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Communication

SF_4•$N(C_2H_5)_3$: The First Conclusively Characterized SF_4 Adduct with an Organic Base†

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Sulfur tetrafluoride and triethylamine react at low temperatures to form a 1:1 adduct. The unambiguous characterization of the SF_4•$N(C_2H_5)_3$, which is only stable at low-temperature, proves the Lewis acid property of SF_4 towards organic Lewis bases. The S–N bond has a length of 2.383(2) Å and is an archetypical example of a dative S^{IV}←N bonding modality.

Sulfur tetrafluoride is a highly reactive gas which has been used as a fluorinating agent in organic chemistry, replacing oxygen by fluorine.[1] It can convert carboxylic acid, carbonyl, and hydroxyl groups into CF_3, CF_2, and CF groups. It has been suggested that a Lewis acid base adduct between the oxygen and the SF_3^+ cation, which is assumed to form in the presence of traces of HF, serves as an intermediate in these fluorination reactions.[1] In order to evaluate proposed reaction mechanisms involving SF_4, it is essential to understand its fundamental Lewis acid base chemistry. While SF_4 acts as a fluoride-ion donor towards Lewis acids, such as BF_3, AsF_5 and SbF_5,[2] it can also act as a weak Lewis acid. The Lewis acidity of SF_4 has been quantified by Christe's fluoride ion affinity scale with a pF^- value of 5.67, which lies between the pF^- values of two other, weakly fluoroacidic main-group fluorides, XeF_4 (5.71) and PF_3 (4.49), reflecting the weak Lewis acidity of SF_4 toward fluoride.[3] The Lewis acid behaviour of SF_4 has been experimentally documented by its reaction with fluoride. The reactions of SF_4 with $[N(CH_3)_4][F]$, CsF, and $[((CH_3)_2N)_3S][(CH_3)_3SiF_2]$ gave the $[N(CH_3)_4][SF_5]$, $Cs[SF_5]$, and $[((CH_3)_2N)_3S][SF_5]$ salts.[4] The crystal structure of $Rb[SF_5]$,[5] $Cs_6[SF_5]_4[HF_2]_2$,[5] and $[Cs(18\text{-crown-}6)_2][SF_5]$,[6] showed the expected square pyramidal geometry of the SF_5^- anion.

The Lewis acid behaviour of SF_4 towards other bases has not been conclusively shown so far. Based on a "crude tensiometric study", Muetterties suggested the formation of SF_4•$N(C_2H_5)_3$ and SF_4•NC_5H_5 adducts.[7] Additional experimental support is based on a matrix-isolation infrared spectroscopic study of adducts between SF_4 and NH_3, NC_5H_5, acetone, and CH_3NH_2. This study, however, was severely hampered by overlap with signals arising from the reactants, and the formation of adducts was only supported by the observation of a few S–F stretching bands attributed to the adducts.[8] An elemental analysis study of potential adducts between SF_4 and pyridine suggested the existence of adducts with 1:1, 1:2, 1:4, and 1:8 ratios of SF_4 versus pyridine at –78 °C.[9] In spite of the lack of the unambiguous characterization of nitrogen-base adducts of SF_4, these findings have found their way into inorganic chemistry textbooks.[10] The goal of the present study was the conclusive study of a Lewis acid-base adduct of SF_4 with a nitrogen base.

Excess sulfur tetrafluoride reacts with triethylamine upon melting at –120 °C, yielding a colourless solution (eqn (1)).

$$SF_4 + N(C_2H_5)_3 \underset{> -45\ ^\circ C}{\overset{< -45\ ^\circ C}{\rightleftharpoons}} SF_4{\bullet}N(C_2H_5)_3 \qquad (1)$$

