

Development of Nitrogen-donor ligated transition metal complexes for water oxidation

T Makhado



orcid.org/0000-0003-0804-3278

Thesis accepted in fulfilment of the requirements for the degree *Doctor of Philosophy in Science with Chemistry* at the North-West University

Promoter: Prof AJ Swarts

Co-promoter: Prof HCM Vosloo

Co-promoter: Prof RJ Kriek

Graduation August 2021

30090938

ABSTRACT

A series of previously reported bis(pyrazol-1-ylmethyl)pyridine ligands, bearing different donating groups on the pyrazolyl moiety (H, Me, *t*-Bu, Ph), was successfully synthesised and characterised. The ligands 2,6-bis((1H-pyrazol-1-yl)methyl)pyridine (**L1**), 2,6-bis((3,5-dimethyl-1H-pyrazol-1-yl)methyl)pyridine (**L2**), 2,6-bis((3,5-di-*tert*-butyl-1H-pyrazol-1-yl)methyl)pyridine (**L3**), and 2,6-bis((3,5-diphenyl-1H-pyrazol-1-yl)methyl)pyridine (**L4**) were reacted with CuCl₂·2H₂O to form Cu(II) complexes **C3.1** to **C3.4**, respectively. Ligand **L2** was reacted with Cu(OTf)₂ to form a Cu(II) complex **C3.5**. The ligands (**L1-L4**) were further reacted with Cu(MeCN)₄PF₆ to form complexes **C4.1** to **C4.4**, respectively. Reacting the ligands **L1-L4** with CoCl₂·6H₂O resulted in Co(II) complexes **C5.1** to **C5.4**, while reacting **L2** with Co(BF₄)₂·6H₂O resulted in the formation of complex **C5.5**. The complexes were characterised by a variety of spectroscopic and analytical techniques, including Fourier-transform infrared (FTIR) spectroscopy, magnetic susceptibility, nuclear magnetic resonance (NMR) spectroscopy in the case of diamagnetic complexes **C4.1** to **C4.4**, electrospray ionisation mass spectrometry (ESI-MS), elemental analysis, and single-crystal XRD. Water-soluble Cu(II) complexes **C3.1** to **C3.5** were investigated towards chemical and electrocatalytic water oxidation. The copper(II) complexes showed activity in chemical water oxidation with cerium ammonium nitrate (CAN) as the primary oxidant, with the complex containing the methyl-substituted pyrazolyl moiety, complex **C3.2** being the most active among the chloride-containing complexes with a turnover number (TON) of 4.22 and turnover frequency (TOF) of 0.033 s⁻¹. Replacing the chloride anion with tetrafluoroborate (**C3.5**) improved the TOF to 0.115 s⁻¹. The complexes showed activity in electrocatalytic water oxidation at pH 7, with overpotentials ranging from 683 to 823 mV. Investigations into the homogeneity of the molecular complex revealed that the Cu(II) complexes mediated electrocatalytic water oxidation proceeds via heterogeneous catalysis. The Cu(II) complexes act as pre-catalysts in the electrodeposition of CuO nanoparticles on the glassy carbon electrodes, which are responsible for water oxidation. Novel Cu(I) complexes were investigated in chemical and electrocatalytic water oxidation reactions. CAN, sodium *m*-periodate, and sodium persulfate were investigated as chemical oxidants in chemical water oxidation. Complexes **C4.1** to **C4.4** showed catalytic activity towards chemical water oxidation in the presence of CAN as the primary oxidant at 25 °C. Complex **C4.2**, which contains a methyl-substituted pyrazole on the ligand scaffold was the most active with a turnover number (TON) of 4.6 and a turnover frequency (TOF) of 0.31 s⁻¹. The least active catalyst was complex **C4.4**, which contains a phenyl substituted pyrazole on the ligand with a TON of 2.3 and a TOF of 0.0086 s⁻¹. This observed difference in catalytic activity between the complexes illustrated the key role that electronic effects play during catalysis. Other oxidants evaluated with **C4.2** were sodium *m*-

periodate (TON, 3.77; TOF 0.14 s⁻¹) and sodium persulfate (TON, 4.02; TOF 0.044 s⁻¹); however, CAN exhibited the greatest activity. Complexes **C4.1** to **C4.4** were investigated towards electrocatalytic water oxidation at a neutral pH of 6.5. Complex **C4.2** was also the most active in electrocatalytic water oxidation, exhibiting an overpotential of 674 mV and TOF of 9.77 s⁻¹ (at 1.7 V vs NHE), which is better than most reported copper(II) complexes. These Cu(I) complexes, **C4.1** to **C4.4**, show potential as efficient chemical and electrocatalytic water oxidation catalysts, which can be achieved by fine-tuning the steric and electronic properties of the catalysts.

Cobalt(II) complexes **C5.1** to **C5.5** were active in electrocatalytic water oxidation at pH 5. The complexes were efficient in water oxidation at overpotentials ranging from 565 to 635 mV. The lowest overpotential was achieved by complex **C5.2** and the highest overpotential was achieved by complex **C5.3**. The complexes were highly active with TOFs as high as 855 s⁻¹ achieved by complex **C5.5**. Although the Co(II) complexes showed the highest TOFs, they were not as stable under electrochemical conditions as electrodeposition of CoO_x nanoparticles could be observed. This suggested that Co(II) complexes were not entirely homogeneous. The complexes also showed activity towards chemically-driven water oxidation in acidic media with CAN as the primary oxidant. Complex **C5.2** resulted in the highest TON of 5.37 and TOF of 0.31 s⁻¹ while the least active complex was **C5.4** with a TON of 1.45 and TOF of 0.0075 s⁻¹.

Key terms: water oxidation, homogeneous catalysis, electrocatalysis, nitrogen-donor ligands, Cu(II), Cu(I), Co(II)

ACKNOWLEDGEMENTS

All thanks and glory to God for sustaining me until now and for all the strength and wisdom to carry out this project. I would like to express my sincere gratitude to my supervisor Prof AJ Swarts. I really appreciate all your help and guidance, I definitely come out of this a better writer and scientist. Sincere gratitude to Prof RJ Kriek for all the input towards the project and for providing facilities for electrochemical studies. Many thanks to Prof HCM Vosloo for all the input towards the project and editing of the thesis.

I would also like to thank the Catalysis and Synthesis group students and staff, particularly Lindie Marais and Vincent Vermaak, thank you for all your valuable contributions. Special appreciation to Dr. Jordaan and Dr. Otto from the Lab for Analytical Services (LAS) for assistance with the characterization of materials. A very special thank you to Mrs. Stoppel for all the help and support, you have been amazing. Appreciation to Electrochemistry for Energy & Environment group for all the help with electrochemistry, especially Dr. Iqbal and Dr. Oyetade.

Appreciation to the NWU and the Focus Area for Chemical Resource Beneficiation (CRB) for the facilities and support. Financial support from the National Research Fund and NWU is greatly acknowledged.

I would also like to thank Prof J Steenkamp from NWU Centre of Excellence for Pharmaceutical Sciences (Pharmacem™) for all the help with DLS analysis. Appreciation to Cassiem Joseph from Stellenbosch University for helping with solving and refining crystal structures. Many thanks to Dr. B Das from Stockholm University in Sweden for all the insights and his contributions to electrocatalysis work.

Grateful for the support from my family, especially my partner, Phathutshedzo Mukwevho, my mom, Ndivhuho Mercy Makhado, and my sisters; Ntovhe, Ndidzu, Rumani, Tshifhiwa, and my niece Maluta. Special thanks to all my friends who were always so encouraging throughout this journey.

TABLE OF CONTENTS

Abstract.....	ii
Acknowledgements.....	iv
List of figures.....	ix
List of schemes.....	xiv
List of tables.....	xv
List of abbreviations	xvi
Conference contributions and publications.....	xvii

Chapter 1: Introduction of nitrogen-donor ligated transition metal complexes as water oxidation catalysts

1.1 Introduction.....	1
1.2 Aim and objectives	2
1.3 Outline of the thesis.....	3
1.4 References.....	4

Chapter 2: Literature review

2.1 Hydrogen: A renewable energy source	6
2.2 Water splitting towards hydrogen production.....	6
2.3 Natural photosynthesis vs artificial photosynthesis.....	7
2.3.1 Natural photosynthesis	7
2.3.2 Artificial photosynthesis	9
2.4 Homogeneous molecular systems as water oxidation catalysts	10
2.4.1 Basic mechanism of homogeneous water oxidation.....	10
2.4.2 Water nucleophilic attack	10
2.4.3 Radical coupling of two metal oxos (I2M).....	11
2.5 Different approaches taken in water oxidation.....	12
2.5.1 Chemical water oxidation.....	13
2.5.1.1 Chemical oxidants	13
2.5.1.2 Catalysts used in water oxidation.....	14
2.5.1.2.1 Ruthenium and iridium complexes	14

2.5.1.2.2	Manganese complexes.....	18
2.5.1.2.3	Iron(II) complexes.....	19
2.5.1.2.4	Copper(II) complexes	22
2.5.1.2.5	Cobalt complexes	22
2.5.2	Electrocatalytic water oxidation.....	23
2.5.2.1	Parameters for evaluating a molecular electrocatalyst	24
2.5.2.2	Catalysts used in electrocatalytic water oxidation	26
2.5.2.2.1	Manganese complexes.....	26
2.5.2.2.2	Nickel(II) complexes	26
2.5.2.2.3	Cobalt complexes	29
2.5.2.2.4	Copper(II) complexes	31
2.6	Conclusions	33
2.7	References	34

Chapter 3: Synthesis and characterization of bis(pyrazolyl)pyridine copper(II) complexes as catalysts in chemical and electrocatalytic water oxidation

3.1	Introduction.....	39
3.2	Results and discussion	41
3.2.1	Synthesis and characterisation of complexes, C3.1 to C3.5	41
3.2.2	Chemical water oxidation catalysed by complexes, C3.1 to C3.5	44
3.2.3	Electrocatalytic water oxidation mediated by complexes C3.1 to C3.5	47
3.2.3.1	Evidence of heterogeneous nanoparticles	52
3.3	Conclusions	54
3.4	Experimental	54
3.4.1	General considerations	54
3.4.2	Synthesis of ligands and complexes.....	55
3.4.2.1	Synthesis of 2,6-bis((1H-pyrazol-1-yl)methyl)pyridine (L1).....	55
3.4.2.2	Synthesis of 2,6-bis((3,5-dimethyl-1H-pyrazol-1-yl)methyl)pyridine (L2)	55
3.4.2.3	Synthesis of 2,6-bis((3,5-di-tert-butyl-1H-pyrazol-1-yl)methyl)pyridine (L3)... ..	55
3.4.2.4	Synthesis of 2,6-bis((3,5-diphenyl-1H-pyrazol-1-yl)methyl)pyridine (L4)	56

3.4.2.5 Synthesis of complex C3.1	56
3.4.2.6 Synthesis of complex C3.2	56
3.4.2.7 Synthesis of complex C3.3	56
3.4.2.8 Synthesis of complex C3.4	57
3.4.2.9 Synthesis of complex C3.5	57
3.4.3 Electrocatalytic water oxidation	57
3.4.4 Chemical water oxidation	58
3.5 References	58
Chapter 4: Synthesis and characterisation of bis(pyrazol-1-ylmethyl)pyridine-ligated Cu(I) complexes as catalysts in chemical and electrochemical water oxidation	
4.1 Introduction.....	61
4.2 Results and discussion	62
4.2.1 Ligand and complex synthesis	62
4.2.2 Cu(I)-catalysed chemically-driven water oxidation.....	68
4.2.3 Cu(I)-catalysed electrocatalytic water oxidation.....	74
4.2.3.1 The effect of catalyst structure on electrocatalytic water oxidation	74
4.2.3.2 Kinetic studies	78
4.2.3.3 pH dependence studies	81
4.2.3.4 Evidence for homogeneous catalysis.....	81
4.2.3.5 Stability of the catalyst	83
4.3 Conclusions.....	84
4.4 Experimental Section.....	85
4.4.1 General considerations	85
4.4.2 Synthesis of complexes.....	85
4.4.2.1 Synthesis of complex C4.1	85
4.4.2.2 Synthesis of complex C4.2	85
4.4.2.3 Synthesis of complex C4.3	86
4.4.2.4 Synthesis of complex C4.4	86
4.4.3 Crystallographic data collection.....	87

4.4.4 Chemical water oxidation	87
4.4.5 Electrocatalytic water oxidation	87
4.5 References	88

Chapter 5: Synthesis, characterization and catalytic evaluation of bis(pyrazol-1-ylmethyl)pyridine-ligated Co(II) complexes in water oxidation reactions

5.1 Introduction.....	92
5.2 Results and discussion	94
5.2.1 Synthesis and characterisation of cobalt complexes C5.1 to C5.5	94
5.2.2 Electrocatalytic water oxidation using cobalt complexes C5.1-C5.5	96
5.2.2.1 The effect of catalyst structure on electrocatalytic water oxidation	97
5.2.2.2 Kinetic studies	98
5.2.2.3 Investigating the integrity of the molecular catalyst	101
5.2.3 Chemical water oxidation catalysed by cobalt complexes C5.1 to C5.5	105
5.3 Conclusions.....	107
5.4 Experimental	108
5.4.1 General considerations	108
5.4.2 Synthesis of complexes.....	108
5.4.2.1 Synthesis of Complex C5.1	108
5.4.2.2 Synthesis of Complex C5.2	108
5.4.2.3 Synthesis of complex C5.3	109
5.4.2.4 Synthesis of complex C5.4	109
5.4.2.5 Synthesis of complex C5.5	109
5.4.3 Chemical water oxidation	109
5.4.4 Electrocatalytic water oxidation	110
5.5 References	110

Chapter 6: Concluding remarks and future recommendations

6.1 Concluding remarks.....	112
6.2 Future recommendations.....	113

LIST OF FIGURES

Chapter 2: Literature review

Figure 2.1: The hydrogen economy: Ways to produce, store and use hydrogen in, applications in different sectors.	6
Figure 2.2: Illustration of the artificial photosynthesis assembly made up of a photosensitizer (PS), water oxidation catalyst (WOC), and hydrogen evolving catalyst (HEC) in the production of solar fuels.....	9
Figure 2.3: $[\text{Ru}^{\text{II}}(\text{tpy})(\text{bpm})(\text{OH}_2)](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ water oxidation catalyst.	14
Figure 2.4: Mononuclear and dinuclear ruthenium complexes investigated in chemical water oxidation.	16
Figure 2.5: Ruthenium complexes used in chemical water oxidation using $[\text{Ru}^{\text{III}}(\text{bpy})_3](\text{PF}_6)_3$ as a chemical oxidant.	16
Figure 2.6: Iridium complexes for water oxidation.	17
Figure 2.7: A dinuclear manganese complex $[\text{H}_2\text{O}(\text{tpy})\text{Mn}(\text{O})_2\text{Mn}(\text{tpy})\text{OH}_2](\text{NO}_3)_3$ studied in chemical water oxidation.....	18
Figure 2.8: Tetradentate iron complexes used in chemical water oxidation catalysis.....	20
Figure 2.9: Iron complexes used in chemical water oxidation.	21
Figure 2.10: A copper complex $[(\text{L})\text{Cu}^{\text{II}}(\text{NO}_3)]$ ($\text{L} = (\text{E})$ -3-(pyridin-2-yl diazenyl)naphthalen-2-ol)) studied in chemical water oxidation with CAN as the primary oxidant.	22
Figure 2.11: Cobalt complexes studied in chemical water oxidation.	23
Figure 2.12: Nickel complexes efficient in electrocatalytic water oxidation.	27
Figure 2.13: Cobalt complexes used in electrocatalytic water oxidation.	30
Figure 2.14: Copper complexes used in electrocatalytic water oxidation.	31

