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Pentafluorophenyl trinuclear [Pt_2Hg] and hexanuclear [Pt_4Hg_2] anionic complexes containing unbridged Pt–Hg bonds and OH bridges

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Abstract

Two unprecedented reactions between $(NBu_4)_2[Pt(C_6F_5)_4]$ or $(NBu_4)_2[Pt(\mu\text{-}Cl)(C_6F_5)_2]_2$ and $Hg(NO_3)_2$ lead to trinuclear $(NBu_4)_2[(C_6F_5)_3Pt(\mu\text{-}OH)(\mu\text{-}HgC_6F_5)Pt(C_6F_5)_3]$ (**1**) or hexanuclear $(NBu_4)_2[(\mu\text{-}OH)_2\{C_6F_5)_2Pt(\mu\text{-}OH)(\mu\text{-}HgCl)Pt(C_6F_5)_2\}_2]$ (**2**), respectively. The structures of both complexes have been established by X-ray studies and contain OH bridges between each pair of platinum atoms and donor–acceptor Pt→Hg bonds unsupported by any covalent bridges. The crystallographic parameters are as follows: **1**: monoclinic, $C2/c$ with $a=19.787(6)$, $b=21.495(6)$, $c=18.242(5)$ Å, $\beta=96.18(3)°$, $D_{calc}=1.948$ g cm^{-3} for $Z=4$ formula units and $R=0.037$ utilizing 3090 data with $F_o^2 \geqslant 3\sigma(F_o^2)$, **2**: triclinic, $P\bar{1}$ with $a=14.23(1)$, $b=17.81(2)$, $c=20.55(2)$ Å, $\alpha=87.03(7)$, $\beta=83.92(7)$, $\gamma=83.46(5)°$, $D_{calc}=2.129$ g cm^{-3} for $Z=2$ and $R=0.079$ using 6507 reflections with $F_o^2 \geqslant 2.5\sigma(F_o^2)$.

Introduction

The ability of perhalophenyl platinate(II) complexes to act as Lewis bases allows the synthesis of polynuclear complexes which contain Pt-to-M (M = Ag, Sn, Pb) donor bonds [1]. Most of the hitherto reported complexes are heteronuclear derivatives containing Pt and Ag, obtained by using $AgClO_4$, $AgNO_3$ or $O_3ClOAgL$ (L = neutral ligands) as Lewis acids and mono- or binuclear pentahalophenyl platinate(II) complexes as the basic components. The structure of the resulting polynuclear complexes is strongly dependent on the platinum substrates and on the acid centres. So, by adequate choice of the platinum fragment, polynuclear Pt–Ag complexes containing one or two Pt–Ag bonds totally unsupported by any covalent bridging ligands as well as derivatives which contain Pt–Ag bonds supported by other bridging ligands have been prepared. This work has been the subject of a recent review [1].

Moreover, in most of these Pt→Ag complexes the perhalophenyl groups play a special structural role, since they are usually oriented in such a way that one of the *o*-X substituents (X = F, Cl) makes a 'short non-bonding contact' with the silver atom (*o*-X...Ag) which seems to contribute to the stability of the cluster. Although most of our efforts have been concentrated on the Pt–Ag derivatives, which are now fairly well represented by a variety of compounds with different structures, very recently we have extended our interest to other post-transition metals such as Sn and Pb, and we have synthesized the heteronuclear complexes $(NBu_4)[Sn\{Pt(\mu\text{-}Cl)(C_6F_5)_2\}_3]$ [2] and $(NBu_4)_2[Pb\{Pt(C_6F_5)_4\}_2]$ [3], which display very peculiar structures. In the former, a $[Pt_3(\mu\text{-}Cl)_3(C_6F_5)_6]^{3-}$ unit with a puckered Pt_3Cl_3 six-membered ring is bonded to the Sn(II) atom through three platinum to tin (Pt→Sn) bonds, and, in the latter, a central Pb(II) atom is linearly coordinated to two Pt(II) atoms, the lone pair of Pb(II) being stereochemically inactive.

In following our interest in such a type of complexes, we report here the reactions between the mononuclear $(NBu_4)_2[Pt(C_6F_5)_4]$ or the dinuclear $(NBu_4)_2[Pt(\mu\text{-}Cl)(C_6F_5)_2]_2$ [4] and $Hg(NO_3)_2$, which lead to heteronuclear Pt→Hg complexes. As a distinctive feature, unobserved so far, in this reaction a transfer of one anionic ligand (C_6F_5 or Cl, respectively) from the platinum(II) coordination sphere to the Hg centre takes place.

Experimental

Elemental analyses were performed with a Carlo Erba EA 1108 microanalyser. IR spectra were recorded

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(4000–200 cm^{-1}) on a Perkin-Elmer 883 spectrometer using Nujol mulls between polyethylene sheets. ^{19}F NMR spectra were recorded on a Varian Unity 300. Literature methods were used for the preparation of $(NBu_4)_2[Pt(C_6F_5)_4]$ and $(NBu_4)_2[Pt(\mu\text{-}Cl)(C_6F_5)_2]_2$ [4].

Synthesis of $(NBu_4)_2[(C_6F_5)_3Pt(\mu\text{-}OH)(\mu\text{-}HgC_6F_5)Pt(C_6F_5)_3]$ *(1)*

To a MeOH solution (20 ml) of $(NBu_4)_2[Pt(C_6F_5)_4]$ (0.300 g, 0.225 mmol) a quantity of $Hg(NO_3)_2$ (0.121 g, 0.372 mmol) was added, and the mixture was stirred at room temperature for 3 h. The resulting orange–yellow solution was evaporated to *c*. 10 ml and then deionized H_2O (50 ml) was added to produce the precipitation of a yellow solid which was washed with two portions (10 ml) of H_2O. The bulk solid was purified by passing its CH_2Cl_2 solution through a silica-gel column and eluting with CH_2Cl_2. The resulting solution was evaporated to dryness, and the residue was washed with n-hexane. Yield 87%. *Anal.* Calc. for $Pt_2HgF_{35}ON_2C_{74}H_{73}$: N, 1.2; C, 39.3; H, 3.2. Found: N, 1.3; C, 38.9; H, 3.4%. IR: ν(O–H), 3629s, 534m; C_6F_5, 801vs, 775s (X-sensitive) [5], 1636w, 1608w, 964vs.

