These results are in agreement with results obtained in eutectic perchloric acid.[1] The K_f ratio obtained in that solvent was 0.53. The temperature difference between the melting point of the two solvents, 38°C, indicates that dimerization of HNO_3 is not confined to temperatures as low as −60°C. Proof of dimerization at −22°C as well as at −60°C indicates that dimerization of HNO_3 in these solvents may well take place even at room temperature.

The two solvents are comparable in two important aspects: (a) the formal (H^+) concentration is 5.2 *M* in eutectic perchloric acid and 5.1 *M* in eutectic trifluoroacetic acid; (b) water constitutes 89.0 mol % in eutectic perchloric acid and 89.4 mol % in HTFAc. The similarity between the solvents leaves unanswered the question as to whether dimerization takes place in other H^+ concentrations. Dimerization in aqueous solutions of pure nitric acid itself, in concentration of ~5 *N*, is a distinct possibility in the light of results of the other two solvents. A detailed Raman study is being undertaken in order to test this hypothesis. Raman studies may also furnish an answer to the major problem which cannot be solved by cryoscopic data, namely that of the structure and bonding of the nitric dimer.[1]

Cryoscopic investigation of ionic species in acidic or basic aqueous solvents may provide a new source of information on the constitution of some important solute species in aqueous solutions. A wide range of eutectic aqueous solutions, ranging from strong acids to strong bases, may be used at different pH ranges, including solutes such as amphoteric metal anions in basic solutions. Forthcoming papers in this series will deal with solute species in new solvents of this type.

Registry No. HTFAc, 76-05-1; $Zn(CF_3COO)_2$, 21907-47-1; $Mg(CF_3COO)_2$, 38482-84-7; $Fe(CF_3COO)_2$, 5781-22-6; $Fe(CF_3COO)_3$, 21907-43-7; $Cr(CF_3COO)_3$, 16712-29-1; $Th(CF_3COO)_4$, 16424-71-8; HCl, 7647-01-0; H_2SO_4, 7664-93-9; $HClO_4$, 7601-90-3; HNO_3, 7697-37-2.

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Some Sulfur(VI)–Nitrogen Compounds Which Contain $CF_3SF_4^-$

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Photolysis reactions of CF_3SF_4Cl with H_2, CF_3CN, and ClCN give $CF_3SF_4SF_4CF_3$, $CF_3SF_4N{=}C(Cl)CF_3$, and $CF_3SF_4N{=}CCl_2$, respectively. Cesium fluoride fluorinates the $CF_3SF_4N{=}C(Cl)CF_3$ to $CF_3SF_4N{=}CFCF_3$ and fluorinates and isomerizes $CF_3SF_4N{=}CCl_2$ to $CF_3SF_3{=}NCF_3$. The >C=N– and >S=N– systems undergo nucleophilic attack by ClF and HF to prepare the new chloramines, $CF_3SF_4N(Cl)CF_2CF_3$ and $CF_3SF_4N(Cl)CF_3$, and amines, $CF_3SF_4N(H)CF_2CF_3$ and $CF_3SF_4N(H)CF_3$. These compounds are stable and boil 20–40° higher than their SF_5 analogs.

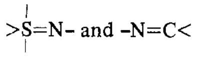
Introduction

Several straightforward synthetic routes to CF_3SF_4Cl enhance its attractiveness as a precursor for a variety of CF_3SF_4-containing compounds which are comparable in stability to their SF_5 analogs[1] but which have the advantage of being somewhat less volatile. Chlorine reacts with CF_3SF_3 in the presence of CsF to give *trans*-CF_3SF_4Cl.[2] Although we find that ClF with CF_3SF_3 results in a quantitative preparation of the latter compound, the preferred route is the reaction of CF_3SSCF_3 with ClF[3] in a molar ratio of 1:>8

$$CF_3SSCF_3 + ClF \xrightarrow{25°} CF_3SF_4Cl\ (70\%)$$

The radical reactions of CF_3SF_4Cl with olefins and fluoroolefins[4] are essentially the same as those of the extensively studied SF_5Cl.[5-11] The photochemical reduction of SF_5Cl by hydrogen provides a facile route to S_2F_{10}.[5]

