

Heterometallic Pd^{II}–Ni^{II} Complexes with *meso*-Substituted Dibenzotetraaza[14]annulene: Double C–H Bond Activation and Formation of a Rectangular Tetradibenzotetraaza[14]annulene

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Supporting Information

ABSTRACT: Three isomeric 2[Pd^{II}–Ni^{II}] metal complexes, derived from indoleninyl *meso*-substituted dibenzotetraaza[14]annulene, were synthesized. The resulting dimers feature Ni⋯Ni or, alternatively, Ni⋯ π interactions in staggered or slipped cofacial structures. A remarkable insertion of palladium into two different C–H bonds yielded a 4[Pd^{II}–Ni^{II}] rectangular complex with dimensions of 8.73 \times 10.38 Å.

Over the past 2 decades, metal-ion-directed assembly has been widely used in the construction of discrete supramolecular architectures.^{1–6} A common synthetic strategy in this field is utilizing the highly directional properties of coordinative bonds in square-planar palladium and platinum complexes. While square assemblies are often favored in this class of complexes, especially when the spacer is rigid, using flexible or semiflexible spacers has led to smaller assemblies, i.e., triangles or ellipses.^{2–4} A more recent trend in the field is the development of supramolecular structures that incorporate functional ligands such as perylene diimide dyes,⁵ salens, and porphyrins.^{4,6} Dibenzotetraaza[14]annulenes (Figure 1) are

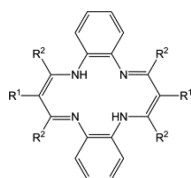


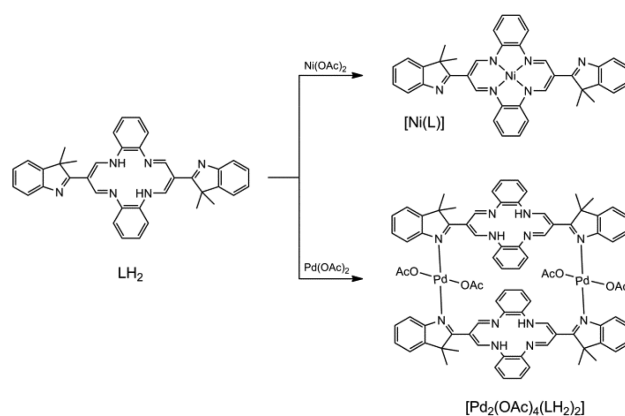
Figure 1. Dibenzotetraaza[14]annulenes.

among the well-studied macrocyclic systems in structural chemistry, coordination chemistry, and materials sciences.⁷ Similar to porphyrins, they possess an N₄ core, which can accommodate various metal ions. However, compared to the 16-membered ring of porphyrin, their ring is composed of 14 atoms, which results in a relatively smaller N₄ core size.

We recently introduced a dibenzotetraaza[14]annulene bearing two 3,3-dimethylindoleninyl fragments at the R¹ positions, R² = H (Figure 1).⁸ It was shown that upon its reaction with nickel(2+), the N₄ core was doubly deprotonated to accommodate the metal atom inside the cavity. Similarly, a

number of first-row transition metals (II/III) were inserted in the central cavity. Instead of occupying the cavity, the relatively larger second-row palladium(II) ion coordinated to the indole nitrogen donor; thus, the macrocycle acted as a neutral ditopic ligand to doubly bridge pairs of palladium atoms, while the central core remained free (Scheme 1). In the formation of the

Scheme 1



dimer, the indole rings were twisted by ca. 40° with respect to the tetraaza[14]annulene system. The two parallel tetraaza rings in this structure were separated by 3.32 Å. In comparison, the dimeric platinum(II) complex of the ditopic di-4-pyridyltetraaza[14]annulene, reported by Beves et al.,³ adopts an ellipse structure with an interplanar separation of more than 7 Å.

A logical extension of our previous work was to synthesize the heterometallic structures with the N₄ core occupied by a small first-row transition-metal ion, while the indole nitrogen atoms were coordinated to the larger palladium(II) ion. Considering the flexibility of the ligand and the short interplanar distance observed in the palladium complex (3.32 Å), we expected that this approach would furnish a cofacial arrangement of tetraaza[14] rings benefiting from metal– π or short metal–metal contacts. In the present work, we report the results of our attempts to synthesize the palladium(II)–

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nickel(II) mixed-metal complexes derived from LH₂. The diamagnetic nature of the square-planar palladium(II) and nickel(II) complexes enabled us to study the solution structures by NMR spectroscopy. The reaction of [Ni(L)] with an equimolar amount of Pd(OAc)₂ in acetic acid gave a mixture of crystals of two dimeric isomers, **1** and **2**, with over 90% being isomer **1**, as suggested by ¹H NMR spectroscopy (Figure S7 in the Supporting Information, SI). As shown by X-ray crystallography, in both structures, pairs of palladium centers are doubly bridged by indole nitrogen atoms of the nickel complex molecules. Two monodentate acetato ligands complete the square-planar geometry around each palladium atom. In structure **1** (Figure 2), Pd1 adopts a trans

