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Synthesis and characterization of binuclear Pt(IV) complexes and tetranuclear mixed valence complexes of Platinum(II)-Platinum(IV)

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The binuclear platinum(IV) complexes $[NBu_4]_2[Pt^{IV}_2(\mu\text{-}Cl)_2(C_6F_5)_4Cl_4]$ (**2**) and $[Pt^{IV}_2(\mu\text{-}C_8H_6N_4)_2(C_6F_5)_4Cl_4]$ (**4**) have been synthesized by oxidative addition of chlorine to the binuclear platinum(II) species, but $[NBu_4]_2[Pt^{IV}_2(\mu\text{-}OH)_2(C_6F_5)_4Cl_4]$ (**3**) has been synthesized by substitution of the chloride bridges of the platinum(IV) complex. The square planar platinum environments of the Pt(II) starting materials change, as expected, to Pt(IV) octahedral environments with the chloride ligands in *trans*-position. Only minor changes in the Pt-X ($X = Cl_{bridge}$, OH) interatomic distances are produced because of the oxidation.

Depending on the size of the bridging ligands and also probably the anionic character of the diplatinum(IV) complexes, the apical chloride ligands can still act as bridges toward other Pt centers. Thus, the organometallic tetra-nuclear mixed-valence platinum(IV)-platinum(II) complexes with formulas $[NBu_4]_2[\{Pt^{IV}(\mu\text{-}X)(C_6F_5)_2\}_2(\mu\text{-}Cl)_4\{Pt^{II}(C_6F_5)_2\}_2]$ [X = Cl (**5**), OH (**6**)] were obtained by reaction of **2** and **3** with *cis*-$[Pt^{II}(C_6F_5)_2(thf)_2]$. The structures of complexes **2**, **4** and **6** have been determined by single-crystal X-ray diffraction studies. These crystal structures confirm that the oxidative addition of the chlorine molecule to the platinum(II) complexes **2** and **3** takes place on the axial positions of the platinum centers suggesting a SN_2 mechanism. On the other hand, the central core of the anion of **6** has a chair like conformation and the long Pt···Pt distances (>3.2 Å) clearly exclude any Pt.···Pt interaction.

On the other hand, ***cis*-**$[(C_6F_5)_2Pt(\mu\text{-}C_8H_6N_4)Pt(C_6F_5)_2]$ **(1)** can be reduced either electrochemically or by reacting with $[CoCp_2]$ to the anion $[Pt_2(\mu\text{-}C_8H_6N_4)(C_6F_5)_4]^-$ which in the last case, can be isolated as complex **7**. According to the EPR studies the anion is not a mixed Pt(II)/Pt(I) compound but a binuclear Pt(II) derivative with the anion $[C_8H_6N_4]^-$ as bridging ligand.

1. Introduction

Platinum(IV) organometallic complexes are usually obtained by oxidation of platinum(II) precursors [1] with halogens (Cl_2, Br_2, I_2, $PhICl_2$) [2–5] or organic halogenated molecules (MeI, EtI, $PhCH_2Br$, …) [6–8]. The oxidative addition process over mononuclear platinum(II) complex produces, in most cases, the mononuclear platinum(IV) species [5,9,10] but in some occasions complexes which show cubane-like structures [11,12], oligomer chains [7,13] or supramolecular polymers [14] are obtained. Only a few binuclear platinum(IV) complexes containing two octahedral Pt(IV) environments sharing an edge or a face have been reported and structurally characterized [15–20].

Mixed-valence platinum(II)-platinum(IV) complexes are also known and have been structurally characterized [21–42]. Most of these compounds display linear structures with $[\cdots Pt^{II}L_4\cdots X\text{-}Pt^{IV}L_4\text{-}X\cdots]_n$ (X = Cl, Br, I) chains, that can be single (1D), ladder type or double (2D) laying along one crystallographic axis in which square-planar coordinated Pt(II) ions and octahedral coordinated Pt(IV) ions are alternately arranged and that have drawn much attention because of their nonlinear optical and luminescence properties [21–23,34,35]. Also, a small amount of discrete bi-, tri-, and tetranuclear mixed-valence platinum(II)-platinum(IV) complexes have been described [24–30,33,36–42].

On the other hand, partial oxidative addition of binuclear Pt(II) complexes allows to prepare the binuclear platinum(II)-

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platinum(IV) anions $[I_4Pt^{IV}(\mu\text{-}I)_2Pt^{II}I_2]^{2-}$ [21–27], $[NBu_4][(C_6F_5)_2Pt^{II}(\mu\text{-}PPh_2)_2Pt^{IV}(\kappa^2,N,C{-}C_{13}H_8N)I_2]$ [38,39], $[NBu_4]_2[Pt^{IV}Pt^{II}_3(C_6Cl_5)_8(\mu\text{-}OH)_2(\mu_3\text{-}OH)_2]$ [40] and $[Pt_2(C_6F_5)_4(C_5H_4NS)_2X]$ ($X = Cl, Br, I$). These later are interesting since they have been synthesized as intermediates in the Pt(II)–Pt(II) to Pt(IV)–Pt(IV) sequence [41]. A singular oxidative addition reaction has been described from $[Pt(PEt_3)_3]$ and 1,2-disilylbenzene in 1:1 ratio at 60 °C yielding the binuclear neutral complex $[(PEt_3)_2Pt^{II}(\mu\text{-}HSiC_6H_4SiH_2)_2Pt^{IV}(PEt_3)_2]$ [28]. In addition, $[Pt_3X_{12}]^{2-}$ ($X = Cl, Br$) are trinuclear platinum(II)-platinum(IV) mixed valence complexes [26], and they consist in three linearly arranged platinum atoms ($Pt^{IV}{-}Pt^{II}{-}Pt^{IV}$) connected by halo-bridging ligands. The chloride-compound was isolated from a mixture of Pt(IV) complexes, probably being the result of the reductive elimination of Cl_2 from the $[Pt_3Cl_{14}]^{2-}$ anion at the central platinum atom, while the bromide derivative has been deliberately synthesized by reaction between $[PtBr_6]^{2-}$ and $[PtBr_4]^{2-}$ in 2:1 ratio, Very recently, Belli Dell'Amico et al. have published the synthesis and structural characterization of the pentanuclear mixed-valence Pt(II)–Pt(IV) complex anion $[Pt_5Cl_{20}]^{2-}$ which has been prepared by using Pt(IV) derivatives as starting materials [42].

Puddephatt and co-workers synthesized some platinum(II)-platinum(IV) cationic complexes from binuclear platinum(II) complexes by oxidative addition of halogen over one of the two platinum(II) atoms, and the resulting binuclear products, which have three bridging ligands, suffer an intramolecular transfer reaction of a methyl group [29]. More recently Puddephatt has described a strategy to synthesize organoplatinum dendrimers by using a reagent containing alkyl halide and diimine functionalities. The successive growth of the nuclearity needs the coordination of one platinum(II) fragment to the non bonded diimine part in a previous step to the new oxidative addition; so the process involves as intermediates mixed-valence platinum(II)-platinum(IV) complexes [7,36].

In this paper we describe the synthesis of three new neutral and anionic binuclear Pt(IV) complexes, two of which can be used as starting materials for the preparation of the first tetra-nuclear platinum(II)-platinum(IV) mixed-valence complexes. These anionic organometallic platinum(II)-platinum(IV) complexes are synthesized by addition of the stoicheiometric amount of a platinum(II) reagent [*cis*-$[Pt(C_6F_5)_2(thf)_2]$ to binuclear platinum(IV) complexes in a different way from the route used by Thiele and coworkers [partial oxidation of the correspondent platinum(II) anions with X_2 ($X = Br, I$)] [26,27] or by Puddephatt and co-workers (in which an oxidative addition to binuclear platinum(II) complexes and further group transfer between the platinum atoms are involved) [29,30].