Synthesis of $(NBu_4)_2[(\mu\text{-}OH)_2\{(C_6F_5)_2Pt(\mu\text{-}OH)(\mu\text{-}HgCl)Pt(C_6F_5)_2\}_2]$ *(2)*

$Hg(NO_3)_2$ (0.141 g, 0.434 mmol) was added to a CH_2Cl_2 solution of $(NBu_4)_2[Pt(\mu\text{-}Cl)(C_6F_5)_2]_2$ (0.350 g, 0.217 mmol), and the mixture was stirred at room temperature for 14 h. The resulting reddish suspension was filtered to eliminate the excess of $Hg(NO_3)_2$, the solution was evaporated to dryness, and the residue was stirred with 15 ml of deionized H_2O for 2 h. The red solid was washed with several portions of H_2O and air dried. **2**, 0.28 g, 83% yield. *Anal.* Calc. for $Pt_4Hg_2Cl_2F_{40}O_4N_2C_{80}H_{76}$: N, 0.9; C, 30.6; H, 2.4. Found: N, 1.1; C, 30.8; H, 2.6%. IR: ν(O–H), 3604s, 3560s, 563m, 518m; C_6F_5, 809s, 805s, (X-sensitive) [5], 964s; ν(Hg–Cl), 318m.

Crystal structure of $(NBu_4)_2[[(C_6F_5)_3Pt(\mu\text{-}OH)(\mu\text{-}HgC_6F_5)Pt(C_6F_5)_3]$ *(1)*

Air-stable orange–yellow crystals were produced by placing a layer of n-hexane over a saturated CH_2Cl_2 solution of compound **1** at −30 °C. The measurement of diffraction data was undertaken at −40 °C. Routine procedures were used to determine the lattice dimensions and Laue group, which were verified by normal-beam oscillation photography. The crystal was found to be *C*-centered monoclinic, with unit cell dimensions as given in Table 1. During intensity data collection, the intensities of three standard reflections, re-measured every three hours, showed no appreciable change as a function of time. An absorption correction was based on complete Ψ-scans of five reflections and on measurements of 22 moderately intense reflections and all of their symmetry equivalents.

Systematic absences were consistent with either of the space groups *Cc* or *C*2/*c*. The structure was developed and successfully refined in the centric group *C*2/*c*. The positions of the heavy atoms were given correctly by both direct methods and automatic Patterson interpretation [6], and the remaining non-hydrogen atoms were located and refined in an alternating series of difference maps and least-squares calculations. All non-hydrogen atoms were refined with anisotropic displacement parameters. The refinement converged with the final residuals given in Table 1. A final difference map did not show any peaks which could have been interpreted as possible positions for the hydrogen atom of the hydroxide bridging ligand. We did not include this or any other hydrogen atoms in the structural model.

Crystal structure of $(NBu_4)_2[(\mu\text{-}OH)_2\{(C_6F_5)_2Pt(\mu\text{-}OH)(\mu\text{-}HgCl)Pt(C_6F_5)_2\}_2]$ *(2)*

Red laminar crystals were grown by diffusion of a layer of n-hexane into a CH_2Cl_2 solution of the compound at −30 °C.

The crystals were found to lose solvent rapidly, to the extent that nearly a dozen attempts to mount crystals for diffraction proved fruitless. Crystals covered with silicon grease did not survive the few seconds needed to transfer them into the cold stream of the low temperature device of the diffractometer. It proved practically impossible to manipulate crystals for any period of time, or to measure or cut them. In the end, a crystal that later proved to be somewhat larger than the X-ray beam was covered with lithium grease and rapidly transferred to the diffractometer. As we did not know even the chemical nature of compound **2**, we proceeded with an analysis of this crystal, even knowing that the precision of the results would be diminished because of the use of a large crystal.

The collection of geometrical and intensity data was conducted via common techniques. The dimensions of the triclinic lattice were verified by six continuous scans ('Q-scans') of reciprocal lattice lines. Data were collected at −50 °C, and the intensities of three monitor reflections remained nearly constant through the course of data collection. A scan step of 0.03° ω was used (with ω–2θ scans), and each step was counted for a time that varied, under computer control, between 0.5 and 2.0 s. Measurements for the purpose of absorption correction comprised full Ψ-scans of five reflections, along with the measurement of 62 additional reflections and their symmetry equivalents. Crystal data for complex **2** are summarized in Table 1.

The six independent heavy atoms of the asymmetric unit were located by direct methods [6] and the re-

TABLE 1. Crystal data for $(NBu_4)_2[(C_6F_5)HgPt_2(\mu\text{-}OH)(C_6F_5)_6]$ (**1**) and $(NBu_4)_2[(HgCl)_2\{Pt(\mu\text{-}OH)(C_6F_5)_2\}_4]\cdot 1.75CH_2Cl_2$ (**2**)

	1	**2**
Formula	$Pt_2HgF_{35}N_2C_{74}H_{73}O$	$Pt_4Hg_2Cl_2F_{40}N_2C_{80}H_{76}O_4\ \frac{7}{4}CH_2Cl_2$
Formula weight	2262.1	3290.5
Space group	$C2/c$	$P\bar{1}$
a (Å)	19.787(6)	14.228(12)
b (Å)	21.495(6)	17.813(12)
c (Å)	18.242(5)	20.55(2)
α (°)	90	87.03(7)
β (°)	96.18(3)	83.92(7)
γ (°)	90	83.46(5)
V, Å^3	7714(4)	5141(8)
Z	4	2
D_{calc} (g/cm^3)	1.948	2.126
μ (Mo Kα) (cm^{-1})	59.75	90.11
Radiation (graphite monochromated)		Mo Kα (λ_α = 0.71073 Å)
Temperature (°C)	-40 ± 1	-50 ± 1
R^a	0.0370	0.0792
$R_w{}^b$	0.0465	0.0961
Quality of fit indicator^c	1.037	1.500

$^aR=\Sigma||F_o|-|F_c||/\Sigma|F_o|$ $^bR_w=[\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$. ^{c}Quality of fit $=[\Sigma w(|F_o|-|F_c|)^2/(N_{obs}-N_{param})]^{1/2}$

maining non-hydrogen atoms were located and refined in a series of alternating least-squares refinement and difference Fourier maps. In all, 144 non-hydrogen atomic sites were established (for the 100 atoms of the hexanuclear dianion, for the 34 atoms of the two independent tetrabutylammonium cations and for the 10 sites for the three dichloromethane moieties, one of which had one atom (C70a, C70b) disordered over two sites). The specific volume of the final structural model, then, was 17.9 Å^3 per non-hydrogen atom. We did not attempt to incorporate any hydrogen atom sites into the structural model.

