# **Electronic Supplementary Information**

## An Unexpected Role of the Monodentate Ligand in Photocatalytic

## Hydrogen Production of the Pentadentate Ligand-based Cobalt

## Complexes

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#### **Experimental Section**

#### Materials

CoCl<sub>2</sub>·6H<sub>2</sub>O, ascorbic acid (H<sub>2</sub>A), AgNO<sub>3</sub>, and AgSO<sub>3</sub>CF<sub>3</sub> were purchased from Alfa Aesar and used as received. [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub> and 2-picolyl chloride hydrochloride was purchased from Sigma-Aldrich. Di(2-pyridyl) ketone oxime was purchased from TCI. All solvents were of analytical purity and used without further treatment. Distilled water was used in all experiments. *Trans*-[Co(Py)<sub>4</sub>Cl<sub>2</sub>]Cl·6H<sub>2</sub>O,<sup>1</sup> di(2-pyridyl) methylamine<sup>2</sup> and 1,1-di(pyridin-2-yl)-*N*,*N*-bis(pyridin-2-ylmethyl)methanamine (N4Py)<sup>3</sup> were prepared by literature methods.

#### Synthesis

[Co(N4Py)Cl]Cl<sub>2</sub> (**1**). *Trans*-[Co(Py)<sub>4</sub>Cl<sub>2</sub>]Cl·6H<sub>2</sub>O (59 mg) was added to a solution of N4Py (37 mg) in CH<sub>2</sub>Cl<sub>2</sub> (5 mL). The mixture was stirred for 60 min and the formed pink solid was isolated by filtration. Yield, 81%. Single crystals of **1** suitable for X-ray crystallographic analysis were obtained by recrystallization of the pink precipitate from EtOH with Et<sub>2</sub>O vapor diffusion. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>OD) δ: 9.47 (d, J = 5.7 Hz, 2H), 8.93 (d, J = 5.3 Hz, 2H), 8.27 (q, J = 7.6 Hz, 4H), 8.01 (t, J = 7.7 Hz, 2H), 7.65 (ddd, J = 12.3, 10.3, 4.2 Hz, 4H), 7.44 (d, J = 7.9 Hz, 2H), 6.96 (s, 1H), 5.18 (dd, J = 45.5, 18.4 Hz, 4H), Figure S1. HR ESI-MS: 460.07326 (Calcd m/z for (C<sub>23</sub>H<sub>20</sub>ClCoN<sub>5</sub>)<sup>+</sup> (M-2Cl<sup>-</sup>-H<sup>+</sup>)<sup>+</sup>: 460.07392), Figure S2. Anal. Calcd for C<sub>23</sub>H<sub>21</sub>Cl<sub>3</sub>CoN<sub>5</sub>·6H<sub>2</sub>O: C, 43.13; H, 5.19; N, 10.93. Found: C, 43.01; H, 5.04; N, 11.00.

 $[Co(N4Py)(NO_3)](NO_3)_2$  (2). To a solution of 1 (26 mg, 0.05 mmol) in 5 mL H<sub>2</sub>O was added dropwise a solution of AgNO<sub>3</sub> (25 mg, 0.15 mmol) in 5 mL of H<sub>2</sub>O. The reaction mixture was refluxed overnight. The formed precipitate was filtered, re-dissolved in minimum amount of methanol, washed with diethyl ether, and dried under vacuum to get the pale brown solid. Yield, 86%. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>OD)  $\delta$ : 9.04 (d, J = 5.7 Hz, 2H), 8.59 (d, J = 5.7 Hz, 2H), 8.31 (m, 4H), 8.08 (t, J = 7.5 Hz, 2H), 7.81 (d, J = 7 Hz, 2H), 7.64 (d, J = 3.3 Hz, 2H), 7.45 (d, J = 7.8 Hz, 2H), 6.85 (s, 1H), 5.01 (dd, J = 37, 14.8 Hz, 4H), Figure S1. HR ESI-MS: 488.09934 (Calcd m/z for (C<sub>23</sub>H<sub>21</sub>CoN<sub>6</sub>O<sub>3</sub>)<sup>+</sup> (M-2NO<sub>3</sub><sup>-</sup> +e<sup>-</sup>)<sup>+</sup>: 488.10071), Figure S2. Anal. Calcd for C<sub>23</sub>H<sub>21</sub>CoN<sub>8</sub>O<sub>9</sub>: C, 45.11; H, 3.46; N, 18.30. Found: C, 45.00; H, 3.60; N, 18.17.