2. Experimental section

2.1. General methods

C, H, and N analyses were carried out with a Perkin-Elmer 240B microanalyzer. IR spectra were recorded over the 4000-200 cm^{-1} range on a Perkin Elmer Spectrum One from Nujol mulls between polyethylene sheets or on a Perkin Elmer Spectrum 100 FT-IR spectrometer with an Universal ATR Sampling Accessory. ^1H and ^{19}F NMR spectra were recorded on a Varian Unity-300 or Gemini or a BRUKER AV-400 in $CDCl_3$, CD_2Cl_2 or d_6-acetone solutions. Some complexes have to be precipitated with n-hexane, in these cases only very small amount of starting materials may remain and were observed by ^{19}F NMR technique. Attempts of recrystallization of them produces partial decomposition in most of the complexes. $[NBu_4]_2[Pt_2(\mu\text{-}Cl)_2(C_6F_5)_4]$ was prepared as described elsewhere [43]. The 2,2' bipyrimidine ligand was purchased and used as received from Lancaster.

Electrochemical studies were carried out using an EG&G model 273 potentiostat in conjunction with a three-electrode cell, in which the working electrode was a platinum disc, the auxiliary electrode a platinum wire, and the reference was an aqueous saturated calomel electrode (SCE) separated from the test solution by a fine-porosity frit and an agar bridge saturated with KCl. Solutions were $5 \cdot 10^{-4}$ mol dm^{-3} in the test compound and 0.1 mol dm^{-3} in $[NBu_4][PF_6]$ as the supporting electrolyte. The solutions were saturated with Ar by bubbling them with this gas before each experiment. At the end of each electrochemical experiment, $[Fe(\eta^5\text{-}C_5H_5)_2]$ was added to the solution as an internal standard for potential measurements. Under the conditions used, the E^o value for the couple $[Fe(\eta^5\text{-}C_5H_5)_2]^+/[Fe(\eta^5\text{-}C_5H_5)_2]$ was 0.47 V. Controlled potential electrochemistry (CPE) was carried out in a two-compartment three electrode cell with a platinum gauze working and counter electrodes in compartments separated by a glass frit; a saturated calomel electrode (SCE) separated from the test solution by a fine-porosity frit and an agar bridge saturated with KCl was used as reference.

EPR data were taken in a Bruker ESP300 spectrometer. The magnetic field was measured with a Bruker ER035 M gaussmeter. A Hewlett-Packard HP5350B frequency counter was used to determine the microwave frequency.

2.2. Preparation of *cis*-$[(C_6F_5)_2Pt(\mu\text{-}C_8H_6N_4)Pt(C_6F_5)_2]$ (**1**)

0.013 g (0.085 mmol) of 2, 2′-bipyrimidine were added to a solution of *cis*-$[Pt(C_6F_5)_2(thf)_2]$ (0.115 g, 0.171 mmol) in 15 ml of $CHCl_3$. Instantaneously, a solid precipitated and the suspension was stirred at room temperature for 15 min. Then the solution was evaporated to 5 mL approximately, and the resulting dark orange solid was filtered off and washed with *n*-hexane. (91% yield). Anal. Found (Calcd. for $C_{32}H_6N_4F_{20}Pt_2$): C, 31.31 (31.59); H, 0.72 (0.50); N, 4.80 (4.60). IR (cm^{-1}): C_6F_5 X-sensitive mode [44] 815 s, 806 s; other, ν(C–F), 965 s; $C_8H_6N_4$, 1586 w, 1557 m, 1503 s, 1419 m, 754 m; ^1H NMR (room temperature), d_6-acetone; δ/ppm: 9.34 ppm(d, 4H), 8.34 ppm (t, 2H). ^{19}F NMR (room temperature), d_6-acetone (282.231 MHz); δ/ppm: 114.93 (d, 4F*o*, $^3J_{Pt\text{-}Fo} = 459.82$ Hz), –115.01 (d, 4F*o*, $^3J_{Pt\text{-}Fo} = 460.95$ Hz), –158.50 (t, 4F*p*, $^4J_{Fp\text{-}Fo} = 38.65$ Hz), –161.00 (m, 8Fm). FAB+ (*m/z*): $[Pt_2(C_6F_5)_4(C_8H_6N_4)]$: 1216.

2.3. Preparation of $[NBu_4]_2[Pt_2(\mu\text{-}Cl)_2(C_6F_5)_4Cl_4]$ (**2**)

To a solution of $[NBu_4]_2[Pt_2(\mu\text{-}Cl)_2(C_6F_5)_4]$ (0.150 g, 0.093 mmol) in Me_2CO (10 mL), NBu_4Cl (0.052 g, 0.186 mmol) and a Cl_2/CCl_4 solution in excess were added. After 15 min stirring at room temperature, the resulting yellow solution was evaporated to dryness. The residue was washed with water (3x10 mL), an after that the residue was dissolved in CH_2Cl_2 (10 ml) and treated with $MgSO_4$, which after some minutes stirring was separated by filtration through Celite. The resulting CH_2Cl_2 solution was evaporated to dryness and the residue was treated with Et_2O yieding a pale-yellow solid (**2**) which was filtered off and air dried. Yield: 61%. Anal. Found (Calcd. for $C_{56}H_{72}Cl_6F_{20}N_2Pt_2$): C, 38.43 (38.20); H, 3.81 (4.14); N, 1.53 (1.60). IR (cm^{-1}): C_6F_5: ν(C–F), 966 vs; X-sensitive mode [44], 790 m; others, 2963 m, 2876 w, 1504 s, 1458 sh, 1444 vs, 1380 w, 1367 w, 1261 w, 1105 w, 1066 s, 1028 w, 1002 w; (NBu_4^+), 879 w, 739 w; $\nu(Pt{-}Cl)_{terminal}$, 327 s; $\nu(Pt{-}Cl)_{bridge}$ 264 vs. ^{19}F NMR in CD_2Cl_2 (376.309 MHz) δ/ppm: –112.78 ppm (F_o, d, 4F), $^3J_{Fm-Fo} = 24.69$ Hz, $^3J_{Pt-Fo} = 102.14$ Hz; –115.77 ppm (F_o, d, 4F), $^3J_{Fm-Fo} = 24.89$ Hz, $^3J_{Pt-Fo} = 112.97$ Hz; –164.43 ppm (F_p, t, 4F); –166.59 ppm (F_m, m, 4F); –167.29 ppm (F_m, m, 4F).

2.4. Preparation of $[NBu_4]_2[Pt_2(\mu\text{-}OH)_2(C_6F_5)_4Cl_4]$ (**3**)

To a solution of $[NBu_4]_2[Pt_2(\mu\text{-}Cl)_2(C_6F_5)_4Cl_4]$ **(2)** (0.073 g, 0.041 mmol) in Me_2CO (10 mL), NBu_4OH (1 M in H_2O) (66 mg, 0.082 mmol) was added. After 2 h stirring at room temperature, the solvent was evaporated to dryness. The residue was washed with water (3x10 mL), after that the residue was dissolved in CH_2Cl_2 (10 ml) and treated with $MgSO_4$, which after some minutes stirring was separated by filtration through Celite. The resulting CH_2Cl_2 solution was evaporated to dryness and the residue was washed with iPrOH (3 × 1ml) and Et_2O giving a yellow oily residue which could be spectroscopically identified as $[NBu_4]_2[Pt_2(\mu\text{-}OH)_2(C_6F_5)_4Cl_4]$ (**3**). IR (cm^{-1}): C_6F_5: ν(C—F), 965 vs; X-sensitive mode [44], 790 m; others, 2963 m, 2876 w, 1504 m, 1459 s, 1380 m, 1361 m, 1065 s, 1028 w, 1002 w; (NBu_4^+), 879 w, 739 w; $\nu(Pt\text{—}Cl)_{terminal}$, 337 m; ν(O—H), 3585 w. ^{19}F RMN in CD_2Cl_2 (376.309 MHz) δ/ppm: −117.67 ppm (F_o, d, 4F), $^3J_{Fm-Fo} = 25.01$ Hz, $^3J_{Pt-Fo} = 115.86$ Hz; −121.03 ppm (F_o, d, 4F), $^3J_{Fm-Fo} = 30.01$ Hz, $^3J_{Pt-Fo} = 91.84$ Hz; −169.04 ppm (F_p, t, 4F); −169.99 ppm (F_m, m, 4F); −170.75 ppm (F_m, m, 4F).

