## Design, Synthesis and Characterization of Binuclear Ni(II) Complexes with Inherent Helical Chirality.

Vadim A. Soloshonok\* and Hisanori Ueki

<sup>#</sup>Department of Chemistry and Biochemistry, University of Oklahoma, Norman, OK 73019

vadim@ou.edu

**List of Contents** 

Experimental Section, General method	S2
Experimental Section, General Procedure for the synthesis of binuclear	
Ni(II) complex	S2
<b>Experimental Section</b> , Physical properties for ( <i>P/M</i> )-5	S2
Experimental Section, Physical properties for ( <i>P/M</i> )-7a	<b>S</b> 3
<b>Experimental Section</b> , Physical properties for ( <i>P</i> / <i>M</i> )- <b>7b</b>	<b>S</b> 3
<b>Experimental Section</b> , Physical properties for ( <i>P/M</i> )-7c	S4
<b>Experimental Section</b> , Physical properties for $(P,S,S)$ -9 and $(M,S,S)$ -9	S4
<b>Figure 1</b> CD spectrum of $(P)$ and $(M)$ -9.	<b>S</b> 6
Figure 2 UV-visible spectrum of ( <i>P</i> ) and ( <i>M</i> )-9.	S7
<sup>1</sup> H NMR of ( <i>P</i> / <i>M</i> )- <b>5</b>	<b>S</b> 8
<sup>1</sup> H NMR of $(P/M)$ -7a	<b>S</b> 9
<sup>1</sup> H NMR of ( <i>P</i> / <i>M</i> )- <b>7b</b>	<b>S</b> 10
<sup>1</sup> H NMR of ( $P/M$ )-7c	<b>S</b> 11
<sup>1</sup> H NMR of ( $P,S,S$ )-9	S12
<sup>1</sup> H NMR of $(M,S,S)$ -9	<b>S</b> 13
<b>Figure 3</b> Space filling model of $(P/M)$ -5.	S14

## **Experimental section**

*General*. Unless otherwise noted, all reagents and solvents were obtained from commercial suppliers and used without further purification. Unless indicated, <sup>1</sup>H and <sup>13</sup>C NMR spectra, were taken in CDCl<sub>3</sub> solutions at 300 and 75 MHz, respectively, on an instrument in the University of Oklahoma NMR Spectroscopy Laboratory. Chemical shifts refer to TMS and CDCl<sub>3</sub> as the internal standards.

All new compounds were characterized by <sup>1</sup>H and <sup>13</sup>C NMR.

General Procedure for the synthesis of binuclear Ni(II) complexes. To a flask containing Ni(II) glycine complex (0.10 g scale) and 3 ml of CH<sub>3</sub>CN, was added KO'Bu (4.0 eq.) at rt and the reaction mixture was stirred at rt under aerobic condition until the starting **1a-d** consumed completely as controlled by TLC. After evaporation of solvent, water and calculated amount of 5% AcOH aq. (4.0 eq.) was added and extracted with  $CH_2Cl_2$  three times. The combined organic layer was dried over MgSO<sub>4</sub> anhydrous. After evaporation of solvents and short path flash silica gel column (4 g of silica gel was used.), the desired binuclear Ni(II) complex was obtained in high yield.

The binuclear Ni(II) complexes are relatively unstable on TLC and silica gel column. Therefore, silica gel column for their purification should be run quickly to prevent from decomposition.

(P/M)-5: Yield 96%. <sup>1</sup>H NMR  $\delta$  6.66 (2 H, d, J = 4.99 Hz), 6.79 (2 H, ddd, J = 7.33, 5.87, 1.46 Hz), 6.94 (2 H, t, J = 7.18 Hz), 7.10-7.40 (12 H, m), 7.66 (2 H, td, J = 7.62, 1.47 Hz), 7.78 (2 H, d, J = 7.63Hz), 8.74 (2 H, d, J = 8.21 Hz), 9.56 (2 H, d, J = 7.18 Hz). <sup>13</sup>C NMR  $\delta$  121.0, 123.3, 125.3, 126.4, 128.3, 128.6, 129.2, 129.6, 130.2, 130.4, 130.8, 138.3, 139.6, 142.3, 148.0, 154.0, 167.2, 168.3. HRMS [M+H<sup>+</sup>] found *m/s* 715.0959, calcd for  $C_{38}H_{27}N_6Ni_2O_2$  715.0824. mp >230 °C (decomp.).

The crystal of (P/M)-5 for X ray crystallography was grown by vapor-diffusion method using CHCl<sub>3</sub> and MeOH as solvents.

