172. *Some Reactions and Derivatives of Bis(trifluoromethylseleno)mercury.*

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The vibrational spectra of bis(trifluoromethylseleno)mercury at 200—4000 cm.$^{-1}$ have been recorded and analysed in terms of group frequencies. Physical methods have been used to investigate its reactions with (*a*) HgX_2 ($X = Cl,Br,I,CN,SCN,CH_3{\cdot}CO_2$) and (*b*) halide ions. In (*a*), equilibrium constants for the formation of derivatives of formulæ CF_3SeHgX ($X =$ Cl,Br,I,SCN) have been determined, and solid half-halides ($X =$ Cl, Br, or I) have been obtained; in (*b*), complex anions of formulæ $(CF_3Se)_2HgX_2^{2-}$ and $[(CF_3Se)_2Hg]_2X^-$ are formed, but there is much less evidence to indicate the formation of 1 : 1 species.

THE reactions of bis(trifluoromethylthio)mercury with mercuric halides, with electron-pair donors, with halide ions, and with mercuric salts of oxy-anions have been investigated using a wide range of physical methods; [1-3] we have studied some of the analogous reactions of bis(trifluoromethylseleno)mercury, using Raman and infrared spectroscopy, conductiometric titrations and *X*-ray powder photography. The general pattern of our results follows that obtained with the sulphur compound, but there are some differences in detail.

The Raman spectra of methanolic solutions of bis(trifluoromethylseleno)mercury and mercuric chloride, bromide or iodide contained bands due to the starting-compounds, and, in addition, scattering that we have assigned to half-halides formed by the reactions

$$(CF_3Se)_2Hg + HgX_2 \rightleftharpoons 2CF_3SeHgX$$

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[1] Jellinek and Lagowski, *J.*, 1960, 810.
[2] Downs, Ebsworth, and Emeléus, *J.*, 1961, 3187.
[3] Downs, Ebsworth, and Emeléus, *J.*, 1962, 1254.

The equilibrium constant where X = Cl was determined from the Raman spectra, and a rough value similarly obtained for the bromide system. The low solubilities of mercuric iodide and thiocyanate in methanol precluded the use of this method, but made it possible to calculate the equilibrium constants directly from solubility measurements. It was only possible to make qualitative estimates of the equilibrium constants for the cyanide and acetate; the results of all these studies are summarized in Table 1. They are similar to those found for the analogous CF_3S derivatives.

TABLE 1.

Equilibrium constants for the reactions of the sulphur and the selenium mercurials with mercuric derivatives.

HgX_2	$(CF_3S)_2Hg$ [a]	$(CF_3Se)_2Hg$
Cl	20 ± 10	20 ± 2
Br	2·3 ± 0·3	15 ± 10
I	1·67 ± 0·15	2·03 ± 0·02
SCN	1·35 ± 0·06	2·34 ± 0·06
CN	Low	Low
CH_3CO_2	High	High

[a] Refs. 2 and 12.

We have prepared the half-chloride, bromide, and iodide as crystalline solids; at least one other compound containing mercury, CF_3Se-groups and iodine was also obtained, but this could not be characterized. The residue obtained after evaporation of the solvent from solutions of bis(trifluoromethylseleno)mercury and mercuric thiocyanate appeared to be a mixture of the two starting-components. No solid half-bromide or -iodide of the CF_3S-series has been isolated, though these compounds are formed in solution.

The in-phase (Hg–Se) stretching frequency at ~180 $cm.^{-1}$ drops as the donor power of the solvent increases, the other modes being relatively unaffected. The drop is greatest in pyridine and in concentrated sulphuric acid, and for the sulphur compound an analogous decrease has been associated with complex-formation.[2] No direct relationship between the dielectric constant of the solvent and the relative shift, such as reported for the mercuric halides,[4] was observed here; in this case the relative shifts were considerably smaller. We were unable to isolate a solid adduct of bis(trifluoromethylseleno)mercury and pyridine, though an equimolar adduct with pyridine has recently been isolated in this Department;[5] we did prepare complexes of the mercurial with triphenylphosphine in (1 : 1) and (2 : 1) molar ratio, but neither was soluble enough in any solvent we tried to allow us to determine the in-phase (Hg–Se) stretching frequency. The stability of the mercurial to concentrated sulphuric acid is surprising, and it is not easy to see what complex species is likely to be formed in that system. Unexpectedly, the photosensitivity of solutions of the mercurial was found to depend markedly on solvent. Solutions in pyridine or methanol were often stable for periods of hours in the Raman spectrometer, but in an " inert " solvent such as carbon tetrachloride or benzene, decomposition began in 5—10 minutes. The increase in stability in donor solvents appears to be accompanied by a shift in the ultraviolet absorption peaks to shorter wavelengths, but in some cases the absorptions of the solvents mask the peaks of the solute.

