

## ***Supporting Information***

### **Base-Enhanced Electrochemical Water Oxidation by a Nickel Complex in Neutral Aqueous Solution**

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#### **Materials and Methods**

##### **Materials and Characterization**

All chemicals were used without further purification and buffer solutions were prepared with reagent-grade water (18 M $\Omega$ -cm resistivity). The 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (TMC) ligand and Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O were purchased from Sigma Aldrich Chemie B.V. FTO-coated glass was purchased from Wuhan Geao science (thickness ~ 2.2 mm, transmittance > 90%, resistance ~ 50 m $\Omega$ /cm<sup>2</sup>). Scanning electron microscopy (SEM) and energy Dispersive Spectroscopy (EDS) analyses were conducted by FEI Nova NanoSEM 450

instrument equipped with an EDS detector. UV-Vis spectrum were recorded on a Thermo Scientific Evolution 220 spectrophotometer. Electrochemical measurements were performed with a CHI760E or a PG-STAT302N electrochemical workstation.

### **Complex and electrolyte preparation**

The preparation of  $[\text{Cu}(\text{TMC})(\text{H}_2\text{O})](\text{NO}_3)_2$  was described in our previous work.<sup>[1]</sup>  $[\text{Ni}(\text{TMC})(\text{CH}_3\text{CN})](\text{NO}_3)_2$  was prepared by following the protocol of the copper analogue with high yield (85%).<sup>[1]</sup> In brief,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.291 g, 1.0 mmol) was added to a acetonitrile solution of TMC ligand (0.256 g, 1.0 mmol). The mixture was stirred at room temperature for 4 hours. The resulting solution was then concentrated to ~ 5 mL under vacuum followed by adding 50 mL diethyl ether to precipitate the complex. The precipitation was generated immediately which was filtered and washed with small amount of acetonitrile and then large scale of diethyl ether. The product was obtained in a yield of 85%. The structure was confirmed by high-resolution mass spectroscopy and single-crystal X-ray diffraction analysis. TOF-MS: Calcd for  $[\text{Ni}(\text{TMC})]^{2+}/2$  ( $\text{C}_{14}\text{H}_{32}\text{NiN}_4$ ): 157.0990; found: 157.0996. The crystals was obtained by diffusion of diethyl ether to 10 mM of  $[\text{Ni}(\text{TMC})(\text{CH}_3\text{CN})](\text{NO}_3)_2$  acetonitrile solution at room temperature. In two weeks, the crystal is collectable and suitable for structure analysis, which was used for electrochemistry analysis.

The pH of solutions were detected by pH meter until getting the goal pH value. Phosphate and borate buffers were prepared by mixing  $\text{Na}_2\text{HPO}_4$  and  $\text{NaH}_2\text{PO}_4$  and  $\text{H}_3\text{BO}_3$  and  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$  in proper ratios, respectively. Acetate and phthalate buffer were obtained by adding the diluted NaOH to the sodium salts solutions until pH 7. The ionic strength of the buffer solutions were compensated to 0.5 M by  $\text{KClO}_4$ .

### **Electrochemical measurement**

All of the electrochemical measurements were conducted with the three-electrode system which consisted of a working electrode, a platinum wire counter electrode, and a Ag/AgCl reference electrode ( $\sim 0.197$  V vs. NHE). Unless stated otherwise, all potentials were reported vs. NHE. Prior to measurement, the glassy carbon electrode was first polished with  $0.2 \mu\text{m}$   $\text{Al}_2\text{O}_3$  slurry and then  $0.05 \mu\text{m}$   $\text{Al}_2\text{O}_3$  for 2 min, respectively. For FTO electrode, prior to the experiments, the glass slides were cleaned by sonication in acetone, ethanol and reagent-grade water.

