TABLE II

X-RAY POWDER PATTERN OF KH_2PO_5[a]

d (obsd.)	I/I_0	d (calcd.)	hkl
14.8[b]	5		
13.4[b]	4		
10.3[b]	1		
8.7[b]	3		
7.5[b]	2		
6.97[b]	1		
5.45	12	5.49	010
4.67	6	4.67	100
4.59	6	4.56	011
4.21	12	4.22	002
3.92[b]	4		
3.73[c]	8		
3.62[b]	23		
3.55	100	3.56	110
3.34	31	3.33	012
3.29	50	3.28	111
3.16	34	3.13	102
3.02[c]	2		
2.91[c]	7		
2.831[b]	18		
2.748	8	2.745	020
2.729	20	2.718	112
2.647[b]	14		
2.591	15	2.608	021
2.500	8	2.500	013
2.449[b]	4		
2.358	6	2.366 2.337	120 200
2.287	9	2.299 2.277	022 121
2.254	5	2.252	201
2.206	6	2.205	113
2.166	8	2.150	210
2.068	10	2.083	211

[a] Obtained with a Norelco spectrometer and Cu Kα radiation. [b] Unidentified impurity. [c] KH_2PO_4.

fied impurity, believed to be a hydrate of KH_2PO_5 or possibly a potassium peroxodiphosphate. It was possible to distinguish the lines from KH_2PO_5 by indexing them on the basis of the above unit cell.

The infrared spectra of KH_2PO_5 and a related compound, $KHSO_5 \cdot H_2O$, are given in Table III; the tentative assignments of the observed frequencies are included. Comparison of the infrared spectra of KH_2PO_5 with those of $KHSO_5 \cdot H_2O$ provides definite evidence that (1) the band at 2940 cm.$^{-1}$ is due to –OO–H stretching; the shift from 3320 cm.$^{-1}$ in solid hydrogen peroxide[10] is probably due to intramolecular hydrogen bonding to the –P–O group, as can be shown by Stuart–Briegleb atomic models; (2) the band at 770 cm.$^{-1}$ is due to –O–O stretching; this frequency occurs in solid hydrogen peroxide at 878 cm.$^{-1}$.[10]

So far, chemical properties of the peroxophosphates have not been studied extensively. The discoverers of H_3PO_5, Schmidlin and Massini,[2] reported that H_3PO_5 oxidizes Mn(II) to MnO_4^-, a property that is not shown by H_2SO_5, and, therefore, recommended H_3PO_5 as a reagent for manganese (the solution must, of course, be free of hydrogen peroxide). Fichter and Bladergroen[4] claimed that instead of MnO_4^-, $MnPO_4$ is formed ($MnPO_4$ is also purple), since they could not obtain the absorption spectrum of MnO_4^-. Using spot tests and absorption spectra for identification, we have found that in neutral solution Mn(II) is oxidized to MnO_2 by KH_2PO_5; in 0.1 *N* H_2SO_4 the permanganate ion is formed. Potassium dihydrogen peroxophosphate oxidizes Cl^- to Cl_2; again this oxidation takes place more readily in 0.1 *N* H_2SO_4. No reaction was apparent with $Cr(NO_3)_3$. Further studies of the chemical properties of peroxophosphates will be conducted.

TABLE III

INFRARED SPECTRA

Frequency, cm.$^{-1}$	Tentative assignment
	KH_2PO_5[a]
2940 m[c]	–OO—H stretching (intramolecular hydrogen bonding to –P═O)
2700 s	–PO—H stretching
1700 m (br)	Combination or overtone band
1450 s (sp)	–OO—H bending
1300 m	–POH deformation mode
1200 m 1100 s 920 s 860 m	–P═O or –P—OH stretching
770 s	–O—O– stretching
	$KHSO_5 \cdot H_2O$[b]
3380 s	–O—H stretching in H_2O
3000 m	–OO—H stretching (intramolecular hydrogen bonding to –S═O)
1615 w	Combination band
1290 w 1090 m	–S═O stretching
725 s	–O—O– stretching

[a] Obtained with a Perkin-Elmer Model 237 spectrophotometer using Irtran-2 windows; Kel-F No. 90 (1450–2940 cm.$^{-1}$ bands) and Apiezon M (770–1300 cm.$^{-1}$ bands) greases were used. [b] Obtained with a Perkin-Elmer Model 112 spectrophotometer using sodium chloride optics; a Nujol mull was used. [c] s, strong; m, medium; w, weak; br, broad; sp, sharp.

