

Article

Crystal Structures and Magnetic Properties of Diaquatetrapyridinenickel(II) and Diaquatetrapyridinecobalt(II) Complexes

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Abstract: Metal complexes with pyridine ligands (py) have not been crystallographically characterized in large numbers, while a large number of 2,2'-bipyridine (bpy) complexes have been structurally characterized. Against this background of scarcity of py complexes, the aim of this study was to characterize the structures and magnetic properties of complexes with pyridine ligands. In this study, new py complexes, *trans*-[Ni(H₂O)₂(py)₄][BPh₄]₂·4py (**1**) and *trans*-[Co(H₂O)₂(py)₄][BPh₄]₂·4py (**2**), were prepared and characterized by the single-crystal X-ray diffraction method and magnetic measurements. In the crystal structure analysis, both complexes were found to have octahedral *trans*-N₂O₄ coordination geometry, and the coordination of the *trans*-aqua ligands was found to be enhanced by the hydrogen-bonded pyridine molecules as a base. In the simultaneous analysis of magnetic susceptibility and magnetization, both complexes were found to show strong magnetism in one direction ($\chi_z > \chi_x, \chi_y; M_z > M_x, M_y$), and this was explained by the enhancement of the axial aqua ligands. In the nickel(II) complex, the strong axial ligand field was found to cause negative zero-field splitting ($D < 0$) to show the magnetic behavior, while in the cobalt(II) complex, the strong axial π -orbital effect was found to cause negative ligand field splitting (Δ) in the ⁴T₁ ground state to show the magnetic behavior.

Keywords: pyridine ligand; nickel(II) complex; cobalt(II) complex; crystal structure; magnetic properties; angular overlap model (AOM)



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1. Introduction

Pyridine is a popular organic solvent, and it works as a monodentate ligand. Metal complexes with pyridine ligands (py), however, have not been crystallographically characterized in large numbers [1–4], while a large number of 2,2'-bipyridine (bpy) complexes have been structurally characterized [5–11]. Octahedral tris-bpy complexes are sterically favorable, forming the *D*₃-symmetric complexes [6–11], but octahedral hexa-py complexes, in the *T_h* symmetry [4], are relatively less sterically favorable due to the steric repulsion at *cis*-positions (Figure 1). Moreover, py ligands are often lost as vapors, while bpy ligands will never be lost in such a way. Based on this background of the scarcity of py complexes, the aim of this study was to characterize the structures and magnetic properties of pyridine-ligand complexes. Fortunately, new py complexes, [Ni(H₂O)₂(py)₄][BPh₄]₂·4py (**1**) and [Co(H₂O)₂(py)₄][BPh₄]₂·4py (**2**), were crystallographically characterized in this study (Scheme 1), and their magnetic behavior has been successfully analyzed.

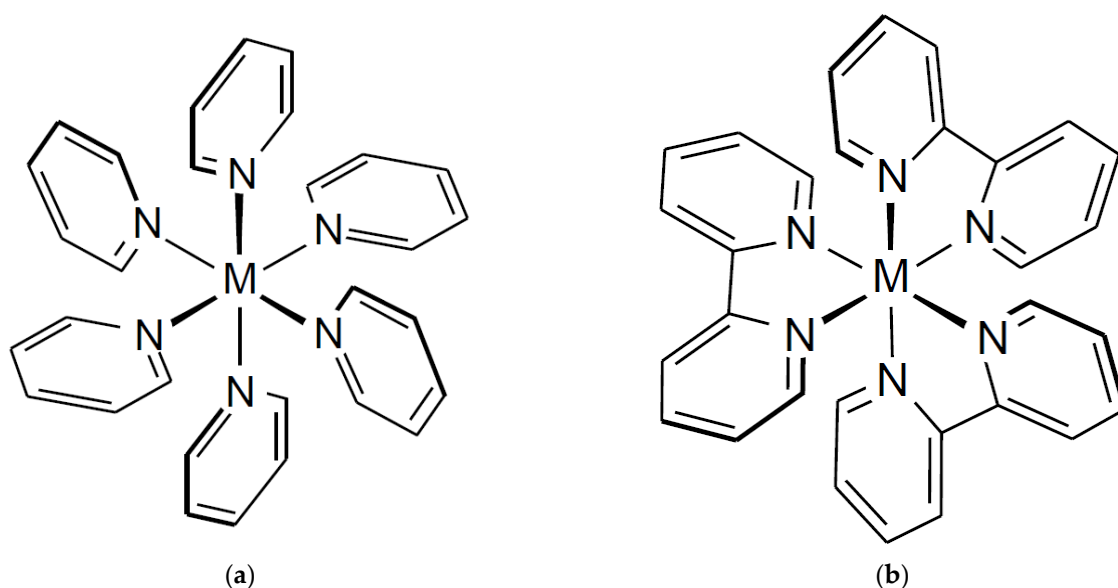
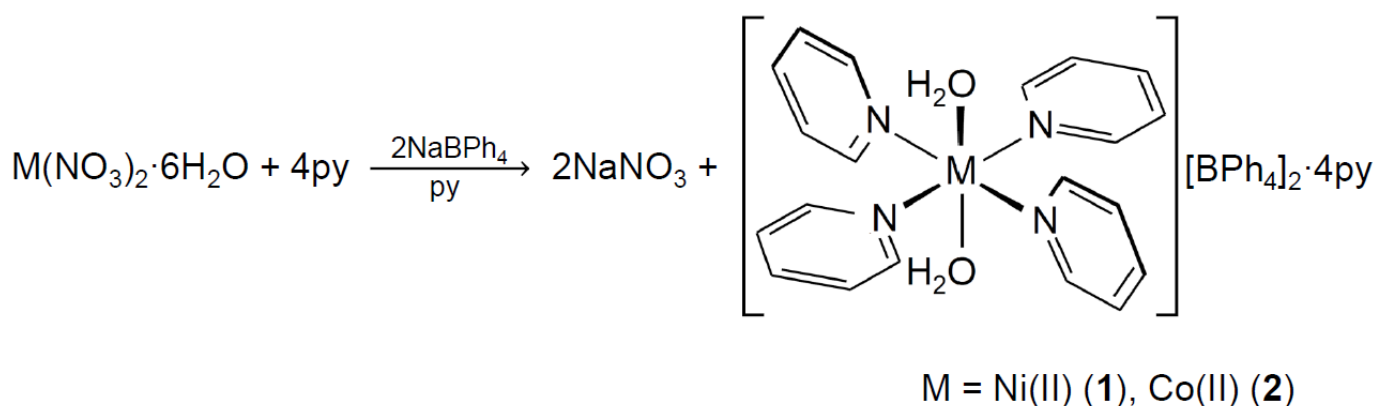


Figure 1. Chemical structures of pyridine and bipyridine complexes: (a) T_h symmetric $[M(py)_6]$ complex; (b) D_3 symmetric $[M(bpy)_3]$ complex.



