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# Intermolecular stacking of a tetranuclear cyclic Pt(II) complex: NMR characterization and X-ray crystal structure of cis–trans–cis–trans tetra[μ-2,6-diethynyl-4-nitroaniline-bis(tri(p-tolyl)phosphine)platinum(II)]

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## Abstract

The synthesis and characterization of a tetranuclear Pt complex, cis–trans–cis–trans tetra[μ-2,6-diethynyl-4-nitroaniline-bis(tri(p-tolyl)phosphine) platinum(II)], namely $[L_2Pt\text{-}DENA]_4$ with L = tri-p-tolylphosphine, is reported. The complex was obtained by the dehydrohalogenative condensation of 2,6-diethynyl-4-nitroaniline (DENA) with cis-[dichlorobis(tri(p-tolyl)phosphine)platinum(II)]. The single crystal structure determination of $[L_2Pt\text{-}DENA]_4$ indicated the formation of a neutral molecular cycle with four alternating platinum units in cis and trans configurations, all bridged with DENA spacers with the presence of solvent (toluene) crystallization molecules. A twisted tetranuclear cyclic feature was identified. The formation of intermolecular stacks of the tetranuclear complex in solution was assessed by means of nuclear Overhauser enhancement spectroscopy (NOESY) and rotating frame Overhauser effect spectroscopy (ROESY) characterizations.

*Keywords:* Cyclic platinum complexes; X-ray; 2D NMR spectra

## 1. Introduction

Interest in nanoscale molecular devices prompted the scientific research to develop chemical routes to achieve selected architectures by self-assembly of macrocyclic multinuclear complexes and related nanoscale supramolecular species. The synthesis and properties of metal-containing molecular rectangles obtained from different transition metals (Re, Pd, Pt, Ag, Cu, Ni, Zn, Co) and rigid bifunctional ligands have been recently reported [1] and outstanding examples of self-assembled metallomacrocycles, with a variety of symmetric shapes, i.e. triangles, squares, hexagons, etc. have been the main object of study by several

research groups [2–5]. These features usually come out when cis-blocked square-planar Pt(II) and Pd(II) complexes are used as the precursors [6–9]. One of the goals of this research is the construction of molecular structures at nanometric scale by using the metal coordination driving force for self-organization. The formation of these structures and their supramolecular assembling behavior [10] suggest promising expectations for the development of advanced technologies.

Our group studied π-conjugated polymers and oligomers based on platinum-acetylide units in a linear rigid rod structure, derived from the reaction of different organic spacers with cis and trans metal dichlorides [11a,11b,11c] and some of them were used in the development of chemical sensors [12a,12b,12c]. In the framework of our research, the building-block approach was tested also for

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the preparation of closed shapes which were found among the side products of the polymerization reactions. Among different functional molecules, we focused our research on the use of 2,6-diethynyl-4-nitroaniline (DENA) and the Pt(II) square planar complex in *cis* configuration, i.e. *cis*-[Pt(PTol₃)₂Cl₂], (PTol₃ = tri-*p*-tolylphosphine). Charge transfer between electron withdrawing and electron donor groups, in our case NO₂ and NH₂ moieties in *para* position in the phenyl ring, is at the basis of different optoelectronic properties and applications such as, for example, linear and non-linear optics and molecular recognition. The square-planar ligand sphere offers the advantage of a restricted number of isomers (when compared to octahedrally coordinated metal centers) and linear or closed-shapes can be obtained and easily recognized. A helicoidal polymeric structure containing DENA units has been recently obtained and the formation of intermolecular stacks recognized by means of NOESY investigation [11b]. Then, our purpose was to achieve a closed-shape likely to be a suitable cage for the detection of selected molecules. Upon modification of the reaction conditions, a planar, hexagonal structure with six Pt(II) centers bridged by six DENA molecules was expected. In this paper, we report that the reaction of an excess of DENA in the presence of *cis*-[Pt(PTol₃)₂Cl₂], gave rise to an unexpected constrained structure with a twisted cyclic shape, containing only four Pt atoms in an alternating *cis–trans* geometry. X-ray diffraction (XRD) together with NOESY and ROESY NMR analyses allowed the molecular structure of the novel tetranuclear complex to be elucidated.

## 2. Results and discussion

The DENA molecule was chosen for the study of the effect of nitro and amino groups in *para* position for the phenyl ring and for the possible intermolecular interactions that may also occur in a closed shape molecule. *cis*-[Pt(PTol₃)₂Cl₂] was used as the precursor, for its chemical stability, as well as on the basis of our previous studies on the formation of both *cis* and *trans* bis-acetylide complexes [13a,13b], thus allowing for the possibility of bonding both *cis* and *trans* sequences in the cage, in some analogy with the rational design reported by Manna and coworkers [7].

