The Protonation of Dithiocarbamic Acid in Superacids HF/MF_5: Synthesis and Characterization of $H_2NC(SH)_2^+$ MF_6^- (M = As, Sb)

Joachim Axhausen, Geraldine Rühl and Andreas Kornath

Department Chemie, Ludwig-Maximilians-Universität München, Butenandtstrasse 5 – 13, 81377 München, Germany

Reprint requests to Prof. Dr. Andreas Kornath. Fax: +49-89-2180-77867.
E-mail: andreas.kornath@cup.uni-muenchen.de

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Dithiocarbamic acid reacts in the superacidic media HF/MF_5 (M = As, Sb) under formation of the corresponding salts $H_2NC(SH)_2^+$ MF_6^-. The colorless compounds are stable in an inert gas atmosphere up to −20 °C. The salts have been characterized by NMR, IR and Raman spectroscopy. Reactions in DF/AsF_5 were carried out to obtain $D_2NC(SD)_2^+$ AsF_6^- in order to confirm the assignments of the observed vibrational modes. Additionally, quantum-chemical calculations of the free cation, $[A_2NC(SA)_2]^+$ (A = H, D), and of the $[A_2NC(SA)_2(3HF)]^+$ unit on the PBE1BPE/6-311G(3df,3pd) level of theory are discussed.

Key words: Dithiocarbamic Acid, Superacids, Vibrational Spectroscopy, NMR Spectroscopy, Protonation

Introduction

The synthesis of dithiocarbamic acid from ammonia and carbon disulfide has been known since the 19th century [1 – 3]. The synthesis was improved in the 1960s by Gattow and Hahnkamm who also conducted extensive analyses of physical data [4 – 10]. Several dithiocarbamates are used in industrial applications, particularly the salts of ethylene bis(dithiocarbamate) with Na, Mn, Zn, Fe, and Cu, called Nabam, Maneb, Zineb, Ferbam or Cufraneb, are common fungicides in agriculture [11 – 14]. Compared with the unstable carbamic acid that immediately decomposes to carbon dioxide and ammonia [15, 16], dithiocarbamic acid decomposes much more slowly ($\tau_{1/2} = 15.7 \pm 0.3$ h) [5] at room temperature. The decomposition takes place according to Eqs. 1 and 2.

$$2\,H_2NC(S)SH \xrightarrow{20\,^\circ C} NH_4^+\,[SC(S)(NH_2)]^- + CS_2 \quad (1)$$

$$NH_4^+\,[SC(S)(NH_2)]^- \xrightarrow{20\,^\circ C} NH_4^+\,SCN^- + H_2S \quad (2)$$

With regard to protonated dithiocarbamic acid, only a few theoretical studies which predict a slightly higher proton affinity for the sulfur site than for the nitrogen site have been published [17, 18]. However, no experimental evidence for a protonated dithiocarbamic acid has been reported.

Results and Discussion

Synthesis and properties of $H_2NC(SH)_2^+$ MF_6^- (M = As, Sb)

The salts were prepared in quantitative yield in a two-step synthesis according to Eqs. 3 and 4. Dithiocarbamic acid was freshly prepared prior to use [4, 5].

$$2\,HF + MF_5 \xrightarrow{0\,^\circ C} H_2F^+\,MF_6^- \quad (M = \text{As, Sb}) \quad (3)$$

$$H_2NC(S)SH + H_2F^+\,MF_6^- \xrightarrow{-40\,^\circ C} H_2NC(SH)_2^+\,MF_6^- + HF \quad (M = \text{As, Sb}) \quad (4)$$

In the first step, the superacidic medium was formed to ensure the highest possible concentration of H_2F^+ MF_6^- (M = As, Sb) in a homogeneous HF solution. In the second step, dithiocarbamic acid was added to the frozen superacid. During the warm-up process up to −40 °C, dithiocarbamic acid dissolved

in the melting superacidic medium. After removal of solvent and excess reactants at −78 °C, the products $H_2NC(SH)_2^+ MF_6^-$ (M = As, Sb) were obtained as colorless powders. Both salts are stable up to −20 °C under an inert-gas atmosphere.

NMR spectra

$H_2NC(SH)_2^+ AsF_6^-$ was dissolved in sulfur dioxide and analyzed by NMR spectroscopy at −44 °C. The ^{1}H NMR spectrum shows two broad signals at 6.05 ppm (s, 2H, S*H*) and 8.95 ppm (s, 2H, NH_2), respectively. The ratio of both signal areas (integrals) is approximately 2 : 2. The ^{14}N NMR spectrum displays a peak of the NH_2 group at −233 ppm (s, *N*H_2). Furthermore, the F atoms of the hexafluoridoarsenate anion are detected at −59 ppm (s, As*F*$_6^-$) in the ^{19}F NMR spectrum.

