It was found that the Ti^{4+} ion enters the tetrahedral as well as the octahedral site in the garnets. In the system $\{Y_{3-x-y}Ca_{x+y}\}Zr_yTi_xGa_{5-x-y}O_{12}$ single-phase specimens were prepared with $x = 1.20$ and 1.50 and $y = 1.00$ (Table I). Because the Zr^{4+} ions prefer exclusively the octahedral sites[2] at least 0.20 and 0.50 Ti^{4+} ion, respectively, were substituted tetrahedrally. When $x = 0.30$ and $y = 2.00$ the amount of tetrahedral Ti^{4+} is 0.30. By the same reasoning the garnet in the system $\{Y_{3-x-y}Ca_{x+y}\}Zr_yTi_xFe_{5-x-y}O_{12}$ with $x = 0.60$ and $y = 1.50$ (Table I) contains at least 0.10 Ti^{4+} ion in tetrahedral coordination.

The lattice constants of the systems $\{Y_{3-x}Ca_x\}$-$Ti_xM_{5-x}O_{12}$ ($M = Ga^{3+}$ or Fe^{3+}) increase with increasing x. When $M = Fe^{3+}$ this increase may be attributed to the Ca^{2+} ion, which is larger than the Y^{3+} ion,[11] while the octahedral Ti^{4+} ion is probably a little smaller than the octahedral Fe^{3+} ion. When $M = Ga^{3+}$ most of the increase is caused by the Ca^{2+} ion but some may be attributed to the tetrahedral Ti^{4+} ion, which is prob-

ably larger than the tetrahedral Ga^{3+} ion. In this system x_{max} is larger when $M = Ga^{3+}$ than when $M = Fe^{3+}$, probably because the tetrahedral Ga^{3+} ion is smaller than the tetrahedral Fe^{3+} ion relative to the ionic size in octahedral coordination. This presumably leads to a more favorable octahedral to tetrahedral metal-oxygen distance ratio relative to the requirements of the structure.

In the systems $\{Y_{3-x}Ca_x\}Ti_xM_{5-x}O_{12}$ and $\{Y_3\}$-$[Cr_xM_{2-x}](M_3)O_{12}$ where $M = Ga^{3+}$ or Fe^{3+}, the maximum amount of Ti^{4+} ion which can be substituted for M^{3+} is always greater than the maximum amount of Cr^{3+} ion which can be substituted within a given system. This results from the distribution of the Ti^{4+} ions over two sites which may lead to a more favorable structural situation in these garnets; it also suggests that the Ti^{4+} ion is larger than the Cr^{3+} ion.

Acknowledgment.—The author wishes to thank S. Geller for suggesting this project and for helpful discussion.

(11) S. C. Abrahams and S. Geller, *Acta Cryst.*, **11**, 437 (1958).

The Preparation and Properties of Trifluoromethoxy Sulfur Pentafluoride [CF₃OSF₅] and *cis*-Bis(trifluoromethoxy)tetrafluorosulfur(VI) [(CF₃O)₂SF₄][1]

By LEONARD C. DUNCAN and GEORGE H. CADY

Trifluoromethoxy sulfur pentafluoride and *cis*-bis(trifluoromethoxy)tetrafluorosulfur(VI) were prepared by the ultraviolet irradiation of gaseous mixtures of SF_4 with either CF_3OF or CF_3OOCF_3. The products have been characterized and the structures confirmed by mass, infrared, and nuclear magnetic resonance spectra.

Trifluoromethyl hypofluorite can be added across double bonds with cleavage at the O–F bond to yield, in the case of ethylene, $CF_3OCH_2CH_2F$,[2,3] and in the case of carbonyl fluoride, CF_3OOCF_3.[4] It has now been found that trifluoromethyl hypofluorite also can be added to sulfur tetrafluoride to give trifluoromethoxy sulfur pentafluoride.[5] *cis*-Bis(trifluoromethoxy)tetrafluorosulfur(VI) is also produced.

