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Enantioselective assembling into tetra- and octanuclear structures by deprotonation of copper(II) complexes of *N*-[(5-methylimidazol-4-yl)methylidene]-DL-phenylalanine and its L-form ligand

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ABSTRACT

Two copper(II) complexes with the protonated ligands $[Cu^{II}ClHL^{DL}]$ and $[Cu^{II}ClHL^{L}]$ were prepared, where HL^{DL} denotes *N*-[(5-methylimidazol-4-yl)methylidene]-DL-phenylalanine and HL^{L} denotes its L-form ligand. The deprotonation of $[Cu^{II}ClHL^{DL}]$ at the imidazole moiety gave an imidazolato-bridged cyclic tetranuclear arrayed $[Cu^{II}L^{D}(H_2O)]$ and $[Cu^{II}L^{L}(H_2O)]$ species, while the deprotonation of $[Cu^{II}ClHL^{L}]$ gave an octanuclear structure $[Cu^{II}_8L^{L}_8{\cdot}4H_2O]$ in which two cyclic tetranuclear species are linked by an intertetramer Cu–O (carboxylate) coordination bond.

1. Introduction

The fields of crystal engineering and supramolecular chemistry have attracted much attention in the past three decades, where an assembly process of well-designed molecular building block plays a crucial role [1]. Self-assembly process involving a metal ion is especially attractive and useful for the constructions of supramolecule, molecular architecture, and functional inorganic–organic porous compound, in which the assembly interaction may arise from coordination bonds and/or hydrogen bonds, which are substantially strong, selective, and directional [2] to construct the assembly structures. Among the number of useful building blocks, metal complexes of polydentate ligands involving imidazole group are useful building block, as they show versatile assembly process by intermolecular coordination bond of imidazolate nitrogen, imidazole···imidazolate (NH···N) hydrogen bond, and imidazole···halogen anion (NH···X) hydrogen bond [3]. Among the assembly processes, chiral assembly process is an important subject in chemistry, biology, and material science [4]. However, chiral assembly process is difficult to control, as we know that chirality is positioned at the top of the stereo-structural classes. While numerous studies have been devoted to elucidate the detailed mechanism of enantioselectivity [5] and tremendous developments have been achieved in the latest decade, the study on chiral assembly process is still challenging.

Previously, Matsumoto et al. reported pH-dependent monomer ↔ oligomer inter-conversion of Cu^{II} complexes with tridentate ligands (*N*-(2-R-imidazol-4-ylmethylidene)-2-aminoethylpyridine ($[Cu^{II}ClHL^{2\text{-}R}]^+$; R = Me, Ph), where the tridentate ligands $HL^{2\text{-}Me}$ and $HL^{2\text{-}Ph}$ are the 1:1 condensation products of 2-aminoethylpyridine and either 2-methyl-4-formylimidazole and 2-phenyl-4-formylimidazole [6]. The pH-dependent inter-conversion reactions of $4{\times}[Cu^{II}ClHL^{2\text{-}Me}]^+ \leftrightarrow [Cu^{II}L^{2\text{-}Me}]_4^{4+}$ and $6{\times}[Cu^{II}ClHL^{2\text{-}Ph}]^+ \leftrightarrow [Cu^{II}L^{2\text{-}Ph}]_6^{6+}$ are schematically shown in Scheme 1. The Cu^{II} complex with the tridentate ligand has one potential donor coordination site at the imidazole moiety and one acceptor coordination site at the substitutable equatorial coordination site. In the acidic condition, the Cu^{II} complex exists as the protonated mononuclear species of $[Cu^{II}ClHL^{2\text{-}R}]^+$. In the alkaline condition the deprotonation at the imidazole moiety promotes a self-assembly process, arising from coordination of the imidazolate nitrogen atom to a Cu^{II} ion of an adjacent unit, to yield oligomers such as $[Cu^{II}L^{2\text{-}Me}]_4^{4+}$ and $[Cu^{II}L^{2\text{-}Ph}]_6^{6+}$. It is understood that the Cu^{II} complex with the tridentate ligand is the simplest self-complementary molecule to a self-assembly process, in which the steric effect of the substituent R determines the structure and nuclearity of the resulting assembly complex.

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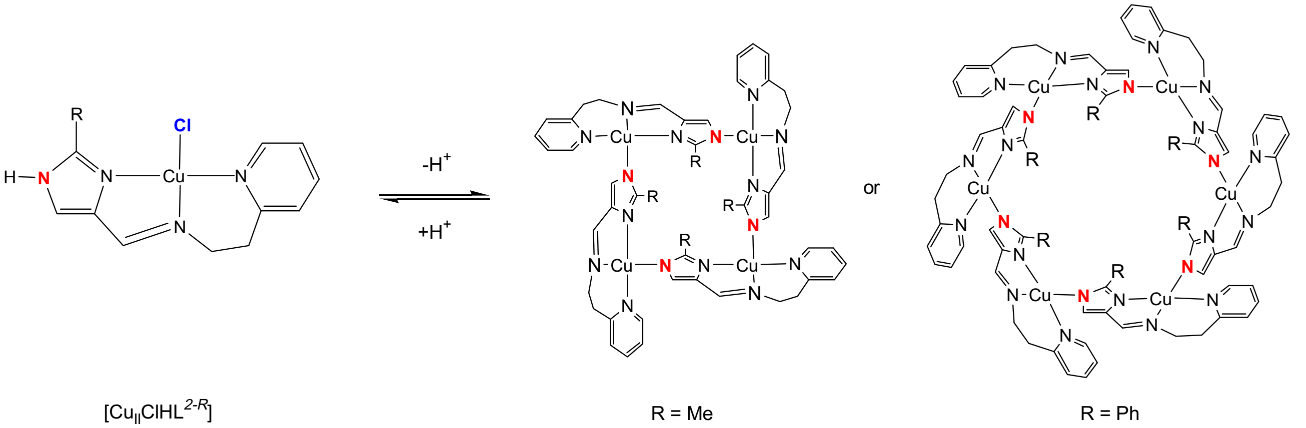
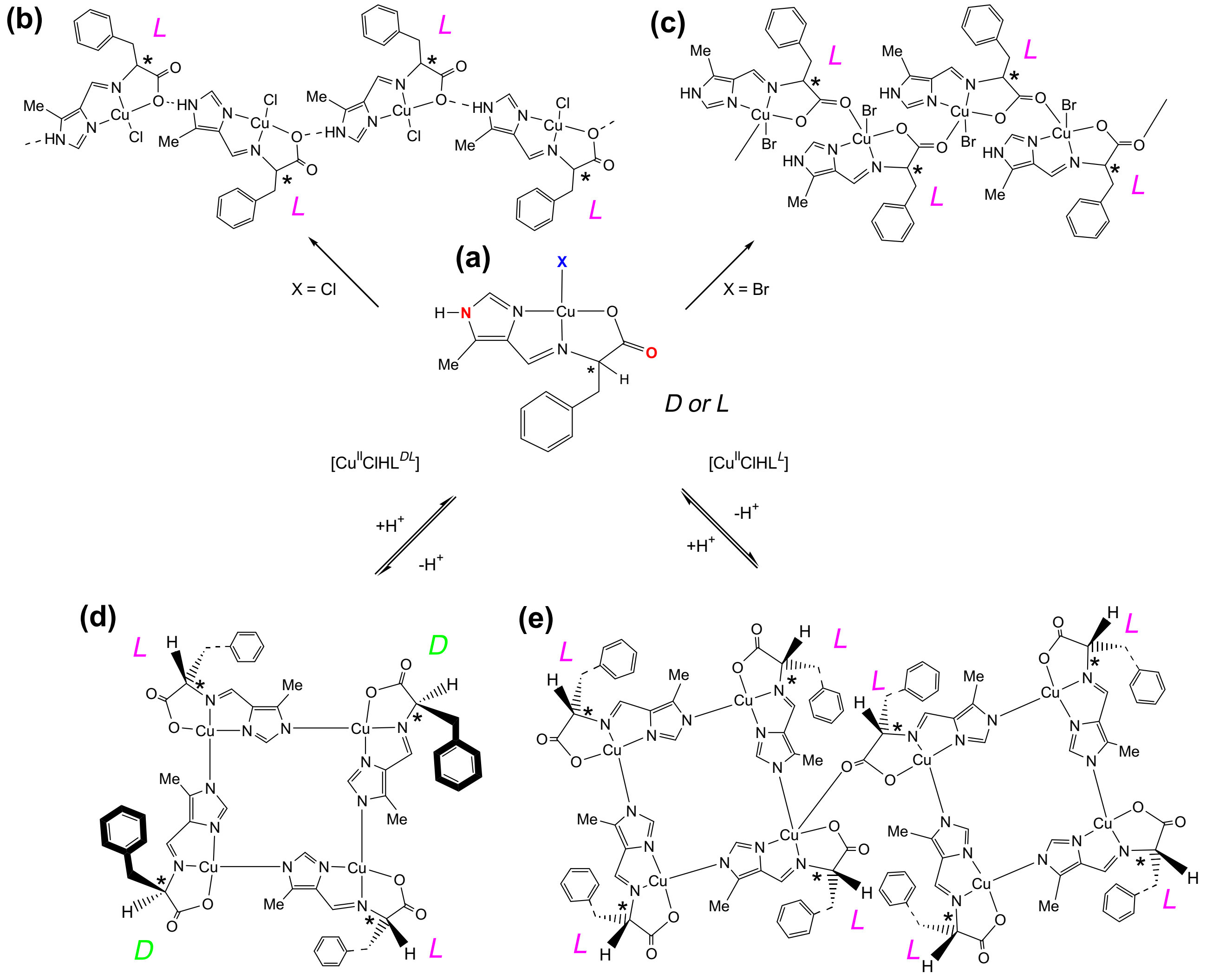


