

A Ferromagnetic Chain of Imidazolato-Bridged One-Dimensional Copper(II) Complex

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A mononuclear copper(II) complex, [2-ethoxy-6-{{3-(2-methyl-4-imidazolylmethyleneamino)propyl}iminomethyl}phenolato]copper(II) perchlorate [CuHL]ClO₄ and its deprotonated complex at the imidazole moiety, [CuL]_n, were prepared. The structure of [CuHL]ClO₄ consists of a cation [CuHL]⁺ exhibiting a four-coordinated square-planar geometry and an anion ClO₄[−], while [CuL]_n assumes an imidazolato-bridged zigzag-chain structure, in which the copper(II) ion is coordinated by the imidazolato nitrogen atom of the adjacent molecule with Cu–N = 2.258(5) Å and the two adjacent CuL units assumes a perpendicular orientation. The temperature-dependent magnetic susceptibilities from 2.0 to 300 K and field-dependent magnetization at 2.0 K demonstrate that [CuHL]ClO₄ is a magnetically isolated copper(II) molecule while [CuL]_n is a ferromagnetic chain. The magnetic susceptibility data of [CuL]_n were analyzed by Baker's model based on $H = -2J\Sigma S_{A_j}S_{A_{j+1}}$ for chain of equally spaced copper(II) ions to give the best-fit parameters of $g = 2.08$ and $J = +0.63 \text{ cm}^{-1}$.

In the last three decades, the field of molecular-based magnets has shown a spectacular advance, in which the concept of magnetic orthogonality introduced by Kahn has played a leading role for development.¹ Owing to this concept, one can easily predict the magnetic properties between two adjacent magnetic centers. As the simplest case consisting of one unpaired electron per metal ion, the magnetic properties of binuclear copper(II) complexes have been extensively studied.² However, ferromagnetic coupling is rarely observed. Hatfield, Hodgson, et al. investigated the magneto–structural correlation of planar hydroxo-bridged copper(II) binuclear complexes and found that the magnetic coupling constant J is correlated linearly to the bridging angle α of Cu–O–Cu.³ The ferromagnetic coupling observed at $\alpha < 97.5^\circ$ is rationalized by accidental orthogonality.¹ Ferromagnetic coupling has been also observed in alkoxo-bridged cubane-type tetranuclear copper(II) complexes, where each copper(II) ions assume a square-pyramidal coordination geometry and the two adjacent equatorial coordination planes are nearly perpendicular to each other.⁴ Due to the perpendicular arrangement of the two adjacent coordination planes, a strict orthogonality is preserved so that ferromagnetic coupling is always expected. If such a perpendicular arrangement is extended from two adjacent molecular units to one-dimensional (1D) infinite lattice, the resulting 1D chain would be a ferromagnetic chain. From a structural viewpoint, a copper(II) complex with the 1:1:1 condensation product of 2-methylimidazole-4-carbaldehyde, 1,3-propanediamine, and 3-ethoxysalicylaldehyde would show such properties.⁵ As schematically drawn in Figure 1, the copper(II) complex [CuHL]⁺ can play the role of a self-complementary building block to form a self-assembled 1D

chain structure, since the complex potentially involves not only an acceptor coordination ability at the vacant axial position but also a donor coordination ability at the imidazolato nitrogen atom. When the proton of the imidazole moiety is dissociated, the self-assembly reaction (the imidazolato nitrogen atom of a molecule generated by the deprotonation axially coordinates to copper(II) ion of the adjacent molecule) is triggered and leads to the assembly structure. The protonated copper(II) complex assumes a square-planar coordination geometry with N₃O donor atoms, whereas the deprotonated copper(II) species assumes a square-pyramidal coordination geometry with N₄O donor atoms, where the axial coordination site is occupied by an imidazolato nitrogen atom of an adjacent molecular unit to give an imidazolato-bridged 1D structure. Although twenty years ago, one of the present authors investigated the structures and magnetic properties of several such complexes, at that time he could not confirm the ferromagnetic chain properties, due to the very weak magnetic interaction and the magnetic susceptibility data from room to liquid nitrogen temperature are not enough for detection. In this study, the analogous copper(II) complex, [2-ethoxy-6-{{3-(2-methyl-4-imidazolylmethyleneamino)propyl}iminomethyl}phenolato]copper(II) perchlorate [CuHL]ClO₄ and its deprotonated complex [CuL]_n, are newly prepared and their structures and magnetic properties are investigated and it is found that [CuL]_n is a ferromagnetic chain.