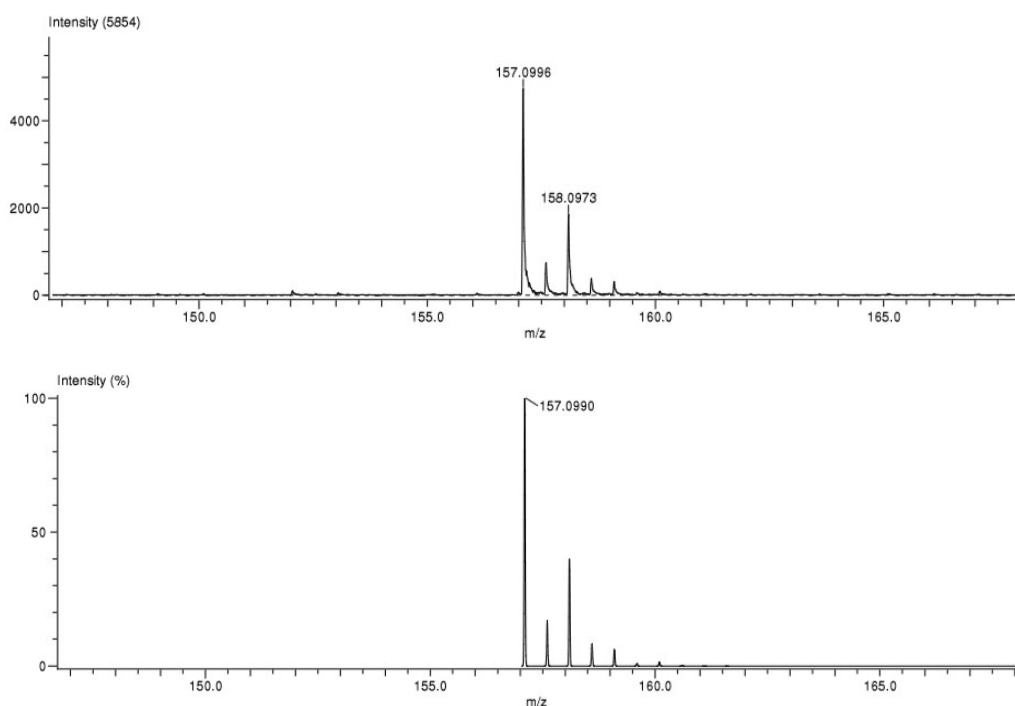


Figure S1. High-resolution mass spectrum for the charged species  $[\text{Ni}(\text{TMC})]^{2+}/2$  observed (above) and simulated isotopic distribution (below).

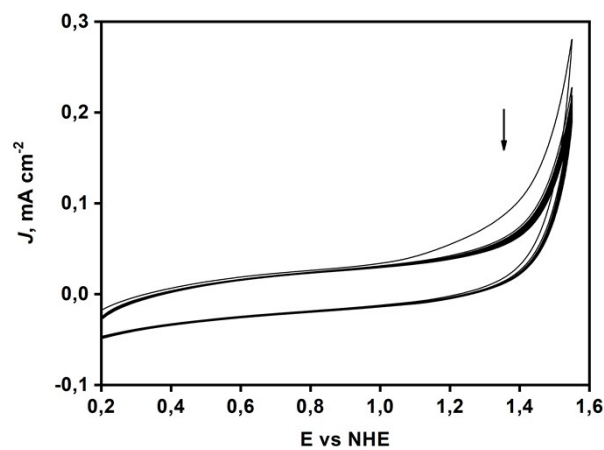


Figure S2. Successive cyclic voltammogram scans of 1 mM  $\text{Ni}(\text{NO}_3)_2$  in 0.1 M pH 7 phosphate buffer with a glassy carbon working electrode, a Ag/AgCl reference electrode and a Pt counter electrode, scan rate of  $100 \text{ mV s}^{-1}$ .

