

## Design, Synthesis, and Characterization of Binuclear Ni(II) Complexes with Inherent Helical Chirality

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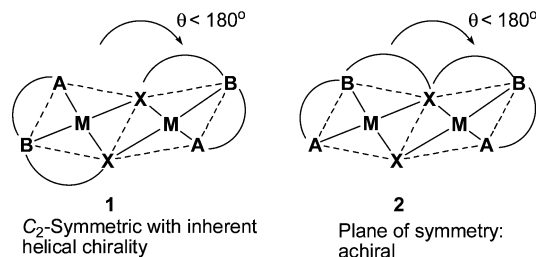
Received October 9, 2006; E-mail: vadim@ou.edu

The helix is an old and ever fascinating example of conformational chirality. Its importance in nature is exemplified by various biological molecules such as nucleic acids<sup>1</sup> and peptides<sup>2</sup> in which the helicity predetermines their higher-order structures and elaborate biological functions.<sup>3</sup> A huge scientific effort has been devoted to understand<sup>4</sup> and mimic<sup>5</sup> natural helical chirality. A great variety of molecules with a helical structure have been prepared and used in virtually all areas of physical sciences, most notably in catalysis,<sup>6</sup> supramolecular chemistry,<sup>7</sup> and chiral nanotechnology.<sup>8</sup> In particular, sterically induced out-of-plane deformations in mononuclear<sup>9</sup> and polynuclear complexes of d<sup>8</sup> transition metals<sup>10</sup> were found to be efficient approaches in making helical molecules of these types. On the other hand, another type of nonplanar geometry which can give rise to helical conformation is provided by the bending of a C<sub>2</sub>-symmetric molecule at the line perpendicular to its axis of symmetry, as shown in Figure 1. However, this type of nonplanar topology is synthetically challenging and remains virtually unexplored.<sup>11</sup>

Here we describe a general synthetic approach to a novel type of double bridged binuclear complexes with unusually distorted square planar coordination geometry around the Ni(II) atoms. These molecules are inherently helically chiral as a result of their folded, ridge–tile conformation. These complexes are neutral, well-soluble in organic solvents, and remarkably chemically and configurationally stable: properties which allow for a systematic study of their unknown chemical, physical and chiroptical properties.

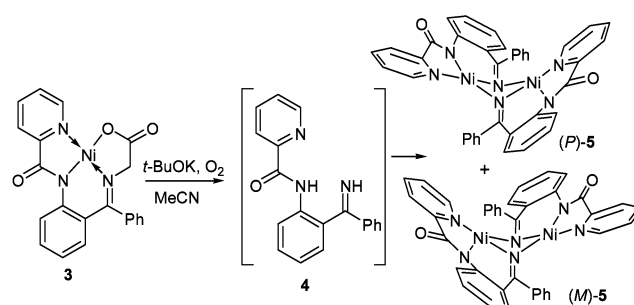
To realize the desired folded, ridge–tile-like topological mode of nonplanarity we envisioned that such conformation could be possible if two C<sub>2</sub>-symmetric metal tetra-coordinated planes in a binuclear complex can be bent along the X,X (Figure 1). However, from the synthetic standpoint at least three challenging issues of this type of chemical architecture should be addressed: first, to control the chemoselectivity of a metal-chelation providing for preferential formation of C<sub>2</sub>-symmetric complex **1** over achiral dimer **2**; second, to make the metal-coordinated planes adopt a bent and potentially more stereochemically congested arrangement versus planar and therefore achiral structure; third, to make such ridge–tile deformation to be configurationally stable, thus preventing its racemization via rapid inversion. To address the first issue, we assumed that X, B, and A elements might be covalently bonded comprising a whole tridentate ligand. Next, the required bending can be provided by repulsive steric interactions between a substituent on X of one ligand with the A element of another ligand. Finally, to provide for the configurational stability of **1**, the bridging elements X should have a planar geometry like in sp<sup>2</sup>-hybridized nitrogen atom. On top of these structural features, further requirements for models **1** to be chemically stable and neutral were also incorporated in our design.

In connection with our project on asymmetric synthesis of  $\alpha$ -amino acids,<sup>12</sup> we found that tridentate ligands **4** (Scheme 1) possessing the desired structural features can be generated in situ



**Figure 1.** 1. Two modes of bending (angle  $\theta$ ) of two square planar-coordinated ligands along the X–X axis.

## Scheme 1

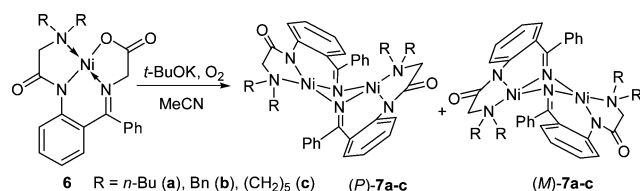


(up to 6%) by treatment of Ni(II) complex of glycine **3** with NaOH in DMF.<sup>13</sup> Under optimized conditions, using acetonitrile as a solvent and *t*-BuOK as a base and running the reaction in open air at room temperature, a quantitative transformation of the starting complex **3** into binuclear complex **5** was observed.