Acknowledgments.—We wish to thank Dr. J. L. Margrave for a sample of $KHSO_5 \cdot H_2O$. A helpful discussion with Dr. W. H. Fletcher is acknowledged.

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[10] K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, New York, N. Y., 1963, p. 97.

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The Preparation of Difluoroaminotrifluoromethoxytetrafluorosulfur(VI), $CF_3OSF_4NF_2$

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Trifluoromethyl hypofluorite reacts with sulfur tetrafluoride to form CF_3OSF_5[1,2] and $(CF_3O)_2SF_4$.[2] If oxygen[1] is present the compounds $CF_3OSF_4OSF_5$, $CF_3OSF_4OOSF_5$, and $CF_3OSF_4OOSF_4OCF_3$ are also

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(1) G. Pass and H. L. Roberts, *Inorg. Chem.*, **2**, 1016 (1963).

(2) L. C. Duncan and G. H. Cady, in press.

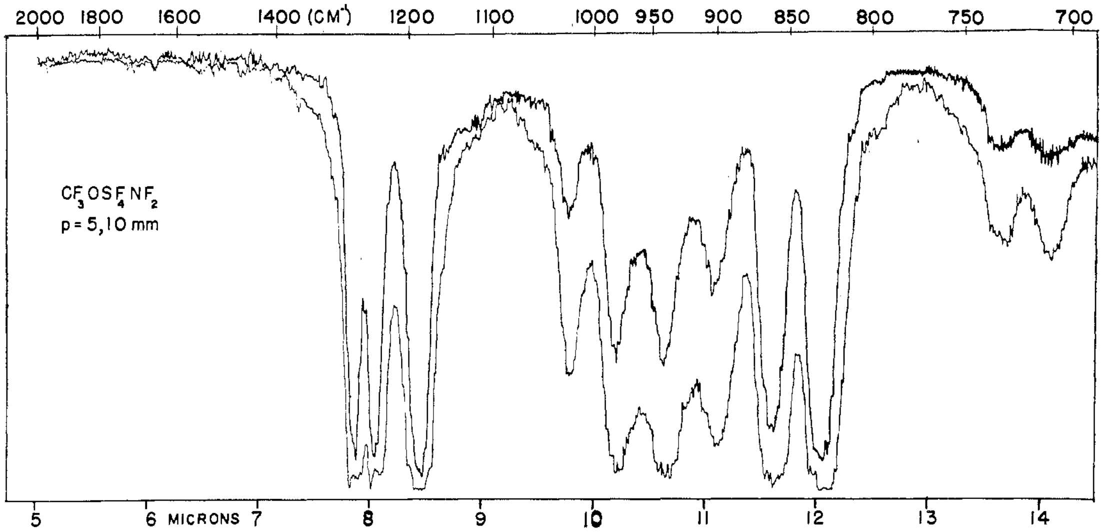

Fig. 1.—Infrared spectrum of $CF_3OSF_4NF_2$.

