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Addition Compounds of Bis(trifluoromethyl)mercury with Tetraphenylphosphonium and Tetraphenylarsonium Halides and Thiocyanates

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Abstract

Addition compounds of $Hg(CF_3)_2$ with $[Ph_4P]X$ and $[Ph_4As]X$ in the 1:1 ratio for X = Cl, Br, I, as well as in the 1:2 ratio for X = SCN, were isolated from aqueous solution and identified by elemental analysis and infrared spectroscopy. Molar conductance of the thiocyanate compounds in nitrobenzene solution points to its complex-salt nature defined as $[Ph_4P]_2[Hg(CF_3)_2(SCN)_2]$ and $[Ph_4As]_2[Hg(CF_3)_2(SCN)_2]$, but not for the halide compounds. However, in the monoclinic crystals of the choride compound, as shown by X-ray diffractometry, pairs of $Hg(CF_3)_2$ molecules are bridged over by two chlorides in a centro-symmetrical dimer with the CHgC bond angle of 160.5(8)° and the Hg...Cl bond length of 2.823(3) and 2.837(4) Å. The structure was refined to the *R* factor of 0.053. When X = CN no addition compounds were obtained, the reaction products were HCF_3 and the complex salts $[Ph_4P]_2[Hg(CN)]_4$ and $[Ph_4As]_2[Hg(CN)]_4$, not described so far.

Introduction

The coordination ability of mercury in organomercurials is small. This well known fact has not yet been understood properly because mercury in its inorganic compounds has a strong tendency to increase its coordination by interacting with the atoms from the surroundings. The effective coordination of mercury, actually observed in crystal structure, is based upon the characteristic coordination [1] but with a more or less deformed geometry according to the strength and direction of the interaction.

Diphenylmercury in the adduct with dimethyl and tetramethyl 1,10-phenanthroline [2] retains the C–Hg–C collinearity, while perfluorated diphenylmercury in the adduct with bis(diphenylarsino)methane [3] loses it to the value of 173° for the C–Hg–C bond angle. That the ligand effect on the R–Hg–R geometry depends upon the nature of R is evidenced also by the C–Hg–C bond angle of 165.6° in bis(phenylethynyl)mercury in the adduct with 1,10-phenanthroline [4, 5] as well as the Hg...N distances of 2.68 Å as compared with 2.85 Å in the analogous diphenylmercury adduct [2].

Mixed organomercurials, RHgX, are more susceptible to deformation under the influence of ligands. The C–Hg–C angle in 1,10-phenanthroline adduct with phenylmercury cyanide [6, 7] and trichloromethylmercury chloride [8] is 167.5 and 150°, respectively. In the reaction of neutral ligands with salt-like organomercurials the X in RHgX is replaced by the ligand, giving $RHgL^+X^-$ as in the case of methylmercury nitrate with 1,10-phenanthroline [9] and 3,3-bipyridyl [10].

In perfluorated organomercurials mercury has a considerably stronger acceptor ability as shown already by Emeléus and Lagowski for bis(trifluoromethyl)mercury [11]. They proved the existence of the $Hg(CF_3)_2X^-$ and $Hg(CF_3)_2X_2^{2-}$ anions in aqueous solution for X = Cl, Br, I, but were able to isolate only complexes containing $Hg(CF_3)_2I_2^{2-}$. From CF_3HgI the complex containing $CF_3HgI_3^{2-}$ was obtained. Later on the $Hg(CF_3)_2$ complexes with neutral ligands were proved to exist in benzene solution [12] but only the 1:1 *N*-pyridine oxide complex was isolated from the carbon tetrachloride solution [13]. The $Hg(CF_3)_2$ complexes with 1,10-phenanthroline and 2,2'-dipyridyl were obtained by decarboxylation of the corresponding complex with $Hg(OCOCF_3)_2$ [14].

We started our study with the idea that the $Hg(CF_3)_2$ halide complexes, which were proved to exist in solution [11], could only be isolated as crystalline solids if a suitable cation was chosen. Actually, we have been successful by using tetraphenylphosphonium and tetraphenylarsonium salts and we found that $Hg(CF_3)_2$ with $[Ph_4P]X$ and $[Ph_4As]X$, where X = Cl, Br, I, gave only the 1:1 adducts, while the 1:2 adduct was obtained only for X = SCN. The reaction with cyanide resulted in the formation of the corresponding tetracyanomercurate with the evolution of fluoroform.