Results and Discussion

Syntheses and Characterizations of [CuHL]ClO₄ and [CuL]_n. The copper(II) complexes with the 1:1:1 condensation product of 2-methylimidazole-4-carbaldehyde, 1,3-propanediamine, and 3-ethoxysalicylaldehyde were prepared by a

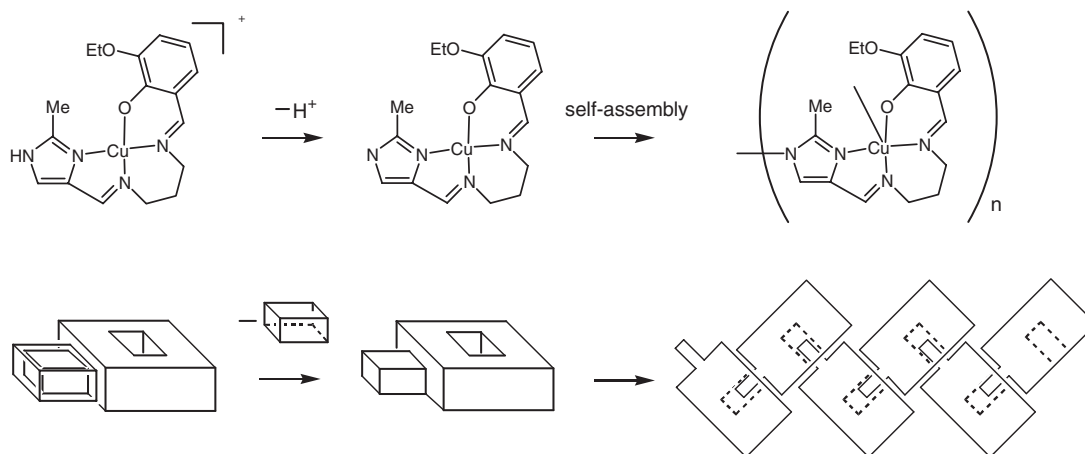


Figure 1. (top) Self-assembly reaction from $[\text{CuHL}]^+$ to its deprotonated 1D complex $[\text{CuL}]_n$. (bottom) The schematic drawing of the assembly reaction. The imidazole hydrogen is drawn by a cap, and the donor and acceptor coordination sites are drawn by $\square$ and $\square$, respectively.

Table 1. X-ray Crystallographic Data for $[\text{CuHL}]\text{ClO}_4$ and $[\text{CuL}]_n$

	$[\text{CuHL}]\text{ClO}_4$	$[\text{CuL}]_n$
Formula	$\text{C}_{17}\text{H}_{21}\text{ClCuN}_4\text{O}_6$	$\text{C}_{17}\text{H}_{20}\text{CuN}_4\text{O}_2$
Fw	476.38	375.92
Crystal system	monoclinic	orthorhombic
Space group	$P2_1/c$ (No. 14)	$Pbca$ (No. 61)
$a/\text{\AA}$	7.027(4)	9.318(4)
$b/\text{\AA}$	12.235(4)	15.310(7)
$c/\text{\AA}$	23.267(9)	23.043(8)
$\beta/^\circ$	92.512(17)	90
$V/\text{\AA}^3$	1998.4(14)	3287(2)
Z	4	8
$D_{\text{calcd}}/\text{Mg m}^{-3}$	1.583	1.519
$\mu(\text{Mo K}\alpha)/\text{mm}^{-1}$	1.26	1.34
R^a	0.0446	0.0524
wR^b	0.0337	0.1102

Data with a) $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. b) $wR = [\Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w|F_o|^2]^{1/2}$.

step-by-step procedure according to methods reported previously.^{5b,5c} At first, a precursor complex with the 1:1 condensation product of 3-(ethoxysalicylaldehyde and 1,3-propanediamine, [bis{6-[(3-aminopropyl)iminomethyl]-2-ethoxyphenolato}]nickel(II), was synthesized by adopting the method of Elder.⁶ A methanolic solution of the 1:1 ligand was obtained by refluxing the nickel(II) complex and two equivalents of dimethylglyoxime for 2 h in methanol and then by filtering out deep red colored bis(dimethylglyoximate)-nickel(II). To the yellow colored filtrate of the 1:1 ligand was added a methanol solution of one equivalent of 2-methylimidazole-4-carbaldehyde. To the resulting 1:1:1 ligand solution, a methanolic solution of copper(II) acetate monohydrate and then a methanolic solution of sodium perchlorate were added. Green fine crystals precipitated were collected and then recrystallized from a mixture of *N,N*-dimethylformamide and methanol to give deep-green rod-like crystals with the formula $[\text{CuHL}]\text{ClO}_4$. The deprotonated complex, $[\text{CuL}]_n$, was obtained as light-green platelet crystals by mixing a methanolic solution of

