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Construction of one-dimensional homochiral helical supramolecular stereoismers using chiral macrocyclic nickel(II) complexes as building blocks

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ABSTRACT

One one-dimensional right-handed helical chain of $\{[Ni(\mathit{RR}\text{-L})][Ni(CN)_4]\cdot 2H_2O\}_n$ (Δ-**2**$\cdot(2H_2O)_n$) was successfully constructed by the reaction of the $[Ni(\alpha\text{-}\mathit{RR}\text{-L})]^{2+}$ and $[Ni(CN)_4]^{2-}$ in acetonitrile/water (1:1) (L = 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane), and another two one-dimensional left-handed helical chains of $\{[Ni(\mathit{SS}\text{-L})][Ni(CN)_4]\cdot 2H_2O\}_n$ (Λ-**2**$\cdot(2H_2O)_n$) and $\{[Ni(\mathit{SS}\text{-L})][Ni(CN)_4]\cdot 1.25H_2O\}_n$ (Λ-**3**$\cdot(1.25H_2O)_n$) were obtained from the reaction of $[Ni(\alpha\text{-}\mathit{SS}\text{-L})]^{2+}$ with $[Ni(CN)_4]^{2-}$. The reaction of $[Ni(CN)_4]^{2-}$ building blocks with $[Ni(\alpha\text{-}\mathit{SS}\text{-L})]^{2+}$ in acetonitrile/methanol (1:1) gave a one-dimensional left-handed helical chain of $\{[Ni(\mathit{SS}\text{-L})][Ni(CN)_4]\cdot MeCN\}_n$ (Λ-**2**$\cdot(MeCN)_n$). In all supramolecular isomers, the $[Ni(\mathit{RR}\text{-L})]^{2+}$/$[Ni(\mathit{SS}\text{-L})]^{2+}$ cations are alternately bridged by $[Ni(CN)_4]^{2-}$ anions through cyano-groups to form one-dimensional helical chains. The homochiral natures of four complexes were confirmed by the results of solid-state circular dichroism spectra measurements.

1. Introduction

Chirality is of fundamental importance for life and plays a key role in biological systems and pharmacy [1], while the relationship between chirality and helicity in the origin of asymmetry in living systems remains unclear [2]. Recently, the designed constructions of helical supramolecular stereisomers has been the topic of much interest in using chiral [3] or achiral [4] building blocks to understand the helicity of DNA and proteins in biological systems. We have found that a racemic nickel(II) complex, $[Ni(\alpha\text{-}\mathit{rac}\text{-L})]^{2+}$, and its two chiral enantiomers of $[Ni(\alpha\text{-}\mathit{SS}\text{-L})]^{2+}$ and $[Ni(\alpha\text{-}\mathit{RR}\text{-L})]^{2+}$ are beneficial for the constructions of one-dimensional helical chains (L = 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, Scheme 1) [5]. Lu et al. [5b] previously predicted that seven supramolecular isomers and stereoisomers of $\{[Ni(\mathit{rac}\text{-L})][Ni(CN)_4]\}_2$ (**1**), $\{[Ni(\mathit{RR}\text{-L})][Ni(CN)_4]\}_n$ (Δ-**2** and Δ-**3**), $\{[Ni(\mathit{SS}\text{-L})][Ni(CN)_4]\}_n$ (Λ-**2** and Λ-**3**), $\{[Ni(\mathit{rac}\text{-L})][Ni(CN)_4]\}_n$ (*meso*-**2** and *meso*-**3**) (see Scheme 2) could be formed by the reactions of $[Ni(\alpha\text{-}\mathit{rac}\text{-L})]^{2+}$ with $[Ni(CN)_4]^{2-}$, and four supramolecular isomers and stereoisomers of **1**, Δ-**2**, *meso*-**2** and Δ-**3** were successfully constructed. Isomer **1** possesses of a [2 + 2] type of molecular square, and isomers Δ-**2** and Δ-**3** show a motif of one-dimensional right-handed homochiral helical chains, with chiral space groups of $P2_12_12_1$ and $P3_121$, respectively. While the one-dimensional right-handed and left-handed helical chains are alternatedly packed in *meso*-**2** to give a *meso* stereoisomer of *meso*-**2**, with a central symmetrical space group of $P2_1/n$.

Lu et al. [5d,f] have demonstrated that the helicity of one-dimensional chains is much dependent on the chirality of the building blocks, when chiral $[Ni(\alpha\text{-}\mathit{SS}\text{-L})]^{2+}$ was used as building block, the right-handed helical chains were formed, while the left-handed helical chains were obtained using chiral $[Ni(\alpha\text{-}\mathit{RR}\text{-L})]^{2+}$ as building block. This reminds us that Λ-**2** and Λ-**3** could be generated if chiral $[Ni(\alpha\text{-}\mathit{SS}\text{-L})]^{2+}$ and $[Ni(CN)_4]^{2-}$ are used as building blocks.

