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A chiral [2]catenane self-assembled from *meso*-macrocycles of palladium(II)

Tara J. Burchell,[a] Dana J. Eisler[b] and Richard J. Puddephatt*[a]

[a] *Department of Chemistry, The University of Western Ontario, London, ON N6A 5B7, Canada. E-mail: pudd@uwo.ca; Fax: + (519) 661 3022*

[b] *Department of Chemistry, University of Calgary, Calgary, AB T2N 1N4, Canada*

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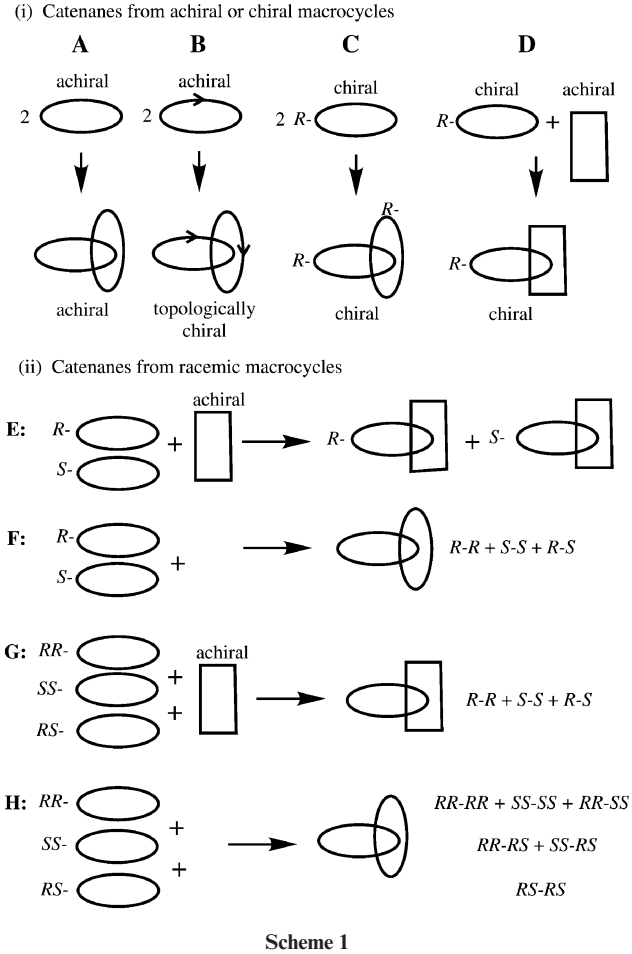
Reaction of *trans*-$[PdX_2(SMe_2)_2]$ (X = Cl or Br) with the chiral ligand LL = 1,1′-binaphthyl-2,2′-(NHC(= O)-3-$C_5H_4N)_2$ gave the [2]catenane complexes *trans*-$[\{(PdX_2)_2(\mu\text{-LL})_2\}_2]$, which are formed by self-assembly from 4 units each of *trans*-PdX_2 and LL. The catenation is favored by the formation of multiple hydrogen bonds between the constituent macrocycles (4 × NH · · · ClPd, 2 × NH · · · O=C). If the ligand LL is racemic, each macrocycle *trans*-$[(PdX_2)_2(\mu\text{-LL})_2]$ is formed in the meso form *trans*-$[(PdX_2)_2(\mu\text{-}R\text{–LL})(\mu\text{-}S\text{–LL})]$ but the resulting [2]catenane is chiral as a direct result of the catenation step. This is the first time that this form of chiral [2]catenane has been observed. The enantiomers of the [2]catenane further self-assemble in the crystalline form, through secondary intermolecular Pd · · · X bonding, to form a racemic infinite supramolecular polymer of [2]catenanes.

Introduction

There is great current interest in the synthesis and properties of catenanes, as promising components of functional molecular materials.[1,2] Many elegant strategies for synthesizing catenanes have been developed, ranging from purely statistical, to directed self-assembly and metal templating strategies.[3,4] The simplest approach to [2]catenane formation is the self-assembly from molecular rings, aided by favorable secondary bonding interactions between the two rings.[5,6] For example, Fujita and coworkers have used the fragment *cis*-$[Pd(H_2NCH_2CH_2NH_2)]^{2+}$ along with bridging bis(pyridine) ligands to form a host of macrocycles, which may self-assemble to give catenanes through favorable secondary interactions between aromatic groups.[5] The equilibration between macrocycles and [2]catenane is made possible by the lability of palladium(II) towards ligand substitution reactions.[5]

