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A luminescent Pt_3Pb cluster with three $Pt(II) \rightarrow Pb(II)$ bonds

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Dedicated to Professor P. Royo on the occasion of his 65th anniversary.

Abstract

The reaction between the pentafluorophenylplatinate derivative $(NBu_4)_2[Pt_2(\mu\text{-}Cl)_2(C_6F_5)_4]$ and $Pb(ClO_4)_2$ (1.5:1) in dry tetrahydrofuran yields the tetranuclear complex $(NBu_4)[Pb\{Pt(\mu\text{-}Cl)(C_6F_5)_2\}_3]$ (**1**). The crystal structure of this compound has been analyzed by X-ray diffraction and reveals the presence of three Pt → Pb metal–metal bonds. This complex shows luminescence at low temperature.

Keywords: Platinum complexes; Pentafluorophenyl derivatives; Pt → Pb bonds; Luminescent properties

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1. Introduction

Complexes containing Pt–Pb bonds are very rare. The few known examples are: (a) the Pt(0)–Pb(II) derivative $[Pt_2(P_2phen)_3Pb](ClO_4)_2$ [P_2phen = 2,9-bis(diphenylphosphine)-1,10-phenanthroline], with a nearly linear Pt–Pb–Pt core [1]; (b) the Pb(II) → Pt(II) complexes $[(Ph_3P)_2PhPt\text{–}PbPh_3]$ [2] and $[PtCl(PbPh_2Cl)(N\text{–}N)(olefin)]$ (R = Me, Ph; N–N = chelating ligand) [3], which possess Pb(II) → Pt(II) donor–acceptor bonds; and (c) the complexes containing Pt(II) → Pb(II) donor–acceptor bonds, namely $(NBu_4)_2[Pb\{Pt(C_6F_5)_4\}_2]$ [4], $[(CH_3CO_2)Pb(crown\text{-}P_2)Pt(CN)_2](CH_3CO_2)$ [5] and $(NBu_4)[(C_6F_5)_3Pt(\mu\text{-}Pb)(\mu\text{-}X)Pt(C_6F_5)_3]$ (X = Cl, OH) [6], which are formed by reacting the square-planar platinum substrate with $Pb(NO_3)_2$ or $Pb(CH_3CO_2)_2$.

The pentafluorophenyl derivatives are members of a family of complexes formed with different degrees of difficulty by reaction of the anionic pentafluorophenyl platinate with $[ML_n]^{m+}$ cations [7]. The formation of these complexes has been explained as a result of donor–acceptor interactions between the basic centers and the acidic $[ML_n]^{m+}$ fragments. Another important factor which seems to facilitate the formation of the complexes, is the presence of pentafluorophenyl groups and their orientations which lead, in most cases, to close *o*-F···M interactions which confer stability upon the whole molecule. In some cases the skeletons of the platinate fragments undergo structural change in order to facilitate more and better Pt → M interactions.

We report here the synthesis and structural characterization of a new heteronuclear Pt–Pb complex that has emerged as part of our ongoing research into this type of system. This compound contains three Pt → Pb bonds unsupported by covalent bridging ligands, an arrangement that coincides with the presence of short contacts between the Pb atom and some of the *ortho*-F atoms of the pentafluorophenyl groups. The luminescent properties of this complex at room temperature have also been studied.

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2. Results and discussion

2.1. Synthesis of the complex

The complex $(NBu_4)[Pb\{Pt(\mu\text{-}Cl)(C_6F_5)_2\}_3]$ (**1**) was obtained by the reaction of $(NBu_4)_2[Pt_2(\mu\text{-}Cl)_2(C_6F_5)_4]$ and $Pb(ClO_4)_2$ (prepared in situ by reaction of $PbCl_2$ and $AgClO_4$) in dry THF (Eq. (1)). The formation of AgCl does not affect the reaction; and it is eliminated, together with NBu_4ClO_4, by treating the reaction mixture with dry diethyl ether, in which they are insoluble. The complex is isolated from the ether solution by adding *n*-hexane. It is important to maintain the given stoichiometry, since an excess of $AgClO_4$ could produce the elimination of the Cl bridging ligand of the platinum substrate, resulting in decomposition products.

$$\begin{aligned}&1.5(NBu_4)_2[Pt_2(\mu Cl)_2(C_6F_5)_4] + PbCl_2 + 2AgClO_4\\ &\quad \rightarrow 2AgCl\downarrow + 2NBu_4ClO_4\\ &\qquad + (NBu_4)[Pb\{Pt(\mu Cl)(C_6F_5)_2\}_3] \quad (\mathbf{1})\end{aligned} \tag{1}$$

