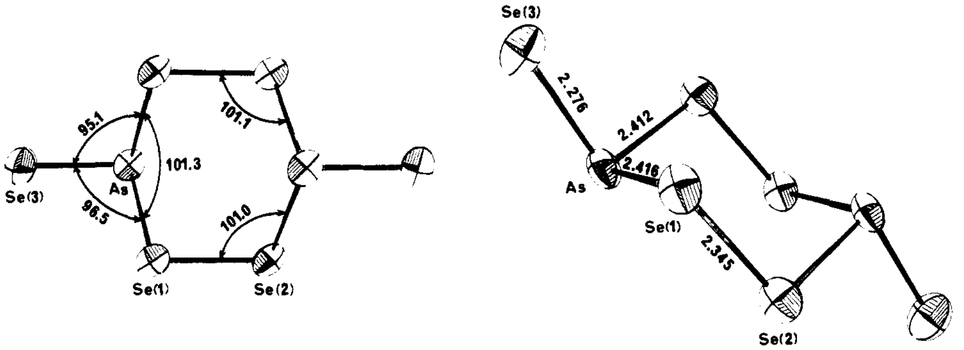

Figure 2. Two views of polyanion $As_2Se_6^{2-}$ in $(2,2,2\text{-crypt-Na}^+)_2As_2Se_6^{2-}$: (a) view perpendicular to cyclic Se plane showing the C_i symmetry; (b) view approximately down the pseudo-twofold axis. Thermal ellipsoids are shown at the 50% probability level.

Results and Discussion

The final positional parameters for the 31 nonhydrogen atoms in $(\text{crypt-Na}^+)_2As_2Se_6^{2-}$ are listed in Table I. Bond distances and angles inside the anion are given in Table II. Thermal parameters for all atoms, bond distances and some angle data for the cation (Tables A and B), as well as the listing of observed and calculated structure factors are given in the supplementary material. The packing in the unit cell is represented on Figure 1. The structure of the cation is similar to those described in other crypt-Na^+ compounds with cells of low symmetry.[9,11] Since the Na^+ ion is considered undersized for the 2,2,2-crypt cavity, this introduces some strain in the ligand, as reflected by nonnegligible differences in distances between sodium and oxygen atoms (2.48, 2.51, 2.62, 2.66, and 2.79 Å; $\sigma = 0.01$ Å) as well as in distances with nitrogen (2.81 (1) and 3.18 (1) Å) while the sodium is off the midpoint of the N-N axis by 0.20 (1) Å with a $N-Na^+-N$ angle of 178.2 (4)°.

As it was previously reported for $(\text{crypt-K}^+)_2Bi_4^{2-}$,[14] the two centrosymmetry-related cations nearly adopt a hexagonal stacking with y and z coordinates of sodium and both nitrogen atoms close to $^1/_3$ and $^2/_3$, corresponding to a position on the threefold axis of a proper hexagonal cell, causing the pseudoequality of b and c parameters and the angle α to be close to 120°.

The most interesting feature of the structure is the hitherto unknown $As_2Se_6^{2-}$ polyanion which is represented on Figure 2. It consists of a six-membered ring in chair conformation (As_2Se_4) bonded, through the trans arsenic atoms, to two exocyclic selenium atoms in equatorial position, so the molecule is bound by six heteroatomic As-Se and two homoatomic Se-Se bonds. As indicated by Figure 2a,b, the anion displays a symmetry close to C_{2h} with a pseudo-twofold axis passing through the midpoint of the Se(1)-Se(2) bonds and a mirror plane perpendicular to it, which would contain the As and Se(3) atoms.

In this anion, the bonding scheme conforms to the classical valence rules; the value of 2.345 (2) Å for Se-Se agrees with twice the covalent radius of selenium (1.17 Å).[20] For the As-Se cyclic bonds, distances of 2.412 (2) and 2.416 (2) Å are not much larger than the sum of the covalent radii of the elements (2.38 Å) and close to those observed in As_4Se_4[21] with a mean value of 2.39 Å. On the other hand, the arsenic to terminal selenium bond length of 2.276 (2) Å indicates some multiple-bond character as observed for exo As-S bonds in the anion $As_4S_6^{2-}$.[5] The shortest contacts between selenium and carbon atoms in the cation are greater than 3.71 Å and obviously exceed the sum of the van der Waals radii of the atoms (3.60 Å, Bondi[22]); this excludes any, even very weak, hydrogen-bonding interaction, especially to the exocyclic selenium atoms.

