

ChemSusChem

Supporting Information

Nickel is a Different Pickle: Trends in Water Oxidation Catalysis for Molecular Nickel Complexes

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1. Materials and methods

All reagents were purchased from commercial suppliers and used without further purification. All complexes were prepared according to literature procedures and spectroscopic analysis was in line with the reported values. Complex **1**,¹ complex **2**,²⁻³ complex **3**,^{1,4} complex **4** & **5**,³ complex **6**,⁵ complex **7**,⁶ complex **8** & **9**,⁷⁻⁸ complex **10**,⁹⁻¹⁰ complex **11**,¹¹ complex **12**,¹² and complex **13**.¹² Milli-Q Ultrapure grade water (> 18.2 M Ω cm resistivity) was used for all experiments and for the preparation of aqueous buffer solutions.

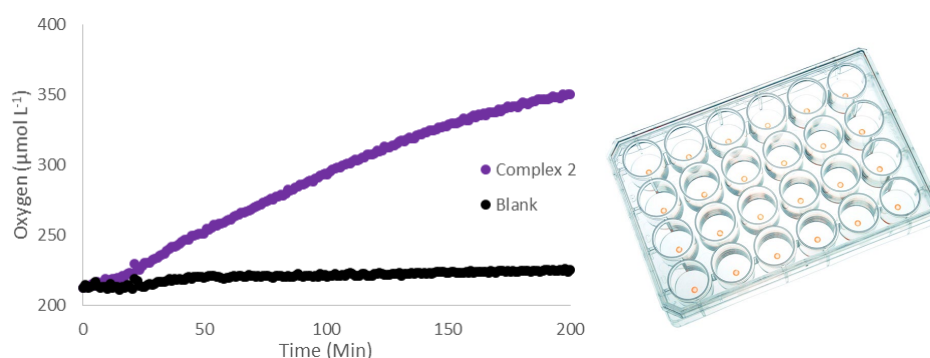
2. Oxodish results¹⁴

For each Oxodish run a freshly unpacked OxoDish 24-well sensor plate (OD24) was placed on the SensorDish Reader. All experiments containing a nickel-based complex (0.1 mM), control experiments (0.1 mM) and blank experiments were performed at four different conditions; 100 mM CAN in MilliQ water, 50 mM NaIO₄ in MilliQ water, 50 mM NaIO₄ in a pH 7 0.1 M phosphate buffer, and 50 mM Oxone in 0.5 M acetate buffer with pH 4.5. For each experiment the wells were filled with a stock solution of oxidant (1 mL), and after equilibration, a stock solution of nickel catalyst was added (0.2 mL, final concentration of nickel of 0.1 mM, pure MilliQ was used to dissolve the catalyst for all examples, except for catalysts **10-13** and **15** for which a few drops of MeCN were added to aid solubility). Then the sensor plate was sealed and the fluorescence response was followed for 2 h. See reference for more information.¹⁴ In Supporting Information Table S1 the results from the Oxodish experiments are reported.

Complex	CAN	NaIO ₄	NaIO ₄ in Pi buffer	Oxone in OAc buffer
-	-	-	-	-
2	-	-	-	60
3	-	-	-	60
4	-	-	-	60
5	-	-	-	-
8	-	-	-	120
9	-	-	-	120
10	-	-	-	-
11	-	-	-	-
12	-	-	-	-
13	-	-	-	-
Ni(ClO ₄) ₂	-	-	-	-
Ni(OAc) ₂	-	-	-	-
NiO ^a	-	-	-	-

Supporting Information Table S1. Oxygen evolution results evaluated with the Oxodish of 0.1 mM nickel complexes and nickel salts at various oxidative conditions. The color indicates the final O₂ concentration: yellow = 270-380 nmol mL⁻¹; no color = no activity (< 270 nmol mL⁻¹). The number in the cell represents the time in minutes in which the maximum O₂ concentration is reached. a) NiO was added as suspension.

