Low temperature vibrational Spectra of $([CISO_2NH_3]^*)_2[[GeF_6]^{2-}: (a) IR spectrum, (d) Raman spectrum; <math>[CISO_2NH_3]^*[AsF_6]^-: (b)$ IR spectrum, (c) Raman spectrum; $CISO_2NH_2: (e)$ Raman spectrum.

FULL PAPER

$([CISO_2NH_3]^+)_2[GeF_6]^{2-}$		[CISO	2NH3]⁺[AsF6]⁻	[CISO ₂ NH ₃] ⁺	[CISO ₂ NH ₃]⁺·HF	Assigr	ment	¥
(a) IR	(d) Raman	(b) IR	(c) Raman	calcd. ^[a]	calcd. ^[a]			
3146 (m)			3171 (1)	3514 (145/22)	3519 (134/21)	V12	A"	$v_{as}(NH_2)$
3048 (m)			3085 (4)	3492 (142/29)	3446 (134/48)	ν ₁	A'	$v_{iph}(NH_3)$
2828 (m)	2828 (5)	2828 (m)		3389 (138/93)	3163 (948/143)	ν2	A'	$v_{\text{ooph}}(NH_3)$
1726 (w)		1726 (w)				$\nu_5 + \nu_8$		
1550 (w)				1612 (39/3)	1620 (30/2)	V13	A"	δ (NH ₂)
		1528 (m)	1528 (2)	1610 (35/3)	1608 (169/2)	V3	A'	δ (NH ₂)
1458 (w)	1455 (9)	1451 (m)	1460 (14)	1548 (165/7)	1541 (168/7)	V14	A"	vas(SO ₂)
1426 (s)				1404 (162/0)	1450 (144/1)	V4	A'	δ (NH ₂)
1218 (w)	1215 (1)	1216 (m)	1207 (33)	1264 (122/21)	1262 (120/21)	ν ₅	A'	vs(SO ₂)
1193 (m)	1190 (27)	1184 (m)	1188 (10)					
1062 (vw)	1068 (17)	1066 (m)	1068 (24)	943(60/2)	1009 (39/2)	V ₆	A'	ρ (NH ₃)
1016 (w)			1012 (1)	936 (11/2)	973 (8/2)	V15	A"	τ (NH ₂)
562 (w)	560 (3)		562 (4)	596 (154/4)	618 (165/3)	V7	A'	δ (SO ₂)
				569 (90/10)	592 (87/13)	V8	A'	δ (CISO)
485 (w)	486 (12)	484 (w)	484 (14)	448 (5/13)	469 (27/8)	V9	A'	v (SN)
	420 (100)		421 (100)	417 (2/7)	421 (1/9)	V10	A'	v (SCI)
438 (w)				351 (0/2)	361 (1/2)	V16	A"	δ (NSO)
				281 (6/2)	285 (27/2)	V17	A"	τ (SO ₂)
			198 (2)	233 (11/2)	273 (15/2)	V11	A'	δ (CISN)
				162 (0/0)	162 (4/1)	V ₁₈	Α"	δ (NH ₃)
			716 (14)					v[MF ₆]⁻
596 (vs)	605 (15)	700 (s)	697 (9)	1				ν[MF ₆]⁻
			688 (4)					v[MF ₆]⁻
		587 (m)	584 (33)					v[MF ₆]⁻
		391 (m)	401 (5)					δ[MF ₆]⁻
508 (w)	219 (2)		275 (6)					δ[MF ₆]⁻
	126 (28)		248 (1)					δ[MF ₆]⁻
								δ[MF ₆]⁻

Table 3. Observed vibrational frequencies $[cm^{-1}]$ of $([CISO_2NH_3]^+)_2[GeF_6]^2^-$, $[CISO_2NH_3]^+[AsF_6]^-$ and calculated vibrational frequencies $[cm^{-1}]$ of $[CISO_2NH_2]^+$ HF.

