Correlation among Crystal Shape, Absolute Configuration, and Circular Dichroism Spectrum of Enantiomorphs of Tris[2-(((2-phenylimidazol-4-yl)methylidene)amino)ethyl]aminemetal(II) Nitrate−Methanol (1/1)

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A series of metal(II) complexes of a tripod-type ligand with the chemical formulas $[M(H_3L)](NO_3)_2 \cdot MeOH$ (M = Mn (**1**), Fe (**2**), Co (**3**), Ni (**4**), Zn (**6**)) and $[Cu(H_3L)](NO_3)_2 \cdot CH_3CN \cdot H_2O$ (**5**) were synthesized and characterized (H_3L = tris[2-(((2-phenylimidazol-4-yl)methylidene)amino)ethyl]amine). The crystal structures were determined, in which those of **1**−**4** and **6** are isomorphous and conglomerates, because they crystallize into the acentric space group $P2_12_12_1$. Each metal(II) ion of **1**−**4** and **6** assumes an octahedral coordination environment with the N_6 donor atoms of the tripod ligand and becomes either a *C* (clockwise) or an *A* (anticlockwise) enantiomorph because of the screw arrangement of the tripod-type ligand around the metal(II) ion. The crystals were divided into two groups, where their crystal shapes are mirror images and their CD spectra show enantiomeric patterns. The circular dichroism (CD) spectrum of the crystal used for the X-ray analysis was measured. The absolute configuration of the enantiomorph of the crystal used for the X-ray analysis was determined by the Flack parameter. The correlation among the crystal shape, the absolute configuration, and the CD spectral pattern was thus confirmed for **1**−**4** and **6**. On the other hand, **5** assumes a square pyramidal coordination geometry with the N_5 donor atoms, and hence, there are no optical isomers.

Introduction

Chirality is expressed on both the molecular and supramolecular levels.[1−13] When a chiral molecule crystallizes to form a crystalline racemate, it would be (1) a racemic compound, (2) a conglomerate (racemic mixture), or (3) a racemic solid solution.[14] L. Pasteur first discovered that ammonium sodium tartrate is a conglomerate on the basis of the observation of the two crystal shapes with mirror images.[15] Since this historic discovery, the elucidation of the correlation among the absolute configuration of the chiral molecule, the circular dichroism (CD) spectrum, and the crystal shape is an essential and relevant feature in chiral chemistry.

Previously, we have reported that the nickel(II) complex of a tripod-type ligand $[Ni(H_3L)](NO_3)_2 \cdot MeOH$, **4** ($H_3L$ = tris[2-(((2-phenylimidazol-4-yl)methylidene)amino)ethyl]amine) is a conglomerate.[16] The chemical structure of **4** is shown in Chart 1. Complex **4** becomes either a *C* (clockwise) or an *A* (anticlockwise) enantiomorph because of the screw arrangement of the tripod-type ligand around the Ni(II) ion. Unfortunately the correlation among the absolute configuration, CD spectrum, and crystal shape could not be elucidated because the CD spectrum of the crystal used for the X-ray analysis could not be measured by the Nujol mull method because of the small size of the crystal and the weak CD intensity in the visible region.

In this study, we focused on the elucidation of the correlation among them. A series of metal(II) complexes of the tripod ligand with the chemical formulas $[M(H_3L)](NO_3)_2 \cdot MeOH$ (M = Mn (**1**), Fe (**2**), Co (**3**), Ni (**4**), Zn (**6**)) and $[Cu(H_3L)](NO_3)_2 \cdot CH_3CN \cdot H_2O$ (**5**) including **4** reported previously have been synthesized and characterized to investigate the effect of the metal ion on the coordination geometry and crystal packing. The good crystals were grown by careful recrystallization, and they were divided into two groups whose crystal shapes are mirror images.

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Their CD spectra for the two different crystal shapes were measured. The KBr disk method was applied because the CD measurements by the Nujol mull method could not be carried out in the UV region. The crystal structures have been determined by the single-crystal X-ray diffraction analyses, and the absolute configurations of the chiral molecules were assigned on the basis of the Flack parameters.[17] The CD spectra of the crystals used for the X-ray analyses were measured by the KBr disk method. We report the correlation among the crystal shape, the absolute configuration of the chiral molecule, and the CD spectral pattern for the conglomerates.

Results and Discussion

Synthesis and Characterization. The tripod-type Schiff base ligand (H_3L = tris[2-(((2-phenylimidazol-4-yl)methylidene)-amino)ethyl]amine) was prepared by a 3:1 condensation reaction of 2-phenyl-4-formylimidazole and tris(2-aminoethyl)amine in methanol. The reaction mixture was subsequently used for the syntheses of the metal(II) complexes without isolation of the ligand. The complexes were easily prepared by mixing the ligand solution and metal(II) nitrate hexahydrate in methanol in a 1:1 molar ratio according to a similar procedure adopted for the synthesis of **4**,[16] where Mn(II), Fe(II), Co(II), Ni(II), Cu(II), and Zn(II) ions were used. The C, H, and N microanalyses agreed with the chemical formulas $[M(H_3L)](NO_3)_2 \cdot MeOH$ (M = Mn (**1**), Fe (**2**), Co (**3**), Ni (**4**), Zn (**6**)) and $[Cu(H_3L)](NO_3)_2 \cdot CH_3CN \cdot H_2O$ (**5**). The infrared spectra of these complexes showed the characteristic absorption bands attributable to the imidazole ν_{N-H} (2300−3400 cm^{-1}), Schiff base $\nu_{C=N}$ (1605−1650 cm^{-1}), and the nitrate ν_{N-O} (1384 cm^{-1}) as the counteranion.[18] The molar electrical conductivities of **1**−**6** were measured in 10^{-3} M methanol solutions, and the values of 165−194 S cm^2 mol^{-1} are in the expected range for 2:1 electrolytes in methanol.[19]