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The isolated products are individual crystalline substances with characteristic X-ray diffraction patterns. The X-ray structure analysis was successfully applied only in the case of the chloride compound, $Hg(CF_3)_2\cdot[Ph_4P]Cl$. The crystals of the thiocyanate compound, $Hg(CF_3)_2\cdot 2[Ph_4P]SCN$, for which a complex anion $[(CF_3)_2Hg(SCN)_2]^{2-}$ had been expected according to the electric conductance data, were not suitable for a complete X-ray structure analysis. Thus we still call both of them addition compounds since their complex nature has not been fully established.

Experimental

General Information

Bis(trifluoromethyl)mercury was prepared by decarboxylation of mercury(II) trifluoroacetate according to Knunyants *et al.* [15]. Tetraphenylphosphonium and tetraphenylarsonium chloride (analytical reagents) by Fluka A.G., Busch, Schweiz were used without further purification. All other chemicals were also analytical grade reagents.

The mercury content of the adducts was determined by the EDTA complexometric titration of the solution obtained by dissolving the specimen in aqua regia [16]. The tetraphenylphosphonium and tetraphenylarsonium were determined as perchlorates according to Willard and Perkins [17], the halogens by Volhard titration and gravimetrically as silver salts, the thiocyanate after oxidation as barium sulphate. Fluoroform was identified by infrared spectra in a cell of 10 cm in length at a pressure of 273 mm Hg. Decomposition points (uncorrected) were determined in a Thiele capillary melting point apparatus.

Infrared spectra were recorded on a double-beam Perkin-Elmer 337 Grating Infrared Spectrophotometer in the 4000 to 400 cm^{-1} region using KBr pellets.

Conductivities were measured in nitrobenzene solutions at 25 °C with a Tacussel electronic model CD 7A conductivity bridge using a glass cell fitted with platinized electrodes previously calibrated with standard potassium chloride solution [18].

Preparation of Compounds

$[Ph_4P]Cl\cdot Hg(CF_3)_2$ and $[Ph_4As]Cl\cdot Hg(CF_3)_2$

$[Ph_4P]Cl$ (1.50 g, 0.004 mol) or $[Ph_4As]Cl$ (1.67 g, 0.004 mol) dissolved in water (100 ml) was added to an aqueous solution of $Hg(CF_3)_2$ (1.35 g, 0.004 mol in 50 ml H_2O) at room temperature. The white crystalline precipitate (tiny needles) was filtered off, washed with water and dried under vacuum. Decomposition at 165 °C. Yield: 1.6 g (56%) and 1.51 g (50%) for tetraphenylphosphonium and tetraphenylarsonium derivative, respectively. *Anal.* Calc. for $Hg(CF_3)_2\cdot[Ph_4P]Cl$: Hg, 28.12; $[Ph_4P]$, 47.57; Cl, 4.97. Found: Hg, 28.38; $[Ph_4P]$, 48.02; Cl, 4.94%. IR (cm^{-1}): 3090–3000(w mult.), 1590(s), 1498(s), 1450(vs), 1345(m), 1330(m), 1150–1100(vs), 1028(vs, br), 995(vs), 760(s), 725(s), 694(s), 528(vs). Calc. for $Hg(CF_3)_2\cdot[Ph_4As]Cl$; Hg, 26.48; $[Ph_4P]$, 50.61; Cl, 4.68. Found: Hg, 26,68; $[Ph_4As]$, 50.18: Cl, 4.34%. IR (cm^{-1}): 3070–3040(w), 1585(m), 1490(s), 1445(vs), 1350(m), 1320(m), 1128(vs), 1030(vs, br), 998(vs), 740(s), 689(s), 478(s), 470(s), 465(s).