We now wish to report the preparation of a new series of $CF_3SF_4N<$ compounds which arise from the photolysis of CF_3SF_4Cl with nitriles and the subsequent substitution of fluorine for chlorine by using CsF as a fluorinating reagent. The relative reactivities of



$$>\underset{|}{\overset{|}{S}}{=}N- \text{ and } -N{=}C<$$

are markedly demonstrated by comparing the ease of saturation of the double bond in $CF_3SF_3{=}N{-}CF_3$ and in $CF_3SF_4N{=}CFCF_3$ with ClF and HF.

Results and Discussion

The charge distribution within the $CF_3SF_4^{\delta-}Cl^{\delta+}$ molecule suggests that reactions with compounds which contain negative chlorine should be useful in synthesizing new CF_3SF_4X compounds. This is supported by the reaction with hydrogen chloride to form chlorine where the likely intermediate, CF_3SF_4H, if formed, is not isolable, viz.

$$CF_3SF_4Cl + HCl \rightarrow Cl_2 + [CF_3SF_4H] \rightarrow CF_3SF_3 + HF(SiF_4)$$

Similarly, thermolysis of CF_3SF_4Cl and NOCl results in decomposition products and chlorine which suggests that CF_3SF_4NO could have been an unstable intermediate

$$CF_3SF_4Cl + NOCl \xrightarrow{180°} Cl_2 + [CF_3SF_4NO] \rightarrow CF_3NO + SF_4$$

Identical products are formed when these reactants were subjected to photolysis through quartz at 25°.

As is the case with SF_5Cl, photolysis of CF_3SF_4Cl with H_2 enhances the formation of the very stable disulfur decafluoride analog, $CF_3SF_4SF_4CF_3$. Unfortunately, in all photolysis reactions described below, a large fraction of the CF_3SF_4Cl

Table I. Boiling Points of CF_3SF_4X and SF_5X (°C)

X	SF_5X[a]	CF_3SF_4X
-Cl	−19	20.1[b]
$-SF_5(CF_3SF_4-)$	27	89
$-N{=}C(Cl)CF_3$	58–61	85
$-N{=}CCl_2$	86–88	96
$-N(H)CF_3$	28.5–31	62
$-N(Cl)CF_3$	41–43	76
$-N(H)CF_2CF_3$	45.5–47	76
$-N(Cl)CF_2CF_3$		94
$SF_4{=}NCF_3$	0.5–1.0	
$(CF_3SF_3{=}NCF_3)$		32

[a] Reference 1. [b] Reference 3.

reactant is consumed in the formation of the latter compound. While CF_3SF_4Cl does not react with CF_3CN or ClCN when irradiated through Pyrex glass, irradiation of equimolar mixtures through quartz gives rise to either $CF_3SF_4N{=}CClCF_3$ or $CF_3SF_4N{=}CCl_2$ and $(CF_3SF_4)_2$.

$$CF_3SF_4Cl + R_fCN \rightarrow \underset{40\%}{CF_3SF_4N{=}CClR_f}$$

$$R_f = CF_3, Cl$$

The chlorine atom in these azamethines is readily replaced by fluoride ion. For example, with the SF_5 analogs[1]

$$SF_5N{=}C(Cl)CF_3 + NaF \xrightarrow[150°]{DMSO} SF_5N{=}CF(CF_3)$$

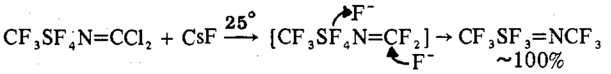
and

$$SF_5N{=}CCl_2 + NaF \xrightarrow[150°]{DMSO} \underset{80\%}{SF_5N{=}CF_2} + \underset{15\%}{CF_3N{=}SF_4}$$

In our work CsF proved to be an excellent nucleophile displacing chlorine readily

$$CF_3SF_4N{=}C(Cl)CF_3 + CsF \xrightarrow{70°} \underset{\sim 100\%}{CF_3SF_4N{=}CFCF_3}$$