[Co(N4Py)(CF<sub>3</sub>SO<sub>3</sub>)](CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub> (**3**). To a solution of **1** (15.9 mg, 0.03 mmol) in 5 mL MeOH was added dropwise a solution of Ag(CF<sub>3</sub>SO<sub>3</sub>) (25 mg, 0.1 mmol) in 5 mL of MeOH. The reaction mixture was refluxed overnight. The formed precipitate was filtered, re-dissolved in minimum amount of methanol, washed with diethyl ether, and dried under vacuum to get the pale brown solid. Yield, 70%. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>OD)  $\delta$ : 8.89 (d, J = 5.7 Hz, 2H), 8.71 (d, J = 5.6 Hz, 2H), 8.48-8.32 (m, 4H), 8.13 (t, J = 7.8 Hz, 2H), 7.95-7.72 (m, 4H), 7.49 (d, J = 7.8 Hz, 2H), 6.74 (s, 1H), 5.03 (s, 4H), Figure S1. HR ESI-MS: 575.06698, 592.06886 (Calcd m/z for (C<sub>24</sub>H<sub>21</sub>CoF<sub>3</sub>N<sub>5</sub>O<sub>3</sub>S)<sup>+</sup> (M-2CF<sub>3</sub>SO<sub>3</sub><sup>-</sup> + e<sup>-</sup>)<sup>+</sup> 575.06492 and (C<sub>24</sub>H<sub>22</sub>CoF<sub>3</sub>N<sub>5</sub>O<sub>4</sub>S)<sup>+</sup> (M-2CF<sub>3</sub>SO<sub>3</sub><sup>-</sup> + OH<sup>-</sup>)<sup>+</sup> 592.06766), Figure S2. Anal. Calcd for C<sub>26</sub>H<sub>21</sub>CoF<sub>9</sub>N<sub>5</sub>O<sub>9</sub>S<sub>3</sub>·2H<sub>2</sub>O: C, 34.33; H, 2.77; N, 7.70. Found: C, 34.30; H, 2.69; N, 7.75.

[Co(N4Py)(H<sub>2</sub>O)](CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub> (**4**). To a solution of **1** (15.9 mg, 0.03 mmol) in 5 mL H<sub>2</sub>O was added dropwise a solution of Ag(CF<sub>3</sub>SO<sub>3</sub>) (25 mg, 0.1 mmol) in 5 mL of H<sub>2</sub>O. The reaction mixture was refluxed overnight. The formed precipitate was filtered, re-dissolved in minimum amount of methanol, washed with diethyl ether, and dried under vacuum to get the brown solid. Yield, 81%. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>OD)  $\delta$ : 8.94 (d, J = 5.6 Hz, 2H), 8.73 (d, J = 5.7 Hz, 2H), 8.39 (dt, J = 15.2, 7.6 Hz 4H), 8.14 (t, J = 7.7 Hz, 2H), 7.83 (dt, J = 13.1, 6.3 Hz 4H), 7.51 (d, J = 7.7 Hz, 2H), 6.78 (s, 1H), 5.17-4.99 (m, 4H), Figure S1. HR ESI-MS: 221.55781, 592.06896 (Calcd m/z for (C<sub>23</sub>H<sub>22</sub>CON<sub>5</sub>O)<sup>2+</sup>

 $(M-3CF_3SO_3^--H^+)^{2+}$  221.55782 and  $(C_{24}H_{22}CoF_3N_5O_4S)^+$   $(M-2CF_3SO_3^--H^+)^+$  592.06766), Figure S2. Anal. Calcd for  $C_{26}H_{23}CoF_9N_5O_9S_3\cdot 2.5H_2O$ : C, 33.34; H, 3.01; N, 7.48. Found: C, 33.27; H, 3.10; N, 7.41.