Scheme 1. Synthetic scheme for 1 and 2.

2. Materials and Methods

2.1. Measurements

Elemental analyses (C, H, and N) were performed at the Elemental Analysis Service Centre of Kyushu University. IR spectra were recorded on a Jasco FT/IR-4100 FT-IR spectrometer. Magnetic susceptibility measurements were performed with a Quantum Design MPMS-7 SQUID magnetometer. The temperature dependence of the susceptibility was measured in the temperature range from 1.9 to 300 K with a static field of 5 kOe. Field dependence of the magnetization was measured in the field range from 0 to 50 kOe at 2 K. The polycrystalline samples were ground into fine powder in an agate mortar and densely packed in a gelatin capsule to prevent field-induced orientation of the powder particles. All data were corrected for diamagnetism of the capsule and the samples by means of Pascal's constants.

2.2. Materials

All the chemicals were commercial products and used as supplied. Pyridine, nickel(II) nitrate–water (1/6), cobalt(II) nitrate–water (1/6), 2-propanol were supplied by Nacalai Tesque Inc., Kyoto, Japan. Sodium tetraphenylborate was supplied by Dojindo Laboratories, Kumamoto, Japan.

2.3. Preparations

[Ni(H₂O)₂(py)₄][BPh₄]₂·4py 1. To a heated pyridine solution (2.0 mL) of Ni(NO₃)₂·6H₂O (0.29 g, 1.0 mmol) was added a heated pyridine solution (2.0 mL) of sodium tetraphenylborate (0.62 g, 2.0 mmol). After cooling, white precipitate (sodium nitrate) was removed by decantation. After adding 2-propanol (9.0 mL), pale blue microcrystals were obtained and recrystallized from pyridine/2-propanol to give blue crystals (Figure S1a). Yield 0.33 g (24%). The sample for elemental analysis was dried *in vacuo* over P₂O₅, and one pyridine molecule was found to be lost from the crystal structure. (Found: C, 77.20; H, 6.20; N, 7.70; Ni, 4.25%. Calc. for C₈₃H₇₉B₂N₇NiO₂ ([Ni(H₂O)₂(py)₄][BPh₄]₂·3py): C, 77.45; H, 6.20; N, 7.60; Ni, 4.55%). Selected IR data [$\tilde{\nu}$ /cm^{−1}] using KBr disk: 3056–2984, 1596, 1442, 1069, 1006, 751, 734, 703, 612.

[Co(H₂O)₂(py)₄][BPh₄]₂·4py 2. This complex was obtained similarly to complex 1, using Co(NO₃)₂·6H₂O as the metal source. The color of complex 2 was orange (Figure S1b). Yield 0.34 g (25%). The sample for elemental analysis was dried *in vacuo* over P₂O₅, and one pyridine molecule was found to be lost from the crystal structure. (Found: C, 77.35; H, 6.00; N, 7.65; Co, 4.60%. Calc. for C₈₃H₇₉B₂CoN₇O₂ ([Co(H₂O)₂(py)₄][BPh₄]₂·3py): C, 77.45; H, 6.20; N, 7.60; Co, 4.55%). Selected IR data [$\tilde{\nu}$ /cm^{−1}] using KBr disk: 3057–2985, 1597, 1442, 1069, 1006, 751, 735, 703, 612.

2.4. Crystallography

Single-crystal X-ray diffraction data were obtained with a Rigaku XtaLAB AFC11 diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). A single crystal was mounted with a glass capillary and flash-cooled with a cold N₂ gas stream. Data were processed using the CrysAlis Pro (1.171.39.43a, 2018) software packages. The structure was solved by intrinsic phasing methods using the SHELXT [12] software packages and refined on F^2 (with all independent reflections) using the SHELXL [13] software packages. The non-hydrogen atoms were refined anisotropically, and hydrogen atoms, except for those of water molecules were refined using the riding model. Hydrogen atoms for water molecules were located by Fourier difference map. The Cambridge Crystallographic Data Centre (CCDC) deposition numbers are included in Table 1.

Table 1. Crystallographic data and refinement parameters of 1 and 2.

Compound	Complex 1	Complex 2
Empirical formula	C ₈₈ H ₈₄ B ₂ N ₈ NiO ₂	C ₈₈ H ₈₄ B ₂ CoN ₈ O ₂
Formula weight	1365.96	1366.18
Crystal system	orthorhombic	orthorhombic
Space group	<i>Pna</i> 2 ₁	<i>Pna</i> 2 ₁
<i>a</i> /Å	28.4603(10)	28.5839(14)
<i>b</i> /Å	11.4004(5)	11.3675(5)
<i>c</i> /Å	22.6229(6)	22.6811(8)
<i>V</i> /Å ³	7340.2(5)	7369.7(6)
<i>Z</i>	4	4
Crystal dimensions/mm	0.24 × 0.14 × 0.12	0.22 × 0.17 × 0.10
<i>T</i> /K	100	100
λ /Å	0.71073	0.71073
ρ_{calcd} /g cm ^{−3}	1.236	1.231
μ /mm ^{−1}	0.320	0.288
<i>F</i> (000)	2888	2884
2 θ_{max} /°	55	55
No. of reflections measured	15,854	14,855
No. of independent reflections	11,529 ($R_{\text{int}} = 0.0651$)	9696 ($R_{\text{int}} = 0.1526$)
Data/restraints/parameters	15,854/5/926	14,855/5/926
$R1$ ($I > 2.00\sigma(I)$) ¹	0.0467	0.0786
$wR2$ (All reflections) ²	0.1012	0.1816
Goodness of fit indicator	1.006	0.992
Highest peak, deepest hole/e Å ^{−3}	0.250, −0.446	0.569, −0.873
CCDC deposition number	2219439	2219440

¹ $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$, ² $wR2 = [\sum (w(F_o^2 - F_c^2)^2) / \sum w(F_o^2)]^{1/2}$.

2.5. Computation

Magnetic analyses were conducted by MagSaki software series [14–17]; Magsaki(B) W0.7.9 was used for the nickel(II) complex, and Magsaki(A) W1.0.14 for the cobalt(II) complex. Angular overlap model (AOM) calculations were performed using the AOMX program.