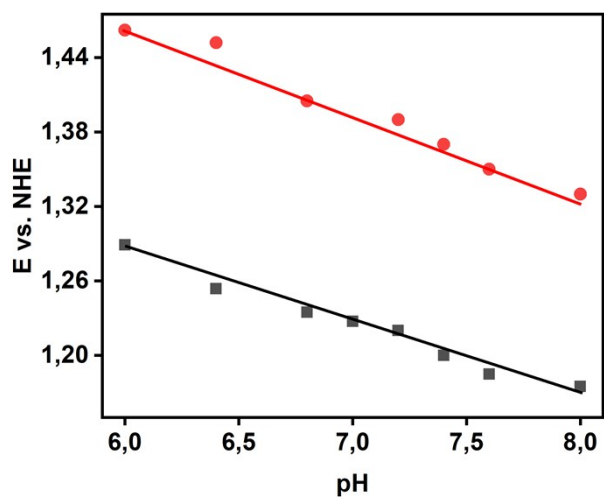


Figure S3. Pourbaix diagram for complex **1** between pH 6-8 phosphate buffer.

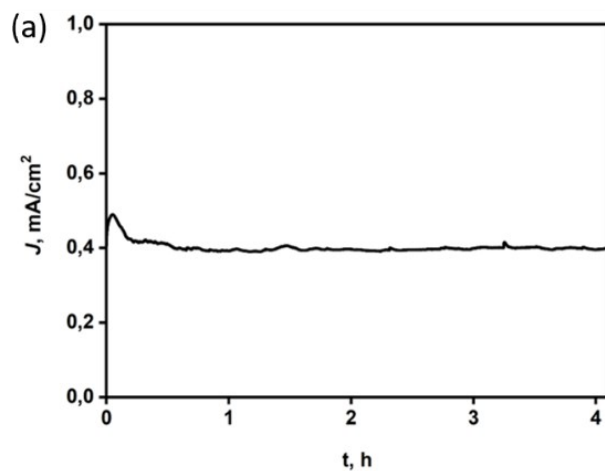


Figure S4. Catalytic current obtained at the controlled potential electrolysis with stirring in the presence of 1 mM complex **1** at an FTO electrode ( $1 \times 2$  cm) in 0.1 M phosphate buffer (pH 7.0) at 1.4 V vs. NHE.

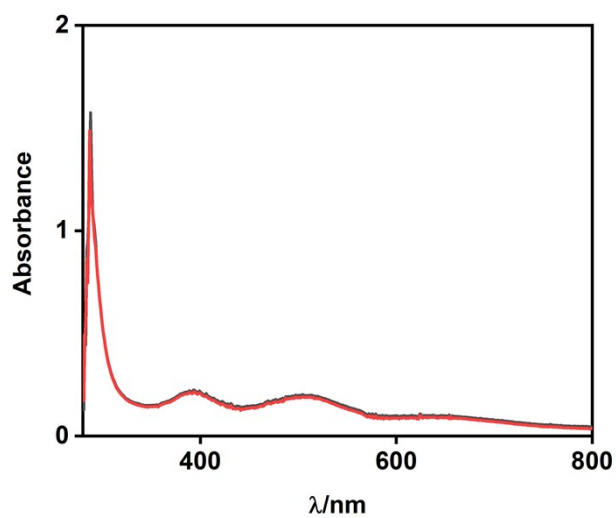


Figure S5. UV-visible spectra of **1** in 0.1 M phosphate buffer at pH 7.0 before (black) and after (red) 4 hours electrolysis.

