Inorganic Chemistry
Communication
pubs.acs.org/IC

Hierarchical Helix of Helix in the Crystal: Formation of Variable-Pitch Helical π-Stacked Array of Single-Helical Dinuclear Metal Complexes

Shigehisa Akine,* Hiroki Nagumo, and Tatsuya Nabeshima*

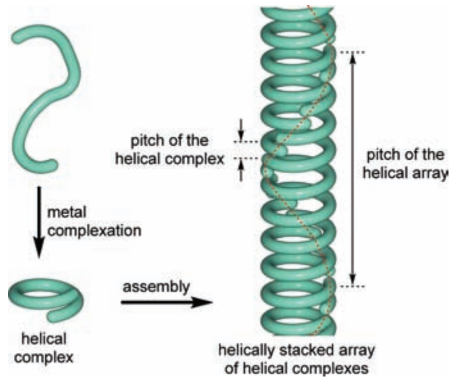
Faculty of Pure and Applied Sciences, University of Tsukuba, 1-1-1 Tennodai, Tsukuba, Ibaraki 305-8571, Japan

Supporting Information

ABSTRACT: Unique *helix of helix* structures were formed via intermolecular π-stacking and metal−metal interactions in the crystal of single-helical dinuclear complexes $[L^2M_2]$ (M = Pd, Ni) having an acyclic bis(N_2O_2)-type ligand. The difference in the helical winding angle of the constituents (401.7° for $[L^2Pd_2]$; 421.3° for $[L^2Ni_2]$) led to variation of the helical pitches of the helical array (7_2 helix for $[L^2Pd_2]$; 6_2 helix for $[L^2Ni_2]$).

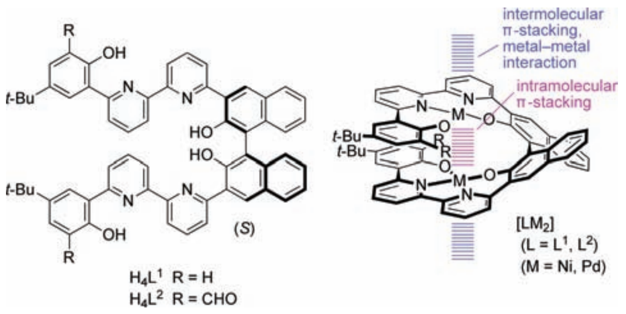
The helical structure is a basic structural motif in biomolecules such as the DNA double helix or protein α-helix. These helical motifs play an important role in storing genetic information, protein−DNA binding, etc. Some of the helical structures further form a helical structure at a higher order, i.e., a hierarchical *helix of helix*, as seen in the supercoiled DNAs[1] or coiled-coil structures in proteins.[2] Such hierarchical helical structures are also found in artificial systems; the representative examples are a spiral structure of helical polyacetylene fibrils[3] and a cholesteric liquid crystal with a helical twist.[4] An alternative approach to obtaining hierarchical *helix of helix* structures is the helical assembling of *discrete* flexible molecules (Scheme 1). In this approach, each of the discrete molecules is folded into a helix, which further aggregates into a higher order helix via noncovalent interactions. We have recently reported that a single-helical metal complex forms a helical array in the crystalline state, which well approximates a superhelical structure.[5]

Scheme 1. Schematic Drawing of a Helically Stacked Array of Helical Molecules as a Hierarchical *Helix of Helix*



We have focused on a hierarchical assembly of helical molecules by taking advantage of the π-stacking and metal−metal interactions. The 1D-stacked array of helical molecules would provide novel electric or optical properties with a helical chirality that is derived from the helicity of the constituents. An aromatic ligand H_4L^1 based on a bipyridine−phenol repeating unit, which we recently reported,[6] is a candidate for this purpose (Chart 1). This ligand molecule consisting of eight aromatic moieties formed a single-helical structure with an intramolecularly π-stacked structure when complexed with metal ions in a square-planar geometry. This planar metal complex moiety also serves as a π surface for the intermolecular π-stacking and metal−metal interactions, which would contribute to the formation of a higher-order structure. In this paper, we report the first hierarchical 1D-stacked array with a *helix of helix* structure, i.e., a helically stacked array formed from a discrete single-helical dinuclear complex of the ligand H_4L^2. The helical pitch was efficiently controlled by changing the metal incorporated into the helical scaffold.