TABLE I

DENSITIES OF $CF_3OSF_4NF_2$

Temp., °C.	0.0	8.8	15.8	27.9	33.3
Density, g./cc.	1.827	1.793	1.770	1.726	1.702

TABLE II

VAPOR PRESSURES OF $CF_3OSF_4NF_2$

P, mm.	Temp., °K.	*P*, mm.	Temp., °K.
109.0	257.1	459.0	288.1
127.2	260.0	491.6	289.4
145.9	262.7	527.8	291.3
204.4	269.4	563.1	293.1
238.1	273.0	596.9	294.2
270.0	275.4	628.5	295.7
297.9	277.5	662.5	297.1
324.5	279.7	691.2	298.1
360.7	282.4	(760.0)	(302.5)
390.6	285.2		
425.4	286.3		

formed. In this investigation CF_3OF and SF_4 were allowed to react in the presence of N_2F_4 in order to learn whether a product containing both NF_2 and CF_3O groups would be formed. This turned out to be the case. The reaction may have proceeded by a series of steps such as proposed by Pass and Roberts[1] with an initiation step such as

$$CF_3OF + SF_4 \longrightarrow CF_3O\cdot + SF_5\cdot$$

and then further steps as

$$CF_3O\cdot + SF_4 \longrightarrow CF_3OSF_4\cdot$$

$$CF_3OSF_4\cdot + N_2F_4 \longrightarrow CF_3OSF_4NF_2 + NF_2\cdot$$

and termination as

$$SF_5\cdot + NF_2\cdot \longrightarrow SF_5NF_2$$

$$2CF_3O\cdot \longrightarrow CF_3OOCF_3$$

The NF_2 and CF_3O groups were found to be located in *cis* positions with respect to each other.

Experimental

Reactions.—In a typical reaction 3.3 g. of N_2F_4, 4.3 g. of SF_4, and 3.8 g. of CF_3OF were held in a 10-cc. Monel reactor at room temperature for 7 days. The tube was then opened and the volatile products were separated by fractional codistillation.[3] They were, in order of decreasing volatility, CF_3OF, SiF_4, COF_2, N_2F_4, ?, SOF_2, CF_3OOCF_3, SF_5NF_2, and $CF_3OSF_4NF_2$ (~14%). All the above substances except the unidentified material and the least volatile product were identified by their characteristic infrared spectra.

Properties of Difluoroaminotrifluoromethoxytetrafluorosulfur(VI).—Experimental measurements gave an average molecular weight of 245.1 compared to a molecular weight of 245.1 calculated for $CF_3OSF_4NF_2$. Densities at five temperatures shown in Table I correspond to a volume coefficient of expansion at 0° of 2.03×10^{-3}. Vapor pressures shown in Table II indicate a heat of vaporization from the Clausius–Clapeyron equation of 6.87 kcal./mole, a normal boiling point of 29.3°, and a Trouton constant of 22.7 e.u. The infrared spectrum of $CF_3OSF_4NF_2$ is shown in Fig. 1. The compound is colorless and slowly reacts with glass at room temperature forming $(NO)_2SiF_6$. The analysis for nitrogen was carried out by weighing the nitrogen produced in the reaction of $CF_3OSF_4NF_2$ with molten potassium. *Anal.* Calcd.: N, 5.72. Found: N, 5.8. The analysis for fluorine was carried out by comparing the integrated F^{19} CF n.m.r. resonance areas of samples containing known weights of $CF_3OSF_4NF_2$ and CCl_3F. *Anal.* Calcd.: F (CF), 23.25. Found: F (CF), 23.48. The integrated F^{19} n.m.r. resonance areas of a pure sample of the compound indicated that for every three fluorine atoms bound to carbon, there were 2.01 bound to nitrogen, and 4.08 bound to sulfur. Total fluorine found, 71.1%; theoretical, 69.8%. The F^{19} n.m.r. spectrum of $CF_3OSF_4NF_2$ at 56.4 Mc. is shown in Fig. 2. Since the compound is a disubstituted derivative of SF_6, the CF_3O and NF_2 groups may be either in *cis* or *trans* configurations, causing the spectrum to be one of the following types: (1) an $A_4X_3Y_2$ system (*trans*), (2) an $A_2BCX_3Y_2$ system (*cis*), (3) a mixture of the two systems. The type of complex character of the $>SF_4$ region in the spectrum clearly rules out the first possibility. It appears that the second system is the one which exists. The *trans* isomer, if present at all, is not present in a substantial proportion, because the integrated resonance areas indicate that for every three fluorine atoms in the X position there is one (1.07 observed) in the C position. The spin coupling constants and chemical shifts listed in Fig. 2(i) were obtained with the help of a computer from the observed spectra at both 40 and 56.4 Mc. In spite of considerable effort being spent on the problem, some doubt remains about the precise values of a few of the parameters. The values in the table give a calculated spectrum which agrees rather well but not

