atom and a π^* molecular orbital of the P→S bond, although it is important to realize that $(CH_3)_4P_2$ absorbs in the same region.[9] The presence of a P→S bond would therefore eliminate structures III and IV, leaving I as the correct structure.

Further spectroscopic evidence for structure I is the strong Raman band at 445 cm.$^{-1}$. This band can be assigned to P–P stretching on the basis that it is very close to the value assigned to this vibration in P_2H_4 (437 cm.$^{-1}$),[10] $(C_2H_5)_4P_2$ (424 cm.$^{-1}$),[11] and $(C_4H_9)_4P_2$ (419 cm.$^{-1}$).[11] Structure I is the only one that would exhibit a P–P stretching frequency.

The infrared bands at 773 and 747 cm.$^{-1}$ are close to the P–C asymmetric stretch in $(CH_3)_3P$ and related molecules[12] and are therefore assigned to this vibration. The P–C bending mode and the modes involving the CH_3 groups are also tentatively assigned by comparison with analogous CH_3-substituted phosphorus compounds.[12]

The crystals of $(CH_3)_4P_2S_2$ are usually acicular and frequently clump together forming hollow cylinders. Most crystals are twinned, but X-ray diffraction photographs from single crystal fragments show that the diffraction symbol is $^2/_mC$, $a = 18.82$ Å., $b = 10.64$ Å., $c = 6.74$ Å., $\beta = 94.4°$. Diffraction spectra, *hkl*, are present only when $h + k = 2n$ so that the three space groups C2, Cm, and $C^2/_m$ are consistent with the diffraction data. The *hk*0 zone shows strong pseudo-hexagonal character and spectra are present only for $h = 3n$; the relationship $a \simeq \sqrt{3}b$ exists also for the monoclinic unit cell. The *c* axis is the needle axis and most crystals display parallel extinction between crossed polaroids as well as orthorhombic diffraction symmetry because of the twinning in the *a,b* plane. There are six formula weights in the unit cell and the calculated density 1.38 g./cc. is near values reported for similar compounds.[8] The pseudo-hexagonal cell contains three molecules and the *c* axis is approximately equal to the length of the molecule of formula I, further strengthening the conclusion that it is the correct choice. The centers of the six molecules can be located in one twofold and one fourfold site in each of the three possible space groups. The twofold locations in C2, Cm, and $C^2/_m$ require a molecular symmetry of 2, m, or $^2/_m$, respectively, and our infrared data as well as the structure of $(C_2H_5)_4P_2S_2$ (8) indicate that the most probable molecular symmetry is $^2/_m$.

In summary the above data make it fairly conclusive that the structure of $(CH_3)_4P_2S_2$ is I. We have repeated the spectrum of $(CH_3)_4P_2S_2$ at 100 Mc. (it was formerly done at 60 Mc.[1]) and find good agreement on the line separations as reported by Harris and Hayter.[1] This indicates that the spectrum is due to spin–spin splitting rather than a chemical shift difference. The reason for the variation in magnitude of J_{PP} between directly bonded phosphorus nuclei in the few known cases is not clear.

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CONTRIBUTION FROM THE GORGAS LABORATORY,
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The Fluoro-O-fluorosulfatomethanes

BY MAX LUSTIG

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The new compounds difluorobis(O-fluorosulfato)-methane, $F_2C(OSO_2F)_2$, and fluorotris(O-fluorosulfato)-methane, $FC(OSO_2F)_3$, were prepared by the reaction of peroxydisulfuryl difluoride, $S_2O_6F_2$, with dibromodifluoro- and tribromofluoromethane, respectively.

$$CBr_2F_2 + S_2O_6F_2 \longrightarrow F_2C(OSO_2F)_2 + Br_2$$

$$CBr_3F + {}^3/_2S_2O_6F_2 \longrightarrow FC(OSO_2F)_3 + {}^3/_2Br_2$$

The fluoropoly(O-fluorosulfato)methanes are the first examples of compounds containing more than one O-fluorosulfate group attached to a single carbon atom. A similar reaction employing CBr_4 did not yield the tetrakis compound, but, rather, a compound tentatively identified as $O{=}C(OSO_2F)_2$.

The first member of the series of fluoro-O-fluorosulfatomethanes, F_3COSO_2F, was first prepared in small yield by the reaction of sulfur dioxide and trifluoromethyl hypofluorite[1] and later in high yield by combining CF_3I,[2] CF_3Br, or CF_3Cl[3] with $S_2O_6F_2$. However, the reaction of CCl_4 with the latter gives $S_2O_5F_2$, $COCl_2$, and/or CO_2 as the products,[4] rather than mixed chloro(O-fluorosulfato)methanes.