Chapter 3: Synthesis and characterization of bis(pyrazolyl)pyridine copper(II) complexes as catalysts in chemical and electrocatalytic water oxidation

Figure 3.1 ^1H (Dichloromethane- d_2) NMR spectrum of ligand L2	42
Figure 3.2: $^{13}\text{C}\{\text{H}\}$ (Dichloromethane- d_2) NMR of L2	42
Figure 3.3: ESI-MS spectrum of complex C3.2	43
Figure 3.4: Oxygen evolution curves of complexes C3.1 and C3.2 with water as the solvent.	45
Figure 3.5a:Oxygen evolution curves showing the catalytic region after catalyst addition performed in a mixture of MeCN:H ₂ O (1:1); 3.5b: Oxygen evolution curves of complex C3.1 to C3.5 in chemical water oxidation after 5 minutes' reaction time.	46

Figure 3.6: Cyclic voltammograms of complex C3.2 (0.5 mM) in 0.1 M Bu ₄ NPF ₆ in MeCN (blue) and C3.2 in 0.1 M Bu ₄ NPF ₆ in MeCN with added 5% (v/v) phosphate buffer at pH 7 (orange) recorded at a scan rate of 50 mV s ⁻¹ .	48
Figure 3.7: Cyclic voltammograms of 0.1 mM C3.1 to C3.5 in 0.2 M phosphate buffer pH 7 recorded at a scan rate of 100 mV s ⁻¹ .	48
Figure 3.8: CVs of 0.5 mM C3.1-C3.5 in 0.1 M Bu ₄ NPF ₆ in MeCN showing the Cu(III)/Cu(II) redox couple recorded at a scan rate of 10 mV s ⁻¹ . The y axis shows the normalised current.	49
Figure 3.9: CVs showing 0.5 mM C3.2 in phosphate buffer pH 7 cycled 20 times at 100 mV s ⁻¹ .	52
Figure 3.10: CVs of 0.1 mM C3.2 in 0.2 M phosphate buffer at pH 7 after 6 cycles, the rinsed electrode in 0.2 M phosphate buffer (blank), and the polished electrode in the blank solution recorded at 100 mV s ⁻¹ .	53
Figure 3.11: CVs of 0.1 mM C3.2 in 0.2 M phosphate buffer at pH 6 after 6 cycles, the rinsed electrode in 0.2 M phosphate buffer (blank), and the polished electrode in the blank solution recorded at 100 mV s ⁻¹ .	53
Chapter 4: Synthesis and characterisation of bis(pyrazol-1-ylmethyl)pyridine-ligated Cu(I) complexes as catalysts in chemical and electrochemical water oxidation	
Figure 4.1: ¹ H (Dichloromethane-d ₂) NMR spectrum of ligand C4.2	63
Figure 4.2: ¹³ C{H} (Dichloromethane-d ₂) NMR of C4.2	64
Figure 4.3: ESI-MS spectrum of complex C4.2	65
Figure 4.4: Ellipsoid diagrams of C4.2 , C4.3 , and C4.4 , respectively, drawn at 50% probability. Hydrogen atoms were omitted for clarity.	66
Figure 4.5: Oxygen evolution curves for Cu(I) complexes C4.1 to C4.4	69
Figure 4.6: CVs of the Cu(I) complexes (0.5 mM) performed in 0.1 M Bu ₄ NPF ₆ in acetonitrile with the glassy carbon as the working electrode, platinum wire as a counter electrode, and Ag/AgCl as the reference electrode. The scan rate was 10 mV s ⁻¹ . Inset: A cyclic voltammogram showing irreversible wave assigned to the first oxidation of Cu(I) to Cu(II) for complex C4.2 . The reversible waves showing the reversible Cu(III)/Cu(II) couple of C4.1 to C4.4	71
Figure 4.7: Initial rate data of the catalyst system studied using C4.2 and 110 mM CAN as the primary oxidant showing a second-order at low concentrations and b, first-order at higher concentrations	72
Figure 4.8: Effect of CAN on the activity of the catalyst studied using 25 μM C4.2	73
Figure 4.9: CVs of Cu(I) complexes C4.1 to C4.4 [0.42 mM] in a mixture of MeCN and 20% (v/v) phosphate buffer (0.2 M, pH 6.5) recorded at a scan rate of 100 mV s ⁻¹ .	74

Figure 4.10: CVs of Cu(I) complex C4.2 [0.5 mM] in a solution of MeCN and 0.1 M NBu ₄ PF ₆ (blue) and C4.2 [0.42 mM] in a mixture of MeCN and 20% (v/v) phosphate buffer (0.2 M, pH 6.5) (orange) recorded at a scan rate of 100 mV s ⁻¹	75
Figure 4.11: The effect of concentration of the catalytic current at 1.7 V studied using complex C4.2 at pH 6.5.	79
Figure 4.12: Scan rate dependence of 0.42 mM C4.2 scanned at 100 to 4 000 mV/s. Inset: Linear scan rate dependence of the catalytic current at 1.7 V versus the square root of the scan rate.....	79
Figure 4.13: A graph of catalytic current/peak current (I_{cat}/I_p) as a function of $1/(v)^{1/2}$ studied using complex C4.2	80
Figure 4.14: CVs showing the effect of pH on the activity of the catalyst studied by complex 0.42 mM C4.2 in a mixture of MeCN and 20% (v/v) phosphate buffer (0.2 M) pH 4 to 6.5 recorded at a scan rate of 100 mV s ⁻¹ . Inset: The effect of pH on the onset potential studied in 0.42 mM C4.2 a mixture of MeCN and 20% (v/v) phosphate buffer (0.2 M) pH. The onset potential was determined using the tangent method.	81
Figure 4.15: CVs in a mixture of MeCN and 20% (v/v) phosphate buffer (0.2 M, pH 6.5) of 0.42 mM C4.2 (blue) after six cycles, followed by a rinsed electrode in a fresh blank solution (orange) and a new polished electrode in blank solution (grey), recorded at a scan rate of 100 mV s ⁻¹	82
Figure 4.16: a Data graph of the background against a 0.42 mM C4.2 in a mixture of MeCN and 20% (v/v) phosphate buffer (0.2 M, pH 6.5) in the absence of the electrolyte; b, particle distribution in the absence of the supporting electrolyte determined by DLS measurements post-electrolysis of 0.42 mM C4.2 in a mixture of MeCN and 20% (v/v) phosphate buffer (0.2 M, pH 6.5)	83
Figure 4.17: CVs in a mixture of MeCN and 20% (v/v) phosphate buffer (0.2 M, pH 6.5) of 0.42 mM C4.2 scanned 150 times at a scan rate of 100 mV s ⁻¹	83
Figure 4.18: CVs in a mixture of MeCN and 20% (v/v) phosphate buffer (0.2 M, pH 6.5) of 0.42 mM C4.2 (blue) after 150 cycles, followed by a rinsed electrode in a fresh blank solution (orange) and a new polished electrode in blank solution (grey), recorded at a scan rate of 100 mV s ⁻¹	84
Chapter 5: Synthesis, characterization, and catalytic evaluation of bis(pyrazol-1-ylmethyl)pyridine-ligated Co(II) complexes in water oxidation reactions	
Figure 5.1: ESI-MS spectrum of complex C5.2 showing the subsequent loss of chloride anions.	95
Figure 5.2: CVs of cobalt complexes C5.1 to C5.5 (0.1 mM) in 0.2 M phosphate buffer at pH 5 recorded at a scan rate of 100 mV s ⁻¹	96

Figure 5.3: CVs of complex C5.2 (0.5 mM) performed in 0.1 M Bu ₄ NPF ₆ in DMF (Blue) and C5.2 performed in 0.1 M Bu ₄ NPF ₆ in DMF with added 5% (v/v) phosphate buffer at pH 5 recorded at a scan rate of 100 mV s ⁻¹	97
Figure 5.4 a:, CVs showing C5.2 in 0.2 M phosphate buffer at varying concentrations (0.03 mM-0.1 mM) recorded at 100 mV s ⁻¹ and 5.4b: the effect of concentration on the catalytic current at 1.7 V studied using complex C5.2 in 0.2 M phosphate buffer at pH 5.....	99
Figure 5.5: CVs showing the effect of scan rate on the catalytic current studied using 0.1 mM C5.2	100
Figure 5.6: A plot of I_{cat}/I_p versus $1/(\text{Scan rate})^{1/2}$	101
Figure 5.7: CVs of 0.1 mM C5.1 in phosphate buffer at pH 7 at the end of the 6 th cycle showing the presence of nanoparticles detected by a metal-ion scavenger method, b Checking for electrodeposited material on the GCE surface.	102
Figure 5.8: CVs of C5.2 (0.5 mM) dissolved in 0.2 M phosphate buffer at pH 7 cycled 20 times at a scan rate of 100 mV.s ⁻¹	103
Figure 5.9: a, SEM image (scale 30 μm) of the bare polished GCE. SEM images b, (scale 300 μm), c, (scale 100 μm), and d, (scale 10 μm) showing the GCE post-electrocatalysis of 0.5 mM C5.2 in phosphate buffer at pH 7 after 20 CV cycles.	103
Figure 5.10: EDS pattern of the GCE post-electrocatalysis of 0.5 Mm 5.2 in phosphate buffer after 20 CV cycles.....	104
Figure 5.11: CV of 0.1 mM 5.1 in 0.2 M phosphate buffer pH 5, and CV of the rinsed GCE in phosphate buffer only (blank) and new polished GCE in the blank.	105
Figure 5.12a: The oxygen evolution curves showing how the reaction proceeds for the first 10 seconds, the arrow shows the catalyst addition to the reaction mixture. 5.12b: Oxygen evolution curves of cobalt(II) complexes C5.1 to C5.5 showing the TON for 5 minutes' reaction time.	106

Appendix: Supplementary information

Figure S1: ¹ H NMR spectrum for L1	S1
Figure S2: ¹³ C{H} NMR for ligand L1	S2
Figure S3: H NMR spectrum for L3	S2
Figure S4: ¹³ C{H} NMR spectrum for L3	S3
Figure S5: ¹ H NMR spectrum for L4	S3
Figure S6: ¹³ C{H} NMR spectrum for L4	S4
Figure S7: FTIR spectrum for L1	S4
Figure S8: FTIR spectrum for L2	S5

Figure S9: FTIR spectrum for L3	S5
Figure S10: FTIR spectrum for L4	S6
Figure S11: FTIR spectrum for C3.1	S6
Figure S12: FTIR spectrum for C3.2	S7
Figure S13: FTIR spectrum for C3.3	S7
Figure S14: FTIR spectrum for C3.4	S8
Figure S15: FTIR spectrum for C3.5	S8
Figure S16: ESI-MS Spectrum for C3.1	S9
Figure S17: ESI-MS Spectrum for C3.3	S9
Figure S18: ESI-MS Spectrum for C3.4	S9
Figure S19: ESI-MS Spectrum for C3.5	S10
Figure S20: A tangent method for the determination of onset potential for complex C3.2 ..	S10
Figure S21: ^1H NMR spectrum of complex C1 in Acetone-d ₆	S11
Figure S22: $^{13}\text{C}\{\text{H}\}$ NMR spectrum of complex C1 in Acetone-d ₆	S11
Figure S23: ^1H NMR spectrum of an <i>in situ</i> synthesised L1 and CuCl complex in CDCl_3 ..	S12
Figure S24: $^{13}\text{C}\{\text{H}\}$ NMR spectrum in situ synthesised L1 and CuCl complex in CDCl_3	S12
Figure S25: ^1H NMR spectrum for C4.2	S13
Figure S26: $^{13}\text{C}\{\text{H}\}$ NMR spectrum for C4.2	S13
Figure S27: ^1H NMR spectrum for C4.3	S14
Figure S28: $^{13}\text{C}\{\text{H}\}$ NMR spectrum for complex C4.3	S14
Figure S29: ^1H NMR spectrum for C4.4	S15
Figure S30: $^{13}\text{C}\{\text{H}\}$ NMR spectrum for C4.4	S16
Figure S31: FTIR spectrum for C4.1	S16
Figure S32: FTIR spectrum for C4.2	S17
Figure S33: FTIR spectrum for C4.3	S17
Figure S34: FTIR spectrum for C4.4	S18
Figure S35: ESI-MS Spectrum for C4.1	S18
Figure S36: ESI-MS Spectrum for C4.2	S18
Figure S37: ESI-MS Spectrum for C4.3	S19
Figure S38: ESI-MS Spectrum for C4.4	S19
Figure S39: The oxygen evolution curves of Cu(I) complexes C4.1 to C4.4 after 5 minutes' reaction time.	S19
Figure S40: FTIR spectrum for C5.1	S20
Figure S41: FTIR spectrum for C5.2	S20
Figure S42: FTIR spectrum for C5.3	S21
Figure S43: FTIR spectrum for C5.4	S21
Figure S44: FTIR spectrum for C5.5	S22

Figure S45: ESI-MS Spectrum for C5.1	S22
Figure S46: ESI-MS Spectrum for C5.3	S23
Figure S47: ESI-MS Spectrum for C5.4	S23
Figure S48: ESI-MS Spectrum for C5.4	S24
Figure S49: Linear graphs showing the slopes of the TON graph for complexes C5.1-C5.5	S24

LIST OF SCHEMES

Chapter 2: Literature review

Scheme 2.1: The Kok cycle illustrating the different oxidation states of manganese in the OEC.	8
Scheme 2.2: The general mechanism showing the WNA O-O bond formation cycle.....	11
Scheme 2.3: Water nuclear attack O-O bond formation.	11
Scheme 2.4: The general mechanism showing the I2M O-O bond formation cycle.....	12
Scheme 2.5: I2M O-O bond formation.....	12
Scheme 2.6: A general representation of chemical water oxidation in the presence of a chemical oxidant.	13
Scheme 2.7: An example of a proposed mechanism of chemical water oxidation by a ruthenium dimer.	15
Scheme 2.8: Proposed mechanism of chemical water oxidation using a manganese dimeric complex 18	19
Scheme 2.9: Proposed mechanism for chemical water oxidation catalysed by $[\text{Fe}^{\text{II}}(\text{X})_2(\text{LN}^4)]$ complexes using CAN as the primary oxidant.	21
Scheme 2.10: A scheme illustrating water oxidation under applied voltage.....	24
Scheme 2.11: An example of a proposed mechanism in electrocatalytic water oxidation catalysed by $[\text{L-Ni}^{\text{II}}-\text{OH}_2]\text{Cl}_2$ (L = PY5) complex in phosphate buffer.....	29
Scheme 2.12: Mechanism of an N, N'-bis(2'-pyridinecarboxamide)-1,2-benzene ligated complex (37).	30
Scheme 2.13: Proposed electrocatalytic water oxidation by a negatively charged copper complex.	32

Chapter 3: Synthesis and characterization of bis(pyrazolyl)pyridine copper(II) complexes as catalysts in chemical and electrocatalytic water oxidation

Scheme 3.1: Synthesis route for copper(II) complexes C3.1 to C3.5	41
Scheme 3.2: Chemical water oxidation catalysed by Cu(II) complexes C3.1 to C3.5	44

Scheme 3.3: Electrocatalytic water oxidation catalysed by Cu(II) complexes C3.1-C3.5 dissolved in 0.2 M phosphate buffer at pH 7.	47
Chapter 4: Synthesis and characterisation of bis(pyrazol-1-ylmethyl)pyridine-ligated Cu(I) complexes as catalysts in chemical and electrochemical water oxidation	
Scheme 4.1: Preparation of the bis(pyrazol-1-ylmethyl)pyridine Cu(I) complexes, C4.1 to C4.4	62
Scheme 4.2: Chemically driven water oxidation catalysed by C4.1 to C4.4	68
Scheme 4.3: Electrocatalytic water oxidation using Cu(I) complexes C4.1 to C4.4	74
Chapter 5: Synthesis, characterization, and catalytic evaluation of bis(pyrazol-1-ylmethyl)pyridine-ligated Co(II) complexes in water oxidation reactions	
Scheme 5.1: Cobalt complexes investigated towards chemical and electrocatalytic water oxidation.	94
Scheme 5.2: Electrocatalytic water oxidation of cobalt complexes C5.1 to C5.5 in phosphate buffer at pH 5	96
Scheme 5.3: Chemical water oxidation catalysed by complexes C5.1-C5.5 with CAN as the primary oxidant.	105

