Inorg. Chem. **1998,** *37,* 3553−3560

Zigzag-Chain and Cyclic-Tetrameric Compounds Derived by Deprotonation of Mononuclear Copper(II) Complexes with *N,N′*-Bis(2-substituted-imidazol-4-ylmethylidene)-1,4-diaminobutane (2-Substituent = H, Me): Synthesis, Characterization, Structure, Substituent Effect, and Interconvertibility

Masaaki Mimura,[†] Toshihiro Matsuo,[†] Toshio Nakashima,[‡] and Naohide Matsumoto*,[†]

Department of Chemistry, Faculty of Science, Kumamoto University, Kurokami 2-39-1,
Kumamoto 860, Japan, and Faculty of Education, Oita University, Dan-noharu 700, Oita 870-11, Japan

Received December 29, 1997

Two copper(II) complexes with *N,N′*-bis(2-substituted-imidazol-4-ylmethylidene)-1,4-diaminobutane (2-substituent = H, **1**; Me, **2**) were synthesized, and their deprotonation assembly behavior was studied. X-ray analyses of **1** and **2** revealed that the molecules assume a butterfly shape bent by a line of N(2)−Cu−N(4) where the angle of N(3)−Cu−N(5) representing the extent of the molecular bend is 150.9(2)° and 105.66(8)° for **1** and **2**, respectively. Due to the molecular bend, two imidazole moieties (sites A and B) are recognized as two inequivalent groups for the deprotonation process in which the imidazole group of site A is in an equatorial CuN_3 plane, while that of site B is in a CuN_2 plane bent from the equatorial coordination plane. **1** dissociates a proton of site B first to give an infinite zigzag-chain compound **1′**, while **2** dissociates a proton of site A first to give a cyclic-tetranuclear compound **2′**. **2′** undergoes a further deprotonation to give an electrically neutral di-deprotonated complex **2″**. The interconversion between the protonated monomer and the deprotonated oligomer/polymer was investigated by pH-dependent potentiometric and absorption spectrometric titrations.

Introduction

The self-assembly process involving a metal ion has attracted much attention in the past 10 years because a metal ion together with its ligand contains a variety of structural information to guide the self-assembly reaction.[1−3] Recent attention has focused particulary on the construction of various supramolecular structures such as molecular squares,[4,5] cylindrical molecular boxes,[6] molecular cages,[7] and helical structures,[8] as well as on the supramolecules exhibiting switching ability,[9,10] whose structure and/or physicochemical properties change by an input of external information.

We previously studied a pH-dependent self-assembly system of metal complexes in which a protonated building unit and its deprotonated oligomer or polymer were interconverted depending on the pH.[11−16] Copper(II) complexes with either a tridentate or a quadridentate ligand involving one imidazole moiety per molecule can function as building modules for the assembly process, because such complexes potentially have not only donor coordination ability at the imidazolate nitrogen atom but also acceptor coordination ability at the vacant or substitutable coordination site. Under the acidic condition of a pH region lower than the dissociation constant pK_d, the donor ability at the imidazole is inhibited by the proton and no assembly process occurs. Under alkaline conditions, the imidazolate nitrogen atom coordinates to a copper(II) ion of the adjacent unit; as a result the assembly structure is constructed. The assembly structure of a copper(II) complex with one donor and one acceptor site per molecule is easily predictable, if we consider the ligand framework affording the steric requirement and the favorable coordination number and geometry of the metal ion. For this system to be developed further, the assembly behavior of a metal complex with multiple donor and/or acceptor sites must be investigated, although predicting the final assembly structure should be more difficult. As the simplest system of such complexes, we investigated copper(II) complexes with the

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* To whom correspondence should be addressed.

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[‡] Oita University.

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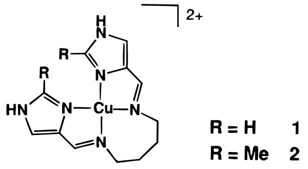
S0020-1669(97)01609-1 CCC: $15.00

Chart 1



quadridentate ligands involving two imidazole moieties per molecule, **1** and **2** (Chart 1), where the ligands used were *N,N′*-bis(2-substituted-imidazol-4-ylmethylidene)-1,4-diaminobutane (2-substituent = H, Me). We report here the synthesis, characterization, structure, and interconvertibility of the protonated (**1**, **2**), mono-deprotonated (**1′**, **2′**), and di-deprotonated (**2″**) complexes and describe how the assembly structures are constructed.

Experimental Section

General Procedures. All chemicals and solvents used for the synthesis were reagent grade. Reagents used for physical measurements were spectroscopic grade.

$[Cu(H_2L^1)](NO_3)_2{\cdot}0.5H_2O$, 1. To a solution of 4-formylimidazole (10 mmol) in 30 mL of methanol was added 1,4-diaminobutane (5 mmol), and the solution was stirred at 50 °C for 30 min. To the resulting solution was added a solution of $Cu(NO_3)_2{\cdot}3H_2O$ (5 mmol) in 20 mL of methanol. After 10 min of stirring, the solution was filtered, and the filtrate was left to stand for several days. The blue crystals which precipitated during that time were collected by suction filtration, washed with a small amount of methanol, and dried in vacuo. Yield: 1.63 g (74%). Anal. Calcd for $C_{12}H_{16}N_8O_6Cu{\cdot}0.5H_2O$: C, 32.69; H, 3.89; N, 25.42. Found: C, 32.84; H, 3.86; N, 25.43. IR (KBr): ν_{N-H}, 3150−3125; $\nu_{C=N}$, 1635; ν_{N-O}, 1385 cm^{-1}. UV/vis in H_2O [λ_{max}/nm (ϵ/dm^3 cm^{-1} mol^{-1})]: 642 (62). UV/vis solid (λ_{max}/nm): 681. $\Lambda_M(H_2O)$: 207 S mol^{-1} cm^2. Mp: >280 °C.