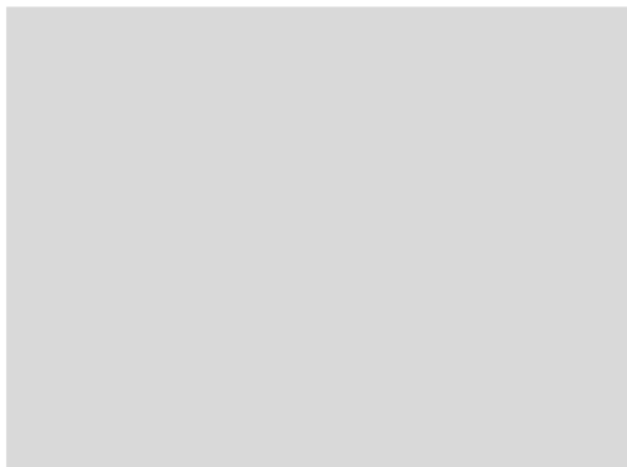


Figure S6. Charge passed through FTO working electrode in phosphate buffer at pH 7 in the presence of various catalyst concentration (0-2 mM).

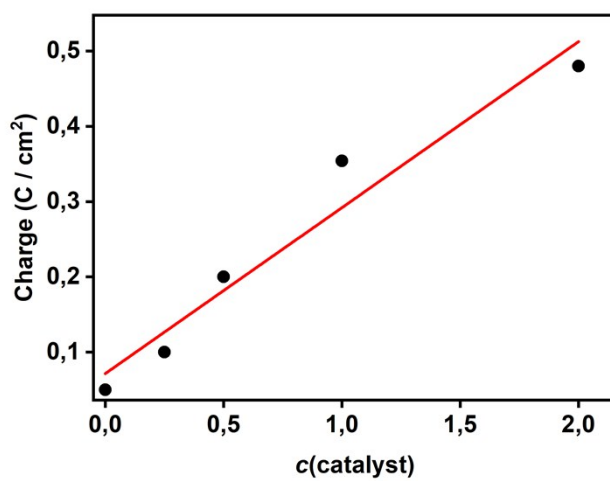


Figure S7. Dependence of integral charges on catalyst concentration in phosphate buffer at pH 7.

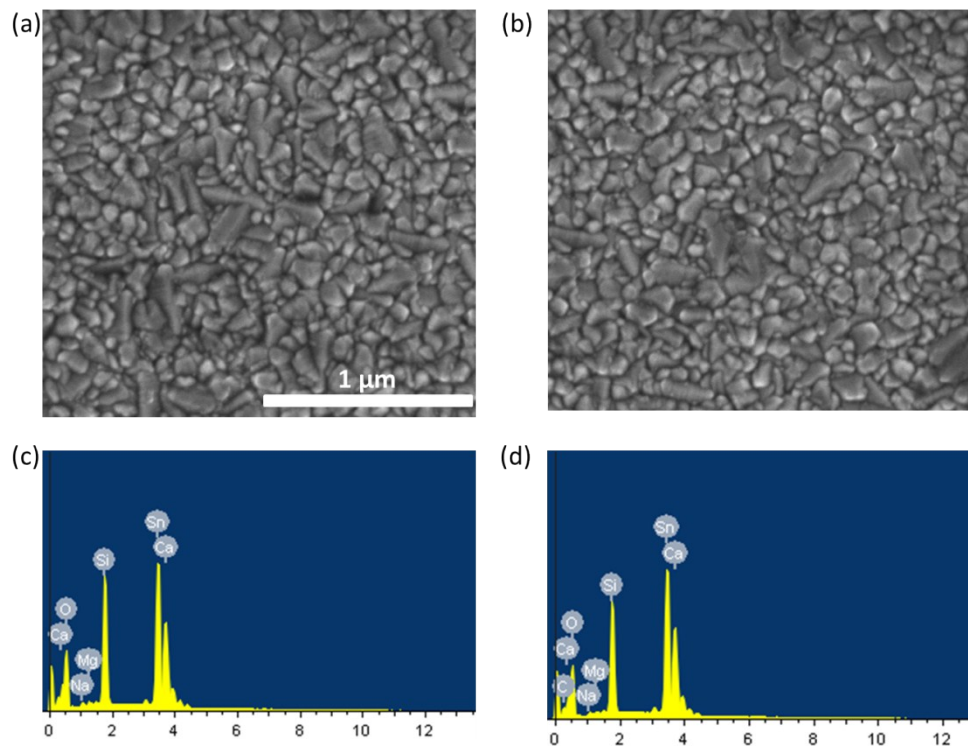


Figure S8. Energy-dispersive X-ray spectra (EDS) and scanning electron microscopes (SEM) images of the FTO anode before (left) and after (right) continuous electrolysis at 1.4 V in 0.1 M pH 7 phosphate buffer containing 1.0 mM complex **1**.