Removal of excess SF_4 at –90 °C yields a colourless solid, having a distinct low-temperature Raman spectrum (vide infra) and its mass balance being consistent with the 1:1 adduct. The adduct is soluble in SF_4, $N(C_2H_5)_3$, and CH_2Cl_2 at –80 °C. The adduct decomposes above –45 °C under dynamic vacuum (4 mTorr) resulting in a very pale brown clear liquid, which was confirmed by Raman spectroscopy to be triethylamine contaminated by small amounts of unidentified impurities. Fluorine-19 NMR spectra of SF_4•$N(C_2H_5)_3$ in excess SF_4 and in excess $N(C_2H_5)_3$ at –78 and –80 °C gave rise to single resonances at 56.3 and 68.8 ppm, respectively, indicating rapid exchange of the fluorine environments under these conditions. Fluorine-19 NMR spectroscopy of CH_2Cl_2 solutions at –80 °C, on the other hand, gave rise to two triplets at 85.9 and 33.3 ppm with $^2J(^{19}F-^{19}F)$ = 80.1 Hz arising from free SF_4, indicating the full dissociation of SF_4•$N(C_2H_5)_3$ in CH_2Cl_2.

Crystals of SF_4•$N(C_2H_5)_3$ were grown by slow evaporation of liquid SF_4 between –120 and –90 °C. The adduct crystallizes in the triclinic space group $P\overline{1}$ and its geometry is shown in Fig. 1.

The crystal structure of SF_4•$N(C_2H_5)_3$ shows that SF_4 retains its seesaw geometry upon adduct formation with the nitrogen coordinating in the equatorial plane, resulting in a pseudo-

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octahedral structure with F(1), F(2), the nitrogen and the lone pair in the equatorial plane. As a consequence of the coordination of nitrogen trans to F(2) (N(1)–S(1)–F(2): 173.54(6)°), the equatorial SF_2 angle is compressed to 91.80(7)° compared to 103.8(6)° in free SF_4 and the lone pair is forced into the position trans to the S–F(1) bond. The S---N distance is 2.3844(19) Å, which is one of the longest reported S^{+IV}–N bonds. A longer S---N distance was observed in the Cs^+ salt of the $(O_2S)_2N_3^-$ anion, in which one nitrogen of the azido group coordinates to two SO_2 molecules with S---N distances of 2.201(5) and 2.437(4) Å.[11] All S–F bonds in the adduct are elongated compared to those in free SF_4, reflecting the increase in the ionic character of S–F bonding in the adduct as a consequence of donation of electron density from the coordinating nitrogen to sulfur. The axial (1.6807(14) and 1.6815(14) Å) and equatorial S–F bonds (1.5555(14) and 1.5943(14) Å) are significantly longer than those of free SF_4 (axial: 1.643(5) Å; equatorial: 1.542(5) Å).[12] The length of the S–F(1) bond (1.5555(14) Å), which is trans to the lone pair, is similar to the axial S–F bond length (1.559 Å) in the SF_5^- anion.[5]

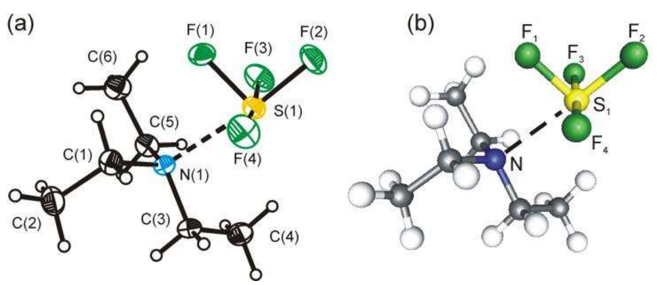

Fig. 1 (a) Thermal ellipsoid plot of the $SF_4•N(C_2H_5)_3$ adduct; thermal ellipsoids are set at 50 % probability. (b) Calculated geometry of $SF_4•N(C_2H_5)_3$ at the DFT level of theory. Bond lengths (Å) and angles (deg) (calculated values in italics): S---N(1) 2.3844(19), *2.626*; S–F(1) 1.5555(14), *1.586*; S–F(2) 1.5943(14), *1.607*; S–F(3) 1.6807(14), *1.710*; S–F(4) 1.6815(14), *1.714*; F(1)–S–F(2) 91.70(7), *94.6*; F(1)–S–F(3) 86.47(7), *87.0*; F(3)–S–F(4) 172.13(6), *173.3*; N(1)–S–F(2) 173.54(6), *176.6*; N(1)–S–F(4) 90.74(7), *89.6*.

