

# Copper(II) Complexes of *N,N'*-Bis((2-substituted-imidazol-4-yl)methylene)-3,3'-diaminodipropylamine (2-Substituent = H, Me): $\Delta$ and $\Lambda$ Enantiomorphs of the Protonated Complex and Helical Structure of the Deprotonated Complex Formed by Hydrogen Bonds

Hitoshi Miyasaka,<sup>\*,†</sup> Shingo Okamura,<sup>†</sup> Toshio Nakashima,<sup>‡</sup> and Naohide Matsumoto<sup>\*,§</sup>

Department of Chemistry, Faculty of Science, Kyushu University, Hakozaki 6-10-1, Higashi-ku, Fukuoka 812, Japan, Faculty of Education, Oita University, Dan-noharu 700, Oita 870-11, Japan, and Department of Chemistry, Faculty of Science, Kumamoto University, Kurokami 2-39-1, Kumamoto 860, Japan

Received April 1, 1997<sup>⊗</sup>

Copper(II) complexes with the quinquedentate ligands  $H_2L^n$  ( $n = 1, 2$ ) of the 1:2 condensation products of 3,3'-diaminodipropylamine and each of 4-formylimidazole and 4-formyl-2-methylimidazole have been synthesized and characterized, where the complexes have the general formula of  $[Cu(H_2L^n)]X_2$  and are abbreviated as  $1X_2$  and  $2X_2$  ( $n = 1, 2$  for 2-substituent = H, Me;  $X = ClO_4, NO_3, Cl$ ). X-ray crystal structures of  $1(NO_3)_2$  and  $2(Cl)_2$  were determined:  $1(NO_3)_2$ , monoclinic, space group  $P2_1/c$  (No. 14),  $a = 9.610(4) \text{ \AA}$ ,  $b = 13.463(5) \text{ \AA}$ ,  $c = 15.568(5) \text{ \AA}$ ,  $\beta = 98.12(3)^\circ$ , and  $Z = 4$ ;  $2(Cl)_2$ , monoclinic, space group  $P2_1/n$  (No. 14),  $a = 9.884(2) \text{ \AA}$ ,  $b = 15.073(3) \text{ \AA}$ ,  $c = 15.295(2) \text{ \AA}$ ,  $\beta = 98.57(2)^\circ$ , and  $Z = 4$ . The complex assumes  $\Delta$  or  $\Lambda$  enantiomorphs due to the spiral arrangement of the quinquedentate ligand around the copper(II) ion, and these  $\Delta$  and  $\Lambda$  enantiomorphs of the cation for  $1(NO_3)_2$  and  $2(Cl)_2$  coexist as the racemic form in the crystals. When the protonated complexes were treated with NaOH, the mono-deprotonated complexes with the formula  $[CuHL^n]ClO_4$ ,  $1'ClO_4$  ( $n = 1$ ) and  $2'ClO_4$  ( $n = 2$ ), were obtained. Crystal data for  $1'ClO_4$ : *Pbca* (No. 61) with  $a = 13.211(3) \text{ \AA}$ ,  $b = 25.387(3) \text{ \AA}$ ,  $c = 10.939(3) \text{ \AA}$ , and  $Z = 8$ ;  $2'ClO_4$ , *Pbca* (No. 61) with  $a = 16.554(4) \text{ \AA}$ ,  $b = 20.609(4) \text{ \AA}$ ,  $c = 12.423(3) \text{ \AA}$ , and  $Z = 8$ . The structures consist of an electronically monocationic copper(II) complex involving a deprotonated imidazole moiety and a protonated imidazole moiety per molecular unit and a mononegative anion  $ClO_4^-$ , where an imidazolate nitrogen atom N(2) of the copper(II) complex is hydrogen bonded to the imidazole nitrogen atom N(6)\* (\* denotes the symmetry operation of  $1/2 + x, 1/2 - y, -z$ ) of the adjacent unit with the hydrogen bond distance of  $N(2) \cdots N(6)^*$  of 2.842(6) for  $1'ClO_4$  and 2.815(4)  $\text{ \AA}$  for  $2'ClO_4$  to give a one-dimensional helical structure running along the *a*-axis. Through the hydrogen bonds, the  $\Delta$  isomer only aggregates with the  $\Delta$  isomer and the  $\Lambda$  isomer only aggregates with the  $\Lambda$  isomer to give an extended helical chain structure described as  $\Delta\Delta\Delta\Delta\dots$  or  $\Lambda\Lambda\Lambda\Lambda\dots$ , respectively.

## Introduction

The fields of crystal engineering and supramolecular chemistry have attracted much attention, because the development of the fields is essential for creating new functional materials and their study is one of the major challenges of modern science.<sup>1</sup> A number of the synthetic strategies based on the self-assembly reaction have been proposed to synthesize supramolecular and extended multidimensional compounds.<sup>1,2</sup> Among them, the so-called helicate, double-helical and triple-helical metal complexes, derived from the spontaneous assembly of metal ion and oligo(2,2'-bipyridine) analogs, are the highlight

of supramolecular chemistry.<sup>3</sup> On the other hand, the field of metal complex-based magnets has made tremendous progress in synthetic design, and a number of complexes with multidimensional structures have been synthesized.<sup>4</sup>

One of the recent interests of the field of supramolecular chemistry is to design and synthesize supramolecular compounds exhibiting switching ability, whose structure and/or physical and chemical properties change by input of external information.<sup>5</sup> Electroswitching interconversion between a double helical binuclear Cu(I) complex and a single strand Cu(II) complex, the electrochemical interconversion of the location of a copper ion between Cu(I) in the  $[12]-S_2N_2$  site and Cu(II) in the  $[15]-$

\* Author to whom correspondence should be addressed.

<sup>†</sup> Kyushu University.

<sup>‡</sup> Oita University.

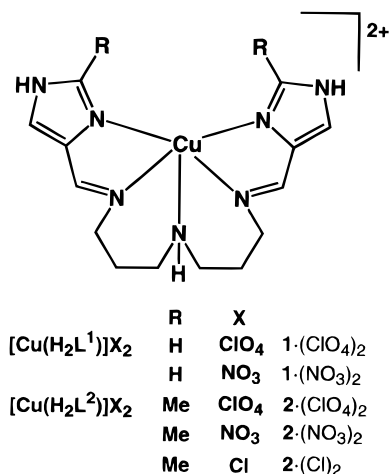
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Chart 1



N<sub>2</sub>O<sub>3</sub> site of a heterotopic macrotricyclic ligand, and the other switching processes have been extensively studied.<sup>5</sup> We have studied the pH-dependent self-assembly behavior of copper(II) complexes with quadridentate or tridentate ligands involving an imidazole moiety per molecule, in which the copper(II) complex exists as a monomer under the protonated lower pH region and it exists as a polymer or oligomer formed by the coordination of the imidazolite nitrogen to the adjacent molecular unit under the deprotonated higher pH region. In such a system, the interconversion between monomer and the self-assembled polymer or oligomer is available by controlling the pH.<sup>6</sup>

In this study, we have prepared the copper(II) complexes of the quinquedentate Schiff base ligands involving two imidazole moieties H<sub>2</sub>L<sup>n</sup> with the general formula of [Cu(H<sub>2</sub>L<sup>n</sup>)]X<sub>2</sub> (*n* = 1, 2; X = ClO<sub>4</sub>, NO<sub>3</sub>, Cl), where the ligands used are the 1:2 condensation products of 3,3'-diaminodipropylamine and each of 4-formylimidazole and 4-formyl-2-methylimidazole, and the schematic drawings of the complexes together with the abbreviations are given in Chart 1.

