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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 $H_2L^{L\text{-}phe}$ tridentate ligands. The coordination geometry around the nickel(II) ion is described as octahedral. In the crystal, **2** consists of $[Ni(HL^{D\text{-}phe})_2]$ and $[Ni(HL^{L\text{-}phe})_2]$ molecule that are related and forms a heterochiral 3D structure via hydrogen bonding through the crystal solvents.

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 imidazolate nitrogen; (2) imidazole···imidazolate (NH···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···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., $[Cu^{II}X(HL^{D\text{-}phe})]$ 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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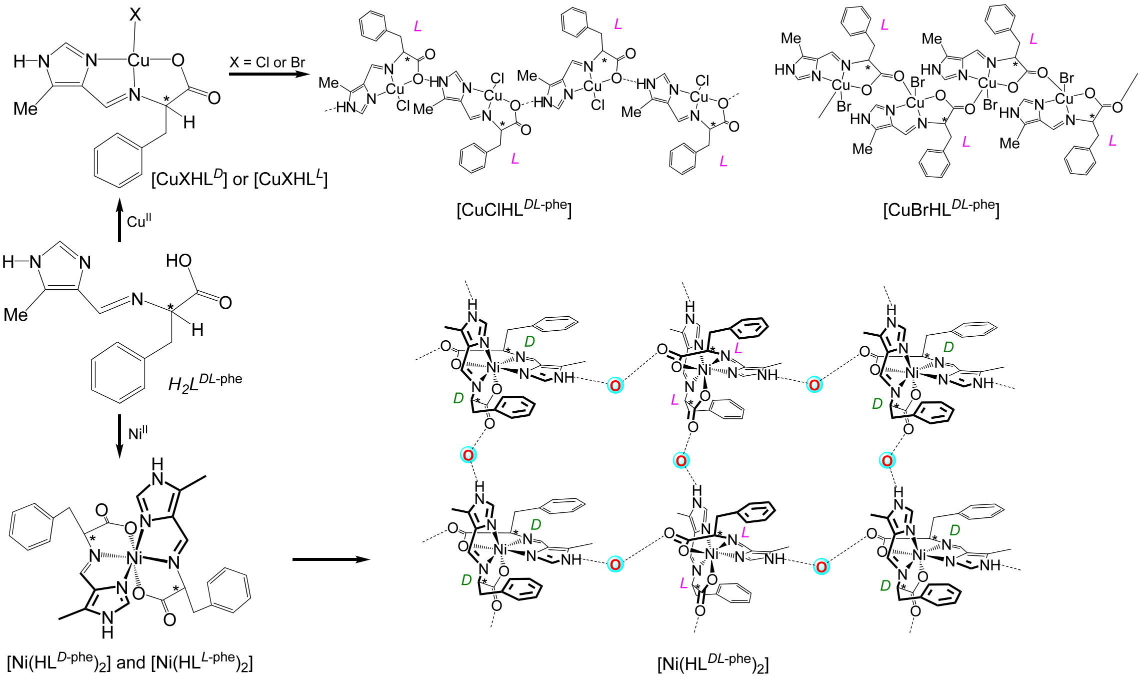

Scheme 1. [$Cu^{II}X(HL^{DL\text{-phe}})$] and [$Ni(HL^{DL\text{-phe}})_2$] and their enantioselective assembling. Homochiral 1D assembly structures of [$Cu^{II}X(HL^{DL\text{-phe}})$] (X = Cl, Br) constructed by intermolecular imidazole···carboxylate hydrogen bond (X = Cl), and intermolecular coordination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

