*Journal of Organometallic Chemistry, 443* (1993) C19–C21

JOM 23195PC

## Preliminary Communication

# Crown compounds for anions. A spinning top-shaped complex of cyclic pentameric perfluoroisopropylidenemercury with two chloride anions

V.B. Shur, I.A. Tikhonova, F.M. Dolgushin, A.I. Yanovsky, Yu.T. Struchkov, A.Yu. Volkonsky, E.V. Solodova, S.Yu. Panov, P.V. Petrovskii and M.E. Vol'pin

*A.N. Nesmeyanov Institute of Organoelement Compounds of the Russian Academy of Sciences, Vavilov St. 28, Moscow 117813 (Russian Federation)*

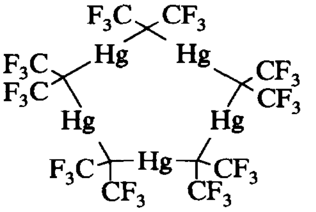
(Received July 29, 1992)

### Abstract

It has been found that cyclic pentameric perfluoroisopropylidenemercury, $[(CF_3)_2CHg]_5$, is capable of forming complexes with $[PPh_4]^+Cl^-$ and $[PPh_4]^+Br^-$ of the type $\{[(CF_3)_2CHg]_5X_2\}^{2-}[PPh_4]_2^+$ ($X = Cl$ or Br). According to an X-ray diffraction study, the chloride anions in the complex of $[(CF_3)_2CHg]_5$ with $[PPh_4]^+Cl^-$ are located above and below the mercury-containing metallacycle, each $Cl^-$ anion being coordinated with all the five mercury atoms of $[(CF_3)_2CHg]_5$.

In the course of our studies [1–6] on the development of crown compounds, effective in coordinating anions, we have recently found that cyclic trimeric perfluoro-*o*-phenylenemercury $(o\text{-}C_6F_4Hg)_3$ (**I**) is capable of forming complexes with $[PPh_3Me]^+I^-$, $[PPh_4]^+Br^-$ and $[PPh_4]^+Cl^-$ of the composition $[(o\text{-}C_6F_4Hg)_3X]^-[PR_3R']^+$ ($X = I$, $R = Ph$, $R' = Me$ (**II**); $X = Br$, $R = R' = Ph$ (**III**)) and $\{[(o\text{-}C_6F_4Hg)_3]_3X_2\}^{2-}[PR_3R']_2^+$ ($X = Cl$, $R = R' = Ph$) [2–6]. An X-ray diffraction study of the complexes **II** and **III** has shown that they have an unusual structure of the polydecker bent sandwiches $[(\cdots I \cdots X \cdots)_n]^{n-}$, in which every halogenide anion is coordinated with six mercury atoms of two neighbouring molecules of **I** [3–6].

Here we report that similar capacity to bind halogenide anions with formation of complexes is displayed by cyclic pentameric perfluoroisopropylidenemercury $[(CF_3)_2CHg]_5$ (**IV**) [7], which contains five mercury atoms in a planar ten-membered cycle.



(**IV**)

The complexes are readily obtained by mixing **IV** with $[PPh_4]^+Cl^-$, $[PPh_4]^+Br^-$ or $[PPh_3Me]^+I^-$ in ethanol at room temperature. The isolated compounds are fine-crystalline colourless solids, readily soluble in acetone and less soluble in EtOH. Complexes of **IV** with $[PPh_4]^+Cl^-$ and $[PPh_4]^+Br^-$ are of the type $\{[(CF_3)_2CHg]_5X_2\}^{2-}[PPh_4]_2^+$ ($X = Cl$ (**V**), Br (**VI**)), *i.e.* contain two halogenide anions per one molecule of **IV**. According to X-ray photoelectron spectra, all five mercury atoms in **V** and **VI** are equivalent, as are both the halogenide anions.

The structure of complex **V** was determined by an X-ray diffraction study ($-65$°C, $\lambda$(Mo K$\alpha$), $\theta/2\theta$-scan mode, $\theta \leqslant 23°$, an empirical absorption correction based on the $\psi$-scans of 15 reflections has been applied, $\mu(\text{Mo K}\alpha) = 110.43$ cm$^{-1}$, $R = 0.037$ for 5352 unique reflections with $I > 3\sigma(I)$). Crystals of **V** are triclinic, at $-65$°C $a = 12.623(3)$, $b = 13.790(4)$, $c = 23.481(5)$ Å, $\alpha = 76.09(2)$, $\beta = 80.59(2)$, $\gamma = 63.40(2)°$, $V = 3540(2)$ Å$^3$, $d_{calc} = 2.348$ g cm$^{-3}$, $Z = 2$, space group $P\bar{1}$.

