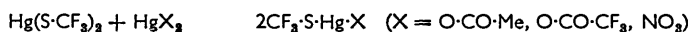


240. *Spectroscopic Studies of the Reaction of Bis(trifluoromethylthio)mercury with Salts of Oxyacids.*

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The interaction of bis(trifluoromethylthio)mercury with the salts of oxyacids has been studied by the use of Raman and infrared spectroscopy. Mercuric acetate, trifluoroacetate, and nitrate yield in solution the corresponding trifluoromethylthiomeric derivatives in equilibrium with the reactants. With silver acetate, trifluoroacetate, nitrate, and perchlorate, there is evidence that reversible complex-formation takes place. Oxysalts of other metals do not react with bis(trifluoromethylthio)mercury.

THE Raman effect has recently been used to compare the reactions of bis(trifluoromethylthio)mercury with mercuric and ionic halides.<sup>1</sup> We have now extended this work to mercuric acetate, trifluoroacetate, and nitrate. The Raman spectrum of an aqueous or methanolic solution containing equimolar amounts of bis(trifluoromethylthio)mercury and the appropriate mercuric salt contains lines attributable to the corresponding trifluoromethylthiomeric derivative in equilibrium with the reactants:



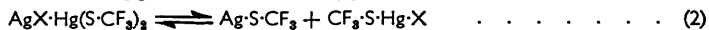
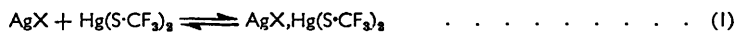
For all three systems, the equilibrium lies well to the right and samples of trifluoromethylthiomeric acetate (which has previously been reported<sup>2</sup>) and trifluoromethylthiomeric trifluoroacetate have been obtained by evaporation of the solution, followed by vacuum-sublimation of the solid residue. Solutions of bis(trifluoromethylthio)mercury and mercuric nitrate in dilute nitric acid yield a solid sparingly soluble in cold water; its analysis and infrared spectrum indicate that it is trifluoromethylthiomeric nitrate hemihydrate. Trifluoromethylthiomeric acetate and trifluoroacetate are relatively low-melting solids which can be sublimed *in vacuo* at about 100°. While the acetate appears to be a molecular compound, there is evidence that the trifluoroacetate and nitrate may ionise to some extent in aqueous solution.

In contrast, the corresponding silver oxysalts usually react with bis(trifluoromethylthio)mercury in a suitable solvent to give complexes of low stability. The intense Raman line at about 240 cm.<sup>-1</sup>, associated with the in-phase Hg-S stretching mode, is shifted to lower frequencies, as in the reaction of the mercury compound with pyridine and tetramethylammonium halides.<sup>1</sup> Owing to the differing solubility relationships, it has not been possible to investigate the behaviour of all the silver salts under strictly comparable

<sup>1</sup> Downs, Ebsworth, and Emel us, *J.*, 1961, 3187.

<sup>2</sup> Emel us and Pugh, *J.*, 1960, 1108.

conditions, but there appear to be two distinct equilibria, each of which may be involved to a greater or lesser degree:



(X = NO<sub>3</sub>, ClO<sub>4</sub>, O·CO·Me, O·CO·CF<sub>3</sub>).

The Raman spectra of an acetonitrile solution of silver nitrate and bis(trifluoromethylthio)mercury, and of a methanolic solution of silver perchlorate and the mercury compound, indicate the equilibrium formation of an adduct according to equation (1). The spectrum of a benzene solution of silver trifluoroacetate and the mercurial shows, however, that, when the molar ratio  $R = \text{Hg}(\text{S}\cdot\text{CF}_3)_2 : \text{Ag}\cdot\text{O}\cdot\text{CO}\cdot\text{CF}_3$  is less than unity, no appreciable concentration of uncomplexed mercurial is present, implying that in this case reaction (1) proceeds almost to completion; when  $R$  exceeds 1, the bands characteristic of both the free mercurial and the adduct are observed. Reaction (2) in the above scheme is involved in the silver acetate–bis(trifluoromethylthio)mercury system. Silver acetate is readily soluble in solutions of the mercury compound in acetonitrile, and the Raman spectrum of the solution reveals not only reversible complex-formation, but also the presence of trifluoromethylthiomeric acetate, formed as in equation (2).