3. Results and Discussion

3.1. Preparation of Complexes 1 and 2

A mononuclear nickel(II) complex, $[\text{Ni}(\text{H}_2\text{O})_2(\text{py})_4][\text{BPh}_4]_2 \cdot 4\text{py}$ (**1**), and a mononuclear cobalt(II) complex, $[\text{Co}(\text{H}_2\text{O})_2(\text{py})_4][\text{BPh}_4]_2 \cdot 4\text{py}$ (**2**), were newly synthesized in this study. In both the IR spectra of **1** and **2** (Figure 2a,b), two strong bands were observed at around 1442 and 1596–1597 cm^{-1} and were assigned to the ring stretching of the pyridine moiety, where the corresponding bands were observed at around 1430–1480 cm^{-1} and 1580–1600 cm^{-1} for the free pyridine ligand. The ring stretching bands of the tetraphenylborate anion were observed at around 1577, 1479, and 1425 cm^{-1} , which were close to those of NaBPh_4 (1578, 1478, and 1427 cm^{-1}). In both the IR spectra of **1** and **2**, the intense bands at around 703 and 735 cm^{-1} were characteristic of the tetraphenylborate anion. Both complexes were characterized by elemental analysis and a single-crystal X-ray diffraction study. It should be noted that pyridine molecules in the crystal structures were found to be easily lost by drying, heating, grinding, and the passage of time.

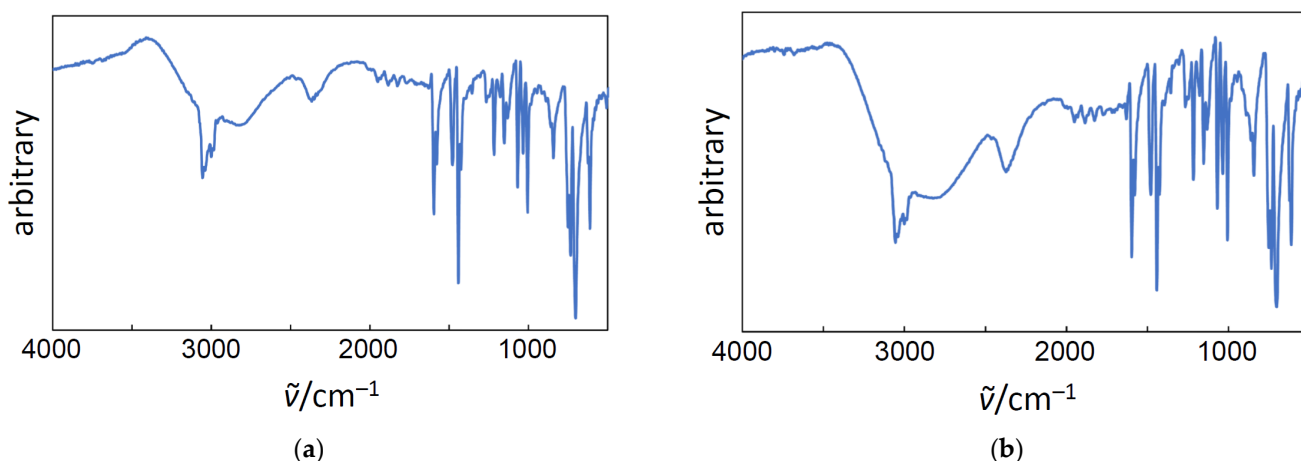


Figure 2. IR spectra of **1** and **2**: (a) $[\text{Ni}(\text{H}_2\text{O})_2(\text{py})_4][\text{BPh}_4]_2 \cdot 4\text{py}$ (**1**); (b) $[\text{Co}(\text{H}_2\text{O})_2(\text{py})_4][\text{BPh}_4]_2 \cdot 4\text{py}$ (**2**).

3.2. Crystal Structures of Complexes 1 and 2

Crystallographic data of $[\text{Ni}(\text{H}_2\text{O})_2(\text{py})_4][\text{BPh}_4]_2 \cdot 4\text{py}$ (**1**) and $[\text{Co}(\text{H}_2\text{O})_2(\text{py})_4][\text{BPh}_4]_2 \cdot 4\text{py}$ (**2**) are summarized in Table 1.

3.2.1. Crystal Structure of $[\text{Ni}(\text{H}_2\text{O})_2(\text{py})_4][\text{BPh}_4]_2 \cdot 4\text{py}$ (**1**)

Crystals of **1** consists of $[\text{Ni}(\text{H}_2\text{O})_2(\text{py})_4]^{2+}$ complex cations, tetraphenylborate anions ($[\text{BPh}_4]^-$), and pyridine molecules in a 1:2:4 molar ratio. The crystal structure of the $[\text{Ni}(\text{H}_2\text{O})_2(\text{py})_4]^{2+}$ complex cation is depicted in Figure 3, together with the surrounding four pyridine molecules. The selected bond distances and angles are summarized in Tables 2 and 3. In the complex cation, four pyridine and two aqua ligands coordinate to the central nickel(II) ion, forming an octahedral coordination geometry with N_4O_2 donor sets. The two aqua ligands are at the *trans* positions, and each aqua ligand is hydrogen-bonded to two pyridine molecules. The $\text{O} \cdots \text{N}$ distances in the hydrogen bonds fell in the range of 2.676(4)–2.763(5), which was shorter than the sum of traditional van der Waals radii (3.07 Å) [18]. In the *trans*- N_4O_2 coordination geometry, the Ni–O distances [2.028(3)–2.052(3) Å] were shorter than the Ni–N distances [2.157(3)–2.164(3) Å]. The shorter Ni–O distances are consistent with the hydrogen bonding with basic pyridine molecules, making the aqua

ligands similar to hydroxido ligands to some extent. Therefore, the axial ligand field is expected to be stronger than the equatorial ligand field.

