

Electronic Supplementary Information (ESI)

Conversion of D-Penicillaminato Trinuclear to Mononuclear Palladium(II) Structure by Diamine Ligands: Remarkable Enantioselectivity toward Racemic 1,2-Cyclohexanediamine

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Experimental

Preparation of [Pd(D-pen-*N,S*)(en)] (1).

To a solution containing [Pd₃(D-pen-*N,S,O*)₃]·4H₂O (0.10 g, 0.12 mmol) in water (20 mL) was added an aqueous solution of ethylenediamine (1.5 M, 0.32 mL, 0.48 mmol). The orange mixture was stirred at room temperature for 10 min, during which time the solution color turned to yellow. The yellow solution was concentrated to ca. 2 mL with a rotary evaporator, and then 30 mL of ethanol was added to it. The resulting yellow powder of [Pd(D-pen-*N,S*)(en)]·H₂O (**1**·H₂O) was collected by filtration and washed with ethanol. Yield: 0.091 g (76% based on Pd). Anal. Calcd for [Pd(pen)(en)]·H₂O = C₇H₁₉N₃O₃PdS: C, 25.34; H, 5.77; N, 12.67%. Found: C, 25.57; H, 5.67; N, 12.56%. Absorption spectrum in H₂O [$\tilde{\nu}$, 10³ cm⁻¹ (log ϵ , M⁻¹cm⁻¹): 25.91 (2.08 sh), 32.15 (2.92), 41.32 (4.00). CD spectrum in H₂O [$\tilde{\nu}$, 10³ cm⁻¹ ($\Delta\epsilon$, M⁻¹cm⁻¹): 32.38 (+2.32), 41.86 (+5.49), 46.43 (-17.6). IR spectrum (cm⁻¹, KBr disk): 1594 (COO⁻). ¹H NMR spectrum in D₂O (ppm from DSS): δ 1.29 (s, 3H), 1.43 (s, 3H), 2.68-2.90 (m, 4H), 3.21 (s, 1H). Single-crystals of **1**·H₂O suitable for X-ray analysis were obtained by recrystallization from water/ethanol at room temperature.

Preparation of [Pd(D-pen-*N,S*)(*S,S*-chxn)] (2_S).

To a solution containing [Pd₃(D-pen-*N,S,O*)₃]·4H₂O (0.10 g, 0.12 mmol) in water (20 mL) was added racemic (*R,R/S,S*) 1,2-cyclohexanediamine (0.9 mL, 0.72 mmol). The orange mixture was stirred at room temperature for 2 h, during which time the solution color turned to yellow. The yellow solution was allowed to stand at room temperature for several days. The resulting yellow crystals of [Pd(D-pen)(*S,S*-chxn)]·H₂O (**2_S**·H₂O), which are poorly soluble in water, were collected by filtration and washed with water. Yield: 0.11 g (80% based on Pd). Anal. Calcd for [Pd(pen)(chxn)]·H₂O = C₁₁H₂₅N₃O₃PdS: C, 34.24; H, 6.53; N, 10.89%. Found: C, 34.05; H, 6.44; N, 10.87%. Absorption spectrum in H₂O [$\tilde{\nu}$, 10³ cm⁻¹ (log ϵ , M⁻¹cm⁻¹): 25.31 (2.16 sh), 32.45 (2.96), 41.05 (4.48). CD spectrum in H₂O [$\tilde{\nu}$, 10³ cm⁻¹ ($\Delta\epsilon$, M⁻¹cm⁻¹): 31.79 (+1.77), 41.25 (+3.99), 46.86 (-21.3). IR spectrum (cm⁻¹, KBr disk): 1594 (COO⁻). ¹H NMR spectrum in D₂O (ppm from DSS): δ 1.11-1.28 (m, 4H), 1.29 (s, 3H), 1.42 (s, 3H), 1.62-1.67 (m, 2H), 1.95 (d, *J* = 14.1 Hz, 1H), 2.03 (d, *J* = 12.9 Hz, 1H), 2.38-2.44 (m, 2H), 3.20 (s, 1H). One of the crystals thus obtained was used for single-crystal X-ray analysis.

