ChemPubSoc Europe
DOI: 10.1002/chem.201404782
CHEMISTRY
A European Journal
Full Paper

Helical Structures

One-Handed Single Helicates of Dinickel(II) Benzenehexapyrrole-α,ω-diimine with an Amine Chiral Source

Chaolu Eerdun, Satoshi Hisanaga, and Jun-ichiro Setsune*[a]

Abstract: Benzenehexapyrrole-α,ω-dialdehyde, composed of a pair of formyltripyrrole units with a 1,3-phenylene linker, was metallated to give dinuclear single-stranded helicates. X-ray studies of the bis-nickel(II) complex showed a helical C_2 form with a pair of helical–metal coordination planes of a 3N+O donor set. The terminal aldehyde was readily converted into the imine by optically active amines, whereby helix-sense bias was induced. Bis-nickel(II) and bis-palladium(II) complexes of the benzenehexapyrrole-α,ω-diimines were studied to show that an enantiomer pair of the helical C_2 form are interchanged by slow flipping of each coordination plane and fast rotation around the C(benzene)–C(pyrrole) bond. The helical screw in the bis-nickel(II) complexes was biased to one side in more than 95% diastereoselectivity, which was achieved by using a variety of optically active amines, such as (*R*)-1-cyclohexylethylamine, (*S*)-1-phenylethylamine, ʟ-Phe(OEt) (Phe = phenylalanine), and (*R*)-valinol. The nickel complexes showed much better diastereoselectivity than the corresponding palladium complexes.

Introduction

Helicates are one of the most intriguing structural motifs for asymmetric molecular architecture as they are regarded as abiotic mimics for helices in biomaterials.[1] In view of their application to biological systems or chirality-related smart materials, significant effort in molecular design and synthesis has focused on inducing absolute helicity.[2] Optically pure double- and triple-stranded helicates (M_2L_2 and M_2L_3) have so far been synthesized, and their rigorous choice of helical sense is owed to the chirality introduced at the ligand terminus or in the linker.[3,4] However, a full bias of helix sense is still difficult to achieve especially in the case of single-stranded helicates, although they have recently drawn considerable attention due to their novel dynamic conformational change, such as inversion and transfer of helical chirality.[5] The ML- and M_2L-type helicates of the widely used oligopyridine ligands are also known,[6,7] but they are racemic, except for a few cases.[7a,b] Single-stranded helicates tend to be in fast equilibrium between right- and left-handed helices due to their relatively flexible structure, which also raises problem of the determination of optical purity. Dinuclear single-stranded M_2L complexes in which both ends of a ligand backbone are folded upon coordination to metal ions are of special interest because of the possible interplay between a bimetallic chemical process at the metal sites and the helical-backbone conformation. In fact, the helix sense was biased by ditopic binding of a chiral guest in the Zn_2L complexes,[8] which is useful for chirality sensing.[9] On the other hand, predetermined one-handed M_2L helicates can regulate stereochemistry in the chemical process at the metal sites.

Open-chain oligopyrroles are regarded as a unique scaffold for helices with intense absorptions in the visible region. Their hydrogen-bonding ability causes helical conformation to happen spontaneously[10a,b] or on anion binding,[10c,d] and their metal-coordinating ability leads to the formation of various helicates.[11–15] Single-stranded ML and M_2L,[11,12] double-stranded M_2L_2,[11c,f,13] triple-stranded M_2L_3,[14] and triangular M_3L_3 complexes[13f,15] have been reported, but most of these studies employed tetrapyrroles, and the helicity control was intended in a limited number of reports;[10a,c,11e–j,13a,b] that is, the chirality introduced at the end group and at the central part of tetrapyrroles was utilized to induce helical-sense bias diastereoselectively in the case of ZnL and Zn_2L_2 helicates.[11e–g,13a,b] It is remarkable that a M_2L-type helicate, in which a pair of zinc(II) bilinones are coupled by a chiral diol linker, has demonstrated full helix-sense bias,[16] but helicates of such long-chain oligopyrroles are very rare in spite of their potential applicability (Figure 1).[17] Helicates of pentapyrrole, hexapyrrole, heptapyrrole, and octapyrrole have recently been reported, but their helicity control has remained unexplored.[17] In principle, the chirality at the linker has a more direct influence on the helical twist,[2g] but the chirality at the ligand terminus is more convenient to introduce. We recently reported that hexapyrrole-α,ω-dialdehyde **1′** forms a helical dinuclear palladium(II) complex **1′Pd$_2$** and its terminal aldehyde group is readily converted into the imine moiety. The helicate **3′Pd$_2$**, which comprises (*R*)-

---

[a] Dr. C. Eerdun, S. Hisanaga, Prof. Dr. J.-i. Setsune
Department of Chemistry
Graduate School of Science, Kobe University
1-1 Rokkodai-cho, Nada-ku, Kobe 657-8501 (Japan)
Fax: (+81) 78-803-5770
E-mail: setsunej@kobe-u.ac.jp

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201404782.

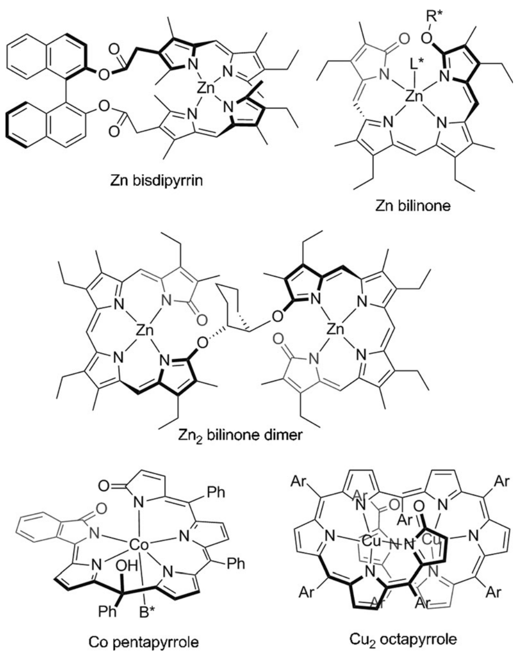
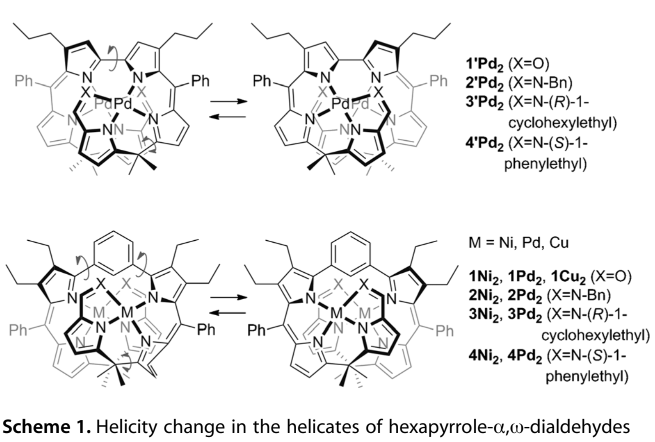


Figure 1. Some single helicate structures of open-chain oligopyrroles. L*, R*, and B* are chiral sources.

1-cyclohexylethylamine, generated a major *P*-helical conformational isomer with 85% diastereoselectivity (Scheme 1).[17a] However, helicity control was far less effective for other amine chiral sources, partly because of the complicated behavior of the conformational changes. Thus, this study aims to demonstrate molecular design of M_2L-type helicates of long-chain oligopyrroles that allows structural diversity for the straightforward introduction of one-handed helicity with high stability against racemization. Herein, we describe dinickel(II) complexes of the open-chain oligopyrrole **1 Ni$_2$**, which was highly effective in the diastereoselective control of the helix sense by introducing a variety of chiral amine groups at the end position.



Scheme 1. Helicity change in the helicates of hexapyrrole-α,ω-dialdehydes and diimines with and without a benzene linker.