Experimental

Materials.—Trifluoromethyl hypofluorite[6] was obtained as the product of a flow reaction of carbon monoxide and fluorine at $350°$. Bistrifluoromethyl peroxide[4] was prepared by passing streams of fluorine and carbon monoxide through a "catalytic"

flow reactor[6] with the flow rates: F_2, 4 l./hr., and CO, 2.7 l./hr. The products of this reaction were collected in a trap held at $-183°$. The peroxide was refined by pumping the product mixture under vacuum through a train consisting of: (1) a 0.75-m. length of 30-mm. tubing packed with granulated soda lime, (2) a trap held at $-78°$, and (3) a trap held at $-183°$. The F_2, CF_3OF, CO_2, and COF_2 present in the crude material were absorbed by the soda lime. The water and oxygen formed in the soda lime column, along with CF_3OOCF_3 and CF_4, then passed through the trap at $-78°$ where water was condensed, then to the trap at $-183°$ where the peroxide was deposited while the CF_4 and O_2 present passed on to the vacuum pump. The CF_3OOCF_3 obtained in this manner was used without further purification. Sulfur tetrafluoride was supplied by E. I. du Pont de Nemours and Co., Inc., and was used directly from the cylinder.

Reactions.—Equimolar amounts of gaseous CF_3OF and SF_4 were introduced into a 3-l. Pyrex bulb to a total pressure of 252 mm. A quartz glass finger containing a water-cooled Hanau 4.5-watt mercury arc lamp projected ultraviolet light into the bulb. After irradiation for 3 days the volatile products were condensed and separated by fractional codistillation.[7] They were, in order of decreasing volatility, CF_3OF, SiF_4, COF_2, SO_2F_2, SOF_2, CF_3OOCF_3, CF_3OSF_5, $(CF_3O)_2SF_4$, and a small amount of a still less volatile material which was not identified.

(1) Presented at the Northwest Regional Meeting of the American Chemical Society, June 20, 1962.

(2) G. H. Cady, Abstracts, XVII International Congress of Pure and Applied Chemistry.

(3) J. A. C. Allison and G. H. Cady, *J. Am. Chem. Soc.*, **81**, 1089 (1959).

(4) R. S. Porter and G. H. Cady, *ibid.*, **79**, 5628 (1957).

(5) (a) This compound has been reported by G. Pass and H. L. Roberts, *Inorg. Chem.*, **2**, 1016 (1963); (b) the n.m.r. spectrum of a sample prepared by the authors was published previously (C. I. Merrill, S. M. Williamson, G. H. Cady, and D. Eggers, Jr., *ibid.*, **1**, 215 (1962).

(6) K. B. Kellogg and G. H. Cady, *J. Am. Chem. Soc.*, **70**, 3986 (1948).

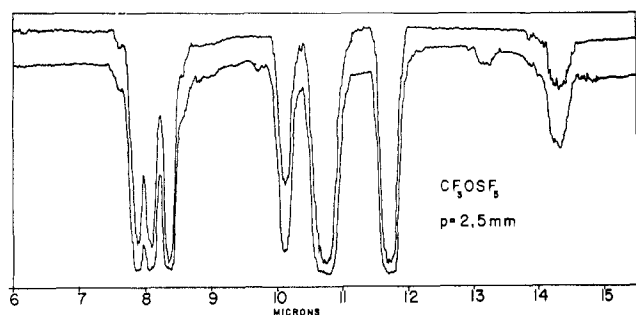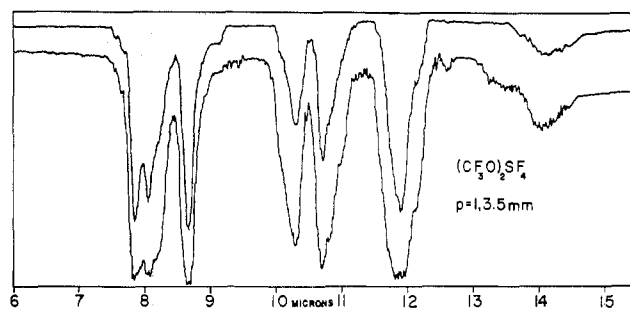(7) G. H. Cady and D. P. Siegwarth, *Anal. Chem.*, **31**, 618 (1959).

Figure 1.

All of the above substances, except the last three, were identified by their characteristic infrared spectra. The yield of CF_3OSF_5 was approximately 10%, and that of $(CF_3O)_2SF_4$ about 8%, of that theoretically possible from the amount of SF_4 used.