Magnetic Properties. The magnetic susceptibilities were measured under an applied magnetic field of 1 T in the 4−300 K temperature range. **6** is diamagnetic because of the d^{10} electronic configuration of Zn(II) ion. The magnetic behavior of **1**−**5** is shown in Figure 1 in the form of the μ_{eff} vs T plots, where μ_{eff} is the effective magnetic moment per metal and T the absolute temperature. The effective magnetic moments of **1**−**5** are nearly constant over the whole temperature range except for the lower temperature region, and the reciprocal magnetic susceptibilities follow the Curie law, demonstrating that the complexes can be described as magnetically isolated systems. The effective magnetic moments of **1**−**5** are compatible with the spin-only values expected for $S = {}^5/_2$ (d^5, Mn(II)), $S = 2$ (d^6, Fe(II)), $S = {}^3/_2$ (d^7, Co(II)), $S = 1$ (d^8, Ni(II)), and $S = {}^1/_2$ (d^9, Cu(II)), respectively.[20−22] The magnetic measurements demonstrate that complexes **1**−**4** exhibit their high-spin electronic configurations.

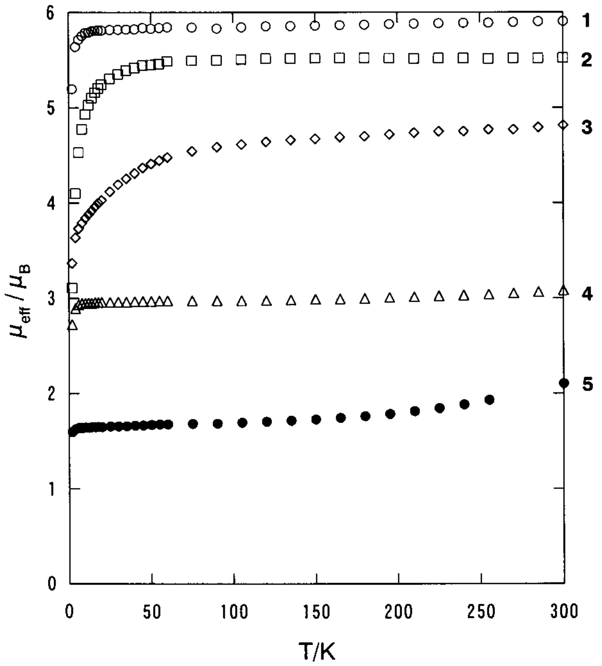

Figure 1. Magnetic behavior of **1**−**5** in the form of a μ_{eff} vs T plot, where the μ_{eff} is the effective magnetic moment per metal and T the absolute temperature.

Crystal Shapes. All the complexes could be obtained as well-grown crystals by careful recrystallization of their methanol solutions at room temperature. The crystal colors of **1**−**6** are pale-green, yellow-orange, red-orange, light-blue, green, and colorless, respectively. The crystal shapes of **1**−**4** and **6**, except for the Cu(II) complex **5**, are very similar, consistent with the fact that they are isomorphous as confirmed later by the X-ray analyses (Table 1). The well-grown crystals of **1**−**4** and **6** can be divided into two groups by observation with a microscope, as Pasteur did for ammonium sodium tartrate.[15] Figure 2 shows a photograph of the two crystal shapes for **3**, indicating that the two crystal shapes in parts a and b are mirror images.

Structural Descriptions of 1−4 and 6. The crystallographic data for all the complexes including **4** reported previously[16] are given in Table 1. **1**−**4** and **6** crystallize into the acentrosymmetric space group $P2_12_12_1$ and are isomorphous. Each crystal structure consists of a metal(II) complex cation $[M(H_3L)]^{2+}$, two nitrate ions as the counteranions, and a methanol molecule

Chart 1. Chemical Structure of $[M(H_3L)]^{2+}$ and *C* (Clockwise) and *A* (Anticlockwise) Enantiomorphs Due to the Screw Arrangement of the Tripod-Type Ligand around the M(II) Ion

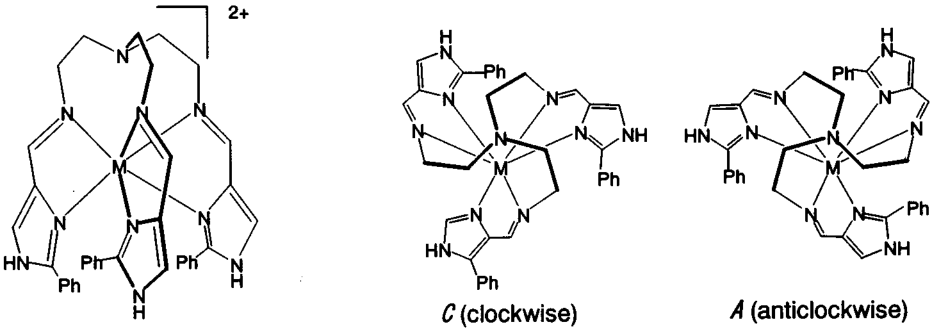

Table 1. X-ray Crystallographic Data for $[M(H_3L)](NO_3)_2 \cdot MeOH$ (M = Mn (**1**), Fe (**2**), Co (**3**), Ni (**4**), Zn (**6**)) and $[Cu(H_3L)](NO_3)_2 \cdot CH_3CN \cdot H_2O$ (**5**)

