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Synthesis and structural characterization of the luminescent tetranuclear complex $[NBu_4]_2[(C_6F_5)_6(\mu\text{-}OH)_3Pt_3HgCl]$ with Pt–Hg bonds unsupported by covalent bridging ligands

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Abstract

The tetranuclear cluster $[NBu_4]_2[(C_6F_5)_6(\mu\text{-}OH)_3Pt_3HgCl]$ is obtained by reacting the mononuclear platinum complex $[NBu_4]_2[Pt(C_6F_5)_3Cl]$ with $Hg(NO_3)_2$ followed by appropriate work-up. The X-ray study reveals that the compound possesses three donor–acceptor Pt → Hg bonds unsupported by any covalent bridges. The crystallographic parameters are: monoclinic, $P2_1/n$ with $a = 11.9770(10)$, $b = 26.092(3)$, $c = 24.991(2)$ Å, $\beta = 92.900(10)°$, $D_{calc} = 2.009$ Mg m^{-3} for $Z = 4$ and $R = 0.076$ utilizing 13 657 data with $F_o^2 \geq 2\sigma(F_o^2)$. The UV–vis spectrum of the solid sample has been studied revealing that the compound is strongly luminescent.

Keywords: Luminescence; Platinum–mercury bond; Donor–acceptor bond

1. Introduction

It has been proved that the platinum centres in perhalophenyl anionic complexes have a basic character and that they react with Lewis-acid metal complexes or metal salts [M] to form heteropolynuclear complexes with donor–acceptor Pt → M bonds. Most of these polynuclear complexes contain Pt → Ag bonds [1] but derivatives with other acidic metal centres, such as Sn(II) [2], Pb(II) [3], Hg(II) [4] or Tl(II) [5], have been prepared as well.

In most of the cases studied to date, the final heteropolynuclear compound forms as a result of interaction between the platinum-containing starting anion and the acidic metal substrate [M]. Thus, $[NBu_4]_2[\textit{trans}\text{-}Pt(C_6F_5)_2Cl_2]$ and $[NBu_4][Pt(C_6F_5)_3(tht)]$ react with $AgClO_4$ or $O_3ClOAgL$, yielding the tetranuclear $[NBu_4]_2[\{(C_6F_5)_2PtCl_2\}_2(\mu\text{-}Ag)_2]$ [6] and the trinuclear $[(C_6F_5)_3(tht)PtAgL]$[7] derivatives, respectively. In only a few cases does the platinate complex react with the substrate [M], producing a chemical transformation to a heteropolynuclear complex; e.g $[NBu_4]_2[Pt(C_6F_5)_3Cl]$ reacts with $AgClO_4$ first forming $[NBu_4]_2[Pt_2(\mu\text{-}C_6F_5)_2(C_6F_5)_4]$ and then yielding the trinuclear derivative $[NBu_4]_2[(C_6F_5)_4(\mu\text{-}C_6F_5)_2Pt_2AgOEt_2]$ [8].

In addition, platinate complexes containing halogen ligands are useful in the synthesis of new heteropolynuclear compounds of this type, since the halogen can serve as either a bridging or terminal ligand in addition to being easily substituted. Regarding heteronuclear complexes as such, mercury has turned out to be useful in their preparation, and a great variety of high-nuclearity heterometallic clusters with M–Hg bonds have been reported [9]. Here we report the reaction between a mononuclear platinum complex containing a terminal chlorine ligand, $[NBu_4]_2[Pt(C_6F_5)_3Cl]$, and $Hg(NO_3)_2$, which yields a tetranuclear complex containing the $[Pt_3Hg]$ core. Its optical behaviour has also been studied.