2.5. Preparation of $[Pt_2(\mu\text{-}C_8H_6N_4)Cl_4(C_6F_5)_4]$ (**4**)

To a suspension of **1** (0.030 g, 0.025 mmol) in 10 ml of CH_2Cl_2, 5 ml of a saturated solution of Cl_2 in CCl_4 were added. The orange suspension changed to a yellow solution. After 14 h stirring at room temperature the resulting pale yellow suspension was evaporated to dryness and the yellow residue was washed with *n*-hexane and filtered. 77% yield. Anal. Found (Calcd. for $C_{32}H_6N_4Cl_4F_{20}Pt_2$): C, 28.09 (28.29); H, 0.45 (0.44); N, 4.20 (4.12). IR (cm^{-1}): C_6F_5 X-sensitive mode [44] 809 s, 800 s; ν(C—F) 974 vs; $C_8H_6N_4$, 1594 vs, 1520 vs, 1425 vs, 821 m, 754 s; ν(Pt—Cl) 354 s ^1H NMR (room temperature), d_6-acetone; δ/ppm: 9.78 (t, 4H), 8.81 (m, 2H). ^{19}F NMR (room temperature), d_6-acetone (282.231 MHz); δ/ppm: 118.04 (d, $4F_0$, $^3J_{Pt\text{-}Fo} = 103.35$ Hz), −118.24 (d, $4F_0$, $^3J_{Pt\text{-}Fo} = 102.39$ Hz), −158.80 (m, $4F_p$), −162.79 (m, $4F_m$), −163.99 (m, $4F_m$).

2.6. Preparation of $[NBu_4]_2[\{Pt(\mu\text{-}Cl)(C_6F_5)_2\}_2(\mu\text{-}Cl)_4\{Pt(C_6F_5)_2\}_2]$ (**5**)

To a solution of $[NBu_4]_2[Pt_2(\mu\text{-}Cl)_2(C_6F_5)_4Cl_4]$ (**2**) (0.100 g, 0.057 mmol) in CH_2Cl_2 (40 mL), *cis*-$[Pt(C_6F_5)_2(thf)_2]$ (0.076 g, 0.114 mmol) was added. After 5 min stirring at room temperature, the resulting red solution was evaporated to dryness. The residue was treated with *n*-hexane (15 mL) yielding a red solid (**5**) which was filtered off. Yield: 58%. Anal. Found (Calcd. for $C_{80}H_{72}Cl_6F_{40}N_2Pt_4$): C, 33.96 (34.14); H, 2.87 (2.58); N, 1.26 (1.00). IR (cm^{-1}): C_6F_5 X-sensitive mode [44], 801 s; ν(C—F), 974 s, 960 s; others, 1638 w, 1607 w, 1504 vs; ν(Pt—Cl), 343 w, 279 w. ^{19}F NMR (room temperature), CD_2Cl_2 (282.231 MHz); δ/ppm: 114.79 (d, $2F_0$, $^3J_{Pt\text{-}Fo} = 95$ Hz), −118.81 (d, $2F_0$, $^3J_{Pt\text{-}Fo} = 134$ Hz), −120.32 (d, $2F_0$), −124.94 (d, $2F_0$, $^3J_{Pt\text{-}Fo} = 96$ Hz), −119.51 (d, $4F_0$, $^3J_{Pt\text{-}Fo} = 483$ Hz), −120.48 (d, $4F_0$, $^3J_{Pt\text{-}Fo} = 509$ Hz), −157.83 (m, $2F_p$), −158.13 (m, $2F_p$), −163.19 (t, $1F_p$), −163.25 (t, $1F_p$), −164.82 (t, $2F_p$), −162.89 (m, $6F_m$), −163.64 (m, $2F_m$), −165.48 (m, $4F_m$), −166.63 (m, $4F_m$).

2.7. Preparation of $[NBu_4]_2[\{Pt(\mu\text{-}OH)(C_6F_5)_2\}_2(\mu\text{-}Cl)_4\{Pt(C_6F_5)_2\}_2]$ (**6**)

To a solution of $[NBu_4]_2[Pt_2(\mu\text{-}OH)_2(C_6F_5)_4Cl_4]$(**3**) prepared as described above (approx. 0.12 mmol) in CH_2Cl_2 (40 mL), *cis*-$[Pt(C_6F_5)_2(thf)_2]$ (0.155 g, 0.232 mmol) was added. After 5 min stirring at room temperature, the resulting red solution was evaporated to dryness. The residue was treated with *n*-hexane (15 mL) yielding a red solid (**6**) that was filtered off. Yield: 72%. Anal. Found (Calcd. for $C_{80}H_{74}Cl_4F_{40}N_2O_2Pt_4$): C, 34.36 (34.59); H, 2.99 (2.68); N, 1.02 (1.01). IR (cm^{-1}): C_6F_5 X-sensitive mode [44], 803 s; ν(C—F), 972 s, 956 s; others, 1639 w, 1607 w, 1502 vs, ν(O—H) 3574 m; ν(Pt—Cl) 352 w, 282 w. ^{19}F NMR (room temperature), CD_2Cl_2 (282.231 MHz); δ/ppm: 115.38 (d, $2F_0$, $^3J_{Pt\text{-}Fo} = 100$ Hz), −119.09 (d, $2F_0$, $^3J_{Pt\text{-}Fo} = 127$ Hz), −120.89 (d, $2F_0$), −125.40 (d, $2F_0$, $^3J_{Pt\text{-}Fo} = 100$ Hz), −120.34 (d, $4F_0$), −120.70 (d, $4F_0$), −158.26 (t, $1F_p$), −158.66 (t, $1F_p$), −159.53 (m, $2F_p$), −164.74 (t, $1F_p$), −165.57 (t, $2F_p$), −167.09 (t, $1F_p$), −163.59 (m, $4F_m$), −164.55 (m, $2F_m$), −166.12 (m, $2F_m$), −167.09 (m, $8F_m$)

2.8. Preparation of $[CoCp_2][Pt_2(\mu\text{-}C_8H_6N_4)(C_6F_5)_4]$ (**7**)

To an orange solution of $[Pt_2(\mu\text{-}C_8H_6N_4)(C_6F_5)_4]$ (**1**) (0.054 g, 0.044 mmol) in 10 mL of thf, Cp_2Co (purified by sublimation (0.008 g, 0.044 mmol) was added. The color of the solution changed immediately to red. After 30 min stirring, the solution was evaporated to dryness and the residue was treated with n-hexane. Yield: 69%. Anal. Found (Calcd. for $C_{42}H_{16}N_4F_{20}CoPt_2$): C, 35.76 (35.88); H, 1.42 (1.15); N, 4.10 (3.98). IR (cm^{-1}): C_6F_5 X-sensitive mode [44], 809 s, 800 s; ν(C—F), 959 s; other, $C_8H_6N_4$: 1580 m, 1504 s, 1417 w, 668 w. FAB- (*m*/*z*):$[Pt_2(C_6F_5)_4(C_8H_6N_4)]$:1216.

