Inorg. Chem. **1996,** *35,* 1918−1925

Acyclic Sulfur−Nitrogen Compounds. Syntheses and Crystal and Molecular Structures of Bis((trifluoromethyl)sulfonyl)amine ($(CF_3SO_2)_2NH$), Magnesium Hexaaquo Bis((trifluoromethyl)sulfonyl)amide Dihydrate ($[Mg(H_2O)_6][(CF_3SO_2)_2N]_2\cdot 2H_2O$), and Bis(bis(fluorosulfonyl)amino)sulfur ($(FSO_2)_2NSN(SO_2F)_2$)

A. Haas,[†] Ch. Klare,[†] P. Betz,[‡] J. Bruckmann,[‡] C. Krüger,[‡] Y.-H. Tsay,[‡] and F. Aubke*,[§]

Lehrstuhl für Anorganische Chemie II, Ruhr-Universität Bochum, D-44780 Bochum, Germany,
Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, D-45470 Mülheim, Germany,
and Department of Chemistry, The University of British Columbia, 2036 Main Mall,
Vancouver, BC V6T 1Z1, Canada

Received June 26, 1995[⊗]

The syntheses of three acyclic (fluorosulfonyl)− or ((trifluoromethyl)sulfonyl)−nitrogen derivatives and their crystal and molecular structures are reported. The structures of bis((trifluoromethyl)sulfonyl)amine (**1**; $(CF_3SO_2)_2NH$) and the corresponding anion in magnesium hexaaquo bis((trifluoromethyl)sulfonyl)amide dihydrate (**2**; $[Mg(H_2O)_6][(CF_3SO_2)_2N]_2\cdot 2H_2O$) shed some light on the observed high gas-phase acidity of $(CF_3SO_2)_2NH$. Extensive electron delocalization in the anion $[(CF_3SO)_2N]^-$ from planar, sp^2-hybridized nitrogen into 3d orbitals of sulfur results in a noticeable shortening of the S−N bond on deprotonation. Similar electron delocalization is observed for the third compound, bis(bis(fluorosulfonyl)amino)sulfur (**3**; $(FSO_2)_2NSN(SO_2F)_2$), which features planar nitrogens with nearly six equidistant S−N bonds and extremely short S−O and S−F bonds. Compounds **2** and **3** have not been reported previously. Their unexpected, accidental formation and their characterization will be discussed. Compound **1** crystallizes in the space group *Pccn* (No. 56) with $a = 16.404(3)$ Å, $b = 5.535(1)$ Å, $c = 9.557(2)$ Å, and $Z = 4$. Compound **2** crystallizes in the space group $P2_1/n$ (No. 14) with $a = 6.400(1)$ Å, $b = 14.300(1)$ Å, $c = 14.421(1)$ Å, $\beta = 97.45(1)°$, and $Z = 2$. Compound **3** crystallizes in the space group $P2_1/c$ (No. 14) with $a = 12.762(1)$ Å, $b = 6.744(1)$ Å, $c = 13.627(1)$ Å, $\beta = 91.42(1)°$, and $Z = 4$.

Introduction

According to a recent comprehensive study of gas-phase acidities,[1] the nitrogen acid $(CF_3SO_2)_2NH$[2] ranks among the strongest neutral Brønsted acids and the term "gas-phase superacid" has been suggested.[1] This remarkably high acidity of $(CF_3SO_2)_2NH$ in the gas phase has been attributed to a pronounced electron delocalization over the approximately tetrahedral $O_2S(R)N$ ($R = CF_3$) skeletal groups, both in $(CF_3SO_2)_2NH$ and more so in its conjugate anion $[(CF_3SO_2)_2N]^-$,[1] which facilitates dissociation of the proton in the gas phase.[1,3]

It is the intent of this study to probe the nature of the proposed[1,3] electron delocalization for $(CF_3SO_2)_2NH$ and its conjugate anion, where no structural data exist.[2]

Charge delocalization via $p\pi \rightarrow d\pi$ bonding within the S−N moiety should result in appreciable multiple-bond character for this moiety and should produce short S−N bonds and a planar environment for nitrogen. More extensive lone-pair delocalization is expected for the anion $[(CF_3SO_2)_2N]^-$, resulting in even shorter S−N bonds. Hence, the molecular structures of both species connected by proton transfer according to

$$(CF_3SO_2)_2NH \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} [(CF_3SO_2)_2N]^- \tag{1}$$

are of interest. We report here the molecular structures of $(CF_3SO_2)_2NH$ and of $[Mg(H_2O)_6][(CF_3SO_2)_2N]_2\cdot 2H_2O$, determined by single-crystal X-ray diffraction. The results are expected to show whether structural factors play a role in the high gas-phase acidity of $(CF_3SO_2)_2NH$.[1]

A similar study has previously been reported for the pair $(C_6H_5SO_2)_2NH$ and its anion $[(C_6H_5SO_2)_2N]^-$ with Na^+ as countercation.[4] Also known are the molecular structures of two related amines, $(CH_3SO_2)_2NH\cdot H_2O$[5] and $(C_2H_5SO_2)_2NH$.[6a] Of remote relevancy are also structural data on cyclic sulfonimide salts of the acid $(CF_2)_nSO_2NHSO_2$ with $n = 3, 4$.[6b] Included in our structural comparison is also a discussion of intermolecular association via hydrogen bonds observed for these nitrogen acids.[4,6] For $[Mg(H_2O)_6][(CF_3SO_2)_2N]_2$, which crystallizes as a dihydrate, interionic association via hydrogen bonds is expected as well.

Judging by the reported[2a] pK_a values in water and acetic acid, $(FSO_2)_2NH$[7,8] appears to be as strong an acid as $(CF_3SO_2)_2NH$. Neither the gas-phase acidity nor the molecular structure of this

---

[†] Ruhr-Universität Bochum.

[‡] Max-Planck Institut für Kohlenforschung.

[§] The University of British Columbia.

[⊗] Abstract published in *Advance ACS Abstracts,* February 15, 1996.

(1) Koppel, I. A.; Taft, R. W.; Anvia, F.; Zhu, S.-Z.; Hu, L.-Q.; Sung, K.-S.; DesMarteau, D. D.; Yagupolskii, L. M.; Yagulpolskii, Y. L.; Ignat'ev, N. V.; Kondratenko, N. V.; Volkonskii, A. Y.; Vlasov, V. M.; Notario, R.; Maria, P.-C. *J. Am. Chem. Soc.* **1994**, *116*, 3047.

(2) (a) Foropoulos, J.; DesMarteau, D. D. *Inorg. Chem.* **1984**, *23*, 3720. (b) Haas, A.; Klare, Ch. *Chimica* **1986**, *40*, 100.

(3) (a) DesMarteau, D. D. Proceedings, International Conference on Fluorine Chemistry, Kyoto, Japan, 1994; p 75. (b) DesMarteau, D. D. *J. Fluorine Chem.*, in press.

(4) Cotton, F. A.; Stokely, P. F. *J. Am. Chem. Soc.* **1970**, *92* 294.

(5) Attig, R.; Mootz, D. *Acta Crystallogr.* **1975**, *B31*, 1212.

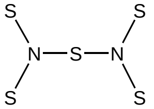
(6) (a) Blachette, A.; Wieland, E.; Schomburg, D.; Adelhelm, M. *Z. Anorg. Allg. Chem.* **1986**, *533*, 7. (b) DesMarteau, D. D.; Zuberi, S. S.; Pennington, W. T.; Randolph, B. B. *Eur. J. Solid State Inorg. Chem.* **1992**, *29*, 777.

(7) Appel, R.; Eisenhauer, G. *Chem. Ber.* **1962**, *95*, 246.

(8) Ruff, J. K.; Lustig, M. *Inorg. Synth.* **1968**, *11*, 138.

0020-1669/96/1335-1918$12.00/0

compound appears to have been reported. The molecular structures of the anion $[(FSO_2)_2N]^-$, with $[(C_6H_5)_4As]^+$ as cation,[9] and of a covalent derivative, $(FSO_2)_2NXeF$,[10] are known. We report here the molecular structure of another covalent derivative of $(FSO_2)_2NH$, bis(bis(fluorosulfonyl)amino)sulfur ($(FSO_2)_2NSN(SO_2F)_2$), which may be viewed as a sulfide of the type R_2S ($R = (FSO_2)_2N$). Again, extensive electron delocalization is observed. The



skeleton invites a structural comparison to cyclic SN compounds[11,12] with alternating sulfur and nitrogen atoms such as $[S_4N_4]^{2+}$.[13]

Experimental Section

(a) Chemicals. NH_3, $MgSO_4{\cdot}6H_2O$, and NaOCl were obtained from commercial sources and used without further purification. Bis((trifluoromethyl)thio)amine ($(CF_3S)_2NH$) was obtained from CF_3SCl and ammonia as described previously.[14] Tetrasulfur tetranitride, S_4N_4, was synthesized according to literature methods.[15,16] Bis(fluorosulfuryl) peroxide, $S_2O_6F_2$, was obtained from Dr. G. Siegemund, Höchst AG Frankfurt, Germany. The method of synthesis was the anodic oxidation of SO_3F^- in HSO_3F.[17] Additional $S_2O_6F_2$ was obtained at UBC by catalytic (AgF_2) fluorination of SO_3.[18] All solvents used were purified by standard procedures.

