Electronic Supplementary Information

Recent Advances in Sulfur Tetrafluoride Chemistry: Syntheses, Structures, and Applications

Kazuhiko Matsumoto,[a,*] Michael Gerken[b,*]

[a]Graduate School of Energy Science, Kyoto University, Yoshida, Sakyo-ku, Kyoto 606-8501, Japan

[b]Canadian Centre for Research in Advanced Fluorine Technologies and Department of Chemistry and Biochemistry, University of Lethbridge, Lethbridge, Alberta T1K 3M4, Canada

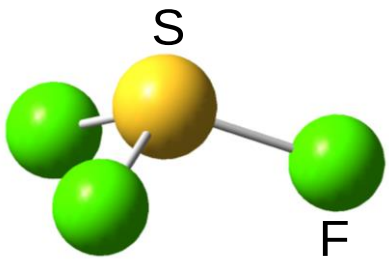
*Corresponding authors

E-mail: k-matsumoto@energy.kyoto-u.ac.jp (K. Matsumoto); michael.gerken@uleth.ca (M. Gerken)

Table S1 Geometrical parameters of $[SF_3]^+$ and related species determined in crystal structures[a]

Salt (CCDC number if available)	S–F [Å]	F–S–F [deg]	S···N [Å]	N···S···N [deg]	N···S–F [deg]
$[SF_3][BF_4]$[1]	1.495(2) 1.499(2)	97.39(12) 97.62(7)	–	–	–
$[SF_3]_2[GeF_5]$[2]	1.519(1) 1.515(2)	96.23(10) 96.12(8)	–	–	–
$[SF_3][W_2O_2F_9]\cdot HF$[3] (CCDC-2031686)	1.509(3) 1.527(3) 1.509(3)	97.38(14) 96.94(16) 97.02(15)	–	–	–
$[SF_3][Mo_2O_2F_9]$[3] (CCDC-2031687)	1.5144(9) 1.5121(9) 1.5102(9)	96.57(5) 97.36(5) 97.65(5)	–	–	–
$[SF_3(NC_5H_5)_2][AsF_6]\cdot 0.5C_5H_5N$[4] (CCDC-2049163)	1.570(3) 1.5626(3) 1.588(3)	88.56(18) 89.96(19) 90.87(18)	2.154(5) 2.054(5)	88.51(18)	82.37(17) 83.84(18) 90.15(18) 89.47(18) 172.39(19) 172.24(19)
$[SF_3(NC_5H_5)_2][SbF_6]\cdot 0.5C_5H_5N$[4] (CCDC-2049164)	1.5605(14) 1.5996(14) 1.6287(15)	90.06(8) 90.73(8) 88.59(8)	2.0596(19) 2.1403(18)	89.40(7)	89.06(8) 84.30(8) 82.42(7) 89.88(7) 172.89(8) 172.43(8)
$[SF_3(NC_5H_5)_2][AsF_6]\cdot CH_2Cl_2$[4] (CCDC-2049165)	1.566(4) 1.620(4) 1.617(4)	89.27(15) 89.78(18) 90.51(14)	2.106(2) 2.098(2)	90.29(10)	82.62(13) 82.89(13) 88.84(16) 89.23(16) 171.88(15) 172.64(15)
$[SF_3(NC_5H_5)_2][SbF_6]\cdot CH_2Cl_2$[4] (CCDC-2049166)	1.571(5) 1.618(4) 1.612(4)	89.3(2) 89.8(2) 91.3(3)	2.108(2) 2.126(2)	90.07(11)	82.34(14) 82.01(14) 88.57(16) 89.48(16) 171.35(18) 172.07(18)
$[SF_3(NC_5H_5)_2][SbF_6]\cdot CH_3CN$[4] (CCDC-2049167)	1.556(3) 1.625(3) 1,598(3)	88.73(18) 90.12(17) 90.73(18)	2.140(4) 2.061(4)	89.60(17)	82.10(16) 83.53(17) 88.70(17) 89.93(17) 172.23(18) 172.21(18)
$[SF_3(phen)][SbF_6]\cdot 2CH_2Cl_2$[4] (CCDC-2049168)	1.553(2) 1.611(3) 1.600(3)	88.79(13) 93.77(15) 89.68(14)	2.137(3) 2.109(3)	78.33(13)	84.00(13) 83.73(13) 93.90(14)