The present complexes assume the characteristics described as follows: (1) The complexes contain two imidazole moieties per unit, and the imidazole protons can dissociate under the proper pH region. The particular species exhibiting a protonated imidazole moiety and a deprotonated imidazole moiety per unit generated by tuning the pH can function as the building component exhibiting a donor and acceptor ability per unit to the assembly process by NH···N hydrogen bonding. (2) Because there is no substitutable or vacant coordination site in the copper(II) complex with the quinquedentate ligand, the association force of the components is limited to the hydrogen bonding between the components. (3) Because the copper(II) complex assumes enantiomers of Δ and Λ due to the spiral arrangement of the quinquedentate ligand coordinated to Cu(II) ion, the complex can function as a chiral component for the self-assembly process. We report here the syntheses,

characterization, and crystal structures of the protonated and the deprotonated complexes.

## Experimental Section

**Physical Measurements.** Elemental analyses for C, H, and N were performed at the Elemental Analysis Service Center of Kyushu University. Copper analyses were made on a Shimadzu AA-680 atomic absorption/ flame emission spectrophotometer. Infrared spectra were measured on KBr disks with JASCO IR-810 and Shimadzu FTIR-8600 spectrophotometers. Electronic spectra were recorded on Shimadzu MPS-2000 spectrophotometer in DMF or water solution ( $1 \times 10^{-3}$  M), and powder reflectance spectra were recorded on this apparatus. Electrical conductivity measurements were carried out on Denki Kagaku Keiki AOL-10 digital conductometer in ca.  $1 \times 10^{-3}$  M solution (DMF or methanol).

**pH Titration.** The potentiometric pH titration was performed about complexes **1**(ClO<sub>4</sub>)<sub>2</sub> and **2**(ClO<sub>4</sub>)<sub>2</sub>. All the titrations were carried out in a thermostated bath at 25 °C and under N<sub>2</sub> atmosphere, and the solvent used in this experiment was water which was extrapure grade, where its resistivity was greater than 18.0 MΩ. The GS-5011c electrode and the potentiometer used in these experiments were supplied from TOA Co, Ltd. The standard electrode potential *E*<sub>0</sub> of the pH electrode was first determined by Gran's plot method.<sup>7</sup>

The electrode potential was converted into the proton concentration scale,  $-\log [H^+] = (E_0(\text{mV}) - E(\text{mV}))/59.15$ , and the degree of dissociation, α, or the average proton coordination number ( $\bar{n}_H$ ) was calculated by Bjerrum's method for the titrations.<sup>8</sup>

**X-ray Structure Analysis.** Crystal data are given in Table 1. Single crystals were prepared by the method described in the synthetic procedure. The single crystals used for the X-ray diffraction studies were cut from a thin plate crystal and encapsulated into Lindemann glass capillaries. All measurements were made on a Rigaku AFC7R diffractometer with graphite-monochromated Mo Kα radiation ( $\lambda = 0.71069 \text{ \AA}$ ) and a 12 kW rotating anode generator. The data were collected at a temperature of  $20 \pm 1 \text{ }^\circ\text{C}$  using the  $\omega-2\theta$  scan technique to a maximum  $2\theta$  value of  $55.0^\circ$  at a scan speed of  $8.0-16.0^\circ/\text{min}$  (in  $\Omega$ ). The weak reflections ( $I < 10.0\sigma(I)$ ) were rescanned (maximum of 5 scans), and the counts were accumulated to ensure good counting statistics. Stationary background counts were recorded on each side of the reflection. The ratio of peak counting time to background counting time was 2:1. The intensities of three representative reflections were measured after every 150 reflection. Over the course of the data collection, the standards reflections were monitored and the decay corrections were applied by a polynomial correction. An empirical absorption correction based on azimuthal scans of several reflections was applied. The data were corrected for Lorentz and polarization effects.

The structures were solved by direct methods<sup>9</sup> and expanded using Fourier techniques.<sup>10</sup> The non-hydrogen atoms were anisotropically refined. Hydrogen atoms were included. Full-matrix least-squares refinements ( $I > 3.00\sigma(I)$ ) were employed, where the unweighted and weighted agreement factors of  $R = \sum ||F_o| - |F_c|| / \sum |F_o|$  and  $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$  were used. The weighting scheme was based on counting statistics. Plots of  $\sum w(|F_o| - |F_c|)^2$  versus  $|F_o|$ , reflection order in data collection,  $(\sin \theta)/\lambda$ , and various classes of indices showed no unusual trends. Neutral atomic scattering factors were taken from Cromer and Waber.<sup>11</sup> Anomalous dispersion effects were included in *F<sub>c</sub>*; the values Δ*f*' and Δ*f*" were those of Creagh

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**Table 1.** Crystallographic Data for All Complexes in This Study

complex	1(NO <sub>3</sub> ) <sub>2</sub>	2(Cl) <sub>2</sub>	1'ClO <sub>4</sub>	2'ClO <sub>4</sub>
chem formula	C <sub>14</sub> H <sub>21</sub> N <sub>9</sub> O <sub>6</sub> Cu	C <sub>16</sub> H <sub>29</sub> N <sub>7</sub> Cl <sub>2</sub> O <sub>2</sub> Cu	C <sub>14</sub> H <sub>20</sub> N <sub>7</sub> ClO <sub>4</sub> Cu	C <sub>16</sub> H <sub>24</sub> N <sub>7</sub> ClO <sub>4</sub> Cu
fw	474.92	485.90	449.36	477.41
space group	<i>P</i> 2 <sub>1</sub> / <i>c</i> (No. 14)	<i>P</i> 2 <sub>1</sub> / <i>n</i> (No. 14)	<i>Pbca</i> (No. 61)	<i>Pbca</i> (No. 61)
<i>a</i> , Å	9.610(4)	9.884(2)	13.211(3)	16.554(4)
<i>b</i> , Å	13.463(5)	15.073(3)	25.387(3)	20.609(4)
<i>c</i> , Å	15.568(5)	15.295(2)	10.939(3)	12.423(3)
β, deg	98.12(3)	98.57(2)		
<i>V</i> , Å <sup>3</sup>	1994(1)	2253.1(7)	3668(1)	4238(1)
Z	4	4	8	8
ρ <sub>obsd</sub> , g cm <sup>-3</sup>	1.582	1.406	1.627	1.496
μ, cm <sup>-1</sup>	11.49	12.31	13.73	11.94
<i>R</i> <sup>a</sup>	0.049	0.042	0.049	0.039
<i>R</i> <sub>w</sub> <sup>b</sup>	0.033	0.039	0.038	0.030

$$^a R = \sum |F_o| - |F_c| / \sum |F_o|. \quad ^b R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2}.$$

and McAuley.<sup>12</sup> The values for the mass attenuation coefficients were those of Creagh and Hubbel.<sup>12</sup> All calculations were performed using the teXsan crystallographic software package of the Molecular Structure Corp.<sup>13</sup>

**Preparations.** All chemicals and solvents used for the syntheses were reagent grade.

**Caution:** *Perchlorate salts are potentially explosive and should only be handled in small quantities*, although we worked with these perchlorate salts without any incident. Heating during the preparation procedure should be carried out not on a hot plate but in a water bath.