Results and Discussion

Synthesis and structure of Pd^{II}, Ni^{II}, and Cu^{II} complexes of benzenehexapyrrole-α,ω-dialdehyde

Benzenehexapyrrole-α,ω-dialdehyde (**1**) was prepared by the reaction of bis-azafulvene **D** and 5-formyl-*gem*-dimethyl-2,2′-dipyrrylmethane followed by oxidation with DDQ (Scheme 2). Bis-azafulvene **D** was prepared starting from 2-carboethoxy-3,4-diethyl-5-iodopyrrole by way of intermediates **A**–**C** through borylation, Suzuki coupling, decarboxylation, Vilsmeier–Haack aroylation, reduction with $NaBH_4$, and $(Boc)_2O$-promoted dehydration according to previous reports.[18] 5-Formyl-*gem*-dimethyl-2,2′-dipyrrylmethane (**E**) was prepared according to previous reports.[17a,19] The reaction of **1** with $PdCl_2(MeCN)_2$, $Ni(OAc)_2$, and $Cu(OAc)_2$ afforded dinuclear metal complexes **1 Pd$_2$**, **1 Ni$_2$**, and **1 Cu$_2$** in yields of 74, 94, and 92%, respectively. These complexes can take an overall *M*- or *P*-helical conformation (Scheme 1). X-ray crystallography of **1 Ni$_2$** shows a helical C_2 form, in which a pair of metal coordination planes of a 3N+O donor set look like folded wings (Figure 2, bottom).[20] Interestingly, the hydrogen (H1 in Figure 2, stick models) at the 2 position of the 1,3-phenylene linker of **1 Ni$_2$** is close to the Ni center, and the distance (2.572 and 2.703 Å) is shorter than the sum of their van der Waals radii (2.83 Å).[21] In contrast, a C_1 form with one wing folded and the other spread is seen in the X-ray study of **1 Cu$_2$** (Figure 2, top). In these dinuclear complexes, each 3N+O metal coordination plane is helically shaped and the central 1,3-di(2-pyrryl)benzene unit is twisted. These components of local helicity dictate their stereochemical features; for example, a pair of helical wings are homochiral in **1 Ni$_2$**, but heterochiral in **1 Cu$_2$**. In the latter case, the 1,3-di(2-pyrryl)benzene unit is twisted to minimize steric constraint in the oligomer chain, thus resulting in a C_1 form rather than a C_s symmetric form. The presence of two rotational axes in the central part of **1 Ni$_2$** allows more flexible behavior in the con-

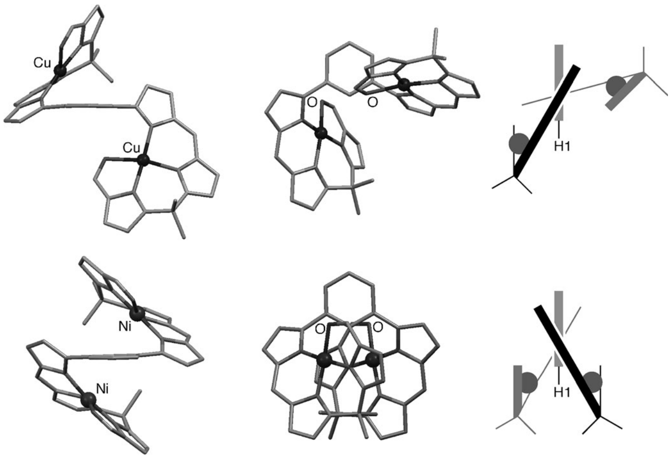
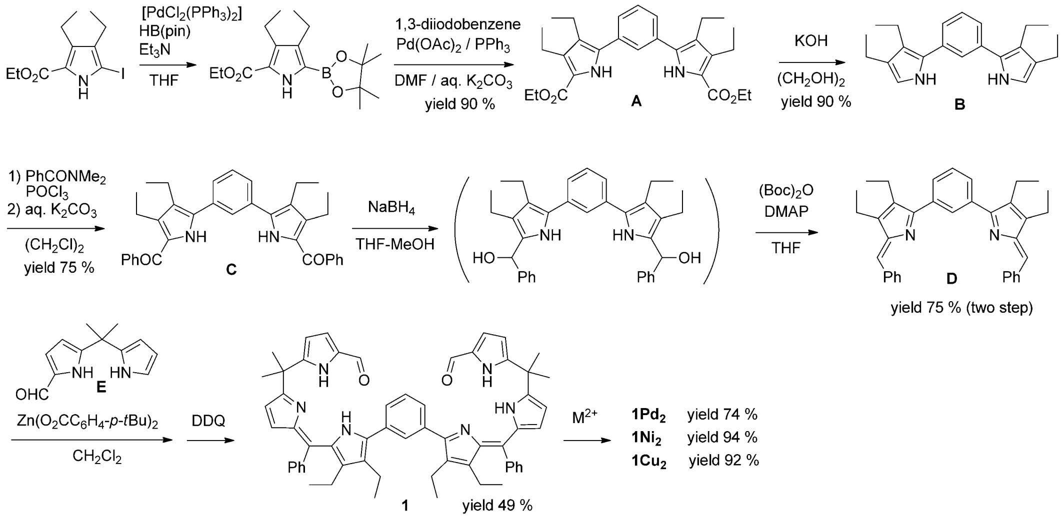


Figure 2. X-ray structures of **1 Ni$_2$** (bottom) and **1 Cu$_2$** (top) from a top view (left) and a front view (center). The alkyl and phenyl groups have been omitted for clarity and a side view of a stick model is shown (right). Selected distances [Å]: Ni1–Ni2 (**1 Ni$_2$**): 5.045(2), Ni1–H1: 2.572(1), Ni2–H1: 2.703(1), Cu1–H1: 2.71(3).



Scheme 2. Synthesis of benzenehexapyrrole-α,ω-dialdehyde **1** and its dinuclear metal complexes **1 Pd$_2$**, **1 Ni$_2$**, and **1 Cu$_2$**. DDQ = 2,3-dichloro-5,6-dicyano-1,4-benzoquinone, DMAP = 4-dimethylaminopyridine, HB(pin) = pinacolborane.

formational changes relative to the dinuclear metal complexes of hexapyrrole-α,ω-dialdehyde (**1′**; Scheme 1).

An enantiomer pair of the helical C_2 forms of **1 Ni$_2$** are interchanged by rotation of both wings around the C(benzene)–C(pyrrole) bond and flipping of the terminal formylpyrrole unit when the inside and outside methyl groups (H8 and H9 in Figure 3) at the *gem*-dimethylmethylene bridge are exchanged. In fact, a pair of broad singlets due to these two methyl groups at $\delta = 1.77$ and 1.68 ppm at −60 °C in the ^{1}H NMR spectrum of **1 Ni$_2$** coalesced at around −10 °C and then gave a sharp singlet at $\delta = 1.58$ ppm at 60 °C. A singlet due to the 1,3-phenylene 2-proton (H1 in Figure 3) underwent a remarkable high-frequency shift from $\delta = 8.5$ to 9.48 ppm on increasing the temperature from −60 to 60 °C. This outcome means that the helical C_2 forms are in rapid equilibrium with some other conformational isomers, even at −60 °C. A similar feature was seen in the variable-temperature (VT) ^{1}H NMR spectra of **1 Pd$_2$** (see Figure S2 in the Supporting Information).

Conformational changes of Pd^{II} and Ni^{II} complexes of benzenehexapyrrole-α,ω-diimines

Because bulky substituents at both ends of the ligand significantly alter the kinetics and thermodynamics of the conformational changes,[17a] **1 Ni$_2$** and **1 Pd$_2$** were treated with benzylamine, (*R*)-1-cyclohexylethylamine, and (*S*)-1-phenylethylamine at reflux in THF to give the corresponding α,ω-diimines **2 Ni$_2$**, **3 Ni$_2$**, **4 Ni$_2$**, **2 Pd$_2$**, **3 Pd$_2$**, and **4 Pd$_2$**, respectively, in good yields. The ^{1}H NMR spectrum of the α,ω-di(*N*-benzyl)imine complex **2 Pd$_2$** at 60 °C shows two sets of signals of a twofold symmetric pattern with the ratio of 1:1 (Figure 4 and Figure S3 in the Supporting Information). The first set (signals with numbers without asterisk in Figure 4) contains a pair of doublets at $\delta = 4.05$ and 3.57 ppm and a pair of multiplets at $\delta = 2.62$ and 2.38 ppm due to the methylene protons of the *N*-benzyl and ethyl groups (H16 and H4, respectively; Scheme 3). The second set (signals with numbers with an asterisk in Figure 4) contains a pair of doublets at $\delta = 4.00$ and 3.57 ppm (H16*) and a pair of multiplets at $\delta = 3.02$ and 2.27 ppm (H4*). These signals

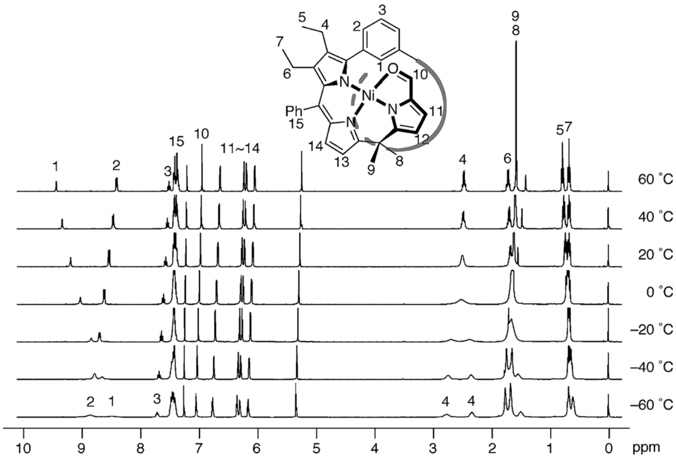


Figure 3. VT ^{1}H NMR spectra of **1 Ni$_2$** in CDCl$_3$.