Registry No. $(2,2,2\text{-crypt-Na}^+)_2As_2Se_6^{2-}$, 81205-87-0.

Supplementary Material Available: Listings of thermal parameters for all atoms, bond distances and some angle data for the cation (Tables A and B), and observed and calculated structure factors (13 pages). Ordering information is given on any current masthead page.

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Reactions of ((Pentafluorosulfanyl)imino)difluorosulfane, $SF_5N{=}SF_2$, with Titanium(IV) Chloride, $TiCl_4$, Tin(IV) Chloride, $SnCl_4$, and Antimony(V) Chloride, $SbCl_5$. Preparation and Characterization of ((Pentafluorosulfanyl)imino)chlorofluorosulfane, $SF_5N{=}SClF$

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((Pentafluorosulfanyl)imino)dichlorosulfane, $SF_5N{=}SCl_2$, was first synthesized[1] by the reaction between pentafluorosulfanylamine, SF_5NH_2, and sulfur dichloride, SCl_2. A yield of 90% was reported; however, all subsequent attempts to repeat this reaction have resulted in <10% yield of $SF_5N{=}SCl_2$.[2] It is also curious to note that Clifford and Goel recovered only 4.26% of the expected quantity of sulfur in the initial reaction.

Aluminum chloride,[3] phosphorus pentachloride,[4] and silicon tetrachloride[5] were used in the chlorination of ((perfluoroalkyl)imino)difluorosulfanes. Recently $SF_5N{=}SCl_2$ was synthesized in 75% yield by the reaction between $SF_5N{=}SF_2$ and PCl_5.[6,7] However, the purification of the main product is rendered difficult by the byproduct chlorofluorophosphoranes. These compounds have physical properties

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similar to $SF_5N{=}SCl_2$, thus making separation difficult.

The ideal chlorinating agent for $SF_5N{=}SF_2$ would have to produce nearly quantitative yield and provide ease of separation from either highly volatile or nonvolatile byproducts formed. Clifford and Shanzer[7] prepared $SF_5N{=}SCl_2$ in low yield when $SiCl_4$ was used. If the yield from this reaction could be increased, the highly volatile SiF_4 produced would meet the alternate criterion. Several chlorides produce solid fluorides, among these are $AlCl_3$, $SnCl_4$, and $TiCl_4$. Surprisingly, the reaction with $AlCl_3$ as a chlorinating agent was found to be unsuccessful.[7]

We report here four routes to the formation of $SF_5N{=}SCl_2$, two of which afford multigram quantities of $SF_5N{=}SCl_2$ safely and cleanly with minimal problems of separation. In the study reported herein, our attempts at dichlorination of $SF_5N{=}SF_2$ led not only to the expected product but also to the new compound, $SF_5N{=}SClF$, which we believe to be the first example of a mixed halide of the type $SF_5N{=}SXY$.

Results and Discussion

The reaction between $TiCl_4$ and $SF_5N{=}SF_2$ occurred almost immediately, forming a yellowish orange solid. The compound $SF_5N{=}SCl_2$ was separated from the reaction mixture in a yield of >89%. This reaction best met the two criteria of high yield and ease of purification. However, when $TiCl_4$ was used in excess, the product, $SF_5N{=}SCl_2$, was not separable from the unused $TiCl_4$ even after repeated trap-to-trap distillations. However, with $SF_5N{=}SF_2$ in slight excess, the problem of separation was eased significantly, since the more volatile $SF_5N{=}SF_2$ could be easily separated from $SF_5N{=}SCl_2$. The complete consumption of $TiCl_4$ was ensured by allowing all of the volatile reaction products to stand with an excess of $SF_5N{=}SF_2$ for a few hours. The full recovery of $SF_5N{=}SF_2$ confirmed that there was no unreacted $TiCl_4$. A small quantity of $SF_5N{=}SClF$ was isolated when the reaction conditions were changed slightly.