(*P/M*)-**7a**: Yield >99%. <sup>1</sup>H NMR δ 0.47 (2 H, m), 0.60-1.15 (12 H, m), 1.00 (6 H, t, J = 7.33 Hz), 1.15-1.42 (6 H, m), 1.78-2.00 (6 H, m), 2.73 (2 H, d, J = 15.8 Hz), 2.94 (2 H, m), 4.76 (2 H, d, J = 15.8 Hz), 5.21 (2 H, m), 6.75-6.95 (6 H, m), 7.19-7.29 (4 H, m), 7.40 (2 H, m), 7.54 (2 H, m), 8.16 (2 H, d, J = 8.21 Hz), 8.42 (2 H, bd, J = 7.62 Hz). <sup>13</sup>C NMR δ 13.7, 13.9, 20.3, 20.9, 28.8, 30.5, 59.2, 61.8, 62.5, 120.3, 122.7, 128.0, 129.1, 129.4, 129.5, 130.2, 130.5, 141.3, 141.8, 166.9, 174.6. HRMS [M] found *m/s* 842.3, calcd for C<sub>46</sub>H<sub>58</sub>N<sub>6</sub>Ni<sub>2</sub>O<sub>2</sub> 842.3. mp 290.2 °C (decomp.).

This compound was used for variable temperature studies taking NMR data at various temperature (20, 40, 60, 80 and 100  $^{\circ}$ C).

The crystal of (P/M)-7a for X ray crystallography was grown by vapor-diffusion method using C<sub>2</sub>HCl<sub>2</sub> and MeOH as solvents.

(*P/M*)-**7b**: Yield 51%. <sup>1</sup>H NMR δ 1.75 (2 H, d, *J* = 13.2 Hz), 2.77 (2 H, d, *J* = 12.8 Hz), 2.78 (2 H, d, *J* = 15.2 Hz), 3.04 (2 H, d, *J* = 13.0 Hz), 3.63 (2 H, d, *J* = 12.8 Hz), 4.67 (2 H, d, *J* = 15.2 Hz), 6.82 (2 H, ddd, *J* = 8.06, 6.89, 1.17 Hz), 6.91 (2 H, dd, *J* = 8.06, 1.76 Hz), 7.00-7.07 (6 H, m), 7.16-7.44 (22 H, m), 7.62 (2 H, m), 7.99 (2 H, dd, *J* = 8.35, 1.17 Hz), 8.67 (2 H, bd, *J* = 7.47 Hz). <sup>13</sup>C NMR δ 59.5, 59.8, 60.0, 120.4, 123.2, 127.2, 128.0, 128.1, 128.1, 128.3, 128.7, 129.2, 129.3, 129.6, 129.9, 130.3, 130.3, 131.2, 131.9, 132.4, 132.6, 141.2, 141.8, 167.5, 173.9. mp 316.1 °C (decomp.).

The crystal of (P/M)-7b for X ray crystallography was grown by vapor-diffusion method using CHCl<sub>3</sub> and MeOH as solvents.

(*P/M*)-**7c**: Yield 98%. <sup>1</sup>H NMR δ 0.40 (2 H, m), 0.46-0.55 (4 H, m), 1.19 (2 H, bd, J = 13.8 Hz), 1.27-1.63 (6 H, m), 1.85-2.08 (4 H, m), 3.76 (2 H, d, J = 15.4 Hz), 4.13 (2 H, bd, J = 13.5 Hz), 4.53 (2 H, d, J = 15.2 Hz), 6.83 (2 H, ddd, J = 8.06, 7.03, 1.17 Hz), 6.93 (2 H, bd, J = 7.62 Hz), 6.97 (2 H, dd, J = 8.06, 1.47 Hz), 7.18-7.29 (4 H, m), 7.38 (2 H, tt, J = 7.47, 1.17 Hz), 7.59 (2 H, td, J = 7.63, 1.32 Hz), 8.20 (2 H, dd, J = 8.50, 1.18 Hz), 8.54 (2 H, ddd, J = 7.63, 1.47, 1.32 Hz). <sup>13</sup>C NMR δ 18.1, 20.1, 22.2, 50.8, 58.0, 61.1, 120.4, 123.0, 127.0, 128.1, 128.8, 128.9, 129.5, 130.1, 130.6, 131.1, 141.4, 141.7, 166.7, 173.3. HRMS [M+Na<sup>+</sup>] found *m/s* 777.1897, calcd for C<sub>40</sub>H<sub>42</sub>N<sub>6</sub>NaNi<sub>2</sub>O<sub>2</sub> 777.1974. mp >340 °C (decomp.).