					93.24(14) 169.71(14) 169.95(14)
$[SF_3(NCCH_3)_2][SbF_6]$[4] (CCDC-2049169)	1.509(2) 1.5119(19)	96.44(9) 95.03(17)	2.621(3) 2.462(3)	101.21(15)	80.62(8) 81.78(12) 175.35(10)
$[F_3S(NSF_3)_2][AsF_6]$[5]	1.511(1) 1.519(1) 1.520(1)	96.2(1) 96.8(1) 96.3(1)	2.552(2) 2.511(2)	96.3(1)	83.1(1) 81.1(1) 83.2(1) 84.2(1) 177.3(1) 179.5(1)



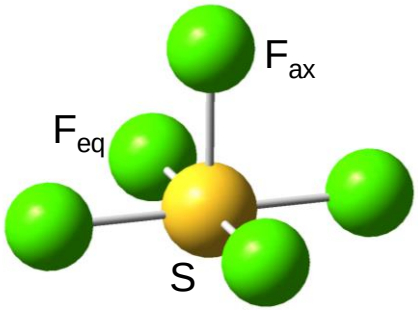
SF_3^+

Table S2 Geometrical parameters of $[SF_5]^-$ and related species determined in crystal structures[a]

Salt (CCDC number if available)	S–F_{ax} [Å]	S–F_{eq} [Å]	F_{ax}–S–F_{eq} [deg]	cis F_{eq}–S–F_{eq} [deg]	trans F_{eq}–S–F_{eq} [deg]
$Rb[SF_5]$[6]	1.559(15)	1.707(14) 1.729(13)	83.4(7) 86.6(7)	88.5(7) 88.5(6)	169.8(7)
$Cs_6[SF_5]_4[HF_2]_2$[6]	1.560(5)	1.481(30) 1.781(15)	79.8(5) 91.0(11)	88.2(13) 92.2(13)	177.9(15) 159.7(6)
$[Cs(18\text{-crown-}6)_2][SF_5]$[7] (complete F_{ax}/F_{eq} disorder)	1.576(8) 1.59(2) 1.574(8) 1.56(2)	1.59(2) 1.55(2)	90.9(5) 89.5(6)	89.1(5) 90.5(6)	179.921 180.000
$[HNC_5H_3(CH_3)_2]_2F[SF_5]\cdot SF_4$[8] (CCDC-1477905)	1.564(2)	1.730(2) 1.763(2) 1.719(2) 1.664(2)	86.74(13) 85.13(13) 83.96(13) 85.99(15)	98.98(13) 90.35(13) 88.89(10) 89.35(11)	171.08(13) 170.70(13)
$[HNC_5H_3(CH_3)_2]_2F[SF_5]\cdot 4SF_4$[9] (CCDC-932409)	1.586(2)	1.709(4) 1.698(3) 1.663(3) 1.718(5)	85.9(2) 87.02(13) 84.28(19) 82.0(2)	88.03(19) 87.8(3) 90.67(19) 91.6(3)	170.1(3) 168.5(2)
	1.506(5)	1.697(8) 1.699(7) 1.657(7) 1.594(17)	78.2(4) 83.2(3) 93.0(3) 89.7(7)	86.9(6) 93.1(8) 93.7(6) 85.2(8)	172.7(8) 175.08(6)
$[C_6H_{12}N_2H]_2F[SF_5]\cdot 6SF_4$[10] (CCDC-1994898)	1.428(10)	1.678(6) 1.719(5) 1.596(11) 1.751(12)	99.2(7) 98.8(6) 85.7(6) 86.7(8)	75.2(6) 102.4(5) 103.5(6) 78.5(5)	175.1(4) 174.1(8)
	1.514(8)	1.678(6) 1.719(5) 1.624(9) 1.739(9)	85.9(6) 87.9(5) 87.3(4) 87.2(6)	84.3(5) 94.6(4) 95.6(5) 85.0(4)	175.1(4) 173.2(6)
$[Cs(tetraglyme)_2][SF_5]$[11] (CCDC-1861202)	1.498(6)	1.676(5) 1.691(5) 1.702(5) 1.713(5)	84.8(4) 86.0(4) 84.2(4) 83.8(3)	85.0(5) 87.3(9) 93.9(7) 91.9(7)	169.9(6) 166.0(7)
$[P(NIiPr)_3F][SF_5]$[12] (CCDC-1585869)	1.585(3)	1.697(5) 1.690(5) 1.754(5) 1.727(4)	85.2(2) 85.4(2) 82.6(2) 84.9(2)	88.4(3) 91.7(4) 89.9(3) 88.0(3)	167.6(3) 170.2(2)
	1.417(7)	1.716(4) 1.707(4) 1.621(5) 1.767(4)	85.5(2) 85.2(3) 88.5(3) 82.8(2)	87.9(2) 89.1(2) 90.6(3) 91.1(3)	167.9(2) 174.0(3)

