

Construction of 18-membered monometallic macrocycles by a *trans*-spanning ligand



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ABSTRACT

The metallomacrocycles **4** and **5** have been constructed by self-assembling between Pd^{II} or Pt^{II} with the polydentated ligand 1,3-bis((2-((pyridin-2-ylmethyl)thio)phenyl)thio)propane (**3**) and their structures were determined by IR, NMR spectroscopy, HR-MS mass spectrometry and by single-crystal X-ray diffraction analysis. The molecular structures of **4** and **5** reveal the formation of discrete 18-membered monometallic macrocycles generated by the assembly of one ligand and one metal atom. In this process ligand **3** acts in a *trans*-spanning mode via the nitrogen atoms of the pyridine rings. In a DMSO-*d*₆ solution the metallomacrocycles **4** and **5** experiment a disassembly process.

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1. Introduction

Over the last years, the rational design, synthesis and construction of exotic molecules such as triangles, squares and rectangles, helicates, knots, catenanes, capsules and molecular containers have received a significant amount of attention due to their great variety of structural and potential applications in different fields such as separation catalysis, sensors, molecular electronics, ion transport, molecular recognition and drug delivery [1–6]. Construction of homo- and heterometallomacrocycles has been achieved by self-assembly between a ligand which may contain single- or multiple donor atoms (O, S, P and N atoms) and be either rigid or flexible and a transition-metal which functions as an acceptor [7–21]. Today, a great number of synthetic strategies based on self-assembly reactions are employed to synthesize metallomacrocycles; in all of them the influence of steric and electronic factors of the ligand that control different properties such as macrocycle size, macrocycle cavities and reactivity at the metal center on the self-assembly process have to be taken into account [11,22–27]. Thus, polyfunctional ligands that contain *ortho*-, *meta*- or *para*-pyridyl substituted rings in their structure have been widely employed to construct a great variety of metallomacrocycles based on self-assembly processes due to their ability

to act as *trans*-spanning or *cis*-chelating ligands through non-covalent metal-nitrogen interactions [8,28–41].

Herein, we describe the construction of novel 18-membered monometallic macrocycles with palladium (II) or platinum (II) as metal centers. Metallomacrocycles **4** and **5** were obtained by self-assembly between 1,3-bis((2-((2-pyridinylthio)methyl)phenyl)thio)propane (**3**) with PdCl₂ and PtCl₂, respectively. In this process the ligand favors a *trans*-spanning mode because the nitrogen atoms of the pyridine rings orient themselves towards the metal center. Metallomacrocycles **4** and **5** had been characterizing by IR, HR-MS spectrometry, X-ray analysis and their behavior in DMSO-*d*₆ solutions has been investigated by ¹H NMR spectroscopy.

2. Experimental

2.1. Materials and instrumentation

All chemicals used are commercially available and were used without further purification. Melting points were measured in a Mel-Temp II instrument and are uncorrected. Elemental analyses of the compounds were determined on a Perkin-Elmer Series II CHNS/O Analyzer. IR spectra (Perkin-Elmer 2000 FTIR) were recorded (4000–400 cm⁻¹ range) as KBr pellets. Raman spectra were obtained in a Perkin-Elmer Spectrum GX NIR FT-RAMAN spectrometer and were measured in the solid state (3600–100 cm⁻¹ range) with 10–280 mW laser power having 4.0 cm⁻¹ resolution; under these conditions metallomacrocycles **4** and **5** were

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Table 1
Details of crystal data and structure refinement parameters for **4** and **5**.