The organometallic cyclic tetranuclear complex, [L₂Pt-DENA]₄, was prepared by the dehydrohalogenation reaction pathway reported in Scheme 1.

The synthetic pathway was suggested by the well known dehydrohalogenation method [14] and a main product, i.e. the tetranuclear complex [L₂Pt-DENA]₄, was isolated among other oligomeric compounds, by careful chromatography purification of the crude reaction products. An excess of DENA (complex/monomer molar ratio 1/10) and short reaction time were used in order to obtain the closed structure at a high yield. The pure complex [L₂Pt-DENA]₄ could be isolated as bright and transparent yellow crystals which contain crystallization molecules of toluene, when crystallized from neat toluene or toluene/hexane; other crystallization solvents did not afford crystals good enough for XRD measurements and even the yellow crystals from toluene withered when taken away from their solution.

A complete traditional spectroscopic characterization was performed on the solvent free complex. The characterization suggested a non-linear structure; the molecular geometry of the tetranuclear complex was conclusively determined by X-ray diffraction analysis. XRD together with 2D ROESY and NOESY ¹H NMR spectra also led to an insight into the intermolecular interaction.

The FTIR spectrum of [L₂Pt-DENA]₄ confirmed the formation of a coupling product through the linking of Pt–acetylide bond: the presence of the bands at 2105 cm⁻¹ ($v$C≡C), 3473, 3360 cm⁻¹ ($v$NH₂), and the absence of the bands at 3293 cm⁻¹ ($v$≡C–H) and 320 cm⁻¹ ($v$Pt–Cl) indicated that the complex had no acetylenic or chloride moieties as terminal groups, thus preliminary suggesting the closed shape.

The geometric arrangement of the ligands around Pt was assessed from ³¹P NMR spectra. Two signals with their satellites were observed at 15.05 ppm with $^1J_{Pt–P}$ = 2345 Hz, and at 16.94 ppm with $^1J_{Pt–P}$ = 2576 Hz, due to phosphines bonded to platinum in *cis* or *trans* configurations respectively, with an intensity ratio 1:1. The presence of two signals with different $^1J_{Pt–P}$ in the ³¹P NMR spectrum, together with the absence of Cl or acetylenic terminal groups, as ascertained from IR spectra, indicated that a partial isomerization reaction from *cis* to *trans* configurations around the Pt center occurred during the reaction,
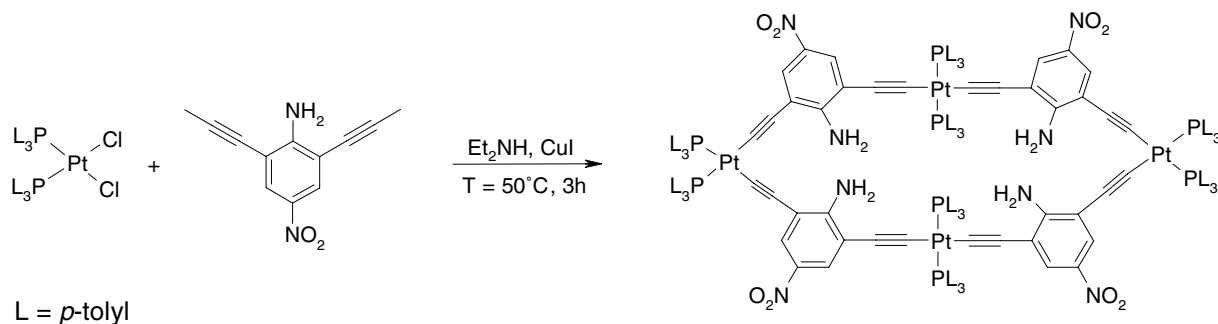


Scheme 1. Reaction pathway for the synthesis of [L₂Pt (DENA)]₄ complex.

leading to the closed-shape structure reported in Scheme 1. This assessment was confirmed by the comparison of $^{31}P$ NMR spectrum with that of the $[L_2Pt\text{-}DENA]_n$ polymer, which showed an overall *trans* structure around the Pt centers in the helicoidal chain and the $^{31}P$ NMR resonance with $^1J_{Pt-P} = 2610$ Hz [11b].