A mixture of equimolar amounts of CF_3OF and SF_4 with a total pressure of 408 mm. was heated in a 1.5-l. nickel reactor which has been described previously.[8] The pressure was recorded at frequent temperature intervals and it was found that the pressure of the mixture increased in direct proportion to the absolute temperature up to 150°. Above this temperature the pressure *vs.* temperature curve "flattened," indicating a reaction which caused a decrease in the number of molecules. The product contained CF_3OSF_5 and $(CF_3O)_2SF_4$, but the yields were small.

The best yield (about 35%) of CF_3OSF_5 was obtained by the reaction of 2.5 g. of CF_3OF and 2.5 g. of SF_4 in a 5-cc. Monel tube held at 100° for 1 week. The yield of $(CF_3O)_2SF_4$ was negligible in this case.

CF_3OSF_5 and $(CF_3O)_2SF_4$ were both obtained in about 10% yields from the ultraviolet irradiation, at room temperature, of an equimolar gaseous mixture of CF_3OOCF_3 and SF_4 with a total pressure of 500 mm. in a 3-l. vessel.

General Methods.—**Infrared spectra** were studied using a Perkin-Elmer Model 21 infrared spectrometer with a sodium chloride prism. The gaseous samples were contained in a 10-cm. glass cell with silver chloride windows. **N.m.r. spectra** were obtained through the use of a Varian Model 4311B high resolution spectrometer with a 40-Mc. oscillator. **Mass spectra** were recorded using a Consolidated Engineering Corporation Type 21-103 mass spectrometer. **Vapor densities** were determined using a glass bulb of 258 ml. volume. Liquid densities were found using a single capillary pycnometer. **Melting points** were obtained by warming the solids slowly in a closed 5-mm. o.d. Pyrex tube contained in a cold isopentane bath. **Vapor pressures** were determined using a method previously described.[6]

Properties of Trifluoromethoxy Sulfur Pentafluoride.—Experimental measurements gave an average molecular weight of 213.4 compared to a molecular weight of 212.1 calculated for CF_3OSF_5. The density of liquid CF_3OSF_5, as determined at five temperatures in the range −30 to −5° (see Table I), gave an extrapolated density at 0° of 1.772 g./cc. and a volume coefficient of expansion at 0° of 2.32×10^{-3}. The observed melting point was $-143.0 \pm 0.5°$. Vapor pressures, shown in Table II, indicated a boiling point of $-11.0°$, a molar heat of vaporization of 5.84 kcal., and a Trouton constant of 22.3 e.u. The experimental data fit the expression $\log p_{mm} = -1.2757/T \times 10^3 + 7.7485$.

TABLE I

DENSITIES OF CF₃OSF₅

Temp., °C.	−29.5	−25.3	−19.5	−11.9	−4.5
Density, g./cc.	1.889	1.872	1.851	1.821	1.790

Figure 2.

TABLE II

VAPOR PRESSURES OF CF₃OSF₅

P, mm.	Temp., °K.	*P*, mm.	Temp., °K.
47.5	214.3	378.9	246.7
76.2	217.9	419.4	248.8
102.2	222.6	466.3	251.1
137.8	227.6	513.6	252.8
171.9	231.5	553.9	255.0
206.8	234.8	602.1	256.8
232.4	237.1	650.2	258.5
262.6	239.3	687.0	259.8
294.4	241.6	717.7	260.9
341.0	244.3	754.4	262.0
		(760.0)	(262.2)

The infrared spectra at 2 and 10 mm., shown in Fig. 1, contained strong bands at 1275 cm.$^{-1}$ (7.84 μ), 1238 cm.$^{-1}$ (8.07 μ), and 1198 cm.$^{-1}$ (8.34 μ) due to the CF₃–O group. The strong bands at 934 cm.$^{-1}$ (10.70 μ) and at 854 cm.$^{-1}$ (11.70 μ) were attributed to the SF₅ group. Cross, *et al.*,[9] have shown that in compounds containing the SF₅ group, intense absorption bands occur in the region from 850 to 920 cm.$^{-1}$, and Sheppard[10] has found that the lower limit of this region may be extended to 820 cm.$^{-1}$. It appears from the spectrum of CF₃OSF₅ that the upper limit of this region must be extended to at least 935 cm.$^{-1}$. It is believed that the strong band at 698 cm.$^{-1}$ (14.30 μ) is also due to the SF₅ group. This band is within the –SF₅ absorption region 706 cm.$^{-1}$ for SF₅Cl[9] and 690 cm.$^{-1}$ for SF₅Br.[11] The weak band centered at 759 cm.$^{-1}$ (13.16 μ) and the strong band at 990 cm.$^{-1}$ (10.10 μ) were not assigned. The mass spectrum of CF₃OSF₅ above mass number 44 included, in order of decreasing intensity, the following ions: SF₅⁺, CF₃⁺, SOF₃⁺, COF⁺, SF₃⁺, SF₂⁺, SF⁺, SOF⁺, S³⁴F₅⁺, and SF₄⁺. The nuclear magnetic resonance spectrum of this compound has been shown in another publication[5b] to be that expected for the structure CF₃OSF₅.