Table 2. Selected Bond Distances ($\text{\AA}$) and Angles ($^\circ$) for $[\text{CuHL}]\text{ClO}_4$ and $[\text{CuL}]_n$

	$[\text{CuHL}]\text{ClO}_4$	$[\text{CuL}]_n$
Cu–O(1)	1.881(2)	1.923(3)
Cu–N(1) ^a		2.258(5)
Cu–N(2)	1.999(2)	2.016(4)
Cu–N(3)	2.006(2)	2.042(3)
Cu–N(4)	1.968(2)	1.975(5)
O(1)–Cu–N(2)	90.25(9)	90.31(19)
O(1)–Cu–N(4)	93.45(9)	91.7(2)
N(2)–Cu–N(3)	81.58(10)	81.6(2)
N(3)–Cu–N(4)	94.54(10)	92.3(2)
O(1)–Cu–N(3)	171.59(10)	162.84(19)
N(2)–Cu–N(4)	174.14(11)	164.76(19)

a) The symmetry operation of $-1/2 + x, 1/2 - y, -z$.

$[\text{CuHL}]\text{ClO}_4$ and a methanolic solution of triethylamine under diluted conditions at ambient temperature. Reflectance spectra showed a maximum in the visible region at 512 and 535 nm for $[\text{CuHL}]\text{ClO}_4$ and $[\text{CuL}]_n$, respectively, demonstrating the different coordination geometry of the copper(II) ion in these two complexes.

Structural Descriptions of $[\text{CuHL}]\text{ClO}_4$ and $[\text{CuL}]_n$. The crystal structures of $[\text{CuHL}]\text{ClO}_4$ and $[\text{CuL}]_n$ were determined by single-crystal X-ray diffraction analyses. Crystallographic data and relevant bond distances and angles are given in Tables 1 and 2, respectively.

Figures 2 and 3 show an ORTEP drawing with the selected atom numbering scheme and the packing diagram of $[\text{CuHL}]\text{ClO}_4$, respectively. The crystal structure consists of a complex cation $[\text{CuHL}]^+$ and an anion ClO_4^- , as shown in Figure 3. The shortest distance between an oxygen atom of the perchlorate ion and the Cu^{II} ion is $\text{Cu}–\text{O}5 = 2.709(2) \text{\AA}$, a distance too long for an axial coordination bond. Thus, the coordination geometry of copper(II) ion can be described as square planar with N_3O donor atoms of the quadridentate ligand HL with the coordination bond distances of $\text{Cu}–\text{O}1 = 1.881(2)$, $\text{Cu}–\text{N}2 = 1.999(2)$, $\text{Cu}–\text{N}3 = 2.006(2)$, and $\text{Cu}–\text{N}4 = 1.968(2) \text{\AA}$.

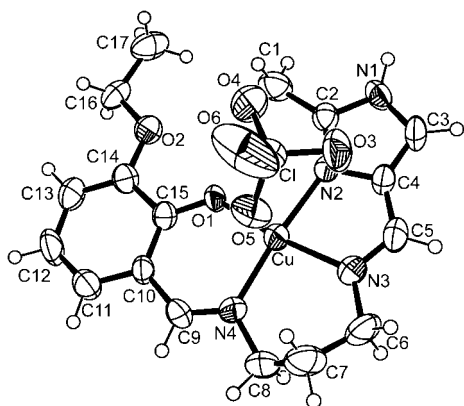


Figure 2. ORTEP drawing of $[\text{CuHL}]\text{ClO}_4$ with the atom numbering scheme.