Catenanes can exhibit interesting and unusual forms of chirality, as illustrated in Scheme 1.[7,8] When individual macrocycles are achiral, the resulting [2]catenanes may also be achiral[3–6] but, if there is a directionality associated with the rings, they can be topologically chiral [Scheme 1, **A** and **B**].[7] For example, Sauvage and Vögtle reported chiral [2]catenanes of type **B** based on the directional macrocycles **I** and **J** (Scheme 2).[7c–e,h] Enantiomerically pure macrocycles always yield chiral catenanes [Scheme 1, **C** and **D**], and several examples are now known.[8] For example, the Sauvage group reported recently [2]catenanes containing a chiral binaphthol unit in each macrocycle **K** (Scheme 2).[8a] The formation of [2]catenanes from macrocycles derived from a racemic mixture of chiral precursors is illustrated in Scheme 1(ii). If a macrocycle contains a single chiral centre and combines with a non-chiral macrocycle, a racemic mixture of *R* and *S* [2]catenanes is formed [Scheme 1, **E**]. Stoddart and coworkers have prepared catenanes of type **E** (Scheme 1) from a racemic mixture of axially chiral binaphthyl-substituted crown ethers and non-chiral macrocycles.[8b,c] If two enantiomeric rings, each containing a single chiral centre, self-assemble, then the resulting [2]catenane may be either chiral (*RR*, *SS*) or achiral (*RS*) [Scheme 1, **F**]. The Stoddart group has reported catenanes of type **F**, but by combination of unlike rings such that four diastereomers were obtained (*RR*′, *SS*′, *RS*′, *SR*′).[8]

If each macrocycle is self-assembled from a racemic (*R*,*S*) precursor and contains *two* chiral units, then it can be either chiral (*RR*, *SS*) or achiral (*meso*, *RS*), and a still more complex mixture of [2]catenanes is possible, as illustrated in Scheme 1, **G**



Scheme 1

and **H**. Combination of pairs of chiral macrocycles can give the [2]catenanes described as *RR*–*RR*, *SS*–*SS*, and *RR*–*SS*, while similar combination of pairs of achiral macrocycles will give the [2]catenane *RS*–*RS*, and combination of chiral and achiral macrocycles can give the [2]catenanes *RR*–*RS* and *SS*–*RS* (Scheme 1, **H**). There may be the additional complication of chirality arising from the catenation step itself, as described below. There appear to be no reported examples of catenation of type **H** (Scheme 1) from like macrocycles.[8] Stoddart[8d] has used

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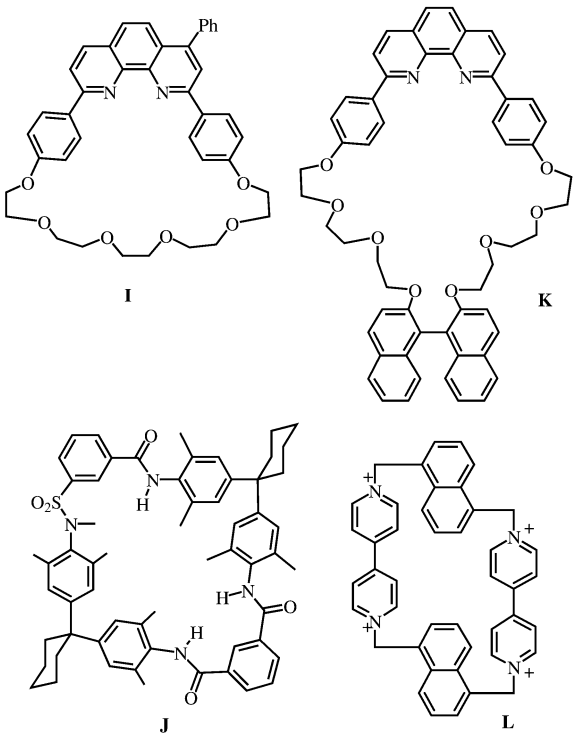


Scheme 2

the electron poor ring complex **L** (Scheme 2), as a mixture of racemic and *meso* isomers, to form [2]catenanes with electron rich macrocyclic polyethers as illustrated in Scheme 1, **G** and found that catenation was favoured for the racemic (*RR*, *SS*) isomer over the *meso* (*RS*) isomer, but it is not possible to form [2]catenanes from like rings in this system.

This article reports the first compounds to be formed by a catenation process of type **H** (Scheme 1), involving catenation of identical *meso* macrocycles. The self-assembly relies on dynamic coordination chemistry at palladium(II), using ligands with hydrogen bonding functionality incorporated to favour catenation of the self-assembled macrocycles. The self-assembly from racemic (*R*,*S*) ligand proves to be highly stereoselective in the system studied, and gives only the *RS*–*RS* combination in the [2]catenane product. Although each macrocycle is *meso* (*RS*) and so achiral, with C_{2h} symmetry, the [2]catenane has C_2 symmetry and is chiral. The development of the chemistry of [2]catenanes based on coordination compounds has relied to a significant extent on the use of labile palladium(II) compounds, but all reported examples have had the *cis* stereochemistry at palladium(II);[5] the compounds reported below are the first with *trans* stereochemistry.