Although trifluoromethylthiosilver,  $\text{Ag}\cdot\text{S}\cdot\text{CF}_3$ , has been prepared by the reaction of silver nitrate with bis(trifluoromethylthio)mercury under aqueous conditions,<sup>3</sup> we have found that the reaction gives a precipitate of the equimolar adduct; loose lattice-compounds with indefinite composition of this adduct with the mercurial may result unless an excess of silver nitrate is used. At about 100° the adduct decomposes into the starting materials, and trifluoromethylthiosilver could not be obtained under any of the conditions tried. Evaporation of the solvent from a solution containing bis(trifluoromethylthio)mercury and either silver trifluoroacetate or silver perchlorate in 1 : 1 proportion yields solids which are unstable to dissociation in that the relatively volatile mercurial can be removed by prolonged pumping at room temperature. Aqueous solutions of the mercury compound and silver acetate (in equimolar proportions), when mixed, give a precipitate of trifluoromethylthiosilver in 60–70% yield based on the reaction:



Trifluoromethylthiosilver is virtually insoluble in water,<sup>4</sup> and the fact that it is not produced quantitatively in this reaction provides further corroboration of the suggested scheme of equilibria.

From the experimental results, it is not possible to reach any definite conclusion about the nature of the complex species, which appear to be formed only by silver salts. The oxysalts of metals such as potassium, copper(II), lead(II), and thallium(I), which do not form stable trifluoromethylthio-compounds, do not react with bis(trifluoromethylthio)mercury,<sup>5</sup> implying that trifluoromethylthiosilver is formed in the reactions of the mercury compound with silver oxysalts. In support of this, evidence has been obtained which indicates the formation of complex trifluoromethylthio-compounds between trifluoromethylthiosilver and mixtures of bis(trifluoromethylthio)mercury with mercuric oxysalts.

The infrared spectra of the trifluoromethylthiomeric derivatives and various complexes isolated show a number of changes in the bands associated with the C–F stretching modes, and in the characteristic frequencies of the oxyanion, with respect to the reactants. Although the molecular symmetry of these derivatives remains obscure, there are certain common factors. Thus, there is a significant change in the contour of the intense band associated with the C–F stretching modes when compared with the corresponding broad,

<sup>3</sup> Man, Coffman, and Muetterties, *J. Amer. Chem. Soc.*, 1959, **81**, 3575.

<sup>4</sup> Emelús and MacDuffie, *J.*, 1961, 2597.

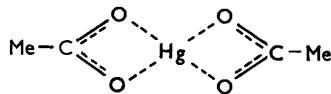
<sup>5</sup> Downs, Ph.D. Thesis, Cambridge, 1961.

rather ill-defined band centred about  $1100\text{ cm}^{-1}$  in the spectrum of pure bis(trifluoromethylthio)mercury. In all cases, moreover, mercury-oxygen co-ordination is implied by the relatively complex pattern of the bands due to the CO-O stretching modes in the acetate and trifluoroacetate derivatives, and by similar modifications in the N-O stretching frequencies of the nitrate derivatives.

## RESULTS

*A. Raman Spectra.*—(1) *Equilibria with mercuric salts.* Both aqueous and methanolic solutions were examined; in all cases  $\sim 10\%$  of the appropriate acid was added to suppress hydrolysis and give a solution clear enough for Raman work. In this and other respects, the interpretation of the spectra is less straightforward than in the case of the mercuric halides.<sup>1</sup> No measurements were made at frequencies greater than  $1100\text{ cm}^{-1}$  owing to the feeble scattering in this region of all the mercury compounds concerned, and to the appearance of solvent bands; it was impracticable to observe changes in the CO-O stretching vibrations (in the region  $1400\text{--}1700\text{ cm}^{-1}$ ) of the acetate and trifluoroacetate.

The intense line at  $240\text{ cm}^{-1}$  due to the in-phase Hg-S stretching vibration of pure bis(trifluoromethylthio)mercury ( $\nu_{\text{Hg-S}}$ ) is accompanied by a new strong line at  $247\text{--}257\text{ cm}^{-1}$   $\nu'_{\text{Hg-S}}$  in solutions containing the mercuric oxysalts; in the nitrate and the trifluoroacetate systems, the exact frequency depends upon the solvent, and is higher for aqueous than for methanolic solutions. In general, no lines can be definitely ascribed to Hg-O stretching modes. The line at  $276\text{ cm}^{-1}$  in the Raman spectrum of an aqueous solution of mercuric acetate has been tentatively assigned by Fonteyne<sup>6</sup> to the totally symmetric vibration of the  $\text{HgO}_4$  group in the molecule