LIST OF TABLES

Chapter 2: Literature review

Table 2.1: Catalytic activities of manganese-based complex 18 using different oxidants. ...	18
Table 2.2: A summary of nickel complexes in electrocatalytic water oxidation.....	28
Table 2.3: Cobalt complexes in electrocatalytic water oxidation.	31
Table 2.4: A summary of copper(II) complexes used in electrocatalytic water oxidation.....	33

Chapter 3: Synthesis and characterization of bis(pyrazolyl)pyridine copper(II) complexes as catalysts in chemical and electrocatalytic water oxidation

Table 3.1: FTIR stretching frequencies of (C=N) (py) in the ligands and complexes.....	43
Table 3.2: Copper(II) chemically driven water oxidation.	47
Table 3.3: Copper (II) complexes as pre-catalysts in electrocatalytic water oxidation.....	51

Chapter 4: Synthesis and characterisation of bis(pyrazol-1-ylmethyl)pyridine-ligated Cu(I) complexes as catalysts in chemical and electrochemical water oxidation

Table 4.1: FTIR stretching frequencies of (C=N) (py) in the ligands and complexes.....	64
Table 4.2: Crystal data and refinement for C4.2 , C4.3 , and C4.4	67
Table 4.3: Selected bond lengths and bond angles for C4.2 , C4.3 , and C4.4	68

Table 4.4: Summary of results of different copper(I) complexes towards chemical water oxidation with CAN	70
Table 4.5: The effect of a chemical oxidant on the TON and TOF of water oxidation	73
Table 4.6: Calculated overpotentials of copper complexes C4.1 to C4.4 at pH 6.5.....	77
Chapter 5: Synthesis, characterization, and catalytic evaluation of bis(pyrazol-1-ylmethyl)pyridine-ligated Co(II) complexes in water oxidation reactions	
Table 5.1: FTIR stretching frequencies of (C=N) (py) in the ligands and complexes.....	95
Table 5.2: A summary of activities of Co complexes C5.1 to C5.5 in comparison to previous studies.....	98
Table 5.3: Summary of results of different Cobalt (II) complexes on chemical water oxidation with CAN	107

LIST OF ABBREVIATIONS

BM	Bohr magnetons
CAN	Cerium ammonium nitrate
CE	Counter electrode
CV	Cyclic voltammetry
CVs	Cyclic voltammograms
DLS	Dynamic light scattering
eq	equivalents
FTIR	Fourier-transform infrared
GCE	Glassy carbon electrode
HER	Hydrogen evolution reaction
N4	Tetrazadentate (N,N,N,N)
NHE	Normal hydrogen electrode
NMR	Nuclear magnetic resonance
OEC	Oxygen evolving center
OER	Oxygen evolution reaction
OTf	Triflate anion
PS	Photosystem
py	pyridine
pz	pyrazole
rds	Rate determining step
TOF	Turnover Frequency
TON	Turnover number

Tpy 2,2':6',2''-terpyridine
WE Working electrode
WNA Water nucleophilic attack
WOC Water oxidation catalyst

CONFERENCE CONTRIBUTIONS AND PUBLICATIONS

Conferences attended

T Makhado, RJ Kriek, HCM Vosloo , AJ Swarts. Copper(I) chemically-driven water oxidation. Poster presented at the 29th annual conference of the Catalysis Society of South Africa "From Nano material to Industrial Process". 10-13 November 2019, Langebaan, Western Cape, South Africa.

Articles published from this research.

T. Makhado, B. Das, R. J. Kriek, H. C. M. Vosloo and A. J. Swarts. *Sustainable Energy Fuels*, 2021, **5**, 2771-2780
DOI: 10.1039/D1SE00402F

Chapter 1: Introduction of nitrogen-donor ligated transition metal complexes as water oxidation catalysts

1.1 Introduction

The growing demand for energy and the environmental impacts from the use of fossil fuels has increased research in renewable energy sources. Hydrogen is a clean and renewable energy source that is an alternative to fossil fuels.¹⁻² Water splitting is one of the greener ways to produce molecular hydrogen from water, which is an abundant natural resource. One of the half-reactions in water splitting is water oxidation, also known as the oxygen evolution reaction (OER). Water oxidation is a multi-electron process coupled with multi-proton transfer in an uphill energy transformation, and therefore the use of catalysts is required.³

Naturally, water oxidation occurs in the oxygen-evolving complex (OEC) which is situated in photosystem II, which consists of a bioinorganic Mn_4Ca core that has inspired the development of molecular water oxidation catalysts in artificial photosynthesis.⁴⁻⁵ The reason why water oxidation is more commonly investigated is that it has much slower reaction kinetics in comparison to the hydrogen evolution reaction (HER). Therefore, water oxidation is regarded as a limiting factor when considering water splitting efficiency.⁶⁻⁹ The water oxidation reaction involves the transfer of four electrons and four protons *en route* to producing one dioxygen molecule from two water molecules, as shown in equation 1.1.



Different approaches to water oxidation reactions using molecular complexes have been undertaken, which include photocatalytic, chemical, and electrocatalytic water oxidation.¹⁰ The oxidation of water using chemical oxidants has been extensively studied over the years.^{3, 11-12} Chemical water oxidation is mostly applicable in catalyst screening and optimisation as it allows for rapid screening of complexes. Chemical oxidants, also referred to as sacrificial oxidants, must have a reduction potential that is high enough to oxidise the metal centre of the water oxidation catalyst forming a metal oxo complex.¹³⁻¹⁵ Chemical oxidants that have been used in water oxidation reactions include CAN, sodium peroxodisulfate, ruthenium(III) trisbipyridine cation, potassium peroxymonosulfate (oxone), and sodium periodate.¹⁵

Electrocatalytic water splitting involves the production of oxygen and hydrogen under applied potential difference. Electrocatalytic water splitting is vital in the development of technologies such as electrolyzers and fuel cells.¹⁶⁻¹⁷ The reaction takes place in an electrochemical setup consisting of a reference, counter, and working electrodes. The two half-reactions involved in electrocatalytic water splitting are the water oxidation reaction that takes place at the anode and the HER, which occurs at the cathode.¹⁷ The water oxidation reaction is the rate-limiting

reaction in the overall water splitting, which influences the efficiency of an electrolyser. Challenges in electrocatalytic water oxidation include the development of stable, affordable, and environmentally friendly catalysts, which are efficient for water oxidation at low overpotential having high turnover rates. The application of molecular catalysts towards electrocatalytic water oxidation is a recent concept and they are not as active in comparison to heterogeneous catalysts and metal oxides. However, the use of molecular catalysts enables the investigation of the mechanistic aspects of water oxidation and the identification of active intermediates.¹⁸ Insights into the mechanisms and active intermediates involved in water oxidation can be used to develop more efficient catalysts. The ligand framework of molecular water oxidation catalysts can be modified to enhance the activity, which is one of the attractive features of molecular water oxidation catalysts. Several studies have shown that substituents on the ligand framework can have a significant effect on the efficiency of water oxidation^{10, 19-20}

To date, the most efficient molecular catalysts for both chemical and electrocatalytic water oxidations are based on ruthenium and iridium, which are rare, toxic, and expensive metals.^{3-4, 21} There has been an increasing number of reports on homogeneous water oxidation using first-row transition metals such as iron, cobalt, copper, and manganese.²²⁻²⁶ However, there are still gaps in the development of copper-based chemical water oxidation catalysts. Copper(II)-based chemical water oxidation has been sparingly explored; meanwhile, there are no reports on copper(I)-based water oxidation catalysts in both chemical and electrochemical water oxidation.

1.2 Aim and objectives

Aim

This study aims to develop abundant, cheap, and environmentally friendly first-row transition metal complexes based on copper(II), copper(I), and cobalt(II), as homogeneous water oxidation catalysts.

Objectives

- To synthesise and characterise previously reported tridentate bis(pyrazol-1-ylmethyl)pyridine ligands bearing different groups on the pyrazolyl moiety.
- To synthesise and characterise bis(pyrazol-1-ylmethyl)pyridine ligated Cu(II), Cu(I), and Co(II), complexes. The complex characterisation will be carried out using techniques such as mass spectrometry, elemental analysis, FTIR spectroscopy, magnetic susceptibility, and single-crystal XRD.

- c) To study the synthesised complexes in detail as chemical water oxidation catalysts using chemical oxidants. The effect of different donating groups on the pyrazole (catalyst structure), initial rate data (catalyst and oxidant concentration), and the effect of using different chemical oxidants will be investigated.
- d) To study the synthesised complexes as electrocatalytic water oxidation catalysts under applied voltage. The effect of pH on the onset potential and the effect of catalyst structure on overpotentials will be investigated. The effect of scan rates on catalytic current and the stability of the catalysts over time will also be studied.

1.3 Outline of the thesis

The thesis is made up of six chapters. **Chapter 2**, which is the **literature review**, outlines the importance of water oxidation in hydrogen production and how natural photosynthesis has inspired the development of water oxidation catalysts. **Chapter 2** also highlights homogeneous chemical and electrocatalytic water oxidation catalysts that have been reported. **Chapter 3** focuses on **chemical and electrochemical water oxidation catalysed by water-soluble bis(pyrazolyl)pyridine copper(II) complexes**. This chapter outlines the results of chemically-driven and electrocatalytic water oxidation using copper(II) complexes. The chapter also probes the nature of the catalytically active species in electrocatalytic water oxidation. **Chapter 4** focuses on **chemical and electrochemical water oxidation mediated by bis(pyrazol-1-ylmethyl)pyridine-ligated Cu(I) complexes**. This chapter highlights the synthesis and characterisation of novel bis(pyrazol-1-ylmethyl)pyridine-ligated Cu(I) complexes and their activity in chemical and electrocatalytic water oxidation. Towards chemically-driven water oxidation, the effects of parameters such as catalyst structure, catalyst concentration, oxidant concentration were evaluated. In electrocatalytic water oxidation, the effect of catalyst structure, pH and catalyst concentration was investigated. **Chapter 5** entitled, “**Water oxidation catalysed by bis(pyrazolyl)pyridine cobalt(II) complexes: Investigating the stability of the complexes**”, highlights the electrocatalytic and chemical water oxidation using Co(II) complexes. The homogeneity of the catalyst system in electrocatalytic water oxidation was thoroughly investigated. **Chapter 6**, gives a summary of the main findings of the project and recommendations for future studies.

1.4 References

1. Kärkäs, M. D.; Åkermark, B., Dalton Trans. 2016, 45 (37), 14421-14461.
2. Crabtree, G. W.; Dresselhaus, M. S., MRS Bull. 2008, 33 (4), 421-428.
3. Blakemore, J. D.; Crabtree, R. H.; Brudvig, G. W., Chem. Rev. 2015, 115 (23), 12974-13005.
4. Yagi, M.; Kaneko, M., Chem. Rev. 2001, 101 (1), 21-35.
5. Yamazaki, H.; Shouji, A.; Kajita, M.; Yagi, M., Coord. Chem. Rev. 2010, 254 (21-22), 2483-2491.
6. Gong, M.; Li, Y.; Wang, H.; Liang, Y.; Wu, J. Z.; Zhou, J.; Wang, J.; Regier, T.; Wei, F.; Dai, H., J. Am Chem. Soc. 2013, 135 (23), 8452-8455.
7. Kanan, M. W.; Nocera, D. G., Science 2008, 321 (5892), 1072-1075.
8. Koper, M. T. M., J. Electroanal. Chem. 2011, 660 (2), 254-260.
9. Tahir, M.; Pan, L.; Idrees, F.; Zhang, X.; Wang, L.; Zou, J.-J.; Wang, Z. L., Nano Energy 2017, 37, 136-157.
10. Berardi, S.; Drouet, S.; Francàs, L.; Gimbert-Suriñach, C.; Guttentag, M.; Richmond, C.; Stoll, T.; Llobet, A., Chem. Soc. Rev. 2014, 43 (22), 7501-7519.
11. Blakemore, J. D.; Schley, N. D.; Balcells, D.; Hull, J. F.; Olack, G. W.; Incarvito, C. D.; Eisenstein, O.; Brudvig, G. W.; Crabtree, R. H., J. Am. Chem. Soc. 2010, 132 (45), 16017-16029.
12. Matheu, R.; Garrido-Barros, P.; Gil-Sepulcre, M.; Ertem, M. Z.; Sala, X.; Gimbert-Suriñach, C.; Llobet, A., Nat. Rev. Chem. 2019, 3 (5), 331-341.
13. Zysman-Colman, E., Iridium (III) in optoelectronic and photonics applications. John Wiley & Sons: 2017.
14. Ottone, C.; Hernández, S.; Armandi, M.; Bonelli, B., Sacrificial Oxidants as a Means to Study the Catalytic Activity of Water Oxidation Catalysts. In Testing Novel Water Oxidation Catalysts for Solar Fuels Production, Springer: 2019; pp 29-47.
15. Parent, A. R.; Crabtree, R. H.; Brudvig, G. W., Chem. Soc. Rev. 2013, 42 (6), 2247-2252.
16. Dau, H.; Limberg, C.; Reier, T.; Risch, M.; Roggan, S.; Strasser, P., ChemCatChem 2010, 2 (7), 724-761.
17. Hong, W. T.; Risch, M.; Stoerzinger, K. A.; Grimaud, A.; Suntivich, J.; Shao-Horn, Y., Energy Environ. Sci. 2015, 8 (5), 1404-1427.
18. Schley, N. D.; Blakemore, J. D.; Subbaiyan, N. K.; Incarvito, C. D.; Dsouza, F.; Crabtree, R. H.; Brudvig, G. W., J. Am Chem. Soc. 2011, 133 (27), 10473-10481.
19. Abdel-Magied, A. F.; Arafa, W. A. A.; Laine, T. M.; Shatskiy, A.; Kärkäs, M. D.; Åkermark, B.; Johnston, E. V., ChemCatChem 2017, 9 (9), 1583-1587.

Chapter 1: Introduction of nitrogen-donor ligated transition metal complexes as water oxidation catalysts

20. Navarro, M.; Smith, C. A.; Li, M.; Bernhard, S.; Albrecht, M., *Chem. Eur. J.* 2018, 24 (24), 6386-6398.
21. Shaffer, D. W.; Xie, Y.; Concepcion, J. J., *Chem. Soc. Rev.* 2017, 46 (20), 6170-6193.
22. Fillol, J. L.; Codolà, Z.; Garcia-Bosch, I.; Gàmez, L.; Pla, J. J.; Costas, M., *Nat. Chem.* 2011, 3 (10), 807-813.
23. Liu, T.; Zhang, B.; Sun, L., *Chem. Asian J.* 2019, 14 (1), 31-43.
24. Panchbhai, G.; Singh, W. M.; Das, B.; Jane, R. T.; Thapper, A., *Eur. J. Inorg. Chem.* 2016, 2016 (20), 3262-3268.
25. Zhang, P.; Wang, M.; Yang, Y.; Yao, T.; Sun, L., *Angew. Chem. Int. Ed.* 2014, 53 (50), 13803-13807.
26. Zhang, T.; Wang, C.; Liu, S.; Wang, J. L.; Lin, W., *J. Am. Chem. Soc.* 2014, 136 (1), 273-281

Chapter 2: Literature review

2.1 Hydrogen: A renewable energy source

Global energy demand is increasing rapidly due to population growth and economic development. Although fossil fuels are still the main source of energy, a major drawback of using fossil fuels is the emission of greenhouse gases, such as carbon dioxide. Therefore, a more sustainable energy future will have to focus on the transition from the use of fossil fuels to renewable and environmentally friendly energy sources. Hydrogen releases energy upon reaction with oxygen, producing water as the only by-product, making it an attractive renewable energy source for the future.¹⁻³ One of the ways to produce hydrogen is the reforming of natural gas, which is not ideal as it results in the emission of carbon dioxide. Another way of producing environmentally friendly hydrogen is via solar-hydrogen technology. Solar-hydrogen technology uses water, an abundant raw material, to produce hydrogen in a process known as water splitting.⁴⁻⁵ Figure 2.1 summarises the hydrogen economy from production, storage, and some of the hydrogen applications in fuel cells.