Scheme 1. Assembly process of a simplest self-complementary molecule. The building block $[\mathrm{Cu^{II}ClHL^{2\text{-}R}}]^+$exhibits a potential donor coordination site and a substitutable acceptor coordination site and the assembly reaction is motivated by the deprotonation at the imidazole moiety to produce the imidazolate-bridged cyclic oligomer. The nuclearity depends on the steric effect of the substituent R.



Scheme 2. (a) Structure of $[\mathrm{Cu^{II}ClHL^{DL}}]$ showing two potential donor coordination sites of imidazolate nitrogen and carboxylate oxygen (red colored atoms) and a substitutable acceptor coordination site (blue colored X). (b) Homochiral 1D assembly structure of $[\mathrm{Cu^{II}ClHL^{DL}}]$ constructed by intermolecular imidazole···carboxylate hydrogen bond. (c) Homochiral 1D assembly structure of $[\mathrm{Cu^{II}BrHL^{DL}}]$ generated by intermolecular coordination bond between carboxylate oxygen and $\mathrm{Cu^{II}}$ ion. (d) An imidazolate-bridged cyclic tetranuclear structure of the deprotonated form of $[\mathrm{Cu^{II}ClHL^{DL}}]_4$, where the array of the ligand chirality is LDLD. (e) Octanuclear structure of the deprotonated form of $[\mathrm{Cu^{II}ClHL^{L}}]$ (Color online).

In order to develop the assembly process from the simplest self-complementary molecule like $[\mathrm{Cu^{II}ClHL^{2\text{-}R}}]^+$ to more functional secondary self-complementary molecule, we designed the Cu^{II} complex with new tridentate ligand involving one imidazole and one amino acid moieties $[\mathrm{Cu^{II}XHL^{DL}}]$, where $\mathrm{H_2L^{DL}}$ denotes the 1:1 condensation product of DL-phenylalanine and 4-formylimidazole derivatives, and X denotes chloride or bromide [7]. The mono-deprotonated ligand $\mathrm{HL^{DL}}$ of the tridentate ligand at the carboxyl group coordinates to a Cu^{II} ion to give the complex $[\mathrm{Cu^{II}XHL^{DL}}]$. The Cu^{II} complex $[\mathrm{Cu^{II}XHL^{DL}}]$ has two potential donor coordination sites at the imidazole nitrogen of the formylimidazole moiety and at the carboxyl oxygen of the amino acid moiety as well as one acceptor coordination site at the substitutable X. Previously we have studied the Cu^{II} complex $[\mathrm{Cu^{II}XHL^{DL}}]$ and showed that such Cu^{II} complex can function as a self-complementary molecule to construct assembly structure even in the protonated form at the imidazole moiety [7]. As shown in Scheme 2(a), the Cu^{II} complex $[\mathrm{Cu^{II}XHL^{DL}}]$ showed two kinds of assembly processes: (1) intermolecular imidazole–carboxylate (NH···O) hydrogen bond gives a homochiral 1D assembly chain. (2) Intermolecular coordination bond from a carboxylate oxygen of a molecule to a Cu^{II} ion of adjacent molecule (–C=O–Cu) gives a homochiral 1D structure. It should be noted that such homochiral 1D assembly structures are enantioselectively constructed from the mixture of self-complementary building blocks $[\mathrm{Cu^{II}XHL^{D}}]$ and $[\mathrm{Cu^{II}XHL^{L}}]$.

If the deprotonation at the imidazole moiety of the Cu^{II} complex $[\mathrm{Cu^{II}XHL^{DL}}]$ was performed, it is anticipated that another kinds of assembly structures can be generated. Further, the tridentate ligand involves an asymmetric carbon atom at the phenylalanine moiety, it is also anticipated that the chirality of the phenylalanine would influence the resulting assembly structure. In this study, two Cu^{II} complexes $[\mathrm{Cu^{II}ClHL^{DL}}]$ and $[\mathrm{Cu^{II}ClHL^{L}}]$ were prepared, where two tridentate ligands $\mathrm{H_2L^{DL}}$ and $\mathrm{H_2L^{L}}$ denote *N*-[5-methylimidazol-4-yl)methylidene]-DL-phenylalanine and its L-form ligand *N*-[5-methylimidazol-4-yl)methylidene]-L-phenylalanine, respectively. And the deprotonated complexes at the imidazole moieties of $[\mathrm{Cu^{II}ClHL^{DL}}]$ and $[\mathrm{Cu^{II}ClHL^{L}}]$ were prepared and the assembly products were studied by the single-crystal X-ray diffraction analyses and several physical measurements, in order to investigate two points: (1) What is the assembly structure generated by the deprotonation of the imidazole moiety of the complementary complex? (2) Is there difference between the assembly structures of the deprotonated products of $[\mathrm{Cu^{II}ClHL^{DL}}]$ and $[\mathrm{Cu^{II}ClHL^{L}}]$? As given in Scheme 2, the deprotonated products of $[\mathrm{Cu^{II}ClHL^{DL}}]$ and $[\mathrm{Cu^{II}ClHL^{L}}]$ are a cyclic tetramer with alternate array of $[\mathrm{Cu^{II}L^{D}}]$ and $[\mathrm{Cu^{II}L^{L}}]$ species bridged by imidazolato group and an octamer in which two cyclic tetramers are linked by a carboxylate-bridge, respectively. We report here the synthesis, characterization, and molecular structures.

2. Experimental

2.1. General procedure

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

2.2. Synthesis of the ligands

2.2.1. Preparation of N-[5-methylimidazol-4-yl)methylidene]-DL-phenylalanine abbreviated as H_2L^{DL}

The ligand $\mathrm{H_2L^{DL}}$ was prepared by mixing DL-phenylalanine and 5-methyl-4-formylimidazole with 1:1 molar ratio in a mixed solution of methanol and water according to the previously reported method [7]. The ligand solution thus prepared was used for the synthesis of $[\mathrm{Cu^{II}ClHL^{DL}}]$ (**1**) without further purification and isolation.

2.2.2. Preparation of N-[5-methylimidazol-4-yl)methylidene]-L-phenylalanine abbreviated as H_2L^{L}

The tridentate ligand $\mathrm{H_2L^{L}}$ was prepared by the 1:1 condensation reactions of L-phenylalanine (166 mg, 1 mmol) and 5-methyl-4-formylimidazole (110 mg, 1 mmol) in 40 mL of a mixed solution of methanol and water (2/1 by volume) on a hot plate for 30 min. The ligand solution thus prepared was used for the synthesis of Cu^{II} complex without further purification and isolation.