The low frequency is in keeping with the fourfold co-ordination of the mercury atom, but the evidence is inconclusive; in no case has a definite value been obtained for the Hg-O stretching frequency in a simple (linear) molecule. When bis(trifluoromethylthio)mercury is added to a solution of mercuric acetate, the line at  $276\text{ cm}^{-1}$  is replaced by one at  $297\text{ cm}^{-1}$ ; changes in the other frequencies characteristic of the  $-\text{Hg}\cdot\text{O}\cdot\text{CO}\cdot\text{Me}$  group are slight. This is consistent with Fonteyne's assignment for the Hg-O stretching frequency, which would be expected to change most markedly when one of the acetate groups is replaced by a trifluoromethylthio-group.

The Raman spectra of solutions containing mercuric nitrate and trifluoroacetate indicate that the corresponding trifluoromethylthiomeric derivatives are dissociated. Although there is no definite evidence for the formation of the  $\text{CF}_3\cdot\text{S}\cdot\text{Hg}^+$  ion in such solutions, very weak lines in the region  $270\text{--}360\text{ cm}^{-1}$  may be due to complex cations such as  $\text{CF}_3\cdot\text{S}\cdot\text{Hg}^+$ ,  $\text{MeOH}$ , and  $\text{CF}_3\cdot\text{S}\cdot\text{Hg}^+\cdot\text{OH}_2$ , which could also account for the dependence of  $\nu'_{\text{Hg-S}}$  upon the solvent; similar observations have been made concerning the Raman spectra of solutions of mercuric nitrate,<sup>7</sup> which are thought to contain complex cations of the type  $\text{Hg}^{2+}(\text{OH}_2)_2$  and  $\text{Hg}^+\cdot\text{OH}$ . These lines are, however, too feeble for accurate measurements. There is no change in the characteristic frequencies of the trifluoroacetate and nitrate ions in the range  $200\text{--}1100\text{ cm}^{-1}$ , but the presence of free acid would make it difficult to detect small frequency shifts. Conductivity measurements also suggest that trifluoromethylthiomeric trifluoroacetate is ionised in aqueous solution, but have very limited helpfulness since equilibria are involved.<sup>8</sup>

The principal Raman frequencies are contained in Table 1, together with the appropriate assignments.

(2) *Adduct formation.* In solutions containing bis(trifluoromethylthio)mercury and silver nitrate, acetate, trifluoroacetate, or perchlorate, complex-formation is inferred from the appearance in the Raman spectra of new lines associated with  $\text{CF}_3\cdot\text{S}\cdot\text{Hg}$  groups of complex species (see Table 2); the lines characteristic of the oxyanions are not significantly affected, and have been omitted from the Table.

<sup>6</sup> Fonteyne, *Natuurw. Tijds.*, 1943, **25**, 108.

<sup>7</sup> Bernstein, Pars, and Blumenthal, *J. Amer. Chem. Soc.*, 1957, **79**, 1579.

TABLE 1.

Principal Raman frequencies of solutions containing equimolar amounts of bis(trifluoromethylthio)mercury and a mercuric oxysalt.

Assignment	$\Delta\nu$ (cm. <sup>-1</sup> )		
	Acetate	Trifluoroacetate	Nitrate
$\nu$ Hg-S of Hg(S-CF <sub>3</sub> ) <sub>2</sub> .....	240sh	239sh	240·5s
$\nu$ Hg-S of CF <sub>3</sub> S·Hg·X .....	248vs	253·5 vs <sup>a</sup> (257 vs) <sup>b</sup>	247·5 vs <sup>a</sup> (252 vs) <sup>b</sup>
$\nu$ Hg-O of CF <sub>3</sub> S·Hg·X .....	297m		
$\nu$ C-S [ $\delta$ CF <sub>3</sub> (sym.)] of Hg(S-CF <sub>3</sub> ) <sub>2</sub> .....	400s	400s	400m
$\nu$ C-S [ $\delta$ CF <sub>3</sub> (sym.)] of CF <sub>3</sub> S·Hg·X .....	410s	412s	408s
$\delta$ CF <sub>3</sub> (sym.) ( $\nu$ C-S) of Hg(S-CF <sub>3</sub> ) <sub>2</sub> and CF <sub>3</sub> S·Hg·X.....	753m	752m	751m

<sup>a</sup> For methanolic solutions. <sup>b</sup> For aqueous solutions.