(b) Instrumentation. Elemental analyses were carried out at the Lehrstuhl für Anorganische Chemie II, Ruhr-Universität Bochum, using a Carlo Erbo analyzer (No. 1106). Infrared spectra were obtained on KBr pellets using a Bruker IFS 85 Fourier transform spectrometer. NMR spectra were recorded with a Bruker WM 500 Fourier transform spectrometer. Deuterioacetone was employed as internal lock. TMS was used as the standard for ^1H and ^{13}C NMR spectra, and $CFCl_3$ was employed for referencing ^{19}F NMR spectra. Moisture-sensitive materials were manipulated inside a drybox made by M. Braun Co., München, Germany. Volatile materials were handled using high-vacuum techniques.

(c) Synthetic Procedures and Crystal Preparation. (i) Bis((trifluoromethyl)sulfonyl)amine, $(CF_3SO_2)_2NH$ (1). Bis((trifluoromethyl)sulfonyl)amine ($(CF_3SO_2)_2NH$) was obtained as reported,[2b] by the oxidation of bis((trifluoromethyl)thio)amine ($(CF_3S)_2NH$) with aqueous sodium hypochlorite (NaOCl) at 20 °C, and liberated from the sodium salt by addition of concentrated (97%) H_2SO_4. Product purification was achieved by sublimation. At 20 °C and 10^{-2} bar pressure, crystals formed on a water-cooled finger. The yield was 92%. The compound was characterized by microanalysis, its ^1H and ^{19}F NMR spectra and the melting point of 50−51 °C, which all agreed well with previously reported data.[2a]

(ii) Magnesium Hexaaquo Bis((trifluoromethyl)sulfonyl)amide Dihydrate, $[Mg(H_2O)_6][(CF_3SO_2)_2N]_2{\cdot}2H_2O$ (2). A suspension of 0.1 g (0.33 mmol) of $Na[(CF_3SO_2)_2N]$ in 10 mL of diethyl ether and 0.04 g of $MgSO_4{\cdot}6H_2O$ were combined, and subsequently 0.5 mL of bromine, dissolved in 4 mL of ether, was added into a two-necked flask equipped with a reflux condenser and a drying tube filled with $CaCl_2$. After the reaction mixture was heated for 4 h and the suspension cooled to room temperature, the solid precipitate, presumed to be NaBr, was removed by filtration and the volume of the filtrate was reduced to yield a yellow oil. After redissolution of this oil in diethyl ether, colorless crystals were isolated by filtration and found suitable for a single-crystal X-ray diffraction study. The yield was about 40%. The composition was established by microanalysis. Anal. Calcd for $C_4H_{16}O_{16}N_2F_{12}S_4Mg$: C, 6.59; N, 3.84; H, 2.21. Found: C, 6.7; N, 3.8; H, 2.2. ^{19}F NMR: −78.6 ppm (s). IR (KBr pellets): 3460 (s, br), 1630 (m), 1346 (m), 1329 (s), 1240 (s, sh), 1199 (vs), 1135 (s), 1050 (s), 792 (s), 765 (m), 739 (s), 640 (m), 610 (m), 585 (m), 555 (m), 510 (s) cm^{-1}.

(iii) Bis(bis(fluorosulfonyl)amino)sulfur, $(FSO_2)_2NSN(SO_2F)_2$ (3). Small amounts of this material were obtained as a byproduct during the oxidation of S_4N_4 (550 mg or 2.98 mmol) with an excess of about 12 g of bis(fluorosulfuryl) peroxide ($S_2O_6F_2$) at 65 °C in a glass reaction vial of ∼50 mL volume fitted with a Young valve. This method was reported to produce $[S_4N_4](SO_3F)_2$ quantitatively at 25 °C.[19] Under the conditions described, the total amount of product was 1.2815 g, obtained after removing all excess $S_2O_6F_2$ in vacuo, slightly more than the expected amount of $[S_4N_4](SO_3F)_2$ of 1.141 g. During an attempt to remove any volatile byproducts under a dynamic vacuum while the reactor was heated to 70 °C in a water bath, small amounts (∼40−50 mg) of colorless, prismatic crystals sublimed to the upper part of the reactor. The very hygroscopic crystals melted at 96 °C to a yellow-brown liquid and decomposed at 122 °C with gas evolution. Anal. Calcd for $N_2O_8F_4S_5$: S, 40.86; N, 7.14. Found: S, 40.5; N, 7.3.

(d) X-ray Crystallography. (i) X-ray Intensity Measurements. Suitable colorless crystals of the compounds **1**−**3** were mounted under argon in glass capillaries. Unit cell parameters were obtained by least-squares refinement of 75 automatically centered reflections. Intensity data were measured on an Enraf-Nonius CAD4 diffractometer with Mo Kα radiation by the $\omega-2\theta$ scan technique for **1**−**3**, where the time spent measuring the background was half that taken to measure the peak. The intensities of three standard reflections were regularly checked every 100 reflections to detect variations during data collection. Data were corrected for Lorentz and polarization effects; an absorption correction was applied for **1**.

(ii) Structure Solutions. The structures of **2** and **3** were solved by direct methods; the structure of **1** was solved by the heavy-atom method. Subsequent refinement was accompanied by the full-matrix least-squares method. A correction for the effects of anomalous dispersion was included in the structure factor calculations. Atomic scattering curves were taken from ref 20. Computer programs used in these investigations include modified versions of DATAP[21] for data reduction, TRACER[22] for cell reduction, DIFABS[23] for absorption correction, and SHELX-86[24] for crystal structure solution. GFMLX, a locally modified version of ORFLS,[25] was used for least squares for structure refinement, DAESD,[26] for the calculation of distances and angles, and XANADU,[27] for the calculation of best planes and torsion angles. ORTEP[28] was employed to obtain thermal ellipsoids. Details of data collection, structure solution, and refinement for compounds **1**−**3** are given in Table 1.

---

(9) Isenberg, W.; Noltemayer, M.; Sheldrick, G. M. *Acta Crystallogr.* **1982**, *B38*, 2887.
(10) Sawyer, J. F.; Schrobilgen, G. J.; Sutherland, S. J. *Inorg. Chem.* **1982**, *21*, 4064.
(11) Chivers, T. *Chem. Rev.* **1985**, *85*, 341.
(12) Oakley, R. T. *Prog. Inorg. Chem.* **1988**, *36*, 299.
(13) Gillespie, R. J.; Kent, J. P.; Sawyer, J. F.; Slim, D. R.; Tyrer, D. J. *Inorg. Chem.* **1981**, *20*, 3799.
(14) Haas, A.; Lorenz, R. *Z. Anorg. Allg. Chem.* **1971**, *385*, 33.
(15) Becke-Goehring, M. *Inorg. Synth.* **1960**, *6*, 123.
(16) Villena-Blanco, M.; Jolly, W. L. *Inorg. Synth.* **1967**, *9*, 98.
(17) Dudley, F. B. *J. Chem. Soc.* **1963**, 3407.
(18) Cady, G. H.; Shreeve, J. M. *Inorg. Synth.* **1963**, *7*, 124.
(19) Sharma, R. D.; Aubke, F.; Paddock, N. L. *Can. J. Chem.* **1981**, *59*, 3157.
(20) *International Tables for X-ray Crystallography*; Vol. IV. Kynoch Press: Birmingham, U.K. (present distributor D. Reidel: Dordrecht, The Netherlands), 1974; pp 99−102, 149.
(21) DATAP: Coppens, P.; Leiserowitz, L.; Rabinovich, D. *Acta Crystallogr.* **1965**, *18*, 1035.
(22) TRACER: Lawton, S. L.; Jacobson, R. A. United States Energy Commission Report IS 1141; Iowa State University: Ames, IA.
(23) DIFABS: Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158.
(24) Goddard, R. *SHELX-86*; Clarendon Press: Oxford, U.K., 1985; p 175.
(25) GFMLX, a highly modified version of ORFLS by: Busing, W. R.; Martin, K. O.; Levy, H. A. Report ORNL-TM-305; Oak Ridge National Laboratory: Oak Ridge, TN, 1962.
(26) DAESD:Davis, R. E.; Harris, D. R., 1970, Roswell Park Mem. Inst., USA.
(27) XANADU: Roberts, P.; Sheldrick, G. M., 1976, Univ. of Cambridge, England.
(28) ORTEP: Johnson, C. K. Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.

