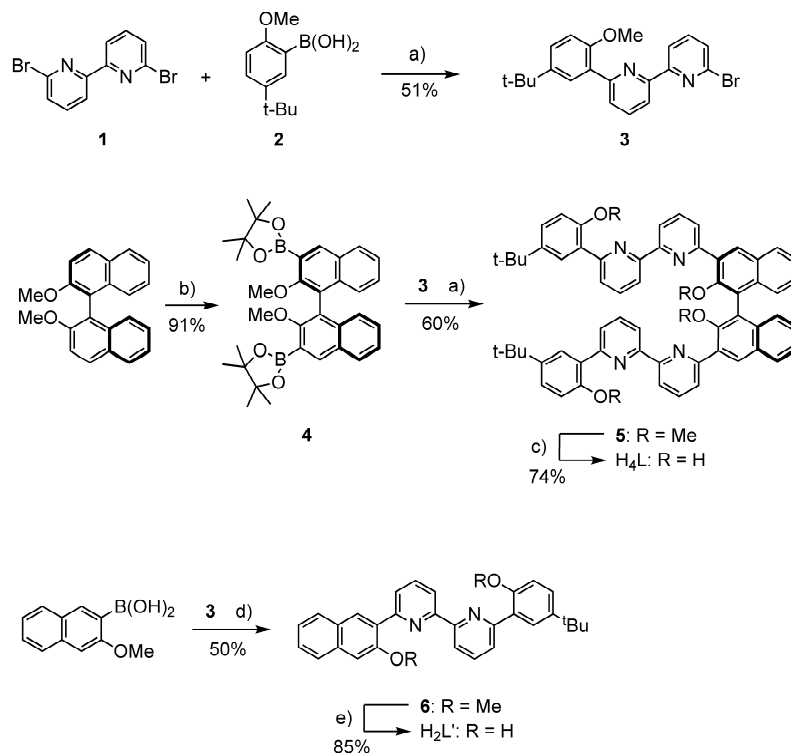


**Highly-Cooperative Double Metalation of a Bis(N<sub>2</sub>O<sub>2</sub>) Ligand Based on Bipyridine-Phenol Framework Driven by Intramolecular  $\pi$ -Stacking of Square Planar Nickel(II) Complex Moieties**

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**Supplementary Information**

## 1. Synthesis and characterization of ligands and metal complexes.



Scheme 1. Synthesis of ligands  $\text{H}_4\text{L}$  and  $\text{H}_2\text{L}'$ . Reagents and conditions: *a*)  $[\text{Pd}(\text{PPh}_3)_4]$ ,  $\text{Na}_2\text{CO}_3$ , toluene/ $\text{H}_2\text{O}$ , *b*) (i) *n*-BuLi, TMEDA, ether (ii)  $\text{B}(\text{OMe})_3$  (iii) dil. HCl (iv) pinacol, toluene, *c*)  $\text{BBr}_3$ ,  $\text{CH}_2\text{Cl}_2$ , *d*)  $[\text{Pd}(\text{PPh}_3)_4]$ ,  $\text{Na}_2\text{CO}_3$ , toluene/ $\text{MeOH}/\text{H}_2\text{O}$ , *e*) HBr, AcOH.

**General Procedures.** All experiments were carried out under argon atmosphere unless otherwise noted. Toluene, diethyl ether, and methanol (dehydrated) were used for the organic syntheses. Aqueous solution of sodium carbonate was degassed prior to use. Dichloromethane and *N,N,N',N'*-tetramethylethylenediamine were distilled under argon atmosphere from calcium hydride prior to use. Commercial chloroform, acetonitrile, and methanol were used without purification for the synthesis of metal complexes. All chemicals were of reagent grade and used as received. Column chromatography was performed with Kanto Chemical silica gel 60N (spherical, neutral). Gel permeation chromatography (GPC) was performed by an LC-9201 equipped with JAI gel 1H + 2H columns (Japan Analytical Industry) with chloroform as eluent. Melting points were determined on a Yanaco melting point apparatus and not corrected. NMR spectra were recorded on a Bruker ARX400 (<sup>1</sup>H, 400 MHz; <sup>13</sup>C, 100 MHz) or a Bruker Avance600 (<sup>1</sup>H, 600 MHz) spectrometer. Mass spectra (ESI-TOF, positive mode) were recorded on an Applied Biosystems QStar Pulsar i spectrometer. Absorption spectra were recorded on a JASCO Ubest V660 spectrometer.

