A possible explanation for the third conclusion is the effect of steric factors, which are of great importance in complex stability. From their consideration one would expect the following order of increasing stability in the alkyl thiourea complexes: tri-alkyl < di-alkyl < mono-alkyl. The results given in Tables XIV and XVI show this to be the case. Steric factors, however, do not account for the fact that ethylthiourea complexes are more stable than those of methylthiourea.

An alternative explanation for the three conclusions listed above might be advanced by taking into consideration the peculiar symmetry of the thiourea molecule, which is, to some degree, similar to the guanidine molecule. Davis and Elderfield[10] noted that mono-alkyl and N,N′-dialkylguanidines are less basic than the parent molecule. Furthermore, they found that the ethyl group has a smaller effect than the methyl in decreasing the basicity. Pauling[11] explained the decreased basicity of the substituted guanidines as an effect of the alkyl group on the resonance energy of the unusually symmetric parent molecule. If, in agreement with Pauling's explanation, it is assumed that the methyl homologs of thiourea have a lower resonance stabilization than the corresponding ethyl homologs, one would expect the energetics of coördination to favor greater stability of the ethylated complexes, provided the resonance energy is not lost in complex formation, but is able to contribute to the stability of the complex, presumably by resonance involving the metal ion. The fact that diethylthiourea forms less stable complexes than ethylthiourea and that the complexes of di- and tri-methylthiourea show less stability than those of methylthiourea supports this assumption. A recent study[12] of the kinetics of decomposition of thiourea and several homologs of thiourea also suggests that alkylation of the parent thiourea molecule decreases its resonance stabilization.

In many cases of complex formation involving ligands of similar structure, differences in energies of coördination are relatively large when compared to differences in energies of solvation. Since the data presented in this paper clearly show that the order of increasing stability for the complexes of the alkyl-substituted thioureas is the same in four solvent systems of different dielectric constant and that the order is preserved for both metal ions studied, it is apparent that the observed differences in stability are due primarily to the structure of the ligand and not to the nature of the solvent or of the metal ion.

It seems probable, however, from the data in the tables that solvation does play an important role in determining the stability of the complexes of the parent molecule, thiourea. These complexes do not occupy a fixed position in the order of increasing stabilities (Tables XIV, XVI) but tend to be among the least stable in aqueous solution, of intermediate stability in the 50% mixtures and of stability comparable to the ethylthiourea complexes in 70% dioxane. This solvent effect was not unexpected. While the dipole moments for the other ligands differ by small amounts, thiourea has a dipole moment which is considerably larger.[13] Consequently, thiourea complexes would tend to dissociate more readily in a solution of high dielectric constant, such as water, whereas their dissociation would be repressed in a low dielectric medium such as 70% dioxane.

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[10] T. L. Davis and R. C. Elderfield, THIS JOURNAL, **54**, 1499 (1932).

[11] L. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1948, p. 214.

[12] W. H. R. Shaw and D. G. Walker, THIS JOURNAL, **80**, 5337 (1958).

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NOTRE DAME, INDIANA

[CONTRIBUTION NO. 522 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND COMPANY]

Synthesis and Properties of Bis-(trifluoromethylthio)-mercury

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Bis-(trifluoromethylthio)-mercury, $Hg(SCF_3)_2$, was obtained in 72% yields from carbon disulfide and mercury(II) fluoride at 250°. Physical and chemical properties of this mercurial are described.

A simple and direct synthesis of bis-(trifluoromethylthio)-mercury, $Hg(SCF_3)_2$, has been found in the reaction of mercury(II) fluoride and carbon disulfide.[1,2] The reaction, effected either in a sealed reactor or by passing the disulfide over heated HgF_2 at 250°, has given the mercurial in yields averaging 72%. Small amounts of CF_3SCF_3 and CF_3SSCF_3 are formed under these conditions. Above 300°, CF_3SSCF_3 becomes the major product. Source of the sulfides is probably the pyrolysis of

$$3HgF_2 + 2CS_2 \longrightarrow 2HgS + Hg(SCF_3)_2$$

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[1] E. L. Muetterties. U. S. Patent 2,729,663 (Jan. 3, 1956).

[2] This mercurial was first prepared by Brandt, Emeleus and Haszeldine (*J. Chem. Soc.*, 2198 (1952)) by irradiating a mixture of bis-(trifluoromethyl)-disulfide and mercury for 4 days in a sealed tube.