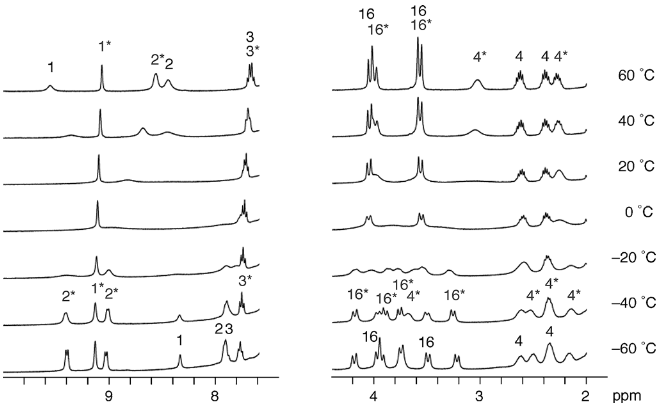
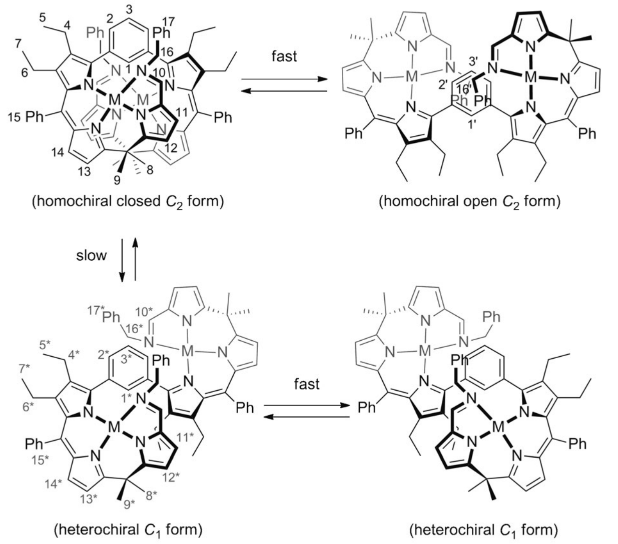


Figure 4. VT ^{1}H NMR spectra (part) of **2 Pd$_2$** in CDCl$_3$. Each signal is associated with the proton numbered in the structure diagram in Scheme 3.



Scheme 3. Conformational changes of dinuclear metal(II) complexes of benzenehexapyrrole-α,ω-di(*N*-benzylimine) (M = Pd, Ni) through fast rotation around the C(benzene)–C(pyrrole) bond and slow flipping of the terminal *N*-benzylformimidoylpyrrole moiety.

became broader with decreasing temperature until approximately 0–−20 °C, and a well-resolved signals of a dissymmetric spectral pattern appeared at −60 °C for the second set of signals, whereas the first set of signals retained the twofold symmetric spectral pattern throughout the temperature range. Consequently, six doublets in total were observed for the N-CH_2-Ph proton (H16 and H16*) in the chemical-shift range δ = 4.2 and 3.2 ppm at −60 °C. The second component of the dissymmetric spectral pattern is populated twice as much as the first component of the twofold symmetric spectral pattern at −60 °C. As the ratio of these two components varied with temperature (from 1:1 at 60 °C to 1:2 at −60 °C), they are in equilibrium and the interchange is very slow on the NMR timescale because signals due to both components appeared separately, even at 60 °C. The signals due to the 1,3-phenylene 4- and 6-protons (H2*) of the second component are remarkably influenced by the temperature change; that is, a broad signal at δ = 8.55 ppm at 60 °C became too broad to be seen at 0 °C and then appeared again as a pair of doublets at δ = 9.39 and 9.03 ppm at −60 °C. In contrast, a singlet and triplet at δ = 9.06 and 7.64 ppm, respectively, at 60 °C due to the 1,3-phenylene 2- and 5-protons (H1* and H3*, respectively) of the second component are almost unchanged in their chemical shift and signal shape throughout the temperature range. This VT NMR profile of the second component is consistent with a heterochiral C_1 form seen in the X-ray structure of **1 Cu$_2$**; namely, one wing is folded and the other spread in a heterochiral C_1 form at −60 °C, but it appears C_s symmetric at 60 °C owing to the rapid rotation of both wings around the C(benzene)–C(pyrrole) bond (Scheme 3). The magnetic circumstances of the 1,3-phenylene 2- and 5-protons (H1* and H3*, respectively) should be constant, even if both wings change their positions in the heterochiral C_1 form, meanwhile the magnetic circumstances of the 1,3-phenylene 4- and 6-protons (H2*) are not constant. This dissymmetric conformation was further supported by the NOESY correlation of the 1,3-phenylene 2-proton (H1*) with one of the methylene protons of the *N*-benzyl and ethyl (H16* and H4*, respectively) groups at δ = 4.00 and 3.02 ppm (see Figure S4 in the Supporting Information). On the other hand, all the proton signals due to the 1,3-phenylene linker of the first component are significantly influenced by the temperature change; that is, broad signals at δ = 9.56 (H1), 8.44 (H2), and 7.66 (H3) ppm at 60 °C became too broad to be seen at 0 °C, and then signals appeared at δ = 8.33 (H1) and 7.90 (H2 and H3) ppm at −60 °C. As in the case with the second component, extreme broadening of these signals at around 0 °C is also ascribable to the restricted rotation of both wings around the C(benzene)–C(pyrrole) bond, thus causing an interchange between a closed C_2 form and an open C_2 form (Scheme 3). At −60 °C, the interchange between these two C_2 forms is not only frozen on the NMR timescale, but also fully biased to one side.

In contrast to this complicated ^{1}H NMR spectrum of **2 Pd$_2$**, the ^{1}H NMR spectrum of dinickel(II) benzenehexapyrrole-α,ω-di(*N*-benzylimine) (**2 Ni$_2$**) at 60 °C shows a single set of signals of a twofold symmetric pattern (Figure 5 a, bottom). Two methyl singlets due to the *gem*-dimethylmethylene bridge (H8 and H9) appear separately at δ = 1.47 and 1.20 ppm, and the diastereotopic nature of the methylene protons of the ethyl (H4 and H6) and *N*-benzyl (H16) groups was clearly seen in the chemical-shift region between δ = 1.5 and 4 ppm. These spectral features are consistent with a helical C_2 form that does not undergo helicity change at 60 °C, at least on the NMR timescale. Signal broadening was observed at approximately 0 to −20 °C, which is very similar to the case of **2 Pd$_2$**, and two sets of signals due to the twofold symmetric molecular conformations appeared at lower temperatures in a ratio of 0.2:1 at −60 °C (see Figure 5 b (bottom) and Figure S6 in the Support-