### **6-Bromo-6'-(5-*tert*-butyl-2-methoxyphenyl)-2,2'-bipyridine (3)**

6,6'-Dibromo-2,2'-bipyridine (**1**) (0.517 g, 1.65 mmol), 5-*tert*-butyl-2-methoxyphenylboronic acid (**2**) (0.286 g, 1.37 mmol), and tetrakis(triphenylphosphine)palladium(0) (0.0892 g, 0.0772 mmol) were placed in a 50 mL two-necked flask. Toluene (15 mL) and saturated aqueous solution of sodium carbonate (3 mL) were added to the mixture in one portion. The mixture was stirred at 75 °C for 60 h. After cooling, water and chloroform were added and the organic layer was separated. The aqueous layer was extracted with chloroform (3 × 30 mL). The combined organic layer was dried over anhydrous magnesium sulfate and concentrated to dryness. The crude product was purified by column chromatography on silica gel using chloroform/hexane (2/1, v/v) as eluent to give **3** (0.276 g, 0.695 mmol, 51%) as colorless crystals, m.p. 112.1–112.9 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ=1.38 (s, 9H), 3.86 (s, 3H), 6.97 (d, *J* = 8.6 Hz, 1H), 7.42 (dd, *J* = 8.6, 2.6 Hz, 1H), 7.47 (d, *J* = 7.6 Hz, 1H), 7.66 (t, *J* = 7.6 Hz, 1H), 7.82 (t, *J* = 7.9 Hz, 1H), 7.91 (dd, *J* = 7.9, 0.9 Hz, 1H), 7.98 (d, *J* = 2.6 Hz, 1H), 8.34 (dd, *J* = 7.6, 0.9 Hz, 1H), 8.52 ppm (d, *J* = 7.9 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ=31.56 (CH<sub>3</sub>), 34.23 (C), 55.73 (CH<sub>3</sub>), 111.22 (CH), 119.19 (CH), 119.74 (CH), 125.84 (CH), 126.90 (CH), 127.71 (CH), 128.09 (C), 128.36 (CH), 136.57 (CH), 139.13 (CH), 141.41 (C), 143.54 (C), 153.82 (C), 155.07 (C), 155.60 (C), 157.80 ppm (C); elemental analysis calcd (%) for C<sub>21</sub>H<sub>21</sub>BrN<sub>2</sub>O: C 63.48, H 5.33, N 7.05; found: C 63.31, H 5.49, N 6.87.

**(*S*)-2,2'-(2,2'-Dimethoxy-1,1'-binaphthyl-3,3'-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)**  
**(4)**

To a stirred suspension of (*S*)-2,2'-dimethoxy-1,1'-binaphthyl (2.52 g, 8.02 mmol) and *N,N,N',N'*-tetramethylethylenediamine (3.6 mL, 24 mmol) in diethyl ether (300 mL) was added *n*-butyllithium (2.8 M hexane solution, 8.7 mL, 24 mmol) at 0 °C. After the mixture was stirred for 4 h at room temperature, trimethyl borate (2.7 mL, 24 mmol) was added dropwise at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred for 2 h. The mixture was acidified with hydrochloric acid (4 M, 10 mL) and stirred for 1 h. The organic layer was separated, and the aqueous layer was extracted with diethyl ether. The combined organic layer was concentrated to dryness to give pale yellow oil. The crude boronic acid was dissolved in toluene (50 mL) and pinacol (1.92 g, 16.2 mmol) was added to the mixture, which was refluxed with a Dean-Stark trap for 3 h. After cooling, water (20 mL) was added and the organic layer was separated. The aqueous layer was extracted with chloroform (3 × 30 mL). The combined organic layer was dried over anhydrous magnesium sulfate and concentrated to dryness. The crude product was purified by column chromatography on silica gel using ethyl acetate/hexane (1/5, v/v) as eluent to give **4** (4.11 g, 7.27 mmol, 91%) as pale yellow crystals, m.p. 124.3–125.2 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ=1.40 (s, 24H), 3.45 (s, 6H), 7.11 (d, *J* = 7.7 Hz, 2H), 7.22 (t, *J* = 7.7 Hz, 2H), 7.34 (t, *J* = 7.7 Hz, 2H), 7.90 (d, *J* = 7.7 Hz, 2H), 8.42 ppm (s, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ=24.85 (CH<sub>3</sub>), 61.92 (CH<sub>3</sub>), 83.67 (C), 123 (br, C), 124.40 (CH), 124.71 (C), 125.76 (CH), 127.12 (CH), 128.41 (CH), 130.06 (C), 135.98 (C), 138.64 (CH), 159.74 ppm (C); elemental analysis calcd (%) for C<sub>34</sub>H<sub>40</sub>B<sub>2</sub>O<sub>6</sub>•0.25CHCl<sub>3</sub>: C 69.00, H 6.81; found: C 68.75, H 6.75.