2.1 Example of Oxodish data



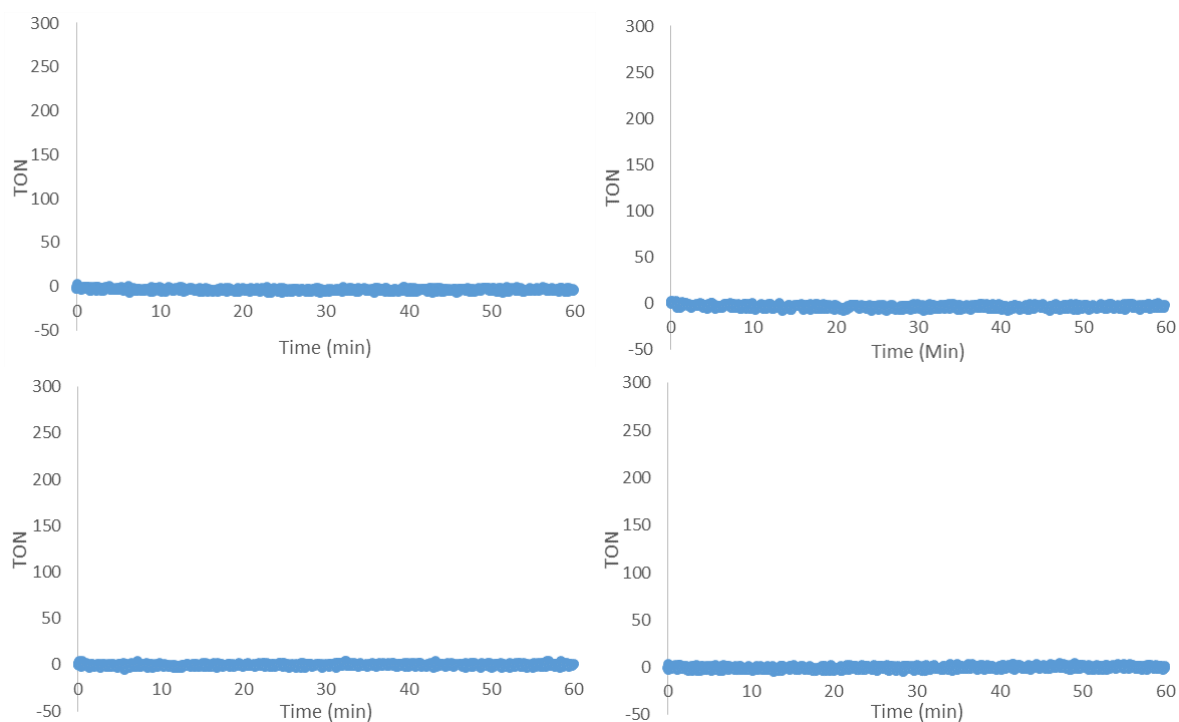
Supporting Information Figure S1. Oxygen evolution by 0.10 mM nickel cyclam **2** at pH 5.0 in a 0.5 M acetate buffer using 0.10 M Oxone as oxidant (Oxygen measured using the oxodish, left). Photo of an Oxodish 24-well sensor plate (right).

3. Oxygen evolution measured by manometry

Kinetic experiments were performed using the Man on the Moon pressure transducer (Series X102, <https://www.manonthemoontech.com/>). For each experiment the total reaction volume was 5.0 ml, with a total schlenk volume of 20.5 ml. A 0.5 M sodium acetate buffer was used of a desired pH. First, a stock solution of Oxone was added (resulting in final concentrations of 0.05 M - 0.50 M, adjusted to the correct pH with 1.0 M NaOH at high Oxone concentrations)). Secondly, a stock solution of the catalyst was added (resulting in a final concentrations of 0.01 – 1.0 mM). Then the reaction was monitored until a constant pressure was attained. Measurements where the pressure dropped quickly after reaching a maximum were discarded as this indicates a leak (occurred in less than 5% of the experiments). Using the ideal gas law and the volume of the schlenk, the quantity of produced oxygen was determined.

3.1 Oxygen evolution activity of nickel salts

Several nickel salts (NiCl_2 , $\text{Ni}(\text{ClO}_4)_2$, $\text{Ni}(\text{NO}_3)_2$ and $\text{Ni}(\text{OAc})_2$) were evaluated under the same oxygen evolution conditions as control experiments to establish the influence of the ligand on any observed catalytic activity.