The reaction between $SnCl_4$ and $SF_5N{=}SF_2$ is slower than the reaction with $TiCl_4$ and proceeds with the formation of a yellowish white solid. The problem with the slow rate of chlorination of $SF_5N{=}SF_2$ in this reaction can be alleviated by heating the mixture to 100 °C for 24 h. However, when either of the reactants was used in excess, the reaction was not complete even when the mixture was heated. A difficulty arose with the fractionation of the volatile products, with the main product $SF_5N{=}SCl_2$ and unused $SnCl_4$ remaining in the same trap (−63 °C). This problem was solved by allowing this mixture of volatile products to react with $(CH_3)_3SiH$. The $SnCl_4$ chlorinated the trimethylsilane, yielding $(CH_3)_3SiCl$, HCl, and $SnCl_2$.[8,9] Since $SF_5N{=}SCl_2$ was less volatile than and did not react with the new products, HCl and $(CH_3)_3SiCl$, we were able to separate the $SF_5N{=}SCl_2$ in high purity from these secondary $SnCl_4$ reaction products. The yield obtained in this reaction was >63%. Although this is a high-yield method for preparing $SF_5N{=}SCl_2$, the difficulties such as slow chlorination and need for an additional reagent, $(CH_3)_3SiH$, made this method more expensive and time consuming. Although we were unable to isolate the new compound, $SF_5N{=}SClF$, among the final products in this reaction, a band observed at 1275 cm^{-1} due to the $-N{=}S<$ stretching mode which is quite different from those in $SF_5N{=}SF_2$ and $SF_5N{=}SCl_2$ indicated that this reaction also produced the mixed halide $SF_5N{=}SClF$.

In another experiment, the reaction of $SnCl_4$ and $SF_5N{=}SF_2$ was monitored by recording the infrared spectra of the reactants during the course of the reaction. The band due to the $-N{=}S<$ stretching mode disappeared in the infrared spectrum of the products after 2 weeks of the reaction.

The reaction between $SbCl_5$ and $SF_5N{=}SF_2$ is very slow, and heating the reactants at 100 °C was necessary to initiate the reaction. Separation was not a problem in this reaction; however, the volatile byproduct, SbF_5, fluorinates[10] the $SF_5N{=}SCl_2$ and therefore a low yield was observed. A small quantity of $SF_5N{=}SClF$ was identified among the products.

Roesky et al.[11] found that fluorosulfonamide reacts with thionyl chloride to give ((fluorosulfonyl)imino)oxosulfane. On the other hand, the reaction of chlorosulfonamide and thionyl chloride produces ((chlorosulfanyl)imino)dichlorosulfane.[12]

$$FSO_2NH_2 + SOCl_2 \rightarrow FSO_2N{=}S{=}O + 2HCl$$

$$ClSO_2NH_2 + 2SOCl_2 \rightarrow ClSO_2N{=}SCl_2 + 2HCl + SO_2$$

Thus, SF_5NH_2 was allowed to react with refluxing $SOCl_2$ (79 °C) for 24 h in one experiment and at room temperature for 2 weeks in a second experiment. In both cases, the products were $SF_5N{=}SCl_2$, $SF_5N{=}SClF$, SO_2, and SOF_2. The starting material, SF_5NH_2, is always in equilibrium with HF (and NSF_3)[13] which readily fluorinates thionyl chloride if present.[14] The byproduct HCl was not recovered because it rapidly reacts with NaF in the scrubber to form NaCl and $NaHF_2$. It is evident that this reaction follows the same path of Roesky's reactions.

In reactions of $SF_5N{=}SF_2$ with PCl_5,[6,7] $AlCl_3$,[7] $SiCl_4$,[7] $SbCl_5$, $SnCl_4$, or $TiCl_4$, there seems to be a correlation between the yield and the ability of the chlorinating agent to expand its coordination sphere as well as on the relative Lewis acidity of the chlorinating agent. (Some studies[15] have shown the relative acceptor strength to decrease in the series $SbCl_5 > AlCl_3 > TiCl_4 > SnCl_4 > SiCl_4 \approx PCl_5$.) This correlation can most aptly be seen in the comparisons of $SiCl_4$ with $SnCl_4$, PCl_5 with $SbCl_5$, $SiCl_4$ with PCl_5, and $SnCl_4$ with $SbCl_5$.

Titanium tetrachloride has available inner d orbitals, with which it can expand its coordination sphere, as well as a relatively high Lewis acidity and the Ti–F bond strength is very high (139.7 kcal/mol).[16] These factors may account for the high yield.

