

Preparation and Characterization of Anion-Dependent Octahedral Nickel(II) Geometric Isomers

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Recently we are interested in multidentate ligands containing hydroxyl and pyridine groups capable of binding two or more metal ions.¹ Metal complexes including Ni(II) ion with polynucleating ligands could display significant coordination chemistry, catalytic activity, and magnetic properties.² Among these, stereoisomerism have been attracted in coordination chemistry for a long time, because it happens ligand interchange in solution and appears important properties, *i.e.*, color and chirality.³ For example, [Co(en)₂Cl₂]Cl complex has different colors and structures, *i.e.*, green for *trans* and violet for *cis* (en = ethylenediamine).⁴ Furthermore, *cis*-[Co(en)₂Cl₂]⁺ has two chiral isomers (Δ and Λ).^{4,5} We have reported the structures and magnetic properties of various metal complexes with *N,N*-bis(2-pyridylmethyl)-2-aminoethanol/-ate, in which they have had from mononuclear to tetranuclear structures depending on anions.^{1,6} In this context, we have tried to prepare multinuclear nickel(II) complexes with *N*-(2-pyridylmethyl)-iminodiethanol (H₂pmide). Unexpectedly, we have obtained two monomeric nickel(II) complexes with two H₂pmide ligands. They have different colors and structures depending on the counterions (NO₃⁻ and Cl⁻). Herein, we report the synthesis, structures, and physical properties of nickel(II) complexes, [Ni(H₂pmide)₂](NO₃)₂ (**1**) and [Ni(H₂pmide)₂]Cl₂ (**2**). H₂pmide is coordinated to nickel(II) ion as tridentate ligand, not tetradentate one.

The reaction of two equivalents of H₂pmide and 1 equiv. of Ni(NO₃)₂·6H₂O/NiCl₂·6H₂O in MeCN/MeOH under aerobic conditions affords air stable **1** and **2** in good yields, respectively. The colors of **1** and **2** are pink and blue, respectively. The composition and structures of **1-2** were determined by elemental analysis, infrared spectrum, UV/Vis spectrum, and single crystal X-ray diffraction analysis. The IR spectrum of **1** had peaks characteristic of coordinated H₂pmide and NO₃⁻ anion.⁷ The IR spectrum of **1** showed a very strong absorption at 3392 cm⁻¹ that is assigned to the hydroxyl groups of coordinated H₂pmide ligands. The bands of the C-H of H₂pmide appeared at 3085 and 2975 cm⁻¹. The band of the N-O of nitrate ion showed at 1384 cm⁻¹. The IR spectrum of **2** had peaks characteristic of coordinated H₂pmide. The IR spectrum of **2** showed a strong absorption at 3357

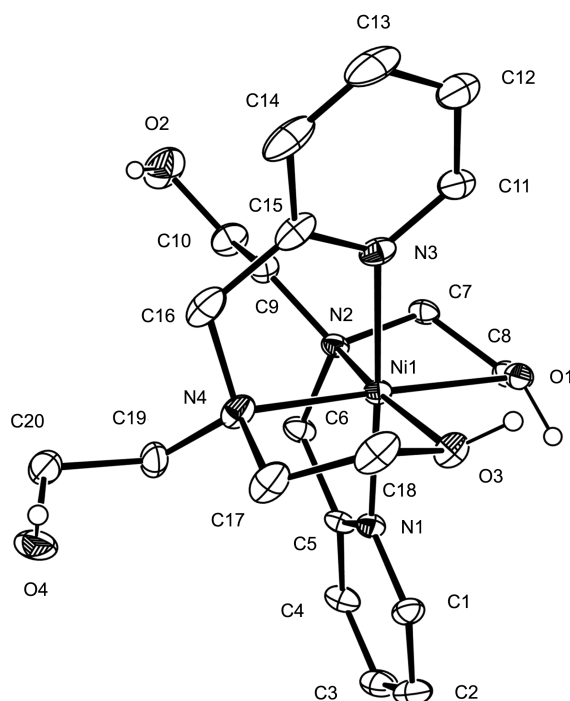


Figure 1. ORTEP view of **1**. The atoms are represented by 30% probable thermal ellipsoid. Hydrogen atoms and NO₃⁻ anions are omitted for clarity.

and 3325 cm⁻¹ that is assigned to the hydroxyl groups of coordinated H₂pmides. The bands of the C-H of H₂pmide appeared at 3046 and 2968 cm⁻¹.⁷ Taking into account the powder and simulated patterns of **1** and **2**, the coherence of peak angles and intensities is very good. Based on these results we are able to conclude that the crystalline solids **1** and **2** have high phase purities (Figures S1 and S2).

