

ELECTRONIC SUPPORTING INFORMATION (ESI)

for

A platinum(II)-palladium(II)-nickel(II) heterotrimetallic coordination polymer showing a cooperative effect on catalytic hydrogen evolution

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General methods.

trans-[Pt(NH₃)₂(D-Hpen)₂] was prepared according to a previously reported method.^{S1} The IR spectra were measured with a JASCO FT/IR-4100 infrared spectrophotometer using KBr disks. The ¹H NMR spectra were measured on JEOL RESONANCE ECS-400 and JEOL RESONANCE ECA-500 NMR spectrometers at room temperature in D₂O. Sodium 4,4-dimethyl-4-silapentane-1-sulfonate (DSS) was used as the internal reference. Elemental analyses (C, H, N) were performed at Osaka University. Voltammetry and controlled potential electrolysis were carried out at room temperature in a three-electrode cell under N₂ using a CHI720E potentiostat. The working electrode was a sample-modified glassy carbon electrode (ϕ 3.0 mm) prepared by drying 5 μ L of the sample solution or suspension (5 mg in 0.05 mL of lower aliphatic alcohols/water containing 5% of Nafion[®] (Aldrich)) on the electrode surface. The counter electrode was a platinum wire, and the reference electrode was an Ag/AgCl (3.0 M NaCl aq.) electrode. A 500 μ L sample was analyzed after 15 min using a gas chromatograph (Shimadzu GC-2014AT) with a thermal conductivity detector operating at 50°C. Ar was used as the carrier gas, and H₂ was detected on an activated molecular sieve column (ShincarbonST, Restek). Single-crystal X-ray diffraction measurements were performed on a RIGAKU RAXIS 7/FR-E imaging plate with graphite-monochromated Mo K α radiation (λ = 0.71075 Å) at 200 K. The intensity data were collected by the ω -scan technique and empirically corrected for absorption. The structures of the complexes were solved by direct methods using SHELXS-2014.^{S2} Structural refinements were carried out using full matrix least-squares (SHELXL-2014).^{S2} Non-hydrogen atoms were refined anisotropically, except for the N and O atoms of the disordered nitrate anion and water molecules. Hydrogen atoms were placed at calculated positions, except for the water molecules. SIMU and ISOR restraints were used to model a part of the penicillamine backbone in [H₄2]Cl₄. Cl atoms were disordered in some parts. All of the structural parameters are summarized in Table S1.

References.

- S1. Y. Kurioka, N. Kuwamura, N. Yoshinari, A. Igashira-Kamiyama and T. Konno, *Chem. Lett.*, 2015, **44**, 1330-1332.
- S2. G. M. Sheldrick, *Acta Crystallogr.*, 2008, **A64**, 112-122.

Preparation of complexes.

Preparation of $[\text{Pd}_2\text{Pt}_2(\text{NH}_3)_4(\text{D-pen})_4]$ ([2]).

To a brown suspension containing 0.43 g (1.9 mmol) of $\text{Pd}(\text{OAc})_2$ in 50 mL of water was added 1.0 g (1.9 mmol) of *trans*- $[\text{Pt}(\text{NH}_3)_2(\text{D-Hpen})_2]$. The mixture was stirred at room temperature for 4 h, which gave a clouded brown solution. After the filtration of unreacted $\text{Pd}(\text{OAc})_2$, the filtrate was evaporated to dryness. The orange residue was washed with EtOH. Yield: 1.29 g (92%). Calcd. for $[\text{Pd}_2\text{Pt}_2(\text{NH}_3)_4(\text{D-pen})_4] \cdot 12\text{H}_2\text{O}$: C, 16.27; H, 4.92; N, 7.59%. Anal. Found: C, 16.32; H, 4.76; N, 7.43%.

Preparation of $[\text{Pd}_2\text{Pt}_2(\text{NH}_3)_4(\text{D-Hpen})_4]\text{Cl}_4$ ($[\text{H}_42]\text{Cl}_4$).