The reactions with alkali metal and quaternary ammonium halides were investigated in the solid state (using powder photography) and in both dilute and concentrated solutions. In the solid state, there is evidence to indicate the formation of species of formulæ $[(CF_3Se)_2Hg]_2X^-$ and $(CF_3Se)_2HgX_2^{2-}$, where X is Cl, Br, or I, but only for the bromide is there any suggestion of a (1 : 1) species. The conductimetric results are harder to interpret. In methanol, it appears that the ions $(CF_3Se)_2HgI^-$ and $(CF_3Hg)_2HgI_2^{2-}$ are formed; in acetone, the latter ion (and its bromide equivalent) is produced, but there was nothing to

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[4] Allen and Warhurst, *Trans. Faraday Soc.*, 1958, **54**, 1786.

[5] Dunn and Emeléus, personal communication.

show that a (1 : 1) species was present, though a (2 : 1) complex is formed at low halide concentrations. Perhaps solvation stabilizes the (1 : 1) species in methanol; there is evidence that polynuclear iodo-complexes of mercury, though stable in acetone, dissociate in methanol into (presumably solvated) HgI_2 and HgI_3^-.[6] The increase in conductivity of the solutions of ionic halides with addition of excess of the mercurial is hard to understand, particularly since there were none of the usual signs of decomposition, such as shifting conductivity values or the appearance of colours, smells, or precipitates.

The infrared and Raman spectra afford qualitative evidence of the formation of complexes with halide ion. The Raman line at 178 cm.$^{-1}$ of the mercurial in acetone shifts to lower frequencies with increasing halide concentration up to a molar ratio of (1 : 1), while for iodide ion a new band appears at a lower frequency, which we have assigned to the (Hg–I) stretching mode of an iodo-complex. It has not proved possible, however, to increase the relative concentration of halide ion beyond the equimolar limit in solutions sufficiently concentrated to give reasonably strong Raman spectra. This is surprising, because the solid residue left after attempts have been made to dissolve mixtures richer in halide is the alkylammonium halide, even though there is no evidence from powder photography or from conductiometric work in this solvent to suggest that an insoluble (1 : 1) complex is formed. It seems likely that the solubility limit is dictated by the low solubility of the alkylammonium halides themselves in acetone, and that some complex species (either a 2 : 1 or a 1 : 1 that is only formed in concentrated solution) is sufficiently dissociated to give a high enough concentration of halide ion to prevent the dissolution of more of the alkylammonium salt. The absence of equimolar complexes is in contrast with the behaviour of the sulphur mercurial, all of the complexes of which with alkali or alkylammonium halides are described as of the (1 : 1) type.[1,2]

EXPERIMENTAL

Preparation of Bis(trifluoromethylseleno)mercury.[7–9]—Bistrifluoromethyl diselenide, obtained by heating silver trifluoroacetate with selenium to 280°, is converted in high yield to bis(trifluoromethylseleno)mercury by shaking it with mercury (Found: *M*, cryoscopic in benzene, 509; m. p. 52°. Calc. for $C_2F_6HgSe_2$: *M*, 496·5; m. p.,[5] 51°).

Physical properties. The ultraviolet spectra in different media, obtained at wavelengths >210 mμ using a Perkin-Elmer 137 recording spectrometer, are given in Table 2. The frequency of the band at 219 mμ in methanol solution was not altered by the addition of pyridine in 1 : 1 or 2 : 1 molar ratio [py : $Hg(SeCF_3)_2$].

TABLE 2.

Ultraviolet spectra of $(CF_3Se)_2Hg$ in different media.