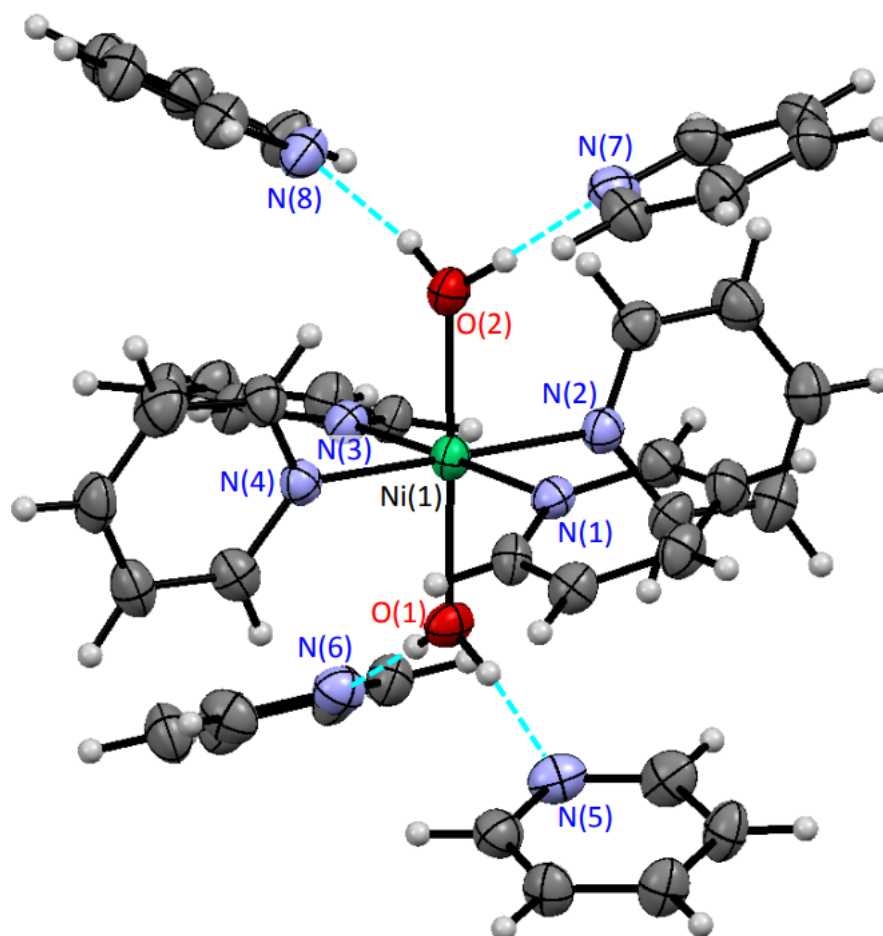


Figure 3. Crystal structure of $[\text{Ni}(\text{H}_2\text{O})_2(\text{py})_4]^{2+} \cdot 4\text{py}$ unit in **1**. Thermal ellipsoids are drawn at the 50% probability level.

Table 2. Selected distances for **1**.

Atom–Atom	Distance/Å	Atom–Atom	Distance/Å
Ni(1)–O(1)	2.052(3)	Ni(1)–O(2)	2.028(3)
Ni(1)–N(1)	2.163(3)	Ni(1)–N(2)	2.157(3)
Ni(1)–N(3)	2.164(3)	Ni(1)–N(4)	2.157(3)
O(1)···N(5)	2.726(4)	O(1)···N(6)	2.763(5)
O(2)···N(7)	2.687(4)	O(2)···N(8)	2.676(4)

Table 3. Selected angles for **1**.

Atom–Atom–Atom	Angle/°	Atom–Atom–Atom	Angle/°
O(1)–Ni(1)–O(2)	178.58(13)	O(1)–Ni(1)–N(1)	90.40(12)
O(1)–Ni(1)–N(2)	90.39(13)	O(1)–Ni(1)–N(3)	87.88(13)
O(1)–Ni(1)–N(4)	90.54(13)	O(2)–Ni(1)–N(1)	90.99(12)
O(2)–Ni(1)–N(2)	89.94(12)	O(2)–Ni(1)–N(3)	90.73(12)
O(2)–Ni(1)–N(4)	89.16(12)	N(1)–Ni(1)–N(2)	89.21(10)
N(1)–Ni(1)–N(3)	178.18(12)	N(1)–Ni(1)–N(4)	89.35(12)
N(2)–Ni(1)–N(3)	91.37(12)	N(2)–Ni(1)–N(4)	178.29(13)
N(3)–Ni(1)–N(4)	90.09(10)		

3.2.2. Crystal Structure of $[\text{Co}(\text{H}_2\text{O})_2(\text{py})_4][\text{BPh}_4]_2 \cdot 4\text{py}$ (2)

The crystal of **2** was found to be isomorphous to that of **1**. Crystals of **2** consist of $[\text{Co}(\text{H}_2\text{O})_2(\text{py})_4]^{2+}$ complex cations, tetraphenylborate anions, and pyridine molecules in a 1:2:4 molar ratio. The crystal structure of the $[\text{Co}(\text{H}_2\text{O})_2(\text{py})_4]^{2+}$ complex cation and four hydrogen-bonded pyridine molecules are shown in Figure 4. The selected bond distances and angles are summarized in Tables 4 and 5. The hydrogen bonds between the aqua ligand and pyridine molecules were confirmed by the $\text{O} \cdots \text{N}$ distances [2.676(8)–2.761(8) Å] shorter than the sum of traditional van der Waals radii (3.07 Å) [18]. The octahedral coordination geometry was tetragonally compressed along the $\text{O}-\text{Co}-\text{O}$ axis, with the $\text{Co}-\text{O}$ distances [2.016(4)–2.048(4) Å] shorter than the $\text{Co}-\text{N}$ distances [2.190(6)–2.221(6) Å]. The shorter $\text{Co}-\text{O}$ distances are consistent with the hydrogen bonding with basic pyridine molecules, enhancing the $\text{Co}-\text{O}$ coordination bonds. Therefore, as in **1**, the axial ligand field is expected to be stronger than the equatorial ligand field.

