290. *The Formation of Halogenoperfluoroalkylmercurates.*[1]

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Conductometric titrations of perfluoroalkylmercury compounds with potassium halides and ammonium thiocyanate indicate the formation of halogenoperfluoroalkylmercurate(II) anions in aqueous solution. Addition of solutions containing the 5 : 6-benzoquinolinium ion or the ethylenediamine complexes of zinc(II), copper(II), cadmium(II), or nickel(II) to mixed solutions of alkali iodides and bis(trifluoromethyl)mercury, trifluoromethylmercuric iodide, or heptafluoro-*n*-propylmercuric iodide precipitates salts containing the anions $[Hg(CF_3)I_3]^{2-}$, $[Hg(CF_3)_2I_2]^{2-}$, or $[Hg(C_3F_7)I_3]^{2-}$.

THE existence of anions containing the trifluoromethyl group has been established in the trifluoromethylantimonic acid series,[2] and the experiments described below were made to determine if analogous halogenoperfluoroalkylmercurate(II) anions are also stable. Such anions would be derivatives of tetrahalogenomercurate(II) ions, which are well known, and for which the stability decreases in the order iodo- > bromo- > chloro-. The ion $(HgF_4)^{2-}$ is known but is hydrolysed by water. It was found in preliminary experiments that the *X*-ray diffraction pattern of the residue on evaporation of an aqueous solution of a potassium halide and bis(trifluoromethyl)mercury, or heptafluoro-*n*-propylmercuric

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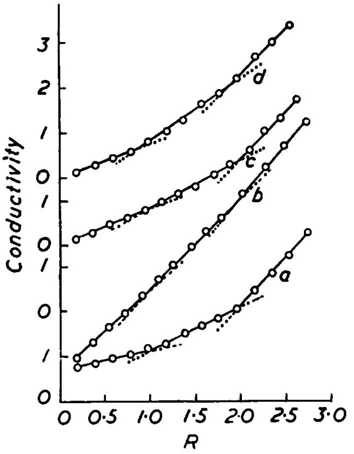
[1] For a preliminary account of this work, see Emeléus and Lagowski, *Proc. Chem. Soc.*, **1958**, **231**.
[2] Emeléus and Moss, *Z. anorg. Chem.*, 1955, **282**, 24.

iodide, in a 1 : 1 or 2 : 1 molar ratio did not contain lines characteristic of the reactants. With a ratio 3KI : $Hg(CF_3)_2$, the characteristic lines of potassium halide were observed, but none of those of the mercurial. Moreover, whereas heptafluoro-*n*-propylmercuric iodide was very sparingly soluble in water, it dissolved readily in presence of halide ions. These observations led to an examination of the formation of halogenoperfluoroalkylmercurate(II) ions by conductometric titration. Typical results are shown in the Figure for titration of aqueous solutions of bis(trifluoromethyl)mercury with potassium (*a*) chloride, (*b*) thiocyanate, (*c*) iodide, and (*d*) bromide. The abscissæ are all on the same scale but are adjusted vertically for clarity. The mercurial itself has a small conductivity,[3] and this is increased by addition of halide, though by less than would arise from the halide alone. Breaks are expected to accompany the formation of new ionic species only if there are relatively large changes in ionic mobility and also in thermodynamic stability. The evidence afforded by the titration results is not, therefore, decisive but must be considered in conjunction with the preparative work described later which has led to the isolation of compounds containing some of the ions postulated.

The results for the three halides in the Figure could be fitted to smooth curves but, the preparative work being borne in mind, it is justifiable to represent them as falling on straight lines which intersect in each case at halide : mercurial ratios of 1 : 1 and 1 : 2, indicating the formation of the new ionic species $[Hg(CF_3)_2X]^-$ and $[Hg(CF_3)_2X_2]^{2-}$. No compounds containing ions of the first type have been prepared, though two were made which contained $[Hg(CF_3)_2I_2]^{2-}$ (see Table). The results of the titration with ammonium thiocyanate (Fig., *b*) were inconclusive since no breaks were found.



Plot of conductivity × 10^2 (*ohm*$^{-1}$ *cm.*$^{-1}$) *against R, the ratio of halide to* $Hg(CF_3)_2$ *concentration* (*mole l.*$^{-1}$).

