457. Some Complex Compounds of Fluoroalkyl- and Fluoroaryl-mercurials.

By H. B. POWELL, MAUNG TIN MAUNG, and J. J. LAGOWSKI.

Complex compounds of the type $Hg(R_f)_2L$ and $Hg(R_f)_2L_2$ (R_f = fluoroalkyl and fluoroaryl; L = piperidine, pyridine, triphenylphosphine, triphenylarsine, acetone, ethanol, dimethyl sulphoxide, pyridine *N*-oxide, tri-(*p*-tolyl) thiophosphate, and dimethyl sulphide) have been shown by oscillometric titration to exist in benzene solution.

COMPLEX compounds of mercuric halides and pseudohalides have been reported with the neutral donor ligands triphenylphosphine,[1] triphenylarsine,[1] dimethyl sulphoxide,[2] and certain amines; [3] the stoicheiometry of these compounds is usually represented by either HgX_2L or HgX_2L_2. Little is known about the relative stability of these complexes except that oxygen is apparently a very weak electron-donor to mercury and that those of type HgX_2L are less stable than the corresponding HgX_2L_2 complexes. Some mercury complexes with pyridine *N*-oxide, dimethyl sulphoxide, tetrahydrothiophen oxide, and thioxan oxide have recently been formulated to contain sexi-co-ordinated mercury.[4] No co-ordination compounds of alkyl- or aryl-mercurials with neutral ligands have been reported previously, although the species $[MeHgOH_2]^+$ and $[MeHgSMe_2]^+$ were recently postulated to explain the Raman lines observed for aqueous solutions of methylmercuric

---

[1] Cass, Coates, and Hayter, *J.*, 1955, 4007; Evans, Mann, Peiser, and Purdie, *J.*, 1940, 1209.

[2] Meek, Straub, and Drago, *J. Amer. Chem. Soc.*, 1960, **82**, 6013.

[3] Sidgwick, " The Chemical Elements and Their Compounds," Oxford Univ. Press, 1950, Vol. I, pp. 327—333 and references therein.

[4] Carlin, Roitman, Dankleff, and Edwards, *J. Inorg. Chem.*, 1962, **1**, 182.

nitrate.[5] Bis(trifluoromethyl)mercury forms complex ions with halide ions,[6] and an aquo-species of this compound has been suggested to explain the conductivity of aqueous solutions of $(CF_3)_2Hg$.[7] We now present evidence that fluoroalkyl- and fluoroaryl-mercurials form complex compounds with a variety of neutral ligands in benzene solution. Because some of these complex compounds are difficult to isolate and the supply of several of the mercurials was limited, oscillometric titrations of benzene solutions of the mercurial and ligand were employed to demonstrate the existence of the complexes.

Oscillometric techniques have been used for classical acid–base titrations [8] and have recently been adapted to studying the interactions between electron-pair donor and acceptors.[9] Oscillometry employs an oscillating or resonant circuit (1—10 megacycles) in which are incorporated the electrical properties of the substance under investigation. The substance is coupled to the circuit by making it the principal dielectric component of a condenser cell (see Fig. 1). During a titration, the addition of titrant changes the electrical properties of the circuit, which in turn alters the capacitance and natural frequency of the circuit. The circuit can be brought back into resonance by varying an external capacitance. Both the dielectric constant and conductivity of the sample contribute to the electrical properties of the circuit, but in solvents such as benzene where conductivity can be neglected the principal effect on the oscillating circuit is a change in the capacitance. Since this depends on the dipole moment of the titrant, inflections in the plot of instrument reading (arbitrary units that are proportional to the capacitance of the solution) against the volume of titrant added are attributed to a change in the nature of the species in solution. Oscillometric titrations (cf. Fig. 2) indicate that all the mercurials studied form both 1 : 1 and 2 : 1 (mole ratio of ligand to mercurial) complex compounds with piperidine, pyridine, triphenylphosphine, dimethyl sulphoxide, ethanol, and pyridine *N*-oxide in benzene solution (see Table). Several of the mercurials were titrated with these

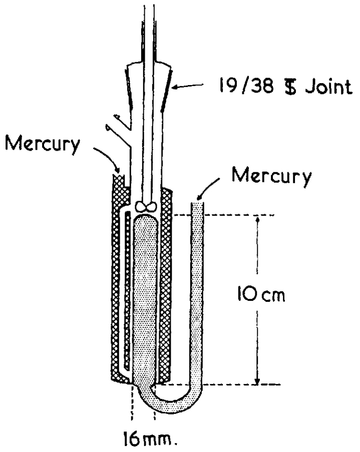

FIG. 1. Oscillometric titration cell (designed by Robert E. Cuthrell of this laboratory). (1½ mm. between cell walls.)

