Electronic Supplementary Information (ESI)

for

A [NiFe]hydrogenase model that catalyses the release of hydrogen from formic acid

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Experimental

Materials and methods. All experiments were carried out under an N_2 or Ar atmosphere by using standard Schlenk techniques and a glovebox. Concentrated HNO_3/H_2O, distilled H_2O, NaOH and HCOONa were purchased from Wako Pure Chemical Industries, Ltd. Concentrated DNO_3/D_2O (99% D), D_2O (99.9% D), 40wt% NaOD/D_2O (99% D), DCOONa (99% D) and were purchased from Cambridge Isotope Laboratories, Inc. H_2 (99.9999%) and CO_2 (99.99%) gases were purchased from Taiyo Toyo Sanso Co., Ltd. $[Ni^{II}L(H_2O)(\mu\text{-}H)Ru^{II}(\eta^6\text{-}C_6Me_6)](NO_3)$ {[**2**](NO_3), L = *N*,*N'*-dimethyl-3,7-diazanonane-1,9-dithiolato} and $[Ni^{II}LRu^{II}(H_2O)(\eta^6\text{-}C_6Me_6)](NO_3)_2$ {[**3**]$(NO_3)_2$} were prepared by the methods described in the literature.[1]

Electrospray ionization mass spectrometry (ESI-MS) data were obtained by a JEOL JMS-T100LC AccuTOF. IR spectra of solid compounds in KBr disks were recorded on a Thermo Nicolet NEXUS 8700 FT-IR instrument from 650 to 4000 cm^{-1} using 2 cm^{-1} standard resolution at 25 °C. UV-vis spectra were recorded on a JASCO V-670 UV-Visible-NIR Spectrophotometer at 25 °C (light pass length: 0.10 cm). Elemental analysis data was obtained by a PerkinElmer 2400II series CHNS/O analyser. H_2 gas was detected and quantified by a Shimadzu GC-14B and GC-8A gas chromatograph {He carrier, 10% $MnCl_2$-alumina column (model: Shinwa OGO-SP) at –196 ˚C (liquid N_2)}. CO_2 gas was detected by a Shimadzu GC-2014 gas chromatograph.

pH (or pD) values of the aqueous solutions were determined by a pH meter (TOA, HM20J) equipped with a pH combination electrode (TOA, GST-5725C). Values of pD were corrected by adding 0.4 to the observed values (pD = pH meter reading + 0.4).[2,3] The pH (or pD) of aqueous solutions was adjusted by HNO_3/H_2O (or DNO_3) and NaOH/H_2O (NaOD/D_2O).

$[Ni^{II}L(HCOO)(\mu\text{-}H)Ru^{II}(\eta^6\text{-}C_6Me_6)]$ (1). Complex **1** can be prepared from [**2**](NO_3) (method A) and [**3**]$(NO_3)_2$ (method B) as starting materials as follows. **Method A.** An aqueous solution (2.0 mL) of HCOONa (0.547 g, 8.04 mmol) was added to an aqueous solution (2.0 mL) of [**2**](NO_3) (50.1 mg, 0.0804 mmol). The resulting solution was allowed to stand overnight to gradually precipitate brown crystals, which were collected by filtration and dried *in vacuo* {yield: 73% based on [**2**](NO_3)}. **Method B.** An aqueous solution (5.0 mL) of HCOONa (1.54 g, 22.7 mmol) was added to an aqueous solution (5.0 mL) of [**3**]$(NO_3)_2$ (152 mg, 0.222 mmol). The resulting solution was allowed to stand for 4 h to gradually precipitate brown crystals, which were collected by filtration and dried *in vacuo* {yield: 34% based on [**3**](NO_3)$_2$}. Positive-ion ESI-MS (in H_2O at pH 7.0): *m/z* 543.2 {[**1** – HCOO]$^+$, relative intensity (*I*) = 100% in the range of *m/z* 200–2000}. Negative-ion ESI-MS (in H_2O at pH 7.0): *m/z* 633.2 ([**1** + HCOO]$^-$, *I* = 100% in the range of *m/z* 200–2000). FT-IR (cm^{-1}, KBr disk): 1349, 1760, 2649. Anal. Calcd for [**1**].2H_2O: $C_{22}H_{44}N_2NiO_4RuS_2$: C, 42.31; H, 7.1; N, 4.49. Found: C, 42.34; H, 7.0; N, 4.39.

