11.4. The base peak corresponding to the ion $\mathrm{ClF_2^+}$ was most unexpected inasmuch as under the same conditions in our instrument no m/e 73 was observed from $\mathrm{ClF_3}$ except those for chlorine.[7]

Chlorine pentafluoride appears to be less corrosive to metals than $\mathrm{ClF_3}$. A large sample has been stored in a Hoke 304 stainless steel cylinder for over 4 years without detectable decomposition. Contrary to the initial report on $\mathrm{ClF_5}$[1] we have found $\mathrm{ClF_5}$ to be extremely reactive toward water and water vapor. The hydrolysis of $\mathrm{ClF_5}$ was carefully studied in Kel-F and the experimentally established stoichiometry is indicated as

$$\mathrm{ClF_5 + 2H_2O \longrightarrow FClO_2 + 4HF}$$

Subsequent decomposition of $\mathrm{FClO_2}$ (in metal systems) no doubt accounts for the presence of $\mathrm{Cl_2}$, $\mathrm{ClO_2}$, and $\mathrm{FClO_3}$ frequently encountered in contaminated $\mathrm{ClF_5}$. These same products are encountered whenever $\mathrm{ClF_5}$ comes into contact with a hydroxylic function in any form.

When $\mathrm{ClF_5}$ was handled in Kel-F or Teflon apparatus above its boiling point, it was found to be appreciably and rapidly soluble in the polymer. After the $\mathrm{ClF_5}$ had been in contact with the polymer at room temperature for 1 day, it was found that neither evacuation under high vacuum nor washing with water removed all of the $\mathrm{ClF_5}$ from the polymer; only after pumping for days in a vacuum system were the last traces of $\mathrm{ClF_5}$ removed.

As predicted, $\mathrm{ClF_5}$ is a vigorous fluorinating agent. With the possible exception of carbon, the first-row nonmetals did not react with $\mathrm{ClF_5}$ at 150° in 16 hr. In contrast, second- and third-row nonmetals except chlorine were reactive even at ambient temperature. Carbon reactivity varied with its form. Activated charcoal reacted vigorously at ambient temperature to form $\mathrm{Cl_2}$, $\mathrm{CF_4}$, $\mathrm{CF_3Cl}$, and $\mathrm{C_2F_6}$. Lampblack with 1% volatile impurities reacted only partially at 150°. Graphite powder and pressed graphite rod took up $\mathrm{ClF_5}$ corresponding to 10 wt % of the graphite but only $\mathrm{ClF_5}$ was found in the volatiles recovered. Basic hydrolysis of such graphitic material was accompanied by a deflagration and yielded products similar to those of $\mathrm{ClF_5}$ hydrolyses. The graphite rod crumbled on prolonged exposure to $\mathrm{ClF_5}$. The above results suggest an intercalation compound between graphite and $\mathrm{ClF_5}$.

Among the products of reaction between $\mathrm{ClF_5}$ and basic, neutral, and acidic hydroxides were HF, $\mathrm{O_2}$, chlorine, and chlorine dioxide. $\mathrm{ClF_5}$ attacked CO, PO, and SO multiple bonds but not NO or ClO multiple bonds. Of particular interest was the scant amount of toxic, noxious, or otherwise hazardous gas products in the reactions of $\mathrm{ClF_5}$ with $\mathrm{Na_2B_4O_7 \cdot Na_2S_2O_3 \cdot 9H_2O}$ and $\mathrm{NaHCO_3}$. Metal fluoride hydrates reacted with $\mathrm{ClF_5}$ at ambient temperature with the exception of $\mathrm{MgF_2 \cdot}x\mathrm{H_2O}$ which had to be warmed for complete reaction.