TABLE 2.

Raman frequencies of solutions containing equimolar amounts of bis(trifluoromethylthio)mercury and a silver oxysalt.

Assignment	Silver salt:	Acetate	Trifluoroacetate	Nitrate	Perchlorate <sup>a</sup>
	Solvent:	Acetonitrile	Benzene	Acetonitrile	Methanol
$\Delta\nu$ (cm. <sup>-1</sup> )					
? Adduct .....		220sh?			222sh?
$\nu$ Hg-S of adduct .....		229vs	228vs	229vs	230vs
$\nu$ Hg-S of Hg(S-CF <sub>3</sub> ) <sub>2</sub> .....		239s		240s	240s
$\nu$ Hg-S of CF <sub>3</sub> S·Hg·O·CO·Me .....		247sh			
$\nu$ C-S [ $\delta$ CF <sub>3</sub> (sym.)] of adduct .....		<sup>b</sup>	389m	394m	390m
$\nu$ C-S [ $\delta$ CF <sub>3</sub> (sym.)] of Hg(S-CF <sub>3</sub> ) <sub>2</sub> ...				401m	
$\delta$ CF <sub>3</sub> (sym.) ( $\nu$ C-S) of S-CF <sub>3</sub> groups		754m	755m	755m	

<sup>a</sup> Gave poor solutions for Raman work. <sup>b</sup> Lines obscured by strong solvent band.

Most significant is the appearance in all cases of a new, intense line at about 230 cm.<sup>-1</sup> in addition to, or in place of, the line at 240 cm.<sup>-1</sup> of the pure mercurial. The frequency varies little from compound to compound, and seems to be characteristic of this class of adduct; it should be compared with the corresponding value of about 220 cm.<sup>-1</sup> for the adducts with tetramethylammonium halides and pyridine.<sup>1</sup> There may be a shoulder at about 220 cm.<sup>-1</sup> in the spectra of solutions containing silver perchlorate and acetate, possibly corresponding to a second complex. The other prominent line close to 400 cm.<sup>-1</sup> for the mercury compound is also accompanied, or replaced, by a new line at about 390 cm.<sup>-1</sup>. No new bands definitely attributable to Hg-O stretching modes have been observed in any of the solutions studied.

By themselves, these results do not indicate the type or stoichiometry of the complexes formed. It has been shown that trifluoromethylthiosilver dissolves in acetonitrile solutions of the mercurial, whose Raman spectrum is unaffected; the possibility of the formation of complexes such as Ag·S·CF<sub>3</sub>·Hg(S·CF<sub>3</sub>)<sub>2</sub> has consequently been ruled out. On the other hand, when mercuric acetate is added to the system, the spectrum becomes indistinguishable from that of a mixture of silver acetate and the mercury compound dissolved in acetonitrile. Similarly, although trifluoromethylthiosilver is almost insoluble in benzene, it dissolves in benzene solutions containing bis(trifluoromethylthio)mercury and mercuric trifluoroacetate; the spectrum shows a new line at ~230 cm.<sup>-1</sup>, as observed for the Ag·O·CO·CF<sub>3</sub>·Hg(S·CF<sub>3</sub>)<sub>2</sub> complex. It therefore seems that the complex species should be regarded as adducts of trifluoromethylthiosilver with trifluoromethylthiomeric oxysalts. Conductimetric studies of solutions containing silver oxysalts and the mercurial give little help in determining what species may be present, since the complexes do not appear to be ionic, and equilibria are involved.<sup>5</sup>

B. *Infrared Spectra.*—The infrared spectra of the solid trifluoromethylthiomeric salts and adducts have been recorded in the range 400—4000 cm.<sup>-1</sup>. The salient features associated with the vibrations of the S-CF<sub>3</sub>, CO·O, and NO groups are presented in Tables 3 and 4.

The C-F vibrations of the S-CF<sub>3</sub> group are generally characterised by two relatively sharp bands at about 1080 and 1150 cm.<sup>-1</sup>, although trifluoromethylthiomeric acetate gives a single band at about 1090 cm.<sup>-1</sup>, as do the adducts of bis(trifluoromethylthio)mercury with tetramethylammonium halides.<sup>5</sup> The frequencies of the oxyanions in the various derivatives

TABLE 3.  
Certain infrared frequencies of solid acetates and trifluoroacetates (cm.<sup>-1</sup>).