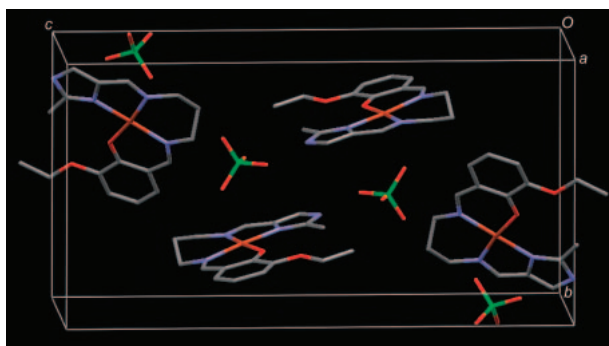


Figure 3. Packing diagram of $[\text{CuHL}]\text{ClO}_4$, showing that the cation $[\text{CuHL}]^+$ and anion ClO_4^- exist separately.

The copper(II) ion is positioned almost in the plane, with the deviation of $0.056 \text{ \AA}$ from the plane of N_3O .

Figure 4 shows an ORTEP drawing of $[\text{CuL}]_n$ with the atom numbering scheme, where the same atom numbering scheme of $[\text{CuHL}]\text{ClO}_4$ was adopted. The copper(II) ion assumes a square-pyramidal coordination geometry with N_3O donor atoms of the tetradentate ligand in the equatorial plane and an imidazolato nitrogen atom of the adjacent molecular unit at the axial position. The coordination bond distances are $\text{Cu}-\text{O1} = 1.923(3)$, $\text{Cu}-\text{N2} = 2.016(4)$, $\text{Cu}-\text{N3} = 2.042(3)$, and $\text{Cu}-\text{N4} = 1.975(5) \text{ \AA}$ for the equatorial plane and $\text{Cu}-\text{N1}^* = 2.258(5) \text{ \AA}$ for the axial coordination (* denotes the symmetry operation of $-1/2 + x, 1/2 - y, -z$). The copper(II) ion is displaced by $0.265 \text{ \AA}$ from the equatorial plane toward the axial coordination atom N1^* . Compared with the coordination bond distances of $[\text{CuHL}]\text{ClO}_4$ in the equatorial plane, the coordination bond distances of $[\text{CuL}]_n$ are longer than the corresponding values of $[\text{CuHL}]\text{ClO}_4$. As the result of the axial coordination of $\text{Cu}-\text{N1}^*$, zigzag-chain structure is formed, where the two adjacent molecules within a chain are related by a symmetry operation of a two-fold screw axis along the a axis. Figure 5 shows a 1D zigzag-chain structure constructed by the imidazolato-bridges of $\text{Cu}-\text{N1}^* = 2.258(5) \text{ \AA}$. The dihedral angle between the two adjacent coordination planes is 75.23° , where the coordination plane is defined by the atoms of Cu , O1 , N2 , N3 , and N4 . The coordination plane of the adjacent unit almost lies on the coordination bonds of $\text{Cu}-\text{N2}$ and $\text{Cu}-\text{N4}$.

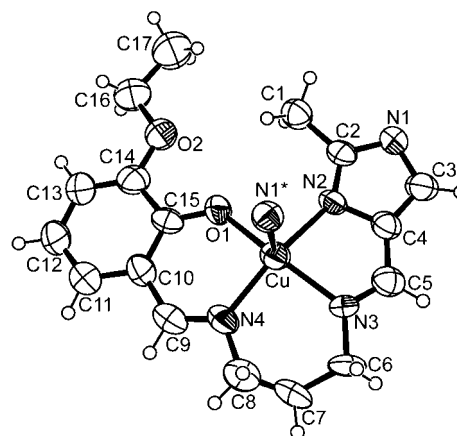


Figure 4. ORTEP drawing of $[\text{CuL}]_n$ with the atom numbering scheme, the same atom numbering of $[\text{CuHL}]\text{ClO}_4$. The axial coordination atom N1^* (* denotes the symmetry operation of $-1/2 + x, 1/2 - y, -z$) and the coordination bond of $\text{Cu}-\text{N1}^*$ are drawn.

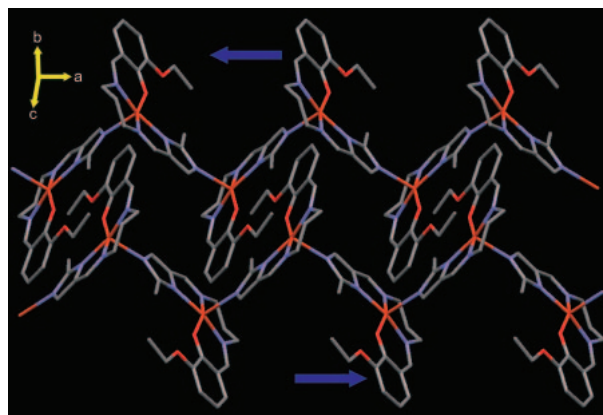


Figure 5. Zigzag chains of $[\text{CuL}]_n$ running along the a axis. The two adjacent chains run along the opposite directions.

