Synthesis, Characterization, and Spontaneous Resolution of Chiral Nickel(II) Complexes with the Tripod Ligand Tris[2-(((2-phenylimidazol-4-yl)methylidene)amino)ethyl]amine

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The chiral nickel(II) complexes of a tripod-type ligand with the chemical formulas $[Ni(H_3L)](NO_3)_2 \cdot MeOH$ (**1**), $[Ni(H_3L)](ClO_4)_2 \cdot MeOH$ (**2**), and $[Ni(H_3L)](C_6H_5COO)_2 \cdot 6H_2O$ (**3**) were synthesized and characterized (H_3L = tris[2-(((2-phenylimidazol-4-yl)methylidene)amino)ethyl]amine). The crystal structures of **1**−**3** were determined by their single-crystal X-ray analyses. **1**, $C_{37}H_{40}N_{12}O_7Ni$: orthorhombic, $P2_12_12_1$; $a = 14.198(2)$ Å, $b = 22.422(2)$ Å, $c = 12.019(2)$ Å, $Z = 4$. **2**, $C_{37}H_{40}N_{10}O_9Cl_2Ni$: orthorhombic, $P2_12_12_1$; $a = 14.206(2)$ Å, $b = 22.735(3)$ Å, $c = 12.696(3)$ Å, $Z = 4$. **3**, $C_{50}H_{58}N_{10}O_{10}Ni$: triclinic, $P\bar{1}$; $a = 14.191(5)$ Å, $b = 16.048(4)$ Å, $c = 13.692(4)$ Å, $\alpha = 115.25(2)°$, $\beta = 111.07(3)°$, $\gamma = 64.75(2)°$, $Z = 2$. Each complex has an octahedral coordination environment for the nickel(II) ion, formed by the six nitrogen donor atoms, and is either a Δ (clockwise) or a Λ (anticlockwise) enantiomorph, depending on the screw arrangement of the tripod-type ligand around the nickel(II) ion. The circular dichroism (CD) spectrum of a powdered sample of a crystal of **1** showed a positive and a negative peak at 915 and 630 nm, respectively, and that of another crystal showed an enantiomeric pattern. The observation of the Cotton effect and the crystal structure provided evidence for spontaneous resolution of the chiral complex molecule.

Introduction

Chirality is an important concept not only in chemistry but also in living organisms, pharmaceuticals, and the chemical industry. When a chiral molecule crystallizes to form a crystalline racemate, the product is either (1) a racemic compound, (2) a racemic mixture (conglomerate), or (3) a racemic solid solution.[1] The separation of two enantiomers forming a conglomerate does not require any optically active auxiliary agent, since resolution spontaneously occurs during the course of crystallization. Spontaneous resolution, which is characteristic of a conglomerate, was first observed in ammonium sodium tartrate by Pasteur in 1848.[2] Since this historic discovery, a large number of chiral molecules have been synthesized and investigated, but only a limited number of these molecules are known to be conglomerates.[1,3,4]

In this study, we synthesized the chiral nickel(II) complexes of a tripod-type ligand with the chemical formulas $[Ni(H_3L)](NO_3)_2 \cdot MeOH$ (**1**), $[Ni(H_3L)](ClO_4)_2 \cdot MeOH$ (**2**), and $[Ni(H_3L)](C_6H_5COO)_2 \cdot 6H_2O$ (**3**) (H_3L = tris[2-(((2-phenylimidazol-4-yl)methylidene)amino)ethyl]amine) (see Chart 1). Each complex is either a Δ (clockwise) or a Λ (anticlockwise) enantiomorph, depending on the screw arrangement of the tripod-type ligand around the Ni(II) ion, as shown in Chart 2. Because **1** and **2** are found to be conglomerates, we report the syntheses, crystal structures, and circular dichroism (CD) spectra of these complexes.