To a brown solution containing 0.062 g (0.21 mmol) of $\text{Na}_2[\text{PdCl}_4]$ in 2 mL of H_2O was added 0.10 g (0.19 mmol) of *trans*- $[\text{Pt}(\text{NH}_3)_2(\text{D-Hpen})_2]$ in 3 mL of H_2O . The orange mixture was stirred at 0°C for 1 h to give a yellow solution. EtOH was diffused into the solution for 3 days to produce yellow crystals. Yield: 25 mg (16%). Calcd. for $[\text{Pd}_2\text{Pt}_2(\text{NH}_3)_4(\text{D-Hpen})_4]\text{Cl}_4 \cdot 12\text{H}_2\text{O}$: C, 14.81; H, 4.72; N, 6.91%. Anal. Found: C, 14.76; H, 4.76; N, 6.96%.

Preparation of $[\{\text{Ni}(\text{H}_2\text{O})_4\}\{\text{Pd}_2\text{Pt}_2(\text{NH}_3)_4(\text{D-pen})_4\}]\text{Cl}_2$ ([3]Cl₂).

To an orange solution containing 0.10 g (0.068 mmol) of $[\text{Pd}_2\text{Pt}_2(\text{NH}_3)_4(\text{D-pen})_4]$ in 15 mL of water was added 0.16 g (0.68 mmol) of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ in 3 mL of water. After the solution was evaporated to dryness, to the black-green residue was added 5 mL of water. The mixture was stood at room temperature for 7 days. The resulting green platelet crystals were collected by filtration and washed with 5 mL of water. Yield: 0.07 g (60%). Calcd. for $[\{\text{Ni}(\text{H}_2\text{O})_4\}\{\text{Pd}_2\text{Pt}_2(\text{NH}_3)_4(\text{D-pen})_4\}]\text{Cl}_2 \cdot 15\text{H}_2\text{O}$: C, 13.87; H, 5.01; N, 6.47%. Anal. Found: C, 13.88; H, 4.80; N, 6.49%.

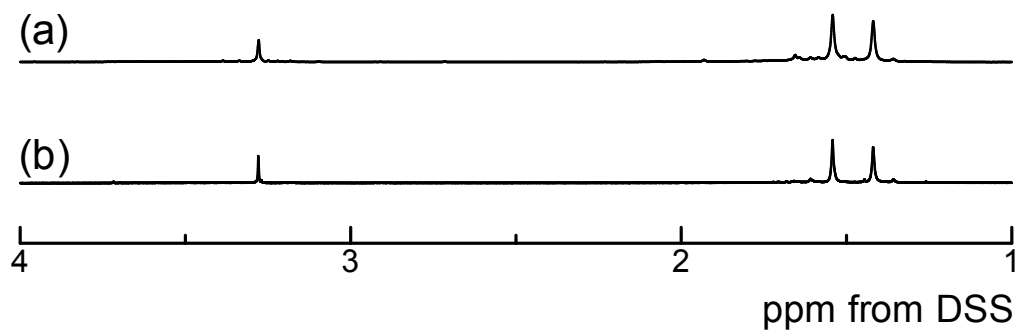


Fig. S1. ¹H NMR spectra of (a) the reaction solution of [H₂1] with Na₂[PdCl₄], and (b) [2] in D₂O.