Experimental Details

Materials.—Chlorine trifluoride was obtained from the Matheson Co. The reactors used for the pressure fluorinations were either Monel or 304 stainless steel and equipped with Hoke M343 valves. The discharge apparatus used for the synthesis of $\mathrm{ClF_5}$ was similar to that described elsewhere.[8]

Preparation by Electrical Discharge.—A 60-l. stainless steel tank was filled to 1 atm with a mixture of 10 parts of fluorine and 1 part of chlorine (by volume). The gas was pumped through an electrical discharge cell cooled in a solid $\mathrm{CO_2}$ and trichloroethylene mixture, a U trap at −196°, and a manostat of the bubbler type filled with Fluorolube oil that maintained a pressure in the train of 30 mm; the pump was protected by a fluorine absorber made of NaCl and soda lime and a liquid nitrogen trap. The contents of the −196° trap adjacent to the discharge apparatus was fractionated in a metal vacuum line through traps cooled to −112, −126, and −196°. The middle trap contained $\mathrm{ClF_5}$, and the other traps contained $\mathrm{ClF_3}$ and ClF, respectively. The yield was of the order of 1 cc of $\mathrm{ClF_5}$/4000 cc of gas mixture used.

Synthesis of $\mathrm{ClF_5}$ from Alkali Metal Chlorotetrafluorides.—A previously passivated 500-ml stainless steel Hoke cylinder was loaded with 76.0 g (0.5 mole) of anhydrous cesium fluoride in a drybox, and 50 g (0.55 mole) of $\mathrm{ClF_3}$ was condensed therein from a metal vacuum line. The reactor was heated for 4 hr at 80°. Most of the $\mathrm{ClF_3}$ was found to have reacted after this treatment. Fifteen liters (0.67 mole) of fluorine was then condensed into the reactor which was then heated for 22 hr at 150°. After removal of the excess fluorine, 26 g (0.2 mole) of pure $\mathrm{ClF_5}$, representing a 40% conversion, was distilled out of the reactor. Essentially the same procedure was employed with RbF and KF; the conversions with KF were not as high and ranged between 10 and 25%.

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[7] B. L. Tuffly, V. E. Bedwell, and E. F. C. Cain, "Proceedings of Ninth Annual Meeting of ASTM Committee E-14 on Mass Spectrometry," Chicago, Ill., 1961.

[8] W. Maya, *Inorg. Chem.*, **3**, 1063 (1964).

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Complexes of Sulfur Dioxide with Ionic Azides

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Numerous reactions between sulfur dioxide and inorganic salts have been reported. For example, potassium cyanide,[1] potassium iodide,[2] and alkali metal fluorides[3] are known to combine with sulfur dioxide, and in many cases the products undergo irreversible reactions. However, the reaction of an azide salt with sulfur dioxide has not been described.

During the course of a study of azides, it was observed that the alkali metal azides reversibly absorb sulfur dioxide at room temperature. The apparent ease of

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[1] F. Seel and E. Muller, *Ber.*, **88**, 1747 (1955); J. M. Ross and W. C. Smith, *J. Am. Chem. Soc.*, **86**, 2861 (1964).

[2] J. Jander and G. Turk, *Angew. Chem.*, **75**, 792 (1963).

[3] F. Seel and L. Riehl, *Z. Anorg. Allgem. Chem.*, **282**, 293 (1955).

sulfur dioxide absorption increases with the atomic number of the cation as does the intensity of an accompanying yellow color. Complete removal of the sulfur dioxide from the complex leaves the azide in an extremely finely divided form.

The product from sodium azide and sulfur dioxide was isolated and a preliminary characterization was carried out. The weight increase due to sulfur dioxide indicated a composition near $3NaN_3 \cdot 4SO_2$. Both the X-ray (Table I) and infrared (Figure 1) spectra of the product show that sodium azide is no longer present as a distinct species. The infrared spectrum is similar to those of organic sulfonyl azides and suggests the presence of a covalent azide. The doublet at 2150–2080 cm^{-1} may be assigned to N_3 asymmetric stretching, the 1185-cm^{-1} band to N_3 symmetric stretching, and the bands at 1065 and 980 cm^{-1} to SO_2. Sodium azide absorbs only at 2100 cm^{-1}.