Vibrational spectra of $H_2NC(SH)_2^+ SbF_6^-$, $H_2NC(SH)_2^+ AsF_6^-$, and $D_2NC(SD)_2^+ AsF_6^-$

The IR and Raman spectra of $H_2NC(SH)_2^+ SbF_6^-$, $H_2NC(SH)_2^+ AsF_6^-$, and $D_2NC(SD)_2^+ AsF_6^-$ are shown in Fig. 1. The observed frequencies are summarized in Tables 1 and 2. The vibrational modes were assigned by comparison with quantum-chemically calculated frequencies. The quantum-chemical calculations are discussed below. The symmetric and antisymmetric NH_2 stretching vibrations are detected in the IR spectra as broad bands at 3338 and 3108 cm^{-1} (AsF_6^-) and at 3299 and 3127 cm^{-1} (SbF_6^-). The SH stretching vibrations occur in the IR spectra as weak broad bands at 2564 (AsF_6^-) and 2595 cm^{-1} (SbF_6^-), whereas the Raman spectra display an intensive line at 2602 cm^{-1} and a weaker line at 2573 cm^{-1}, respectively. In the case of $H_2NC(SH)_2^+ AsF_6^-$, only one SH stretching vibration at 2568 cm^{-1} is observed. In order to confirm the protonation, the synthesis was carried out in DF/AsF_5 to obtain the deuterated isotopomers. The frequencies are summarized in Table 2. In accordance with the Teller-Redlich rule [19], the ν(SD) modes are observed in the region around 1800 cm^{-1}. The CN and CS stretching vibrations are strongly coupled with the deformation vibrations of the NH_2 group. The deformation vibrations were assigned in accordance with the theoretical calculations.

For hexafluoridoarsenate and hexafluoridoantimonate anions with an ideal O_h symmetry five vibrations are expected to which the mutual exclusion rule applies. In the case of $H_2NC(SH)_2^+ AsF_6^-$, five vibrations are observed in the expected regions. For $D_2NC(SD)_2^+ AsF_6^-$ and $H_2NC(SH)_2^+ SbF_6^-$, only the most intense vibrational modes are observed, and these all obey the mutual exclusion rule. Therefore, there is no evidence for a lowering of the symmetry of the MF_6^- octahedra.

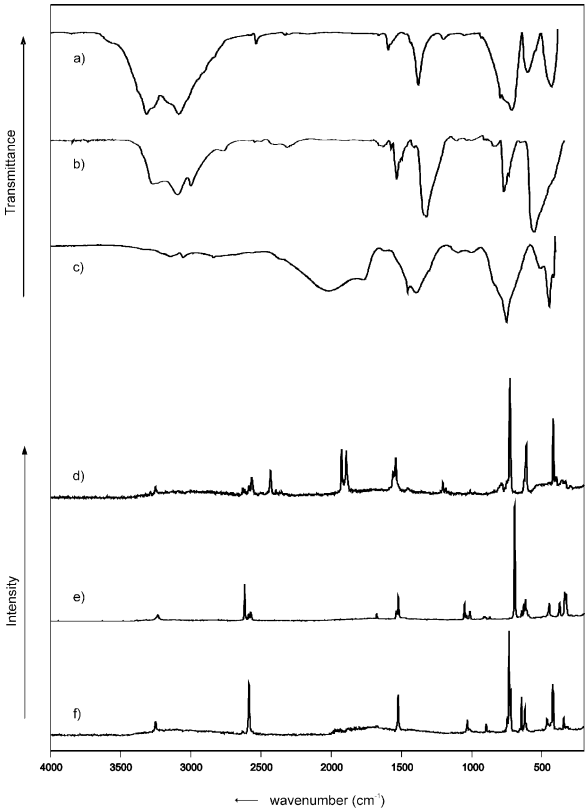

Fig. 1. Low-temperature vibrational spectra: $[H_2NC(SH)_2]^+$ $[AsF_6]^-$ (a) IR and (f) Raman; $[H_2NC(SH)_2]^+$ $[SbF_6]^-$ (b) IR and (e) Raman; $[H_2NC(SD)_2]^+$ $[AsF_6]^-$ (c) IR and (d) Raman.