Results and discussion

The 1,1′-binaphthyl group is widely used as a chiral unit in asymmetric catalysis and in molecular recognition processes, so ligands were designed using this group in the backbone. The readily available 1,1′-binaphthyl-2,2′-diamine $C_{20}H_{12}(NH_2)_2$ was easily converted to the corresponding bis(pyridine) ligand $C_{20}H_{12}(NHC(=O)\text{-}3\text{-}C_5H_4N)_2$, **1**, by reaction with 3-$ClC(=O)C_5H_4N{\cdot}HCl$ and base. The ligand was prepared in both the racemic, *rac*-**1**, and enantiomerically pure form, *R*-**1**, by using the corresponding diamine precursor. The structure of *rac*-**1** was determined, and is shown in Fig. 1. The chiral molecules associate in an $\cdots R\cdots S\cdots R\cdots S\cdots$ fashion through intermolecular hydrogen bonding of an N–H group of one enantiomer with a pyridyl nitrogen atom of the other enantiomer [N(3)$\cdots$N(4A) = 2.991(4) Å] to form a polymeric structure. There is also an intramolecular hydrogen bond between an N–H and C=O group of each molecule [N(2)$\cdots$O(2) = 2.948(3) Å]

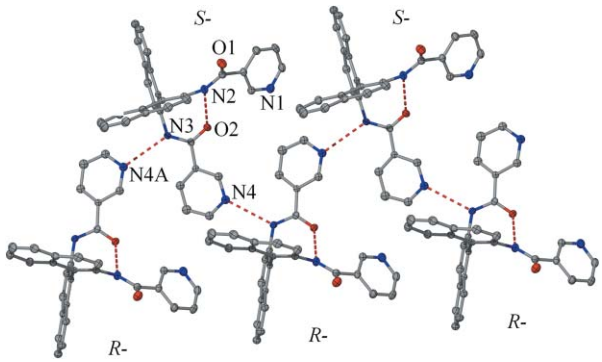
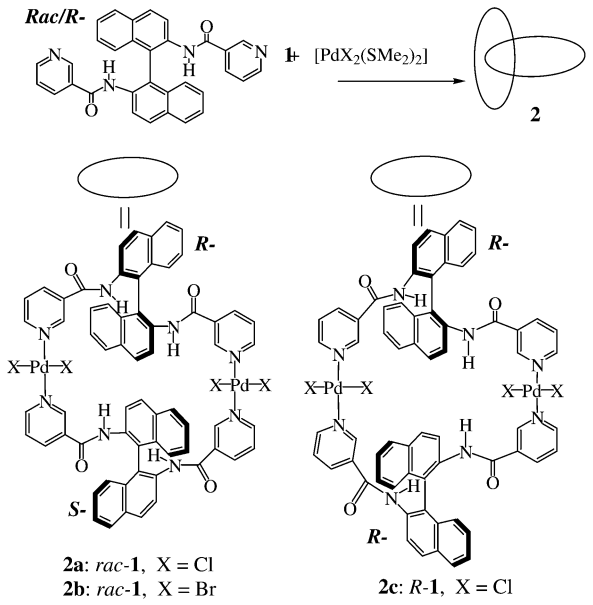


Fig. 1 The conformation of ligand *rac*-**1** and the zig-zag polymeric structure formed by intermolecular N–H$\cdots$N interactions.

(Fig. 1) that limits the span of the pyridyl donors [N(1)$\cdots$N(4) = 6.6 Å]. All NH groups are involved in hydrogen bonding while only half of the pyridine and carbonyl groups are.

The reaction of ligands *rac*-**1** and *R*-**1** with *trans*-[$PdX_2(SMe_2)_2$], X = Cl, Br, occurred by displacement of the weakly coordinating SMe_2 groups by the pyridyl groups of **1** to form chiral [2]catenanes, **2a–c**, as shown in Scheme 3. The [2]catenanes **2** were obtained as yellow solids, which were soluble in DMSO but sparingly soluble in other common organic solvents.