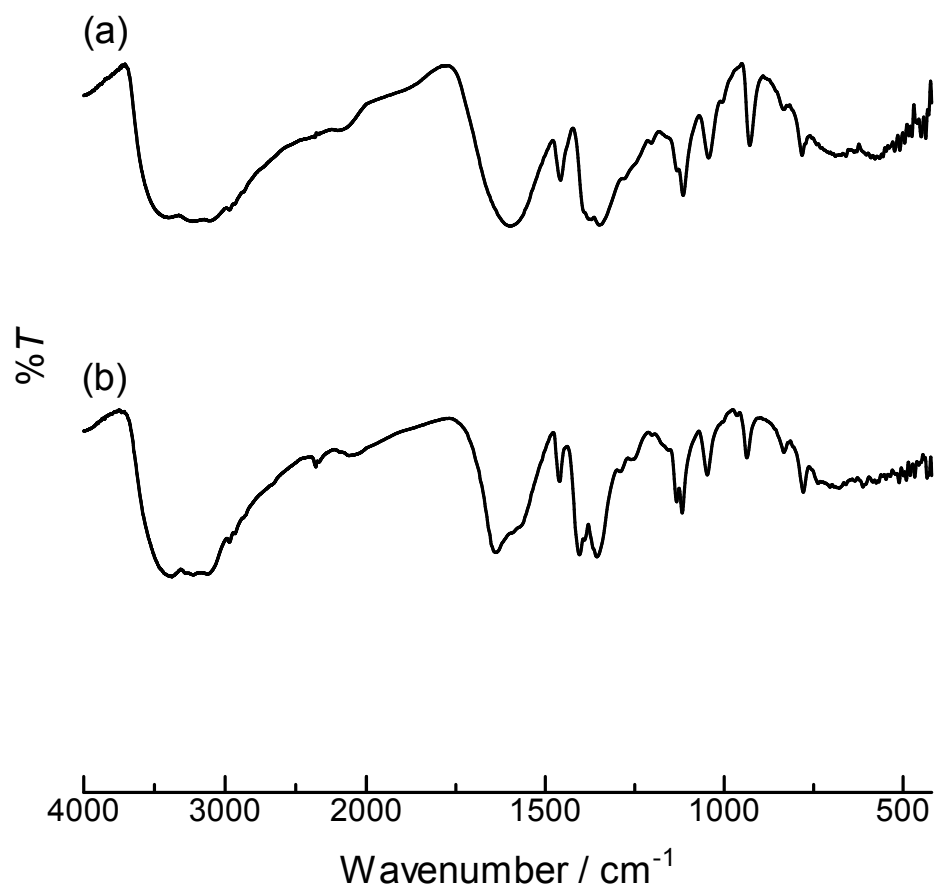


Fig. S2. IR spectra of (a) [2] and (b) [3]Cl₂.