**[Cu(H<sub>2</sub>L<sup>1</sup>)](ClO<sub>4</sub>)<sub>2</sub>, 1(ClO<sub>4</sub>)<sub>2</sub>.** To a solution of 4-formylimidazole (961 mg, 10 mmol) in 40 cm<sup>3</sup> of ethanol was added 3,3'-diaminodipropylamine (656 mg, 5 mmol), and the solution was stirred at 50 °C for 30 min. To the resulting solution was added a solution of Cu(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O in 10 cm<sup>3</sup> of ethanol, and the blue solution was stirred at 50 °C for several minutes. After cooling to room temperature, blue precipitated microcrystals were collected by suction filtration, washed with ethanol and dried in vacuo. Blue microcrystalline yield: 91%. Recrystallization can be performed by slow evaporation from methanol to obtain single crystals. Anal. Calcd for C<sub>14</sub>H<sub>21</sub>N<sub>9</sub>O<sub>6</sub>Cl<sub>2</sub>Cu: C, 30.58; H, 3.85; N, 17.83; Cu, 11.56. Found: C, 30.62; H, 3.95; N, 17.52; Cu, 11.61. IR (KBr): ν<sub>N-H</sub>(imidazole), 1510 and 3346 cm<sup>-1</sup>; ν<sub>C=N</sub>(imine), 1636 cm<sup>-1</sup>; ν<sub>Cl-O</sub>(perchlorate), 1080–1160 cm<sup>-1</sup>. UV/vis spectra (DMF) [λ<sub>max</sub>/nm (ε/cm<sup>2</sup> mmol<sup>-1</sup>): 701 (190), 320 (sh) (1900), 270 (25 700). Solid (λ<sub>max</sub>/nm): 685, 340, 280. Λ<sub>M</sub>: 130 S cm<sup>2</sup> mol<sup>-1</sup> in DMF.

**[Cu(HL<sup>1</sup>)]ClO<sub>4</sub>, 1'ClO<sub>4</sub>.** To the solution of complex 1(ClO<sub>4</sub>)<sub>2</sub> (275 mg, 0.5 mmol) in 30 cm<sup>3</sup> of methanol was added a solution of NaOH (40 mg, 1 mmol) in 5 cm<sup>3</sup> of water at room temperature. During the addition of NaOH, the color of the solution changed from blue to green, and the solution was stirred for 30 min at room temperature. The green solution was then filtered off, and the filtrate was kept to stand for 1 week. Purple rhombic crystals were obtained and collected by suction filtration, washed with a minimum amount of ethanol, and dried in vacuo. These crystals were suitable for single-crystal X-ray crystallography. Purplish blue crystal yield: 50%. Anal. Calcd for C<sub>14</sub>H<sub>20</sub>N<sub>7</sub>O<sub>4</sub>ClCu: C, 37.42; H, 4.49; N, 21.82; Cu, 14.14. Found: C, 37.45; H, 4.43; N, 21.69; Cu, 14.04. IR (KBr): ν<sub>N-H</sub>(imidazole), 1527 and 3246 cm<sup>-1</sup>; ν<sub>C=N</sub>(imine), 1609 and 1641 cm<sup>-1</sup>; ν<sub>Cl-O</sub>(perchlorate), 1070–1130 cm<sup>-1</sup>. UV/vis spectra (DMF) [λ<sub>max</sub>/nm (ε/cm<sup>2</sup> mmol<sup>-1</sup>): 713 (150), 311 (15 400), 270 (20 200), 260 (sh) (18 000). Solid (λ<sub>max</sub>/nm): 620, 405, 380, 310. Λ<sub>M</sub>: 67 S cm<sup>2</sup> mol<sup>-1</sup> in DMF.

**[Cu(H<sub>2</sub>L<sup>1</sup>)](NO<sub>3</sub>)<sub>2</sub>, 1(NO<sub>3</sub>)<sub>2</sub>.** This complex was prepared as described for 1(ClO<sub>4</sub>)<sub>2</sub> using Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O instead of Cu(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O. Single crystals suitable for X-ray crystallography were prepared by slow evaporation in methanol solution. Blue crystal yield: 91%. Anal. Calcd for C<sub>14</sub>H<sub>21</sub>N<sub>9</sub>O<sub>6</sub>Cu: C, 35.41; H, 4.46; N, 26.54; Cu, 13.38.

Found: C, 35.32; H, 4.47; N, 26.45; Cu, 13.71. IR (KBr): ν<sub>N-H</sub>(imidazole), 1508; ν<sub>C=N</sub>(imine), 1640 cm<sup>-1</sup>; ν<sub>N-O</sub>(NO<sub>3</sub>), 1280–1450 cm<sup>-1</sup>. UV/vis spectra (DMF) (λ<sub>max</sub>/nm (ε/cm<sup>2</sup> mmol<sup>-1</sup>): 704 (190), 282 (sh)(23 000), 272 (26 800). Solid (λ<sub>max</sub>/nm): 695, 350, 295. Λ<sub>M</sub>: 130 S cm<sup>2</sup> mol<sup>-1</sup> in DMF.

**[Cu(H<sub>2</sub>L<sup>2</sup>)](ClO<sub>4</sub>)<sub>2</sub>, 2(ClO<sub>4</sub>)<sub>2</sub>.** To the solution of 2-methyl-4-formylimidazole (1101 mg, 10 mmol) in 40 cm<sup>3</sup> of ethanol was added 3,3'-diaminodipropylamine (656 mg, 5 mmol), and the solution was stirred at 50 °C for 30 min. To the resulting solution was added a solution of Cu(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O in 10 cm<sup>3</sup> of ethanol, and the mixture was stirred at 50 °C for several minutes. After cooling of the solution to room temperature, blue microcrystals precipitated, and these were collected by suction filtration, washed with ethanol, and dried in vacuo. Blue microcrystalline yield: 89%. Recrystallization can be performed by slow evaporation in methanol solution to obtain the blue single crystals. Anal. Calcd for C<sub>16</sub>H<sub>25</sub>N<sub>7</sub>O<sub>8</sub>Cl<sub>2</sub>Cu: C, 33.26; H, 4.36; N, 16.97; Cu, 11.00. Found: C, 33.13; H, 4.33; N, 16.72; Cu, 11.14. IR (KBr): ν<sub>N-H</sub>(imidazole), 1555 and 3315 cm<sup>-1</sup>; ν<sub>C=N</sub>(imine), 1636 cm<sup>-1</sup>; ν<sub>Cl-O</sub>(perchlorate), 1070–1140 cm<sup>-1</sup>. UV/vis spectra (DMF) [λ<sub>max</sub>/nm (ε/cm<sup>2</sup> mmol<sup>-1</sup>): 704 (180), 330 (sh) (1600), 280 (27 000), 260 (sh) (20 000). Solid (λ<sub>max</sub>/nm): 705, 350, 290. Λ<sub>M</sub>: 130 S cm<sup>2</sup> mol<sup>-1</sup> in DMF.