$[Cu(HL^1)]NO_3{\cdot}0.75H_2O$, 1′. To a solution of **1** (2 mmol) in 30 mL of methanol was added a slight excess of triethylamine (2.5 mmol). After the solution was stirred at room temperature, green microcrystals precipitated. These were collected by suction filtration, washed with a small amount of methanol, and dried in vacuo. To obtain crystals suitable for X-ray analysis, the filtrate was allowed to stand for several days. Green crystals thus obtained were used for X-ray analysis and physical measurements. Yield: 0.60 g (78%). Anal. Calcd for $C_{12}H_{15}N_7O_3Cu{\cdot}0.75H_2O$: C, 37.69; H, 4.35; N, 25.65. Found: C, 37.87; H, 4.31; N, 25.67. IR(KBr): ν_{N-H}, 3150−3050; $\nu_{C=N}$, 1625−1610; ν_{N-O}, 1385 cm^{-1}. UV/vis solid (λ_{max}/nm): 793. Mp: >280 °C.

$[Cu(H_2L^2)]Cl{\cdot}NO_3$, 2. To a solution of 2-methyl-4-formylimidazole (10 mmol) in 30 mL of methanol was added 1,4-diaminobutane (5 mmol), and the solution was stirred at 50 °C for 30 min. To the resulting solution were added a solution of $CuCl_2{\cdot}2H_2O$ (5 mmol) in 20 mL of methanol and a solution of NH_4NO_3 (15 mmol) in 10 mL of methanol. The light green solution was stirred for several minutes. The solution was then filtered, and the filtrate was left to stand for several days. The light green crystals which precipitated were collected by suction filtration, washed with a small amount of methanol, and dried in vacuo. Yield: 1.36 g (63%). Anal. Calcd for $C_{14}H_{20}N_7O_3ClCu$: C, 38.80; H, 4.65; N, 22.63. Found: C, 38.86; H, 4.71; N, 22.67. IR (KBr): ν_{N-H}, 3200−3100; $\nu_{C=N}$, 1640−1620; ν_{N-O}, 1385 cm^{-1}. UV/vis in H_2O [λ_{max}/nm (ϵ/dm^3 cm^{-1} mol^{-1})]: 777 (102). UV/vis solid (λ_{max}/nm) 775. $\Lambda_M(H_2O)$: 212 S mol^{-1} cm^2. Mp: >280 °C.

$[Cu(HL^2)]_4(NO_3)_2Cl_2{\cdot}1.25H_2O$, 2′. To a solution of **2** (2 mmol) in 30 mL of methanol was added a slight excess of triethylamine (2.5 mmol). During its addition, the color of the solution changed from light to dark green. After 5 min of stirring at room temperature, the solution was filtered, and the filtrate was left to stand for several days. The dark green crystals obtained were collected by suction filtration, washed with a minimum amount of methanol, and dried in vacuo. Yield: 0.56 g (72%). Anal. Calcd for $C_{56}H_{76}N_{26}O_6Cl_2Cu_4{\cdot}1.25H_2O$: C, 43.20; H, 5.08; N, 23.40. Found: C, 42.94; H, 5.00; N, 23.68. IR (KBr): ν_{N-H}, 3200−3000; $\nu_{C=N}$, 1630−1615; ν_{N-O}, 1385 cm^{-1}. UV/vis in H_2O [λ_{max}/nm (ϵ/dm^3 cm^{-1} mol^{-1})]: 716(174). UV/vis solid (λ_{max}/nm): 740. Λ_M: 109 S mol^{-1} cm^2 in H_2O. Mp: >280 °C.

$[Cu(L^2)]_4{\cdot}H_2O$, 2″. To a solution of **2′** (1 mmol) in 30 mL of methanol was added a slight excess of triethylamine (1.5 mmol). After 5 min of stirring at room temperature, green microcrystals precipitated. These were collected by suction filtration, washed with a minimum amount of methanol, and dried in vacuo. Recrystallization was carried out in a mixed solution of chloroform and methanol at room temperature. Yield: 0.28 g (83%). Anal. Calcd for $C_{14}H_{18}N_6Cu{\cdot}0.25H_2O$: C, 49.69; H, 5.51; N, 24.84. Found: C, 49.83; H, 5.59; N, 24.69. IR (KBr): $\nu_{C=N}$, 1630−1610 cm^{-1}. UV/vis in $CHCl_3$ [λ_{max}/nm (ϵ/dm^3 cm^{-1} mol^{-1})]: 815 (219). UV/vis solid (λ_{max}/nm): 709. Λ_M: 0 S mol^{-1} cm^2 in $CHCl_3$. Mp: >280 °C.

Physical Measurements. Elemental analyses for C, H, and N were performed at the Elemental Analysis Service Center of Kyushu University. Electrical conductivity measurements were carried out on a Horiba DS-14 conductivity meter in a ca. 10^{-3} mol dm^{-3} solution at room temperature. Infrared spectra were measured on KBr disks with JASCO A-102 spectrophotometers. Electronic absorption spectra of the 10^{-3} mol dm^{-3} solutions and the diffuse reflectance spectra of the powdered samples were measured on a Hitachi U-4000 spectrophotometer. Magnetic susceptibilities were measured with a MPMS5 SQUID susceptometer (Quantum Design Inc.) in the temperature range 2−300 K. The calibrations were made with $[Ni(en)_3]S_2O_3$ (en = ethylenediamine).[17] Corrections were applied for diamagnetism calculated from Pascal's constants.[18] Effective magnetic moments were calculated by the equation $\mu_{eff} = 2.828(\chi_A T)^{1/2}$, where χ_A is the magnetic susceptibility per copper.