The existence of three distinct sites for dichloromethane moieties is consistent with the severe and rapid physical decomposition which the crystals were observed to suffer. One of the solvent sites was modelled with full occupancy and refined freely with isotropic displacement parameters. A second moiety (around C60) was assigned a single overall isotropic displacement parameter and a fixed occupancy of 0.5, after an occupancy parameter had refined to almost this value. The third CH_2Cl_2 site (C70a, C70b, Cl71, Cl72) was disordered around a crystallographic inversion centre, with atom Cl71 lying in the centre. The occupancy parameter for this group refined to almost 0.25 (with $U_{overall}$ fixed at 0.12 Å^2), and was fixed at this value later with an overall variable isotropic displacement parameter assigned to the group. The atomic parameters of this group oscillated to the extent that the entire group was held fixed in the final least-squares refinement.

We observed clear and unmistakable symptoms of having used a large crystal. First of all, fifty-three atoms were kept isotropic in the final refinement because their anisotropic displacement tensors had become non-positive definite. Secondly, two strong, low-angle reflections, (101) and (110), emerged with $|F_{obs}| \ll |F_{calc}|$ and they were omitted from the final refinement. Thirdly, the final difference Fourier map had quite dense positive and negative peaks (Table 1) as was to be expected. The largest peaks were located near the core of the hexanuclear anion. (The specific volume of the structural model makes it unlikely that any further chemical moieties remain to be found.)

The final refinement, then, involved a model of 144 atomic sites, of which 81 had anisotropic displacement parameters. A common isotropic displacement parameter was used for each of two dichloromethane molecules. In all, the model comprised 974 parameters, of which 964 were varied in the last least-squares analysis. Because of the number of parameters, the final refinement was done in four blocks. In each block, half of the C_6F_5 ligands and one of the NBu_4 cations were refined, and the two blocks thus generated were repeated with the half set of C_6F_5 ligands and the NBu_4 groups spoonerized. In this way, all covariance matrix elements were computed at least one time during the process. Observational restraints were used for seven bond distances and for four angles within the NBu_4 cations. The refinement converged with the residuals given in Table 1.

The structure determination of compound **2** serves to establish the connectivity and geometry of the hexanuclear complex. While the derived distances and angles are in line with accepted values for groups of known geometry, and while the magnitudes of the displacement parameters show the expected trends, it is undoubtable that the standard deviations of refined and derived parameters are somewhat underestimated. In particular, the use of a large crystal renders nearly impossible the determination and use of the covariances among the observations $|F_{\mathrm{obs}}|$, covariances which, in this case, may well be significant.

Results and discussion

Synthesis

$(\mathrm{NBu_4})_2[\mathrm{Pt(C_6F_5)_4}]$ reacts with an excess of $\mathrm{Hg(NO_3)_2}$ (1:1.65 molar ratio), in MeOH, yielding an orange solution from which yellow $(\mathrm{NBu_4})_2[(\mathrm{C_6F_5})_3\mathrm{Pt}(\mu\text{-}\mathrm{OH})(\mu\text{-}\mathrm{HgC_6F_5})\mathrm{Pt(C_6F_5)_3}]$ (**1**) can be isolated by addition of $\mathrm{H_2O}$, which is the only treatment leading to isolable solids, since otherwise intractable oils are obtained. The formation of **1**, whose structure has been established by an X-ray study, is schematized in eqn. (1).

$$\begin{aligned}&(\mathrm{NBu_4})_2[\mathrm{Pt(C_6F_5)_4}] + \mathrm{Hg(NO_3)_2} + \mathrm{H_2O} \longrightarrow\\&\quad(\mathrm{NBu_4})_2[(\mathrm{C_6F_5})_3\mathrm{Pt}(\mu\text{-}\mathrm{OH})(\mu\text{-}\mathrm{HgC_6F_5})\mathrm{Pt(C_6F_5)_3}]\\&\quad+ 2\mathrm{NBu_4NO_3} + \mathrm{C_6F_5H} \qquad (1)\end{aligned}$$

The reaction involves the transfer of a $\mathrm{C_6F_5}$ ligand from the platinum centre to the mercury one and the hydrolysis of another $\mathrm{C_6F_5}$ ligand. This course of the reaction is unprecedented: neither $\mathrm{Ag^+}$, $\mathrm{Sn^{2+}}$ or $\mathrm{Pb^{2+}}$ react in such a way. A tentative explanation might be as follows: relativistic effects, which enhance the stability of the 6s orbital, make the bare $\mathrm{Hg^{2+}}$ ion a very strong electrophile and the usual share of electron density with one $\mathrm{Pt \rightarrow Hg}$ or two $\mathrm{Pt \rightarrow Hg \leftarrow Pt}$ platinum centres in the anionic pentahalophenyl complexes is not enough to satisfy the electron density requirements of the $\mathrm{Hg^{2+}}$ cation. Instead, an anionic $\mathrm{C_6F_5}$ ligand is abstracted from the coordination sphere of the platinum in $[\mathrm{Pt(C_6F_5)_4}]^{2-}$ to give an $(\mathrm{Hg{-}C_6F_5})^+$ moiety, leaving a coordinatively unsaturated '$(\mathrm{C_6F_5})_3\mathrm{Pt}$' fragment which, in order to complete its coordination sphere, interacts with a second $[\mathrm{Pt(C_6F_5)_4}]^{2-}$ anion to form a $\mathrm{C_6F_5}$-bridged dinuclear moiety $[(\mathrm{C_6F_5})_3\mathrm{Pt}(\mu\text{-}\mathrm{C_6F_5})\mathrm{Pt(C_6F_5)_3}]^{2-}$ anion, a potentially chelating ligand which binds the mercury atom in the $(\mathrm{Hg{-}C_6F_5})^+$ moiety and undergoes hydrolysis in the $\mathrm{C_6F_5}$ bridging group to give $\mathrm{C_6F_5H}$ and the resulting $[(\mathrm{C_6F_5})_3\mathrm{Pt}(\mu\text{-}\mathrm{OH})(\mu\text{-}\mathrm{HgC_6F_5})\mathrm{Pt(C_6F_5)_3}]^{2-}$ anion.