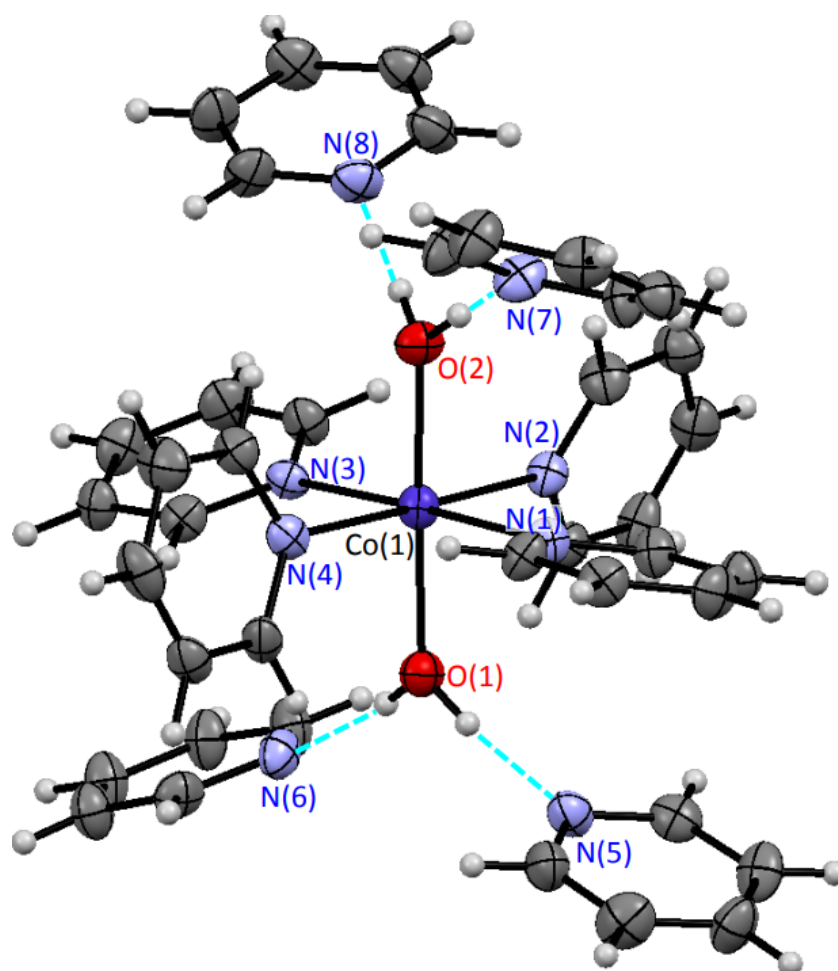


Figure 4. Crystal structure of $[\text{Co}(\text{H}_2\text{O})_2(\text{py})_4]^{2+} \cdot 4\text{py}$ unit in **2**. Thermal ellipsoids are drawn at the 50% probability level.

Table 4. Selected distances for **2**.

Atom–Atom	Distance/Å	Atom–Atom	Distance/Å
Co(1)–O(1)	2.048(4)	Co(1)–O(2)	2.016(4)
Co(1)–N(1)	2.218(6)	Co(1)–N(2)	2.213(6)
Co(1)–N(3)	2.221(6)	Co(1)–N(4)	2.190(6)
O(1) $\cdots$ N(5)	2.761(8)	O(1) $\cdots$ N(6)	2.716(8)
O(2) $\cdots$ N(7)	2.676(8)	O(2) $\cdots$ N(8)	2.682(8)

Table 5. Selected angles for **2**.

Atom–Atom–Atom	Angle/°	Atom–Atom–Atom	Angle/°
O(1)–Co(1)–O(2)	178.2(3)	O(1)–Co(1)–N(1)	87.9(2)
O(1)–Co(1)–N(2)	90.1(2)	O(1)–Co(1)–N(3)	90.0(2)
O(1)–Co(1)–N(4)	90.6(2)	O(2)–Co(1)–N(1)	90.4(2)
O(2)–Co(1)–N(2)	89.6(2)	O(2)–Co(1)–N(3)	91.7(2)
O(2)–Co(1)–N(4)	89.7(2)	N(1)–Co(1)–N(2)	91.9(2)
N(1)–Co(1)–N(3)	177.88(19)	N(1)–Co(1)–N(4)	89.64(18)
N(2)–Co(1)–N(3)	88.64(18)	N(2)–Co(1)–N(4)	178.4(2)
N(3)–Co(1)–N(4)	89.9(2)		

3.3. Magnetic Properties of Complexes **1** and **2**

3.3.1. Magnetic Properties of **1**

The temperature dependence of magnetic susceptibility (χ_A) and field-dependence of magnetization (M) were measured for **1**. The $\chi_A T$ vs. T plot and M vs. H plot are shown in Figure 5. The $\chi_A T$ value at 300 K was $1.33 \text{ cm}^3 \text{ K mol}^{-1}$, which was slightly larger than the spin-only value ($1.00 \text{ cm}^3 \text{ K mol}^{-1}$) for the $S = 1$ system. When decreasing the temperature, the $\chi_A T$ value was almost constant; but below 10 K, the value dropped to show the minimum ($0.90 \text{ cm}^3 \text{ K mol}^{-1}$) at 1.9 K. This behavior suggests very small intermolecular interaction with surrounding nickel(II) centers. In magnetization, the $M/N\beta$ value would saturate to 2.0, and this was consistent with the $S = 1$ system. The magnetic data were analyzed by the field-dependent magnetic susceptibility equations (Equations (1)–(6)) and the magnetization equations (Equations (7)–(10)) on the basis of the local Hamiltonian, $\mathbf{H} = g_u \beta S_u H_u + D[S_z^2 - S(S + 1)/3]$. In Equations (1)–(6), the axial zero-field splitting (D), temperature-independent paramagnetism (χ_{tip}), and intermolecular interaction (zJ) were considered. The field-dependent magnetization was simultaneously analyzed using Equations (7)–(10), considering the axial zero-field splitting and intermolecular interaction. In Equations (9) and (10), the integral for the powder average was approximated by the expanded sum [19,20]. Equations (1)–(10) are suitable in simultaneous analysis of magnetic susceptibility and magnetization even when $|D|$ is not so large.

$$\chi_z = \frac{N \left(g_z \beta \exp\left(\frac{-D+g_z \beta H}{kT}\right) - g_z \beta \exp\left(\frac{-D-g_z \beta H}{kT}\right) \right)}{H \left(1 + \exp\left(\frac{-D+g_z \beta H}{kT}\right) + \exp\left(\frac{-D-g_z \beta H}{kT}\right) \right)} + \chi_{\text{tip},z} \quad (1)$$

$$\chi_x = \frac{N \left(\frac{-2g_x^2 \beta^2}{\sqrt{4g_x^2 \beta^2 H^2 + D^2}} \exp\left(\frac{\sqrt{4g_x^2 \beta^2 H^2 + D^2} - D}{2kT}\right) + \frac{2g_x^2 \beta^2}{\sqrt{4g_x^2 \beta^2 H^2 + D^2}} \exp\left(\frac{-\sqrt{4g_x^2 \beta^2 H^2 + D^2} - D}{2kT}\right) \right)}{H \left(\exp\left(\frac{-D}{kT}\right) + \exp\left(\frac{\sqrt{4g_x^2 \beta^2 H^2 + D^2} - D}{2kT}\right) + \exp\left(\frac{-\sqrt{4g_x^2 \beta^2 H^2 + D^2} - D}{2kT}\right) \right)} + \chi_{\text{tip},x} \quad (2)$$

$$\chi_{\text{av}} = \frac{\chi_z + 2\chi_x}{3} \quad (3)$$

$$\chi_A = \frac{\chi_{\text{av}} T}{T - zJ(\chi_{\text{av}} / (Ng_{\text{av}}^2 \beta^2))} \quad (4)$$

$$\chi_{A,z} = \frac{\chi_z T}{T - zJ(\chi_{\text{av}} / (Ng_{\text{av}}^2 \beta^2))} \quad (5)$$