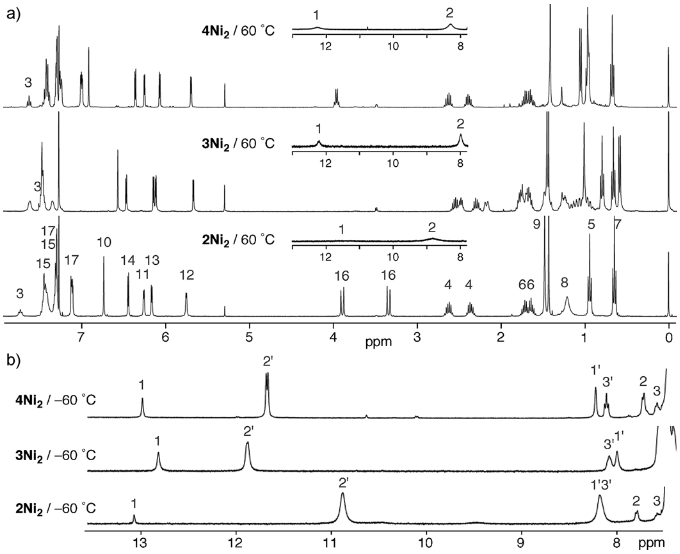
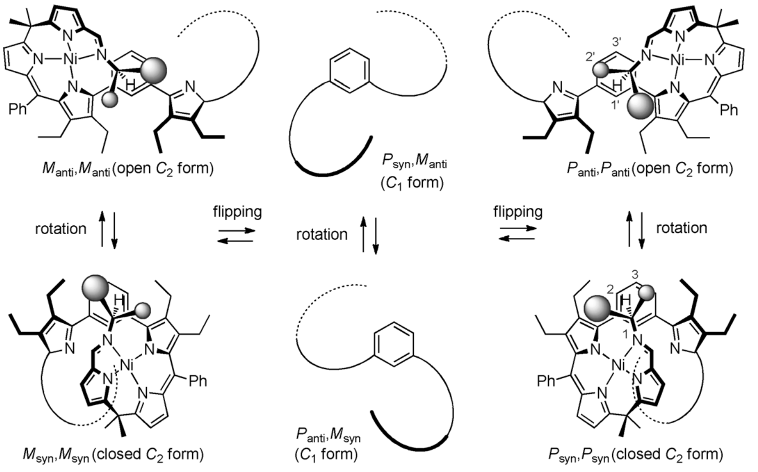


Figure 5. ^{1}H NMR spectra of **2 Ni$_2$**, **3 Ni$_2$**, and **4 Ni$_2$** in CDCl$_3$ at a) 60 and b) −60 °C (a high-frequency region). See Scheme 3 for the numbering of each signal of **2 Ni$_2$**.

ing Information). A major component shows a pair of doublets at $\delta=3.93$ and 3.50 ppm (H16′ in Figure S6 in the Supporting Information) due to the *N*-CH_2-Ph proton and one set of signals at $\delta=10.88$ (H2′) and 8.20 ppm (H1′ and H3′) due to the 1,3-phenylene protons, whereas a minor component shows another pair of doublets at $\delta=3.80$ and 3.37 ppm (H16 in Figure S6 in the Supporting Information) due to the *N*-CH_2-Ph proton and another set of signals at $\delta=13.07$ (H1), 7.82 (H2), and 7.60 ppm (H3) due to the 1,3-phenylene protons. This temperature dependency is explained in terms of an interchange between a closed C_2 form and an open C_2 form, but it is remarkable that the heterochiral C_1 form of **2 Ni$_2$** has never been observed.



Scheme 4. Conformational changes of dinickel(II) benzenehexapyrrole-α,ω-di(*N*-alkylimine) with a *R* stereogenic center at the imine moiety as in the case of **3 Ni$_2$**.

The ^{1}H NMR spectra of **3 Ni$_2$** and **4 Ni$_2$** at 60 °C, which indicates twofold symmetry, are very similar to that of **2 Ni$_2$** despite the presence of a stereogenic center at the imine unit that might otherwise induce a mixture of diastereomeric helicates (depicted in Scheme 4 and Figure 5 a, top and middle). Therefore, the helix sense of **3 Ni$_2$** and **4 Ni$_2$** is biased almost completely to one side. An unusual ^{1}H NMR chemical shift ($\delta=12.2$ ppm for **3 Ni$_2$** and **4 Ni$_2$**) of the 1,3-phenylene 2-protons (H1) suggests a direct magnetic or electronic influence of the Ni center in its proximity, as expected from the very short Ni–H distance shown in the X-ray study of **1 Ni$_2$** (Figure 2). The ^{1}H NMR spectrum of **4 Ni$_2$** at 60 °C shows one set of signals in a small fraction: a singlet at $\delta=10.78$ ppm due to the 1,3-phenylene 2-proton (H1), a triplet at $\delta=7.80$ ppm due to the 1,3-phenylene 5-proton (H3), and eight doublets at $\delta=6.56$–5.88 ppm due to the pyrrole β-protons (H11–H14 in Figure S7 in the Supporting Information). This spectral pattern is consistent with a heterochiral C_1 form. In spite of the rapid rotation of both wings around the C(benzene)–C(pyrrole) bond at 60 °C, this heterochiral C_1 form does not look C_s symmetric owing to the presence of the stereogenic center at both ends. The diastereomeric ratio of **4 Ni$_2$** estimated at 20 °C is 95:5 for C_2/C_1, and the helical sense excess is 95 % because the net helicity due to the heterochiral C_1 form should be negligible. The ^{1}H NMR signals of the major C_2 form of **2 Ni$_2$**, **3 Ni$_2$**, and **4 Ni$_2$** are split into two sets of a twofold symmetric pattern at −60 °C in ratios of 0.2:1, 1:1, and 0.6:1, respectively (see Figure 5 b and Figure S8 in the Supporting Information). In the case of **4 Ni$_2$**, a singlet at $\delta=12.97$ ppm (H1) is associated with the 1,3-phenylene 2-protons of the closed C_2 form and a doublet at $\delta=11.68$ ppm (H2′) is associated with the 1,3-phenylene 4- and 6-protons of the open C_2 form (Figure 5 b, top). Such high-frequency chemical shifts are consistent with the position of those protons being very close to the nickel center (Scheme 3). The ^{1}H NMR signals due to the 1,3-phenylene moiety of **2 Ni$_2$** and **3 Ni$_2$** could be assigned on the basis of the chemical shifts for **4 Ni$_2$**. Thus, it is concluded that an open C_2 form is preferred to a closed C_2 form at −60 °C (Figure 5 b), but a closed form is predominant at 60 °C. As discussed above, the C_2 forms interchange by the rotation of both wings around the C(benzene)–C(pyrrole) bond by keeping the helical sense. However, the flipping motion of the terminal *N*-alkylformimidoylpyrrole moiety that causes helical-chirality change is very slow.

Highly diastereoselective helicate formation

As noted above, the ^{1}H NMR spectroscopic analysis of **3 Ni$_2$** and **4 Ni$_2$** is indicative of highly diastereoselective control of the helix sense. In fact, a strong Cotton effect ($\Delta\varepsilon=517\,\mathrm{M^{-1}\,cm^{-1}}$) with a positive sign appeared at $\lambda=587$ nm in the CD spectrum of **3 Ni$_2$** (Figure 6, left). A mirror-image CD spectrum was observed for the complex **3* Ni$_2$**, which was prepared from **1 Ni$_2$** and (*S*)-1-cyclohexylethylamine. A strong Cotton effect ($\Delta\varepsilon=-386\,\mathrm{M^{-1}\,cm^{-1}}$) with a negative sign was also observed for **4 Ni$_2$** with an *S*-stereogenic center at the imine substituent. Theoretical CD spectra for a closed C_2 form, an open C_2 form, and a C_1 form were calculated by using TD-DFT with the model structures based on the X-ray studies of **1 Ni$_2$** and **1 Cu$_2$** (see Figures S14 and S15 in the Supporting Information). Both C_2 model forms of *P,P* helicity showed a strong first Cotton effect with a positive sign that is similar

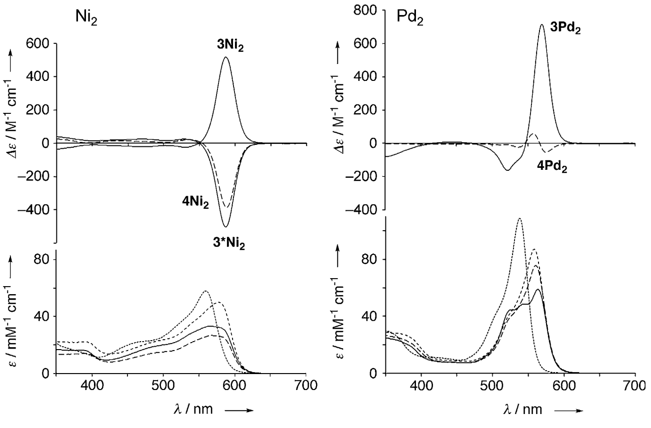


Figure 6. Left: UV/Vis (bottom) and CD (top) spectra of **1 Ni$_2$** (dotted line), **2 Ni$_2$** (broken line), **3 Ni$_2$** (solid line), **3* Ni$_2$** (solid line), and **4 Ni$_2$** (long broken line) in CH_2Cl_2. Right: spectra of the corresponding Pd complexes.

to the experimental CD spectrum of **3 Ni$_2$**, whereas the first Cotton effect of a C_1 model form is much weaker.