Theoretical calculations

Structure optimizations of $[H_2NC(SH)_2]^+$ and $[D_2NC(SD)_2]^+$ were performed with the PBE1PBE method using the 6-311G(3df,3pd) basis set. Subsequently, vibrational frequencies in the harmonic approximation as well as IR and Raman intensities were calculated. Our previous studies on comparable molecules have shown that the method is suitable for such cations [20 – 22]. Because of a large overestima-

Table 1. Experimental vibrational frequencies (cm^{-1}) of $[H_2NC(SH)_2]^+$ $[MF_6]^-$ (M = As, Sb) and calculated vibrational frequencies (cm^{-1}) of $[H_2NC(SH)_2(3HF)]^+$.

$H_2NC(SH)_2^+$ AsF_6^-		$H_2NC(SH)_2^+$ SbF_6^-		$[H_2NC(SH)_2(3HF)]^+$		Assignment
IR	Raman	IR	Raman	calcd.[a]	(IR/Raman)	
3338 vs, br		3299 s, br		3422	(469 / 69)	$\nu_{as}(NH_2)$
3108 vs, br	3243 (13)	3127 s, br	3230 (6)	3299	(519 / 125)	$\nu_s(NH_2)$
2564 w	2568 (48)	2595 w	2602 (32)	2541	(55 / 141)	ν(SH)
			2573 (4)	2512	(230 / 141)	ν(SH)
1641 w			1649 (5)	1616	(135 / 4)	$\delta(NH_2)$
1431 m	1490 (38)	1490 vs, br	1492 (21)	1459	(90 / 18)	ν(CN) + $\delta(NH_2)$
1252 w		1248 vw		1254	(89 / 0)	$\delta(NH_2)$
	990 (13)		1014 (14)	983	(32 / 9)	δ(CSH)
			974 (8)	961	(2 / 5)	δ(CSH)
853 s, sh	854 (9)	870 s	873 (4)	851	(63 / 2)	ν(CS) + $\delta(NH_2)$
			832 (3)	701	(75 / 0)	$\delta(NH_2)$
				655	(61 / 0)	$\delta(NH_2)$
	599 (34)		603 (9)	592	(13 / 15)	δ(SCS)
				540	(11 / 0)	$\delta(NCS)_{oop}$
				419	(22 / 3)	$\delta(NCS)_{ip}$
	414 (8)		403 (15)	416	(3 / 1)	δ(CSH)
			329 (15)	294	(36 / 1)	δ(CSH)
	293 (11)		293 (24)	285	(41 / 1)	δ(SCS)
664 vs, br	689 (100)	658 vs, br	651 (100)	}		
	575 (21)		575 (18)	}	$[MF_6]^-$	(M = As, Sb)
395 s	373 (44)			}		

[a] Calculated at the PBE1PBE/6-311G(3df,3pd) level of theory; frequencies are scaled by a factor of 0.95; calculated IR intensities in km mol^{-1}; Raman activities in $Å^4$ μ^{-1} for calculated frequencies and in % for experimental frequencies.

Table 2. Experimental vibrational frequencies (cm^{-1}) of $[D_2NC(SD)_2]^+$ $[AsF_6]^-$ and calculated vibrational frequencies (cm^{-1}) of $[D_2NC(SD)_2(3HF)]^+$.

$D_2NC(SD)_2^+$ AsF_6^-		$[D_2NC(SD)_2(3HF)]^+$		Assignment
IR[a]	Raman[a]	calcd.[b]	(IR / Raman)	
	(3244 (9))*	2538	(250 / 34)	$\nu_{as}(ND_2)$
(3042 w)*	2413 (21)	2388	(314 / 56)	$\nu_s(ND_2)$
2824 w				2x ν(CN)
1987 s, br	1899 (40) (2601 (3))*	1825	(27 / 71)	ν(SD)
	1865 (39) (2549 (16))*	1804	(112 / 69)	ν(SD)
1744 m, sh				
1054 w	1069 (13)	1142	(6 / 2)	$\delta(ND_2)$
(1420 s)*	1509 (33)	1484	(190 / 20)	ν(CN) + $\delta(ND_2)$
1355 s		1110	(107 / 1)	$\delta(ND_2)$
		727	(3 / 8)	δ(CSD)
		682	(18 / 2)	δ(CSD)
	744 (13)	763	(22 / 1)	ν(CS) + $\delta(ND_2)$
		490	(32 / 0)	$\delta(ND_2)$
457 w, sh		469	(24 / 0)	$\delta(ND_2)$
		274	(62 / 1)	δ(SCS)
		570	(21 / 0)	$\delta(NCS)_{oop}$
		376	(19 / 3)	$\delta(NCS)_{ip}$
		560	(13 / 14)	δ(CSD)
		304	(6 / 0)	δ(CSD)
		274	(62 / 1)	δ(SCS)
703 vs, br	686 (100)	}		
	566 (44)	}	$[MF_6]^-$	(M = As, Sb)
392 s	377 (64)	}		

[a] Frequencies marked with an asterisk (*) belong to a species with incomplete H/D exchange; [b] calculated at the PBE1PBE/6-311G(3df,3pd) level of theory; frequencies are scaled by a factor of 0.95; calculated IR intensities in km mol^{-1} and Raman activities in $Å^4$ μ^{-1} for calculated frequencies and in % for experimental frequencies.