Experimental

Reagents.—Peroxydisulfuryl difluoride[4] and the bromofluoromethanes[5] were made by literature methods. Tetrabromomethane was distributed by Baker and Adamson Products, Allied Chemical Corp.

General Procedure.—Transfer of gaseous substances was accomplished by use of a standard Pyrex vacuum apparatus. The reactor used for the preparation of $F_2C(OSO_2F)_2$ and $FC(OSO_2F)_3$ was a 100-ml. Pyrex bulb with a side arm attached through a stopcock. The $S_2O_6F_2$ was measured into the bulb and then condensed into the side arm and the stopcock was closed. The appropriate bromofluoromethane was then placed into the bulb. The peroxide was allowed to warm to room temperature and then the stopcock was opened, permitting it to diffuse slowly into the bulb and react with the appropriate substrate.

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TABLE I

INFRARED SPECTRA OF THE FLUORO-O-FLUOROSULFATOMETHANES

F_3COSO_2F		$F_2C(OSO_2F)_2$		$FC(OSO_2F)_3$	
Cm.$^{-1}$	Tentative assignments	Cm.$^{-1}$	Tentative assignments	Cm.$^{-1}$	Tentative assignments
1493 s	S=O asym. str.[a,b]	1506 s	S=O asym. str.[a,b]	1503 s	S=O asym. str.[a,b]
1269 s	S=O sym. str.[a,b]	1277 s	S=O sym. str.[a,b]	1264 s	S=O sym. str.[a,b]
1149 s	C—F str.[c]	1193 s	C—F str.[c]	1114 s	C—F str.[c]
976 s		1123 s, complex	C—F str.[d]	998 s	
843 s	S—F str.[a]	1002 m		870 sh	
799 m	S—O str.[d,e]	885 sh		846 vs	S—F str.[a]
		847 vs	S—F str.[a]	800 m	S—O str.[d,e]
		808 w	S—O str.[d,e]	*ca.* 679 w	
		781 w	S—O str.[d,e]		
		709 w			

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TABLE II

FLUORINE NUCLEAR MAGNETIC RESONANCE SPECTRA

F_3COSO_2F				$F_2C(OSO_2F)_2$					$FC(OSO_2F)_3$				
Frequency, ϕ	J_{F-F}, c.p.s.	Type of splitting	Assignment	Frequency, ϕ	Area ratio	J_{FF}, c.p.s.	Type of splitting	Assignment	Frequency, ϕ	Area ratio	J_{FF}, c.p.s.	Type of splitting	Assignment
−46.1	8	Quadruplet	SF	−48.5	1.03	8	Triplet	SF	−50.0	3.24	8	Doublet	SF
56.7	8	Doublet	CF	53.6	1.00	8	Triplet	CF	63.9	1.00	8	Quadruplet	CF

The quantity of each reactant used was determined by measuring its respective vapor at a known pressure, volume, and temperature (*PVT* measurement) into the reactor assuming ideal gas behavior. For the attempted preparation of $C(OSO_2F)_4$, solid CBr_4 was weighed into a Pyrex bulb and the peroxide was slowly added into the reactor.

The relative amount of each component present in a gaseous mixture was analyzed by mass spectrometry. A *PVT* measurement of the mixture was then used to calculate the total amount of each species. If a liquid component was present it was weighed after purification. Infrared spectra in the 2.15–15 μ region were obtained with a Perkin-Elmer Infracord using a 10-cm. path length gas cell with NaCl windows and the mass spectra with a Consolidated Engineering Corp. Model 21-620 spectrometer using a heated cycloid tube and an ionization potential of 100 v. The instrument was calibrated using pure gaseous samples. The ^{19}F n.m.r. spectra of the O-fluorosulfate products were obtained using a Varian Model V4310 spectrometer at 40 Mc. Samples were measured at ambient temperature in 5-mm. o.d. Pyrex tubes using CCl_3F as an internal standard.

Preparation of $F_2C(OSO_2F)_2$.—Equimolar quantities (0.31 mmole) of both reactants were combined in the manner described above. The appearance of the bromine color was observed immediately and droplets of liquid formed in the reactor near the stopcock. The reactor did not heat noticeably during the reaction. The product mixture was allowed to stand for 1 hr. of ambient temperature and was found to contain $F_2C(OSO_2F)_2$, 0.19 mmole[6]; Br_2, 0.19 mmole; $S_2O_5F_2$, 0.06 mmole; COF_2, 0.03 mmole; and CO_2, 0.01 mmole by mass spectral analysis and *PVT* measurement. The mixture was pumped through traps held at −80 and −196° for 4 hr. The O-fluorosulfate and a trace of Br_2 were retained in the former while the remainder of the mixture was in the latter. The crude ester was then further purified by passage through a 15-ft. perfluorotri-*t*-butylamine on Chromosorb P gas partition chromatographic column maintained at 40°.

