

New self-assembled dinuclear Pd(II) and Pt(II) metallomacrocycles of a 4,4'-bipyridin-1-ium ligand with an inner cavity

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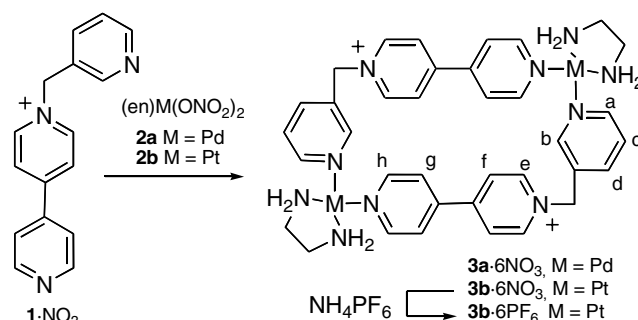
Abstract—New dinuclear Pd(II) and Pt(II) metalocycles of 1-(pyridin-4-ylmethyl)-4,4'-bipyridin-1-ium ligand with an inner cavity were prepared and its inclusion complexes in solution studied. The cavity of macrocycle **6b** presents a nearly optimal size to form supramolecular complexes through π -stacking interactions with electron-rich aromatic units. On the contrary, the distance between the two pseudoparallel bipyridinium units in **3b** is too short to allow the insertion of aromatic guests. © 2006 Elsevier Ltd. All rights reserved.

Metal-coordination-directed self-assembly of well-defined 2D and 3D molecular assemblies is a growing area at the forefront of supramolecular chemistry.¹ In this context, metallomacrocycles such as molecular triangles, squares, pentagons, and hexagons have been synthesized in the last few years.² However, rectangular molecular structures have remained relatively rare.³ In addition to the remarkable self-assembly formation reactions and the unusual structures, metalocyclophanes have attracted attention due to their potential for the molecular recognition of substrates.⁴

Here, we describe the formation of a new class of rectangular-shaped metallomacrocycles using 4,4'-bipyridine based ligands and Pd and Pt complexes.

The ligands **1**·NO₃ and **4**·NO₃ used in this work were prepared by reaction of 4,4'-bipyridine with the corresponding bromomethylpyridine. After counterion exchange, the pyridine ligands were obtained in 44% and 48% yield, respectively.

The metallomacrocycles **3a,b** were prepared from 3-pyridine ligand **1**·NO₃ and **2a,b** (Scheme 1). The addition of 1 equiv of (en)Pd(NO₃)₂ to a solution of **1**·NO₃ in D₂O



Scheme 1.

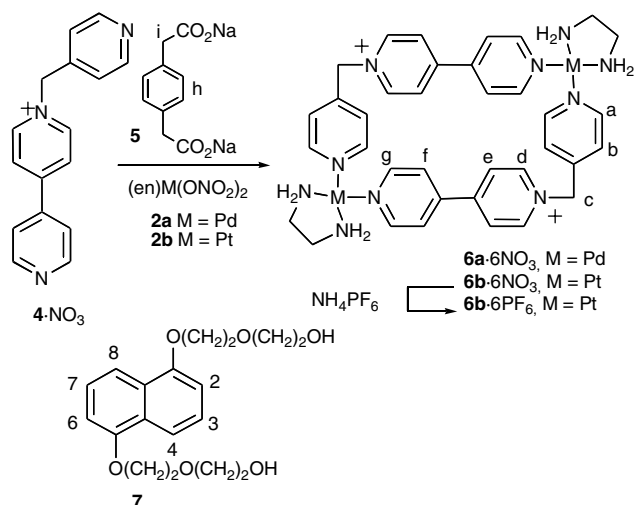
at room temperature resulted in the formation of **3a**·6NO₃ as the only product. Self-assembly proceeded instantaneously and in a wide range of concentrations (0.5–20 mM). The ¹H NMR spectrum of **3a**·6NO₃ shows that the H_{a–d} signals have shifted downfield from those of the free ligand ($\Delta\delta = 0.31, 0.08, 0.18, 0.32$ ppm, respectively), as expected for coordination of the pyridyl nitrogen atom to the metal center.⁵ Similarly, signals of C_{a,b,h} have shifted downfield ($\Delta\delta = 3.48, 3.40, 3.08$ ppm, respectively) in the ¹³C NMR spectrum. The diffusion coefficients obtained from DOSY⁶ (diffusion-ordered NMR spectroscopy) NMR experiments of **1**·NO₃, **2a** and **3a**·6NO₃ show that the metalocycle is significantly larger than its components. The structure of **3a**·6NO₃ was also confirmed by MS (ESI), which shows a peak at $m/z = 540$ (M–2NO₃+2CH₃OH)⁺².