Complex **1 Ni$_2$** was treated with (*S*)-1-(1-naphthyl)ethylamine, (*R*)-1-(2-naphthyl)ethylamine, L-alanine ethyl ester, L-phenylalanine ethyl ester, (*R*)-2-ethylglycinol, (*S*)-phenylalaninol, (*R*)-valinol, and (*R*)-2-phenylglycinol to give the corresponding α,ω-diimines **5 Ni$_2$**–**12 Ni$_2$**, respectively, in good yields (Figure 7). These dinickel(II) complexes also showed strong CD signals with *g* factor ($\Delta\varepsilon/\varepsilon$) in the range $g = 4.6–16.8 \times 10^{-3}$ (see Table 1 and Figures S12 and S13 in the Supporting Information). Table 1 shows that the helix sense of four nickel complexes **3 Ni$_2$**, **4 Ni$_2$**, **8 Ni$_2$**, and **11 Ni$_2$** is biased to one side with more than 95 % diastereoselectivity of the C_2 form based on the ^{1}H NMR spectroscopic analysis (see Figures S9–S11 in the Supporting Information) and a *g* factor is in the range $g = 14.0–16.8 \times 10^{-3}$. Because these helicates are contaminated with a small amount of a heterochiral C_1 form, their helix-sense excess is also more than 95 %. In the cases of **7 Ni$_2$** and **9 Ni$_2$** with lower *g* factors (-8.9 and 11.2×10^{-3}), the ^{1}H NMR spectroscopic analysis indicated the presence of considerable amounts (18 and 10 %, respectively) of the minor C_2 form (denoted as C_2* in Table 1) that has an opposite helical sense to that of the major C_2 form (Figures S10 and S11 in the Supporting Information). The ^{1}H NMR spectrum of **7 Ni$_2$** shows two sets of twofold symmetric signals due to major and minor C_2 forms in the ratio of 4.3:1 (Figure 8). In contrast to L-alanine ethyl ester as an amine chiral source in **7 Ni$_2$**, L-phenylalanine ethyl ester induced full bias of the helical sense in **8 Ni$_2$**, which shows the largest *g* factor in Table 1. On the other hand, relatively weak CD signals for **5 Ni$_2$**, **10 Ni$_2$**, and **12 Ni$_2$** with *g* factors of $g = -9.4$, -4.6, and 10.9×10^{-3} are ascribed to the presence of a C_1 form in considerable amounts (i.e., 15, 48, and 32 %, respectively; Figures S10 and S11 in the Supporting Information). Although ^{1}H NMR signals due to these C_1 forms are well resolved, signals due to the C_2 forms of **5 Ni$_2$** and **12 Ni$_2$** are so broad that it was not possible to see definitely whether a minor C_2 form (C_2*) exists or not. However, the magnitude of their *g* factors suggest a very high C_2/C_2* ratio, even if both C_2 forms coexist.

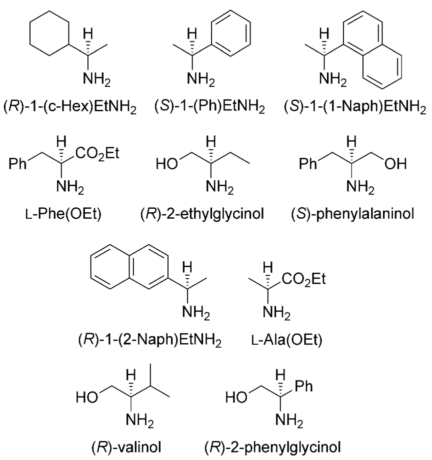


Figure 7. Optically active amines used for helicity control.

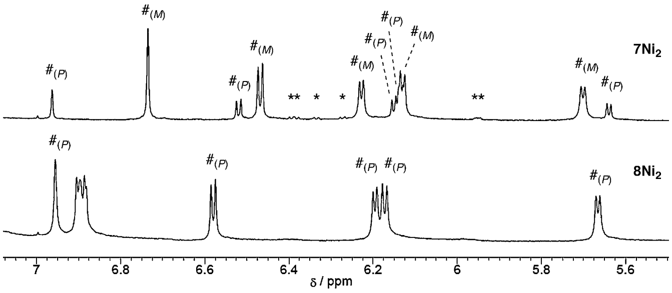


Figure 8. ^{1}H NMR spectra of **7 Ni$_2$** (top) and **8 Ni$_2$** (bottom) at 20 °C in CDCl$_3$. The formimidoyl proton (singlet) and the pyrrole β proton (doublet) of the C_2 (#) and C_1 (*) forms.

Table 1. Chiroptical properties of dinuclear Pd^{II} and Ni^{II} complexes of benzenehexapyrrole-α,ω-diimines and their diastereomeric ratio ($C_2/C_1/C_2$*).

	Amine[a]	Vis/CD (1st CE)[b] λ_{max} [nm]	(θ_{mdeg}/A_{abs}) [$g \times 10^3$][c]	Helical sense (d.r. $C_2/C_1/C_2$*)[d]
3 Pd$_2$	(*R*)-1-(c-Hex)EtNH$_2$	564/570	399/12.1	*P* (≈75/≈25/tr)
4 Pd$_2$	(*S*)-1-(Ph)EtNH$_2$	560/575	−24/−0.73	*M* (30 > /≈70/–)[e]
3 Ni$_2$	(*R*)-1-(c-Hex)EtNH$_2$	566/587	514/15.6	*P* (> 96/4 > /–)
3* Ni$_2$	(*S*)-1-(c-Hex)EtNH$_2$	566/587	−501/−15.2	*M* (> 96/4 > /–)
4 Ni$_2$	(*S*)-1-(Ph)EtNH$_2$	567/588	−487/−14.5	*M* (95/5/–)
5 Ni$_2$	(*S*)-1-(1-Naph)EtNH$_2$	579/589	−311/−9.4	*M* (85 > /15/–)[e]
6 Ni$_2$	(*R*)-1-(2-Naph)EtNH$_2$	573/589	437/13.3	*P* (94/4/2)
7 Ni$_2$	L-Ala(OEt)	565/589	−292/−8.9	*M* (77/5/18)
8 Ni$_2$	L-Phe(OEt)	564/586	553/16.8	*P* (> 98/2 > /–)
9 Ni$_2$	(*R*)-2-ethylglycinol	565/587	369/11.2	*P* (88/2/10)
10 Ni$_2$	(*S*)-phenylalaninol	573/590	−151/−4.6	*M* (48/48/4)
11 Ni$_2$	(*R*)-valinol	568/590	−462/−14.0	*M* (97/3/–)
12 Ni$_2$	(*R*)-2-phenylglycinol	578/588	360/10.9	*P* (68 > /32/–)[e]

[a] Amines used for the imine formation. [b] The λ_{max} value measured in CH$_2$Cl$_2$. [c] Anisotropic factor $g = \Delta\varepsilon/\varepsilon = \theta_{mdeg}/32\,980(A_{abs})$ measured in CH$_2$Cl$_2$. [d] The diastereomeric ratio (d.r.) [%] of a major C_2, C_1, and a minor C_2 (C_2*) form was estimated on the basis of ^{1}H NMR spectroscopy analysis performed in CDCl$_3$ at 20 °C. [e] The C_2/C_2* ratio was not determined exactly due to very broad ^{1}H NMR signals at 20 °C.