TABLE I

COMPARISON OF X-RAY POWDER DIFFRACTION PATTERNS[a]

$NaN_3 \cdot 1.3SO_2$		$NaNa_3$	
d spacing	Rel intens, %	*d* spacing	Rel intens, %
1.8226	12.2	1.547	11.2
1.8790	8.9	1.792	11.7
1.8945	12.2	1.823	36.2
1.9060	18.9	2.189	29.8
1.9456	13.3	2.429	100.0
2.0170	12.2	2.913	100+[b]
2.4149	20.0	3.097	20.2
2.5902	77.8	5.046	5.3
2.7281	28.8		
2.9005	27.8		
2.9955	19.6		
3.0930	44.4		
3.2406	7.3		
3.3781	40.0		
3.7509	13.3		
4.0368	95.5		
4.3078	13.3		
4.5250	100.0		

[a] Cu Kα; Ni filter; *d* spacings obtained from strip-chart recordings; the intensities were obtained from peak heights. [b] Off-scale.

Ammonium azide, tetramethylammonium azide, and dibenzyldimethylammonium azide also absorb sulfur dioxide. The product from the last salt is fairly stable. The weight increase and vapor pressure data indicate the product has a composition near $3(\text{azide}) \cdot 2SO_2$. The infrared spectrum is essentially a superimposition of the spectra of the sodium azide–sulfur dioxide product and the quaternary ammonium chloride.

With a few exceptions, the chemical properties of these complexes are the same as those of the parent azides. This suggests that they are bound by weak rather than by strong bonds. However, in some cases the complex appears to be directly involved in the reaction. For example, triphenylphosphine causes the slow liberation of nitrogen from a mixture of sodium azide and sulfur dioxide. No solid product containing nitrogen could be detected, but sodium bisulfite, triphenylphosphine oxide, and triphenylphosphine sulfide were isolated.[4] Although it is well known that covalent azides liberate nitrogen in the presence of phosphines,[5] there is no record of ionic azides doing this.

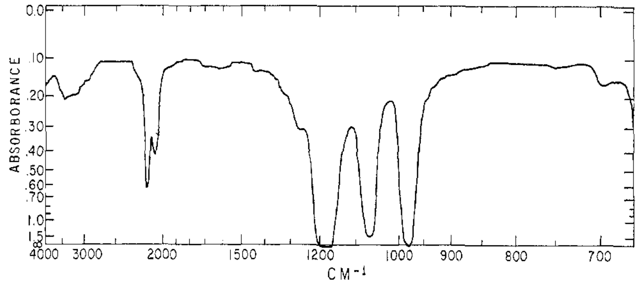

Figure 1.– Infrared spectrum of $NaN_3 \cdot 1.3SO_2$ (KBr pellet).

In another example of complex participation, the addition of phosgene to a mixture of sodium azide and sulfur dioxide leads to the formation of small amounts of carbonyl azide and sulfuryl azide chloride, $ClSO_2N_3$. In control experiments with sulfur dioxide and phosgene, sulfuryl chloride, an intermediate in a demonstrated route to sulfuryl azide chloride,[6] could not be detected. Furthermore, a mechanism involving the formation of chlorine azide and its addition to sulfur dioxide is eliminated by the apparent failure of Ruff to detect sulfuryl azide chloride in systems containing these reagents.[7] Consequently, a mechanism involving chlorination of the complex or of an equilibrium species such as the azidosulfinate ion appears likely.

Since molecular chlorine was not detected chromatographically in the phosgene, either phosgene or a species generated from it in the polar system is the active chlorinating agent.

The complexes are useful in the preparation of organic azides. Chemical or physical activation of the azide salt is unnecessary, and in many cases the reactions are rapid, clean, and efficient. Workup is simplified by the low boiling point of the solvent. An example is provided to illustrate the technique.

ω-Hydroperfluorononanoyl azide is formed in the reaction of the corresponding acyl chloride with sodium azide in liquid sulfur dioxide. The acyl azide decomposes normally to yield the isocyanate. The reaction sequence was confirmed by the isolation and identification of ethyl-ω-hydroperfluorooctyl carbamate.