2.3. Synthesis of the copper(II) complexes

2.3.1. Preparation of $[Cu^{II}ClHL^{DL}]$ (**1**)

The complex $[\mathrm{Cu^{II}ClHL^{DL}}]$ was prepared according to the method reported previously [7]. Green ble needles. *Anal.*Calc. for $[\mathrm{Cu^{II}ClHL^{DL}}] = \mathrm{C_{14}H_{14}N_3O_2ClCu}$: C, 47.33; H, 3.97; N, 11.83. Found: C, 47.39; H, 3.96; N, 11.84%.

2.3.2. Preparation of $[Cu^{II}L^{DL}(H_2O)]_4$ (**1′**)

To a solution of $[\mathrm{Cu^{II}ClHL^{DL}}]$ (178 mg, 0.5 mmol) in 50 mL of water was added 1 equivalent of aqueous 0.1 M NaOH solution. The mixture was stirred for 30 min at room temperature and then filtered. The filtrate was allowed to stand for several days, during which time blue green needle crystals precipitated. They were collected by suction filtration. Blue green needles. *Anal.* Calc. for $[\mathrm{Cu^{II}L^{DL}(H_2O)}] = \mathrm{C_{14}H_{13}N_3O_2Cu{\cdot}H_2O}$: C, 49.92; H, 4.49; N, 12.48. Found: C, 49.41; H, 4.51; N, 12.09%.

2.3.3. Preparation of $[Cu^{II}ClHL^{L}]$ (**2**)

To the solution of the ligand $\mathrm{H_2L^{L}}$ (1 mmol) was added a solution of $\mathrm{Cu^{II}Cl_2{\cdot}2H_2O}$ (170 mg, 1 mmol) in methanol (10 mL). The mixture was gently warmed and stirred for 30 min on a hot plate and then filtered. The filtrate was allowed to stand for several days, during which time green blue needle crystals precipitated. They were collected by suction filtration, washed with methanol and dried. Green blue needles. *Anal.*Calc. for $[\mathrm{Cu^{II}ClHL^{L}}] = \mathrm{C_{14}H_{14}N_3O_2ClCu}$: C, 47.33; H, 3.97; N, 11.83. Found: C, 47.51; H, 3.90; N, 11.76%.

2.3.4. Preparation of $[Cu^{II}L^{L}]_8{\cdot}xH_2O$ (**2′**)

To a solution of $[\mathrm{Cu^{II}ClHL^{L}}]$ (178 mg, 0.5 mmol) in 50 mL of water was added 1 equivalent of 0.1 M NaOH aqueous solution. The mixture was stirred for 30 min at room temperature and then filtered. The filtrate was allowed to stand for several days, during which time crystals precipitated. They were collected by suction filtration. Blue green needles. *Anal.* Calc. for $[\mathrm{Cu^{II}L^{L}}]{\cdot}2.8\mathrm{H_2O} = \mathrm{C_{14}H_{13}N_3O_2Cu{\cdot}2.8H_2O}$: C, 45.54; H, 5.08; N, 11.38. Found: C, 45.45; H, 5.12; N, 11.30%.

2.4. Physical measurements

Elemental C, H, and N analyses were carried out by Ms. Kikue Nishiyama at the Center for Instrumental Analysis of Kumamoto University. Thermogravimetric analyses (TGA) were performed on a TG/DTA6200 (Seiko Instrument Inc.), where the sample of ca. 2 mg was heated from room temperature to 120 °C. UV–Vis electronic spectra were measured on a Shimadzu UV-2450 UV–Vis spectrophotometer. pH-dependent electronic spectral changes were recorded at room temperature upon sequential addition of 0.1 M aqueous NaOH and HCl solutions for the forward and reverse titrations, respectively. An aqueous solution of the protonated complex (0.05 mmol of the complex in 10 mL of water/methanol = 50/50 vol %) was prepared. A spectrum was recorded after each 0.1 mL addition of a 0.1 M NaOH solution, until 1 equivalent of NaOH was added. Immediately after, electronic spectra were recorded for the reverse titration, following each 0.1 mL addition of a

0.1 M HCl solution to the solution resulting from the forward titration. The spectra were corrected for the volume variation due to the addition of the NaOH and HCl solutions. FAB-MS spectra were measured in methanol on a JEOL JMS-700 mass spectrometer; 3-nitrobenzyl alcohol was used as the matrix. Magnetic susceptibilities were measured with a MPMS SQUID susceptometer (Quantum Design Inc.) in the 2–300 K temperature range under the external magnetic field of 0.5 T. The calibrations were made with palladium. Corrections for diamagnetism were applied by using Pascal's constants [8]. Corrections for gelatin capsule were applied.

2.5. X-ray crystal structure analyses

A crystal of $[\mathrm{Cu^{II}L^{DL}(H_2O)}]_4$ (**1′**) is selected from the solution, mounted on a glass rod and coated with epoxy resin quickly, and then used for the X-ray diffraction study at room temperature. A crystal of $[\mathrm{Cu^{II}L^{L}}]_8 \cdot x\mathrm{H_2O}$ (**2′**) was handled similarly to that of **1′** and further the X-ray diffraction measurement was carried out at 150 K. All measurements were made on a Rigaku RAXIS RAPID imaging plate area detector with graphite monochromated Mo Kα radiation ($\lambda = 0.71075$ Å). The structures were solved by direct methods and expanded using the Fourier technique. The phenylalanine moiety of **1′** was not well refined by the conventional least-squares due to the large thermal motion and disorder. The phenyl group of the phenylalanine moiety was restrained and refined by the isotropic thermal parameters. Hydrogen atoms were fixed in calculated positions and refined by using a riding model. Hydrogen atoms of water molecules were not included. Due to the large numbers of the atomic parameters of over 180 non-hydrogen atoms and the poor quality of the crystal data due to the partial decomposition, the structure of **2′** was refined by least squares with isotropic displacement parameters except for eight Cu atoms and unit weight. The oxygen atoms of the water molecules were well located on the D-Fourier and 26 oxygen atoms were determined. The 26 water content of $[\mathrm{Cu^{II}L^{L}}]_8 \cdot 26\mathrm{H_2O}$ on the basis of the X-ray analysis is compatible with $[\mathrm{Cu^{II}L^{L}}]_8 \cdot 22.4\mathrm{H_2O}$ by the elemental analysis and $[\mathrm{Cu^{II}L^{L}}]_8 \cdot 24\mathrm{H_2O}$ by TGA. All calculations were performed by using the Crystal Structure crystallographic software package [9]. The crystallographic data of **1′** and **2′** are given below and the relevant coordination bond distances are given in Table 1.

$[\mathrm{Cu^{II}L^{DL}(H_2O)}]_4$ (**1′**), formula = $\mathrm{C_{14}H_{15}CuN_3O_3}$, M = 336.84, tetragonal, space group = $I4_1/a$ (No. 88), $a = b = 14.759(4)$ Å, $c = 26.895(8)$ Å, $V = 5858(3)$ Å^3, $Z = 16$, $D_{\mathrm{calc}} = 1.527$ g cm^{-3}, μ(Mo Kα) = 1.504 mm^{-1}, $T = 296$ K, R with $I > 2.0\sigma(I) = 0.1322$, $Rw(F^2)$ with all data = 0.2915, GOF = 0.997.

$[\mathrm{Cu^{II}L^{L}}]_8 \cdot 26\mathrm{H_2O}$ (**2′**), formula = $[\mathrm{Cu^{II}L^{L}}]_8 + 26\mathrm{H_2O} = \mathrm{C_{112}H_{160}Cu_8N_{24}O_{42}}$, M = 3023.00, orthorhombic, space group = $P2_12_12_1$ (No. 19), $a = 15.4925(8)$ Å, $b = 24.9090(13)$ Å, $c = 35.0759(16)$ Å, $V = 13535.9(12)$ Å^3, $Z = 4$, $D_{\mathrm{calc}} = 1.483$ g cm^{-3}, μ(Mo Kα) = 1.320 mm^{-1}, $T = 150$ K, R with $I > 2.0\sigma(I) = 0.1274$, $Rw = 0.1433$, GOF = 1.326.