Keywords: Metallomacrocycles; Host–guest chemistry; Bipyridinium.

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In contrast to this, platinum macrocycle **3b**·6NO₃ could not be prepared at room temperature. The addition of 1 equiv of (en)Pt(NO₃)₂ to a solution of **1**·NO₃ (10 mM) in D₂O at room temperature afforded a complex mixture of kinetic products. However, when the temperature was raised to 100 °C for 7 days no peaks other than those of **3b**·6NO₃ could be observed in the ¹H NMR spectrum.⁷ Under these conditions, Pt(II)–pyridine coordinate bond becomes labile and the equilibrated structure of macrocycle **3b**·6NO₃ is formed.⁸ The macrocycle could be isolated as its hexafluorophosphate salt (**3b**·6PF₆) by adding an excess of NH₄PF₆ to a water solution of **3b**·6NO₃. Again, the H_{a–d} and C_{a,b,h} signals have shifted downfield from those of the free ligand in the ¹H NMR and ¹³C NMR spectra, respectively. The formation of **3b**·6PF₆ was also supported by MS (ESI). Mass spectrum clearly shows a peak at *m/z* = 647 (M–4PF₆–2H)²⁺. Moreover, the observed isotopic distribution of this peak is in accordance with the theoretical one based on the dinuclear metallocycle **3b**·6PF₆.

Addition of 1 equiv of palladium complex (**2a**) to a solution of bipyridinium ligand **4**·NO₃ (10 mM) in D₂O at room temperature resulted in the formation of a major product (**6a**·6NO₃) and other minor components (Scheme 2). The composition of this mixture remained unchanged in the 0.5–20 mM range. The ¹H NMR spectrum shows the characteristic downfield shiftings expected for coordination of the pyridyl nitrogen atoms to the Pd atom (Fig. 1a and b). Moreover, MS (ESI) confirmed the structure of **6a**·6NO₃, showing a peak at *m/z* = 540 [M–2NO₃+2CH₃OH]²⁺. Minor components disappeared when disodium *p*-phenyldiacetic dicarboxylate (**5**) (1 equiv) was added to a solution of **6a**·6NO₃ (10 mM). Then, only one compound was detected in the ¹H NMR spectrum (Fig. 1b,c), which shows the upfield shift of the signal for the aromatic protons of the guest (H_h, Δδ = 1.31 ppm) as a result of the C–H–π interaction with the pyridine ring in the short side of the rectangle. The protons of this pyridine ring are



Scheme 2.

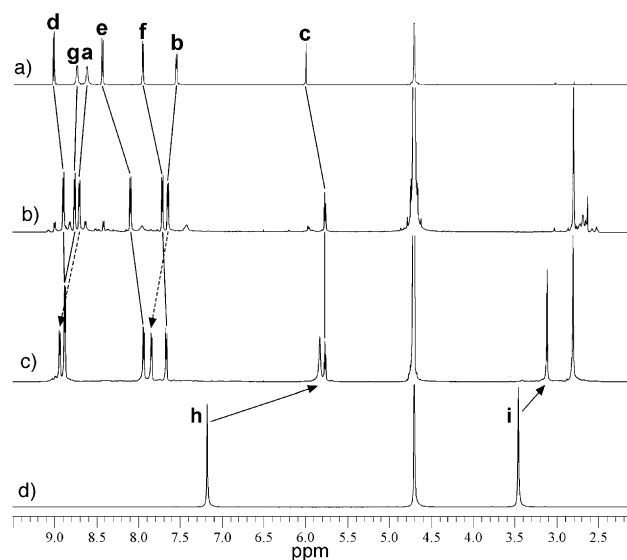


Figure 1. Partial ¹H NMR (300 MHz, D₂O, 298 K) spectra of (a) **4**·NO₃, (b) **4**·NO₃ (10 mM) + **2a** (10 mM), (c) **4**·NO₃ (10 mM) + **2a** (10 mM) + **5** (10 mM), (d) **5**.

downfield shifted (H_{a,b} dotted arrows in Fig. 1) indicating the insertion of **5** into **6a**·6NO₃.