	1	**2**	**3**	**4**[a]	**5**	**6**
formula	$C_{37}H_{40}N_{12}O_7Mn$	$C_{37}H_{40}N_{12}O_7Fe$	$C_{37}H_{40}N_{12}O_7Co$	$C_{37}H_{40}N_{12}O_7Ni$	$C_{38}H_{41}N_{13}O_7Cu$	$C_{37}H_{40}N_{12}O_7Zn$
fw	819.74	820.65	823.73	823.50	837.36	830.18
space group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$	$P\bar{1}$	$P2_12_12_1$
a, Å	14.206(1)	14.221(2)	14.228(6)	14.198(2)	13.236(3)	14.233(2)
b, Å	22.690(3)	22.553(2)	22.514(6)	22.422(2)	13.741(2)	22.512(3)
c, Å	12.168(2)	12.064(2)	12.015(9)	12.019(2)	12.178(2)	12.049(4)
α, deg	90	90	90	90	108.05(1)	90
β, deg	90	90	90	90	96.98(2)	90
γ, deg	90	90	90	90	103.49(2)	90
V, Å3	3922.2(8)	3869.4(8)	3849(3)	3826.4(6)	2002.4(8)	3861(1)
Z	4	4	4	4	2	4
D_{calcd}, g cm^{-3}	1.388	1.409	1.421	1.429	1.389	1.428
μ, cm^{-1}	4.01	4.55	5.12	5.73	6.08	7.02
R,[b] R_w[c]	0.047, 0.030	0.082, 0.062	0.041, 0.026	0.040, 0.043	0.054, 0.041	0.048, 0.054

[a] Reference 16. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, $w = 1/\sigma(F_o)^2$.

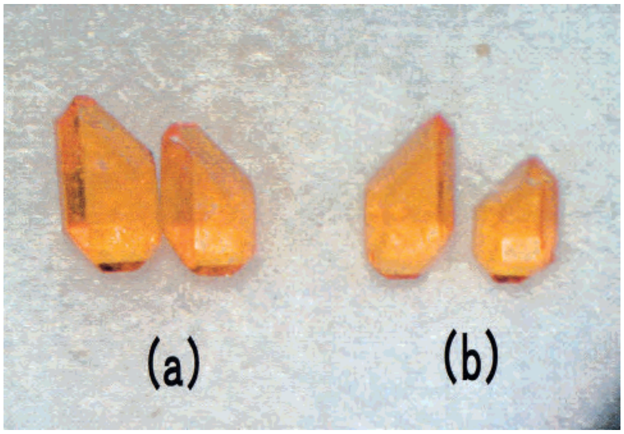

Figure 2. Photograph of the two crystal shapes (a and b) for **3** showing that the two crystal shapes are mirror images.

as the crystal solvent. The hydrogen-bonded chain structure of **3** is shown in Figure 3. Three imidazole nitrogen atoms of the tripod ligand of the complex cation form hydrogen bonds (NH···O) with the methanol molecule and the two nitrate anions form them through the imidazole protons, where the N···O distances are N(7)···O(7)(methanol) = 2.742(5) Å, N(4)···O(6) = 2.757(6) Å, N(10)···O(2) = 2.862(6) Å, respectively. The oxygen atom O(7) of the methanol is further hydrogen-bonded to the oxygen atom O(1) of one nitrate ion of the adjacent molecular unit with a hydrogen bond distance of O(7)···O(1) = 2.822(5) Å. Thus, the adjacent metal complex cations are connected by the three hydrogen bonds through a methanol and a nitrate ion, N(7)···O(7)H···O(1)N(11)O(2)···N(10)*, to form a 1D helical chain structure running along the *c* axis. The hydrogen bond distances for all the complexes are listed in Table 2.