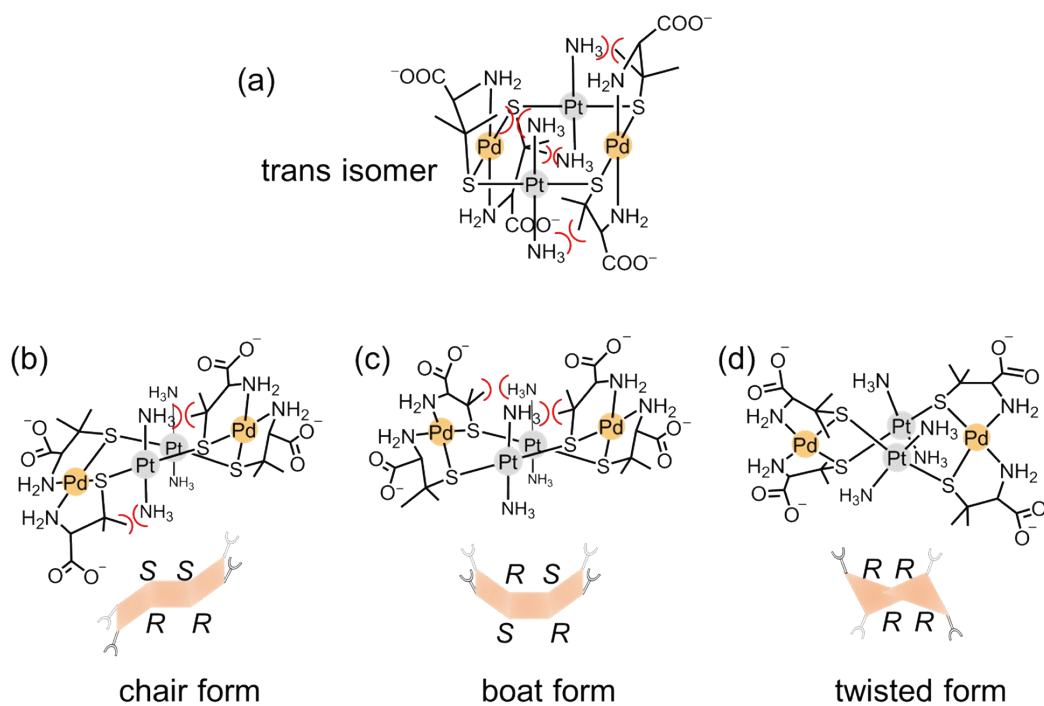


Fig. S3. Model structures of (a) the trans isomer and cis isomers with (b) the chair form, (c) boat form, and (d) twisted form of $[\text{Pd}_2\text{Pt}_2(\text{NH}_3)_4(\text{D-pen})_4]$. The red curve indicates the steric repulsions between methyl and ammine groups.

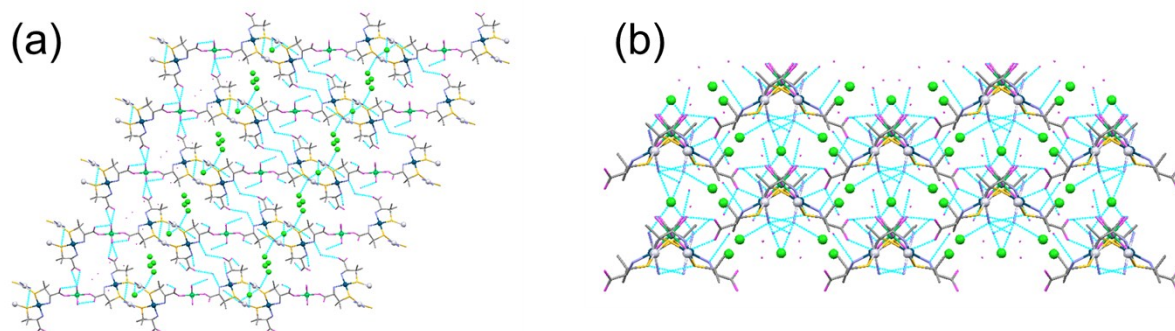
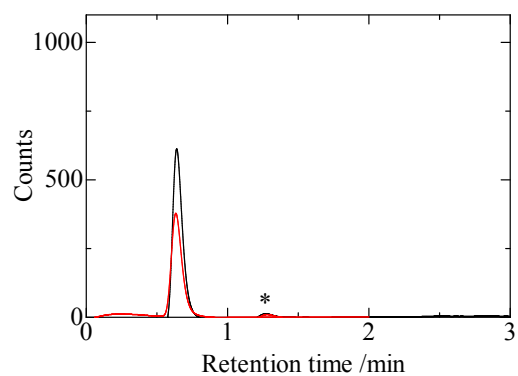


Fig. S4. Packing structure of $[3]Cl_2$ viewed from the (a) b axis and (b) c axis. The green ball represents a chloride ion. H atoms are omitted for clarity. Blue dashed lines represent hydrogen bonds.

(a)



(b)

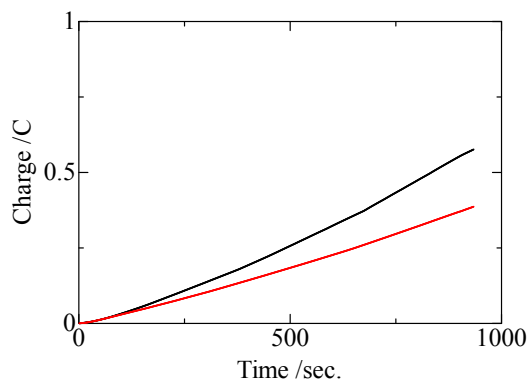


Fig. S5. (a) Gas chromatogram of the head space (500 μL) after the electrolysis of **[3]**Cl₂ (black line) and **[2]** (red line) attached to the glassy carbon electrode in H₂O/CH₃CN (v/v = 1/9) containing 0.1 M LiClO₄ at an applied voltage of -1.2 V for 15 min. (*) indicates O₂ gas contamination. (b) Charge vs. time plot of the electrolysis.

