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# Self-assembly of organometallic polymers through hydrogen bonding: A diplatinum(IV) complex with a single bridging halide ligand

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Dedicated to Professor Malcolm Chisholm, master of molecular architecture, in recognition of his outstanding contributions to inorganic chemistry.

#### Abstract

The reaction of [PtMe<sub>2</sub>(bu<sub>2</sub>bipy)], bu<sub>2</sub>bipy = 4,4'-di-*t*-butyl-2,2'-bipyridine (1) with RCH<sub>2</sub>Br occurs by *trans* oxidative addition to give the platinum(IV) complexes [PtBrMe<sub>2</sub>(CH<sub>2</sub>R)(bu<sub>2</sub>bipy)],  $R = C_6H_4CO_2H$  (2);  $R = C_6H_4CH_2CO_2H$  (3) and these reacted with half an equivalent of Ag[PF<sub>6</sub>] to give the unusual diplatinum(IV) complexes [{PtMe<sub>2</sub>(CH<sub>2</sub>R)(bu<sub>2</sub>bipy)}<sub>2</sub>(µ-Br)][PF<sub>6</sub>],  $R = C_6H_4CO_2H$  (4);  $R = C_6H_4CH_2CO_2H$  (5). These diplatinum(IV) complexes, each of which contains a hydrogen bonding carboxylic acid group, are connected only by an unsupported bridging bromide ligand. In the solid state, complex 4 forms a self-assembled zig-zag polymer through intermolecular hydrogen bonding between pairs of carboxylic acid groups. © 2005 Elsevier Ltd. All rights reserved.

Keywords: Platinum; Self-assembly; Polymer; Hydrogen bond

## 1. Introduction

Hydrogen bonding is widely used in supramolecular chemistry, such as in crystal engineering and in the design of molecular materials [1–3]. However, this approach has natural limitations in organometallic chemistry, since many alkyl-metal bonds react with the functional groups (e.g. OH or NH bonds) typically used as hydrogen bond donors [4]. Although methylplatinum(II) bonds can be cleaved by carboxylic acids [5], the reactions of [PtMe<sub>2</sub>(bu<sub>2</sub>bipy)], bu<sub>2</sub>bipy = 4,4'-di-*t*-butyl-2,2'-bipyridine (1) with BrCH<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>H and BrCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>CO<sub>2</sub>H occur selectively by *trans* oxidative addition of the C–Br bond to give the platinum(IV) complexes **2** and **3**, rather than by protonolysis of a methylplatinum(IV) bonds are typically inert towards protonolysis [4,5], with the notable exception of

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tetramethylplatinum(IV) compounds [9], the organoplatinum(IV) products, **2** and **3** of Scheme 1, that contain a carboxylic acid functional group are stable compounds. In the solid state, they form dimers by self-assembly as illustrated for complex **2** in Scheme 1 [6].

In order to form polymers by self-assembly, it is necessary to have at least two hydrogen-bonding donor/acceptor pairs per molecule. One way to prepare such "building block" molecules is to abstract the bromide ligand from 2 or 3 in the presence of an assembling ligand such as 4,4'-bipyridine, and the diplatinum(IV) complexes formed in this way have been shown to self-assemble to give unusual supramolecular polymers [6–8]. This paper reports a simpler way to prepare diplatinum(IV) complexes by formation of a bridging halide linking group, and shows that self-assembly can then give a supramolecular polymer.

# 2. Experimental

All reactions were performed under a nitrogen atmosphere by using standard Schlenk techniques. NMR and

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Scheme 1. Reagents are: (i) BrCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>H and (ii) BrCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>CO<sub>2</sub>H.

IR spectra were recorded by using a Varian Gemini 400 NMR and a Perkin-Elmer FT-IR 2000 spectrometer, respectively. Compound **1** was prepared using a method reported in the literature [10].