2.2. Structure of the complex

The structure of (**1**) was determined by X-ray diffraction analysis. Fig. 1 shows the anion of the complex and Fig. 2 shows the central core. Table 1 collects selected bond distances and angles. The asymmetric unit contains two molecules that are nearly equal, with very similar bond distances and angles, the small differences being attributed to packing effects. The following description refers to only one of the nearly identical anions. The tetranuclear complex is best described on the basis of a '$Pt_3(\mu\text{-}Cl)_3(C_6F_5)_6$' unit in which there is a six-membered, puckered Pt_3Cl_3 ring with Pt and Cl atoms occupying alternate positions (see Fig. 2). The ring is capped on one side by a Pb atom that is bonded to the three Pt centers by platinum-to-lead donor–acceptor bonds, with Pt–Pb–Pt angles ranging from 83.75(2) to 85.63(2)°. The Pt_3Cl_3 moiety acts as a tridentate ligand, with the Pt centers serving as donor atoms towards the Pb atom. The Pt–Pb distances range from 2.825(1) to 2.843(1) Å and are only slightly longer than the sum of the covalent radii of the two atoms. These distances are comparable to, although slightly

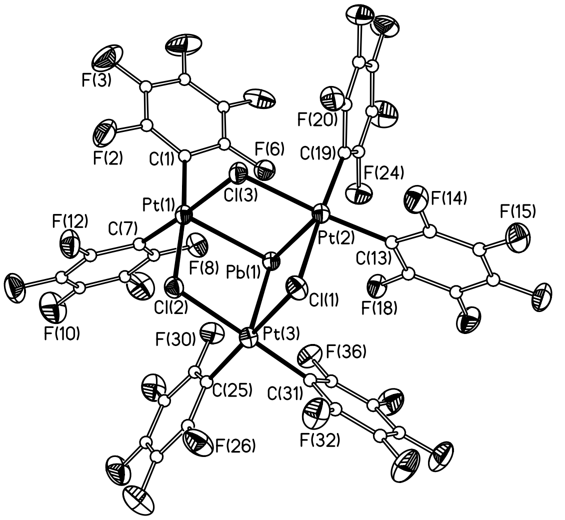

Fig. 1. Drawing of one anion from the crystal structure of **1**.

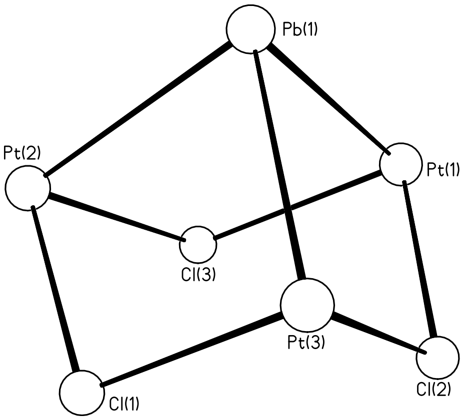

Fig. 2. Core of the anion $[Pb\{Pt(\mu\text{-}Cl)(C_6F_5)_2\}_3]^-$, from the crystal structure.

Table 1
Selected bond distances (Å) and angles (°) for $(NBu_4)[Pb\{Pt(\mu\text{-}Cl)(C_6F_5)_2\}_3]$