Properties of $F_2C(OSO_2F)_2$.—The compound is a colorless liquid which melts at −101 ± 1°, although it does not crystallize easily. *Anal.* Calcd. for $CF_4O_6S_2$: F, 30.7. Found: F, 31.5. The molecular weight by vapor density measurement was found to be 247; calcd. 248. By determining the effusion rate of molecules through the leak in the mass spectrometer inlet system,[7,8] the molecular weight of the compound was calculated to be 249 ± 5. The determination was made by measuring the peak height decrease with time due to the fragment ion corresponding to mass number 149. The infrared, ^{19}F n.m.r., and mass spectra are summarized below.

Preparation of $FC(OSO_2F)_3$.—A procedure similar to that described above was used employing 0.48 mmole of CBr_3F and 0.72 mmole of $S_2O_6F_2$. The reaction was observed to start immediately and, as in the above case, droplets of liquid formed in the reactor near the stopcock. The reaction mixture was allowed to stand for 1 hr. Analysis showed $FC(OSO_2F)_3$, 0.30 mmole; Br_2, 0.61 mmole; $S_2O_5F_2$, 0.084 mmole; $FC(=O)OSO_2F$,[9] 0.084 mmole; CO_2, 0.10 mmole; and traces of CBr_3F, O_2, SiF_4, and an unidentified substance. The mixture was pumped through a trap maintained at −45° which retained the $FC(OSO_2F)_3$. It was found to be pure since further rectification using the chromatographic column described above at 40° revealed only one substance. A small amount of an oily material remained in the reactor.

Properties of $FC(OSO_2F)_3$.—The compound is a colorless liquid and melts at −20.0 ± 1.5°. *Anal.* Calcd. for $CF_4O_9S_3$: C, 3.95; F, 23.75. Found: C, 3.66; F, 23.17. Its molecular weight determined by mass spectroscopy (described above) by observing the ion corresponding to m/e 47 was found to be 320 ± 10; calcd. 328. The spectral properties of $FC(OSO_2F)_3$ are recorded below. The spectra of F_3COSO_2F are included for comparison. The ^{19}F n.m.r. spectrum of the latter has only been partially described,[1] while its mass spectrum has not been reported previously. Resonances in the −50 ϕ region are diagnostic of the $-OSO_2F$ group fluorine atom since this frequency is relatively invariant,[10] whereas fluorine absorptions due to the $-SO_2F$ group can be found within a very large frequency range.[11]

The mass spectra of $F_2C(OSO_2F)_2$ and $FC(OSO_2F)_3$ are also characteristic. The following are the mass numbers, species, and relative intensities of some of the major absorptions. $F_2C(OSO_2F)_2$: 47, COF^+, 76.3; 48, SO^+, 6.5; 64, SO_2^+, 3.7; 66, COF_2^+, 1.2; 69, CF_3^+, 1.6; 83, SO_2F^+, 100; 85, $^{34}SO_2F^+$, SiF_3^+,[12] 6.9; 149, $F_2C(OSO_2F)^+$, 40.8; 151, $F_2C(O^{34}SO_2F)^+$. $FC(OSO_2F)_3$: 47, COF^+, 100; 48, SO^+, 3.9; 64, SO_2^+, 1.8; 83, SO_2F^+, 26.7; 85,

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(6) This value may be low due to dissolution of the $F_2C(OSO_2F)_2$ in Kel-F stopcock grease and oil which was used to lubricate the stopcocks and cover the mercury manometers in the vacuum apparatus and to loss from purification.

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(12) Traces of SiF_4^+.

$^{34}SO_2F$, SiF_3,[12] 2.0; ~310, $C(OSO_2F)_3^+$, 1.5. F_3COSO_2F: 47, COF^+, 4.0; 48, SO^+, 2.3; 64, SO_2^+, 1.3; 67, SOF^+, 2.6; 69, CF_3^+, 100.0; 70, $^{13}CF_3^+$, 1.3; 83, SO_2F^+, 16.1; 85, $^{34}SO_2F^+$, SiF_3^+, 1.0. It is observed that the ion corresponding to mass number 47, COF^+, increases in the expected manner as the number of oxygen atoms bound to a single carbon increases. The SO_2F^+ ion is generally of high intensity in these as well as other reported O-fluorosulfate compounds.[10,13]

