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# Chemical Communications

## COMMUNICATION

# Orientational self-sorting: formation of structurally defined $Pd_4L_8$ and $Pd_6L_{12}$ cages from low-symmetry dipyridyl ligands

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**Tetra- and hexanuclear coordination cages were obtained in reactions of [Pd(CH₃CN)₄](BF₄)₂ with low-symmetry dipyridyl ligands. In both cases, only one structurally defined complex was formed out of a vast pool of potential isomers.**

Metal-ligand assemblies of the general formula $[Pd_nL_{2n}]^{2n+}$ can be obtained from ditopic N-donor ligands, L, and $Pd^{2+}$ ions.[1] Typically, these assemblies display high stability in solution and in the solid state, enabling diverse applications. For example, $[Pd_nL_{2n}]^{2n+}$ complexes have been employed as hosts for bioactive compounds,[2] as nanoreactors for chemical transformations,[3] as network junctions in gels,[4] and as links for nanoparticles.[5]

Most $[Pd_nL_{2n}]^{2n+}$ complexes reported to date show high symmetry. Assemblies with reduced symmetry can be obtained by using two types ligand L and L' for the assembly process, and different heteroleptic structures with defined geometry have been reported over the last years.[6,7] An alternative approach to synthesize $[Pd_nL_{2n}]^{2n+}$ complexes with reduced symmetry is the utilization of bridging ligands with two distinct binding sites.[8,9] Several groups have investigated the formation of dinuclear $[Pd_2L_4]^{4+}$ cages from low-symmetry N-donor ligands.[9] The assembly process can give rise to four distinct isomers, which differ in the relative orientation of the ligands (Fig. 1). Certain ligands were found to give selectively one isomer. However, a computational analysis of a small library of $[Pd_2L_4]^{4+}$ complexes has shown that the energy difference between the four isomers is often not large enough for providing a good selectivity.[9a]

For $[Pd_nL_{2n}]^{2n+}$ complexes with more than two $Pd^{2+}$ ions, the number of possible isomers when using low-symmetry ligands quickly increases. In order to identify these isomers, we used the "orbit-stabilizer" method[10] of counting configurations modulo symmetries. In each case, the symmetries generate a

subgroup of the hyperoctahedral group, allowing us to reduce the orbit computations to multiplication by signed permutation matrices. The matrix calculations were then carried out on a computer (for details, see the Electronic Supplementary Information, ESI).
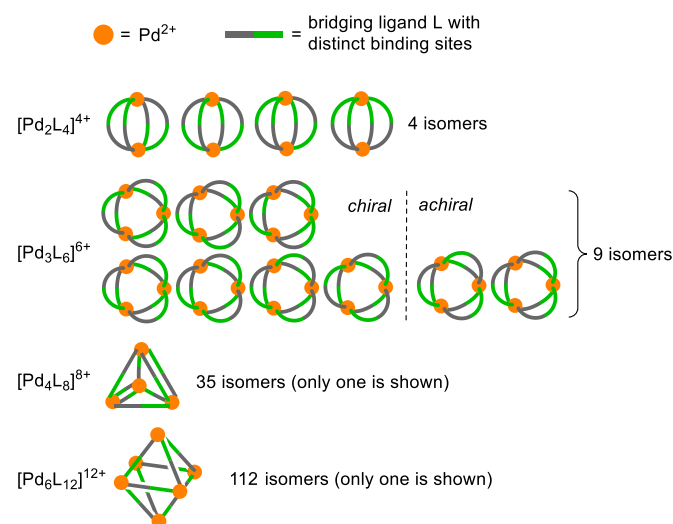


**Fig 1.** Potential isomers for metal-ligand assemblies of the general formula $[Pd_nL_{2n}]^{2n+}$ ($n$ = 2, 3, 4, or 6). The isomers differ in the relative orientation of the bridging ligands L, which have two distinct binding sites. The number of isomers increases from 9→16, 35→68, and 112→186 if enantiomers are considered as well.