Chart 1. Chemical Structure of $[Ni(H_3L)]^{2+}$

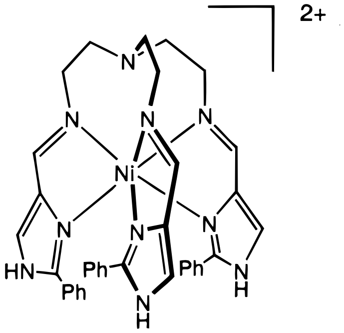
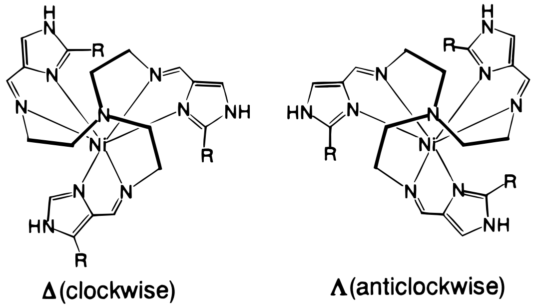


Chart 2. Δ (Clockwise) and Λ (Anticlockwise) Enantiomorphs Due to the Screw Arrangement of the Tripod-Type Ligand around the Ni(II) Ion



Results and Discussion

Syntheses and Characterizations. The tripod-type Schiff-base ligand H_3L was prepared by a 3:1 condensation reaction of 2-phenyl-4-formylimidazole with tris(2-aminoethyl)amine in methanol. The reaction mixture was subsequently used for the syntheses of the nickel(II) complexes without isolation of the

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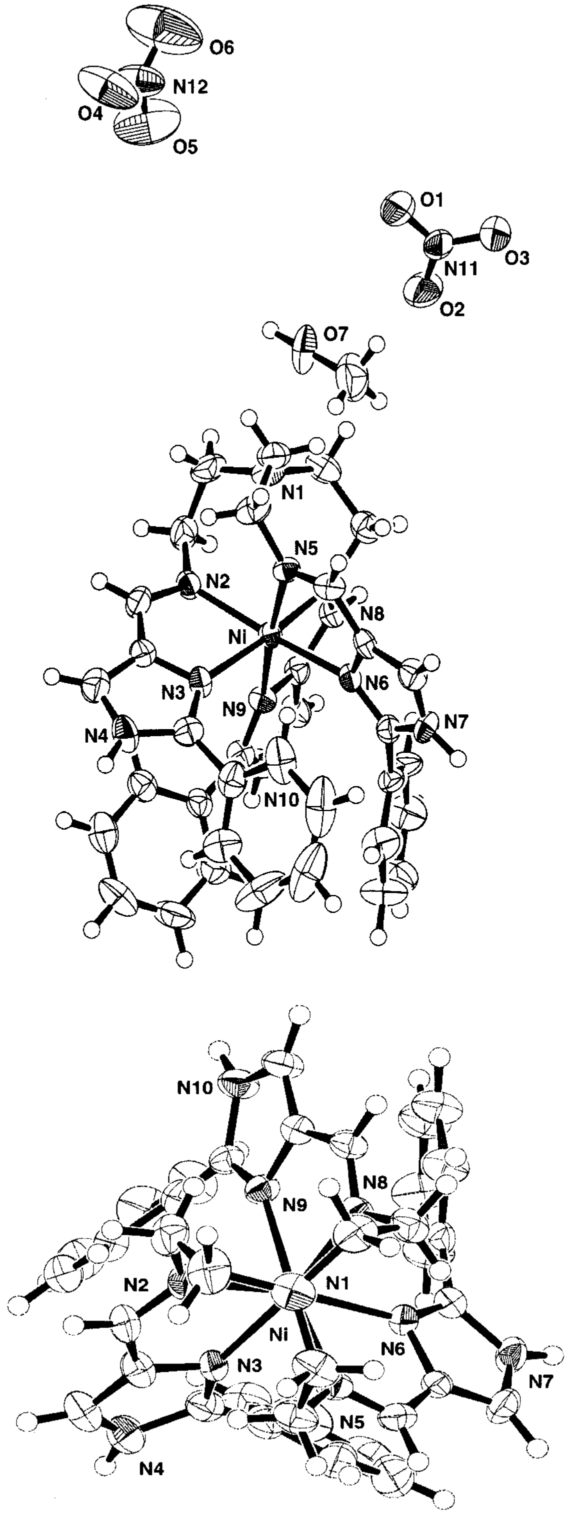

Figure 1. Top: ORTEP drawing of **1**, with a selected atom-numbering scheme, showing the Λ enantiomorph (anticlockwise molecule) and 50% probability ellipsoids. Bottom: ORTEP drawing of the cation of **1** viewed down the pseudo-3-fold axis showing an anticlockwise structure.