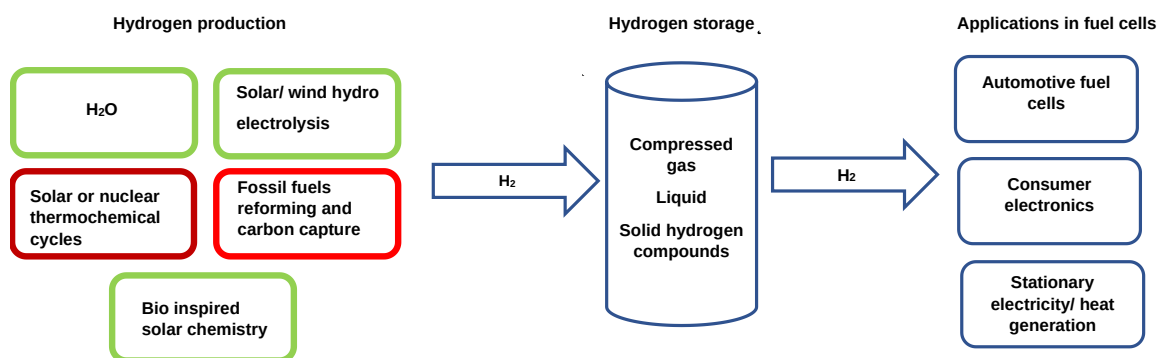
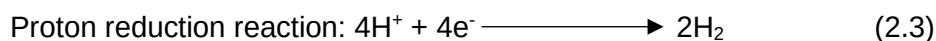
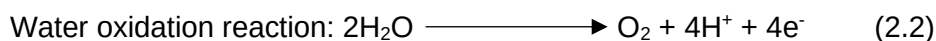
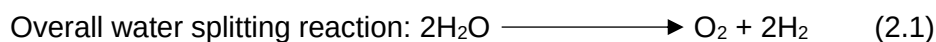


Figure 2.1: The hydrogen economy: Ways to produce, store and use hydrogen in, applications in different sectors (adapted from reference 6).

2.2 Water splitting towards hydrogen production

Water splitting (2.1) is a process wherein water is converted into oxygen and hydrogen. The two reactions involved in water splitting are the water oxidation reaction commonly known as the OER where oxygen is produced (2.2), and the proton reduction reaction known as HER (2.3) where hydrogen is produced.⁷ Water oxidation is the reaction of interest in water splitting as it is thermodynamically challenging and the rate-determining step in the overall water splitting, which requires a catalyst to overcome the activation barrier. This is because water oxidation involves the transfer of four electrons and four protons in a process of producing one dioxygen molecule from two water molecules.



2.3 Natural photosynthesis vs artificial photosynthesis

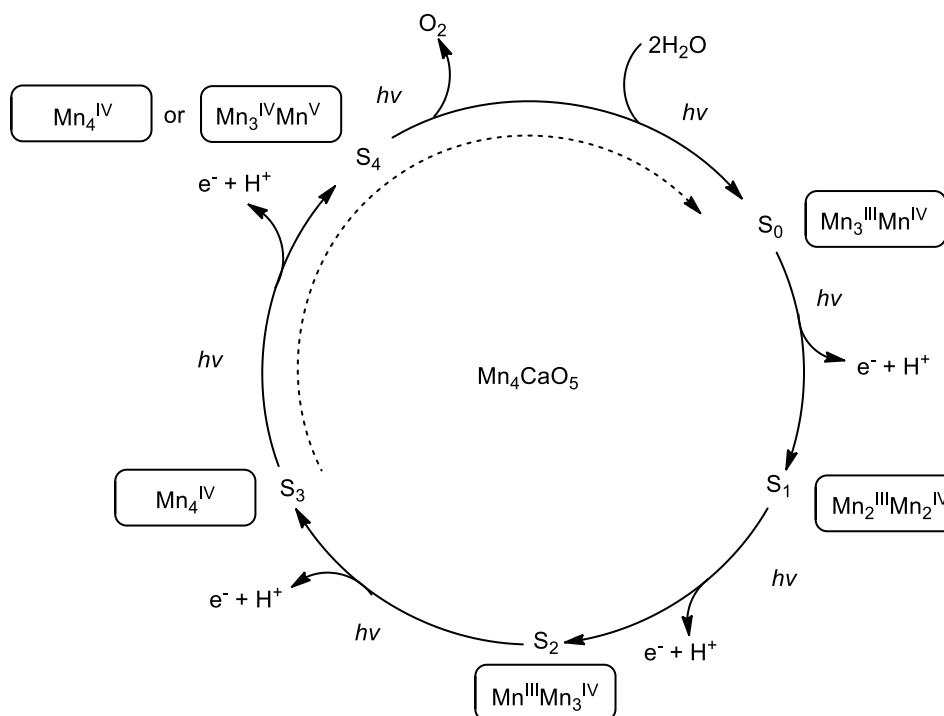
Nature often inspires the synthesis of new chemical compounds and the development of efficient catalysts for various processes. This area of chemistry inspired by nature is known as biomimetic chemistry.⁸ Natural photosynthesis has sustained life on earth through the conversion of solar energy to chemical energy. In artificial photosynthesis, the natural process is mimicked through the development of synthetic artificial leaves.⁹

2.3.1 Natural photosynthesis

In natural photosynthesis, light energy is used in the oxidation of water to dioxygen. This process takes place in the enzyme co-factor complex photosystem II (PSII).¹⁰⁻¹² During the water oxidation reaction, four protons, and four electrons are released. The protons from PSII contribute to the membrane-spanning proton motive force, while the released electrons are used in the reduction of plastoquinone to plastoquinols.¹³

Biological water oxidation is catalysed by the OEC situated in the PSII. The core of the OEC has been studied by techniques such as X-ray crystallography,^{10, 14} and electron paramagnetic resonance (EPR) spectroscopy.¹⁵ The OEC is made up of a pentanuclear cluster that contains four manganese atoms and one calcium atom (Mn_4CaO_5). The manganese cluster is held together by surrounding μ -oxo and μ -hydroxo ligands in a cubane arrangement, wherein the three manganese centres are capped by a calcium atom and the fourth dangling manganese is connected to the cubane via two of its oxo groups.^{10, 16-17}

The OEC is conserved as the site of water oxidation in all known oxygenic phototrophs. The manganese cluster is progressively oxidised through a tyrosine residue in a one-electron step using the single-photon photochemistry of the P_{680} chlorophylls.¹⁸ After four electrons are removed from the OEC, sufficient potential has been accumulated for oxygen evolution from water to occur.¹⁹ The water oxidation by the manganese cluster can be explained by the Kok cycle (Scheme 2.1).



Scheme 2.1: The Kok cycle illustrating the different oxidation states of manganese in the OEC.^{16, 20}

The Kok cycle reflects that the liberation of O_2 requires four-electron transfers. The cycle encompasses a four-quantum process wherein four consecutive flash excitations of chlorophyll-a electron donor, P_{680} forms an oxidant P_{680}^+ that induces four increasingly oxidised states of the Mn_4CaO_5 cluster with each excitation adding +1 charge.²⁰⁻²¹ Each oxidation state is termed the S-state (S_0 – S_4) with S_0 being the most reduced state and S_4 being the most oxidized state in the catalytic cycles. The first three steps, i.e., S_0 – S_1 , S_1 – S_2 , and S_2 – S_3 , are where charge accumulation takes place. The dark stable S_1 state, which evolves from the S_0 oxidation state via a proton-coupled electron transfer (PCET) process, is transformed into the S_2 state after a single electron loss. This is followed by the transition of S_2 – S_3 associated with the loss of one proton and another electron. After the charge accumulation on the Mn_4CaO_5 cluster on the S_3 oxidation state, the oxidation state of Mn is IV, the highest oxidation state that can be reached through one-electron oxidation. Following the charge arrangements, the highly active S_4 oxidation state is predicted to contain a Mn^{IV} oxyl radical or Mn^{V} oxo species.²¹ The S_4 oxidation state is very short-lived, making it difficult to obtain experimental evidence of the structure and reaction steps involved.^{19, 21} The formation of S_4 immediately releases molecular oxygen through a peroxo transition state, and the S_0 state is regenerated.^{16, 20, 22-23} The natural photosynthetic system, i.e., the structure and function of the OEC, inspires the development of artificial photosynthetic assemblies including water splitting catalysts.

2.3.2 Artificial photosynthesis

Artificial photosynthesis mimics the natural photosynthesis system in the development of efficient water oxidation catalysts. The construction of an artificial photosynthetic system requires one-electron transfer events to be coupled to catalytic units that are capable of mediating four-electron and four proton transfers in the splitting of water. In an artificial photosynthesis assembly, the light-harvesting unit and the reaction centre must be coupled to water splitting catalysts to eventually produce chemical fuels, as shown in Figure 2.2.²⁴ In an artificial photosynthetic system, a chromophore (photosensitiser) can be attached to a semiconductor. Upon illumination, a charge-separated state is formed by electron transfer from the photo-excited chromophore to the conduction band of the semiconductor. The charge-separated state must be sufficiently long-lived to allow the chromophore to abstract an electron from the catalyst, thereby regenerating the chromophore and the one-electron oxidised catalyst. After four successive charge separations and associated electron abstractions, the catalyst refills the holes by abstracting the electrons from H_2O , thereby oxidising it to molecular oxygen. The electrons abstracted from H_2O are ultimately delivered to a reduction catalyst, which mediates the reduction of protons to form H_2 .¹⁶

The challenge in the assembly of an artificial photosystem is the development of water oxidation catalysts.²⁵ Water oxidation is an energy-demanding reaction; therefore, catalysts should be able to accumulate several oxidising equivalents, forming the essential O–O bond, while operating close to the thermodynamic potential of 1.23 V.

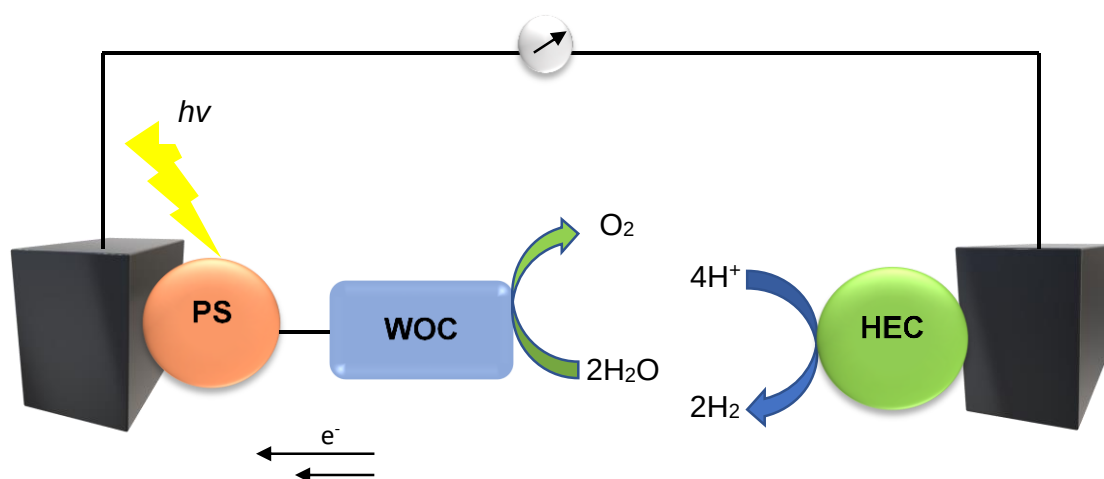


Figure 2.2: Illustration of the artificial photosynthesis assembly made up of a photosensitizer (PS), water oxidation catalyst (WOC), and hydrogen evolving catalyst (HEC) in the production of solar fuels (adapted from reference 16).

2.4 Homogeneous molecular systems as water oxidation catalysts

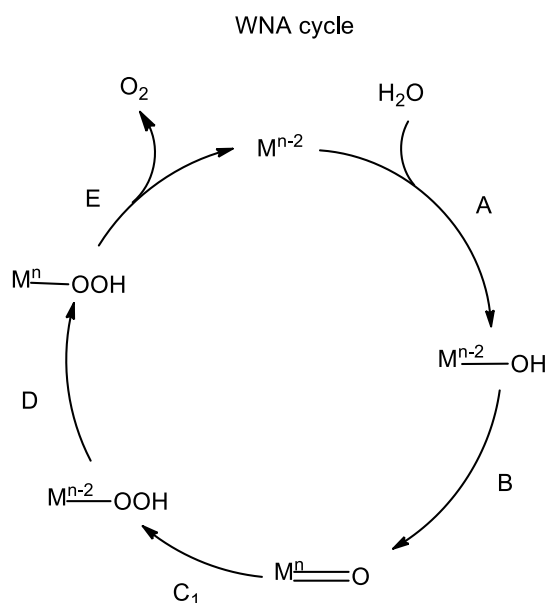
Although heterogeneous water oxidation catalysts were known long before the homogeneous analogues, homogeneous water oxidation catalysts are worth investigating. In comparison to well-established and efficient heterogeneous water oxidation catalysts, homogeneous water oxidation catalysts can easily be modified through ligand modification. Another advantage of using molecular systems in water oxidation catalysis is the ease of deducing the catalytic mechanism in solution.