Preparation of [Pd(D-pen-*N,S*)(*R,R*-chxn)] (2_R).

To a solution containing [Pd₃(D-pen-*N,S,O*)₃]·4H₂O (0.20 g, 0.24 mmol) in water (20 mL) was

added a solution containing *R,R*-1,2-diaminocyclohexane hydrochloride (0.18 g, 0.96 mmol) in a 0.1 M potassium hydroxide aqueous solution (2 mL, 2.0 mmol). The orange mixture was stirred at room temperature for 3 h, during which time the solution color turned to yellow. The yellow solution was passed through a QAE-Sephadex A-25 column (Cl⁻ form, 3 × 10 cm) by eluting with water. The eluate was then passed through an SP-Sephadex C-25 column (Na⁺ form, 3 × 10 cm) by eluting with water. The resulting yellow eluate was evaporated with a rotary evaporator to give a yellow powder of [Pd(D-pen)(*R,R*-chxn)] (**2_R**). Yield: 0.31 g (91% based on Pd). Anal. Calcd for [Pd(pen)(chxn)]·NaCl·2.5H₂O = C₁₁H₂₈ClN₃NaO_{4.5}PdS: C, 28.03; H, 5.99; N, 8.92%. Found: C, 27.98; H, 6.13; N, 8.75%. IR spectrum (cm⁻¹, KBr disk): 1595 (COO⁻). ¹H NMR spectrum in D₂O (ppm from DSS): δ 1.13-1.28 (m, 4H), 1.29 (s, 3H), 1.42 (s, 3H), 1.97 (d, *J* = 12.2 Hz, 1H), 2.05 (d, *J* = 12.0 Hz, 1H), 2.43 (d, *J* = 3.7 Hz, 2H), 3.22 (s, 1H). Complex **2_R** is highly soluble in water, and the slow evaporation of the reaction solution did not give any solid sample until dryness.

Conversion from [Pd(D-pen-*N,S*)(*R,R*-chxn)] (**2_R**) to [Pd(D-pen-*N,S*)(*S,S*-chxn)] (**2_S**).

To a solution containing [Pd(D-pen-*N,S*)(*R,R*-chxn)]·NaCl·2.5H₂O (0.03 g, 0.06 mmol) in water (1 mL) was added *S,S*-1,2-diaminocyclohexane (0.01 g, 0.11 mmol). The mixture was allowed to stand at room temperature for 2 days, which gave yellow crystals of **2_S**·H₂O. Yield: 0.01 g (40%).

X-ray structure determination.

Single-crystal X-ray diffraction measurements for **1**·H₂O and **2_S**·H₂O were made on a Rigaku RAXIS-RAPID imaging plate area detector with a graphite monochromated Mo-Kα radiation. The intensity data were collected by the ω scan mode. The intensities were corrected for Lorentz and polarization effects. Empirical absorption corrections were also applied. The structures were solved by direct methods. The structures were refined with full-matrix least-squares on *F*². H atoms bound to C and N atoms were placed at calculated positions and refined as riding models. H atoms of water molecules were found from a difference Fourier map and were refined with restrained geometrical parameters [O–H = 0.85(2) Å, H···H = 1.38(2) Å, and *U*_{iso} = 1.2U_{eq}(O)]. All non-hydrogen atoms were refined anisotropically. All calculations were performed using the Yadokari-XG 2009 software package¹ except for refinement, which was performed using SHELXL-97.²

DFT calculations.

The DFT calculations were performed with the Gaussian 03 program³ at the B3LYP⁴ level using a

Lan12DZ⁵ basis set for [Pd(D-pen-*N,S*)(*R,R*-chxn)] (**2_R**) and [Pd(D-pen-*N,S*)(*S,S*-chxn)] (**2_S**). Solvent effects (H₂O) were evaluated by using the PCM. The resulting optimized structure of **2_R** and **2_S** are illustrated in Figure S5. The selected bond distances and relative free energy of these complexes are listed in Table S3. In each of the optimized structures of **2_R** and **2_S**, the carboxylate group of D-pen adopts an equatorial orientation, as found in the crystal structure of **2_S**·H₂O. The relative free energies of **2_R** and **2_S** are almost the same as each other, which is compatible with the equal formation of **2_R** and **2_S** in the reaction solution.