2. Results and discussion

The addition of $Hg(NO_3)_2$ to a colourless solution of $[NBu_4]_2[Pt(C_6F_5)_3Cl]$ in CH_2Cl_2 in a 1:1 molar ratio, followed by 2 h stirring at room temperature (r.t.), gave

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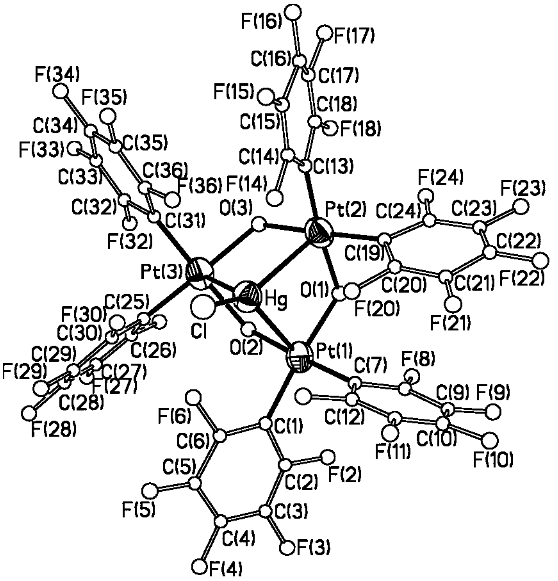

Fig. 1. Drawing of the anion from the crystal structure of $[NBu_4]_2[(C_6F_5)_6(\mu\text{-}OH)_3Pt_3HgCl]$, showing the atom labelling scheme. Heavy atoms are represented by their 50% probability ellipsoids.

a red solution, which after filtration, evaporation to dryness, and addition of a mixture of $^{i}PrOH/H_2O$ to the residue rendered an orange complex of stoichiometry $[NBu_4]_2[(C_6F_5)_6(\mu\text{-}OH)_3Pt_3HgCl]$. The formation of this complex is the result of partial decomposition of the platinate substrate, which loses a pentafluorophenyl and the chloro ligand in a hydrolysis process which introduces the OH groups. The latter bridge the platinum centres in the resulting trinuclear fragment '$[Pt_3(\mu\text{-}OH)_3(C_6F_5)_6]^{3-}$', which is capped by the $HgCl^+$ species through three Pt–Hg bonds.

The structure of **1** has been established by an X-ray diffraction study.

2.1. Crystal structure of $[NBu_4]_2[(C_6F_5)_6(\mu\text{-}OH)_3Pt_3HgCl]$

The structure of the anionic complex in $[NBu_4]_2[(C_6F_5)_6(\mu\text{-}OH)_3Pt_3HgCl]$ with the atom numbering scheme is shown in Fig. 1. Selected bond distances and angles are listed in Table 1.

The tetranuclear cluster can be described as a $[(C_6F_5)_6(\mu\text{-}OH)_3Pt_3]^{3-}$ unit with a puckered central six-membered $Pt_3(\mu\text{-}OH)_3$ ring in which the three platinum atoms are interconnected by three bridging hydroxy ligands and linked to the HgCl fragment by three platinum-to-mercury donor–acceptor bonds. Thus, the puckered $Pt_3(\mu\text{-}OH)_3$ ring acts as a tridentate ligand to the $[HgCl]^+$ unit. Each platinum atom is located in a square-pyramidal environment with the Hg atom in the apical position. The basal plane is defined by the *ipso*-C atoms of two *cis*-C_6F_5 groups and the oxygen atoms of two bridging hydroxy ligands. The Pt–Hg bonds form angles of 10.5° (Pt1), 14.4° (Pt2) and 19.8°(Pt3) with the perpendiculars to their respective basal planes. The Pt–Hg distances (2.750(1)–2.875(1) Å) are in the range found for other complexes with Pt → Hg donor–acceptor bonds [4] and are longer than those observed in complexes displaying Pt–Hg covalent bonds (around 2.5 Å) [10].

Table 1
Selected bond distances (Å) and angles (°) and their estimated standard deviations for $[NBu_4]_2[(C_6F_5)_6(\mu\text{-}OH)_3Pt_2HgCl]$