On the other hand, the binuclear derivative $(\mathrm{NBu_4})_2[\mathrm{Pt}(\mu\text{-}\mathrm{Cl})(\mathrm{C_6F_5})_2]_2$ reacts with $\mathrm{Hg(NO_3)_2}$ (molar ratio 1:2) in $\mathrm{CH_2Cl_2}$ yielding, after the adequate treatment for crystallization (which includes the addition of $\mathrm{H_2O}$, see 'Experimental'), a red solid of a complicated stoichiometry, $(\mathrm{NBu_4})_2[(\mu\text{-}\mathrm{OH})_2\{(\mathrm{C_6F_5})_2\mathrm{Pt}(\mu\text{-}\mathrm{OH})(\mu\text{-}\mathrm{HgCl})\mathrm{Pt(C_6F_5)_2}\}_2]$ (**2**), whose nature has been established by a single crystal X-ray diffraction study. In this case the formation of the complex is the result of both a hydrolysis of the platinum substrate and the transfer of chloride from the platinum to the mercury centre (eqn. (2)).

$$\begin{aligned}&2(\mathrm{NBu_4})_2[\mathrm{Pt}(\mu\text{-}\mathrm{Cl})(\mathrm{C_6F_5})_2]_2 + 2\mathrm{Hg(NO_3)_2} + 4\mathrm{H_2O} \longrightarrow\\&\quad(\mathrm{NBu_4})_2[(\mu\text{-}\mathrm{OH})_2\{(\mathrm{C_6F_5})_2\mathrm{Pt}(\mu\text{-}\mathrm{OH})(\mu\text{-}\mathrm{HgCl})\mathrm{Pt(C_6F_5)_2}\}_2]\\&\quad+ 2\mathrm{NBu_4}^+ + 4\mathrm{H}^+ + 4\mathrm{NO_3}^- + 2\mathrm{Cl}^- \qquad (2)\end{aligned}$$

This reaction is also unprecedented. Although it could be envisaged in a similar way to that discussed above (eqn. (1)), it is more complicated because the expected trinuclear $[(\mathrm{C_6F_5})_2\mathrm{Pt}(\mu\text{-}\mathrm{OH})(\mu\text{-}\mathrm{HgCl})(\mathrm{Pt(C_6F_5)_2}]^{2-}$ anion further reacts to give the hexanuclear complex which appears as the end-product (eqn. (2)).

Structure of 1

General crystallographic information is given in Table 1. Positional parameters are listed in Table 2. Selected bond distances and bond angles are given in Table 3. The structure of the anion is shown in Fig. 1. It is a trinuclear derivative containing two Pt and one Hg atoms, and can be considered as formed by the interaction of the anion $[(\mathrm{C_6F_5})_3\mathrm{Pt}(\mu\text{-}\mathrm{OH})\mathrm{Pt(C_6F_5)_3}]^-$ with the $[\mathrm{Hg(C_6F_5)}]^+$ cation through two $\mathrm{Pt \rightarrow Hg}$ donor acceptor bonds unsupported by any covalent bridging ligand. The Pt–Hg distance (2.718(1) Å) is near the high end of the range found in other polynuclear complexes containing Pt–Hg bonds [7–17], in keeping with the donor-acceptor ($\mathrm{Pt \rightarrow Hg}$) nature of this bond [9].

Each platinum centre is in a distorted square-pyramidal environment, with three $\mathrm{C_6F_5}$ groups and one OH bridging group lying in the base of the pyramid and the Hg atom in the apical position. The platinum atom is less than 0.1 Å out of the basal plane and the Pt–Hg bond forms an angle of 13.5° with the perpendicular to the basal plane. As in other complexes containing the '$\mathrm{Pt(C_6F_5)_3X}$' fragment [18–20] the Pt–C distances of the $\mathrm{C_6F_5}$ groups in mutually *trans* positions are identical (within experimental error: 2.07(1), 2.10(1) Å), while the Pt–C distance corresponding to the $\mathrm{C_6F_5}$ *trans* to the OH is shorter (2.02(1) Å) indicating that $\mathrm{C_6F_5}$ groups display a higher *trans* influence than does the OH ligand. The Pt–O distance (2.074(6) Å) is similar to those found in other μ-hydroxo platinum(II) complexes with OH bridging two platinum centres [21–25] and slightly shorter than Pt–O distances found in μ^3-hydroxo platinum complexes [26–28] and the angle Pt–O–Pt (116.0(5)°) is larger than those found in most μ-hydroxo platinum complexes [21, 22, 24–27]. However,

TABLE 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $(NBu_4)_2[Hg(C_6F_5)Pt_2(\mu\text{-}OH)(C_6F_5)_6]$ (**1**)

	x	y	z	U_{eq}[a]
Hg(1)	0(1)	1583(1)	2500	38(1)
Pt(1)	838(1)	2547(1)	2935(1)	38(1)
O(1)	0	3058(5)	2500	47(5)
C(1)	446(6)	2472(7)	3954(6)	39(5)
C(2)	241(8)	2989(7)	4317(9)	53(6)
C(3)	−29(8)	2979(8)	4981(10)	60(7)
C(4)	−85(8)	2426(9)	5324(8)	61(7)
C(5)	139(8)	1902(9)	5003(10)	66(7)
C(6)	380(7)	1936(7)	4338(8)	48(6)
F(2)	299(5)	3559(4)	3991(5)	83(4)
F(3)	−203(5)	3518(5)	5293(5)	100(5)
F(4)	−330(5)	2426(5)	5979(5)	97(5)
F(5)	72(6)	1353(5)	5346(5)	97(5)
F(6)	574(4)	1381(3)	4063(4)	59(3)
C(7)	1238(6)	2684(6)	1941(7)	39(5)
C(8)	1393(7)	2232(7)	1464(8)	45(5)
C(9)	1607(8)	2322(8)	766(9)	56(6)
C(10)	1671(8)	2913(8)	520(9)	58(7)
C(11)	1543(7)	3380(7)	977(9)	57(6)
C(12)	1315(6)	3277(6)	1668(8)	42(5)
F(8)	1350(4)	1618(4)	1662(4)	70(3)
F(9)	1716(5)	1837(5)	320(5)	82(4)
F(10)	1863(5)	3027(5)	−143(5)	88(4)
F(11)	1605(5)	3993(4)	744(5)	83(4)
F(12)	1175(5)	3783(4)	2069(5)	71(4)
C(13)	1708(6)	2153(7)	3395(7)	39(5)
C(14)	1921(6)	1543(7)	3407(7)	46(5)
C(15)	2530(8)	1354(8)	3775(8)	60(7)
C(16)	2945(7)	1780(11)	4152(8)	70(8)
C(17)	2792(9)	2389(11)	4153(9)	73(8)
C(18)	2158(7)	2567(8)	3783(8)	56(6)
F(14)	1527(4)	1097(4)	3050(4)	57(3)
F(15)	2702(4)	748(5)	3745(5)	80(4)
F(16)	3548(5)	1561(7)	4497(6)	118(6)
F(17)	3201(5)	2805(6)	4505(6)	112(5)
F(18)	2015(4)	3180(4)	3815(5)	75(4)
C(19)	0	611(9)	2500	45(7)
C(20)	−324(7)	272(7)	2994(9)	51(6)
C(21)	−348(8)	−380(8)	2990(11)	72(8)
C(22)	0	−684(10)	2500	77(11)
F(20)	−671(4)	562(4)	3497(5)	71(4)
F(21)	−682(5)	−686(4)	3481(6)	99(5)
F(22)	0	−1322(6)	2500	127(8)
N(1)	3019(6)	208(5)	1472(7)	55(5)
C(101)	3084(8)	929(6)	1445(8)	59(6)
C(102)	3541(9)	1188(7)	2097(9)	73(7)
C(103)	3512(11)	1875(8)	2127(10)	88(8)
C(104)	4014(10)	2151(10)	2715(11)	103(9)
C(105)	3737(8)	−108(8)	1635(10)	76(7)
C(106)	4247(8)	63(8)	1094(10)	81(8)
C(107)	4954(9)	−24(9)	1484(12)	99(9)
C(108)	5488(10)	101(10)	986(13)	110(10)
C(109)	2710(8)	−27(8)	732(8)	68(7)
C(110)	1977(8)	240(8)	539(9)	68(7)
C(111)	1680(9)	−125(10)	−145(12)	103(9)
C(112)	959(10)	147(10)	−423(10)	104(9)
C(113)	2591(8)	52(7)	2111(9)	66(7)
C(114)	2376(9)	−639(8)	2118(11)	85(8)
C(115)	2067(9)	−746(9)	2843(11)	97(9)
C(116)	1793(10)	−1374(10)	2945(15)	141(12)