As a C_1 form seems to contribute little to the whole chiroptical property due to its heterochiral nature, the diastereoselectivity of the major C_2 form would be directly related to the CD intensity, except for **7 Ni$_2$** and **9 Ni$_2$**. It is true that the magnitude of the *g* factor is more or less dependent on the structure of the amine used, but the observed *g* factor is roughly proportional to the diastereoselectivity of the major C_2 form determined by NMR spectroscopic analysis. In most cases, the *R* amine preferentially induces *P*-helix sense; however, exceptions to this relationship are **8 Ni$_2$** and **11 Ni$_2$**. The structure models for **3 Ni$_2$** in Scheme 4 indicate that the sterically most demanding ligand at the *R* stereogenic center undergoes steric constraint from the twisted dipyrrylbenzene unit to a greater extent in the *M*-helical C_2 forms than in the *P*-helical C_2 forms. This behavior explains the helical sense preferred for **3 Ni$_2$**–**7 Ni$_2$**, in which a methyl group and a larger substituent are at the stereogenic center. In the case of **8 Ni$_2$**–**12 Ni$_2$**, in which bulky and polar ligands are at the stereogenic center, the helix sense is quite sensitive to the nature of each ligand and the combination of these ligands. Consequently, the amino acid ester and the amino alcohol that lead to a very high diastereoselective control of helix sense have been found. The ^{1}H NMR spectra of **3 Pd$_2$** and **4 Pd$_2$** are not so simple as those of **3 Ni$_2$** and **4 Ni$_2$** because of the lower diastereoselectivity and signal-broadening phenomenon (see Figure S5 in the Supporting Information). A helical C_2 form is predominant for **3 Pd$_2$** with approximately 75 % diastereoselectivity, but a heterochiral C_1 form is predominant for **4 Pd$_2$** with approximately 70 % diastereoselectivity (Table 1). Consequently, the CD signal of **4 Pd$_2$** is very weak (Figure 6, right). Because the average Pd–L bond length is longer by 0.14 Å than the average Ni–L bond length if **1′ Pd$_2$** and **1 Ni$_2$** are compared,[17a] the formimidoyltripyrrolic coordination plane of the palladium center is larger than that of the nickel center. It is remarkable that such geometrical difference between the palladium and nickel centers sensitively affects their diastereoselectivity for the helical conformations;

furthermore, the very high ratios of C_2/C_1 and $C_2/C_2{}^*$ were demonstrated for **2 Ni$_2$**, **3 Ni$_2$**, and **4 Ni$_2$**.

Conclusion

The dinuclear metal complexes of open chain benzenehexapyrrole-α,ω-dialdehyde have been synthesized and X-ray crystallographic studies revealed a helical C_2 form for the dinickel(II) complex and a heterochiral C_1 form for the dicopper(II) complex. The conformational changes of the corresponding α,ω-diimine complexes were investigated by NMR spectroscopic analysis. The presence of two rotational axes in the central 1,3-dipyrrylbenzene unit allows fast conformational changes and keeps the helical sense. This outcome led to the fast interconversion between an open C_2 form and a closed C_2 form and also averaged the magnetic circumstances of both wings in the C_1 form of **2 Pd$_2$**. The helical sense of each metal site is inverted by flipping of the terminal formimidoylpyrrole unit. Such helicity change is very slow, but actually led to a change in the C_2/C_1 ratio of **2 Pd$_2$** with temperature. The helix sense of dinickel(II) benzenehexapyrrole-α,ω-diimines was biased to one side with high diastereoselectivity by using a variety of chiral amines, such as aliphatic amines, aryl-substitued alkylamines, amino acid esters, and amino alcohols. It is remarkable that the nickel complexes are far superior to the corresponding palladium complexes in the diastereoselective control of the helix sense. Coupling two helical wings of the metal coordination plane through an appropriate linker led to a high helix-sense bias with a strong CD signal due to the exciton coupling between both wings. The generated single helicates are stable enough to be purified by using chromatography, but the chiral auxiliary is easily exchangeable, which is advantageous in developing a library of enantiopure helicates with a wide variety of functions.

Experimental Section

Synthesis of 1 Ni$_2$: A mixture of benzenehexapyrrole-α,ω-dialdehyde (**1**; 50 mg, 54 μmol) and Ni(OAc)$_2$·4 H$_2$O (36 mg, 0.14 mmol) in CH$_2$Cl$_2$ (6 mL) and MeOH (2 mL) was stirred for 2 h at room temperature, and the reaction mixture turned from orange to red. The solvents were removed under vacuum and column chromatography on alumina afforded a red fraction with CH$_2$Cl$_2$ as the eluent. Recrystallization from CH$_2$Cl$_2$/MeOH gave a red precipitate of **1 Ni$_2$** in 94 % yield. ^{1}H NMR (400 MHz, CDCl$_3$, 20 °C): $\delta = 9.24$ (s, 1 H; 1,3-phenylene-2-*H*), 8.58 (d, $J = 7.6$ Hz, 2 H; 1,3-phenylene-4,6-*H*), 7.60 (t, $J = 7.6$ Hz, 1 H; 1,3-phenylene-5-*H*), 7.52–7.38 (m, 10 H; *meso*-phenyl-*H*), 7.01 (s, 2 H; C*H*O), 6.71, 6.11 (2×d, $J = 4.2$ Hz, 2×2 H; pyrrole-β-*H*), 6.29, 6.25 (2×d, $J = 4.2$ Hz, 2×2 H; pyrrole β-*H*), 2.51 (br s, 4 H; CH_2CH$_3$), 1.68 (q, $J = 7.6$ Hz, 4 H; CH_2CH$_3$), 1.62 (s, 12 H; C(CH_3)$_2$), 0.73, 0.67 ppm (2×t, $J = 7.2$ Hz, 2×6 H; CH$_2$CH_3); UV/Vis (CH$_2$Cl$_2$): λ_{max} ($\log\varepsilon$) = 285 (4.56), 322 (4.57), 465 (sh, 4.34), 560 nm (4.76); MS (ESI): *m*/*z* calcd for $C_{60}H_{56}N_6O_2Ni_2 + H^+$: 1009.32; found: 1009.32; elemental analysis (%) calcd for $C_{60}H_{56}N_6O_2Ni_2{\cdot}CH_2Cl_2$: C 66.88, H 5.34, N 7.67; found: C 67.13, H 5.45, N 7.65.

Synthesis of 3 Ni$_2$: A mixture of **1 Ni$_2$** (20 mg, 18 μmol), (*R*)-(−)-1-cyclohexylethylamine (160 μL) and dry THF (5 mL) was stirred for 6 h under reflux, and the reaction mixture turned red. After the solvent was removed under vacuum, column chromatography on alumina with CH$_2$Cl$_2$ as the eluent gave a red fraction. Recrystallization from CH$_2$Cl$_2$/MeOH afforded a red powder of dinickel(II) benzenehexapyrrole-α,ω-di[*N*-(*R*)-1-cyclohexylethylimine] (**3 Ni$_2$**) in 78 % yield. ^{1}H NMR (400 MHz, CDCl$_3$, 60 °C): $\delta = 12.2$ (br s, 1 H; 1,3-phenylene-2-*H*), 8.0 (br s, 2 H; 1,3-phenylene-4,6-*H*), 7.46 (t, $J = 7.8$ Hz, 1 H; 1,3-phenylene-5-*H*), 7.58, 7.32 (2×br, 2×2 H; phenyl-*H*), 7.46–7.40 (m, 6 H; phenyl-*H*), 6.54 (s, 2 H; C*H*=*N*-CHMe), 6.44, 6.12 (2×d, $J = 4.2$ Hz, 2×2 H; pyrrole-β-*H*), 6.09, 5.64 (2×d, $J = 3.7$ Hz, 2×2 H; pyrrole β-*H*), 2.47 (quin, $J = 6.0$ Hz, 2 H; *N*-C*H*Me), 2.16 (d, $J = 12.0$ Hz, 2 H; cyclohexyl-*H*), 1.80–1.60 (m, 6 H; cyclohexyl-*H*), 1.46 (m, 4 H; cyclohexyl-*H*), 1.30–1.18 (m, 4 H; cyclohexyl-*H*), 1.18–0.90 (m, 6 H; cyclohexyl-*H*), 2.54, 2.28 (2×m, 2×2 H; CH_2CH$_3$), 1.76, 1.65 (2×m, 2×2 H; CH_2CH$_3$), 1.44 (s, 6 H; C(CH_3)$_2$), 1.00 (br s, 6 H; C(CH_3)$_2$), 0.79, 0.66 (2×t, $J = 7.4$ Hz, 2×6 H; CH$_2$CH_3), 0.58 ppm (d, $J = 6.8$ Hz, 6 H; *N*-CHCH_3); UV/Vis (CH$_2$Cl$_2$): λ_{max} ($\log\varepsilon$) = 291 (sh, 4.65), 307 (4.67), 386 (4.21), 495 (sh, 4.29), 566 (4.52), 580 nm (sh, 4.51); CD (CH$_2$Cl$_2$): λ_{max} ($\Delta\varepsilon$) = 319 (−108.6), 587 nm (517.3); MS (ESI): *m*/*z* calcd for $C_{76}H_{86}N_8Ni_2 + H^+$: 1227.57; found: 1227.72; elemental analysis (%) calcd for $C_{76}H_{86}N_8Ni_2{\cdot}2\,H_2O$: C 72.16, H 7.17, N 8.86; found: C 72.07, H 6.98, N 8.79.