Chart 1. Acyclic Pyridine−Phenol Ligands for the Formation of Hierarchical *Helix of Helix* Structures



The ligand H_4L^2 with formyl groups was synthesized from a precursor bearing 1,3-dioxolan-2-yl groups using a method analogous to the synthesis of the parent ligand H_4L^1.[7] The helical dinuclear palladium(II) complex $[L^2Pd_2]$ was obtained in 77% yield by a reaction with palladium(II) acetate in *N,N*-dimethylformamide (DMF).[7] The single crystals of $[L^2Pd_2]$ were grown by the vapor-phase diffusion of diethyl ether into the DMF solution. X-ray crystallographic analysis[8,9] (Figure 1) revealed that the asymmetric unit of the crystal contains seven crystallographically independent molecules whose structures are essentially similar to each other. While a number of crystals containing several crystallographically independent molecules in the asymmetric unit have been reported, the ones containing

Received: February 24, 2012
Published: May 9, 2012

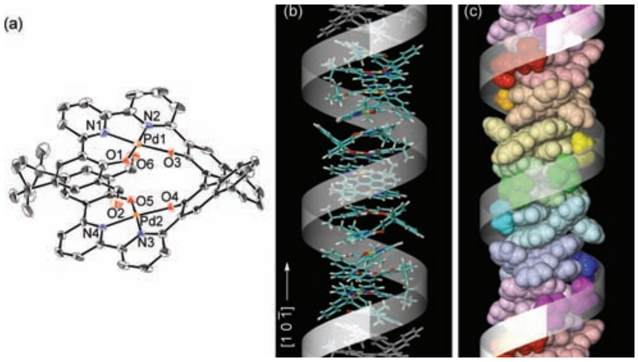


Figure 1. (a) ORTEP drawing (30% probability) of one of the seven crystallographically independent molecules of [L^2Pd_2]. Hydrogen atoms are omitted for clarity. (b and c) Wireframe and space-filling models of a 1D helically stacked array of [L^2Pd_2] in the crystal. A helical ribbon is approximately overlaid on the positions of the *tert*-butyl groups to show the helical twisting.

seven are quite rare.[10] Each molecule of [L^2Pd_2] has two square-planar metal moieties lying almost parallel to one another at a distance of 3.4 Å (Figure 1a). The dihedral angles of the binaphthyl group range from 66 to 75°, and the helix winding angles[11] are in the range of 387−422°. The structures are better described as a one-turn single-helical structure, whose helical handedness is forced to be right-handed because of the chiral (*S*)-2,2′-binaphthyl group.[12] Such a structural feature of the dinuclear complex [L^2Pd_2] was similar to that of the nickel(II) complex [L^1Ni_2] without having formyl groups.[6]

The molecular arrangement in the crystal of [L^2Pd_2] is also noteworthy. The seven crystallographically independent molecules are stacked on top of each other in the direction of [1 0 $\bar{1}$], forming an infinite 1D array continuing to the neighboring cells (Figure 1b,c). The two neighboring molecules are stacked in such a way that they twist around the axis of the 1D array by 91−127°.[13] As a result, the seven molecules form a right-handed two-turn twist (7_2 helically stacked array; seven repeat units per two turns) with a helical pitch of 22.5 Å, while each of the molecules adopted a single-helical structure with a helical pitch of 3.4 Å. Thus, a hierarchical *helix of helix* is formed in the crystal.