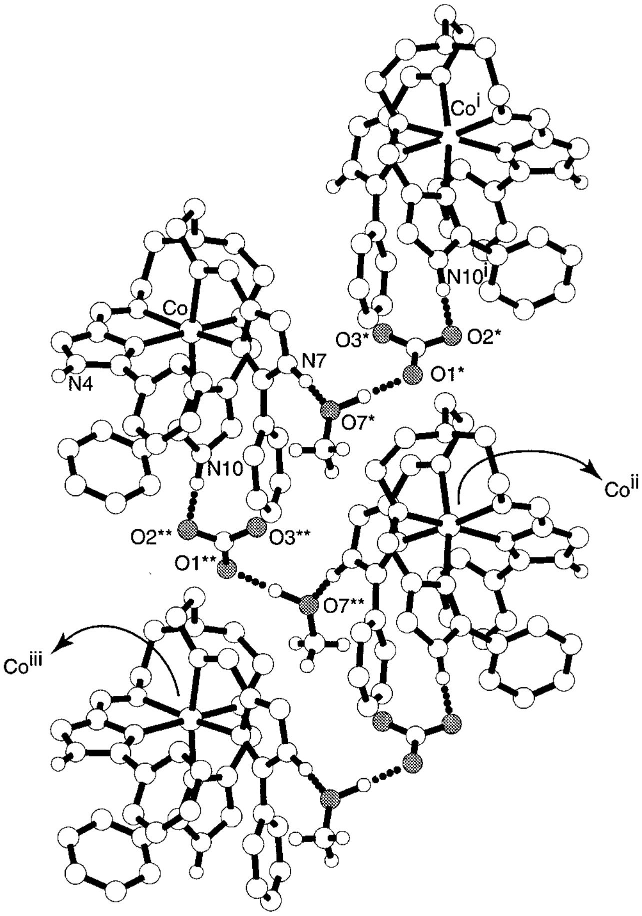

Figure 3. Hydrogen-bonded 1D chain structure of **3**. Three imidazole nitrogen atoms of the tripod ligand form hydrogen bonds (N(7)···O(7)-(methanol) = 2.742(5) Å, N(4)···O(6) = 2.757(6) Å, N(10)···O(2) = 2.862(6) Å). The oxygen atom O(7) of the methanol molecule is further hydrogen-bonded to the oxygen atom O(1) of one nitrate ion of the adjacent molecular unit with a distance of O(7)···O(1) = 2.822(5) Å. The adjacent metal complex cations are thus connected by the three hydrogen bonds through a methanol molecule and a nitrate ion, N(7)···O(7)H···O(1)N(11)O(2)···N(10)*, to form a 1D helical chain structure running along the *c* axis. The symmetry codes are as follows: (i) $-x + {}^3/_2, -y, z - {}^1/_2$; (ii) $-x + {}^3/_2, -y, z + {}^1/_2$; (iii) $x, y, z + 1$.

The ORTEP drawing of **3** with the atom numbering scheme is given in Figure 4. Selected bond distances, angles, and hydrogen bond distances with their estimated standard deviations for **1**−**6** are summarized in Table 2. Each metal(II) ion assumes an octahedral coordination environment with the N_6 donor set of the tripod-type ligand, including three imidazole and three imine nitrogen atoms. The distances of the six M−N bonds are as follows: Mn(II), 2.230(5)−2.366(5) Å; Fe(II). 2.146(7)−2.289(7) Å; Co(II), 2.134(4)−2.236(4) Å; Ni(II), 2.087(5)−2.190(5) Å; Zn(II), 2.120(6)−2.306(6) Å. These values are in

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Table 2. Relevant Bond Distances (Å) and Angles (deg), and Hydrogen Bond Distances (Å) Less Than 3.00 Å with the Estimated Standard Deviations in Parentheses for **1**−**6**

	1	**2**	**3**	**4**[a]	**5**	**6**
			Bond Distance			
M(1)−N(2)	2.230(5)	2.146(7)	2.132(4)	2.120(6)	2.025(3)	2.196(6)
M(1)−N(3)	2.366(5)	2.289(7)	2.232(4)	2.131(5)		2.204(6)
M(1)−N(5)	2.283(5)	2.210(8)	2.167(4)	2.130(5)	2.035(3)	2.190(6)
M(1)−N(6)	2.297(5)	2.207(7)	2.202(4)	2.122(6)	2.116(3)	2.194(6)
M(1)−N(8)	2.278(5)	2.191(7)	2.169(4)	2.089(5)	2.234(4)	2.120(6)
M(1)−N(9)	2.289(5)	2.209(7)	2.170(4)	2.188(5)	2.049(3)	2.306(6)
N···O[b]	2.75(1)	2.77(1)	2.776(6)	2.869(9)	2.733(5)	2.756(8)
N···O	2.87(1)	2.75(1)	2.863(6)	2.781(9)	2.896(5)	2.863(9)
N···O	2.71(1)	2.88(1)	2.756(6)	2.768(8)	2.860(5)	2.764(9)
O···O[b]	2.80(1)	2.81(1)	2.797(6)	2.798(8)	2.940(6)	2.816(9)
			Bond Angles			
N(2)−M(1)−N(3)	75.0(3)	77.1(3)	78.1(2)	79.4(2)		77.7(2)
N(2)−M(1)−N(5)	95.4(2)	95.4(3)	94.7(2)	92.7(2)	92.0(1)	93.9(2)
N(2)−M(1)−N(6)	167.1(2)	169.8(3)	171.5(2)	171.0(2)	157.6(1)	169.8(2)
N(2)−M(1)−N(8)	98.3(2)	98.6(3)	97.5(2)	93.6(2)	105.4(1)	94.1(2)
N(2)−M(1)−N(9)	93.1(2)	91.7(3)	90.5(2)	89.9(2)	90.2(1)	90.4(2)
N(3)−M(1)−N(5)	91.8(3)	90.2(3)	89.4(1)	88.6(2)		90.2(2)
N(3)−M(1)−N(6)	96.4(3)	96.2(3)	96.7(2)	96.9(2)		96.7(2)
N(3)−M(1)−N(8)	170.3(3)	174.5(3)	174.6(2)	172.2(2)		169.3(2)
N(3)−M(1)−N(9)	99.0(3)	99.6(3)	99.3(1)	97.0(2)		95.0(2)
N(5)−M(1)−N(6)	74.9(2)	76.7(3)	78.4(1)	78.9(2)	80.6(1)	77.5(2)
N(5)−M(1)−N(8)	95.9(2)	93.8(3)	94.2(2)	95.3(2)	97.5(1)	97.3(2)
N(5)−M(1)−N(9)	167.7(2)	169.0(3)	170.7(1)	174.2(2)	176.4(1)	173.8(2)
N(6)−M(1)−N(8)	91.4(2)	88.4(3)	88.1(1)	90.4(2)	96.5(1)	92.5(2)
N(6)−M(1)−N(9)	97.8(2)	97.0(3)	97.1(2)	98.7(2)	98.4(1)	98.6(2)
N(8)−M(1)−N(9)	74.1(2)	76.8(3)	77.4(1)	79.4(2)	79.1(1)	77.9(2)

[a] Reference 16. [b] Methanol oxygen except for **5**.