X-ray Structure analysis of $[NBu_4]_2[Pt_2(\mu\text{-}Cl)_2Cl_4(C_6F_5)_4]$ (2), $[Pt_2(\mu\text{-}C_8H_6N_4)Cl_4(C_6F_5)_4]\cdot 4Me_2CO$ ($4\cdot 4Me_2CO$) and $[NBu_4]_2[\{Pt(\mu\text{-}OH)(C_6F_5)_2\}_2(\mu\text{-}Cl)_4\{Pt(C_6F_5)_2\}_2]\cdot CH_2Cl_2$ ($6\cdot CH_2Cl_2$).

Relevant crystallographic information for these structures is collected in Supplementary Material (Table 1). Suitable crystals for X ray diffraction studies were obtained by slow diffusion of *n*-hexane into solutions of the complexes in Me_2CO (**2** and **4**) or CH_2Cl_2 (**6**) at 4 °C.

Crystals of the complexes were mounted at the end of quartz fibers and held in place with epoxy adhesive. Diffraction measurements were made on an Enraf-Nonius CAD-4 diffractometer, using graphite monochromated Mo-K_α *X*-radiation. Lorentz and polarization corrections were applied.

The structures were solved by direct methods. All non-hydrogen atoms of the complex anion and the cation were assigned anisotropic displacement parameters. The hydrogen atoms were constrained to idealized geometries and assigned isotropic displacement parameters equal to 1.2 times (1.5 times for the methyl carbon atoms) the U_{iso} values of their respective parent atoms. For **2,** some very diffuse electron density were found in the final stages of the refinement. After several unsuccessful attempts to model this density as *n*-hexane, one of the crystallization solvents, the SQUEEZE procedure as implemented in the program PLATON [45] was used to deal with this problem. Besides, one of the methyl carbon atoms of the NBu_4^+ cation is disordered over two positions and their occupancies were refined to 0.7/0.3, and the CH_2—CH_3 distance were constrained to an idealized value. For **6**, one methyl carbon atom of the NBu_4 group was modeled as a pair of atomic sites with occupancy of 0.5 each and the hydrogen atoms of these atoms and the other methyl carbon atoms were omitted. Five atomic sites in an interstitial zone were modeled as a pair of partially occupied, disordered CH_2Cl_2 molecules, sharing a common carbon atom. Each of the CH_2Cl_2 moieties was assigned 0.25 occupancy; thus, the common C site had 0.50 occupancy. A common anisotropic displacement parameter was refined for the five atoms of the disordered CH_2Cl_2 moieties. Loose restraints to equality were applied to the C—Cl distance and Cl—C—Cl angles. Full-matrix least-squares refinement of these models against F^2 converged to final residual indices given in Table 1 of the Supplementary Material. The structures were refined using the SHELXL-93 program [46].

Selected crystallographic data, data collection and structure

Table 1
Spin-Hamiltonian parameters of some $\{(bpym)[PtR_2]_2\}^{-}$ radicals.

	g_1	g_2	g_3	g	Δg	A_1(MHz)	A_2(MHz)	A_3(MHz)	ref.
$\{(bpym)[PtMe_2]_2\}^{\cdot-}$	2.055	2.011	1.895	1.987	0.160	43	51	(53)	53
$\{(bpym)[PtCl_2]_2\}^{\cdot-}$	2.049	2.008	1.902	1.986	0.147	111	143	<80	50
$\{(bpym)[PtMes_2]_2\}^{\cdot-}$	2.0435	2.0091	1.916	1.990	0.128	-	45	-	18
$\{(bpym)[PtMes_2]_2\}^{\cdot-}$	2.040	2.008	1.917	1.988	0.123	49	53	(54)	53
$\{(bpym)[Pt(C_6F_5)_2]_2\}^{\cdot-}$	**2.029**	**2.009**	**1.934**	**1.991**	**0.095**	**65**	**40**	**-**	[a]

[a] Included in this article.

refinement parameters are available in Supporting Information. CCDC 1911936-1911938 contains supplementary crystallographic data on this paper. These data are available, free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

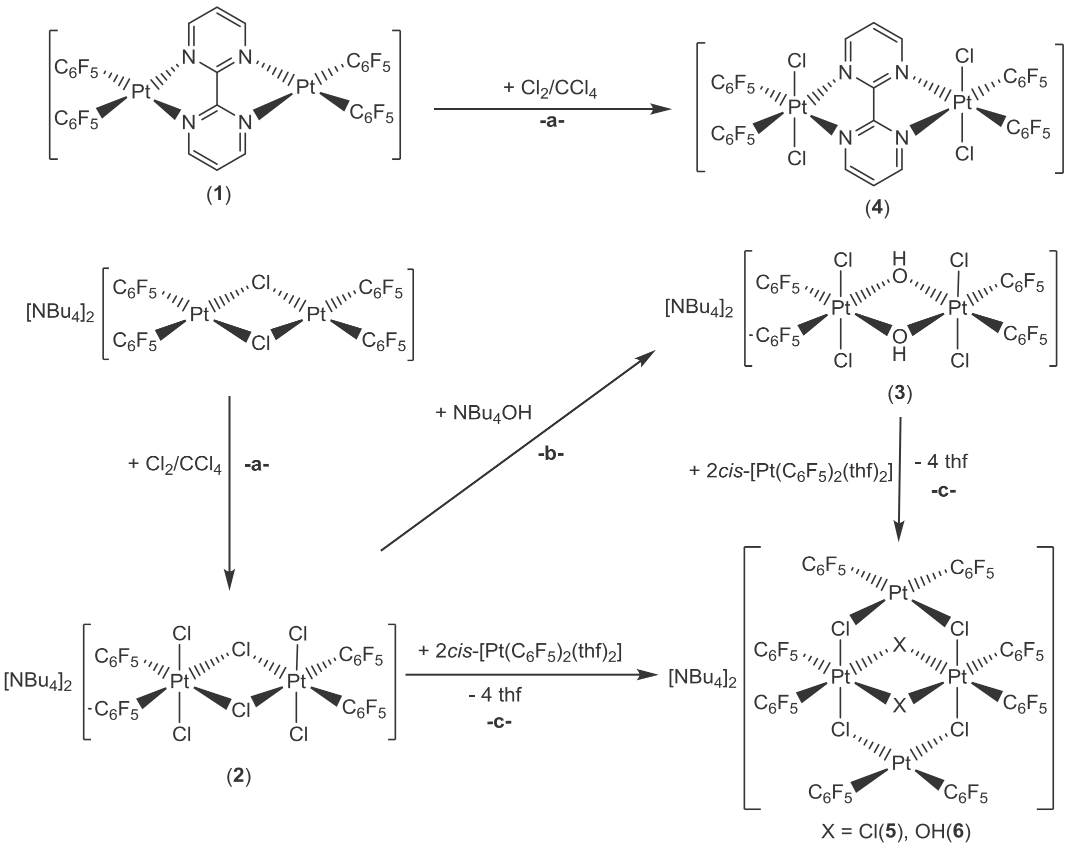
3. Results and discussion

The anionic complex $[NBu_4]_2[Pt_2(\mu\text{-}Cl)_2(C_6F_5)_4]$ was prepared as described elsewhere[37] and the neutral binuclear platinum(II) complex *cis*-$[(C_6F_5)_2Pt(\mu\text{-}C_8H_6N_4)Pt(C_6F_5)_2]$ (**1**) (See Scheme 1) was prepared by reaction of *cis*-$[Pt(C_6F_5)_2(thf)_2]$ and the ligand 2,2′-bipyrimidine, which is able to act as a bridge between the metal centers [18,47,48].