$[R_3P{=}N^tBuH][SF_5]$[13]	1.548(15)	1.683(16)	88.0(8)	78.1(12)	169.6(14)
(R = –N=P(NEt$_2$)$_3$)		1.664(18)	87.2(11)	91(2)	168.0(19)
(CCDC- 2002669)		1.84(3)	87.1(10)	92.5(12)	
		1.598(18)	88.2(9)	98(2)	

[a] NIiPr: 1,3-diisopropyl-4,5-dimethylimidazolin-2-ylidenamino.

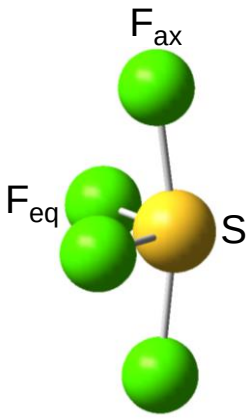


SF_5^-

Table S3 Geometrical parameters of SF_4 in its pure and adducted forms determined in crystal structures.

Salt (CSD or CCDC number if available)	S–F_{ax} [Å]	S–F_{eq} [Å]	F_{ax}–S–F_{ax} [deg]	F_{eq}–S–F_{eq} [deg]	S···X (X = F, O or N) [Å]
SF_4[9] (CSD-425996)	1.647(5) 1.676(5) 1.671(5) 1.635(4)	1.527(4) 1.535(4) 1.553(4) 1.474(6)	172.6(3) 171.6(3)	101.0(2) 99.6(3)	F 2.954(5) F 3.031(5) F 2.975(4) F 3.261(6)
$[HNC_5H_3(CH_3)_2]_2F[SF_5]\cdot SF_4$[8] (CCDC-1477905)	1.6557(12) 1.6736(12)	1.5415(11) 1.5538(13)	170.94(7)	97.39(7)	F 2.5116(12)
$[HNC_5H_3(CH_3)_2]_2F[SF_5]\cdot 4SF_4$[9] (CCDC-932409)	1.650(2) 1.706(2)	1.545(2) 1.549(2)	171.31(11)	97.43(11)	F 2.487(2) F 2.818(2)
$[C_6H_{12}N_2H]_2F[SF_5]\cdot 6SF_4$[10] (There is one highly disordered SF_4 molecule) (CCDC-1994898)	1.692(4) 1.693(4) 1.690(4) 1.669(4) 1.668(4) 1.669(4) 1.686(5) 1.669(5) 1.656(5) 1.657(5)	1.539(4) 1.584(3) 1.551(4) 1.577(4) 1.545(4) 1.561(4) 1.547(4) 1.553(4) 1.505(5) 1.520(5)	172.76(19) 171.2(2) 172.6(2) 168.4(3) 171.9(3)	95.4(2) 96.08(19) 98.5(2) 99.0(3) 101.2(3)	N 2.514(5) N 2.594(5) F 2.662(5) F 2.613(6) F 3.119(8)
$SF_4\cdot NC_5H_5$[14] (CCDC-1037495)	1.677(2) 1.652(2)	1.5345(15) 1.5599(14)	172.60(10)	95.57(8)	N 2.514(2)
$SF_4\cdot 4\text{-}NC_5H_4(CH_3)$ [14] (CCDC-1037496)	1.660(2) 1.665(2)	1.526(2) 1.551(2)	172.36(11)	95.74(9)	N 2.513(3)
$SF_4\cdot 4\text{-}NC_5H_4N(CH_3)_2$[14] (CCDC-1037497)	1.682(2) 1.684(2)	1.561(2) 1.616(2)	169.70(14)	89.98(11)	N 2.141(2)
$[HNC_5H_5]F\cdot SF_4$[8] (CCDC-1477908)	1.6622(11) 1.6680(11) 1.6632(11) 1.6671(11)	1.5398(9) 1.5425(9) 1.5382(9) 1.5440(9)	172.03(5) 171.93(5)	98.49(5) 98.69(6)	F 2.6826(9) F 2.7739(9) F 2.6923(9)
$[HNC_5H_5][HF_2]\cdot 2SF_4$[8] (CCDC-1477906)	1.643(3) 1.648(3) 1.652(3) 1.670(3)	1.537(2) 1.537(2) 1.535(2) 1.535(2)	171.21(18) 170.90(19)	99.71(17) 99.47(18)	F 2.876(3) F 2.840(3)
$[HNC_5H_4(CH_3)]F\cdot SF_4$[8] (CCDC-1477909)	1.650(4) 1.652(4)	1.543(4) 1.544(4)	172.06(6)	97.80(7)	F 2.632(6)
$[HNC_5H_4N(CH_3)_2][HF_2]\cdot 2SF_4$[8] (CCDC-1477911)	1.6489(15) 1.6747(16) 1.6326(15) 1.6619(16) 1.6499(15) 1.6728(16) 1.6545(15) 1.6825(16)	1.5421(14) 1.5461(14) 1.5330(15) 1.5418(13) 1.5417(14) 1.5432(15) 1.5355(14) 1.5455(13)	171.03(8) 170.69(8) 170.94(8) 171.85(7)	99.24(9) 98.80(8) 99.02(9) 99.04(9)	F 2.6783(18) F 2.8702(18) F 2.7133(18) F 2.800(2) F 2.758(2) F 2.7666(18) F 2.6787(19) F 2.8410(17)
$[HNH_4C_5{-}C_5H_4N]F\cdot 2SF_4$[8] (CCDC-1477904)	1.644(2) 1.650(2)	1.521(2) 1.559(2)	173.90(14)	96.06(11)	N 2.613(3)