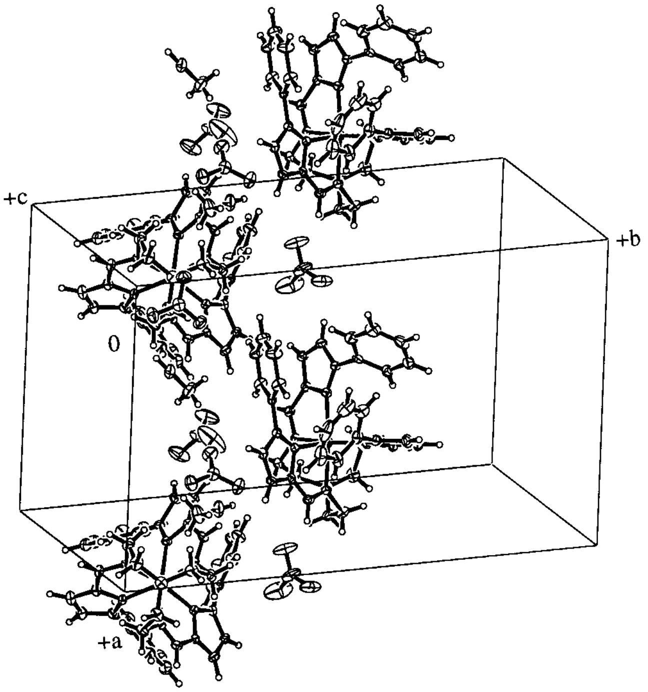

Figure 2. Packing diagram of **1** showing that only the Λ enantiomorph (anticlockwise molecule) is involved in the crystal.

ligand. The nickel(II) complex $[Ni(H_3L)](NO_3)_2 \cdot MeOH$ (**1**) was prepared by mixing the ligand solution and nickel(II) nitrate hexahydrate in methanol in a 1:1 molar ratio. Similar reaction procedures were adopted for the syntheses of $[Ni(H_3L)](ClO_4)_2 \cdot MeOH$ (**2**) and $[Ni(H_3L)](C_6H_5COO)_2 \cdot 6H_2O$ (**3**). The infrared spectra of these complexes show characteristic bands attributable to the imidazole ν_{N-H} (2300−2840 cm^{-1}), the Schiff-base $\nu_{C=N}$ (1644−1649 cm^{-1}), and the counteranion nitrate ν_{N-O} (1384 cm^{-1}), perchlorate ν_{Cl-O} (1057−1176 cm^{-1}), or benzoate (1596 cm^{-1}) absorptions.[5] The molar electrical conductivities of **1**−**3** in 10^{-3} M solutions of *N*,*N*-dimethylformamide are 132, 132, and 15 S cm^2 mol^{-1}, respectively. The values for **1** and **2** are in the expected range for 1:2 electrolytes in *N*,*N*-dimethylformamide.[6] The magnetic susceptibilities of the powdered samples were measured in the temperature range 2−300 K under an external magnetic field of 10 000 G, giving effective magnetic moments that are practically constant at ca. 3.0 μ_B. These values are in the expected range for discrete mononuclear high-spin Ni(II) complexes.[7−9]

Structural Descriptions of 1−3. The crystal structure of each complex consists of a dipositive nickel(II) complex cation with a nitrate, perchlorate, or benzoate counteranion and methanol or water molecules as the crystal solvents. Because the cations of these complexes assume similar molecular structures the same atom-numbering scheme was adopted for each. The ORTEP drawing of **1** is shown in Figure 1. The ORTEP drawings with atom-numbering schemes for **2** and **3** are deposited in the Supporting Information. The ORTEP drawing of the cation viewed down the pseudo-C_3 axis of **1**, given in Figure 1, shows the anticlockwise enantiomorph. A packing diagram of the molecule in the unit cell of **1** is shown in Figure 2. Selected bond distances and angles with their estimated standard deviations for **1**−**3** are summarized in Table 1.