The IR spectrum of complex **1** is very informative about the structural disposition of the ligands. The similar intensity of the absorptions at 1586 and 1557 cm^{-1} indicates the bis-chelate bridging coordination of the 2,2′-bipyrimidine ligand [48]. Moreover, the presence of only two signals in the ^{1}H NMR spectrum of **1** in 2:1 ratio point to a symmetrical arrangement of the N-donor ligand in the complex. In fact, its coordination features are most suitable to synthesize binuclear complexes in which the 2,2′-bipyrimidine ligand bridges two platinum centers with a coplanar disposition of their environments [18,47–49]. The mass spectrum confirms the binuclear nature of complex **1**.

The electronic properties of the 2,2′-bipyrimidine cause that the complexes that contain it suffer chemical and electrochemical reduction processes similar to other cases [50]. For this reason we have studied the redox behavior of complex **1** by electrochemical methods. Fig. 1 shows the cyclic voltammogram registered at 200 mVs^{-1} in MeCN and using a platinum disc as working electrode. There are two reduction waves connecting with two electrochemically reversible reduction processes, the first one corresponding to an electrochemically reversible system ($E_{1/2(red)} = -0.33$ V) and the second one at lower potential ($E_{1/2(red)} = -1.05$ V).

Aiming to know the number of electrons involved in these reductions, we carried out the electrolysis at controlled potential of a solution of complex **1** in MeCN. A potential of −0.55 V was applied to 100 mL of a solution 0.001 M of **1** containing NBu_4PF_6 (0.1 M) as supporting electrolyte. Once 9.65C were transferred to the solution, a strong decrease in the intensity was observed. Moreover, a change



Scheme 1. Synthesis of dinuclear platinum(IV) complexes **2, 3** and **4**, and the tetranuclear mixed valence platinum(II)-platinum(IV) complexes **5** and **6**.

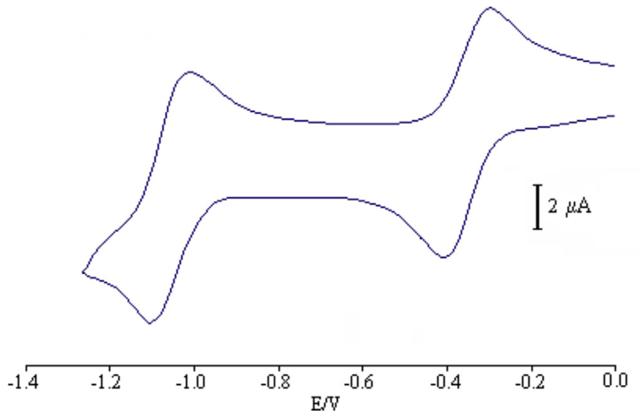


Fig. 1. Cyclic voltammogram of *cis*-[$(C_6F_5)_2Pt(\mu\text{-}C_8H_6N_4)Pt(C_6F_5)_2$] (**1**) in MeCN.

in the solution color is observed from orange to brown. The cyclic voltammetry of the resulting solution shows a null intensity of the electrical current at −0.55 V, which confirms that the process corresponding to the wave at −0.33 V has been completed after the transference of an equimolecular amount of electrons, thus indicating that the wave observed at −0.33 V in the CV is due to the binuclear anion $\mathbf{1}^{-}$ (see Fig. 1 in Supplementary Material).

3.1. EPR studies of complex cis-[$(C_6F_5)_2Pt(\mu\text{-}C_8H_6N_4)Pt(C_6F_5)_2$] (1)

The Electron Paramagnetic Resonance (EPR) spectrum of a frozen solution (CH_2Cl_2/thf 1:2) of a in situ electrochemically generated radical anion of *cis*-[$(C_6F_5)_2Pt(\mu\text{-}C_8H_6N_4)Pt(C_6F_5)_2$]$^{-}$ ($\mathbf{1}^{-}$) is shown in Fig. 1. At first glance it can be associated to a slightly orthorhombic S = ½ entity. While the high field feature at $g_z = 1.934$ does not show any resolved structure, the "perpendicular" low field feature consists of several overlapped lines. A detailed analysis of this structure indicated that the different lines can be grouped in two sets, one of them consists of four lines 11.2 mT (A = 65(2) MHz) apart centered at about $g_x = 2.029$ and the other is formed by five lines 7 mT (A = 40(2) MHz) apart centered at about $g_y = 2.009$. Both sets of lines are indicated in Fig. 2 with cross and stars, respectively. The lower trace in the figure shows the second derivative spectrum; a comparison of both traces reinforces the former analysis. Moreover, it seems sensible to consider the cross-marked quartet as a part of a five lines feature, the high field small signal being masked into the start labeled quintet.

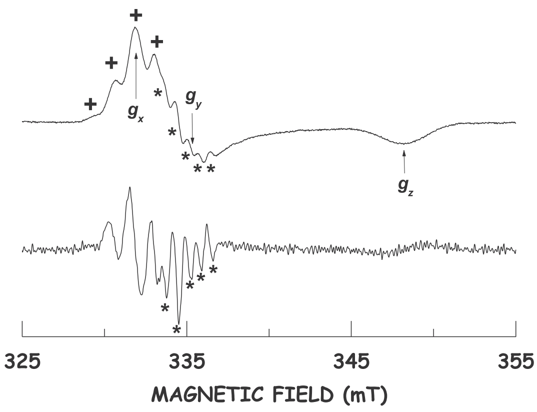


Fig. 2. Electron Paramagnetic Resonance spectrum (upper trace) and the second derivative (lower trace) of a frozen solution (CH_2Cl_2/thf 1:2) of a in situ generated radical anion $\mathbf{1}^{-}$.

The EPR spectra of frozen solutions of some similar mononuclear and binuclear platinum radical have been reported [18,50–54]. In all the cases the EPR spectrum is described as due to a S = ½ entity with a slightly orthorhombic *g*-tensor and the structure of the features, when resolved, is associated with the hyperfine interaction with the ^{195}Pt nucleus (I = ½, natural abundance 33.8%). The assignment of this structure to the hyperfine interaction with the Pt nuclei is supported by some DFT calculation [50–53].

For those complexes, from the EPR and DFT calculations it was inferred the equivalence of the platinum centers and the localization of the added electron on the bipyrimidine bridging ligand [18,50,53]. Taking into account the similarity of our EPR signal with those previously reported, a similar assignment can be done. In our case we obtain for the spectroscopic relevant parameters the values: $g_x = 2.029(2)$, $g_y = 2.009(2)$, $g_z = 1.934(2)$, $A_x = 65(2)$ MHz, $A_y = 40(2)$ MHz which are included in Table 1 where can be easily compared with the similar complexes already described.

In the present case the anisotropy of the *g*-tensor, measured as the difference of the extreme principal *g*-values, Δg, is lower than that observed in the other $\{(bpym)[PtR_2]_2\}^{\cdot-}$ radicals while the isotropic contribution, $g = (g_x + g_y + g_z)/3$ is practically independent on the ligand R.

We have also synthesized the reduced anion as complex [$CoCp_2$][$Pt_2(\mu\text{-}C_8H_6N_4)(C_6F_5)_4$] (**7**) by reaction of the neutral complex **1** with Cp_2Co freshly sublimated. It has been isolated and its elemental analyses, infrared spectrum and EPR confirm its stoicheiometry and paramagnetic character. (see Experimental) The paramagnetic behavior of complex **7** precludes the attempts to do the ^{1}H or ^{19}F NMRs spectra.