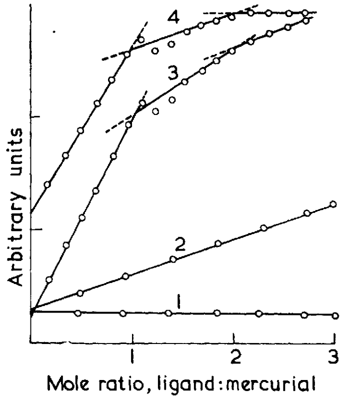

FIG. 2. Oscillometric titration curve for the titration of (1) $(CF_3)_2Hg$ with pure solvent, (2) solvent with piperidine, and (3) $(CF_3)_2Hg$ with piperidine; (4) is the differential curve for the titration of $(CF_3)_2Hg$ with piperidine.

---

[5] Goggin and Woodward, *Trans. Faraday Soc.*, 1962, **58**, 1495.

[6] Emeléus and Lagowski, *J.*, 1959, 1497.

[7] Lagowski, Ph.D. Diss., Cambridge, 1959.

[8] Pungor, *J. Electroanalyt. Chem.*, 1962, **3**, 289; see also articles in *Analyt. Chem.*, 1952, **24**, 1236, *et seq.*

[9] Powell and Lagowski, Proc. Seventh Internat. Conference on Co-ordination Chemistry, Stockholm, Sweden, June 1962, p. 223; Hitchcock and Elving, *ibid.*, p. 226.

Results of the oscillometric titrations of some fluoroalkyl- and fluoroaryl-mercurials with selected ligands.

	$C_5H_{11}N$	C_5H_5N	PPh_3	$AsPh_3$	Me_2CO	EtOH	Me_2SO	C_5H_5NO	$(p\text{-}C_7H_7O)_3PS$	Me_2S
$(CF_3)_2Hg$	1 : 1 M*	1 : 1 M	1 : 1 S	—†	1 : 1 D	1 : 1 M	1 : 1 M	1 : 1 W	1 : 1 M	1 : 1 M
	2 : 1 M	2 : 1 M	2 : 1 W	2 : 1 D	—	2 : 1 W	2 : 1 W	2 : 1 W	2 : 1 W	2 : 1 W
$(C_2F_5)_2Hg$	1 : 1 M	1 : 1 M	1 : 1 D	1 : 1 W	1 : 1 W	1 : 1 W	1 : 1 M	1 : 1 M	—	1 : 1 M
	2 : 1 M	2 : 1 M	2 : 1 M	2 : 1 D	2 : 1 W	2 : 1 W	2 : 1 W	2 : 1 M	2 : 1 W	2 : 1 M
$[(CF_3)_2CF]_2Hg$ ...	1 : 1 M	1 : 1 S	1 : 1 M	1 : 1 D	1 : 1 M	1 : 1 D	1 : 1 S	1 : 1 S	1 : 1 W	
	2 : 1 S	2 : 1 W	2 : 1 M	2 : 1 W	2 : 1 W	2 : 1 M	2 : 1 D	2 : 1 S	—	
$(CF_3{\cdot}CFH)_2Hg$ ...	1 : 1 S	1 : 1 M	1 : 1 W	1 : 1 D	1 : 1 W	1 : 1 M	1 : 1 W	1 : 1 D	1 : 1 D	1 : 1 S
	2 : 1 M	2 : 1 W	2 : 1 W	—	—	2 : 1 M	2 : 1 M	2 : 1 W	2 : 1 W	2 : 1 M
$(CF_3{\cdot}CH_2)_2Hg$ ...	1 : 1 D	1 : 1 W	1 : 1 W	1 : 1 W	1 : 1 M	1 : 1 M	1 : 1 M	1 : 1 W	—	1 : 1 D
	2 : 1 W	2 : 1 W	2 : 1 W	—	—	2 : 1 W	2 : 1 W	2 : 1 M	—	2 : 1 D
$(o\text{-}CF_3{\cdot}C_6H_4)_2Hg$	1 : 1 S	1 : 1 M	1 : 1 S	1 : 1 M	1 : 1 M	1 : 1 M	1 : 1 M	1 : 1 M	1 : 1 W	
	2 : 1 S	2 : 1 W	2 : 1 W		2 : 1 M	2 : 1 M	2 : 1 S	2 : 1 D	2 : 1 D	
$(m\text{-}CF_3{\cdot}C_6H_4)_2Hg$	1 : 1 M	1 : 1 M	1 : 1 M	1 : 1 S	1 : 1 M	1 : 1 D	1 : 1 M	1 : 1 D	1 : 1 W	
	2 : 1 W	2 : 1 W	2 : 1 M	2 : 1 S	2 : 1 M	2 : 1 W	2 : 1 S	2 : 1 W	—	
$(p\text{-}CF_3{\cdot}C_6H_4)_2Hg$	1 : 1 S	1 : 1 D	1 : 1 W				1 : 1 M			
	2 : 1 M	2 : 1 W	2 : 1 D				2 : 1 M			
Ph_2Hg	1 : 1 S	1 : 1 D	1 : 1 W	1 : 1 W	1 : 1 M	1 : 1 W	1 : 1 M	1 : 1 D	1 : 1 W	
	2 : 1 S	2 : 1 W	2 : 1 M	2 : 1 D	2 : 1 M	2 : 1 M	2 : 1 M	2 : 1 W	2 : 1 D	