**(*S*)-6',6''-(2,2'-Dimethoxy-1,1'-binaphthyl-3,3'-diyl)bis(6-(5-*tert*-butyl-2-methoxyphenyl)-2,2'-bipyridine)** (**5**)

Compound **3** (0.243 g, 0.611 mmol), diboronate ester **4** (0.172 g, 0.303 mmol), and tetrakis(triphenylphosphine)palladium(0) (0.0346 g, 0.0299 mmol) were placed in a 50-mL two-necked flask and toluene (10 mL) and saturated aqueous solution of sodium carbonate (2 mL) were added to the mixture in one portion. The mixture was stirred at 80 °C for 48 h. After cooling, water was added and the organic layer was separated. The aqueous layer was extracted with chloroform (3 × 20 mL). The combined organic layer was dried over anhydrous magnesium sulfate and concentrated to dryness. The crude product was purified by using GPC to give **5** (0.173 g, 0.183 mmol, 60%) as colorless crystals, m.p. 161.2–163.4 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ=1.41 (s, 18H), 3.35 (s, 6H), 3.88 (s, 6H), 6.99 (d, *J* = 8.7 Hz, 2H), 7.28–7.30 (m, 4H), 7.43 (dd, *J* = 8.7, 2.6 Hz, 2H), 7.45 (ddd, *J* = 10.2, 6.0, 2.2 Hz, 2H), 7.89 (t, *J* = 7.8 Hz, 2H), 7.90 (t, *J* = 7.9 Hz, 2H), 7.95 (dd, *J* = 7.9, 1.1 Hz, 2H), 8.06 (d, *J* = 8.1 Hz, 2H), 8.07 (dd, *J* = 7.8, 0.9 Hz,

2H), 8.09 (d,  $J = 2.6$  Hz, 2H), 8.59 (dd,  $J = 7.8, 0.9$  Hz, 2H), 8.63 (s, 2H), 8.64 ppm (dd,  $J = 7.9, 1.1$  Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 31.57$  ( $\text{CH}_3$ ), 34.21 (C), 55.72 ( $\text{CH}_3$ ), 61.26 ( $\text{CH}_3$ ), 111.27 (CH), 119.03 (CH), 119.55 (CH), 124.62 (CH), 125.08 (CH), 125.23 (CH), 125.78 (CH), 126.05 (C), 126.73 (CH), 126.79 (CH), 128.37 (C), 128.43 (CH), 128.77 (CH), 130.89 (C), 131.85 (CH), 133.63 (C), 134.30 (C), 136.47 (CH), 137.05 (CH), 143.49 (C), 154.29 (C), 155.13 (C), 155.44 (C  $\times$  2), 155.72 (C), 156.44 ppm (C); elemental analysis calcd (%) for  $\text{C}_{64}\text{H}_{58}\text{N}_4\text{O}_4 \cdot 2\text{H}_2\text{O}$ : C 78.18, H 6.36, N 5.70; found: C 78.16, H 6.09, N 5.45.