Potentiometric pH Titration. Potentiometric pH titrations were carried out in a thermostated bath at 25 °C and under a 99.9995% N_2 atmosphere. Extra pure grade water was used (resistivity higher than 18.0 MΩ). The GS-5015c electrode and potentiometer were supplied by the TOA Co. Ltd. The standard electrode potential (E_0) was first determined by Gran's plot method.[19] About 100 mL of 0.15 ionic strength solution containing 0.24 mmol of metal complex and sodium chloride was titrated with a 0.10 M NaOH + 0.05 M NaCl solution. Immediately after forward titration the resulting solution was titrated back with a 0.10 M HCl + 0.05 M NaCl solution. The electrode potentials were converted into a proton concentration scale ($-\log [H^+] = (E_0(mV) - E(mV))/59.15$)), and the degree of association n was calculated by Bjerrum's method for the forward and reverse titrations, respectively.[20]

pH-Dependent Electronic Spectra. Electronic spectral changes for the forward titration with the addition of 0.1 M aqueous NaOH solution and for the reverse titration with the addition of 0.1 M HCl solution were measured at room temperature. An aqueous solution of the protonated complex (0.24 mmol of the complex in 80 mL of water) was prepared. The spectra were measured at every addition of 0.4 mL of 0.1 M NaOH solution until the total volume of the NaOH solution reached 4.8 mL. Then, by adding 0.4 mL of 0.1 M HCl solution at a time, the electronic spectra for the reverse procedure were measured. The spectra were corrected for the volume due to the addition of 0.1 M NaOH and HCl solutions.

X-ray Data Collection, Reduction, and Structure Determination. Since crystals of **2″** gradually decompose, they were encapsulated into a Lindeman glass capillary containing a small amount of mother liquid. Each of the other crystals was coated with epoxy resin and mounted on a glass rod. All measurements were made on a Rigaku AFC7R diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 69 Å) and a 12 kW rotating anode generator. The data were collected at a temperature of 20 ± 1 °C using a $\theta-2\theta$ scan technique at a scan speed of 16.0 °/min. The maximum 2θ of **2′** was 48°, and the values for the other compounds were set to be 50°. The weak

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Table 1. Crystallographic Data for All Complexes in This Study[a]

compound	**1**	**1′**	**2**	**2′**	**2″**
formula	$C_{12}H_{16}N_8O_6Cu$	$C_{12}H_{15}N_7O_4Cu$	$C_{14}H_{20}N_7O_3ClCu$	$C_{56}H_{76}N_{26}O_9Cl_2Cu_4$	$C_{14}H_{18}N_6O_5Cu$
fw	431.85	384.84	433.36	1582.48	413.88
space group	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$I4_1/a$ (No. 88)
a, Å	8.568(2)	13.024(1)	10.697(1)	17.776(2)	23.114(3)
b, Å	11.703(1)	9.848(1)	12.729(2)	18.809(2)	23.114(3)
c, Å	8.469(1)	13.067(1)	7.1662(9)	11.687(3)	14.973(6)
α, deg	94.56(1)	90	96.73(1)	103.04(1)	90
β, deg	92.52(1)	110.184(6)	98.17(1)	99.77(1)	90
γ, deg	90.01(1)	90	107.830(9)	98.532(9)	90
V, Å	845.6(2)	1573.0(2)	906.1(2)	3679(1)	7999(3)
Z	2	4	2	2	16
ρ_{calcd}, g cm^{-3}	1.696	1.625	1.688	1.428	1.374
μ, cm^{-1}	13.43	14.23	13.83	12.81	11.27
R,[b] R_w,[c] %	5.2, 4.3	2.7, 2.4	3.0, 4.2	6.3, 5.9	4.8, 3.2

[a] The reflection data were measured at 20 ± 1 °C. Mo Kα radiation ($\lambda = 0.710\,69$ Å) was used. [b] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [c] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$. $w = 1/\sigma(F_o)^2$.

reflections ($I < 10.0\sigma(I)$) were rescanned (maximum of 3 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 reflections, ensuring a good stability of intensities during data collection. An empirical absorption correction based on azimuthal scans of several reflections was applied. The data were also corrected for Lorentz and polarization effects.

The structures were solved by direct methods[21,22] and expanded using Fourier techniques.[23] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms at the ideal calculated positions were included in the structure factor calculation but were not refined. Full-matrix least-squares refinement based on the observed reflections ($I > 3.00\sigma(I)$) was employed, using the unweighed and weighed agreement factors of $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$ The structures except for **1** were solved without disorder. The methylene chain of the ligand backbone of **1** is disordered, and the thermal parameters of the atoms are large. The weighing scheme was based on counting statistics. Neutral atomic scattering factors were taken from *International Tables for X-ray Crystallography*.[24,25] Anomalous dispersion effects were included in F; the values $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.[26] All calculations were performed using the teXsan crystallographic software package of the Molecular Structure Corporation.[27] Crystal data and details of the structure determination are summarized in Table 1.

Results and Discussion

Synthesis and Characterization of Complexes. The quadridentate Schiff-base ligands, *N*,*N*′-bis(2-substituted-imidazol-4-ylmethylidene)-1,4-diaminobutane H_2L^1 (2-substitutent = H) and H_2L^2 (2-substitutent = Me), were prepared by the 1:2 condensation reaction of 1,4-diaminobutane and 4-formylimidazole or 2-methyl-4-formylimidazole in methanol, respectively, and the reaction mixtures were subsequently used for the synthesis of copper(II) complexes. The copper(II) complexes with the formulas $[Cu(H_2L^1)](NO_3)_2$, **1**, and $[Cu(H_2L^2)]ClNO_3$, **2**, were obtained by the reaction of copper(II) nitrate trihydrate or copper(II) chloride dihydrate with each of the quadridentate ligands at a molar ratio of 1:1 in methanol. The IR spectra of **1** and **2** showed the characteristic bands assignable to the C═N stretching vibration of the Schiff-base ligand at 1640−1610 cm^{-1}, the imidazole N−H vibration at 3200−3000 cm^{-1}, and the N−O vibration of the nitrate ion at 1385 cm^{-1}.[28] The molar electrical conductivities of **1** and **2** are 207 and 212 S mol^{-1} cm^2 in ca. 10^{-3} mol dm^{-3} aqueous solution, respectively. The observed values are in the expected range for 1:2 electrolytes in water,[29] indicating that the anions do not coordinate to copper(II) ion and that the two imidazole protons associate in the aqueous solutions.