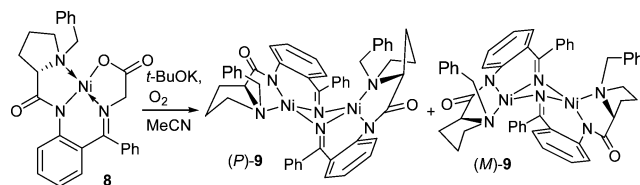
Crystallographic analysis of product **5** revealed its desired folded, ridge–tile-like topology via bending the Ni(II) coordination planes along the bridging imine nitrogens. The angle of bending  $\theta$  was found to be 138.86(17)° thus putting the Ni(II) atoms in close proximity to each other (2.6672(6) Å) to assume a Ni<sub>2</sub>Ni bond.<sup>14,15</sup> From the stereochemical stand point, the unit cell of the crystals of compound **5** contains both enantiomers (*P*)-**5** and (*M*)-**5** of right- and left-handed helicity. It is also interesting to mention that the distance between the para hydrogens of the picolinic acid moieties in the enantiomers **5** is very close to 1 nm (1.0071).

Since picolinic acid derived compound **5** had some limited degree of structural flexibility and potential functionalization, we decided to explore our recently developed modular approach for preparation of achiral glycine Ni(II) complexes<sup>12b</sup> for synthesis of various molecules with ridge–tile-like topological mode of nonplanarity and therefore helical chirality. We found that the glycine derivatives **6** derived from the dibutyl-, dibenzyl-, and picolinamine modules, under the standard conditions smoothly produced the corresponding folded binuclear complexes **7** as racemic mixtures of (*P*)- and (*M*)-enantiomers (Scheme 2). Interestingly, the bending angles  $\theta$  and the deviation from the planarity of the bridging imine nitrogens were quite similar to that of the sp<sup>2</sup> containing picolinic acid derived complex **5**. Thus, bending angles  $\theta$  for **7a–c** were found to be:

Scheme 2



Scheme 3



132.25(8)° (a), 137.21(15)° (b), and 130.83(8)° (c), respectively. The deviation of the bridging imine nitrogens was ranging from 0.322 to 0.882 Å and the Ni,Ni distances were 2.6427(4) (a), 2.6952(9) (b), 2.6156(3) Å (c).

Finally to prepare this new type of helical molecules in enantiomerically pure form and taking advantage of the modular nature of our design, we synthesized chiral complex **8** and subjected it to the standard dimerization procedure. The application of chiral complex **8** resulted in formation of two diastereomers (*M,S,S*)-**9** and (*P,S,S*)-**9**, isolated in quantitative yield and in a ratio of 21:79, respectively (Scheme 3). The diastereomers (*P,S,S*)-**9** and (*M,S,S*)-**9** were easily separated by regular column chromatography on silica gel and fully characterized including X-ray crystallographic studies. As it follows from the structure of the diastereomer (*M,S,S*)-**9**, the corresponding *N*-benzyl groups are in close proximity to each other rendering (*M,S,S*)-**9** relatively unstable as compared to major diastereomer (*P,S,S*)-**9** in which the *N*-benzyl groups point away from each other. This different mode of stereochemical interactions in the diastereomers (*P,S,S*)-**9** and (*M,S,S*)-**9** is probably responsible for some geometric differences between them. Thus, both diastereomers exhibited significant folded, ridge–tile structures, however the torsion angles  $\theta$  between two square planar faces were 132.80–(8)° for (*P,S,S*)-**9** and 136.02(7)°, slightly larger, for (*M,S,S*)-**9**. Moreover, as a result of different torsion angles  $\theta$ , short Ni–Ni distances were found to be also different, measuring 2.6341(3) Å for (*P,S,S*)-**9** and 2.6813(4) Å for (*M,S,S*)-**9**. Examination of the chiroptical properties, such as CD spectra and optical rotation, revealed that diastereomers (*P,S,S*)-**9** and (*M,S,S*)-**9** behave rather as helical pseudo-enantiomers. Thus, extraordinary large  $[\alpha]_D$  values of  $-1022$  for (*M,S,S*)-**9** and  $+1222$  for (*P,S,S*)-**9** as well as strong and opposite Cotton effects in the CD spectra indicated that helical chirality virtually completely overwhelmed the two stereogenic centers in the compounds (*P,S,S*)-**9** and (*M,S,S*)-**9**.<sup>16</sup>

Finally, to demonstrate thermal stability of these ridge–tile shaped compounds, we took <sup>1</sup>H NMR spectra of complex **7a** in toluene. Thus, heating compound **7a** gradually from ambient temperature to 100 °C did not result in any changes or broadening of peaks, indicating the absence of any transformations.

In summary, we report the first example of design and synthesis of helical molecules using ridge–tile-like topological mode of nonplanarity. The modular nature of the design of starting glycine derivatives renders this approach general for the preparation of structurally varied and functionalized derivatives of this type of

bended molecules with inherent helical chirality. Moreover, we demonstrated that the introduction of elements of central chirality in the design allowed preparation and optical separation of the helical stereoisomers but contributed little to their chiroptical properties. Chemical stability as well as the rigid and stable ridge–tile-like structure of these helical molecules was also demonstrated. Taking into account these structural features, one can expect that these novel type of helical molecules might be useful structural elements in macromolecular design or can be used as chiral nanoscale building blocks in the field of chiral nanotechnology.

**Acknowledgment.** The authors are thankful to Dr Takada (JASCO corp.) for the CD spectra. This work was supported by the Department of Chemistry and Biochemistry, University of Oklahoma. The authors gratefully acknowledge generous financial support from Central Glass Company (Tokyo, Japan) and Ajinomoto Company (Tokyo, Japan).

**Supporting Information Available:** Experimental procedures, characterizations of new compounds, and crystallographic data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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JA0671215