As in the case of macrocycle **3b**·6NO₃, platinum complex **6b**·6NO₃ could not be obtained at room temperature. The addition of 1 equiv of (en)Pt(NO₃)₂ to a solution of **4**·NO₃ (10 mM) in D₂O at room temperature gave a complex mixture of kinetic products. When the temperature was raised to 100 °C for 7 days a major compound (**6b**·6NO₃) and other minor components could be observed in the ¹H NMR spectrum. Longer reaction times (14 d) and dilution (10–2 mM) did not affect the composition of the mixture. However, the addition of 1 equiv of sodium *p*-phenyldiacetic dicarboxylate (**5**) caused dramatic changes in the ¹H NMR spectrum. The upfield shift of the signals of **5** (Δδ = 1.33 and Δδ = 0.30 ppm for H_h and H_i, respectively) and the downfield shifted signals of H_{a,b} strongly suggest that **5** is inserted into the cavity of metallomacrocycle. The template effect of **5** has allowed the isolation on a preparative scale of pure empty⁹ macrocycle **6b**·6PF₆ as its hexafluorophosphate salt. The ¹H and ¹³C NMR spectra of **6b**·6PF₆, together with its MS (ESI) spectrum provide good evidence for the formation of the macrocycle.

When two molecules of ligand **1**·NO₃ and two metal ions are assembled to form the dinuclear metallocycles, two different stereoisomers, *syn* and *anti*, can be envisaged as a result of the relative orientation of the 3-pyridine planes. Metallocycles **3a,b** can exist as two stereoisomers, the chiral C₂ (*syn*) stereoisomer, and the achiral C_s (*anti*) stereoisomer. Of the two possible stereoisomers (*syn* and *anti*), only one has been experimentally observed. The ¹H NMR spectra of **3a,b** showed one species and remained unchanged in a wide concentration range (0.25–10 mM in D₂O), suggesting that no aggregation or significant structural variation occur. Unfortunately, no single crystals of **3a,b** suitable for X-ray crystallographic analysis could be obtained.

The **3b** and **6b** systems were characterized by means of DFT calculations (B3LYP model).¹⁰ In these calculations the 6-31G(d) basis set was used for the ligand atoms, while for Pt atoms the effective core potential of Wadt and Hay (Los Alamos ECP) included in the LanL2DZ basis set was applied.¹¹ The calculated geometries are shown in Figure 3 (see also Supporting Information). For **3b** we have modeled the two possible stereoisomers possessing C_2 (*syn*) and C_s (*anti*) symmetries. The metal centers show a square planar geometry, in which bond distances and angles are in the usual range.¹² From the conformational energies of the *syn* and *anti* isomers of **3b** we have calculated an in vacuo relative free energy, $\Delta G_{298K}^{\circ} = G_{anti}^{\circ} - G_{syn}^{\circ}$, of $-0.14 \text{ kcal mol}^{-1}$. Likewise, from the results obtained in aqueous solution (COSMORS model)¹³ we have obtained a relative free energy, $\Delta G^{\text{sol}} = G_{anti}^{\text{sol}} - G_{syn}^{\text{sol}}$, of $-1.37 \text{ kcal mol}^{-1}$. Thus, our quantum mechanical calculations predict the *anti* isomer being the most stable one both in vacuo and in solution. Figure 2 shows distances between non-bonded atoms of the metallomacrocycles that give an estimate of the size of the macrocyclic cavity. Our results show that **6b** presents a larger macro-