	1.633(2)	1.510(2)	174.25(15)	98.75(14)	F 2.562(3)
	1.651(2)	1.553(2)			
$[HNH_4C_5{-}C_5H_4NH]2F{\cdot}4SF_4$[8]	1.642(3)	1.512(3)	174.23(16)	99.83(16)	F 2.838(3)
(CCDC-1477903)	1.643(3)	1.534(3)			
	1.653(2)	1.536(2)	172.39(11)	97.97(13)	F 2.658(2)
	1.680(2)	1.547(2)			F 2.695(3)
$SF_4{\cdot}N(C_2H_5)_3$[15]	1.6807(14)	1.5555(14)	172.13(6)	91.80(7)	N 2.3844(19)
(CCDC-883511)	1.6815(14)	1.5943(14)			
$C_6H_{12}N_2{\cdot}2SF_4$[10]	1.685(3)	1.561(3)	171.01(11)	92.66(11)	N 2.362(4)
(CCDC-1994897)	1.685(3)	1.596(3)			
	1.684(3)	1.574(3)	170.86(10)	92.27(9)	N 2.337(4)
	1.697(3)	1.595(3)			
$C_6H_{12}N_4{\cdot}2SF_4$[10]	1.683(2)	1.5647(16)	172.50(10)	94.50(12)	N 2.774(3)
(CCDC-1994893)	1.676(2)	1.5648(16)			N 2.774(3)
	1.670(3)	1.543(3)	172.1(3)	95.0(5)	N 2.460(3)
	1.626(3)	1.578(3)			
$[C_6H_{12}N_4H][HF_2]{\cdot}SF_4$[10]	1.658(8)	1.572(10)	169.4(7)	98(2)	N 2.791(2)
(CCDC-1994894)	1.668(11)	1.572(10)			
$[C_7H_{13}NH]F{\cdot}3.5SF_4$[10]	1.654(2)	1.5415(18)	171.54(12)	97.54(11)	F 2.4945(13)
(CCDC-1994895)	1.677(2)	1.551(2)			
$(SF_4{\cdot}OC_4H_8)_2$[16]	1.6430(17)	1.5344(17)	173.77(11)	98.25(10)	O 2.7766(17)
(CCDC-1507217)	1.6610(18)	1.5448(16)			O 2.8022(19)
	1.6503(19)	1.5465(17)	171.62(11)	98.46(10)	O 2.7892(17)
	1.6557(19)	1.5468(16)			O 2.793(2)
$SF_4{\cdot}(OC_4H_8)_2$[16]	1.649(2)	1.5275(19)	171.84(12)	96.68(11)	O 2.687(2)
(CCDC-1507218)	1.658(2)	1.5350(19)			O 2.701(2)
	1.643(2)	1.5341(18)	171.12(11)	96.50(10)	O 2.678(2)
	1.653(2)	1.5454(18)			O 2.737(2)
	1.641(2)	1.5316(19)	172.02(11)	96.73(11)	O 2.662(2)
	1.641(2)	1.5438(19)			O 2.792(2)
	1.626(2)	1.5352(19)	172.63(12)	97.07(10)	O 2.703(2)
	1.641(2)	1.5457(18)			O 2.731(2)
$SF_4{\cdot}(O{=}C_5H_8)_2$[16]	1.6579(10)	1.5455(10)	171.85(6)	98.24(6)	O 2.7592(12)
(CCDC-1507216)	1.6674(10)	1.5478(10)			O 2.7880(12)
$SF_4{\cdot}CH_3OC_2H_4OCH_3$[16]	1.6602(10)	1.5473(7)	171.41(5)	99.03(5)	O 2.8692(9)
(CCDC-1507214)	1.6736(10)	1.5474(7)			O 2.8692(9)
$C_8H_{10}N_4O_2{\cdot}2SF_4{\cdot}HF$[16]	1.6462(14)	1.5354(13)	172.50(7)	99.74(8)	O 2.8586(17)
(CCDC-1507215)	1.6717(14)	1.5440(13)			O 2.9954(18)
	1.6556(14)	1.5466(12)	171.48(6)	99.30(7)	O 2.8034(19)
	1.6706(13)	1.5483(13)			F 2.7932(15)