[a] Calculated at the PBE1PBE/6-311G++(3pd,3df) level of theory. IR intensity in km·mol⁻¹ and Raman intensities in Å⁴·μ⁻¹. Abbrevations for IR intensities: v=very, s=strong, m=medium, w=weak. Raman activity is normalized in which the most Raman active mode is normalized to be 100. M= Ge; As

Theoretical Calculations. Quantum chemical calculations were carried out using the hybrid DFT method PBE1PBE employing the 6–311G++(3pd,3df) basis set. To support the vibrational spectroscopic investigations of the [CISO₂NH₃]⁺ cation the frequencies were calculated in harmonic approximation. [CISO₂NH₃]⁺ was calculated as free cation as well as HF adduct in the gas phase. Especially in case of the NH stretching vibrations the calculated frequencies summarized in Table 3. From Table 1 it can be assumed that the cationic structure is stronger influenced by [GeF₆]^{2–} than by [AsF₆][–] due to the closer

match of the structural parameters for the calculated $[\text{CISO}_2\text{NH}_3]^+$ cation. This finding prompted us to a further theoretical investigation on the M06/aug-cc-pVTZ level of theory including all anions showing contacts to the cation. Therefore the units $([\text{CISO}_2\text{NH}_3^+])_2[\text{GeF}_6]^{2^-}$ and $[([\text{CISO}_2\text{NH}_3]^+([\text{AsF}_6]^-)_2]^-$ were calculated using the structural parameters observed in the crystal structures (Figure 5). A comparison of the calculated and the observed bond angles and bond lengths is given in Table 3. The quantum chemical calculations support the hypothesis that the cationic structure of $[\text{CISO}_2\text{NH}_3]^+$, especially the S–N bond, is remarkably influenced depending on the counterion.

FULL PAPER

elongation of the sulfur-nitrogen bond. It was found that depending on the counterion the sulfur-nitrogen bond is significantly different, 1.725(3) Å in (I) and 1.765(3) Å in (II). Quantum chemical calculations involving all interacting anions confirm the significant influence of the counterions on the structure of the [CISO₂NH₃]⁺ cation.

Experimental Section

Caution! Avoid contact with any of these materials. HCl and HF are formed through hydrolysis of these compounds, respectively. HF burns skin and causes irreparable damage. Safety precautions should be taken when using and handling these materials.

Apparatus and Materials. All experimental work was carried out by using standard Schlenk techniques using a stainless-steel vacuum line. The reactions were performed in FEP/PFA reactors which were closed with a stainless-steel valve. Data collections for (I) and (II) were performed with an Oxford Xcalibur3 diffractometer equipped with a Spellman generator (voltage 50 kV, current 40 mA) and a KappaCCD detector, operating with MoK α radiation (λ =0,717 Å). Data collection was performed at 173(2) K using the CrysAlisCCD software, the data reductions were carried out using CrysAlis RED software.^[16] The solution and refinement of the structure was performed with the programs SHELXL^[17] and SHELXS-97^[18] implemented in the WinGX software package^[19] and checked with the software PLATON.^[20] The absorption correction was achieved with the SCALE3 ABSPACK multi-scan method.^[21] Infrared spectra were recorded in the range between 4000 cm⁻¹ and 350 cm⁻¹ at a temperature of -196°C using a Bruker Vertex 70V FTIR spectrometer. The Raman spectroscopic studies were carried out with a Bruker MultiRAM which is equipped with a Nd:YAG laser (λ =1064 nm). The spectra were recorded in a range between 4000 cm⁻¹ and 250 cm⁻¹. Quantum chemical calculations were carried out with the Gaussian 09 program package.^[22] All calculations were performed employing the hybrid method PBE1PBE and the base set 6-311++G(3df,3pd). CISO₂NCO (Sigma Aldrich) was distilled several times prior to use. HCOOH was dried over B_2O_3 . GeF₄ and AsF₅ were synthesized from the elements and purified by fractionated distillation.

Synthesis of CISO₂NH₂. An amount of 3.59 g (25.3 mmol) CISO₂NCO was stirred at 0°C and 1.16 g (0.95 ml, 25.3 mmol) dry HCOOH was added dropwise to the reaction vessel under dry nitrogen atmosphere. A colorless solid was formed rapidly under gas formation.