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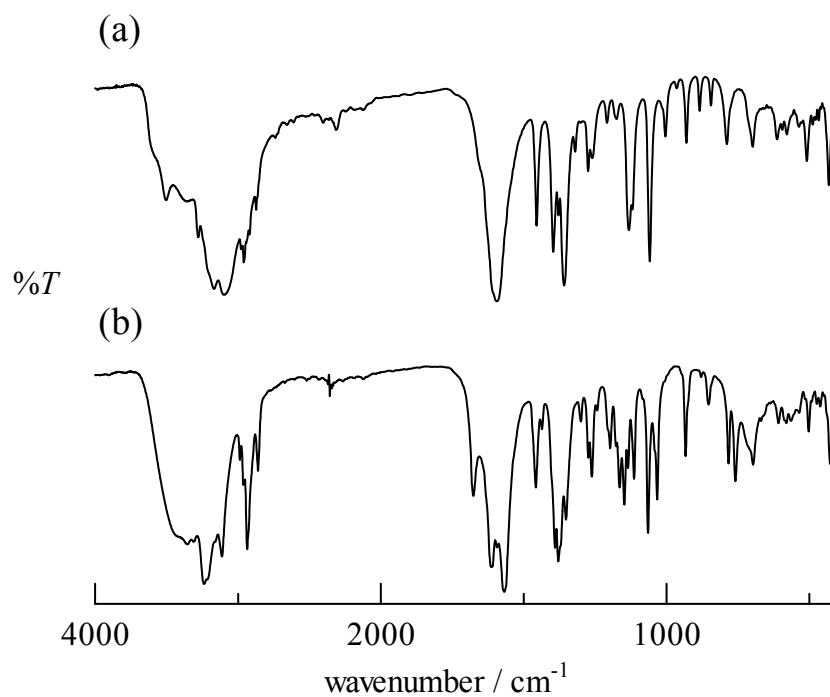


Fig. S1. IR spectra of (a) 1·H₂O and (b) 2_S·H₂O (KBr pellet).

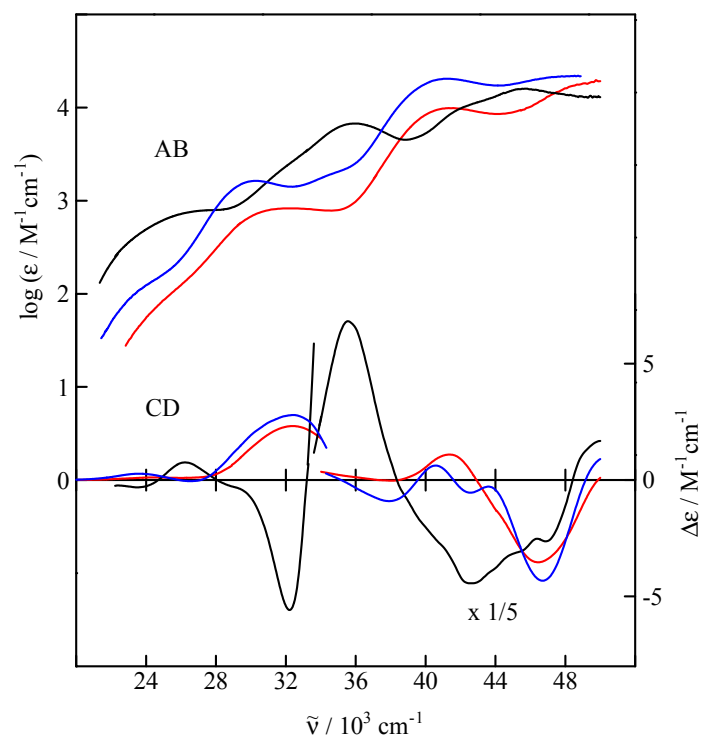


Fig. S2. Absorption (AB) and circular dichroism (CD) spectra of $[\text{Pd}_3(\text{D-pen-N,O,S})_3] \times 1/3$ (black), $\text{K}_2[\text{Pd}(\text{D-pen})_2]$ (blue), and **1** (red) in water.