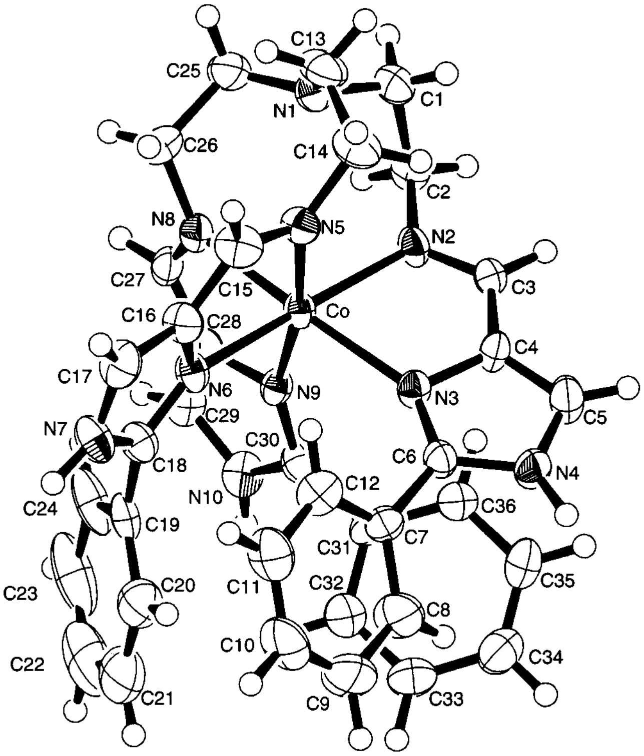

Figure 4. ORTEP drawing of **3** with the atom numbering scheme showing the C enantiomorph (clockwise molecule) and 50% probability ellipsoids.

the expected range for their high-spin metal(II) complexes with the same coordination number and donor atoms.

Each metal(II) complex becomes either a *C* (clockwise) or an *A* (anticlockwise) enantiomorph because of the screw arrangement of the tripod-type ligand around the metal(II) ion, where the complex has a pseudo-C_3 axis running from the central amine nitrogen atom to the metal(II) ion. Because the complexes crystallize into the acentric space group $P2_12_12_1$, the crystal, which was subjected to the X-ray analysis, should consist of one of two enantiomorphs. The absolute configurations of **1**−**4** and **6** were determined to be the C enantiomorph for all the complexes, on the basis of the analysis of their Flack parameters.[17] The refined Flack parameters are −0.022(5), −0.023(8), −0.008(2), 0.013(1), and −0.007(3) for **1**−**4** and **6**, respectively. The present X-ray analyses demonstrate that **1**−**4** and **6** are conglomerates and that the separation of the two enantiomers spontaneously occurred during the course of the crystallization. Jacques et al. reported that between 5% and 10% of all racemates form conglomerates[23] and that chiral molecules exhibiting a C_3 axis have a much higher tendency to undergo spontaneous resolution.[24] It can thus be considered that the present complexes with a pseudo-C_3 axis and with a 1D hydrogen-bonded chain structure show great probability to conglomerate.

Structural Description of 5. The complex of **5** crystallizes into a space group $P\bar{1}$ with $Z = 2$, and the crystal structure consists of a copper(II) complex cation, two nitrate anions as the counteranions, and one acetonitrile and one water molecule as the crystal solvents. The molecular structure of the complex cation is shown in Figure 5. The copper(II) ion assumes a square pyramidal coordination geometry with the N_5 donor atoms with bond distances of 2.025(3)−2.234(4) Å, in which the N(3) atom of one of the three imidazole groups is free from coordination. Therefore, there is no C_3 molecular axis in this molecule. The adjacent two Cu(II) complexes are linked by the two hydrogen bonds through a nitrate ion to form a 1D chain structure. Figure 6 shows the hydrogen-bonded 1D chain structure, where the N···O distances are N(4)···O(1) = 2.896(5) Å and N(10)···O(3) = 2.860(5) Å. The remaining imidazole

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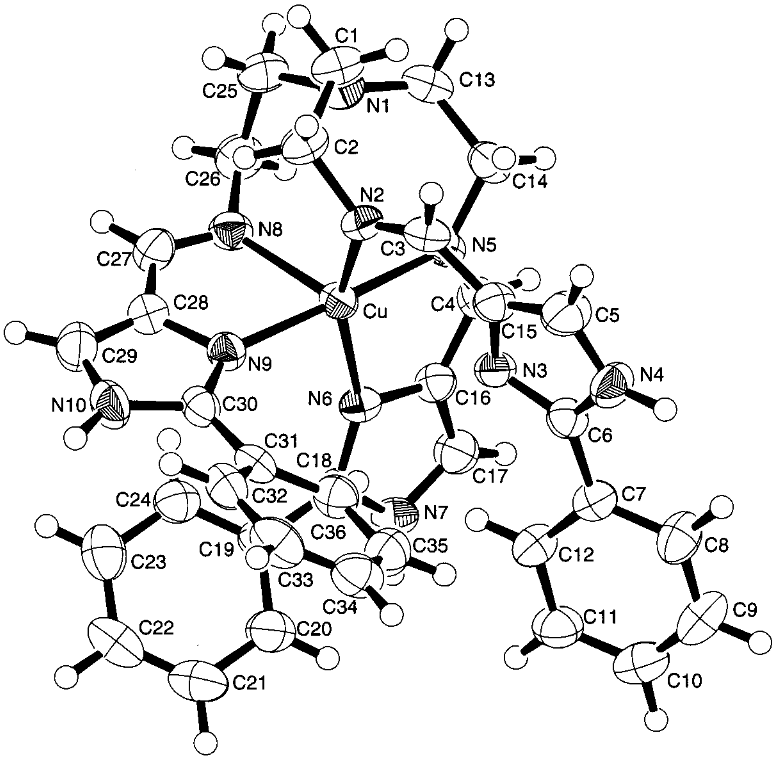

Figure 5. ORTEP drawing of the cation for **5** with the atom numbering scheme showing 50% probability ellipsoids.