Trifluoromethoxy sulfur pentafluoride is colorless and low in reactivity as might be expected from its similarity to a saturated perfluoro ether.[12] The analysis was accomplished on the products of the fusion of a known quantity of the compound with an excess of sodium. *Anal.* Calcd.: S, 15.1; F, 71.2. Found: S, 15.0; F, 70.2.

Properties of *cis*-Bis(trifluoromethoxy)tetrafluorosulfur(VI).—Molecular weight determinations gave an average value of 278.2 (theoretical, 278.1). Densities at four temperatures shown in Table III correspond to a volume coefficient of expansion at 0° of 1.85×10^{-3}. The melting point of this compound was not found. In all attempts the material became a glass when cooled below $-130°$. Vapor pressures shown in Table IV indicate a heat of vaporization of 6.89 kcal./mole, a normal boiling point

(8) W. P. Van Meter and G. H. Cady, *J. Am. Chem. Soc.*, **82**, 6005 (1960).

(9) L. H. Cross, G. Cushing, and H. L. Roberts, *Spectrochim. Acta*, **17**, 344 (1961).

(10) W. A. Sheppard, *J. Am. Chem. Soc.*, **84**, 3064 (1962).

(11) C. I. Merrill and G. H. Cady, to be published.

(12) A. M. Lovelace, D. A. Rausch, and W. Postelnek, "Aliphatic Fluorine Compounds," American Chemical Society Monograph Series 138, Reinhold Publishing Co., New York, N. Y., 1958.
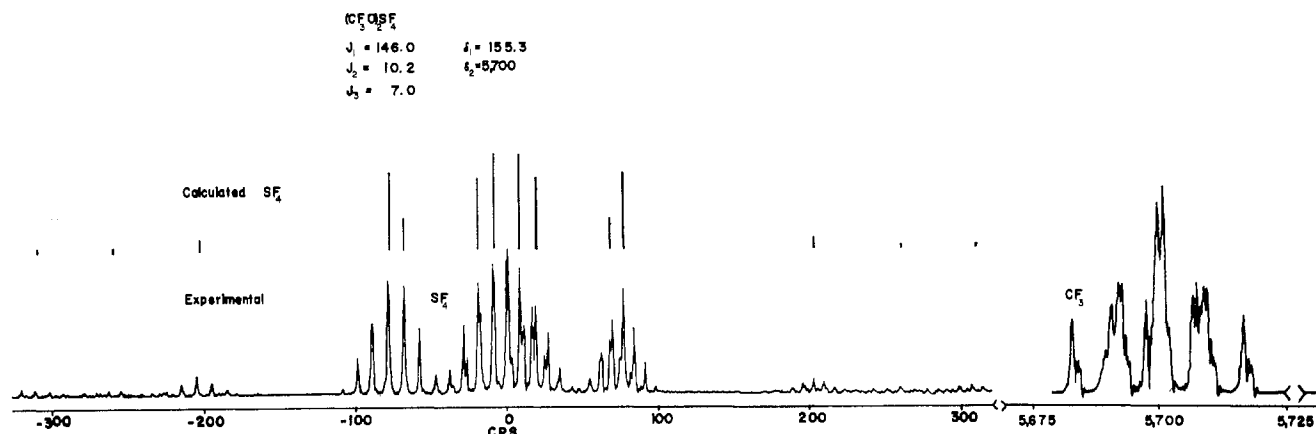
$(CF_3O)_2SF_4$

$J_1 = 146.0$ $\delta_1 = 155.3$
$J_2 = 10.2$ $\delta_2 = 5700$
$J_3 = 7.0$

Figure 3.