[Ni^{II}L(DCOO)(μ-D)Ru^{II}(η^6-C_6Me_6)] (double D-labelled 1). A solution of DCOONa (151 mg, 2.19 mmol) in D_2O (0.5 mL) was added to a solution of [**3**](NO_3)$_2$ (15 mg, 0.0219 mmol) in D_2O (0.5 mL). The resulting solution was allowed to stand for 4 h to gradually precipitate brown crystals, which were collected by filtration and dried *in vacuo* {yield: 34% based on [**3**](NO_3)$_2$}. Positive-ion ESI-MS (in D_2O at pD 7.0): *m/z* 544.2 ([**1** – DCOO]$^+$, *I* = 100% in the range of *m/z* 200–2000). Negative-ion ESI-MS (in D_2O at pD 7.0): *m/z* 636.3 ([double D-labelled **1** + DCOO]$^+$, *I* = 100% in the range of *m/z* 200–2000). FT-IR (cm^{-1}, KBr disk): 1248, 1329, 2114.

Typical procedure for H_2 and CO_2 evolution from HCOOH catalysed by 2. A 3 mL vial was charged with 7.3 nmol of [**2**](NO_3) and 146 μmol of HCOONa in H_2O (510 μL) at pH 1.6–9.0, and was capped with a septum under an N_2 atmosphere. The vial was heated at 60 °C for 1 h. The gas present in the vial was sampled using a gas-tight syringe and analysed for H_2 and CO_2 gases by GC.

X-ray crystallographic analysis. A brown crystal of **1** used for X-ray analysis was obtained from its aqueous solution. Crystallographic data for **1**·5H_2O has been deposited with the Cambridge Crystallographic Data Centre as Supplementary Publication No. CCDC 1016741. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK {Fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk}. Measurements were made on a Rigaku/MSC Saturn CCD diffractometer with confocal monochromated Mo$K\alpha$ radiation (λ = 0.7107 Å). Data were collected and processed using the CrystalClear program (Rigaku). All calculations were performed using the CrystalStructure crystallographic software package except for refinement, which was performed using SHELXL-97.

Although five O atoms (O3, O4, O5, O6 and O7) are assigned as waters, the electron densities of H atoms binding to the O atoms are not found. Thus, refinement was carried out without these H atoms and the calculated molecular weight is different from the reported molecular weight. The short distances between O atoms (O3, O4, O5, O6 and O7) should be caused by hydrogen bonds.

