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# Monochloride complex of five-mercury anticrown $[(CF_3)_2CHg]_5$ and reinvestigation of crystal structure of this anticrown

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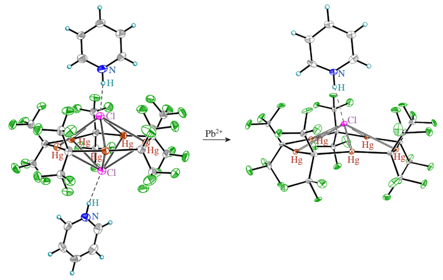
**Reexamination of crystal structure of five-mercury anticrown $[(CF_3)_2CHg]_5$ revealed that instead of the previous definition as a co-crystal of this anticrown with water and pyridine $\{[(CF_3)_2CHg]_5\}\cdot 2Py\cdot 2H_2O$, the compound actually represented its bipyramidal dichloride complex, $(PyH)_2\{[(CF_3)_2CHg]_5\}Cl_2$. Treating it with lead(II) benzoate gave pyramidal monochloride complex $(PyH)\{[(CF_3)_2CHg]_5\}Cl$.**

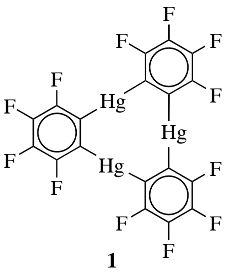


*Keywords*: anti-Werner complexes, anticrown, mercury, organofluorine compounds, chlorine, lead.

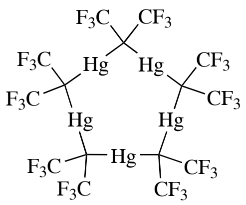
One of the important problems of modern supramolecular chemistry is the development of highly efficient and selective anion receptors. A considerable progress in this area was achieved in the 1960–1980s when the first publications on the binding of anions by macrocycles containing several positively charged ammonium groups in the ring appeared.[1] Another promising approach for solving the problem is the use of neutral macrocyclic multidentate Lewis acids called anticrowns as anion receptors (see, *e.g*., reviews[2–10] and papers[11–13]). Anticrowns are able to form unusual complexes, in which the anionic guest is cooperatively coordinated by all Lewis acid centres of the macrocycle.

Among the presently known types of anticrowns, especially high efficiency is displayed by perfluorinated polymercuramacrocycles **1**–**4**. The presence of electron-withdrawing fluorine atoms in such anticrowns leads to a strong increase in the Lewis acidity of the mercury centres and strength of mercury–carbon bonds. The most studied[14] among the known anticrowns is three-mercury macrocycle $(o\text{-}C_6F_4Hg)_3$ **1**. This anticrown is capable of forming extremely stable complexes of unique structures with various anions and neutral Lewis bases. The complexing properties of other anticrowns,[15,16] especially cyclic pentameric perfluoroisopropylidenemercury $[(CF_3)_2CHg]_5$ **2**,[17] are much less studied, mostly due to their low synthetic availability.

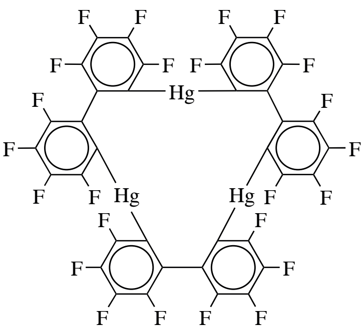
First, we reinvestigated the crystal structure of the above-mentioned five-mercury anticrown **2**. According to an X-ray diffraction study, it turned out that it actually represented bipyramidal dichloride complex **5**, $(PyH)_2\{[(CF_3)_2CHg]_5\}Cl_2$, *viz.* $(PyH)_2(\mathbf{2}\cdot Cl_2)$, instead of a co-crystal of this anticrown with water and pyridine $\{[(CF_3)_2CHg]_5\}\cdot 2Py\cdot 2H_2O$, as reported previously.[18] The presence of chloride ions in complex **5** was confirmed by a Beilstein test and ESI-MS (see the Online Supplementary Materials). Taking into account that complex **5** was obtained in accordance with the previously published procedure for the synthesis of macrocycle **2**, one can assume that in all previous works, this dichloride complex would have been taken instead of macrocycle **2**. Therefore, it can be considered that the previously observed reactions of formation of complexes of this mercury



**1**



**2**



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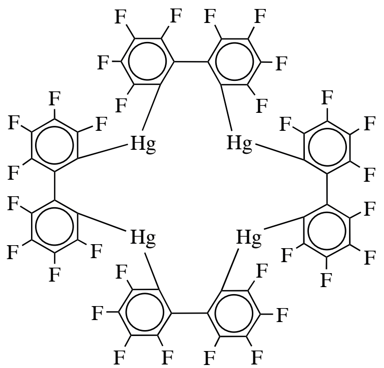

**4**

macrocycle with halide ions[19] were in fact the exchange reactions of the cation and the bound anion in complex **5**. Also, the possibility of using **2** as a phase-transfer catalyst for nitration with dilute nitric acid in the absence of a promoting NaCl additive[20] should be explained by the fact that it was already present in the form of a chloride adduct.