Solvent	$\lambda_{max.}$ (mμ)	
C_6H_{12}	234	291
C_6H_6	—	291
CCl_4	—	289
CH_3OH	219	274
	($\varepsilon = 2 \times 10^4$)	($\varepsilon = 1{\cdot}1 \times 10^3$)
CH_3OH + pyridine (1 : 1,py : Hg)	219	Masked
CH_3OH + pyridine (2 : 1,py : Hg)	219	Masked

The infrared spectra were recorded by means of a Perkin-Elmer model 21 double-beam recording spectrometer, fitted with sodium chloride, potassium bromide or cæsium bromide prisms; the spectra were also recorded at frequencies between 400 and 200 cm.$^{-1}$ using a Grubb-Parsons DM-4 double-beam grating instrument. Frequencies are believed to be accurate to

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[6] Deacon and West, *J.*, 1961, 3929.

[7] Dale, Thesis, Cambridge, 1955; Dale, Emeléus, and Haszeldine, *J.*, 1958, 2939.

[8] Dunn, Thesis, Cambridge, 1963.

[9] Emeléus and Welcman, *J.*, 1963, 1268.

about ± 2 cm.$^{-1}$ for all but broad and diffuse bands. The compounds were studied as mulls in Nujol or hexachlorobutadiene, or in solution; some of the solutions, which were found to dissolve alkali metal halides, were held in Polythene bags. The Raman spectrometer used was a Hilger model E612 instrument with standard source unit; spectra were excited by the primary Hg 4358A line, other primary lines of shorter wavelength being suppressed by filter solutions of sodium or potassium nitrite in water. The spectra were recorded by means of a pen recorder operated by the amplified output from a photomultiplier. The level of background makes it unlikely that bands within 120 cm.$^{-1}$ of the exciting line would have been detected with any certainty. The states of polarization of relatively strong lines were determined qualitatively by the method of polarized incident light,[10] successive records being taken with suitably orientated polaroid cylinders surrounding the sample-tube. The appropriate sharp bands in the spectra of carbon tetrachloride, benzene, or acetone were used for calibration, and the frequencies quoted are believed to be accurate to about ± 2 cm.$^{-1}$ for all but the broad or very weak bands.

TABLE 3.

Vibrational spectra of bis(trifluoromethylseleno)mercury in various media (frequencies in cm.$^{-1}$).

Infrared			Raman	
CCl_4	Me_2CO	Mull	CH_3OH	Assignment
1272w	—	1275w	—	734 + 536
1134vs, b	1114vs, vb	1132vs, b	—	ν (CF) asym.
1096 1085 } vs	1093 1086 } vs	1092 1082 } vs	—	ν (CF) sym.
1069vs	1063vs	1058vs	—	734 + 330
		734m	735m, p	δ (CF_3) sym. in-phase ? and out-of-phase
		654vw	—	2 × 330
		536w	—	(CF_3) asym.
		330m, b	334m, p	δ (C–Se) in-phase ? and out-of-phase
		—	305w, b, dp	(CF_3) rock
		233w, b	—	(HgSe) out-of-phase
		n.s.	178vs, p	(Hg–Se) in-phase

s = strong, m = medium intensity, w = weak, v = very, b = broad, p = polarised, dp = depolarized, n.s. = not studied in this region.

The observed infrared and Raman spectra are summarized in Table 3, with group assignments. The overall molecular symmetry of bis(trifluoromethylseleno)mercury is likely to be low, but it is probable that co-ordination at mercury is roughly linear, and that the ($HgSe_2$) modes obey the selection rules of a linear skeleton. Vibrations of the two " halves " of the molecule are described as " in-phase " or " out-of-phase," to avoid confusion with the internally symmetric or anti-symmetric modes of the CF_3Se-groups. The only modes that give polarized Raman lines are in-phase, symmetric modes.