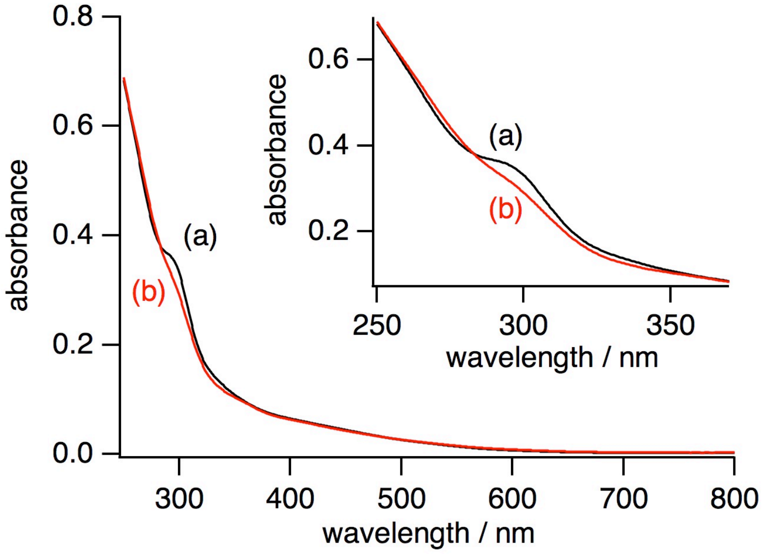

Fig. S1 A UV-vis spectral change from (a) $[Ni^{II}L(H_2O)(\mu\text{-}H)Ru^{II}(\eta^6\text{-}C_6Me_6)]^+$ (**2**) to (b) $[Ni^{II}L(HCOO)(\mu\text{-}H)Ru^{II}(\eta^6\text{-}C_6Me_6)]$ (**1**) upon the addition of one equivalent of HCOONa (2.34 μmol) into **2** (2.34 μmol) in H_2O (2.0 mL). Insert: UV-vis spectra enlarged in the region between 250 and 370 nm.

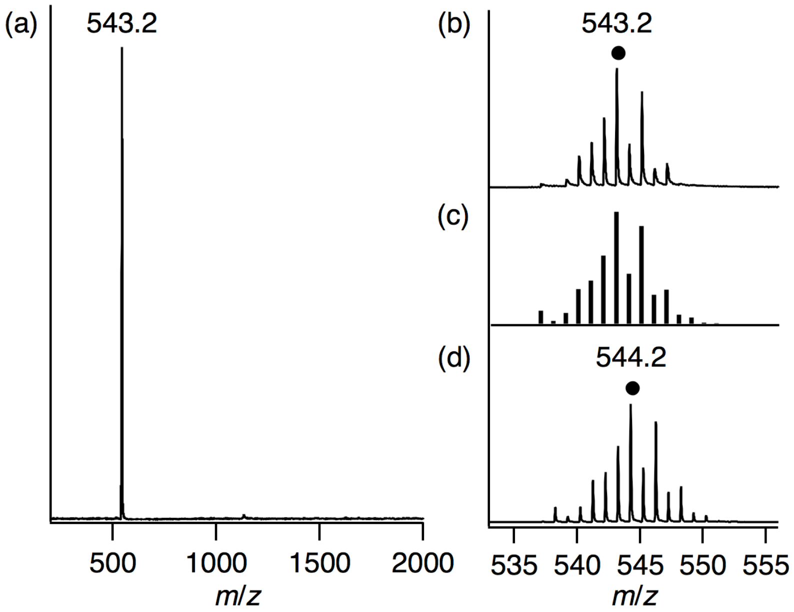

Fig. S2 (a) A positive-ion ESI mass spectrum of [Ni^{II}L(HCOO)(μ-H)Ru^{II}(η^6-C_6Me_6)] (**1**) in H_2O at pH 7.0. (b) Signal at *m*/*z* 543.2 corresponds to [**1** – HCOO]$^+$. (c) Calculated isotopic distribution corresponds to [**1** – HCOO]$^+$. (d) A positive-ion ESI mass spectrum of [Ni^{II}L(DCOO)(μ-D)Ru^{II}(η^6-C_6Me_6)] (double D-labelled **1**) in D_2O at pD 7.0. Signal at *m*/*z* 544.2 corresponds to [double D-labelled **1** – DCOO]$^+$.