Complex **5** has a bipyramidal structure with chloride anions located at the vertices of this bipyramid above and below the mean plane of the five mercury centres (Figure 1).[†] Both chloride anions are cooperatively bound to all five mercury sites of the anticrown. The Cl(1) and Cl(2) distances to the $Hg_5$ plane are 1.65 and 1.74 Å, respectively. The Hg–Cl bonds in **5** are 3.233(3)–3.354(3) (*av.* 3.31 Å) which is less than sum of the van der Waals radii of mercury (1.73–2.00 Å)[21,22] and chlorine (1.8 Å).[23] Additionally, each chloride anion in **5** is hydrogen-bonded to pyridinium cation [the Cl(1)···N(1) distance is 2.92(2) Å and the Cl(2)···N(2) distance is 3.04(1) Å], and these H-bonds are slightly tilted from the perpendicular to the $Hg_5$ midplane (by 3.0 and 15.9°, respectively). The parameters of the N–H···Cl hydrogen bonds in **5** are consistent with the literature data for similar interactions. For example, in a pyridinium chloride crystal the N···Cl distance is 3.01 Å.[24] The C–Hg–C bond angles are close to 180° [174.8(4)–176.9(4), *av.* 175.7°]. It should be noted that the intramolecular Cl(1)···Cl(2) separation in **5** is 3.389(4) Å, which is shorter than sum of the van der Waals radii of two chlorine atoms. Apparently, this is a case of forced contact caused by the cooperative $Hg_5\cdots Cl^-$ interactions, which significantly exceed the energy of Coulomb repulsion between two negatively charged ions.

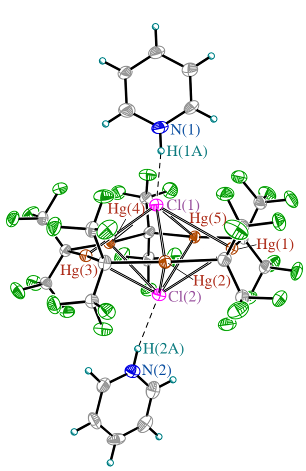

**Figure 1** ORTEP representation of the molecular structure of complex **5** with thermal ellipsoids drawn at the 30% probability level.

In the previously described dichloride complex $(PPh_4)_2\{[(CF_3)_2CHg]_5\}Cl_2$, the chloride anions do not take part in non-covalent intermolecular interactions with counter cations and the Hg–Cl distances lie in the range of 3.089(6)–3.388(8) Å (*av.* 3.24 Å),[19] which is on average 0.07 Å shorter than in complex **5**. In a $^{19}$F NMR spectrum of **5** in acetone-$d_6$, the $CF_3$ groups resonate at –45.9 ppm ($^3J_{FHg}$ = 237 Hz in satellites).

With the intention to get the chloride-free five-mercury anticrown **2** from the dichloride complex **5**, the latter was reacted in ethanol with equimolar amount of lead(II) benzoate $(PhCOO)_2Pb$ suspension, giving, however, the colourless crystals of complex **6** being a monochloride analogue of **2**, namely, $(PyH)\{[(CF_3)_2CHg]_5\}Cl$, *i.e.* (PyH)(**2**·Cl). The yield of **6** was 31%. Attempts to remove the chloride anion using silver salt resulted only in a multicomponent mixture of products. A $^{19}$F NMR spectrum of **6** in acetone-$d_6$ shows a singlet at –46.1 ppm ($^3J_{FHg}$ = 231 Hz in satellites).