Table 1. Crystallographic Data for $(CF_3SO_2)_2NH$ (**1**), $[Mg(H_2O)_6][(CF_3SO_2)_2N]_2{\cdot}2H_2O$ (**2**), and $(FSO_2)_2NSN(SO_2F)_2$ (**3**)

	1	**2**	**3**
a, Å	16.404(3)	6.400(1)	12.762(1)
b, Å	5.535(1)	14.300(1)	6.744(1)
c, Å	9.557(2)	14.421(1)	13.627(1)
β, deg	90.0	97.45(1)	91.42(1)
V, Å^3	867.7	1308.8	1172.5
Z	4	2	4
fw	281.2	728.7	392.3
space group [No.]	*Pccn* [56]	$P2_1/n$ [14]	$P2_1/c$ [14]
ρ_{calcd}, g cm^{-3}	2.15	1.85	2.22
μ, cm^{-1}	6.9	5.18	10.4
Kα radiation, Å	0.710 69	0.710 69	0.710 69
T, °C	20	20	20
R,[a] R_w[b] ($w = 1/\sigma^2(F_o)$)	0.037, 0.049	0.060, 0.075	0.066, 0.072

[a] $R = [\Sigma(F_o - F_c)/\Sigma(F_o)]/2$. [b] $R_w = [\Sigma w(F_o - F_c)/\Sigma w(F_o)^2]/2$.

Results and Discussion

(a) Synthetic Aspects and Crystal Preparation. For the synthesis of bis((trifluoromethyl)sulfonyl)amine ($(CF_3SO_2)_2NH$) the oxidation of $(CF_3S)_2NH$,[14] dissolved in pentane by NaOCl in aqueous solution at 20 °C, was chosen.[2b] This method appeared to be simpler than the multistep procedure used in the original synthesis of $(CF_3SO_2)_2NH$,[2a] which in turn was adapted from a more general synthetic procedure by Meussdörfer and Niederprüm.[29] Crystals suitable for a molecular structure determination were obtained by sublimation at 20 °C and at 10^{-2} Torr. The sodium salt $Na[(CF_3SO_2)_2N]$, obtained as an intermediate,[2a] was used as starting material in the preparation of $[Mg(H_2O)_6][(CF_3SO_2)_2N]_2{\cdot}2H_2O$.

The synthesis of this salt, as described in the Experimental Section, appears to be needlessly complex, which requires an explanation. During an unsuccessful attempt to oxidize $Na[(CF_3SO_2)_2N]$ with bromine in diethyl ether in the hope of synthesizing a salt of the cation $[(CF_3SO_2)_2N]^+$, small amounts of a crystalline, white material were isolated and used in a single-crystal X-ray diffraction study. The resulting molecular structure, which contains an octahedrally coordinated species, was initially interpreted as that of $[(CF_3SO_2)_2N]_2[SiF_6]{\cdot}2H_2O$. Close inspection of the structural parameters, in particular of the Si−F bond distances in the "anion" which are about 0.35 Å longer than in $K_2[SiF_6]$,[30] and S−N distances of the "cation", which do not agree with those found for the related cation $[N(SCl)_2]^+$ [31a] but show some resemblance to those reported for $Na[(C_6H_5SO_2)_2N]$,[4] have resulted in a reformulation of the compound as $[Mg(H_2O)_6][(CF_3SO_2)_2N]_2{\cdot}2H_2O$. As a likely source of the $[Mg(H_2O)_6]^{2+}$ cation, the use of $MgSO_4$ as drying agent for an ether extract of $Na[(CF_3SO_2)_2N]$ from the aqueous medium[2b] has to be considered. To confirm this assumption, the reaction of Br_2 with $Na[(CF_3SO_2)_2N]$ was repeated under identical conditions, but with a small amount of $MgSO_4{\cdot}6H_2O$ added. The crystalline material was produced in a quantity sufficient to allow characterization of the salt by microanalysis and ^{19}F NMR and IR spectroscopy. The IR spectrum in the anion region is found to be identical with that of $Cs[(CF_3SO_2)_2N]$ reported previously.[2a] The single crystals obtained in this manner after recrystallization from ether were of better quality than the original ones, and the quality of the structure determination was improved markedly.

It hence appears that the formation reaction of $[Mg(H_2O)_6][(CF_3SO_2)_2N]_2$ is a simple metathesis with the starting material according to

$$[Mg(H_2O_6)]SO_4 + 2Na[(CF_3SO_2)_2N] \rightarrow [Mg(H_2O)_6][(CF_3SO_2)_2N]_2 + Na_2SO_4 \quad (2)$$

The role of the bromine in the formation reaction is unclear. Its addition may even be unnecessary, in view of an earlier report[32] that the reaction of $Ag[(CF_3SO_2)_2N]$ with Br_2 does not lead to $(CF_3SO_2)NBr$, which is obtained differently.[32] The relatively low yield of $[Mg(H_2O)_6][(CF_3SO_2)_2N]_2$, which crystallizes as a dihydrate, suggests the presence of other products, which we have not been able to identify. It seems clear, however, that the cation $[(CF_3SO_2)_2N]^+$ cannot be obtained by this route and remains unknown.

Equally perplexing and unexpected is the synthesis of bis(bis(fluorosulfonyl)amino)sulfur ($(FSO_2)_2NSN(SO_2F)_2$, **3**), the third compound to be structurally characterized in this study. The compound is formed in rather low yield, but its isolation by sublimation produces single crystals suitable for a single-crystal X-ray diffraction study. Unfortunately, the amounts obtained were so small as to only permit, in addition to the determination of the molecular structure, microanalysis and a melting point determination.

The previously reported reaction of S_4N_4 and $S_2O_6F_2$,[19] according to

$$S_4N_4 + S_2O_6F_2 \xrightarrow{25\ °C} [S_4N_4](SO_3F)_2 \quad (3)$$

leads quantitatively to an ionic material, with the presence of the square-planar cation $[S_4N_4]^{2+}$ subsequently confirmed by a single-crystal X-ray diffraction study.[13] On the other hand, the radical $(CF_3)_2NO$ achieves tetrasubstitution and binds to all four sulfur atoms in $S_4N_4[ON(CF_3)_2]_4$.[33] An attempt to achieve further oxidation of S_4N_4 by $S_2O_6F_2$ at elevated temperatures, where a higher concentration of $SO_3F^\bullet$ radicals is present,[34] results in a greater than expected weight increase, but only $(FSO_2)_2NSN(SO_2F)_2$ is isolated as a byproduct in addition to the main product, $[S_4N_4](SO_3F)_2$.

The observation that $(FSO_2)_2NSN(SO_2F)_2$ is only produced when $S_2O_6F_2$ has been prepared by anodic oxidation of SO_3F^- in HSO_3F[17] suggests that small amounts of fluorosulfuric acid (HSO_3F) may be the active species in the generation of the byproduct. With $S_2O_6F_2$, obtained by catalytic fluorination of SO_3,[35] only $[S_4N_4](SO_3F)_2$ is obtained quantitatively.[19] Reportedly HSO_3F is used in the synthesis of $(FSO_2)_2NH$.[36,37] The reaction of HSO_3F with S_4N_4 in SO_2 as solvent has been studied[13,38] but fails to shed any light on the situation, on account of its complexity. Besides $[S_4N_4](SO_3F)_2$,[13] additional cationic sulfur−nitrogen compounds appear to form in systems such as $[S_6N_4](SO_3F)_2$ and $[S_6N_4](S_2O_2F)_2$ as well as sulfamic acid (NH_2SO_3H) and the adduct $S_4N_4{\cdot}SO_3$.[38] Additional products or intermediates are probable.

It hence appears that the formation of $(FSO_2)_2NSN(SO_2F)_2$ in this manner is rather fortuitous and that the synthesis is probably better achieved by other routes. The molecular structure of the compound reveals some interesting features, however, which will be discussed subsequently.

---

(29) Meussdörfer, J. N.; Niederprüm, H. *Chem. Ztg.* **1972**, *96*, 582.
(30) Loehlin, J. H. *Acta Crystallogr.* **1984**, *C40*, 570.
(31) (a) Glemser, O.; Krebs, B.; Wegener, J.; Kindler, E. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 598. (b) Glemser, O.; Kindler, E.; Krebs, B.; Mews, R.; Schnepel, F. M.; Wegener, J. *Z. Naturforsch.* **1980**, *35B*, 657.
(32) Singh, S.; DesMarteau, D. D. *Inorg. Chem.* **1986**, *25*, 4596.
(33) Emeléus, H. J.; Poulet, A. J. *J. Fluorine Chem.* **1971/72**, *1*, 13.
(34) Dudley, F. B.; Cady, G. H. *J. Am. Chem. Soc.* **1963**, *85*, 3375.
(35) Dudley, F. B.; Cady, G. H. *J. Am. Chem. Soc.* **1951**, *73*, 513.
(36) Becke-Goehring, M. *Adv. Inorg. Chem. Radiochem.* **1962**, *2*, 159.
(37) Glemser, O.; Mews, R. *Adv. Inorg. Chem. Radiochem.* **1972**, *14*, 333.
(38) Gillespie, R. J.; Kent, J. P.; Sawyer, J. F. *Inorg. Chem.* **1981**, *20*, 3784.