The reaction between $S_2O_6F_2$ and CBr_4 using a 2:1 molar ratio gave product results similar to those reported by Shreeve,[4] who used CCl_4 as the substrate, *i.e.*, CO_2 and $S_2O_5F_2$. These were produced in nearly a 1:2 molar ratio. However, in the case involving CBr_4 a trace quantity of another compound was isolated which may have the structure $O{=}C(OSO_2F)_2$. This compound slowly decomposed to yield equimolar quantities of CO_2 and $S_2O_5F_2$. In the mass spectrometer using a heated cycloid tube only CO_2 and $S_2O_5F_2$ were observed, again in equimolar quantities. The infrared spectrum of this compound showed a band in the carbonyl region at 1886 cm.$^{-1}$ and absorptions at 1504, 1266, 847, 758, and 708 cm.$^{-1}$ which are frequencies characteristic of the $-OSO_2F$ group. Other bands at 1136 and 1028 cm.$^{-1}$ are unassigned. The ^{19}F n.m.r. spectrum shows one singlet resonance at $-51.6\ \phi$ in the SF region of the fluorosulfate group. Pyrosulfuryl fluoride has one resonance at $-47.2\ \phi$. The compound was never obtained in a pure state so no further analysis was attempted.

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Contribution from the School of Chemistry,
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The Metal–Metal Bond in the Copper(II) Acetate Dimer. Nuclear Magnetic Resonance Evidence for a δ Bond

By D. J. Royer

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Considerable uncertainty seems to exist concerning the nature of the Cu–Cu interaction in the copper acetate complex, $Cu_2(C_2H_3O_2)_4 \cdot 2H_2O$. That a relatively strong interaction takes place is indicated by the Cu–Cu distance of 2.64 Å.[1] and by the singlet character of the ground state.[2] However, the nature of this interaction seems to be the subject of some disagreement. Arguments based on theoretical calculations, on the visible spectrum, and on the electron spin resonance spectrum have been advanced for a σ bond[3] and for a δ bond.[4]

In essence the problem reduces to finding the relative order of the three highest energy molecular orbitals derived from the d orbitals of the two copper atoms. It is generally agreed[3,4] that these three orbitals are the a_{2u} (σ^*) molecular orbital derived from the d_{z^2} atomic orbitals which lie along the Cu–Cu axis and the b_{1g} (δ) and b_{2u} (δ^*) molecular orbitals derived from the $d_{x^2-y^2}$ atomic orbitals which lie normal to the Cu–Cu axis. The three possible arrangements of these molecular orbitals are

—b_{2u} (δ^*)	—b_{2u} (δ^*)	—a_{2u} (σ^*)
—b_{1g} (δ)	—a_{2u} (σ^*)	—b_{2u} (δ^*)
—a_{2u} (σ^*)	—b_{1g} (δ)	—b_{1g} (δ)
A	B	C

Since there are four electrons to place in these three orbitals, the highest energy orbital will be vacant in the ground state. Thus orders A and B, where the δ^* orbital is vacant and the σ^* orbital is filled, correspond to the formation of a δ bond between the two copper atoms while order C, where the σ^* orbital is vacant and the δ^* orbital is filled, corresponds to a σ bond. Order A is favored by Ross and co-workers,[4] while order C has been suggested by Forster and Ballhausen.[3] The purpose of this report is to present some single crystal nuclear magnetic resonance results which seem to strongly support order B.

The nuclear quadrupole splitting of the nuclear magnetic resonance of a nucleus with a spin greater than $^1/_2$, $I > {}^1/_2$, is dependent upon the nonspherical components of the electric field gradient tensor, V_{ij}, at the site of the nucleus.[5] The single crystal n.m.r. spectrum of a material which contains such a nucleus thus gives some information about the electronic structure of the material.[6]

In the case at hand, the quadrupole splitting of the copper-63 resonance, $I = {}^3/_2$, should give some information about the electronic distribution in the copper acetate dimer. If the difference between the component of the electric field gradient tensor along the Cu–Cu axis, $V_{\mathrm{Cu,Cu}}$, of the dimer in the ground state and in the lowest triplet state can be determined, it should be possible to tell which of the three orders given above is the correct one. In order A the ground state, $(a_{2u})^2(b_{1g})^2$, and the triplet state, $(a_{2u})^2(b_{1g})(b_{2u})$, should have essentially the same electron density along the Cu–Cu axis because both b_{1g} and b_{2u} contain a nodal axis corresponding to the Cu–Cu axis. Thus $V_{\mathrm{Cu,Cu}}$ should be essentially the same in the two states. Since only the traceless portion of the tensor can be measured, there might be a small increase in the measured value for the triplet due to a slight decrease in the components of the tensor normal to the Cu–Cu axis, but the effect should be small.

In order B, the transition from the ground state to the triplet state corresponds to transferring one electron from the a_{2u} orbital which lies along the Cu–Cu axis to the b_{2u} orbital which has no electron density along this axis. Thus the electron density along the Cu–Cu axis should be smaller and the electron density

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