Experimental Section

Sodium Azide–Sulfur Dioxide Complex.—To 1.0 g (15.4 mmoles) of recrystallized, anhydrous sodium azide in a glass pressure vessel was added 2.2 g (34.8 mmoles) of sulfur dioxide with liquid nitrogen cooling. The sealed flask was warmed to room temperature, and the mixture was stirred for 1 hr. The flask was carefully opened to a calibrated volume under high vacuum. The pressure reached 486 mm in a 990-cc volume. This pressure was 172 mm less than that noted for the same amount of sulfur dioxide alone. The gas was completely pumped

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[4] E. Fluck and H. Binder, *Angew. Chem. Intern. Ed. Engl.*, **4**, 359 (1965), reported that the heating of mixtures of phosphines and sulfur dioxide yielded the phosphine oxides and sulfides.

[5] J. E. Franz and C. Osuch, *Tetrahedron Letters*, **13**, 841 (1963), noted, in addition to the expected phosphinimine, the formation of triphenylphosphine oxide, phenyl sulfide, and phenyl disulfide from benzenesulfonyl azide and triphenylphosphine in hot acetonitrile or chloroform.

[6] R. J. Shozda and J. A. Vernon, *J. Org. Chem.*, **32**, 2876 (1967).

[7] J. K. Ruff, *Inorg. Chem.*, **4**, 567 (1965).

out, and fresh sulfur dioxide was added. The above procedure was repeated five times, and the equilibrium pressure decreased each time until a value of 366 mm was duplicated in the two final additions. The solid complex (2.29 g) was removed from the flask. The product gave an acidic reaction in water and slowly lost sulfur dioxide on standing in air.

In a similar way, sulfur dioxide was absorbed by lithium, potassium, rubidium, and cesium azide.

Dibenzyldimethylammonium Azide–Sulfur Dioxide Complex. By the above procedure 3.0 g (11.2 mmoles) of anhydrous dibenzyldimethylammonium azide[6] was contacted with 4.2 g (66 mmoles) of sulfur dioxide to form a yellow solution. The vapor pressure at 25° in a 982–998-cc volume was noted as measured amounts of sulfur dioxide were removed from the system. The data are shown in Table II. When the mole ratio of sulfur dioxide to azide was decreased to 1, the mixture became solid. When the mole ratio was decreased to 0.7, the vapor pressure was 4 mm. The 3.5 g of solid (mp 75–80°) was removed from the flask. A comparison of the infrared spectrum of the product with that of the corresponding quaternary ammonium chloride and azide indicated the presence of bands due to the complex at 2010–2050 (doublet), 1190, 1110, and 985 cm^{-1}.

TABLE II

VAPOR PRESSURE OF THE SYSTEM

$(C_6H_5CH_2)_2N^+(CH_3)_2N_3^- + SO_2$[a]

Total mmoles of SO_2	Vapor pressure, mm
7.84	4
8.33	10
9.82	30
17.6	156
37.3	394
47.0	456
51.8	526
59.1	624
66.4	710

[a] 25°, 982–998-cc volume, 11.2 mmoles of azide.

Dibenzyldimethylammonium chloride did not absorb sulfur dioxide, while ammonium azide and tetramethylammonium azide did.

Reaction of Sodium Azide and Triphenylphosphine in Liquid Sulfur Dioxide.—A mixture of 1.3 g (20 mmoles) of sodium azide, 5.24 g (20 mmoles) of triphenylphosphine, and 29 g of sulfur dioxide was stirred 7 days at 25° in a glass pressure flask. Periodically, the flask was cooled in liquid nitrogen, and the nitrogen generated in the reaction was pumped out. At the end of the reaction period, about 20 mmoles of nitrogen had formed. The sulfur dioxide was then distilled from the purple reaction mixture. The remaining solid was extracted with chloroform to leave a residue which was extracted into water and filtered. The water extract was evaporated to leave 0.7 g of a white solid which was shown to be sodium bisulfite by X-ray analysis. The chloroform extract was evaporated, and the solid was purified by fractional crystallization from methanol to yield 3.2 g of triphenylphosphine oxide and 1.5 g of triphenylphosphine sulfide which were identified by their melting points and infrared spectra.