* S = strong, M = medium, W = weak, D = doubtful; this does not necessarily indicate the relative strengths of the complexes formed. † The titration was performed, but no inflection was observed.

ligands to mole ratios greater than 2 : 1, but there was no indication that higher complexes were formed. All mercurials studied formed a 1 : 1 and a 2 : 1 complex with acetone except $(CF_3)_2Hg$, $(CF_3{\cdot}CHF)_2Hg$, and $(CF_3{\cdot}CH_2)_2Hg$ which formed only 1 : 1 complexes.

It is perhaps surprising that bis(trifluoromethyl)mercury does not form a 2 : 1 complex whereas bis(pentafluoroethyl)mercury does, since the electronic effects of these two perfluoroalkyl groups on the mercury atom are essentially the same.[10] In general, the inflections in the titration curves obtained on using acetone, triphenylarsine, and tri-(*p*-tolyl) thiophosphate as the ligands were less distinct than those observed with other ligands.

Because of its volatility and the resulting difficulties in its use as a titrant, dimethyl sulphide was used in only four titrations.

It is interesting that complex formation is indicated with diphenylmercury and with methylmercuric chloride. Complexes of the latter could be of the type which Goggin and Woodward [5] suggested exist in aqueous solution; however their solubility in benzene does not indicate an ionic structure.

The absence of an inflection in a titration curve does not preclude the formation of a complex. The slopes of oscillometric titration curves obtained on using benzene as a solvent depend primarily on a change in the dielectric constant of the solution, and a change in slope occurs because the nature of the species present in solution changes. Since the dielectric constant of these solutions depends on the dipole moment of the species present as well as on the dielectric constant of the solvent, an unfavourable combination of dipole moment of the species being destroyed and of that being produced in a titration could produce a break not readily detected with the equipment employed.

EXPERIMENTAL

Bis(trifluoromethyl)- and bis(pentafluoroethyl)-mercury were prepared by Emeléus and Haszeldine's method,[11] and bis-(1,2,2,2-tetrafluoroethyl)-, bis-(2,2,2-trifluoroethyl)-, and bis-(heptafluoroisopropyl)-mercury by Krespan's method.[12]

Bis-(*o*-, *m*-, and *p*-trifluoromethylphenyl)mercury were prepared from the corresponding

---

[10] Lagowski, *Quart. Rev.*, 1959, **13**, 233; Powell and Lagowski, *J.*, 1962, 2047.

[11] Emeléus and Haszeldine, *J.*, 1949, 2953.

[12] Krespan, *J. Org. Chem.*, 1960, **25**, 105.

trifluoromethylphenyl iodides through the lithium derivatives; the latter were prepared in ether [13] and treated with the required quantity of mercuric chloride to form the mercurials.[14]

A Sargent model V oscillometer equipped with a cell compensator was used in all the titrations. Except for some early exploratory work, titrations were conducted with the cell compensator set at 800 units; the oscillometer was balanced against the standard capacitor incorporated in the cell compensator.

The authors thank Miss Patricia Janda for her assistance in the titrations with acetonitrile as solvent, the Robert A. Welch Foundation for a fellowship (H. B. P.), and the Burmese Government for a scholarship (M. T. M.).

DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF TEXAS,
AUSTIN 12, TEXAS, U.S.A.

[*Received, October* 11*th*, 1962.]

---

[13] Pierce, McBee, and Judd, *J. Amer. Chem. Soc.*, 1954, **76**, 474.

[14] Maung Tin Maung, M.S. Thesis, University of Texas, 1962.