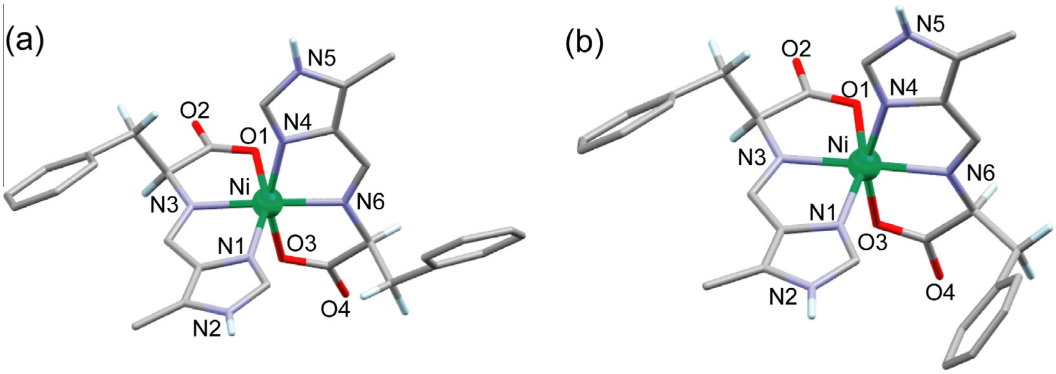

Fig. 1. Molecular structures of (a) [$Ni(HL^{L\text{-phe}})_2$]·2MeOH·H$_2$O (**1**) and (b) the mononuclear unit [$Ni(HL^{L\text{-phe}})_2$] with the L isomer of the ligand of [$Ni(HL^{DL\text{-phe}})_2$]·7H$_2$O (**2**) with the selected atom numbering scheme.

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 [$Ni(HL^{DL\text{-phe}})_2$]·6H$_2$O.

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 [$Ni^{II}(HL^{L\text{-phe}})_2$]·MeOH·3H$_2$O (**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 $H_2L^{L\text{-phe}}$ 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 [$Ni^{II}(HL^{L\text{-phe}})_2$]·MeOH·3H$_2$O = $C_{29}H_{38}N_6O_8Ni$: 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·3H$_2$O (13.1%) when heated to a temperature region lower than 120 °C.

In a cooling mode, a 5.2% weight increase corresponding to two H_2O molecules (5.6%) was observed.

2.2.2. Preparation of $[Ni^{II}(HL^{DL\text{-}phe})_2]\cdot 6H_2O$ (**2**)

A solution of DL-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. A solution of $Ni^{II}(CH_3COO)_2\cdot 4H_2O$ (124 mg, 0.5 mmol) in 10 mL of methanol was then added to the solution of the $H_2L^{DL\text{-}phe}$ 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 blue platelet crystals precipitated; the crystals were collected by suction filtration, washed with ether, and dried. Yield: 124 mg (22%). Elemental *Anal.* Calc. for $[Ni^{II}(HL^{DL\text{-}phe})_2]\cdot 6H_2O = C_{28}H_{40}N_6O_{10}Ni$: C, 49.50; H, 5.93; N, 12.37. Found: C, 49.44; H, 5.88; N, 12.32%. Dry samples were used for TGA. **2** showed a 15.8% weight loss corresponding to the calculated values of $6H_2O$ molecules (15.9%) when heated to a temperature region lower than 120 °C. In a cooling mode, a 2.7% weight increase corresponding to one H_2O molecule (2.8%) was observed.

2.3. Physical measurements

Elemental C, H, and N analyses were performed at the Center for Instrumental Analysis of Kumamoto University, Japan. Infrared spectra were recorded at room temperature using a JEOL JIR-6500 W spectrometer with the samples in KBr disks. Thermogravimetric analyses (TGA) were performed on a TG/DTA6200 instrument (Seiko Instrument Inc.), which involved heating $\sim$2 mg of the sample from room temperature to 210 °C at a rate of 5 °C min^{-1}.

Table 1
Crystallographic data of nickel(II) complexes $[Ni(HL^{L\text{-}phe})_2]\cdot 2MeOH\cdot H_2O$ and $[Ni(HL^{DL\text{-}phe})_2]\cdot 7H_2O$.