While the chloroazamethine is stable indefinitely in Pyrex, the fluorinated molecule on standing undergoes polymerization to form a white crystalline solid which attacks glass (SiF_4) and forms other unidentified compounds. It was not possible to isolate the totally fluorinated azamethine in the case of $CF_3SF_4N{=}CF_2$, but rather a fluoride ion shift occurs according to



$$CF_3SF_4N{=}CCl_2 + CsF \xrightarrow{25°} [CF_3SF_4N{=}CF_2] \rightarrow \underset{\sim 100\%}{CF_3SF_3{=}NCF_3}$$

That an analogous shift does not occur with $CF_3SF_4N{=}CFCF_3$ may be because of steric reasons with too little space being available around the nitrogen and carbon to permit the formation of $CF_3SF_4\bar{N}CF_2CF_3$ as a viable intermediate.

Although polar additions to carbon–nitrogen double bonds have been well studied, little work has been reported on either polar or radical reactions which lead to the saturation of the $S^{VI}{=}N$ bond. Earlier work in these laboratories has demonstrated that $S^{IV}{=}N-$ bonds, when subjected to ClF at −78°, are severed readily to form $>SF_2$ and $-NCl_2$ compounds.[12] Under ionic conditions (CsF), elemental fluorine converts $R_fN{=}SF_2$ to $R_fN(F)SF_5$, whereas without fluoride ion SF_6 and $(R_fN{=})_2SF_2$ form.[13] The compounds $CF_3SF_4N{=}CFCF_3$ and $CF_3SF_3{=}NCF_3$ provide an opportunity to compare the relative susceptibilities of

$$>\overset{|}{\underset{|}{S}}{=}N- \text{ and } >C{=}N-$$

bonds in similar chemical environments to polar additions. While chlorine monofluoride adds readily and quantitatively to $CF_3SF_3{=}NCF_3$ at 50° or in the presence of CsF at 25°

Table II. Thermodynamic Data, Elemental Analyses, and Infrared Spectra

Compd	ΔH_v[a]	ΔS_v, eu	A[b]	B	Elemental analyses, % F	S	N	C	Cl(H)	Infrared spectra, cm^{-1}
$CF_3SF_4SF_4CF_3$	7.8	21.5	7.82	1792	74.5 (75.1)[c]	18.29 (18.10)		6.58 (6.80)		1255 (vs), 1155 (vs), 890 (vs), 880 (m), 650 (ms), 565 (ms)
$CF_3SF_4NC(Cl)CF_3$	7.5	20.9	7.53	1664	61.8 (61.8)	10.76 (10.40)	4.74 (4.50)	11.57 (11.70)	11.21 (11.40)	1690 (s), 1290 (s), 1250 (vs), 1200 (s), 1165 (s), 970 (s), 865 (s), 830 (ms), 725 (ms), 670 (m). 620 (w)
$CF_3SF_4NCCl_2$	7.4	20.0	7.02	1527	49.2 (48.71)	11.77 (11.72)	6.17 (5.13)	8.90 (8.75)	25.92 (25.64)	1640 (s), 1250 (vs), 1155 (ms), 930 (s), 845 (s), 815 (ms), 750 (m), 650 (m), 620 (m)
$CF_3SF_4NCFCF_3$	Polymerizes				70.05 (71.82)					1755 (s), 1345 (s), 1315 (w), 1250 (vs), 1200 (s), 1160 (ms), 1120 (s), 865 (vs), 800 (ms), 745 (m), 730 (s), 650 (mw), 630 (m), 565 (w)
$CF_3SF_3NCF_3$	7.2	23.5	8.01	1572	72.5 (70.95)	13.44 (13.27)	5.82 (5.80)	9.51 (9.95)		1345 (vs), 1280 (s), 1250 (s) 1230 (s), 1200 (s), 1155 (s), 1113 (s), 860 (s), 820 (ms), 790 (vs), 750 (m), 640 (m)
$CF_3SF_4N(H)CF_3$	6.2	18.5	6.92	1352	72.4 (72.8)	12.40 (12.26)	5.21 (5.34)	8.99 (9.23)	0.50 (0.39)	3470 (m), 1460 (s), 1280 (s), 1250 (vs), 1185 (vs), 1155 (s), 970 (m), 860 (vs), 720 (m), 660 (ms)
$CF_3SF_4N(Cl)CF_3$	8.2	23.4	8.01	1785	64.0 (64.4)	11.11 (10.84)	4.52 (4.75)	7.96 (8.13)	11.80 (12.04)	1250 (vs), 1210 (s), 1180 (s), 1160 (s), 860 (vs), 770 (m), 720 (m), 660 (s), 645 (ms)
$CF_3SF_4N(H)CF_2CF_3$	6.4	18.4	6.90	1401	71.8 (73.3)	10.31 (10.28)	4.55 (4.70)	11.32 (11.60)	0.40 (0.35)	3470 (m), 1470 (ms), 1340 (s), 1250 (s), 1230 (vs), 1180 (s), 1080 (s), 840 (vs), 740 (w), 670 (s)
$CF_3SF_4N(Cl)CF_2CF_3$	8.6	23.5	8.02	1882	65.70 (66.08)	9.27 (9.27)	3.93 (4.05)	9.87 (10.43)	10.24 (10.15)	1335 (wm), 1240 (vs), 1210 (m), 1150 (s), 1080 (s), 870 (vs), 830 (ms), 780 (w), 750 (w), 670 (s)