Scheme 3

The structure of compound **2a** is shown in Fig. 2. It shows the presence of a [2]catenane formed by interlocking of two 30-membered macrocycles. Each macrocycle contains two ligands **1** and two *trans*-$PdCl_2$ units, and so the [2]catenane is formed by 4 + 4 self-assembly. The secondary bonding between the macrocycles that favours [2]catenane formation is unusual. Thus, there are four intermolecular N–H$\cdots$ClPd hydrogen bonds [N(2)/(2A)$\cdots$Cl(3A)/(3) = 3.330(9) Å, N(7)/(7A)$\cdots$Cl(4A)/(4) = 3.61(2) Å] and two intermolecular N–H$\cdots$O=C [N(6)/(6A)$\cdots$O(2A)/(2) = 2.89(2) Å] hydrogen bonds (Fig. 2). It is likely that the NH$\cdots$ClPd hydrogen bonds make a major contribution to the intermacrocycle binding, and this is notable since most catenanes contain only hydrogen bonds between organic groups, dipolar attractions between polar groups or π-stacking forces between arene units.[3–8] Each [2]catenane **2a** contains two NH groups and six carbonyl groups that are not involved in hydrogen bonding. The conformation of the bis(pyridine) ligands is more open in the [2]catenane **2a** compared to the free ligand *rac*-**1** (Fig. 1) and the distance between the pyridyl

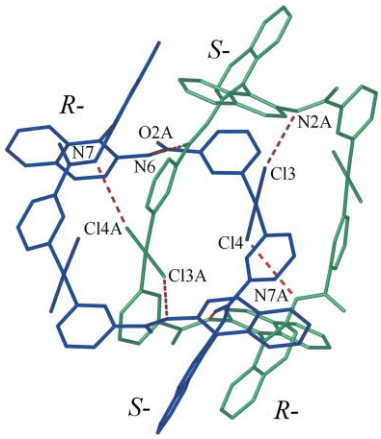


Fig. 2 Structure of one enantiomer of the chiral [2]catenane **2a**. Selected bond lengths and angles: Pd(1)–N(1) = 1.996(9) Å, Pd(1)–N(8) = 2.023(9) Å, Pd(2)–N(4) = 1.994(10) Å, Pd(2)–N(5) = 2.000(9) Å, Pd(1)–Cl(1) = 2.291(4) Å, Pd(1)–Cl(2) = 2.296(4) Å, Pd(2)–Cl(3) = 2.291(3) Å, Pd(2)–Cl(4) = 2.303(3) Å, N(1)–Pd(1)–N(8) = 178.1(4)°, N(4)–Pd(2)–N(5) = 174.4(3)°, Cl(1)–Pd(1)–Cl(2) = 177.56(12)°, Cl(3)–Pd(2)–Cl(4) = 179.76(13)°. (symmetry code: $-x + 1$, y, $-z + 3/2$)

nitrogen atoms is correspondingly greater in **2a**, [N(1) ··· N(4) = 10.0 Å, N(5) ··· N(8) = 10.2 Å]. This conformational change is necessary to create a large enough cavity in each macrocycle to allow the catenation. The intramolecular N–H ··· O=C hydrogen bonds that were present in the free ligand *rac*-**1** (Fig. 1) are replaced by the intermacrocycle N–H ··· ClPd hydrogen bonds in **2a**. The IR spectrum of *rac*-**1** contains a broad N–H stretch at 3280 cm^{-1}, assigned to the similar strength N–H ··· O and N–H ··· N hydrogen bonding groups, while the IR spectrum of **2a** contains N–H stretches at 3279, 3403 and 3503 cm^{-1} for the more varied NH groups in **2a**. Complexes **2a**, **2b** and **2c** have similar IR spectra.

Each macrocycle in **2a** exists in the *meso* (*R*,*S*) form, containing one ligand *R*-**1** and one ligand *S*-**1**, and has approximate C_{2h} symmetry, with the mirror plane perpendicular to the macrocycle. However, when the two achiral rings interlock, the mirror plane is lost and the catenane **2a** is chiral and has crystallographic C_2 symmetry (Fig. 2). The overall chirality of the catenane can be described as *R*-(*R*,*S*)$_2$ or *S*-(*R*,*S*)$_2$, where the first descriptor refers to the chirality associated with catenation step. In the solid state, the enantiomers of the [2]catenane **2a** further self-assemble through weak intermolecular interactions (Pd ··· Cl = 3.52Å)[9] to form a racemic infinite polymer of catenanes ··· *R*-(*R*,*S*)$_2$ ··· *S*-(*R*,*S*)$_2$ ··· (Fig. 3).

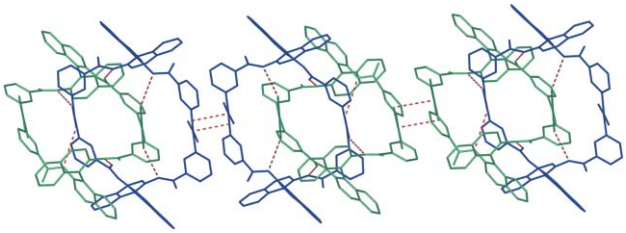


Fig. 3 One-dimensional polymer of [2]catenanes **2a** formed through intermolecular Pd ··· Cl interactions.

