



Assembly structures of 1:2 nickel(II) complex of 5-methylimidazol-4-yl-methylidene-L-phenylalanine and 1:2 nickel(II) complex of its racemic ligand

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ABSTRACT

1:2 Nickel(II) complexes of 5-methylimidazol-4-yl-methylidene-L-phenylalanine ($H_2L^{L\text{-phe}}$) and its racemic ligand ($H_2L^{DL\text{-phe}}$) were synthesized and the crystal structures of the resultant $[Ni(HL^{L\text{-phe}})_2] \cdot MeOH \cdot 3H_2O$ (**1**) and $[Ni(HL^{DL\text{-phe}})_2] \cdot 6H_2O$ (**2**) complexes were determined. Complex **1** crystallized in an acentrosymmetric monoclinic space group, $P2_1$ (No. 4). The nickel(II) ion is coordinated by $(N_2O)_2$ donor atoms from two tridentate $H_2L^{L\text{-phe}}$ ligands and has an octahedral coordination environment. In the crystal, **1** contains only the L-isomer and forms a homochiral 2D structure through hydrogen bonding between the adjacent complex molecules. In contrast, Complex **2** crystallized into a centrosymmetric monoclinic space group, $P2_1/c$ (No. 14). The nickel(II) ion is coordinated by $(N_2O)_2$ donor atoms from two $H_2L^{DL\text{-phe}}$ tridentate ligands. The coordination geometry around the nickel(II) ion is described as octahedral. In the crystal, **2** consists of $[Ni(HL^{DL\text{-phe}})_2]$ and $[Ni(HL^{L\text{-phe}})_2]$ molecule that are related and forms a heterochiral 3D structure via hydrogen bonding through the crystal solvents.

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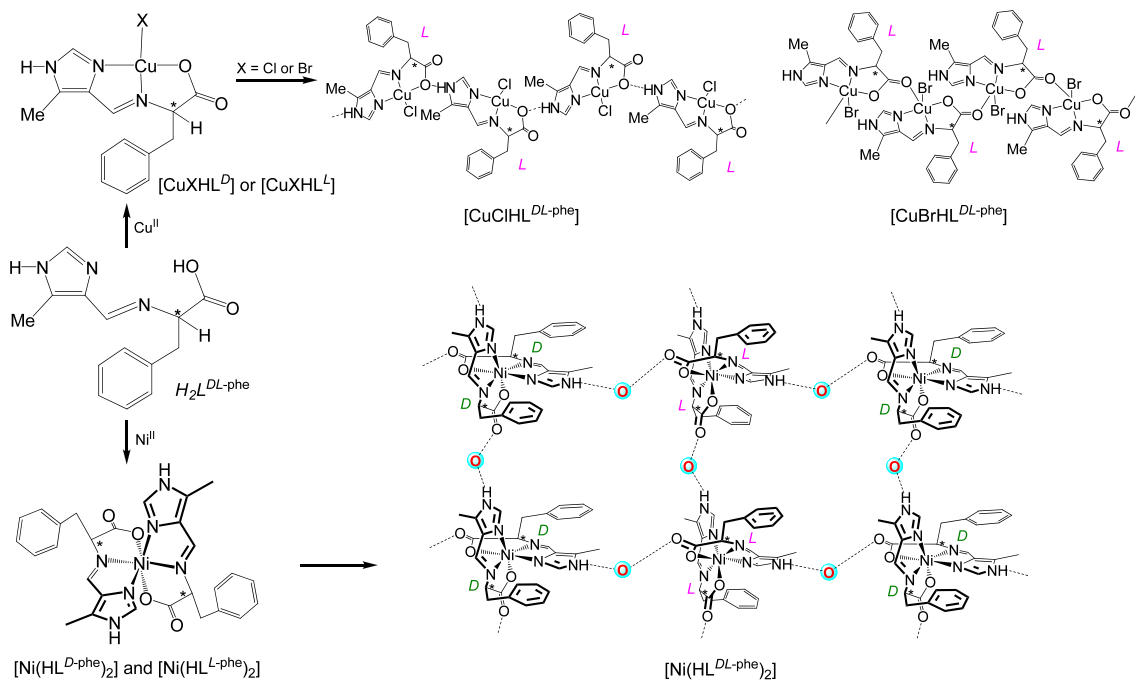
1. Introduction