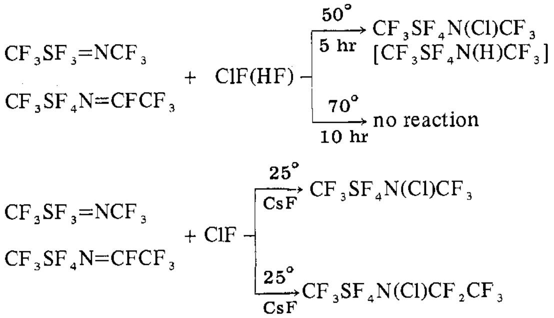
[a] Calculated values in kcal mol^{-1}. [b] $\log P_{Torr} = A - B/T$. [c] Calculated values.

Table III. Nuclear Magnetic Resonance Data (Shifts Relative to $CFCl_3$ or $(CH_3)_4Si$)[a]

	Chemical shift, ppm							
Compd	CF_3S	CF_3C	CF	CF_2	CF_3-N	SF_4	H	*J*, Hz
$CF_3SF_4SF_4CF_3$	65.6 (p)					−12.6 (q)		SF_4-CF_3 = 21.7 CF_3-CF_3 = 0.0
$CF_3SF_4N{=}C\begin{matrix}Cl\\CF_3\end{matrix}$	65 (p)	71.5 (s)				−41.7 (q)		SF_4-CF_3 = 23.1 CF_3-CF_3 ~ 0 CF_3C-SF_4 ~ 0
$CF_3SF_4N{=}C\begin{matrix}Cl\\Cl\end{matrix}$	65 (p)					−41.5 (q)		SF_4-CF_3 = 23.1
$CF_3SF_4N{=}C\begin{matrix}F\\CF_3\end{matrix}$	64.0 (p)	73.0 (d)	29.3 (p of q)			−46.2 (p)		CF_3-CF = 16.3 SF_4-CF_3 = 22.3 SF_4-CF = 22.3 CF_3S-CF_3 ~ 0
CF_3SF_4NH-CF_3	64.5 (p)				56.5 (p of d)	−53.2 (mult)	5.8 (br)	H-NCF_3 = 4.6 SF_4-NCF_3 = 12 SF_4-SCF_3 = 23.5
CF_3SF_4NCl-CF_3	65.5 (p)				62.0 (p)	−44.3 (mult)		SF_4-$NCCF_3$ = 12.0 SF_4-SCF_3 = 23.6
CF_3SF_4NH-CF_2CF_3	64.5 (p of d)	85.5 (s)		94 (h)		−55.3 (q of t of d)	5.6 (br)	SF_4-CF_2 = 11.8 SF_4-SCF_3 = 23.5 CF_3S-CF_3N ~ 0 SF_4-H = 3.5 CF_2S-CF_2 ~ 0 CF_3S-H ~ 1
CF_3SF_4NCl-CF_2CF_3	65.0 (p)	80.0 (p) (mult)		94.5 (p of q)		−47.3 (mult)		SF_4-SCF_3 = 24.2 SF_4-CF_2 = 18 SF_4-CF_3C = 1.3 CF_3S-CF_3 ~ 0 CF_3C-CF_2 = 2.5
$CF_3SF_3{=}N$-CF_3	62.0 (t of d of q)				49.3 (br, t)	Eq −70.0 (1) Ax −60.0 (2) (d of mult)		SF_1-SCF_3 = 13.8 SF_1-SF_2 = 182 SF_2-SCF_3 = 27 SF_2-NCF_3 = 13 SF_1-NSF_3 = 3.8 CF_3S-CF_3N = 0.4