Bond distances			
Pb(1)–Pt(3)	2.8247(9)	Pb(1)–Pt(1)	2.8334(9)
Pb(1)–Pt(2)	2.8426(11)	Pt(1)–C(1)	2.005(8)
Pt(1)–C(7)	2.011(8)	Pt(1)–Cl(2)	2.408(2)
Pt(1)–Cl(3)	2.412(2)	Pt(2)–C(13)	2.008(8)
Pt(2)–C(19)	2.012(9)	Pt(2)–Cl(1)	2.405(2)
Pt(2)–Cl(3)	2.410(2)	Pt(3)–C(25)	2.022(9)
Pt(3)–C(31)	2.029(9)	Pt(3)–Cl(2)	2.399(2)
Pt(3)–Cl(1)	2.425(2)		
Bond angles			
Pt(3)–Pb(1)–Pt(1)	84.95(3)	Pt(3)–Pb(1)–Pt(2)	83.75(2)
Pt(1)–Pb(1)–Pt(2)	85.63(2)	C(1)–Pt(1)–C(7)	86.6(3)
C(1)–Pt(1)–Cl(2)	174.3(3)	C(7)–Pt(1)–Cl(2)	91.7(2)
C(1)–Pt(1)–Cl(3)	91.5(2)	C(7)–Pt(1)–Cl(3)	177.1(2)
Cl(2)–Pt(1)–Cl(3)	90.03(7)	C(1)–Pt(1)–Pb(1)	101.0(2)
C(7)–Pt(1)–Pb(1)	98.7(2)	Cl(2)–Pt(1)–Pb(1)	84.69(6)
Cl(3)–Pt(1)–Pb(1)	83.84(5)	C(13)–Pt(2)–C(19)	89.0(3)
C(13)–Pt(2)–Cl(1)	88.5(2)	C(19)–Pt(2)–Cl(1)	174.6(2)
C(13)–Pt(2)–Cl(3)	173.4(2)	C(19)–Pt(2)–Cl(3)	90.4(2)
Cl(1)–Pt(2)–Cl(3)	91.52(8)	C(13)–Pt(2)–Pb(1)	102.9(2)
C(19)–Pt(2)–Pb(1)	98.6(2)	Cl(1)–Pt(2)–Pb(1)	86.54(5)
Cl(3)–Pt(2)–Pb(1)	83.68(5)	C(25)–Pt(3)–C(31)	90.3(3)
C(25)–Pt(3)–Cl(2)	89.7(3)	C(31)–Pt(3)–Cl(2)	178.8(2)
C(25)–Pt(3)–Cl(1)	171.4(3)	C(31)–Pt(3)–Cl(1)	91.3(3)
Cl(2)–Pt(3)–Cl(1)	88.47(8)	C(25)–Pt(3)–Pb(1)	101.6(3)
C(31)–Pt(3)–Pb(1)	96.2(2)	Cl(2)–Pt(3)–Pb(1)	85.03(6)
Cl(1)–Pt(3)–Pb(1)	86.57(5)	Pt(2)–Cl(1)–Pt(3)	103.11(8)
Pt(3)–Cl(2)–Pt(1)	105.29(8)	Pt(2)–Cl(3)–Pt(1)	106.27(8)

longer than, those found in other Pt–Pb complexes containing Pt(II)→Pb(II) bonds: $(NBu_4)_2[Pb\{Pt(C_6F_5)_4\}_2]$ 2.769(2), 2.793(2) Å [4]; $(NBu_4)[(C_6F_5)_3Pt(\mu\text{-}Pb)(\mu\text{-}Cl)Pt(C_6F_5)_3]$ 2.721(1), 2.729(1) Å [6]; $(NBu_4)[(C_6F_5)_3Pt(\mu\text{-}Pb)(\mu\text{-}OH)Pt(C_6F_5)_3]$ 2.701(1), 2.712(1) Å [6]. Shorter Pb(II)→Pt(II) distances have been found in complexes in which Pb(II) acts as donor atom and Pt(II) as acceptor: $[(Ph_3P)_2PhPt\text{–}PbPh_3]$ 2.698(8) Å [2]; $[PtCl(PbPh_2Cl)(dmphen)(dimethyl\ maleate)]$ 2.642(1) Å [3]. An extremely long Pt(II)–Pb(II) distance has been found in $[(CH_3CO_2)Pb(crown\text{-}P_2)Pt(CN)_2](CH_3CO_2)$, 3.312(2) Å [5], although the presence of a Pt–Pb bond has been questioned in that case.