Bond distances			
Pt(1)–C(1)	1.99(2)	Pt(1)–C(7)	1.95(2)
Pt(1)–O(2)	2.06(1)	Pt(1)–O(1)	2.08(1)
Pt(1)–Hg	2.764(1)	Pt(2)–C(13)	1.97(3)
Pt(2)–C(19)	1.98(2)	Pt(2)–O(1)	2.077(13)
Pt(2)–O(3)	2.09(1)	Pt(2)–Hg	2.750(1)
Pt(3)–C(25)	1.97(2)	Pt(3)–C(31)	1.99(3)
Pt(3)–O(3)	2.08(1)	Pt(3)–O(2)	2.10(1)
Pt(3)–Hg	2.875(1)	Hg–Cl	2.370(5)
Bond angles			
C(1)–Pt(1)–C(7)	87.8(9)	C(1)–Pt(1)–O(2)	176.1(8)
C(1)–Pt(1)–O(2)	94.9(6)	C(7)–Pt(1)–O(1)	93.0(8)
C(1)–Pt(1)–O(1)	171.5(7)	O(2)–Pt(1)–O(1)	83.9(5)
C(7)–Pt(1)–Hg	98.5(7)	C(1)–Pt(1)–Hg	102.2(7)
O(2)–Pt(1)–Hg	83.6(3)	O(1)–Pt(1)–Hg	86.1(4)
C(13)–Pt(2)–C(19)	89.9(9)	C(13)–Pt(2)–O(1)	171.2(9)
C(19)–Pt(2)–O(1)	90.1(7)	C(13)–Pt(1)–O(3)	92.2(8)
C(19)–Pt(2)–O(3)	173.3(8)	O(1)–Pt(2)–O(3)	86.9(5)
C(13)–Pt(2)–Hg	102.0(8)	C(19)–Pt(2)–Hg	105.3(7)
O(1)–Pt(2)–Hg	86.5(3)	O(3)–Pt(2)–Hg	80.5(3)
C(25)–Pt(3)–C(31)	92(1)	C(25)–Pt(3)–O(3)	175.7(8)
C(31)–Pt(3)–O(3)	87.5(9)	C(25)–Pt(3)–O(2)	89.7(8)
C(31)–Pt(3)–O(2)	172.9(9)	O(3)–Pt(3)–O(2)	90.4(5)
C(25)–Pt(3)–Hg	106.6(7)	C(31)–Pt(3)–Hg	106(1)
O(3)–Pt(3)–Hg	77.6(4)	O(2)–Pt(3)–Hg	80.1(3)
Cl–Hg–Pt(2)	136.2(1)	Cl–Hg–Pt(1)	136.9(1)
Pt(2)–Hg–Pt(1)	76.56(4)	Cl–Hg–Pt(3)	126.4(1)
Pt(2)–Hg–Pt(3)	79.79(4)	Pt(1)–Hg–Pt(3)	78.3(1)
Pt(1)–O(1)–Pt(2)	110.7(5)	Pt(1)–O(2)–Pt(3)	117.6(5)
Pt(3)–O(3)–Pt(2)	119.6(6)		

The mercury atom is located in a distorted tetrahedral environment formed by the three platinum atoms and the chlorine ligand, the Pt–Hg–Pt angles being significantly smaller than 109.67° (Pt–Hg–Pt2, 76.56(4)°; Pt2–Hg–Pt3, 79.79(4)°; Pt1–Hg–Pt3, 78.26(4)°) and the Cl–Hg–Pt angles larger than that (Cl–Hg–Pt1, 136.9(1)°; Cl–Hg–Pt2, 136.2 (1)°; Cl–Hg–Pt3, 126.4(1)°). The platinum···platinum distances lie in the normal range for complexes containing double bridges between platinum(II) atoms, signaling the absence of any bond between these metal centres: Pt1···Pt2, 3.415(1); Pt1···Pt3, 3.609(1); Pt2···Pt3, 3.559(1) Å.

The Pt–C and Pt–O bond distances are in the usual range of values and very similar to the values reported for $[NBu_4]_2[Pt_2(\mu\text{-}OH)_2(C_6F_5)_4]$ [11]; however, it should be noted that the Pt–O–Pt and O–Pt–O angles in the dinuclear complex (Pt–O–Pt, 101.4°; O–Pt–O, 78.6°)

are smaller than the values found in **1**: Pt1–O1–Pt2, 110.7°; Pt1–O2–Pt3, 117.6°; Pt3–O3–Pt2, 119.6°; O3–Pt3–O2, 90.4°; O2–Pt1–O1, 83.9°; O1–Pt2–O3, 86.9°.