[a] s, singlet; d, doublet; t, triplet; q, quartet; p, pentet; h, sextet; b, broad; mult, multiplet.

to form the chloroamine, even at 70° it does not attack $CF_3SF_4N{=}CFCF_3$. The latter is saturated at 25° in the presence of CsF. Hydrogen fluoride behaves similarly in the absence of CsF.



$$\left.\begin{matrix}CF_3SF_3{=}NCF_3\\CF_3SF_4N{=}CFCF_3\end{matrix}\right\} + ClF(HF) \begin{cases}\xrightarrow[5\text{ hr}]{50°} CF_3SF_4N(Cl)CF_3\ [CF_3SF_4N(H)CF_3]\\ \xrightarrow[10\text{ hr}]{70°} \text{no reaction}\end{cases}$$

$$\left.\begin{matrix}CF_3SF_3{=}NCF_3\\CF_3SF_4N{=}CFCF_3\end{matrix}\right\} + ClF \begin{cases}\xrightarrow[CsF]{25°} CF_3SF_4N(Cl)CF_3\\ \xrightarrow[CsF]{25°} CF_3SF_4N(Cl)CF_2CF_3\end{cases}$$

No fragmentation occurs. These reactions support the prediction that nucleophilic attack would occur more readily at the positive sulfur center.

The positive nature[14] of the chlorine in $CF_3SF_4N(Cl)CF_3$ and $CF_3SF_4N(Cl)CF_2CF_3$ permits the synthesis of the amines by reaction with hydrogen chloride.

$$CF_3SF_4N(Cl)R_f + HCl \xrightarrow{25°} CF_3SF_4N(H)R_f + Cl_2$$
$$R_f = CF_3, C_2F_5$$

In Table I are given the boiling points of the compounds CF_3SF_4X and SF_5X. Based on these data, the effect of replacing one fluorine by a trifluoromethyl group is to increase the boiling point by 20–40°. Thus, the new compounds reported here not only have the same thermal stability and inert nature associated with their SF_5 analogs but have the decided advantage of exhibiting much lower vapor pressures at ambient temperature.

Experimental Section

Apparatus. Infrared spectra were taken using a Perkin-Elmer Model 457 infrared spectrometer using a 10 cm gas cell fitted with KBr windows, and were calibrated against known absorption bands in polystyrene film. Fluorine nuclear magnetic resonance spectra were determined with a Varian HA-100 NMR spectrometer using Freon 11 as an internal standard and proton NMR spectra were obtained on a Varian EM-360 with TMS as an internal reference. Mass spectra were obtained using a Hitachi Perkin-Elmer Model RMU-6E mass spectrometer at 70 eV. Beller Mikroanalytisches Laboratorium performed the elemental analyses. Samples were purified by gas chromatography utilizing columns constructed of 0.25-in. copper tubing packed with 20% Kel-F 3 oil or FS-1265 on Chromosorb P.

Reagents. Chlorine monofluoride was purchased from Ozark-Mahoning Co. Chlorine monofluoride should be handled with caution, since it is a very strong oxidizing agent. Bis(trifluoromethyl)disulfane and trifluoroacetonitrile were obtained from PCR, Inc. Cesium fluoride and hydrogen fluoride were supplied by American Potash and Union Carbide, respectively.