$[Ph_4P]X\cdot Hg(CF_3)_2$ and $[Ph_4As]X\cdot Hg(CF_3)_2$
X = Br or I

A solution of $Hg(CF_3)_2$ (1.35 g, 0.004 mol) in water (50 ml) was mixed with a solution of KBr (0.47 g, 0.004 mol in 10 ml H_2O) or KI (0.66 g, 0.004 mol in 10 ml H_2O) and to the mixture an aqueous solution of $[Ph_4P]Cl$ (1.50 g, 0.004 mol in 100 ml H_2O) or $[Ph_4As]Cl$ (1.67 g, 0.004 mol in 150 ml H_2O) was added at room temperature. The white crystalline precipitate was filtered off, washed with water and dried under vacuum. Tiny plates and needles with decomposition at 170 and 165 °C with the yield 2.2 g (73%) and 2.72 g (84%) for the phosphonium bromide and iodide adduct, respectively, and tiny needles with decomposition at 170 and 180 °C with the yield of 2.56 (80%) and 3.0 (88%), for the arsonium bromide and iodide, respectively were obtained. *Anal.* Calc. for $Hg(CF_3)_2\cdot[Ph_4P]Br$: Hg, 26.47; $[Ph_4P]$, 44.78; Br, 10.54. Found: Hg, 26.14; $[Ph_4P]$, 44.88; Br, 10.59%. IR (cm^{-1}): 3080–3000(w), 1590(s), 1490(s), 1450(vs), 1350(m), 1330(m), 1140–1100(vs), 1030(vs, br), 998(vs), 755(m), 725(s), 692(s), 529(vs). Calc. for $Hg(CF_3)_2\cdot[Ph_4P]I$: Hg, 24.92; $[Ph_4P]$, 42.17; I, 15.77. Found: Hg, 25.32; $[Ph_4P]$, 42.43; I, 15.57%. IR (cm^{-1}): 3080–3000(w), 1590(s), 1490(s), 1450(vs), 1350(m), 1325(m), 1140–1100(vs), 1035(vs, br), 998(vs), 760(m), 725(s), 691(s), 528(vs). Calc. for $Hg(CF_3)_2\cdot[Ph_4As]Br$: Hg, 25.02; $[Ph_4As]$, 47.81; Br, 9.97. Found: Hg, 24.94; $[Ph_4As]$, 48.34; Br, 9.59%. IR (cm^{-1}): 3075–3045(w), 1590(m), 1490(s), 1450(vs), 1350(m), 1320(m), 1130(vs), 1030(vs, br), 998(vs), 742(s), 690(s), 480(s), 473(s), 467(s). Calc. for $Hg(CF_3)_2\cdot[Ph_4As]I$: Hg, 23.63; $[Ph_4As]$, 45.16; I, 14.95. Found: Hg, 23.48; $[Ph_4As]$, 44.48; I, 14.77%. IR (cm^{-1}): 3070–3040(w), 1590(m), 1490(s), 1445(vs), 1345(m), 1319(m), 1125(vs), 1032(vs, br), 998(vs), 740(s), 690(s), 478(s), 472(s), 459(s).

$[Ph_4P]_2(SCN)_2\cdot Hg(CF_3)_2$ and $[Ph_4As]_2(SCN)_2\cdot Hg(CF_3)_2$

To a mixture of the aqueous solutions of $Hg(CF_3)_2$ (0.67 g, 0.002 mol in 25 ml H_2O) and KSCN (0.39 g, 0.004 mol in 10 ml H_2O) a solution of

[Ph_4P]Cl (1.50 g, 0.004 mol in 100 ml H_2O) or [Ph_4As]Cl (1.67 g, 0.004 mol in 150 ml H_2O) was added at room temperature. The white crystalline precipitate (fine needles in both cases) was filtered off, washed with water and dried under vacuum. Yield 1.9 g (86%) and 2.3 g (95%) with decomposition at 172 and 192 °C for the phosphonium and arsonium adduct, respectively. *Anal.* Calc. for $Hg(CF_3)_2 \cdot [Ph_4P]_2(SCN)_2$: Hg, 17.70; [$Ph_4P$], 59.88; SCN, 10.25. Found: Hg, 17.99; [Ph_4P], 60.63; SCN, 10.21%. IR (cm^{-1}): 3080–3000(w), 2059(vs), 1590(s), 1490(s), 1440(vs), 1345(m), 1320(m), 1135–1105(vs), 1050(vs, br), 995(vs), 755(s), 725(s), 692(s), 528(vs), 460(w), 450(m). Calc. for $Hg(CF_3)_2 \cdot [Ph_4As]_2(SCN)_2$: Hg, 16.42; [$Ph_4As$], 62.77; SCN, 9.51. Found: Hg, 16.49; [Ph_4As], 63.29; SCN, 9.94%. IR (cm^{-1}): 3080–3040(w), 2059(vs, sh), 1580(m), 1485(s), 1440(vs), 1350(m), 1320(m), 1135(vs), 1050(vs, br), 998(vs), 745(s), 691(s), 479(s), 461(s).