Each complex has an octahedral coordination environment for the Ni(II) ion, formed by the N_6 donor set of the tripod-type ligand, including three imidazole and three imine nitrogen atoms. The distances of the six Ni−N bonds are in the ranges 2.089(5)−2.188(5) Å for **1**, 2.098(8)−2.155(9) Å for **2**, and

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Table 1. Relevant Bond Distances (Å) and Angles (deg) with Estimated Standard Deviations in Parentheses for $[Ni(H_3L)](NO_3)_2\cdot MeOH$ (**1**), $[Ni(H_3L)](ClO_4)_2\cdot MeOH$ (**2**), and $[Ni(H_3L)](C_6H_5COO)_2\cdot 6H_2O$ (**3**)

	1	**2**	**3**
Bond Distances			
Ni−N(2)	2.120(6)	2.098(8)	2.076(8)
Ni−N(3)	2.131(5)	2.151(7)	2.135(8)
Ni−N(5)	2.130(5)	2.124(8)	2.140(8)
Ni−N(6)	2.122(6)	2.138(8)	2.150(8)
Ni−N(8)	2.089(5)	2.105(8)	2.103(8)
Ni−N(9)	2.188(5)	2.155(9)	2.149(7)
Bond Angles			
N(2)−Ni−N(3)	79.4(2)	79.5(3)	78.5(3)
N(2)−Ni−N(5)	92.7(2)	93.7(3)	93.8(3)
N(2)−Ni−N(6)	171.0(2)	172.6(3)	171.6(3)
N(2)−Ni−N(8)	93.6(2)	94.0(3)	93.3(3)
N(2)−Ni−N(9)	89.9(2)	89.5(3)	90.3(3)
N(3)−Ni−N(5)	88.6(2)	89.1(3)	91.0(3)
N(3)−Ni−N(6)	96.9(2)	97.4(3)	98.9(3)
N(3)−Ni−N(8)	172.2(2)	172.6(3)	170.4(3)
N(3)−Ni−N(9)	97.0(2)	97.0(3)	95.5(3)
N(5)−Ni−N(6)	78.9(2)	79.4(3)	78.3(3)
N(5)−Ni−N(8)	95.3(2)	95.0(4)	94.4(3)
N(5)−Ni−N(9)	174.2(2)	173.6(4)	172.9(3)
N(6)−Ni−N(8)	90.4(2)	89.4(3)	90.0(3)
N(6)−Ni−N(9)	98.7(2)	97.6(3)	97.8(3)
N(8)−Ni−N(9)	79.4(2)	79.2(3)	79.6(3)

2.076(8)−2.150(8) Å for **3**. As shown in Chart 2 and Figure 2, each nickel(II) complex can be either a Δ (clockwise) or a Λ (anticlockwise) enantiomorph, depending on the screw arrangement of the tripod-type ligand around the nickel(II) ion. Because **1** and **2** crystallize in an acentrosymmetric space group, $P2_12_12_1$, their crystals should consist of one of two enantiomorphs. On the basis of the analysis of the Flack parameter,[10] it was found that the crystals of **1** and **2** used for the present X-ray analyses consist of the Λ (anticlockwise) enantiomorph, as shown in Figure 2 for **1**. The present X-ray analyses demonstrate that the separations of the two enantiomers spontaneously occurred during the crystallizations and that **1** and **2** are conglomerate. In contrast, the crystal structure of **3** consists of the Δ (clockwise) and Λ (anticlockwise) enantiomorphs related by a symmetry operation of inversion, as **3** crystallizes in the centrosymmetric space group $P\bar{1}$. The above results suggest that there are important effects due to the counteranion, the solvent of recrystallization, and the crystal solvent on the crystal packing (Which does the complex form, a racemic compound or a racemic mixture (conglomerate)?).

The imidazole nitrogen atoms of the tripod-type ligand form hydrogen bonds (NH···O) with the methanol and water molecules of the crystal solvents and with counteranions through the imidazole proton. The N···O distances assigned to the hydrogen bonds are listed in Table 2. It should be noted that there is no multidimensional network structure due to the hydrogen bonds. In contrast, the water molecules and oxygen atoms of the benzoate in **3** form a complex network due to the hydrogen bonds, as shown in Figure 3 and Table 2.