Complex	$[Ni(HL^{L\text{-}phe})_2]\cdot 2MeOH\cdot H_2O$	$[Ni(HL^{DL\text{-}phe})_2]\cdot 7H_2O$
Formula	$C_{30}H_{38}N_6O_7Ni$	$C_{28}H_{42}N_6O_{11}Ni$
Formula weight	653.37	697.37
Crystal system	monoclinic	monoclinic
Space group	$P2_1$ (No. 4)	$P2_1/c$ (No. 14)
a (Å)	10.389(1)	12.2143(9)
b (Å)	12.096(2)	11.4255(7)
c (Å)	13.439(2)	24.292(2)
β (°)	100.530(4)	95.427(2)
V ($Å^3$)	1660.4(4)	3374.9(4)
Z	2	4
T (K)	250	250
D_{calcd} (g cm^{-1})	1.307	1.372
R, Rw	0.0753, 0.1712	0.0751, 0.1992
Flack parameter	0.07(3)	

Table 2
Relevant coordination bond and hydrogen bond distances of $[Ni(HL^{L\text{-}phe})_2]\cdot 2MeOH\cdot H_2O$.

Complex	$[Ni(HL^{L\text{-}phe})_2]\cdot 2MeOH\cdot H_2O$
Coordination bond distances (Å)	
Ni—N1 (imidazole)	2.118(5)
Ni—N3 (imine)	1.994(7)
Ni—N4 (imidazole)	2.102(8)
Ni—N6 (imine)	1.995(8)
Ni—O1 (carboxylate)	2.122(5)
Ni—O3 (carboxylate)	2.111(7)
Hydrogen bond distances (Å)	
O1 (carboxylate)···O5^{*1} (water)	2.771(7)
O2 (carboxylate)···N2^{*2} (imidazole)	2.652(8)
O3 (carboxylate)···O7^{*3} (methanol)	2.840(18)
O4 (carboxylate)···O5^{*3} (water)	2.735(10)
O4 (carboxylate)···O6^{*3} (methanol)	2.82(4)
O5 (water)···N5 (imidazole)	2.732(10)

Symmetry operations:
(*1), $-x+2, y-1/2, -z+2$; (*2), $x+1, y, z$; (*3), $x, y-1, z$.

2.4. X-ray crystal structure analyses

Crystals of **1** and **2** were selected from the solution, mounted on a glass rod, and quickly coated with epoxy resin; they were then used for the X-ray diffraction study at 250 K. The X-ray diffraction data were collected using a Rigaku RAXIS RAPID imaging plate area detector with graphite monochromated Mo Kα radiation (λ = 0.71069 Å). The structures were resolved using direct methods and expanded using the Fourier technique. Hydrogen atoms were fixed at the calculated positions and refined using a riding model. All calculations were performed using the Crystal Structure crystallographic software package [35,36].

3. Results and discussion

3.1. Synthesis and characterization of nickel(II) complexes

Tridentate ligands, i.e., $H_2L^{L\text{-}phe}$ and $H_2L^{DL\text{-}phe}$, were prepared via a 1:1 condensation reaction of 5-methyl-4-formylimidazole and either L-phenylalanine or DL-phenylalanine in a mixed solvent comprising methanol and H_2O (2:1 by volume); the resulting ligand solution was used for the synthesis of the metal complex without isolating the ligand. The nickel(II) complexes, i.e., $[Ni^{II}(HL^{L\text{-}phe})_2]\cdot MeOH\cdot 3H^2O$ (**1**) and $[Ni^{II}(HL^{DL\text{-}phe})_2]\cdot 6H_2O$ (**2**), were prepared by mixing $Ni^{II}(CH_3COO)_2\cdot 4H_2O$ with $H_2L^{L\text{-}phe}$ and $H_2L^{DL\text{-}phe}$, respectively, in a 1:2 M ratio in the mixed solvent. After slow crystallization at room temperature, complexes **1** and **2** were obtained as light purple platelet and light blue platelet crystals, respectively. The relatively low yields ($\sim$20%) were probably due to the high solubility of the complex in the crystallization solvent. C, H, and

Table 3
Relevant coordination bond and hydrogen bond distances of $[Ni(HL^{DL\text{-}phe})_2]\cdot 7H_2O$.