Each platinum atom has a distorted square-pyramidal coordination environment with the Pb atom occupying the apical position and the square plane being formed by the two C_{ipso} atoms of the C_6F_5 groups and two bridging Cl atoms; the platinum atom lies out of the plane of the square by less than 0.11 Å in all cases. The distances and angles in the square planes range within the expected values, and the Pt→Pb vectors form angles of 6.6(1) to 8.8(1)° with the perpendiculars to their respective basal planes. This small deviation from perpendicularity suggests good overlap between the orbitals involved in the Pt→Pb bond. The C_6F_5 rings form dihedral angles with the corresponding basal planes which range from 87.8(2) to 59.9(2)°. The orientation of the C_6F_5 rings enables the formation of *o*-F···Pb interactions in some cases (*o*-F···Pb distances: F(6), 2.800; F(30), 2.917; F(18), 2.991; F(36), 2.997; F(8), 3.088; F(24), 3.213 Å). These contacts, albeit weak, are not negligible and play an important role in the stability of the complex; they are comparable to the values found in other complexes with similar structures. The parameter ρ (experimental distance/sum of covalent radii) [8], which serves as a basis of comparison with other complexes in which these contacts are present, has values between 1.33 and 1.52, which are smaller than the values obtained for $(NBu_4)[Sn\{Pt(\mu\text{-}Cl)(C_6F_5)_2\}_3]$ [9], implying stronger interactions. These contacts can account for the fact that the Pb atom is otherwise naked. The core of the compex is very similar to that found in the complexes $(NBu_4)[Sn\{Pt(\mu\text{-}Cl)(C_6F_5)_2\}_3]$ [9] or $(NBu_4)_2[(C_6F_5)_6(\mu\text{-}OH)_3Pt_3HgCl]$ [10], in which there are also three Pt→M bonds.

2.3. NMR studies

The ^{19}F-NMR spectrum of **1** was recorded at room temperature, revealing the presence of a single type of C_6F_5 ligand with separate resonances for all five F atoms within the ring (2 *ortho*, 2 *meta* and 1 *para*). One of the *o*-F signals (*exo o*-F) appears as an apparent doublet centered at −119.5 ppm, with well-defined platinum satellites ($^3J_{F-Pt} = 325$ Hz). The other *o*-F signal (*endo o*-F) is centered at −127.5 ppm and also appears as a doublet, but with two sets of satellites, ascribed to coupling to ^{195}Pt ($^3J_{F-Pt} = 382$ Hz) and to ^{207}Pb nuclei ($J_{F-Pb} = 1140$ Hz). The experimentally observed *o*-F–Pb coupling shows that the *o*-F–Pb contacts found to exist in the solid state (vide supra) are maintained in solution. In the *meta* region there are also two separate sets of signals centered at −162.3 and −163.3 ppm, corresponding to the chemically inequivalent *exo* and *endo* nuclei. Finally, the *p*-F appears as a pseudo-triplet centered at −158.4 ppm.

2.4. Optical properties

In the last few years the photophysics of homo Pt(II)–Pt(II) and heteropolynuclear [Pt(II)/d^{10} or Pt(II)/d^{10}ns^2] complexes has attracted a considerable attention. Many of these complexes have been described to exhibit visible luminescence which display a notable dependence to the presence of d^8···M bonding interactions. In this context the optical properties of **1** have been examined.

The electronic absorption spectra in solid state and in solution ($CHCl_3$) show similar features. In solid state two bands are found at 302 and 405 nm (Fig. 3) which are observed at 310 and 406, respectively, in solution. The high energy band is tentatively assigned to the transition localized in the p-orbitals of the pentafluorophenyl rings, while the low energy band is probably related to orbitals in the tetranuclear cluster. In agreement with this assignment the dinuclear platinum complex $(NBu_4)_2[Pt_2(C_6F_5)_4(\mu\text{-}Cl)_2]$ (which has been used as starting material) show only bands at high energy ($CHCl_3$, 291 and 333 nm). **1** is not emissive in fluid solution ($CHCl_3$) at room temperature and only very weak yellow emission ($\lambda_{max} = 531$ nm) is observed in solid state at room temperature by exciting at 443 nm. However, a strong luminescence is seen both in the solid state and in frozen solution at low temperature (77 K;

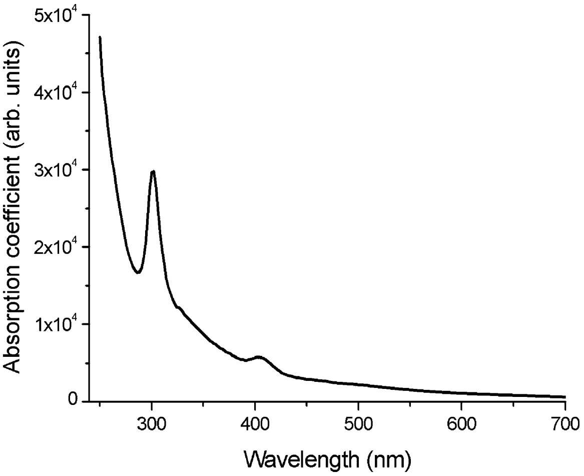

Fig. 3. Absorption spectrum at room temperature.