Compound	$\nu\text{CO}_2$ (asym.)	$\nu\text{CO}_2$ (sym.)	$\nu\text{C-F}^a$	$\delta\text{CF}_3$ (sym.) <sup>a</sup> ( $\nu\text{C-S}$ )
$\text{Hg}(\text{O}\cdot\text{CO}\cdot\text{Me})_2$	1616sh			
	1600vs	1383sh		
	1566vs	1368s		
	1547sh			
$\text{CF}_3\cdot\text{S}\cdot\text{Hg}\cdot\text{O}\cdot\text{CO}\cdot\text{Me}$	1633sh	1394s	1095vs	755s
	1600vs	1377s		
	1568sh			
$\text{Hg}(\text{O}\cdot\text{CO}\cdot\text{CF}_3)_2$	1715sh	1416s, br	1196vs	
	1680vs	1381sh	1145vs	
	1638sh			
$\text{CF}_3\cdot\text{S}\cdot\text{Hg}\cdot\text{O}\cdot\text{CO}\cdot\text{CF}_3$	1687sh		1208sh	
	1671vs	1448s	1190vs, br	750s
	1640sh	1434s	1140vs	
	1608sh		1074vs	
$\text{Ag}\cdot\text{O}\cdot\text{CO}\cdot\text{CF}_3$	1677sh	1454s	1207vs	
	1623vs		1190vs	
			1145vs	
$(\text{CF}_3\cdot\text{S})_2\text{Hg}\cdot(\text{Ag}\cdot\text{O}\cdot\text{CO}\cdot\text{CF}_3)_z$	1708sh		1225sh	
	1679vs	1451s	1195vs	754s
	1622vs		1144vs	
			1079vs	

TABLE 4.  
Infrared frequencies of solid nitrates (cm.<sup>-1</sup>).

Mode	Compound			
	(9) AgNO <sub>3</sub>	Hg(S·CF <sub>3</sub> ) <sub>2</sub> ·AgNO <sub>3</sub>	(7) Hg(NO <sub>3</sub> ) <sub>2</sub> ·H <sub>2</sub> O	CF <sub>3</sub> ·S·Hg·NO <sub>3</sub> ·½H <sub>2</sub> O
$\nu\text{NO}_2$ (asym.) * .....		1436sh	1460sh	1436sh
$\nu_2 \text{NO}_3^-$ .....	1348vs	1376vs	1375vs	1383vs
$\nu\text{NO}_2$ (sym.) * .....		1284vs	1300vs, br	1312sh
$\nu\text{C-F}$ (sym. and asym.) <sup>a</sup> ...		1212m		1194vs
		1148vs		1143vs
		1073vs		1082vs
$\nu\text{N-O}$ ( $\nu_1\text{NO}_3^-$ ) * .....	Forbidden	1040sh	1036w	1033sh
$\nu_2 \text{NO}_3^-$ .....	835w		837m	833w
				825w
O·NO <sub>2</sub> non-planar rocking *		804m	806w	816m
$\delta\text{CF}_3$ ( $\nu\text{C-S}$ ) <sup>a</sup> .....		752s		760s
$\nu_4 \text{NO}_3^-$ .....	733w		737vw	726m
			700w	718m

\* Additional active modes introduced by co-ordination.

<sup>a</sup> For pure Hg(S·CF<sub>3</sub>)<sub>2</sub>,<sup>1</sup> the corresponding values are:  $\nu\text{C-F}$  (sym. and asym.) 1123, 1103, 1083 (all vs, br)  $\delta\text{CF}_3$  ( $\nu\text{C-S}$ ) 751s.