Physical Properties of $SF_5N{=}SClF$

The new compound $SF_5N{=}SClF$ was characterized by ^{19}F NMR, mass, and infrared spectroscopy. The mass spectrum of $SF_5N{=}SClF$ had fragments at *m/e* 210 and at *m/e* 208 corresponding to the parent ion minus one fluorine as well as an intense fragment at *m/e* 192 indicating loss of chlorine from the parent ion to form $SF_5N{=}SF^+$. The other fragments, $SF_5N{=}S^+$ (*m/e* 173), SF_5^+ (*m/e* 127), $FClS{=}N^+$ (*m/e* 102, 100), SF_3^+ (*m/e* 89), and SF_2^+ (*m/e* 70), observed in the mass spectrum, identified the compound as the mixed halide, $SF_5N{=}SClF$.

The typical AB_4X complex spin pattern observed for $SF_5N{=}SClF$ in the ^{19}F NMR spectrum shows a clear distinction from that of $SF_5N{=}SF_2$ and $SF_5N{=}SCl_2$. The NMR parameters are given in the Experimental Section.

The formulation of the compound as $SF_5N{=}SClF$ may be further proved by comparison of its observed infrared spectrum

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with the published infrared spectra of $SF_5N{=}SF_2$[18] and $SF_5N{=}SCl_2$.[1] The stretching mode due to $-N{=}S<$ is significantly different from those of $SF_5N{=}SF_2$ and $SF_5N{=}SCl_2$. The S^{IV}–F and S^{IV}–Cl stretching modes appear in the expected regions, that is, in between the values observed for the difluoride and the dichloride. The spectroscopic parameters for $SF_5N{=}SClF$ are consistent with those of the known mixed halide $FC(O)N{=}SClF$.[17] The striking difference between these two molecules is that $SF_5N{=}SClF$ does not disproportionate to the difluoride and dichloride at room temperature as is reported to be in case with $FC(O)N{=}SClF$.[17]

Experimental Section

Materials. ((Pentafluorosulfanyl)imino)difluorosulfane, $SF_5N{=}SF_2$, was prepared by the reaction[18] of SF_4 and NSF_3 in the presence of the catalyst HF. Pentafluorosulfanylamine, SF_5NH_2, was prepared by the reaction of NSF_3 and HF as described elsewhere.[13] Titanium tetrachloride, stannic chloride, antimony pentachloride, thionyl chloride, sulfur dichloride, and chlorine were taken from laboratory stock and were distilled. The purity of these reagents was checked (IR spectrum and vapor pressure) before each use.

Spectra. Infrared spectra were obtained on either a Beckman 20A-X or a Perkin-Elmer 283-B instrument and were run in a 10-cm gas cell. Fluorine-19 NMR spectra were recorded on a Varian EM-390 at 84.6 MHz and referenced to internal CCl_3F. The method of Harris and Packer[19] was used to calculate the chemical shifts and coupling constants of the AB_4 portion of the ^{19}F NMR spectra. Mass spectra were obtained on a Finnigan Model 3200 quadrupole mass spectrometer.

Reaction of $TiCl_4$ and $SF_5N{=}SF_2$. The compound $SF_5N{=}SF_2$ (11.20 mmol) and $TiCl_4$ (1.862 g, 9.8 mmol) were taken in a 250-mL flask at −196 °C. The mixture was allowed to warm to −78 °C and was kept at this temperature for several hours. The mixture was then slowly warmed to room temperature over a period of 18 h after which time a yellow-orange preciptitate had formed inside the reaction flask. After keeping this mixture at room temperature for 3 days, the volatile products were separated by conventional vacuum distillation. The trap at −64 °C contained mainly $SF_5N{=}SCl_2$ (2.13 g, 8.73 mmol; 89.1% yield based on $TiCl_4$ consumed) and the trap at −196 °C contained a small quantity (1.20 mmol) of unreacted $SF_5N{=}SF_2$. The yellow-orange precipitate which remained in the flask was not identified.

