



# Efficient $\pi$ -stacking with benzene provides 2D assembly of *trans*-[PtCl<sub>2</sub>(*p*-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CN)<sub>2</sub>]

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## ARTICLE INFO

### Article history:

Received 29 May 2015

Received in revised form

5 September 2015

Accepted 29 September 2015

Available online 13 October 2015

### Keywords:

$\pi$ -stacking

Platinum(II)

*p*-trifluoromethylbenzonitrile

X-ray structure

DFT calculations

## ABSTRACT

The new platinum(II) complex *trans*-[PtCl<sub>2</sub>(*p*-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CN)<sub>2</sub>], which was obtained upon treatment of [PtCl<sub>2</sub>(MeCN)<sub>2</sub>] with excess of *p*-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CN, co-crystallizes with benzene giving 2D layers formed by complex–benzene and complex–complex  $\pi$ -stacking interactions. These interactions were detected by X-ray crystallography and their nature was analyzed by DFT calculations (M06 functional), including AIM analysis, inspection of NBO atomic charges, and evaluation of the vertical total energies for dissociation in the model supramolecular cluster. The crystal packing insignificantly effect the structure of the supramolecular associates and  $\pi$ -stacking interactions are rather weak.

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## 1. Introduction

Intermolecular interactions involving aromatic rings are among the key factors determining both chemical and biological recognition [1–3]. The nature of these interactions is electrostatic and  $\pi$ -stacking can be described as a quadrupole–quadrupole interaction [1,3–5]. The alternation of compounds with positive and negative quadrupole moments leads to formation of enduring  $\pi$ – $\pi$  interactions [2,3]. Stacking can be also considered within donor–acceptor model especially when charge transfer complexes are formed [6]. Benzene, substituted benzenes, and many phenyl containing compounds are used as  $\pi$ -stacking donors, and their fluorinated analogs act as  $\pi$ -stacking acceptors [3,5].

Organometallic and coordination compounds featuring aromatic ligands are also known to be used for molecular assembly by  $\pi$ -stacking.  $\pi$ -Systems of these ligands are often polarized by the coordination to metal centers of various nature giving many examples of supramolecular ordering due to  $\pi$ – $\pi$  contacts [6].

*p*-Trifluoromethylbenzonitrile (**1**) is a representative organonitrile bearing electron withdrawing substituent. The metal-bound cyano and trifluoromethyl substituents make its aromatic  $\pi$ -system

electron poor. Accordingly, this compound and its complexes in principle can be used as an acceptor for  $\pi$ -stacking assembly, however, this was never studied experimentally.

Although **1** was synthesized [7] long ago, only few examples of its complexes [8–14] were reported and only one platinum(II) complex, viz. *cis*-[PtCl<sub>2</sub>(*p*-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CN)<sub>2</sub>] [15] is known. In this work, we prepared the *trans*-isomer, *trans*-[PtCl<sub>2</sub>(*p*-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CN)<sub>2</sub>] (**2**), which was obtained (see Experimental) by modification of the method previously applied for the synthesis of *trans*-[PtCl<sub>2</sub>(PhCN)<sub>2</sub>] [16]. We observed that **2** co-crystallizes with benzene forming 1:1 solvate, which demonstrates extended  $\pi$ -stacking between the complex and solvent molecules. The nature of these interactions was analyzed by DFT calculations (M06 functional), including AIM analysis, inspection of NBO atomic charges and evaluation of the vertical total energies for dissociation in the model supramolecular cluster. All our results are consistently disclosed in sections that follow.