Although this type of pentafluorophenyl containing platinum complex with Pt → M donor–acceptor bonds usually displays *o*-F···M contacts [1c], in this case the *o*-F···Hg distances are rather long (Hg–*o*-F distances: for F(6), 2.966; F(20), 3.106; F(36), 3.142; F(12), 3.152; F(14), 3.168; F(30), 3.429 Å) indicating very weak, if any, *o*-F···Hg interactions. Since the Hg ion is located in a four-coordinate environment, the *o*-F···Hg contacts may not be necessary for the stability of the complex.

The trinuclear platinum fragment in **1** has no independent existence as a stable complex, its stoichiometry being equal to that of the very stable dinuclear anion $[Pt_2(\mu\text{-}OH)_2(C_6F_5)_4]^{2-}$ [11]; so the presence of this trinuclear framework in the tetranuclear cluster must be a consequence of the formation of the three Pt–Hg bonds. A similar structural disposition of platinum atoms has been described for a tetranuclear tin-containing complex, $[NBu_4]_2[(C_6F_5)_6(\mu\text{-}Cl)_3Pt_3Sn]$ [3], which displays three $Pt^{II} \rightarrow Sn^{II}$ bonds instead of the $Pt^{II} \rightarrow Hg^{II}$ bonds and three chlorine ligands bridging the platinum atoms instead of the hydroxo groups of **1**.

This type of cluster, in which Hg or the HgR^+ fragment caps an M_3 triangle, is well known. The triangular M_3 unit is formed by transition metals in low oxidation states and usually displays metal-metal bonds between the metal atoms. The M_3 triangle capped by Hg may be a self-standing complex [12] or part of a higher nuclearity cluster (homo or hetero-metallic) [13]. There is one compound, $[NMe_4][\{Co(CO)_4\}_3(\mu\text{-}Hg)]$, in which the Hg centre participates in three Co–Hg bonds while the Co centres do not form Co–Co bonds [14].

As far as Pt–Hg complexes are concerned, three structural types containing triangular platinum(0) fragments are known: (i) complexes in which the Hg atom or HgL unit is bonded to the three platinum atoms of the triangle with similar Hg–Pt bond distances [15]; (ii) complexes in which the Hg atom bridges two Pt_3 fragments, forming six Hg–Pt bonds [16]; and (iii) compounds with an Hg_2 dimer unit bridging two Pt_3 triangles, with each mercury atom bonded to three platinum atoms [17]. The trinuclear Pt cluster in all of these cases is formed by Pt(0), not Pt(II), centres. Complex **1**, $[NBu_4]_2[(C_6F_5)_6(\mu\text{-}OH)_3Pt_3HgCl]$, could in principle be viewed as belonging to type (i) in this classification scheme, but it must be noted that in **1** there are no Pt–Pt bonds and the oxidation state of Pt is II. Several platinum(II) complexes displaying Pt–Hg donor–acceptor bonds have been reported, but in these cases the mercury atom is generally bonded to one or in a very few cases to two platinum atoms [18].

The ^{1}H-NMR spectrum of $[NBu_4]_2[(C_6F_5)_6(\mu\text{-}OH)_3Pt_3HgCl]$ in $CDCl_3$ at r.t. shows the four signals corresponding to the tetrabutylammonium cation but not the signal corresponding to the bridging OH ligands, probably because of proton exchange with water present in the solvent. The ^{19}F-NMR spectrum in $CDCl_3$ indicates that the complex $[NBu_4]_2[(C_6F_5)_6(\mu\text{-}OH)_3Pt_3HgCl]$ does not persist either at r.t. or at −60°C. At r.t., in the *ortho*-fluorine region only one signal can be detected (−119.92 (2F,*o*-F,$^3J_{Pt-o-F} = 524$ Hz)) the coupling constant of which permits us to assign it to the C_6F_5 groups of the complex $[NBu_4]_2[Pt_2(\mu\text{-}OH)_2(C_6F_5)_4]$. The signals corresponding to the *m*-F and *p*-F atoms of these groups are also observed in the spectrum (−165.04 (*p*-F,1F) and −166.89 (*m*-F,2F) ppm). In addition, two more signals (−162.34 (*p*-F,2F) and −165.67 (*m*-F,4F)) in the *p*-F and *m*-F region are also detected, indicating that there are other types of C_6F_5 groups present. However, the corresponding *o*-F signals are not observed. This seems to indicate that these latter C_6F_5 groups belong to a complex (or complexes) involved in a fluxional process. At −60°C, the ^{19}F-NMR spectrum shows, in addition to the signals due to the dinuclear complex $[NBu_4]_2[Pt_2(\mu\text{-}OH)_2(C_6F_5)_4]$, two signals in the *o*-F region at −110.89 ($^3J_{Pt-o-F} = 507.1$ Hz) and −123.22 ($^3J_{Pt-o-F} = 292.1$ Hz) ppm; in the *p*-F and *m*-F region two signals of equal intensities at −164.88 and −165.42 ppm due to *m*-F atoms and another signal at −161.66 ppm due to a *p*-F atom are observed. These data suggest that in solution the binuclear derivative and one other pentafluorophenyl platinum containing complex, — as yet unidentified — are present.