SF_4

References

1. D. D. Gibler, A. Zalkin, C. J. Adams, N. Bartlett and M. Fischer, *Inorg. Chem.*, 1972, **11**, 2325-2329.
2. T. E. Mallouk, G. L. Rosenthal, G. Muller, R. Brusasco and N. Bartlett, *Inorg. Chem.*, 1984, **23**, 3167-3173.
3. D. Turnbull, P. Chaudhary, D. Leenstra, P. Hazendonk, S. D. Wetmore and M. Gerken, *Inorg. Chem.*, 2020, **59**, 17544-17554.
4. D. Turnbull, P. Chaudhary, P. Hazendonk, S. D. Wetmore and M. Gerken, *Inorg. Chem.*, 2021, **60**, 3893-3901.
5. G. L. Smith and G. J. Schrobilgen, *Inorg. Chem.*, 2009, **48**, 7714-7728.
6. J. Bittner, J. Fuchs and K. Seppelt, *Z. Anorg. Allg. Chem.*, 1988, **557**, 182-190.
7. M. Clark, C. J. Kellenyuen, K. D. Robinson, H. Zhang, Z. Y. Yang, K. V. Madappat, J. W. Fuller, J. L. Atwood and J. S. Thrasher, *Eur. J. Solid State Inorg.*, 1992, **29**, 809-833.
8. J. T. Goettel, N. Kostiuk and M. Gerken, *Inorg. Chem.*, 2016, **55**, 7126-7134.
9. J. T. Goettel, N. Kostiuk and M. Gerken, *Angew. Chem. Int. Ed.*, 2013, **52**, 8037-8040.
10. N. Kostiuk, J. T. Goettel and M. Gerken, *Inorg. Chem.*, 2020, **59**, 8620-8628.
11. K. Matsumoto, Y. Haruki, S. Sawada, S. Yamada, T. Konno and R. Hagiwara, *Inorg. Chem.*, 2018, **57**, 14882-14889.
12. F. Buss, C. Muck-Lichtenfeld, P. Mehlmann and F. Dielmann, *Angew. Chem. Int. Ed.*, 2018, **57**, 4951-4955.
13. R. F. Weitkamp, B. Neumann, H. G. Stammler and B. Hoge, *Chem. Eur. J.*, 2021, **27**, 6460-6464.

14. P. Chaudhary, J. T. Goettel, H. P. A. Mercier, S. Sowlati-Hashjin, P. Hazendonk and M. Gerken, *Chem. Eur. J.*, 2015, **21**, 6247-6256.

15. J. T. Goettel, P. Chaudhary, P. Hazendonk, H. P. A. Mercier and M. Gerken, *Chem. Commun.*, 2012, **48**, 9120-9122.

16. J. T. Goettel and M. Gerken, *Inorg. Chem.*, 2016, **55**, 12441-12450.