**[Cu(HL<sup>2</sup>)]ClO<sub>4</sub>, 2'ClO<sub>4</sub>.** To the solution of complex 2(ClO<sub>4</sub>)<sub>2</sub> (289 mg, 0.5 mmol) in 40 cm<sup>3</sup> of methanol was added a solution of NaOH (40 mg, 1 mmol) in 5 cm<sup>3</sup> of water at room temperature. During the addition of NaOH, the color of the solution changed from blue to green, and the solution was stirred for 30 min at room temperature. This green solution was then filtered off, and the filtrate was kept to stand for 1 week. Green rhombic crystals were obtained and collected by suction filtration, washed with a minimum amount of ethanol, and dried in vacuo. These crystals were suitable for single crystal X-ray crystallography. Green crystal yield: 53%. Anal. Calcd for C<sub>16</sub>H<sub>24</sub>N<sub>7</sub>O<sub>4</sub>ClCu: C, 40.25; H, 5.07; N, 20.54; Cu, 13.31. Found: C, 40.14; H, 5.09; N, 20.42; Cu, 13.23. IR (KBr): ν<sub>N-H</sub>(imidazole), 1558 cm<sup>-1</sup>; ν<sub>C=N</sub>(imine), 1607 and 1636 cm<sup>-1</sup>; ν<sub>Cl-O</sub>(perchlorate), 1060–1150 cm<sup>-1</sup>. UV/vis spectra (DMF) [λ<sub>max</sub>/nm (ε/cm<sup>2</sup> mmol<sup>-1</sup>): 700 (160), 324 (16 800), 279 (20 700), 260 (sh) (16 800). Solid (λ<sub>max</sub>/nm): 695, 415, 385, 310. Λ<sub>M</sub>: 62 S cm<sup>2</sup> mol<sup>-1</sup> in DMF.

**[Cu(H<sub>2</sub>L<sup>2</sup>)](NO<sub>3</sub>)<sub>2</sub>·0.5H<sub>2</sub>O, 2(NO<sub>3</sub>)<sub>2</sub>.** This complex was prepared as described for 2(ClO<sub>4</sub>)<sub>2</sub> using Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O instead of Cu(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O. Recrystallization can be performed by slow evaporation in methanol solution to obtain the single crystals. Blue crystalline yield: 78%. Anal. Calcd for C<sub>16</sub>H<sub>26</sub>N<sub>9</sub>O<sub>7</sub>Cu: C, 37.54; H, 5.12; N, 24.62; Cu, 12.41. Found: C, 37.49; H, 5.13; N, 24.63; Cu, 12.71. IR (KBr): ν<sub>N-H</sub>(imidazole), 1556; ν<sub>C=N</sub>(imine), 1632 cm<sup>-1</sup>; ν<sub>N-O</sub>(NO<sub>3</sub>), 1320–1400 cm<sup>-1</sup>. UV/vis spectra (DMF) [λ<sub>max</sub>/nm (ε/cm<sup>2</sup> mmol<sup>-1</sup>): 703 (170), 280 (27200), 270 (sh) (21 100). Solid (λ<sub>max</sub>/nm): 685, 350, 300. Λ<sub>M</sub>: 130 S cm<sup>2</sup> mol<sup>-1</sup> in DMF.

**[Cu(H<sub>2</sub>L<sup>2</sup>)](Cl)<sub>2</sub>, 2(Cl)<sub>2</sub>.** This complex was prepared as described for 2(ClO<sub>4</sub>)<sub>2</sub> using Cu(Cl)<sub>2</sub>·2H<sub>2</sub>O instead of Cu(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O. The single crystals for X-ray crystallography can be prepared by slow evaporation in methanol solution. Blue crystal yield: 85%. Anal. Calcd for C<sub>16</sub>H<sub>25</sub>N<sub>7</sub>Cl<sub>2</sub>Cu: C, 42.72; H, 5.60; N, 21.79; Cu, 14.13. Found: C, 42.52; H, 5.43; N, 21.45; Cu, 13.46. IR (KBr):

(12) Creagh, D. C.; Hubbel, J. H. *International Tables for Crystallography*; Wilson, A. J. C. Ed.; Kluwer Academic Publishers: Boston, MA, 1992; Vol. C, Table 4.2.4.3, pp 200–206. Creagh, D. C.; McAuley, W. J. *International Tables for Crystallography*; Wilson, A. J. C., Ed.; Kluwer Academic Publishers: Boston, MA, 1992; Vol. C, Table 4.2.6.8, pp 219–222.

(13) teXsan: Crystal Structure Analysis Package, Molecular Structure Corp., 1985, 1992.

$\nu_{\text{N-H}}$ (imidazole), 1555;  $\nu_{\text{C=N}}$ (imine), 1640  $\text{cm}^{-1}$ . UV/vis spectra (DMF) [ $\lambda_{\text{max}}/\text{nm}$  ( $\epsilon/\text{cm}^2 \text{mmol}^{-1}$ ): 696 (190), 327 (sh) (1700), 279 (25 000), 261 (sh) (19 900).  $\Lambda_{\text{M}}$ : 160  $\text{S cm}^2 \text{mol}^{-1}$  in MeOH.

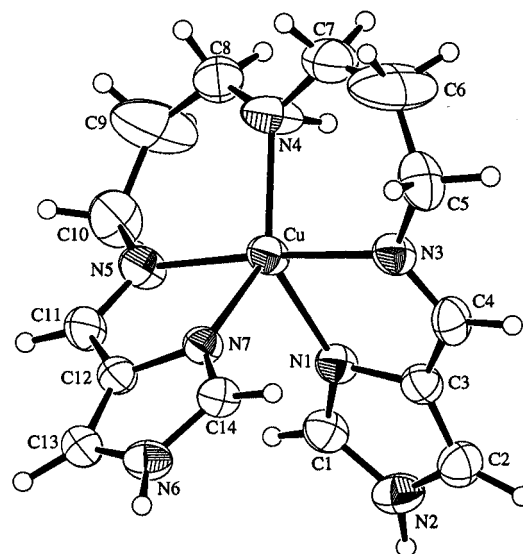
## Results and Discussion

**Syntheses and Characterization of the Protonated Complexes 1 and 2.** Copper(II) complexes of the quinquedentate Schiff base ligands  $\text{H}_2\text{L}^n$  ( $n = 1, 2$ ) with the formula of  $[\text{Cu}(\text{H}_2\text{L}^n)]\text{X}_2$  were synthesized by mixing copper(II) salt and  $\text{H}_2\text{L}^n$  ( $n = 1, 2$ ) in ethanol, where the ligands involving two imidazole moieties are the 2:1 condensation products of 3,3'-diaminodipropylamine and each of 4-formylimidazole and 4-formyl-2-methylimidazole. Elemental analyses of the complexes agree with the chemical formula of  $[\text{Cu}(\text{H}_2\text{L}^n)]\text{X}_2$  ( $n = 1, 2$ ;  $\text{X} = \text{ClO}_4, \text{NO}_3, \text{Cl}$ ), and the infrared spectra exhibit the absorptions assigned to  $\nu_{\text{N-H}}$  at ca. 1500 and 3300  $\text{cm}^{-1}$ ,  $\nu_{\text{C=N}}$  at 1600–1640  $\text{cm}^{-1}$ , and the counteranion. The molar electrical conductivities measured in the DMF or methanol solutions are in the expected range for 2:1 electrolytes.