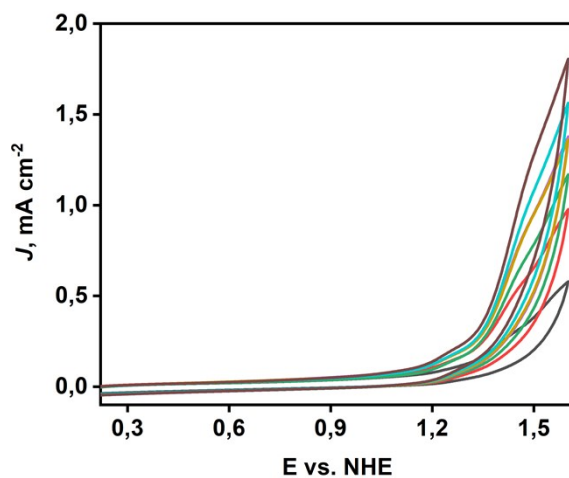


Figure S9. Cyclic voltammograms of **1** in 0.1 M pH 7 phosphate at a scan rate of 100 mV s<sup>-1</sup> with the concentration of **1** varied from 0.3 to 1.5 mM.

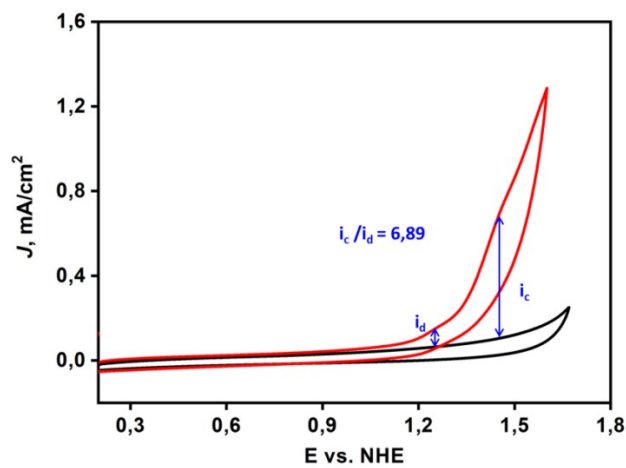


Figure S10. Cyclic voltammograms in the presence of 1 mM complex **1** (red) and absence of catalyst (black) in 0.1 M pH 7 phosphate at a scan rate of 100 mV s<sup>-1</sup>.

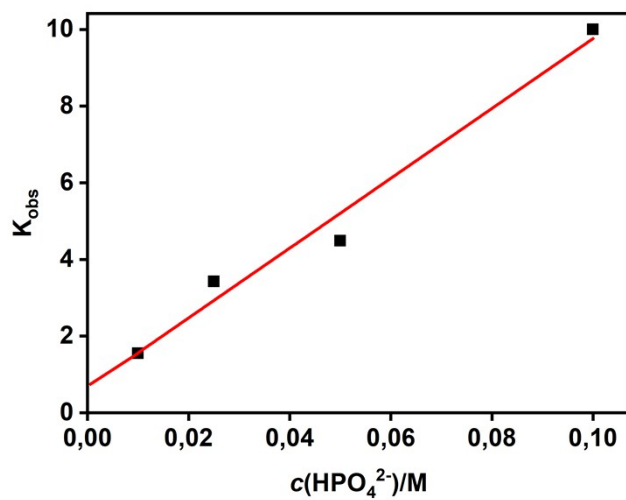


Figure S11.  $K_{obs}$  of complex **1** measured in the range phosphate concentration of 0.01 to 0.1 M.