Mono-deprotonated complexes with the formulas $[Cu(HL^1)](NO_3)$, **1′**, and $[Cu(HL^2)]\cdot 0.5(ClNO_3)$, **2′**, were obtained as green crystals by the treatment of **1** and **2** with 1 equiv or a slight excess of triethylamine in methanol. The IR spectra of **1′** and **2′** showed the imidazole N−H vibration at 3200−3000 cm^{-1} and the N−O vibration of the nitrate ion at 1385 cm^{-1}.[28] As **1′** is insoluble in common organic solvents, the electrical conductivity of the solution cannot be measured. The electrical conductivity per Cu of **2′** is 109 S mol^{-1} cm^2 in water, a value in the expected range for 1:1 electrolytes,[29] indicating that the anion does not coordinate to the copper(II) ion and that the ligand is in the singly deprotonated form.

Due to the insolubility of **1′** in common organic solvents, no further deprotonation reaction could be carried out. **2′** is moderately soluble in methanol, and the di-deprotonated complex **2″** was easily obtained as green crystals by the addition of 1.5 equiv of triethylamine to the methanol solution of **2′**. The characteristic IR bands due to the imidazole N−H vibration and the N−O vibration of the nitrate ion disappear in the spectrum of **2″**. **2″** is insoluble in methanol and water and moderately soluble in chloroform and dichloromethane. The electrical conductivity is nearly equal to 0 in chloroform, indicating that the ligand is in the doubly deprotonated form.

Structural Description of 1 and 1′. Selected bond distances and angles with their estimated standard deviations in parentheses for all of the complexes are given in Table 2. ORTEP drawings of mononuclear complex **1** and one-dimensional

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Table 2. Selected Bond Distances (Å) and Angles (deg) for All Complexes in This Study

	1	**1′**	**2**	**2′**	**2″**
Bond Distances (Å)					
Cu−N(2)	1.959(3)	1.987(2)	1.979(2)	1.983(6)−1.959(6)	2.013(9)
Cu−N(3)	2.035(4)	2.114(2)	2.138(2)	2.027(7)−2.046(6)	2.052(9)
Cu−N(4)	1.976(4)	2.003(2)	1.997(2)	2.018(6)−2.038(6)	2.01(1)
Cu−N(5)	1.998(4)	2.014(2)	2.125(2)	2.165(7)−2.219(7)	2.18(1)
Cu−O(2)	2.370(4)				
Cu−Cl(1)			2.2918(8)		
Cu−N*[a]		2.122(2)		1.995(6)−2.006(6)	1.987(9)
Bond Angles (deg)					
N(2)−Cu−N(3)	82.0(1)	80.54(7)	80.10(8)	81.2(3)−81.9(3)	80.8(4)
N(2)−Cu−N(4)	173.9(2)	170.19(7)	170.73(9)	168.4(3)−171.8(3)	169.2(5)
N(2)−Cu−N(5)	101.0(1)	95.49(7)	95.23(8)	98.7(3)−99.9(3)	103.9(5)
N(3)−Cu−N(4)	97.2(2)	96.21(7)	92.83(8)	88.2(3) −90.6(3)	88.5(4)
N(3)−Cu−N(5)	150.9(2)	142.04(7)	105.66(8)	103.3(3)−109.5(3)	106.3(3)
N(4)−Cu−N(5)	82.6(2)	81.33(7)	80.83(8)	79.1(3)−79.3(3)	79.9(5)
N−Cu−N*[b]		109.44(7)		96.9(2)−97.9(2)	95.4(4)

[a] Cu−N* distance (N* denotes the imidazolate nitrogen atom of the adjacent unit). [b] N−Cu−N* angle referring to Cu and two nitrogen atoms of two bridging imidazolate groups.

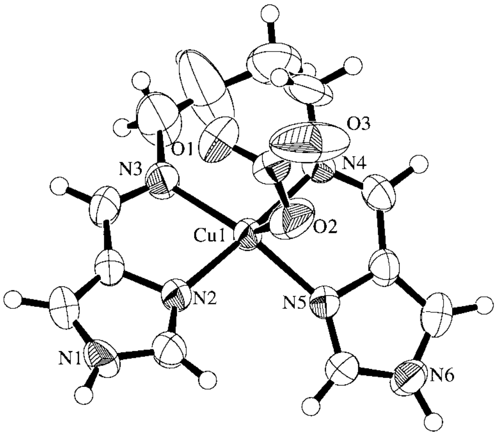

Figure 1. ORTEP drawing of the cation for **1**, showing 50% probability ellipsoids.

compound **1′** are shown in Figures 1 and 2, respectively, where the same atom-numbering scheme is used for both compounds.

The crystal of **1** consists of a copper(II) complex with a quadridentate ligand and two nitrate anions. The copper(II) ion assumes a pentacoordinated geometry with N_4 donor atoms of the quadridentate ligand with bond distances of 1.959(3)−2.035(4) Å and an oxygen atom O(2) of a nitrate ion with 2.370(4) Å. The coordinated nitrate anion is further hydrogen-bonded to an imidazole nitrogen atom of the adjacent unit with N(6)···O(2) = 2.928(5) Å and N(6)···O(3) = 2.968(6) Å. Another nitrate anion is free from coordination but is hydrogen-bonded to an imidazole nitrogen atom with N(1)···O(5) = 2.775(5) Å. The most noteworthy structural feature, found in all of the complexes of this study, is that the molecule is bent by a line consisting of N(2), Cu, and N(4) atoms so that the molecule assumes a butterfly shape. The angle of N(3)−Cu−N(5), representing the extent of the bend, is 150.9(2)° for **1**.

The crystal of **1′** assumes an imidazolate-bridged zigzag-chain structure, where mono-deprotonated molecules are connected by the coordination bond between the copper(II) ion of a unit and a deprotonated imidazolate nitrogen atom of the adjacent unit with a Cu−N(6)* distance of 2.122(2) Å. The nitrate anion is free from coordination but is hydrogen-bonded to the imidazole nitrogen atom with N(1)···O(1) = 2.789(3) Å. The copper(II) ion assumes a pentacoordinated geometry with N_5 donor atoms of the quadridentate ligand of a unit with four Cu−N distances of 1.987(2)−2.114(2) Å and an imidazolate nitrogen atom of the adjacent unit with Cu−N(6)* = 2.122(2) Å. The angle of N(3)−Cu−N(5) is 142.04(7)°.