$Hg(SCF_3)_2$. At 350°, the mercurial does, in fact, decompose to give the disulfide and the monosulfide.

Some of the physical properties determined for $Hg(SCF_3)_2$ are listed in Table I. The mercurial tends to crystallize in plates which show birefringence under the microscope. Attempts to index the complex X-ray pattern were unsuccessful. The major features of the infrared spectrum (melt and CS_2 solution) are a broad absorption at 1100 cm.$^{-1}$ characteristic of the C–F stretch with overtones at higher wave numbers and a relatively sharp absorption at 759 cm.$^{-1}$ that may be the C–S vibration. The F^{19} magnetic resonance spectrum at 40 Mc. consists of an intense resonance at +2287 c.p.s. ($\delta CF_3COOH = O$) and two weak satellites at +2146 and +2428 c.p.s. The intense resonance is assigned to the CF_3 fluorine atoms in the $(CFS_3)_2$-Hg molecule where the mercury atoms are the even numbered isotopes (μ = O). The satellite resonances are ascribed to those molecules where the mercury atom is Hg^{199} ($I = {}^1/_2$), and the value of the F^{19}–Hg^{199} coupling constant is 258 c.p.s. Failure to see a satellite quadruplet from F^{19}–Hg^{201} coupling may be because of broadening due to quadrupole relaxation effects on the Hg^{201} nucleus ($I = {}^3/_2$ and $Q = 0.5 \times 10^{-24}$ cm.^{2}).

TABLE I

PHYSICAL PROPERTIES OF $Hg(SCF_3)_2$

M.p., °C.	39–40
F.p., °C.	39.1
Vapor pressure at 55°	3 mm.
Vapor pressure at 120°	125 mm.
Log $p = -\frac{A}{T} + B$(95° to 151°)	$A = 2551, B = 8.49$
Extrapd. b.p. (760 mm)., °C.	181.5
Heat of vaporization, kcal.	11.7
Trouton constant	25.6
$d^{25}{}_0$ (solid), g./cc.	2.911
$d^{45.4}{}_0$ (liquid), g./cc.	2.98
Mol. wt. (water – f.p. dep.)	412 (av.)
Mol. wt. (benzene – f.p. dep.)	470 (av.)
Mol. wt., theory	402.6
Absorption max. (aqueous soln.), mμ	240
Molar extinction coefficient	179

Bis-(trifluoromethylthio)-mercury is soluble in a wide range of solvents, and, in the case of donor solvents, there is significant heat evolution indicating complex formation. Several new crystalline compounds, *e.g.*, $Hg(SCF_3)_2 \cdot 2P(C_6H_5)_3$ and $Hg(SCF_3)_2 \cdot H\overset{S}{\overset{\|}{C}}N(CH_3)_2$, were isolated from the solutions. The relative stability of adducts appears to be $PR_3 > NR_3 > SR_2 > OR_2$ which order is analogous to that of mercuric halide complexes. The behavior of the mercurial as an acceptor molecule possibly explains its essentially normal molecular weight (Table I) in water, a donor molecule and its association in benzene.[3]

Most metals, *e.g.*, lead and thallium, react with $Hg(SCF_3)_2$ with formation of the corresponding metal fluoride and colored compounds of which

TABLE II

REACTIONS OF $Hg(SCF_3)_2$ WITH ORGANIC HALIDES

Halide	$Hg(SCF_3)_2$, g.	Reaction temp., °C.	Product	Yield, %	Analytical Found C	Found H	Found F	Found S	Theory C	Theory H	Theory F	Theory S	B.p., °C.	$n^{25}D$
31 g. CH_3COCl	80	~50	CH_3COSCF_3	51	25.40	2.47	39.70	22.22	25.00	2.10	39.65	22.24	80–83	1.3640
35 g. C_2H_5COCl	80	~50	$C_2H_5COSCF_3$	46	31.32	3.45	...	...	30.32	3.19	...	...	99–100	1.3754
39 g. CF_3COCl[a]	76	~40	CF_3COSCF_3	23	...	...	...	...	...	...	...	...	24–26	....
8 g. t-C_4H_9Cl	24	Reflux	$C_4H_9SCF_3$	47	38.41	5.80	35.20	...	37.98	5.74	36.10	...	78	1.3658
$C_6H_5CH_2Cl$	..	Reflux	$C_6H_5CH_2SCF_3$	..	50.36	3.45	29.97	...	50.00	3.68	29.66	...	172	....
35 g. $CH_2{=}CHCH_2Cl$[b]	60	Reflux	$C_3H_5SCF_3$	23	34.29	3.71	...	...	33.81	3.59	...	...	61	....
25 g. CCl_3SCl[b,c]	27	~30	CCl_3SSCF_3	80	10.21	42.76[d]	22.18	26.03	9.55	42.29[d]	22.66	25.49	74 (60 mm.)	1.4739