### Ligand $\text{H}_4\text{L}$ .

To a stirred solution of **5** (0.173 g, 0.183 mmol) in dichloromethane (15 mL) was added boron tribromide (0.2 mL, 2.1 mmol) at 0 °C under nitrogen atmosphere. The reaction mixture was stirred for 4 h at room temperature. After the addition of water at 0 °C, the mixture was stirred for 1 h at room temperature. The organic layer was separated and the aqueous layer was extracted with chloroform (3  $\times$  50 mL). The combined organic layer was dried over anhydrous magnesium sulfate and concentrated to dryness to give  $\text{H}_4\text{L}$  (0.120 g, 0.135 mmol, 74%) as yellow crystals, m.p. > 300 °C;  $^1\text{H}$  NMR (600 MHz,  $[\text{D}_6]\text{DMSO}$ ):  $\delta = 1.25$  (s, 18H), 6.87 (d,  $J = 8.4$  Hz, 2H), 7.07 (d,  $J = 8.4$  Hz, 2H), 7.28–7.38 (m, 6H), 7.93 (d,  $J = 2.4$  Hz, 2H), 7.96 (d,  $J = 8.0$  Hz, 2H), 8.08 (t,  $J = 8.0$  Hz, 2H), 8.09 (d,  $J = 8.0$  Hz, 2H), 8.25 (d,  $J = 8.0$  Hz, 2H), 8.28 (d,  $J = 8.4$  Hz, 2H), 8.42 (t,  $J = 8.0$  Hz, 2H), 8.73 (d,  $J = 8.0$  Hz, 2H), 9.02 (s, 2H), 12.60 (s, 2H), 14.06 ppm (s, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 31.48$  ( $\text{CH}_3$ ), 34.14 (C), 117.83 (CH), 117.89 (C), 118.28 (C), 119.00 (CH), 119.08 (CH), 119.55 (CH), 120.74 (CH), 121.07 (C), 122.89 (CH), 123.03 (CH), 124.60 (CH), 127.47 (CH), 127.48 (CH), 127.55 (C), 128.84 (CH), 129.11 (CH), 135.36 (C), 139.17 (CH), 139.26 (CH), 141.50 (C), 150.91 (C), 151.84 (C), 154.45 (C), 157.13 (C), 157.34 (C), 157.63 ppm (C); elemental analysis calcd (%) for  $\text{C}_{60}\text{H}_{50}\text{N}_4\text{O}_4 \cdot \text{H}_2\text{O}$ : C 79.27, H 5.77, N 6.16; found: C 79.55, H 5.69, N 5.98.

### Nickel complex $[\text{LNi}_2]$ .

A solution of nickel(II) acetate tetrahydrate (9.6 mg, 38.6  $\mu\text{mol}$ ) in methanol (3 mL) and acetonitrile (3 mL) were added to a solution of  $\text{H}_4\text{L}$  (17.2 mg, 19.3  $\mu\text{mol}$ ) in chloroform (3 mL), and the resulting solution was kept at room temperature. From the solution, nickel complex  $[\text{LNi}_2]$  was obtained as dark red crystals (8.0 mg, 6.7  $\mu\text{mol}$ , 35%),  $^1\text{H}$  NMR (600 MHz,  $[\text{D}_6]\text{DMSO}$ ):  $\delta = 1.11$  (s, 18H), 5.48 (d,  $J = 8.7$  Hz, 2H), 6.21 (dd,  $J = 8.7, 2.3$  Hz, 2H), 7.03 (d,  $J = 2.3$  Hz, 2H), 7.09–7.12 (m, 4H), 7.15–7.17 (m, 2H), 7.73 (d,  $J = 7.8$  Hz, 2H), 7.81 (d,  $J = 7.8$  Hz, 2H), 7.87 (t,  $J = 7.8$  Hz, 2H), 7.89 (d,  $J = 8.3$  Hz, 2H), 7.99 (d,  $J = 7.9$  Hz, 2H), 8.23 (t,  $J = 7.9$  Hz, 2H), 8.57 (s, 2H), 8.64 ppm (d,  $J = 7.9$  Hz, 2H); ESI-MS:  $m/z$  1003.3 ( $[\text{M}+\text{H}]^+$ ); elemental analysis calcd (%) for  $\text{C}_{60}\text{H}_{46}\text{N}_2\text{O}_2\text{Ni}_2 \cdot \text{CHCl}_3 \cdot \text{CH}_3\text{CN} \cdot 1.5\text{H}_2\text{O}$ : C 63.49, H 4.48, N 5.88; found: C 63.44, H 4.40, N 5.70.