2.4.1 Basic mechanism of homogeneous water oxidation

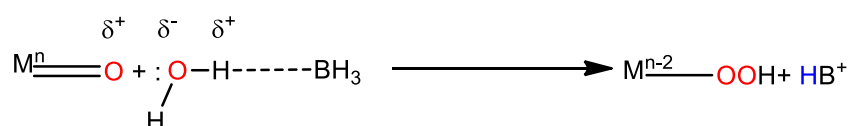
The general mechanism of water oxidation is shown in Scheme 2.2 and Scheme 2.4. Steps **A**, **B**, **D**, and **E** take place the same way on both Scheme 2.2 and Scheme 2.4. However, the O-O bond formation step **C** can take place through different mechanisms. The first event in water oxidation is the binding of water (**A**) in a case where a water molecule is not already bound. The water-binding is followed by oxidative water activation, which forms a high valent metal-oxo or metal oxyl intermediate (**B**). The metal oxo undergoes oxygen-oxygen (O-O) bond formation, which can happen in two ways, namely water nucleophilic attack (WNA) (**C1** in Scheme 2.2) and radical coupling reactions (I2M) (**C2** in Scheme 2.4). After the O-O bond formation, further oxidation, and deprotonation reactions take place (**D**). Lastly, molecular oxygen is released, and the initial state of the catalyst is regenerated by the coordination of the novel substrate (**E**). In summary, the steps involved in water oxidation are water oxidative activation, O-O bond formation, oxidative activation of peroxide intermediates, and lastly, oxygen evolution.³⁰

2.4.2 Water nucleophilic attack

In the WNA mechanism, water oxidation takes place at a single site. This key step involves the attack of a water molecule on an electron-deficient metal-oxo species with a simultaneous proton transfer to a hydrogen bound proton acceptor to generate a hydroperoxide intermediate (Scheme 2.3). Limits to the catalytic rates for single-site catalysis can be the oxidation, O-O bond formation, or oxygen evolution step. Each of the steps has a first-order dependence on the catalyst and the oxidation steps are also first order in respect of the oxidant.³⁰



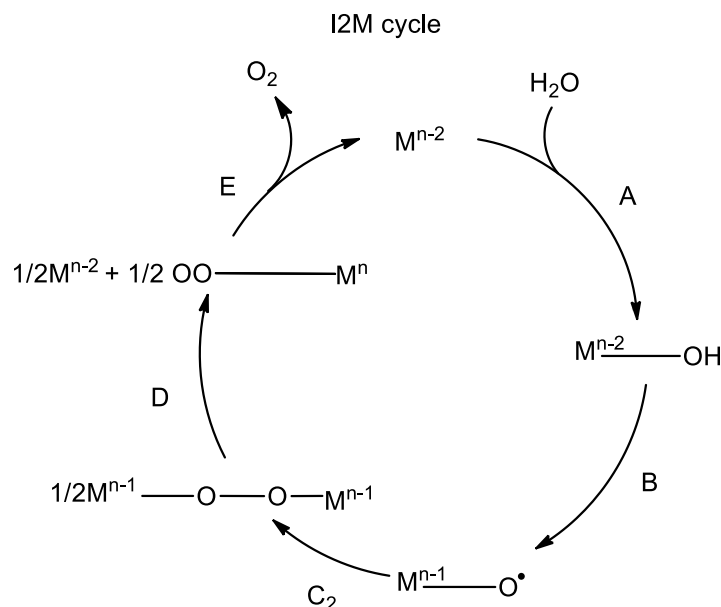
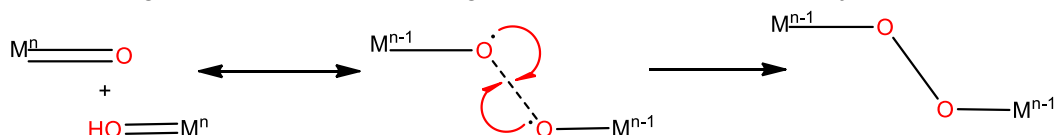
Scheme 2.2: The general mechanism showing the WNA O-O bond formation cycle.³⁰



Scheme 2.3: Water nuclear attack O-O bond formation.³⁰

2.4.3 Radical coupling of two metal oxos (I2M)

The I2M mechanism is favoured by more electron-rich catalysts, which have more oxyl radical character in their activated state, which results in M-O antibonding character. Upon formation of the O-O bond by the coupling of two metal oxyl radicals, a peroxo bridge between the two metal centres is formed (Scheme 2.5). The rate-determining step in these systems can be the oxidation step, the oxo-oxo coupling step, or the oxygen release step. Biomolecular systems are more sensitive to catalyst concentration; therefore, catalysts that require an intermolecular coupling step will be rate-limited by that step at low enough catalyst concentrations.³⁰

Scheme 2.4: The general mechanism showing the I2M O-O bond formation cycle.³⁰Scheme 2.5: I2M O-O bond formation.³⁰

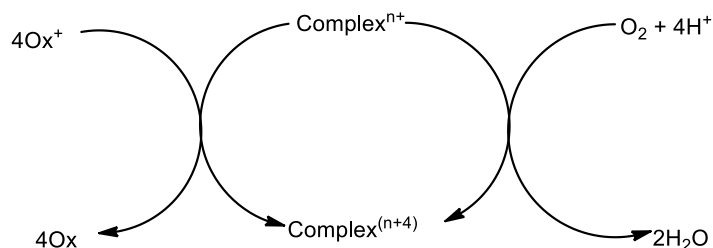
This mechanism is favoured by more electron-rich catalysts having more oxyl radical character in their activated state, which results in M-O antibonding character. Upon formation of the O-O bond by the coupling of two metal oxyl radicals, a peroxo bridge between the two metal centres is formed (Scheme 2.5). The rate-determining step in these systems can be the oxidation step, the oxo-oxo coupling step, or the oxygen release step. Biomolecular systems are more sensitive to catalyst concentration; therefore, catalysts that require an intermolecular coupling step will be rate-limited by that step at low enough catalyst concentrations.³⁰

2.5 Different approaches taken in water oxidation

Different activation approaches for evaluating water oxidation have been reported including chemical, electrocatalytic, and photochemical water oxidation.³¹⁻³² In chemical water oxidation, sacrificial oxidants are used to activate the metal centre for water oxidation while electrocatalytic water oxidation is potential controlled with water oxidation taking place under applied voltage. Photochemical water oxidation, in contrast, involves the use of light during water oxidation. Chemical and electrocatalytic water oxidation will be discussed in detail in the following sections.

2.5.1 Chemical water oxidation

The catalytic oxidation of water using chemical oxidants (Scheme 2.6) has been extensively studied over the years.^{13, 32-35} Chemical water oxidation is mostly used in catalyst screening and optimization. Measurements using sacrificial oxidants allow for rapid screening of complexes and to study the effect of varying reaction conditions. Chemical oxidants, also referred to as sacrificial oxidants, must have reduction potentials that are sufficient to oxidize the water oxidation catalysts.³⁶⁻³⁷



Scheme 2.6: A general representation of chemical water oxidation in the presence of a chemical oxidant.³²

2.5.1.1 Chemical oxidants

CAN has been extensively investigated as the sacrificial oxidant of choice in water oxidation reactions. CAN is capable of driving water oxidation catalysis in one-electron steps, which is relevant to the conditions present in a photo-electrochemical cell. CAN is readily available commercially and has a strong absorption band in the ultraviolet-visible (UV-Vis) spectrum at 300 to 450 nm, which can be used to track the consumption of the oxidant during catalysis. The drawback of using CAN as an oxidant is that it is only stable at low pH (pH ~1). Another oxidant that has been investigated in water oxidation includes ruthenium(III) tris(bipyridine) cation $[\text{Ru}(\text{bpy})_3](\text{PF}_6)$. The drawback of using this ruthenium cation as a primary oxidant is that it is expensive. Sodium *m*-periodate has also been investigated in water oxidation with some transition metals. Unlike CAN and $[\text{Ru}(\text{bpy})_3](\text{PF}_6)$, sodium *m*-periodate is a two-electron oxidant. Sodium *m*-periodate is stable at pH 2 - 7.5 and allows for investigation of water oxidation catalysts at neutral pH, which best mimics PSII. The drawback with the use of sodium *m*-periodate is that it can potentially act as an oxo-transfer reagent, which could lead to the production of extra oxygen which is not due to water oxidation.³⁸ Other oxidants include sodium peroxodisulfate and potassium peroxymonosulfate (oxone).³⁷

2.5.1.2 Catalysts used in water oxidation

2.5.1.2.1 Ruthenium and iridium complexes

The first homogeneous water oxidation catalyst known as Meyer's blue dimer was reported in 1982 by Meyer *et al.*³⁹ The oxo-bridged ruthenium dimer $[(\text{bpy})_2(\text{H}_2\text{O})\text{RuORu}(\text{H}_2\text{O})(\text{bpy})_2]^{4+}$ contains bipyridine ligands and catalysed water oxidation in the presence of a sacrificial oxidant CAN with a TON of 13.2 and TOF of 0.0042 s^{-1} . Another homogeneous ruthenium dimeric system, $[\text{Ru}_2^{\text{II}}(\mu\text{-OAc})(\text{bpp})(\text{trpy})_2]^{2+}$ (bpp = 2,2'-(1H-pyrazole-3,5-diyl)dipyridine, trpy = 2,2':6',2''-terpyridine) used in chemical water oxidation was reported by Llobet and colleagues⁴⁰ in 2004. The bpp ligand aided in enforcing the cis geometry of the two ruthenium centres. The addition of the metal complex to CAN resulted in the evolution of oxygen at the rate of 0.014 s^{-1} . Ruthenium complexes have played a vital role in the mechanistic studies of homogeneous water oxidation and the characterisation of the intermediates detailed in Scheme 2.7.⁴¹⁻⁴³ Meyer *et al.*⁴¹ reported on the first single-site mechanistic study using ruthenium complex **1**, which was proposed based on electrochemical data and UV-visible spectroscopy.

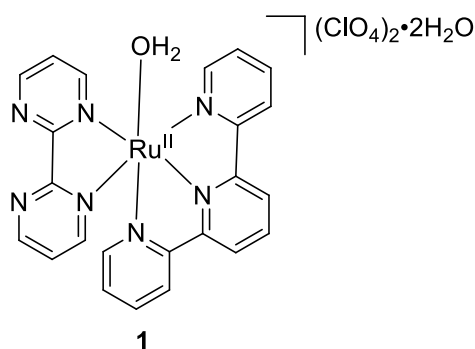
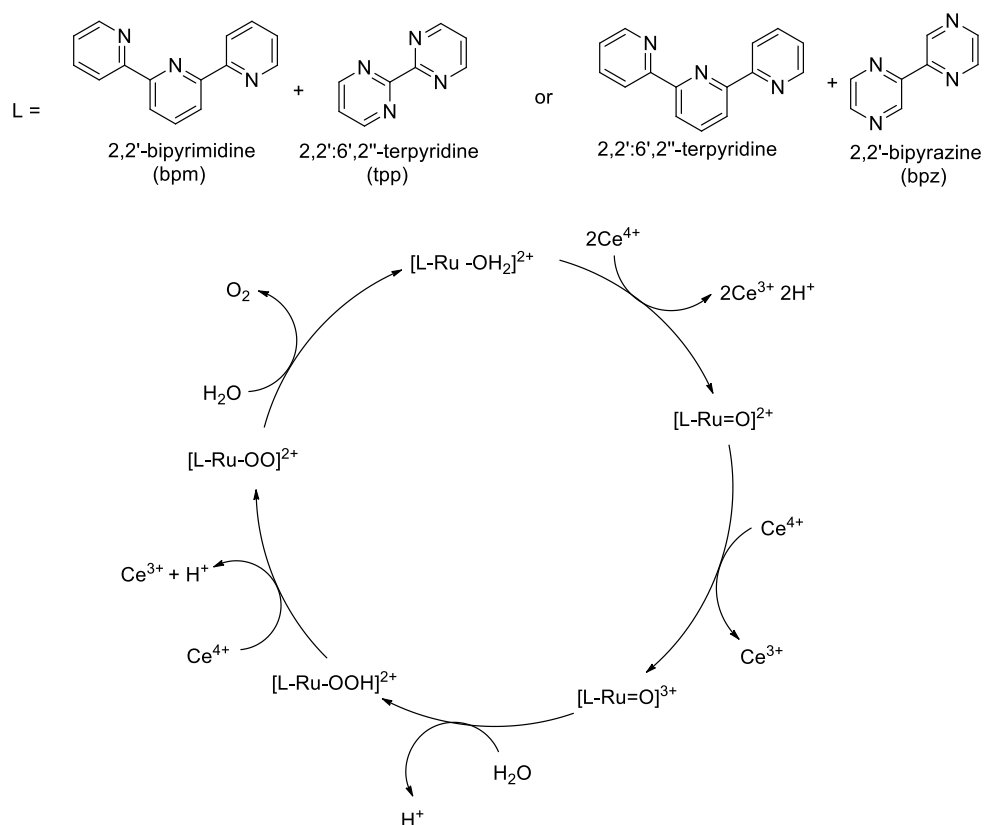


Figure 2.3: $[\text{Ru}^{\text{II}}(\text{tpy})(\text{bpm})(\text{OH}_2)] (\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ water oxidation catalyst.

Scheme 2.7 shows a proposed mechanism of CAN driven water oxidation catalysed by $[\text{Ru}(\text{tpy})(\text{bpm})(\text{OH}_2)]^{2+}$ (**1**) and $[\text{Ru}(\text{tpy})(\text{bpz})(\text{OH}_2)]^{2+}$ (tpy = 2,2':6',2''-terpyridine, bpm = 2,2'-bipyrimidine, bpz = 2,2'-bipyrazine). Upon the addition of 2 equivalents of Ce(IV) to a solution of $[\text{Ru}(\text{tpy})(\text{bpm})(\text{OH}_2)]^{2+}$ in 0.1 M HNO_3 the catalyst is oxidized to a high valent $\text{Ru}(\text{tpy})(\text{bpm})(\text{O})^{2+}$ intermediate. Further addition of one equivalence of Ce(IV) to $[\text{Ru}=\text{O}]^{2+}$, or 3 equivalents of Ce(IV) to $[\text{Ru}(\text{OH}_2)]^{2+}$ results in the formation of an intermediate $[\text{Ru}=\text{O}]^{3+}$, which is short-lived. The $[\text{Ru}=\text{O}]^{3+}$ undergoes an O-O bond formation via WNA by the second water molecule to give a peroxide cation, $[\text{Ru}(\text{tpy})(\text{bpm})(\text{OOH})]^{2+}$, which was characterised by redox titration. The peroxidic cation $[\text{Ru}(\text{tpy})(\text{bpm})(\text{OOH})]^{2+}$ is very unstable, decomposing in minutes to give $[\text{Ru}-\text{OH}_2]^{2+}$, which releases oxygen, and the catalyst is regenerated.

Chapter 2: Literature review



Scheme 2.7: An example of a proposed mechanism of chemical water oxidation by a ruthenium dimer.⁴¹

Thummel *et al.*⁴⁴ reported dinuclear ruthenium complexes ligated by 3,6-bis-[6'-(1'',8''-naphthyrid-2''-yl)-pyrid-2'-yl]pyridazine and mononuclear complexes containing a 2,2'-(4-(*tert*-butyl)pyridine-2,6-diyl)bis(1,8-naphthyridine) scaffold (Figure 2.4). Both the dinuclear and mononuclear complexes were active in water oxidation in the presence of CAN as the chemical oxidant. For both dinuclear and mononuclear complexes, the highest turnover numbers are observed with 4-methylpyridine (**3** and **6**) as the axial ligand with TONs of 3200 and 580, respectively. In comparison with other reported systems, the 4-methylpyridine makes the catalyst more robust. The dinuclear complexes were more active as compared to the mononuclear complexes.

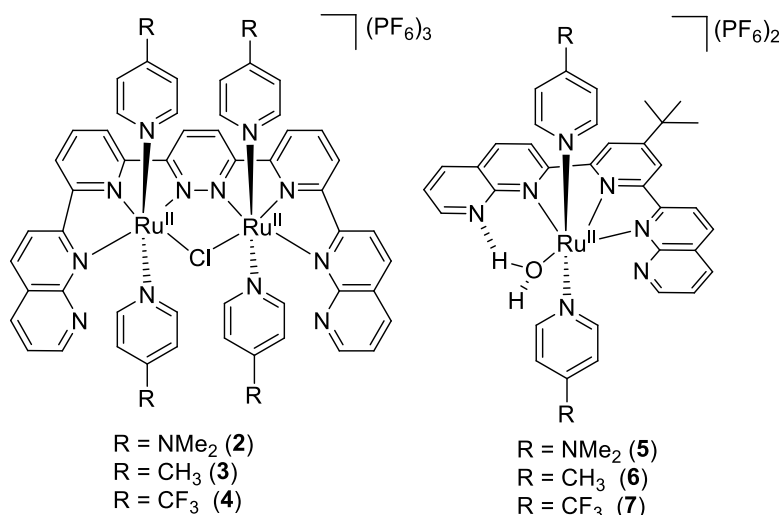
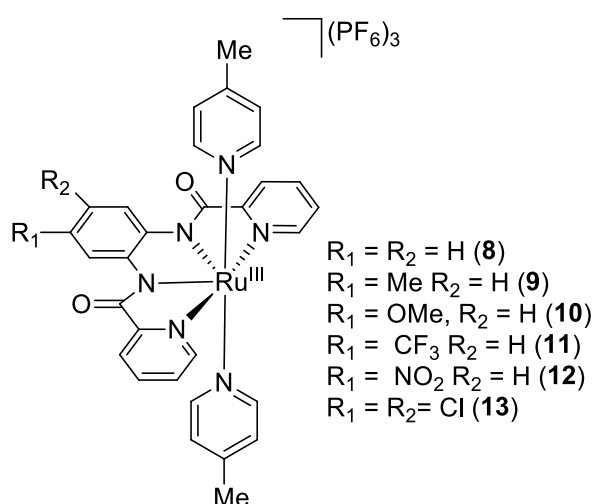


Figure 2.4: Mononuclear and dinuclear ruthenium complexes investigated in chemical water oxidation.