The fields of crystal engineering and supramolecular chemistry have attracted much attention during the past three decades, because a well-designed molecular building block is crucial for the formation of a functional supramolecular assembly [1]. Self-assembly involving metal ions is especially useful for the construction of functional supramolecules; for example, metal-directed assembly has been successfully employed to construct various supramolecular architectures such as helices [2–6], grids [7,8], boxes [9,10], rods [11], and tubes [12], in which the assembly interactions may involve coordination or hydrogen bonds. Such interactions are quite strong, selective, and directional, and, in some cases, sustainable [13–16]. Among the many useful building blocks for metal complexes, imidazole-containing polydentate ligands have several advantages for versatile assembly of different structures because of the multitude of coordination modes available: (1) intermolecular coordination through the imidazole nitrogen; (2) imidazole...imidazole ($NH \cdots N$) hydrogen bonding; and (3) imidazole...halogen anion ($NH \cdots X^-$) hydrogen bonding [17–20]. Because the metal complex and/or ligands are often chiral [21–23], these complexes are useful for investigating the chiral assembly process [24–30].

In previous papers, we studied the enantioselective assembly of a copper(II) complex with a chiral-imidazole-containing tridentate ligand, i.e., $[Cu^{II}Cl(HL^{DL\text{-phe}})]$, where $H_2L^{DL\text{-phe}}$ is 5-methylimidazol-4-yl-methylidene-DL-phenylalanine; this ligand is the 1:1 condensation product of DL-phenylalanine and 5-methyl-4-formylimidazole [31–34]. $[Cu^{II}X(HL^{DL\text{-phe}})]$ can function as a self-complementary chiral building block in the construction of assembly structures [31–34]. As shown in Scheme 1, this Cu^{II} complex can undergo two types of assembly processes: (1) intermolecular imidazole-carboxylate ($NH \cdots O$) hydrogen bonding to form a homochiral 1D assembly chain, or (2) intermolecular coordination bonding between a carboxylate oxygen of one molecule to a Cu^{II} ion of an adjacent molecule ($=O-Cu$) to form a homochiral 1D structure. It should be noted that such homochiral 1D assembly structures are enantioselectively constructed from a mixture of self-complementary building blocks, i.e., $[Cu^{II}X(HL^{DL\text{-phe}})]$ and $[Cu^{II}X(HL^{L\text{-phe}})]$. To further investigate the chiral discrimination of the metal complexes, we also studied the nickel(II) complexes. In contrast to the 1:1 Cu complex, i.e., $[Cu^{II}X(HL^{DL\text{-phe}})]$, the nickel(II) ion reacts with $H_2L^{DL\text{-phe}}$ to form a 1:2 complex, i.e., $[Ni(HL^{DL\text{-phe}})_2]$. The metal complex formation with the particular ligand depends predominantly on the kind of metal ion and its oxidation state. Generally $Cu(II)$ ion reacts with the NO-Schiff-base ligand to produce four- or five-coordinated complex, whereas $Ni(II)$ ion gives low-spin four coordinated complex or high-spin six-coordinated complex. In the present case, $Cu(II)$ ion with the tridentate ligand forms the 1:1

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Scheme 1. $[Cu^{II}X(HL^{DL-phe})]$ and $[Ni(HL^{DL-phe})_2]$ and their enantioselective assembling. Homochiral 1D assembly structures of $[Cu^{II}X(HL^{DL-phe})]$ ($X = Cl, Br$) constructed by intermolecular imidazole...carboxylate hydrogen bond ($X = Cl$), and intermolecular coordination bond between carboxylate oxygen and Cu^{II} ion ($X = Br$). The 1:2 complex $[Ni(HL^{DL-phe})_2]$ and its assembly structure $[Ni(HL^{DL-phe})_2]$.