Most of the assignments follow by comparison with the spectra of CF_3Br [11] and $(CF_3S)_2Hg$.[2] There appears to be less coupling between the in-phase (C–Se) stretching modes and the symmetrical (CF_3) deformation modes than in the sulphur compound, since the CF_3– deformation frequencies are much the same in the two compounds. Moreover, the band at 645 cm.$^{-1}$, at first sight analogous to the out-of-phase symmetric (CF_3) deformation mode of $(CF_3S)_2Hg$ at 686 cm.$^{-1}$, is still present in the spectra of the half-halides CF_3SeHgX (see below), and so for the selenium compounds has been put down to an overtone or combination mode. As with the sulphur compound, the frequency of $\nu_s(HgSe_2)$ is solvent-dependent, appearing at 182 cm.$^{-1}$ in CCl_4, 181 cm.$^{-1}$ in CH_3COOH, 179 cm.$^{-1}$ in C_6H_6 and in CH_3CN, 178 cm.$^{-1}$ in acetone and in methanol, at 167 cm.$^{-1}$ in pyridine and at 164 cm.$^{-1}$ in concentrated sulphuric acid.

Reactions with Hg(II) *Compounds*.—(*a*) *Raman spectra*. Solutions of $(CF_3Se)_2Hg$ and mercuric chloride, bromide, iodide, cyanide, thiocyanate, or acetate in methanol gave Raman

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[10] Rank and Kagarise, *J. Opt. Soc. Amer.*, 1950, **40**, 89.
[11] Edgell and May, *J. Chem. Phys.*, 1954, **22**, 1808.

lines due to the " half "-compounds CF_3SeHgX, besides the spectra of the starting-compounds; the frequencies of the mixed species agree reasonably well with those predicted using the frequencies of the " simple " compounds [2] (see Table 4).

TABLE 4.

Raman lines ($\Delta\nu < 450$ cm.$^{-1}$) in methanolic solutions containing $(CF_3Se)_2Hg$ and HgX_2.

	X					
Assignment	Cl	Br	I	CN[a]	SCN	CH_3CO_2
ν_s(HgSe) of $(CF_3Se)_2Hg$	178	179	179	178	178	176
ν(HgSe) of CF_3SeHgX (obs.)	207	188	—	208	202	203
(calc.)	203	187	228	208	205	
ν(HgX) of CF_3SeHgX (obs.)	—	—	161	—	288	294
(calc.)	354	260	155	427	286	
ν_s(HgX) of HgX_2	323	203	146	411	—	—
CF_3 rock (all CF_3Se-species)	310	—	308	308	—	—
ν(C–Se) (all CF_3Se-species)	339	—	333	334	333	336

Spaces indicate bands not observed.

[a] In this system there was a line at 272 cm.$^{-1}$, assigned to a bending-mode of $Hg(CN)_2$.

For the chloride, the equilibrium constant was determined with reasonable accuracy from the Raman spectra. Because of overlapping bands, the value for the bromide system could only be estimated very roughly from the spectra. A method devised by Downs [2,12] in which the increased solubility of HgX_2 (X is I or SCN) in solutions of $(CF_3Se)_2Hg$ is measured by direct weighing, was found to give accurately reproducible results for the iodide and thiocyanate. The values obtained are given in Table 1.

(*b*) *Solid compounds.* (i) We obtained trifluoromethylselenomercuric chloride by evaporation of the solvent from a methanolic solution of mercuric chloride and $(CF_3Se)_2Hg$ (m. p. 175—177°, lit.,[9] 175—177°).

(ii) *Trifluoromethylselenomercuric bromide* was obtained similarly from methanolic solutions containing bis(trifluoromethylseleno)mercury and mercuric bromide, and was purified by recrystallization from benzene (Found: Hg, 46·4; Se, 18·4. $CBrF_3HgSe$ requires: Hg, 46·8; Se, 18·5%). The pale yellow crystalline solid, m. p. 160—162° (decomp.), is more photosensitive than the half-chloride or bis(trifluoromethylseleno)mercury itself.