### 6-(5-*tert*-Butyl-2-methoxyphenyl)-6'-(3-methoxynaphthalene-2-yl)-2,2'-bipyridine (**6**)

Compound **3** (0.394 g, 0.992 mmol), 3-methoxynaphthalen-2-ylboronic acid (0.203 g, 1.01 mmol), and tetrakis(triphenylphosphine)palladium(0) (0.0133 g, 0.0115 mmol) were placed in a 50-mL two-necked flask and toluene (10 mL) methanol (1 mL), and saturated aqueous solution of sodium carbonate (2 mL) were added to the mixture in one portion. The mixture was stirred at 80 °C for 20 h. After cooling, water (10 mL) was added and the organic layer was separated. The aqueous layer was extracted with chloroform. The combined organic layer was dried over anhydrous magnesium sulfate and concentrated to dryness. The crude product was subjected to chromatography on silica gel using chloroform as eluent and then purified by GPC to afford **6** (0.235 g, 0.495 mmol, 50%) as colorless crystals, m.p. 87.3–89.6 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ=1.41 (s, 9H), 3.88 (s, 3H), 4.01 (s, 3H), 6.98 (d, *J* = 8.7 Hz, 1H), 7.28 (s, 1H), 7.38 (ddd, *J* = 7.8, 6.9, 1.2 Hz, 1H), 7.42 (dd, *J* = 8.7, 2.6 Hz, 1H), 7.48 (ddd, *J* = 7.8, 6.9, 1.2 Hz, 1H), 7.79 (d, *J* = 7.8 Hz, 1H), 7.84 (t, *J* = 7.7 Hz, 1H), 7.87 (t, *J* = 7.8 Hz, 1H), 7.91 (dd, *J* = 7.7, 1.0 Hz, 1H), 7.92 (d, *J* = 7.8 Hz, 1H), 7.93 (dd, *J* = 7.8, 1.1 Hz, 1H), 8.07 (d, *J* = 2.6 Hz, 1H), 8.43 (s, 1H), 8.54 (dd, *J* = 7.7, 1.0 Hz, 1H), 8.55 ppm (dd, *J* = 7.8, 1.1 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ=31.58 (CH<sub>3</sub>), 34.23 (C), 55.53 (CH<sub>3</sub>), 55.74 (CH<sub>3</sub>), 106.05 (CH), 111.29 (CH), 119.02 (CH), 119.30 (CH), 123.90 (CH), 125.10 (CH × 2), 126.30 (CH), 126.68 (CH), 126.73 (CH), 128.40 (CH), 128.48 (C), 128.49 (CH), 128.87 (C), 130.82 (C), 131.33 (CH), 134.59 (C), 136.37 (CH × 2), 143.51 (C), 154.76 (C), 155.13 (C), 155.31 (C), 155.51 (C), 155.87 (C), 156.24 ppm (C); elemental analysis calcd (%) for C<sub>32</sub>H<sub>30</sub>N<sub>2</sub>O<sub>2</sub>•1.25H<sub>2</sub>O: C 77.32, H 6.59, N 5.64; found: C 77.39, H 6.23, N 5.45.

### Ligand H<sub>2</sub>L'

To a stirred solution of **6** (0.177 g, 0.372 mmol) in acetic acid (7 mL) was added hydrobromic acid (47%, 0.5 mL) and the resulting solution was refluxed overnight. After cooling, the mixture was neutralized with saturated aqueous solution of sodium hydrogencarbonate and extracted with chloroform (3 × 30 mL). The combined organic layer was dried over anhydrous magnesium sulfate and concentrated to dryness. The residue was recrystallized from chloroform/methanol to give H<sub>2</sub>L' (0.142 g, 0.317 mmol, 85%) as yellow crystals, m.p. 249.5–250.5 °C, <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ=1.39 (s, 9H), 7.03 (d, *J* = 8.6 Hz, 1H), 7.33 (ddd, *J* = 8.2, 6.9, 1.2 Hz, 1H), 7.40 (s, 1H), 7.43 (dd, *J* = 8.6, 2.4 Hz, 1H), 7.46 (ddd, *J* = 8.2, 6.9, 1.2 Hz, 1H), 7.72 (d, *J* = 8.2 Hz, 1H), 7.84 (d, *J* = 8.2 Hz, 1H), 7.86 (d, *J* = 2.4 Hz, 1H), 8.03–8.10 (m, 3H), 8.17 (dd, *J* = 7.1, 1.6 Hz, 1H), 8.20 (d, *J* = 7.1 Hz, 1H), 8.21 (d, *J* = 8.0 Hz, 1H), 8.40 (s, 1H), 13.92 (s, 1H), 13.98 ppm (s, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ=31.57(CH<sub>3</sub>), 34.25 (C), 112.20 (CH), 117.99 (C), 118.05 (CH), 119.04 (CH), 119.70 (CH), 120.01 (CH), 120.83 (CH), 121.46 (C), 122.99 (CH), 123.51 (CH), 126.04 (CH), 127.56 (CH), 127.60 (CH), 127.71 (C), 128.45 (CH), 129.38 (CH), 135.99 (C), 139.19 (CH),

139.45 (CH), 141.80 (C), 151.98 (C), 152.47 (C), 156.41 (C), 157.28 (C), 157.71 (C), 158.33 ppm (C); ESI-MS:  $m/z$  447.2 ( $[M+H]^+$ ); elemental analysis calcd (%) for  $C_{30}H_{26}N_2O_2$ : C 80.69, H 5.87, N 6.27; found: C 80.34, H 6.01, N 6.19.