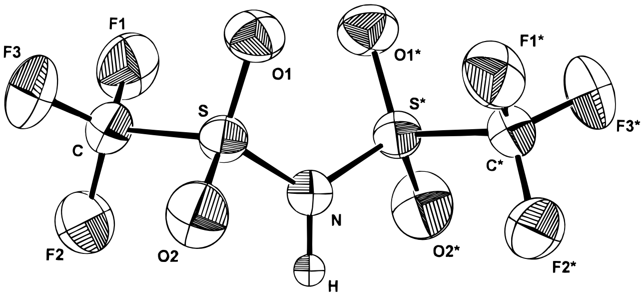


Figure 1. Molecular structure of bis((trifluoromethyl)sulfonyl)amine ($(CF_3SO_2)_2NH$; 50% probability ellipsoids).

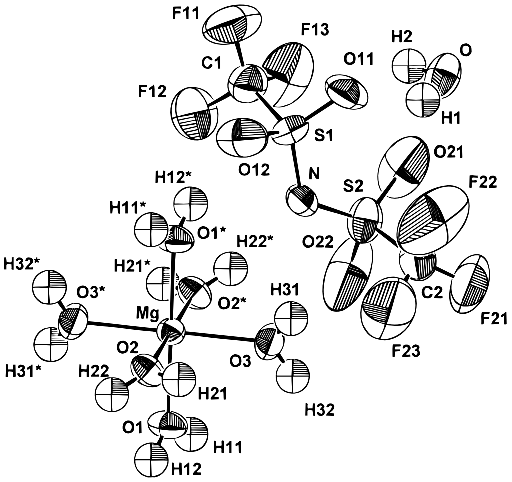


Figure 2. Molecular structure of magnesium hexaaquo bis((trifluoromethyl)sulfonyl)amide dihydrate ($[Mg(H_2O)_6][(CF_3SO_2)_2N]_2\cdot 2H_2O$; 50% probability ellipsoids).

In summary, a straightforward synthetic method[2b] and two unexpected and accidental formation reactions are employed to produce single crystals of the three acyclic S–N compounds which are studied here: $(CF_3SO_2)_2NH$ (**1**), $[Mg(H_2O)_6][(CF_3SO_2)_2N]_2\cdot 2H_2O$ (**2**), and $(FSO_2)_2NSN(SO_2F)_2$ (**3**). While the formation reactions differ widely, there are common structural features which permit a comparison.

(b) Molecular Structures of $(CF_3SO_2)_2NH$, $[Mg(H_2O)_6][(CF_3SO_2)_2N]_2\cdot 2H_2O$, and $(FSO_2)_2NSN(SO_2F)_2$. The three molecular structures will be discussed in the order shown in the title. The discussion will focus on three interrelated aspects: (i) a description of the molecular structures, (ii) the discussion of bonding features observed for all compounds, including comparisons to related precedents, and (iii) a brief description of the intermolecular association via hydrogen bonds for the nitrogen acids $(RSO_2)_2NH$ (R = CF_3, C_6H_5,[4] CH_3,[5] or C_2H_5[6]) and interionic interactions observed for $[Mg(H_2O)_6][(CF_3SO_2)_2N]\cdot 2H_2O$ which again involve hydrogen bonds.

ORTEP drawings of compounds **1**–**3** are shown in Figures 1–3, which also introduce the numbering system employed here. The packing of $[Mg(H_2O)_6][(CF_3SO_2)_2N]_2\cdot 2H_2O$ in the unit cell is shown in Figure 4. Tables 2, 4, and 6 list final atomic coordinates and equivalent isotropic thermal parameters for compounds **1**–**3**. Selected bond distances and angles for **1**–**3** are summarized in Tables 3, 5, and 7, respectively. Some representative intermolecular and interionic bond distances, which illustrate hydrogen bonding in $[Mg(H_2O)_6][(CF_3SO_2)_2N]\cdot 2H_2O$, are collected in Table 8. Finally, in Tables 9 and 10 important structural features for various $(RSO_2)_2N$ derivatives (R = CF_3, CH_3,[5] C_2H_5,[6a] C_6H_5[4]) and for $(FSO_2)_2N$ derivatives such as $[(FSO_2)_2N]^-$, as the tetraphenylarsonium salt,[9] and $(FSO_2)_2N-XeF$[10] are compared.

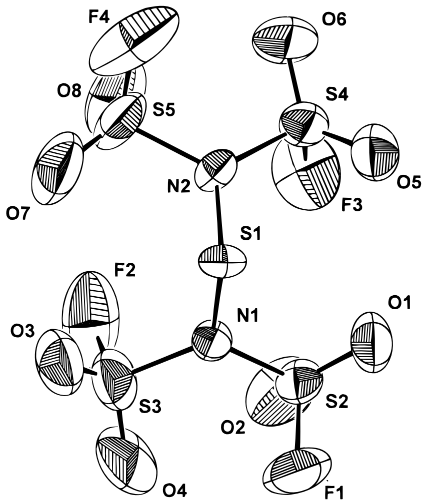


Figure 3. Molecular structure of bis(bis(fluorosulfonyl)amino)sulfur ($(FSO_2)_2NSN(SO_2F)_2$; 50% probability ellipsoids).

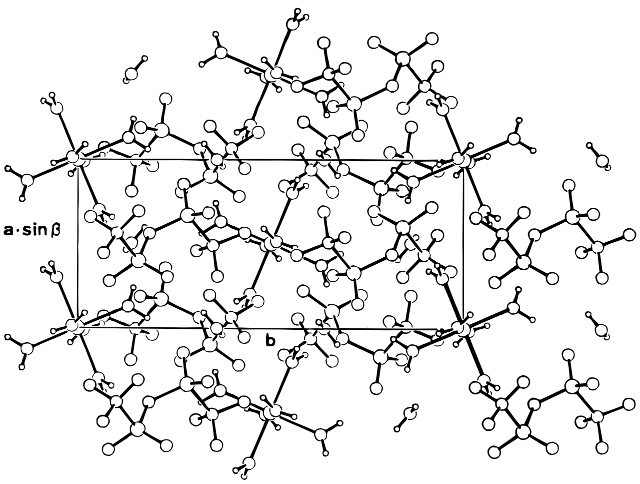


Figure 4. Packing of $[Mg(H_2O)_6][(CF_3SO_2)_2N]_2\cdot 2H_2O$.

Table 2. Atomic Coordinates and Equivalent Isotropic Thermal Parameters[a] (Å^2) for $(CF_3SO_2)_2NH$ (**1**)

atom	*x*	*y*	*z*	U_{eq}
S	0.1818(1)	0.0752(1)	0.0828(1)	0.040
F1	0.1065(1)	0.4604(4)	0.1712(2)	0.071
F2	0.0734(1)	0.3513(5)	−0.0356(2)	0.080
F3	0.0309(1)	0.1512(5)	0.1423(2)	0.085
O1	0.2056(1)	0.0292(4)	0.2210(2)	0.055
O2	0.1618(1)	−0.1075(4)	−0.0152(2)	0.066
C	0.0922(2)	0.2745(7)	0.0921(3)	0.051
N	0.2500	0.2500	0.0079(3)	0.042
H	0.2500	0.2500	−0.095(5)	0.068

[a] $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i^*a_j^*(\bar{a}_i\cdot\bar{a}_j)$.