#### Instrumentation

<sup>1</sup>H NMR spectra were obtained on a Bruker DMX-400 MHz spectrophotometer. High-resolution mass spectrometry (HR-MS) spectra were determined on a Brucker APEX IV (7.0 T) FT\_MS. The dynamic light scattering measurements were operated on Dybapro NanoStar (Wyatt Technology). UV–vis absorption spectra were recorded on a Shimadzu UV-2450 spectrophotometer. Fluorescence emission spectra were taken on a Hitachi F-4600 fluorescence spectrophotometer. The redox potentials in acetonitrile were measured on an EG&G Model 283 Potentiostat/Galvanostat in a three-electrode cell with a glassy carbon working electrode, a platinum-plate counter electrode, and a SCE (saturated calomel electrode) reference electrode, using 0.1 M tetra-*n*-butylammonium hexafluorophosphate as supporting electrolyte. Before each scan the glassy carbon electrode was polished using a 0.05 μm polycrystalline diamond suspension and rinsed with acetone.

#### H<sub>2</sub> Evolution Experiments

A total of 10 mL of aqueous solution containing optimized concentrations of PS (photosensitizer), WRC (water reduction catalyst), and SR (sacrificial reductant) was put into a 40 mL glass vial equipped with a rubber-septum-sealed outlet. After bubbling with argon for 25 min, 3 mL of methane was injected into the reaction vessel to serve as the internal standard for H<sub>2</sub> quantification. Then the vial was irradiated with visible light, which was obtained from a 1000 W solar simulator (Oriel 91192) using a 400-nm-long pass glass filter and a distilled water pool to cut off the UV and IR light. The production of H<sub>2</sub> was monitored and quantified by gas chromatography on a Shimadzu GC-2014 (thermal conductivity detector, 5 Å molecular sieve, 30 m × 0.53 mm column, N<sub>2</sub> gas carrier).

Photocatalytic reactions were carried out in varied conditions (Figure S3) to select a proper PS to match the combination of **1** and ascorbic acid, serving as WRS and SR, respectively. More experiments were performed to find the optimal concentrations of  $[Ru(bpy)_3]^{2+}$ , **1**, and ascorbic acids, as well as the more suitable medium and initial pH, for maximizing the H<sub>2</sub> evolution volume (Figure S4-S9).



**Scheme S1.** General reaction mechanisms for the Co complex-based catalytic proton reduction and the chemical structure of a cobaloxime hydride as an example of Co(III)H intermediate.





Figure S1. <sup>1</sup>H NMR spectra of 1 (a), 2 (b), 3 (c), and 4(d) in  $CD_3OD$ .

а









d



Figure S2. High resolution mass spectra of 1 (a), 2 (b), 3 (c) and 4(d).



**Figure S3**. Molecular structure of **1** with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.



**Figure S4.** Photocatalytic H<sub>2</sub> production over time of the multi-component systems containing 50  $\mu$ M **1**, 0.1 M ascorbic acid, and 100  $\mu$ M different PS in aqueous solutions.



**Figure S5.** Photocatalytic H<sub>2</sub> production over time of the multi-component system containing 100  $\mu$ M [Ru(bpy)<sub>3</sub>]<sup>2+</sup>, 50  $\mu$ M **1**, and 0.1 M ascorbic acid in aqueous solutions with varied initial pH.



**Figure S6.** Photocatalytic H<sub>2</sub> production over time of the multi-component system containing 100  $\mu$ M [Ru(bpy)<sub>3</sub>]<sup>2+</sup>, 50  $\mu$ M **1**, and 0.1 M ascorbic acid in water or 1:1 organic solvent/water.