So that the complete consumption of $TiCl_4$ could be ensured, the product, $SF_5N{=}SCl_2$, was once again mixed with 2.0 mmol of $SF_5N{=}SF_2$ and was kept at room temperature for 3 days. Lack of formation of a solid and the recovery of 2.0 mmol of $SF_5N{=}SF_2$ confirmed that all the $TiCl_4$ had been consumed in the initial reaction. In another procedure $SF_5N{=}SF_2$ (10.30 mmol) and $TiCl_4$ (0.78 g, 4.10 mmol) were condensed into a 100-mL glass reaction flask at −196 °C. The reaction vessel was warmed to −78 °C and held at that temperature for approximately 1 h, after which time the reaction mixture was allowed to warm slowly to room temperature. After 3 h the volatile products were removed to the vacuum line for separation by trap-to-trap distillation. Unreacted $SF_5N{=}SF_2$ (6.25 mmol) was found in the −196 °C trap. Repeated redistillation of the contents of the −70 °C trap yielded $SF_5N{=}SClF$ (0.10 mmol, 2.44% yield; collected at −70 °C) and $SF_5N{=}SCl_2$ (3.8 mmol, 92.68% yield; collected at −64 °C). The yellow-orange solid produced was not identified. A small quantity of $SF_5N{=}SClF$ was observed by means of its IR and NMR spectra, and we found that this mixed halide did not disproportionate into $SF_5N{=}SF_2$ and $SF_5N{=}SCl_2$ at room temperature.

Physical Properties of $SF_5N{=}SClF$. IR (gas) 1275 (s), 902 (vs), 858 (vs), 703 (m), 600 (s), 470 (m) cm^{-1}; mass spectrum (70 eV) *m/e* (relative intensity) 210, 208 $[M - F]^+$ (0.6, 1.4), 192 $[M - Cl]^+$ (29.3), 173 $[SF_5N{=}S]^+$ (0.4), 143 (1.8), 129, 127 $[SF_5]^+$ (4.3, 83.5), 124 (1.2), 108 (3.9), 107, 105 (6.4, 15.8), 102, 100 $[N{=}SClF]^+$ (1.3, 3.4), 91, 89 $[SF_3]^+$ (2.8, 51.9), 86 (3.3), 85 (1.8), 84 (0.8), 81 (1.1), 72, 70 $[SF_2]^+$ (0.9, 17.2), 67 (3.8), 65 (17.2), 64 (4.8), 51 (8.3), 48, 46 $[SN]^+$ (7.4, 100.0), 38 (1.9), 37 (1.6), 36 (5.3), 35 (5.0), 32 (3.8); ^{19}F NMR (relative to CCl_3F, solvent $CDCl_3$) ϕ (SF_A) 71.0 (n, SF_A), 79.0 (d of m, SF_b), $\phi(SF_X)$ 63.9 (qu, J_{AB} = 156.3 Hz, J_{BX} = 13.7 Hz).

Reaction of $SnCl_4$ and $SF_5N{=}SF_2$. The compound $SF_5N{=}SF_2$ (30.0 mmol) was allowed to react with constant stirring with anhydrous $SnCl_4$ (8.92 g, 34.18 mmol) in a 500-mL flask at room temperature. After several hours a white precipitate formed and the solution mixture attained a pale yellow color. After 15 days the volatile products were fractionated through a series of traps at −23, −64, −78, and −196 °C. The nonvolatile solid residue was not identified. The trap at −196 °C contained unreacted $SF_5N{=}SF_2$ (2.21 g, 10.49 mmol). The remaining volatile products (SF_5NSCl_2 and $SnCl_4$) were collected in both −64 and −78 °C traps. Several trap-to-trap distillations failed to separate $SnCl_4$ from $SF_5N{=}SCl_2$. Finally, trimethylsilane, $(CH_3)_3SiH$ (23.34 mmol), was condensed into the flask and was allowed to react with the mixture of $SnCl_4$ and $SF_5N{=}SCl_2$ at room temperature. A white precipitate ($SnCl_2$) formed immediately. After 2 h, the volatile products were fractionated through a series of traps. The traps contained the following: at −23 °C, nothing; at −64 °C, pure $SF_5N{=}SCl_2$ (4.62 g, 19.01 mmol, 63.37% yield); at −95 °C, $(CH_3)_3SiCl$ (22.40 mmol); at −196 °C, HCl (2.8 mmol). A large quantity of noncondensable gas (H_2) produced during the reaction was pumped off.