Supporting Information Figure S2. Oxygen evolution by 0.10 mM of NiCl_2 (top left), $\text{Ni}(\text{ClO}_4)_2$ (top right), $\text{Ni}(\text{NO}_3)_2$ (bottom left) and $\text{Ni}(\text{OAc})_2$ (bottom right) at a pH of 5.0 in a 0.50 M acetate buffer using 0.10 M Oxone as oxidant (TON determined by manometry).

4. H₂O¹⁸ labeling experiments

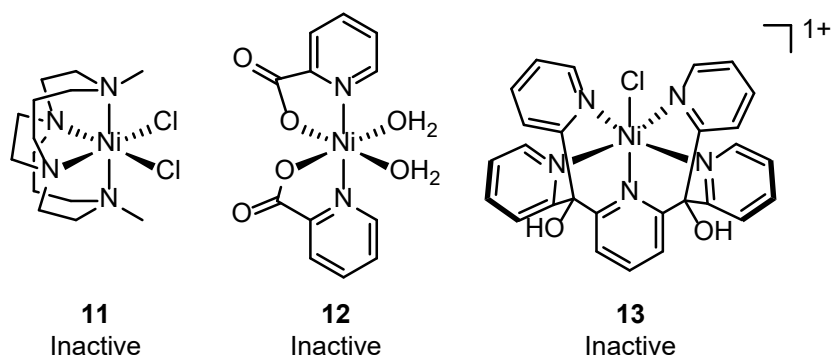
We performed H₂O¹⁸ labeling experiments to investigate whether nickel complex **1** acts as a water oxidation catalyst or if it has catalytic activity in Oxone decomposition. When performing oxygen evolution studies in O¹⁸ labeled water, increase in O₂³² would be expected if the oxygen produced originates from Oxone, while the ratio of O₂³⁶/O₂³⁴ would remain similar. If the catalyst is capable of using water as substrate and oxidizing water, and oxygen evolution experiment with O¹⁸ labeled water would result in an increase in the amount of O₂³⁶, while the amount of O₂³² and O₂³⁴ remain roughly similar, thus an increase in the ratio of O₂³⁶/O₂³⁴ would be expected. Oxygen evolution labeling experiments were carried out with ~80% O¹⁸ labeled water using 0.1 mM of **1** at a pH of 5.0 in a 0.10 M acetate buffer using 0.10 M Oxone as oxidant in a 4 mL vial. Five minutes after water oxidation was initiated, 1 mL of headspace was injected in a GC-vial. Then an aliquot of the GC-vial was injected into a GC-MS system. Due to a leak in the mass spectrometer, O₂³² labeled oxygen was present in a large excess and no considerable changes in N₂²⁸ and O₂³² were observed. When a run without a catalyst was injected into the GC, the ratio of the area of O₂³⁶/O₂³⁴ was 0.1 (Supporting Information Figure S3). When a run with the catalyst was injected, a significant increase in the amount of O₂³⁶ was observed, the ratio of the area of O₂³⁶/O₂³⁴ was 10.7 (Supporting Information Figure S3). From this significantly higher O₂³⁶/O₂³⁴ ratio, we conclude that at least part of the oxygen evolved during oxygen evolution experiments originates from water and the complex is thus capable of oxidizing water.



Supporting Information Figure S3. MS spectrum of the oxygen evolution reaction in a 0.10 M acetate buffer using 0.10 M Oxone with ~80% O¹⁸ labeled water at a pH of 5.0 without (top) and with 0.10 mM of nickel complex **1** (bottom) .

