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Fluorothiazynes, 50 years old and still exciting: electrophilic attack at the thiazyl nitrogen of $NSF_2NS(O)F_2$

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Dedicated to Professor Oskar Glemser on behalf of his 93rd birthday.

Abstract

One of the most interesting compounds in sulfur nitrogen fluorine chemistry is $N{\equiv}SF_2{-}N{=}S({=}O)F_2$ (**3**) (reported by Glemser and Höfer 30 years ago): in the NS backbone a triple and a double bond are connected by a single bond. Electrophiles (metal cations, fluoro Lewis acids, "CH_3^{+}") attack this multifunctional system exclusively at the thiazyl nitrogen of the triple bond. $[M(NSF_2NS(O)F_2)_4][AsF_6]_2$ (M = Ni (**4b**), Cu (**4c**)), $[Re(CO)_5(NSF_2NS(O)F_2)][AsF_6]^-$ (**5**), $F_5A{\cdot}NSF_2NS(O)F_2$ (A = As (**6**), Sb (**7**)), $F_3B{\cdot}NSF_2NS(O)F_2$ (**8**) and $[H_3CNSF_2NS(O)F_2]^+[AsF_6]^-$ (**9**) were isolated. The X-ray structures of **4c**, **6**, **8** and **9** are reported, bonding in these complexes is compared with the recently reported related $NSAr_2NS(X)Ar_2$ (X = O, NH) species.

Keywords: Thiazyl compounds; Thiazynes; Sulfur nitrogen multiple bonds; Electrophilic attack; Fluoro Lewis acids; Coordination compounds; Alkylation; X-ray structures

1. Introduction

From the reaction of S_4N_4 and AgF_2 almost 50 years ago Glemser and coworkers isolated thiazylfluoride N≡SF and thiazyltrifluoride $N{\equiv}SF_3$ [1], the first compounds outside carbon chemistry containing nonmetal triple bonds. These two compounds served as starting materials for a vast number of acyclic and cyclic inorganic, organic and organometallic sulfur nitrogen species [2]. Only specialists in a few laboratories were able to prepare these compounds [3], their chemistry being investigated by a very limited number of research groups. This might change because Yoshimura et al. reported a completely different easy route to diarylfluorothiazynes. From the reaction of *SS*-diaryl-*N*-bromosulfilimines Ar_2SNBr and tetra-*n*-butyl ammonium fluoride [4] and very recently from Ar_2SNH and Selectfluor [5] they obtained the corresponding diaryl fluoro thiazynes $N{\equiv}S(Ar)_2F$. Similar to NSF_3 the sulfur bonded fluorine is readily exchanged by nucleophiles. Structure determinations of $NS(Ar)_2F$ and of the products $N{\equiv}SAr_2R$ (R = Ph, OPr, $NSPh_2$) showed SN bond distances in the range 144–147 pm [6], not much longer than the SN bond distances reported for NSF_3 in the gas phase (141.6 pm) [7].

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As expected from theoretical calculations the shortest SN bond distance is found for NSF_3, due to negative hyperconjugation between n(N) and σ^*(S–F) [8]. Substitution of the sulfur bonded fluorines e.g. by alkyl, aryl, aryloxy or amino substituents should increase the SN and SF bond distances. Surprisingly the structure determination of $(–CH_2–N(CH_3)SF_2{\equiv}N)_2$ showed an SN bond distances of 141.2(2) pm [9], even shorter than the distance determined for NSF_3 in the gas phase. As expected the SF bond distance was elongated to 157.5(1) pm from 155.2(3) pm in NSF_3. This prompted us to investigate the structure of NSF_3 in the solid state (at 120(2) K), for which we determined $d(N{\equiv}S) = 139.9(3)$ pm and $d(SF) = 153.1(3)$ pm [9]. Even shorter NS and SF bonds were determined when NSF_3 and derivatives thereof act as ligands in coordination chemistry [10].