$$\chi_{A,x} = \frac{\chi_x T}{T - zJ(\chi_{\text{av}} / (Ng_{\text{av}}^2 \beta^2))} \quad (6)$$

$$M_z = \frac{N \left(g_z \beta \exp\left(\frac{-D+g_z \beta H}{kT}\right) - g_z \beta \exp\left(\frac{-D-g_z \beta H}{kT}\right) \right)}{1 + \exp\left(\frac{-D+g_z \beta H}{kT}\right) + \exp\left(\frac{-D-g_z \beta H}{kT}\right)} \quad (7)$$

$$M_x = \frac{N \left(\frac{-2g_x^2\beta^2}{\sqrt{4g_x^2\beta^2H^2+D^2}} \exp\left(\frac{\sqrt{4g_x^2\beta^2H^2+D^2}-D}{2kT}\right) + \frac{2g_x^2\beta^2}{\sqrt{4g_x^2\beta^2H^2+D^2}} \exp\left(\frac{-\sqrt{4g_x^2\beta^2H^2+D^2}-D}{2kT}\right) \right)}{\exp\left(\frac{-D}{kT}\right) + \exp\left(\frac{\sqrt{4g_x^2\beta^2H^2+D^2}-D}{2kT}\right) + \exp\left(\frac{-\sqrt{4g_x^2\beta^2H^2+D^2}-D}{2kT}\right)} \quad (8)$$

$$M_\theta(\theta) = \frac{M_z \left(\cos\left(\frac{(\theta-0.5)\pi}{180}\right) \right)^2 + M_x \left(\sin\left(\frac{(\theta-0.5)\pi}{180}\right) \right)^2}{\left| M_z \left(\cos\left(\frac{(\theta-0.5)\pi}{180}\right) \right)^2 + M_x \left(\sin\left(\frac{(\theta-0.5)\pi}{180}\right) \right)^2 \right|} \sqrt{M_z^2 \left(\cos\left(\frac{(\theta-0.5)\pi}{180}\right) \right)^2 + M_x^2 \left(\sin\left(\frac{(\theta-0.5)\pi}{180}\right) \right)^2} \quad (9)$$

$$M_{av} = \sum_{\theta=1}^{90} M_\theta(\theta) \left(\cos\left(\frac{(\theta-1)\pi}{180}\right) - \cos\left(\frac{\theta\pi}{180}\right) \right) \quad (10)$$

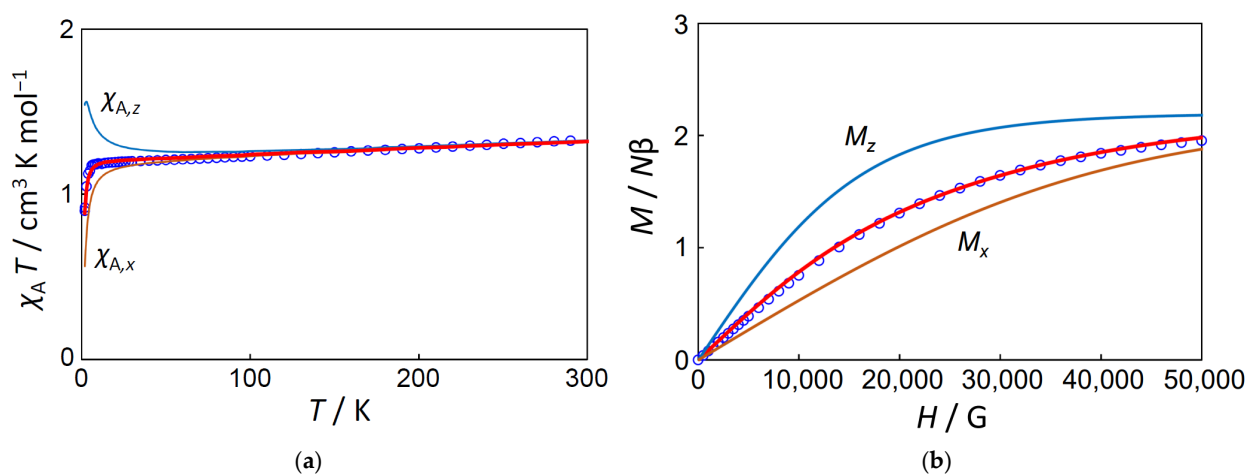


Figure 5. The $\chi_A T$ vs. T plot and M vs. H plot for **1**. The observed data (○) and theoretical curves (— for average, — for the z component, and — for the x component) with the best-fitting parameter set ($g, D, zJ, \chi_{\text{tip}}$) = (2.19, -3.5 cm^{-1} , -0.40 cm^{-1} , $398 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$). (a) The $\chi_A T$ vs. T plot; (b) The M vs. H plot.

In the magnetic analysis, the g -anisotropy and the χ_{tip} -anisotropy were not considered. As a result of the simultaneous analysis, the best-fitting parameter set was obtained as ($g, D, zJ, \chi_{\text{tip}}$) = (2.19, -3.5 cm^{-1} , -0.40 cm^{-1} , $398 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$). The small but negative D value suggests that the axial ligand field is stronger than the equatorial ligand field [21]. This is consistent with the *trans*- Ni_4O_2 coordination geometry with two aqua ligands whose ligand fields were enhanced by the hydrogen-bonded pyridine as a base. In both the $\chi_A T$ vs. T plot (Figure 5a) and the M vs. H plot (Figure 5b), the theoretical z components are larger than the theoretical x components. However, the anisotropy was not so large, and the g -anisotropy was not obvious in the present magnetic measurements. Compared with the observed D value with other nickel(II) complexes, the magnitude was consistent with others [21]. For related $[\text{Ni}(\text{py})_4\text{Cl}_2]$ and $[\text{Ni}(\text{py})_4\text{Br}_2]$ complexes with weak axial ligands, positive D values (4.8 and 6.9 cm^{-1} , respectively) were observed [22], and this was consistent with complex **1** with strong axial ligands showing a negative D value.