In the titration of trifluoromethylmercuric bromide with the same halides there were breaks at 1 : 1 and 1 : 2 for potassium iodide and at 1 : 2 for the bromide, but no breaks were observed with potassium chloride. The formation of $[Hg(CF_3)BrI]^-$, $[Hg(CF_3)BrI_2]^{2-}$, and $[Hg(CF_3)Br_3]^{2-}$ may be deduced, but it is probable that $[Hg(CF_3)Br_2]^-$, $[Hg(CF_3)BrCl]^-$, and $[Hg(CF_3)BrCl_2]^{2-}$ are unstable. In the titration of trifluoromethylmercuric iodide with potassium chloride, bromide, and iodide there are in each case breaks at halide : mercurial ratios of 1 : 1 and 1 : 2, indicating the formation in solution of the ionic species $[Hg(CF_3)IX]^-$ and $[Hg(CF_3)IX_2]^{2-}$ (X = Cl, Br, or I), and several derivatives containing the ion $[Hg(CF_3)I_3]^{2-}$ were isolated (Table). There were no clear breaks in the titration curves for ammonium thiocyanate in this case. With heptafluoro-*n*-propylmercuric iodide breaks occurred at 1 : 1 and 2 : 1 ratios with potassium iodide and bromide, and with potassium chloride there was an ill-defined break at a 1 : 2 ratio. These results can be interpreted in the same way, those for the potassium iodide titration being supported by

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[3] Emeléus and Haszeldine, *J.*, 1949, 2948, 2953.

the preparation of a compound containing $[Hg(C_3F_7)I_3]^{2-}$. It seems from this evidence that the anions become less stable in passing from the iodo- to the chloro-type.

Anionic complexes of mercury containing organic radicals, other than cyanide, have not been previously reported, although compounds of the type $LiMPh_3$ have been characterised for the other elements of Group IIB.[4] Their relative stabilities are in the order $LiZnPh_3 > LiCdPh_3 > LiPh + HgPh_2$ (no compound formed). The nature of these compounds is unknown, but the order of stability is the reverse of that of the tetrahalogenometallate ions. Only zinc alkyls react with alkyls of the alkali or the alkaline-earth metals to form compounds containing tetra-alkylmetallate ions[5] and, though perfluoroalkyl derivatives of zinc[6] and cadmium[7] have been described, no derived complexes, other than solvates of the zinc compounds, are known.

The interpretation of the results of conductometric titrations is supported by the preparation of compounds containing halogenoperfluoroalkylmercurate ions. Salts of ethylenediamine–transition metal complexes were chosen as precipitating reagents because they give insoluble compounds with tetrahalogenomercurate anions. The compounds containing tris(ethylenediamine)zinc(II) or bis(ethylenediamine)cadmium(II) were white, those with tris(ethylenediamine)nickel(II) violet, and those with bis(ethylenediamine)-copper(II) dark purple. All resembled the corresponding compounds containing the tetrahalogenomercurate anions. The insoluble compounds isolated contained $[Hg(CF_3)I_3]^{2-}$, $[Hg(C_3F_7)I_3]^{2-}$, or $[Hg(CF_3)_2I_2]^{2-}$ (see Table). Attempts to isolate bromo- and chloro-perfluoroalkylmercurate derivatives of the cations examined were unsuccessful, although tetraphenylarsonium chloride, when added to an aqueous solution of bis(trifluoromethyl)mercury containing chloride ions, gave an immediate white precipitate which gave trifluoromethane on alkaline hydrolysis. This preliminary result indicates that derivatives of other anions could probably be isolated by a suitable choice of cation, but the relative stabilities of anions cannot be deduced from the ease of isolation of these derivatives. Aqueous solutions of trifluoromethylmercuric iodide containing potassium iodide lose trifluoromethane forming a yellow solution which presumably contains tetra-iodomercurate ions.[1] A similar decomposition may have occurred in the attempted preparation of bis(ethylenediamine)cadmium(II) di-iodobis(trifluoromethyl)mercurate(II), the product from which contained too high a proportion of iodine. The decomposition in presence of iodide ion probably occurs as follows:

$$Hg(CF_3)_2I_2^{2-} + I^- + H_2O \longrightarrow Hg(CF_3)I_3^{2-} + CHF_3 + OH^-$$