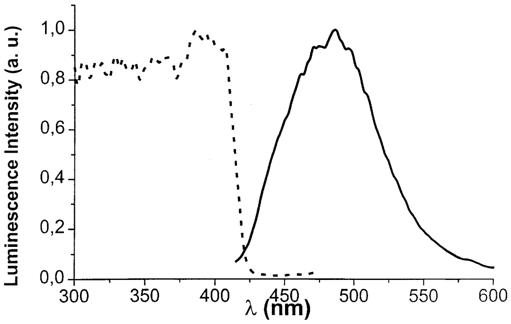

Fig. 4. Normalized emission (—) and excitation (···) spectra of **1** in the solid state at 77 K.

Figs. 4 and 5). Excitation of **1** in the solid state al low temperature in the range 390–410 nm results in an intense yellow–green broad emission centered at 485 nm. A clear blue shift is observed in frozen $CHCl_3$ solution ($\lambda_{max} = 458$ nm) being the radiative lifetime (77 ms) suggestive of a triplet parentage. The excitation spectrum show a peak maximum at 406 nm which closely resembles that of the low energy absorption band, indicative of their similar origin. The emission of **1** is notably blue-shifted when compared with those observed for the related tetranuclear complex $(NBu_4)_2[(C_6F_5)_6(\mu\text{-}OH)_2Pt_3HgCl]$ [11] which contains a similar tetranuclear $[Pt_3Hg]$ core [$CHCl_3$ (77 K) $\lambda_{emi} =$ 622 nm; solid (r.t.) $\lambda_{emi} = 653$ nm], thus suggesting a significant contribution of the Pt–M bonds within the core to the orbitals involved in the optical transition. Although more experimental data on related systems should be desirable, the emission observed for **1** is tentatively assigned to originate from the triplet states of cluster $[Pt_3Pb]$-to-ligands (C_6F_5) charge-transfer.

3. Conclusions

The formation and properties of this tetranuclear Pt_3Pb complex **1** allow us to draw the following conclusions:

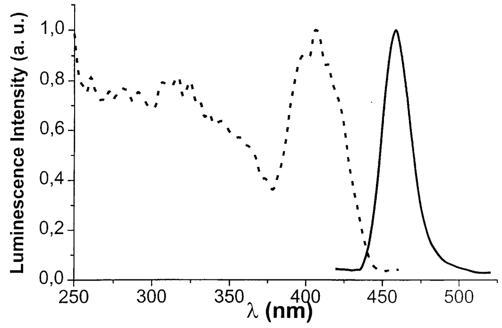

Fig. 5. Normalized emission (—) and excitation (···) spectra of **1** in frozen $CHCl_3$ solution at 77 K.

a) The ability of both metal centers to engage in such interactions under appropriate conditions has been demonstrated, in spite of the scant number of complexes containing Pt–Pb bonds.
b) The *o*-F atoms of the pentafluorophenyl rings stabilize the whole anion and play an important structural role.
c) There is a template effect involving the Pb^{2+} ion, as has also been observed for Sn^{2+}, which facilitates the formation of the trinuclear anion $[Pt_3(\mu\text{-}Cl)_3(C_6F_5)_6]^{3-}$; the latter has not been isolated except in these cases. Such a trinuclear Pt_3Cl_3 ring allows the formation of three Pt → Pb vectors nearly perpendicular to the platinum basal planes, and thus produces better overlap between the orbitals involved in the bonds.

4. Experimental

Literature methods were used for the preparation of $(NBu_4)_2[trans\text{-}Pt_2(\mu\text{-}Cl)_2(C_6F_5)_2]$ [11]. All solvents and chemicals were analytical reagent grade. C, H and N analyses were carried out on a Perkin–Elmer 240 microanalyzer. The IR spectrum was recorded (4000–200 cm^{-1}) on a Perkin–Elmer 883 spectrophotometer from Nujol mulls between polyethylene sheets. The ^{19}F-NMR spectrum was recorded on a Varian Unity 300 spectrometer from a $CDCl_3$ solution. UV–vis absorption spectra were recorded on a Hitachi U-3400 spectrophotometer. Emission and excitation spectra and emission lifetime measurements were obtained on a Perkin–Elmer Luminescence Spectrometer LS 50B.