Like for the other $(RSO_2)_2NH$ compounds, the molecular structure of $(CF_3SO_2)_2NH$ is characterized by a 2-fold crystallographic axis passing through the central N–H bonds. The coordination environment around nitrogen is planar, and the point group is C_2. As seen in Figure 1, the two CF_3 groups are on opposite sides of the central S–NH–S plane. The S–N distances is at 1.644(1) Å, identical within standard deviations with those for the other $(RSO_2)NH$ compounds,[4,6] while the S–O bond distances appear to be marginally shorter in $(CF_3SO_2)_2NH$. However, the S–C bond is, at 1.840(3) Å, noticeably long, compared to an average distance of 1.756(18) Å for this bond type.[39]

Similarly long S–C bonds are found for the structurally related trifluoromethanesulfonate group. For example, in

Table 3. Selected Bond Distances (Å) and Bond Angles (deg) for $(CF_3SO_2)_2NH$ (**1**)

Bond Distances			
S−O1	1.401(2)	S−O2	1.417(2)
S−C	1.840(3)	S−N	1.644(1)
F1−C	1.298(4)	F2−C	1.330(3)
F3−C	1.307(3)	N−H	0.99(4)
Bond Angles			
N−S−C	102.2(1)	N−S−O2	106.9(1)
N−S−O1	109.1(1)	C−S−O2	106.0(1)
C−S−O1	106.6(1)	O2−S−O1	123.9(1)
F3−C−F2	109.0(2)	F3−C−F1	109.8(2)
H−N−S	115.8(3)	S*−N−S	128.4(2)

Table 4. Atomic Coordinates and Equivalent Isotropic Thermal Parameters (Å^2)[a] for $[Mg(H_2O)_6][(CF_3SO_2)_2N]\cdot 2H_2O$ (**2**)

atom	*x*	*y*	*z*	U_{eq}
S(1)	0.1697(2)	0.7848(1)	0.3365(1)	0.051(1)
S(2)	−0.0986(2)	0.6578(1)	0.2328(1)	0.066(1)
Mg	0.0000	0.0000	0.0000	0.034(0)
F(11)	0.0658(6)	0.9327(2)	0.4218(3)	0.118(3)
F(12)	−0.0411(7)	0.8078(3)	0.4764(2)	0.134(3)
F(13)	−0.1911(5)	0.8626(3)	0.3488(3)	0.135(3)
F(21)	−0.0532(7)	0.5683(3)	0.0824(2)	0.133(3)
F(22)	0.1953(9)	0.6582(4)	0.1312(4)	0.203(6)
F(23)	0.160(1)	0.5335(4)	0.1949(3)	0.203(5)
O	0.0020(4)	0.6387(2)	0.6133(2)	0.068(2)
O(1)	0.1288(4)	0.8693(2)	−0.0062(2)	0.052(1)
O(2)	−0.2993(3)	0.9452(2)	−0.0287(2)	0.045(1)
O(3)	−0.0130(4)	0.9859(2)	0.1403(2)	0.055(2)
O(11)	0.1857(5)	0.8386(2)	0.2555(2)	0.076(2)
O(12)	0.3544(5)	0.7739(2)	0.4019(3)	0.090(2)
O(21)	−0.1938(7)	0.7331(4)	0.1800(3)	0.149(4)
O(22)	−0.2193(8)	0.5829(4)	0.2590(3)	0.176(5)
N	0.0622(5)	0.6859(2)	0.3206(2)	0.053(2)
C(1)	−0.0088(8)	0.8501(3)	0.4001(4)	0.070(3)
C(2)	0.064(1)	0.6023(4)	0.1552(4)	0.081(4)

[a] $U_{eq} = {}^{1}/_{3}\sum_i\sum_j U_{ij}a_i^*a_j^*(\bar{\mathbf{a}}_i\cdot\bar{\mathbf{a}}_j)$.

Table 5. Bond Distances and Bond Angles for $[Mg(H_2O)_6][(CF_3SO_2)_2N]_2\cdot 2H_2O$ (**2**)

Bond Distances			
S(1)−O(11)	1.413(3)	S(1)−O(12)	1.423(4)
S(1)−N	1.577(3)	S(1)−C(1)	1.814(5)
S(2)−O(21)	1.411(5)	S(2)−O(22)	1.402(6)
S(2)−N	1.576(3)	S(2)−C(2)	1.810(6)
Mg−O(1)	2.050(2)	Mg−O(2)	2.062(2)
Mg−O(3)	2.047(2)	Mg−O(1)*	2.050(2)
Mg−O(2)*	2.062(2)	Mg−O(3)*	2.047(2)
F(11)−C(1)	1.297(6)	F(12)−C(1)	1.296(6)
F(13)−C(1)	1.311(6)	F(21)−C(2)	1.305(7)
F(22)−C(2)	1.239(9)	F(23)−C(2)	1.258(8)
Bond Angles			
C(1)−S(1)−N	104.1(2)	C(1)−S(1)−O(12)	104.1(2)
C(1)−S(1)−O(11)	104.8(2)	N−S(1)−O(12)	107.9(2)
N−S(1)−O(11)	116.5(2)	O(12)−S(1)−O(11)	117.7(2)
C(2)−S(2)−N	103.9(2)	C(2)−S(2)−O(22)	102.4(3)
C(2)−S(2)−O(21)	104.1(3)	N−S(2)−O(22)	107.7(2)
N−S(2)−O(21)	115.5(2)	O(22)−S(2)−O(21)	121.0(3)
O(3)*−Mg−O(2)*	90.3(1)	O(3)*−Mg−O(1)*	91.2(1)
O(3)*−Mg−O(3)	180.0(1)	O(3)*−Mg−O(2)	89.7(1)
O(3)*−Mg−O(1)	88.8(1)	O(2)*−Mg−O(1)*	90.8(1)
O(2)*−Mg−O(3)	89.7(1)	O(2)*−Mg−O(2)	180.0(1)
O(2)*−Mg−O(1)	89.2(1)	O(1)*−Mg−O(3)	88.8(1)
O(1)*−Mg−O(2)	89.2(1)	O(1)*−Mg−O(1)	180.0(1)
O(3)−Mg−O(2)	90.3(1)	O(3)−Mg−O(1)	91.2(1)
O(2)−Mg−O(1)	90.8(1)	F(21)−C(2)−S(2)	110.0(4)
S(2)−N−S(1)	125.0(2)	F(13)−C(1)−F(12)	108.3(5)
F(13)−C(1)−F(11)	106.6(4)	F(13)−C(1)−S(1)	111.0(4)
F(12)−C(1)−F(11)	108.4(4)	F(12)−C(1)−S(1)	111.7(4)
F(11)−C(1)−S(1)	110.8(4)	F(23)−C(2)−F(22)	108.9(6)
F(23)−C(2)−F(21)	105.8(5)	F(23)−C(2)−S(2)	110.4(4)
F(22)−C(2)−F(21)	110.9(5)	F(22)−C(2)−S(2)	110.8(5)

Table 6. Atomic Coordinates and Equivalent Isotropic Thermal Parameters[a] (Å^2) for $(FSO_2)_2NSN(SO_2F)_2$ (**3**)

atom	*x*	*y*	*z*	U_{eq}
S1	0.2301(1)	0.2109(2)	0.3135(1)	0.043
S2	0.1352(1)	−0.1840(2)	0.2937(1)	0.057
S3	0.3605(1)	−0.1411(3)	0.2781(2)	0.084
S4	0.1365(1)	0.2358(2)	0.5075(1)	0.061
S5	0.3606(1)	0.2873(4)	0.4908(1)	0.091
F1	0.1349(3)	−0.2488(6)	0.1878(3)	0.104
F2	0.3922(3)	−0.1772(9)	0.3819(4)	0.143
F3	0.1341(3)	0.0149(6)	0.5273(3)	0.117
F4	0.3445(5)	0.4956(8)	0.5260(4)	0.158
O1	0.0480(3)	−0.0692(6)	0.3064(4)	0.098
O2	0.1583(4)	−0.3538(7)	0.3475(4)	0.105
O3	0.4263(3)	0.0068(8)	0.2441(4)	0.097
O4	0.3441(5)	−0.3137(9)	0.2281(6)	0.162
O5	0.0486(3)	0.2766(7)	0.4499(3)	0.085
O6	0.1619(4)	0.332(1)	0.5942(3)	0.121
O7	0.4343(4)	0.287(1)	0.4200(4)	0.139
O8	0.3681(4)	0.1682(9)	0.5735(4)	0.115
N1	0.2423(3)	−0.0370(5)	0.2955(3)	0.044
N2	0.2419(3)	0.2423(5)	0.4363(3)	0.045

[a] $U_{eq} = {}^{1}/_{3}\sum_i\sum_j U_{ij}a_i^*a_j^*(\bar{\mathbf{a}}_i\cdot\bar{\mathbf{a}}_j)$.