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

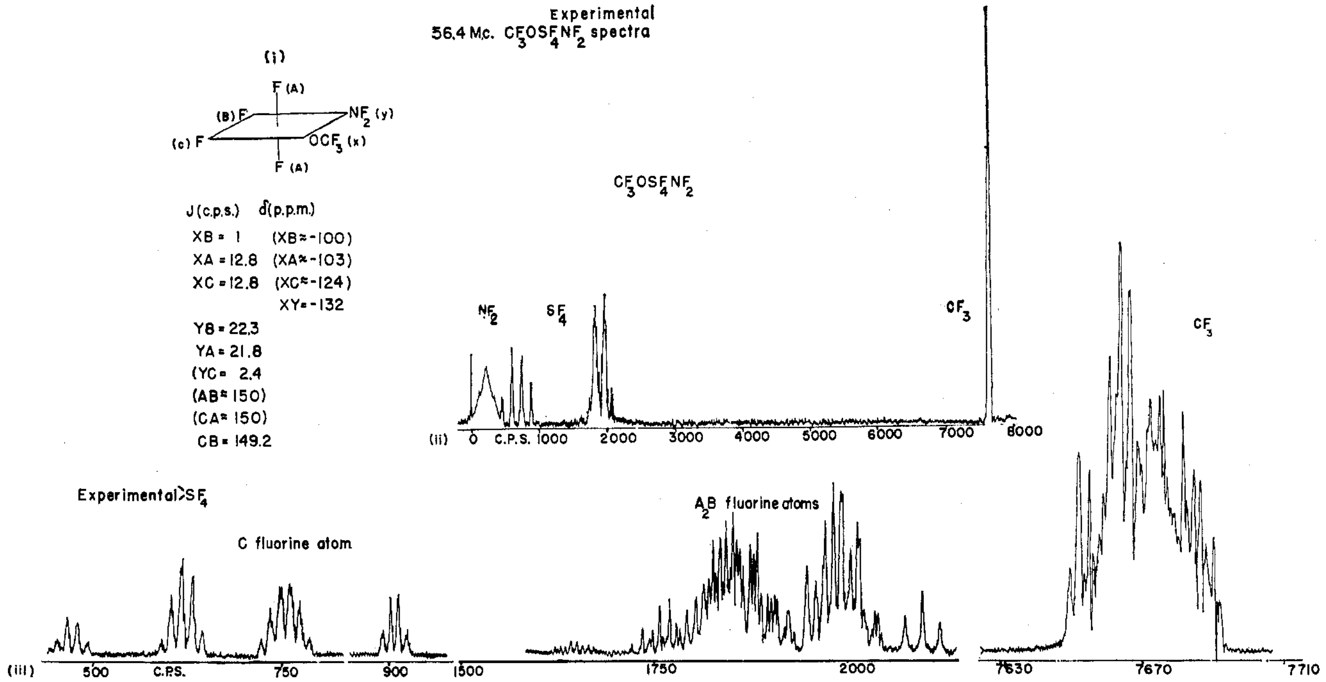

Fig. 2.—(i) Proposed structure of $CF_3OSF_4NF_2$, spin coupling constant, and chemical shifts. (ii) Experimental spectrum at high scan rate. (iii) $>SF_4$ and CF_3 portions of the spectrum at low scan rates.

perfectly with that observed. Agreement is very good for the part of the spectrum caused by the fluorine in position C.

The N^{14} to NF coupling constant was 110 c.p.s.