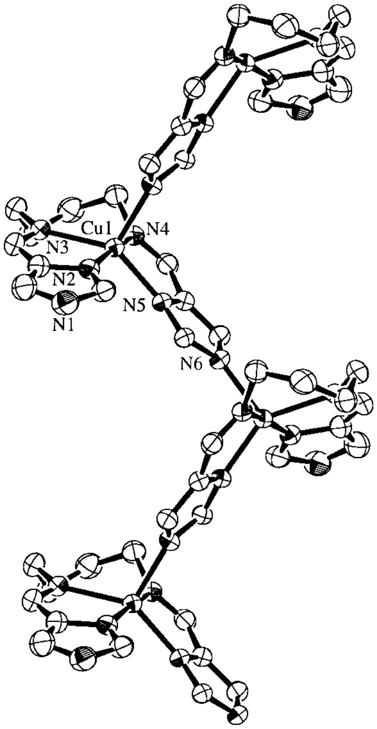

Figure 2. ORTEP drawing of one-dimensional chain structure of **1′**, showing 50% probability ellipsoids. The atom numbering of the unique atoms is given, and hydrogen atoms are omitted for clarity.

Structural Description of 2, 2′, and 2″. ORTEP drawings of mononuclear **2** and tetranuclear **2′** and **2″** are shown in Figures 3, 4, and 5, respectively. The copper(II) ion of **2** assumes a pentacoordinated geometry with N_4 donor atoms of the quadridentate ligand with bond distances of 1.979(2)−2.138(2) Å and a chloride ion with a distance of 2.2918(8) Å. The angle of N(3)−Cu-N(5) is 105.66(8)°, indicating that **2** is much more bent than **1**. The nitrate anion is free from coordination, but one oxygen atom of the nitrate O(2) bridges two adjacent cations by a hydrogen bond to give a cyclic-dimeric structure consisting of two $[CuH_2L^2]^{2+}$ cations and two NO_3^- anions, where O(2) is hydrogen-bonded to two imidazole nitrogen atoms with N(1)···O(2) = 2.785(3) Å and N(6)*···O(2) = 2.828(3) Å.

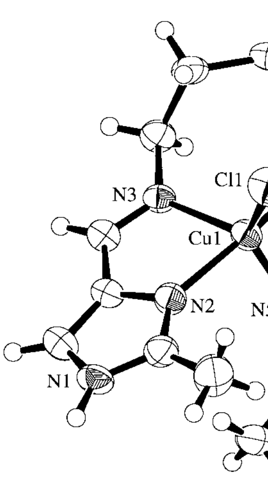

Figure 3. ORTEP drawing of the cation for **2**, showing 50% probability ellipsoids.

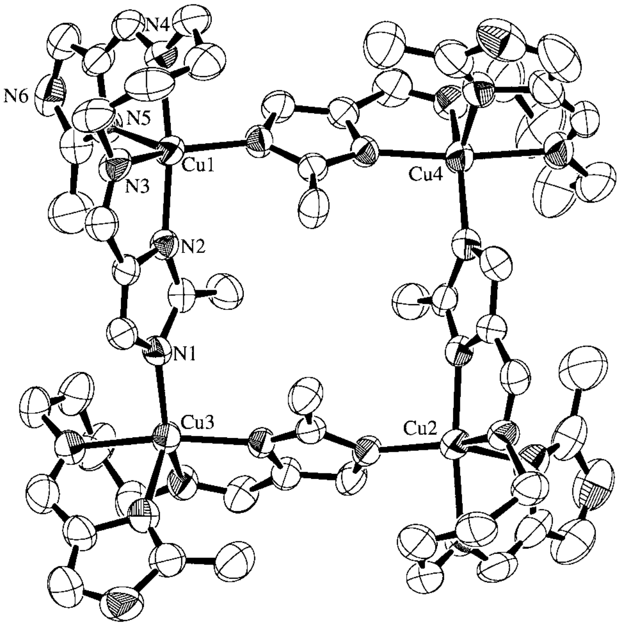

Figure 4. ORTEP drawing of **2′**, showing the cavity and 50% probability ellipsoids. Hydrogen atoms are omitted for clarity.

The crystal of **2′** consists of an imidazolate-bridged cyclic-tetranuclear molecule described as a molecular square, two nitrate and two chloride anions, and water molecules as the crystal solvents, where Cu−Cu distances with and without an imidazolate bridge are 6.076(1)−6.133(1) and 8.473(2)−8.570(1) Å, respectively. In the cyclic structure, the four formulas are connected by a coordination bond between the copper(II) ion and the imidazolate nitrogen atom of the adjacent unit with bond distances of 1.995(6)−2.006(6) Å. Each copper(II) ion assumes a pentacoordinated geometry with N_5 donor atoms of the ligand and an adjacent imidazolate nitrogen atom. The angle of the molecular bend, N(3)−Cu−N(5), is 103.3(3)−109.5(3)°.

2″ crystallizes in the tetragonal space group $I4_1/a$, and the four formula units form an imidazolate-bridged cyclic-tetranuclear structure, where Cu−Cu distances with and without the imidazolate bridge are 6.160(2) and 8.061(2) Å, respectively, and four copper(II) ions array in a tetrahedral distortion. Each copper(II) ion assumes a pentacoordinated geometry with N_5 donor atoms of the ligand of a unit with four Cu−N distances of 2.01(1)−2.18(1) Å and an imidazolate nitrogen atom of the adjacent unit with a distance of 1.987(9) Å. The angle of N(3)−Cu−N(5) is 106.3(3)°.