(iii) *Trifluoromethylselenomercuric iodide* was prepared by fractional sublimation in an evacuated glass tube surrounded by a copper cylinder,[12] the base of which was maintained at 45° (4—7 days), of a fused mixture (approximately equimolar) of mercuric iodide and bis-(trifluoromethylseleno)mercury (Found: Hg, 41·8; Se, 16·3. CF_3HgISe requires: Hg, 42·2; Se, 16·6%). The compound was obtained as lemon-yellow crystals, softening with decomposition at 110°, stable in the dark at room temperature, but darkening in light and decomposing to give mercuric iodide at 45° in 12 hr. Orange-yellow cubic crystals of slightly higher volatility, and with infrared spectrum and *X*-ray powder photograph different from those of $(CF_3Se)_2Hg$ or CF_3SeHgI, were also obtained from the vacuum sublimation. The infrared spectrum contained a band at 1100 cm.$^{-1}$, a frequency at which absorption is observed in the spectra of adducts of bis(trifluoromethylseleno)mercury with halide ions, but not in the spectra of bis(trifluoromethylseleno)mercury or the half-halides. When fractionally sublimed, this substance partly decomposed, and gave mercuric iodide, the half-iodide, and bis(trifluoromethylseleno)mercury; an equimolar mixture of the half-iodide and bis(trifluoromethylseleno)-mercury after being ground in a mortar gave an orange-yellow powder, the *X*-ray powder photograph and infrared spectrum of which contained the features of the orange compound described above, besides those of the half-iodide and the mercurial. The orange-yellow crystals obtained from the sublimation are thus an addition-compound of the half-iodide and the mercurial. Attempts to analyse the compound were, however, unsuccessful. The selenium content was closer to that calculated for a 1 : 2 than for a 1 : 1 complex [Found: Se, 22·2,

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[12] Downs, Thesis, Cambridge, 1961.

21·2. $CF_3SeHgI\cdot(CF_3Se)_2Hg$ requires Se, 24·4; $(CF_3SeHgI)_2\cdot(CF_3Se)_2Hg$ requires Se, 21·8%]. The compound was not soluble enough in benzene for its molecular weight to be determined cryoscopically, and it appeared to react with dioxan. It was kept in a closed container in the dark for several weeks without apparent decomposition, but on a watch-glass in a dark cupboard it gradually turned pale yellow, forming crystals which were identified spectroscopically as the half-iodide. The compound softened at ~100°.

The three half-halides are isomorphous; the lattice constants increase from chloride to iodide. The infrared and Raman spectra are closely similar; apart from the changes in ν(HgSe), the chief differences from the mercurial are in the antisymmetric (CF) stretching modes, which give a band at ~1170 cm.$^{-1}$, some 40 cm.$^{-1}$ higher than in the mercurial and 90 cm.$^{-1}$ higher than in the adducts, and in the lowering of the (C–Se) stretching frequency. The relatively small changes in CF_3Se frequencies as the halogen atom is changed suggest that there is relatively little coupling with the (Hg–X) modes. The spectra are set out in Table 5.

TABLE 5.

Infrared spectra of the half-halides CF_3SeHgX (in cm.$^{-1}$).

Cl	Br	I	Assignment
1280w	1278w	1277w	736 + 536
1172s	1172s	1174s	ν(CF) asym.
1140vs	1139vs	1136vs	
1080vs	1079vs	1078vs	ν(CF) sym.
1055vs	1053vs	1050vs	736 + 320
738m	736m	736m	$\nu(CF_3)$ sym.
745vw, b	638vw, b	635vw, b	2 × 320
539w	536w	536w	$\nu(CF_3)$ asym.
323m	321m	319m	ν(C–Se)
286 271 m	249m, b	[161 Raman]	ν(Hg–X)

Reactions with Ionic Halides.—(*a*) *Raman spectra.* Tetramethylammonium iodide, only slightly soluble in acetone, is soluble in acetone solutions of bis(trifluoromethylseleno)mercury up to a molar ratio of 1 : 1, and the insoluble residue from a 2 : 1 ($Me_4NI\cdot Hg$) mixture was shown spectroscopically to be Me_4NI. The Raman spectra of mixed solutions at molar ratios between 0 and 1 : 1 contained lines at 160—178 cm.$^{-1}$ which are assigned to the in-phase ($HgSe_2$) stretching mode, lowered in frequency by complex-formation; the lowering is very roughly proportional to the added iodide concentration. A new line at ~140 cm.$^{-1}$ in solutions rich in iodide was assigned to the (HgI) stretching mode of a complex anion $[(CF_3Se)_2HgI_n]^{-n}$. Other lines at 332(w) and 735(w) differed little in frequency from those of the mercurial; a line due to the cation was also observed at 529 cm.$^{-1}$. Lithium iodide reacted with the mercurial when the compounds were ground together, producing a deep red colour, and a brick-red precipitate slowly formed when concentrated solutions of the two compounds in acetone were mixed.