Reaction of $Hg(CF_3)_2$ with KCN and [Ph_4P] Cl, [Ph_4As] Cl

To a solution of $Hg(CF_3)_2$ (0.34 g, 0.001 mol) and [Ph_4P]Cl (0.75 g, 0.002 mol) in water (50 ml), KCN (0.26 g, 0.004 mol) dissolved in a little water (5 ml) was added. In order to measure the volume of gas evolved (HCF_3) the reaction was carried out in a round flask (100 ml) connected by means of a Tygon tube with a graduated cylinder in which the gas was collected over water. The reaction mixture was kept warm until the cessation of the gas evolution. The gas volume was measured at 25 °C and 750 mm Hg, the value corrected for the water vapour tension and reduced to STP. Calc. for $Hg(CF_3)_2$: HCF_3, 44.8 ml. Found: HCF_3, 43.5 ml. [Ph_4As]Cl reacts in the same way.

[Ph_4P]$_2$[$Hg(CN)_4$] and [Ph_4As]$_2$[$Hg(CN)_4$]

In order to isolate the mercury complex formed in the preceding reaction the following procedure was used. To a solution of $Hg(CF_3)_2$ (0.67 g, 0.002 mol) and KCN (0.52 g, 0.008 mol) in water (50 ml), an aqueous solution of [Ph_4P]Cl (1.5 g, 0.004 mol, 100 ml H_2O) was added. The white crystalline precipitate (fine needles) was washed with water and dried under vacuum. Decomposition at 210 °C. Yield 1.77 g (90%). *Anal.* Calc. for $[Ph_4P]_2 \cdot [Hg(CN)_4]$: Hg, 20.40; [$Ph_4P$] 69.02. Found: Hg, 19.52; [Ph_4P], 69.18%. IR (cm^{-1}): 3080–3040(w), 2138(m), 1590(m), 1485(s), 1440(vs), 1345(m), 1320(m), 1190(vs), 1165(vs), 1108(vs), 1031(w), 999(s), 757(s), 725(vs), 690(vs), 528(vs). In the same way the analogous arsonium complex was isolated as white crystalline precipitate (fine needles). Decomposition at 238 °C. *Anal.* Calc. for $[Ph_4As]_2$-[$Hg(CN)_4$]: Hg, 18.72; [Ph_4As], 71.56. Found: Hg, 18.99; [Ph_4As], 71.25%. IR (cm^{-1}): 3080–3020(w), 2140(m), 1585(m), 1485(vs), 1445(vs), 1340(m), 1320(m), 1187(vs), 1165(vs), 1080(vs), 1025(w), 999(s), 757(vs), 690(vs), 420(s).

TABLE I. Crystal and X-ray Data

Compound	$Hg(CF_3)_2 \cdot [PPh_4]Cl$
Formula	$C_{26}H_{20}ClF_6HgP$
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	10.783(2)
b (Å)	14.023(6)
c (Å)	18.719(5)
β (°)	111.42(3)
V (Å^3)	2635(2)
Z	4
Formula weight	713.45
D_c (g cm^{-3})	1.798
$F(000)$	1386
μ(Mo Kα) (cm^{-1})	61.70
λ(Mo Kα) (Å)	0.7107
Transmission max.–min.	0.085–0.151
Crystal size (mm)	0.71 × 0.54 × 0.48
Diffractometer	Philips 1100
Scan mode	$\theta - 2\theta$
θ range (°)	2–31
Total no. reflections	4077
No. reflections in the refinement	3193
Criterion for observed reflections	$I > 4\sigma(I)$; $F_o/\Delta F > 5$ for $F_o < 0.048(F_o)_{max}$
R factor	0.053
R_w factor	0.070
Weighting scheme (w)	$\sigma^{-2}(F_o)$
Programs used	XRAY76, CSU, ORTEP

Crystal Structure Solution and Refinement

Three-dimensional diffraction data were recorded on a Philips PW 1100 four-circle automatic diffractometer using graphite monochromatized Mo Kα radiation. The collection method and crystal data are given in Table I. Data of the unit cell parameters, determined by centering of 20 reflections within the range of $6° < \theta < 8°$, were refined through the orientation matrix by means of least-square method. Significant variations of the intensities were not observed for three monitored reflections measured every two hours. The absorption correction was made according to [19].