3.3.2. Magnetic Properties of $[\text{Co}(\text{H}_2\text{O})_2(\text{py})_4][\text{BPh}_4]_2 \cdot 4\text{py}$ (**2**)

The temperature dependence of magnetic susceptibility (χ_A) and field-dependence of magnetization (M) were measured for **2** (Figure 6). The $\chi_A T$ value at 300 K ($3.33 \text{ cm}^3 \text{ K mol}^{-1}$) was much larger than the spin-only value ($1.88 \text{ cm}^3 \text{ K mol}^{-1}$) for the $S = 3/2$ system, but was close to the theoretical value ($3.38 \text{ cm}^3 \text{ K mol}^{-1}$) for the uncoupled $S = 3/2$ and $L = 3$ system, suggesting the orbital contribution in the octahedral high-spin state. When decreasing the temperature, the $\chi_A T$ value gradually decreased; and below 10 K, the value slightly dropped to the minimum ($2.23 \text{ cm}^3 \text{ K mol}^{-1}$) at 1.9 K. Judging from the

$\chi_A T$ slope and minimum $\chi_A T$ value, the temperature-dependent behavior was found to be typical of spin-orbit splitting with the negative axial splitting parameter, Δ [23], defined in the Hamiltonian, $\mathbf{H} = \Delta(\mathbf{L}_z^2 - 2/3) - (3/2)\kappa\lambda\mathbf{L}\cdot\mathbf{S} + \beta[-(3/2)\kappa\mathbf{L}_u + g_e \mathbf{S}_u]\cdot\mathbf{H}_u$ ($u = x, y, z$) [24], suggesting very small intermolecular interactions. In magnetization, the $M/N\beta$ value was going to saturate to ~ 2.3 , which was consistent with the effective $1/2$ spin system with the g -factor of ~ 4.3 , resulting in the spin-orbit coupling in the octahedral high-spin cobalt(II) complexes. The magnetic data were analyzed by the magnetic susceptibility equations (Equations (11)–(16)) [14,15,25,26] and magnetization equations (Equations (9), (10), (17) and (18)) [19,20,23], considering the spin-orbit coupling (λ), orbital reduction factor (κ), axial distortion (Δ), and intermolecular interaction. In Equations (11)–(16), the intermolecular interaction was considered using the Weiss constant, θ , which can be converted to zJ . Twelve microstates ($n = \pm 1 - \pm 6$) originate from the 4T_1 term were considered, and their zero-field energies ($E_n^{(0)}$), first-order Zeeman coefficients ($E_{n,u}^{(1)}$) and second-order Zeeman coefficients ($E_{n,u}^{(2)}$) ($u = z, x$) were used [15,25] in the equations. It should be noted that the admixing effect is included in the parameter κ [24,25]. For the powder average of the principal magnetization (Equations (17) and (18)), expanded equations (Equations (9) and (10)) [19,20] were used. In considering the intermolecular interaction in the magnetization simulation, the $T - \theta$ value was used instead of T , because the slope ($\partial M/\partial H$) of magnetization, approximated with $\chi T/(T - \theta)$, can be further approximated by χ at $(T - \theta)$ K.

$$\chi_A = \frac{\chi_z + 2\chi_x}{3} \quad (11)$$

$$\chi_z = N \frac{F_1}{F_2} + \chi_{\text{tip}} \quad (12)$$

$$\chi_x = N \frac{F_3}{F_2} + \chi_{\text{tip}} \quad (13)$$

$$F_1 = \sum_{n=\pm 1} \left(\frac{E_{z,n}^{(1)2}}{k(T-\theta)} - 2E_{z,n}^{(2)} \right) \exp\left(\frac{-E_n^{(0)}}{kT}\right) + \sum_{n \neq \pm 1} \left(\frac{E_{z,n}^{(1)2}}{kT} - 2E_{z,n}^{(2)} \right) \exp\left(\frac{-E_n^{(0)}}{kT}\right) \quad (14)$$

$$F_2 = \sum_n \exp\left(\frac{-E_n^{(0)}}{kT}\right) \quad (15)$$

$$F_3 = \sum_{n=\pm 1} \left(\frac{E_{x,n}^{(1)2}}{k(T-\theta)} - 2E_{x,n}^{(2)} \right) \exp\left(\frac{-E_n^{(0)}}{kT}\right) + \sum_{n \neq \pm 1} \left(\frac{E_{x,n}^{(1)2}}{kT} - 2E_{x,n}^{(2)} \right) \exp\left(\frac{-E_n^{(0)}}{kT}\right) \quad (16)$$

$$M_z = \frac{N \sum_n \left(-E_{n,z}^{(1)} - 2E_{n,z}^{(2)} H \right) \left(-\frac{E_n^{(0)} + E_{n,z}^{(1)} H + E_{n,z}^{(2)} H^2}{kT} \right)}{\sum_n \left(-\frac{E_n^{(0)} + E_{n,z}^{(1)} H + E_{n,z}^{(2)} H^2}{kT} \right)} \quad (n = \pm 1 - \pm 6) \quad (17)$$

$$M_x = \frac{N \sum_n \left(-E_{n,x}^{(1)} - 2E_{n,x}^{(2)} H \right) \left(-\frac{E_n^{(0)} + E_{n,x}^{(1)} H + E_{n,x}^{(2)} H^2}{kT} \right)}{\sum_n \left(-\frac{E_n^{(0)} + E_{n,x}^{(1)} H + E_{n,x}^{(2)} H^2}{kT} \right)} \quad (n = \pm 1 - \pm 6) \quad (18)$$

The best-fitting parameter set was obtained as $(\lambda, \kappa, \Delta, zJ [\theta]) = (-142 \text{ cm}^{-1}, 0.90, -1670 \text{ cm}^{-1}, -1.4 \text{ cm}^{-1} [-0.23 \text{ K}])$. The negative Δ value is consistent with the above estimation from the $\chi_A T$ vs. T curve, and the negative Δ value indicates that the 4E state generated from the 4T_1 ground term by tetragonal distortion is lower than the 4A_2 state in the D_4 symmetry of the *trans*- N_4O_2 geometry. The magnitude of Δ was slightly larger than other octahedral high-spin cobalt(II) complexes ($-1200 \sim +730 \text{ cm}^{-1}$) [27]. In both the $\chi_A T$ vs. T plot (Figure 6a) and the M vs. H plot (Figure 6b), the theoretical z components are larger than the theoretical x components. From the best-fitting parameter set, the g_z and g_x

values were calculated as 8.20 and 1.28, respectively. The average g value was calculated as 4.85, indicating the saturated magnetization value of 2.4 for the effective $1/2$ spin state. This saturation value is consistent with the observed magnetization.