Complex	$[Ni(HL^{DL\text{-}phe})_2]\cdot 7H_2O$
Coordination bond distances (Å)	
Ni—N1 (imidazole)	2.093(5)
Ni—N3 (imine)	2.012(4)
Ni—N4 (imidazole)	2.107(5)
Ni—N6 (imine)	2.006(4)
Ni—O1 (carboxylate)	2.107(4)
Ni—O3 (carboxylate)	2.089(4)
Hydrogen bond distances (Å)	
O1 (carboxylate)···O6^{*1} (water)	2.719(6)
O2 (carboxylate)···O7^{*2} (water)	2.874(6)
O2 (carboxylate)···O9^{*2} (water)	2.724(6)
O3 (carboxylate)···O11^{*3} (water)	2.762(6)
O4 (carboxylate)···O5^{*4} (water)	2.722(6)
O4 (carboxylate)···O8^{*3} (water)	2.807(6)
O5 (water)···O6 (water)	2.737(6)
O5 (water)···N5 (imidazole)	2.734(6)
O6 (water)···O10^{*8} (water)	2.882(7)
O7 (water)···O8 (water)	2.901(6)
O7 (water)···O11 (water)	2.873(6)
O7 (water)···N2 (imidazole)	2.886(7)
O8 (water)···O9 (water)	2.908(7)
O9 (water)···O10 (water)	2.771(7)
O10 (water)···O11 (water)	2.808(7)
O10 (water)···O11^{*13} (water)	2.766(7)

Symmetry operations:
(*1), $-x+1, -y+2, -z+1$; (*2), $x, -y+3/2, z-1/2$;
(*3), $-x+2, y-1/2, -z+3/2$; (*4), $x+1, y, z$;
(*8), $x-1, -y+5/2, z-1/2$; (*13), $-x+2, -y+2, -z+2$.

N elemental analyses of **1** and **2** agreed with the chemical formulae of $[Ni^{II}(HL^{L\text{-}phe})_2]\cdot MeOH\cdot 3H_2O$ and $[Ni^{II}(HL^{DL\text{-}phe})_2]\cdot 6H_2O$, respectively.

3.2. Crystal structure of nickel(II) complexes

The crystal structures of **1** and **2** were determined by single-crystal X-ray diffraction analyses at 250 K. The molecular structures of **1** and **2** are shown in Fig. 1, while Table 1 shows the crystallographic data; Tables 2 and 3 list the relevant bond lengths and hydrogen bond distances.

Complex **1** crystallized into an acentrosymmetric monoclinic space group, $P2_1$ (No. 4), with $Z = 2$ and the formula of $[Ni(HL^{L\text{-}phe})_2]\cdot 2MeOH\cdot H_2O$. The number of the crystal solvents is not compatible with $[Ni(HL^{L\text{-}phe})_2]\cdot MeOH\cdot 3H_2O$ by the elemental analyses. The samples used for the X-ray and elemental analyses are same products. Crystals for X-ray diffraction analyses were selected from the solution, whereas crystals for the elemental analyses were kept in open atmosphere. Therefore, it suggested that the crystal solvents are eliminated and absorbed. The Flack parameter was refined to nearly zero, which is consistent with the chirality of L-phenylalanine used forthe synthesis. 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; the coordination bond distances are as follows: Ni–N(1) (imidazole) = 2.118(5) Å; Ni–N(3) (imine) = 1.994(7) Å; Ni–O(1) (carboxylate) = 2.122(5) Å; Ni–N(4)(imidazole) = 2102(8) Å; Ni–N(6) (imine) = 1.995(8) Å; and Ni–O(3) (carboxylate) = 2.111(7) Å. The Ni–N (imine) distance is shorter than the Ni–N (imidazole) and Ni–O (carboxylate) distances.