The statistical analysis provided the following results: For trinuclear $[Pd_3L_6]^{6+}$ complexes, one finds 9 isomers, which are distinguished by the relative orientation of the bridging ligands (Fig. 1). Out of those 9 isomers, 7 are chiral. If enantiomers are taken into account, the total number of isomers for $[Pd_3L_6]^{6+}$ assemblies is therefore 16. For tetrahedral complexes with eight ligands, 35 different isomers can potentially form, 33 of which are chiral (isomers including pairs of enantiomers: 68). Octahedral $[Pd_6L_{12}]^{24+}$ complexes could give rise to 112 isomers, 74 of which are chiral (isomers including pairs of enantiomers: 186). To the best of our knowledge, attempts to synthesize such

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higher nuclearity $[Pd_nL_{2n}]^{2n+}$ complexes have not been reported so far.

Below, we show that it is possible to obtain structurally defined $[Pd_4L_8]^{8+}$ and $[Pd_6L_{12}]^{12+}$ complexes from low-symmetry dipyridyl ligands in a process that we would like to describe as 'orientational self-sorting'.[11,12] The new Pd cages have been characterized comprehensively, including single-crystal X-ray analyses, and preliminary results regarding their host properties are provided.

For our investigations, we have synthesized the dipyridyl ligands **L1** and **L2** (Scheme 1, for details, see ESI). Ligand **L1** features a 4-pyridyl group, which is connected via a 1,3-phenylene spacer to a 3-pyridyl group. In ligand **L2**, the phenylene spacer is replaced by a bridging thiophenyl group.
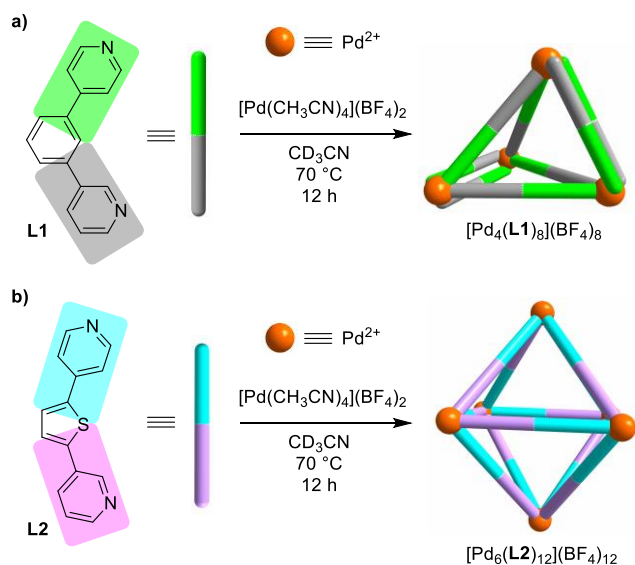


**Scheme 1.** Synthesis of the coordination cages $[Pd_4(L1)_8](BF_4)_8$ and $[Pd_6(L2)_{12}](BF_4)_{12}$. The abstract representation of the cage structures indicates the relative orientation of the dipyridyl ligands.

The reaction of **L1** with $[Pd(CH_3CN)_4](BF_4)_2$ (0.5 equiv) in $CD_3CN$ (70 °C, 12 h) resulted in the clean (> 90%) formation of a new complex, as evidenced by NMR spectroscopy ($^1H$, $^{13}C$, DOSY). Two sets of signals for the bridging ligand were observed, indicating that **L1** is present in two distinct coordination environments (Fig. 2a and 2b).

A similar observation was made for the reaction of **L2** with $[Pd(CH_3CN)_4](BF_4)_2$: after tempering the reaction mixture at 70 °C for 12 h, the $^1H$ NMR spectrum suggested the formation a defined complex, with two sets of signals for the bridging ligand **L2** (Fig. 2c and 2d). The reaction mixture was slightly turbid. In order to verify that the precipitates are not side products, we have isolated all products by precipitation with diethyl ether, and we have then analyzed the products in $d_6$-DMSO. A clean solution was obtained, and the NMR spectrum indicated the formation of a defined assembly in high yield (>95%).