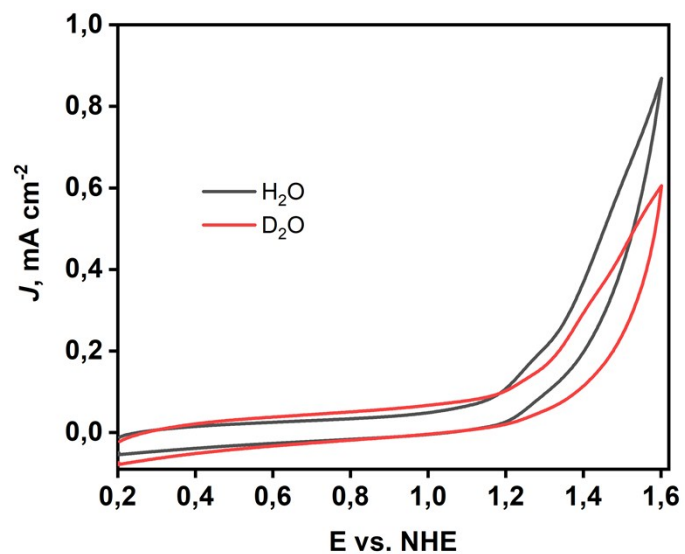


Figure S12. Cyclic voltammograms of complex **1** in neutral H<sub>2</sub>O and D<sub>2</sub>O phosphate buffers with the same catalyst concentration of 0.5 mM.

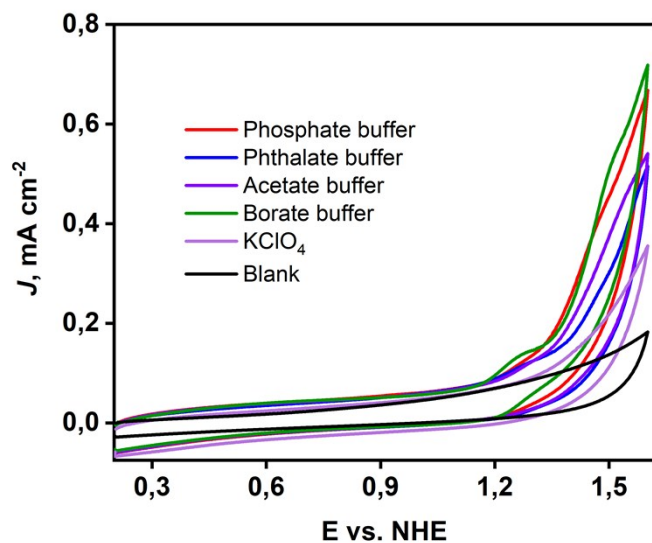


Figure S13. Cyclic voltammograms of complex **1** (0.5 mM) in various solutions at pH 7, the ionic strength was compensated to be 0.5 M with KClO<sub>4</sub>.

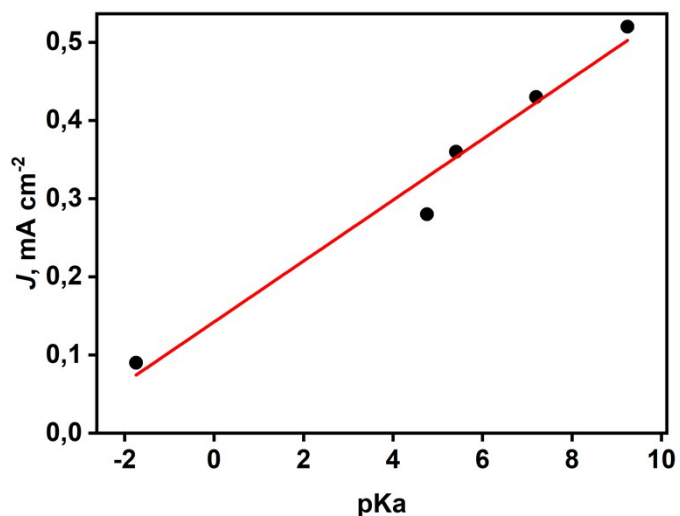


Figure S14. Dependence of pKa of buffers on the catalytic current density measured in the same conditions.