A $[\text{Ru}(\text{bda})(\text{isoq})_2]$ (H_2bda = 2,2'-bipyridine-6,6'-dicarboxylic acid; isoq = isoquinoline) was reported as an efficient chemical water oxidation catalyst in the presence of CAN.⁴⁵ The complex resulted in a TOF of 303 s^{-1} , which is comparable to reaction rate ($100\text{-}400 \text{ s}^{-1}$) of the OEC of PSII. The complex was found to be more active than the frequently reported $[\text{Ru}(\text{bda})(\text{pic})_2]$ (pic = 4-picoline). Abdel-Magied *et al.*⁴⁶ studied the effect of different substituents on water oxidation catalysis using mononuclear tetradentate ruthenium complexes (Figure 2.5). Water oxidation was investigated at a neutral pH using $[\text{Ru}(\text{bpy})_3](\text{PF}_6)$ (bpy = 2,2'-bipyridine) as the chemical oxidant. Complexes containing electron-donating substituents, methyl (Me) (**9**) and methoxy (OMe) (**10**) were found to be more efficient with a TON of 26 and a TOF of 0.50 s^{-1} for complex **9** and a TON of 21 and a TOF of 0.45 s^{-1} for complex **10**.

Figure 2.5: Ruthenium complexes used in chemical water oxidation using $[\text{Ru}^{\text{III}}(\text{bpy})_3](\text{PF}_6)_3$ as a chemical oxidant.

The efficiency of iridium complexes in chemical water oxidation is comparable to that of ruthenium complexes. The first reported iridium complexes are cyclometalated aquo complexes ($[\text{Ir}^{\text{III}}(\text{R}_1\text{R}_2\text{ppy})_2(\text{OH}_2)_2]^+$) (ppy = phenylpyridine) containing a bis-phenylpyridine ligand framework.⁴⁷ The oxidation of the complex with CAN as the primary chemical oxidant resulted in oxygen evolution in a homogeneous aqueous solution. The initial rate was $10 \sim 50 \text{ mmol h}^{-1}$ with a TOF of $0.93 \sim 4.6 \times 10^{-3} \text{ s}^{-1}$. The effect of donating groups on iridium complexes in water oxidation catalysis was studied by Navarro *et al.*⁴⁸

Pyridylidene amide ligated iridium complexes (**14-17**), shown in Figure 2.6, were studied using CAN as the chemical oxidant. Upon the introduction of electron-donating groups on the complex, the TOF increased from 1600 h^{-1} to 3300 h^{-1} . The study investigated the effect of different substituents on the water oxidation activity, which shows that the ligand framework plays a vital role in the activity of the water oxidation catalyst.

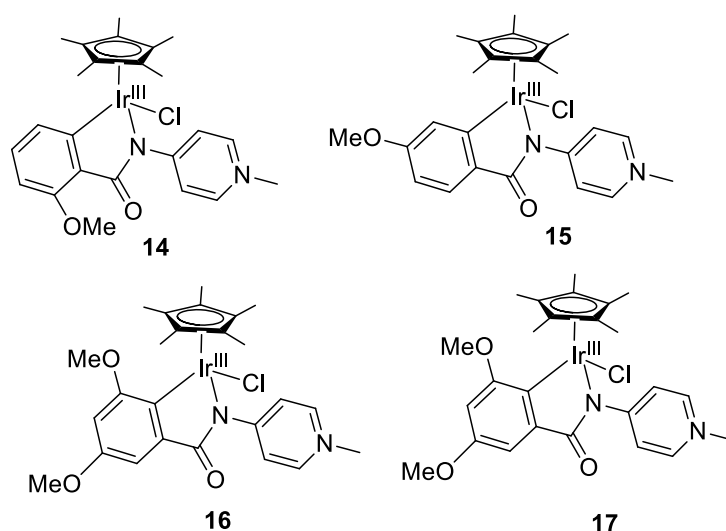


Figure 2.6: Iridium complexes for water oxidation.

Although ruthenium and iridium complexes are efficient water oxidation catalysts, the drawback of using these metals is that they are rare, toxic, and expensive. Over the years, there has been a growing number of reports on chemically-driven homogeneous water oxidation using first-row transition metals such as iron, cobalt, copper, and manganese as catalysts.

2.5.1.2.2 Manganese complexes

Manganese complexes best mimic natural photosynthesis as the PSII responsible for water oxidation in nature contains a manganese atom. This makes exploring manganese complexes as water oxidation catalysts an interesting topic. Manganese is also a cheap and abundant metal that exhibits redox flexibility which activates the generation of high valent species that oxidises water. A dinuclear complex $[\text{H}_2\text{O}(\text{terpy})\text{Mn}(\text{O})_2\text{Mn}(\text{tpy})\text{OH}_2](\text{NO}_3)_3$ (**18**) shown in Figure 2.7 has been studied using different oxidants as summarised in Table 2.1. The complex shows activity towards chemical water oxidation in the presence of NaOCl (TON 4, TOF 0.0033 s^{-1}), CAN (TON 17, TOF 320), and oxone (TON >50, TOF 0.034 s^{-1}). Tagore *et al.*⁴⁹ observed low oxygen evolution with complex **18** using CAN as the primary oxidant with a TON of 0.54. The use of clay compounds as support for complex **18** using CAN as the primary oxidant improved the activity significantly to a TON of 17 and a TOF of 320 s^{-1} .⁵⁰⁻⁵¹

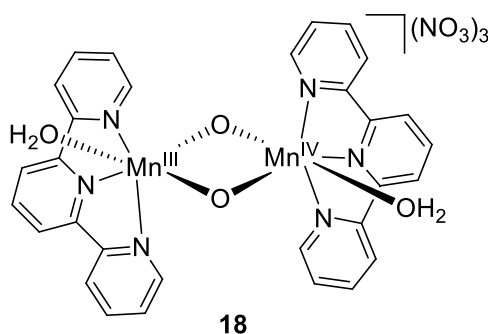


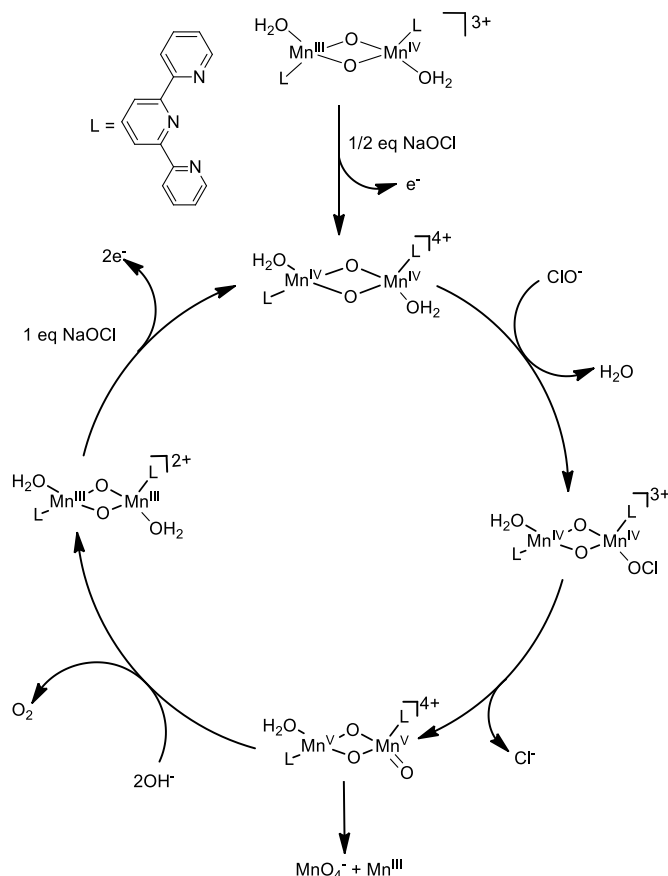
Figure 2.7: A dinuclear manganese complex $[\text{H}_2\text{O}(\text{tpy})\text{Mn}(\text{O})_2\text{Mn}(\text{tpy})\text{OH}_2](\text{NO}_3)_3$ studied in chemical water oxidation.

Table 2.1: Catalytic activities of manganese-based complex **18** using different oxidants.

Cat	Oxidant	TON	TOF	Reference
18	NaOCl	4	0.0033	52
18	Oxone	>50	0.034	35
18	CAN	0.54	-	49
18	CAN	17	320	50-51

The mechanism for O_2 formation from the reaction of complex **18** with sodium hypochlorite is shown in Scheme 2.8. Complex **18** initially reacts rapidly to form the Mn(IV/IV) dimer. The Mn(IV/IV) dimer can then react with sodium hypochlorite to form a Mn(V)=O dimeric intermediate, the species that are featured in the O–O bond-forming step. The proposed mechanism for O–O bond formation involves an attack of OH on the Mn=O to form a peroxo dimer, which rapidly reacts with two further oxidising equivalents and releases O_2 .

Permanganate would form in a competing reaction by disproportionation of the Mn(V/V) dimer to give Mn(VII) and Mn(III).



Scheme 2.8: Proposed mechanism of chemical water oxidation using a manganese dimeric complex **18**.⁵²

2.5.1.2.3 Iron(II) complexes

The interest towards iron-based water oxidation catalysts is due to the redox chemistry of the metal, which is necessary for electron transfer processes during water oxidation catalysis. Additionally, iron is one of the most abundant and inexpensive redox-active metals.⁵³⁻⁵⁵ Fillol *et al.*⁵⁶ reported efficient water oxidation catalysts based on nitrogen-based iron complexes, [Fe(X)₂(L^{N4})](L^{N4}) (L^{N4} = 1-(2'-pyridylmethyl)-4,7-dimethyl-1,4,7-triazacyclononane) (**Me₂Pytacn**) (N,N'-dimethyl-N,N'-bis(2-pyridylmethyl)-cyclohexane-1,2-diamine (**mcp**), N,N'-dimethyl-N,N'-bis(2-pyridylmethyl)-ethane-1,2-diamine (**mep**), N,N'-bis(2-pyridylmethyl)-2,2'-bipyrrlidine (**bpbp**) and tris-(2-pyridylmethyl)amine(**tpa**); X = Cl, OTf)) **19-23** (Figure 2.8). The complexes achieved a TON of 360 when using CAN and >1000 when sodium *m*-periodate was used as the oxidant.⁵⁶

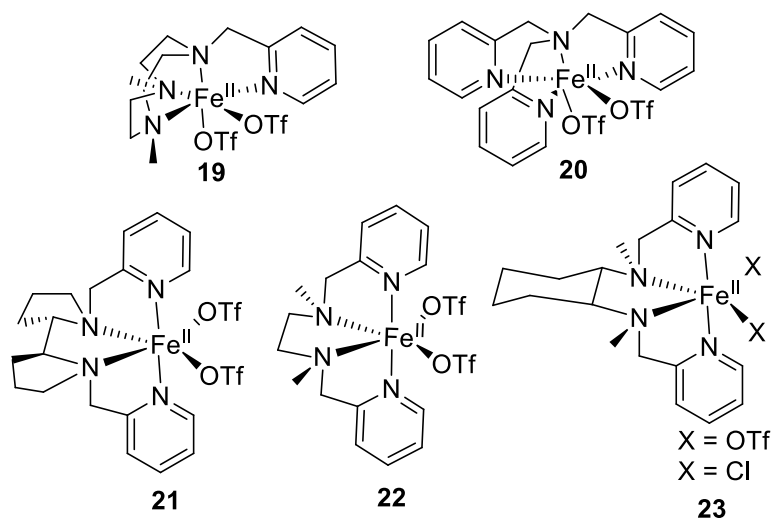
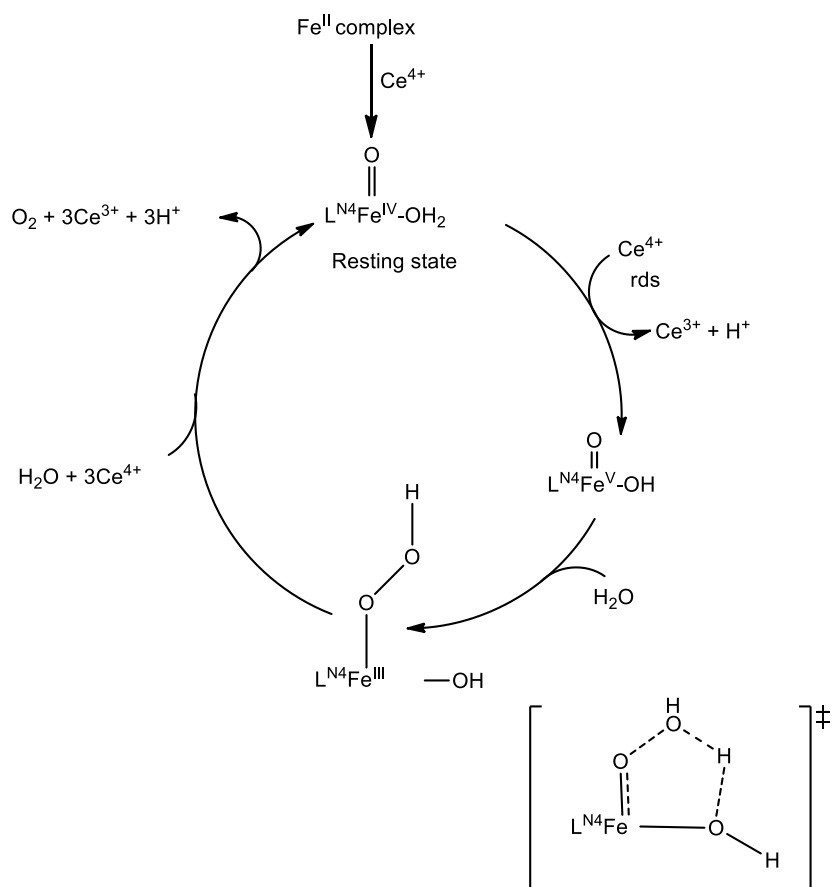


Figure 2.8: Tetradentate iron complexes used in chemical water oxidation catalysis.⁵⁶

The mechanism of the chemically-driven water oxidation reactions is illustrated in Scheme 2.9 below. Spectroscopic monitoring demonstrates that the initial Fe(II) complexes $[\text{Fe}(\text{X})_2(\text{L}^{\text{N}4})]$ are oxidised immediately by excess Ce(IV), which results in the formation of the resting-state water-oxo compound $[\text{Fe}^{\text{IV}}(\text{O})(\text{H}_2\text{O})(\text{L}^{\text{N}4})]^{2+}$. The bimolecular rate law extracted from the kinetic analysis suggests that the RDS involves further $1e^-$ oxidation of the oxo-iron(IV) complex by Ce(IV), to form a highly oxidising $[\text{Fe}^{\text{V}}(\text{O})(\text{OH}_2)(\text{L}^{\text{N}4})]^{3+}$ intermediate. Given the high oxidation state of the metal centre, the water ligand must be nucleophilic and the $[\text{Fe}^{\text{V}}(\text{O})(\text{OH})(\text{L}^{\text{N}4})]^{2+}$ intermediate is expected to be formed. Subsequent attack of a water molecule, assisted by a hydrogen-bond interaction with the hydroxide ligand, forms the O–O bond, which reduces the Fe(V) to form the $[\text{Fe}^{\text{III}}(\text{OOH})(\text{H}_2\text{O})(\text{L}^{\text{N}4})]^{2+}$ intermediate $\text{L}^{\text{N}4}\text{Fe}^{\text{III}}\text{--OOH}$. The closure of the catalytic cycle can be envisioned as two possible pathways. The first possibility comprises further oxidation of intermediate $\text{L}^{\text{N}4}\text{Fe}^{\text{III}}\text{--OOH}$ to give $\text{L}^{\text{N}4}\text{Fe}^{\text{IV}}\text{--OOH}$ or $\text{L}^{\text{N}4}\text{Fe}^{\text{V}}\text{--OOH}$, and O_2 extrusion via reduction of the metal centre to Fe(II) or Fe(III), respectively. The second possibility involves protonation of the hydroperoxide ligand in $\text{L}^{\text{N}4}\text{Fe}^{\text{III}}\text{--OOH}$ extruding H_2O_2 and forming a Fe(III) species that is oxidized rapidly by Ce(IV), and thereby closes the catalytic cycle.