Acknowledgements

This work was supported by a Grant-in-Aid for Scientific Research (no. 24550050) from the Japan Society for the Promotion of Science (JSPS).

Keywords: chirality · helical structures · metalation · oligopyrroles · porphyrinoids

[1] a) J.-M. Lehn, A. Rigault, J. Siegel, J. Harrowfield, B. Chevrier, D. Moras, *Proc. Natl. Acad. Sci. USA* **1987**, *84*, 2565 – 2569; b) M. Albrecht, *Chem. Rev.* **2001**, *101*, 3457 – 3497; c) C. Piguet, G. Bernardinelli, G. Hopfgartner,

Chem. Rev. **1997**, *97*, 2005 – 2062; d) D. J. Hill, M. J. Mio, R. B. Prince, T. S. Hughes, J. S. Moore, *Chem. Rev.* **2001**, *101*, 3893 – 4011; e) G. Maayan, *Eur. J. Org. Chem.* **2009**, 5699 – 5710; f) M. Berg, A. Lützen, in *Metallofoldamers, Supramolecular Architectures from Helicates to Biomimetics* (Eds: G. Maayan, M. Albrecht), Wiley, Chichester, **2013**, pp. 125 – 158.

[2] a) A. von Zelewsky, *Coord. Chem. Rev.* **1999**, *190 – 192*, 811 – 825; b) O. Mamula, A. von Zelewsky, *Coord. Chem. Rev.* **2003**, *242*, 87 – 95; c) U. Knof, A. von Zelewsky, *Angew. Chem. Int. Ed.* **1999**, *38*, 302 – 322; *Angew. Chem.* **1999**, *111*, 312 – 333; d) C. He, Y. Zhao, D. Guo, Z. Lin, C. Duan, *Eur. J. Inorg. Chem.* **2007**, 3451 – 3463; e) E. C. Constable, *Chem. Soc. Rev.* **2013**, *42*, 1637 – 1651; f) J. Crassous, *Chem. Commun.* **2012**, *48*, 9684 – 9692; g) S. E. Howson, P. Scott, *Dalton Trans.* **2011**, *40*, 10268 – 10277.

[3] a) G. Baum, E. C. Constable, D. Fenske, C. E. Housecroft, T. Kulke, *Chem. Eur. J.* **1999**, *5*, 1862 – 1873; b) G. Baum, E. C. Constable, D. Fenske, C. E. Housecroft, T. Kulke, M. Neuburger, M. Zehnder, *J. Chem. Soc. Dalton Trans.* **2000**, 945 – 959; c) G. Baum, E. C. Constable, D. Fenske, C. E. Housecroft, T. Kulkea, *Chem. Commun.* **1998**, 2659 – 2660; d) C.-S. Tsang, H.-L. Yeung, W.-T. Wong, H.-L. Kwong, *Chem. Commun.* **2009**, 1999 – 2001; e) C. Provent, S. Hewage, G. Brand, L. J. Charbonnière, A. F. Williams, G. Bernardinelli, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1287 – 1289; *Angew. Chem.* **1997**, *109*, 1346 – 1348; f) C. Provent, E. Rivara-Minten, S. Hewage, G. Brunner, A. F. Williams, *Chem. Eur. J.* **1999**, *5*, 3487 – 3494; g) S. E. Howson, A. Bolhuis, V. Brabec, G. J. Clarkson, J. Malina, A. Rodger, P. Scott, *Nat. Chem.* **2012**, *4*, 31 – 36; h) L. Cardo, V. Sadovnikova, S. Phongtongpasuk, N. J. Hodges, M. J. Hannon, *Chem. Commun.* **2011**, *47*, 6575 – 6577; i) F. Stomeo, C. Lincheneau, J. P. Leonard, J. E. O'Brien, R. D. Peacock, C. P. McCoy, T. Gunnlaugsson, *J. Am. Chem. Soc.* **2009**, *131*, 9636 – 9637; j) M. Albrecht, *Synlett* **1996**, 565 – 567.

[4] a) C. J. Carrano, K. N. Raymond, *J. Am. Chem. Soc.* **1978**, *100*, 5371 – 5374; b) W. Zarges, J. Hall, J.-M. Lehn, C. Bolm, *Helv. Chim. Acta* **1991**, *74*, 1843 – 1853; c) H. Mürner, A. von Zelewsky, G. Hopfgartner, *Inorg. Chim. Acta* **1998**, *271*, 36 – 39; d) U. Kiehne, A. Lützen, *Org. Lett.* **2007**, *9*, 5333 – 5336; e) J. Bunzen, T. Bruhn, G. Bringmann, A. Lützen, *J. Am. Chem. Soc.* **2009**, *131*, 3621 – 3630; f) E. J. Enemark, T. D. P. Stack, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 996 – 998; *Angew. Chem.* **1995**, *107*, 1082 – 1084; g) M. Albrecht, I. Janser, S. Kamptmann, P. Weis, B. Wibbeling, R. Fröhlich, *Dalton Trans.* **2004**, 37 – 43; h) M. Albrecht, S. Schmid, M. deGroot, P. Weis, R. Fröhlich, *Chem. Commun.* **2003**, 2526 – 2527; i) J. Hamblin, L. J. Childs, N. W. Alcock, M. J. Hannon, *J. Chem. Soc. Dalton Trans.* **2002**, 164 – 169; j) V. Amendola, L. Fabbrizzi, C. Mangano, P. Pallavicini, E. Roboli, M. Zema, *Inorg. Chem.* **2000**, *39*, 5803 – 5806; k) S. G. Telfer, R. Kuroda, T. Sato, *Chem. Commun.* **2003**, 1064 – 1065.

[5] a) Z. Dong, S. Bai, G. P. A. Yap, J. M. Fox, *Chem. Commun.* **2011**, *47*, 3781 – 3783; b) Z. Dong, R. J. Karpowicz, Jr., S. Bai, G. P. A. Yap, J. M. Fox, *J. Am. Chem. Soc.* **2006**, *128*, 14242 – 14243; c) H. Miyake, K. Yoshida, H. Sugimoto, H. Tsukube, *J. Am. Chem. Soc.* **2004**, *126*, 6524 – 6525; d) H. Miyake, M. Ueda, S. Murota, H. Sugimoto, H. Tsukube, *Chem. Commun.* **2012**, *48*, 3721 – 3723; e) S. Akine, S. Hotate, T. Nabeshima, *J. Am. Chem. Soc.* **2011**, *133*, 13868 – 13871; f) S. Akine, S. Sairenji, T. Taniguchi, T. Nabeshima, *J. Am. Chem. Soc.* **2013**, *135*, 12948 – 12951.

[6] R. B. Prince, T. Okada, J. S. Moore, *Angew. Chem. Int. Ed.* **1999**, *38*, 233 – 236; *Angew. Chem.* **1999**, *111*, 245 – 249.

[7] a) H.-L. Kwong, H.-L. Yeung, W.-S. Leea, W.-T. Wong, *Chem. Commun.* **2006**, 4841 – 4843; b) H.-L. Yeung, W.-Y. Wong, C.-Y. Wong, H.-L. Kwong, *Inorg. Chem.* **2009**, *48*, 4108 – 4117; c) C. M. Chamchoumis, P. G. Potvin, *J. Chem. Soc. Dalton Trans.* **1999**, 1373 – 1374; d) P. K.-K. Ho, S.-M. Peng, J.-Y. Wong, C.-M. Che, *J. Chem. Soc. Dalton Trans.* **1996**, 1829 – 1834; e) E. C. Constable, M. D. Ward, D. A. Tocher, *J. Chem. Soc. Dalton Trans.* **1991**, 1675 – 1683; f) C. J. Cathey, E. C. Constable, M. J. Hannon, D. A. Tocher, M. D. Ward, *J. Chem. Soc. Chem. Commun.* **1990**, 621 – 622; g) P. K.-K. Ho, K.-K. Cheung, S.-M. Peng, C.-M. Che, *J. Chem. Soc. Dalton Trans.* **1996**, 1411 – 1417; h) Y.-J. Fu, W.-Y. Sun, W.-N. Dai, M.-H. Shu, F. Xue, D.-F. Wang, T. C. W. Mak, W.-X. Tang, H.-W. Hu, *Inorg. Chim. Acta* **1999**, *290*, 127 – 132.