Complex **2** crystallized into a centrosymmetric monoclinic space group, $P2_1/c$ (No. 14), with the formula of $[Ni(HL^{DL\text{-}phe})_2]\cdot 7H_2O$. The number of the crystal solvents is not compatible with $[Ni(HL^{DL\text{-}phe})_2]\cdot 6H_2O$ by the elemental analyses. The same products used as samples for the X-ray diffraction and elemental analyses. Crystals for X-ray diffraction analyses were selected from the solution, whereas crystals for the elemental analyses were kept in open atmosphere. Therefore, it suggested that water molecules of the crystal solvents are eliminated. The crystal structure consists of $[Ni(HL^{D\text{-}phe})_2]$ and $[Ni(HL^{L\text{-}phe})_2]$ molecules that are related by inversion because the $P2_1/c$ space group has an inversion center. Fig. 1(b) shows the molecular structure of $[Ni(HL^{L\text{-}phe})_2]$, where two tridentate ligands coordinated to the Ni^{II} ion have the same chirality but two $H_2L^{L\text{-}phe}$ ligands differ with respect to the orientation of the phenyl group. The nickel(II) ion is coordinated by $(N_2O)_2$ donor atoms from two $H_2L^{L\text{-}phe}$ tridentate ligands. The coordination geometry around the nickel(II) ion is described as octahedral; the coordination bond distances are as follows: Ni–N(1) (imidazole) = 2.093(5) Å; Ni–N(3) (imine) = 2.012(4) Å; Ni–O(1) (carboxylate) = 2.107(4) Å; Ni–N(4) (imidazole) = 2.107(5) Å; Ni–N(6)