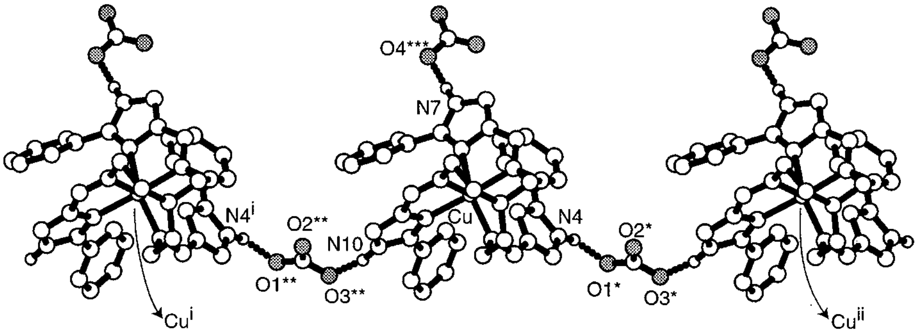

Figure 6. Hydrogen-bonded 1D structure of **5** running along the *a* axis, where the distances are N(4)$\cdots$O(1)* = 2.896(5) Å, N(10)$\cdots$O(3)** = 2.860(5) Å, and N(7)$\cdots$O(4)*** = 2.733(5) Å. The symmetry codes are as follows: (*) $-x, -y, -z$; (**) $1 - x, -y, -z$; (***) $1 - x, 1 - y, -z$; (i) $1 + x, y, z$; (ii) $1 + x, y, z$.

group is hydrogen-bonded to the other nitrate ion with a distance N(7)$\cdots$O(4) = 2.733(5) Å.

Correlation among Crystal Shape, Absolute Configuration, and CD Spectrum. The CD spectra of **1**−**4** and **6** were measured by the KBr disk method. In the previous paper,[16] the CD spectrum of the nickel complex (**4**) in a Nujol mull was measured in the region 400−1000 nm by the opal glass technique.[25] In this ligand field transition region, the CD spectrum of a large-size crystal (ca. 3 mm × 3 mm × 4 mm) of **4** exhibited a positive and a negative peak,[16] but the CD spectrum of the crystal used for the X-ray analysis could not be measured because of the small size of the crystal (ca. 0.2 mm × 0.2 mm × 0.3 mm) and the weak CD intensity in this region. The CD measurements could not be carried out in the UV region because the intensity of the light after passage of an opal glass plate was very weakened. In the present study, CD spectra were measured with the KBr method, and the measurement region could be extended to lower wavelengths to 260 nm. Figure 7 shows the CD spectra of **3**. The CD intensity at ca. 320 nm attributable to the imine $\pi-\pi^*$ transition is much larger than that in the region 500−550 nm because of the ligand field transitions. Since it was found that **1**−**4** and **6** exhibit strong CD signals at ca. 320 nm, the sign of the CD band at ca. 320 nm was used to investigate the correlation among the crystal shape, the absolute configuration, and the CD spectrum.

The crystals of **3** were obtained as well-grown orange crystals from careful recrystallization. They can be divided into two groups whose crystal shapes are mirror images, as observed with a microscope, as shown in Figure 2. The CD spectra for the two different crystal shapes were measured, and those of **3** are shown in Figure 7. It was found that the crystal (see Figure 2a) exhibits a CD spectral pattern (Figure 7), while the crystal shown in Figure 2b exhibits the enantiometric pattern (Figure 7). The crystal in Figure 2a with the crystal shape of **3** was subjected to single-crystal X-ray analysis, and the absolute configuration of the chiral molecule was determined by the Flack parameter to be the *C* enantiomorph. The CD spectrum of crystal **3** used for the X-ray analysis was measured and showed the same CD pattern as that for crystal in Figure 2a. As a result, one can conclude that the crystal in Figure 2a with the crystal shape of

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[25] Taniguchi, Y.; Shimura, Y. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 2847.

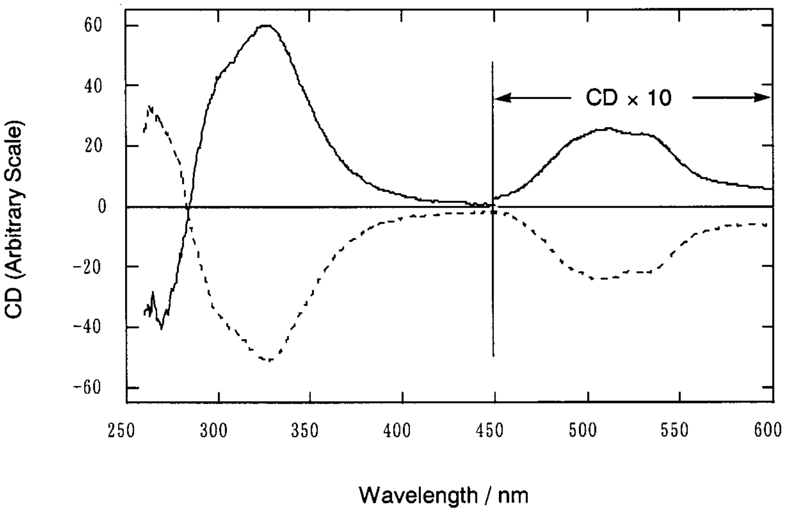

Figure 7. CD spectra of **3**. A crystal piece of **3** was selected and ground into a powder, and the CD spectrum was measured using the KBr disk method in the wavelength regions 400−650 and 260−600 nm. One crystal showed positive peaks at 320 and 525 nm, while the other showed an enantiomeric CD pattern.