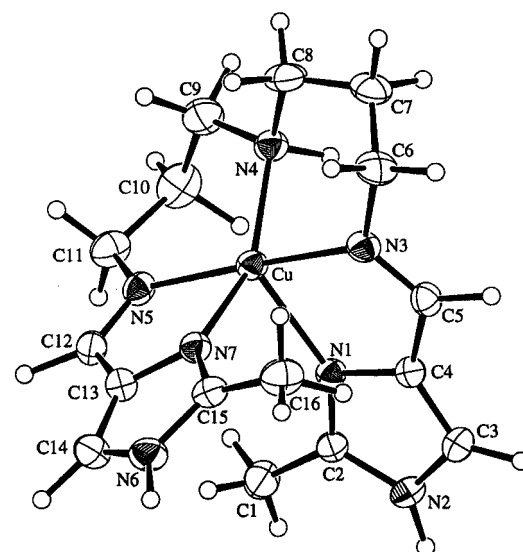
**Syntheses and General Properties of Complexes 1'ClO<sub>4</sub> and 2'ClO<sub>4</sub>.** Deprotonated complexes, 1'ClO<sub>4</sub> and 2'ClO<sub>4</sub>, were obtained as well-grown purplish blue and green colored crystals from slow evaporation of the solutions containing 2 equiv of NaOH and the corresponding protonated complexes 1(ClO<sub>4</sub>)<sub>2</sub> and 2(ClO<sub>4</sub>)<sub>2</sub> in methanol/water, respectively. Elemental analyses agree with the formula of  $[\text{CuHL}^n]\text{ClO}_4$  ( $n = 1, 2$ ) consisting of a monocationic cation and an anion, suggesting that the monodeprotonated compound with the chemical formula of  $[\text{CuHL}^n]\text{ClO}_4$  ( $n = 1, 2$ ) more easily crystallized than the di-deprotonated compound with the formula of  $[\text{CuL}^n]$ . Infrared absorptions attributable to  $\nu_{\text{N-H}}$ ,  $\nu_{\text{C=N}}$ , and perchlorate anion were observed. The molar electrical conductivities measured in ca.  $1 \times 10^{-3}$  M DMF solutions are in the range expected for 1:1 electrolytes. The electronic absorption UV/vis spectra of the DMF solutions and the reflectance spectra of the powdered samples were measured in the range 270–900 nm. The reflectance spectrum of 1(ClO<sub>4</sub>)<sub>2</sub> exhibits a broad d–d transition band at the maxima 685 nm, while the deprotonated complex 1'ClO<sub>4</sub> exhibits it at 620 nm. When 1'ClO<sub>4</sub> was dissolved in DMF, the d–d transition band shifted from 620 to 713 nm, accompanying the color change from purplish blue to green. The drastic color change is due to the difference in the coordination geometry around the Cu(II) ion between the solid state and the solution state of 1'ClO<sub>4</sub>. The reflectance spectra of 2(ClO<sub>4</sub>)<sub>2</sub> and 2'ClO<sub>4</sub> showed the d–d transition band at 705 and 695 nm, respectively, and the corresponding d–d transition in the DMF solution is observed at 704 and 700 nm, respectively.

**Descriptions of Crystal Structures 1(NO<sub>3</sub>)<sub>2</sub> and 2(Cl)<sub>2</sub>.** The crystal structures of 1(NO<sub>3</sub>)<sub>2</sub> and 2(Cl)<sub>2</sub> consist of a dicationic copper(II) complex and two electronically mononegative anions, in which two imidazole nitrogen atoms of the cation, N(2) and N(6), are hydrogen-bonded to the counteranions through the imidazole hydrogen atoms. The hydrogen bond distances are N(2)⋯O(2) = 2.830(5) Å and N(6)⋯O(6) = 2.858(5) Å for 1(NO<sub>3</sub>)<sub>2</sub> crystallized as the NO<sub>3</sub> salt and N(2)⋯Cl(1) = 3.124(3) Å and N(6)⋯Cl(1) = 3.076(3) Å for 2(Cl)<sub>2</sub> crystallized as the chloride salt.

The ORTEP drawings of the cation of these complexes with the atom-numbering schemes are shown in Figures 1 and 2. Selected bond distances and angles with their estimated standard deviations are summarized in Table 2. In these complexes, the Cu(II) ion assumes a similar pentacoordinated geometry with the N<sub>5</sub> donor atoms consisting of two imidazole moieties, two imine, and one amino nitrogen of the quinquedentate ligand.



**Figure 1.** ORTEP drawing of the cation  $[\text{Cu}(\text{H}_2\text{L}^1)]^{2+}$  ( $\Delta$  enantiomorph) for  $1(\text{NO}_3)_2$  with the atom-numbering scheme, showing 30% probability ellipsoids.



**Figure 2.** ORTEP drawing of the cation  $[\text{Cu}(\text{H}_2\text{L}^2)]^{2+}$  ( $\Delta$  enantiomorph) for  $2(\text{Cl})_2$  with the atom-numbering scheme, showing 30% probability ellipsoids.

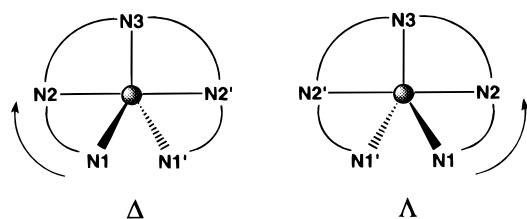
in the five-coordinated complex introduced by Reedijk,<sup>14</sup>  $\tau = (\beta - \alpha)/60$ , are  $\tau = 0.66$  and  $0.42$  for  $1(\text{NO}_3)_2$  and  $2(\text{Cl})_2$ , respectively, where  $\alpha$  and  $\beta$  represent two basal angles ( $\beta > \alpha$ ), and the parameters for an ideal square pyramid and trigonal bipyramid are  $\tau = 0$  ( $\alpha = \beta = 180^\circ$ ) and  $\tau = 1$  ( $\alpha = 120^\circ$ ,  $\beta = 180^\circ$ ), respectively. The coordination geometry around Cu(II) of these complexes is described as an intermediate between square pyramid and trigonal bipyramid; however,  $1(\text{NO}_3)_2$  is more close to a trigonal-bipyramid and  $2(\text{Cl})_2$  is a square pyramid. It is noteworthy that the two Cu–N(imidazole nitrogen) bond distances are not equal to each other, but one of them, Cu–N(1), is substantially longer than the other, Cu–N(7), as given by the bond distances of  $[\text{Cu}-\text{N}(1), \text{Cu}-\text{N}(7)] = [2.124(4), 2.078(4) \text{ \AA}]$  for  $1(\text{NO}_3)_2$  and  $[2.207(3), 2.060(3) \text{ \AA}]$  for  $2(\text{Cl})_2$ , respectively.

The most interesting feature of the structure is that the cation assumes a  $\Delta$  or  $\Lambda$  enantiomorph due to the spiral coordination arrangement of the quinquedentate ligand around the copper-

(14) Addison, A. W.; Rao, T. N.; Reedijk, J.; van Rijn, J.; Verschoor, G. *C. J. Chem. Soc., Dalton Trans.* **1984**, 1349.