# 2.1. $[{PtMe_2(bu_2bipy)(CH_2C_6H_4CO_2H)}_2(\mu-Br)][PF_6]-(4[PF_6])$

To a solution of [PtMe<sub>2</sub>(bu<sub>2</sub>bipy)] (100 mg) in acetone (30 mL) was added bromotoluic acid (44 mg), and the solution was stirred for 30 min., after which time a solution of AgPF<sub>6</sub> (26 mg) in acetone (5 mL) was added. After stirring for further 30 min, the mixture was filtered through Celite and evaporated under vacuum to give a white solid. Yield: 86%. *Anal.* Calc. for C<sub>56</sub>H<sub>74</sub>BrF<sub>6</sub>N<sub>4</sub>O<sub>4</sub>PPt<sub>2</sub>: C, 45.38; H, 5.03; N, 3.78. Found: C, 45.07; H, 5.21; N, 3.55%. NMR in acetone-*d*<sub>6</sub>:  $\delta$ (<sup>1</sup>H) = 1.04 [s, 12H, <sup>2</sup>*J*(PtH) = 70 Hz, PtMe]; 1.44 [s, 36H, bu]; 2.82 [s, 4H, <sup>2</sup>*J*(PtH) = 90 Hz, PtCH<sub>2</sub>]; 6.35 [m, 4H, C<sub>6</sub>H<sub>4</sub> H<sup>2</sup>]; 7.25 [m, 4H, C<sub>6</sub>H<sub>4</sub> H<sup>3</sup>]; 7.70 [m, 4H, bipy H<sup>5</sup>]; 8.45 [m, 4H, bipy H<sup>3</sup>]; 8.60 [m, 4H, bipy H<sup>6</sup>]. IR (Nujol mull): *v*(CO) = 1697 cm<sup>-1</sup>, *v*(OH) = 2624, 2548 cm<sup>-1</sup>.

# 2.2. $[{PtMe_2(bu_2bipy)(CH_2C_6H_4CH_2CO_2H)}_2(\mu-Br)] - [PF_6] (5[PF_6])$

This was prepared similarly from  $[PtMe_2(bu_2bipy)]$  (100 mg), bromomethylphenylacetic acid (46 mg) and AgPF<sub>6</sub> (26 mg). Yield: 87%. *Anal.* Calc. for C<sub>58</sub>H<sub>78</sub>BrF<sub>6</sub>N<sub>4</sub>-

O<sub>4</sub>PPt<sub>2</sub>: C, 46.13; H, 5.20; N, 3.71. Found: C, 45.71; H, 5.21; N, 3.58%. NMR in acetone- $d_6$ :  $\delta({}^{1}\text{H}) = 1.02$  [s, 12H,  ${}^{2}J(\text{PtH}) = 70$  Hz, PtMe]; 1.48 [s, 36H, bu]; 2.75 [s, 4H,  ${}^{2}J(\text{PtH}) = 90$  Hz, PtCH<sub>2</sub>]; 6.15 [m, 4H, C<sub>6</sub>H<sub>4</sub> H<sup>2</sup>]; 7.45 [m, 4H, C<sub>6</sub>H<sub>4</sub> H<sup>3</sup>]; 7.70 [m, 4H, bipy H<sup>5</sup>]; 8.3–8.6 [m, br, 8H, bipy H<sup>3</sup> + bipy H<sup>6</sup>]. IR (Nujol mull):  $\nu(\text{CO}) = 1696 \text{ cm}^{-1}$ ,  $\nu(\text{OH}) = 2652$ , 2516 cm<sup>-1</sup>.

#### 2.3. X-ray structure determination

Crystals of  $4[PF_6] \cdot 4C_6H_6$  were grown by slow diffusion of benzene into an acetonitrile solution. A colorless plate was mounted on a glass fiber. Data were collected at 200 K using a Nonius Kappa CCD diffractometer with collect (Nonius, B.V., 1998) software. The unit cell parameters were calculated and refined from the full data set. Crystal cell refinement and data reduction were carried out using the Nonius DENZO package. After data reduction, the data were scaled based on equivalent reflections using SCALEPACK (Nonius, B.V. 1998). The crystal data and refinement parameters are listed in Table 1. The SHELX-TL 5.1 (Sheldrick, G.M., Madison, WI) program package was used to solve the structure by direct methods. There was some disorder in the hexafluorophosphate anion, which was modeled as a mixture of two 50:50 occupancy groups, with the phosphorus fluorine bond lengths restrained to be equal and allowed to refine. Several of the solvent molecules were disordered and were modeled as isotropic 50:50 mixtures.

Table	e 1					
Cryst	tal data and	structure r	efinement for	complex	$4[PF_6] \cdot 40$	$C_6H_6$

Empirical formula	$C_{80}H_{98}BrF_6N_4O_4PPt_2$		
Formula weight	1794.68		
Temperature (K)	200(2)		
Wavelength (Å)	0.71073		
Crystal system	monoclinic		
Space group	P2(1)/n		
Unit cell dimensions			
a (Å)	14.57770(10)		
b (Å)	32.5272(3)		
<i>c</i> (Å)	19.4740(2)		
β (°)	101.894(1)		
Volume ( $Å^3$ )	9035.8(4)		
Ζ	4		
Density (calculated) (Mg/m <sup>3</sup> )	1.319		
Absorption coefficient (mm <sup>-1</sup> )	3.608		
<i>F</i> (000)	3592		
Reflections collected	51 358		
Independent reflections	$20503 \ [R_{\rm int} = 0.048]$		
Completeness to $\theta = 27.48^{\circ}$ (%)	99.0		
Absorption correction	integration		
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0707, wR_2 = 0.2073$		
R indices (all data)	$R_1 = 0.1083, wR_2 = 0.2361$		

All other non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were calculated geometrically and were riding on their respective carbon atoms.