This helically stacked array presumably resulted from multiple noncovalent interactions between the neighboring molecules. Each two neighboring molecules face one another in such a way that the square-planar palladium planes are stacked parallel on top of each other. The intermolecular Pd−Pd distances are in the range of 3.16−3.37 Å, which are typical values for the $Pd^{II}-Pd^{II}$ contact.[10d,14] The terminal phenol rings of the two neighboring molecules are also stacked in a parallel fashion at a distance of around 3.4 Å, indicative of a π-stacking interaction. These two kinds of noncovalent interactions are responsible for the formation of the 1D-stacked array. In addition, the pyridyl protons, B2 and B3 (Figure 2), interact with the naphthalene ring of the neighboring molecule in a C−H···π fashion (H···π distances, 2.5−2.8 Å). This attractive interaction as well as the steric hindrance of the *tert*-butyl groups makes each two neighboring molecules twisted at approximately 100° in the same direction, leading to the formation of the unique 7_2 helically stacked array.[15]

There still remains the possibility that the 1D helically stacked array in the crystal of [L^2Pd_2] resulted from just the crystal-packing force. However, intermolecular noncovalent interactions were also observable in solution. The ^1H NMR spectra of [L^2Pd_2] in $(CD_3)_2SO$ showed a significant dependence on the concentration (Figure 2). As the concentration increased, the protons on the phenol ring (A2 and A3), pyridine rings (B1−B3 and C1−C3), and the formyl groups shifted upfield, while the naphthalene protons D2−D5 showed slight downfield shifts. This result suggests intermolecular interactions in which the phenol−bipyridine moiety of the [L^2Pd_2] molecule is in the shielding region of the neighboring molecules. The spectral changes were analyzed by using self-association equilibrium with the equal *K* model,[16] giving an equilibrium constant of 35.7 ± 0.8 M^{-1} (Figure 2).

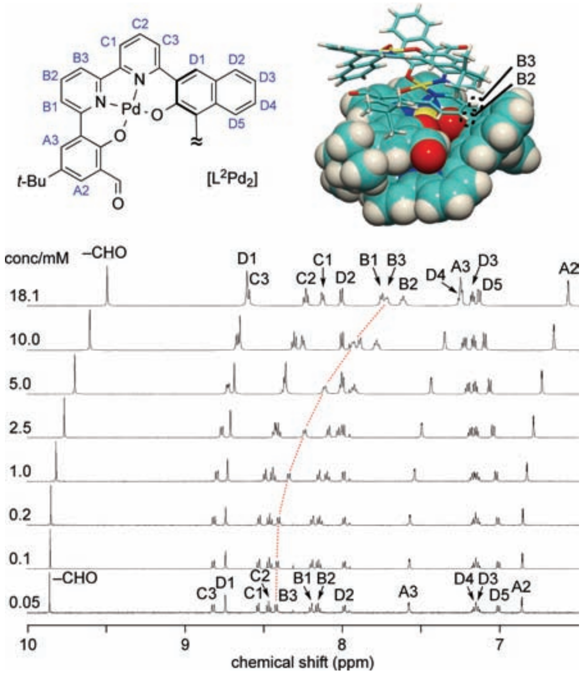


Figure 2. Concentration dependence of the ^1H NMR spectra (aromatic region) of [L^2Pd_2] (600 MHz, $(CD_3)_2SO$, 298 K). The stacking structure of [L^2Pd_2] in the crystal is also shown.

Of these spectral changes, the largest upfield shift was observed for the pyridyl proton B3. This proton should interact with the naphthalene π surface of the neighboring molecules via C−H···π interaction, as is observed in the crystal structure (Figure 2). The rotational nuclear Overhauser effect (ROE) correlation between the pyridyl proton C1 and the naphthalene proton D5 also supports a structural similarity to that of the crystal structure in which the corresponding distances are in the range of 2.5−3.0 Å. Therefore, the attractive noncovalent interaction significantly contributes to the formation of the helical array of [L^2Pd_2] in the crystal.

Once we knew that [L^2Pd_2] underwent aggregation in solution, it was obvious that this unique 7_2 helically stacked array was formed not by unpredictable interactions such as packing forces but was inevitably produced by directional and attractive noncovalent interactions. We expected that modification of the helical constituent at the *lower hierarchical level* changes the structural feature of the helically stacked array at the *higher hierarchical level*.