**Table 2.** Selected Bond Distances (Å) and Angles (deg) of the Protonated Complexes **1**(NO<sub>3</sub>)<sub>2</sub> and **2**(Cl)<sub>2</sub>

	<b>1</b> (NO <sub>3</sub> ) <sub>2</sub>	<b>2</b> (Cl) <sub>2</sub>
Bond Distances (Å)		
Cu–N(1)	2.124(4)	2.207(3)
Cu–N(3)	1.985(3)	1.991(3)
Cu–N(4)	1.978(3)	2.032(3)
Cu–N(5)	1.977(4)	2.005(3)
Cu–N(7)	2.078(4)	2.060(3)
Bond Angles (deg)		
N(1)–Cu–N(3)	80.7(1)	79.8(1)
N(1)–Cu–N(4)	127.5(2)	116.6(1)
N(1)–Cu–N(5)	96.4(2)	99.14(10)
N(1)–Cu–N(7)	96.5(1)	90.78(10)
N(3)–Cu–N(4)	92.2(2)	87.0(1)
N(3)–Cu–N(5)	175.5(2)	177.6(1)
N(3)–Cu–N(7)	95.8(1)	96.7(1)
N(4)–Cu–N(5)	92.3(2)	95.3(1)
N(4)–Cu–N(7)	136.1(2)	152.6(1)
N(5)–Cu–N(7)	81.1(1)	81.2(1)

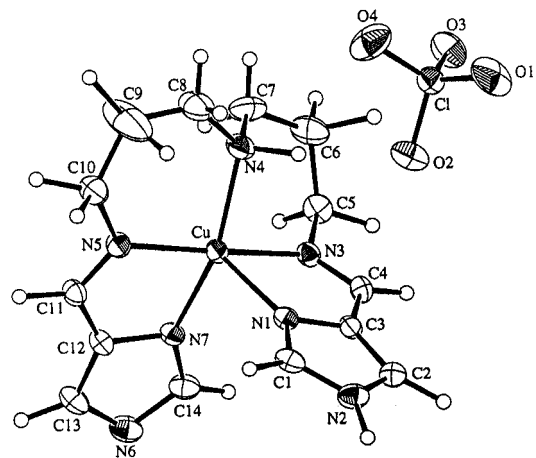
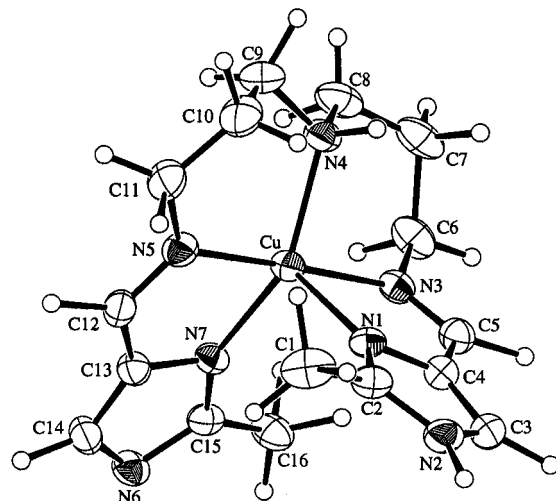
**Chart 2**

(II) ion. The  $\Delta$  and  $\Lambda$  enantiomorphs were defined as shown in Chart 2, at first, the front imidazole nitrogen is defined as N1 against the back imidazole nitrogen N1'; next, when the direction of the chelate ligand (N1→N2→N3→N2'→N1') is clockwise, this enantiomorph is a  $\Delta$ -isomer, and when it is anticlockwise, it is a  $\Lambda$ -isomer.<sup>15,16</sup>

As **1**(NO<sub>3</sub>)<sub>2</sub> and **2**(Cl)<sub>2</sub> crystallized in the centrosymmetric space groups  $P2_1/c$  and  $P2_1/n$  with  $Z = 4$ , respectively, the  $\Delta$  and  $\Lambda$  enantiomorphs of the cation coexist as the racemic form in the crystal.

**Description of Crystal Structures of Deprotonated Complexes 1'ClO<sub>4</sub> and 2'ClO<sub>4</sub>.** The crystals of the deprotonated complexes assume a structural feature similar to each other consisting of an electronically monovalent copper(II) complex and a mononegative anion ClO<sub>4</sub><sup>-</sup>, where an imidazolate nitrogen atom N(2) of a copper(II) complex is hydrogen bonded to the imidazole nitrogen atom N(6)\* of the adjacent unit to form an intermolecular hydrogen-bonded one-dimensional structure. The ORTEP drawings of the cations of **1'**ClO<sub>4</sub> and **2'**ClO<sub>4</sub> with the atom-numbering schemes are shown in Figures 3 and 4, respectively. The one-dimensional helical structure formed by the hydrogen bonding of **1'**ClO<sub>4</sub> is shown in Figure 5. Selected bond distances and angles with their estimated standard deviations are summarized in Table 3.

Each copper(II) ion assumes a pentacoordinated geometry with the N<sub>5</sub> donor atoms consisting of two imidazole, two imine, and one central amino nitrogen atom of the quinquedentate ligand. The coordination geometry around the Cu(II) ion is described as an intermediate geometry between the square pyramid and trigonal bipyramid, and the structural index parameter for the coordination geometry defined by Reedijk<sup>14</sup>

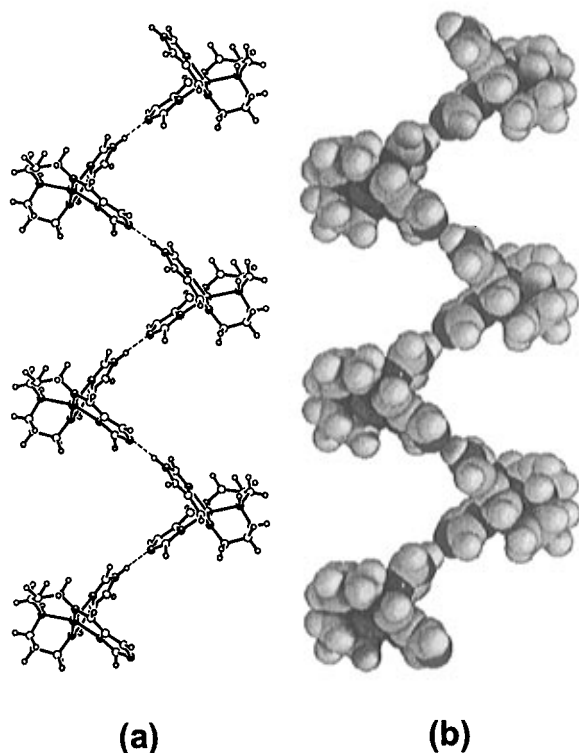
**Figure 3.** ORTEP drawing of [Cu(HL<sup>1</sup>)]ClO<sub>4</sub> ( $\Delta$  enantiomorph) for **1'**ClO<sub>4</sub> with the atom-numbering scheme, showing 30% probability ellipsoids.**Figure 4.** ORTEP drawing of the cation [Cu(HL<sup>2</sup>)]<sup>+</sup> ( $\Lambda$  enantiomorph) for **2'**ClO<sub>4</sub> with the atom-numbering scheme, showing 30% probability ellipsoids.

is  $\tau = 0.29$  and  $\tau = 0.52$  for **1'**ClO<sub>4</sub> and **2'**ClO<sub>4</sub>, respectively. The parameter  $\tau = 0.29$  of the deprotonated complex **1'**ClO<sub>4</sub> is considerably smaller than  $\tau = 0.66$  of the protonated complex **1**(NO<sub>3</sub>)<sub>2</sub>, indicating that the coordination geometry of the protonated and deprotonated complexes for **1** is quite different from each other within a pentacoordination mode, the coordination geometry of the deprotonated complex **1'**ClO<sub>4</sub> is closer to a square-pyramidal coordination geometry, and the coordination geometry is very influenced by the formation of hydrogen bonds in the crystal and it also may be influenced by the different of packing forces of counteranions. On the other hand, the parameter of the protonated complex **2**(Cl)<sub>2</sub>,  $\tau = 0.44$ , is compatible with  $\tau = 0.52$  of the deprotonated complex **2'**ClO<sub>4</sub>. The difference of the coordination geometries for **1'**ClO<sub>4</sub> and **2'**ClO<sub>4</sub>, in which the index parameter for the coordination geometry  $\tau = 0.29$  and  $\tau = 0.52$ , respectively, affected the electronic d–d transition energies of the Cu(II) ion; for **1'**ClO<sub>4</sub>, the transition exhibits at 620 nm, while for **2'**ClO<sub>4</sub> it exhibits at 695 nm on the powder reflectance spectra.