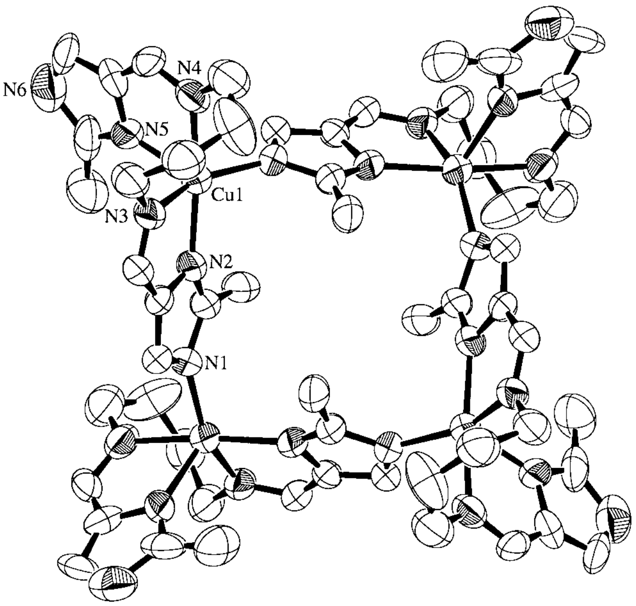

Figure 5. ORTEP drawing of **2″**, showing the cavity and 30% probability ellipsoids. Hydrogen atoms are omitted for clarity.

Magnetic Properties. The effective magnetic moment per copper of **1**, μ_{eff}, is nearly constant in the temperature range measured, and the value of 1.81 μ_B is compatible with the spin-only value, 1.73 μ_B, expected for $S = {}^1/_2$, indicating that **1** behaves as a magnetically diluted spin system of $S = {}^1/_2$ as confirmed by X-ray analysis. On the other hand, the μ_{eff} value of **1′** decreases gradually from 1.78 μ_B at 300 K to 0.38 μ_B at 2 K, suggesting the operation of a weak antiferromagnetic interaction. The magnetic susceptibility data were analyzed by eq 1[30,31] on the basis of the Bonner and Fisher model for a one-dimensional infinite-chain structure for $J < 0$, where the spin Hamiltonian is defined as $H = -2J\sum S_iS_{i+1}$.

$$\chi_A = (Ng^2\beta^2/kT)(0.25 + 0.14995x + 0.30094x^2)/(1.0 + 1.9862x + 0.68854x^2 + 6.0626x^3) + N\alpha$$

$$\text{with} \qquad x = |J|/kT \qquad (1)$$

The best-fit parameters of $g = 2.018(5)$, $J = -8.3(1)$ cm^{-1}, and the linear agreement factor $R = 0.9993$ were obtained, where $N\alpha$ denotes the temperature independent paramagnetism and the value of 60×10^{-6} cm^3 mol^{-1} was used. The coupling constant of $J = -8.3(1)$ cm^{-1} is compatible with those of the imidazolate-bridged one-dimensional compounds reported previously.[15] The magnetic behaviors of **2**, **2′**, and **2″** are shown in Figure 6 in the form of χ_A vs T plots. The effective magnetic moment of **2** remained constant in the temperature range measured, and the behavior was essentially the same for **1**, indicating that **2** is a magnetically diluted $S = {}^1/_2$ system due to an unpaired electron given by the d^9 electronic configuration of the Cu(II) ion. On the other hand, the μ_{eff} values of **2′** and **2″** at room temperature are 1.51 and 1.58 μ_B, respectively, values substantially smaller than the spin-only value of 1.73 μ_B for $S = {}^1/_2$. On lowering of the temperature, the μ_{eff} values decrease

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(31) Bonner, J. C.; Fisher, M. E. *Phys. Rev.* **1964**, *135*, A640.

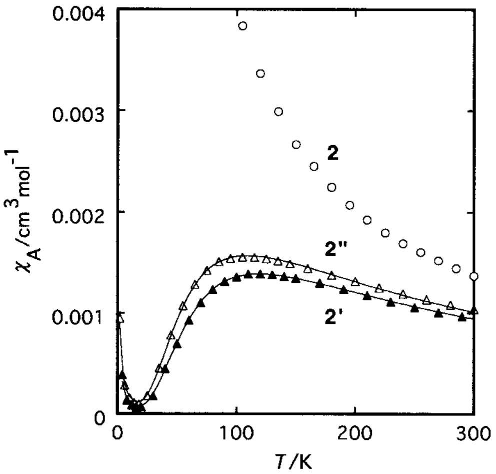

Figure 6. Plots of χ_A versus T for **2, 2′**, and **2″**. The solid lines of **2′** and **2″** represent the theoretical curves with best-fit parameters of $g = 2.015(4)$ and $J = -53.1(2)$ cm^{-1} for **2′** and $g = 2.062(4)$ and $J = -48.8(2)$ cm^{-1} for **2″**, respectively.

gradually. The χ_A vs T curves show a maximum at 115 and 105 K for **2′** and **2″**, respectively, typical magnetic behavior for a polynuclear Cu(II) system involving even numbers of Cu(II) ions and exhibiting antiferromagnetic coupling.[32] The magnetic susceptibility data were interpreted quantitatively by eq 2 based on a cyclic-tetranuclear structure,[15,33,34] where the spin Hamiltonian is defined as $H = -2J(S_1S_2 + S_2S_3 + S_3S_4 + S_4S_1)$.

$$\chi_A = (Ng^2\beta^2/2kT)(2 + 5\exp(2K) + \exp(-2K)/(7 + \exp(2K) + 3\exp(-2K) + \exp(-4K))(1 - \rho) + \rho(Ng^2\beta^2/4kT) + N\alpha \quad \text{with} \quad K = J/kT \qquad (2)$$

The best-fit parameters are $J = -53.1(2)$ cm^{-1} and $g = 2.015(4)$, $\rho = 0.013$, and $R = 0.9995$ for **2′** and $J = -48.8(2)$ cm^{-1}, $g = 2.062(4)$, $\rho = 0.019$, and $R = 0.9994$ for **2″**, where ρ and R represent the paramagnetic impurity and linear agreement factor. The theoretical curves with these parameters are represented by the solid lines in Figure 6. The magnitudes of the antiferromagnetic interaction for the present complexes are compatible with those of the imidazolate-bridged cyclic-tetranuclear copper(II) complexes with tridentate ligands reported previously.[15]