The self-assembly, as represented in the solid state structure, is highly selective (several single crystals were examined and they were all isomorphous with the data crystal). Thus, the racemic ligand could give rise to either chiral or achiral macrocycles (*RR*, *SS*, *RS*), and the catenanes might contain any combination of these (Scheme 1, **H**), but only one form (*RS*–*RS*) is observed. A partial structure determination of [2]catenane **2b** was carried out, and it was found to be isomorphous and isostructural with **2a**, though problems with crystal twinning prevented full refinement. It is probable that it is the intercatenane association in the solid state that causes the very low solubility of compounds **2a** and **2b**.

Does the catenane structure survive in solution? The ESI-MS of the catenane **2a** in CH_2Cl_2/MeOH, with formic acid added to aid ionization, contained envelopes of peaks centred at m/z = 1662 $[Pd_4Cl_7(\mathbf{1})_2]^+$, 1483 $[Pd_3Cl_5(\mathbf{1})_2]^+$ and 1307 $[Pd_2Cl_3(\mathbf{1})_2]^+$, but no parent ion at m/z = 2680 $[Pd_4Cl_8(\mathbf{1})_4]^+$. The spectra indicate the presence of a tetrapalladium complex, with subsequent loss of $PdCl_2$ units, as expected for the [2]catenane. However, they do not prove that the [2]catenane is the dominant species in solution. Thus, the peak at m/z = 1307 is also consistent with the presence of the simple macrocycle. The ESI-MS of complex **2c** was very similar to that of **2a**.

The ^{1}H NMR spectra of ligand *rac*-**1** and catenane **2a** in DMSO-d_6 are shown in Fig. 4(a) and (b). At a concentration of 5.2×10^{-3} M, the NMR spectrum of **3a** is indicative of catenane formation [Fig. 4(b)], as indicated by the presence of four distinct NH resonances (each catenane contains 8 NH groups, and there is only a two-fold symmetry axis) and multiple pyridyl proton resonances. The spectrum is broad, indicative of non-rigidity, but it is reproducible and is unchanged after several days, indicating that there is little dissociation to simple macrocycles and little displacement of the bis(pyridine) ligands by DMSO under these conditions. However, at lower concentration [2.4×10^{-4} M, Fig. 4(c)], significant reaction with DMSO occurred to give free ligand *rac*-**1**. In confirmation, addition of extra ligand *rac*-**1** caused the equilibrium to move back to favoring **2a**. There was no evidence for the simple macrocycle in the dmso solution, and so the self-assembly of the new dissymmetric [2]catenane appears to be selective. The ^{1}H NMR spectra of complexes **2b** and **2c** in dmso-d_6 were similar, and so we suggest that the enantiopure catenane **2c** has a similar structure and H-bonding interactions as the catenanes self-assembled from the racemic ligand. The catenane complexes are sparingly soluble in most organic solvents, so a complete NMR study was not possible. However, the ^{1}H NMR of a dilute solution of **2a** in CD_2Cl_2/CD_3OD was obtained and contained four equal intensity NH resonances at δ = 9.41, 9.43, 9.61 and 9.66, as expected for the [2]catenane structure. At room temperature, the COSY NMR contained correlations between the pairs of NH resonances at δ = 9.41 and 9.43 and δ = 9.61 and 9.66, which were not present at −20 °C, indicating that the correlations arise as a result of an undefined dynamic exchange process. The

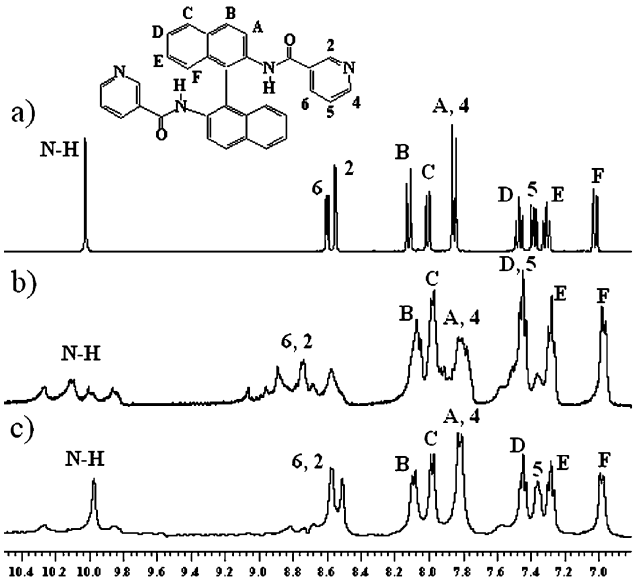
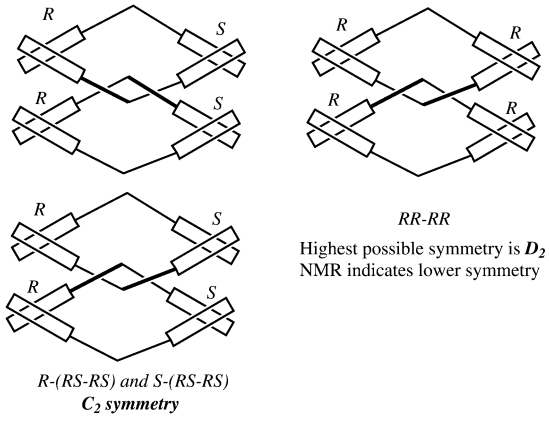