$$Hg(CF_3)I_3^{2-} + I^- + H_2O \longrightarrow HgI_4^{2-} + CHF_3 + OH^-$$

Tris(ethylenediamine)zinc(II) di-iodobis(trifluoromethyl)mercurate(II) and tris(ethylenediamine)nickel(II) di-iodobis(trifluoromethyl)mercurate(II) dissolve in hot water or hot aqueous potassium iodide solutions and liberate trifluoromethane quantitatively. Cations which would not form precipitates with di-iodobis(trifluoromethyl)mercurate anions readily did so in 70—80% yield with tri-iodo(trifluoromethyl)mercurate(II) ions. Tris(ethylenediamine)zinc(II), bis(ethylenediamine)copper(II), tris(ethylenediamine)-nickel(II), bis(ethylenediamine)cadmium(II), and di-(5 : 6-benzoquinolinium) tri-iodo(trifluoromethyl)mercurate(II) were soluble, with reaction, in hot water, and trifluoromethane was formed quantitatively. In decomposing these compounds for analysis it was found that the $Hg-C_3F_7$ bond was less readily broken than $Hg-CF_3$. An attempt to isolate silver tri-iodoheptafluoro-*n*-propylmercurate(II) by the addition of silver nitrate to a solution of heptafluoro-*n*-propylmercuric iodide containing potassium iodide (all substances in stoicheiometric amounts) was unsuccessful: there was an immediate precipitate of silver iodide which was identified by its *X*-ray pattern.

[4] Wittig and Hornberger, *Annalen*, 1952, **557**, 11.

[5] Hurd, *J. Org. Chem.*, 1948, **13**, 711; Gilman, Meals, O'Donnell, and Woods, *J. Amer. Chem. Soc.*, 1943, **65**, 268; Gilman and Woods, *ibid.*, 1945, **67**, 520.

[6] Haszeldine and Walaschewski, *J.*, 1953, 3607; Miller, Bergman, and Fainberg, *J. Amer. Chem. Soc.*, 1957, **79**, 4159.

[7] Haszeldine, *Nature*, 1951, **168**, 1028.

EXPERIMENTAL

Trifluoromethylmercuric iodide, m. p. 112°, was prepared by irradiating trifluoroiodomethane with mercury and was then converted into trifluoromethylmercuric bromide, m. p. 83°. Bis(trifluoromethyl)mercury was prepared from trifluoroiodomethane and cadmium amalgam.[3] Mercury (10 ml.) was sealed with heptafluoroiodopropane [7] in an evacuated tube and heated at 220° for 24 hr. in a rocking furnace. The white crystalline product was extracted with ether and gave *heptafluoro*-n-*propylmercuric iodide* (10·4 g.) which was sublimed at 80° in nitrogen to lustrous white plates, m. p. 77·0—77·5° (Found: C_3F_7, 34·1; I, 25·2%. C_3F_7IHg requires C_3F_7, 34·0; I, 25·6%), soluble in common organic solvents but not in water. Heptafluoroiodopropane (4·89 g.) was recovered.

Conductivities were measured at 20° in a cell of 5 ml. capacity, closed by a rubber serum cap, through which the potassium halide solution was added with a calibrated Agla micrometer syringe. About 4 ml. of mercurial solution of known concentration were used, the cell being shaken after each addition of titrant. Measurements were made with an A.C. bridge with a visual null-point indicator.[8] Since the volume of titrant was not negligible compared with the volume of mercurial solution, the resistance measurements were corrected for dilution. All solutions were prepared in distilled water except those of heptafluoro-*n*-propylmercuric iodide, which was dissolved in aqueous methanol (1 : 1 w/w). All the mercurials were resublimed immediately before use. Samples for *X*-ray examination were prepared by dissolving stoicheiometric mixtures of potassium halide and bis(trifluoromethyl)mercury or heptafluoro-*n*-propylmercuric iodide in acetone, with the addition of a little water in the case of potassium chloride and bromide. The solvent was evaporated in a vacuum at room temperature, and the samples were handled subsequently in a dry-box in nitrogen.

The same general procedure was used in preparing all the compounds containing the halogenoperfluoroalkylmercurate ions: details are given for the typical preparation of tris(ethylenediamine)zinc(II) tri-iodo(trifluoromethyl)mercurate(II). Analytical data for the remaining compounds are given in the Table.