The mass spectrum of the $SF_5N{=}SCl_2$ prepared by this method showed the fragments $SF_4N{=}S^{37}Cl_2^+$ (*m/e* 228), $SF_4NS^{35}Cl^{37}Cl^+$ (*m/e* 226), $SF_4N{=}S^{35}Cl_2^+$ (*m/e* 224), $SF_5N{=}S^{37}Cl$ (*m/e* 210), $SF_5N{=}S^{35}Cl^+$ (*m/e* 208), SF_5^+ (*m/e* 127), SF_3^+ (*m/e* 89), and $N{\equiv}S^+$ (*m/e* 46) only.

Reaction of $SbCl_5$ and $SF_5N{=}SF_2$. The compound $SF_5N{=}SF_2$ (10.0 mmol) was condensed onto $SbCl_5$ (4.0 mmol) at −196 °C for 2 days. Separation of the products was accomplished by use of −6, −45, −78, −112, and −196 °C traps. The −6 °C trap contained SbF_5 and unreacted $SbCl_5$; the −45 °C trap contained $SF_5N{=}SCl_2$, the −112 °C trap, $SF_5N{=}SF_2$, and the −196 °C trap, traces of HCl and SiF_4. The −78 °C trap contained both $SF_5N{=}SCl_2$ and $SF_5N{=}SF_2$ plus a third compound subsequently identified as $SF_5N{=}SClF$. The yield of $SF_5N{=}SCl_2$ was approximately 35% (3.5 mmol).

Reaction of $SOCl_2$ and SF_5NH_2. Method A. Anhydrous hydrogen fluoride (1.5 ml, 75 mmol) and NSF_3 (37.5 mmol) were condensed in a steel cylinder at −196 °C and allowed to react at room temperature for 1 h prior to the addition of $SOCl_2$ (37.5 mmol). The reaction mixture was then heated at 79 °C for 24 h, at which time the volatile products of the reaction were condensed into a NaF scrubber. The volatile materials were later distilled through a series of −10, −78, and −196 °C traps, the −196 °C trap containing primarily SOF_2. The contents of the −78 °C trap were redistilled twice with a −45 °C trap collecting 0.7 mmol of $SF_5N{=}SCl_2$ (2% yield) and a −63 °C trap collecting a small quantity of a new compound later identified as $SF_5N{=}SClF$.

Method B. Anhydrous hydrogen fluoride ($^1/_8$ mL, 6.25 mmol) and NSF_3 (6.0 mmol) were condensed into a Kel-F reactor and allowed to react overnight before addition of $SOCl_2$ (6 mmol). The reaction mixture was allowed to react at room temperature for 2 weeks and was then placed on a NaF scrubber prior to distillation. The −196 °C of the first distillation again contained primarily SOF_2; the contents of the −78 °C were redistilled through −45 and −196 °C traps. The −45 °C trap contained 0.3 mmol of $SF_5N{=}SCl_2$ (9.6% yield), identified by IR, NMR, and mass spectrometry. A low-intensity peak at *m/e* 102 corresponding to $[SF_5N{=}SF]^+$ in the mass spectrum gave some evidence for a trace impurity of $SF_5N{=}SClF$.

Reaction of SCl_2 and SF_5NH_2 with Cl_2. The compound NSF_3 (10.0 mmol) and anhydrous HF (20 mmol) were combined in a 30-mL steel cylinder and left for 4 h at room temperature. The cylinder was then cooled to −196 °C, and SCl_2 (10.0 mmol) and Cl_2 (10.0 mmol) were condensed into it. The cylinder was slowly warmed to room temperature over a period of 6 h. After distillation, $SF_5N{=}SCl_2$ (~4 mmol, 40% yield) was recovered in the −45 °C trap. The −196 °C trap contained HCl, SF_4, NSF_3, SCl_2, and some Cl_2.

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Registry No. $SF_5N{=}SClF$, 80997-19-9; $SF_2N{=}SCl_2$, 25502-15-2; $SF_5N{=}SF_2$, 13774-70-4; $TiCl_4$, 7550-45-0; $SnCl_4$, 7646-78-8; $SbCl_5$, 7647-18-9; $SOCl_2$, 7719-09-7; SF_5NH_2, 15192-28-6; NSF_3, 15930-75-3; SCl_2, 10545-99-0; Cl_2, 7782-50-5.

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