In the $^1H$ NMR spectrum (Fig. 1, Table 1) all the resonances expected for our complex appeared split into doublets due to the presence of both *cis* and *trans* configurations around Pt in $[L_2Pt\text{-}DENA]_4$.

The doublet signals at 1.80 and 2.21 ppm (integral ratio 1:1) were attributed to the proton resonance of the methyl in PTol₃ ligand for a *cis* and *trans* configuration, respectively, as assigned by comparison with the methyl resonance (s, 2.28 ppm) of the precursor *cis*-[Pt(PTol₃)₂Cl₂]. The proton resonances of the *p*-nitroaniline moiety (ArH₁ and ArH₂) look as a double doublet at 6.35 and 7.68 ppm, due to the anisotropic effect of the phenyls of –Pt(PTol₃)₂ moiety that was arranged in both *cis* and *trans* configurations in the molecular structure. The presence of *cis* and *trans* configurations around Pt(II) centers provoked also the splitting of the Hα and Hβ resonances of the phenyls in PTol₃ (double doublets at 6.83, 6.88 ppm for Hβ₁ and Hβ₂, and 7.19, 7.46 ppm for Hα₁ and Hα₂). The assign-

ment of proton resonances is reported in Table 1. The definitive attribution of which resonances among Hα and Hβ belonged to *cis* and which belonged to *trans* moiety was assessed by the ROESY spectrum, that will be hereafter discussed, and by considering the resonances of the tolyl group of the precursor *cis*-[Pt(PTol₃)₂Cl₂] assigned to Hα (q, 7.33 ppm) and Hβ (d, 6.92 ppm), –CH₃ (s, 2.28 ppm).

The NH₂ group of DENA moiety gave a broad signal at 4 ppm, whose assignment was attributed considering the exchange property of these hydrogens with H₂O (CDCl₃ impurity). All the reported assignments were supported by the ratios of the corresponding peak integrals (see Section 4).

More information on the molecular structure and dynamics of molecular moieties can be achieved by the study of the relaxation times ($T_1$). In fact, it is known that the experimental time $T_1$ is correlated to the mobility of molecular moieties. $T_1$ is strictly depending on correlation time ($\tau_C$) for molecular reorientation, an intrinsic dynamic parameter defining the motional state of the different groups within the molecule. Consequently, the knowledge of the correlation time is crucial in order to define the motional state of the different groups.

The correlation time values can be obtained from mono-selective and biselective relaxation times measurements [15], but can be also derived from the frequency dependence of $^1H$ $T_1$ [16]

$$\frac{T_1^{ns}(\omega_1)}{T_1^{ns}(\omega_2)} = \frac{5 + 8\omega_2^2\tau_C^2}{5 + 8\omega_1^2\tau_C^2} \cdot \frac{1 + 5\omega_1^2\tau_C^2 + 4\omega_1^4\tau_C^4}{1 + 5\omega_2^2\tau_C^2 + 4\omega_2^4\tau_C^4} \quad (1)$$

where $\omega_1$ and $\omega_2$ are the resonance frequencies, in our case 300 and 200 MHz respectively, and $T_1^{ns}$ are the non-selective spin lattice relaxation times. Hence, $\tau_C$ for any proton can be evaluated from the knowledge of the $T_1^{ns}$ values at two different frequencies. The observed $T_1^{ns}$ values at two different frequencies are listed in Table 1 together with the $\tau_C$ and the related chemical shifts. The calculated plot of $\tau_C$ vs the $T_1^{ns}(300)/T_1^{ns}(200)$ ratio is shown in Fig. 2.

Our results indicate that the methyl groups are more entangled than the phenyl to which they are bound, due to relatively strong interactions among close molecules. Moreover, the correlation times of the ArH₁ at 6.35 ppm show a higher mobility with respect to the ArH₂ at 7.68 ppm. thus supporting the hypothesis of intermolecular stacking. It is note worthy that the chemical shifts of $[L_2Pt\text{-}DENA]_4$ resonances do not change upon diluting the sample solution in the concentration range from $7.0 \times 10^{-5}$ M to $2.8 \times 10^{-3}$ M, thus indicating that, should stacking interactions occur, they can be considered fairly strong interactions.