[8] S. Wezenberg, G. Salassa, E. Escudero-Adán, J. Benet-Buchholz, A. Kleij, *Angew. Chem. Int. Ed.* **2011**, *50*, 713 – 716; *Angew. Chem.* **2011**, *123*, 739 – 742.

[9] a) G. A. Hembury, V. V. Borovkov, Y. Inoue, *Chem. Rev.* **2008**, *108*, 1 – 73; b) N. Berova, G. Pescitelli, A. G. Petrovic, G. Proni, *Chem. Commun.* **2009**, 5958 – 5980; c) C. Wolf, K. W. Bentley, *Chem. Soc. Rev.* **2013**, *42*, 5408 – 5424.

[10] a) S. E. Boiadjiev, D. A. Lightner, *J. Am. Chem. Soc.* **2000**, *122*, 378 – 383; b) G. D. Pantos, M. S. Rodríguez-Morgade, T. Torres, V. M. Lynch, J. L. Sessler, *Chem. Commun.* **2006**, 2132 – 2134; c) Y. Haketa, Y. Bando, K. Takaishi, M. Uchiyama, A. Muranaka, M. Naito, H. Shibaguchi, T. Kawai, H. Maeda, *Angew. Chem. Int. Ed.* **2012**, *51*, 7967 – 7971; *Angew. Chem.* **2012**, *124*, 8091 – 8095; d) Y. Haketa, H. Maeda, *Chem. Eur. J.* **2011**, *17*, 1485 – 1492.

[11] a) M. Bröring, in *Handbook of Porphyrin Science, Vol. 8* (Eds: K. M. Kadish, K. M. Smith, R. Guilard), World Scientific, Singapore, **2010**, pp. 343 – 501, and references therein; b) T. E. Wood, A. Thompson, *Chem. Rev.* **2007**, *107*, 1831 – 1861; c) G. Struckmeier, U. Thewalt, J.-H. Fuhrhop, *J. Am. Chem. Soc.* **1976**, *98*, 278 – 279; d) M. Bröring, C. D. Brandt, J. Lex, H.-U. Humpf, J. Bley-Escrich, J.-P. Gisselbrecht, *Eur. J. Inorg. Chem.* **2001**, 2549 – 2556; e) A. Al-Sheikh-Ali, K. S. Cameron, T. S. Cameron, K. N. Robertson, A. Thompson, *Org. Lett.* **2005**, *7*, 4773 – 4775; f) A. Al-Sheikh-Ali, R. E. Benson, S. Blumentritt, T. S. Cameron, A. Linden, D. Wolstenholme, A. Thompson, *J. Org. Chem.* **2007**, *72*, 4947 – 4952; g) T. Mizutani, S. Yagi, T. Morinaga, T. Nomura, T. Takagishi, S. Kitagawa, H. Ogoshi, *J. Am. Chem. Soc.* **1999**, *121*, 754 – 759; h) T. Mizutani, S. Yagi, A. Honmaru, S. Murakami, M. Furusyo, T. Takagishi, H. Ogoshi, *J. Org. Chem.* **1998**, *63*, 8769 – 8784; i) T. Mizutani, S. Yagi, A. Honmaru, H. Ogoshi, *J. Am. Chem. Soc.* **1996**, *118*, 5318 – 5319; j) T. Mizutani, N. Sakai, S. Yagi, T. Takagishi, S. Kitagawa, H. Ogoshi, *J. Am. Chem. Soc.* **2000**, *122*, 748 – 749.

[12] a) M. Bröring, C. D. Brandt, E. Cónsul-Tejero, *J. Organomet. Chem.* **2005**, *690*, 5290 – 5299; b) M. Bröring, E. Cónsul-Tejero, *Z. Anorg. Allg. Chem.* **2005**, *631*, 1793 – 1798.

[13] a) T. E. Wood, N. D. Dalgleish, E. D. Power, A. Thompson, X. Chen, Y. Okamoto, *J. Am. Chem. Soc.* **2005**, *127*, 5740 – 5741; b) T. E. Wood, A. C. Ross, N. D. Dalgleish, E. D. Power, A. Thompson, X. Chen, Y. Okamoto, *J. Org. Chem.* **2005**, *70*, 9967 – 9974; c) Y. Zhang, A. Thompson, S. J. Rettig, D. Dolphin, *J. Am. Chem. Soc.* **1998**, *120*, 13537 – 13538; d) Q. Chen, Y. Zhang, D. Dolphin, *Tetrahedron Lett.* **2002**, *43*, 8413 – 8416; e) A. Thompson, D. Dolphin, *J. Org. Chem.* **2000**, *65*, 7870 – 7877; f) L. Ma, J.-Y. Shin, B. O. Patrick, D. Dolphin, *CrystEngComm* **2008**, *10*, 1531 – 1533; g) W. S. Sheldrick, J. Engel, *J. Chem. Soc. Chem. Commun.* **1980**, 5 – 6; h) C. Mwakwari, F. R. Fronczek, K. M. Smith, *Chem. Commun.* **2007**, 2258 – 2260; i) R. G. Khoury, L. Jaquinod, K. M. Smith, *Tetrahedron* **1998**, *54*, 2339 – 2346; j) M. Bröring, S. Link, C. D. Brandt, E. Cónsul-Tejero, *Eur. J. Inorg. Chem.* **2007**, 1661 – 1670.

[14] Z. Zhang, D. Dolphin, *Chem. Commun.* **2009**, 6931 – 6933.

[15] A. Thompson, S. J. Rettig, D. Dolphin, *Chem. Commun.* **1999**, 631 – 632.

[16] a) S. Yagi, R. Yamada, T. Takagishi, N. Sakai, H. Takahashi, T. Mizutani, S. Kitagawa, H. Ogoshi, *Chem. Commun.* **1999**, 911 – 912; b) S. Yagi, K. Hamakubo, S. Ikawa, H. Nakazumi, T. Mizutani, *Tetrahedron* **2008**, *64*, 10598 – 10604.

[17] a) C. Eerdun, S. Hisanaga, J. Setsune, *Angew. Chem. Int. Ed.* **2013**, *52*, 929 – 932; *Angew. Chem.* **2013**, *125*, 963 – 966; b) S. Saito, K. Furukawa, A. Osuka, *J. Am. Chem. Soc.* **2010**, *132*, 2128 – 2129; c) K. Yamanishi, M. Miyazawa, T. Yairi, S. Sakai, N. Nishina, Y. Kobori, M. Kondo, F. Uchida, *Angew. Chem. Int. Ed.* **2011**, *50*, 6583 – 6586; *Angew. Chem.* **2011**, *123*, 6713 – 6716; d) M. Bröring, S. Link, S. Köhler, E. Cónsul-Tejero, *Z. Anorg. Allg. Chem.* **2004**, *630*, 817 – 820.

[18] a) J. Setsune, A. Tanabe, J. Watanabe, S. Maeda, *Org. Biomol. Chem.* **2006**, *4*, 2247 – 2252; b) J. Setsune, M. Toda, K. Watanabe, P. K. Panda, T. Yoshida, *Tetrahedron Lett.* **2006**, *47*, 7541 – 7544.

[19] D. K. Dogutan, M. Ptaszek, J. S. Lindsey, *J. Org. Chem.* **2007**, *72*, 5008 – 5011.

[20] CCDC 970642 (**1 Ni$_2$**) and CCDC 970643 (**1 Cu$_2$**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data request/cif. Experimental procedures, details on the X-ray diffraction studies, and spectroscopic data of all the compounds are provided in the Supporting Information.

[21] A. Bondi, *J. Phys. Chem.* **1964**, *68*, 441 – 451.

Received: August 8, 2014
Published online on November 4, 2014