We synthesized the corresponding dinuclear nickel(II) complex [L^2Ni_2] in a similar manner,[7] whose structure was determined by X-ray crystallographic analysis[8,9] (Figure 3a).

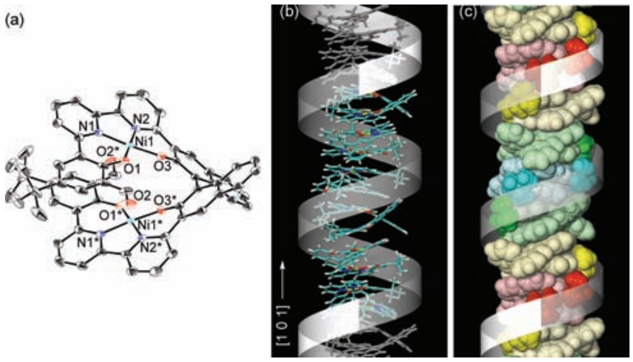


Figure 3. (a) ORTEP drawing (30% probability) of one of the four crystallographically independent molecules of [L^2Ni_2]. Hydrogen atoms are omitted for clarity. (b and c) Wireframe and space-filling models of a 1D helically stacked array of [L^2Ni_2] in the crystal. A helical ribbon is approximately overlaid on the positions of the *tert*-butyl groups to show the helical twisting.

This crystal contains four crystallographically independent molecules (molecules 1−4) of [L^2Ni_2], two of which (molecules 1 and 4) have a crystallographically imposed 2-fold axis. These four kinds of molecules formed an array of 1,2,3,4,3,2,1..., which forms the 1D-stacked *helix of helix* structure (Figure 3b,c) similar to the palladium(II) analogue. It is worth noting that [L^2Ni_2] formed a 6_2 helically stacked array instead of the 7_2 one. The helical pitch is now 19.0 Å, which is considerably shorter than that of [L^2Pd_2] (22.5 Å) by ca. 3.5 Å.

The change in the pitch of the higher-order helix can be ascribed to the slight structural differences in the helical constituents at the *lower hierarchical level*. Although the overall molecular structure of [L^2Ni_2] (Figure 3a) is similar to that of [L^2Pd_2], different bond distances (Ni−O 1.815−1.838 Å and Ni−N 1.860−1.878 Å for [L^2Ni_2]; Pd−O 1.933−1.996 Å and Pd−N 1.947−2.002 Å for [L^2Pd_2]) resulted in a difference in the average helix winding angles of each helical constituent (421.3° for [L^2Ni_2]; 401.7° for [L^2Pd_2]). The difference of approximately 20° well accounts for the difference in the helical twisting per molecule, $720°/6 = 120°$ for [L^2Ni_2] and $720°/7 = 102.9°$ for [L^2Pd_2] because each two neighboring molecules are stacked in a similar way. Thus, [L^2Ni_2] requires a lower number of molecules for two turns (e.g., six molecules for two turns) than [L^2Pd_2] (seven molecules for two turns).

One of the significant features of the *helix of helix* structures reported here is that a helical molecule at the *lower hierarchical level* formed a helically stacked array at a *higher hierarchical level*. An organic ligand having chiral information can define the handedness of helices *at both the lower and higher hierarchical levels*. This implies that a finely designed helical constituent leads to the formation of well-controlled helically stacked arrays, which would be useful for various kinds of helicity-based functions, such as self-replication, amplification, or transcription of the chirality information. We are now investigating such a sophisticated function based on the hierarchical *helix of helix*.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Syntheses and characterization of ligand H_4L^2 and metal complexes [L^2M_2] (M = Pd, Ni), details of crystallographic analysis, and determination of the self-association constant for [L^2Pd_2]. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: akine@chem.tsukuba.ac.jp (S.A.), nabesima@chem.tsukuba.ac.jp (T.N.).