### **Nickel complex [L'Ni]**

A solution of nickel(II) acetate tetrahydrate (8.4 mg, 33.4  $\mu$ mol) in methanol (2 mL) was added to a solution of ligand  $H_2L'$  (14.7 mg, 32.9  $\mu$ mol) in chloroform (2 mL) at room temperature. Vapor phase diffusion of diethyl ether into the solution afforded [L'Ni] (14.1 mg, 23.1  $\mu$ mol, 70%) as red needles,  $^1H$  NMR (400 MHz,  $[D_6]DMSO$ ):  $\delta$ =1.32 (s, 9H), 6.87 (d,  $J$  = 8.8 Hz, 1H), 7.11 (ddd,  $J$  = 8.4, 7.1, 1.4 Hz, 1H), 7.19 (s, 1H), 7.30 (dd,  $J$  = 8.8, 2.2 Hz, 1H), 7.33 (ddd,  $J$  = 8.4, 7.1, 1.4 Hz, 1H), 7.54 (d,  $J$  = 8.4 Hz, 1H), 7.80 (d,  $J$  = 8.4 Hz, 1H), 7.81 (s, 1H), 8.23 (t,  $J$  = 8.3 Hz, 1H), 8.34 (t,  $J$  = 7.7 Hz, 1H), 8.39 (d,  $J$  = 7.7 Hz, 1H), 8.46 (d,  $J$  = 8.3 Hz, 1H), 8.49 (d,  $J$  = 8.3 Hz, 1H), 8.67 (s, 1H), 8.68 ppm (d,  $J$  = 7.7 Hz, 1H); ESI-MS:  $m/z$  503.1 ( $[M+H]^+$ ); elemental analysis calcd (%) for  $C_{30}H_{26}N_2O_2Ni \cdot 0.9CHCl_3$ : C 60.78, H 4.11, N 4.59; found: C 60.63, H 4.23, N 4.44.

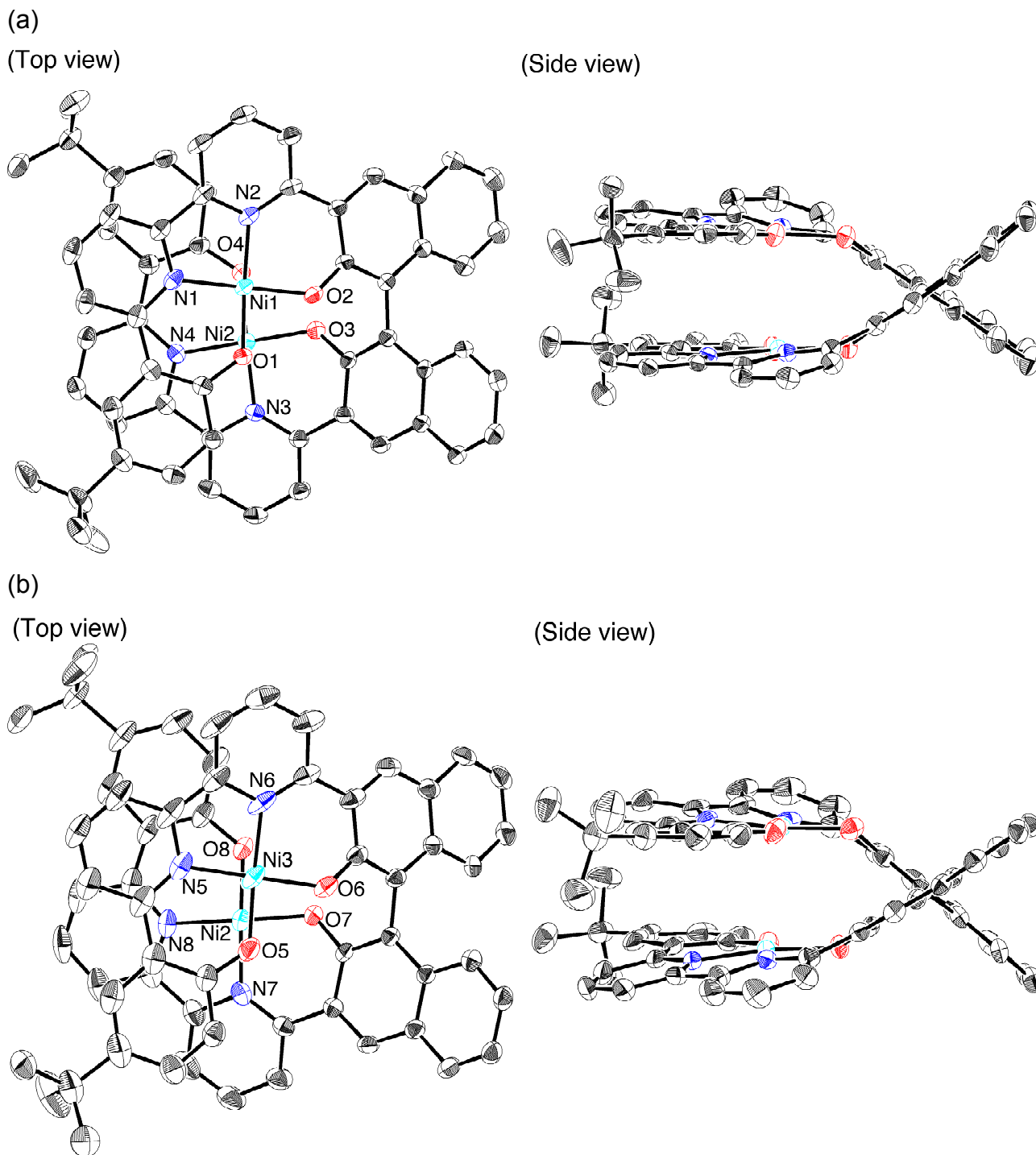
## 2. X-ray crystallographic analysis of [LNi<sub>2</sub>].