The experimental geometry of $SF_4•N(C_2H_5)_3$ is in excellent agreement with that optimized at the B3LYP level of theory using the aug-cc-pVTZ basis set for all atoms (Figure 1), even reproducing the conformation of the ethyl groups in the crystal structure. The main difference between the calculated and experimental geometries is that the calculated S---N distance (2.626 Å) underestimates the strength of interaction between the Lewis acid and base.

The nature of the $SF_4•N(C_2H_5)_3$ adduct is fundamentally different from compounds that also contain a SF_4 moiety, such as $F_4S{=}NH_2^+$ [13] and $F_4S{=}CH_2$,[14] since in these compounds, sulfur is doubly bonded to N and C, while sulfur has a lone pair and accepts a coordinative bond to nitrogen in the adduct of this study. The difference is reflected by the substantially smaller S–F bond lengths and significantly larger equatorial F–S–F angle compared to the values for $SF_4•N(C_2H_5)_3$.

The $SF_4•N(C_2H_5)_3$ adduct was also characterized by low-temperature Raman spectroscopy. The Raman spectra of $SF_4•N(C_2H_5)_3$ as well as that of the reactants SF_4 and $N(C_2H_5)_3$ are depicted in Figure 2. In order to aid with the assignment of the Raman spectrum, the vibrational frequencies of $SF_4•N(C_2H_5)_3$, SF_4 and $N(C_2H_5)_3$ were calculated at the B3LYP level of theory. The experimental and calculated vibrational frequencies of the N---SF_4 moiety of $SF_4•N(C_2H_5)_3$ are listed in Table 2, while a complete list of vibrational frequencies are given in the supporting information. The Raman spectrum of the adduct contains signals associated with the SF_4 and $N(C_2H_5)_3$ moieties.

The signals of both moieties are shifted and exhibit splittings compared to those of the parent Lewis acid and base. Gaseous SF_4 has C_{2v} symmetry, with the symmetric and asymmetric stretches of the equatorial SF_2 appearing at 892 and 867 cm^{-1}.[15] The symmetric and asymmetric stretches of the axial SF_2 moiety have significantly lower frequencies, *i.e.*, 558 and 730 cm^{-1}.[15]

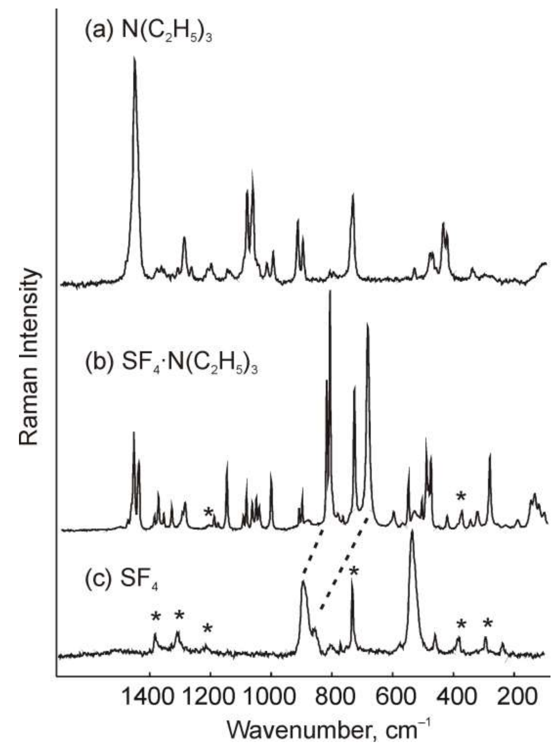

Fig. 2 Raman spectra of (a) solid $N(C_2H_5)_3$, (b) solid $SF_4•N(C_2H_5)_3$, and liquid SF_4 at –110 °C. Asterisks (*) denote bands arising from the FEP sample tube.