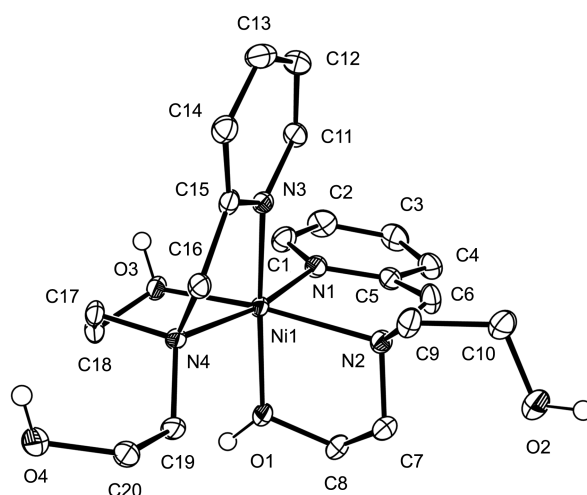
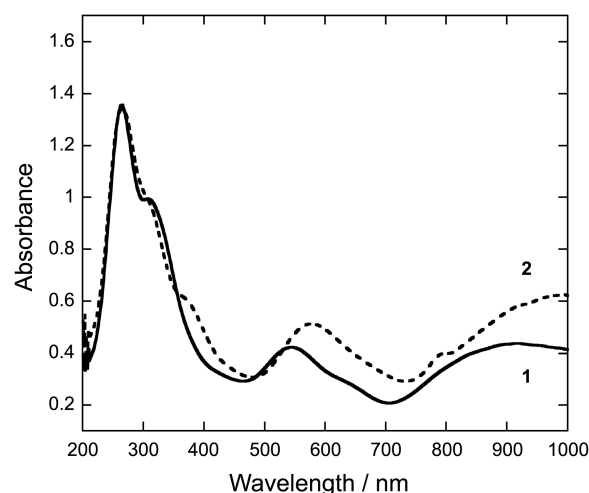
1 crystallizes in the monoclinic *P*2₁ space group, and the unit cell includes two mononuclear complex molecules. An atom labeling ORTEP drawing of **1** is shown in Figure 1, and Table 1 lists the selected bond lengths and angles. The nickel(II) ion exhibits a distorted octahedral geometry. Two H₂pmide ligands are coordinated to nickel(II) ion as tridentate and *facial* type.⁸ That is, a hydroxyl group and tertiary nitro-

Table 1. Selected Bond Distances (Å) and Angles (°) for **1** and **2**

1		2	
Ni1-N1	2.034(3)	Ni1-N1	2.074(2)
Ni1-N2	2.152(3)	Ni1-N2	2.205(2)
Ni1-N3	2.044(3)	Ni1-N3	2.039(2)
Ni1-N4	2.160(3)	Ni1-N4	2.204(2)
Ni1-O1	2.100(3)	Ni1-O1	2.045(2)
Ni1-O3	2.101(3)	Ni1-O3	2.093(1)
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N1-Ni1-N2	82.4(1)	N1-Ni1-N2	81.72(6)
N1-Ni1-N3	177.2(1)	N1-Ni1-N3	96.37(6)
N1-Ni1-N4	95.0(1)	N1-Ni1-N4	169.50(6)
N1-Ni1-O1	88.0(1)	N1-Ni1-O1	89.89(6)
N1-Ni1-O3	93.4(1)	N1-Ni1-O3	88.77(6)
N3-Ni1-N4	82.4(1)	N3-Ni1-N4	80.08(6)
N3-Ni1-O1	94.7(1)	N3-Ni1-O1	170.67(6)
N3-Ni1-O3	87.3(1)	N3-Ni1-O3	98.03(6)