Further insight into the intra and intermolecular correlations occurring in the tetranuclear complex can be achieved by 2D NOESY and ROESY $^1H$ NMR spectra recorded at different mixing times. ROESY experiment is of advantage for molecules of intermediate size; so, our molecule being an intermediate size system, its ROESY
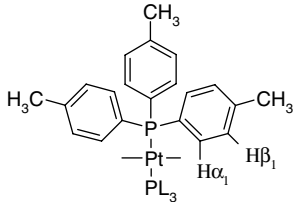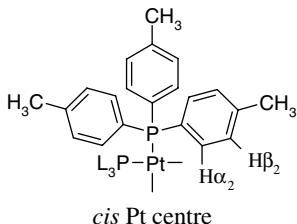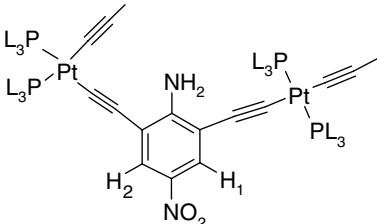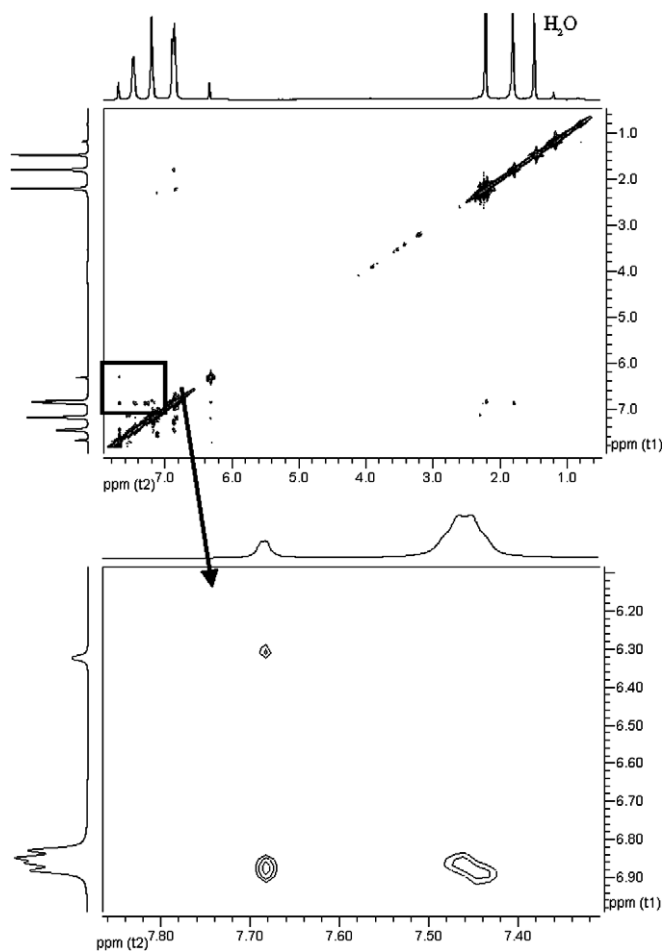


Fig. 1. ROESY NMR spectrum of [L₂Pt (DENA)]₄ in CDCl₃.

Table 1
Relaxation times and chemical shift values for [L$_2$Pt-DENA]$_4$

| Chemical structures of [L$_2$Pt-DENA]$_4$ moieties | | $\delta$ Chemical shift (ppm) | $T_1$ 300 MHz (s) | $T_1$ 200 MHz (s) | $\tau_c$ (s × 10$^{-11}$) |
|---|---|---|---|---|---|
| *trans* Pt centre | CH$_3$ | *trans* 2.20 (s) | 0.760 | 0.498 | 27.7 |
| | | *cis* 1.80 (s) | 0.714 | 0.406 | 43.2 |
| *cis* Pt centre | Tolyl | H$\beta_1$ 6.83 (d) | 0.633 | 0.547 | 11.8 |
| | | H$\beta_2$ 6.88 (d) | 0.520 | 0.441 | 12.8 |
| | Tolyl | H$\alpha_1$ 7.19 (d) | 0.497 | 0.407 | 14.3 |
| | | H$\alpha_2$ 7.46 (q) | 0.691 | 0.577 | 13.5 |
| | NH$_2$ | 4.00 (b) | – | – | – |
| | ArH | ArH$_1$ 6.35 (d) | 2.373 | 1.680 | 22.0 |
| | | ArH$_2$ 7.68 (d) | 1.609 | 0.843 | 59.7 |

s, singlet; d, doublet; b, broad; q, quartet L = *p*-tolyl.

spectrum is reported in Fig. 1 confirming NOESY data. The most intense contacts in ROESY spectrum appeared to be 2.21 (methyl of *cis* moiety) −6.83 (Hβ$_1$), 1.80 (methyl



Fig. 2. Relaxation time ratio at two different static magnetic fields vs correlation time $\tau_c$.