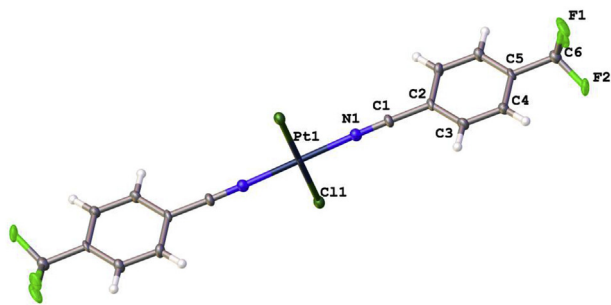
## 2. Results and discussion

### 2.1. Structure of **2** in **2**•C<sub>6</sub>H<sub>6</sub>

Molecules of **2** in **2**•C<sub>6</sub>H<sub>6</sub> exhibit square planar environment of the platinum atom with the *trans*-configuration of both the Cl and nitrile ligands (Fig. 1). Planes of substituent phenyls are

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**Fig. 1.** Molecular structure of **2** in  $2\bullet\text{C}_6\text{H}_6$  with the atomic numbering scheme. Thermal ellipsoids are drawn with the 50% probability.

perpendicular to the  $\text{PtCl}_2\text{N}_2$  plane. The F1 atom lies in the latter plane demonstrating high degree of order even in the individual molecule of the complex.

Coordination to the  $\text{Pt}^{\text{II}}$  center has no significant effect on structure of the nitrile and the latter possesses equal bond lengths with the corresponding values for uncomplexed **1** (Table 1) [17]. The  $\text{Pt1}-\text{Cl1}$  [2.3060(12) Å] and the  $\text{Pt1}-\text{N1}$  [1.966(4) Å] bonds have similar lengths compared to the corresponding bonds in *trans*- $[\text{PtCl}_2(\text{PhCN})_2]$  (2.2923(9) Å and 1.9783(9) Å, respectively).

## 2.2. Stacking interactions in $2\bullet\text{C}_6\text{H}_6$

Stacking interactions between the complex molecules and benzene provide stacked 2D layers (Figure 2).

Benzene molecules are located between two nitrile ligands from two different complex molecules, demonstrating an equivalent stacking with two ligand rings.  $\pi$ -Stacking between two ligand rings is wider and weaker, which can be explained by their electrophilic nature and steric effect of the  $\text{CF}_3$  groups. Parameters of the  $\pi$ -stacking are given in Table 2.

Noteworthy that, apart from the classic stacking, interactions between the carbon atoms from the cyano groups and  $\pi$ -system of benzene molecules was observed. It is expected that these carbon atoms are acceptors, whereas benzene molecules act as donors. Indeed, this type of interaction was confirmed by theoretical calculations (see later). One should mention that contacts between the cyano carbons and the carbons from the benzene ring are equal [ $d(\text{C}\cdots\text{C}) = 3.405(7)$  Å, less than  $2R_{\text{vdw}}(\text{C}) = 3.54$  Å [18]] insofar as positions of solvent molecules are symmetrical.

## 2.3. The $\text{C}-\text{H}\cdots\text{Cl}$ contacts in $2\bullet\text{C}_6\text{H}_6$

The stacked layers (Fig. 2) bound by the  $\text{C}-\text{H}\cdots\text{Cl}$  hydrogen bonds (Fig. 4). It should also be noted that projections (formed by aromatic rings) and depressions (platinum, chloride atoms, and trifluoromethyl areas) of one 2D layer fit nicely to projections and depressions of another.

**Table 1**  
Selected bond lengths of **2** in  $2\bullet\text{C}_6\text{H}_6$ . The data for **1** are given to comparison.

Bond length, Å	<b>2</b>	<b>1</b>
Pt1–Cl1	2.3060(12)	–
Pt1–N1	1.966(4)	–
N1–C1	1.141(7)	1.1482(14)
C1–C2	1.430(6)	1.4500(13)
C2–C3	1.394(4)	1.3974(15)
C3–C4	1.380(5)	1.3911(13)
C4–C5	1.391(4)	1.3921(13)
C5–C6	1.500(7)	1.5051(13)

Each of two complex molecules are linked by the two equal  $\text{C}-\text{H}\cdots\text{Cl}$  bonds (Fig. 5). The distance between the Cl1 and H4 atoms is slightly less than the sum of their vdW radii ( $2.8375(6) < 2.86$  Å [18]), carbon $\cdots$ chlorine distance is also less the sum of vdW radii ( $3.517(4) < 3.53$  Å [18]). Although the corresponding angle is not large [ $130.9(3)^\circ$ ], this contact should be interpreted as hydrogen bonding accordingly to the IUPAC criterion [19].