5 Additional evaluated nickel complexes

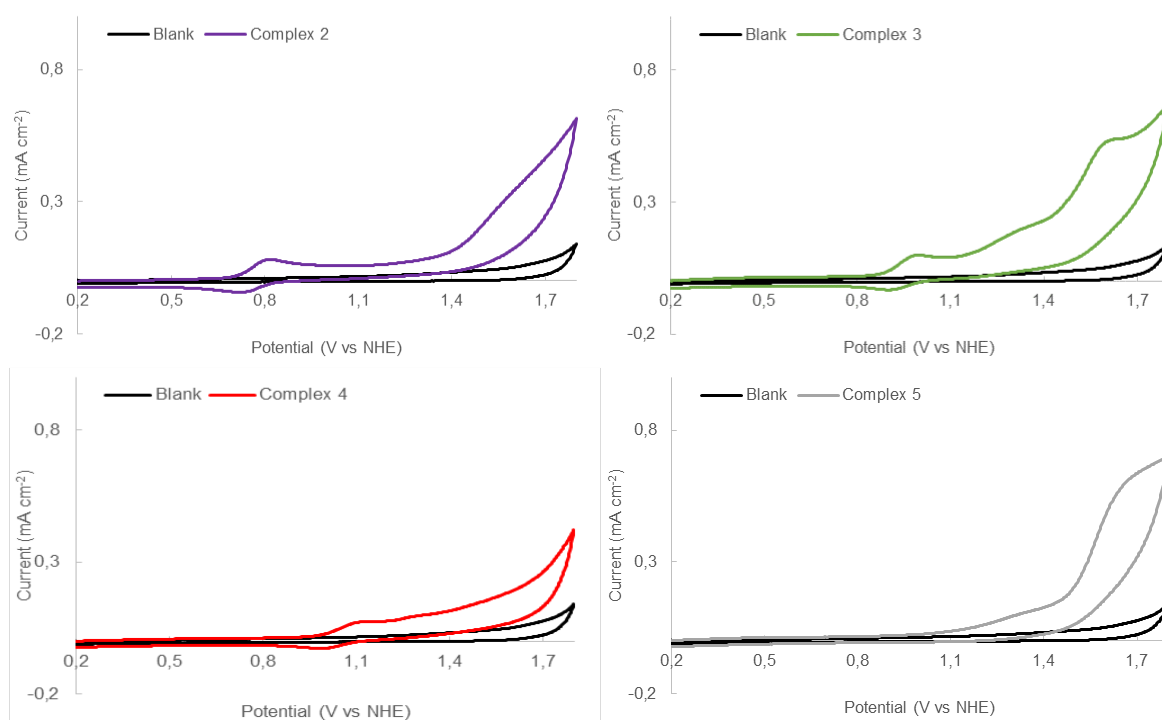
Complexes **11-13** were evaluated using either the Oxodish or manometry measurements, but proved inactive in oxygen evolution using either CAN, NaIO₄, or Oxone.



Supporting Information Figure S4. Complexes **11-13** are inactive in oxygen evolution under the tested conditions.

6. Electrochemical studies

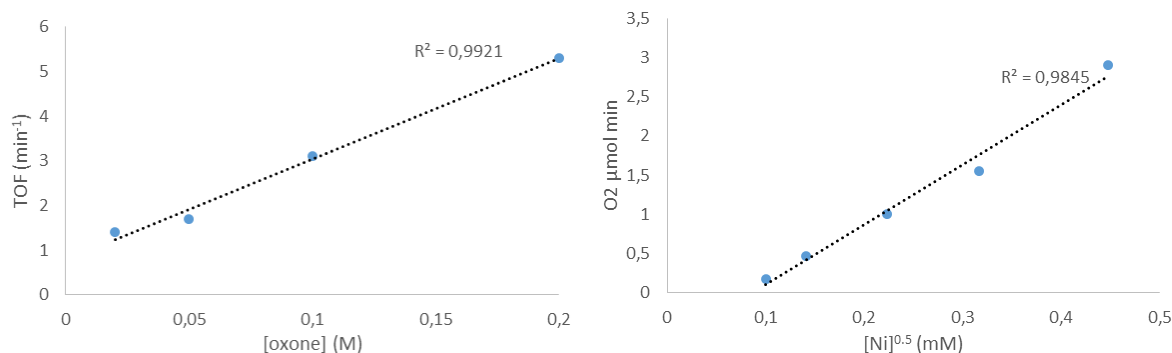
Cyclic voltammetry (CV) measurements were recorded on an Autolab PG-STAT302N potentiostat with a three electrode system. A freshly polished glassy carbon (GC) working electrode, a platinum coil counter electrode and a leak free Ag/AgCl reference electrode were used.



