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Fluorine-19 Chemical Shifts in Nuclear Magnetic Resonance Spectra of Fluorosulfate-Containing Compounds

BY FREDERICK A. HOHORST AND JEAN'NE M. SHREEVE

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Since the synthesis of peroxydisulfuryl difluoride ($\mathrm{S_2O_6F_2}$) by Dudley and Cady,[1] the number of compounds containing the fluorosulfate group, $\mathrm{OSO_2F}$, has increased rapidly inasmuch as reactions of the former or its derivatives provide a facile route to the introduction of this group into fluoroolefins and simple inorganic molecules. In characterizing some of these fluorosulfates, the chemical shift of the fluorine bonded to sulfur was reported with respect to an internal or an external standard. The literature reports no attempts to compare the magnitudes of the chemical shifts as a function of chemical or molecular environment. However, it has been stated that resonances in the −50-ppm region are diagnostic of the fluorine in fluorosulfate since the frequency in organic molecules seems to be relatively constant.[2] In order to study this relationship, several of these compounds have been synthesized and their nuclear magnetic resonance spectra have been measured with trichlorofluoromethane as the internal reference.

Experimental Section

The compounds examined were prepared through the use of conventional methods. A Varian Model 4311B high-resolution spectrometer equipped with a 40-Mc oscillator was used to determine the nuclear magnetic resonance spectra. Reproducibility of chemical shift values was about ±0.1 ppm for consecutive measurements on the same or different preparations of a compound or for measurements separated by 24 hr. The samples were contained in sealed 5-mm o.d. Pyrex tubes heated to 35° prior to use to check pressure stability. Roughly 50% solutions (by volume) were prepared with $\mathrm{CCl_3F}$, which had been dried over $\mathrm{P_2O_5}$, as the reference compound. In the case of $\mathrm{HOSO_2F}$, because of immiscibility with $\mathrm{CCl_3F}$, an external reference was used. $\mathrm{CCl_3F}$ was sealed into a 2-mm o.d. tube, and this was placed in the liquid $\mathrm{HOSO_2F}$. External references were also used with $\mathrm{ClOSO_2F}$ and $\mathrm{BrOSO_2F}$.

In Table I, the fluorosulfate compounds are listed with the respective chemical shifts given in ppm.

TABLE I

$\mathrm{F^{19}}$ CHEMICAL SHIFTS OF $\mathrm{OSO_2F}$ IN FLUOROSULFATE-CONTAINING COMPOUNDS RELATIVE TO $\mathrm{CCl_3F}$

Compound	Shift, ppm	Compound	Shift, ppm
$\mathrm{ClOSO_2F}$[a]	−33.9[h]	$\mathrm{FO_2SOSO_2F}$[b]	−48.8
$\mathrm{FOSO_2F}$[b]	−36.3	$\mathrm{CF_2(OSO_2F)_2}$[e]	−48.7
$\mathrm{CF_3OOSO_2F}$	−37.9	$\mathrm{C_2F_5OSO_2F}$[a]	−49.6
$\mathrm{FO_2SOOSO_2F}$[b]	−40.4	$\mathrm{O_2S(OSO_2F)_2}$	−49.6
$\mathrm{BrOSO_2F}$	−41.3[h]	$\mathrm{NF_2CF_2CF_2OSO_2F}$[f]	−50.4
$\mathrm{FOOSO_2F}$[b]	−42.6	$\mathrm{C_2F_4(OSO_2F)_2}$	−50.7
$\mathrm{NF_2OSO_2F}$	−44.1	$\mathrm{CF_3CBrFCF(OSO_2F)CF_3}$[g]	−51.0
$\mathrm{CF_3OSO_2F}$	−46.8	$\mathrm{CF_3CF_2CF(OSO_2F)CF_3}$[c]	−51.2
$\mathrm{CF_3C(O)OSO_2F}$[c,d]	−47.4	$\mathrm{HOSO_2F}$	−65.6[h]
$\mathrm{CClF_2OSO_2F}$[d]	−48.0		