Fig. 4 ^{1}H NMR spectrum of: (a) ligand *rac*-**1**; (b) 5.2×10^{-3} M solution of **2a** (equilibrium favours catenane); (c) 2.4×10^{-4} M solution of **2a** (equilibrium favours *rac*-**1**).

equilibrium in this solvent system again appears to favour the [2]catenane.

Conclusions

In summary, the chiral [2]catenanes **2a**–**c** were prepared by 4 + 4 self-assembly of *trans*-PdX_2 groups and chiral bis(amidopyridyl)binaphthyl ligands. When a racemic mixture of the chiral ligand, *rac*-**1**, was used in the catenane synthesis, the self-assembly occurred in a highly selective fashion in the crystalline product and, though the evidence is less definitive, in the solution phase product also. The macrocycles formed only in the *meso* (*RS*) form. These macrocycles further self-assembled to give the [2]catenanes **2a** and **2b**, as the *RS*-*RS* stereoisomers. Thus, of the six possible stereoisomers formed by random 4 + 4 self-assembly (**H**, Scheme 1), only one is formed in the crystalline product. Of the several forms of chirality exhibited by [2]catenanes (Scheme 1), the type in which a [2]catenane is formed by combination of two identical macrocycles, each with *meso* stereochemistry, appears to be new. It is particularly noteworthy that each individual macrocycle is *meso* and has approximate C_{2h} symmetry, but the [2]catenane is dissymmetric with C_2 symmetry as a result of the catenation step. The [2]catenane enantiomers are described as *R*-(*RS*-*RS*) and *S*-(*RS*-*RS*), illustrated in simplified form in Scheme 4. Crystals of the racemic [2]catenane **2a** contain self-assembled chains of these enantiomers connected through secondary Pd···Cl bonding. It has not been possible to grow crystals of the chiral [2]catenane **2c** for structure determination so its detailed stereochemistry is undetermined. Scheme 4 illustrates that both the constituent macrocycles and the [2]catenane **2c** have highest possible symmetry D_2. However, the ^{1}H NMR spectrum of complex **2c** contains four NH resonances, as for the complexes **2a** and **2b** with lower symmetry C_2. This lower symmetry is expected to result from the rigid [2]catenane and particularly from the presence of only two NH···O=C hydrogen bonds.



Scheme 4

The ability to organize self-assembled functional molecules into ordered arrays is an important step in the development of molecular materials. This work shows that self-assembly of novel [2]catenanes in solution can be combined with solid state self-assembly to give ordered arrays of the [2]catenanes. The key is to have enough functional groups in the precursor molecules to direct first the molecular self-assembly, then the supramolecular self-assembly of the [2]catenane and, finally, the solid state self-assembly to give the supramolecular polymer of chiral [2]catenanes.

Experimental

NMR spectra were recorded using a Varian Inova 400 NMR spectrometer. ^{1}H and ^{13}C chemical shifts are reported relative to tetramethylsilane (TMS). The NMR labeling is defined in Fig. 4. IR spectra were recorded using a Bruker Vector 33 spectrometer as KBr pellets.