**Figure S7**. Photocatalytic H<sub>2</sub> production over time of the multi-component systems containing 100  $\mu$ M [Ru(bpy)<sub>3</sub>]<sup>2+</sup>, 0.1 M ascorbic acid, and varied concentrations of **1** in water.



**Figure S8**. Photocatalytic H<sub>2</sub> production over time of the multi-component systems containing 50  $\mu$ M **1**, 0.1 M ascorbic acid, and varied concentrations of [Ru(bpy)<sub>3</sub>]<sup>2+</sup> in water.

![](_page_9_Figure_2.jpeg)

**Figure S9**. Photocatalytic H<sub>2</sub> production over time of the multi-component systems containing 100  $\mu$ M [Ru(bpy)<sub>3</sub>]<sup>2+</sup>, 50  $\mu$ M **1**, and varied concentrations of ascorbic acid in water.

![](_page_10_Figure_0.jpeg)

**Figure S10.** Particle size distribution of the aqueous solution containing 100  $\mu$ M [Ru(bpy)<sub>3</sub>]<sup>2+</sup>, 50  $\mu$ M **1**, and 0.1 M ascorbic acid before (a) and after (b) irradiation of 2 h.

![](_page_10_Figure_2.jpeg)

**Figure S11**. Absorption spectra of the system containing 100  $\mu$ M [Ru(bpy)<sub>3</sub>]<sup>2+</sup>, 50  $\mu$ M **1**, and 0.1 M ascorbic acid in aqueous solution at initial pH 4 upon irradiation. The observed changes are mainly due to the damage of [Ru(bpy)<sub>3</sub>]<sup>2+</sup>.

![](_page_11_Figure_0.jpeg)

**Figure S12.** Photocatalytic H<sub>2</sub> production over time of the multi-component system containing 100  $\mu$ M [Ru(bpy)<sub>3</sub>]<sup>2+</sup>, 50  $\mu$ M **2**, and 0.1 M ascorbic acid in different electrolyte solutions with initial pH of 4.0.

![](_page_11_Figure_2.jpeg)

**Figure S13.** Photocatalytic H<sub>2</sub> production over time of the multi-component system containing 100  $\mu$ M [Ru(bpy)<sub>3</sub>]<sup>2+</sup>, 50  $\mu$ M **3**, and 0.1 M ascorbic acid in different electrolyte solutions with initial pH of 4.0.

![](_page_12_Figure_0.jpeg)

**Figure S14.** Photocatalytic H<sub>2</sub> production over time of the multi-component system containing 100  $\mu$ M [Ru(bpy)<sub>3</sub>]<sup>2+</sup>, 50  $\mu$ M **4**, and 0.1 M ascorbic acid in different electrolyte solutions with initial pH of 4.0.

![](_page_12_Figure_2.jpeg)

**Figure S15.** Photocatalytic H<sub>2</sub> production over time of the multi-component system containing 100  $\mu$ M [Ru(bpy)<sub>3</sub>]<sup>2+</sup>, 50  $\mu$ M **1**, and 0.1 M ascorbic acid with different electrolytes in 9:1 H<sub>2</sub>O/DMF solutions with initial pH of 4.0.

	V(H <sub>2</sub> ) in water (mL) <sup>a</sup>	V(H <sub>2</sub> ) in 0.3 M NaCl (mL)ª	V(H <sub>2</sub> ) in 0.1 M Na <sub>2</sub> SO <sub>4</sub> (mL) <sup>a</sup>	V(H <sub>2</sub> ) in 0.3 M NaSO <sub>3</sub> CF <sub>3</sub> (mL) <sup>a</sup>	V(H₂) in 0.3 M NaClO₄ (mL)ª	V(H <sub>2</sub> ) in 0.3 M NaNO <sub>3</sub> (mL)ª	E <sub>co(III)/Co(II)</sub> (V, vs SCE) <sup>b</sup>	E <sub>Co(II)/Co(I)</sub> (V, vs SCE) <sup>b</sup>
Complex 1	0.165	0.328	0.239	0.182	0.065	0.005	0.14	-1.46
Complex <b>2</b>	0.0305	0.0349	0.0326				-0.050	-1.25
Complex 3	0.114	0.192	0.139	0.145			-0.027	-1.23
Complex 4	0.114	0.192	0.139	0.145			0.10	-1.44

Table S1. Photocatalytic hydrogen production and electrochemical data for complex 1-4.

a. Data obtained after 3 h irradiation.

b. Peak potentials determined by cyclic voltammetry in anhydrous and deoxygenated CH<sub>3</sub>CN solution.