Table III

Densities of $(CF_3O)_2SF_4$

Temp., °C.	0.0	9.7	20.2	35.2
Density, g./cc.	1.851	1.818	1.781	1.732

Table IV

Vapor Pressures of $(CF_3O)_2SF_4$

P, mm.	Temp., °K.	P, mm.	Temp., °K.
52.8	246.1	449.5	288.9
107.6	258.5	497.4	291.8
137.6	263.2	537.5	293.4
171.9	267.4	574.8	295.1
214.1	272.1	607.4	296.5
250.2	275.5	647.2	298.2
281.9	278.1	681.4	299.4
308.8	280.1	706.6	300.4
339.2	282.2	736.9	301.6
375.0	284.6	750.2	302.0
413.6	286.7	(760.0)	(302.2)

of 29.1°, and a Trouton constant of 22.8 e.u. The data fit the expression $\log P_{mm} = -1.5061/T \times 10^3 + 7.8661$.

The infrared spectrum of $(CF_3O)_2SF_4$ shown in Fig. 2 had strong bands at 1273 cm.$^{-1}$ (7.85 μ), 1242 cm.$^{-1}$ (8.05 μ), and 1146 cm.$^{-1}$ (8.72 μ) due to the CF_3-O group. The strong absorptions at 935 cm.$^{-1}$ (10.69 μ), 840 cm.$^{-1}$ (11.89 μ), and 712 cm.$^{-1}$ (14.03 μ) were attributed to the SF_4 group. Another strong absorption occurred at 972 cm.$^{-1}$ (10.28 μ). The mass spectrum was due to the following ions, in order of decreasing intensity: CF_3^+, SOF_3^+, SF_3^+, SF_2^+, SOF^+, $S^{34}F_3^+$, SOF_2^+, COF_2^+, and SF_5^+. The SF_5^+ peak, mass 127, was weak in relative intensity and was attributed to a trace impurity of CF_3OSF_5 in this sample.

The compound is colorless and does not react with water at room temperature. A sample stored over a 10 M sodium hy-

droxide solution for 3 months showed no reaction, and another sample showed no change on being contacted with calcium at 100° for 1 hr. The analysis was carried out on the products of the reaction of this material with molten potassium. *Anal.* Calcd.: S, 11.5; F, 68.3. Found: S, 11.6; F, 67.8. The F^{19} n.m.r. spectrum of *cis*-bis(trifluoromethoxy)tetrafluorosulfur-(VI) at 40 Mc. is shown in Fig. 3. The part of the spectrum due to F atoms bound to the sulfur is a symmetrical group of fourteen bands, each of which is split seven times. If, in this molecule, the trifluoromethoxy groups were *trans*, all of the SF_4 fluorine atoms would be equivalent, yielding a single resonance, split seven times by the six neighboring CF_3 fluorines. It is evident from this spectrum that the two trifluoromethoxy groups must be in a *cis* configuration,[13] giving rise to two different pairs of fluorine atoms bound to the sulfur. In order to show that the experimental spectrum was actually that of a *cis*-disubstituted derivative of SF_6, a theoretical spectrum was calculated for an A_2B_2 model using a generalized seven-spin n.m.r. program.[14] It was found that the computed spectrum could be matched to the experimental SF_4 portion of the spectrum (see Fig. 3) using a chemical shift $\Delta \nu$ of 155.3 c.p.s. (3.88 p.p.m.) and a spin coupling constant J_1 of 146.0 c.p.s. The CF_3 portion of the spectrum was shifted $\Delta \nu = 5700$ c.p.s. (1425 p.p.m.) to higher field strength. Spin coupling constants between the CF and SF atoms were $J_2 = 7$ and $J_3 = 9$ c.p.s.

It is interesting that in this case of "addition" of CF_3OOCF_3 to sulfur tetrafluoride, exclusively the *cis* product is formed. This *cis* configuration has also been shown to be the preferred orientation in the formation of tetrafluorobisfluorosulfonato sulfur-(VI)[13] and bis(pentafluorosulfoxo) sulfur tetrafluoride.[15]

(13) J. M. Shreeve and G. H. Cady, *J. Am. Chem. Soc.*, **83**, 4524 (1961).
(14) Program provided by K. B. Wiberg.
(15) C. I. Merrill and G. H. Cady, *J. Am. Chem. Soc.*, **85**, 912 (1963).