[a] The equivalent isotropic U is defined as one third of the trace of the orthogonalized U_{ij} tensor.

TABLE 3. Selected bond distances (Å) and angles (°) for $(NBu_4)_2[Hg(C_6F_5)Pt_2(\mu\text{-}OH)(C_6F_5)_6]$ (**1**)

Distances			
Hg(1)–Pt(1)	2.718(1)	Hg(1)–C(19)	2 09(2)
Pt(1)–C(1)	2.10(1)	Pt(1)–C(7)	2.08(1)
Pt(1)–C(13)	2.02(1)	Pt(1)–O(1)	2.074(6)
Hg(1)–F(6)	2.985(8)		
Angles			
Pt(1)–Hg(1)–Pt(1A)	80.7(1)	Pt(1)–Hg(1)–C(19)	139.7(1)
Hg(1)–Pt(1)–O(1)	81.6(3)	Hg(1)–Pt(1)–C(1)	85.9(4)
O(1)–Pt(1)–C(1)	91.3(3)	Hg(1)–Pt(1)–C(7)	97.6(3)
O(1)–Pt(1)–C(7)	87.4(3)	C(1)–Pt(1)–C(7)	176.1(5)
Hg(1)–Pt(1)–C(13)	105.5(4)	O(1)–Pt(1)–C(13)	172.8(5)
C(1)–Pt(1)–C(13)	88.8(5)	C(7)–Pt(1)–C(13)	92 0(5)
Pt(1)–O(1)–Pt(1A)	116.0(5)		

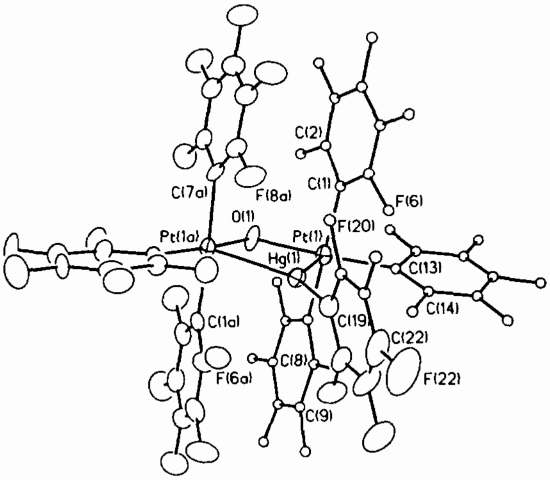

Fig. 1. Drawing of the complex anion from the crystal structure of $(NBu_4)_2[(C_6F_5)_3Pt(\mu\text{-}OH)(\mu\text{-}HgC_6F_5)Pt(C_6F_5)_3]$ (**1**). The atom labelling scheme is indicated; atom numbers increase sequentially around the phenyl rings, and fluorine atom numbers correspond to those of the parent carbon atoms. Atoms O(1), Hg(1), C(19), C(22) and F(22) lie on a crystallographic two-fold axis. For clarity, displacement ellipsoids (30% probability) are shown only for Pt, Hg, O and a unique set of C and F atoms.

this value is in the range found in $[Pt(en)(OH)Pt]^{4+}$ [23] or in $[Pt_3(\mu^3\text{-}OH)(\mu\text{-}OPPh_2)_3(PR_3)_3]^{2+}$ [28].

On the other hand, mercury is located in an almost planar trigonal environment formed by the two platinum centres and the C_{ipso} atom of the C_6F_5 group, the corresponding angles around Hg being very different (Pt–Hg–C(19) = 139.7(1)°, Pt(1)–Hg–Pt(1a) = 80.7(1)°). Finally there is a pair of close non-bonding *o*-F...Hg contacts (Hg...F(6), 2.985(8) Å) related to each other by the crystallographic two-fold axis that passes though the Hg atom. The angle F–Hg–F is 163.3(3)°.

Spectroscopic data are given in 'Experimental'.

Structure of 2

Figure 2 shows the hexanuclear anion $[(HgCl)_2\{Pt_2(\mu\text{-}OH)(C_6F_5)_2\}_4]^{2-}$ along with the atom labelling scheme.