Potentiometric pH Titration. The interconversion between the Cu(II) monomer and deprotonated oligomer or polymer was investigated by potentiometric pH titration. Figure 7 shows the results of forward and reverse titrations carried out in water at 25 °C for **1** and **2**. The degree of proton association n calculated by Bjerrum's method[20] decreased from 2 to 0 for the forward titration and increased from 0 to 2 for the reverse titration. The imidazole proton did not dissociate when **1** and **2** were dissolved in water (ca. 0.25×10^{-3} mol dm^{-3} aqueous solution), because the electrode potentials were almost constant. In the forward titration process of **1** and **2**, green powders began to precipitate at $n = 1.5$ and $n = 0.5$, respectively, and they dissolved at the same points for the reverse procedures. Due to the precipitation, the forward and reverse titration curves show a slight disagreement. For **2**, curves in the range $n = 1-2$ showed a sigmoidal shape and were almost the same, indicating that the interconversion between the protonated monomer **2** and the monodeprotonated tetramer **2′** is reversible in the aqueous solution. From these titrations the first and second dissociation constants pK_{d1} and pK_{d2} were determined to be (pK_{d1} and pK_{d2}) = (8.2, 8.8) and (7.9, 9.9) for **1** and **2**, respectively.

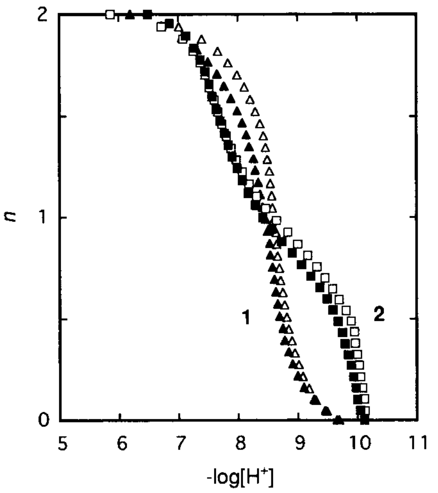

Figure 7. pH-dependent potentiometric titration curves for the forward and reverse titrations of **1** and **2**, where a plot of the degree of proton association n versus pH is given.

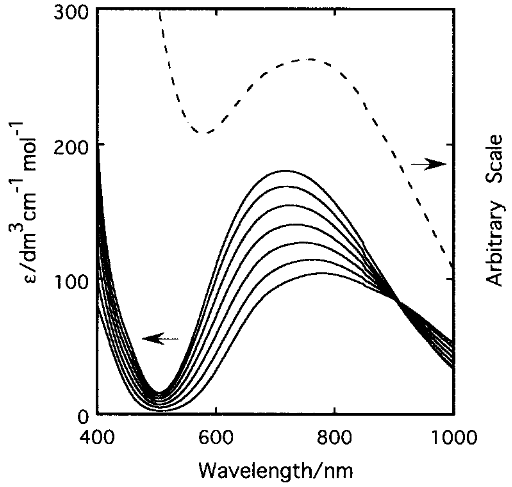

Figure 8. pH-dependent electronic spectra of **2**. An aqueous solution of **2** (0.24 mmol in 80 mL of water) was prepared. The spectrum of the solution was measured at every addition of 0.4 mL of 0.1 M NaOH solution. The spectra were corrected by the volume deviation due to the addition of 0.1 M NaOH solution. The dotted line represents a spectrum when 2 equiv NaOH solution were added to the aqueous solution of **2**.

pH-Dependent Absorption Spectra in Water. The aqueous solutions of the protonated complexes **1** and **2** (0.24 mmol in 80 mL of water) were prepared, and the electronic absorption spectra were measured at every addition of 0.4 mL of 0.1 M NaOH aqueous solution until the total volume of the NaOH solution (4.8 mL) neutralized the two imidazole protons per complex. Then, to the solution was added 0.1 M HCl solution in 0.4 mL increments for the reverse procedure, and the electronic spectra were measured. The result for **2** is shown in Figure 8.

The spectrum of **1** without NaOH solution exhibited a broad band at 642 nm with the molar extinction coefficient $\epsilon = 62$ dm^3 mol^{-1} cm^{-1} assignable to a d−d band. On addition of 0.1 M NaOH solution, the solution became cloudy due to the

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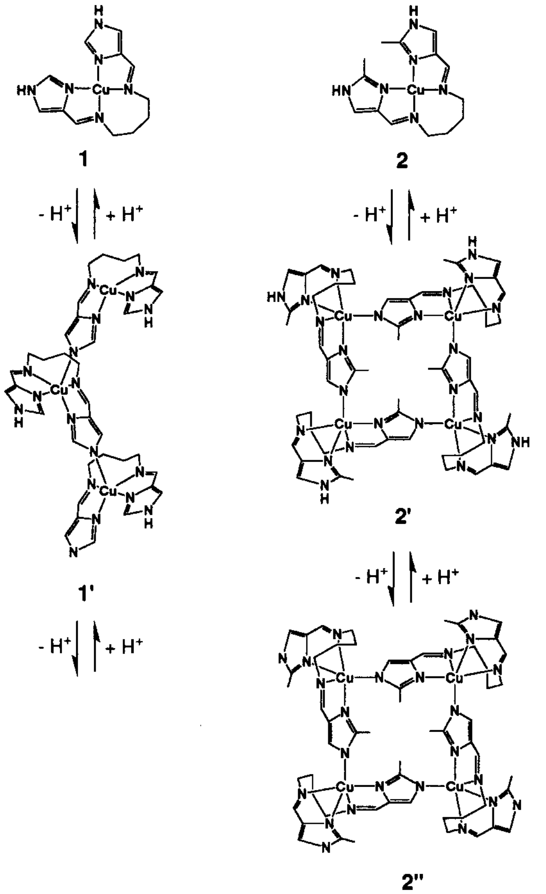
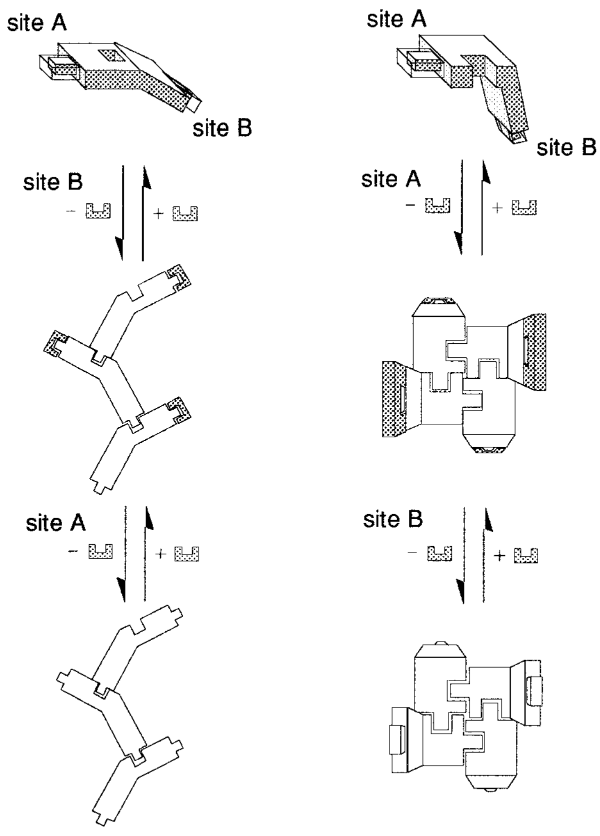
(32) Kahn, O. *Molecular Magnetism*; VCH: Weinheim, Germany, 1993.
(33) Nakao, Y.; Mori, W.; Okuda, N.; Nakahara, A. *Inorg. Chim. Acta.* **1979**, *35*, 1.
(34) Mohanta, S.; Nanda, K. K.; Werner, R.; Haase, W.; Mukherjee, A. K.; Dutta, S. K.; Nag, K. *Inorg. Chem.* **1997**, *36*, 4656.