As a better understanding on the correlations between the chirality of building blocks and helicity of one-dimensional chains, two supramolecular stereoisomers of Λ-**2** and Λ-**3** were successfully constructed. The results further confirm the conclusion that the helicity of one-dimensional chains is much dependent on the chirality of the building blocks.

2. Experimental

2.1. Materials and instrumentation

The macrocyclic ligand (L) and its nickel(II) complex were prepared according to the literature method [6], and separated as the racemic form of *rac*-L. The chiral enantiomers of $[Ni(\alpha\text{-}\mathit{SS}\text{-L})](ClO_4)_2$ and $[Ni(\alpha\text{-}\mathit{RR}\text{-L})](ClO_4)_2$ were prepared according to the previously reported methods [5c]. All of the other chemicals are commercially

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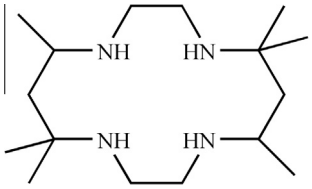


Scheme 1. Sketch of the ligand L.

available and used without further purification. Elemental analyses were determined using Elementar Vario EL elemental analyser. The IR spectra were recorded in the 4000–400 cm^{-1} region using KBr pellets and a Bruker EQUINOX 55 spectrometer. The solid-state circular dichroism (CD) spectra were recorded on a JASCO J-810 Spectropolarimeter with KBr pellets.

Caution! Perchlorate salts of metal complexes with organic ligands are potentially explosive. They should be handled with care, and prepared only in small quantities. X-ray structure determination.

2.2. X-ray crystallographic study

Single-crystal data for Λ-**2**·$(MeCN)_n$ was collected on a CrysAlis CCD, Gemini S Ultra (Oxford Diffraction Ltd.), with Cu-Kα radiation (= 1.54178 Å). The empirical absorption corrections were applied using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. Single-crystal data for Δ-**2**·$(2H_2O)_n$, Λ-**2**·$(2H_2O)_n$ and Λ-**3**·$(1.25H_2O)_n$ were collected on a Bruker Smart 1000 CCD diffractometer, with Mo-Kα radiation (= 0.71073 Å). All empirical absorption corrections were applied by using the SADABS program [7]. The structures were solved using direct methods, which yielded the positions of all non-hydrogen atoms. These were refined first isotropically and then anisotropically. Hydrogen atoms attached to carbon atoms were located geometrically and refined using the riding model, and the hydrogen atoms attached to nitrogen and oxygen atoms were located from the difference maps and refined with isotropic thermal parameters. All calculations were performed using the SHELXTL system of computer programs [8]. The crystallographic data for Δ-**2**·$(2H_2O)_n$, Λ-**2**·$(2H_2O)_n$, Λ-**2**·$(MeCN)_n$ and Λ-**3**·$(1.25H_2O)_n$ are summarized in Table 1. The selected bond lengths and angles are listed in Table 2.

2.3. Synthesis

2.3.1. {[Ni(RR-L)][Ni(CN)$_4$]·2H$_2$O}$_n$ (Δ-**2**·$(2H_2O)_n$), {[Ni(RR-L)][Ni(CN)$_4$]·1.25H$_2$O}$_n$ (Δ-**3**·$(1.25H_2O)_n$) and [Ni(RR-L)][Ni(CN)$_4$(H$_2$O)]·H$_2$O (*a*-**4**·H_2O)

A water solution (20 mL) of $K_2[Ni(CN)_4]\cdot 2H_2O$ (0.139 g, 0.5 mmol) was layered with an acetonitrile solution (20 mL) of [Ni(α-*RR*-L)]$(ClO_4)_2$ (0.270 g, 0.5 mmol). After about one month, thin block-shaped purple crystals of Δ-**2**·$(2H_2O)_n$, prism-shaped purple crystals of Δ-**3**·$(1.25H_2O)_n$ and block-shaped blue crystals of *a*-**4**·H_2O formed along the wall of the tube. They were separated manually. Yield: 17% for Δ-**2**·$(2H_2O)_n$, 37% for Δ-**3**·$(1.25H_2O)_n$, and 5% for *a*-**4**·H_2O. $C_{20}H_{40}N_8Ni_2O_2$ (Δ-**2**·$(2H_2O)_n$): Calc. C, 44.32; H, 7.44; N, 20.68. Found C, 44.49; H, 7.54; N, 20.53%. $C_{20}H_{38.5}N_8Ni_2O_{1.25}$ (Δ-**3**·$(1.25H_2O)_n$): Calc. C, 45.45; H, 7.34; N, 21.20. Found C, 45.59; H, 7.37; N, 21.29%. $C_{20}H_{40}N_8Ni_2O_2$ (*a*-**4**·H_2O): Calc. C, 44.32; H, 7.44; N, 20.68. Found C, 44.50; H, 7.26; N, 20.73%. IR (KBr) cm^{-1}: ν_{CN} 2155 (coordinated) and 2125 (uncoordinated) for Δ-**2**·$(2H_2O)_n$; 2154 (coordinated) and 2123 (uncoordinated) for Δ-**3**·$(1.25H_2O)_n$; 2154 (coordinated) and 2124 (uncoordinated) for *a*-**4**·H_2O.