2.2. Optical properties

Many compounds containing heteronuclear d^8-d^8 or d^{10}-d^8 clusters are luminescent, a property linked to the electronic distribution around the metal clusters. Before the luminescence of compound **1** is discussed, it should be noted that the binuclear derivative $[NBu_4]_2[Pt_2(\mu\text{-}OH)_2(C_6F_5)_4]$, which has the same stoichiometry and Pt environment as the trinuclear platinate fragment bonded to $HgCl^+$ in compound **1**, has interesting luminescence (see Fig. 2). This compound is slightly emissive in the solid state at r.t., exhibiting a structured vibronic band at ca. 423 nm with a spacing of ca. 3014 cm^{-1} for the vibrational progression. This emission can be assigned to a metal-to-ligand transition. In $CHCl_3$ solution at r.t. no luminescence is detected; however, at low temperature (77 K, $CHCl_3$, glass) the complex shows an intense yellow emission at ca. 538 nm (18 587 cm^{-1}) with a full width at half maximum (FWHM) of 3368 cm^{-1}. This change in the luminescent behaviour at low temperature can be attributed to stronger Pt···Pt interactions. The emission of the Pt_3Hg cluster shows an intense orange luminescence at 653 nm (15 310 cm^{-1}) with an FWHM of 3180 cm^{-1}, in the solid state at r.t. In $CHCl_3$ solution at r.t., an extremely weak

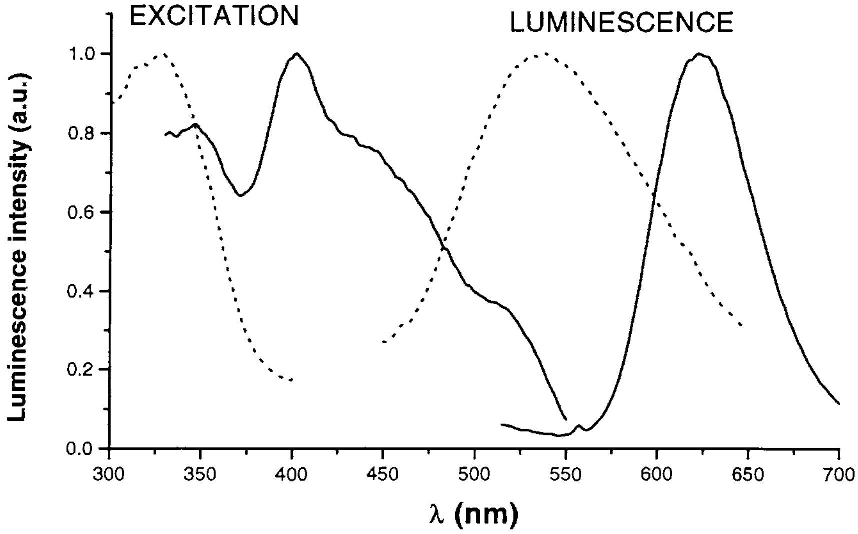

Fig. 2. Emission and excitation spectra of $[NBu_4]_2[(C_6F_5)_6(\mu\text{-OH})_3Pt_3HgCl]$ (—) and $[NBu_4]_2[Pt_2(\mu\text{-OH})_2(C_6F_5)_4]$ (- - -) in degassed $CHCl_3$ at 77 K.