### 3. Results and discussion

The synthesis of the building blocks for self-assembly was achieved according to Scheme 2. The organoplatinum(IV) complexes 2 and 3, each of which contains a single carboxylic acid substituent, were prepared in situ by reaction of  $[PtMe_2(bu_2bipy)]$  with the corresponding benzyl bromide derivative according to Scheme 1. Reaction of these complexes with silver hexafluorophosphate in a 2:1 molar ratio occurred by bromide abstraction, to give insoluble AgBr, and then by formation of a bridging bromide group to give the cationic diplatinum(IV) complexes 4 and 5, which were isolated as the hexafluorophosphate salts. In these reactions, it can be considered that the bromo ligand of one platinum(IV) center acts as a ligand at the



Scheme 2. In the self-assembled polymer only the core atoms of the  $bu_2bipy$  ligands are shown.

second platinum(IV) center by occupying the coordination site which is opened up by the bromide abstraction step.

The complexes 4 and 5 are air-stable complexes which are soluble in organic solvents such as acetone and dichloromethane. In acetone- $d_6$  solution, the <sup>1</sup>H NMR spectrum of complex 4 contained a single methylplatinum resonance at  $\delta({}^{1}H) = 1.04$ , with coupling constant  ${}^{2}J(PtH) = 70$  Hz, showing that all methylplatinum(IV) groups are equivalent. The benzylic protons also occurred as a singlet resonance at  $\delta = 2.82$ , with coupling constant  ${}^{2}J(PtH) = 90$  Hz. The infrared spectrum of complex 4 as a Nujol mull contained a band due to v(C=0) at 1697 cm<sup>-1</sup> and bands due to v(OH) at 2624 and 2548 cm<sup>-1</sup>. The NMR data are fully consistent with the proposed structure of 4 in solution (Scheme 2), while the IR data indicate the presence of hydrogenbonded carboxylic acid groups in the solid state [8,9]. Complex 5 was characterized spectroscopically in a similar way.

The molecular structure of complex 4 is shown in Fig. 1. It confirms the overall stereochemistry deduced from the spectroscopic data, with the methylplatinum groups *trans* to the bipyridine ligand and the substituted benzyl group trans to bromide. The bromide ligand bridges the two platinum atoms with roughly equal distances Pt(1)-Br(1) =2.560(2) Å and Pt(2)-Br(1) = 2.565(2) Å. The large angle  $Pt(1)-Br(1)-Pt(2) = 127.88(8)^{\circ}$  and correspondingly long distance  $Pt \cdot \cdot \cdot Pt = 4.60$  Å are clear indications that there is no platinum-platinum bonding interaction [10]. Thus, the natural bond angle M-X-M is close to 90° for complexes containing a bridging halide and no other bridging halides [10]. An M–X–M angle much less than 90° then indicates the presence of a metal-metal bonding interaction, while an M–X–M angle much greater than 90° indicates both the lack of an attractive force between the metals and the presence of steric interactions around the bridging halide [10–15].

The molecules of complex **4** associate through complementary hydrogen bonding between carboxylic acid

C(1R)

Pt(2

C(2R)

1(3)

C(115

Br(1) N(2

C(1Q)

C(20)

C(11C

O(1Q)





Fig. 2. Part of the zig-zag polymeric chain structure formed by selfassembly through hydrogen bonding between units of complex **4**.

substituents, as shown in Fig. 2. The intermolecular hydrogen bonding between the V-shaped building blocks **4** naturally leads to formation of a zig-zag polymeric structure. The O···O distances O(1Q)···O(1R) = 2.62(2) Å and O(2Q)···O(2R) = 2.71(2) Å are in the expected range for hydrogen bonds in carboxylic acids [5–7,9].

There are very few diplatinum complexes that have been characterized to contain a single unsupported halide bridge, and particularly few organoplatinum(IV) examples [11–14], so the characterization of the molecular structure of complex 4 is significant. More noteworthy is the observation that this is the first time that a complex of this type has been used in the self-assembly of supramolecular polymeric structures. Since the oxidative addition of alkyl halides to platinum(II) is a versatile method for the synthesis of alkyl(halogeno)platinum(IV) complexes containing functionally substituted alkyl groups [5–7], the finding that these monoplatinum(IV) complexes can easily be converted to the diplatinum(IV) complexes with bridging halide provides a valuable new method for the synthesis of bifunctional organodiplatinum(IV) complexes for use in the self-assembly of molecular materials.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly. 2005.08.020.

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