Preparation of CF_3SF_4Cl. Bis(trifluoromethyl)disulfane (5 mmol) and chlorine monofluoride (42 mmol) were combined at −196° in a 75-ml Hoke stainless steel cylinder. After 10 hr at 25°, the reaction products were separated crudely by trap-to-trap distillation. The major product CF_3SF_4Cl, which was retained in the trap at −98°, was purified by using an 8-ft Kel-F column. The yield of CF_3SF_4Cl approached 70%.

Reaction of CF_3SF_4Cl with HCl. An equimolar mixture of CF_3SF_4Cl (1.5 mmol) and HCl was held in a 25-ml Pyrex glass vessel at 25° for 24 hr. The products were separated by trap-to-trap distillation and identified as CF_3SF_3 (1.2 mmol) and SiF_4 by infrared spectrum and as Cl_2 (1.2 mmol) by color and molecular weight. Unreacted CF_3SF_4Cl was also recovered.

Reaction of CF_3SF_4Cl with NOCl. A 50-ml Pyrex glass vessel which contained equimolar amounts (1.5 mmol) of CF_3SF_4Cl and NOCl was heated at 150° for 12 hr. After separation, CF_3NO, SiF_4, and unreacted CF_3SF_4Cl were identified by using infrared. Chlorine was also found. The yield of CF_3NO was 40%. Similar products were found after uv irradiation of the reaction mixture in a quartz vessel.

Preparation of $CF_3SF_4SF_4CF_3$. A 2:1 mmol mixture of CF_3SF_4Cl and hydrogen in a 300-ml Pyrex vessel was photolyzed by using a Hanovia Utility model uv lamp for 10 hr. After trap-to-trap fractionation, a 50% yield of $CF_3SF_4SF_4CF_3$ was found in a trap cooled to −78°.

Preparation of $CF_3SF_4NC(Cl)CF_3$. Irradiation of a mixture of CF_3CN (6 mmol) and CF_3SF_4Cl (5 mmol) in a quartz vessel for 12 hr gave, after trap-to-trap separation and subsequent purification by using a 6-ft FS-1265 GC column, $CF_3SF_4NC(Cl)CF_3$ (2.5 mmol) and $CF_3SF_4SF_4CF_3$ (1 mmol).

Preparation of $CF_3SF_4NCCl_2$. Using the same reaction and purification conditions as above, CF_3SF_4Cl (5 mmol) was reacted with ClCN to give $CF_3SF_4NCCl_2$ (2.3 mmol) and $CF_3SF_4SF_4CF_3$ (1 mmol).

Preparation of $CF_3SF_4NCFCF_3$. One millimole of $CF_3SF_4N\text{-}C(Cl)CF_3$ was condensed onto an excess of CsF in a 75-ml Hoke reaction vessel and was heated at 100° for 4 hr. Nearly quantitative conversion to $CF_3SF_4NCFCF_3$ occurs.

Preparation of $CF_3SF_3{=}NCF_3$. When $CF_3SF_4NCCl_2$ was condensed on excess CsF in a Hoke vessel and allowed to remain at 25° for 10 hr, a volatile compound identified as $CF_3SF_3NCF_3$ in >99% yield was found.

Preparation of $CF_3SF_4N(Cl)CF_3$. After 5 hr at 60°, a mixture of $CF_3SF_3NCF_3$ (1 mmol) and ClF (1.5 mmol) reacted to form $CF_3SF_4N(Cl)CF_3$ in a yield >98%. For final purification an 8-ft Kel-F column was used. When CsF is present, $CF_3SF_4N(Cl)CF_3$ is formed in similar yields at 25°.

Preparation of $CF_3SF_4N(H)CF_3$. Hydrogen fluoride (2 mmol) was reacted with $CF_3SF_3NCF_3$ (1 mmol) in a 75-ml Hoke reaction vessel at 60° for 5 hr. The reaction mixture was transferred into a second Hoke vessel which contained NaF. After 12 hr at 25°, the volatile mixture was separated by trap-to-trap distillation. Retained in a trap at −78° was $CF_3SF_4N(H)CF_3$ in 40% yield.