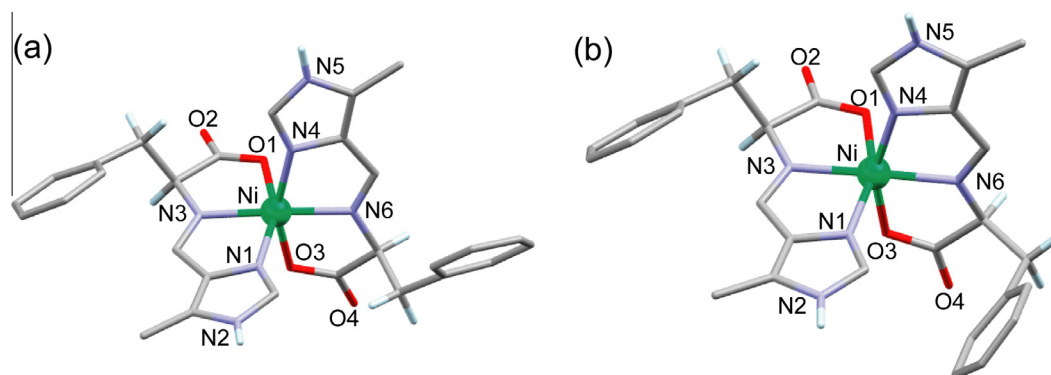


Fig. 1. Molecular structures of (a) $[Ni(HL^{L-phe})_2] \cdot 2MeOH \cdot H_2O$ (1) and (b) the mononuclear unit $[Ni(HL^{L-phe})_2]$ with the L isomer of the ligand of $[Ni(HL^{L-phe})_2] \cdot 7H_2O$ (2) with the selected atom numbering scheme.

complex, while nickel(II) ion gives high-spin 1:2 complex. The tridentate ligand plays an uninegative ligand and the 1:2 Ni(II) complex with preferable six-coordination number is electronically neutral and stable complex. Other types of chiral assemblies were also found in the Ni^{II} complex: we report here the synthesis, molecular structure, and chirally discriminative assembly of $[Ni(HL^{DL-phe})_2] \cdot 6H_2O$.

2. Experimental

2.1. General

All chemicals and solvents were obtained from Tokyo Kasei Co., Ltd., and Wako Pure Chemical Industries, Ltd., and were of reagent grade and used without further purification. All the synthetic procedures were carried out in an open atmosphere.

2.2. Synthesis of nickel(II) complexes

2.2.1. Preparation of $[Ni^{II}(HL^{L-phe})_2] \cdot MeOH \cdot 3H_2O$ (1)

A solution of L-phenylalanine (165 mg, 1 mmol) in 5 mL of methanol and 5 mL of water was added to a solution of 5-methyl-4-formylimidazole (110 mg, 1 mmol) in 5 mL of methanol, and the mixture was stirred on a hot plate at 60 °C for 60 min. The ligand solution was then cooled to room temperature and used for the synthesis of the nickel(II) complex. Accordingly, a solution of $Ni^{II}(CH_3COO)_2 \cdot 4H_2O$ (124 mg, 0.5 mmol) in 10 mL of methanol was added to a solution of the H_2L^{L-phe} ligand (1 mmol). The mixture was stirred at room temperature for 60 min and then filtered. The filtrate was allowed to stand for several days, during which time light purple platelet crystals precipitated. Yield: 115 mg (20%). Elemental Anal. Calc. for $[Ni^{II}(HL^{L-phe})_2] \cdot MeOH \cdot 3H_2O = C_{29}H^{38}N_6O_8Ni$: C, 52.99; H, 5.82; N, 12.78. Found: C, 52.78; H, 5.48; N, 13.07%. Dry samples were used for TGA. **1** showed a 12.5% weight loss corresponding to a calculated values of $MeOH \cdot 3H_2O$ (13.1%) when heated to a temperature region lower than 120 °C.

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