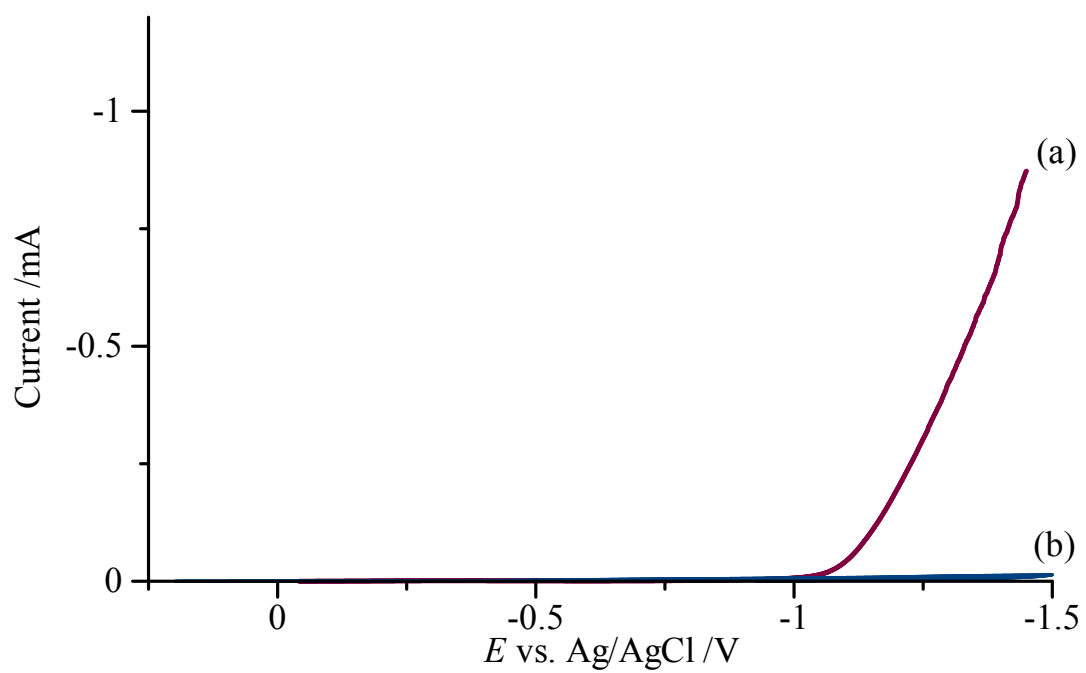


Fig. S6. Linear sweep voltammograms of $[3]Cl_2$ attached to a glassy carbon electrode in (a) H_2O/CH_3CN ($v/v = 1/9$) and (b) acetonitrile, both containing 0.1 M $LiClO_4$.