An equimolar mixture of $CF_3SF_4N(Cl)CF_3$ (1 mmol) and HCl was condensed into a Pyrex vessel at −183° and allowed to warm slowly to 25°. A quantitative yield of $CF_3SF_4N(H)CF_3$ was found.

Preparation of $CF_3SF_4N(Cl)CF_2CF_3$. Into a 75-ml vessel at −183° which contained CsF were condensed $CF_3SF_4N{=}CFCF_3$ (2 mmol) and ClF (3 mmol). The mixture was allowed to remain at 25° for 8 hr. A quantitative yield of $CF_3SF_4N(Cl)CF_2CF_3$ was obtained.

Preparation of $CF_3SF_4N(H)CF_2CF_3$. In a Pyrex vessel at 25°, equimolar amounts of $CF_3SF_4N(Cl)CF_2CF_3$ (1 mmol) and HCl were reacted to give $CF_3SF_4N(H)CF_2CF_3$ in >99% yield.

The spectral, analytical, and thermodynamic data for these new compounds are given in Tables II and Table III.

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Registry No. CF_3SF_4Cl, 25030-42-6; $CF_3SF_4SF_4CF_3$, 1580-11-6; $CF_3SF_4NC(Cl)CF_3$, 56868-52-1; $CF_3SF_4NCCl_2$, 56868-53-2; $CF_3SF_4NCFCF_3$, 56868-55-4; $CF_3SF_3{=}NCF_3$, 56868-56-5; $CF_3SF_4N(Cl)CF_3$, 56868-57-6; $CF_3SF_4N(H)CF_3$, 56868-58-7; $CF_3SF_4N(Cl)CF_2CF_3$, 56868-59-8; $CF_3SF_4N(H)CF_2CF_3$, 56868-60-1; ClF, 7790-89-8; CF_3SF_3, 374-10-7; NOCl, 2696-92-6; CF_3NO, 334-99-6; H_2, 1333-74-0; CF_3CN, 353-85-5; ClCN, 506-77-4; CsF, 13400-13-0; HF, 7664-39-3; HCl, 7647-01-0; CF_3SSCF_3, 372-64-5.

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Convenient Preparation and Physical Properties of Lithium Intercalation Compounds of Group 4B and 5B Layered Transition Metal Dichalcogenides

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n-Butyllithium in hexane solution has been found to be a mild and efficient reagent for intercalation of lithium into the layered MX_2 compounds (M = Ti, Zr, Hf, V, Nb, Ta; X = S, Se, Te), most of which were prepared in this study. All the compounds attained a limiting composition of $LiMX_2$ except VSe_2 which formed Li_2VSe_2. For the group 5B compounds this is more lithium than can be intercalated at high temperatures or from lithium–ammonia solutions. The tellurides, which decompose under previous reaction conditions, were intercalated using *n*-BuLi. Crystallographic, magnetic susceptibility, pressed pellet dc conductivity, and superconductivity data are reported. Only the $LiZrX_2$ compounds were superconducting. All compounds have a low room-temperature resistivity (10^{-2}–10^{-3} Ω cm in pressed powders) except Li_2VSe_2 which has $\rho_{298°K} = 6 \times 10^3$ Ω cm. Li_2VSe_2 contains V^{2+} having $S = {}^3/_2$ and $g = 1.98$ and possible antiferromagnetic ordering below 20°K. Only $LiTiSe_2$ gave any indication in magnetic susceptibility of a possible charge density wave instability similar to those observed in d^1 MX_2 compounds.

A number of alkali metal intercalates of the groups 4B, 5B, and 6B layered transition metal dichalcogenides have been reported.[1–7] These compounds have been prepared either by combination of the elements at high temperature, by treating the parent MX_2 with a solution of the alkali in liquid ammonia, or by treatment with lithium naphthalide. These methods have drawbacks, particularly for lithium intercalation. High-temperature methods may lead to decomposition or only partial