The structure was solved by means of standard Patterson and Fourier syntheses. In the final cycles of full-matrix least-squares refinement, performed by means of the X-RAY76 program [20], the mercury, phosphorus and chlorine atom coordinates were treated anisotropically. The minimization function was $\Sigma w(|F_o| - |F_c|)^2$, where $w = \sigma^{-2}(F_o)$. Scattering factors and correction for anomalous dispersion were taken from Cromer and Mann [21] and Cromer and Libermann [22]. Positions of the hydrogen atoms were calculated with the C–H

TABLE II. Fractional Atomic Coordinates and Equivalent Isotropic Temperature Factors

	x/a	y/b	z/c	U_{eq} or U
Hg	0.1224(1)	0.4003(0)	0.5705(0)	53(0)
Cl	−0.0444(3)	0.4099(3)	0.4142(2)	58(1)
P	0.3571(3)	0.0202(2)	0.6177(2)	45(1)
F(1)	−0.149(1)	0.377(1)	0.574(1)	9(0)
F(2)	−0.051(1)	0.245(1)	0.580(1)	10(0)
F(3)	0.003(1)	0.338(1)	0.679(1)	11(0)
F(4)	0.324(3)	0.408(2)	0.503(2)	25(1)
F(5)	0.362(2)	0.506(2)	0.584(1)	22(1)
F(6)	0.397(3)	0.372(2)	0.603(2)	21(1)
C(1)	−0.025(2)	0.340(1)	0.602(1)	7(0)
C(2)	0.303(2)	0.422(2)	0.561(1)	10(1)
C(11)	0.409(1)	−0.098(1)	0.616(1)	5(0)
C(12)	0.319(1)	−0.173(1)	0.602(1)	6(0)
C(13)	0.356(1)	−0.267(1)	0.597(1)	7(0)
C(14)	0.484(2)	−0.287(1)	0.605(1)	7(0)
C(15)	0.578(2)	−0.214(1)	0.621(1)	8(0)
C(16)	0.541(1)	−0.121(1)	0.625(1)	6(0)
C(21)	0.500(1)	0.100(1)	0.642(1)	4(0)
C(22)	0.522(1)	0.151(1)	0.587(1)	5(0)
C(23)	0.639(2)	0.206(1)	0.607(1)	7(0)
C(24)	0.727(2)	0.208(1)	0.682(1)	7(0)
C(25)	0.702(2)	0.159(1)	0.738(1)	8(0)
C(26)	0.584(1)	0.102(1)	0.716(1)	6(0)
C(31)	0.285(1)	0.031(1)	0.690(1)	5(0)
C(32)	0.198(2)	0.104(1)	0.688(1)	8(0)
C(33)	0.154(2)	0.115(1)	0.750(1)	9(0)
C(34)	0.192(2)	0.047(1)	0.809(1)	7(0)
C(35)	0.275(2)	−0.026(1)	0.809(1)	8(0)
C(36)	0.322(2)	−0.033(1)	0.751(1)	6(0)
C(41)	0.241(1)	0.053(1)	0.523(1)	5(0)
C(42)	0.208(2)	−0.011(1)	0.466(1)	7(0)
C(43)	0.123(2)	0.020(1)	0.393(1)	10(1)
C(44)	0.068(2)	0.105(1)	0.380(1)	7(0)
C(45)	0.103(2)	0.172(1)	0.437(1)	8(0)
C(46)	0.191(2)	0.146(1)	0.510(1)	7(0)

bond distance and the CCH bond angle of 1.09 Å and 120°, respectively, by means of the CSU program [23]. This program was also used for the analysis of the interatomic geometry within the unit cell. The thermal parameters of the hydrogen atoms were set equal to the equivalent isotropic thermal parameters of the corresponding carbon atom, and their atomic coordinates not refined. The atomic coordinates and thermal parameters are listed in Table II. See also 'Supplementary Material'. Calculations were carried out on the UNIVAC 1110 of the University Computing Centre in Zagreb.