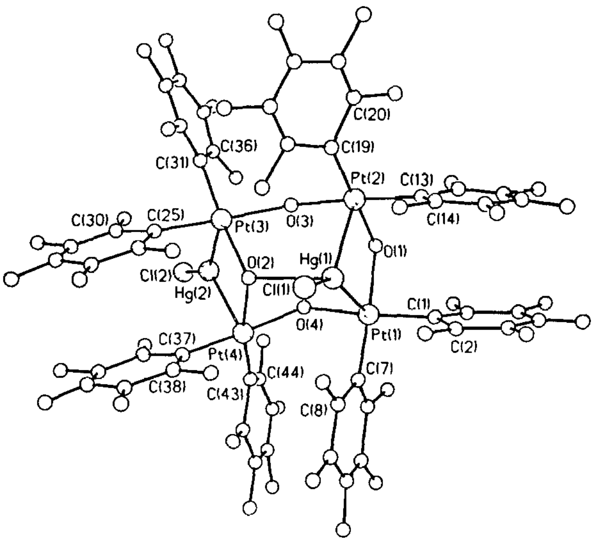

Fig. 2. Drawing of the hexanuclear dianion $[(\mu\text{-OH})_2\{(C_6F_5)_2Pt(\mu\text{-OH})(\mu\text{-HgCl})Pt(C_6F_5)_2\}_2]^{2-}$ (2). Atoms are numbered sequentially within the phenyl rings, and fluorine atoms have the same numbers as the carbon atoms to which they are attached

General information is given in Table 1, atomic coordinates are listed in Table 4 and selected distances and angles are presented in Table 5. As described in 'Experimental', the structure determination of compound **2** serves to establish the composition and overall stereochemistry of the system. The derived geometrical parameters have large estimated standard deviations, for the reasons laid out in 'Experimental', and so we do not attempt any finely detailed comparisons of distances and angles. The core of the anion is best described as a puckered eight-membered ring, $(Pt\text{–}OH\text{–})_4$, to which two units of (HgCl) are bound, each through two Pt–Hg bonds (Fig. 2). Each platinum centre also has two C_6F_5 ligands *cis* to each other, in such a way that the platinum centre has, at the base of its coordination shell, a square plane of two carbon and two oxygen atoms. The coordination about each platinum centre is completed by a mercury atom, which sits at the apex of a square pyramid. The platinum–mercury and platinum–oxygen distances found for complex **2** are quite similar to those in the trinuclear complex **1**. As far as the Pt–C distances in **2** (which have large yet still underestimated standard deviations) can be compared with results from other structures, they too are similar on the whole to those found in **1**. The bond angles about two of the bridging oxygen atoms – O(1) and O(2), which bridge pairs of platinum atoms that also bond mercury – are near the tetrahedral value (Pt(1)–O(1)–Pt(2), 108(1)°; Pt(3)–O(2)–Pt(4), 108(1)°). The angles about the other two oxygen atoms are more open: Pt(2)–O(3)–Pt(3), 133(1)°; Pt(1)–O(4)–Pt(4), 125(1)°. By analogy to the case of compound **1**, the eight-membered skeletal ring

TABLE 4. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $(NBu_4)_2[(HgCl)_2(Pt(\mu\text{-OH})(C_6F_5)_2)_4] \cdot 1.75\ CH_2Cl_2$ (2)

	x	y	z	U_{eq}[a]
Hg(1)	3593(1)	6190(1)	2688(1)	33(1)
Pt(1)	1707(1)	6174(1)	2737(1)	31(1)
Pt(2)	3440(1)	5557(1)	1536(1)	30(1)
Pt(3)	3755(1)	7674(1)	1104(1)	29(1)
Pt(4)	2201(1)	8149(1)	2414(1)	30(1)
Hg(2)	2103(1)	8528(1)	1121(1)	34(1)
Cl(1)	4954(8)	6343(7)	3203(6)	51(5)
Cl(2)	1044(7)	9287(6)	495(5)	44(4)
Atomic coordinates are given $\times 10^3$ for the following atoms				
O(1)	199(2)	570(1)	180(1)	27(6)
O(2)	349(2)	752(1)	211(1)	25(6)
O(3)	316(2)	664(1)	107(1)	32(6)
O(4)	164(2)	719(1)	218(1)	33(6)
C(1)	163(3)	517(2)	316(2)	29(9)
C(2)	217(4)	482(3)	366(2)	61(14)
C(3)	214(4)	405(3)	394(2)	55(13)
C(4)	144(3)	363(3)	377(2)	60(21)
C(5)	86(3)	396(3)	333(2)	50(12)
C(6)	94(3)	475(3)	304(2)	59(21)
F(2)	296(2)	517(2)	382(1)	80(13)
F(3)	271(2)	375(2)	432(2)	125(18)
F(4)	139(3)	300(2)	404(2)	141(21)
F(5)	18(2)	358(2)	312(2)	109(17)
F(6)	36(2)	501(2)	261(2)	91(15)
C(7)	128(3)	671(2)	352(2)	39(11)
C(8)	195(4)	697(3)	399(3)	66(15)
C(9)	148(5)	740(3)	456(3)	74(17)
C(10)	57(5)	746(3)	471(2)	77(27)
C(11)	−7(3)	729(3)	431(2)	43(11)
C(12)	36(3)	687(3)	368(2)	51(12)
F(8)	278(2)	692(2)	386(1)	75(13)
F(9)	203(3)	762(2)	495(2)	114(18)
F(10)	8(2)	781(2)	524(2)	92(15)
F(11)	−105(3)	736(2)	444(2)	137(21)
F(12)	−30(2)	660(2)	332(2)	96(15)
C(13)	354(3)	451(2)	198(2)	33(10)
C(14)	415(3)	425(3)	239(2)	54(13)
C(15)	412(3)	355(2)	273(2)	51(19)
C(16)	350(3)	307(3)	263(3)	56(20)
C(17)	292(4)	336(2)	220(2)	52(19)
C(18)	298(3)	400(2)	185(2)	42(11)
F(14)	483(2)	468(1)	255(1)	69(12)
F(15)	476(3)	335(1)	318(1)	94(15)
F(16)	345(3)	247(1)	299(2)	103(16)
F(17)	221(2)	287(2)	206(2)	109(17)
F(18)	228(2)	417(1)	141(2)	69(12)
C(19)	477(3)	544(2)	118(2)	36(10)
C(20)	529(3)	480(3)	79(2)	41(11)
C(21)	611(4)	473(3)	54(2)	50(12)
C(22)	666(4)	528(3)	53(3)	49(12)
C(23)	635(3)	587(2)	91(2)	37(17)
C(24)	547(3)	594(3)	118(2)	42(11)
F(20)	468(2)	426(1)	69(1)	68(12)
F(21)	651(2)	409(2)	18(1)	79(13)
F(22)	760(2)	519(2)	31(2)	86(14)
F(23)	692(2)	641(2)	94(2)	92(15)
F(24)	514(2)	656(1)	153(1)	51(6)
C(25)	437(3)	861(2)	113(2)	35(10)

