TABLE 1

NMR studies of $Hg(SCF_3)_2$ and $Hg(SeCF_3)_2$[a]

Nucleus	$Hg(SCF_3)_2$	$Hg(SeCF_3)_2$
^{13}C δ(ppm) (ref. TMS)	131.013 [q, $^1J(C–F)=307.9$ Hz][b]	121.26 [q, $^1J(C–F)=332.4$ Hz][c]
^{19}F δ(ppm) (ref. $CFCl_3$)	−20.882 [s, no $^2J(C–F)$ obs.][d]	−15.385 [weak d, $^2J(F–Se)=37.9$ Hz][e, f]
^{77}Se δ(ppm) (ref. Me_2Se)		412.429 [q, $^2J(Se–F)=38.3$ Hz $^1J(Se–Hg)=24$ Hz]
^{199}Hg δ(ppm) (ref. Me_2Hg)	−1231.2 (s) (acetone)	−1481.5 (s)

[a] All spectra recorded in $CDCl_3$ solution, except where indicated: s = singlet, d = doublet, q = quartet. High frequency δ was positive. TMS internal standard, others external.

[b] Lit. value $^1J(^{13}C–F)=308.3$ Hz, from ^{19}F spectrum [7].

[c] Lit. value $^1J(^{13}C–F)=332.5$ Hz [7], 329.6 Hz [8] from ^{19}F spectrum.

[d] Lit. value $\delta(CF_3)=-21.28$ ppm [9].

[e] Lit. value $\delta(CF_3)=-15.53$ ppm, $CFCl_3$ as solvent [8].

[f] Lit. value $^2J(^{77}Se–F)=39.8$ Hz, from ^{19}F spectrum [8].

spectra have allowed $^1J(^{13}C–F)$ values to be determined from the ^{13}C satellites: $Hg(SCF_3)_2$, 308.3 Hz [5]; $Hg(SeCF_3)_2$, 332.5 Hz [7] and 329.6 Hz [8], which are very close to the values for $^1J(^{13}C–F)$ reported here and deduced from the ^{13}C NMR spectra. A value of $J=282$ Hz, deduced from the ^{19}F NMR spectrum of $Hg(SCF_3)_2$ was probably erroneously assigned to $^3J(^{199}Hg–F)$ rather than $^1J(^{13}C–F)$ [9]. The coupling constant $^2J(^{77}Se–F)$ has also been deduced from the ^{19}F NMR spectrum of $Hg(SeCF_3)_2$ [8] and the value 39.8 Hz is almost the same as that obtained in the present work from either the ^{19}F or ^{77}Se NMR spectra. It was not possible to observe any mercury to fluorine coupling in the fluorine spectrum [8] or in the ^{199}Hg spectra reported here; however a mercury–selenium coupling, $^1J(^{199}Hg–^{77}Se)$, was observed in the selenium spectrum but not in the mercury spectrum of $Hg(SeCF_3)_2$. The chemical shift of ^{77}Se in trifluoromethaneselenol has been observed at $\delta=287$ ppm [6] and is similar to the value found in $Hg(SeCF_3)_2$. The ^{77}Se chemical shifts reported for a series of thioselenides, such as CF_3SeSCF_3 $\delta=590$ ppm, are much larger and may be due to the partial double-bond character of the Se–S bond [10], whereas in chloroform solutions of $Hg(SePh)_2$ the ^{77}Se chemical shift is reported as being 248.3 ppm [11]. The mercury chemical shifts reported are similar to those found in analogous aromatic thiolates $Hg(SC_6F_5)_2$, $\delta=-1242.9$ ppm; $Hg(SC_6F_4H\text{-}p)_2$, $\delta=-1224.4$ ppm, both measured in acetone [12]; $Hg(SPh)_2$, $\delta=-1065$ ppm; and $Hg(SePh)_2$, $\delta=-1512$ ppm, measured in chloroform solutions [11].