Table 2. Hydrogen-Bond Distances (Å) for $[Ni(H_3L)](NO_3)_2\cdot MeOH$ (**1**), $[Ni(H_3L)](ClO_4)_2\cdot MeOH$ (**2**), and $[Ni(H_3L)](C_6H_5COO)_2\cdot 6H_2O$ (**3**)

D	A	D···A
	H-Bonds for **1**	
N(7)	O(2)	2.869(9)
N(10)	O(4)	2.781(9)
N(4)	O(7)	2.768(8)
O(1)	O(7)	2.798(8)
	H-Bonds for **2**	
N(7)	O(9)	2.76(1)
N(4)	O(5)	2.84(1)
N(10)	O(2)	3.09(1)
	H-Bonds for **3**	
N(10)	O(2)	2.70(1)
N(4)	O(3)	2.72(1)
N(7)	O(7)	2.87(1)

Possible Intermolecular H-Bonds for **3**

D	A	D···A	D	A	D···A
O(1)	O(9)	2.83(1)	O(1)	O(9)	2.70(1)
O(5)	O(4)	2.80(1)	O(5)	O(6)	2.92(2)
O(6)	O(3)	2.83(1)	O(6)	O(7)	2.94(1)
O(7)	O(8)	2.74(1)	O(8)	O(9)	2.82(1)
O(9)	O(10)	2.97(3)			

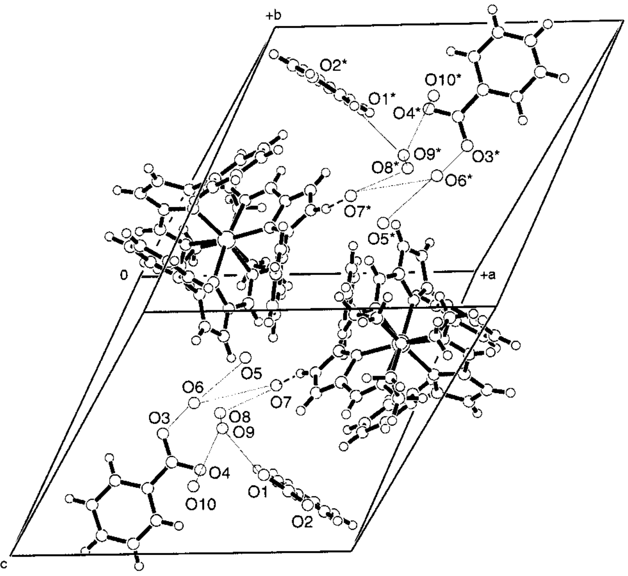

Figure 3. Packing diagram of **3** showing that the Δ (clockwise) and the Λ (anticlockwise) enantiomorphs are involved in the crystal.

CD Spectra. A crystal of **1** was selected and ground into a powder. A CD spectrum of the powdered sample was recorded in the 400−1000 nm range by the Nujol mull method. This spectrum showed a positive and a negative peak at 915 and 630 nm, respectively, and the spectrum of another crystal showed an enantiomeric CD pattern. The CD spectra of these two crystals of **1** are shown in Figure 4. The observation of the Cotton effect provides more evidence that spontaneous resolution took place during the course of crystallization.

Concluding Remarks. The chiral nickel(II) complexes of a tripod-type ligand with the chemical formulas $[Ni(H_3L)](NO_3)_2\cdot MeOH$ (**1**), $[Ni(H_3L)](ClO_4)_2\cdot MeOH$ (**2**), and $[Ni(H_3L)](C_6H_5COO)_2\cdot 6H_2O$ (**3**) have been synthesized and characterized. In each complex, the screw coordination arrangement of the tripod-type ligand around the nickel(II) ion induces chirality, resulting in a Δ (clockwise) or a Λ (anticlockwise) enantiomer. The single-crystal X-ray analyses and CD spectra confirmed that **1** and **2** are conglomerate. Intermolecular interactions, including cation−cation, cation−anion, anion−anion, and ion−crystal solvent, were investigated. However, no intermolecular interactions were found, except for hydrogen bonds. The hydrogen bonds do not form multidimensional extended network structures. We could not determine the mechanisms whereby **1** and **2** crystallize as conglomerates.

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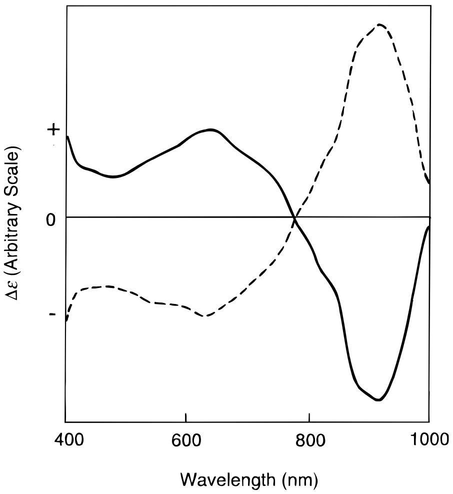

Figure 4. CD spectra of powdered samples of **1**. Two crystals of **1** were selected and ground into powder, and the CD spectra were recorded by the Nujol mull method. One crystal showed a positive and a negative peak at 915 and 630 nm, respectively, and the other showed an enantiomeric CD pattern.