Reaction of Sodium Azide and Phosgene in Liquid Sulfur Dioxide.—A mixture of 0.5 g (7.7 mmoles) of sodium azide, 2.1 g (21 mmoles) of phosgene, and 12.2 g of sulfur dioxide was stirred 21 hr at 25° in a glass pressure flask. The volatile portion of the mixture was distilled through a Dry Ice cooled trap on a high-vacuum line to collect 0.18 ml of a colorless liquid in the trap. Infrared analysis indicated that the product consisted of nearly equal amounts of carbonyl azide[8] and sulfuryl azide chloride.[6]

ω-Hydroperfluorononanoyl Azide.—ω-Hydroperfluorononanoyl chloride, prepared by the procedure of Carnahan and Sampson,[9] was isolated as a colorless liquid; bp 28° (0.5 mm); infrared peak at 1805 cm^{-1}. A mixture of 2.3 g (5.2 mmoles) of the acyl chloride, 0.4 g (6.1 mmoles) of sodium azide, and 20.5 g of sulfur dioxide was stirred overnight at room temperature. The sulfur dioxide was removed under vacuum and the residue was mixed with methylene chloride to extract the product. Distillation afforded 1.95 g (80%) of ω-hydroperfluorononanoyl azide; bp ~25° (0.06 mm). The product displayed infrared absorption at 2160–2190 (doublet), 1740–1749 (doublet), and 1110–1310 cm^{-1}.

In another experiment, the crude product from 0.8 g of sodium azide and 4.6 g of acyl chloride was extracted with toluene and heated until the solvent slowly refluxed. During 2-hr time, 225 cc (92%) of gas was evolved. The resulting solution of ω-hydroperfluorooctyl isocyanate was stirred 1 hr with 7 ml of anhydrous ethanol to form ethyl-ω-hydroperfluorooctyl carbamate. The carbamate was purified by distillation to yield 3.5 g (66%) of a solid, bp ~40° (0.005 mm), mp 43–45°. The product showed infrared absorption at 3360 and 1540 (NH), 1740 (C=O), and 1060–1350 cm^{-1}.

Anal. Calcd for $C_{11}H_7F_{16}NO_2$: C, 27.00; H, 1.45; F, 62.2; N, 2.90. Found: C, 27.00; H, 1.65; F, 60.5; N, 2.86.

In a like manner, benzyl azide, methanesulfonyl azide, and *p*-toluenesulfonyl azide were obtained in high yields.

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[8] T. Curtius and K. Heidenreich, *J. Prakt. Chem.*, **52**, 454 (1895).

[9] J. E. Carnahan and H. J. Sampson, U. S. Patent 2,646,499 (1953).

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Proton Magnetic Resonance Shifts and Spin Delocalization in Nickel(II) Complexes with Macrocyclic Schiff Base Ligands

BY GERD N. LA MAR

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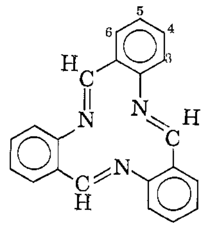
It has recently been shown that in the course of investigating the metal template effect on certain chemical reactions,[1,2] one of the products resulting from the self-condensation of *o*-aminobenzaldehyde in the presence of nickel(II) is a complex containing the macrocyclic ligand tribenzo[*b,f,j*][1,5,9]triazacycloduodecine, abbreviated TRI, with structure **1**.[3]



1

Several complexes containing this ligand have been prepared containing either one or two TRI molecules,[2-4] though the 5-Cl-substituted ligand, 5-Cl-TRI, has been prepared only with one TRI.[4] Both the magnetic and spectral data for $Ni[TRI]_2(NO_3)_2 \cdot H_2O$ are consistent with a pseudo-octahedral configuration about the

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[1] G. A. Melson and D. H. Busch, *J. Am. Chem. Soc.*, **87**, 1706 (1965).

[2] L. T. Taylor, S. C. Vergez, and D. H. Busch, *ibid.*, **88**, 3170 (1966).

[3] E. B. Fleischer and E. Klem, *Inorg. Chem.*, **4**, 637 (1965).

[4] D. H. Busch and L. T. Taylor, private communication.