![](_page_13_Figure_4.jpeg)

**Figure S16.** <sup>1</sup>H NMR spectra of 2-picolyl chloride hydrochloride (20 mM) in d<sup>6</sup>-DMSO. (a) 2-picolyl chloride hydrochloride + excess  $K_2CO_3$ ; (b) 2-picolyl chloride hydrochloride alone; (c) 2-picolyl chloride hydrochloride + excess trifluoroacetic acid.

![](_page_14_Figure_0.jpeg)

**Figure. S17** <sup>1</sup>H NMR spectra of **1** (5.0 mM) in D<sub>2</sub>O. (a) **1** alone; (b) **1** + H<sub>2</sub>A (25.0 mM); (c) **1** + H<sub>2</sub>A (25.0 mM) + TEA (75.0 mM).

We also measured <sup>1</sup>H NMR spectra of **1** in D<sub>2</sub>O. Upon addition of excess ascorbic acid, a set of new signals appear in the range of 6.5-9.0 ppm (Figure S17). The new signals may result from the N4Py ligand with one pyridyl arm protonated. In this case, the bridge CH chemical shift also has a change. The signals from ascorbic acid interfere with the observation of the change of the bridge CH<sub>2</sub> resonance. Further addition of TEA, however, makes all NMR signals disappear, probably due to the strong reduction ability of ascorbic acid in basic solution, leading to the reduction of the diamagnetic Co(III) complex to the paramagnetic Co(II) one.

![](_page_15_Figure_0.jpeg)

![](_page_15_Figure_2.jpeg)

![](_page_16_Figure_0.jpeg)

**Figure S18**. Cyclic voltammograms of **1** (a), **2** (b), **3** (c) and **4** (d) in  $CH_3CN$  in the presence of varied concentrations of acetic acid. Scan rate is 100 mV/s.

![](_page_16_Figure_2.jpeg)

Figure S19. Luminescence spectra of  $[Ru(bpy)_3]^{2+}$  (10  $\mu$ M) in water in the presence of different quencher.

![](_page_17_Figure_0.jpeg)

**Figure S20.** <sup>1</sup>H NMR spectra of **1** and **4** in  $D_2O$ . (a) the sample of freshly prepared **1**; (b) the sample of **1** stored for 4 h; (c) the sample of freshly prepared **4**.

![](_page_17_Figure_2.jpeg)

**Figure S21.** (a) Cyclic voltammograms of **1** in D<sub>2</sub>O obtained in a continuous CV measurement. Scan rate, 50 mV/s. Working electrode, glassy carbon; reference electrode, SCE; counter electrode, Pt plate; 0.1 M Na<sub>2</sub>SO<sub>4</sub> as supporting electrolyte; N<sub>2</sub> atmostphere. (b) <sup>1</sup>H NMR spectrum of the electrolyzed solution of **1** in D<sub>2</sub>O after 80 cycles of scan. (c) <sup>1</sup>H NMR spectrum of **1** in D<sub>2</sub>O. (d) <sup>1</sup>H NMR spectrum of **4** in D<sub>2</sub>O.

There are discernible differences between the <sup>1</sup>H NMR spectra of **1** and **4**, particularly for the two groups of chemical shifts at low field and the splitting pattern of the bridge  $CH_2$  resonance of the N4Py ligand (Figure S20). As a result, we examined <sup>1</sup>H NMR spectra of **1** in D<sub>2</sub>O as a function of time with that of **4** as reference. No any spectrum changes were found between the

sample of freshly prepared and that of stored for 4 h (Figure S20), indicating that the monodentate ligand substitution by water is negligible during the examined period of time for **1** in its Co(III) state.