are close to those in the corresponding simple mercuric salts. The relatively complex pattern of the band normally ascribed to the asymmetric CO·O stretching mode of pure mercuric acetate and trifluoroacetate is reproduced in the spectra of trifluoromethylthiomeric acetate and trifluoroacetate; accordingly, some form of metal-oxygen co-ordination is indicated in all four compounds. The corresponding mode, appearing as a single band at 1623 cm.<sup>-1</sup> in the spectrum of pure silver trifluoroacetate, is accompanied by a new strong band at 1679 cm.<sup>-1</sup> in that of the adduct with bis(trifluoromethylthio)mercury, to be explained by a change in symmetry of the simple trifluoroacetate ion. Furthermore, the spectra of the nitrates, including the mercuric and trifluoromethylthiomeric derivatives, and the adduct AgNO<sub>3</sub>·Hg(S·CF<sub>3</sub>)<sub>2</sub>, also exhibit modifications in the absorption bands normally shown by simple nitrates. Apart from the three infrared-active fundamentals of the nitrate ion, additional bands are observed which

can be accounted for in terms of covalent bonding of the nitrate group through one oxygen atom, with a resultant lowering of symmetry.<sup>8</sup>

#### EXPERIMENTAL

The preparation of bis(trifluoromethylthio)mercury and the techniques used for studying the Raman spectra of the various solutions are described elsewhere.<sup>1</sup> For the Raman work, a Hilger E612 spectrometer was employed with the mercury line at 4358Å as the exciting line; the spectra were reproduced directly by means of a pen recorder operated by the amplified output from a photomultiplier unit. The Raman lines were calibrated from the position of appropriate sharp bands in the spectra of pure carbon tetrachloride, benzene, and acetone; the frequencies in the range 100—1100 cm.<sup>-1</sup> (correct to about 2 cm.<sup>-1</sup> for all but the weak and diffuse bands) are listed below:

Pure Hg(O-CO-Me)<sub>2</sub>: 276m, 496m, 693m, 937s.  
 Hg(O-CO-Me)<sub>2</sub> + Hg(S-CF<sub>3</sub>)<sub>2</sub>: 240sh, 248vs, 297m, 400s, 410s, 471w, 503m, 697m, 753m, 933s.  
 Pure Hg(O-CO-CF<sub>3</sub>)<sub>2</sub>: 276w, 299w, 340w, br, 413w, 605w, 731w, 791w, br, 852s.  
 Hg(O-CO-CF<sub>3</sub>)<sub>2</sub> + Hg(S-CF<sub>3</sub>)<sub>2</sub>: 239sh, 253·5—257vs, 276w, 299w, 340w, br?, 400s, 412s, 420w, 468w, 607vw, 729w, 752m, 854s.  
 Pure Hg(NO<sub>3</sub>)<sub>2</sub>: 718w, 1045vs.  
 Hg(NO<sub>3</sub>)<sub>2</sub> + Hg(S-CF<sub>3</sub>)<sub>2</sub>: 240·5s, 247·5—252vs, 295w?, 400m, 408s, 718w, 751m, 1045vs.  
 AgNO<sub>3</sub> + Hg(S-CF<sub>3</sub>)<sub>2</sub>: 229vs, 240s, 394s, 401s, 718vw, 755m, 1035s.  
 AgClO<sub>4</sub> + Hg(S-CF<sub>3</sub>)<sub>2</sub>: 222sh?, 230vs, 240s, 390m.  
 Ag-O-CO-CF<sub>3</sub> + Hg(S-CF<sub>3</sub>)<sub>2</sub>: 228vs, 389s, 463w, 755m, 889m, 935s.  
 Ag-O-COMe + Hg(S-CF<sub>3</sub>)<sub>2</sub>: 220sh?, 229vs, 239s, 247sh, 754m, 935m.

The infrared spectra were recorded between 400 and 4000 cm.<sup>-1</sup> with a Perkin-Elmer model 21 double-beam spectrometer fitted with a sodium chloride or potassium bromide prism. The solids were examined as mulls with Nujol or hexachlorobutadiene.

*Preparation of Solid Derivatives.*—The solid obtained by evaporating a solution of mercuric acetate (1·51 g.) and bis(trifluoromethylthio)mercury (1·91 g.) in methanol gave, on vacuum-sublimation at 100°, trifluoromethylthiomeric acetate (1·72 g.) (Found: F, 15·5; Hg, 55·1; S, 8·9. Calc. for C<sub>3</sub>H<sub>3</sub>F<sub>3</sub>HgO<sub>2</sub>S: F, 15·8; Hg, 55·6; S, 8·9%) and bis(trifluoromethylthio)mercury (0·94 g.). Trifluoromethylthiomeric acetate melts at 80—85° and decomposes at 170°.