luminescence is observed; however, at 77 K ($CHCl_3$, glass) the complex displays strong luminescence with a maximum at 622 nm (16 077 cm^{-1}) and an FWHM of 1711 cm^{-1}. The peaks of the excitation spectrum (maxima at 347, 402, 441 and 512 nm in $CHCl_3$ solution at 77 K; and 480 nm in the solid state) correspond to the observed electronic absorption energies, indicating that the electronic states involved in absorption in the range 400–480 nm are also probably implicated in the strong luminescence. Nevertheless, a large Stokes shift is observed (3454 cm^{-1}), which would indicate a strong configurational modification accompanying optical excitation.

The optical properties appear to be dominated by the tetranuclear Pt_3Hg core. A possible assignment for the origin of the emission involves a metal–metal (Pt–Hg) based charge transfer.

This optical behaviour also indicates that the tetranuclear compound is not present in solution at r.t.

3. Experimental section

3.1. General procedures

C, H, and N analyses were carried out with a Perkin–Elmer 240B microanalyzer. IR spectra were recorded over the range 4000–200 cm^{-1} on a Perkin–Elmer 883 spectrophotometer using nujol mulls between polyethylene sheets. The ^1H- and ^{19}F-NMR spectra were recorded on a Varian Unity-300 spectrometer in $CDCl_3$ solutions. UV–vis absorption spectra were recorded on a Hitachi U-3400 spectrophotometer (solid state) and on a Hewlett–Packard 8453 spectrophotometer (solution). Photoluminescence spectra were measured by excitation with light from a 1000 W tungsten lamp passed though a 0.22 m double monochromator. Fluorescence was detected through a 0.5 m monocromator with a photomultiplier detector. The luminescence spectra were corrected for instrumental response. Luminescence as well as excitation spectra were recorded on a Perkin–Elmer Luminescence Spectrometer LS 50B with a red-sensitive Type R928 photomultiplier. $[NBu_4]_2[Pt(C_6F_5)_3Cl]$ was prepared as described elsewhere [19]. $Hg(NO_3)_2$ was obtained from commercial sources and used as delivered.

3.2. Preparation of $[NBu_4]_2[(C_6F_5)_6(\mu\text{-OH})_3Pt_3HgCl]$

$Hg(NO_3)_2$ (0.080 g, 0.25 mmol) was added to a CH_2Cl_2 solution (20 ml) of $[NBu_4]_2[Pt(C_6F_5)_3Cl]$ (0.300 g, 0.247 mmol), and the mixture was stirred at r.t. for 2 h. The resulting reddish suspension was filtered to eliminate the excess of $Hg(NO_3)_2$. The solution was evaporated to dryness, and to the residue 10 ml of ^{i}PrOH and 40 ml of H_2O were added, rendering an orange solid which was filtered off and washed with ^{i}PrOH and *n*-hexane. (Yield: 69%.)

3.3. Analytical and spectroscopic data

Anal. Found (Calc. for $Pt_3HgClF_{30}O_3N_2C_{68}H_{75}$): N, 1.37(1.19); C, 35.10(34.61); H 3.21(3.20). IR data (cm^{-1}): ν(O–H) 3591(m); C_6F_5 X-sensitive [20]: 808(s), 801(s); C_6F_5 others: 1638(w), 1608(w), 1504(vs), 1066(vs), 961(vs); ν(Hg–Cl) 315(w). ^1H-NMR data [CD_3Cl, r.t.], ppm: NBu_4^+: 0.96 (t, 12H, CH_3), 1.43 (sextuplet, 8H, α-CH_2), 1.73 (m, 8H, β-CH_2), 3.43 (m, 8H, γ-CH_2).

3.4. Preparation of crystals of $[NBu_4]_2[(C_6F_5)_6(\mu\text{-}OH)_3Pt_2HgCl]$ for the X-ray structure determination

Suitable crystals for X-ray purposes were obtained by slow diffusion of an *n*-hexane layer into a CH_2Cl_2 solution of $[NBu_4]_2[(C_6F_5)_6(\mu\text{-}OH)_3Pt_2HgCl]$ at 4°C.