To design a species that induces spontaneous resolution, a chiral molecule with enantioselective homochiral discrimination and a 3D network structure due to substantially strong intermolecular interactions should be developed, i.e., a self-complementary metal complex with assembly character and a chiral recognition unit. A metal complex with a multidentate ligand involving an imidazole group, which has not only donor ability but also acceptor ability both in coordination bonds and in hydrogen bonds,[11−14] is a good candidate for this purpose. Studies along this line are currently in progress.[15−19]

Experimental Section

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

Warning! *Perchlorate salts are potentially explosive and should be handled only in small quantities and with care.*

Tris[2-(((2-phenylimidazol-4-yl)methylidene)amino)ethyl]-amine (H_3L). A methanolic solution of 2-phenyl-4-formylimidazole (2.582 g, 15 mmol, in 10 mL) was added to a methanolic solution of tris(2-aminoethyl)amine (0.731 g, 5 mmol, in 10 mL). The methanol was evaporated, giving an oily material, and then diethyl ether (50 mL) was added. Scratching the oily material with a spatula resulted in the formation of a yellow powder. Anal. Calcd for $C_{35}H_{36}N_{10}\cdot MeOH$: C, 69.35; H, 6.29; N, 21.86. Found: C, 69.54; H, 6.39; N, 21.59. ^1H NMR (300 MHz, $CDCl_3$; δ): 8.11 (s, 3H, CH), 8.0−7.0 (m, 18H, Ar H), 3.65 (br t, 6H, $=NCH_2CH_2$), 2.84 (br t, 6H, $=NCH_2CH_2$). Mp: 153−155 °C.

$[Ni(H_3L)](NO_3)_2\cdot MeOH$ (1). A methanolic solution of 2-phenyl-4-formylimidazole (2.583 g, 15 mmol, in 10 mL) was added to a methanolic 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 tripod-type ligand. A methanolic solution of nickel(II) nitrate hexahydrate (1.454 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 the light-blue crystals that had precipitated were collected by suction filtration, washed with a small amount of methanol, and dried in vacuo. Yield: 2.260 g (55%). 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. IR (KBr; cm^{-1}): ν_{N-H} (imidazole), 2840−2300; $\nu_{C=N}$ (imine), 1648; ν_{N-O} (nitrate), 1384. Λ_M: 132 S cm^2 mol^{-1} in DMF. Mp: 275 °C dec. CD (Nujol, λ_{max}/nm): 950.

$[Ni(H_3L)](ClO_4)_2\cdot MeOH$ (2). The complex was prepared as described for **1** using nickel(II) perchlorate hexahydrate (1.828 g, 5 mmol) instead of nickel(II) nitrate hexahydrate. The product was obtained as blue crystals. Yield: 0.370 g (8%). Anal. Calcd for $C_{37}H_{40}N_{10}O_9Cl_2Ni$: C, 49.47; H, 4.49; N, 15.59. Found: C, 49.27; H, 4.56; N, 15.48. IR (KBr; cm^{-1}): ν_{N-H} (imidazole), 2830−2500; $\nu_{C=N}$ (imine), 1649; ν_{Cl-O} (perchlorate), 1176, 1110, 1057. Λ_M: 132 S cm^2 mol^{-1} in DMF. Mp: >300 °C.

$[Ni(H_3L)](C_6H_5COO)_2\cdot 6H_2O$ (3). To the ligand solution (5 mmol in 20 mL of methanol) was added a methanol solution of nickel(II) chloride hexahydrate (1.189 g, 5 mmol). The mixture was stirred at room temperature for 30 min, after which an aqueous solution of sodium benzoate (1.44 g, 10 mmol) was added. The mixture was stirred for 30 min and then filtered. The filtrate was allowed to stand for several days, after which the light-blue microcrystals that had precipitated were collected by suction filtration, washed with a small amount of methanol, and dried in vacuo. Yield: 1.356 g (29%). Anal. Calcd for $C_{50}H_{49}N_{10}O_{5.5}Ni$: C, 63.96; H, 5.30; N, 14.75. Found: C, 64.11; H, 5.27; N, 14.95. The crude product was recrystallized as light-blut crystals from a mixture of methanol and water. Anal. Calcd for $C_{50}H_{58}N_{10}O_{10}Ni$: C, 59.01; H, 5.74; N, 13.76. Found: C, 59.76; H, 5.74; N, 14.04. IR (KBr; cm^{-1}): ν_{O-H} (hydrogen-bonded carboxylic acid), 3370−2500; $\nu_{C=N}$ (imine), 1644; $\nu_{C=O}$ (carboxylic acid), 1596 cm^{-1}. Λ_M: 15 S cm^2 mol^{-1} in DMF. Mp: 225 °C dec.

