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Crown compounds for anions. Unusual complex of trimeric perfluoro-*o*-phenylenemercury with the bromide anion having a polydecker sandwich structure

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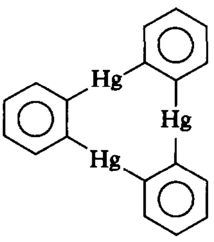
Abstract

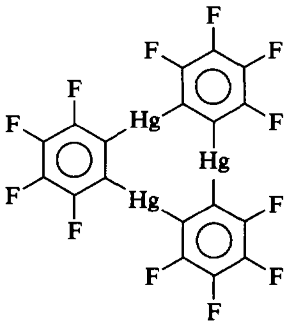
Here we show that cyclic trimeric perfluoro-*o*-phenylenemercury $(o\text{-}C_6F_4Hg)_3$ is capable of forming complexes with $[PPh_4]^+Br^-$, $[PPh_3Me]^+I^-$ and $[PPh_4]^+Cl^-$ of the composition $[(o\text{-}C_6F_4Hg)_3X]^-[PR_3R']^+$ ($X = Br$, $R = R' = Ph$; $X = I$, $R = Ph$, $R' = Me$) or $\{[(o\text{-}C_6F_4Hg)_3]_3X_2\}^{2-}[PR_3R']_2^+$ ($X = Cl$, $R = R' = Ph$). An X-ray study of the complex with $[PPh_4]^+Br^-$ revealed that it has the unusual structure of the polydecker bent sandwich wherein each Br^- anion is coordinated with six mercury atoms of two neighbouring molecules of $(o\text{-}C_6F_4Hg)_3$.

The problem of creating effective crown compounds for anions has received considerable attention in recent years (see e.g. refs. 1–7). Such crown compounds have to contain in macrocyclic chain either several positively charged onium groups or several atoms posessing Lewis acidity.

We have shown previously [4,5] that trimeric *o*-phenylenemercury (I), having a planar cyclic structure [8], is capable of forming complexes with halogenide anions (I^-, Br^-, Cl^-) in dihalomethane solutions and can catalyze the azocoupling reaction of phenyldiazonium halogenides $PhN_2^+X^-$ ($X = Cl$, Br) with β-naphthol in two phase H_2O–CH_2Br_2 media. The complexation of I with halogenide anions is proved by ^{199}Hg NMR spectroscopy, although all attempts to isolate the individual complexes failed. Here we report that when the considerably more electron accepting trimeric perfluoro-*o*-phenylenemercury(II) [9,10] is used instead of I, the resulting complexes with halogenide anions (I^-, Br^-, Cl^-) can be isolated as definite compounds [11,12].



(I)



(II)

The complexes are readily obtained by mixing II with $[PPh_4]^+Br^-$, $[PPh_3Me]^+I^-$ and $[PPh_4]^+Cl^-$, respectively in CH_2Br_2 or ethanol at room temperature. The isolated compounds are fine-crystalline colorless solids, readily soluble in acetone, less soluble in CH_2Br_2 and practically insoluble in aromatic and aliphatic hydrocarbons. According to elemental analysis, the complexes of II with $[PPh_4]^+Br^-$ and $[PPh_3Me]^+I^-$ can be formulated as $[(o\text{-}C_6F_4Hg)_3X]^-[PR_3R']^+$, where X = Br, R = R' = Ph (III); X = I, R = Ph, R' = Me (IV).

^{19}F NMR spectra of III and IV in acetone-d_6 show two multiplets (of equal intensity), typical for AA'XX' systems, as well as the satellite signals due to spin coupling between ^{19}F and ^{199}Hg nuclei. A similar ^{19}F NMR spectrum is observed in the case of II but it differs markedly in its parameters from the spectra of III and IV. According to X-ray photoelectron spectra, the complexation of Br^- and I^- with II to form III and IV leads to considerable increase in electron density on mercury atoms and to decrease on halogen atoms.

Slow evaporation of the solution of III in CH_2Br_2 gave crystals of the solvate III · CH_2Br_2 suitable for X-ray study. They are monoclinic; at −120 °C: $a = 15.326(3)$, $b = 26.772(5)$, $c = 31.585(6)$ Å, $\beta = 95.10(5)°$, $V = 12908(4)$ Å^3, $D_{calc} = 2.496$ Mg m^{-3}, space group $P2_1/n$, $Z = 12$ (three independent PPh_4^+ cations, three independent Br^- anions and three independent molecules of II and solvate CH_2Br_2 molecules).