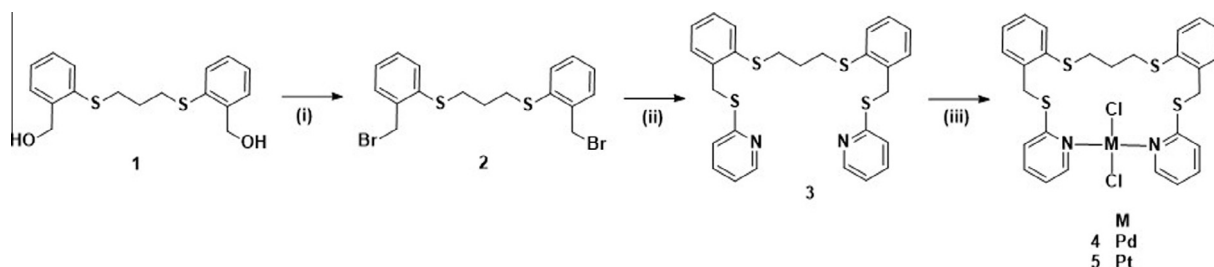
Metallomacrocyclic	4	5
Empirical formula	C ₅₆ H ₅₅ N ₅ S ₈ C ₁₄ Pd ₂	C ₅₆ H ₅₅ N ₅ S ₈ Cl ₄ Pt ₂
Mr	1409.13	1586.51
T (K)	293(2)	293(2)
Wavelength (Å)	1.54184	1.54184
Crystal size (mm)	0.23 × 0.07 × 0.03	0.64 × 0.24 × 0.14
Crystal system	monoclinic	monoclinic
Space group	C2/m	C2/m
a (Å)	15.5753(8)	16.0747(2)
b (Å)	16.8796(6)	17.1321(3)
c (Å)	11.7473(5)	11.63808(15)
α (°)	90	90
β (°)	105.382(5)	102.9518(14)
γ (°)	90	90
V (Å ³)	2977.8(2)	3123.51(8)
Z	2	2
ρ _{calc} (mg/mm ⁻³)	1.572	1.687
μ (mm ⁻¹)	9.474	12.643
F (000)	1428.0	1556.0
2θ range for data collection (°)	7.806–134.03	7.646–148.956
Index ranges	–18 ≤ h ≤ 18, –20 ≤ k ≤ 19, –14 ≤ l ≤ 14	–20 ≤ h ≤ 20, –21 ≤ k ≤ 20, –14 ≤ l ≤ 14
Absorption correction	analytical	analytical
Reflections collected	9804	27772
Unique reflections, R _{int}	2762, 0.0380	3309, 0.0635
Data/restraints/parameters	2762/358/293	3309/362/293
Goodness-of-fit (GOF) on F ²	1.049	1.105
R ₁ , wR ₂ [I ≥ 2σ(I)]	0.0554, 0.1539	0.0366, 0.0999
R ₁ , wR ₂ [all data]	0.0678, 0.1687	0.0387, 0.1026
Largest difference in peak/hole [e Å ⁻³]	1.10/–0.9	1.81/–0.79

photosensitive and underwent photodecomposition. Mass spectrometric measurements were recorded on a HR-LC 1100/MSD TOF Agilent Technology in positive-ion mode by direct insertion and simulations were performed with IsoPro 3.1 Software [42]. A Varian Inova 400 NMR spectrometer was used to record ¹H NMR and ¹³C{¹H} NMR spectra at 20 °C, in CDCl₃ or, where necessary, in DMSO-*d*₆; ¹H, 399.78 MHz and residual protio-solvent signal was utilized as reference. PdCl₂ and PtCl₂, HBr, 2-mercaptopyridine and Cs₂CO₃, were obtained from Sigma–Aldrich and were used as received, 1,3-bis-(2-hydroxymethylphenylthio)propane (**1**) was prepared as previously described [43].

2.2. Synthesis of compound **2** and ligand **3**

2.2.1. Synthesis of 1,3-bis((2-(bromomethyl)phenyl)thio)propane (**2**)

1,3-Bis-(2-hydroxymethylphenylthio)propane (15.6 mmol, 5 g) was dissolved in 50 mL of toluene and hydrobromic acid, 48% (50 mL) was added; the mixture was refluxed for 5 days. The two phases were then separated and the organic phase was dried with



Scheme 1. Synthetic route established for preparation of ligand **3** and metallomacrocycles **4** and **5**. (i) HBr, toluene, reflux, 5 days; (ii) 2-mercaptopyridine, Cs₂CO₃, toluene, reflux, 16 h; (iii) PdCl₂ or PtCl₂, acetonitrile, reflux, 16 h.