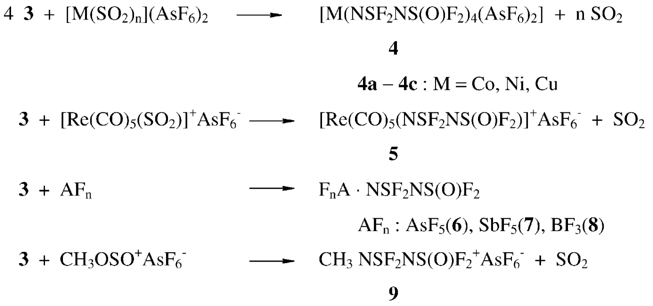
Substitution of the sulfur bonded fluorine, especially by *N*-substituents (e.g. NR_2, $NS(O)F_2$), increases the donor properties of the thiazyl nitrogen. Even dialkylation of NSF_2NMe_2 to give $Me_2NSF_2NMe_2^{2+}$ [11] is possible. An especially interesting chemistry is expected for $N{\equiv}SF_2–N{=}S(O)F_2$ [12], a NSF_3 derivative with a SN single, double and triple bond in one molecule, as we demonstrated recently by the structure determination of $[Co(N{\equiv}SF_2–N{=}S(O)F_2)_4][AsF_6]_2$ [13]. In the present paper we report on interactions of $N{\equiv}SF_2–N{=}S(O)F_2$ with metal cations, Lewis acids (AsF_5 and BF_3) and the alkylation with CH_3OSO^+ to give the corresponding complexes, adducts and salts. The structures of these compounds are described and the bonding properties will be compared with those of the related aryl system $N{\equiv}SPh_2–N{=}S(X)Ph_2$ (X = O, NH) [14,15] and $HN{=}SPh_2–N{=}S(X)Ph_2$ [15] recently reported by Yoshimura, Fujii et al.

2. Results and discussion

Glemser and coworkers showed that OSF_4 reacts with $Me_3SiN{=}SF_2{=}NSiMe_3$ (isolated from the reaction of NSF_3 with $LiN(SiMe_3)_2$ [16] to give $N{\equiv}SF_2–N{=}S(O)F_2$ (**3**), a colourless, extremely reactive liquid [12] (Scheme 1).

Similarly, the thermally rather unstable sulfur(IV)derivative $N{\equiv}SF_2–N{=}SF_2$ is prepared from **2** and SF_4 [17].

As mentioned in Section 1, the structure of **3** is of special interest because of the unusual bonding situation, According to the VB description, a SN triple and a SN double bond are connected by a SN single bond. Because of the low melting point of **3** an X-ray structure determination of this compound was not reported. In order to investigate the bonding situation, we introduced **3** as ligand into coordination and organometallic chemistry, we prepared adducts with Lewis acids and a cation by alkylation with $CH_3OSO^+AsF_6^-$ (Scheme 2).



$$4\ \mathbf{3} + [M(SO_2)_n](AsF_6)_2 \longrightarrow [M(NSF_2NS(O)F_2)_4(AsF_6)_2] + n\,SO_2$$

4

4a – **4c** : M = Co, Ni, Cu

$$\mathbf{3} + [Re(CO)_5(SO_2)]^+AsF_6^- \longrightarrow [Re(CO)_5(NSF_2NS(O)F_2)]^+AsF_6^- + SO_2$$

5

$$\mathbf{3} + AF_n \longrightarrow F_nA \cdot NSF_2NS(O)F_2$$

AF_n : AsF_5(**6**), SbF_5(**7**), BF_3(**8**)

$$\mathbf{3} + CH_3OSO^+AsF_6^- \longrightarrow CH_3\,NSF_2NS(O)F_2^+AsF_6^- + SO_2$$

9

Scheme 2.

Compounds **4–9** are thermally stable solids; they were characterised by spectroscopic methods (except **9**) and X-ray structure determinations (**4a**, **4c**, **6**, **8** and **9**). In a short communication, recently, we have already reported on the structure of **4a** [13].

Since a priori $N{\equiv}SF_2–N{=}S(O)F_2$ has to be considered as a multifunctional ligand, electrophilic attack at the thiazyl and at the imino nitrogen should be possible, the oxygen could act as donor, and even fluoride abstraction under formation of cationic species seemed to be not impossible. Hints for this variety come from our earlier results on the reaction of NSF_3 and its derivatives with various acceptors [2,10]; the nitrogen in $HNS(O)F_2$ [18] and $H_3CNS(O)F_2$ [19] is attacked by metal centers and Lewis acids, and $(CH_3)_2NSO_2F$ forms oxygen bonded adducts with Lewis acids [20]. AsF_5 possibly abstracts the fluoride ion from $(H_3CN{=})_2S(F)N(CH_3)_2$ [21].