(*continued*)

TABLE 4. (*continued*)

	x	y	z	U_{eq}[a]
C(26)	497(3)	872(2)	159(2)	39(11)
C(27)	532(3)	940(3)	169(2)	54(20)
C(28)	512(3)	1004(3)	129(2)	48(12)
C(29)	453(3)	997(2)	88(2)	31(10)
C(30)	417(3)	931(3)	75(2)	58(13)
F(26)	528(2)	810(1)	200(1)	49(10)
F(27)	598(2)	938(1)	216(1)	72(12)
F(28)	544(2)	1068(2)	145(2)	89(15)
F(29)	432(2)	1061(1)	47(1)	61(11)
F(30)	357(2)	934(1)	30(1)	47(10)
C(31)	408(3)	772(2)	13(2)	27(9)
C(32)	496(3)	768(3)	−15(2)	51(20)
C(33)	527(4)	769(3)	−79(3)	63(25)
C(34)	451(4)	767(2)	−122(2)	63(23)
C(35)	359(4)	762(2)	−97(2)	44(18)
C(36)	337(3)	767(2)	−30(2)	38(11)
F(32)	570(2)	767(2)	22(1)	58(11)
F(33)	616(2)	766(2)	−104(1)	79(13)
F(34)	479(2)	767(2)	−190(1)	72(13)
F(35)	289(2)	764(2)	−139(1)	80(13)
F(36)	249(2)	762(2)	−12(1)	56(11)
C(37)	278(3)	904(2)	259(2)	32(10)
C(38)	347(3)	902(2)	304(2)	41(11)
C(39)	391(3)	968(3)	319(2)	47(18)
C(40)	378(3)	1032(3)	286(2)	40(11)
C(41)	307(3)	1038(3)	245(2)	48(12)
C(42)	264(2)	974(3)	229(2)	29(9)
F(38)	368(2)	838(1)	339(1)	60(11)
F(39)	454(2)	956(1)	363(1)	60(11)
F(40)	416(2)	1090(1)	302(2)	83(14)
F(41)	291(2)	1107(2)	211(2)	81(9)
F(42)	198(2)	990(1)	88(1)	63(11)
C(43)	98(3)	854(3)	273(2)	47(11)
C(44)	12(3)	862(3)	247(2)	50(12)
C(45)	−83(5)	876(3)	270(3)	78(17)
C(46)	−95(5)	904(4)	330(3)	88(18)
C(47)	−21(4)	908(3)	366(3)	74(15)
C(48)	78(4)	889(3)	340(2)	63(14)
F(44)	12(2)	840(1)	187(1)	62(11)
F(45)	−156(2)	884(2)	247(2)	113(17)
F(46)	−180(2)	933(2)	364(2)	118(17)
F(47)	−19(3)	934(2)	431(2)	97(15)
F(48)	150(2)	889(1)	376(1)	59(7)
N(1)	444(2)	211(2)	503(2)	44(14)
C(101)	529(4)	155(3)	479(2)	69(24)
C(102)	564(4)	161(3)	405(3)	69(24)
C(103)	640(4)	92(4)	388(3)	95(31)
C(104)	679(6)	89(5)	319(3)	135(43)
C(105)	352(3)	198(3)	470(2)	53(20)
C(106)	323(4)	117(3)	481(3)	67(14)
C(107)	236(4)	118(3)	443(3)	84(17)
C(108)	208(4)	39(4)	455(3)	93(19)
C(109)	431(3)	196(3)	578(2)	55(20)
C(110)	346(4)	254(3)	611(2)	68(23)
C(111)	337(4)	223(4)	682(3)	94(28)
C(112)	264(5)	281(4)	725(3)	102(20)
C(113)	464(3)	290(3)	478(2)	54(13)
C(114)	558(3)	309(3)	501(3)	115(33)
C(115)	577(9)	390(3)	488(4)	248(79)
C(116)	582(8)	423(4)	430(4)	312(94)
N(2)	1004(3)	192(2)	140(2)	74(19)
C(201)	929(3)	138(3)	119(2)	55(20)
C(202)	937(3)	55(3)	156(4)	107(33)
C(203)	873(4)	8(4)	124(3)	86(28)
C(204)	776(5)	33(4)	147(3)	117(23)
C(205)	970(5)	264(2)	104(4)	114(35)
C(206)	1023(4)	331(3)	115(4)	147(38)
C(207)	979(4)	396(3)	75(3)	93(19)
C(208)	1023(5)	467(3)	86(4)	177(53)
C(209)	1024(5)	179(4)	210(2)	102(20)
C(210)	930(5)	203(4)	253(4)	114(23)
C(211)	942(5)	183(5)	331(4)	115(28)
C(212)	957(7)	103(3)	340(3)	170(50)
C(213)	1099(4)	165(4)	100(2)	118(24)
C(214)	1119(3)	177(3)	27(2)	79(26)
C(215)	1216(3)	139(4)	4(2)	197(55)
C(216)	1243(3)	155(3)	−66(3)	92(28)
C(50)	−15(6)	337(5)	864(4)	150(29)
Cl(51)	103(2)	341(2)	886(1)	181(10)
Cl(52)	−74(1)	292(1)	926(1)	102(5)
C(60)	699(12)	462(11)	257(9)	163(12)
Cl(61)	792(3)	498(3)	229(2)	163(12)
Cl(62)	702(3)	387(3)	215(2)	163(12)
Cl(71)	0	500	500	272
C(70a)	−51(1)	426(1)	457(1)	272
C(70b)	−81(1)	479(1)	485(1)	272
Cl(72)	−84(1)	382(1)	536(1)	272

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

(–[Pt(OH)]$_4$–) acts as a bidentate chelate ligand to each of two mercury centres.

The two mercury atoms have quite different coordination environments. Hg(2) is three-coordinate, with trigonal planar geometry provided by atoms Cl(2), Pt(3) and Pt(4). As with compound **1**, the Pt–Hg–Pt angle is acute, while the two other angles at the mercury centre are significantly larger than 120° (Tables 3 and 5). Atom Hg(1), on the other hand, has a similar set of three bonds to one chlorine and two platinum atoms, plus an additional, weak bond to oxygen atom O(2) (Hg(1)–O(2), 2.59(2) Å). Thus, the overall coordination about Hg(1) is a trigonal pyramid with a rhombic distortion in the basal plane. The observed bonding to atom O(2) is pyramidal, in agreement with the stoichiometric requirement that this be a hydroxide group.