Table 1
Coordination bond lengths (Å) for $[\mathrm{Cu^{II}L^{DL}(H_2O)}]_4$ (**1′**) and $[\mathrm{Cu^{II}{}_8L^{L}{}_8(H_2O)_4}] \cdot 22\mathrm{H_2O}$ (**2′**).

$[\mathrm{Cu^{II}L^{DL}(H_2O)}]$ (**1′**)			
Cu–N2	1.98(2)	Cu–N3	1.91(2)
Cu–O2	1.98(2)	Cu–N1	1.96(2)
Cu–O3	2.32(2)		
$[\mathrm{Cu^{II}{}_8L^{L}{}_8(H_2O)_4}] \cdot 22\mathrm{H_2O}$ (**2′**)			
Cu1–O1	2.06(3)	Cu1–N1	2.00(3)
Cu1–N3	2.04(4)	Cu1–N11	1.94(4)
Cu1–O22	2.51(3)		
Cu2–O3	2.00(3)	Cu2–O17	2.34(3)
Cu2–N2	1.98(3)	Cu2–N4	2.02(3)
Cu2–N6	1.92(3)		
Cu3–O5	2.01(2)	Cu3–O10	2.29(2)
Cu3–N5	1.98(2)	Cu3–N7	2.03(2)
Cu3–N9	1.99(3)		
Cu4–O7	2.01(3)	Cu4–O18	2.30(3)
Cu4–N8	1.95(2)	Cu4–N10	2.04(3)
Cu4–N12	1.97(3)		
Cu5–O9	2.01(2)	Cu5–O19	2.29(2)
Cu5–N13	2.07(2)	Cu5–N15	1.97(3)
Cu5–N23	2.01(3)		
Cu6–O11	2.00(2)	Cu6–N14	1.95(2)
Cu6–N16	1.99(2)	Cu6–N18	1.95(3)
Cu7–O13	2.02(2)	Cu7–O20	2.36(3)
Cu7–N17	1.94(2)	Cu7–N19	2.04(2)
Cu7–N21	1.99(2)		
Cu8–O15	2.00(2)	Cu8–N20	1.98(2)
Cu8–N22	2.04(2)	Cu8–N24	1.96(2)

3. Results and discussion

3.1. Synthesis and characterization of copper(II) complexes

Tridentate ligand $\mathrm{H_2L^{DL}}$ (or $\mathrm{H_2L^{L}}$) with $\mathrm{N_2O}$ donor atoms was prepared by the 1:1 condensation reaction of 5-methyl-4-formylimidazole and DL-phenylalanine or L-phenylalanine. When ligand $\mathrm{H_2L^{DL}}$ (or $\mathrm{H_2L^{L}}$) was reacted with $\mathrm{Cu^{II}Cl_2 \cdot 2H_2O}$ in 1:1 molar ratio in methanol, the reaction produces the $\mathrm{Cu^{II}}$ complex with the formula $[\mathrm{Cu^{II}ClHL^{L\ or\ DL}}]$, in which the carboxylate moiety in the tridentate ligand is deprotonated. When complex $[\mathrm{Cu^{II}ClHL^{L\ or\ DL}}]$ was treated with 1 equivalent aqueous NaOH solution, the imidazole moiety of $[\mathrm{Cu^{II}ClHL^{L\ or\ DL}}]$ is deprotonated to produce the deprotonated complex with the formula $[\mathrm{Cu^{II}L^{L\ or\ DL}}] \cdot x\mathrm{H_2O}$, in which the di-deprotonated tridentate ligand $\mathrm{L^{L\ or\ DL}}$ at the carboxylate and imidazole moieties coordinates to a $\mathrm{Cu^{II}}$ ion as an electronically di-negative ligand. On slow crystallization at room temperature, the deprotonated complexes $[\mathrm{CuL^{DL\ and\ L}}]_n \cdot x\mathrm{H_2O}$ were obtained as blue green needle crystals, which decompose gradually in open atmosphere due to partial elimination of the crystal solvents. The C, H, and N elemental analyses of the samples kept in open atmosphere agree with the formulas of $[\mathrm{Cu^{II}L^{DL}}] + 1\mathrm{H_2O}$ and $[\mathrm{Cu^{II}L^{L}}] + 2.8\mathrm{H_2O}$. The dried samples were used for thermogravimetric analyses (TGA), magnetic susceptibility measurements, and FAB-MS spectral measurements. TGA were performed as follows: the sample was heated from room temperature to 120 °C at the heating rate of 2 °C min^{-1} and the sample temperature was kept at 120 °C for 6 h and then the temperature was cooled to room temperature. The sample of $[\mathrm{Cu^{II}L^{DL}(H_2O)}]_4$ (**1′**) showed a 2.5% weight loss corresponding to $0.5\mathrm{H_2O}$ per $[\mathrm{Cu^{II}L^{DL}(H_2O)}]$ in the heating process, another 2.5% weight loss corresponding to $0.5\mathrm{H_2O}$ in the keeping the temperature at 120 °C, and a 2.5% weight increase corresponding to $0.5\mathrm{H_2O}$ in the cooling process from 120 °C to room temperature. The sample of $[\mathrm{Cu^{II}L^{L}}]_8 \cdot x\mathrm{H_2O}$ (**2′**) showed a ca. 15% weight loss corresponding to ca. $3\mathrm{H_2O}$ in the heating process per $[\mathrm{Cu^{II}L^{L}}] \cdot (x/8)\mathrm{H_2O}$ and a 6% weight increase corresponding to ca. $\mathrm{H_2O}$ in the cooling process from 120 °C to room temperature. The TGA data are compatible with the water contents of $[\mathrm{Cu^{II}L^{DL}}] \cdot 1\mathrm{H_2O}$ and $[\mathrm{Cu^{II}L^{L}}] \cdot 3\mathrm{H_2O}$. The positive ion FAB-MS spectrum of $[\mathrm{Cu^{II}L^{DL}(H_2O)}]_4$ (**1′**) shows the peaks assigned to a tetramer species of $[\mathrm{Cu^{II}{}_4(L^{DL})_3(HL^{DL})}]^+$. The FAB-MS spectrum of $[\mathrm{Cu^{II}L^{L}}]_8 \cdot x\mathrm{H_2O}$ (**2′**) shows the peaks assignable to a pentamer species of $[\mathrm{Cu^{II}{}_5(L^{L})_4(HL^{L})}]^+$, in addition to the peaks assigned to a tetramer species of $[\mathrm{Cu^{II}{}_4(L^{L})_3(HL^{L})}]^+$.

3.1.1. Structure of $[\mathrm{Cu^{II}L^{DL}(H_2O)}]_4$ (**1′**)

Complex **1′** crystallized in the centrosymmetric space group $I4_1/a$ (No. 88) with the unique formula unit of $[\mathrm{Cu^{II}L^{DL}(H_2O)}]$. The tetranuclear structure of **1′** with the selected atom numbering scheme viewed along a 4_1 screw axis is shown in Fig. 1(a). In a unit cell, two enantiomers of $\mathrm{Cu^{II}}$ complexes with the tridentate ligands consisting of the

D- and L-phenylalanine moieties, that is, $[\mathrm{Cu^{II}L^{D}(H_2O)}]$ and $[\mathrm{Cu^{II}L^{L}(H_2O)}]$ are involved. A $\mathrm{Cu^{II}}$ ion is coordinated by the $\mathrm{N_3O}$ donor atoms of an electronically dinegative tridentate ligand $\mathrm{L^D}$ or $\mathrm{L^L}$, where the imidazole group is deprotonated, in addition to the deprotonation of the carboxylate group. An imidazolate nitrogen atom of $[\mathrm{Cu^{II}L^{D}(H_2O)}]$ coordinates to the $\mathrm{Cu^{II}}$ ion of the adjacent unit of $[\mathrm{Cu^{II}L^{L}(H_2O)}]$ to form a cyclic tetranuclear structure, where $[\mathrm{Cu^{II}L^{D}(H_2O)}]$ or $[\mathrm{Cu^{II}L^{L}(H_2O)}]$ functions as a self-complementary building block, as it contains one donor coordination site at the imidazolate nitrogen and one acceptor coordination site at the vacant equatorial coordination site. The sequence of the chiralities of the cyclic tetramer is ($[\mathrm{Cu^{II}L^{D}(H_2O)}]$–$[\mathrm{Cu^{II}L^{L}(H_2O)}]$–$[\mathrm{Cu^{II}L^{D}(H_2O)}]$–$[\mathrm{Cu^{II}L^{L}(H_2O)}]$). Fig. 1(b), that the cyclic tetramer was viewed perpendicular the 4_1 screw axis, shows the orientations of four phenylalanine moieties and four coordinated water molecules in the cyclic tetramer. Two D-phenylalanine moieties are positioned at one side and the other two L-phenylalanine moieties are positioned at other side. And two water molecules are positioned at one side and the other two water molecules are positioned at another side.