of *trans* moiety) −6.87 (Hβ$_2$). Other correlations were found between the two protons ArH$_1$ and ArH$_2$ (6.35–7.68 ppm) and between these and the protons of the tolyl ligand, i.e.: ArH$_1$ and Hβ$_1$ (6.35–6.83), ArH$_1$ and Hα$_1$ (6.35–7.19), ArH$_2$ and Hβ$_2$ (7.68–6.87), ArH$_2$ and Hα$_2$ (7.68–7.46). Moreover, correlations of Hβ$_1$ with Hα$_1$ (6.83–7.19) for *cis* and of Hβ$_2$ with Hα$_2$ (6.87–7.46) for *trans* configurations were found. It is known that Hα and Hβ *ortho* protons of phenyl rings are placed at a distance of 2.43 Å to then give rise to a strong dipolar contact. In our case, if $r_1 = 2.43$ Å is taken as a ruler for the *ortho* protons, the following relation can be applied,

$$V_1/V_2 = r_2^6/r_1^6 \qquad (2)$$

where $V_1$ and $V_2$ are the integral volumes determined from NOESY spectra concerning a given contact. In our study, $V_1$ was assumed equal to 1 for Hα and Hβ correlations (6.87–7.46 ppm); $V_2 = 0.015$ was experimentally determined from the spectrum for the correlation 6.35–7.68 (i.e. for ArH$_1$ and ArH$_2$). The value $r_2 = 4.9 \pm 0.5$ Å was obtained from Relation (2) and corresponded to the distance of intermolecular contacts. The value of $r_2$ indicated that a weak, but detectable contact occurred between the
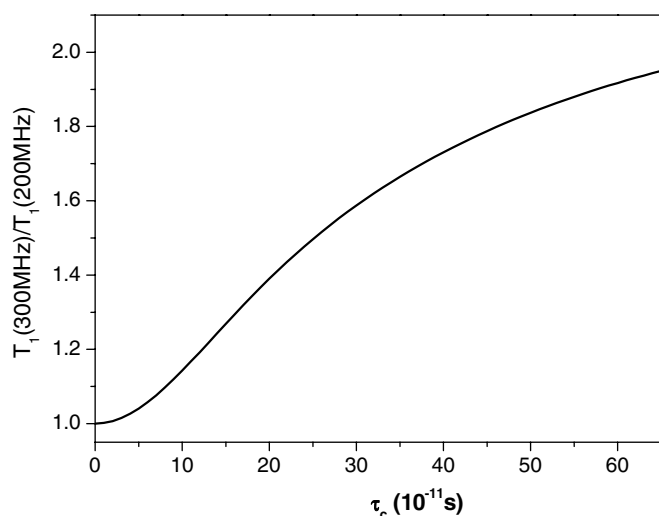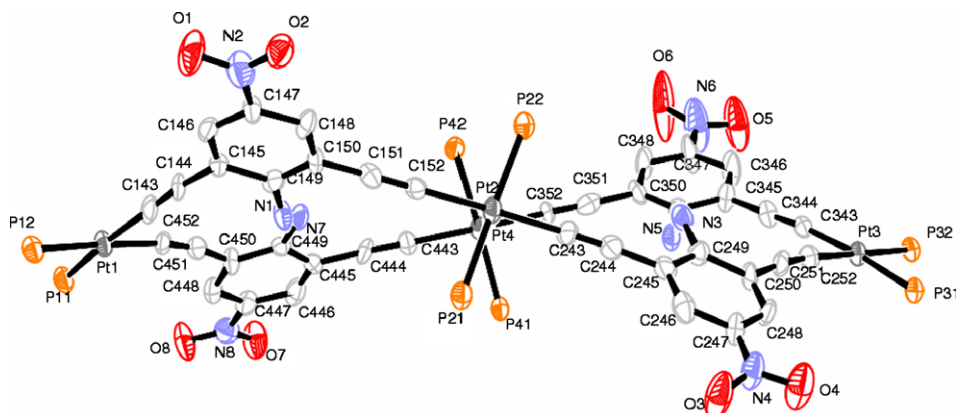
Fig. 3. ORTEP view of [L$_2$Pt-DENA]$_4$ structure showing the twisted cyclic structure. Tolyls of the ligands have been removed for clarity.

aryl groups of different molecules. The correlations due to intermolecular interactions through space were confirmed from the ROESY spectrum by using the same approach (Hα and Hβ distance as a ruler) and Relation (1), already applied to the NOESY spectrum. The methyl–Ar interaction gave support to intermolecular stacking between adjacent cycles.