Results like those with tetramethylammonium iodide were obtained with tetramethylammonium bromide (lithium bromide again causing decomposition) and with lithium chloride, save that no lines were observed that could be assigned to (HgX) stretching modes; the results are summarized in Table 6.

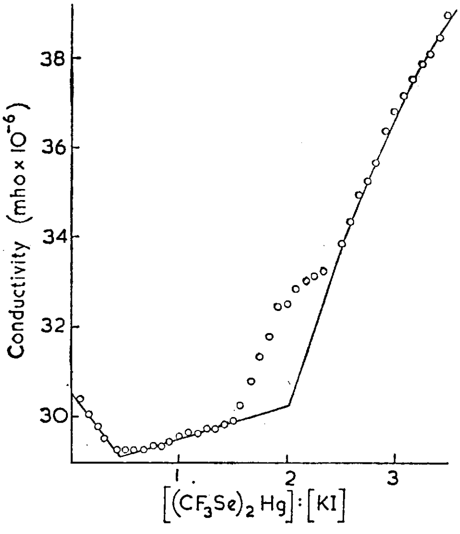
TABLE 6.

Raman lines ($\Delta\nu$ < 300 cm.$^{-1}$) of $(CF_3Se)_2Hg$ in acetone with added X^-.

	Raman shift (cm.$^{-1}$)			
	X = I		Br	Cl
$[X^-]$: [Hg], molar	ν(HgI)	ν_s(HgSe)	ν_s(HgSe)	ν_s(HgSe)
	—	178	178	178
1 : 4	—	173	n.s.	177
1 : 2	140	169	171	173
3 : 4	n.s.	n.s.	n.s.	167
1 : 1	137	157	164	163

n.s. = not studied at this concentration ratio.

(*b*) *Conductimetric titrations.* (i) *In acetone.* The conductivity of a solution of bis(trifluoromethylseleno)mercury ($1{\cdot}47 \times 10^{-2}$M) in acetone increased with addition of a solution of potassium iodide ($9{\cdot}86 \times 10^{-3}$M) in the same solvent up to a 3 : 1 molar ratio of iodide to mercurial, though there was no evidence of decomposition (such as drifting conductivity, or the formation of coloured precipitates), in contrast with the behaviour of the sulphur-mercurial under these conditions. The conductivity had barely changed after 3 days. Addition of bis(trifluoromethylseleno)mercury solution ($1{\cdot}03 \times 10^{-2}$M) to potassium iodide ($9{\cdot}86 \times 10^{-3}$M) in the same solvent led to a conductivity-curve with a clear break at a molar ratio (iodide : mercurial) of 2 : 1, and a " loop " which can be explained in terms of a partly dissociated 1 : 2 complex anion (see Figure). There was no evidence for a 1 : 1 complex. Similar results were obtained on adding solutions of the mercurial to solutions of potassium bromide in acetone, and a similar titration using lithium chloride led to a curve that showed no significant deviations from linearity; the addition of lithium chloride solution to the mercurial dissolved in methanol led to a curve with slight breaks at 2 : 1, 1 : 1, and 1 : 2 molar ratios. An interesting feature of the experiments in which solutions of the mercurial were added to solutions of the halides is that the conductivity in all cases continued to rise with addition of excess of the mercurial, which is itself virtually a non-conductor, though there were no signs of decomposition.



The conductivity of a solution of KI ($9{\cdot}86 \times 10^{-3}$M) in acetone on addition of a solution of $(CF_3Se)_2Hg$ ($1{\cdot}03 \times 10^{-2}$M) in the same solvent.

(ii) *In methanol.* Addition of bis(trifluoromethylseleno)mercury solution to potassium iodide dissolved in methanol led to decomposition; the addition of aliquot portions at 3½ min. intervals of methanolic potassium iodide solution ($2{\cdot}03 \times 10^{-2}$M) to a methanolic solution of the mercurial ($9{\cdot}33 \times 10^{-3}$M) led to a conductivity curve with clear changes of slope at molar ratios (KI : Hg) of 1 : 1 and 2 : 1.