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by Grants-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

■ REFERENCES

(1) Bauer, W. R.; Crick, F. H. C.; White, J. H. *Sci. Am.* **1980**, *243*, 118−133.

(2) Gruber, M.; Lupas, A. N. *Trends Biochem. Sci.* **2003**, *28*, 679−685.

(3) Akagi, K. *Polym. Int.* **2007**, *56*, 1192−1199.

(4) George, S. J.; Ajayaghosh, A.; Jonkheijm, P.; Schenning, A. P. H. J.; Meijer, E. W. *Angew. Chem., Int. Ed.* **2004**, *43*, 3422−3425.

(5) Akine, S.; Matsumoto, T.; Nabeshima, T. *Chem. Commun.* **2008**, 4604−4606.

(6) Akine, S.; Shimada, T.; Nagumo, H.; Nabeshima, T. *Dalton Trans.* **2011**, *40*, 8507−8509.

(7) For the synthesis of H_4L^2, [L^2Pd_2], and [L^2Ni_2], see the Supporting Information.

(8) For the crystal data for [L^2Pd_2] and [L^2Ni_2], see the Supporting Information.

(9) *SHELXL 97, Program for crystal structure refinement*: Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112−122.

(10) For example, see: (a) Schmitt, M. A.; Choi, S. H.; Guzei, I. A.; Gellman, S. H. *J. Am. Chem. Soc.* **2006**, *128*, 4538−4539. (b) Antolić, S.; Teichert, M.; Sheldrick, G. M.; Kojić-Prodić, B.; Čudić, M.; Horvat, Š. *Acta Crystallogr.* **1999**, *B55*, 975−984. (c) Görbitz, C. H. *Acta Crystallogr.* **2003**, *C59*, o589−o592. (d) Eddings, D.; Barnes, C.; Gerasimchuk, N.; Durham, P.; Domasevich, K. *Inorg. Chem.* **2004**, *43*, 3894−3909. (e) Görbitz, C. H.; Agustsdottir, S.; Bleken, F. *Acta Crystallogr.* **2007**, *C63*, o58−o60.

(11) The molecular winding angles are defined as the sum of the seven A_n−M−A_{n+1} angles, where points A_n ($n = 1, 2, ..., 8$) are the centroids of the aromatic rings (phenol, pyridine, and binaphthyl (1−4, 9, and 10 carbon atoms) and point M is the midpoint of two palladium atoms.

(12) (a) Kesanli, B.; Lin, W. *Coord. Chem. Rev.* **2003**, *246*, 305−326. (b) Jouaiti, A.; Hosseini, M. W.; Kyritsakas, N.; Grosshans, P.; Planeix, J.-M. *Chem. Commun.* **2006**, 3078−3080.

(13) The *intermolecular* helical twisting angles are defined as the torsion angles from one molecule (the midpoint of the binaphthyl C−C bond) to the neighboring one around the axis of the helically stacked array, which was defined as a line parallel to the [1 0 $\bar{1}$] axis, which passes through the centroid of all of the palladium atoms (Pd1−Pd16) of the seven molecules.

(14) For examples of intermolecular Pd^{II}−Pd^{II} contact, see: (a) Penavić, M.; Šoptrajanova, L.; Jovanovski, G.; Šoptrajanov, B. *Acta Crystallogr.* **1986**, *C42*, 1283−1284. (b) Miller, K. J.; Baag, J. H.; Abu-Omar, M. M. *Inorg. Chem.* **1999**, *38*, 4510−4514. (c) Kumari, N.; Prajapati, R.; Mishra, L. *Polyhedron* **2008**, *27*, 241−248. (d) Yue, C.; Jiang, F.; Xu, Y.; Yuan, D.; Chen, L.; Yan, C.; Hong, M. *Cryst. Growth Des.* **2008**, *8*, 2721−2728.

(15) The helical structure with seven repetitive units in the crystalline state is quite rare because most of the reported helical arrays are based on crystallographically allowed (2, 3, 4, and 6) repetitive units.

(16) Martin, R. B. *Chem. Rev.* **1996**, *96*, 3043−3064.