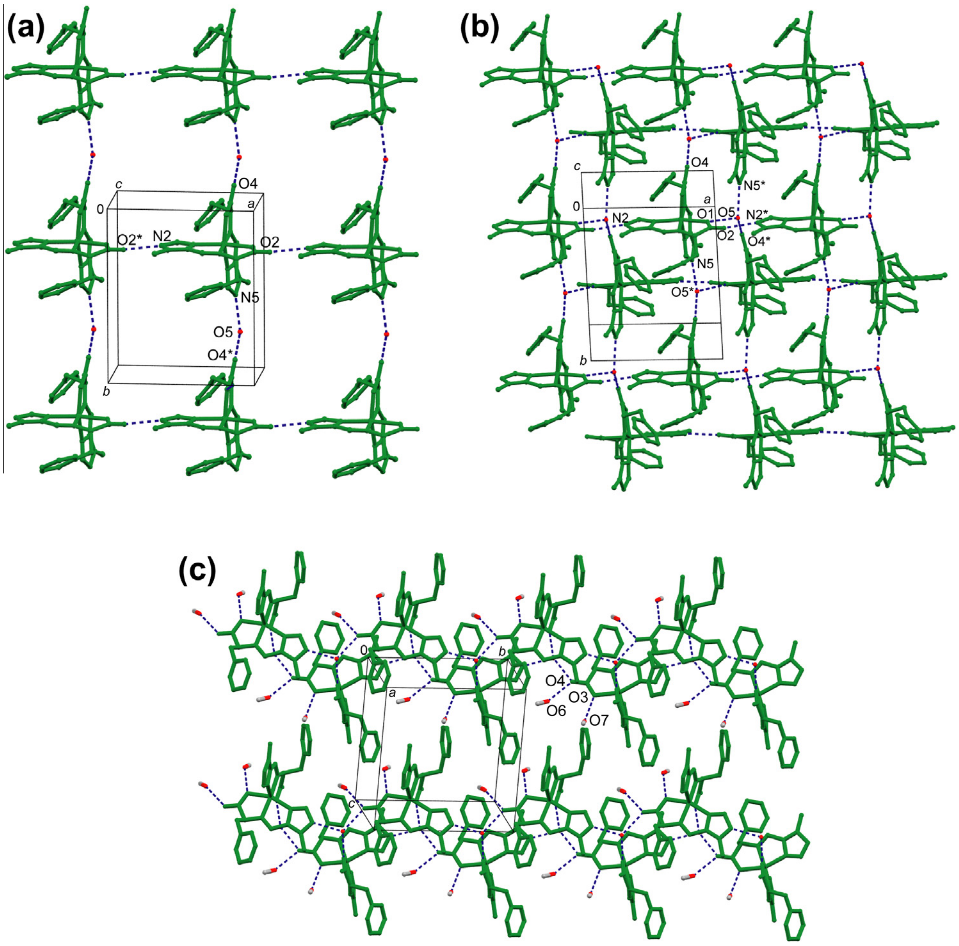

Fig. 2. (a) Homochiral 2D network structure of $[Ni(HL^{L\text{-}phe})_2]\cdot 2MeOH\cdot H_2O$ (**1**) constructed by intermolecular imidazole···carboxylate hydrogen bond of O(2)···N(2) and two hydrogen bonds via water molecule O(5). Green-colored molecule represents an enantiomer consisting of L-phenylalanine moiety. (b) A view of double layer projected onto the layer. Adjacent 2D layers related by 2_1 symmetry operation along the *b*-axis are linked by a water molecule O(5) via hydrogen bonds, forming a double layer. (c) Side view of two double layers. The double layers are stacked along the *c*-axis. Two methanol molecules are hydrogen bonded to carboxylate groups and occupy the void between the double layers. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

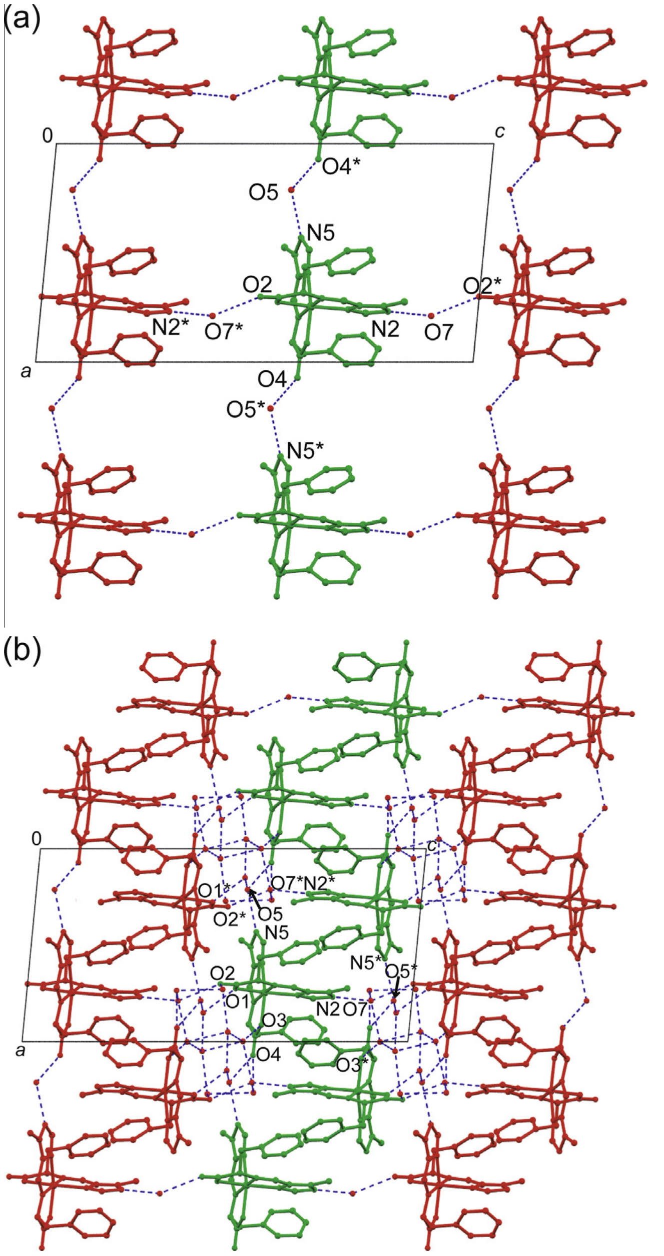

Fig. 3. (a) Heterochiral 2D network structure of $[\mathrm{Ni(HL^{DL\text{-}phe})_2}]\cdot 7\mathrm{H_2O}$ (**2**) constructed by the hydrogen bonds to a water molecule O(5) and O(7), where green- and red-colored molecules represent two enantiomers consisting of L- and D-phenylalanine moieties, respectively. (b) The 2D layers are stacked along the *b*-axis and the adjacent a heterochiral 2D layer is linked by the hydrogen bonds through the water clusters to forms a heterochiral 3D structure.