[a–g] For comparison with previously reported shifts, consult the following: (a) W. P. Gilbreath and G. H. Cady, *Inorg. Chem.*, **2,** 496 (1963); (b) G. Franz and F. Neumayr, *ibid.*, **3,** 921 (1964); (c) J. J. Delfino and J. M. Shreeve, *ibid.*, **5,** 308 (1966); (d) D. D. DesMarteau and G. H. Cady, *ibid.*, **5,** 169 (1966); (e) see ref 2; (f) M. Lustig and J. K. Ruff, *Inorg. Chem.*, **4,** 1441 (1965); (g) B. L. Earl, B. K. Hill, and J. M. Shreeve, *ibid.*, in press. [h] External reference.

Although the observed shifts as a function of the substituent group cannot be simply related to any single factor, the data, in general, appear to be internally consistent, which makes some interesting comparisons possible. (1) Introduction of $\mathrm{CF_2}$ group(s) shifts resonances to lower field: $\mathrm{FOSO_2F > CF_3OSO_2F > C_2F_5OSO_2F}$; $\mathrm{ClOSO_2F > ClCF_2OSO_2F}$; $\mathrm{FO_2SOOSO_2F > FO_2SOCF_2OSO_2F > FO_2SOC_2F_4OSO_2F}$; $\mathrm{NF_2OSO_2F > NF_2C_2F_4OSO_2F}$. (2) Substitution of $\mathrm{SO_3F}$ for fluorine shifts to lower field: $\mathrm{FO_2SOSO_2F > FO_2SOSO_2OSO_2F}$; $\mathrm{CF_3OSO_2F > FO_2SOCF_2OSO_2F}$; $\mathrm{FOSO_2F > FO_2SOOSO_2F}$. (3) Substitution of a halogen or pseudo-halogen for a fluorine may shift to lower field: $\mathrm{CF_3OSO_2F > ClCF_2OSO_2F}$; $\mathrm{FOSO_2F > NF_2OSO_2F}$; $\mathrm{FOSO_2F > BrOSO_2F}$; or to higher field: $\mathrm{FOSO_2F < ClOSO_2F}$. (4) Introduction of an oxygen atom varies: $\mathrm{FOSO_2F > FOOSO_2F}$, while $\mathrm{CF_3OSO_2F < CF_3OOSO_2F}$.

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[1] F. B. Dudley and G. H. Cady, *J. Am. Chem. Soc.*, **79,** 513 (1957).

[2] M. Lustig, *Inorg. Chem.*, **4,** 1828 (1965).

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Trimethylsiloxydimethylgold

BY HUBERT SCHMIDBAUR AND MANFRED BERGFELD

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We wish to report the synthesis of trimethylsiloxydimethylgold, a heterosiloxane species[1] containing the Si–O–Au linkage.

Trimethylgold, prepared according to a method described by Gilman and Woods,[2] was converted to

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[1] H. Schmidbaur, *Angew. Chem.*, **77,** 206 (1965); *Angew. Chem. Intern. Ed. Engl.*, **4,** 201 (1965).

[2] H. Gilman and L. A. Woods, *J. Am. Chem. Soc.*, **70,** 550 (1948).

dimethylgold bromide by reaction with hydrogen chloride in the presence of excess lithium bromide.[2] $(CH_3)_2AuBr$ shows characteristic infrared absorptions at 3000, 2955, 2908, 1405, 1229, 1198, 810, 722, and 530 cm^{-1} (Hostaflon, Nujol), and a proton magnetic resonance signal at -82.3 cps relative to TMS as an internal standard in CCl_4 solution (Varian A 60, 60 Mc, 35°).

Equimolar amounts of dimethylgold bromide and sodium trimethylsiloxide were found to react in diethyl ether solution at room temperature with formation of a sodium bromide precipitate. After filtration

$$(CH_3)_2AuBr + NaOSi(CH_3)_3 \longrightarrow NaBr + \underset{\text{I}}{(CH_3)_2AuOSi(CH_3)_3}$$

and evaporation of the solvent under vacuum a colorless crystalline material was obtained which could be sublimed *in vacuo* at 40° under 0.001 mm pressure. The sublimate, mp 39–40°, is soluble in aprotic organic solvents and stable to dry air, but rather sensitive to moisture. Combustion analysis confirmed the composition $(CH_3)_5AuOSi$, but cryoscopic molecular weight determinations in benzene as a solvent proved the compound to exist as a *dimer*.