The molecule of complex **V** has an unusual shape of a spinning top, the equatorial girdle of which is the mercury-containing metallacycle, whilst the axis direction is fixed by $Cl^-$ anions located above and below the metallacycle plane at approximately equal distances from the mercury atoms (Fig. 1).

A remarkable feature of complex **V** is the coordination of each chloride anion with all five Hg atoms of the cycle. The Hg–Cl(1) and Hg–Cl(2) distances span the ranges of 3.151–3.388 Å (av. 3.284 Å) and 3.089–3.312 Å (av. 3.221 Å), respectively. All Hg–Cl distances are significantly shorter than the sum of the Van der Waals radii of the Hg and Cl atoms (2.1 + 1.8 = 3.9 Å [8]). The existence of Hg–Cl coordinative bonds in **V** is also evidenced by an abnormally short $Cl^- \cdots Cl^-$ distance (3.25(1) Å), *ca.* 0.35 Å shorter than twice the

---

Correspondence to: Professor V.B. Shur.

0022-328X/93/$6.00

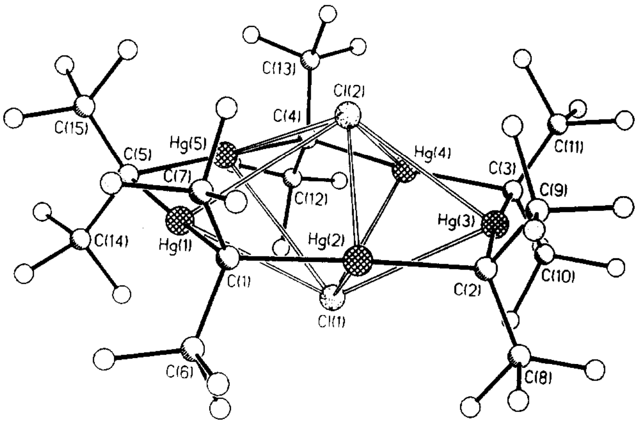


Fig. 1. Structure of the $\{[(CF_3)_2CHg]_5Cl_2\}^{2-}$ anion.

Van der Waals radius of the $Cl^-$ anion [8]. It is clear that the system is able to tolerate this otherwise unbearably shortened distance between two negatively charged $Cl^-$ ions, owing only to energetic gain from the strongly attracting Hg · · · Cl interactions.

Noticeably shorter Hg–Cl distances than those in **V** (2.944(2) Å) have recently been found by Hawthorne *et al.* [9] in the structure of a complex of a carboranylmercury metallacycle $(B_{10}H_{10}C_2Hg)_4$ (**VII**) a chloride anion. In this complex the $Cl^-$ anion is in the centre of a planar 12-membered cycle formed by four mercury and eight *o*-carboranyl carbon atoms. Evidently, in the case of **IV** the formation of a similar complex with $Cl^-$ is precluded by the smaller size of metallacycle in the molecule of **IV** compared with that in **VII**.

In the subsequent paper Hawthorne *et al.* [10] have reported the structure of a complex of **VII** with two iodide anions, which, like the $Cl^-$ anions in **V**, are located above and below the metallacycle plane. However, in contrast to **V**, this complex $[(B_{10}H_{10}C_2Hg)_4 I_2]^{2-}[AsPh_4]_2^+$ (**VIII**) is characterized by a pronounced asymmetry of the halogenide ion coordination. Each $I^-$ anion in **VIII** forms three comparatively short Hg–I bonds (3.277, 3.304 and 3.306 Å) and one considerably longer Hg–I bond (3.774 Å). Such symmetry violation was explained by the electrostatic repulsion of the iodide anions. One can assume that a similar asymmetry in **V** would conflict with the steric requirements of bulky $CF_3$ substituents that would not allow any significant displacement of the $Cl^-$ anions from the non-crystallographic five-fold symmetry axis of molecule **IV**.

