Molecular Structure of $Hg[C(COF)=SF_2=O]_2$

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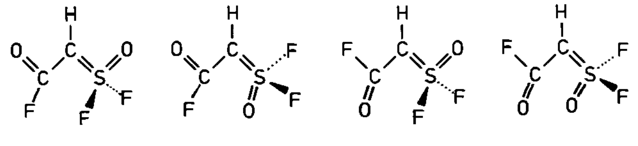
$Hg[C(COF)=SF_2=O]_2$ is prepared by the reaction of $FCO-CH=SF_2=O$ with HgF_2. This compound represents the third known example of an alkylidenesulfur difluoride oxide. Its molecular structure is the same as that of the most abundant of the three isomers of $FCO-CH=SF_2=O$. This is assumed to be the result of weak intramolecular $Hg\cdots O$ contacts. With the exception of the fluorine atoms bound to sulfur, all atoms lie approximately in one plane.

The first alkylidenesulfur difluoride oxide $FCO-CH=SF_2=O$ was detected only recently[1]. It was prepared by careful hydrolysis of $FCO-CH=SF_4$. This reaction cannot be extended to any of the few other known alkylidenesulfur tetrafluorides[2]. $FCO-CH=SF_2=O$ exhibits a peculiar non-rigid behavior. At −70°C the torsion of the CS double bond is frozen, at −136°C the torsion of the CC single bond. The assignment of the three observed AB_2X systems in the ^{19}F-NMR spectra was first based on assumptions on chemical shifts and particularly on coupling constants. This assignment, as published in ref.[1], is possibly not correct because ab initio calculations gave slightly different total energies for the four isomers[3]. Their stability increases as the number of hydrogen–oxygen contacts increases. This results in the sequence of isomers in decreasing stability from left to right as shown in Scheme 1.

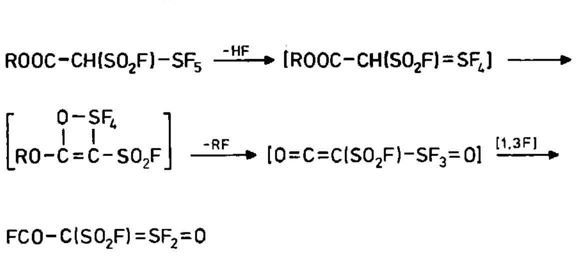
Scheme 1



This remarkable non-rigid behavior would best be investigated if other alkylidenesulfur difluoride oxides, particularly simple ones, were available.

Winter and Gard have studied the formation of $FCO-C(SO_2F)=SF_2=O$ in a complicated reaction involving at least three steps[4]. This compound does not reveal the dynamic behavior and isomerism of $FCO-CH=SF_2=O$.

Scheme 2



We treated $FCO-CH=SF_2=O$ with HgF_2 and obtained the novel compound $Hg[C(COF)=SF_2=O]_2$. The yield is low, but after sublimation a pure material was obtained. According to its ^{19}F-NMR spectrum this compound seems to exist only as a single isomer. Its molecular structure could be solved by single-crystal X-ray analysis (Tables 1–3 and Figure 1).

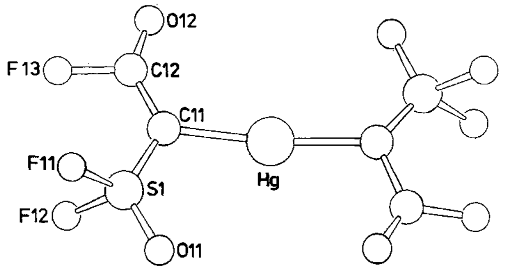


Figure 1. Molecular structure of $Hg[C(COF)=SF_2=O]_2$. The molecule is planar except for the sulfur-bound fluorine atoms. The geometry seems to be fixed by long intramolecular $Hg\cdots O$ contacts

Table 1. Crystallographic data and data collection details

Formula: $Hg[C(COF)=SF_2=O]_2$; a = 358.1(4), b = 898.5(7), c = 1032.9(6) pm; β = 101.10(5)°; V = 590.1 · 10^6pm^3; Z = 2; space group $P2_1$ (No 4); crystal size [mm]: 0.2 × 0.4 × 0.1, temperature: −156°C; octands: $\pm h$, $+k$, $\pm l$; Θ = 2–25°; number of reflections: mesured 1671, independent 930, with $I \geq 3\sigma(I)$ 873; μ = 155.41 cm^{-1}; parameters: 83 (Hg and S anisotrop); R = 0.048, R_w = 0.037; $w = 2.2773/\sigma^2(F_o)$

The structure in the solid state consists of isolated $Hg[C(COF)=SF_2=O]_2$ molecules. A long contact between Hg and O22 of a neighbouring molecule (310.8 pm) seems to cause the small deviation (171.0°) from the usual linear arrangement of HgR_2. The molecule itself is approximately planar except for the fluorine atoms bound to sulfur. Particularly, if only the two halves of the molecule are regarded separately, Hg, C, S, and O atoms form a planar arrangement with a largest deviation of 3 pm (O22) on one side and 11 pm (C11) on the other side from the mean plane. The struc-