Magnetic Properties of $[\text{CuHL}]\text{ClO}_4$ and $[\text{CuL}]_n$. The temperature dependences of the magnetic susceptibilities of $[\text{CuHL}]\text{ClO}_4$ and $[\text{CuL}]_n$ were measured in the temperature range of $2.0\text{--}300.0 \text{ K}$ under an external magnetic field of 0.5 T . Figure 6 shows the plots of $\chi_M T$ vs. T for $[\text{CuHL}]\text{ClO}_4$ and $[\text{CuL}]_n$, where χ_M is the molar magnetic susceptibility per Cu unit and T is the absolute temperature. The $\chi_M T$ vs. T plots of $[\text{CuHL}]\text{ClO}_4$ are nearly constant with a value of $0.41 \text{ cm}^3 \text{ K mol}^{-1}$ over the whole temperature range, a value consistent with that of $0.414 \text{ cm}^3 \text{ K mol}^{-1}$ expected for one copper(II) ($S = 1/2$) ion and $g = 2.10$.

The $\chi_M T$ vs. T plot of $[\text{CuL}]_n$ shows a constant increase on lowering the temperature from 300.0 to 2.0 K . The increase of the $\chi_M T$ value indicates the operation of a ferromagnetic interaction between two adjacent copper(II) ions through the imidazolato group. The Curie–Weiss plots of $1/\chi_M$ vs. T from 2.0 to 40.0 K follow the Curie–Weiss equation of $1/\chi_M = (T - \theta)/C$ with a positive Weiss constant of $\theta = +0.8 \text{ K}$ and a Curie constant of $C = 0.409 \text{ cm}^3 \text{ K mol}^{-1}$. It should be noted that both χ_M and $\chi_M T$ values under 0.5 T continue to increase on lowering the temperature down to 1.8 K , indicating the lack of significant antiferromagnetic interchain interaction.

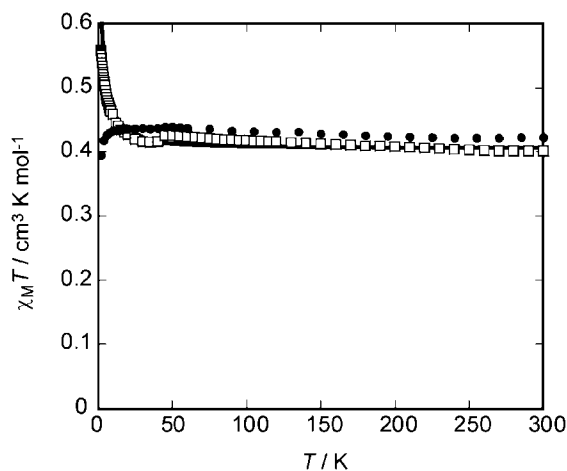


Figure 6. Plots of $\chi_M T$ vs. temperature for $[\text{CuHL}]\text{ClO}_4$ (●) and $[\text{CuL}]_n$ (□). The solid line represents the theoretical curve for $[\text{CuL}]_n$ derived from the eq 1 with the parameters of $g = 2.08$, $J = +0.63 \text{ cm}^{-1}$.

The X-ray analysis of $[\text{CuL}]_n$ demonstrates that the present copper(II) complex is the simplest case of a magnetic chain constituted by equally spaced copper(II) ions with $S_{\text{Cu}} = 1/2$ local spins.¹ For the present case, the spin Hamiltonian in zero-field adapted to describe the isotropic interaction between nearest neighbor ions is $H = -2J \sum S_{A_j} S_{A_{j+1}}$, where the summation runs over the n sites of the chain. When n tends to infinite, there is no analytical method that can be used to determine the energies of the low-lying states and the magnetic susceptibility. The problem may be solved numerically by considering ring chains of increasing size. The method was first applied by Bonner and Fisher in 1964,⁷ but the method is only applicable for antiferromagnetic case $J < 0$.⁷ Alternatively, a high-temperature series expansion, valid for both positive and negative J values, has been proposed by Baker et al.⁸ This method has been applied to the present complex. The expression is given below (1), where the coupling constant J and g value are the best-fit parameters to be determined. The solid line in Figure 6 shows the calculated curve with the best-fit parameters of $g = 2.08$, $J = +0.63 \text{ cm}^{-1}$.