[a] Reaction run in 50 ml. of ether; product identified by F^{19} magnetic resonance spectrum. Condenser was maintained at ~ −78° to contain the low boiling CF_3COCl. [b] Reaction did not proceed until $AgNO_3$ (2 g.) was added. [c] Reaction run in 800 ml. of ether. [d] Chlorine analysis.

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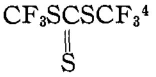
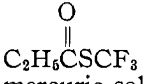
[3] The rather high Trouton constant (25.6) suggests some type of molecular association of the mercurial.

 $CF_3S\underset{\overset{\|}{S}}{C}SCF_3$[4] is one of the components. Copper powder, on the other hand, reacts to form largely mercury and the new compound, $(CuSCF_3)_x$. The mercurial does not undergo simple metathetical reactions with most inorganic and organometallic halides, such as PCl_3 and R_3SiCl; but, in water, it reacts with silver nitrate to form another new salt of the thiol, $AgSCF_3$. Alkyl, aryl and sulfenyl halides did undergo facile metathesis with the mercurial to give novel trifluoromethyl alkyl sulfides, trifluoromethyl thiolacylates and trifluoromethyl disulfides, *e.g.*, $CH_2{=}CHCH_2SCF_3$,  $C_2H_5\overset{\overset{O}{\|}}{C}SCF_3$ and CCl_3SSCF_3. Unlike most simple mercuric salts $Hg(SCF_3)_2$ does not mercurate benzene or thiophene nor does it appear to add to olefinic hydrocarbons.

Experimental

Preparation of $Hg(SCF_3)_2$.—Mercury(II) fluoride (715 g., 3 moles) and carbon disulfide (1 lb., about 6 moles) were heated at 250° for 4 hr. in a one-liter bomb lined with "Hastelloy C." After cooling to room temperature, the carbon disulfide solution of the mercury salt was separated from mercury(II) sulfide by filtration. The sulfide was characterized by X-ray analysis and was shown to be the hexagonal form. The carbon disulfide solution was evaporated, and the low melting solid residue was distilled at 80–81° (21 mm.). Yields of mercury salt obtained ranged from 250–390 g. (average yield, 72%).

Anal. Calcd. for $HgS_2C_2F_6$: C, 5.95; Hg, 49.80. Found: C, 5.83; Hg, 50.96.

A nickel tube (~2" i.d.) was packed with 200 g. of HgF_2 and heated to 250°. Carbon disulfide was volatilized in a stream of nitrogen and passed through the nickel tube for a period of about 3 hr. Volatile products (4 g.) consisted of CF_3SSCF_3 and unreacted CS_2. A total of 43 g. of $Hg(SCF_3)_2$ was recovered from the cooler portions of the reactor tube (yield based on ~36 g. CS_2 = ~48%).

Reaction of mercury(II) fluoride and carbon disulfide at 460° in a sealed vessel gave no $Hg(SCF_3)_2$. Bis-(trifluoromethyl) disulfide was obtained in 23% yield along with small amounts of carbon tetrafluoride.

The mercurial was pyrolyzed in the pressure vessel at 350° for 5 hr. and infrared analysis of the volatile products showed the presence of CF_3SCF_3 and CF_3SSCF_3.

Physical Properties.—Vapor pressure measurements were made with a quartz spiral manometer. Vapor pressures in millimeters are 50°, 2.4; 80°, 18; 90°, 27.5; 100°, 45; 105°, 52; 110°, 65; 115°, 82.5; 120°, 98; 125°, 120; 130°, 147; 135°, 176; 140°, 208; 145°, 247; 150°, 291.