X-ray diffraction data showed that complex **6** had a pyramidal structure with the chloride anion disposed above the mean $Hg_5$ plane of the mercuracycle at a distance of 1.26 Å (Figure 2).[†] The chloride anion in **6** is almost symmetrically bound to all mercury atoms of the anticrown with the Hg–Cl contacts being in the range of 2.954(3)–3.317(3) Å (*av.* 3.15 Å). The Hg–Cl bonds in monochloride **6** are on average 0.16 Å shorter as those in dichloride complex **5**, which may be explained by the absence of the repulsive effect of the second chloride ion. The chloride ion in **6** is hydrogen-bonded to a pyridinium cation with a Cl(1)···N(1) distance of 3.14(1) Å. The C–Hg–C bond angles are non-exclusive [170.8(5)–178.2(5)°, *av.* 173.9°]. In analogous monochloride adducts of four-mercury anticrowns **4** and $(C_2B_{10}H_{10}Hg)_4$ **7**, the bound chloride anion is located much closer to the mean planes (0.79 Å for **4**[16] and 0.383 Å for **7**[25]) of these macrocycles, which can be explained by the smaller size and greater structural rigidity of the cavity of the mercuramacrocycle **2** compared to these anticrowns. The corresponding Hg–Cl distances in these compounds are 2.9221(14)–3.0205(15) Å (*av.* 2.957 Å) and 2.944(2) Å, respectively.

The formation of only monochloride **6** instead of free host **2** under the action of a salt forming an insoluble metal chloride indicates that the five-mercury anticrown binds the chloride anion very strongly, despite the fact that this anion does not fit into its cavity.

In summary, reexamination of the compound previously described as a free cyclic pentameric perfluoroisopropylidene-mercury $[(CF_3)_2CHg]_5$ **2** has shown that it represents in fact dichloride complex of this anticrown **5**, namely, $(PyH)_2(\mathbf{2}\cdot Cl_2)$.

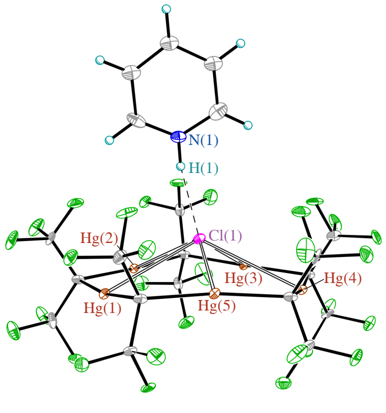

**Figure 2** ORTEP representation of the molecular structure of complex **6** with thermal ellipsoids drawn at the 30% probability level.

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[†] *Crystal data for* **5**. $C_{25}H_{12}Cl_2F_{30}Hg_5N_2$ ($M$ = 1984.22 g mol$^{-1}$), monoclinic, space group $P2_1/c$, $a$ = 16.549(3), $b$ = 14.025(3) and $c$ = 18.106(4) Å, $\beta$ = 91.105(5)°, $V$ = 4201.5(15) Å$^3$, $Z$ = 4, $T$ = 210 K, $\mu(MoK_\alpha)$ = 18.492 mm$^{-1}$, $d_{calc}$ = 3.137 g cm$^{-3}$, 44263 reflections measured (3.67° $\leqslant 2\theta \leqslant$ 58.00°), 11166 unique ($R_{int}$ = 0.0635) which were used in all calculations. The refinement converged to $wR_2$ = 0.1107 and GOF = 0.827 for all independent reflections [$R_1$ = 0.0455 was calculated against $F$ for 8157 observed reflections with $I > 2\sigma(I)$].

*Crystal data for* **6**. $C_{20}H_6ClF_{30}Hg_5N$ ($M$ = 1868.66 g mol$^{-1}$), triclinic, space group $P\bar{1}$, $a$ = 12.8129(16), $b$ = 13.1823(17) and $c$ = 21.548(3) Å, $\alpha$ = 78.002(3), $\beta$ = 81.070(3) and $\gamma$ = 75.252(3)°, $V$ = 3422.5(8) Å$^3$, $Z$ = 4, $T$ = 110 K, $\mu(MoK_\alpha)$ = 22.613 mm$^{-1}$, $d_{calc}$ = 3.627 g cm$^{-3}$, 36173 reflections measured (1.94° $\leqslant 2\theta \leqslant$ 56.00°), 16502 unique ($R_{int}$ = 0.0586) which were used in all calculations. The refinement converged to $wR_2$ = 0.1158 and GOF = 1.055 for all independent reflections [$R_1$ = 0.0506 was calculated against $F$ for 10454 observed reflections with $I > 2\sigma(I)$].

CCDC 2401614 (**5**) and CCDC 2401615 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* https://www.ccdc.cam.ac.uk.

By treating with lead benzoate, one of its chloride anions can be removed with the formation of the monochloride adduct **6**, (PyH)(**2**·Cl). Remarkable structural features of complexes **5** and **6** are the $\eta^5$-coordination of the chloride anions with all mercury atoms of the anticrown as well as the simultaneous participation of these halide ligands in the formation of the hydrogen bonds with the pyridinium counter-cation.

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*Online Supplementary Materials*

Supplementary data associated with this article can be found in the online version at doi: 10.71267/mencom.7803.

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