Synthesis

rac-1,1′-$C_{20}H_{12}$-2,2′-(NHC(O)-3-$C_5H_4N)_2$ *rac*-1

Nicotinic acid (1.23 g, 10.0 mmol) was refluxed in thionyl chloride (10 mL) for 2 h to form the acid chloride. Excess thionyl chloride was removed under vacuum leaving a colourless solid. The solid was suspended in tetrahydrofuran (30 mL), and triethylamine (1.4 mL) was added, followed by addition of a solution of *rac*-2,2′-diamino-1,1′-binaphthyl (1.42 g, 5.0 mmol) in tetrahydrofuran (10 mL). The mixture was heated under reflux for 6 h, then it was allowed to cool and was poured into ice water. The resulting precipitate was filtered, washed with cold water and acetone, and dried. Yield 1.75 g, 75%. IR (KBr): ν(NH) 3280 cm^{-1} (broad); ^{1}H NMR (DMSO-d_6): 10.02 (s, 2H, NH); 8.77 (d, $^3J_{HH}$ = 5 Hz, 2H, H^6 py); 8.55 (s, 2H, H^2 py); 8.12 (d, $^3J_{HH}$ = 9 Hz, 2H, H^B $C_{10}H_6$); 8.01 (d, $^3J_{HH}$ = 8 Hz, 2H, H^C $C_{10}H_6$); 7.85 (d, $^3J_{HH}$ = 9 Hz, 2H, H^A $C_{10}H_6$; d, $^3J_{HH}$ = 5 Hz H^4 py); 7.47 (t, $^3J_{HH}$ = 8 Hz, 2H, H^D $C_{10}H_6$); 7.38 (dd, $^3J_{HH}$ = 5 Hz, 8 Hz, 2H, H^5 py); 7.31 (t, $^3J_{HH}$ = 8 Hz, 2H, H^E $C_{10}H_6$); 7.02 (d, $^3J_{HH}$ = 8 Hz, 2H, H^F $C_{10}H_6$);^{13}C NMR: δ = 165.4, 152.9, 148.6, 135.6, 135.2, 132.8, 132.3, 130.1, 129.7, 129.2, 128.8, 127.5, 126.6, 125.9, 125.6. MS: *m*/*z* Calcd.: 494.1742, Found: 494.1737.

R-1,1′-$C_{20}H_{12}$-2,2′-(NHC(O)-3-$C_5H_4N)_2$ *R*-1

This was prepared similarly from nicotinic acid (0.271 g, 2.2 mmol), triethylamine (0.3 mL) and *R*-2,2′-diamino-1,1′-binaphthyl (0.309 g, 1.1 mmol). Yield 0.282 g, 52%. IR, NMR as for *rac*-1. MS: *m*/*z* Calcd.: 494.1742, Found: 494.1742.

trans-[{$(PdCl_2)_2$(μ-*rac*-1)$_2$}$_2$], 2a

[$PdCl_2(SMe_2)_2$] (0.030 g, 0.10 mmol) was added to a solution of *rac*-1 (0.049 g, 0.10 mmol) in CH_2Cl_2. After several minutes of stirring the product complex precipitated as a pale yellow solid, which was collected by filtration and dried under vacuum. Yield 0.060 g, 90%. IR (KBr): ν(NH) 3279, 3403, 3503 cm^{-1}; ^{1}H NMR (DMSO-d_6): 10.34–9.84 (m, 8H, NH); 9.16–8.51 (m, 16H, H^{2,6} py); 8.18–7.76 (m, 32H, H^4 py, H^{A,B,C} $C_{10}H_6$); 7.67–7.25 (m, 24H, H^5 H^{D,E} $C_{10}H_6$); 7.01 (d, $^3J_{HH}$ = 8 Hz, 8H, H^F $C_{10}H_6$); Anal. Calcd. (%) for $C_{32}H_{22}N_4O_2PdCl_2$: C: 57.21, H: 3.30, N: 8.34 Found: C: 57.33, H: 2.87, N: 8.02.

trans-[{$(PdBr_2)_2$(μ-*rac*-1)$_2$}$_2$], 2b

This was prepared similarly from [$PdBr_2(SMe_2)_2$] (0.039 g, 0.10 mmol) and *rac*-1 (0.049 g, 0.10 mmol). Yield 0.066 g, 87%. IR (KBr): ν(NH) 3267, 3410, 3503 cm^{-1}; ^{1}H NMR (DMSO-d_6): 10.38–9.64 (m, 8H, NH); 9.15–8.31 (m, 16H, H^{2,6} py); 8.11–7.57 (m, 32H, H^4 py, H^{A,B,C} $C_{10}H_6$); 7.52–7.08 (m, 24H, H^5 H^{D,E} $C_{10}H_6$); 6.85 (d, $^3J_{HH}$ = 8 Hz, 8H, H^F $C_{10}H_6$); Anal. Calcd. (%) for $C_{32}H_{22}N_4O_2PdBr_2$: C: 50.52, H: 2.91, N: 7.36 Found: C: 50.16, H: 2.66, N: 6.91.

trans-[{$(PdCl_2)_2$(μ-*R*-1)$_2$}$_2$], 2c

This was prepared similarly from [$PdCl_2(SMe_2)_2$] (0.030 g, 0.10 mmol) and *R*-1 (0.049 g, 0.10 mmol). Yield 0.057 g, 86%. IR (KBr): ν(NH) 3346, 3409, 3503 cm^{-1}; ^{1}H NMR (DMSO-d_6): 10.34–9.79 (m, 8H, NH); 9.10–8.46 (m, 16H, H^{2,6} py); 8.16–7.71 (m, 32H, H^4 py, H^{A,B,C} $C_{10}H_6$); 7.63–7.21 (m, 24H, H^5 H^{D,E} $C_{10}H_6$); 6.96 (d, $^3J_{HH}$ = 8 Hz, 8H, H^F $C_{10}H_6$); Anal. Calcd. (%) for $C_{32}H_{22}N_4O_2PdCl_2$: C: 57.21, H: 3.30, N: 8.34 Found: C: 56.83, H: 2.95, N: 7.79.