Physical Measurements. Elemental analyses for C, H, and N were performed at the Elemental Analysis Service Center of Kyushu University. Infrared spectra were recorded with the KBr disk method using a Perkin-Elmer Paragon 1000 FT-IR spectrometer. Magnetic susceptibilities were measured with an MPMS5 SQUID susceptometer (Quantum Design Inc.) in the 2−300 K temperature range under an externally applied magnetic field of 1 T. The calibration was made with palladium metal. Corrections for diamagnetism were applied using Pascal's constants.[20] Effective magnetic moments were calculated using the equation $\mu_{eff} = (8\chi_A T)^{1/2}$, where χ_A is the magnetic susceptibility per nickel. Circular dichroism spectra were recorded on a JASCO J-720 spectropolarimeter.

X-ray Data Collections and Reductions and Structure Determinations. Each single crystal was mounted on a glass fiber and coated with epoxy 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 by the use of a polynomial expression. An empirical absorption correction based on the azimuthal scans of several reflections was also applied, as were corrections for Lorentz and polarization effects.

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Table 3. Crystallographic Data for All Complexes

	1	**2**	**3**
formula	$C_{37}H_{40}N_{12}O_7Ni$	$C_{37}H_{40}N_{10}O_9Cl_2Ni$	$C_{50}H_{58}N_{10}O_{10}Ni$
fw	823.50	898.39	1017.77
space group	$P2_12_12_1$ (No. 19)	$P2_12_12_1$ (No. 19)	$P\bar{1}$ (No. 2)
a, Å	14.198(2)	14.206(2)	14.191(5)
b, Å	22.422(2)	22.735(3)	16.048(4)
c, Å	12.019(2)	12.696(3)	13.692(4)
α, deg	90	90	115.25(2)
β, deg	90	90	111.07(3)
γ, deg	90	90	64.75(2)
V, Å^3	3826.4(7)	4100.5(10)	2489(1)
Z	4	4	2
D_{calcd}, g cm^{-3}	1.429	1.455	1.36
μ, cm^{-1}	5.73	6.76	4.58
R,[a] R_w[b]	0.040, 0.043	0.070, 0.044	0.087, 0.086

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

The space group $P2_12_12_1$ for **1** and **2** was unequivocally determined by the extinction rule. There were two possible space groups for **3**: $P1$ and $P\bar{1}$. Only $P\bar{1}$ was possible because the structure was well determined and the constituting atoms gave reasonable thermal parameters when $P\bar{1}$ was assumed. The structures were solved by DIRDIF92 (PATTY) and expanded using Fourier techniques.[21,22] The non-hydrogen atoms were anisotropically refined. Hydrogen atoms at their ideal calculated positions were included in the structure factor calculations but not refined. Full-matrix least-squares refinements ($I > 2.00\sigma(I)$) were employed, where the unweighted and weighted agreement factors $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ were used. The weighting scheme was based on counting statistics. Plots of $\sum w(|F_o| - |F_c|)^2$ versus $|F_o|$, the reflection order in data collection, (sin θ)/λ, 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.[10] The x values were 0.055 and 0.096 for **1** and **2**, respectively, indicating that the selected enantiomer was correct in each case.

Neutral-atomic scattering factors were taken from the work of Cromer and Waber.[23] Anomalous dispersion effects were included in F_c; the values of $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.[24] The values for the mass attenuation coefficients were those of Creagh and Hubbel.[25] All calculations were performed using the teXsan crystallographic software package of the Molecular Structure Corp.[26] Crystal data and details of the structure determinations are summarized in Table 3.

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Supporting Information Available: ORTEP drawings for **2** and **3** and X-ray crystallographic files, in CIF format, for the structure determinations of **1**−**3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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