Supporting Information Figure S5. Cyclic voltammety measurements at 100 mV s⁻¹ of nickel complex **2** (top left), **3** (top right), **4** (bottom left) and **5** (bottom right) in a 0.50 M pH 5.0 acetate buffer using a glassy carbon working electrode.

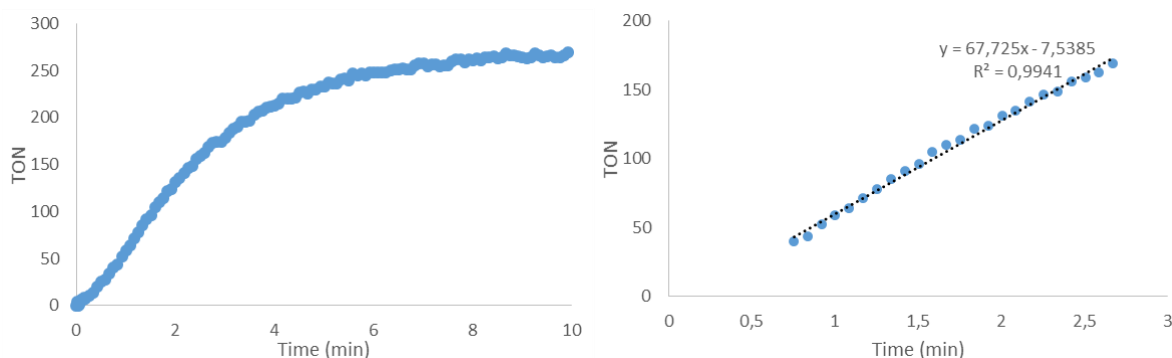
7. Kinetic studies with complex 2, nickel cyclam

In addition to the kinetic studies with complex 1, we also performed kinetic studies with complex 2, which shows the same trends in reaction order; 1st order in Oxone and ½ order in catalyst.

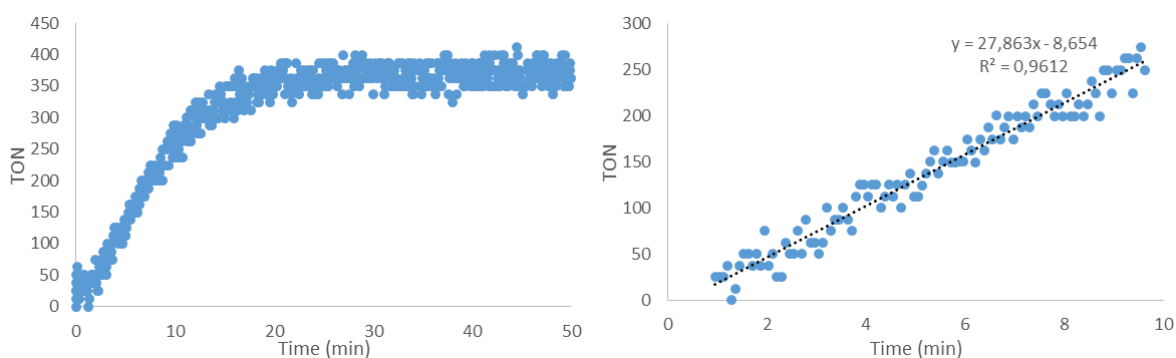


Supporting information Figure S6. Kinetic studies with nickel complex 2. Turnover frequencies per minute of 0.10 mM 2 using various Oxone concentrations in a 1.0 M acetate buffer at a pH of 5.0 (left). Rate of oxygen evolution versus the square root of the concentration of 2 in a 0.50 M acetate buffer at a pH of 5.0 using 0.10 M Oxone as oxidant (right).

8. Oxygen evolution examples



Supporting Information Figure S7 Oxygen evolution by 0.10 mM of nickel complex 1 at a pH of 5.0 in a 1.00 M acetate buffer using 0.50 M Oxone as oxidant (TON determined by manometry). Determination of TON (left) and TOF (right).



Supporting Information Figure S8. Oxygen evolution by 0.01 mM of nickel complex 1 at a pH of 5.0 in a 0.5 M acetate buffer using 0.10 M Oxone as oxidant (TON determined by manometry). Determination of TON (left) and TOF (right).

9. References

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