(imine) = 2.006(4) Å; and Ni–O(3) (carboxylate) = 2.089(4) Å. The Ni–N (imine) distance is shorter than the Ni–N (imidazole) and Ni–O (carboxylate) distances.

The assembly structure of **1** is shown in Fig. 2(a–c). One of the two imidazole nitrogen atoms, N(2), in each nickel(II) complex is hydrogen bonded to a carboxylate oxygen atom, O(2)*, of the adjacent $\mathrm{Ni^{II}}$ complex, which is related by an *a*-transformation (1 + *x*,*y*,*z*), with a hydrogen bond distance (N(2)···O(2)*) of 2.652(8) Å. The intermolecular N(2)···O(2)* hydrogen bond repeats along the *a*-axis to give a 1D chain. Another imidazole nitrogen atom, N(5), of a $\mathrm{Ni^{II}}$ complex is hydrogen bonded to an oxygen atom of a water molecule, O(5), with a distance of 2.732(10) Å;O(5) is further hydrogen bonded to a carboxylate oxygen atom, O(4)*, of the adjacent $\mathrm{Ni^{II}}$ complex, which is related by a *b*-transformation (*x*,1 + *y*,*z*), with a distance (O(5)···O(4)*) of 2.735(10) Å. The 1D chains running along the *a*-axis are linked via an oxygen atom of the water molecule, O(5), through two hydrogen bonds, i.e., N(5)···O(5) and O(5)···O(4)*, to give a 2D layer structure, as shown in Fig. 2(a). The adjacent 2D layer is generated by a 2_1 symmetry operation along the *b*-axis and is stacked along the *c*-axis. The adjacent 2D layers are linked by O(5)···O(1) (carboxylate) andO(5)···O(4)* (carboxylate) hydrogen bonds to form a double-layer structure; the hydrogen bond distances of O(5)···O(1) and O(5)···O(4)* are 2.771(7) and 2.735(10) Å, respectively. The oxygen atom of the water molecule, O(5), of $[\mathrm{Ni(HL^{L\text{-}phe})_2}]\cdot 2\mathrm{MeOH}\cdot\mathrm{H_2O}$ (**1**) forms three hydrogen bonds to the three neighboring $[\mathrm{Ni(HL^{L\text{-}phe})_2}]$ and functions a connector to form the double-layer structure. Fig. 2(b) shows the double-layer structure viewed perpendicular to the 2D layer, i.e., along the *c*-axis. Fig. 2(c) shows a side view of the double layers, which are stacked along the *c*-axis. Two molecules of methanol crystal solvent are hydrogenbonded to carboxylate groups and occupy the void between the double layers.