**Table S1.** Crystallographic data and processing parameters for **1** and **2**

Complex	<b>1</b>	<b>2</b>
Formula	C <sub>16</sub> H <sub>35</sub> N <sub>7</sub> O <sub>6</sub> Ni	C <sub>14</sub> H <sub>36</sub> N <sub>6</sub> O <sub>8</sub> Cu
Formula weight	480.22	480.03
Crystal system	Tetragonal	Triclinic
Space group	P4(3)	P-1
Z	8	2
<i>a</i> / Å	13.4449(7)	9.4885(3)
<i>b</i> / Å	13.4449(7)	10.1789(3)
<i>c</i> / Å	24.078(2)	11.6397(4)
<i>α</i> / deg	90.00	85.237(2)
<i>β</i> / deg	90.00	74.9220(10)
<i>γ</i> / deg	90.00	77.7440(10)
<i>V</i> / Å <sup>3</sup>	4352.5(5)	1060.29(6)

$D_{\text{calcd}} / \text{g m}^{-3}$	1.466	1.504
$\mu / \text{mm}^{-1}$	0.939	1.083
Crystal size / mm	0.17 × 0.15 × 0.10	0.21×0.18×0.17
$\theta$ Range / deg	2.27 / 25.59	2.27 / 27.45
Reflns collected / Indep.	7604 / 6908	3721 / 3520
Parameters refined	551	282
$F(000)$	2048	510
GOF on $F^2$	1.030	1.014
Final $R_1 (I > 2(I))$	0.0466	0.0384
Final $wR_2 (I > 2(I))$	0.0994	0.1001
max. peak/hole / $\text{e \AA}^{-3}$	0.758 / -0.329	0.807 / -0.874

$$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|, wR_2 = [\Sigma(|F_o|^2 - |F_c|^2)^2/\Sigma(F_o^2)]^{1/2}$$

**Table S2** Selected bond lengths (Å) and angles (deg) for **1** and **2**

Complex 1		Complex 2	
Bond	Length (Å)	Bond	Length (Å)
Ni–N1	2.148(4)	Cu–N1	2.097(19)
Ni–N2	2.024(5)	Cu–N2	2.096(2)
Ni–N3	2.175(4)	Cu–N3	2.090(2)
Ni–N4	2.099(3)	Cu–N4	2.090(2)
Ni–N5	2.009(3)	Cu–O1	2.238(2)
Bond	Angle (deg)	Bond	Angle (deg)
N1–Ni–N2	85.68(13)	N1–Cu–N2	86.07(8)
N1–Ni–N3	177.93(14)	N1–Cu–N3	152.88(8)
N1–Ni–N4	93.82(14)	N1–Cu–N4	93.34(8)

N1–Ni–N5	91.69(15)	N1–Cu–O1	102.37(8)
N2–Ni–N3	94.85(13)	N2–Cu–N3	93.36(8)
N2–Ni–N4	153.06(12)	N2–Cu–N4	176.79(7)
N2–Ni–N5	100.86(12)	N2–Cu–O1	91.54(9)
N3–Ni–N4	84.79(14)	N3–Cu–N4	85.72(8)
N3–Ni–N5	90.17(15)	N3–Cu–O1	104.75(8)
N4–Ni–N5	106.07(11)	N4–Cu–O1	91.67(8)

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[1] F. Yu, F. Li, J. Hu, L. Bai, Y. Zhu, L. Sun, *Chem. Commun.*, **2016**, 52, 10377-10380.