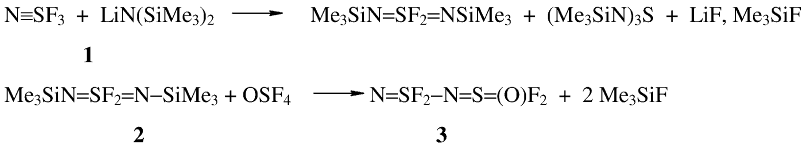
From ^{19}F NMR data we conclude that in the adducts described in this paper exclusively the thiazyl nitrogen is attacked (Table 1).

The chemical shifts of the fluorides at the $N{\equiv}SF_2$ group are displaced on adduct formation high field by 12–25 ppm while the fluorines of the $S(O)F_2$ group are almost not affected.

The IR data are a little confusing. Compared to the free ligand ($\nu_{S{\equiv}N} = 1482\ cm^{-1}$, gas phase) almost no shift is

Table 1
$\delta(^{19}F)$ for $NSF_2NS(O)F_2$ and adducts **5–8**

	$NSF_2NS(O)F_2$	**5**	**6**	**7**	**8**
$\delta(N{\equiv}SF_2)$	100.67	88.83	74.25	75.38	80.88
$\delta(S(O)F_2)$	47.5	47.83	49.22	49.4	48.35



$$N{\equiv}SF_3 + LiN(SiMe_3)_2 \longrightarrow Me_3SiN{=}SF_2{=}NSiMe_3 + (Me_3SiN)_3S + LiF, Me_3SiF$$

1

$$Me_3SiN{=}SF_2{=}N–SiMe_3 + OSF_4 \longrightarrow N{=}SF_2–N{=}S{=}(O)F_2 + 2\,Me_3SiF$$

2 **3**

Scheme 1.

Table 2
Crystal data and structure refinement for $[Cu(NSF_2NS(O)F_2)_4(FAsF_5)_2]$ (**4c**), $AsF_5{}^{\bullet}NSF_2NS(O)F_2$ (**6**), $BF_3{}^{\bullet}NSF_2NS(O)F_2$ (**8**), and $[CH_3{}^{-}NSF_2NS(O)F_2{}^{+}][AsF_6{}^{-}]$ (**9**)

	4c	**6**	**8**	**9**
Empirical formula	$As_2CuF_{28}N_8O_4S_8$	$AsF_9N_2OS_2$	$BF_7N_2OS_2$	$CH_3AsF_{10}N_2OS_2$
Formula weight	1177.94	354.06	251.95	388.09
Temperature	173(2) K	173(2) K	173(2) K	173(2) K
Wavelength	71.073 pm	71.073 pm	71.073 pm	71.073 pm
Crystal system	Tetragonal	monoclinic	monoclinic	monoclinic
Space group	$I4_1/a$	$P2_1/m$	$P2_1/m$	$P2_1/m$
Unit cell dimensions, *a* (pm)	1263.7(5)	585.0(1)	598.3(4)	648.8(7)
b (pm)	1263.7(5)	846.8(2)	780.3(5)	791.4(3)
c (pm)	1748.1(7)	902.5(1)	805.9(4)	1004.6(4)
β (°)	90°	108.90(1)	110.60(4)°	91.37(7)
Volume (nm^3)	2.7916(19)	0.42297(13)	0.3522(4)	0.5157(6)
Z	4	2	2	2
Density (calculated) (mg/m^3)	2.803	2.780	2.376	2.499
Absorption coefficient (mm^{-1})	3.955	4.643	0.853	3.833
$F(000)$	2252	336	244	372
Crystal size (mm^3)	0.6 × 0.5 × 0.4	0.4 × 0.4 × 0.3	0.7 × 0.3 × 0.3	0.6 × 0.5 × 0.2
Theta range for data collection	3.22–27.48	3.39–27.50	2.70–27.50	3.14–27.59
Index ranges	$-16 \leq h \leq 16$, $-16 \leq k \leq 16$, $-22 \leq l \leq 22$	$-7 \leq h \leq 7$, $-11 \leq k \leq 11$, $-11 \leq l \leq 11$	$-7 \leq h \leq 7$, $-8 \leq k \leq 10$, $-10 \leq l \leq 10$	$-1 \leq h \leq 8$, $-10 \leq k \leq 10$, $-13 \leq l \leq 13$
Reflections collected	11611	3626	2925	2742
Independent reflections	1557	1017 [R(int) = 0.0352]	831 [R(int) = 0.0630]	1208 [R(int) = 0.1086]
Completeness to theta (%)	97.2	98.4	95.1	93.6
Absorption correction	Empirical DIFABS	Empirical (DIFABS)	None	Empirical (DIFABS)
Max. and min. transmission	0.8888 and 0.8687	0.803 and 0.415	–	0.581 and 0.114
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	1557/0/117	1017/0/97	831/0/71	1208/0/94
Goodness-of-fit on F^2	1.133	1.364	1.109	1.075
Final R indices [$I > 2\text{sigma}(I)$]	$R_1 = 0.1075$, $wR2 = 0.2162$	$R_1 = 0.0534$, $wR2 = 0.1386$	$R_1 = 0.0559$, $wR2 = 0.1486$	$R_1 = 0.0668$, $wR2 = 0.1588$
R indices (all data)	$R_1 = 0.1099$, $wR2 = 0.2564$	$R_1 = 0.0543$, $wR2 = 0.1389$	$R_1 = 0.0594$, $wR2 = 0.1527$	$R_1 = 0.0862$, $wR2 = 0.1698$
Largest diff. peak and hole, e Å^{-3}	2.619 and −5.134 e Å^{-3}	1.702 and −0.963 e Å^{-3}	1.022 and −0.792 e Å^{-3}	1.218 and −1.196 e Å^{-3}