X-Ray structure determinations

Crystals were mounted on glass fibres. Data were collected using a Nonius-Kappa CCD diffractometer using 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 was carried out using the Nonius DENZO package. The data were scaled using SCALEPACK (Nonius, B.V. 1998). The SHELX-TL V5.1 and SHELX-TL V6.1 (G. M. Sheldrick) program packages were used to solve and refine the structures. The structures were solved by direct methods. Except as mentioned, all non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were calculated geometrically and were riding on their respective carbon atoms. Thermal ellipsoid diagrams are shown at 30% probability.

rac-1,1′-$C_{20}H_{12}$-2,2′-$(NHC(O)\text{-}3\text{-}C_5H_4N)_2$, *rac*-1

Crystals of $C_{32}H_{22}N_4O_2 \cdot THF$ were grown by diffusion of hexane into a THF solution of the compound. Formula $C_{36}H_{30}N_4O_3$, fw = 566.64, monoclinic, space group $P2(1)/n$, $a = 9.966(2)$, $b = 30.966(6)$, $c = 10.167(2)$ Å, $\beta = 113.65(3)°$, $V = 2874.0(10)$ Å^3, $Z = 4$, $T = 150(2)$ K, $\rho_{calcd.} = 1.310$ Mg m^{-3}, $\mu = 0.085$ mm^{-1}, $\lambda = 0.71073$ Å, $\theta_{max} = 25.04°$, 20639 reflections, 5046 independent reflections, GOF = 1.060, $R1\,[I > 2\sigma(I)] = 0.0622$, $wR2 = 0.1754$, largest difference peaks 0.412/−0.405 e Å^{-3}. One of the pyridyl groups was disordered over two positions and was modeled as a 70 : 30 isotropic mixture. The THF solvent molecule was also disordered over two positions and was modeled as a 50 : 50 isotropic mixture with geometric restraints.

trans-[{$(PdCl_2)_2$(μ-*rac*-1)$_2$}$_2$], 2a

Crystals of $C_{128}H_{88}Cl_8N_{16}O_8Pd_4 \cdot 10.1CH_2Cl_2$ were grown by diffusion of hexane into a solution of **2a**, formed *in situ* in dichloromethane (the pure complex does not redissolve in dichloromethane). Formula $C_{138.1}H_{108.2}Cl_{28.2}N_{16}O_8Pd_4$, fw = 3543.08, monoclinic, space group $C2/c$, $a = 33.094(7)$, $b = 14.712(3)$, $c = 35.077(7)$ Å, $\beta = 107.77(3)°$, $V = 16264(6)$ Å^3, $Z = 4$, $T = 150(2)$ K, $\rho_{calcd.} = 1.447$ Mg m^{-3}, $\mu = 0.954$ mm^{-1}, $\lambda = 0.71073$ Å, $\theta_{max} = 21.97°$, 15571 reflections, 9413 independent reflections, GOF = 1.058, $R1\,[I > 2\sigma(I)] = 0.0871$, $wR2 = 0.2563$, largest difference peaks 1.275/−0.648 e Å^{-3}. One ligand was disordered over two positions and was modeled as a 50 : 50 isotropic mixture with geometric restraints. The majority of the solvent molecules were highly disordered and all were modeled with geometric restraints. One solvent molecule was modeled as a 50 : 50 mixture, with one shared chlorine atom at full occupancy. Another solvent was modeled at full occupancy with one of the chlorine atoms disordered over two positions in a 70 : 30 ratio. One solvent molecule was highly disordered around a symmetry element and was modeled as a four part 25 : 25 : 25 : 25 isotropic mixture without hydrogen atoms. One partial occupancy solvent molecule was modeled as a 4 part isotropic mixture with occupancies of 25 : 25 : 15 : 15. A 75% occupancy solvent molecule was modeled with two positions for one of the chlorine atoms in a 40 : 35 ratio. The remaining two partial occupancy solvent molecules (50% and 25%, respectively) were not disordered. For the solvent molecules, only the chlorine atoms with occupancies of at least 50% were refined anisotropically.

CCDC reference numbers 249203 and 249204.

See http://www.rsc.org/suppdata/dt/b4/b413258k/ for crystallographic data in CIF or other electronic format.

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