Chemical Properties.—A. Reaction with Donor Molecules.—$Hg(SCF_3)_2$ evolved heat when dissolved in amines, amides, thioamides, thioesters and sulfoxides, and complexes were crystallized from solutions of the base and the mercurial in dimethoxyethane.

$Hg(SCF_3)_2{\cdot}2P(C_6H_5)_3$, m.p. 166–168° dec. *Anal.* Calcd.: Hg, 21.64; P, 6.69; F, 12.30. Found: Hg, 22.33; P, 7.08; F, 13.07. $Hg(SCF_3)_2{\cdot}HCSN(CH_3)_2$, m.p. 91–92°. *Anal.* Calcd.: S, 19.53; Hg, 40.75; C, 12.23; N, 2.85. Found: S, 19.14; Hg, 39.95; C, 12.46; N, 2.87.

A crystalline solid melting at 85–86° was obtained with trimethylamine but this compound proved rather reactive. It was visibly decomposed on standing before analysis although the carbon value found, 12.42, checked well with the calculated value of 12.99 for a 1:1 complex. The mercurial dissolved in acetonitrile without significant heat evolution. However, evaporation of the solution *in vacuo* (<1 mm.) for 36 hr. yielded no solid but a mobile liquid that contained slightly more than 1% nitrogen by analysis. Similarly, solutions of the mercurial in diethyl ether and in tetramethylene sulfide yielded mobile liquids that, respectively, contained ether and thioether. Addition of tetramethylene sulfide to the diethyl etherate liberated diethyl ether.

B. Reaction with Metals and with $AgNO_3$.—$CuSCF_3$ was prepared by warming a mixture of 6 g. of finely divided copper and 9 g. of $Hg(SCF_3)_2$. At 80–100°, an exothermic reaction took place with the development of a bright orange color. Heating was continued for 30 min. at 150°. After cooling, the solid products were extracted with 500 ml. of ether and evaporation of the extract left a pale green residue of $CuSCF_3$ that could not be completely freed of ether.

Anal. Calcd. for $CuSCF_3$: Cu, 38.60; C, 7.30. Found: Cu, 36.14; C, 8.95.

The copper compound readily complexed with basic solvents and recrystallization from acetonitrile resulted in a 1:1 adduct.

A slurry of thallium amalgam and a dimethoxyethane solution of $Hg(SCF_3)_2$ was warmed to about 50° for 30 min. The slurry was filtered and evaporated. The residue was largely thallium(I) fluoride. Lead powder reacted at ~100° to form lead fluoride and volatile organofluorine compounds. Infrared analysis of the latter indicated  $CF_3S\underset{\overset{\|}{S}}{C}SCF_3$ was present.

$AgSCF_3$ was prepared by adding a solution of 11 g. of silver nitrate in 100 ml. of water to 20 g. of $Hg(SCF_3)_2$ slurried in 100 ml. of water. A white precipitate formed immediately. After stirring for 0.5 hr., the slurry was filtered, and the solid product was washed with water and ether. Yield of crude product was 16 g.; it was recrystallized from acetone.

Anal. Calcd. for $AgSCF_3$: Ag, 51.70; C, 5.74. Found: Ag, 53.70; C, 5.32.

C. Reaction with Organic Halides.—The reactions with organic halides are summarized in Table II.

Toxicity of $Hg(SCF_3)_2$.—Serious skin burns result from contact with $Hg(SCF_3)_2$. Acute oral toxicity tests indicated an approximate lethal dose (ALD) in male albino rats of 130 mg./kg. Acute gastritis was found in animals that died, and there was evidence of injury to the stomach and kidneys in survivors sacrificed 10 days later. The ALD on the basis of mercury content, as well as its other toxic properties, is characteristic of other vesicant mercury compounds such as the mercury phosphates. The sweet and penetrating odor of the mercurial is unmistakable even at 20° where the vapor pressure is less than 0.1 mm.

Acknowledgment.—The toxicity information on bis-(trifluoromethylthio)-mercury was obtained from the Haskell Laboratory for Toxicology and Industrial Medicine of the du Pont Company. We are indebted to Mr. Charles Wortz who made some of the physical measurements.

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[4] This compound has been prepared by Haszeldine and Kidd (*J. Chem. Soc.*, 3871 (1955)) by reaction of CF_3SH and NH_3.

[5] We are grateful to Dr. J. F. Harris of this Laboratory for carrying out this preparation.