3.2. Synthesis of the platinum (IV) complexes: [NBu_4]$_2$[$Pt_2(\mu\text{-}X)_2(C_6F_5)_4Cl_4$] [X = Cl (2), OH (3)] and [$Pt_2(\mu\text{-}C_8H_6N_4)_2(C_6F_5)_4Cl_4$] (4)

The binuclear platinum(IV) complexes [NBu_4]$_2$[$Pt_2(\mu\text{-}Cl)_2(C_6F_5)_4Cl_4$] (**2**) and [$Pt_2(\mu\text{-}C_8H_6N_4)_2(C_6F_5)_4Cl_4$] (**4**) were obtained by addition of a solution of Cl_2 in CCl_4 in excess to the corresponding [NBu_4]$_2$[$Pt_2(\mu\text{-}Cl)_2(C_6F_5)_4$] or *cis*-[$Pt_2(\mu\text{-}C_8H_6N_4)_2(C_6F_5)_4$] (**1**) respectively (see Scheme 1-a). These oxidative addition reactions take place under mild conditions and involve the oxidation of both platinum(II) centers in the binuclear Pt(II) complexes to platinum(IV). The synthesis of complex **3** is quite more complicated since the reaction of the hydroxo Pt(II) derivative [NBu_4]$_2$[$Pt_2(\mu\text{-}OH)_2(C_6F_5)_4$] (prepared as described elsewhere [55]), with a solution of Cl_2 in CH_2Cl_2 under similar conditions to the ones used for the preparation of **2** and **4** results in a mixture of Pt(IV) complexes. In our hands and after several attempts the best way to achieve complex [NBu_4]$_2$[$Pt_2(\mu\text{-}OH)_2(C_6F_5)_4Cl_4$] (**3**) was by reacting the Pt(IV) derivative [NBu_4]$_2$[$Pt_2(\mu\text{-}Cl)_2(C_6F_5)_4Cl_4$] (**2**) with NBu_4OH in 1:2 molar ratio and the oily residue, which could not be isolated as a solid was spectroscopically characterized by IR and NMR. The substitution reaction of the chlorine ligands takes place selectively on the chlorine bridge ligands instead the terminal ones, probably due to the fact that the Pt—Cl bridging bonds are weaker that the terminal ones. Although complex **3** is not obtained as a solid, the use of the oily sample allows the isolation of the mixed Pt(II)/Pt(IV) complex (**6**), as we will see later. The IR spectra (see Experimental) of complexes **2, 3** and **4** show the typical absorptions for the C_6F_5 groups at around 970 and 795 cm^{-1} and the absorptions due to the ν(Pt—Cl) at around 327 and 264 cm^{-1} for complex **2**, at 337 cm^{-1} for complex **3** and at 354 cm^{-1} for complex **4**, It is important to note that the position of the band located around 950 cm^{-1}, assigned to ν(C—F) and related to the oxidation state of the central atom is in all cases in accordance with the oxidation states of the Pt centers [44] (see Table 2). For complex **3** the absorption due to the ν(O–H) appears at 3581 cm^{-1}. The ^1H NMR spectrum of complex **4** only shows two signals at 9.78 and 8.81 ppm in 2:1 ratio indicating a symmetrical disposition of the metal moieties with respect to the bridging ligand.

The ^{19}F NMR spectra of complexes **2**, **3** and **4** are similar and they show only one signal for the *p*-F atoms which suggest the equivalence of all pentafluorophenyl groups in each complex. However, the presence of two separated signals for the *o*-F atoms in a 1:1 ratio and also two more signals for the *m*-F atoms indicates the inequivalence of the analogous fluorine atoms in the ring, because the platinum coordination planes including all the Pt–C bonds are not a symmetry planes at room temperature. This different behavior respect to the dinuclear platinum (II) complexes have to be due to the sterical hindrance caused by the chlorine terminal ligands over and below the dinuclear coordination plane.

3.3. *Crystal structures of* $[NBu_4]_2[Pt_2(\mu\text{-}Cl)_2Cl_4(C_6F_5)_4]\cdot$ *(2),* $[Pt_2Cl_4(C_6F_5)_4(\mu\text{-}C_8N_4H_6)]\cdot 4Me_2CO$ *(4·4Me₂CO)*

Crystallographic data for complexes **2** and **4**$\cdot 4Me_2CO$ are given in Supplementary Material (Table 1), selected bond distances and angles are also given in Supplementary material (Tables 2 and 3 respectively).

The structure of the complex anion of **2**, $[Pt_2(\mu\text{-}Cl)_2Cl_4(C_6F_5)_4]^{2-}$, is shown in Fig. 3. There is a crystallographic inversion center in the middle of the anion. This anion contains two platinum atoms in oxidation state IV with a Pt···Pt distance of 3.664(1) Å which is similar to that found in the starting platinum(II) complex[55] and excludes any intermetallic interaction. The platinum(IV) atoms are bridged by two Cl ligands in a planar arrangement. Moreover, each platinum(IV) center has also coordinated two terminal *cis* C_6F_5 groups in the same plane and two *trans* Cl atoms above and below of the plane, thus resulting an octahedral environment for both metal centers.

The Pt–C distances are equal within the experimental error and similar to the distances found in pentafluorophenylplatinum(II) complexes [56–59]. The Pt–Cl terminal distances are slightly shorter than the Pt–Cl bridging ones, and the value of the distances of each type of Pt–Cl bond are also equal within the experimental error. As expected from an octahedral geometry the bond angles around each platinum(IV) center are close to 90° for *cis* ligands (from 81.6(1)° to 94.4(2)°), and 180° for *trans* ligands [from 174.3(2)° to 178.7(1)°].

The comparison of these structural data with the reported in the literature for the starting complex $[NBu_4]_2[Pt_2(\mu\text{-}Cl)_2(C_6F_5)_4]$ [56] confirms that the skeleton of the binuclear anion of platinum(II) does not suffer important modifications in the bond distances and angles as a result of the oxidation to platinum(IV).

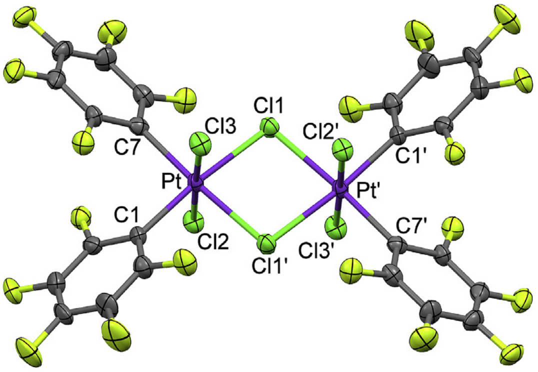


Fig. 3. Molecular structure of the complex anion of $[NBu_4]_2[Pt_2(\mu\text{-}Cl)_2Cl_4(C_6F_5)_4]$ (**2**). Relevant distances: Pt–C(1) 2.076(6), Pt–C(7) 2.090(6), Pt–Cl(1) 2.418(2), Pt–Cl(1′) 2.424(2), Pt–Cl(2) 2.329(2), Pt–Cl(3) 2.329(2). Thermal ellipsoids are represented at the 50% probability level.

Table 2
ν(C–F) of several pentafluorophenyl complexes in oxidation state (O.S.) II and IV.