3 exhibits a CD pattern (Figure 7) and contains the *C* enantiomorph in the crystal cell.

The correlation among the crystal shape, absolute configuration, and CD spectrum for a series of the complexes **1**, **2**, **4**, and **6** were studied as follows. The crystal shapes of **1**−**4** and **6** are very similar because they are isomorphous, as confirmed by X-ray analyses. The absolute configurations of the chiral molecules of the crystals, which were subjected to the X-ray analyses, were determined by the Flack parameters to be the *C* enantiomorph for **1**, **2**, **4**, and **6**. The CD spectra of the crystals **1**, **2**, **4**, and **6** used for the X-ray analyses exhibited a positive CD band at ca. 320 nm. We can conclude that the crystal with the shape of crystal a exhibits a positive CD band at 320 nm and contains the *C* enantiomorph in the crystal cell for **1**−**4** and **6**.

Experimental Section

Caution! *Nitrate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of materials should be prepared, and the samples should be handled with much caution.*

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

$[Mn(H_3L)](NO_3)_2 \cdot MeOH$, 1. A methanol solution of 2-phenyl-4-formylimidazole (2.583 g, 15 mmol, in 10 mL) was added to a methanol solution of tris(2-aminoethyl)amine (0.731 g, 5 mmol, in 10 mL). The mixture was stirred at room temperature for 30 min, and the resulting yellow solution was used in the subsequent reaction without isolation of the ligand. A methanolic solution of $Mn(NO_3)_2 \cdot 6H_2O$ (1.44 g, 5 mmol, in 20 mL) was added to the ligand solution, and the mixture was stirred for 30 min at room temperature and filtered. The filtrate was allowed to stand for several days, after which pale-green crystals that had precipitated were collected by suction filtration, washed with a small amount of methanol, and dried in vacuo. $\Lambda_M = 165$ S cm^2 mol^{-1} in methanol. IR (cm^{-1}): ν_{N-H} 3200−2800; $\nu_{C=N}$ 1650. μ_{eff}/Mn = 5.91 μ_B at 300 K. Anal. Calcd for $C_{37}H_{40}N_{12}O_7Mn$: C, 54.21; H, 4.92; N, 20.50. Found: C, 54.21; H, 4.91; N, 20.58.

$[Fe(H_3L)](NO_3)_2 \cdot MeOH$, 2. A methanol solution of $FeCl_2 \cdot 4H_2O$ (0.994 g, 5 mmol, in 20 mL) was then added to the H_3L ligand solution (5 mmol in 20 mL of methanol). After the reaction mixture was stirred for a while, sodium nitrate (0.850 g, 10 mmol, in 10 mL of methanol) was added to this solution. The reaction mixture was stirred for 30 min and filtered, and the filtrate was allowed to stand for several days. Yellow-orange crystals were formed. $\Lambda_M = 182$ S cm^2 mol^{-1} in methanol. IR (cm^{-1}): ν_{N-H} 3400−2850; $\nu_{C=N}$ 1646. μ_{eff}/Fe = 5.52 μ_B at 300 K. Anal. Calcd for $C_{37}H_{40}N_{12}O_7Fe$: C, 54.15; H, 4.91; N, 20.48. Found: C, 54.04; H, 4.87; N, 20.57.

$[Co(H_3L)](NO_3)_2 \cdot MeOH$, 3. 3 was prepared as red-orange crystals according to a similar method adopted for **1**, using $Co(NO_3)_2 \cdot 6H_2O$ instead of $Mn(NO_3)_2 \cdot 6H_2O$. $\Lambda_M = 181$ S cm^2 mol^{-1} in methanol. IR (cm^{-1}): ν_{N-H} 3200−2800; $\nu_{C=N}$ 1644. μ_{eff}/Co = 4.82 μ_B at 300 K. Anal. Calcd for $C_{37}H_{40}N_{12}O_7Co$: C, 53.95; H, 4.89; N, 20.41. Found: C, 53.98; H, 4.90; N, 20.39.

$[Ni(H_3L)](NO_3)_2 \cdot MeOH$, 4. 4 was prepared as light-blue crystals according to a similar method reported previously.[16] $\Lambda_M = 187$ S cm^2 mol^{-1} in methanol. IR (cm^{-1}): ν_{N-H} 2840−2300; $\nu_{C=N}$ 1648. μ_{eff}/Ni = 3.08 μ_B at 300 K. Anal. Calcd for $C_{37}H_{40}N_{12}O_7Ni$: C, 53.97; H, 4.90; N, 20.41. Found: C, 53.87; H, 4.91; N, 20.39.