## 2.4. Theoretical considerations

In order to quantitatively estimate energies of the  $\pi$ -stacking and determine the influence of crystal packing effects, appropriate theoretical DFT study was performed. Primarily, we optimized the structure of the isolated heterotrimeric cluster  $2\bullet 2\bullet\text{C}_6\text{H}_6$  (**A**) (Fig. 3) using the experimental X-ray geometry as a starting point. Such approach allows excluding the crystal packing effects from consideration and to study short contacts only within this cluster. If the crystal packing effects are significant, the structure should change appreciably on going from the solid state to the gas phase otherwise the geometry is expected to be preserved in the isolated form [20].

The results of our theoretical calculations are given below. The structure of cluster **A** in the isolated state did not significantly change compared to the experimental X-ray data (Fig. 3), except the orthogonal orientation of the *p*- $\text{CF}_3\text{C}_6\text{H}_4\text{CN}$  ligands that are not involved in the  $\pi$ -stacking relatively to other *p*- $\text{CF}_3\text{C}_6\text{H}_4\text{CN}$  ligands participating in non-covalent interactions. The maximum deviation between theoretical and experimental bond lengths was found for the Pt–Cl bonds (0.05 Å), whereas this difference for other bonds of cluster **A** does not exceed 0.018 Å, falling in the  $3\sigma$  interval of the experimental data; theoretical and experimental characteristic parameters of the  $\pi$ -stacking are presented in Table 3.

Additional information on the nature of the stacking interactions in **A** can be obtained by the topological analysis of the electron density distribution (AIM method) [21]. We found (i) two bond critical points (3, –1) for stacking interactions between the *p*- $\text{CF}_3\text{C}_6\text{H}_4\text{CN}$  ligands (*meta*-C – *meta*-C type) in **2**; (ii) two bond critical points (3, –1) for  $\pi$ -stacking interactions between one *p*- $\text{CF}_3\text{C}_6\text{H}_4\text{CN}$  ligand in **2** and benzene molecule; (iii) bond critical point (3, –1) for interaction of benzene molecule with the C atom of the cyano group in one *p*- $\text{CF}_3\text{C}_6\text{H}_4\text{CN}$  ligand of **2** (Table 3 and Fig. 3). These interactions are very weak and this indirectly indicates the low magnitude of electron density and the positive values of Laplacian and energy density in appropriate bond critical points (3, –1). Based on the approaches proposed by Espinosa et al. [22] and Vener et al. [23], one can state that the energy of these contacts does not exceed 1.1 kcal/mol.

The NBO atomic charges [24] were also calculated for the carbon atoms involved in the weak interactions in **A**. The values of charges on the *meta*-carbon atoms in the aryl rings of the *p*- $\text{CF}_3\text{C}_6\text{H}_4\text{CN}$  ligands are around –0.21, and the corresponding stacking interaction between two molecules of **2** is assumed to be non-polar [2,3,5,6]. Analogous situation was verified for the benzene–complex stacking (values of NBO atomic charges on carbon atoms in benzene molecule and in phenyl ring as part of the *p*- $\text{CF}_3\text{C}_6\text{H}_4\text{CN}$  ligand are –0.25 and –0.17, respectively). However, partial charge on the cyano group carbon atom is positive (0.50), whereas benzene carbon atom has negative charge (–0.24) and this interaction is assumed to be polar [2,3,5,6]. The interaction of cyano group with benzene may be also attributed to local dipole interactions as demonstrated in the literature [25,26].

We evaluated the vertical total energies for dissociation of heterotrimeric cluster **A** ( $E_v$ ) by two paths: **A**  $\rightarrow 2\bullet 2 + \text{C}_6\text{H}_6$  ( $E_v = 8.7$  kcal/mol) and **A**  $\rightarrow 2 + 2\bullet\text{C}_6\text{H}_6$  ( $E_v = 11.6$  kcal/mol). It can be concluded that the contribution of these weak interactions to the stabilization of heterotrimeric cluster **A** is 10–31%.

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