COMPOUND	Pt O.S.	ν(C–F) cm^{-1}
cis-$[(C_6F_5)_2Pt(\mu\text{-}C_8H_6N_4)Pt(C_6F_5)_2]$ (**1**)	II	956
$[CoCp_2][Pt_2(\mu\text{-}C_8H_6N_4)(C_6F_5)_4]$ **(7)**.	II	966
$[Pt_2(\mu\text{-}C_8H_6N_4)Cl_4(C_6F_5)_4]$ **(4)**	IV	974
$[NBu_4]_2[Pt_2(\mu\text{-}Cl)_2(C_6F_5)_4]$	II	
$[NBu_4]_2[Pt_2(\mu\text{-}Cl)_2(C_6F_5)_4Cl_4]$	IV	966
$[NBu_4]_2[\{Pt(\mu\text{-}Cl)(C_6F_5)_2\}_2(\mu\text{-}Cl)_4\{Pt(C_6F_5)_2\}_2]$ **(5)**	IV, II	974, 960
$[NBu_4]_2[Pt_2(\mu\text{-}OH)_2(C_6F_5)_4]$	II	953
$[NBu_4]_2[Pt_2(\mu\text{-}OH)_2(C_6F_5)_4Cl_4]$ **(3)**	IV	965
$[NBu_4]_2[\{Pt(\mu\text{-}OH)(C_6F_5)_2\}_2(\mu\text{-}Cl)_4\{Pt(C_6F_5)_2\}_2]$ (**6**)	IV, II	972, 956

The structure of the complex $[Pt_2(\mu\text{-}C_8H_6N_4)_2Cl_4(C_6F_5)_4]$ (**4**) is shown in Fig. 4. As for complex **2,** there is a crystallographic inversion center in the middle of the anion. This molecule contains two platinum atoms in oxidation state IV bridged by a neutral tetradentate N-ligand ($C_8H_6N_4$) coordinated to each platinum atom through two nitrogen atoms in a chelating form. Moreover, each platinum(IV) center is bonded to two terminal *cis* C_6F_5 groups located in the same plane as the neutral ligand. The octahedral environment of the platinum atoms is completed by two *trans* Cl atoms. There are not significant changes in the structure of the coordinated 2,2′-bipyrimidine with respect to the free ligand [60].

The Pt–C and the Pt–Cl distances are similar to the corresponding ones in **2**. The Pt–N distances are in the range found in other platinum(II) or platinum(IV) complexes containing nitrogen donor ligands [2,3,36]. The N(1)–Pt–N(2) angle is quite narrow (77.9(2)°) due to the chelating nature of the bridging ligand, while the other angles around the platinum atom are in the range from 82.6(2)° to 97.3(3)° for *cis* ligands, and from 172.3(1)° to 175.0(3)° for *trans* ligands. The Pt···Pt distance is 5.698(1) Å, within the range of other complexes with this bridging ligand [18].

3.4. *Synthesis of mixed valence platinum(II)-platinum(IV) complexes:* $[NBu_4]_2[\{Pt(\mu\text{-}X)(C_6F_5)_2\}_2(\mu\text{-}Cl)_4\{Pt(C_6F_5)_2\}_2]$ *[X = Cl (5), OH (**6**)]*

The terminal chloro ligands of the binuclear platinum(IV)

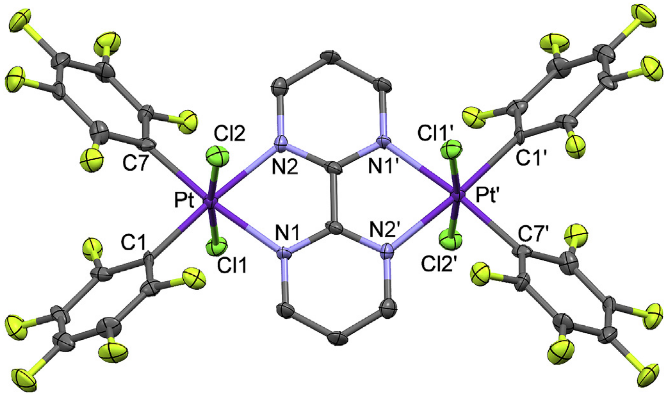


Fig. 4. Molecular structure of complex molecule of $[Pt_2Cl_4(C_6F_5)_4(\mu\text{-}C_8N_4H_6)]\cdot 4Me_2CO$ (**4**$\cdot 4Me_2CO$). Relevant distances: Pt–C(1) 2.033(8), Pt–C(7) 2.033(8) Pt–N(1) 2.133(6), Pt–N(2) 2.153(7), Pt–Cl(1) 2.319(2), PtCl(2) 2.321(2). Thermal ellipsoids are represented at the 50% probability level.

complexes **2**, **3** and **4** are suitable for acting as a bridging group between the platinum(IV) atom and other platinum centers, thus allowing the synthesis of derivatives of higher nuclearity. On the other hand *cis*-$[Pt(C_6F_5)_2(thf)_2]$ has proved to be an excellent synthon for the preparation of polynuclear complexes due to the lability of the thf ligands bonded to the metal center [61–64] generating the coordinatively unsaturated complex fragment "*cis*-$Pt(C_6F_5)_2$", which easily incorporates to other Pt complexes. Bearing this in mind, we carried out the reactions of the Pt(IV) complexes **2** and **3** with the Pt(II) synthon *cis*-$[Pt(C_6F_5)_2(thf)_2]$ in 1:2 molar ratio aiming to prepare Pt complexes of higher nuclearity and in mixed oxidation state [Pt(IV)/Pt(II)]. This synthetic approach is different to those described in the literature for the preparation of Pt(II)–Pt(IV) mixed-valence complexes [15,21–30]. In the reactions of complexes **2** and **3** with *cis*-$[Pt(C_6F_5)_2(thf)_2]$, a dramatic change in the color of the solution is produced due to charge-transfer absorption band indicating the formation of a chloride-bridged mixed valence complexes [21,65]. From these solutions, the tetranuclear Pt(IV)-X-Pt(II) complexes. $[NBu_4]_2[\{Pt(\mu\text{-}X)(C_6F_5)_2\}_2(\mu\text{-}Cl)_4\{Pt(C_6F_5)_2\}_2]$ [X = Cl (**5**), OH (**6**)] are obtained as red solids. The IR spectra of these complexes show two ν(C–F) bands due to the presence of platinum centers in two different oxidation states (see Table 2). In addition, the IR spectra show the absorptions due to the ν(Pt–Cl) at 343 and 279 cm^{-1} for **7** and at 325 and 282 cm^{-1} for **6**, in addition the absorption due to the ν(O–H) at 3574 cm^{-1} for **6**.

The ^{19}F NMR spectra confirm the presence of pentafluorophenyl groups bonded to platinum atoms in different oxidation states. that can be easily distinguished, when the platinum satellites are not overlapped with other signals, because the *ortho*-fluorine atoms corresponding to C_6F_5 groups bonded to Pt(IV) atoms present smaller $^3J(^{195}Pt,^{19}F)$ coupling constants (100–130Hz) than groups bonded to Pt(II) (around 500Hz). The ^{19}F NMR spectra of complexes **5** and **6** show six signals for the *ortho-fluorine* atoms: four signals assigned to the pentafluorophenyl groups bonded to platinum(IV), due to the presence of the platinum(II) units that reduce the symmetry and increase the sterically hindrance over the pentafluorophenyl groups bonded to Pt(IV), and two signals due to the rings bonded to platinum(II) The *meta*-fluorine atoms appear as complex multiplets in which several signals must be overlapped meanwhile the *para*-fluorine atoms may be assigned according their aspect of triplet. It is interesting to mention that, under similar conditions to those used in the synthesis of complexes **5** and **6**, there is no reaction between $[Pt_2(\mu\text{-}C_8H_6N_4)_2Cl_4(C_6F_5)_4]$ (**4**) and *cis*-$[Pt(C_6F_5)_2(thf)_2]$. This could be the result of the longer separation between the Pt(IV) centers in complex **4** created by the 2,2′-bipyrimidine ligand and in consequence between the chloride ligands of both metal atoms that should act as a bridge.