We also carried out continuous CV experiments of **1** in D<sub>2</sub>O as shown in Figure S21a. The electrochemical scan covered a range of -0.2 - 0.3 V *vs* SCE, where Co(III)/Co(II) interconversion will take place. After 80 cycles of scan, a process spending *ca*. 0.5 h, the cyclic voltammograms of **1** remained unchanged. The <sup>1</sup>H NMR spectrum of the electrolyzed solution indicates the formation of trace amount of new species (Figure 21b). Though the chemical nature of the new species is unknown yet, it is clear that less than 10% of **1** underwent chemical transformation during the electrochemical experiment. This result suggests that **1** is still stable enough in its Co(II) state.

One may expect that the leave of the Cl<sup>-</sup> ligand from **1** may be facilitated in the Co(I) state, *i.e.* a shift of the following equilibrium (equation 1) to the right side. This possibility cannot be rule out, however, the monodentate ligand substitution by water is not likely very efficient during the photocatalysis, since the photocatalytic activity of **1** is much higher than that of **4** (Figure 1a). The addition of Cl<sup>-</sup> will undoubtedly restrict such a process and move the equilibrium to the left side, accordingly promoting the photocatalytic activity of **1** more dramatically than the other examined anions (Figure 1b). The results presented in this work suggest that the lability of the monodentate ligand may not benefit the catalytic activity of the pentadentate ligand-based Co complexes, and the employment of new monodentate ligands with stronger binding ability toward Co than that of Cl<sup>-</sup> may lead to more efficient H<sub>2</sub> evolution catalysts.

 $Co-Cl + H_2O \longrightarrow Co-OH_2 + Cl^-$  (eq. 1)

## Table S2. Crystal data and structure refinement for 1. (CCDC 987076)

Empirical formula	C23 H33 Cl3 Co N5 O6
Formula weight	640.82
Temperature	153(2) K
Wavelength	0.71073 A
Crystal system, space group	Orthorhombic, P2(1)2(1)2(1)
Unit cell dimensions	a = 9.173(4) A alpha = 90 deg. b = 13.175(5) A beta = 90 deg. c = 23.399(9) A gamma = 90 deg.
Volume	2828.0(19) A^3
Z, Calculated density	4, 1.505 Mg/m^3
Absorption coefficient	0.937 mm^-1
F(000)	1328
Crystal size	0.47 x 0.10 x 0.04 mm
Theta range for data collection	2.38 to 29.02 deg.
Limiting indices	-12<=h<=12, -17<=k<=17, -31<=l<=31
Reflections collected / unique	36663 / 7514 [R(int) = 0.0668]
Completeness to theta = 29.02	99.70%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9680 and 0.6646
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7514 / 0 / 346
Goodness-of-fit on F^2	1.002

1 = 0.0693, wR2 = 0.1748
R1 = 0.0879, wR2 = 0.1907
-0.03(2)
1.289 and -0.831 e.A^-3

Co(1)-N(3)	1.927(4)
Co(1)-N(2)	1.942(4)
Co(1)-N(4)	1.945(4)
Co(1)-N(5)	1.947(4)
Co(1)-N(1)	1.957(4)
Co(1)-Cl(1)	2.2350(16)
N(1)-C(1)	1.497(6)
N(1)-C(13)	1.512(6)
N(1)-C(7)	1.515(6)
N(2)-C(6)	1.335(6)
N(2)-C(2)	1.373(6)
N(3)-C(12)	1.353(6)
N(3)-C(8)	1.356(7)
N(4)-C(18)	1.340(7)
N(4)-C(14)	1.363(6)
N(5)-C(23)	1.334(6)
N(5)-C(19)	1.362(6)
C(1)-C(2)	1.500(7)
C(1)-H(1A)	0.9900
C(1)-H(1B)	0.9900
C(2)-C(3)	1.380(7)
C(3)-C(4)	1.374(8)
C(3)-H(3)	0.9500
C(4)-C(5)	1.380(8)
C(4)-H(4)	0.9500
C(5)-C(6)	1.384(7)
C(5)-H(5)	0.9500
C(6)-H(6)	0.9500
C(7)-C(8)	1.490(7)
C(7)-H(7A)	0.9900
C(7)-H(7B)	0.9900
C(8)-C(9)	1.360(7)
C(9)-C(10)	1.383(8)
C(9)-H(9)	0.9500
C(10)-C(11)	1.372(9)
C(10)-H(10)	0.9500
C(11)-C(12)	1.381(7)
C(11)-H(11)	0.9500
C(12)-H(12)	0.9500
C(13)-C(14)	1.514(7)