Table 2. Fractional atomic positions of $Hg[C(COF)=SF_2=O]_2$

Atom	x	y	z	U_{eq}
Hg	-0.1505	0.7500	0.0967	0.0041
S1	0.0184	0.7009	0.4035	0.0075
S2	-0.2974	0.7983	-0.2013	0.0099
O11	-0.2076	0.6200	0.3962	0.0160
F11	0.0366	0.8132	0.5163	0.0142
C11	0.1011	0.7460	0.2748	0.0094
F12	0.2364	0.6088	0.4858	0.0231
O12	0.4139	0.8722	0.1868	0.0156
C12	0.3271	0.8356	0.2799	0.0062
F13	0.4617	0.8656	0.4010	0.0173
F21	-0.3021	0.6961	-0.3201	0.0263
O21	-0.0707	0.8809	-0.1828	0.0016
C21	-0.3855	0.7194	-0.0835	0.0084
O22	-0.7203	0.5801	-0.0228	0.0196
F22	-0.5045	0.8950	-0.2767	0.0325
F22	-0.6129	0.6393	-0.0968	0.0029
F23	-0.7480	0.6335	-0.2271	0.0118

Table 3. Selected bond distances [pm] and bond angles [°] of $Hg[C(COF)=SF_2=O]_2$. Each first and second figure denotes atoms with first index 1 and 2, respectively

Hg-C	206(3), 206(3)	C-Hg-C	171(3)
C-C	145(6), 140(4)	Hg-C-C	122(2), 122(2)
C-F	135(3), 140(3)	Hg-C-S	115(3), 115(3)
C-O	119(3), 117(3)	C-C-S	120(3), 123(3)
C-S	154(3), 156(3)	C-S-O	119(2), 121(1)
S-O	141(2), 141(2)	F-S-F	90(1), 92(1)
S-F	151(2)-155(2)		

ture would be comparable to that of the most abundant isomer of $FCO-CH=SF_2=O$. The reason for this may be the maximization of long Hg···O intramolecular contacts (290—322 pm) (four in this particular structure). While all bond lenghts are within the expected range, it is worth pointing out that the CS bond lengths of 154(3), 156(3) pm are those of double bonds. They may be compared to the CS double bond length in alkylidenesulfur tetrafluorides of 155—159 pm[2]; sulfur ylides have CS bond lengths of 170—175 pm[5–8]. If the parent molecule $FCO-CH=SF_2=O$ has a similar strong double bond, and there is no reason to assume that this is not the case, then the explanation of the relative ease of rotation around the CS bond in ref.[1] is correct: This double bond rotates easily not because of intrinsic weakness of the double bond character, but because of the (pseudo) sixfold symmetry of the rotational process.

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Experimental

IR: Perkin-Elmer Model 885 spectrometer, window material KCl. — MS: Varian MAT 112 S high resolution, solid inlet probe. — ^{19}F NMR: Jeol FX 90 Q, $CFCl_3$ as external standard, chemical shifts according to IUPAC conventions. — Starting materials: $FCO-CH=SF_2=O$[1] was prepared according to the literature method. Other reagents were taken from laboratory stock and purified, if necessary, before use.

Bis[1-(difluorooxo-λ^6-sulfanylidene)-2-fluoro-2-oxoethyl]mercury, $Hg[C(COF)=SF_2=O]_2$: A 10 mm wide and 20 cm long glass ampule is filled with 0.40 g (1.67 mmol) of pure HgF_2 with careful exclusion of moisture (dry box!). Using a glass vacuum line and cooling to −196°C 5 ml of CH_2Cl_2 and 0.23 g (1.58 mmol) of $COF-CH=SF_2=O$ are condensed into the ampule, which is then sealed off. On warming the reaction starts with evolution of some gas. The ampule is shaken at room temp. for 1 h and then opened, and all volatile material is pumped off. The yellowish solid residue is sublimed in vacuo at 50°C to a water-cooled finger. Unsublimable HgF_2 remains. Yield: 50 mg (6%) of a colorless, crystalline solid. — IR (KBr): $\tilde{\nu}$ = 3487 (vw) cm^{-1}, 3014 (sh), 2922 (w), 2851 (sh), 1793 (sh), 1753 (vs), 1522 (w), 1468 (w), 1367 (vs), 1349 (sh), 1266 (s), 1233 (sh), 1198 (w), 1119 (s), 1102 (sh), 1068 (sh), 954 (w), 911 (m), 804 (vs), 734 (s), 588 (s), 470 (m), 332 (w). — MS (80 eV, EI; referred to ^{202}Hg, intensities including all isotopes): m/z (%) = 491.884821 (53) [M^+, calcd. 491.884868], 366 (65) [$C_2F_4HgO_2S^+$], 347 (100) [$C_2F_3HgO_2S^+$], 261 (19) [C_2FHgO^+], 202 (29) [Hg^+], 146 (10) [$C_2F_3HO_2S^+$] and smaller fragments. — ^{19}F NMR: δ = 38.8 (CF, t), 62.7 (SF, d); $J_{CF,SF}$ = 12.2, $J_{CF,^{199}Hg}$ = 128.2, $J_{SF,^{199}Hg}$ = 68.4 Hz.

Crystal Structure of $Hg[C(COF)=SF_2=O]_2$: Slow sublimation of this material at 25°C/10^{-4} mbar within 1 week results in colorless, very thin (0.1 mm) plates. Transportation of one selected specimen and mounting on the diffractometer are described in ref.[9,10] Diffractometer: Enraf Nonius Delft CAD-4, Mo-K_α, graphite monochromator, −156°C. The structure is solved by direct methods and difference Fourier synthesis[11]. Finally an absorption correction has been applied[12]. Although the model refined well, the standard deviations of all geometric parameters are quite high because of the acentric space group $P2_1$. Since the small size of the crystal has not allowed us to collect more data, we have refined anisotropically only Hg and S atoms. For details see Table 1—3 and Figure 1. Further details of the crystal structure determination may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2, on quoting the disposatory number CSD-54741, the names of the authors, and the journal citation.

CAS Registry Numbers

$Hg[C(COF)=SF_2=O]_2$: 130120-98-8 / $FCO-CH=SF_2=O$: 115983-29-4 / HgF_2: 7783-39-3

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