3.5. *Crystal structure of $[NBu_4]_2[\{Pt(\mu\text{-}OH)(C_6F_5)_2\}_2(\mu\text{-}Cl)_4\{Pt(C_6F_5)_2\}_2]\cdot CH_2Cl_2$ ($6\cdot CH_2Cl_2$)*

Crystallographic data and selected bond distances and angles for complex **6**$\cdot CH_2Cl_2$ are given in Supplementary material (Tables 1 and 4 respectively). The structure of the complex anion is shown in Fig. 5a and the central core is shown in Fig. 5b. The anion is located around an inversion center in $P2_1/n$. space group. The core of this anion presents a chair like disposition and comprises four platinum atoms, two of them in oxidation state (II) and square planar coordination environment and the other two in oxidation state (IV) and octahedral environments. The platinum(IV) centers are bridged by two hydroxo groups while each platinum(II) center is connected with the two platinum(IV) atoms by bridging chloride ligands. The Pt(II)–Pt(IV) and Pt(IV)–Pt(IV) distances are 3.848(1) Å and 3.289(1) Å respectively, excluding the existence of any metal-metal bonding.

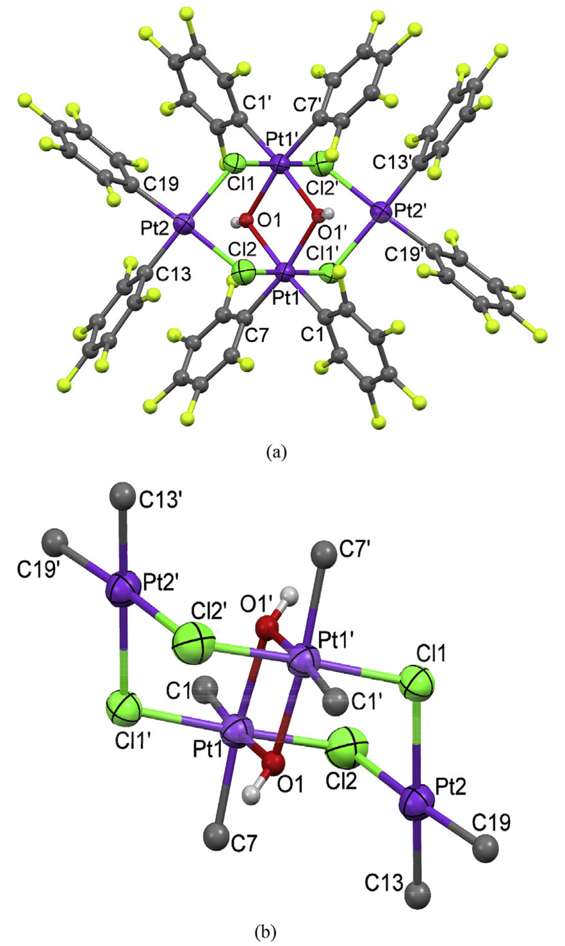


Fig. 5. a) Molecular structure of the complex anion of $[NBu_4]_2[\{Pt(\mu\text{-}OH)(C_6F_5)_2\}_2(\mu\text{-}Cl)_4\{Pt(C_6F_5)_2\}_2]\cdot CH_2Cl_2$ ($\mathbf{6}\cdot CH_2Cl_2$). (b) Detail of the core of the complex anion. Relevant distances: Pt Pt(1)–C(7) 1.984(18), Pt(1)–C(1) 1.992(18), Pt(1)-O(1′) 2.091(12), Pt(1)–O(1) 2.098(11), Pt(1)-Cl(2′) 2.292(6), Pt(1)–Cl(1) 2.341(5), Pt(2)–C(13) 1.908(19), Pt(2)–C(19) 1.997(16), Pt(2)–Cl(2) 2.345(5), Pt(2)–Cl(1) 2.406(4). Thermal ellipsoids are represented at the 50% probability level.

The two Pt(IV) moieties are formed by two μ-OH ligands in *cis* positions, two terminal *cis* C_6F_5 groups and two *trans*-μ-Cl atoms in apical positions thus completing an octahedral environment for both metal centers. The bond angles around each Pt(IV) center range from 76.5(4)° to 97.6(6)° for *cis* ligands, the smallest value corresponding to O–Pt–O, and from 169.7(6)° to 177.1(2)° for *trans* ligands. Each Pt(II) atom has two terminal *cis* C_6F_5 groups and two *cis* Cl atoms which form a *quasi* perfect square planar environment [angles for *cis* ligands range from 88.1(7)° to 93.4(5)°].

Each Pt(II) fragment is connected to each one of the two Pt(IV) centers through one Cl atom acting as bridging ligand and the Pt^{IV}–Cl distances are longer than the Pt^{II}–Cl ones (see Supplementary Material, Table 4). These Pt–Cl bridging distances [range from 2.292(6) to 2.406(4) Å] are similar to those found in other μ-chlorideplatinum(IV)platinum(II) complexes [42]. The values of the Pt^{II}–Cl–Pt^{IV} angles [109.3(2) and 108.3(2)°] are greater than those found in complex $[NEt_4]_2[Pt_2(NO)_2Cl_6]$ [24] which contains two platinum atoms in different oxidation states (IV,II) and where the two metal centers are bridged by a chlorine atom and a NO ligand. The steric requirements of the C_6F_5 groups could be responsible of this broader Pt(II)–Cl–Pt(IV) angle. The Pt–C distances are equal within the experimental error disregarding of the platinum oxidation state, and similar to other complexes containing the $Pt(C_6F_5)_2$ fragment [56–59].

The two square planar environments of the Pt(II) atoms lie parallel to each other due to the symmetry of the anion and these planes form a dihedral angle of 26.6° with the plane containing both Pt(IV) and the oxygen atoms. The dihedral angle between the square planes of Pt(II) and the plane containing the platinum(IV) atoms and chlorine atoms is 119.9°. The structure of complex **6** resemble the pentanuclear complex $[NBu_4]_2[\{Pt^{IV}{}_2(\mu\text{-}Cl)_2(Cl)_8\}_2(\mu\text{-}Pt^{II})]$ [42], where two dinuclear platinum (IV) units are bridged by a platinum(II) center which is bonded to one of the axial chlorine ligand of each platinum(IV).

The comparison of these structural data with the ones reported for complex $[NBu_4]_2[Pt_2(\mu\text{-}OH)_2(C_6F_5)_4]$ [55] confirms that the skeleton of the binuclear complex anion does not suffer any important modifications in the bond distances and angles as consequence of the oxidation reaction to platinum (IV) and the incorporation of the two "*cis*-$Pt^{II}(C_6F_5)_2$" fragments to the Pt(IV) substrates. Additionally, the X-ray structure reveals that the described reactions does not produce any intramolecular reorganization of ligands nor a modification on the oxidation states of the Pt centers.

4. Conclusions

While the binuclear Pt(IV) complexes $[NBu_4]_2[Pt_2(\mu\text{-}X)_2(C_6F_5)_4Cl_4]$ (X = Cl, 2,2′-bipyrimidine) can be obtained by oxidative addition of Cl_2 to the corresponding Pt(II) derivative, the hydroxide-platinum(IV) complex (X = OH) have to be prepared by a substitution process of the Cl^- by OH^- in the chloride-platinum(IV) derivative. These Pt(IV) (X = Cl, OH) complexes produces the mixed valence [Pt(IV)/Pt(II)] tetranuclear derivatives when react with *cis*-$[Pt(C_6F_5)_2(thf)_2]$ because of the lability of the thf ligand in the Pt(II) substrates and the adequate distance between the two apical chloride ligands of the platinum(IV) centers (3.610 Å). The Pt(IV) binuclear units act as a quelate metaloligand towards the *cis*-pentafluorophenylplatinum(II) fragments. However the analogous reaction with complex containing X = 2,2′-bipyrimidine does not form the tetranuclear mixed valence [Pt(IV)/Pt(II)] compound probably because of the inadequate long separation of the chloro ligands (5,385 Å).

Acknowledgements

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jorganchem.2019.06.034.

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