Another important consequence (or perhaps an enabling cause) of the Hg(1)–O(2) interaction is that the two planar Pt–O–Pt–Hg– rings are inclined 48° to each other rather than being parallel. The core of the anion thus has only trivial symmetry.

Finally, as is usual in this type of compound (heteronuclear [L(C$_6$F$_5$)$_n$Pt → ML′] complexes with Pt → M (M = Ag, Sn, Pb) donor acceptor bonds [1]), we observe in **2** short *o*-F...Hg contacts, as follows: Hg(1)...F(2),

TABLE 5. Selected bond distances (Å) and angles (°) for $(NBu_4)_2[(HgCl)_2\{Pt(\mu\text{-}OH)(C_6F_5)_2\}_4]\cdot 1.75\ CH_2Cl_2$ (**2**)

Distances			
Hg(1)–Pt(1)	2.678(4)	Hg(1)–Pt(2)	2.714(4)
Hg(1)–Cl(1)	2.35(1)	Hg(1)–O(2)	2.59(2)
Pt(1)–O(1)	2.12(2)	Pt(1)–O(4)	2.10(2)
Pt(1)–C(1)	1.96(4)	Pt(1)–C(7)	1.92(4)
Pt(2)–O(1)	2.07(2)	Pt(2)–O(3)	2 12(2)
Pt(2)–C(13)	2.02(4)	Pt(2)–C(19)	1.94(4)
Pt(3)–Hg(2)	2.648(4)	Pt(3)–O(2)	2.07(2)
Pt(3)–O(3)	2.12(3)	Pt(3)–C(25)	1.97(4)
Pt(3)–C(31)	2.02(4)	Pt(4)–Hg(2)	2 720(4)
Pt(4)–O(2)	2 10(2)	Pt(4)–O(4)	2.06(3)
Pt(4)–C(37)	1.94(4)	Pt(4)–C(43)	1.86(4)
Hg(2)–Cl(2)	2 35(1)		
Angles			
Pt(1)–Hg(1)–Pt(2)	79.0(1)	Pt(1)–Hg(1)–Cl(1)	150.3(3)
Pt(2)–Hg(1)–Cl(1)	129.9(3)	Pt(1)–Hg(1)–O(2)	91.5(5)
Pt(2)–Hg(1)–O(2)	90.2(5)	Cl(1)–Hg(1)–O(2)	94.9(6)
Hg(1)–Pt(1)–O(1)	85.6(6)	Hg(1)–Pt(1)–O(4)	88 5(7)
O(1)–Pt(1)–O(4)	82.6(9)	Hg(1)–Pt(1)–C(1)	98(1)
O(1)–Pt(1)–C(1)	91(1)	O(4)–Pt(1)–C(1)	171(1)
Hg(1)–Pt(1)–C(7)	102(1)	O(1)–Pt(1)–C(7)	170(1)
O(4)–Pt(1)–C(7)	91(1)	C(1)–Pt(1)–C(7)	95(2)
Hg(1)–Pt(2)–O(1)	85 6(7)	Hg(1)–Pt(2)–O(3)	91.0(7)
O(1)–Pt(2)–O(3)	82.7(9)	Hg(1)–Pt(2)–C(13)	91(1)
O(1)–Pt(2)–C(13)	91(1)	O(3)–Pt(2)–C(13)	173(1)
Hg(1)–Pt(2)–C(19)	100(1)	O(1)–Pt(2)–C(19)	173(1)
O(3)–Pt(2)–C(19)	94(1)	C(13)–Pt(2)–C(19)	93(2)
Hg(2)–Pt(3)–O(2)	88.1(6)	Hg(2)–Pt(3)–O(3)	94.8(6)
O(2)–Pt(3)–O(3)	84.5(9)	Hg(2)–Pt(3)–C(25)	88(1)
O(2)–Pt(3)–C(25)	96(1)	O(3)–Pt(3)–C(25)	177(1)
Hg(2)–Pt(3)–C(31)	97(1)	O(2)–Pt(3)–C(31)	174(1)
O(3)–Pt(3)–C(31)	92(1)	C(25)–Pt(3)–C(31)	88(2)
Hg(2)–Pt(4)–O(2)	85.7(6)	Hg(2)–Pt(4)–O(4)	83.2(7)
O(2)–Pt(4)–O(4)	82 7(9)	Hg(2)–Pt(4)–C(37)	95(1)
O(2)–Pt(4)–C(37)	95(1)	O(4)–Pt(4)–C(37)	177(1)
Hg(2)–Pt(4)–C(43)	98(1)	O(2)–Pt(4)–C(43)	169(2)
O(4)–Pt(4)–C(43)	88(2)	C(37)–Pt(4)–C(43)	95(2)
Pt(3)–Hg(2)–Pt(4)	77 9(1)	Pt(3)–Hg(2)–Cl(2)	145.8(3)
Pt(4)–Hg(2)–Cl(2)	136 2(3)	Pt(1)–O(1)–Pt(2)	110(1)
Hg(1)–O(2)–Pt(3)	122(1)	Hg(1)–O(2)–Pt(4)	110.5(9)
Pt(3)–O(2)–Pt(4)	108(1)	Pt(2)–O(3)–Pt(3)	134(1)
Pt(1)–O(4)–Pt(4)	125(1)		

3.00(3); Hg(1)...F(8), 2.87(3); Hg(1)...F(14), 3.04(2); Hg(2)...F(30), 2.99(2); Hg(2)...F(36), 3.05(3); Hg(2)...F(42), 2.95(2) and Hg(2)...F(44), 3.08(2) Å.

NMR spectra

The ^{19}F NMR spectra of both complexes in $CDCl_3$ at room temperature show very complicated multiplets in the *o*-F and in the *m*- and *p*-F regions, but the complexity of these signals precludes a detailed assignment. The higher solubility of **2** allows a study at different temperatures (−60 °C, room temperature; at higher temperatures decomposition is observed), which indicates the dynamic behaviour of this complex, although the spectra cannot be fully analyzed.

The ^{1}H NMR spectrum of **2** in $CDCl_3$ at room temperature shows, beside the signals due to the NBu_4 groups, three peaks at 2.97 (broad), 2.15 and 1.55 ppm (2:1:1), which can be due to the protons of the OH groups. However, the spectrum of **1**, which is less soluble, shows signals due to the NBu_4 groups but no signals assignable to the OH groups can be observed.

Supplementary material

All the crystallographic material (atomic coordinates, bond lengths, bond angles and anisotropic thermal parameters) is available on request from the authors.

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