4.1. Preparation of $(NBu_4)[Pb\{Pt(\mu\text{-}Cl)(C_6F_5)_2\}_3]$

A mixture of $(NBu_4)_2[trans\text{-}Pt_2(\mu\text{-}Cl)_2(C_6F_5)_2]$ (0.300 g, 0.186 mmol), anhydrous $PbCl_2$ (0.034 g, 0.124 mmol) and $AgClO_4$ (0.051 g, 0.248 mmol) in 40 ml of dry THF was stirred at room temperature (r.t.) under N_2 for 30 min. A white precipitate appeared immediately. The suspension was evaporated to dryness, and the residue was treated with diethyl ether (50 ml). After filtration, a white residue (AgCl and NBu_4ClO_4) was separated, and a yellow solution was obtained. The solution was evaporated to dryness, the resulting oily residue was dissolved in CH_2Cl_2 (10 ml); and upon addition of pentane a pale yellow solid was obtained in 70% yield.

Anal. Calc. for $C_{34}H_{36}Cl_3F_{30}NPbPt_3$: C, 29.14; H, 1.69; N, 0.65. Found: C, 29.46; H, 2.00; N, 1.06%. IR (cm^{-1}): C_6F_5: 1640 (m), 1613 (m), 1510 (vs), 1066 (vs), 961 (vs), 840 and 813 (vs, X-sensitive [12]); ν(Pt–Cl): 299 (m); NBu_4, 885 (m, br).

Table 2
Crystal data and structure refinement parameters for (NBu$_4$)[Pb{Pt(μ-Cl)(C$_6$F$_5$)$_2$}$_3$]

Empirical formula	$C_{52}H_{36}Cl_3F_{30}NPbPt_3$
Formula weight	2143.63
Temperature (K)	193(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a (Å)	12.881(4)
b (Å)	19.021(7)
c (Å)	25.950(10)
α (°)	73.99(2)
β (°)	80.36(1)
γ (°)	80.92(1)
V (Å^3)	5983(4)
Z	4
D_{calc} (Mg m^{-3})	2.380
Absorption coefficient (mm^{-1})	10.063
F(000)	3968
Crystal size (mm)	0.30 × 0.30 × 0.20
Theta range for data collection (°)	0.82–25.77
Index ranges	$-15 \leq h \leq 15$, $-22 \leq k \leq 23$, $0 \leq l \leq 31$
Reflections collected	21 417
Independent reflections	21 417
Refinement method	Full-matrix-block least-squares on F^2
Data/restraints/parameters	20 840/0/1621
Goodness-of-fit on F^2	1.153
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0432$, $wR_2 = 0.1052$
R indices (all data)	$R_1 = 0.0521$, $wR_2 = 0.1138$
Largest difference peak and hole (e Å^{-3})	2.188 and −3.172

$R_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^2]^{1/2}$; goodness-of-fit $= [\Sigma w(F_o^2 - F_c^2)^2/(N_{obs} - N_{param})]^{1/2}$; $w = [\sigma^2(F_o) + (g_1P)^2 + g_2P]^{-1}$; $P = [\max(F_o^2; 0 + 2F_c^2]/3$.

4.2. *Crystal structure of (NBu$_4$)[Pb{Pt(μ-Cl)(C$_6$F$_5$)$_2$}$_3$]*

Suitable crystals were grown by slow diffusion of *n*-hexane into a dichloromethane solution of the complex at −18 °C. A pale yellow prismatic crystal was mounted on a glass fiber in a rapidly cooled perfluoropolyether [13]. Diffraction data were collected on a Stoe-Siemens-Huber four-circle diffractometer coupled to a SiemensCCD area-detector, with graphite-monochromated Mo–K$_\alpha$ radiation. Data were collected at 193 K by the $\theta/2\theta$ method. Three check reflections, measured at regular intervals, showed no significant loss of intensity at the end of data collection. An empirical absorption correction based on ψ-scans was applied, as were Lorentz and polarization corrections. The crystal data, data collection and refinement parameters are summarized in Table 2. The structure was solved by the Patterson method. All non-hydrogen atoms were located in successive difference Fourier syntheses and refined with anisotropic thermal parameters. Hydrogen atoms were added at calculated positions and assigned isotropic displacement parameters fixed at 1.2 or 1.5 times the U_{iso} value of their respective parent carbon atoms. There are some peaks of electron density higher than 1 e Å^{-3} in the final map, located close to the heavy atoms, without any chemical meaning. The refinement was carried out using the program SHELXL-97 [14].

5. Supplementary material

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC number 18803. Copies of this information may be obtained from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk), and are available upon request.

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