 Table S3.
 Bond lengths [Å] and angles [deg] for 1.

C(13)-C(19)	1.539(7)
C(13)-H(13)	1.0000
C(14)-C(15)	1.383(7)
C(15)-C(16)	1.400(8)
C(15)-H(15)	0.9500
C(16)-C(17)	1.386(8)
C(16)-H(16)	0.9500
C(17)-C(18)	1.375(8)
C(17)-H(17)	0.9500
C(18)-H(18)	0.9500
C(19)-C(20)	1.368(7)
C(20)-C(21)	1.393(7)
C(20)-H(20)	0.9500
C(21)-C(22)	1.361(8)
C(21)-H(21)	0.9500
C(22)-C(23)	1.383(7)
C(22)-H(22)	0.9500
C(23)-H(23)	0.9500
O(1)-H(01A)	0.8372
O(1)-H(01B)	0.8385
O(2)-H(2A)	0.8447
O(2)-H(2B)	0.8414
O(3)-H(3A)	0.66(7)
O(4)-H(4A)	0.8327
O(4)-H(4B)	0.8289
O(6)-H(6A)	0.8461
O(6)-H(6B)	0.8445
N(3)-Co(1)-N(2)	88.24(16)
N(3)-Co(1)-N(4)	170.32(18)
N(2)-Co(1)-N(4)	89.80(16)
N(3)-Co(1)-N(5)	91.95(17)
N(2)-Co(1)-N(5)	169.65(17)
N(4)-Co(1)-N(5)	88.28(17)
N(3)-Co(1)-N(1)	85.86(17)
N(2)-Co(1)-N(1)	86.98(16)
N(4)-Co(1)-N(1)	84.57(17)
N(5)-Co(1)-N(1)	82.71(17)
N(3)-Co(1)-Cl(1)	95.70(13)
N(2)-Co(1)-Cl(1)	97.07(12)
N(4)-Co(1)-Cl(1)	93.95(13)
N(5)-Co(1)-Cl(1)	93.21(13)
N(1)-Co(1)-Cl(1)	175.69(12)
C(1)-N(1)-C(13)	114.3(4)