The two Cu–N(imidazole nitrogen) bond distances are not equal to each other, where one of them, Cu–N(1), is substantially longer than the other, Cu–N(7), as given by the bond distances of [Cu–N(1), Cu–N(7)] = [2.280(4), 2.016(4) Å] for **1'**ClO<sub>4</sub> and [2.232(9), 2.032(5) Å] for **2'**ClO<sub>4</sub>. The imidazole moiety with the longer coordination bond distance of Cu–N associates the proton, while that with the shorter distance

(15) *Nomenclature of Inorganic Chemistry, Recommendations 1990*; Blackwell: Oxford, U.K., 1990.

(16) In ref 15, the symbol of chirality used for these complexes is C (clockwise) and A (anticlockwise) instead of  $\Delta$  and  $\Lambda$ . In this paper, the symbols of  $\Delta$  and  $\Lambda$  are used to describe the chirality for the reported complexes, because of the identical chirality for the parental complex and the produced helical chain.



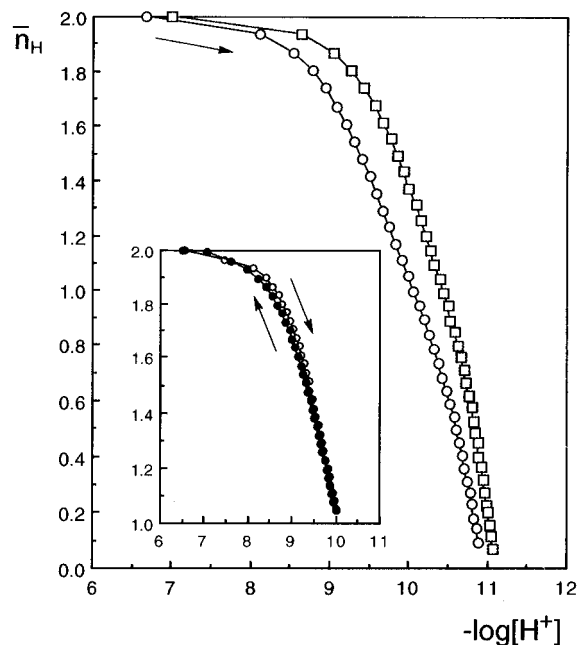
**Figure 5.** Hydrogen-bonded helical chain structure of  $1'\text{ClO}_4$  ( $\Delta$ -helical chain), which is made from  $\Delta$  enantiomorph molecules: (a) Arrangement of spiral complexes where the dashed line exhibits the hydrogen bond; (b) space-filling representation.

**Table 3.** Selected Bond Distances (Å) and Angles (deg) of the Deprotonated Complexes  $1'\text{ClO}_4$  and  $2'\text{ClO}_4$

	$1'\text{ClO}_4$	$2'\text{ClO}_4$
Bond Distances (Å)		
Cu–N(1)	2.280(4)	2.229(3)
Cu–N(4)	2.022(4)	2.030(3)
Cu–N(7)	2.016(4)	2.028(3)
Cu–N(3)	1.980(4)	1.977(3)
Cu–N(5)	2.000(4)	1.994(3)
Bond Angles (deg)		
N(1)–Cu–N(3)	79.0(1)	79.6(1)
N(1)–Cu–N(5)	107.4(2)	97.8(1)
N(3)–Cu–N(4)	85.6(2)	87.3(1)
N(3)–Cu–N(7)	95.2(2)	97.2(1)
N(4)–Cu–N(7)	156.0(2)	146.2(1)
N(1)–Cu–N(4)	107.9(2)	110.8(1)
N(1)–Cu–N(7)	95.8(2)	103.0(1)
N(3)–Cu–N(5)	173.3(2)	177.2(1)
N(4)–Cu–N(5)	94.2(2)	94.5(1)
N(5)–Cu–N(7)	82.2(2)	82.6(1)
Hydrogen Bond (Å)		
N(2)⋯N(6)*	2.842(6)	2.815(4)

dissociates the proton. As the result, the complex involves a deprotonated imidazole moiety and a protonated imidazole moiety per molecular unit. The copper(II) complex assumes  $\Delta$  or  $\Lambda$  enantiomorphs due to the spiral coordination arrangement of the quinquedentate ligand around the copper(II) ion (the definition of  $\Delta$  and  $\Lambda$  enantiomorphs is the same as for the protonated complexes). Since  $1'\text{ClO}_4$  and  $2'\text{ClO}_4$  crystallized in a centrosymmetric space group  $Pbca$  with  $Z = 8$ , the  $\Delta$  and  $\Lambda$  enantiomorphs of the cation coexist as a racemic form in the crystals.

The most striking feature of the crystal structures for the deprotonated complexes is a one-dimensional helical structure formed by the hydrogen bonding between the imidazole nitrogen atom of a unit N(2) and the imidazolite nitrogen of the adjacent unit N(6)\* (\* denotes the symmetry operation of  $1/2 + x, 1/2 -$



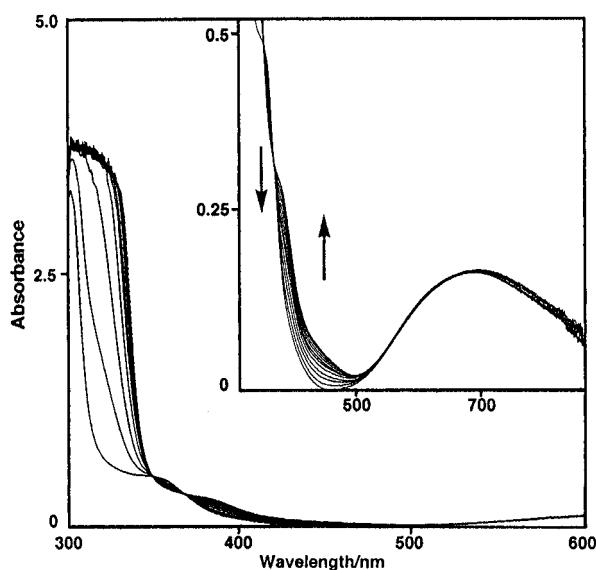
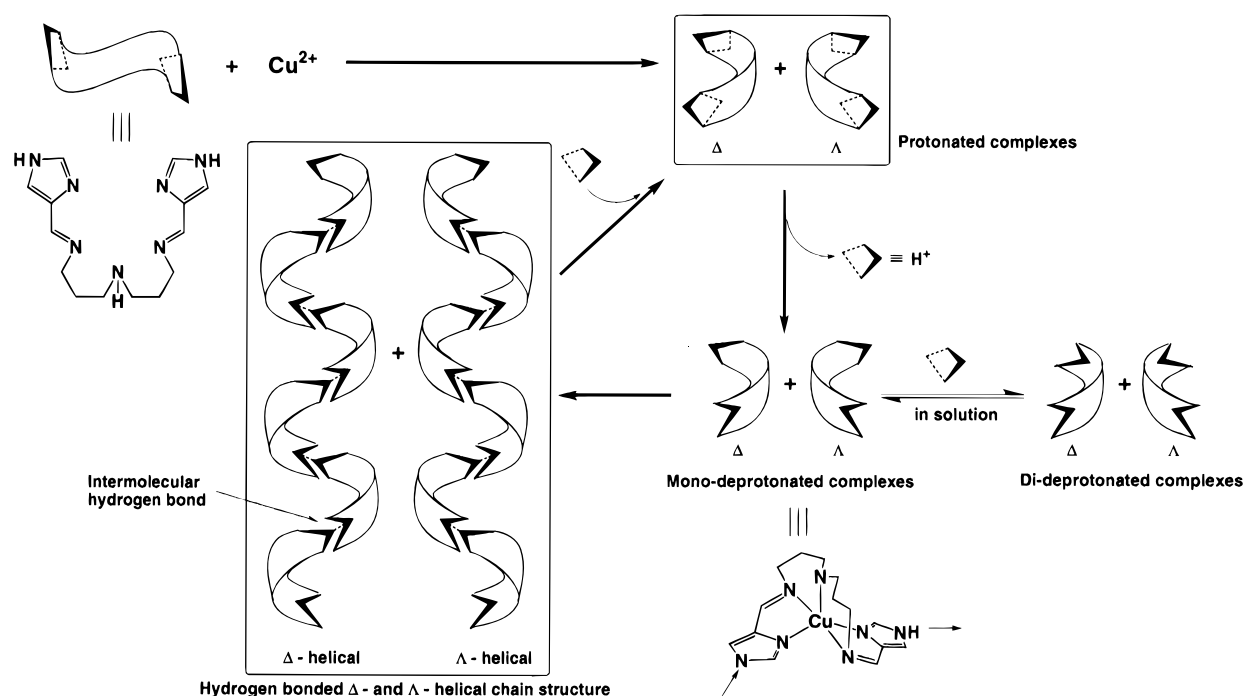
**Figure 6.** pH titrations (forward) for complexes  $1(\text{ClO}_4)_2$  (○) and  $2(\text{ClO}_4)_2$  (□). The inserted figure shows the forward (○) and reverse (●) titrations for complex  $1(\text{ClO}_4)_2$ .