$(CH_3)_2Au(OSO_2CF_3)\cdot H_2O$,[40a] where a monodentate trifluoromethanesulfonate group is observed, *d*(S−C) is 1.816(9) Å. Even longer S−C bonds (1.842−1.895 Å) are found in $K[C(SO_2CF_3)_3]\cdot H_2O$.[40b] It appears that the strong electron-withdrawing fluorine substituents on carbon are a likely cause of the observed bond lengthening, rather than the bulkiness of the CF_3 group, which is unlikely in view of the positioning of the two groups at opposite sides of the S−NH−S plane. The sulfur−carbon distances for the remaining NH derivatives do not vary much from an average value of ∼1.76 Å.[39]

The presence of 1 mol of lattice water in $(CH_3SO_2)_2NH\cdot H_2O$ does not appear to affect the internal bonds of the amine.[5] As the structure indicates, the compound is not an oxonium salt of the type $[H_3O][(CH_3SO_2)_2N]$ but rather a hydrogen-bridged polymer, where lattice water and the amine alternate and form chains via O−H---O bonds, which are then crosslinked by N−H---O bonds into double chains.[5]

A different mode of intermolecular association is encountered for $(CF_3SO_2)_2NH$. The packing in the unit cell is shown in Figure 5. Individual molecules are linked into chains by long (about 2.26 Å) bifurcated hydrogen bonds from the N−H group to two O atoms of two adjacent SO_2 groups. For the remaining two compounds in this group, again different types of intermolecular association via N−H---O hydrogen bonds are noted. For $(C_6H_5SO_2)NH$,[4] rather strong hydrogen bonds to a single oxygen of a neighboring molecule (*d*(N−H---O) = 2.854(6) Å) are reported. The bonds are nearly linear (N−H---O is 168°). Finally, for $(C_2H_5SO_2)_2NH$ dimers are formed by linear N−H---O bonds of 2.87 Å.[6]

In summary, the sulfonylamines $(RSO_2)_2NH$ (R = CH_3,[5] C_2H_5,[6a] C_6H_5,[4]) form approximately linear N−H---O hydrogen bridge bonds, which involve for R = C_2H_5[6a] and C_6H_5[4] sulfonyl oxygen atoms. In $(CH_3SO_2)_2NH\cdot H_2O$,[5] the sulfonyl O atoms are only involved in OH---OS bonds with the lattice water, which cross-links via N−H---O bonds to the amine. Judging by the reported bond distances, the hydrogen bonds are in all instances of comparable strength. For $(CF_3SO_2)_2NH$ weaker bifurcated H bonds are encountered. The ability to form hydrogen bonds is an indication of the acidic nature of the proton in all four amines. The different types of H bonds encountered

---

(39) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2*, **1987**, S1.

(40) (a) Komiya, S.; Huffman, J. C.; Kochi, J. K. *Inorg. Chem.* **1977**, *16*, 2138. (b) Turowsky, L.; Seppelt, K. *Inorg. Chem.* **1988**, 27, 2135.

Table 7. Selected Distances (Å) and Angles (deg) for $(FSO_2)_2NSN(SO_2F)_2$ (**3**)

Bond Distances			
S1−N1	1.698(4)	S1−N2	1.690(4)
S2−N1	1.688(4)	S2−O1	1.371(4)
S2−O2	1.387(5)	S2−F1	1.508(4)
S3−N1	1.686(4)	S3−O3	1.391(5)
S3−O4	1.363(7)	S3−F2	1.482(5)
S4−N2	1.678(4)	S4−O5	1.382(4)
S4−O6	1.379(5)	S4−F3	1.515(4)
S5−N2	1.699(4)	S5−O7	1.364(5)
S5−O8	1.386(6)	S5−F4	1.501(6)
Bond Angles			
N2−S1−N1	105.1(2)	F1−S2−O2	105.2(3)
F1−S2−O1	107.6(3)	O2−S2−O1	124.2(3)
F2−S3−O4	111.8(4)	F2−S3−O3	106.5(3)
O4−S3−O3	122.2(4)	F3−S4−O6	108.3(3)
F3−S4−O5	106.1(3)	O6−S4−O5	124.3(3)
F4−S5−O8	106.8(3)	F4−S5−O7	109.4(4)
O8−S5−O7	122.6(3)	S3−N1−S2	118.7(2)
S3−N1−S1	121.0(2)	S2−N1−S1	120.2(2)
S5−N2−S4	118.1(2)	S2−N2−S1	120.8(2)
S4−N2−S1	121.1(2)		

Table 8. Selected Contacts Involving Hydrogen in $[Mg(H_2O)_6][(CF_3SO_2)_2N]_2{\cdot}2H_2O$ (**2**)

	d (Å)		*d* (Å)
O(11)−H(2)	2.412(3)	O(3)−H(21)	2.845(3)
O(21)−H(1)	1.947(5)	O(12)−H(22)	2.957(3)
O(22)−H(31)	1.908(5)	N−H(22)	2.042(3)
Mg−H(11)	2.558(1)	O(3)−H(22)	2.937(3)
O−H(11)	1.983(3)	Mg−H(31)	2.638(1)
Mg−H(12)	2.648(1)	O(1)−H(31)	2.869(3)
O(2)−H(12)	2.917(2)	F(23)−H(32)	2.929(5)
O(12)−H(12)	2.046(3)	Mg−H(32)	2.643(1)
O−H(21)	1.955(3)	O(1)−H(32)	2.933(3)
O(2)−H(21)	2.729(2)	H(32)−O(11)	2.045(3)

(bifurcated or linear) and the involvement of lattice water in one case allow no relative ranking according to strength of the hydrogen bonds.

Deprotonation of $(CF_3SO_2)_2NH$ produces the corresponding amide, and the structural data reported for $[(C_6H_5SO_2)_2N]^-$ [4] with Na^+ as countercation and for $[(CF_3SO_2)_2N]^-$ with $[Mg(H_2O)_6]^{2+}$ as cation allow a comparison. The relevant structural data for both anions are summarized in Table 9. The presence of lattice water in $[Mg(H_2O)_6][(CF_3SO_2)_2N]_2{\cdot}2H_2O$ and the involvement of both lattice water and coordinated water in hydrogen bonding appear to make little difference in the internal dimensions of the anion. As seen in Table 8, the hydrogen bonds are rather weak with the shortest N---H and O---H bond distances around 2 Å. The same can be said for the sodium salt $Na[(C_6H_5SO_2)_2N]$, where weak Na---O and Na---N contacts between 2.3 and 2.7 Å in length are observed.[4]

Both the internal dimensions of the $[Mg(H_2O)_6]^{2+}$ cation and the involvement of coordinated water in hydrogen bonding follow published precedents. Only a few of the many reported structures of salts with the magnesium hexaaquo ion $[Mg(H_2O)_6]^{2+}$ are cited here, because they involve an oxy anion. Two of the reports are relatively recent. The examples cited consist of X-ray studies of $[Mg(H_2O)_6][S_2O_3]$,[41] $[Mg(H_2O)_6]SO_4$,[42] and $[Mg(H_2O)_6](ClO_2)_2$.[43] A fourth study, that of $[Mg(H_2O)_6]Cl_2$,[44] involves neutron diffraction and is of interest with regard to hydrogen bonding. In our case Mg−O distances (see Table 5) vary little (2.047(2)−2.062(2) Å), with O atoms trans to each other equidistant to Mg. A similar situation is found for the thiosulfate;[41] however, the spread of Mg−O bond distances is wider (2.0404(7)−2.1208(6) Å). Both H---O and weaker H---S contacts are seen. Comparable Mg−O bond lengths, similar distortions of the MgO_6 octahedron, and involvement of coordinated H_2O in H bonding are noted for $[Mg(H_2O)_6]Cl_2$[44] and $[Mg(H_2O)_6]SO_4$.[42] In summary, both the observed bond distances and the involvement of H_2O in hydrogen bonding are not unusual and $[(CF_3SO_2)_2N]^-$ behaves just like other oxyacid anions in this respect.[41,44] Hence, none of the effects discussed below for the anion appear to be caused or influenced by the $[Mg(H_2O)_6]^{2+}$ cation or the lattice water.

The most striking feature observed for $[(CF_3SO_2)_2N]^-$ and its phenyl analogue[4] is the contraction of the S−N bond by ~0.07 Å on deprotonation. As argued previously,[4] more electron density on N will result in more extensive $p\pi \rightarrow d\pi$ bonding for the S−N bond at the expense of the S−O bonds, which appear to lengthen slightly. Comparable, slightly longer S−O bond lengths (1.428−1.437 Å) are found for $[C(SO_2CF_3)_3]^-$.[40b] These effects underline the extensive delocalization of electronic charge in the anion and provide an answer for the observed gas-phase superacidity of $(R_FSO_2)_2NH$ ($R_F = CF_3$, C_4F_9).[1] This extensive electron delocalization results, in the case of $[(CF_3SO_2)_2N]^-$, in a very slight shortening of the S−C bond, which is still at 1.812(5) Å abnormally long.[39]

While in $[Mg(H_2O)_6][(CF_3SO_2)_2N]_2{\cdot}2H_2O$ limited molecular symmetry is noted, with the Mg^{2+} cation found on an inversion center, this is not the case for the third molecule discussed here, initially formulated as a sulfide of the type $[(FSO_2)_2N]_2S$, which exhibits no exact molecular symmetry. As seen in Figure 3, two FSO_2N tetrahedra are joined by a shared nitrogen atom and the resulting $(FSO_2)_2N$ moieties are linked again over the planar (sp^2-coordinated) nitrogen atoms N(1) and N(2) to the central sulfur atom S(1). The N−S(1)−N angle is, at 105.1(2)°, close to the tetrahedral angle and compares well with C-S-C angles (105.9(1)−106.7(1)°) in related compounds such as $(CF_3S)_3C{-}C(SCF_3)_3$.[45a] The two planes defined by S(2)N(1)S(3) and S(4)N(2)S(5) have an interplanar angle of 107°. Both of these planes lie perpendicular to the central N(1)−S(1)−N(2) group.