Details in common: Refinement method full-matrix least-squares on F^2 $\omega - 2\theta$ scans; Siemens P4 diffractometer; refinement based on F^2; $R_1 = \sum||F_o| - |F_c||\sum||F_o|$; $wR2 = \sum w(Fo2 - Fc2)/\sum w(Fo2)21/2$, Programs SHELX-97 [28] and DIAMOND [29].

observed in the AsF_5 and SbF_5 adducts (1481 and 1487 cm^{-1}, respectively) while for the BF_3 adduct a band at 1563 cm^{-1} (Raman) is assigned to $\nu_{S\equiv N}$.

In complexes **4a**–**4c**, ν_{SN} varies from 1495 (**4b**) over 1527 (**4c**) to 1563 cm^{-1} in **4e**, suggesting a different behaviour of the ligands to the different metal centers. The largest shift to higher wave numbers is observed for complex **5** (1603 cm^{-1}), for cation **9** no vibrational spectra were obtainable.

Possible explanations for the unexpected IR data are given by the structures of **4c**, **6**, **8** and **9** and of **4a**.

2.1. X-ray structure investigations of $[Cu(NSF_2NS(O)F_2)_4(AsF_6)_2]$ (**4c**), $F_5As{\cdot}NSF_2NS(O)F_2$ (**6**), $F_3B{\cdot}NSF_2NS(O)F_2$ (**8**), and $[H_3CNSF_2NS(O)F_2]^+(AsF_6)^-$ (**9**)

Single crystals suitable for X-ray structure investigations of **4c** and **9** were obtained by slow evaporation of CH_2Cl_2 solutions under vacuum at −30 °C, of **6** by evaporation of the SO_2 solvent at 25 °C and of **8** by vacuum sublimation. In Table 2 crystal data and details of the structure refinements for **4c**, **6**, **8**, and **9** are given. Figs. 1–4 show the X-ray structures of these compounds together with selected bond angles and bond distances.

As expected from the spectroscopic data the structure determinations show that in the complexes, adducts and in the salt exclusively the nitrogen of the NS triple bond is attacked. In all compounds the bond distances follow the order N(1)S(1) < N(2)S(2) < S(1)N(2). S(1)F is always longer than S(2)F, while the S(2)O bond distances (137.5–138.2 pm) almost do not vary in this series. Remarkable are the large differences in the ANS angles. This variation is independent of the class to which A belongs (metal center, fluoro Lewis acid, CH_3^+); in **4a** this angle is 24° larger than in **4c**,and in **6** this angle is 18° smaller than in **8**. According to Table 3 there is a direct correlation between the ANS angle and the distance N(1)S(1); with increasing angle a decreasing SN distance is observed. These distances also explain the unexpected IR- and Ra-data. The bonding situation and the variation of the bond distances can be described by the valence bond structures I–III (Scheme 3).