Single crystal of [LNi<sub>2</sub>] suitable for X-ray crystallography was obtained from a suspension of [LNi<sub>2</sub>] in methanol/acetonitrile. Intensity data were collected on a Rigaku R-AXIS Rapid diffractometer with MoK $\alpha$  radiation ( $\lambda = 0.71069$  Å). The data were corrected for Lorentz and polarization factors, and for absorption by semiempirical methods based on symmetry-equivalent and repeated reflections. The structure was solved by Patterson methods (DIRDIF 99) and refined by full-matrix least-squares on  $F^2$  using SHELXL 97. The crystallographic data are summarized in Table 1.

**Table 1.** Crystallographic data for [LNi<sub>2</sub>]•4MeOH•2MeCN

[LNi <sub>2</sub> ]•4MeOH•2MeCN	
Formula	C <sub>68</sub> H <sub>68</sub> N <sub>6</sub> Ni <sub>2</sub> O <sub>8</sub>
Formula weight	1214.70
Temperature (K)	120
Crystal size (mm <sup>3</sup> )	0.50 × 0.25 × 0.10
Crystal system	orthorhombic
Space group	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>
<i>a</i> (Å)	15.6037(4)
<i>b</i> (Å)	27.0324(5)
<i>c</i> (Å)	27.9392(5)
<i>V</i> (Å <sup>3</sup> )	11784.9(4)
<i>Z</i>	8
<i>D</i> <sub>calcd</sub>	1.369
Collected reflections	115940
Unique reflections	26976
<i>R</i> <sub>int</sub>	0.0333
2 $\theta$ <sub>max</sub>	54.96
<i>F</i> <sub>000</sub>	5104
$\mu$ (MoK $\alpha$ )	0.702
Limiting indices	$-20 \leq h \leq 20$ $-35 \leq k \leq 29$ $-36 \leq l \leq 35$
Parameters/restraints	1597/110
Flack $\chi$	0.021(7)
Goodness of fit ( $F^2$ )	1.057
<i>R</i> 1 ( $I > 2\sigma(I)$ )	0.0423
<i>wR</i> 2 ( $I > 2\sigma(I)$ )	0.1122
<i>R</i> 1 (all data)	0.0451
<i>wR</i> 2 (all data)	0.1140





**Figure 1.** X-ray crystal structure of  $[LNi_2]$  with thermal ellipsoids drawn at 50% probability level. (a) and (b) denote the two crystallographically independent molecules. Hydrogen atoms and less occupied disordered atoms are omitted for clarity.