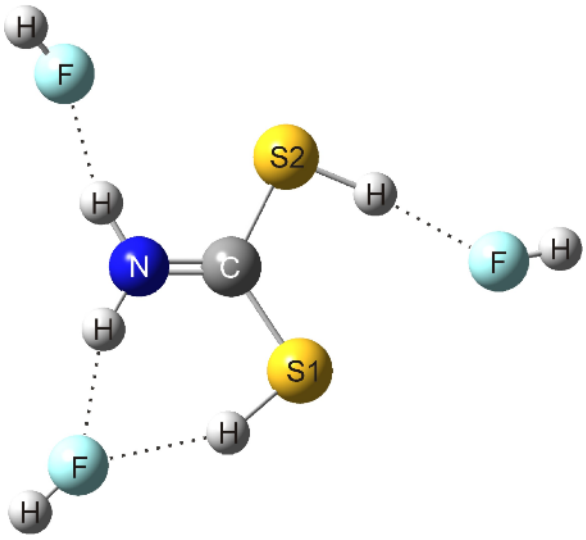

Fig. 2 (color online). Calculated structure of the $[H_2NC(SH)_2(3HF)]^+$ unit.

tion (350 cm^{-1}) of the calculated stretching vibrations $\nu_s(NH_2)$ at 3682 cm^{-1} and $\nu_{as}(NH_2)$ at 3566 cm^{-1}, as well as of both ν(SH) at 2703 and 2687 cm^{-1} compared to the observed frequencies, we assumed that the discrepancies are a result of strong hydrogen bonds in the condensed phase. To simulate this donor-acceptor interaction, three HF molecules were added to the free cation. The resulting $[H_2NC(SH)_2(3HF)]^+$ (Fig. 2) and $[D_2NC(SD)_2(3HF)]^+$ units were again optimized with the PBE1PBE method using the 6-311G(3df,3pd) basis set. This caused only minor changes in geometry as compared to the naked cation (Table 3), but the previously overestimated frequencies of the stretching vibrations shifted remarkably toward the experimental values. Although the addition of HF molecules is a very simple model to simulate interionic interactions, it leads to a satisfactory agreement of calculated and observed frequencies.

For the $[H_2NC(SH)_2(3HF)]^+$ cation, a C–N bond length of 1.306 Å has been calculated. This value is between a typical single C–N (1.47 Å) and double C=N (1.22 Å) bond [23]. An analogous trend is observed for the C–S1 (1.71 Å) and C–S2 (1.72 Å) bonds. Both bonds have a C–S distance between a typical single C–S (1.81 Å) and double C=S (1.61 Å) bond [23]. The N and S atom of the $[H_2NC(SH)_2]^+$ cation are in a planar arrangement around the C atom. This is in accordance with the well-known amino resonance.

Table 3. Calculated distances (Å) and angles (deg) of the free $[H_2NC(SH)_2]^+$ cation and the $[H_2NC(SH)_2(3HF)]^+$ unit.

	$[H_2NC(SH)_2(3HF)]^+$ PBE1PBE 6-311G(3df,3dp)	$[H_2NC(SH)_2]^+$ PBE1PBE 6-311G(3df,3dp)
N–H	1.016 / 1.012	1.011 / 1.009
N–C	1.306	1.310
C–S1	1.715	1.710
C–S2	1.717	1.716
S1–H	1.348	1.347
S2–H	1.350	1.345
C–N–H	120.4 / 121.1	121.3 / 122.0
H–N–H	118.4	116.7
N–C–S1	123.3	123.8
N–C–S2	118.2	117.7
C–S1–H	96.3	97.3
C–S2–H	96.0	95.9

Conclusion

Two salts of the protonated form of dithiocarbamic acid, $H_2NC(SH)_2^+$ SbF_6^- and $H_2NC(SH)_2^+$ AsF_6^-, were prepared and identified for the first time. The colorless compounds are stable under inert gas conditions up to −20 °C. The synthesis was successful in the reaction of freshly prepared dithiocarbamic acid in the superacidic media HF/MF_5 (M = As, Sb). NMR, IR and Raman spectroscopy were employed at low temperatures to characterize the salts. In order to confirm the assignments of the observed vibrational modes, the isotopomer $D_2NC(SD)_2^+$ AsF_6^- was prepared with DF/AsF_5. Quantum-chemical calculations of the free cation $[A_2NC(SA)_2]^+$ (A = H, D) on the PBE1BPE/6-311G(3df,3pd) level of theory did not describe the vibrational spectra precisely enough. To include interionic interactions, a $[A_2NC(SA)_2(3HF)]^+$ model was calculated which led to a satisfactory agreement between calculated and observed vibrational frequencies.