The UV–VIS spectrum of [L$_2$Pt-DENA]$_4$ showed a red shift for the absorption maximum, found at 434 nm, with respect to the precursor organic spacer DENA ($\lambda_{max} = 355$, 382shnm), so that an enhanced electronic delocalization occurring through the Pt centers was assessed, probably involving an overlapping between the π orbitals of the conjugated spacer with the Pt 5d and 6p orbitals, according to the literature [17,18].

The X-ray crystal structure of the complex [L$_2$Pt-DENA]$_4$ is shown in Fig. 3 and crystal data, bond lengths and angles are summarized in Tables 2 and 3.

The molecule is non-planar, cyclic and contains four Pt atoms in square planar configuration, each one carrying two phosphines, bridged by four DENA molecules through C≡C–Pt bonds. Pt atoms with a *cis* geometry cause a sharp turn in the ring and are alternate with Pt centers showing *trans* configuration, which act as linear spacers. The overall shape appears as a twisted cycle, with a distortion from planarity, all the NH$_2$ substituents being oriented

inside the cage and all the NO$_2$ moieties pointing outside. In Fig. 4, it is possible to see the solvated crystal lattice.

The toluene solvent molecules are inserted only between the layers, leaving the cage free. A possible molecular recognition property of [L$_2$Pt-DENA]$_4$ can be envisaged for small molecules, since the open channels of the rather crowded structure would fit a guest of small diameter, suggesting a different behavior from that of triangular hexanu-

Table 3
Crystal data and selected refinement details

| | |
|---|---|
| Empirical formula | $C_{260.50}H_{244}N_8O_8P_8Pt_4$ |
| Formula weight | 4642.76 |
| Temperature (K) | 120(2) |
| Wavelength (Å) | 0.71073 |
| Crystal system | Triclinic |
| Space group | $P\bar{1}$ |
| Unit cell dimensions | |
| $a$ (Å) | 19.9834(3) |
| $b$ (Å) | 24.6245(4) |
| $c$ (Å) | 26.5756(5) |
| $\alpha$ (°) | 114.5350(10) |
| $\beta$ (°) | 97.9090(10) |
| $\gamma$ (°) | 104.1690(10) |
| Volume (Å$^3$) | 11102.2(3) |
| $Z$ | 2 |
| $D_{calcd}$ (Mg/m$^3$) | 1.389 |
| Absorption coefficient (mm$^{-1}$) | 2.631 |
| $F(000)$ | 4718 |
| Crystal | Block; yellow |
| Crystal size | $0.08 \times 0.06 \times 0.06$ mm$^3$ |
| $\theta$ Range for data collection (°) | 2.92–27.48 |
| Index ranges | $-25 \leqslant h \leqslant 25$, $-31 \leqslant k \leqslant 31$, $-34 \leqslant l \leqslant 33$ |
| Reflections collected | 92817 |
| Independent reflections [$R_{int}$] | 50115 [0.2099] |
| Completeness to $\theta = 27.48°$ | 98.5 % |
| Absorption correction | Semi-empirical from equivalents |
| Maximum and minimum transmission | 0.8581 and 0.8171 |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data/restraints/parameters | 50115/409/2122 |
| Goodness-of-fit on $F^2$ | 0.955 |
| Final $R$ indices [$F^2 > 2\sigma(F^2)$] | $R_1 = 0.0847$, $wR_2 = 0.1523$ |
| $R$ indices (all data) | $R_1 = 0.2559$, $wR_2 = 0.2057$ |
| Largest difference peak and hole | 1.613 and $-0.944$ e Å$^{-3}$ |

Table 2
Summary of main bond lengths and angles for the structure of [L$_2$Pt-DENA]$_4$