The coordination geometry around the $\mathrm{Cu^{II}}$ ion is described as a square pyramid, in which the equatorial coordination site is occupied by $\mathrm{N_3O}$ donor atoms of the tridentate ligand and an imidazolate nitrogen atom of the adjacent molecular unit and the axial site is occupied by the oxygen atom of a water molecule. The Cu–ligand distances are Cu–N2 (imidazole) = 1.98(2) Å, Cu–N3 (imine) = 1.91(2) Å, Cu–O2 (carboxylate) = 1.98(2) Å, Cu–N1 (imidazolate) = 1.96(2) Å for equatorial sites, and Cu–O3 (water) = 2.32(2) Å for axial site. The dihedral angle between the equatorial coordination plane of N1, N2, N3, O2 and the imidazolate plane is 47°.

The hydrogen bond O···O distances are listed in Table 2. The water molecule O(3) at the axial coordination site is hydrogen-bonded to two carboxylate oxygen atoms O(1) and O(2) of the adjacent tetramers with the distances of O1···O3 = 2.76(3) Å and O2···O3 = 2.68(3) Å. The cyclic tetramers are connected by the two hydrogen bonds to form a three-dimensional network structure, in which these two hydrogen bonds and the symmetry related hydrogen bonds form cyclic hexanuclear and octanuclear structures. The cyclic hexanuclear structure is constructed by that O3–Cu1–O2 is hydrogen bonded to the symmetry related O3*–Cu1*–O2* with the two hydrogen bonds of O2···O3* and O3···O2*. The cyclic octanuclear structure is constructed by that O2–C7–O1 of carboxylate moiety is hydrogen bonded to the symmetry related O2**–C7**–O1** through two water molecules O3 and O3* with the four hydrogen bonds of O2···O3*, O3*···O1**, O2**···O3***, and O3***···O1.

Table 2
O···O Distances (Å) assigned to hydrogen bonds.

$[\mathrm{Cu^{II}L^{DL}(H_2O)}]$ (**1′**)					
O1···O3	2.76(3)		O2···O3		2.68(3)
$[\mathrm{Cu^{II}_8L^{L}_8(H_2O)_4}]\cdot 22\mathrm{H_2O}$ (**2′**)					
O1∼O16 are the oxygen atoms of the carboxylate moieties of $[\mathrm{Cu^{II}_8L^{L}_8(H_2O)_4}]$, O17∼O20 are the oxygen atoms at the axial coordination positions of $\mathrm{Cu^{II}}$ ions, and O21∼O42 are the oxygen atoms of the crystal waters					
O1···O31	2.88(5)	O2···O34	2.73(5)	O3···O28	2.64(4)
O4···O34	2.68(4)	O6···O25	2.81(3)	O6···O40	2.83(5)
O7···O39	2.73(4)	O8···O42	2.84(3)	O10···O26	2.92(4)
O11···O40	2.93(5)	O12···O23	2.81(4)	O12···O25	2.86(4)
O13···O38	2.67(5)	O14···O22	2.80(3)	O14···O36	2.87(4)
O16···O31	2.67(5)	O16···O35	2.98(4)		
O17···O24	2.83(5)	O17···O32	2.83(5)	O18···O27	2.77(4)
O18···O30	2.74(4)	O18···O34	2.72(4)	O19···O29	2.82(4)
O19···O41	2.67(5)	O20···O23	2.87(4)	O20···O29	2.78(4)
O21···O22	2.80(4)	O21···O27	2.92(5)	O21···O32	2.84(5)
O21···O36	2.81(5)	O22···O24	2.98(4)	O22···O38	2.87(5)
O23···O28	2.91(4)	O24···O26	2.69(4)	O24···O27	2.80(5)
O25···O33	2.76(5)	O26···O30	2.73(4)	O26···O352	2.89(5)
O29···O33	2.67(5)	O30···O38	2.79(5)	O30···O39	2.78(5)
O31···O32	2.61(5)	O33···O37	2.89(5)	O35···O36	2.84(5)
O37···O41	2.67(6)	O39···O41	2.64(6)	O39···O42	2.92(6)

3.1.2. Structure of $[\mathrm{Cu^{II}L^{L}}]_8\cdot 26\mathrm{H_2O}$ (**2′**)

Complex **2′** crystallized in orthorhombic non-centrosymmetric space group $P2_12_12_1$ (No. 19) and the unit cell consists of eight molecules $[\mathrm{Cu^{II}L^{L}}] \times 8$ and the 26 water molecules as the unique unit. The octanuclear structure of **2′** with the selected atom numbering is shown in Fig. 2(a). Due to the large numbers of the atomic parameters, the crystal structure was refined by the use of isotropic thermal parameters for non-hydrogen atoms except for Cu atoms and the number of the water molecules is determined to be 23 on the D-Fourier map. Nevertheless the low accuracy of the crystal structural determination, the overall molecular structure including crystal waters is satisfactory determined. The Flack parameter was refined nearly to zero and the resulting structure consists of eight molecules with L-form $[\mathrm{Cu^{II}L^{L}}]$, where the ligand chirality of *N*-[(5-methylimidazol-4-yl)methylidene]-L-phenylalanine thus determined is consistent with the commercially purchased L-phenylalanine.

Each copper(II) ion is coordinated by $\mathrm{N_3O}$ donor atoms of an electronically di-negative planar tridentate ligand ($\mathrm{L^L}$), where the imidazole group is deprotonated, in addition to the deprotonation

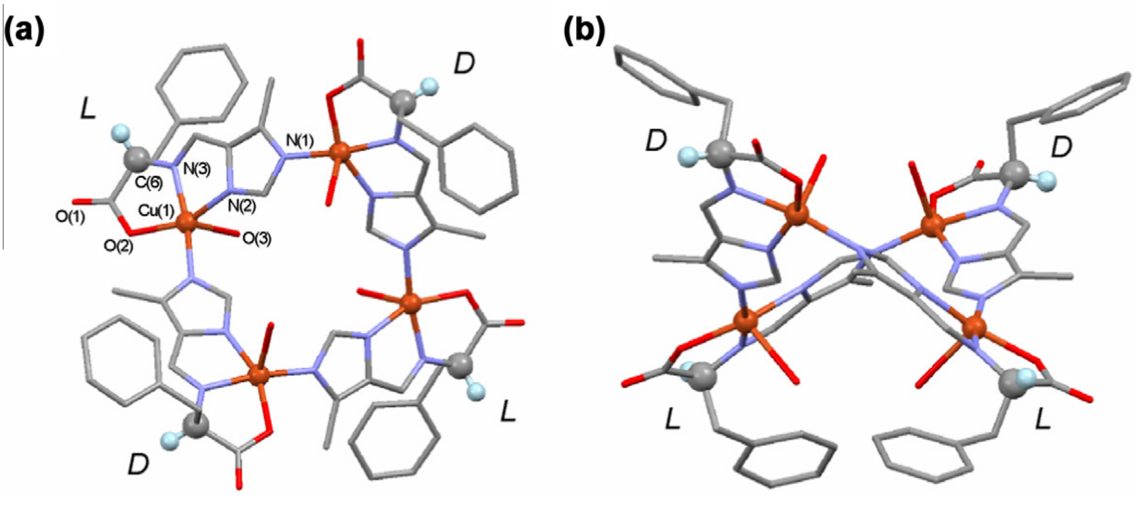


Fig. 1. (a) Cyclic tetranuclear structure of $[\mathrm{Cu^{II}L^{DL}(H_2O)}]_4$ (**1′**) viewed along 4_1 axis with the selected atom-numbering scheme. (b) Side view of the tetramer. The tetrameric structure consists of ($[\mathrm{Cu^{II}L^{D}(H_2O)}]$–$[\mathrm{Cu^{II}L^{L}(H_2O)}]$–$[\mathrm{Cu^{II}L^{D}(H_2O)}]$–$[\mathrm{Cu^{II}L^{L}(H_2O)}]$).