The single resonance line on the low-field side of the NF_2 resonance was believed to be due to an impurity, since its relative intensity varied in different samples. The chemical shift of the CF_3 group was measured relative to $CFCl_3$ (internal) and was found to be δ 55.8 p.p.m. The variation of this quantity with concentration was not examined. A comparison of the CF–SF and NF–SF coupling constants with those of related compounds supports a structure with a F_3CO and an NF_2 group attached to the sulfur atom of the SF_4 group.

TABLE III

COMPARISON OF F^{19} COUPLING CONSTANTS OF $CF_3OSF_4NF_2$ AND RELATED S–F COMPOUNDS

Compound	"Type" fluorine coupling (SF_5 is A_4B system)	J, c.p.s.
CF_3SF_5[a]	CF_3–SF_{A_4}	22.4
(*trans*) $CF_3SF_4NF_2$[b]	CF_3–SF_{A_4}	22
CF_3OSF_5[a]	CF_3–SF_{A_4}	9.9
(*cis*) $(CF_3O)_2SF_4$[c]	CF_3–SF_{A_2}	9.0
$CF_3OSF_4NF_2$	CF_3–SF_{A_2}	12.8
	CF_3–SF_C	12.8
CF_3SF_5[a]	CF_3–SF_B	6.4
CF_3OSF_5[a]	CF_3–SF_B	1.5
$CF_3OSF_4NF_2$	CF_3–SF_B	1
SF_5NF_2[d]	NF_2–SF_{A_4}	19.1
(*trans*) $CF_3SF_4NF_2$[b]	NF_2–SF_{A_4}	20
$CF_3OSF_4NF_2$	NF_2–SF_{A_2}	21.8
	NF_2–SF_B	22.3
SF_5NF_2[d]	NF_2–SF_B	4.1
$CF_3OSF_5NF_2$	NF_2–SF_C	2.4
FSO_3NF_2[e]	NF_2–SF	4.6

[a] C. I. Merrill, S. M. Williamson, G. H. Cady, and D. F. Eggers, Jr., *Inorg. Chem.*, **1**, 215 (1962). [b] A. L. Logothetis, G. N. Sausen, and R. J. Shozda, *ibid.*, **2**, 173 (1963). [c] Ref. 2. [d] These values were obtained from the spectrum of this compound reported by G. H. Cady, D. F. Eggers, Jr., and B. Tittle, *Proc. Chem. Soc.*, 65 (1963). [e] M. Lustig and G. H. Cady, *Inorg. Chem.*, **2**, 388 (1963).

The respective CF_3–SF coupling constants in $CF_3OSF_4NF_2$ are of a magnitude that might be expected for a CF_3 group bound through oxygen, interacting with sulfur fluorines at 90 and 180°. The observed NF–SF coupling constants are also within the range that might be expected for a NF_2 group bound directly to sulfur. The *cis* structure of the compound is in accord with the reported structures of other derivatives of SF_6 formed by direct oxidation of SF_4, *cis*-$(FSO_3)_2SF_4$,[4] *cis*-(F_5SO_2)-SF_4,[5] and *cis*-$(CF_3O)_2SF_4$.[2]

Acknowledgments.—This work was performed in part under contract with the Office of Naval Research and in part under a fellowship of the Allied Chemical Co. The n.m.r. spectra were acquired by B. J. Nist.

[4] J. M. Shreeve and G. H. Cady, *J. Am. Chem. Soc.*, **83**, 4521 (1961).
[5] C. I. Merrill and G. H. Cady, *ibid.*, **85**, 909 (1963).

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The Formation Constants of Lead Perfluorocarboxylate Complexes

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Hershenson, Smith, and Hume[1] found evidence for weak complex formation between nitrate ions and lead ions in aqueous solution. The relative acid strengths of the perfluorocarboxylic acids CF_3COOH and C_3F_7-COOH are comparable to that of nitric acid, and the existence of weak complexes between lead and the anions of these acids might be expected. The only evidence

[1] H. M. Hershenson, M. E. Smith, and D. N. Hume, *J. Am. Chem. Soc.*, **75**, 507 (1953).