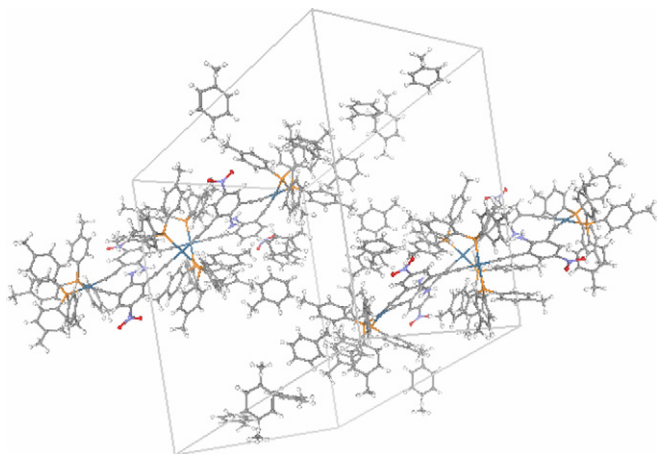| | Range | Average |
|---|---|---|
| Pt–C (*trans*) | 1.960(11)–1.991(11) | 1.980 |
| Pt–C (*cis*) | 1.962(12)–1.984(14) | 1.972 |
| Pt–P (*trans*) | 2.287(4)–2.298(4) | 2.292 |
| Pt–P (*cis*) | 2.290(3)–2.308(3) | 2.296 |
| C≡C | 1.174(14)–1.210(16) | 1.200 |
| P–Pt–P (*trans*) | 175.66(13)–177.94(12) | 176.8 |
| P–Pt–P (*cis*) | 97.30(12)–97.67(11) | 97.49 |
| C–Pt–C (*trans*) | 175.5(5)–175.7(5) | 175.6 |
| C–Pt–C (*cis*) | 86.8(5)–87.1(5) | 86.95 |

Fig. 4. Stereo view of solvated [L₂Pt-DENA]₄.

clear Pt cages, recently synthesized [19], which show a huge cavity of 1.4 nm. Congested cages may find also applications in asymmetric catalysis, such as those reported for dinuclear Pt centers bridging bis(alkynyl)-binaphthalene ligands [20].

Recently reported studies have investigated on the self-organization of self-assembled supramolecular cycles on Au (1 1 1) substrate, which is important for the development of functional nanostructures and devices [10]. Further studies on the synthesis and self organization of twisted shapes are in progress.

## 3. Conclusions

A dehydrohalogenation reaction was run under mild conditions affording the synthesis of a tetranuclear Pt complex, containing 2,6-diethynyl-4-nitroaniline, DENA, as the organic spacer between *cis* and *trans* Pt metal centers. The investigation of the molecular structure was performed by XRD analysis and 2D NMR ROESY and NOESY techniques. The complex was formed by a cyclic structure with the amine groups of the organic spacer directed inside the cage, the nitro groups outside and Pt centers with alternate *cis* and *trans* configurations. ROESY and NOESY spectra showed the correlations supporting the formation of intermolecular stacks in solution. The synthesis of molecular cycles similar to [L₂Pt-DENA]₄ remains under investigation, considering diethynylbiphenyl and 2,6-diethynyl-4-nitrophenol as the organic spacers, with the aim of tailoring the size of the cage and finding the role of the spacer on the deviation from planarity of the cyclic complexes.

## 4. Experimental details

### 4.1. Materials and methods

IR spectra were recorded with a Perkin–Elmer 1700 FTIR spectrophotometer in nujol mulls. Spectra in the 200–500 cm$^{-1}$ range were run on a Perkin–Elmer 1700X 200–500 cm$^{-1}$ interferometer. UV–VIS spectra were measured on a Cary 100 Bruker spectrophotometer in CHCl₃ solution. NMR spectra were collected with a Varian XL 300 spectrometer in CDCl₃. $^{1}$H and $^{13}$C spectra were calibrated with internal standards and $^{31}$P spectra with H₃PO₄ (85%) probe. ROESY and NOESY spectra were collected with a Bruker Avance at 400 MHz for $^{1}$H with a mixing time of 100 ms.

X-ray diffraction study: small crystals were grown from toluene/hexane and transferred to a goniometer head mounted on a Kappa CCD diffractometer, situated at a window of a Bruker–Nonius molybdenum rotating anode generator. Small crystals were grown from toluene/hexane, and initial handling showed them to be extremely solvent dependent. After much effort, a single specimen, $0.08 \times 0.06 \times 0.06$ mm in size, was successfully mounted on a "flagpole" fiber (glass wool fiber attached to the end of a normal-sized fiber in a brass pip), and transferred to a goniometer head mounted on a Kappa CCD diffractometer, situated at a window of a Bruker-Nonius molybdenum rotating anode generator. All aspects of the experiment were conducted with the crystal cooled to 120 K [21]. Unit cell parameters were determined via the Dirax [22] method, using data from phi–chi scans, and intensity data were obtained via phi and omega scans, with ranges computed to fill an asymmetric unit hemisphere, within the COLLECT software [23]. Data reduction used the DENZO [24] procedure, with absorption corrections via the SORTAV program [25]. The structure was solved by direct methods [26], giving the positions of the Pt and P atoms, along with some lighter atoms, and the rest of the structure slowly developed via the least-squares-difference map cycling using SHELX97 [27]. Where appropriate, non-hydrogen atoms were refined in the anisotropic approximation, and hydrogen atoms were included using the relevant AFIX riding models. Development of the structure showed a degree of solvation, with seven molecules of toluene in general positions and one molecule disordered over a centre of symmetry. Definition of the full crystal structure was hampered by the extensive disordering of the solvent molecules and some of the phenyl rings, but the structure of the complex molecule was reliably established. Because of the low precision of the structure, it is not really possible to discuss individual bond lengths.