The assembly structure of **2** is shown in Fig. 3(a) and (b). One of the two imidazole nitrogen atoms, N(5), of a $\mathrm{Ni^{II}}$ complex is hydrogen bonded to an oxygen atom of a water molecule, O(5), with a distance (N(5)···O(5)) of 2.734(6) Å; O(5) is further hydrogen bonded to a carboxylate oxygen atom, O(4)*, of an adjacent $\mathrm{Ni^{II}}$ complex that is related by an *a*-transformation (1 + *x*,*y*,*z*) with O(5)···O(4)* = 2.722(6) Å. Two hydrogen bonds to an oxygen atom in a water molecule, O(5), i.e., N(5)···O(5) and O(5)···O(4)*, are repeated along the *a*-axis to form a 1D chain. A nitrogen atom from the second imidazole group, N(2), of the $\mathrm{Ni^{II}}$ complex is hydrogen bonded to an oxygen atom of a water molecule, O(7), with a distance of 2.886(7) Å; the water molecule is further hydrogen bonded through O(7) to a carboxylate oxygen atom, O(2)*, of the adjacent $\mathrm{Ni^{II}}$ complex, which is related by inversion (−*x*,−*y*,−*z*), with a distance of 2.874(6) Å. The 1D chains running along the *c*-axis are linked via an oxygen atoms of a water molecule, O(7), through two hydrogen bonds, i.e., N(2)···O(7) and O(7)···O(2)*, to provide the 2D layer structure, as shown in Fig. 3(a). The 2D layer structure contains D-isomer (red) or L-isomer (green) chains bonded by two hydrogen bonds to an oxygen atom of a water molecule, O(5), i.e., N(5)···O(5) and O(5)···O(4)*, which run along the *a*-axis. The adjacent chains with opposite chirality are linked by two hydrogen bonds to an oxygen atom of a water molecule, O(7), i.e., N(2)···O(7) and O(7)···O(2)*, to give a heterochiral 2D layer structure. Because the phenyl groups are present on the same side, the layer is hydrophobic. The water clusters are present at the opposite sides of the hydrophobic layer formed by the phenyl group. The adjacent 2D layer is generated by a 2_1 symmetry operation along the *a*-axis and is stacked along the *b*-axis; the layers are connected via hydrogen bonds of the water clusters. As a result, complex **2** features a heterochiral 3D structure, as shown in Fig. 3(b). The O(5) and O(7) atoms of water molecules in $[\mathrm{Ni(HL^{DL\text{-}phe})_2}]\cdot 7\mathrm{H_2O}$ (**2**) are hydrogen bonded to water clusters and function as connectors to form the 3D structure [37,38]. Table 3 summarizes the hydrogen bond O···O distances.

4. Concluding remarks

The 1:2 nickel(II) complex, $[\mathrm{Ni(HL^{L\text{-}phe})_2}]\cdot\mathrm{MeOH}\cdot 3\mathrm{H_2O}$ (**1**) was synthesized using an optically pure ligand of *N*-[(5-methylimidazol-4-yl)methylidene]-L-phenylalanine. Complex **1** contains only the L-isomer and crystallized into an acentrosymmetric monoclinic space group, $P2_1$ (No. 4). The crystal structure formed a homochiral 2D structure through hydrogen bonds between the adjacent complexes. To investigated from the perspective of enantioselective assembly into crystal lattices, the 1:2 nickle(II) complex $[\mathrm{Ni(HL^{DL\text{-}phe})_2}]\cdot 6\mathrm{H_2O}$ (**2**) was synthesized using racemic ligand of

N-[(5-methylimidazol-4-yl)methylidene]-D-phenylalanine and *N*-[(5-methylimidazol-4-yl)methylidene]-L-phenylalanine. In the 1:2 nickle(II) complex, $[\mathrm{Ni}(\mathrm{HL}^{D\text{-}phe})_2]$, $[\mathrm{Ni}(\mathrm{HL}^{L\text{-}phe})_2]$ and $[\mathrm{Ni}(\mathrm{HL}^{D\text{-}phe})(\mathrm{HL}^{L\text{-}phe})]$ are three probable isomers. Complex **2** contains $[\mathrm{Ni}(\mathrm{HL}^{D\text{-}phe})_2]$ and $[\mathrm{Ni}(\mathrm{HL}^{L\text{-}phe})_2]$ molecules that are related by inversion because **2** crystallized into a centrosymmetric monoclinic space group, $P2_1/c$ (No. 14). The crystal structure formed a heterochiral 3D structure via hydrogen bonds through the crystal solvents. The different assembly structures were formed by chiral aggregation and the presence of hydrogen-bonded solvent molecules.

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Appendix A. Supplementary material

CCDC 933581 and 933582 contains the supplementary crystallographic data for $[\mathrm{Ni}(\mathrm{HL}^{L\text{-}phe})_2]\cdot 2\mathrm{MeOH}\cdot \mathrm{H_2O}$ (**1**) and $[\mathrm{Ni}(\mathrm{HL}^{DL\text{-}phe})_2]\cdot 7\mathrm{H_2O}$ (**2**) at 250 K. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2013.06.044.

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