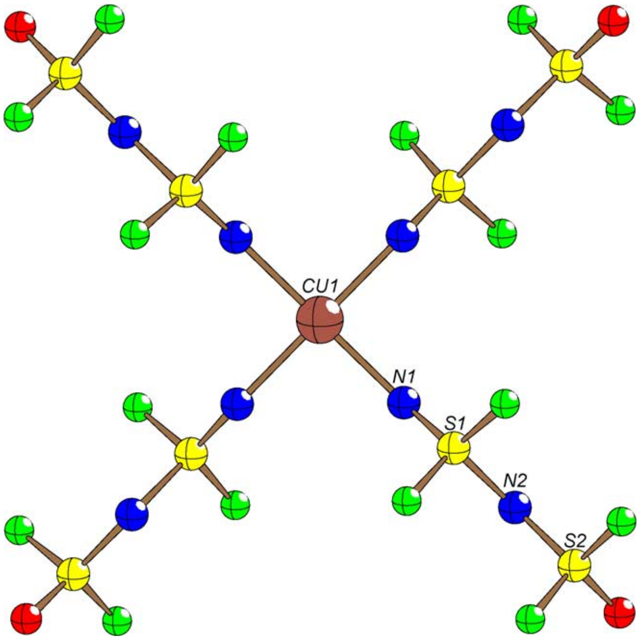


Fig. 1. Selected bond distances (pm) and bond angles (°) in **4c**. Cu1N1 195.2(12), N1S1 143.7(13), S1F1 155.9(12), S1F2 154.1(12), S1N2 155.3(12), N2S2 151.8(11), S2F3 150.5(11), S2F4 149.4(14), S2O1 138.3(14); CuN1S1 142.6(9), N1S1N2 115.7(7), S1N2S2 129.7(8).

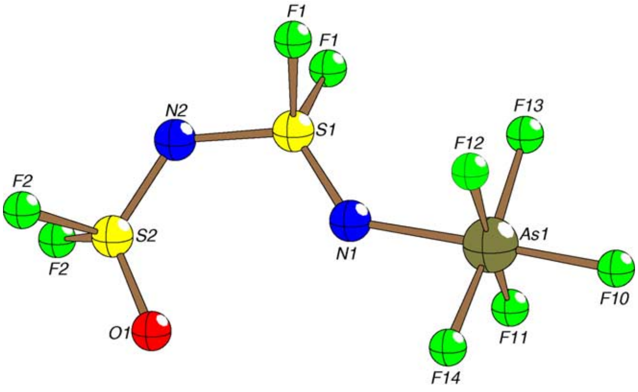


Fig. 2. Selected bond distances (pm) and bond angles (°) in **6**. AsN1 189.9(8), N1S1 143.0(8), S1F1 151.6(4), S1N2 156.7(8), N2S2 149.7(8), S2F2 148.5(5), S2O1 136.8(8); As N1S1 133.6(5), N1S1N2 119.7(4), S1N2S2 125.9(5).

A bonding situation similar to **3** is found in the corresponding aryl derivative $N{\equiv}SAr_2{-}N{=}S({=}O)Ar_2$ [15] and the electronically related imino derivative $N{\equiv}SAr_2{-}N{=}S({=}NH)Ar_2$ [15]. According to the X-ray structure of the latter compound three different types of SN-bonds are found for the N≡S–N=S backbone, the bond distances being in the region of SN triple, single and double bonds. Compared to **3** an increase of the SN bond lengths is expected due to

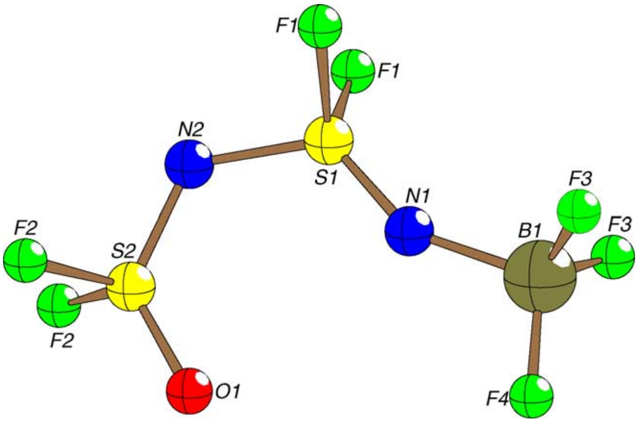


Fig. 3. Selected bond distances (pm) and bond angles (°) in **8**. B1N1 157.1(7), N1S1 139.5(5), S1F1 152.1(2), S1N2 157.8(4), N2S2 150.9(4), S2F2 150.0(2), S2O1 137.7(4), B1F3 132.2(4), B1F4 135.6(7); B1N1S1 151.7(4), N1S1N2 122.6(3), S1N2S2 123.5(3).