C(1)-N(1)-C(7)	111.3(4)
C(13)-N(1)-C(7)	114.4(4)
C(1)-N(1)-Co(1)	109.3(3)
C(13)-N(1)-Co(1)	98.1(3)
C(7)-N(1)-Co(1)	108.4(3)
C(6)-N(2)-C(2)	119.8(4)
C(6)-N(2)-Co(1)	127.1(3)
C(2)-N(2)-Co(1)	112.8(3)
C(12)-N(3)-C(8)	119.1(4)
C(12)-N(3)-Co(1)	126.7(4)
C(8)-N(3)-Co(1)	113.9(3)
C(18)-N(4)-C(14)	120.5(4)
C(18)-N(4)-Co(1)	128.8(4)
C(14)-N(4)-Co(1)	110.6(3)
C(23)-N(5)-C(19)	117.6(4)
C(23)-N(5)-Co(1)	131.1(4)
C(19)-N(5)-Co(1)	111.3(3)
N(1)-C(1)-C(2)	111.1(4)
N(1)-C(1)-H(1A)	109.4
C(2)-C(1)-H(1A)	109.4
N(1)-C(1)-H(1B)	109.4
C(2)-C(1)-H(1B)	109.4
H(1A)-C(1)-H(1B)	108.0
N(2)-C(2)-C(3)	119.9(5)
N(2)-C(2)-C(1)	116.0(4)
C(3)-C(2)-C(1)	124.0(5)
C(4)-C(3)-C(2)	120.1(5)
C(4)-C(3)-H(3)	119.9
C(2)-C(3)-H(3)	119.9
C(3)-C(4)-C(5)	119.6(5)
C(3)-C(4)-H(4)	120.2
C(5)-C(4)-H(4)	120.2
C(4)-C(5)-C(6)	118.7(5)
C(4)-C(5)-H(5)	120.7
C(6)-C(5)-H(5)	120.7
N(2)-C(6)-C(5)	121.9(5)
N(2)-C(6)-H(6)	119.1
C(5)-C(6)-H(6)	119.1
C(8)-C(7)-N(1)	109.5(4)
C(8)-C(7)-H(7A)	109.8
N(1)-C(7)-H(7A)	109.8
C(8)-C(7)-H(7B)	109.8
N(1)-C(7)-H(7B)	109.8
H(7A)-C(7)-H(7B)	108.2
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N(3)-C(8)-C(9)	120.9(5)
N(3)-C(8)-C(7)	116.1(4)
C(9)-C(8)-C(7)	123.0(5)
C(8)-C(9)-C(10)	120.6(6)
C(8)-C(9)-H(9)	119.7
C(10)-C(9)-H(9)	119.7
C(11)-C(10)-C(9)	118.5(5)
C(11)-C(10)-H(10)	120.8
C(9)-C(10)-H(10)	120.8
C(10)-C(11)-C(12)	119.6(5)
C(10)-C(11)-H(11)	120.2
C(12)-C(11)-H(11)	120.2
N(3)-C(12)-C(11)	121.3(5)
N(3)-C(12)-H(12)	119.4
C(11)-C(12)-H(12)	119.4
N(1)-C(13)-C(14)	106.1(4)
N(1)-C(13)-C(19)	104.3(4)
C(14)-C(13)-C(19)	106.7(4)
N(1)-C(13)-H(13)	113.0
C(14)-C(13)-H(13)	113.0
C(19)-C(13)-H(13)	113.0
N(4)-C(14)-C(15)	121.6(5)
N(4)-C(14)-C(13)	111.3(4)
C(15)-C(14)-C(13)	126.8(5)
C(14)-C(15)-C(16)	117.5(5)
C(14)-C(15)-H(15)	121.2
C(16)-C(15)-H(15)	121.2
C(17)-C(16)-C(15)	119.8(5)
C(17)-C(16)-H(16)	120.1
C(15)-C(16)-H(16)	120.1
C(18)-C(17)-C(16)	120.0(5)
C(18)-C(17)-H(17)	120.0
C(16)-C(17)-H(17)	120.0
N(4)-C(18)-C(17)	120.4(5)
N(4)-C(18)-H(18)	119.8
C(17)-C(18)-H(18)	119.8
N(5)-C(19)-C(20)	122.6(5)
N(5)-C(19)-C(13)	110.5(4)
C(20)-C(19)-C(13)	126.8(5)
C(19)-C(20)-C(21)	118.8(5)
C(19)-C(20)-H(20)	120.6
C(21)-C(20)-H(20)	120.6
C(22)-C(21)-C(20)	118.6(5)
C(22)-C(21)-H(21)	120.7

C(20)-C(21)-H(21)	120.7	
C(21)-C(22)-C(23)	120.0(5)	
C(21)-C(22)-H(22)	120.0	
C(23)-C(22)-H(22)	120.0	
N(5)-C(23)-C(22)	122.3(5)	
N(5)-C(23)-H(23)	118.8	
C(22)-C(23)-H(23)	118.8	
H(01A)-O(1)-H(01B)	111.3	
H(2A)-O(2)-H(2B)	110.7	
H(4A)-O(4)-H(4B)	112.6	
H(6A)-O(6)-H(6B)	109.3	

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