In the same way, mercuric trifluoroacetate (2·23 g.) and bis(trifluoromethylthio)mercury (2·10 g.) gave *trifluoromethylthiomeric trifluoroacetate* (1·47 g.) (Found: F, 27·1; Hg, 47·9; S, 7·9. C<sub>3</sub>F<sub>6</sub>HgO<sub>2</sub>S requires F, 27·5; Hg, 48·4; S, 7·7%), m. p. 100—101° (some decomp.).

On cooling, a solution of mercuric nitrate monohydrate (2·57 g.) and bis(trifluoromethylthio)mercury (3·02 g.) in 10% nitric acid (10—15 ml.) yielded crystals of *trifluoromethylthiomeric nitrate hemihydrate*, which were filtered off, washed with water and benzene, and dried (KOH) *in vacuo* (Found: F, 15·0; Hg, 53·4; NO<sub>3</sub>, 16·6; S, 8·45. C<sub>2</sub>H<sub>2</sub>F<sub>6</sub>Hg<sub>2</sub>N<sub>2</sub>O<sub>7</sub>S<sub>2</sub> requires F, 15·3; Hg, 53·8; NO<sub>3</sub>, 16·6; S, 8·6%). The previously reported<sup>2</sup> anhydrous trifluoromethylthiomeric nitrate could not be obtained by vacuum-sublimation at temperatures up to 140°; water and oxides of nitrogen were evolved, but only a trace of bis(trifluoromethylthio)mercury appeared as a sublimate [vap. press.<sup>3</sup> of pure Hg(S-CF<sub>3</sub>)<sub>2</sub> at 140° ~15 cm.]. A yellowish, hygroscopic material remained, which was shown spectroscopically to contain S-CF<sub>3</sub> and NO<sub>3</sub> groups; when heated to 190° it decomposed further to bis(trifluoromethylthio)mercury.

To prepare the 1:1 *adduct of bis(trifluoromethylthio)mercury and silver nitrate*, the mercurial (2·18 g.) was heated with a solution of silver nitrate (1·84 g.; 10 ml.). The precipitate (1·75 g.) was filtered off, washed with water and benzene, and dried (P<sub>2</sub>O<sub>5</sub>) *in vacuo* (Found: Ag, 18·8; F, 9·9; Hg, 35·1; NO<sub>3</sub>, 10·5; S, 5·6. C<sub>2</sub>AgF<sub>6</sub>HgNO<sub>3</sub>S<sub>2</sub> requires Ag, 18·85; F, 10·0; Hg, 35·0; NO<sub>3</sub>, 10·8; S, 5·6%). Repetition of the experiment under a variety of conditions failed to give trifluoromethylthiosilver reported elsewhere<sup>3</sup> as the product. Although the composition of the precipitate depended on the molar proportions of the reactants, the nitrate group was invariably present. Unless an excess of silver nitrate was used, the precipitate contained free bis(trifluoromethylthio)mercury, which could not be recovered by the usual method of vacuum-sublimation at room temperature. The adduct was appreciably soluble in water, acetone,

<sup>8</sup> Gatehouse, Livingstone, and Nyholm, *J.*, 1957, 4222.

and ether, almost insoluble in benzene, but readily soluble in acetonitrile. It melted, with decomposition, at about 170° and did not have an appreciable dissociation pressure below 50° [vap. press.<sup>9</sup> of pure  $\text{Hg}(\text{S}\cdot\text{CF}_3)_2$  at 50°, 0.24 cm.]. At 100°, however, the adduct (612 mg.) gave, after 10—12 hr. *in vacuo*, a sublimate of bis(trifluoromethylthio)mercury (430 mg.) and an involatile residue of silver nitrate (182 mg.). No adducts of other silver salts could be obtained from aqueous solution in this way.

When bis(trifluoromethylthio)mercury (1.63 g.) and silver acetate (0.67 g.), each dissolved in the minimum amount of water, were mixed, a precipitate resulted. Filtration, washing with water and benzene, and drying ( $\text{P}_2\text{O}_5$ ) *in vacuo* gave trifluoromethylthiosilver (0.47 g.) (Found: C, 5.7; Ag, 51.35; S, 15.3. Calc. for  $\text{C}\cdot\text{AgF}_3\text{S}$ : C, 5.7; Ag, 51.65; S, 15.3%); the infrared spectrum was identical with that of a sample prepared from silver fluoride and carbon disulphide.<sup>9</sup>

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<sup>9</sup> MacDuffie, Ph.D. Thesis, Cambridge, 1961.

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