gen of each H₂pmide occupy in equatorial plane and two pyridine moieties of two H₂pmides bind in axial position. The other hydroxyl groups of both H₂pmides are not coordinated. Interestingly, the geometry of two pyridine groups which are resulted from the different H₂pmide ligands displays *trans* configuration in axial positions. The average Ni-N_{tertiary}, Ni-N_{pyridine}, and Ni-O_{hydroxyl} bond distances are 2.156(2), 2.039(2), and 2.101(2) Å, respectively. The average bite distance and angle of the five-membered chelate rings are 2.791(2) Å and 84.94(5)°, respectively.⁹ All hydroxyl groups of **1** are involved in hydrogen-bonding interactions with oxygen atoms of nitrate ions. Owing to these hydrogen-bonding interactions, all nickel(II) complex ions are linked together, resulting in a two-dimensional network extending along the *ac* plane (O3···O5(-x+1, y-1/2, -z+1) 2.661 Å, ∠O3-H3a-O5 163°; O2···O7(-x, y-1/2, -z+1) 3.013 Å, ∠O2-H2-O7 172°; O1···O10 3.033 Å, ∠O1-H1-O10 165°; O4···O9(x-1, y, z-1) 3.046 Å, ∠O4-H4-O9 149°).¹⁰ (Figure S3).

2 crystallizes in the monoclinic *P*2₁/*c* space group, and the unit cell includes four mononuclear complex molecules. An atom labeling ORTEP drawing of **2** is shown in Figure 2, and Table 1 lists the selected bond lengths and angles. The nickel(II) ion shows a distorted octahedral structure. Two H₂pmide ligands are bonded to nickel(II) ion as *facial* type, like **1**.⁸ Unexpectedly, a hydroxyl group and tertiary nitrogen of one H₂pmide are occupied in equatorial plane and those of another H₂pmide are located in *cis* fashion. Thus, two pyridine groups of the different H₂pmide ligands are located in *cis* positions. The remaining hydroxyl groups of both H₂pmides are free. The average Ni-N_{tertiary}, Ni-N_{pyridine}, and Ni-O_{hydroxyl} bond distances are 2.204(1), 2.059(1), and 2.066(1) Å, respectively. The average bite distance and angle of the five-membered chelate rings are 2.774(1) Å and 81.02(3)°, respectively.⁹ The hydroxyl groups of **2** are also involved in hydrogen bondings with chloride anions. First, two adjacent nickel(II) complexes are hydrogen bonded each other *via* chloride anions, which gives rise to a dimer (O3···Cl1(-x+2,

**Figure 2.** ORTEP view of **2**. The atoms are represented by 50% probable thermal ellipsoid. Hydrogen atoms and Cl⁻ anions are omitted for clarity.**Figure 3.** Solid UV/Vis spectra of **1** (solid line) and **2** (dotted line).

-y, -z+2) 3.000 Å, ∠O3-H3a-Cl1 173°; O4···Cl1 3.173 Å, ∠O4-H4-Cl1 172°) (Figure S4).¹⁰ Second, the dimeric units are linked together by H-bonding interaction, leading to a two-dimensional network extending along the *bc* plane (O1···Cl2(-x+2, y-1/2, -z+3/2) 2.945 Å, ∠O1-H1a-Cl2 167°; O2···Cl2 3.184 Å, ∠O2-H2-Cl2 172°) (Figure S4).

The UV/Vis spectra of **1** and **2** in solid state are displayed in Figure 3. The spectrum of **1** shows mainly three maxima at 264, 544, and 917 nm. This appears to be characteristic of the high spin octahedral Ni(II) complexes.¹¹ The lowest energy absorption band in **1**, considered to arise from the ³A_{2g} → ³T_{2g} d-d transition, is appeared at 917 nm and corresponded as exactly Δ_o (= 10Dq).¹² The second transition at 544 nm, presumably responsible for the pink color of solid **1**, would be the ³A_{2g} → ³T_{1g} (from F) transition. The highest energy band is thought to be primarily charge transfer and/or ³A_{2g} → ³T_{1g} (from P) transition. The spectrum of **2** is similar to that of **1**. The characteristic three maxima at 264, 579, and 989 nm are appeared. Compared to that of **1**, the lowest