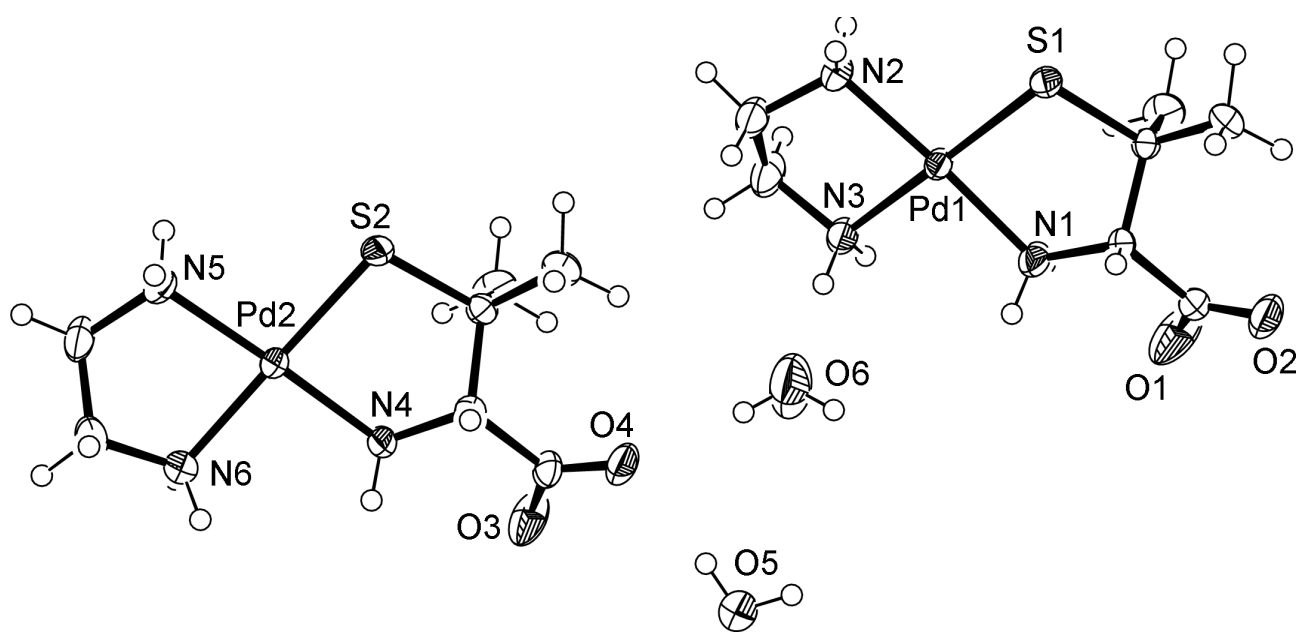


Fig. S3. An ORTEP drawing of the asymmetric unit of $1 \cdot \text{H}_2\text{O}$.

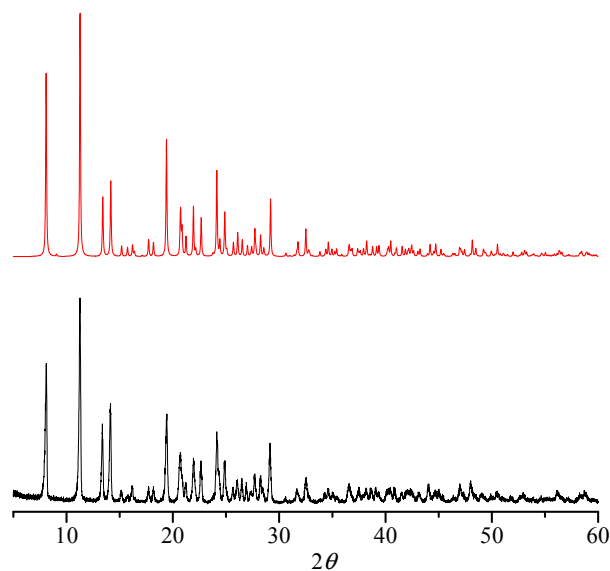


Fig. S4. Observed (black) and calculated (red) PXRD of $2\text{S} \cdot \text{H}_2\text{O}$.