Results and Discussion

The most interesting result of our experiments is the stoichiometry of the adducts. The halide adducts were obtained always in the 1:1 ratio, *i.e.* they are defined by the formulae $Hg(CF_3)_2 \cdot [Ph_4P]X$ and $Hg(CF_3)_2 \cdot [Ph_4As]X$, with X = Cl, Br, I. The same composition resulted even then when the onium salt had been added in considerable excess. On the contrary, the thiocyanate adduct could be obtained only in the 1:2 ratio with the composition defined as $Hg(CF_3)_2 \cdot 2[Ph_4P]SCN$ and $Hg(CF_3)_2 \cdot 2[Ph_4As]$-SCN. All attempts to prepare the fluoride adducts failed. As to the iodide adduct our result is in apparent disagreement with the result reported by Emeléus and Lagowski [11] who identified the 2:1 complexes with the tris(ethylenediamine)zinc and tris(ethylenediamine)nickel(II) cation. The explanation seems to be found in the difference between the cations used, against the complex ionic nature of the halide adducts.

TABLE III. Molar Conductivities in 10^{-3} M Nitrobenzene Solutions at 25 °C

Compound	λ_M (Ω^{-1} cm^2 mol^{-1})
$Hg(CF_3)_2 \cdot [Ph_4P]Cl$	25.91
$Hg(CF_3)_2 \cdot [Ph_4P]Br$	25.55
$Hg(CF_3)_2 \cdot [Ph_4P]I$	26.74
$Hg(CF_3)_2 \cdot [Ph_4P]_2(SCN)_2$	61.53
$Hg(CF_3)_2 \cdot [Ph_4As]Cl$	24.47
$Hg(CF_3)_2 \cdot [Ph_4As]Br$	27.24
$Hg(CF_3)_2 \cdot [Ph_4As]I$	25.69
$Hg(CF_3) \cdot [Ph_4As]_2(SCN)_2$	59.87
$[Ph_4P]_2[Hg(CN)_4]$	49.39
$[Ph_4As]_2[Hg(CN)_4]$	55.62

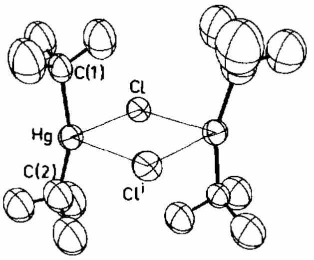

Fig. 1. ORTEP drawing of the $[(F_3C)_2HgCl_2Hg(CF_3)_2]^{2-}$ anion in the crystal structure of the 1:1 addition compound of bis(trifluoromethyl)mercury and tetraphenylphosphonium chloride.

The complex nature of the halide adducts could not be established by the conductivity measurements (Table III) of the nitrobenzene solutions. The values obtained prove the presence of uni-univalent electrolytes [18] which is indicative for the $Hg(CF_3)_2 \cdot [Ph_4P]X$ adduct as well as for the onium salt with the $[Hg(CF_3)_2X]^-$ anion.

Such an anion probably exists in solution but in the solid state it occurs in dimeric form as shown by X-ray structure analysis. The crystals of the chloride adduct are built up of the onium cation

TABLE IV. Selected Interatomic Distances and Angles[a]