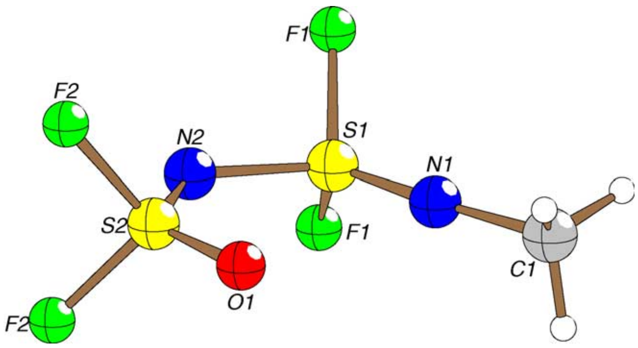
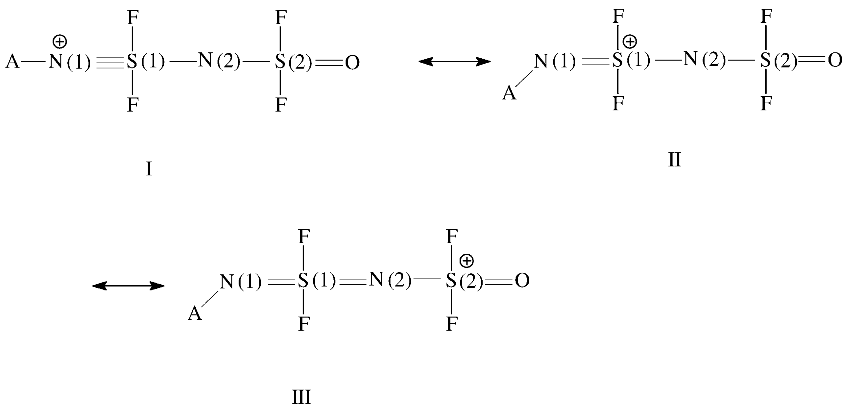


Fig. 4. Selected bond distances (pm) and bond angles in 9. C1N1 140.8(14), N1S1 136.7(10), S1F1 151.8(5), S1N2 155.9(9), N2S2 151.6(9), S2O1 137.5(8), S2F2 148.6(5); C1N1S1 173.8(11), N1S1N2 124.6(6), S1N2S2 122.1(5).

Table 3
Selected bond distances (pm) and bond angles (°) in $A–N^1{\equiv}S^1F_2–N^2{=}S^2({=}O)F_2$

	4a	**4c**	**6**	**8**	**9**
AN	196.9	195.3(10)	189.9(8)	157.1(7)	140.8(14)
N^1S^1	138.9	143.4(11)	143.0(8)	139.5(5)	136.7(10)
S^1N^2	158.8	155.4(10)	156.7(8)	157.8(4)	155.9(9)
N^2S^2	149.9	151.9(9)	149.7(8)	150.9(4)	151.6(9)
S^1F	152.5	155.4(8)	151.6(4)	152.1(2)	151.8(5)
S^2F	151.0	154.0(10)	148.5(5)	150.0(2)	148.6(5)
S^2O	138.2	137.6(12)	136.8(8)	137.7(4)	137.5(8)
AN^1S^1	166.4	142.8(8)	133.6(5)	151.7(4)	173.8(11)
$N^1S^1N^2$	125.2	115.7(7)	119.8(4)	122.6(3)	124.6(6)
$S^1N^2S^2$	123.5	129.6(7)	125.9(5)	123.5(2)	122.1(5)
ν_{SN} (cm^{-1})	1563	1527	1527	1563	–



Scheme 3.

reduced anomeric interactions. In contrast to **3**, the aryl derivatives are reasonably stable against hydrolysis, and a much higher basicity of the thiazyl nitrogen is observed. Protonation [15] and alkylation [16] is possible under mild conditions. In contrast to the adducts and cations of **3** described in this paper, the addition of the electrophiles to the aryl counterparts leads to a significant lengthening of the thiazyl bond [22].

3. Conclusions

Exchange of one fluorine in NSF_3 by the $NS(O)F_2$-group to give $N{\equiv}SF_2–N{=}S({=}O)F_2$ increases the donor properties of the resulting multifunctional system. Reactions with different electrophiles (metal cations, Lewis acids, "CH_3^+") show that exclusively the thiazyl nitrogen, the nitrogen at the triple bond is attacked. The alternation triple–single–double bond in the NSNS backbone of the ligand is maintained in the adducts. The length of this NS bond is dependent on the ANS angle, not on the nature of the ligand. With increasing angle, with increasing s-character of the AN bond, the SN distance decreases.