The 70 eV low resolution electron impact (EI) mass spectra of a number of sulfides, disulfides and trisulfides containing at least one trifluoromethyl group have been examined [13]. In our work, the most abundant ion observed in the spectrum of $Hg(SCF_3)_2$ was $SCF_2^{\cdot+}$ while the $CF_3^{\cdot+}$ ion had a relative

TABLE 2

Mass spectra of $Hg(SCF_3)_2$ and $Hg(SeCF_3)_2$[a]

Ion	EI mode		NCI mode	
	$Hg(SCF_3)_2$	$Hg(SeCF_3)_2$	$Hg(SCF_3)_2$	$Hg(SeCF_3)_2$
XC	36	2	–	–
XCF	32	9	–	–
CF_3	2	100	–	–
X	–	22	–	–
XCF_2	100	66	–	–
XCF_3	3	17	11	100
X_2	0	28	0	0
Hg	22	44	0	0
CF_3X_2	0	19	0	5
$(CF_3X)_2$	0	8	100	6
$HgXCF_3$	0	6	0	0
HgX_2CF_3	0	0	1	4
$Hg(XCF_3)_2$	0	4	1	0

[a] Based on ^{80}Se and ^{202}Hg: X=S or Se.

abundance of only 2% (see Table 2), suggesting that there was little decomposition to mercury and the disulfide, as the $CF_3^{\cdot+}$ ion is the most abundant ion in the spectrum of bis(trifluoromethyl)disulfide, CF_3SSCF_3 [13]. The relative abundances of the peaks around *m/z* 200 can be attributed to an isotopic pattern for the $Hg^{\cdot+}$ ion, but no ion was observed corresponding to the disulfide or the molecular ion. In contrast, the electron impact mass spectrum of mercury(II) pentafluorobenzenethiolate exhibited a weak peak corresponding to the molecular ion, with the most intense ion being $C_6F_5S^{\cdot+}$ [14]. In studies of the 70 eV EI mass spectra of a series of trifluoromethylseleno compounds, CF_3SeX (X=H, Cl, Br, CN, CF_3, $SeCF_3$), the $CF_3^{\cdot+}$ ion was always observed as the most intense peak [15], as found in the EI spectrum of $Hg(SeCF_3)_2$.

In the negative ion chemical ionization (NCI) mass spectra of $Hg(SCF_3)_2$ and $Hg(SeCF_3)_2$, a considerable number of peaks was observed, the most abundant being the disulfide, CF_3SSCF_3, and the trifluoromethylselenide ion, $CF_3Se^{\cdot}$, possibly formed by the decomposition of the diselenide. No mercury ions were detected in these spectra.

Experimental

The NMR spectra were recorded on various instruments, Nicolet 360-BM (^{19}F) (Atlantic Magnetic Resonance Centre), Varian XL-200 (^{77}Se and ^{199}Hg), Bruker ACE-200 (^{13}C) and Bruker AM-400 (^{77}Se and ^{199}Hg). The mass spectra were obtained using a DuPont model 21-104 instrument with indirect introduction (electron impact, EI) and a Finnigan-MAT 4000 instrument with methane reagent gas (negative ion chemical ionization, NCI).

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Mercury(II) trifluoromethane thiolate and selenolate: NMR and mass spectra

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Abstract

The NMR spectra (^{13}C, ^{19}F, ^{77}Se and ^{199}Hg) of mercury(II) trifluoromethane thiolate and selenolate have been examined. The chemical shifts are reported as well as various coupling constants. The electron impact and chemical ionization mass spectra have been measured.

Introduction

The mercury(II) thiolates and selenolates, $Hg(XR)_2$ (X = S or Se), are well-known reagents for the introduction of the XR group into a variety of compounds. Mercury(II) trifluoromethanethiolate, $Hg(SCF_3)_2$, and mercury(II) trifluoromethaneselenolate, $Hg(SeCF_3)_2$, were both first prepared several years ago [1, 2] and subsequently have been used in synthetic reactions for the preparation of numerous compounds containing CF_3S or CF_3Se groups. While the vibrational spectra of both of these compounds have been studied in detail [3, 4], only the ^{19}F NMR spectra have been described and there are no reports of the mass spectra. This paper presents details of the NMR spectra of these compounds as well as the mass spectra.

Results and discussion

Table 1 shows details of the ^{13}C, ^{19}F, ^{77}Se and ^{199}Hg NMR spectra of $Hg(SCF_3)_2$ and $Hg(SeCF_3)_2$. The ^{13}C chemical shifts of the CF_3 group in CF_3SX or CF_3SeX are relatively independent of the group X, the carbon signal being observed within the range 120–130 ppm [5, 6]. Similar chemical shifts were observed for the mercury derivatives. The ^{19}F NMR spectra have been reported previously and the chemical shifts of the trifluoromethyl group lie within the expected range. Careful and detailed analysis of the ^{19}F NMR

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