Scheme 2.9: Proposed mechanism for chemical water oxidation catalysed by $[\text{Fe}^{\text{II}}(\text{X})_2(\text{LN}^4)]$ complexes using CAN as the primary oxidant.

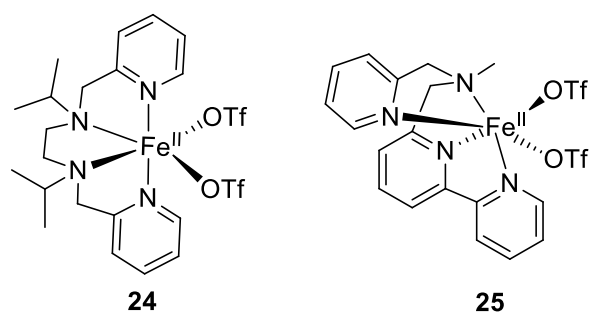


Figure 2.9: Iron complexes used in chemical water oxidation.

Panchbhai *et al.*⁵⁷ evaluated mononuclear tetrazadentate iron catalysts (**24** and **25**) shown in Figure 2.9 using CAN as the oxidant, monitoring the oxygen evolution using the Clark-type oxygraph. The complexes were able to catalyse water oxidation and resulted in a TON of 14 and a TOF of 0.18 s^{-1} .

2.5.1.2.4 Copper(II) complexes

Copper complexes are attractive WOCs owing to their widespread bio-mimetic chemistry with oxygen. However, there is a lack of research in chemically-driven water oxidation using copper complexes. The challenge encountered in chemical water oxidation using copper complexes is the precipitation of CAN under basic conditions.

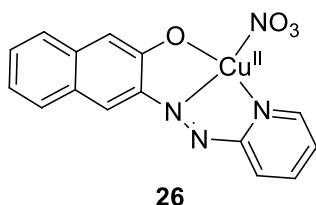


Figure 2.10: A copper complex ($[(L)Cu^{II}(NO_3)]$ ($L = (E)$ -3-(pyridin-2-yl-diazenyl)naphthalen-2-ol)) studied in chemical water oxidation with CAN as the primary oxidant.

Wei *et al.*⁵⁸ have reported $[(L)Cu^{II}(NO_3)]$ ($L = (E)$ -3-(pyridin-2-yl-diazenyl)naphthalen-2-ol) (**26**) (Figure 2.10) as a homogeneous catalyst for water oxidation under both electrochemical and chemical conditions. Under chemically-driven water oxidation conditions, the complex resulted in a TOF of 4.0 kPa h^{-1} .

Najafpour *et al.*⁵⁹ studied the activity of the same copper complex (**26**) in the presence of CAN. No activity was observed as the catalyst was not stable due to the highly acidic environment. At a higher pH (pH 11), the phosphate buffer used resulted in the precipitation of CAN. To date, all of the reports on copper(II) complexes are studied in electrocatalytic water oxidation.

2.5.1.2.5 Cobalt complexes

Reports on homogeneous cobalt complexes are mostly on photochemical water oxidation and only a few on chemically-driven cobalt water oxidation catalysis. Examples of cobalt complexes investigated towards photochemical water oxidation are illustrated in Figure 2.11. Nakazono *et al.*⁶⁰ studied three cobalt porphyrins, CoTMPyP (TMPyP = 5,10,15,20-Tetrakis(1-methyl-4-pyridinio)porphyrin-tetra(p-toluenesulfonate)) (**27**), CoTCPP (TCPP = Tetrakis(4-carboxyphenyl)porphyrin) (**28**) and Co^{III}TPPS (TPPS = meso-tetraphenylporphine-4,4',4'',5,10,15,20-tetrakis(4-sulfophenyl)porphyrin)) (**29**) towards photochemical water oxidation using $Ru^{II}(bpy)_3^{2+}/Na_2S_2O_3$. At pH 11, the Co^{III}TPPS complex (**29**) was the most active with a TON of 121.8 and TOF of 0.170 s^{-1} . The proposed mechanism indicated that the O-O bond formation step involved a bimolecular radical coupling process. Another report on photochemical water oxidation using a cobalt complex was by Das *et al.*⁶¹

A $[Co^{II}(Py_5OH)(Cl)](BF_4)$ (**30**) showed activity towards photochemical water oxidation in the presence of $Ru^{II}(bpy)_3^{2+}$ and $Na_2S_2O_3$ resulting in a TON of 51 and TOF of 1.3 s^{-1} . The ability

of complex **30** to catalyse chemically-driven water oxidation was studied using $\text{Ru}^{\text{II}}(\text{bpy})_3^{2+}$ as the primary oxidant resulting in a TON of 15. The report highlighted the role of the chlorido ligand as part of the catalyst, which was to prevent the formation of Co^{III}_2 species that impede the catalytic activity of the complex in wet acetonitrile. Literature reports above show that the commonly used oxidant is the $\text{Ru}^{\text{II}}(\text{bpy})_3^{2+}$, which is based on a rare, expensive, and toxic ruthenium metal. There are no reports on cobalt-based chemically driven water oxidation using inexpensive primary oxidants such as CAN, creating a gap in research of cobalt-based water oxidation catalysts using easily accessible oxidants.

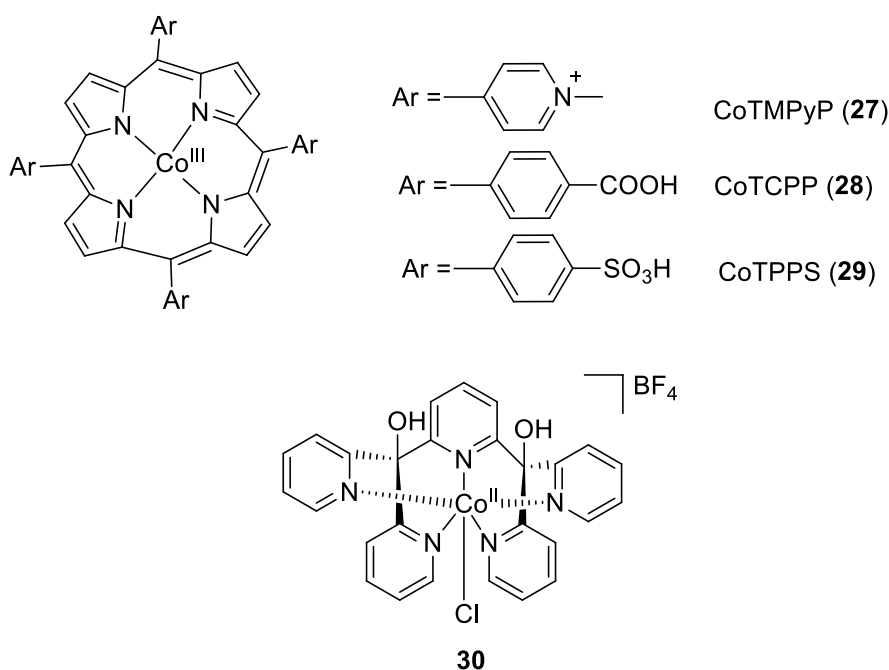
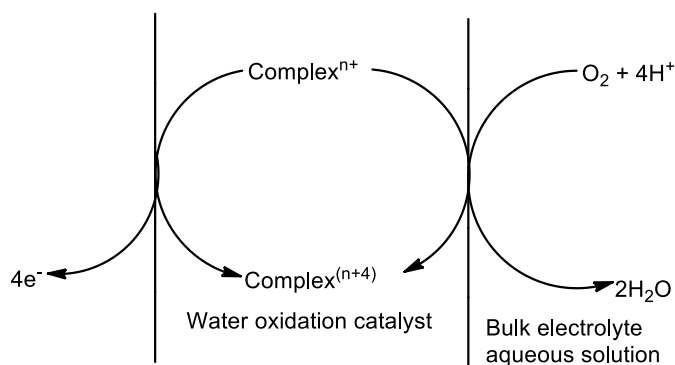


Figure 2.11: Cobalt complexes studied in chemical water oxidation.

2.5.2 Electrocatalytic water oxidation

The electrocatalytic water splitting of water to produce oxygen and hydrogen under applied potential difference is illustrated in Scheme 2.10. The evaluation of homogeneous molecular catalysts differs from that of well-established heterogeneous WOCs. This section details parameters that are necessary for the evaluation of homogeneous electrocatalytic WOCs and some of the first-row metal complexes that have been investigated towards electrocatalytic water oxidation.



Scheme 2.10: A scheme illustrating water oxidation under applied voltage.

2.5.2.1 Parameters for evaluating a molecular electrocatalyst

Overpotential and onset potential

The benchmarking of molecular homogeneous catalysts is not as established in comparison to heterogeneous electrocatalysts. In homogeneous electrocatalytic systems, parameters such as onset potential and overpotential are considered important in deducing the activity of an electrocatalyst. Overpotential is the difference between the equilibrium potential (thermodynamic potential) and the potential at which the catalyst operates at a specific current under specific conditions. The overpotential can be calculated from equation (2.4) where the onset potential (E_{onset}) is where the catalytic current onset occurs.⁶² Both the onset potential and the overpotential can be obtained from the cyclic voltammetry curve.

$$\text{Overpotential} = E_{\text{onset}} - (1.23 - (0.059\text{pH})) \quad (2.4)$$

TOF calculation

The turnover frequency (TOF) is an important parameter to define the activity of the catalyst. TOF is defined as the amount of product converted from the reactant per mol of the effective catalyst per unit time. In homogeneous electrocatalytic water oxidation, the TOF can be derived from the following equations (2.5) to (2.8):

$$i_{\text{cat}} = n_{\text{cat}}FA [\text{Cat}] (k_{\text{cat}}D\text{Cat})^{1/2} \quad (2.5)$$

$$i_p = 0.4633nFA[\text{Cat}] (nFvD\text{Cat}/RT)^{1/2} \quad (2.6)$$

$$i_p = 2.69 \times 10^5 n^{3/2} A D \text{Cat}^{1/2} v^{1/2} \quad (2.7)$$

$$i_{\text{cat}}/i_p = (0.359 n_c/n_p^{3/2} k_{\text{cat}}^{1/2}) 1/v^{1/2} \quad (2.8)$$

Equation (2.5) is the Randles-Sevcik equation, which relates the peak current (i_p) to the number of electrons transferred in the redox event (n), the area of the working electrode (A), catalyst concentration (Cat), and the scan rate (v). Equation (2.7) is the Randles-Sevcik

equation at 25 °C. The ratio of equation (2.5)/(2.7)(i_{cat}/i_p) results in equation (2.8), where n_c is the number of electrons transferred in water oxidation (4 electrons), n_p is the number of transferred electrons during the redox process of the catalyst, which is a non-catalytic redox event, and v is the scan rate. The pseudo-first-order rate constant k_{cat} (TOF), is calculated from the slope of the i_{cat}/i_p vs $1/v^{1/2}$ graph.⁶³⁻⁶⁵

Catalyst stability

Investigating the integrity of the molecular catalyst in homogeneous electrocatalytic water oxidation is important, as highly oxidising conditions can lead to the decomposition of the molecular complex. In many literature reports, complexes are decomposed to form corresponding oxides or hydroxides, which are equally efficient or more than the molecular complex.^{28, 66} Therefore, the analysis of post-reaction electrolytes and electrodes in homogeneous systems is important to establish the true nature of the catalyst, whether homogeneous or heterogeneous. Methods that can be used include spectroscopic methods such as UV-Vis and FTIR, monitor spectral absorbance changes of the complex before and after electrolysis. MS can be used to monitor complexes or free ligands in solution after electrolysis. Physical characterisation methods such as SEM, XPS, and EDX can be used to identify metal oxides formed.⁶⁶⁻⁶⁷ The presence of nanoparticles in the post-electrolysis solution can be confirmed by dynamic light scattering (DLS).⁶⁸⁻⁶⁹ Electrochemical methods involve the investigation of the electrochemical behaviour of the electrolyte pre- and post-electrocatalysis. The electrolyte is measured with a clean polished electrode to observe the possible changes of the complex post-electrocatalysis. Thereafter, the electrode is rinsed without polishing and reused in a fresh electrolyte (blank) to detect the formation of metal oxides or hydroxides deposited on the surface of the electrode. Metal ion scavengers can also be used to confirm the decomposition of the molecular complex. In this case, during the catalysis, other ligands such as bipyridine and EDTA are added into the system to weakly coordinate to the metal centre. The coordination of the ligands can change the electrochemical behaviour of the catalyst system.⁷⁰

2.5.2.2 Catalysts used in electrocatalytic water oxidation

Metals that have been used in electrocatalytic water oxidation include rare and expensive metals such as ruthenium and iridium. The interest in the development of electrocatalytic water oxidation catalysts based on cheap, abundant, and environmentally friendly metals such as copper, nickel, and manganese, has been on the rise.⁷¹⁻⁷³

2.5.2.2.1 Manganese complexes

There have been a few reports of manganese-based electrocatalytic water oxidation. The first manganese electrocatalytic water oxidation catalyst was a manganese porphyrin dimer reported in 1994 by Naruta *et al.*⁷⁴, with the highest TOF being 0.11 min⁻¹. More than 20 years later, a soluble manganese-oxo cluster [Mn₁₂O₁₂(O₂CC₆H₃(OH)₂)₁₆(H₂O)₄] was reported by Mayaan *et al.*⁷⁵ The manganese cluster was found to be a highly active electrocatalytic as a water oxidation catalyst at an overpotential of 334 mV at pH 6. The high activity of the manganese cluster in electrocatalytic water oxidation is attributed to the high nuclearity of the cluster.

2.5.2.2.2 Nickel(II) complexes

Reports on nickel-based electrocatalytic WOCs have been slowly increasing.⁷⁶⁻⁸⁰ Nickel complexes investigated in electrocatalytic water oxidation are summarised in Table 2.2. A nickel complex, [L-Ni^{II}-OH₂]₂Cl₂ (L = 2,6-bis(1,1-bis(2-pyridyl)ethyl)pyridine) (PY5)) (**31**) shown in Figure 2.12 is an active electrocatalyst oxidising water at an overpotential of 907 mV and a high TOF of 145 s⁻¹ in aqueous phosphate buffer solutions (pH 10.8).⁷⁹ Water oxidation catalysis takes place at a single site and proceeds via water nucleophilic attack as shown in Scheme 2.11.