(*c*) X-*Ray powder photography.*—*X*-Ray powder photographs were obtained of mixtures of tetramethylammonium chloride or iodide and the mercurial of molar compositions (2 : 1, 1 : 1, and 1 : 2) that had been thoroughly ground together, giving white crystalline solids that were not hygroscopic. The resulting photographs could be interpreted in terms of three species—the tetramethylammonium halide, a 1 : 2 complex, and a 2 : 1 complex. With tetramethylammonium bromide, patterns were obtained that were very like those for the iodide system, though a few lines in the photograph of the 1 : 1 mixture were not present in the 2 : 1 or the 1 : 2 patterns.

The mercurial decomposed on being ground with the iodides of cæsium, potassium or lithium, or with lithium bromide; mixtures with lithium or potassium chloride gave only the patterns for the metal halides and the mercurial. Mixtures with cæsium chloride or bromide, however, gave some extra lines in addition to those of the pure components.

The 1 : 2 ($Me_4NI{:}Hg$) complex was insoluble in water, and decomposed in the presence of liquid water only after some hours. The 1 : 2 ($Me_4NCl{:}Hg$) complex, though insoluble in water or benzene, was very soluble in acetone; water in which the solid had been shaken gave only a faint cloudiness when treated with silver nitrate, indicating that the complex is not readily hydrolysed.

TABLE 7.

Infrared frequencies of complexes of $(CF_3Se)_2Hg$ with tetramethylammonium halides, studied as mulls.

$[X^-]:[Hg] = 2:1$		$[X^-]:[Hg] = 1:2$			
X = I	Cl	I	Br	Cl	Assignment
1265w	1265w	1270w	1272w	1271w	730 + 530
1080vs, b	1080s, b	1100w, sh	1088vs, vb	1100w, sh	(CF) asym.
		1087vs, b		1081vs, b	(CF) sym.
1050vs	1051s	1057vs	1062vs	1057vs	730 + 330
731m	734m	735m	734m	735m	(CF_3) sym.
654vw	666w	666 657 } w	662w	662w	2 × 330
n.o.	n.o.	532w	532w	533vw	(CF_3) asym.
335m	335m	333m	332m	334m	(CSe)
	226s, b			322m	(HgCl)
—	—	219m	219m, b	218m, b	(HgSe) out-of-phase

w = weak, m = medium intensity, s = strong, v = very, b = broad, n.o. = not observed, n.s. = not studied in this region.

Infrared spectra. The infrared spectra of the 1 : 2 ($X{:}Hg$) complexes are very similar, save for a band at 322 cm.$^{-1}$ in the spectrum of the chloride, which is probably due to the (Hg–Cl) stretching frequency; the bands at ~219 cm.$^{-1}$ in all the spectra may well be associated with (Hg–Se) stretching modes. In the region of 1100 cm.$^{-1}$, it is interesting that the very strong bands at ~1170 cm.$^{-1}$ (for the half-compounds) and at 1130 cm.$^{-1}$ (for the mercurial) are shifted to ca. 1080 cm.$^{-1}$. The spectrum of the 2 : 1 (X : Hg) adducts are very similar, save that the band at 532 cm.$^{-1}$ is missing; the 1 : 2 chloro-adduct shows an additional peak at 221 cm.$^{-1}$.

Triphenylphosphine Complexes.—Complexes of the formulæ $(CF_3Se)_2Hg,P(Ph)_3$ and $(CF_3Se)_2Hg,2P(Ph)_3$ were obtained by mixing strong benzene solutions of the reactants in stoicheiometric proportions, and were recrystallized from benzene (Found: For 1 : 1, C, 31·3; H, 2·3. $C_{20}H_{15}F_6HgPSe$ requires: C, 31·6; H, 1·9%. For 2 : 1, C, 44·4; H, 2·8; Hg, 19·4. $C_{38}H_{30}F_6HgP_2Se$ requires: C, 44·7; H, 2·9; Hg, 19·6%).

Reaction with nitric acid. The mercurial dissolves in concentrated nitric acid with the evolution of brown fumes, the reaction occurring more rapidly on heating; a white crystalline solid separates as the solution cools. This crystalline solid oxidizes hydrochloric acid to chlorine, and was identified as *mercuric trifluoromethylselenonate* (Found: Hg, 35·6; Se, 28·1. $C_2F_6HgO_4Se_2$ requires: Hg, 35·8; Se, 28·2%). The infrared spectra were consistent with this formulation.

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