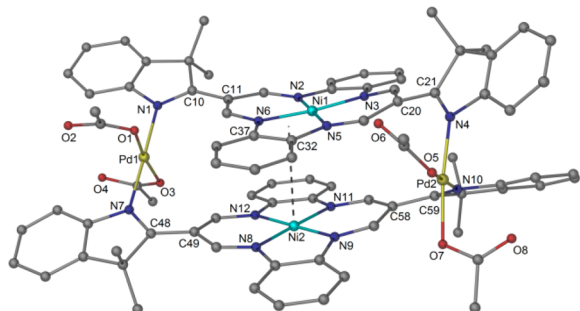


Figure 2. Crystal structure and atomic labeling scheme of **1**. The dashed line represents Ni... π (chelate) interaction.

configuration, while Pd2 has a cis geometry. The two indole rings of the [Ni1(L)] fragment are rotated in the same direction out of the plane of the attached 14-membered tetraaza ring by 28° and 50° about the C10–C11 and C20–C21 linkages, respectively. The indole rings of the [Ni2(L)] fragment are rotated in opposite directions from the plane of the tetraaza ring by +28° and –27° about the C48–C49 and C58–C59 bonds. The two nickel centers are separated by 3.91 Å. Perhaps, one of the significant noncovalent contacts in the molecule is the metal– π (chelate) interaction formed between Ni2 and the Ni1/N5/N6/C32/C37 ring with a metal–centroid distance of 3.35 Å (Figure S8 in the SI).

In structure **2** (Figure 3), both palladium centers have trans square-planar geometry, and the pairs of indole rings of each

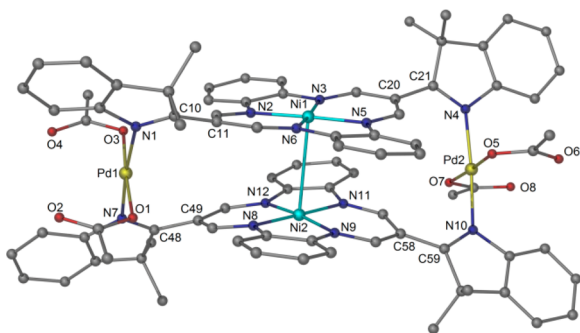


Figure 3. Crystal structure and atomic labeling scheme of **2**.

[Ni(L)] moiety are twisted in the opposite direction out of the plane of the 14-membered tetraazaannulene (by 47–62°). Consequently, the two tetraaza rings are placed above each other and staggered by 38°, which brings the two nickel atoms close together at a distance of 3.22 Å, shorter than the sum of their van der Waals radii, 3.26 Å.⁹ Intermolecular Ni...Ni

contacts in the range of 2.78–3.39 Å have been observed in complexes of octa- and tetraaza[14]annulenes,^{8,10} but a structure with an intramolecular Ni...Ni contact is unique in this class.

Separation of the two isomers could be achieved by taking advantage of the solubility of **2** and insolubility of **1** in acetone. This helped us to study their solution structures by NMR spectroscopy. The ¹H NMR spectra of **1** in CD₂Cl₂ and **2** in acetone-*d*₆, supported by 2D NMR spectroscopy, are in agreement with their crystal structures. The spectrum of **2** shows that in an acetone solution the predominant species possesses D₂ symmetry, consistent with the approximate D₂ symmetry of the molecule in the crystal structure of **2**. Moreover, NMR spectroscopy revealed that in CD₂Cl₂ the structure of **1** slowly transforms to **2**, so that while the proportion of **1** in the initial mixture was up to 90%, it reduced to less than one-third within 5 days (Figure S7 in the SI). Isomerization and transformation also occurred in the acetone solution of **2** to yield red block-shaped crystals of **3**, with a small amount of a red plate-shaped crystal. The structure of the crystal of **3**, shown in Figure 4, is that of a conformational

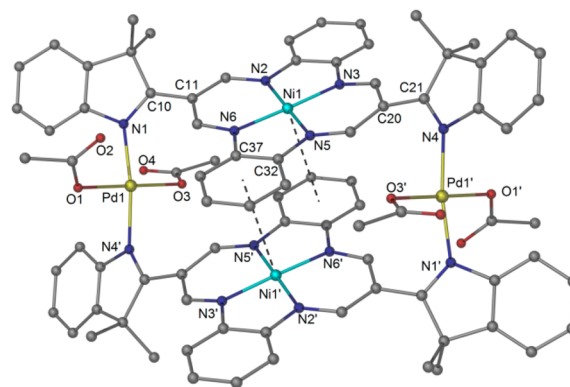


Figure 4. Crystal structure of **3**. Dashed lines represent Ni... π interactions. Symmetry code: ' = $-x + 1, -y + 1, -z + 1$.

isomer of the structure **2**. The two conformers differ by rotation about the indole–tetraazaannulene C–C linkages accompanied by a slipping motion of the two macrocyclic rings. Thus, unlike **2**, in structure **3**, pairs of the indole rings of each [Ni(L)] fragment are twisted in the same direction from the plane of the tetraaza ring, by 45–49°. As a result, the Ni–Ni interaction no longer exists and the two nickel atoms are separated by 5.40 Å. Instead, the structure shows two Ni... π interactions with a Ni–centroid distance of 3.32 Å.