Distances (Å)			
Hg–C(1)	2.067(22)	C(21)–C(22)	1.344(25)
Hg–C(2)	2.042(23)	C(21)–C(26)	1.350(21)
P–C(11)	1.753(14)	C(22)–C(23)	1.408(22)
P–C(21)	1.823(12)	C(23)–C(24)	1.378(22)
P–C(31)	1.797(19)	C(24)–C(25)	1.360(29)
P–C(41)	1.817(15)	C(25)–C(26)	1.430(22)
F(1)–C(1)	1.349(22)	C(31)–C(32)	1.380(23)
F(2)–C(1)	1.392(20)	C(31)–C(36)	1.391(23)
F(3)–C(1)	1.361(26)	C(32)–C(33)	1.414(32)
F(4)–C(2)	1.203(46)	C(33)–C(34)	1.402(23)
F(5)–C(2)	1.333(37)	C(34)–C(35)	1.360(26)
F(6)–C(2)	1.247(35)	C(35)–C(36)	1.359(32)
C(11)–C(12)	1.390(18)	C(41)–C(42)	1.339(23)
C(11)–C(16)	1.408(17)	C(41)–C(46)	1.398(20)
C(12)–C(13)	1.390(20)	C(42)–C(43)	1.408(22)
C(13)–C(14)	1.362(25)	C(43)–C(44)	1.314(21)
C(14)–C(15)	1.394(25)	C(44)–C(45)	1.367(23)
C(15)–C(16)	1.374(21)	C(45)–C(46)	1.398(22)
Hg...Cl	2.823(03)	Hg...Cl^{i}	2.837(04)
Angles (°)			
C(1)–Hg–C(2)	160.5(08)	Hg–C(2)–F(4)	123.6(22)
Cl...Hg...Cl^{i}	87.7(02)	Hg–C(2)–F(5)	117.5(17)
C(11)–P–C(21)	109.8(07)	Hg–C(2)–F(6)	116.3(21)
C(11)–P–C(31)	108.8(07)	F(1)–C(1)–F(2)	100.9(15)
C(11)–P–C(41)	109.4(07)	F(1)–C(1)–F(3)	103.0(15)
C(21)–P–C(31)	108.6(07)	F(2)–C(1)–F(3)	103.7(15)
C(21)–P–C(41)	107.9(07)	F(4)–C(2)–F(5)	102.2(25)
C(31)–P–C(41)	112.3(07)	F(4)–C(2)–F(6)	95.7(27)
Hg–C(1)–F(1)	119.2(13)	F(5)–C(2)–F(6)	96.4(24)
Hg–C(1)–F(2)	113.6(12)		
Hg–C(1)–F(3)	114.5(13)		

[a] Symmetry code: i = $-x, 1-y, 1-z$.

and the dimeric $[(CF_3)_2HgCl_2Hg(CF_3)_2]^{2-}$ anion. The anion is formed from pairs of the $Hg(CF_3)_2$ molecules bridged over by two chloride ions (Fig. 1) at the Hg...Cl distances of 2.823(3) and 2.837(4) Å, considerably less than the sum of corresponding van der Waals radii [1, 24]. The CHgC bond angle is 160.5(8)°, thus the departure from the collinearity of the C–Hg–C bonds is greater than any observed until now [3–10]. But the geometry is still far from the tetrahedral one expected for the ideal case of a complex with the tetra-coordinated mercury atom. Consequently, the chloride-to-mercury donor–acceptor interaction should be estimated as moderate and the compound considered as a complex only in the crystalline state. Such a characterization is justified also by considering the value of the C–Hg bond length of 2.04(2) and 2.07(2) Å, which did not increase in comparison with the value of 2.118(16) Å found in the $Hg(CF_3)_2$ crystals [25]. The interatomic distances and bond angles are given in Table IV. They are in agreement with the values previously observed in analogous compounds.

The conductance of the thiocyanate adduct in nitrobenzene solution agrees well with the value for the 2:1 electrolytes, which means that it can be considered as a phosphonium (or arsonium) salt containing the $[Hg(CF_3)_2(SCN)_2]^{2-}$ complex anion. Consequently, the Hg...S donor–acceptor link is stronger than the Hg...Cl one as expected. Unfortunately, all our attempts to prepare a crystal suitable for X-ray structure analysis have been unsuccessful so far.

In the infrared spectra the absorption bands expected for the onium cation, e.g. ring vibration bands at 1590, 1485 and 1440 cm^{-1}, the P–C stretching vibrations at 725 and 528 cm^{-1} [26], as well as the C–F stretching vibrations in the region of 1150–1025 cm^{-1} [25], were observed. The absorption band at 2059 cm^{-1}, usually observed near 2100 cm^{-1} [27] in the spectra of the thiocyanate compounds, may be assigned to the CN stretching vibration of the nitrogen-to-mercury linked thiocyanate ion, as it had been done previously by Ahuja and Yadava [28] in the case of mercury(II) thiocyanate hexamethylenetetramine.

Supplementary Material

The calculated and observed structure factors, and the anisotropic temperature factors are available from the authors on request.

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