NaSO₄ then filtered through a bed of Celite. The solvent was removed under reduced pressure to give a white solid. Yield: 6.50 g (93%). m.p. = 70 °C. C₁₇H₁₈Br₂S₂ (446.26): Calc. C, 45.76; H, 4.07. Found: C, 45.44; H, 3.99%. ¹H NMR (CDCl₃): δ = 7.38 (2H, dd, ³J = 7.50 Hz, ⁴J = 1.70 Hz, H1), 7.36 (2H, dd, ³J = 7.50 Hz, ⁴J = 1.70 Hz, H4), 7.25 (2H, ddd, ³J = 7.50 Hz, ⁴J = 1.70 Hz, H3), 7.19 (2H, ddd, ³J = 7.50 Hz, ⁴J = 1.70 Hz, H2), 4.68 (4H, s, H7), 3.12 (4H, t, ³J = 7.00 Hz, H8), 2.00 (2H, q, ³J = 7.00 Hz, H9) ppm. ¹³C NMR (CDCl₃): δ 137.9 (C6), 136.2 (C5), 130.9 (C4), 130.4 (C1), 129.4 (C2), 126.9 (C3), 32.9 (C8), 32.2 (C7), 28.2 (C9) ppm. IR (KBr): 3058, 2960, 2922, 2851, 1588, 1567, 1467, 1442, 1218, 1199, 1064, 1040, 819, 756, 730, 682, 605, 596, 495, 446 cm⁻¹.

2.2.2. Synthesis of 1,3-bis((2-((2-pyridinylthio)methyl)phenyl)thio)propane (**3**)

1,3-Bis((2-(bromomethyl)phenyl)thio)propane (11.20 mmol, 5.0 g) and 2-mercaptopyridine (22.40 mmol, 2.50 g) were dissolved in 50 mL toluene, and then Cs₂CO₃ (11.20 mmol, 3.65 g) was added directly into the solution; the mixture was then refluxed for 16 h. After cooling, the resulting suspension was then filtered through Celite. The solvent was removed under reduced pressure to give a yellow oil. Yield 5.10 g (90%). C₂₇H₂₆N₂S₂ (506.76): Calc. C, 63.99; H, 5.17. Found: C, 63.20; H, 5.05%. ¹H NMR (DMSO-*d*₆): δ = 8.46 (2H, ddd, ³J = 4.90 Hz, ⁴J = 1.85 Hz, ⁵J = 0.95 Hz, H14), 7.61 (2H, ddd, ³J = 8.10 Hz, ⁴J = 1.74 Hz, ⁵J = 0.90 Hz, H11), 7.43 (2H, dd, ³J = 7.56 Hz, ⁴J = 1.48 Hz, H1), 7.36 (2H, dd, ³J = 7.84 Hz, ⁴J = 1.10 Hz, H4), 7.25 (2H, ddd, ³J = 8.10 Hz, ⁴J = 1.74 Hz, ⁵J = 0.90 Hz, H10), 7.20 (2H, ddd, ³J = 7.61 Hz, ⁴J = 1.57 Hz, H3), 7.12 (2H, ddd, ³J = 7.38 Hz, ⁴J = 1.27 Hz, H2), 7.10 (2H, ddd, ³J = 3.68 Hz, ⁴J = 1.02 Hz, H13), 4.50 (4H, s, H7), 3.11 (4H, t, ³J = 7.13 Hz, H8), 1.84 (2H, q, ³J = 7.13 Hz, H9) ppm. ¹³C NMR (DMSO-*d*₆): δ = 157.9 (C10), 149.4 (C14), 136.8 (C), 136.7 (C12), 135.5 (C6), 130.2 (C1), 128.7 (C4), 128.1 (C3), 125.9 (C2), 121.7 (C11), 120.0 (C13), 31.9 (C7), 31.4 (C8), 27.9 (C9). IR (KBr): 3055, 2993, 2953, 2924, 2848, 1578, 1467, 1450, 1411, 1279, 1246, 1144, 1125, 1062, 1046, 980, 756, 736, 720, 615, 575, 476 cm⁻¹.

2.3. Synthesis of the metallomacrocycles **4** and **5**

Metallomacrocycles **4** and **5** were synthesized according to the following general method: A mixture of the corresponding metal dichloride in 50 mL of hot acetonitrile was refluxed until the metal salt was dissolved, then the reaction mixture was allowed to cool to room temperature and ligand **3** was added. The mixture was refluxed for 16 h. At the end, the suspension was filtered whilst hot. Finally, the solid filtered was washed with one portion of 20 mL of cold acetonitrile.

2.3.1. Synthesis of the metallomacrocyclic **4**

Compound **4** was prepared from PdCl₂ (1.13 mmol, 200 mg) and 1,3-bis((2-((2-pyridinylthio)methyl)phenyl)thio)propane (**3**) (1.13 mmol, 570 mg), according to the procedure described above

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