of the carboxylate group of the L-phenylalanine moiety. An imidazolate nitrogen atom of a unit $[\mathrm{Cu^{II}L^{L}}]$ thus generated coordinates to the $\mathrm{Cu^{II}}$ ion of the adjacent unit to form a cyclic tetranuclear structure $[\mathrm{Cu^{II}L^{L}}]_4$. Two cyclic tetranuclear units (A and B) are linked by the coordination bond of Cu3–O10 = 2.29(2) Å to form an octanuclear structure.

The coordination geometry for two $\mathrm{Cu^{II}}$ sites (Cu5, and Cu7) of tetramer B is described as a square pyramid due to the axial coordination of water molecule, while the other two sites (Cu6 and Cu8) have a square planar geometry. For every other site of four $\mathrm{Cu^{II}}$ sites for cyclic tetramer B, a water molecule coordinates to a $\mathrm{Cu^{II}}$ ion at the axial coordination site. On the other hand, the coordination

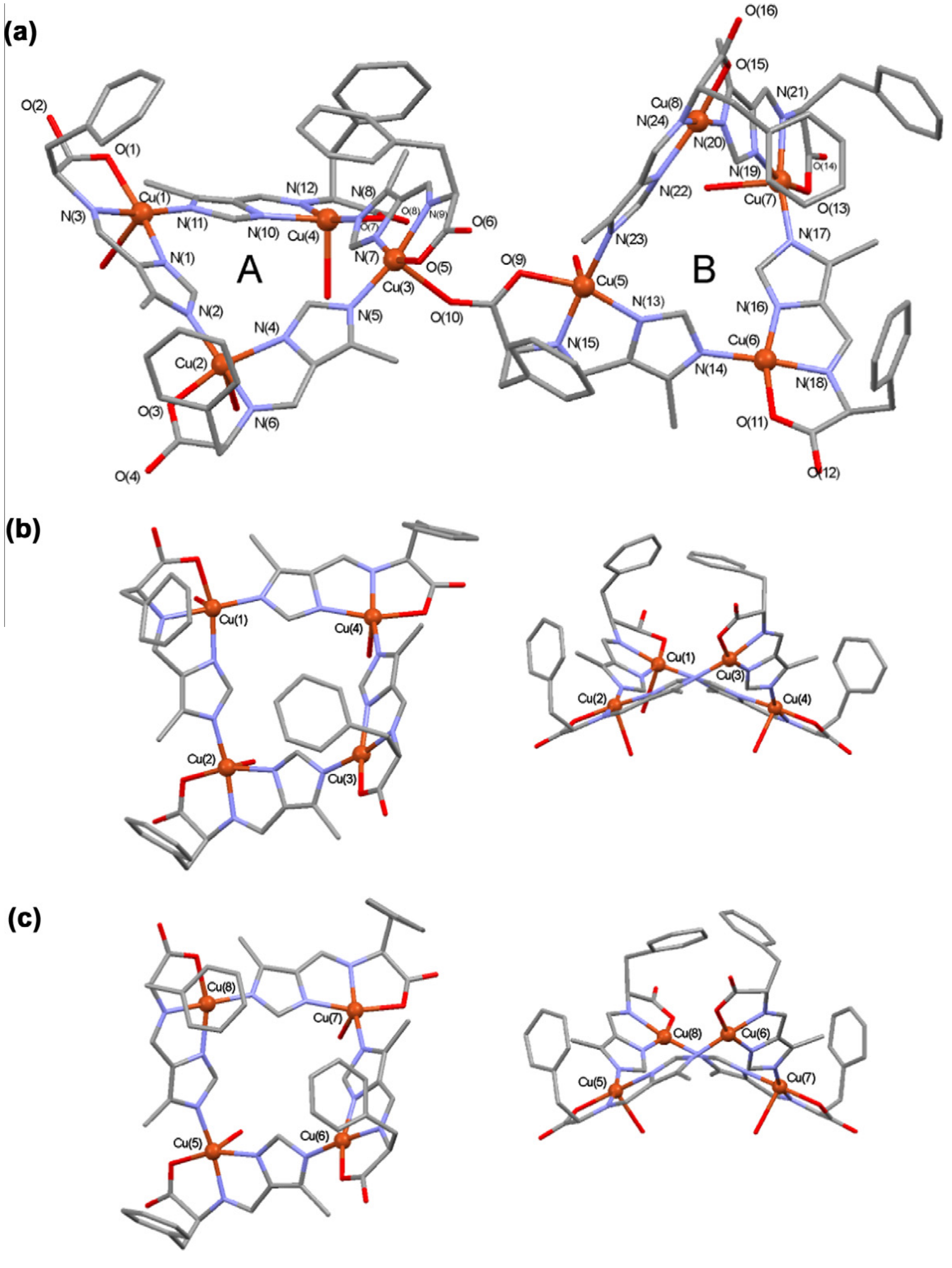


Fig. 2. (a) Octanuclear structure of $[\mathrm{Cu^{II}}_8\mathrm{L^{L}}_8(\mathrm{H_2O})_4]$ (**2′**) with the selected atom-numbering scheme. Two cyclic tetramers A and B are linked by a Cu–O coordination bond. (b) Cyclic structure of tetramer A. A view showing the cavity of tetramer A (left); side view showing the orientation of four phenyl groups of L-phenylalanines (right). (c) Cyclic structure of tetramer B. A view showing the cavity of tetramer B (left); side view showing the orientation of four phenyl groups of L-phenylalanines (right).

geometry for four Cu^{II} sites of a tetramer A (Cu1, Cu2, Cu3, and Cu4) is described as a square pyramid, in which a water molecule occupies the axial coordination site for Cu1, Cu2 and Cu4, while the carboxylate oxygen atom of Cu5 site of other tetramer B occupies the axial site for Cu3 site. It should be noted than the distance of Cu1–O22 = 2.51(3) Å is longer for the other two Cu–water distances. Excluding O22 as the coordinated water molecules, the octamer can be written as a $[Cu^{II}{}_8L^{L}{}_8(H_2O)_4]$, in which each water molecule coordinates axially to a Cu^{II} ion for every other site in a cyclic tetrameric $Cu^{II}{}_4$.

Fig. 2(b) shows the orientations of four L-phenylalanine moieties for tetramer A. Compared with Fig. 1(b), it is apparent that the cyclic tetranuclear structure with all L-phenylalanine moieties of **2**′ differs from that of **1**′ with (DLDL). The side view of the tetramer (Fig. 2(b)) demonstrates that all four phenyl groups of L-phenylalanine moieties are positioned at the same side and the oxygen atoms of water molecules are positioned at the opposite side. The orientation is different from that of $[Cu^{II}L^{DL}(H_2O)]_4$ (**1**′), in which two D-phenylalanine moieties are positioned at one side and the other two L-phenylalanine moieties are positioned at other side (Fig. 1(b)). As the four L-phenylalanine moieties are positioned at one side and oriented so as to enclose a hydrophobic cavity of a cyclic tetramer. On the other hand, the other side was occupied by the coordinated water molecules and provides a hydrophilic space.