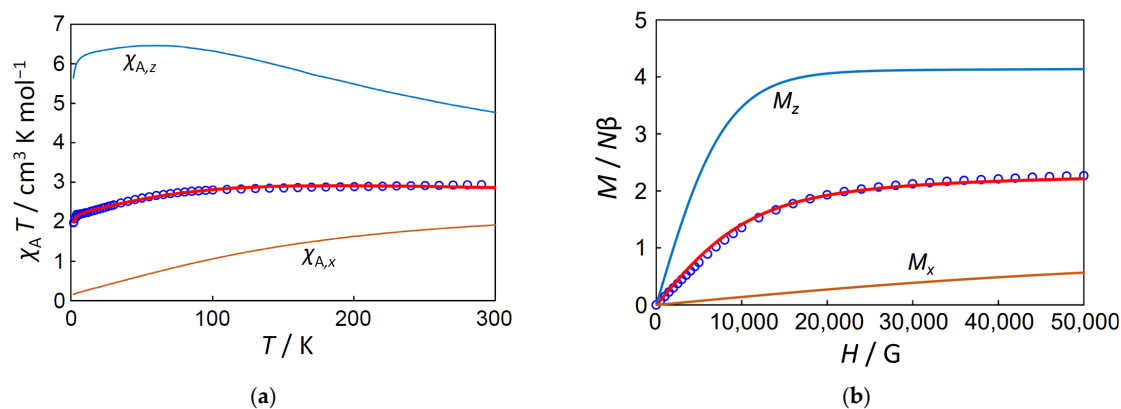


Figure 6. The $\chi_A T$ vs. T plot and M vs. H plot for **2**. The observed data ($\circ$) and theoretical curves (— for average, — for the z component, and — for the x component) with the best-fitting parameter set $(\lambda, \kappa, \Delta, zJ[\theta]) = (-142 \text{ cm}^{-1}, 0.90, -1670 \text{ cm}^{-1}, -1.4 \text{ cm}^{-1} [-0.23 \text{ K}])$. (a) The $\chi_A T$ vs. T plot; (b) The M vs. H plot.

Here, we discuss the reason for the negative Δ value of **2** on the basis of the structure. As discussed in Section 3.2.2, the donation of the *trans*-aqua ligands is enhanced by the hydrogen-bonded pyridine molecules in crystals. At the same time, the π -orbital effect of the aqua ligands is expected to be also enhanced, because both the σ and π angular overlap model (AOM) parameters of hydroxide ligand are found to be stronger than those of aqua ligand [28,29]. Also, the σ and π AOM parameters for py ligands are weaker than those of aqua ligands [28,29]. The energy level diagram for the quartet spin states of octahedral high-spin cobalt(II) complexes is shown in Figure 7 with respect to the enhancement of the axial π AOM parameter, $e_{\pi,ax}$. When the $e_{\pi,ax}$ parameter is zero, the diagram is set to be the perfect O symmetry, and when the $e_{\pi,ax}$ parameter becomes larger, the axial π effect becomes stronger in the D_4 symmetry. This π -orbital effect on the splitting of the 4T_1 ground state is more significant than that of the σ -orbital effect, reported previously [23]. In this way, as shown in Figure 7, the enhancement of the axial π -orbital effect makes the 4E state lower than the 4A_2 state, affording the negative Δ value.

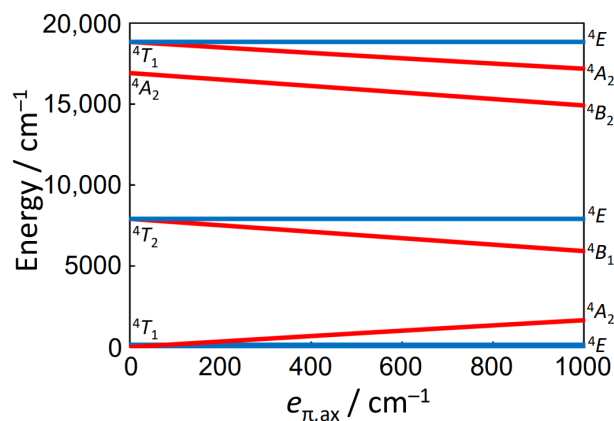


Figure 7. Energy level diagram for octahedral high-spin cobalt(II) complexes with respect to the enhancement of $e_{\pi,ax}$. Racah and AOM parameters: $B = 800 \text{ cm}^{-1}$, $C = 3200 \text{ cm}^{-1}$, $e_{\sigma,av} = 3000 \text{ cm}^{-1}$.

3.4. Structural Consideration for Diaquatetrapyridine Complexes

In the case of crystallographically characterized $[\text{Fe}(\text{py})_6]^{2+}$ complex cation [4], the symmetry was T_h , and the T_h symmetric complex was found to be the only possible

structure for the $[\text{Mg}(\text{py})_6]^{2+}$ complex cation by a theoretical study [30]. This is because the T_h symmetric structure is the best suited to avoid steric repulsion between the bulky py ligands at *cis* positions. In this way for the $[\text{MX}_2(\text{py})_4]$ complex (X: small monoatomic ligand), the *trans*- D_{2h} structure is considered to be the best [31]. When X is replaced with H_2O , however, the symmetry decreases due to the coordination nature of the aqua ligand, and the four py ligands at the equatorial sites are expected to be twisted as observed in the crystal structures of **1** and **2**. When pyridine molecules are hydrogen-bonding to the aqua ligands at the axial positions, the coordination of the aqua ligands will be strengthened, and the twist of the equatorial py ligands is expected to be enhanced.

4. Conclusions

In this study, new py complexes, $[\text{Ni}(\text{H}_2\text{O})_2(\text{py})_4][\text{BPh}_4]_2 \cdot 4\text{py}$ (**1**) and $[\text{Co}(\text{H}_2\text{O})_2(\text{py})_4][\text{BPh}_4]_2 \cdot 4\text{py}$ (**2**) were synthesized and structurally characterized. In crystals, both complex cations were found to have octahedral *trans*- N_2O_4 coordination geometry, and the coordination of the *trans*-aqua ligands was found to be enhanced by the hydrogen-bonded pyridine molecules as a base. In the simultaneous analysis of magnetic susceptibility and magnetization, both complexes **1** and **2** were found to show strong magnetism in one direction ($\chi_z > \chi_x, \chi_y$; $M_z > M_x, M_y$), and this was explained by the enhancement of the axial aqua ligands. In the nickel(II) complex, the strong axial ligand field was found to cause the negative zero-field splitting ($D < 0$), while in the cobalt(II) complex, the strong axial π -orbital effect was found to cause the negative ligand field splitting (Δ).

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/magnetochemistry9010014/s1>, Figure S1: Crystals of **1** and **2**: (a) $[\text{Ni}(\text{H}_2\text{O})_2(\text{py})_4][\text{BPh}_4]_2 \cdot 4\text{py}$ (**1**); (b) $[\text{Co}(\text{H}_2\text{O})_2(\text{py})_4][\text{BPh}_4]_2 \cdot 4\text{py}$ (**2**).

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