$$\begin{aligned} \chi_A &= (Ng^2 \beta^2 / 4kT) [N/D]^{2/3} \text{ with} \\ N &= 1.0 + 5.7979916y + 16.902653y^2 \\ &\quad + 29.376885y^3 + 29.832959y^4 + 14.036918y^5, \\ D &= 1.0 + 2.7979916y + 7.0086780y^2 \\ &\quad + 8.6538644y^3 + 4.5743114y^4, \text{ and } y = J/2kT \quad (1) \end{aligned}$$

The field dependence of the magnetization at 2.0 K was measured from 0 to 5 T. The result is plotted in Figure 7 in the form of $M/N\beta$ vs. H and compared with the theoretical values per Cu atom calculated with the Brillouin function for an isolated copper(II) ion ($S = 1/2$) and for the ferromagnetic ground states of dinuclear and trinuclear linear copper(II) complexes ($S = 1$ and $3/2$). The experimental data of $[\text{CuHL}]\text{ClO}_4$ are consistent with the calculated Brillouin function of $g = 2.10$ and $S = 1/2$ expected for the magnetically isolated copper(II) molecule. The experimental data of $[\text{CuL}]_n$ are larger than the calculated Brillouin function of $g = 2.08$ and $S = 1/2$,

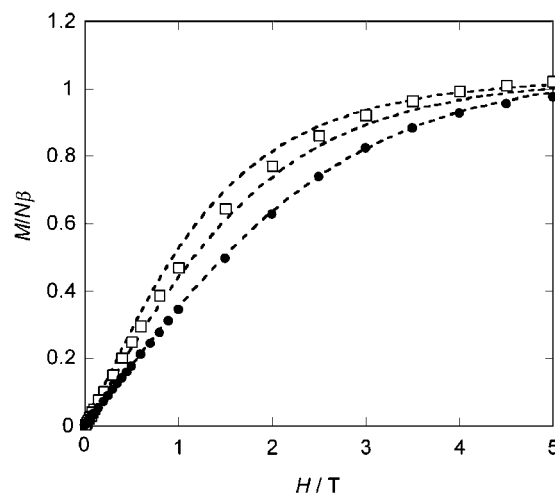


Figure 7. Field dependence of the magnetization of $M/N\beta$ at 2.0 K as a function of the applied magnetic field H (tesla) for $[\text{CuHL}]\text{ClO}_4$ (●) and $[\text{CuL}]_n$ (□). The experimental data of $[\text{CuHL}]\text{ClO}_4$ (●) was reproduced by the Brillouin function for $S = 1/2$ and $g = 2.10$. The upper dotted lines correspond to the theoretical values per Cu atom calculated with the Brillouin functions for the ferromagnetic ground states of isolated dinuclear and trinuclear linear copper(II) complexes ($S = 1$ and $S = 3/2$) with $g = 2.08$.

indicating ferromagnetic coupling as shown by the magnetic susceptibility analysis. The magnetization data of $[\text{CuL}]_n$ are, however, smaller than the values per copper(II) calculated with the Brillouin function for the ferromagnetic ground state of the trinuclear linear copper(II) complex ($S = 3/2$), and close to those of the Brillouin function for the $S = 1$ ferromagnetic ground state of the dinuclear copper(II) complex, consistently with the small value of ferromagnetic coupling constant determined from the magnetic susceptibility analysis.

There are several examples of copper(II) complexes exhibiting ferromagnetic chain character, such as 1D azido-bridged ferromagnetic chain.⁹ To the best of our knowledge, this is the first example of ferromagnetic coupling between two copper(II) ions via imidazolato bridging ligands. Indeed, the observed ferromagnetic coupling constant of $+0.63 \text{ cm}^{-1}$ is very different from those reported for imidazolato-bridged polynuclear copper(II) complexes, in the range -40 to -100 cm^{-1} , in which the imidazolato group bridges both copper(II) ions at their equatorial sites.¹⁰ These fairly large antiferromagnetic interactions result from a superexchange mechanism in which the unpaired electrons of adjacent copper(II) ions occupy the $d_{x^2-y^2}$ orbitals lying in the basal coordination planes interact through the imidazolato bridge.¹¹ On the other hand, when the imidazolato group bridges a copper(II) ion at its equatorial site with another at the axial site, the unpaired electrons occupy, respectively, the orthogonal $d_{x^2-y^2}$ and d_{z^2} orbitals and a small ferromagnetic coupling is expected.