The crystal waters are distributed on the side of the hydrophilic space and form a cluster-like hydrogen-bonded network, as shown in Fig. 3. Adjacent two octamers are connected through hydrogen-bonded water clusters. Of 26 water molecules, 22 water molecules exist as the crystal waters. The hydrogen bond O···O distances are listed in Table 2, where O1–O16 are the oxygen atoms of the carboxylate moieties of $[Cu^{II}{}_8L^{L}{}_8(H_2O)_4]$, O17–O20 are the oxygen atoms at the axial positions of Cu^{II} ions, and O21–O42 are the oxygen atoms of the crystal waters. The 22 crystal waters of O21–O42 are not only self-assembled through hydrogen bonds [10] but also hydrogen-bonded to the water and carboxylate oxygen atoms of $[Cu^{II}{}_8L^{L}{}_8(H_2O)_4]$ to form a complex cluster-like network. It is noteworthy that complex **2**′ has the cluster water network involving cyclic penta-, hexa-, hepta-, and octa-meric O···O structures.

3.2. *Magnetic susceptibility studies of $[Cu^{II}L^{DL}(H_2O)]_4$ (**1**′) and $[Cu^{II}L^{L}]_8{\cdot}22.6H_2O$ (**2**′)*

The magnetic susceptibilities were measured under a 5000 G applied magnetic field in the 1.9–300 K temperature range. The magnetic behaviors of **1**′ and **2**′ are shown in Fig. 4, as χ_A versus T plots and $\chi_A T$ versus T plots, where χ_A is the magnetic susceptibility per Cu and T is the absolute temperature. The $\chi_A T$ value for **1**′ (0.357 $cm^3\ K\ mol^{-1}$) and **2**′ (0.316 $cm^3\ K\ mol^{-1}$) at 300 K are smaller than the spin-only value for $S = 1/2$ (0.375 $cm^3\ K\ mol^{-1}$). The χ_A versus T curves of **1**′ and **2**′ show a maximum at 50 and 95 K, respectively. When the temperature is lowered, the $\chi_A T$ value decreases gradually. All these data indicate the operation of antiferromagnetic interactions between Cu^{II} ions. The magnetic susceptibility data of **1**′ was interpreted quantitatively based on a cyclic tetranuclear structure, by the use of the spin Hamiltonian $\boldsymbol{H} = -2J[\mathbf{S}_1 \cdot \mathbf{S}_2 + \mathbf{S}_2 \cdot \mathbf{S}_3 + \mathbf{S}_3 \cdot \mathbf{S}_4 + \mathbf{S}_4 \cdot \mathbf{S}_1]$, where J is the Heisenberg exchange integral between two adjacent Cu^{II} ions. The magnetic susceptibility per Cu was fitted to the Van Vleck equation (1) [11], where N is Avogadro's number, β *is* the Bohr magneton, k is the Boltzmann constant, g is the Cu^{II} Landé factor, and ρ *is* the molar fraction of non-coupled species. The value of temperature independent paramagnetism, $N\alpha$, and the g value of non-coupled species were fixed at 60×10^{-6} $cm^3\ mol^{-1}$ and 2.00, respectively.

$$\begin{aligned}\chi_A = {} & N\beta^2 g^2/2kT[2 + \exp(-2J/kT) + 5\exp(2J/kT)]/[7 \\ & + \exp(-4J/kT) + 3\exp(-2J/kT) + 5\exp(2J/kT)](1 - \rho) \\ & + (2N\beta^2/kT)\rho + N\alpha \qquad (1)\end{aligned}$$

The magnetic data of **2**′ was interpreted by introducing magnetic interaction J' between adjacent two tetramers, in addition to the Eq. (1). The inter-tetranuclear exchange integral, J', was estimated by the molecular field approximation with the number of interacting nearest neighbors $z = 1$ [12]. The experimental magnetic data of **1**′ and **2**′ are reproduced by the best-fit parameters: $g = 2.06$, $J = -31.6$ cm^{-1}, and $\rho = 1.8\%$ (**1**′); $g = 2.07$, $J = -40.6$ cm^{-1}, $\rho = 0.1\%$ and $J' = -6.5$ cm^{-1} (**2**′).

The fairly large antiferromagnetic interactions result from a super-exchange mechanism in which the unpaired electrons of adjacent Cu^{II} ions occupying the orbitals lying in the basal coordination planes interact through the imidazolate-bridge. The calculated J

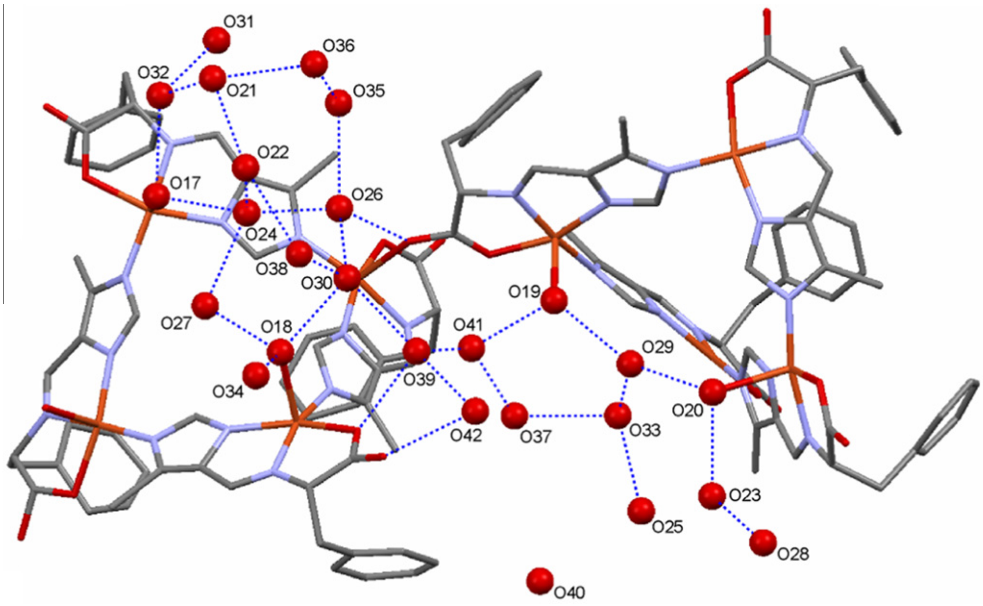


Fig. 3. Cluster waters of $[Cu^{II}{}_8L^{L}{}_8(H_2O)_4]$ (**2**′) with the atom-numbering scheme. Of 26 water molecules, 22 water molecules exist as the crystal waters and form a cluster-like network structure. The crystal waters are distributed on the side of the hydrophilic space.

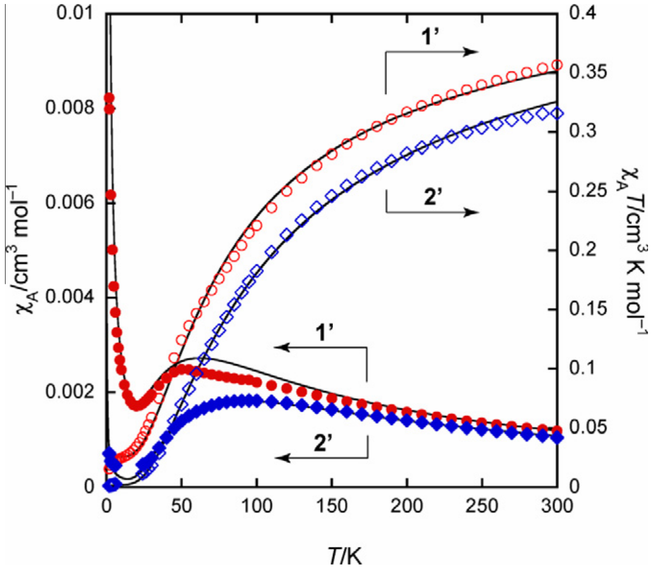


Fig. 4. Plots of χ_A vs. T and $\chi_A T$ vs. T for **1**′ and **2**′. The χ_A and $\chi_A T$ are the values per Cu. The solid lines represent the theoretical curves obtained with the model and best-fit parameters mentioned in the text.

exchange integrals are compatible with those of imidazolate bridged binuclear and polynuclear Cu^{II} complexes in which the imidazolate group bridges the Cu^{II} ions at their equatorial sites [13]. The J value (-40.6 cm^{-1}) of **2**′ is a little larger than that ($J = -31.6$ cm^{-1}) of **1**′, indicating the antiferromagnetic interaction via imidazolate bridge of **2**′ is slightly larger than that of **1**′. This is rationalized by their structures, where the coordination geometry of **1**′ is a square pyramid for all four Cu^{II} sites, while half of the Cu^{II} sites of **2**′ have a square planar and the other half have a square pyramidal. On the other hand, the small inter-tetranuclear antiferromagnetic interaction J' is due to the axial–equatorial bridging through carboxylate with the syn–anti bridging mode [14].