Syntheses of ([CISO₂NH₃]⁺)₂[GeF₆]²⁻ (I) and [CISO₂NH₃]⁺[AsF₆]⁻ (II). For the syntheses of (I) and (II) in the first step CISO₂NH₂ was synthesized through the reaction of equimolar amounts (in a typical reaction each 1.0 mmol) of CISO₂NCO and HCOOH were condensed in an FEP reactor and allowed to warm up to 0°C. The formed colorless solid was then dried overnight in dynamic vacuum. In the second step an excess of HF followed by 3 equivalents of GeF₄ (I) or AsF₅ (II) were condensed at -196° C into the FEP reaction vessel. The mixture was then allowed to warm up to -40° C and was stored for 72 hours at this temperature. Colorless crystals precipitated during this time. Excess GeF₄ and AsF₆, respectively, as well as HF were removed in dynamic vacuum at -78° C for a time period of 14 hours.



Table 3. Comparison of the observed and calculated bond lengths and
bond angles of ([CISO ₂ NH ₃] ⁺) ₂ [GeF ₆] ²⁻ and [CISO ₂ NH ₃] ⁺ [AsF ₆] ⁻ .

	([CIS	O ₂ NH ₃] ⁺) ₂	[CIS	O₂NH₃]⁺·
	[GeF ₆] ²⁻		[A	\sF ₆]⁻
	obsd.	calcd. ^[a]	obsd.	calcd. ^[a]
Bond lengths	[Å]			/ /
S1–O1	1.417(3)	1.421	1.406(2)	1.420
S1–N1	1.725(3)	1.733	1.765(3)	1.781
S1–Cl1	1.956(1)	2.023	1.945(1)	2.022
Bond angles [°]				
01-S1-O2	122.7(2)	124.4	123.6(1)	126.1
01-S1-N1	107.2(2)	106.5	104.9(1)	107.5
01-S1-Cl1	108.6(2)	109.1	111.0(1)	107.9
N1-S1-Cl1	99.6 (1)	97.9	100.3(1)	96.7

[a] Calculated at the M06/aug-cc-pVTZ level of theory.

Conclusions

In the course of this study salts containing the $[CISO_2NH_3]^+$ cation were isolated for the first time using the two binary superacidic systems HF/GeF₄ and HF/AsF₅, respectively. ($[CISO_2NH_3]^+$) $_2[GeF_6]^{2-}$ and $[CISO_2NH_3]^+[AsF_6]^-$ are characterized by single-crystal X-ray structure analyses and low temperature vibrational spectroscopy supported by quantum chemical calculations. The protonation takes selectively place at the nitrogen atom and leads in both cases to a significant

This article is protected by copyright. All rights reserved.

FULL PAPER

Table 4. Crystal data and structure refinement for ([CISO_2NH_3]^+)_2[GeF_6]^- and [CISO_2NH_3]^+[AsF_6]^-

Empirical formula	([CISO₂NH₃]⁺)₂ [GeF ₆]²⁻	[CISO₂NH₃]⁺ [AsF ₆]⁻	CISO ₂ NH ₂
Mr	419.68	305.46	115.54
т [К]	173(3)	123(2)	173(2)
λ (Mo- <i>K</i> α) [Å]	0.71073	0.71073	0.71073
Crystal system	triclinic	monoclinic	orthorhombic
Space Group	<i>P</i> –1	<i>P</i> 2 ₁ /n	Pmc2
a [Å]	5.5686(4)	4.9653(3)	7.7652(6)
b [Å]	5.5718(5)	7.4256(4)	5.7998(4)
c [Å]	10.883(1)	19.3595(1)	8.7627(6)
α [°]	82.637(8)	90	90
β[°]	86.425(7)	90.741(5)	90
γ [°]	61.069(9)	90	90
V[Å ³]	293.09(4)	713.73(7)	394.64(5)
Z	1	4	4
ρ_{calcd} , [gcm ⁻³]	2.378	2.843	1.945
μ[mm ⁻¹]	3.508	5.507	1.313
λ _{Μοκα} [Å]	0.71073	0.71073	0.71073
F(000)	204	584	232
T[K]	173(2)	123(2)	173(2)
hkl range	-6:6;-6;6;- 13:10	-6:6;-10:10;- 26:25	-6:10;-7:7;-11:9
refl. measured	2160	6331	1778
refl. unique	1181	1920	871
Rint	0.0194	0.0337	0.0293
parameters	91	121	63
$R(F)/wR(F^2)^{a)}$	0.0290/0.0706	0.0325/0.0606	0.0334/ 0.0469
weighting scheme ^{b)}	0.0251/0.5437	0.0221/0.1433	0.0121/0.0000
S(GooF) ^{c)}	1.096	1.093	1.020
residual	0.559/0.576	0.416/-0.793	0.323/-0.271
device type	Oxford	Oxford	Oxford
solution/refinement	SHELXS-97 ^[18] SHELXL-97 ^[17]	SHELXS-97 ^[18] SHELXL-97 ^[17]	SHELXS-97 ^[18] SHELXL-97 ^[17]
CCDC	1574006	1574004	1574005

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) GoF = $\{\Sigma [w(F_0^2 - F_c^2)^2] / (n-p)\}^{1/2}$ (n = number of reflexions; p = total number of parameters).