2.3.2. {[Ni(SS-L)][Ni(CN)$_4$]·2H$_2$O}$_n$ (Λ-**2**·$(2H_2O)_n$), {[Ni(SS-L)][Ni(CN)$_4$]·1.25H$_2$O}$_n$ (Λ-**3**·$(1.25H_2O)_n$) and [Ni(SS-L)][Ni(CN)$_4$(H$_2$O)]·H$_2$O (*b*-**4**·H_2O)

A water solution (20 mL) of $K_2[Ni(CN)_4]\cdot 2H_2O$ (0.139 g, 0.5 mmol) was layered with an acetonitrile solution (20 mL) of [Ni(α-*SS*-L)]$(ClO_4)_2$ (0.270 g, 0.5 mmol). After about one month, thin block-shaped purple crystals of Λ-**2**·$(2H_2O)_n$, prism-shaped purple crystals of Λ-**3**·$(1.25H_2O)_n$ and block-shaped blue crystals of *b*-**4**·H_2O formed along the wall of the tube. They were separated manually. Yield: 20% for Λ-**2**·$(2H_2O)_n$, 31% for Λ-**3**·$(1.25H_2O)_n$ and 15% for *b*-**4**·H_2O. $C_{20}H_{40}N_8Ni_2O_2$ (Λ-**2**·$(2H_2O)_n$): Calc. C, 44.32; H, 7.44; N 20.68. Found C, 44.40; H, 7.51; N, 20.57%. $C_{20}H_{38.5}N_8Ni_2O_{1.25}$ (Λ-**3**·$(1.25H_2O)_n$): Calc. C, 45.46; H, 7.34; N, 21.20. Found C, 45.50; H, 7.38; N, 21.25%. $C_{20}H_{40}N_8Ni_2O_2$ (*b*-**4**·H_2O): Calc. C, 44.32; H, 7.44; N, 20.68. Found C, 44.43; H, 7.31; N, 20.79%. IR (KBr) cm^{-1}: ν_{CN} 2154 (coordinated) and 2125 (uncoordinated) for Λ-**2**·$(2H_2O)_n$; 2155 (coordinated) and 2123 (uncoordinated) for Λ-**3**·$(1.25H_2O)_n$; 2155 (coordinated) and 2123 (uncoordinated) for *b*-**4**·H_2O.

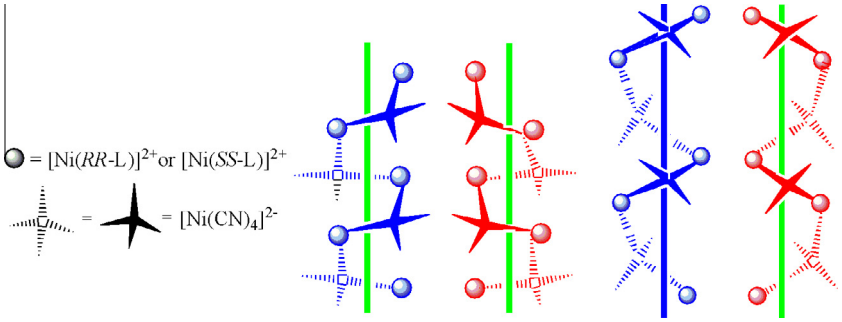
2.3.3. {[Ni(SS-L)][Ni(CN)$_4$]·MeCN}$_n$ (Λ-**2**·$(MeCN)_n$)

A methanol solution (20 mL) of $\{P(C_6H_5)_4\}_2[Ni(CN)_4]$ (0.042 g, 0.05 mmol) was layered with an acetonitrile solution (20 mL) of [Ni(α-*SS*-L)]$(ClO_4)_2$ (0.027 g, 0.05 mmol). After about 2 weeks, prism-shaped purple crystals of Λ-**2**·$(MeCN)_n$ was isolated. Yield: 37%. $C_{22}H_{39}N_9Ni_2$: Calc. C, 48.30; H, 7.18; N, 23.05. Found C, 48.54; H, 7.33; N, 23.29%. IR (KBr) cm^{-1}: ν_{CN} 2154 (coordinated) and 2124 (uncoordinated).

3. Results and discussion

3.1. Synthetic chemistry

It has been reported that two one-dimensional right-handed helical chains of Δ-**2** and Δ-**3** with the formula of [Ni(*RR*-L)][Ni(CN)$_4$] had been constructed based on the [Ni(α-*rac*-L)]$^{2+}$



Scheme 2. Possible supramolecular isomers and stereoisomers based on $[Ni(RR\text{-}L)]^{2+}$/$[Ni(SS\text{-}L)]^{2+}$ and $[Ni(CN)_4]^{2-}$ building blocks.