The crystal of (P/M)-7c for X ray crystallography was grown by vapor-diffusion method using CH<sub>2</sub>Cl<sub>2</sub> and Et<sub>2</sub>O as solvents.

(P,S,S)-9 and (M,S,S)-9 Yield 76%. Ratio (M)-9 / (P)-9 = 21 / 79.

(*M*,*S*,*S*)-**9**: <sup>1</sup>H NMR δ 0.36 (2 H, m), 1.30-1.80 (4 H, m), 1.63-1.80 (2 H, m), 2.29 (2 H, m), 2.42 (2 H, d, J = 12.9 Hz), 2.61 (2 H, m), 3.28 (2 H, d, J = 12.9 Hz), 4.61 (2 H, d, J = 8.21 Hz), 6.79 (2 H, m), 6.90-6.98 (4 H, m), 7.18 (2 H, ddd, J = 7.34, 7.04, 1.76 Hz), 7.22-7.37 (8 H, m), 7.43 (2 H, dd, J = 7.48, 7.33 Hz), 7.64 (2 H, dd, J = 7.48, 7.18 Hz), 7.88-8.06 (4 H, m), 8.20 (2 H, d, J = 8.06 Hz), 8.72 (2 H, d, J = 7.48 Hz). <sup>13</sup>C NMR δ 21.1, 26.7, 55.9, 59.4, 69.7, 120.2, 123.3, 126.9, 127.9, 128.6, 128.9, 129.0, 129.6, 130.2, 130.4, 131.4, 131.8, 133.5, 141.9, 142.0, 167.0, 177.2. HRMS [M+Na<sup>+</sup>] found *m/s* 901.2275, calcd for C<sub>50</sub>H<sub>46</sub>N<sub>6</sub>NaNi<sub>2</sub>O<sub>2</sub> 901.2287. mp 307.8 °C (decomp.). [α]<sub>D</sub><sup>25</sup> -1022 (*c* 0.55, CHCl<sub>3</sub>). (*P*,*S*,*S*)-**9**: <sup>1</sup>H NMR δ 1.51 (2 H, d, J = 13.5 Hz), 1.73 (2 H, m), 2.00-2.30 (4 H, m),

2.70 (2 H, m), 2.85 (2 H, d, J = 13.5 Hz), 3.15 (2 H, m), 3.95 (2 H, m), 5.10 (2 H, m), 6.80 (2 H, ddd, J = 8.06, 6.89, 1.17 Hz), 6.86-7.01 (8 H, m), 7.11-7.20 (8 H, m), 7.28-7.39 (4 H, m), 7.56 (2 H, m), 8.02 (2 H, dd, J = 8.50, 1.17 Hz), 8.47 (2 H, d, J = 7.62 Hz). <sup>13</sup>C NMR  $\delta$  24.3, 30.3, 53.7, 53.7, 58.1, 69.2, 120.2, 122.9, 127.0, 127.9, 128.0, 128.3, 129.1, 129.1, 129.7, 130.0, 130.3, 130.4, 131.3, 131.9, 141.5, 141.9, 167.5, 177.0. HRMS [M+Na<sup>+</sup>] found *m/s* 901.2262, calcd for C<sub>50</sub>H<sub>46</sub>N<sub>6</sub>NaNi<sub>2</sub>O<sub>2</sub> 901.2287. mp 301.4 °C (decomp.). [ $\alpha$ ]<sub>D</sub><sup>25</sup> +1222 (*c* 0.55, CHCl<sub>3</sub>).

The crystal of (M,S,S)-9 for X ray crystallography was grown by vapor-diffusion method using CH<sub>2</sub>Cl<sub>2</sub> and MeOH as solvents.

The crystal of (P,S,S)-9 for X ray crystallography was grown by vapor-diffusion method using CHCl<sub>3</sub> and Et<sub>2</sub>O as solvents.



**Figure 1** CD spectrum of (*P*) and (*M*)-9 in CH<sub>2</sub>Cl<sub>2</sub>. Since even trace amount of (*P*) and (*M*)-9 possessed enough high absorption, the concentration  $[10(\pm 1) \,\mu \text{mol/L}]$  was adjusted to 0.8 abs.

**Figure 2** UV-visible spectrum of (*P*) and (*M*)-9 in CH<sub>2</sub>Cl<sub>2</sub>. Since even trace amount of (*P*) and (*M*)-9 possessed enough high absorption, the concentration  $[10(\pm 1) \,\mu \text{mol}/\text{L}]$  was adjusted to 0.8 abs.















**Figure 3**. Space filling model of (P/M)-5.