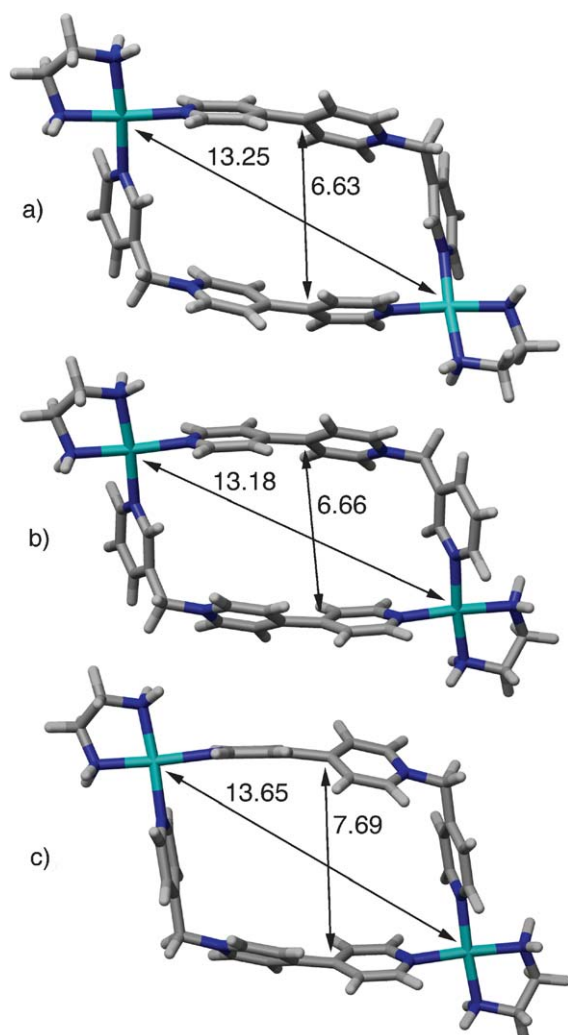


Figure 2. Calculated structures with selected distances (Å) of (a) **3b** (*syn*), (b) **3b** (*anti*) and (c) **6b**.

cyclic cavity than both the *syn* and *anti* stereoisomers of **3b**. The distance between the two pseudoparallel bipyridinium units in **6b** amounts to 7.1–7.7 Å, which is approximately twice the optimal π -stacking distance.¹⁴ Thus, the macrocyclic cavity of **6b** presents a nearly optimal size to form supramolecular complexes through π -stacking interactions with electron-rich aromatic units. However, the distance between the two pseudoparallel bipyridinium units in **3b** is too short to allow the formation of supramolecular complexes through π -stacking interactions, in agreement with the experimental data.

Indeed, the interaction of **6a,b** with diol **7** (Scheme 2) forms a [2]pseudorotaxane in a reversible self-assembly process but no interaction was detected between **3a,b** and **5** or **7**. The addition of 1 equiv of **7** to a 5 mM solution of **6b**·6PF₆ in CD₃NO₂ produced very broad resonances in the ¹H NMR spectrum recorded at 298 K, however they became sharp on cooling the sample down to 250 K. The H-4 and H-8 protons of the 1,5-dioxynaphthalene ring system resonate at very high field ($\delta = 3.12 \text{ ppm}$) as a result of C–H– π interaction with pyridine ring in the short side of the rectangle.¹⁵ The protons of this pyridine rings are high field shifted (dotted arrows in Fig. 3). Twelve doublets can be observed for the α - and β -pyridine protons as a consequence of the imposed C_7 -symmetry by the host and the restricted rotation around platinum–pyridine and pyridine–CH₂ bonds. These facts point out that the dioxynaphthalene system is located inside the metallomacrocyclic system. The association constant of complex **7** \subset **6b**·6PF₆, determined in CH₃NO₂ by UV–vis spectroscopy¹⁷ and following the charge-transfer band at $\lambda = 470 \text{ nm}$, was $1180 \pm 30 \text{ M}^{-1}$.

In conclusion, we described the synthesis of new dinuclear Pd and Pt metallomacrocycles (**3a,b** and **6a,b**). Compounds **6a,b** present an inner cavity suitable for the insertion of aromatic guests and open the way to prepare new catenanes and rotaxanes.

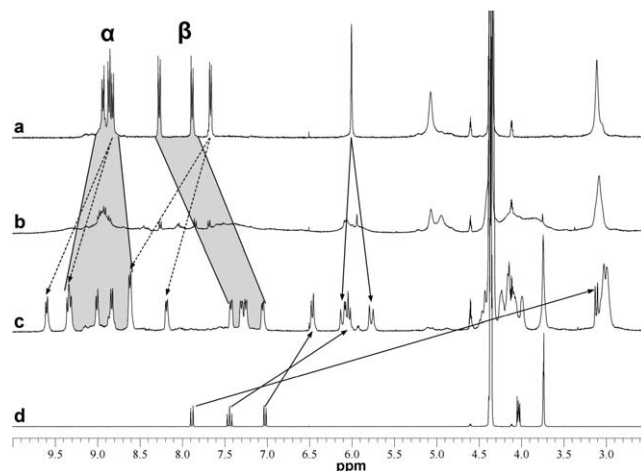


Figure 3. ¹H NMR (300 MHz, CD₃NO₂) of (a) **6b**·6PF₆, (b) 5.0 mM **6b**·6PF₆ + 5.0 mM **7b**, 298 K, (c) 5 mM **6b**·6PF₆ + 5 mM **7b**, 250 K, (d) **7b**.

Acknowledgements

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Supplementary data

Supplementary data (experimental details and characterization, NMR and MS spectra of compounds **1**, **4**, **3a,b** and **6a,b**) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2006.02.146.

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