The high-frequency, equatorial S–F stretching bands are shifted to 826/816 and 691 cm^{-1}, which are assigned to ν(S–F_1) and ν(S–F_2), respectively. Analysis of the potential energy distribution showed that the stretches of these two bonds do not exhibit significant vibrational coupling. The larger difference between the frequencies of these two equatorial S–F stretches (125 cm^{-1}) compared to those in free SF_4 (25 cm^{-1}), in which the two stretches are coupled, is a consequence of the significantly different S–F bond lengths in the adduct. The observation that the calculations underestimate the strength of interaction is reflected by the smaller difference between the calculated equatorial S–F stretching frequencies (64 cm^{-1}) compared to that of the experimental values. The asymmetric and symmetric combination of ν(S–F_3) and ν(S–F_4) appear at 606 and 498 cm^{-1}, which is also significantly lower than the corresponding S–F stretching frequencies of neat SF_4, reflecting more ionic S–F bonding in the adduct. The S---N stretch was not observed, which is consistent with the low calculated Raman intensity and the low calculated vibrational frequency. The calculated S---N stretching frequency of 70 cm^{-1} indicates weak S---N bonding interactions, which is paralleled by the observation of the facile dissociation of the adduct above –45 °C.

Table 2. Observed and Calculated Frequencies for the N---SF_4 moiety of $SF_4 \bullet N(C_2H_5)_3$

Exptl[a]	Calcd[b]	Assignment[c]
826(24)		$\nu(S{-}F_1)$
816(100)	805(76)[130]	
691(80)	741(59)[266]	$\nu(S{-}F_2)$
606(7)	644(1)[467]	$\nu(S{-}F_3) - \nu(S{-}F_4)$
513(10)	481(2)[31]	$\delta(F_1SF_2) + \delta(F_3SF_4)$
498(33)	505(7)[<1]	$\nu(S{-}F_3) + \nu(S{-}F_4)$
	473(2)[11]	$\delta(F_1S_1F_3) - \delta(F_1S_1F_4) + \rho_w(F_1S_1F_2)$
	388(<1)[1]	$\rho_t(F_1S_1F_2) + \delta(F_2S_1F_3) - \delta(F_2S_1F_4)$
353(4)	346(1)[4]	$\rho_r(F_1S_1F_2) + \rho_w(F_3S_1F_4)$
290 (32)	255(4)[<1]	$\delta(F_1S_1F_2) + \rho_w(F_3S_1F_4)$
142(15)	158(<1)[1]	$\rho_t(S_1F_1F_2) + \rho_t(N(C_2H_5)_3)$
	94(<1)[<1]	$\rho_t(S_1F_1F_2) - \rho_r(N(C_2H_5)_3)$
	83(<1)[4]	$\rho_t(S_1F_3F_4) - \rho_t(N(C_2H_5)_3)$
	70(<1)[5]	$\nu(S_1{-}N)$
	30(<1)[<0.1]	$\rho_t(S_1F_2F_3F_4) - \rho_t(N(C_2H_5)_3)$

a Relative intensities are given in parentheses. b Raman intensities, in $Å^4\ u^{-1}$ are given in parentheses, infrared intensities in km mol^{-1} are given in square brackets. c Atom numbering is given in Figure 1.

While, in this study, SF_4 was shown to act as a weak Lewis acid towards organic bases, the heavier analogue TeF_4 acts, as expected, as a stronger Lewis acid and was shown to accommodate two THF donor molecules.[16] Sulfur-nitrogen chemistry is very rich, and S–N bonding in sulfur-nitrogen halides exhibit a wide range of bonding modalities. The bond order of S–N bonds ranges from three ($N{\equiv}SF_3$)[17] to two ($H_2N{=}SF_4^+$)[13] and one ($O_2N{-}SF_5$).[18] The present structure is an important example of the dative N→S bonding modality. The calculated bond dissociation energy for the S---N bond is 13.5 kJ mol^{-1}, which is similar to some hydrogen bonding interactions. The gas-phase ΔH° and ΔG° of reaction (1) were calculated as –15.98 and –98.08 kJ mol^{-1}, respectively.

In conclusion, we report the first nitrogen-base-SF_4 adduct that was synthesized and unambiguously characterized, exemplifying the Lewis acidity of SF_4 towards bases beside fluoride ions. This adduct contains a long dative S---N bond, representing a new bonding modality for N/S/F compounds. The observation that SF_4 and organic bases form adducts that contain weaker S–F bonds may lead to a re-evaluation of reaction mechanisms involving SF_4. An extensive study of the Lewis acid behaviour towards a series of bases is currently being pursued and will be reported elsewhere.

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