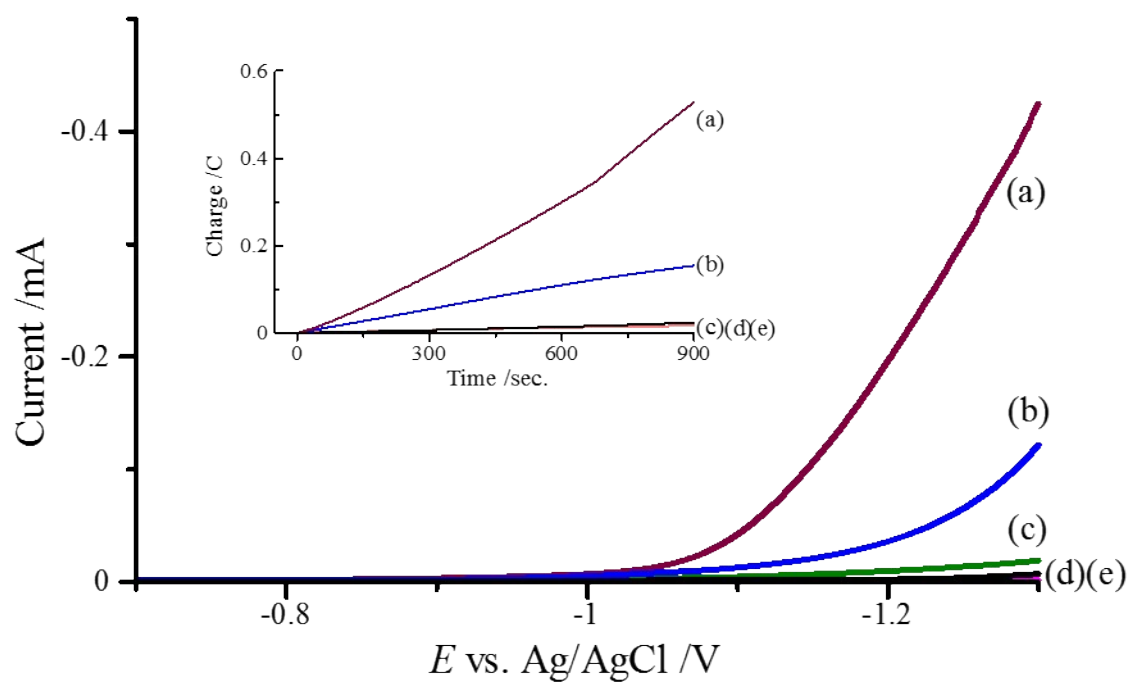


Fig. S7. Linear sweep voltammograms of (e) $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ attached to a glassy carbon electrode (0.07 cm^2), compared with (a) $[\mathbf{3}]\text{Cl}_2$, (b) $[\mathbf{2}]$, and (c) $[\text{H}_2\mathbf{1}]$, and (d) a bare glassy carbon electrode, in $\text{H}_2\text{O}-\text{CH}_3\text{CN}$ ($v/v = 1/9$) containing 0.1 M LiClO_4 . The scan rate is 0.01 V/sec . Inset: Charge build-up versus time in extended potential-controlled electrolysis experiments at the applied potential of -1.20 V .

Table S1. Crystallographic data for [H₄2]Cl₄ and [3]Cl₂.

	[H ₄ 2]Cl ₄	[3]Cl ₂
Formula	C ₂₀ H ₅₂ Cl ₄ N ₈ O _{14.5} Pd ₂ Pt ₂ S ₄	C ₂₀ H ₄₈ Cl ₂ N ₈ NiO ₂₆ Pd ₂ Pt ₂ S ₄
Colour, shape	yellow, block	yellow, platelet
<i>M</i>	1509.71	1677.49
Crystal system	monoclinic	monoclinic
Space group	<i>C</i> 2	<i>C</i> 2
<i>a</i> /Å	16.407(4)	22.503(3)
<i>b</i> /Å	23.902(9)	9.0650(10)
<i>c</i> /Å	14.901(3)	18.450(2)
<i>β</i> /°	103.206(17)	119.332(8)
<i>V</i> /Å ³	5689(3)	3281.0(7)
<i>Z</i>	4	2
<i>T</i> /K	200	200
<i>F</i> (000)	2896	1612
ρ_{calcd} /g cm ⁻³	1.763	1.698
μ (Mo K α) /mm ⁻¹	5.910	5.342
Crystal size /mm ³	0.20 × 0.20 × 0.15	0.10 × 0.08 × 0.03
Limiting indices	-21 ≤ <i>h</i> ≤ 21	-28 ≤ <i>h</i> ≤ 29
	-30 ≤ <i>k</i> ≤ 31	-11 ≤ <i>k</i> ≤ 11
	-19 ≤ <i>l</i> ≤ 19	-23 ≤ <i>l</i> ≤ 19
<i>R</i> ₁ ^a (<i>I</i> > 2σ(<i>I</i>))	0.0324	0.0569
<i>wR</i> ₂ ^b (all data)	0.0998	0.1658
GOF	1.047	1.058
Flack parameter	0.014(3)	0.079(8)
CCDC number	1514220	1514221

^a $R_1 = \sum (|F_o| - |F_c|) / \sum (|F_o|)$.

^b $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$.