Acknowledgements

[1] [2]

[3]

[4] [5]

[6]

[7]

[8]

[9]

[10] [11]

[12]

[13]

[14]

[15]

[16]

[17]

[18]

[19]

[20]

[21]

[22]

Financial support of this work by the Lududwig-Maximilian-University of Munich (LMU), by the Deutsche Forschungsgemeinschaft (DFG) and the F-Select GmbH is gratefully acknowledged.

Keywords: protonation • chlorosulfonamide • superacid chemistry• single-crystal structure• vibrational spectroscopy

R. Graf, Chem. Ber. 1959, 92, 509-513. W. Schneider, G. Kessler, H. A. Lehmann, Z. anorg.allg. Chem. **1968**, *356*, 239-243. R. M. S. Álverez, E. H. Cutín, H. G. Mack, C. O. D. Védova, *J. Mol.* Struct. 1998, 440, 213-219. H. M. Badawi, Spectrochim. Acta 2006, 65A, 453-458. F. M. Menger, L. Mandell, J. Am. Chem. Soc. 1967, 89, 4424-4426. R. G. Laughlin, J. Am. Chem. Soc. 1967, 89, 4268-4271. A. Bagno, G. Scorrano, J. Phys. Chem. 1996, 100, 1545-1553. B. A. Shainyan, N. N. Chipanina, L. P. Oznobikhina, J.Phys.Org. Chem. 2012, 25, 738-747. D. Leitz, M. Hopfinger, K. Stierstorfer, J. Axhausen, A. Kornath, Z. anorg. allg. Chem. 2017, 643, 1202–1207. T. Soltner, PhD Thesis 2011. M. Hopfinger, K. Lux, A. Kornath, ChemPlusChem 2012, 77, 476-481 R. Appel, G. Berger, *Chem. Ber.* **1958**, *91*, 1339-1341. D. Mootz, A. Merschenz-Quack, *Acta Cryst.* **1988**, *C44*, 924-925. R. Minkwitz, P. Garzarek, F. Neikes, A. Kornath, H. Preut, Z. anorg. allg. Chem. 1997, 623, 333-339. E. Hansen, E. Limé, P.-O. Norrby, O. Wiest, J. Phys. Chem 2016, A120, 3677-3682. CrysAlisRED, Version 1.171.35.11 (release 16-05-2011 CrysAlis 171.NET), Oxford Diffraction Ltd., UK, 2011. G. M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structures, University of Göttingen, Germany, 1997. G. M. Sheldrick, SHELXS-97, Program for Crystal Structure Solution, University of Göttingen, Germany, 1997. L. Farrugia, Journal of Applied Crystallography 1999, 32, 837-838. A. L. Spek, PLATON, A Multipurpose Crystallographic Tool, U. Utrecht University, The Netherlands, 1999., **1999**. SCALE3 ABSPACK, An Oxford Diffraction Program, O. Diffraction, Ltd., UK, 2005. H. B. S. G. W. T. M. J. Frisch, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J.A. Montgomery, T. V. Jr., K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian, Inc. 2003, Pittsburgh PA.

FULL PAPER

Entry for the Table of Contents

Layout 1:

FULL PAPER

The protonation of chlorosulfonamide in the binary superacidic systems HF/AsF_5 and HF/GeF_4 leads to the formation of salts containing the $[CISO_2NH_3]^+$ cation. The protonation causes a remarkable elongation of the S–N bond length which is furthermore influenced by the anions.



Protonated Chlorosulfonamide

Dominik Leitz, Karin Stierstorfer, Yvonne Morgenstern, Florian Zischka, Andreas Kornath*

Page No. – Page No.

The Influence of $[AsF_6]^-$ and $[GeF_6]^{2-}$ on the Structure of the $[CISO_2NH_3]^+$ Cation *