The 10-membered $Hg_5C_5$ cycle in **V** exhibits only insignificant deviations from planarity (maximal displacement being 0.1 Å). The endocyclic Hg–C bond lengths are unexceptional (2.051–2.133 Å); the C–Hg–C bond angles in **V** (172.1–176.1°) as well as in **IV** are close to 180°; the Hg–C–Hg bond angles in **V** span the range of 102.0–104.9° (100.0–104.9° in **IV**). Although one of the C–F bond vectors in each of the ten $CF_3$-groups is directed towards the $Cl^-$ anion (the average pseudo-torsion angle Cl · · · C–C–F being 8°), such geometry can hardly be caused by any specific Cl · · · F interaction, taking into account that the relevant Cl · · · F distances in **V** (3.583–3.878 Å) are noticeably longer than the sum of corresponding Van der Waals radii (1.8 + 1.4 = 3.2 Å [8]). The observed C–F vector orientation is evidently due to the quite normal staggered conformation of the substituents around the exocyclic C–$CF_3$ bonds.

An interesting geometrical peculiarity of complex **V** is the significant decrease of its exocyclic $F_3C$–C–$CF_3$ bond angles compared with those in molecule **IV** (average values are 110.7 and 117.1°, respectively). Taking into account rather long Cl · · · F distances in **V** (*vide supra*), these differences in angles can hardly be attributed to steric factors. One may rather suggest, that the electronic effects, *viz.* the increase in electron density at the Hg atoms on going from **IV** to **V**, owing to the coordination of **IV** with $Cl^-$ anions, may cause the decrease in the exocyclic angles. Indeed, according to the VSEPR theory [11], the increase in the Hg–C bonds polarity, induced by coordination, should normally lead to a decrease in the $F_3C$–C–$CF_3$ bond angles.

## References

1 V. B. Shur, I. A. Tikhonova, P. V. Petrovskii and M. E. Vol'pin, *Metalloorg. Khim.*, *2* (1989) 1431; V. B. Shur, I. A. Tikhonova, P. V. Petrovskii and M. E. Vol'pin, *Organomet. Chem. USSR, 2* (1989) 759

2 I. A. Tikhonova, P. V. Petrovskii, S. Yu. Panov, G. G. Furin, V. B. Shur and M. E. Vol'pin, *Vth All-Union Conference on Organometallic Chemistry, Riga-Yurmala, April 1–4, 1991*, Abstracts, p. 90.

3 I. A. Tikhonova, A. I. Yanovsky, Yu. T. Struchkov, P. V. Petrovskii, S. Yu. Panov, G. G. Furin, V. B. Shur and M. E. Vol'pin, *IXth FECHEM Conference on Organometallic Chemistry, Heidelberg, Germany, July 14–19, 1991*, Abstracts, p. 108

4 V. B. Shur, I. A. Tikhonova, A. I. Yanovsky, Yu. T. Struchkov, P. V. Petrovskii, S. Yu. Panov, G. G. Furin and M. E. Vol'pin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1991) 1466

5 V. B. Shur, I. A. Tikhonova, A. I. Yanovsky, Yu. T. Struchkov, P. V. Petrovskii, S. Yu. Panov, G. G. Furin and M. E. Vol'pin, *J. Organomet. Chem.*, *418* (1991) C29

6 V. B. Shur, I. A. Tikhonova, A. I. Yanovsky, Yu. T. Struchkov, P.

V. Petrovskii, S. Yu. Panov, G. G. Furin and M. E. Vol'pin, *Dokl. Akad. Nauk SSSR, 321* (1991) 1002

7 M. Yu. Antipin, Yu. T. Struchkov, A. Yu. Volkonsky and E. M. Rokhlin, *Izv. Akad. Nauk SSSR, Ser. Khim.* (1983) 452

8 S. S. Batsanov, *Zh. Neorg. Khim., 36* (1991) 3015

9 X. Yang, C. B. Knobler and M. F. Hawthorne, *Angew. Chem., Int. Ed. Engl., 30* (1991) 1507

10 X. Yang, C. B. Knobler and M. F. Hawthorne, *J. Am. Chem. Soc., 114* (1992) 380

11 R. J. Gillespie, *Molecular Geometry*, Van Nostrand-Reinhold, London, 1972.