Surprisingly, all six S−N distances are identical within their esd values, even though the formal oxidation state implied by the formulation as sulfide or sulfane would be −2 for S(1), while for the remaining S atoms of the sulfonyl groups the oxidation state is +6. It appears that nitrogen lone-pair electron density is rather evenly distributed over all S−N bonds, regardless of the formal oxidation of the sulfur atoms. All S atoms act as equally effective π-acceptors in this case. Hence, formulation as $(FSO_2)_2NSN(SO_2F)_2$ is in our opinion more appropriate in analogy to $(C_6H_{11})_2NSN(C_6H_{11})_2$.[45b]

Planar, sp^2-hybridized nitrogen is not unusual and is found in all nine structures summarized in Tables 9 and 10, as well as in another acyclic S−N compound, $R_2N{-}S{-}NR_2$[45] (R = cyclohexyl). Here the N−S−N angle of 110.7(2)° is again nearly identical with the tetrahedral angle of 109.3°. However, in $(FSO_2)_2NSN(SO_2F)_2$ the S−N distances are rather long and approach ~1.7 Å. They are the longest of all the S−N distances listed in Tables 9 and 10 and longer than in R_2NSNR_2[45] ($R = C_6H_{11}$), where $d(S{-}N) = 1.657(4)$ Å, or in $S_7NSN(CH_3)_2$, where $d(S{-}N) = 1.606(6)$ Å. Again nearly planar nitrogen atoms are found.

The S−N bonds average 1.69 Å in $(FSO_2)_2NSN(SO_2F)_2$ and

---

(41) Elerman, Y.; Bats, J. W.; Fuess, H. *Acta Crystallogr.* **1983**, *C39*, 515.

(42) Zalkin, A.; Ruben, H.; Templeton, D. H. *Acta Crystallogr.* **1964**, *17*, 235.

(43) Okuda, M.; Ishihara, M.; Yamanaka, M.; Ohba, S.; Saito, Y. *Acta Crystallogr.* **1990**, *C46*, 1755.

(44) Agron, P. A.; Busing, W. R. *Acta Crystallogr.* **1985**, *C41*, 8.

(45) (a) Boese, R.; Haas, A.; Krüger, C.; Möller, G.; Waterfeld, A. *Chem. Ber.* **1994**, *127*, 597. (b) Bruce, R. B.; Gillespie, R. J.; Seim, D. R. *Can. J. Chem.* **1978**, *56*, 2927.

Table 9. Summary of Structural Features of $(RSO_2)_2N$ Derivatives

compd or ion	*d* (S−N) (Å)	∠(S-−N−S) (deg)	*d*(S−O)$_{av}$ (Å)	*d* (S−C) (Å)	*d* (N−H) (Å)	*d* (H---O) (Å)	H bonding	ref
$(CF_3SO_2)_2NH$	1.644(1)	128.4(2)	1.409(2)	1.840(3)	0.99(4)	2.261(2)	chains involving bifurcated H-bonds	*a*
$[(CF_3SO_2)_2N]^-$ with $[Mg(H_2O)_6]^{2+}$ and $2H_2O$	1.577(3)	125.0(2)	1.418(3)	1.812(5)	2.042(3)	*b*	extensive H bonding involving $[Mg(H_2O)_6]^{2+}$ lattice water and $[(CF_3SO_2)N]^-$	*a*
$(C_6H_5SO_2)_2NH$	1.643(5), 1.647(5)	127.7(3)	1.415(5)	1.763(6) 1.756(6)	1.01(6)	1.80(10)	chains with linear N−H---O bonds	4
$[(C_6H_5SO_2)_2N]^-$ with Na^+	1.598(5), 1.571(5)	127.5(3)	1.446(5)	1.777(6), 1.769(6)			Na---O and Na---N contacts 2.342(5)−2.883(5)	4
$(CH_3SO_2)_2NH\cdot H_2O$	1.645	125.0	1.428	1.746	0.89	1.85	double chain, H_2O and $(CH_3SO_2)_2NH$ alternating N−H---O crosslinks	5[c]
$(C_2H_5SO_2)_2NH$	1.645(2)	125.3(1)	1.422(2)	1.755(3)	0.99	1.88	dimers via linear H-bridges	6

[a] This work. [b] For details on H bonding see Table 8. [c] Only ranges of standard deviations are given.

Table 10. Summary of Structural Features of $(FSO_2)_2N$ Derivatives

compd or ion	*d*(S^a−N)$_{av}$[a] (Å)	*d*(S^b−N)$_{av}$[b] (Å)	*d*(S−O)$_{av}$ (Å)	*d*(S−F)$_{av}$ (Å)	∠S−N−S (deg)	comments	ref
$(FSO_2)_2NSN(SO_2F)_2$	1.688(4)	1.698(4), 1.690(4)	1.378(4)	1.502(5)	118.4(2),[b] 120.8(2)[c]	∠N−S(1)−N = 105.1(2)°	*c*
$(FSO_2)_2NXeF$	1.626(3)		1.405(3)	1.532(3)	120.5(2)	(N−Xe) = 2.200(3) Å	10
$[(FSO_2)_2N]^-$ at 112 K + $[(C_6H_5)_4As]^+$	1.567(3)		1.415(3)	1.574(3)	121.4(2)		9

[a] Sa denotes S atom of the sulfonyl group. [b] Sb denotes the central S(1) atom. [c] This work.

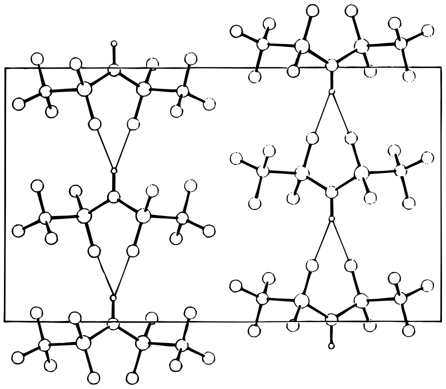


Figure 5. Intermolecular association in $(CF_3SO_2)_2NH$ via bifurcated hydrogen bonds.

rank at the lower end of bond distances of this type in organic molecules.[39] In comparison to the sum of the covalent radii for S and N of 1.77 Å,[46] the multiple-bond character appears to be small. As seen in Table 10 for related molecules, as nitrogen acquires more electron density by forming a polar, covalent bond with xenon in $(FSO_2)_2NXeF$,[10] or in the $[(FSO_2)_2N]^-$ anion,[9] more extensive electron delocalization occurs, and the S−N bond shortens to 1.626(3) Å and for the xenon derivatives to 1.567(3) Å for the anion. The latter value is comparable to 1.577(3) Å for $[(CF_3SO_2)_2N]^-$ (see Table 9).

The short S−N bond distances and the concomitant slight lengthening of both the S−O and S−F bonds suggests a redistribution of π-electron density within the approximately tetrahedral coordination sphere of sulfur. The averaged S−O and S−F bond distances of 1.378(4) and 1.502(5) Å, respectively, for $(FSO_2)_2NSN(SO_2F)_2$ are to our knowledge among the shortest known for neutral compounds. For SO_2F_2,[47b] *d*(S−O) and *d*(S−F) are 1.397(2) and 1.530(2) Å, respectively, and in the structurally related molecule $FOSO_2F$, where the FO group replaces N in the coordination sphere of sulfur, values of 1.409(6) Å (*d*(S−O)) and 1.545(6) (*d*(S−F)) are found, according to a recent electron diffraction study.[48] It would be interesting to include data reported for $[(FSO_2)_3C]^-$,[48b] but they are incomplete. All other S−O bond distances reported are longer, and the average value of 326 data sets is 1.428(10) Å for the $X-SO_2NX_2$ bond type.[39] There are in our view two reasons for the extremely short S−O and S−F bonds in $(FSO_2)_2NSN(SO_2F)_2$. (a) As already mentioned, redistribution of π-electron density around tetrahedral sulfur in the FSO_2N^- moiety, supported by the trends in S−N, S−O and S−F bond distances within the series $(FSO_2)_2NSN(SO_2F)_2$, $(FSO_2)_2NXeF$, and $[(FSO_2)_2N]^-$ (see Table 10), results in very short S−F and S−O bonds. (b) There are for this molecule no significant intermolecular interactions. Hence, the bonding electron density is entirely concentrated in the intramolecular region. This is consistent with the low melting point and the fact that the molecule sublimes. To illustrate this point further, in the series $SbF_n(SO_3F)_{3-n}$ ($n = 0, 1, 2$), where extremely accurate structural data have been obtained,[49] the shortest S−O bond distances are 1.407(3) Å and the O atom is involved in secondary,[50] intermolecular contacts of ∼3 Å while S−F distances average 1.533 Å.[49] We also note from the data in Table 9 that, for the derivatives $(RSO_2)N$ (R = CF_3, CH_3, C_2H_5, C_6H_5), hydrogen bonding is observed and may affect S−O bond distances. It is altogether not surprising that there is no intermolecular interaction for $(FSO_2)_2NSN(SO_2F)_2$ because there are only highly electronegative atoms (F and O) at the periphery of the molecule (see Figure 3) and only weak F---S(1) or O---S(1) contacts are feasible.