Conclusive information about the nuclearity of the assemblies was obtained by high resolution mass spectrometry. For the reaction with **L1**, the dominant peaks in the mass spectrum of the product could be attributed to a tetranuclear

species of the formula $[\{Pd_4(L1)_8\}(BF_4)_x]^{8-x}$ ($x$ = 2–6) (Fig. 2e). The reaction with **L2**, on the other hand, had resulted in the formation of a hexanuclear complex, as evidenced by peaks for $[\{Pd_6(L2)_{12}\}(BF_4)_x]^{12-x}$ ($x$ = 3–9) species (Fig. 2f).
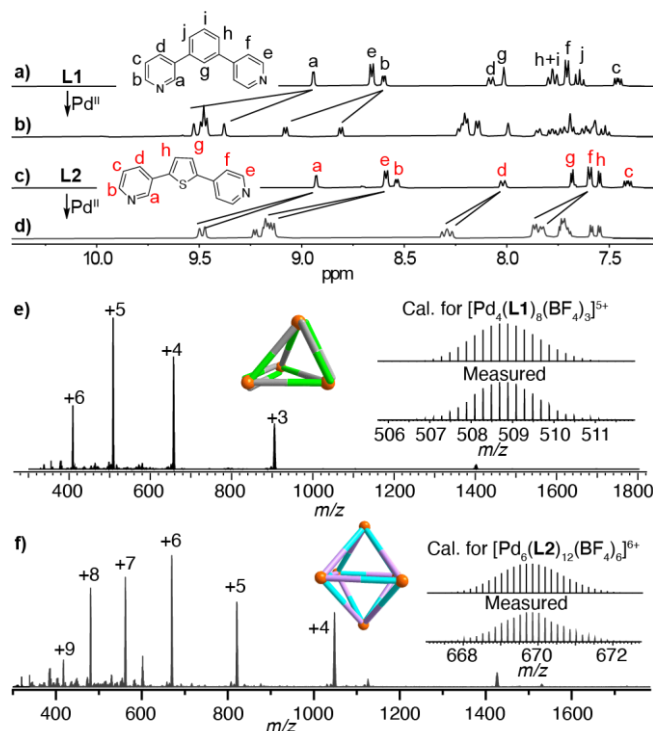


**Fig. 2.** $^1H$ NMR spectra of the ligands **L1** (**a**) and **L2** (**c**), and the corresponding metal-ligand assemblies $[Pd_4(L1)_8](BF_4)_8$ (**b**) and $[Pd_6(L2)_{12}](BF_4)_{12}$ (**d**). High resolution ESI mass spectra of $[Pd_4(L1)_8](BF_4)_8$ (**e**) and $[Pd_6(L2)_{12}](BF_4)_{12}$ (**f**).
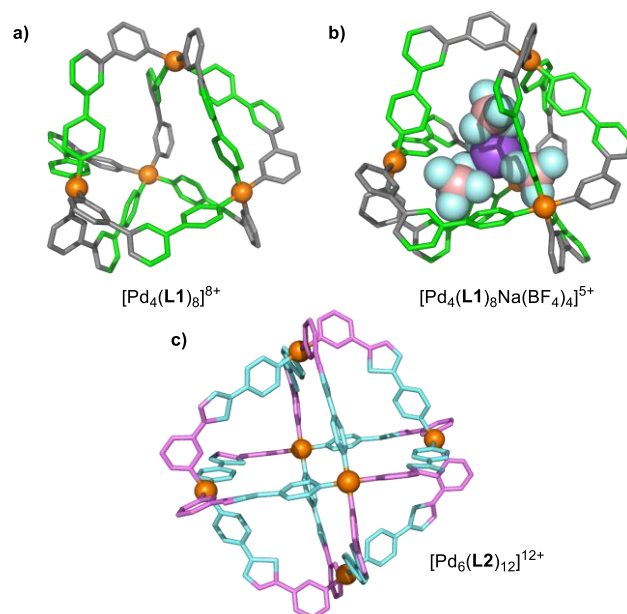


**Fig. 3.** Molecular structures of $[Pd_4(L1)_8]^{8+}$ (**a**) and $[Pd_6(L2)_{12}]^{12+}$ (**c**) as determined by X-ray crystallography. The cage cavity of $[Pd_4(L1)_8]^{8+}$ is filled with a $[Na(BF_4)_4]^{3-}$ complex (**b**). Hydrogen atoms and counter ions are not depicted for clarity. The color coding of the ligand atoms aims to visualize the non-symmetric nature of the ligand.

In order to determine the relative orientation of the ligands in $[Pd_4(L1)_8](BF_4)_8$ and $[Pd_6(L2)_{12}](BF_4)_{12}$, we tried to obtain single crystals for a structural analysis by X-ray diffraction. After several failed attempts to crystallize the pure products, we investigated co-crystallizations in the presence of different salts. Single crystals were obtained for mixtures with $NaBPh_4$, and crystallographic analyses were performed (Fig. 3).