Experimental Section

General

Caution! Avoid contact with any of these reagents and products. Note that hydrolysis of the salts might form HF which burns skin and causes irreparable damage. Appropriate safety precautions should be taken when using and handling these materials.

Apparatus and materials

Synthesis and sample handling was performed by employing standard Schlenk techniques using a stainless-steel vacuum line. Superacid reactions were carried out in FEP/PFA

ampoules which were closed by stainless-steel valves. All reaction vessels and the stainless-steel line were dried with fluorine prior to use. For NMR measurements, slim FEP tubes (external diameter 3 mm) were used and sealed after filling. These sealed tubes were inserted into a glass NMR tube containing about 0.1 mL [D_6]acetone which was used as external standard and lock substance [24]. For IR measurements, a cooled cell with a single-crystal CsBr plate coated with a small amount of the sample was used. IR spectra were recorded in the range between 350 and 4000 cm^{-1} at a temperature of −196 °C with a Bruker Vertex 70V FTIR spectrometer. Raman spectra were recorded in a glass cell cooled with liquid nitrogen with a Bruker MultiRAM FT-Raman spectrometer with Nd:YAG laser excitation up to 1000 mW (at 1064 nm) in the range between 250 and 4000 cm^{-1}. The NMR spectra were recorded with a Delta Jeol 400 ECX instrument at −44 °C.

Synthesis of $H_2NC(SH)_2^+$ SbF_6^-

Antimony pentafluoride SbF_5 (1.00 mmol, 217 mg) and anhydrous hydrogen fluoride HF (3 mL) were condensed into a reactor (FEP tube) at −196 °C. The reactor was warmed up to 0 °C in an ice bath for about 10 min to mix the components and form the superacid system. The reactor was then cooled to −196 °C, and dithiocarbamic acid CH_4NS_2 (1.00 mmol, 93 mg) was added under dry nitrogen atmosphere to the frozen superacid. Dithiocarbamic acid $H_2NC(S)SH$ was prepared as described by Gattow and Hahnkamm by addition of a stoichiometric amount of hydrochloric acid to the ammonium salt NH_4^+ $[SC(S)(NH_2)]^-$ [5]. The reaction mixture was warmed to −40 °C for 10 min and then cooled to −78 °C. Excess hydrogen fluoride was removed in dynamic vacuum at −78 °C. After 24 h, $[H_3C(COH)NH_2]^+$ $[SbF_6]^-$ was obtained as a colorless powder. The salt is stable up to −20 °C under an inert gas atmosphere.

Synthesis of $H_2NC(SH)_2^+$ AsF_6^- and $D_2NC(SD)_2^+$ AsF_6^-

Anhydrous hydrogen fluoride HF (3 mL) or deuterium fluoride DF (3 mL) and arsenic pentafluoride AsF_5 (1.50 mmol, 255 mg) were condensed into a reactor (FEP tube) at −196 °C. The reactor was warmed up to 0 °C in an ice bath for 10 min to mix the components and form the superacid system. The reactor was then cooled to −196 °C, and dithiocarbamic acid CH_4NS_2 (1.0 mmol, 93 mg) was added under dry nitrogen atmosphere to the frozen superacid. The reaction mixture was warmed to −40 °C for 10 min and then cooled to −78 °C. Excess hydrogen fluoride and arsenic pentafluoride were removed in a dynamic vacuum at −78 °C. After 24 h, $[H_2NC(SH)_2]^+$ $[AsF_6]^-$ (or $[D_2NC(SD)_2]^+$ $[AsF_6]^-$) was obtained as a colorless powder. The salt is stable up to −20 °C under an inert gas atmosphere. NMR spectra of $H_2NC(SH)_2^+$ AsF_6^-: ^{1}H NMR (400 MHz, SO_2, −44 °C): $\delta = 6.05$ (S, 2H, S*H*), 8.95 (s, 2H, NH_2). – ^{14}N NMR (29 MHz, SO_2, −44 °C): $\delta = -233$ (s, *N*H_2). – ^{19}F NMR (377 MHz, SO_2, −44 °C): $\delta = -59$ (s, AsF_6^-), −185 (s, H*F*).

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