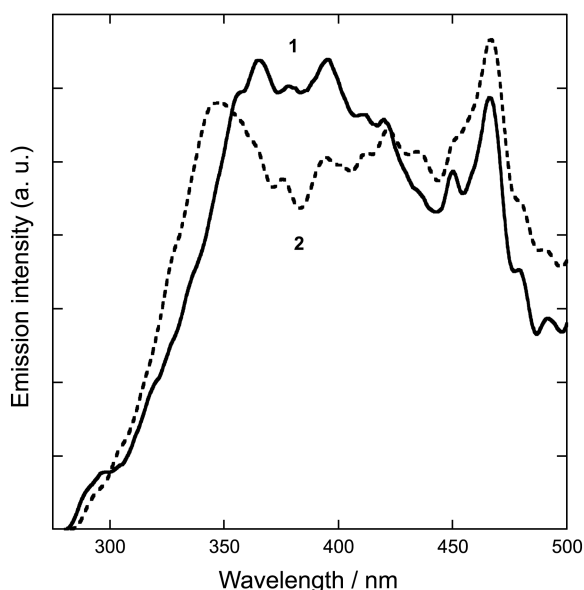


Figure 4. Solid state photo-induced emission spectra of **1** (solid line) and **2** (dotted line) at room temperature with $\lambda_{\text{ex}} = 260$ nm.

energy band (Δ_0) of **2** appears at 989 nm and is red-shifted about 72 nm. This means that the splitting of d orbitals (t_{2g} and e_g) in **2** is smaller than that of **1**. This indicates the *facial/trans* coordination mode of **1** can be induced more stronger field, compared *facial/cis* mode of **2**.¹³ Furthermore, the spin-forbidden transition (${}^3A_{2g} \rightarrow {}^1E_g$) band at 796 nm in **2** occurs as a weak shoulder, due to the low value of Δ_0 .¹⁴ The absorption band corresponding to the ${}^3A_{2g} \rightarrow {}^3T_{1g}$ (from F) transition in **2** is exhibited at 579 nm, which can be attributed to the blue color of **2**. This band also is red-shifted *ca.* 35 nm for **1**. The electronic spectra of **1** and **2** in aqueous and methanol solutions show same patterns, respectively ($\lambda_{\text{max}} = 559, 961$ nm in H_2O ; 566, 950 nm in MeOH). Thus, the geometric isomers of **1** and **2** in aqueous and methanol solutions could not discriminate.

The solid-state photoluminescent properties of **1** and **2** were investigated at room temperature. The luminescent spectra of **1** and **2** are shown in Figure 4. Upon excitation at $\lambda_{\text{ex}} = 260$ nm, **1** and **2** display strong emission bands between 300 and 500 nm in complicated patterns. The spectra of **1** and **2** are shown in quite different shapes between 300 and 440 nm, while those of **1** and **2** are exhibited as same patterns from 440 to 500 nm. The different patterns can be attributed to the *trans/cis* coordination geometries of nickel(II) ions. The emissive behaviors in **1** and **2** can be mostly related to ligand-centered $\pi \rightarrow \pi^*$ or $\pi \rightarrow n$ transitions within the aromatic groups of the H_2pmide ligands.¹⁵

In conclusion, we have prepared monomeric nickel(II) complexes **1** and **2** having different structures (*trans* and *cis*) and colors (pink and blue), due to the different anions (NO_3^- , Cl^-). **1** is displayed *facial/trans* conformation, while **2** is exhibited *facial/cis* mode. The *facial/trans* mode of **1** induces much strong field for the *facial/cis* fashion of **2**. The complexes **1** and **2** have strong hydrogen bondings *via* nitrate and chloride anions, respectively, and show two-di-

mensional network structures. Due to the geometric structures of **1** and **2**, the luminescence behaviors are appeared in different shapes.

Experimental

Materials and Measurements. All chemicals used in the synthesis were of reagent grade and used without further purification. *N*-(2-pyridylmethyl)-iminodiethanol (H_2pmide) was prepared according to literature procedures.¹⁶ UV/Vis absorption spectra were recorded with a SCINCO S-2100 spectrophotometer. Infrared spectra were recorded with a Thermo Fisher Scientific IR200 spectrophotometer ($\pm 1 \text{ cm}^{-1}$) using KBr disk. Elemental analyses were carried out using a Fissons/Carlo Erba EA1108 instrument. X-ray powder diffraction (XRPD) patterns were measured on a Bruker AXS D2 Phaser X-ray Diffractometer with increments of degree and time step of 0.02° and 0.2 sec/step in 2θ . Luminescence spectra were obtained with a SINCO FS-2 fluorescence spectrometer.