$[Cu(H_3L)](NO_3)_2 \cdot CH_3CN \cdot H_2O$, 5. 5 was prepared according to a similar method adopted for **1**, using $Cu(NO_3)_2 \cdot 3H_2O$ instead of $Mn(NO_3)_2 \cdot 6H_2O$. $\Lambda_M = 185$ S cm^2 mol^{-1} in methanol. IR (cm^{-1}): ν_{N-H} 2800−2400; $\nu_{C=N}$ 1645. μ_{eff}/Cu = 2.10 μ_B at 300 K. Anal. Calcd for $C_{36}H_{36}N_{12}O_6Cu$: C, 54.30; H, 4.56; N, 21.11. Found: C, 54.30; H, 4.59; N, 21.08. The crude products were recrystallized from a mixture of acetonitrile/methanol/water. The green crystal thus obtained was coated with epoxy resin and subjected to X-ray analysis. The X-ray analysis reveals that the crystal contains one acetonitrile and one water molecule as the crystal solvents, which are eliminated in the open atmosphere as indicated by the microanalysis.

$[Zn(H_3L)](NO_3)_2 \cdot MeOH$, 6. 6 was obtained as colorless crystals according to a similar method adopted for **1**, using $Zn(NO_3)_2 \cdot 6H_2O$ instead of $Mn(NO_3)_2 \cdot 6H_2O$. $\Lambda_M = 194$ S cm^2 mol^{-1} in methanol. IR (cm^{-1}): ν_{N-H} 2900−2500; $\nu_{C=N}$ 1605. Anal. Calcd for $C_{37}H_{40}N_{12}O_7Zn$: C, 53.53; H, 4.86; N, 20.25. Found: C, 53.54; H, 4.87; N, 20.20.

Physical Measurements. Elemental analyses for C, H, and N were performed at the Elemental Analyses Service Center of Kyushu University. Infrared spectra were recorded using a Perkin-Elmer FT-IR Paragon 1000 spectrometer with KBr disks. Electrical conductivity measurements were carried out on a Horiba DS-14 conductometer in ca. 10^{-3} M methanolic solutions. Magnetic susceptibilities were measured with a MPMS5 SQUID susceptometer (Quantum Design, Inc.) in the 4−300 K temperature range under an externally applied magnetic field of 1 T. The calibration was done with palladium metal. Corrections for diamagnetism were applied using Pascal's constants.[26] Effective magnetic moments were calculated using the equation $\mu_{eff} = (8\chi_A T)^{1/2}$, where χ_A is the magnetic susceptibility per metal. Circular dichroism spectra were measured with a JASCO J-720 spectropolarimeter by the KBr disk method.

X-ray Data Collection, Reduction, and Structure Determination. Each single crystal was mounted on a glass fiber and coated with epoxy

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(26) Kahn, O. *Molecular Magnetism*; VCH: Weinheim, 1993.

resin. All crystallographic measurements were carried out on a Rigaku AFC-7R diffractometer with graphite monochromated Mo Kα radiation ($\lambda = 0.710\,69$ Å) and a 12 kW rotating anode generator. The data were collected at a temperature of 20 ± 1 °C using the $\omega-2\theta$ scan technique to a maximum 2θ value of 50.0° at a scan speed of 8.0−16.0°/min (in ω). The weak reflections ($I < 10.0\,\sigma(I)$) were rescanned (maximum of five scans), and the counts were accumulated to ensure good counting statistics. The intensities of three representative reflections were measured after every 150 reflections. Over the course of the data collection, the standard reflections were monitored and decay corrections were applied through a polynomial expression. An empirical absorption correction based on the azimuthal scans of several reflections was applied. The data were also corrected for Lorentz and polarization effects.

The space group $P2_12_12_1$ for **1**−**3** and **6** was unequivocally determined by the extinction rule ($h00$, h = odd; $0k0$, k = odd; $00l$, l = odd). There are two possible space groups for **5**: $P1$ and $P\bar{1}$. $P\bar{1}$ is chosen because the structure was well determined and the constituent atoms gave reasonable thermal parameters when $P\bar{1}$ was assumed. The structures were solved by DIRDIF92(PATTY) and expanded using Fourier techniques.[27,28] The non-hydrogen atoms were anisotropically refined. Hydrogen atoms at their ideal calculated positions were included in the structure factor calculations but were not refined. Full-matrix least-squares refinements ($I > 2.00\,\sigma(I)$) 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 $\sum w(|F_o| - |F_c|)^2$ vs $|F_o|$, the reflection order in data collection, $\sin\theta/\lambda$, and various classes of indices showed no unusual trends. In the least-squares refinements, the Flack parameter defined as $|F| = (1 - x)|F(+)| + x|F(-)|$ was refined.[17]

Neutral atomic scattering factors were taken from Cromer and Waber.[29] Anomalous dispersion effects were included in F_c; the values $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.[30] The values for the mass attenuation coefficients were those of Creagh and Hubbel.[31] All calculations were performed using the teXsan crystallographic software package from the Molecular Structure Corporation.[32]

Supporting Information Available: Three supplementary ORTEP drawings and X-ray crystallographic files in CIF format for the structure determinations of $[M(H_3L)](NO_3)_2\cdot MeOH$ (M = Mn (**1**), Fe (**2**), Co (**3**), Zn (**6**)) and $[Cu(H_3L)](NO_3)_2\cdot CH_3CN\cdot H_2O$ (**5**). This material is available free of charge via the Internet at http://pubs.acs.org.

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(28) Fan, H.-F. *SAPI91*: *Structure Analysis Programs with Intelligent Control*; Rigaku Corp.: Tokyo, Japan, 1991.

(29) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2A.

(30) Creagh and, D. C.; McAuley, W. J. In *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.

(31) Creagh, D. C.; Hubbel, J. H. In *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.

(32) *teXsan*: *Crystal Structure Analysis Package*; Molecular Structure Corp.: The Woodlands, TX, 1985, 1992.