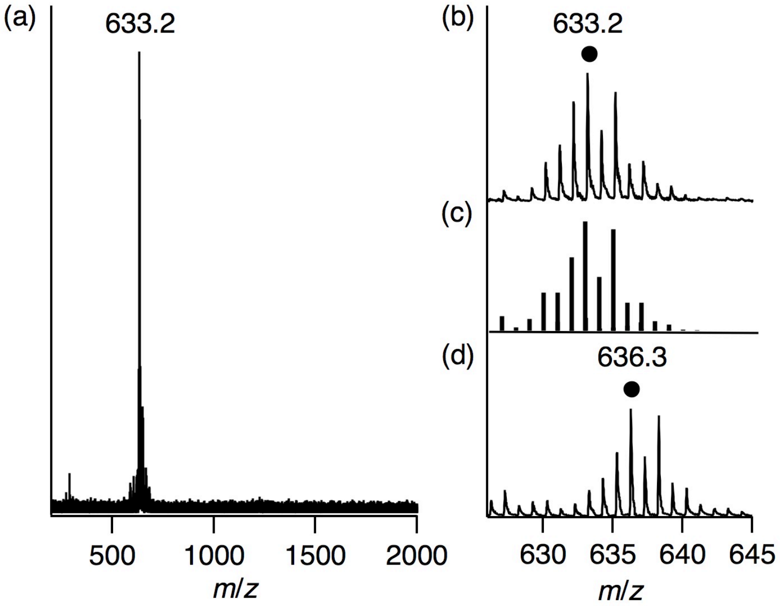

Fig. S3 (a) A negative-ion ESI mass spectrum of [Ni^{II}L(HCOO)(μ-H)Ru^{II}(η^6-C_6Me_6)] (**1**) in H_2O at pH 7.0. (b) Signal at *m*/*z* 633.2 corresponds to [**1** + HCOO]$^-$. (c) Calculated isotopic distribution corresponds to [**1** + HCOO]$^-$. (d) A negative-ion ESI mass spectrum of [Ni^{II}L(DCOO)(μ-D)Ru^{II}(η^6-C_6Me_6)] (double D-labelled **1**) in D_2O at pD 7.0. Signal at *m*/*z* 636.3 corresponds to [double D-labelled **1** + DCOO]$^-$.

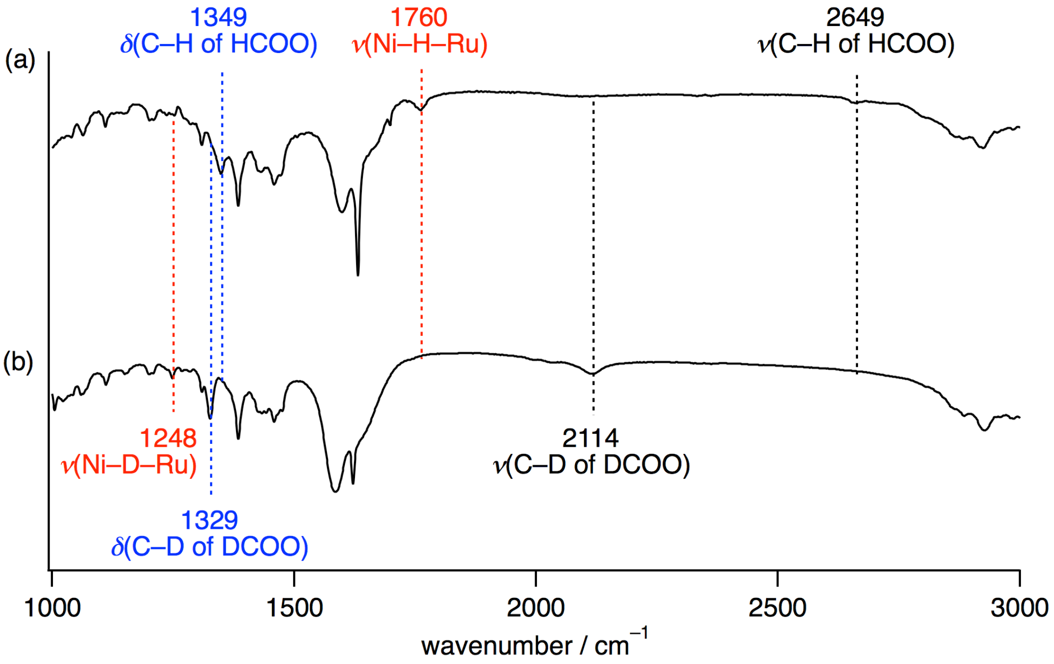

Fig. S4 IR spectra of (a) [$Ni^{II}L(HCOO)(\mu\text{-}H)Ru^{II}(\eta^6\text{-}C_6Me_6)$] (**1**) and (b) [$Ni^{II}L(DCOO)(\mu\text{-}D)Ru^{II}(\eta^6\text{-}C_6Me_6)$] (double D-labelled **1**) as KBr disks.

References

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