3.3. pH-dependent electronic spectra of [Cu^{II}L^{DL}(H$_2$O)]$_4$ (**1**′) and [Cu^{II}L^{L}]$_8$·22.6H$_2$O (**2**′)

The pH-dependent inter-conversion between the protonated monomer and the deprotonated oligomer was studied by the titration of the aqueous solution of **1** and **2** with NaOH or HCl. Fig. 5 shows the pH-dependent electronic spectra for the **1** → **1**′ forward conversion and for the **1**′ → **1** reverse conversion. The spectrum of **1** exhibits a broad band at 692 nm (molar extinction coefficient $\varepsilon = 75$ M^{-1} cm^{-1}) assignable to a d–d transition. On adding a 0.1 M aqueous NaOH solution, this broad band shifts to lower wavelength and the molar extinction coefficient increases. When the amount of NaOH solution added was equimolar, the generated spectrum had a d–d band maximum at 645 nm ($\varepsilon = 117$ M^{-1} cm^{-1}). This spectral change is characterized by an isosbestic point at 726 nm, typical of an equilibrium between the protonated and deprotonated forms. The spectra for the **1**′ → **1** reverse titration exhibit an isosbestic point at the same wavelength and reach the genuine spectrum of **1**, evidencing that the equilibrium is reversible. The pH-dependent inter-conversion for **2** → **2**′ → **2** was studied by the same method. The pH-dependent electronic spectra showed a very similar behavior to that observed for the **1** → **1**′ → **1**, as given in *Fig. S1*. The spectrum of **2** exhibits a d–d band at 691 nm ($\varepsilon = 78$ M^{-1} cm^{-1}). Upon addition of a 0.1 M NaOH solution, the spectrum changed exhibiting an isosbestic point at 732 nm. When the amount of added NaOH solution was equimolar, the spectrum showed a d–d band maximum at 644 nm ($\varepsilon = 118$ M^{-1} cm^{-1}). The pH dependent electronic spectra of **1** and **2** showed no distinct difference, although the deprotonation of **1** and **2** produced tetramer and octamer in the solid states, respectively.

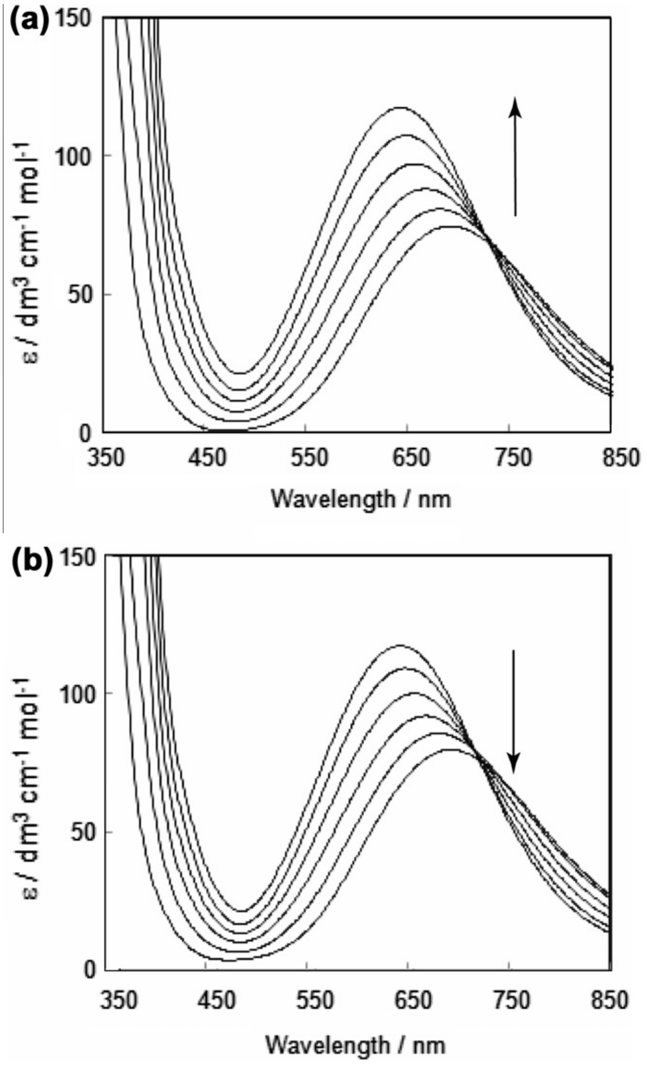


Fig. 5. The pH-dependent electronic spectra of **1** → **1**′ → **1**. (a) Forward titration for **1** → **1**′ during the addition of NaOH aqueous solution (b) reverse titration for **1**′ → **1** during the addition of HCl aqueous solution.

4. Concluding remarks

Copper(II) complexes with tridentate ligands, which were derived from the 1:1 condensation reaction of phenylalanine and 4-formylimidazole derivatives, have been studied, in order to develop self-assembly process from the simplest self-complementary molecule to the advanced multi-functional self-assembly molecule. Two such complexes [Cu^{II}ClHL^{DL}] and [Cu^{II}ClHL^{L}] were prepared, where HL^{DL} denotes a racemic ligand of *N*-[(5-methylimidazol-4-yl)methylidene]-DL-phenylalanine and HL^{L} denotes its optically pure L-form ligand. The Cu^{II} complex [Cu^{II}ClHL^{DL}] or [Cu^{II}ClHL^{L}] has two potential donor coordination sites at the imidazole nitrogen of the formylimidazole moiety and at the carboxylate oxygen of the amino acid moiety as well as one acceptor coordination site at the substitutable Cl$^-$. The complex can be an advanced self-assembly building block, because it contains two different kinds of donor sites and one acceptor site. Further, as the Cu^{II} complex contains an asymmetric carbon atom at the phenylalanine moiety of the tridentate ligand, the assembly process should be also influenced by the element of the chirality. Interestingly the $\mathrm{Cu^{II}}$ complex can function as a self-complementary building block both in the protonated form and the deprotonated form. In the protonated form, the $\mathrm{Cu^{II}}$ complex $[\mathrm{Cu^{II}XHL^{DL}}]$ showed two kinds of enantioselective assembly process to give (1) homochiral 1D assembly structure constructed by intermolecular imidazole⋯carboxylate hydrogen bond and (2) homochiral 1D structure generated by intermolecular coordination bond between a carboxylate oxygen of a molecule and a $\mathrm{Cu^{II}}$ ion of adjacent molecule. The deprotonation of $[\mathrm{Cu^{II}ClHL^{DL}}]$ at the imidazole moiety gave an imidazolato-bridged cyclic tetranuclear structure $[\mathrm{CuL^{DL}(H_2O)}]_4$, while the deprotonation of $[\mathrm{Cu^{II}ClHL^{L}}]$ gave an octanuclear structure $[\mathrm{Cu^{II}}_8\mathrm{L^{L}}_8\mathrm{(H_2O)_4}]$, in which two cyclic tetranuclear species are bridged by a coordination bond between an carboxylate oxygen and a $\mathrm{Cu^{II}}$ ion. The result apparently demonstrates that the chirality is an important factor to construct definitely different assembly structure. The present complexes can be advanced self-complementary building block. The studies along this line should be developed.

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Appendix A. Supplementary data

CCDC 833502 & 833503 contains the supplementary crystallographic data for $[\mathrm{Cu^{II}L^{DL}(H_2O)}]_4$ (**1’**) at 296 K and $[\mathrm{Cu^{II}8L^{L}8(H_2O)_4}]\cdot 22\mathrm{H_2O}$ (**2’**) at 150 K. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2011.11.024.

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