3.5. X-ray structure analysis of $[NBu_4]_2[(C_6F_5)_6(\mu\text{-}OH)_3Pt_2HgCl]$

A crystal of $[NBu_4]_2[(C_6F_5)_6(\mu\text{-}OH)_3Pt_3HgCl]$ (approximate dimensions $0.34 \times 0.32 \times 0.29$ mm) was mounted on a glass fibre and covered with epoxy. Standard procedures were used to gather the data with an automated four-circle diffractometer [21]. Although the lattice paramenters emerged from routine procedures with no difficulty, axial photographs were taken of the *a*-, *b*- and *c*-axes to verify the lattice dimensions. For intensity data collection, ω–θ scans were used with $\Delta\omega = (1.25 + 0.37 \tan \theta)°$. The scan parameters, including the scan type, were chosen on the basis of two-dimensional $(\omega - \theta)$ plots of several reflections. Other parameters relevant to the data collection are given in Table 2. Three monitor reflections, which were re-measured after every 3 h of beam time, decreased by an average of 11% in intensity over the 168 h of total X-ray exposure. An empirical absorption correction was based on ψ-scans of 15 scattering vectors [22].

Table 2
Crystal data and structure refinement for $[NBu_4]_2[(C_6F_5)_6(\mu\text{-}OH)_3Pt_3HgCl]$ [a]

Empirical formula	$C_{68}H_{75}ClF_{30}HgN_2O_3Pt_3$
Formula weight	2359.61
Temperature (K)	296(2)
Wavelength (Å)	0.71073
Crystal system, space group	Monoclinic, $P2_1/n$
Unit cell dimensions	
a (Å)	11.9770(10)
b (Å)	26.092(3)
c (Å)	24.991(2)
α (°)	90
β (°)	92.900(10)
γ (°)	90
Volume (Å^3)	7799.8(13)
Z, D_{calc} (Mg m^{-3})	4, 2.009
Absorption coefficient (mm^{-1})	7.477
$F(000)$	4488
Crystal size (mm)	$0.34 \times 0.32 \times 0.29$
Theta range for data collection (°)	2.01–24.98
Index ranges	$0 \le h \le 14$, $0 \le k \le 30$, $-29 \le l \le 29$
Reflections collected/unique	14398/13657 [$R_{int} = 0.0876$]
Absorption correction	Psi-scans
Max and min transmission	0.900 and 0.773
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	13 641/0/976
Goodness-of-fit on F^2	1.046
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0765$, $wR_2 = 0.0908$
R indices (all data)	$R_1 = 0.2442$, $wR_2 = 0.1386$
Largest difference peak and hole (e Å^{-3})	0.807 and −0.732

[a] $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$; $wR_2 = [\Sigma\, w(|F_o| - |F_c|)^2/\Sigma\, w|F_o|^2]^{1/2}$; goodness-of-fit $= [\Sigma\, w(|F_o| - |F_c|)^2/(N_{obs} - N_{param})]^{1/2}$; $w = 1/\sigma^2(F) + 0.001051F^2$.

The structure was solved and developed by Patterson and Fourier methods. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms of the CH_2 and CH_3 groups were constrained to idealised geometries (C–H, 0.97 Å; H–C–H, 107°), and the isotropic displacement parameter of each of these hydrogen atoms was set to a value of 1.2 times the equivalent isotropic displacement parameter of its parent carbon atom. The hydrogen atoms of the OH groups were omitted.

One methyl carbon atom of one NBu_4 group was modelled as a pair of atomic sites with an occupancy of 0.5 for each methyl congener, and the hydrogen atoms of these moieties and all of the other methyl groups were omitted.

Eight atomic sites in two interstitial zones were modelled as two CH_2Cl_2 molecules (one molecule with occupancy 0.5) with anisotropic displacement for the carbon and chlorine atoms. The hydrogen atoms of these groups were omitted from the model. One chlorine atom of CH_2Cl_2 is disordered over two positions in each solvent molecule (with relative occupancies of 0.5/0.5 and 0.25/0.75, respectively).

The data-to-parameter ratio in the final refinement was 14.0. The structure was refined to F_o^2, and all reflections were used in the least-squares calculations [23]. The residuals and other pertinent parameters are summarized in Table 2.

4. Supplementary material

Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 135277. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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