$y, -z$ ). The hydrogen bond distances of N(2)⋯N(6)\* are 2.842(6) and 2.815(4) Å for  $1'\text{ClO}_4$  and  $2'\text{ClO}_4$ , respectively. Within a helical chain, the  $\Delta$  isomer only aggregates with the  $\Delta$  isomer and the  $\Lambda$  isomer only aggregates with the  $\Lambda$  isomer to give an extended helical chain described as  $\Delta\Delta\Delta\Delta\Delta\dots$  or  $\Lambda\Lambda\Lambda\Lambda\Lambda\dots$ , respectively. If the  $\Delta$  isomer is connected to the  $\Lambda$  isomer by a hydrogen bond, no such extended structure can be constructed. Thus, this assembly process is enantioselective.<sup>17</sup> In the  $bc$ -plane of the crystal lattice,  $\Delta$  and  $\Lambda$  helical chains running along the  $a$ -axis are alternately arrayed, and the counteranion  $\text{ClO}_4^-$  stacks among the chains without coordination to the Cu(II) ion and hydrogen bonding.

**Deprotonation Behavior in Solution.** Deprotonation behaviors of  $1(\text{ClO}_4)_2$  and  $2(\text{ClO}_4)_2$  in aqueous solution were studied by pH titration and electronic spectra. Figure 6 shows the results of the pH titration for  $1(\text{ClO}_4)_2$  and  $2(\text{ClO}_4)_2$  in the plots of the proton number per molecule vs pH. As shown in Figure 6, no stepwise deprotonation reaction was observed, although the crystal structure analysis both for the protonated and deprotonated compounds demonstrated the distinct difference of two imidazole moieties. The pH titration that indicates the first and second deprotonation occurs successively. The pH titration evaluated the  $\text{p}K_1$  and  $\text{p}K_2$  to be 9.3 and 10.5 for  $1(\text{ClO}_4)_2$  and 9.7 and 10.7 for  $2(\text{ClO}_4)_2$ , respectively, and these first and second dissociation values are very similar to each other. Figure 6 demonstrates that the deprotonation–protonation reaction of these complexes is reversible. The pH variation of the UV/vis spectra of complex  $2(\text{ClO}_4)_2$  is shown in Figure 7. The spectra show two isosbestic points at 349 and 368 nm, suggesting that there are equilibrium among protonated/deprotonated species such as  $[\text{Cu}(\text{H}_2\text{L})]^{2+}$ ,  $[\text{Cu}(\text{HL})]^+$ , and  $[\text{Cu}(\text{L})]$ . With the addition of NaOH, the intensity of an absorption band at 390 nm increased and, on the contrary, that of an absorption at 360 nm decreased with the boundary of the isosbestic points. On the other hand, a broad d–d transition band at ca. 700 nm showed no change in the intensity and absorption maxima,

(17) (a) Jacques, J.; Collet, A.; Wilen, S. H. *Enantiomers, Racemates and Resolutions*; Krieger: Malabar, FL, 1991. (b) Cray, D. P.; Mellor, D. P. *Top. Curr. Chem.* **1976**, 63, 1. (c) Lehn, J.-M. *Supramolecular Chemistry*; VCH: Weinheim, Germany, 1995; Section 9.7.

## Scheme 1



**Figure 7.** Variation of UV/vis spectra for complex  $2(\text{ClO}_4)_2$  with addition of an aqueous solution of NaOH. [Complex] =  $1 \times 10^{-3}$  M; added an aqueous solution of NaOH in concentration range  $0-3 \times 10^{-3}$  M.

indicating that the coordination sphere is maintained throughout the deprotonation.

### Concluding Remarks

The self-assembly process of the complexes can be summarized as follows and as shown in Scheme 1: (1) The coordination arrangement of the chainlike quinquedentate ligand around copper(II) ion produces enantiomeric components,  $\Delta$ -

and  $\Lambda$ -enantiomorphs, as a racemic mixture. (2) When one of the two imidazole protons of the copper(II) complex is dissociated, the resulting deprotonated complex can function as a building component exhibiting a donor and an acceptor ability per component. (3) The motive force of the self-assembly of the components is due to hydrogen bonding between an imidazole nitrogen atom of the two neighboring components,  $\text{NH} \cdots \text{N}^*$ . (4) The self-assembly is an enantioselective self-assembly, because the generated helical species consisting of  $\Delta\Delta\Delta\Delta\Delta\dots$  and  $\Lambda\Lambda\Lambda\Lambda\Lambda\dots$  were obtained by the spontaneous selection of components of the same chirality.<sup>17</sup> (5) The reverse deconstruction process is available by dissolving the solid samples and by controlling the pH.

This self-assembly process provides an alternative and a complementary synthetic method of double-stranded metal complexes formed by oligo(2,2'-bipyridine) analogs ligands and copper(I) ions or several metal ions.<sup>3</sup> While the helicate structure of the double-stranded metal complex is formed by the arrangement of the oligopyridine ligand coordinated to the metal ion in a helical fashion, the present helical structure is formed by the hydrogen bonding between the components having the same chirality which is produced at the time of synthesis for the parental complexes. If either of the enantiomorphs,  $\Delta$  and  $\Lambda$ , is used, chiral helical supramolecules can be obtained. We are now studying this procedure.

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**Supporting Information Available:** Four X-ray crystallographic files, in CIF format, are available. Access information is given on any current masthead page.

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