Anal. Calcd: C, 18.97; H, 4.74; mol wt, 632. Found: C, 18.65; H, 4.50; mol wt, 603.

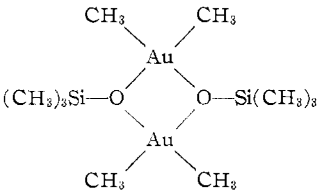
The colorless melt of I is decomposed at 135° with formation of a bright gold mirror at the walls of the tube. The compound gives rise to two singlet signals in its ^1H nmr spectrum, the areas of which were found to be in the relative ratio 3:2: δCH_3Au -57.7 cps, δCH_3Si -8.5 cps (CCl_4 solution). The $(CH_3)_3Si$ signal is accompanied by two small satellite signals due to $^1H-^{29}Si$ coupling with $J(^1H-C-^{29}Si) = 6.5$ cps. In the infrared spectral region 1350–400 cm^{-1} only a small number of bands were detected, and their assignments are given in Table I. These spectra along with the observed diamagnetism of the compound (nmr) are consistent with an inorganic skeleton containing the gold atoms in a square-planar dsp^2 hybridization state. For I therefore a bridged four-membered ring structure is suggested

TABLE I

INFRARED SPECTRUM OF TRIMETHYLSILOXYDIMETHYLGOLD[a]

Cm^{-1}	Assignment	Cm^{-1}	Assignment
1300 w	$\delta_{as}CH_3(Si)$	805 sh	$\rho CH_3(Au)$
1258 s		720 sh	
1245 s		680 m	$\nu_{as}SiC_3$
1210 s	$\delta_{as}CH_3(Au)$	620 w	ν_sSiC_3
910 vs	$\nu Si-O$	588 m	$\nu_{as}AuC_2$
882 vs		577 m	
835 vs	$\rho CH_3(Si)$	478 vs	$\nu Au-O$
748 s		440 sh	

[a] Perkin-Elmer 337, KBr windows, Nujol solution.



As has recently been shown, oxygen-bridged structures are not uncommon in heterosiloxane chemistry,[1] but I is the first example with the heteroatom in a nontetrahedral state of bonding.[3]

Attempts to prepare tris(trimethylsiloxy)gold from $AuBr_3$ and 3 moles of $NaOSi(CH_3)_3$ were successful only at temperatures below $-30°$. A yellow crystalline compound was obtained on recrystallization from diethyl ether, which slowly decomposed above $-20°$. The initial product showed the following infrared absorptions: 1260, 1245, 875 (νSiO), 840, 752, 681, 638, 502 (νAuO), 470 (νAuO). In the ^1H nmr spectrum two signals appeared at δCH_3Si -12.8 and -20.2 cps (ratio 1:2). However, the presence of impurities could not entirely be excluded, as suggested from small additional signals. Again a structure similar to that of I with bridging and terminal siloxy groups is proposed for this compound.[3,4]

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A General Formulation for the Evaluation of Group Overlap Intergals

BY WALTER A. YERANOS

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During the past few years the semiempirical method of Wolfsberg and Helmholz[1] has gained tremendous momentum in the explanation of the magnetic and optical properties of the coordination compounds of the transition metal ions.[2]

As is well known, one of the computational problems encountered in this method is the evaluation of the overlap integrals between the symmetry-adapted functions of the central ion and the ligands, as well as between the ligands themselves. Fortunately, when the ligands lie on the cartesian coordinate system which defines the molecular symmetry, extremely simple techniques[3,4] can be devised for the reduction of the group overlap integrals to *scaled* diatomic overlaps. The latter can then be evaluated either from published tables[5] or by the use of digital computers.[6] Unfortu-

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(6) W. A. Yeranos, Moment Integral Calculations, Q.C.P.E. Program 82, Quantum Chemistry Program Exchange, Indiana University, Bloomington, Ind. 47401.