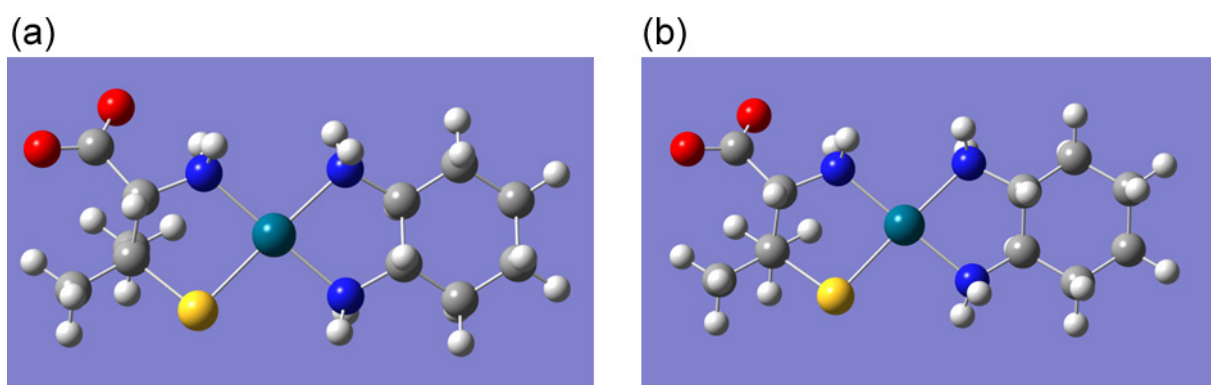


Fig. S5. Perspective views of the optimized structures of (a) **2_S** and (b) **2_R**. Pd: green, C: gray, H: white, N: blue, O: red, S: yellow.

Table S1. Selected bond distances (Å) and angles (°) of **1**·H₂O.

Pd(1)-S(1)	2.2613(12)	Pd(2)-S(2)	2.2625(12)
Pd(1)-N(1)	2.029(3)	Pd(2)-N(4)	2.039(3)
Pd(1)-N(2)	2.053(3)	Pd(2)-N(5)	2.045(3)
Pd(1)-N(3)	2.069(3)	Pd(2)-N(6)	2.083(3)
N(1)-Pd(1)-N(2)	177.52(10)	N(4)-Pd(2)-N(5)	177.01(15)
N(1)-Pd(1)-N(3)	94.00(13)	N(4)-Pd(2)-N(6)	94.22(13)
N(2)-Pd(1)-N(3)	83.69(13)	N(5)-Pd(2)-N(6)	83.55(13)
N(1)-Pd(1)-S(1)	85.97(10)	N(4)-Pd(2)-S(2)	86.09(10)
N(2)-Pd(1)-S(1)	96.39(10)	N(5)-Pd(2)-S(2)	96.17(10)
N(3)-Pd(1)-S(1)	177.06(12)	N(6)-Pd(2)-S(2)	179.01(11)

Table S2. Selected bond distances (Å) and angles (°) of **2_S**·H₂O.

Pd(1)-S(1)	2.2615(11)	Pd(1)-N(2)	2.061(3)
Pd(1)-N(1)	2.042(3)	Pd(1)-N(3)	2.114(4)
N(1)-Pd(1)-N(2)	175.51(16)	N(2)-Pd(1)-S(1)	95.70(10)
N(1)-Pd(1)-N(3)	97.06(13)	N(3)-Pd(1)-S(1)	175.06(10)
N(2)-Pd(1)-N(3)	82.09(13)		

Table S3. Selected bond distances (Å) and total energies (au) of the optimized structures for **2_S** and **2_R**.

	[Pd(D-pen- <i>N,S</i>)(<i>S,S</i> -chxn)] (2_S)	[Pd(D-pen- <i>N,S</i>)(<i>R,R</i> -chxn)] (2_R)
Pd(1)-S(1)	2.379	2.379
Pd(1)-N(1)	2.080	2.082
Pd(1)-N(2)	2.095	2.095
Pd(1)-N(3)	2.153	2.151
Total energy	-884.621957	-884.621996