With σ-bonding in tetrahedrally coordinated sulfur explained by sp^3 hybridization of sulfur, π-bonding, according to ideas initially advanced some time ago by Cruickshank,[51,52] is of the dative $p\pi \rightarrow d\pi$ type. Dative π-bonding involves as donors p-type lone-pair orbitals on electron-rich atoms in the second period (N, O, and F) and $3d_{x^2-y^2}$ and $3d_{z^2}$ orbitals on sulfur. This choice of d orbitals for geometrical overlap reasons fixes the maximum π-bond order at 2. Subsequently, bond lengths,

---

(46) Huheey, J. E.; Keiter, E. A.; Keiter, R. L. *Inorganic Chemistry: Principle, Structure, and Reactivity*, 4th ed.; Harper-Collins: New York, 1993; p 292.

(47) (a) Lide, D. R.; Mann, D. R.; Fristrom, R. M. *J. Chem. Phys.* **1957**, *26*, 734. (b) Hagen, K.; Cross, V. C.; Hedberg, K. *J. Mol. Struct.* **1978**, *44*, 187.

(48) (a) Aubke, F.; Casper, B.; Müller, H. S. P.; Oberhammer, H.; Willner, H. *J. Mol. Struct.* **1995**, *346*, 111. (b) Klöter, G.; Pritzkow, H.; Seppelt, K. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 942.

(49) Zhang, D.; Rettig, S. J.; Trotter, J.; Aubke, F. *Inorg. Chem.* **1995**, *34*, 3153.

(50) Alcock, N. W. *Adv. Inorg. Chem. Radiochem.* **1972**, *15*, 1.

(51) Cruickshank, D. W. J. *J. Chem. Soc.* **1961**, 5486.

(52) Cruickshank, D. W. J. In *Inorganic Sulphur Chemistry*; Nickless, G., Ed.; Elsevier: Amsterdam, 1968; p 7.

bond angles, and S−O vibrational data were correlated,[53] to derive π-bond orders for a wide range of sulfur−oxygen compounds. Dative pπ → dπ bonding appears to be the most pronounced, where F in addition to O is bonded to sp^3-hybridized sulfur.[53] This somewhat dated approach is quite useful in our case, if it is expanded to include both N and F as pπ donor atoms and is not restricted to describe only multiple bonding in S−O compounds.[52,53] The case for fluorine participating in pπ → dπ bonding can be made, on the basis of vibrational spectra where e.g. from SO_2F_2[54] to the isoelectronic SO_3F^- [55] in $CsSO_3F$ $\bar{\nu}$(S−F) ranges from 867 to 715 cm^{-1}.

As seen in Table 10, variations in d(S−N) are more pronounced than trends in d(S−O) and d(S−F). This is in part due to nitrogen being bonded to two sulfur atoms in $[(FSO_2)_2N]^-$,[9] rather than to three in $(FSO_2)_2NSN(SO_2F)_2$, but also to the fact that lone-pair electron density is more readily delocalized from nitrogen than from oxygen or fluorine as discussed elsewhere.[53] As involvement of nitrogen in π back-donation increases, the π-bonding appears to be slightly diminished in the S−O and S−F bonds and vice versa.

A similar effect is seen for the $(RSO_2)_2N^-$ derivatives (Table 9), even though the S−O distances in $(CF_3SO_2)_2NH$ are not quite so short, where F is replaced by CF_3 and where H bonding involves the O atoms of the CF_3SO_2 group (see Figure 4).

(c) Conclusions and Summary. Cruickshank's model of pπ → dπ bonding[51,52] allows us to rationalize trends in S−N, S−O, and S−F bond distances, collected in Tables 9 and 10, if both F and, especially, N are included in addition to O as pπ donor atoms. The VSEPR concept of molecular structure[56,57] permits a good explanation of the geometries for the three molecules reported here, because hydrogen bonding in $(CF_3SO)_2NH$ and in $[Mg(H_2O)_6][(CF_3SO_2)_2N]_2 \cdot 2H_2O$ appears to cause only a minor perturbation. Trigonal-planar, sp^2-hybridized nitrogen is present in all compounds and ions discussed here, with structural information on them collected in Tables 9 and 10. It seems that electron delocalization in all acyclic S−N compounds is as common as it is in cyclic systems.[11,12] In the anions $[(RSO_2)_2N]^-$ (R = CF_3, F,[9] C_6H_5[4]), where electron delocalization is most extensive, the observed S−N distances are shorter than in S_4N_4[58,59] and are comparable to those in planar $[S_4N_4]^{2+}$.[13] Multiple bonding involves planar nitrogen (sp^2) for the most part and tetrahedral sulfur with highly electronegative additional ligands such as F, R_F, and O. Hence, on deprotonation stronger S−N bonds are observed for the anions than for the corresponding nitrogen acids, while the concomitant loss of bond strength in the S−O, and, where applicable, S−F bonds appears to be minor. The suggested stabilization of the gas-phase superacid anions[1,3] by electron delocalization can now be clearly documented for the pair $(CF_3SO_2)_2NH$ and $[(CF_3SO_2)_2N]^-$.

A similar argument can be made for the corresponding carbon acids $(RSO_2)_3CH$ (R = R_F, F) and many of the gas-phase superacids.[1] The reported structure of the anion $[(CF_3SO_2)_3C]^-$ [40b] supports this view. The reported order of gas-phase acidities[1] $FSO_2OH \approx CF_3SO_2OH < (CF_3SO_2)_2NH < (CF_3SO_2)_3CH$ can now easily be understood in terms of anion stablization via electron delocalization in 3d orbitals of sulfur in the RSO_2^- moieties (R = F, CF_3). For $[(CF_3SO_2)_2N]^-$ and $[(CF_3SO_2)_3C]^-$ with respectively two and three such moieties available, more extensive electron delocalization is possible than for the two oxygen acids which have only one RSO_2^- moiety.

In the liquid phase, judging from the reported Hammett function values $-H_0$ of 15.1 for FSO_2OH[60] and 14.3 for CF_3SO_2OH,[61] the two oxygen acids belong to the strongest Brønsted superacids.[60] Here anion stabilization occurs via solvation and involves strong O−H---O hydrogen bonds. Even though no $-H_0$ values for $(CF_3SO_2)_2NH$ and $(CF_3SO_2)_3CH$ appear to have been determined, reduced anion stabilization by solvation is expected because the strength of hydrogen bonds is expected to decrease in the order O−H---O> N−H---O > C−H---O and the observed order of gas-phase acidities for the four acids is expected to be reversed in the liquid state.

The unusual nature of the bonding in these three structures reported is also reflected in the extremely short S−O and S−F bond distances in $(FSO_2)_2NSN(SO_2F)_2$.

Acknowledgment. Financial support by the Heinrich Herz Stiftung is gratefully acknowledged.

Supporting Information Available: Complete crystallographic data and details of data collection, drawings of the molecular structure, and tables of atomic fractional coordinates, atomic thermal parameters, and selected interatomic distances and angles for **1**−**3** (18 pages). Ordering information is given on any current masthead page.

IC9507934

---

(53) Gillespie, R. J.; Robinson, E. A. *Can. J. Chem.* **1963**, *41*, 2074.
(54) Gillespie, R. J.; Robinson, E. A. *Can. J. Chem.* **1961**, *39*, 2171.
(55) Ruoff, A.; Milne, J. B.; Kaufmann, G.; Leroy, M. *Z. Anorg. Allg. Chem.* **1970**, *37*, 119.
(56) Gillespie, R. J. *Molecular Geometry*; Van Norstrand Reinhold: London, 1972.
(57) Gillespie, R. J.; Hargittai, I. *The VSEPR Model of Molecular Geometry*; Allyn and Bacon: Boston, 1991.
(58) Sharma, B. D.; Donohue, J. *Acta Crystallogr.* **1963**, *16*, 891.
(59) Delucia, M. I.; Coppens, P. *Inorg. Chem.* **1978**, *17*, 2336.
(60) Gillespie, R. J.; Peel, T. E. *J. Am. Chem. Soc.* **1973**, *95*, 5173.
(61) O'Donnell, T. A. *Superacids and Acidic Melts as Inorganic Chemical Reaction Media*; VCH: New York, 1993; p 41.