$Cu(C_2H_8N_2)_2HgCF_3I_3$	Found (%)	Reqd. (%)
I	45·1	45·6
Hg	24·7	24·1
Cu	7·28	7·63
CF_3	8·15	8·29

$Ni(C_2H_8N_2)_3HgCF_3I_3$	Found (%)	Reqd. (%)
I	42·3	42·85
Hg	22·3	22·5
Ni	6·38	6·61
CF_3	7·35	7·77
N	10·0	9·47

$Cd(C_2H_8N_2)_2HgCF_3I_3$	Found (%)	Reqd. (%)
I	42·95	43·1
Hg	22·6	22·7
Cd	12·5	12·7
CF_3	7·50	7·81

$(C_{13}H_9NH)_2HgCF_3I_3$	Found (%)	Reqd. (%)
I	37·9	37·6
Hg	19·8	19·9
CF_3	6·66	6·80
N	3·08	2·78

$Zn(C_2H_8N_2)_3HgC_3F_7I_3$	Found (%)	Reqd. (%)
I	38·5	38·2
Zn	7·10	6·55
C_3F_7	16·6	17·0
N	8·65	8·43

$Zn(C_2H_8N_2)_3Hg(CF_3)_2I_2$	Found (%)	Reqd. (%)
I	30·4	30·3
Hg	23·4	23·95
Zn	7·91	7·97
CF_3	16·0	16·5

$Ni(C_2H_8N_2)_3Hg(CF_3)_2I_2$	Found (%)	Reqd. (%)
I	30·6	30·45
CF_3	16·1	16·6
N	9·77	10·0

Preparation of Tris(*ethylenediamine*)*zinc*(II) *Tri-iodo*(*trifluoromethyl*)*mercurate*(II).—To 2M-aqueous potassium iodide (10 ml.) was added trifluoromethylmercuric iodide (0·105 g.) followed by a two-fold excess of tris(ethylenediamine)zinc(II) sulphate, prepared by dissolving the required amount of zinc sulphate in 1M-potassium iodide and adding excess of ethylenediamine. A fine white granular precipitate formed immediately and was filtered on a sintered crucible, washed with cold water, ethanol, and ether, and kept in an evacuated desiccator for 30 min. The dry product weighed 0·195 g. (82% yield on trifluoromethylmercuric iodide) [Found: I, 43·0; Zn, 7·56; CF_3, 7·40%. $Zn(C_2H_8N_2)_3HgCF_3I_3$ requires I, 42·5; Zn, 7·30; CF_3, 7·60%].

In an attempt to prepare bis(ethylenediamine)cadmium(II) di-iodobis(trifluoromethyl)-mercurate(II), a solution prepared from 2M-potassium iodide (20 ml.) and bis(trifluoromethyl)mercury was mixed with excess of a solution of bis(ethylenediamine)cadmium(II) sulphate. A white solid (0·0956 g.) formed after 4 hr. [Found: I, 45·8; CF_3, 2·20%. Calc. for

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[8] Haszeldine and Woolf, *Chem. and Ind.*, 1950, 544.

$Cd(C_2H_8N_2)_2Hg(CF_3)_2I_2$: I, 30·75; CF_3, 16·7%. Calc. for $Cd(C_2H_8N_2)_2HgCF_3I_3$: I, 43·9; CF_3, 7·77%. Calc. for $Cd(C_2H_8N_2)_2HgI_4$: I, 53·85%]. Similar analytical results were obtained in attempts to prepare bis(ethylenediamine)copper(II) di-iodobis(trifluoromethyl)mercurate(II) and di-(5 : 6-benzoquinolinium) di-iodobis(trifluoromethyl)mercurate(II).

Trifluoromethyl and heptafluoropropyl groups were estimated by heating in a sealed tube at 100° for 4 hr. with 15% sodium hydroxide and measuring the CHF_3 or C_3F_7H produced. Zinc was determined as zinc–2-methylquinoline monohydrate,[9] cadmium as cadmium–dipyridine thiocyanate,[10a] nickel as either nickel sulphide or nickel–dipyridine thiocyanate,[10b] copper as bis(ethylenediamine)copper(II) tetraiodomercurate(II), and mercury as mercuric sulphide or bis(ethylenediamine)copper(II) tetraiodomercurate(II).[10c] Compounds containing the di-iodobis(trifluoromethyl)mercurate(II) or tri-iodotrifluoromethylmercurate(II) anion were decomposed for analysis by hot dilute acetic acid. Compounds containing the Hg–C_3F_7 bond were decomposed by hot alcoholic potassium hydroxide. Infrared spectra were recorded as Nujol mulls.

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[9] Flagg, " Organic Reagents Used in Gravimetric and Volumetric Analysis," Interscience Publishers Inc., New York, 1948, 255.

[10] Vogel, " Quantitative Inorganic Analysis," Longmans, Green and Co., London, 1951, (*a*) p. 429, (*b*) p. 458, (*c*) p. 433.