Elemental analyses were performed at the "Laboratorio Servizio Microanalisi - Dipartimento di Chimica" University of Rome "La Sapienza". Solvents and materials were reagent grade (Carlo Erba) and were used without further purification. The precursor complex *cis*-[Pt(PTol₃)₂Cl₂] was prepared by reaction of K₂PtCl₄ and PTol₃ in 1:2 molar ratio in ethanol, with optimization of the reported literature methods [28]; the *cis* configuration was confirmed by the chemical shift value ($\delta = 12.93$ ppm) and $^{1}J_{Pt–P} = 3685$ Hz of $^{31}$P NMR spectrum recorded in CDCl₃. $^{1}$H NMR: (CDCl₃, $\delta$ ppm) 2.28 (s, 18H, CH₃), 6.92 (d, 12H, tolyl Hβ); 7.33 (d, 12H, tolyl Hα); 2,6-diethynyl-4-nitroaniline

(DENA) was prepared following an already reported pathway [11b].

## 4.2. Preparation of cis–trans–cis–trans tetra[μ-2,6-diethynyl-4-nitroaniline-bis(tri-para-tolylphosphine)platinum(II)], [L$_2$Pt-DENA]$_4$

0.250 g ($3 \times 10^{-4}$ mol) of *cis*-[Pt(PTol$_3$)$_2$Cl$_2$] were dissolved in 40 mL of Argon degassed diethylamine and 0.560 g ($3 \times 10^{-3}$ mol) of DENA and 3 mg of CuI as catalyst were added. The reaction was allowed to reach 50 °C and was stirred under argon atmosphere. Further details are reported in the Supporting Information. A yellow solid separated gradually and after 3 h, the crude solid was filtered off and thoroughly washed with ethanol. The product was purified by two subsequent chromatographies: the first one using florisil and toluene/CHCl$_3$ = 1/3 as eluant, while the second one was performed on SiO$_2$ and toluene as an eluant. Crystallization by toluene/hexane of the purified sample gave yellow needles (yield: 1.18 g; $3 \times 10^{-5}$ mol; 40%) that were analyzed by X-ray diffraction. Elemental analysis (%) on solvent free sample (calcd. for [C$_{52}$H$_{46}$N$_2$O$_2$P$_2$Pt]$_4$): C, 63.50 (63.22); H, 4.86 (4.69); N, 2.80 (2.84). IR (nujol mull, cm$^{-1}$) 3469, 3356 ($v$NH$_2$), 2105 ($v$C≡C), 1598 ($v$C=C aromatic), 1500 ($v$NO$_2$), 1098 (PTol$_3$), 514 (PTol$_3$). UV–Vis (CHCl$_3$, nm) $\lambda_{max}$ = 355.0, 382.0 (sh), 434.0. $^1$H NMR: (CDCl$_3$, $\delta$ ppm) 1.80 (s, 36H, CH$_3$ *cis*), 2.20 (s, 36H, CH$_3$ *trans*); 4.00 (b, 8H, NH$_2$); 6.83 (d, 24H, Hβ$_1$); 6.88 (d, 24H, Hβ$_2$); 7.19 (d, 24H, Hα$_1$); 7.46 (q, 24H, Hα$_2$); 6.35 (d, 4H, ArH$_1$); 7.68 (d, 4H, ArH$_2$).$^{13}$C NMR (CDCl$_3$, $\delta$ ppm): 20.9, 21.3 (CH$_3$), 101.1, 106.8, 110.3, 111.5 (–C≡C–), 125.7, 128.5, 136.1, 153.5 (C$_6$H$_2$NO$_2$NH$_2$), 128.0, 128.4, 128.8, 134.6, 140.4, 140.6 (PC$_6$H$_4$Me). $^{31}$P NMR: (CDCl$_3$, $\delta$ ppm) 15.05 ($^1J_{Pt–P}$ = 2345 Hz), 16.94 ($^1J_{Pt–P}$ = 2576 Hz).

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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.jorganchem.2006.09.059.

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