The four $Pd^{2+}$ ions in $[Pd_4(L1)_8]^{8+}$ are arranged in a tetrahedral fashion (Fig. 3a),[13,14] with Pd···Pd distances between 10.195(2) and 10.914(1) Å. Each of the four $Pd^{2+}$ ions are coordinated to two 4-pyridyl groups and to two 3-pyridyl groups with a *cis* arrangement of the different donor groups. In line with the NMR data, two distinct coordination environments are observed for the bridging ligands **L1**: four out of the eight ligands are involved in the formation of macrocyclic $[Pd_2(L1)_2]^{4+}$ subunits, whereas the other four are bridging the $[Pd_2(L1)_2]^{4+}$ subunits. Overall, the cage displays approximate $S_4$ symmetry, which is an unusual point group for coordination cages. The cavity of the assembly is filled with a sodium ion (originating from the additive $NaBPh_4$), which is surrounded by four $BF_4^-$ anions (Fig. 3b). Additional $BF_4^-$ and $BPh_4^-$ anions could be localized outside the cage (not shown in Fig. 3).

The hexanuclear complex $[Pd_6(L2)_{12}]^{12+}$ shows an octahedral arrangement of the $Pd^{2+}$ ions, with the 12 bridging ligands **L2** occupying the edges of the octahedron (Fig 3c).[15,16] The diameter of the cage, as defined by the distance of the $Pd^{2+}$ ions, is 17.5 Å. The cationic cage crystallized with $BPh_4^-$ anions originating from the additive $NaBPh_4$. As in the case of the $[Pd_4(L1)_8]^{8+}$ cage, all $Pd^{2+}$ ions are coordinated in a *cis* fashion to two 4-pyridyl groups and to two 3-pyridyl groups. The eight trigonal faces of the octahedron are made from two types of $[Pd_3(L2)_3]^{6+}$ subunits: there are two triangular faces with exclusive head-to-tail connections of the bridging ligands, and six triangular faces, which also show head-to-head and tail-to-tail connections. The connectivity gives rise to an approximate $S_6$ symmetry for the entire assembly. The geometry observed in the solid state matches well with the NMR data, which show two sets of signals for **L2**.

The results of the crystallographic analysis prompted us to study the solution-based interaction between $[Pd_4(L1)_8]^{8+}$ and $NaBPh_4$. For this purpose, we have performed an NMR titration experiment: increasing amounts of $NaBPh_4$ were added to a solution of the cage in $CD_3CN$, and $^1H$ NMR spectra were recorded after each addition. Binding-induced shifts for some of the $^1H$ NMR signals were observed (see ESI, Fig. S21). We assume that the shifts are related to an anion-mediated complexation of $Na^+$ inside the cage,[17] as observed crystallographically. The isotherm resulting from the titration could be fitted to a 1:1 binding model with an association constant of $K_a = 82$ M$^{-1}$.

To conclude: we have shown that tetra- and hexanuclear cages are obtained in reactions of $[Pd(CH_3CN)_4](BF_4)_2$ with the low-symmetry ligands **L1** or **L2**. In both cases, the analytical data suggest that only one structurally defined complex is formed out of a vast pool of potential constitutional isomers. At the moment, we are not able to provide a rationale for the observed selectivity. Most likely, the preferred formation of a specific isomer is related to the fact that this isomer is favored from an enthalpic point-of-view, with the relative orientation of the ligands providing a good match for the coordination requirements of the $Pd^{2+}$ ions. Overall, the results are evidence that the utilization of low-symmetry ligands is a viable option to prepare higher nuclearity assemblies with defined geometry.

## Author contributions

R.-J.L. and K.S. designed the experiments, R-J.L. performed the experiments and analyzed the data, A.M. performed the mathematical analysis of the isomers, F.F.-T. collected and processed the X-ray data, and R.-J.L. and K.S. co-wrote the manuscript. All authors discussed the results and commented on the manuscript.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

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**Graphic for the TOC:**

Structurally defined $Pd_4L_8$ and $Pd_6L_{12}$ coordination cages are obtained from low-symmetry dipyridyl ligands.