An X-ray diffraction study (−120 °C, λ(Mo-K_α), $\theta/2\theta$-scan, $\theta \leq 22°$, the DIFABS absorption correction [13], μ(Mo-K_α) = 135.6 cm^{-1}, $R = 0.0538$ for 8903 independent reflections with $F^2 \geq 4\sigma(F^2)$) revealed that the crystal of III is built of infinite zigzag chains (along the b-axis direction) which are formed of alternating molecules of II and Br^- anions (the fragment of the chain is shown in Fig. 1). Each Br^- anion in the crystal of III is in contact with six mercury atoms of the two neighbouring molecules of II. It is important to note that all but one Hg · · · Br distances lie within the range of 3.07–3.39 Å and thus are noticeably shorter than the sum of Van der Waals radii of the Hg and Br atoms (1.50 + 1.97 = 3.47 Å [14,15]). This indicates the existence of coordinative bonds between the Br^- anions and Hg atoms in III. However, when compared with the normal covalent Hg–Br bonds (2.539 Å [16]) these coordination Hg · · · Br bonds are considerably weaker and are characterized by the somewhat less pronounced energetic minimum, which is reflected in the large scatter of the Hg · · · Br distances (one of the eighteen such distances involving three independent bromide ions (see Fig. 1) is as short as 3.071(3) Å, whereas the longest is equal to 3.610(3) Å).

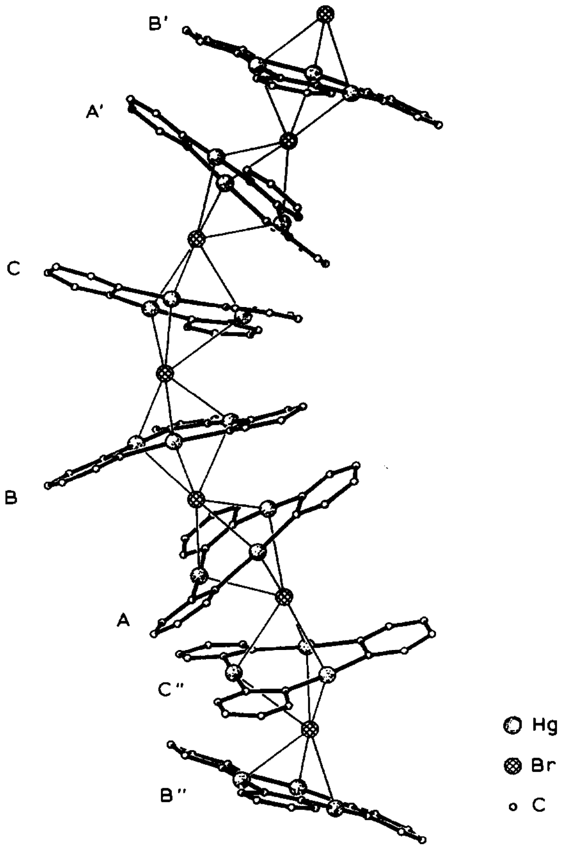


Fig. 1. The fragment of infinite polyanionic chain $[(o\text{-}C_6F_4Hg)_3Br]_n^{n-}$ in the structure of III·CH_2Br_2. The F atoms of phenylene rings are omitted for clarity.

Molecules of II coordinated with Br^- exhibit as a whole considerable deviations from planarity (up to 0.47 Å), their mercury–carbon frameworks being non-planar as well (maximum displacements from the mean planes are as large as 0.23 Å). Only the central 9-membered rings may be considered planar, although even these rings show notable (up to 0.13 Å) deviations from planarity. The mean planes of the rings are non-parallel, dihedral angles between the neighbouring planes A/B, B/C, and C/A' in the chain (see Fig. 1) being equal to 28.2, 28.9, and 32.3° respectively.

Thus the results show that complex III has an unusual structure of a polydecker bent sandwich in the solid state wherein every Br^- anion is coordinated to six mercury atoms of two neighbouring molecules of II. The unique feature of complex III is that the coordinating centres in its structure are not the metal atoms or cations as in the case of normal sandwich complexes but the anions of the metalloid.

It is noteworthy that the reaction of II with $[PPh_4]^+Cl^-$ yields a complex of different composition: $\{[(o\text{-}C_6F_4Hg)_3]_3Cl_2\}^{2-}[PPh_4]_2^+$ (V) [12]. One may suggest that complex V, at least in the solid state, has a structure of triple-decker sandwich: $[II \cdots Cl \cdots II \cdots Cl \cdots II]^{2-}$.

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