4. Experimental

The starting materials $NSF_2NS(O)F_2$ (**3**) [12], $[Ni(SO_2)_2(AsF_6)_2]$ [23], $[Cu(SO_2)_2(AsF_6)_2]$ [23], AsF_5 [24], SbF_5 [25], $[Re(CO)_5SO_2]^+AsF_6^-$ [26], and $CH_3OSO^+AsF_6^-$ [27] were prepared according to the literature. All operations had to be carried out in a dry nitrogen atmosphere due to the moisture sensitivity of the starting materials and the products. Elemental analyses were performed by the Mikroanalytisches Labor Beller, Göttingen.

4.1. *Preparation of* ***4b****,* ***4c*** *and* ***9***

In a dry box 2–3 mmol of the solid starting materials were filled in a λ-shaped glass vessel equipped with a Teflon valve, and onto this at a vacuum line 5–10 ml SO_2 (liquid) and a slight stoichiometric excess of **3** were condensed at −196 °C. The reaction proceeded while warming to room temperature, and clear solutions were formed. Minor impurities were removed by decanting the solutions from one leg of the λ-vessel into the other. Solvent and volatiles were removed at slightly reduced pressure.

*4.1.1. [Ni(NSF$_2$NSOF$_2$)$_4$(AsF$_6$)$_2$] (**4b**)*

0.61 g (3.3 mmol) **3** and 0.42 g (0.74 mmol) [Ni(SO$_2$)$_2$(AsF$_6$)$_2$] gave 0.87 g (0.74 mmol) **4b**. IR (cm^{-1}): 1495 m, 1448 m (sh), 1435 m, 1203 s, 925 m, 900 s, 824 s, 793 m, 772 m (sh), 720 m, 696 vs, 586 m, 511 s, 468 m, 424 w, 399 vs. As$_2$F$_{28}$N$_8$NiO$_4$S$_8$ (1173.05): calc. (found): F 45.35 (45.0), N 9.55 (9.4).

*4.1.2. [Cu(NSF$_2$NSOF$_2$)$_4$(AsF$_6$)$_2$] (**4c**)*

2.3 g (12.5 mmol) **3** and 1.29 g (2.92 mmol) Cu(AsF$_6$)$_2$ gave 3.4 g (2.92 mmol) **4c**. IR (cm^{-1}): 1527 m, 1443 m, 1212 s, 1185 m (sh), 920 m, 900 s, 803 m, 794 m, 705 s, 698 s, 688 s, 668 m, 512 m, 499 m, 440 w, 399 s. As$_2$CuF$_{28}$N$_8$O$_4$S$_8$ (1177.9): calc. (found): F 45.16 (44.6), N 9.51 (9.61).

*4.1.3. [Re(CO$_5$)NSF$_2$NS(O)F$_2$]$^+$(AsF$_6$)$^-$] (**9**)*

From 1.33 g (2.30 mmol) [Re(CO)$_5$SO$_2$]$^+$AsF$_6$$^-$ and 0.47 g (2.55 mmol) **3**, 1.64 g (2.35 mmol) **9** were obtained (mp = 79 °C). IR (cm^{-1}): 2175 m, 2121 s, 2048 vs, 1996 vs, 1977 vs, 1603 s, 1440 m (sh), 1415 s, 1338 m, 1255 s (sh), 1223 vs, 1209 vs, 944 m, 926 s, 827 vs, 766 vs, 700 vs, 678 s (sh), 586 vs, 550 m, 520 m, 500 m, 482 m, 435 s, 398 vs, 340 vs. ^{19}F NMR: SF$_2$ 88.83 (mult.), S(O)F$_2$ 47.83 (mult.), AsF 59.42 (quart.), ^{1}As–F 940 ± 20 Hz. C$_5$AsF$_{10}$N$_2$O$_6$ReS$_2$ (699.3): calc. (found): C 8.59 (8.3), As 10.71 (10.6), F 27.17 (26.4), N 4.01 (3.95).