Scheme 1



Scheme 2



precipitation of mono-deprotonated polymeric species **1′**. On addition of 0.1 M HCl solution in the reverse procedure, **1′** dissolved and the spectrum finally reached its original value.

The initial spectrum of **2** without NaOH solution exhibited a broad band at 777 nm with $\epsilon = 102$ dm^3 mol^{-1} cm^{-1} assignable to a d−d band. On addition of 0.1 M NaOH solution, the color changed from light to dark green, the spectrum changed with an isosbestic point at 900 nm, and the d−d band shifted to a lower wavelength with an increase in intensity. After the addition of 2.4 mL of 0.1 M NaOH aqueous solution, the spectrum exhibited a d−d band with λ_{max}= 720 nm and ϵ = 180 dm^3 mol^{-1} cm^{-1}, which resembled the spectrum of the isolated mono-deprotonated compound **2′** measured in water (λ_{max}= 716 nm, $\epsilon = 174$ dm^3 mol^{-1} cm^{-1}). On further addition of 0.1 N NaOH solution, the solution became cloudy due to the precipitation of electrically neutral di-deprotonated species **2″**. The spectral change exhibited no isosbestic point. In the reverse procedure, on addition of 0.1 M HCl solution, the precipitate began to dissolve gradually when 1.2 mL of the HCl solution was added; the spectrum reached that of **2′** when 1 equiv of HCl was added. On further addition of the HCl solution, the spectrum changed with an isosbestic point at 900 nm and reached the spectrum of **2** finally. These results demonstrate that the interconversion between the Cu(II) monomer and deprotonated oligomer or polymer as given in Scheme 1 is available in this system.

Substituent Effect on the Deprotonation Self-Assembly Process. The X-ray structural analyses of **1′** and **2′** demonstrated that the assembly deprotonation process of **1** with substituent = H and **2** with substituent = methyl produced an infinite zigzag-chain compound **1′** and a cyclic-tetranuclear compound **2′**, respectively. It is proper to consider why such a drastic substituent effect is induced. The most noteworthy structural feature is a molecular bend by a line consisting of N(2), Cu, and N(4) atoms. Due to this molecular bend, the two imidazole moieties can be recognized as distinctly different from each other; i.e., one (hereafter denoted as site A) is in a plane defined by Cu and N$_3$ of the tetradentate N$_4$ ligand, and the other (hereafter denoted as site B) is in a plane defined by Cu, N(4), and N(5). In the present system, either site A or site B can be used for the self-assembly process. In fact, site A is used for the assembly process of **2** and site B is used for that of **1**.

The angles of N(3)−Cu−N(5) for **1** and **1′** with the substituent = H are 150.9(2)° and 142.04(7)°, respectively, and those for **2**, **2′**, and **2″** with substituent = Me are 105.66(8)°, 105.8° (average), and 106.3(3)°, respectively. The larger bend found in **2**, **2′**, and **2″** is ascribed to the steric repulsion between two 2-methylimidazole moieties. Owing to a nearly perpendicular bend for **2**, the distance of Cu−N(5) = 2.125(2) Å of site B is substantially longer than that of Cu−N(2) = 1.979(2) Å of site A, implying that the imidazole proton at N(1) of site A would dissociate first. According to these results, the imidazolate nitrogen atom occupies one of the equatorial coordination sites of the adjacent block to give a cyclic tetramer. On the other hand, due to the spread-out shape of **1**, the distance of Cu−N(2) = 1.959(3) Å is rather compatible with that of Cu−N(5) = 1.998(4) Å; in fact, the imidazole proton of site B dissociates first and the imidazolate nitrogen atom, N(6), occupies an apical position of the adjacent molecule to give an infinite chain. The assembly process can be easily understood

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(36) Carlin, R. L. In *Magneto-Structural Correlations in Exchange Coupled Systems*; Willet, R. D., Gatteschi, D., Kahn, O., Eds.; Reidel: Dordrecht, The Netherlands, 1985; p 127.

by Scheme 2. This difference in the relative orientation between the two adjacent coordination planes can be well detected by the magnetic interaction, since the $\sigma-\sigma$ super exchange mechanism inducing antiferromagnetic coupling is available for **2′** and **2″** and unavailable for **1′**.[32, 35,36]

Acknowledgment. This work was supported in part by a Grant-in-Aid from the Ministry of Education, Science and Culture (No. 09874145).

Supporting Information Available: Five X-ray crystallographic files in CIF format are available on the Internet only. Access information is given on any current masthead page.

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