Preparation of 1. To an MeCN solution (2 mL) of H_2pmide (100 mg, 0.51 mmol) was added an MeCN/MeOH (v/v, 2:1) mixture solution (3 mL) of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (74 mg, 0.25 mmol), and the color became light violet, and the solution was stirred for 30 min at room temperature. After filtrating, pink crystals were obtained by slow diffusion of diethyl ether into the mixture solution of **1**, collected by filtration, and washed with acetonitrile and dried in air. Yield: 129 mg (88%). FT-IR (KBr, cm^{-1}): 3392, 3085, 2975, 1609, 1384, 1068, 1027, 769. UV/Vis (diffuse reflectance spectrum): $\lambda_{\text{max}} = 264, 308$ (sh), 544, 917 nm. Anal. calcd for $\text{C}_{20}\text{H}_{32}\text{N}_6\text{NiO}_{10}$: C, 41.76; H, 5.61; N, 14.61. Found: C, 41.60; H, 5.64; N, 14.37.

Preparation of 2. This complex was obtained as blue crystals in a manner similar to the synthesis of **1** except that $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (61 mg, 0.25 mmol) instead of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was used. Yield: 122 mg (91%). FT-IR (KBr, cm^{-1}): 3357, 3046, 2968, 1609, 1433, 1066, 1028, 780. UV/Vis (diffuse reflectance spectrum): $\lambda_{\text{max}} = 264, 304$ (sh), 360 (sh), 579, 796 (sh, forbidden), 989 nm. Anal. calcd for $\text{C}_{20}\text{H}_{32}\text{Cl}_2\text{N}_4\text{NiO}_4$: C, 46.01; H, 6.18; N, 10.73. Found: C, 45.86; H, 6.24; N, 10.79.

Crystal Structure Determination. Single crystals of **1** and **2** were coated with paratone-*N* oil and the diffraction data measured at 100(2) K with synchrotron radiation ($\lambda = 0.70000 \text{ \AA}$) on an ADSC Quantum-210 detector at 2D SMC with a silicon (111) double crystal monochromator (DCM) at the Pohang Accelerator Laboratory, Korea. The ADSC Q210 ADX program¹⁷ was used for data collection (detector distance is 63 mm, omega scan; $\Delta\omega = 1^\circ$, exposure time is 1 sec per frame) and HKL3000sm (Ver. 703r)¹⁸ was used for cell refinement, reduction and absorption correction. The crystal structures of **1** and **2** were solved by direct methods,¹⁹ and refined by full-matrix least-squares refinement using the SHELXL-97 computer program.²⁰ The positions of all non-hydrogen atoms were refined with anisotropic displacement factors. All hydrogen atoms were placed using a riding

Table 2. Summary of the Crystallographic Data for **1** and **2**

Compound	1	2
Empirical formula	C ₂₀ H ₃₂ N ₆ NiO ₁₀	C ₂₀ H ₃₂ Cl ₂ N ₄ NiO ₄
Formula weight	575.20	522.10
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	8.690(2)	7.684(2)
<i>b</i> (Å)	15.961(3)	9.967(2)
<i>c</i> (Å)	9.692(2)	29.344(6)
β (°)	115.13(3)	92.78(3)
<i>V</i> (Å ³)	1217.1(4)	2244.7(8)
<i>Z</i>	2	4
<i>d</i> _{calc} (g cm ⁻³)	1.570	1.545
λ (Å)	0.70000	0.70000
<i>T</i> (K)	100(2)	100(2)
μ (mm ⁻¹)	0.775	1.028
<i>F</i> (000)	604	1096
Collected	13070	20566
Unique	7358	6303
Observed	6932	5012
Parameters	345	291
GOF	1.068	1.040
<i>R</i> ₁ ^a (4 σ data)	0.0598	0.0412
<i>wR</i> ₂ ^b (4 σ data)	0.1601	0.1076

$${}^aR_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, {}^bWR_2 = \frac{[\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]}{1/2}$$

model, and their positions were constrained relative to their parent atoms using the appropriate HFIX command in SHELXL-97, except the hydrogen atoms of coordinated hydroxyl groups. The crystallographic data and the result of refinements of **1-2** are summarized in Table 2.

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Supporting Information. Powder and simulated XRPD patterns and extended 2-D structures of **1** and **2**. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-955898 (for **1**) and CCDC-955899 (for **2**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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