*4.2. Preparation of **6**, **7** and **8***

At a vacuum line 3–5 mmol of **3** and a slight excess of AsF$_5$ and BF$_3$ (with SbF$_5$ a slight excess of **3** was used) were condensed together with 5 ml SO$_2$ as a solvent into a λ-shaped glass vessel with a Teflon valve. On warming to room temperature the adducts are formed. Volatiles are removed under vacuum at room temperature (for **8** at −30 °C).

*4.2.1. [AsF$_5$·NSF$_2$NS(O)F$_2$] (**6**)*

0.84 g (4.57 mmol) **3** and 0.89 g (5.24 mmol) AsF$_5$ gave 1.58 g (4.46 mmol) **6** (mp = 127 °C). IR (cm^{-1}): 1481 s, 1435 vs, 1332 w, 1258 vs, 1205 w, 1150 w, 1021 w, 968 s, 935 vs, 867 vs, 777 m, 721 vs, 700 vs, 647 m, 600 w, 546 s, 508 m (sh), 501 s, 454 m. ^{19}F NMR: SF$_2$ +74.25 (s, br), S(O)F$_2$ +49.22 (mult.), AsF −30.9 (s, br). AsF$_9$N$_2$OS$_2$ (354.05): calc. (found) As 21.16 (21.1), F 48.29 (48.0), N 7.91 (7.9), S 18.11 (18.2).

*4.2.2. [NSF$_2$NS(O)F$_2$·SbF$_5$] (**7**)*

0.78 g (3.60 mmol) SbF$_5$ and 0.67 g (3.64 mmol) **3** gave 1.43 g (3.57 mmol) **7** (mp = 130 °C). IR (cm^{-1}): 1487 s, 1437 vs, 1338 w, 1246 vs, 1024 w, 967 s, 940 vs, 870 vs, 779 m, 680 s (sh), 662 vs, 625 m, 599 w, 532 s, 501 s, 445 m. ^{19}F NMR: SF$_2$ +75.38 (mult.), S(O)F$_2$ +49.4 (mult.), SbF was too broad to be observed. F$_9$N$_2$OS$_2$Sb (400.88): calc. (found): F 42.65 (42.4), N 6.99 (6.9), S 16.00 (16.1), Sb 30.37 (30.4).

*4.2.3. [NSF$_2$NS(O)F$_2$·BF$_3$] (**8**)*

0.82 g (4.46 mmol) **3** and 0.35 g (5.16 mmol) BF$_3$ gave 1.10 g (4.37 mmol) **8** (mp = 59 °C). Raman (cm^{-1}): 1563 m, 1435 m, 1244 w, 963 s, 948 m (sh), 875 s, 782 vs, 660 vs, 591 w, 510 s, 490 m, 442 m, 397 m, 321 s. ^{19}F NMR: SF$_2$ +80.88 (mult.), S(O)F$_2$ +48.35 (mult.), BF −133.0 (s). BF$_7$N$_2$OS$_2$ (251.94): calc. (found): B 4.29 (4.12), N 11.12 (11.3), S 25.45 (25.4).

*4.3. Preparation of [H$_3$CNSF$_2$NS(O)F$_2$$^+$][AsF$_6$$^-$] (**9**)*

At −196 °C, 0.51 g (15 mmol) CH$_3$F and 2.55 g (15 mmol) AsF$_5$ were condensed together with 20 ml SO$_2$ (liq.) into a glass bomb equipped with a Teflon valve. After warming for 1 h to −20 °C, 2.76 g (15 mmol) **3** were added at −196 °C. The reaction mixture was stirred at room temperature for 1 h, after removal of all volatiles, 5.82 g (15 mmol) of **9** remained as colourless solid (quant. yield).

5. Crystallographic analysis

The crystals were fixed to a glassfiber with KEL-F oil. The X-ray data were collected on a Siemens P4 diffractometer using Mo Kα radiation (λ = 0.71073 Å) and a graphite monochromator. The programs SHELX-97 [28] and DIAMOND [29] were used. The structure was solved by direct methods. Subsequent least squares refinement located the positions of the remaining atoms in the electron density map. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions using a riding mode and refined isotropically in blocks.[1]

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[1] Crystallographic data (excluding structure factors) for the structure of **9** have been deposited this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 253368. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk). Details of the structures for **4c**, **6** and **8** may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Zusammenarbeit, D-76344 Eggenstein-Leopoldshafen, on quoting the dispository numbers, for **6**: CSD 414490, for **4c**: CSD 414491, for **8**: CSD 414492, the name of the authors and this journal.

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