Concluding Remarks

The deprotonation of $[\text{CuHL}]\text{ClO}_4$ motivates a self-assembly reaction to give $[\text{CuL}]_n$. The $[\text{CuL}]_n$ complex assumes an imidazolato-bridged zigzag-chain structure. The temperature-dependent magnetic susceptibilities from 2.0 to 300 K and

field-dependent magnetization at 2.0 K demonstrate that $[\text{CuL}]_n$ is a ferromagnetic chain. The magnetic susceptibility data were analyzed by Baker model for chains of equally spaced copper(II) ions to give the best-fit parameters of $g = 2.08$ and $J = +0.63 \text{ cm}^{-1}$.

Experimental

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

$[\text{CuHL}]\text{ClO}_4$. The precursor complex [bis{6-[(3-aminopropyl)iminomethyl]-2-ethoxyphenolato}]nickel(II) was prepared by the method of Elder.⁵ A methanolic solution of the ligand was obtained by refluxing the Ni^{II} complex (1.504 g, 3 mmol) and two equivalents of dimethylglyoxime (0.697 g, 6 mmol) in 100 mL of methanol for 2 h and cooled to room temperature. Deep red fine crystals of bis(dimethylglyoximate)nickel(II) were removed by suction filtration. To the yellow filtrate of the 1:1 ligand was added one equivalent of 2-methylimidazole-4-carbaldehyde (0.661 g, 6 mmol) in 50 mL of methanol and the mixture was warmed at 50 °C for 1 h and cooled to ambient temperature. To the resulting solution was added a solution of copper(II) acetate monohydrate (1.198 g, 6 mmol) in 50 mL of methanol and then a solution of sodium perchlorate (0.735 g, 6 mmol) in 10 mL of methanol. Moss-green fine crystals precipitated were collected by suction filtration. Crude product, 1.5 g (52%). Recrystallization from a mixture of *N,N*-dimethylformamide and methanol gave deep green rod-like crystals. Anal. Calcd for $\text{C}_{17}\text{H}_{21}\text{O}_6\text{N}_4\text{CuCl}$: C, 42.86; H, 4.44; N, 11.76%. Found: C, 43.19; H, 4.56; N, 11.79%.

$[\text{CuL}]_n$. To a solution of $[\text{CuHL}]\text{ClO}_4$ (281 mg, 0.59 mmol) in 40 mL of methanol was diffused a solution of triethylamine (59 mg, 0.59 mmol) in 20 mL of methanol. Several days later, light green platelet crystals precipitated and they were collected by suction filtration, washed with a small amount of water and dried in air. Yield, 143 mg (64%). Anal. Calcd for $\text{C}_{17}\text{H}_{20}\text{O}_2\text{N}_4\text{Cu}$: C, 54.32; H, 5.36; N, 14.90%. Found: C, 53.80; H, 5.37; N, 14.89%. **CAUTION:** The perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small quantities of the compound should be prepared, and they should be handled with much care.

Physical Measurements. C, H, and N elemental analyses were performed by Miss. Kikue Nishiyama at the Center for Instrumental Analysis of Kumamoto University. Magnetic data were measured with MPM-S5 and MPMS-XL-5 SQUID susceptometers (Quantum Design). Magnetic susceptibilities were measured in a 2.0–300 K temperature range under an applied magnetic field of 0.5 T. Magnetization at 2.0 K was measured from 0 to 5 T. The apparatus was calibrated with palladium metal. Corrections for diamagnetism were applied by using Pascal's constants.¹ Reflectance spectra were measured on a Shimadzu UV-2450 UV–visible spectrophotometer.

X-ray Diffraction Analysis. Diffraction data of $[\text{CuHL}]\text{ClO}_4$

and $[\text{CuL}]_n$ were obtained using a Rigaku R-Axis Rapid diffractometer at 296 K. The structures were solved by direct methods and expanded using the Fourier technique. The non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were fixed at calculated positions and refined using a riding model. All calculations were performed using the CrystalStructure crystallographic software package.¹² Crystallographic data in CIF format for compounds $[\text{CuHL}]\text{ClO}_4$ and $[\text{CuL}]_n$ has been deposited at the deposition numbers 712693 and 712694 of CCDC.

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