As mentioned above, some plate-shaped crystals were grown concomitantly with the block crystals of **3**. The structure of this crystal, **4**, to our surprise, is a centrosymmetric tetrapalladium complex consisting of four doubly deprotonated nickel complexes, [Ni(L-2H)]²⁻ (Figure 5). The formation of such a structure occurred through an interesting and unprecedented reaction for a tetraaza[14]annulene: the β -C–H bond activation to form a Pd–C bond. At the same time, a phenylene C–H bond activation also took place at the palladium center, resulting in the formation of a C,C,N-palladabicyclic. The formation of four such palladabicycles accounts for the creation of a metallacyclic rectangle with dimensions of 8.73 × 10.38 Å, as defined by the palladium centers. The arrangement of the metallacycles in the crystal gives rise to rectangular channels along the crystallographic *b*

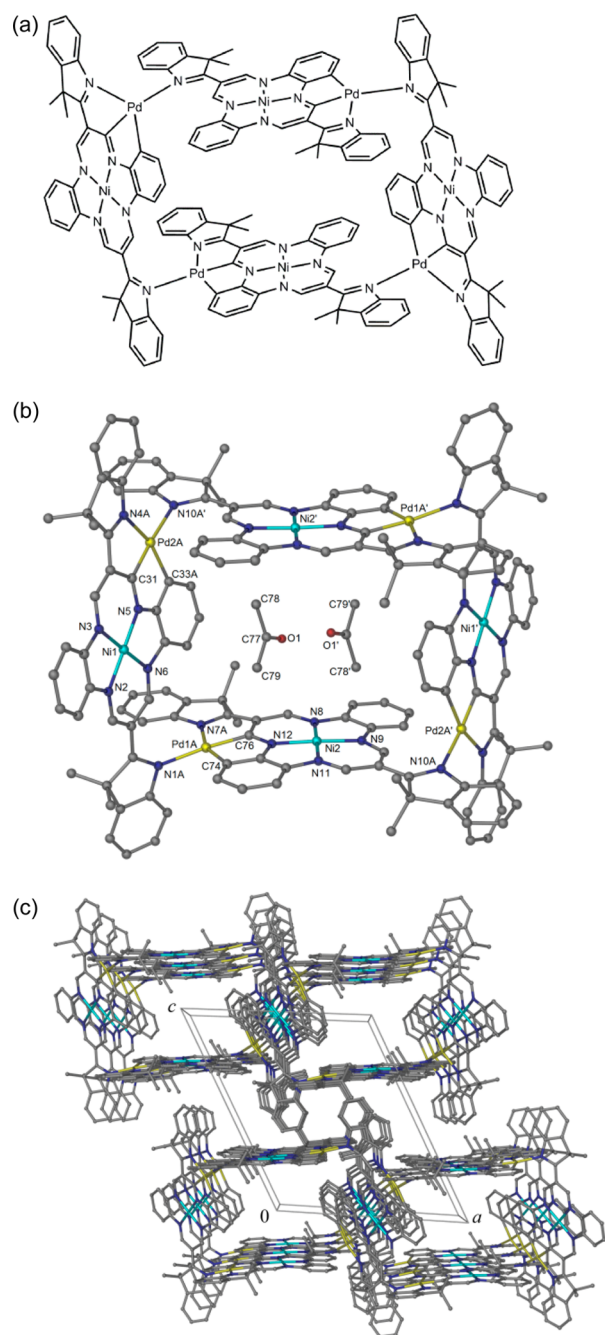


Figure 5. (a) Schematic drawing of molecule 4. (b) Crystal structure of 4 encasing acetone solvent molecules. (c) Crystal packing diagram of molecule 4 showing the rectangular channels.

axis (Figure 5c). These channels are interdigitated along the *a* axis through π - π interactions (Figure S11 in the SI) and are filled with acetone solvent molecules. Additional evidence for the formation of 4 was obtained by MALDI-MS spectroscopy, which shows a peak assignable to the $[M - (C_{28}H_{20}N_5NiPd)]^+$ fragment (Figure S12 in the SI). Regrettably, our repeated attempts to obtain a high-purity sample of 4 failed, which hampered further characterization of the molecule. On the basis of the generally accepted mechanism of the cyclopalladation reactions,¹¹ transformation of the dimeric complex, 2 or 3, to the tetrameric complex 4 is suggested to be through an electrophilic C-H activation pathway, wherein the acetato ligand would abstract the carbon-bound hydrogen atom.

In conclusion, through metal-directed assembly, flexible cofacial and also rectangular assemblies of tetraaza[14]annulene systems were obtained. This approach may lead to systems with tunable cavity sizes and metal-metal distances that have applications in catalysis and molecular switches.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures, NMR and MS spectra, additional views for the crystal structures, X-ray crystallographic files and tables. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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