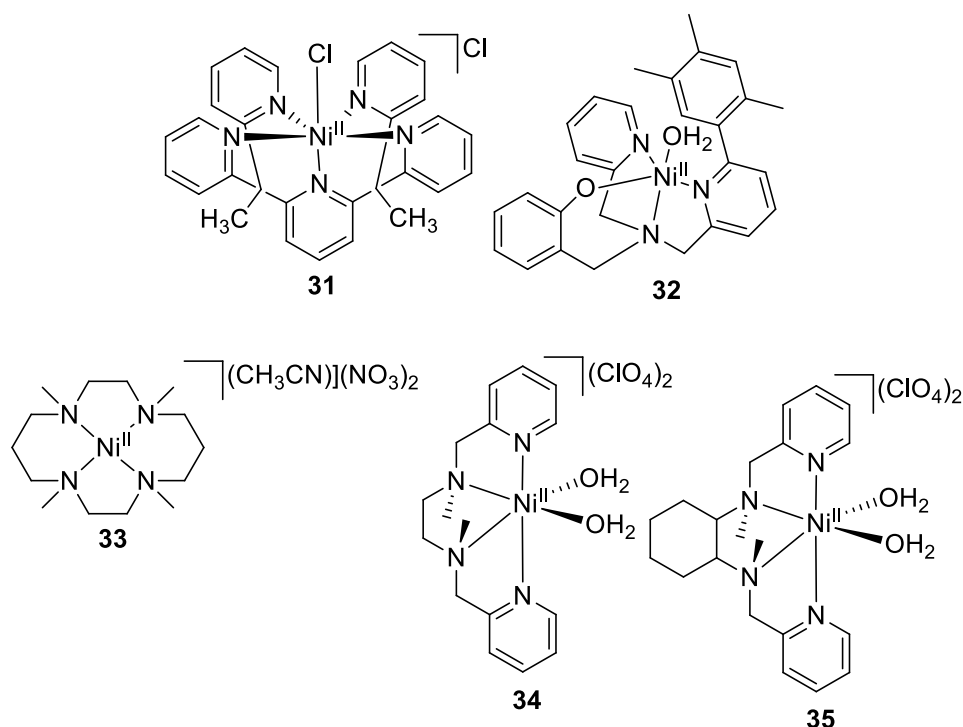


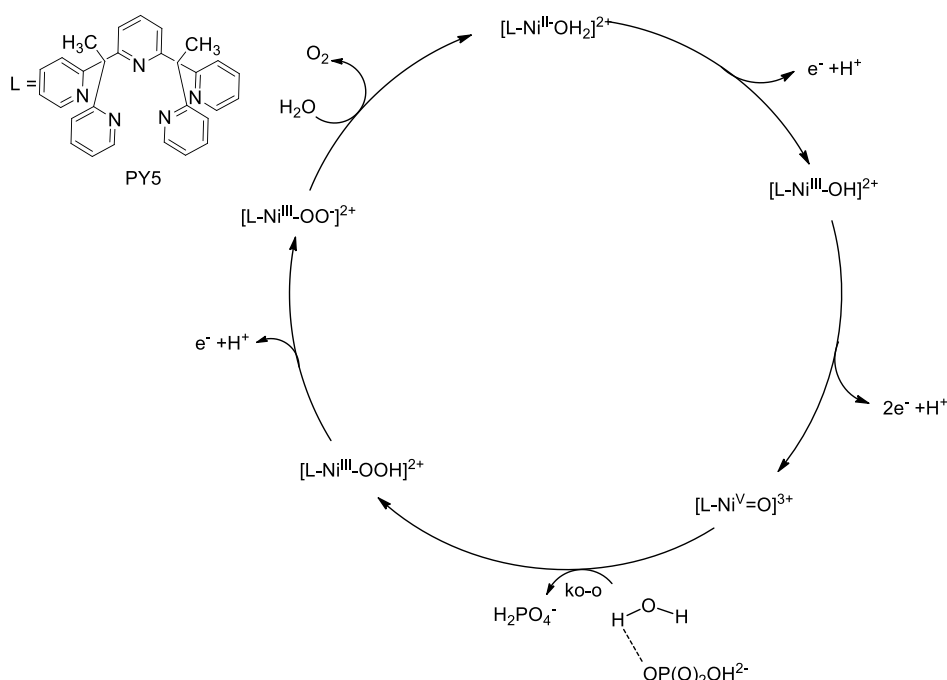
Figure 2.12: Nickel complexes efficient in electrocatalytic water oxidation.

Another example of a nickel-based catalyst efficient in electrocatalytic water oxidation is a bio-inspired nickel complex (**32**) ligated by a redox active ligand, 2-((((6-(2,4-dimethylphenyl)pyridin-2-yl)methyl)(pyridin-2-ylmethyl)amino)methyl)phenol.⁷⁷ The complex was efficient towards electrocatalytic water oxidation at a low overpotential of 383 mV at neutral pH with a TOF of 0.15 s⁻¹. The redox-active ligand was useful in avoiding high valent nickel intermediates. Zhang *et al.*⁸⁰ reported a nickel-based complex, [Ni(TMC)(CH₃CN)](NO₃)₂ (TMC = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane) (**33**) efficient in electrocatalytic water oxidation at an overpotential of 590 mV and a TOF of 9.95 s⁻¹, which is the highest TOF reported for nickel-based complexes studied in solutions at neutral pH. An N, N'-dimethyl-N, N'-bis(pyridin-2-ylmethyl)-1,2-diaminoethane ligated nickel(II) (**34**) complex containing two labile sites, was an efficient electrocatalyst at an overpotential of 753 mV in acetate buffer at pH 6.5. The acetate ions assisted in the formation of active intermediates and atom proton transfers (APT) in O-O bond formation. Another example where the buffer played an essential role in accelerating the proton-coupled electron transfer (PCET) process is with a nickel complex [Ni(mcp)(H₂O)₂](ClO₄)₂ (**35**) (mcp = (1R,2R)-N1,N2-dimethyl-N1,N2-bis(pyridin-2-ylmethyl)cyclohexane). This complex was able to catalyse electrochemical water oxidation at a low overpotential of 480 mV and a TOF of 0.19 s⁻¹.

Table 2.2: A summary of nickel complexes in electrocatalytic water oxidation.

Catalyst	Reaction conditions	Overpotential/mV	Kcat/s ⁻¹	Reference
31	Sodium phosphate buffer (0.2 M, pH 10.8)	907	145	79
32	Sodium phosphate buffer (0.1 M, pH 7)	383	0.15	77
33	Sodium phosphate buffer (0.1 M, pH 7)	590	9.95	80
34	NaOAC (0.3 M, pH 6.5)	753	-	76
35	Sodium phosphate buffer (0.1 M, pH 7)	480	0.19	78

The mechanistic pathway of complex **31** is illustrated in Scheme 2.11. The catalyst, [L-Ni^{II}-OH₂]²⁺ is oxidised to [L-Ni^{III}-OH]²⁺. The [Ni^{III}-OH]²⁺ is further oxidised forming a high valent nickel oxo species ([L-Ni^V=O]³⁺). The [L-Ni^V=O]³⁺ undergoes a PCET process with the phosphate as the proton acceptor resulting in O-O bond formation forming a [L-Ni^{III}-OOH]²⁺ intermediate. Further oxidation of a [L-Ni^{III}-OOH]²⁺ leads to the formation of the peroxido complex, [L-Ni^{III}-OO]²⁺. The decomposition of the peroxido complex releases oxygen and the catalyst is regenerated. All these findings point to a common reaction mechanism for a single-site transition metal-based water oxidation catalyst.



Scheme 2.11: An example of a proposed mechanism in electrocatalytic water oxidation catalysed by $[L-Ni^{II}-OH_2]Cl_2$ ($L = PY5$) complex in phosphate buffer.

2.5.2.2.3 Cobalt complexes

There have been a few cobalt complexes (Figure 2.13) as summarised in Table 2.3, which have been reported as efficient electrocatalytic water oxidation catalysts.^{61, 81} Wang *et al.*⁸² investigated a cobalt porphyrin complex, Co^{III} -TDMIImP (**36**) (TDMIImP = 5,10,15,20-tetrakis-(1,3-dimethylimidazolium-2-yl)porphyrin) capable of catalysing electrochemical water oxidation at an overpotential of 920 mV at neutral pH. In the study, the role of the buffer base, which is to accept protons during O-O bond formation was highlighted. An N,N' -bis(2'-pyridinecarboxamide)-1,2-benzene ligated cobalt complex (**37**) exhibited a high TOF of $\sim 81.54 \text{ s}^{-1}$ at pH 8.6 and an overpotential of 560 mV. The mechanistic route (Scheme 2.12) is analogous to that of ruthenium and nickel complexes. As described in the mechanism, the product of the oxidation is the Co^{IV} species, which is a highly oxidised Co-oxo intermediate. The intermediate is responsible O-O coupling and water oxidation. Another example is a cobalt complex, $L-Co(II)-L$ ($L = (E)$ -4-((2-hydroxynaphthalen-1-yl)diazinyl) benzenesulfonate (**38**) capable of oxidising water under applied voltage. The complex was efficient in electrocatalytic water oxidation at an overpotential of 520 mV and a high TOF of 5 s^{-1} in phosphate buffer at pH 9.

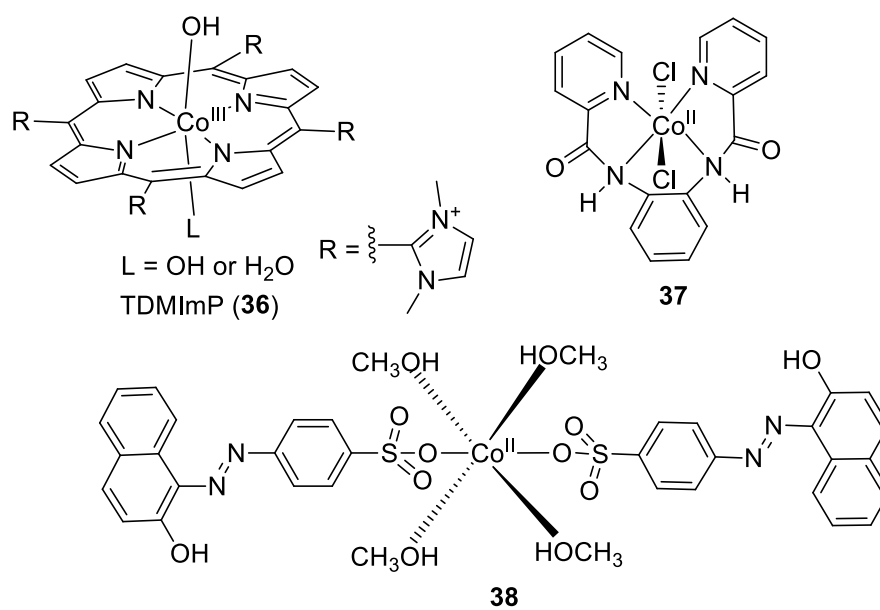


Figure 2.13: Cobalt complexes used in electrocatalytic water oxidation.

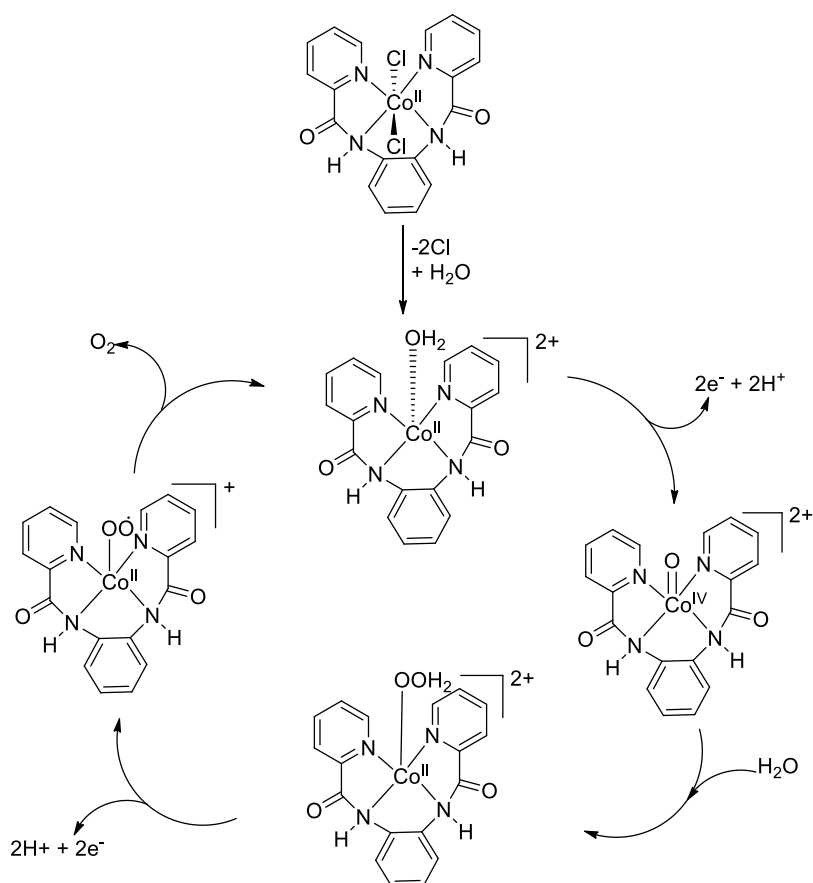
Scheme 2.12: Mechanism of an N, N'-bis(2'-pyridinecarboxamide)-1,2-benzene ligated complex (**37**).⁸¹

Table 2.3: Cobalt complexes in electrocatalytic water oxidation.

Catalyst	Reaction conditions	Overpotential/mV	$K_{\text{cat}}/\text{s}^{-1}$	Reference
36	Sodium phosphate buffer (0.20 M, pH 7)	920	-	82
37	Sodium phosphate buffer (0.25 M, pH 8.6)	560	81.54	81
38	Sodium phosphate buffer (pH 9)	520	5	83

2.5.2.2.4 Copper(II) complexes

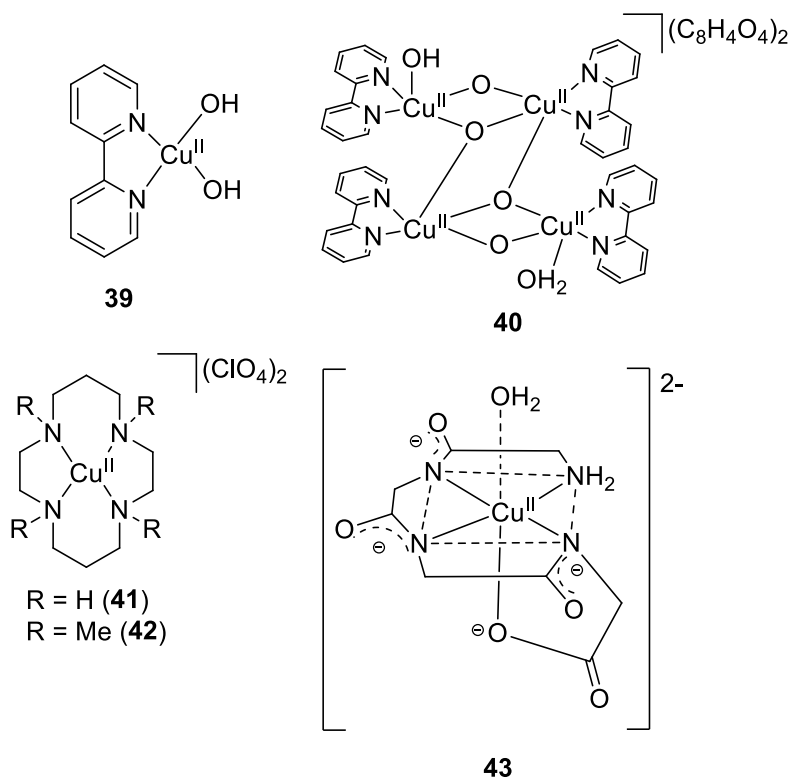
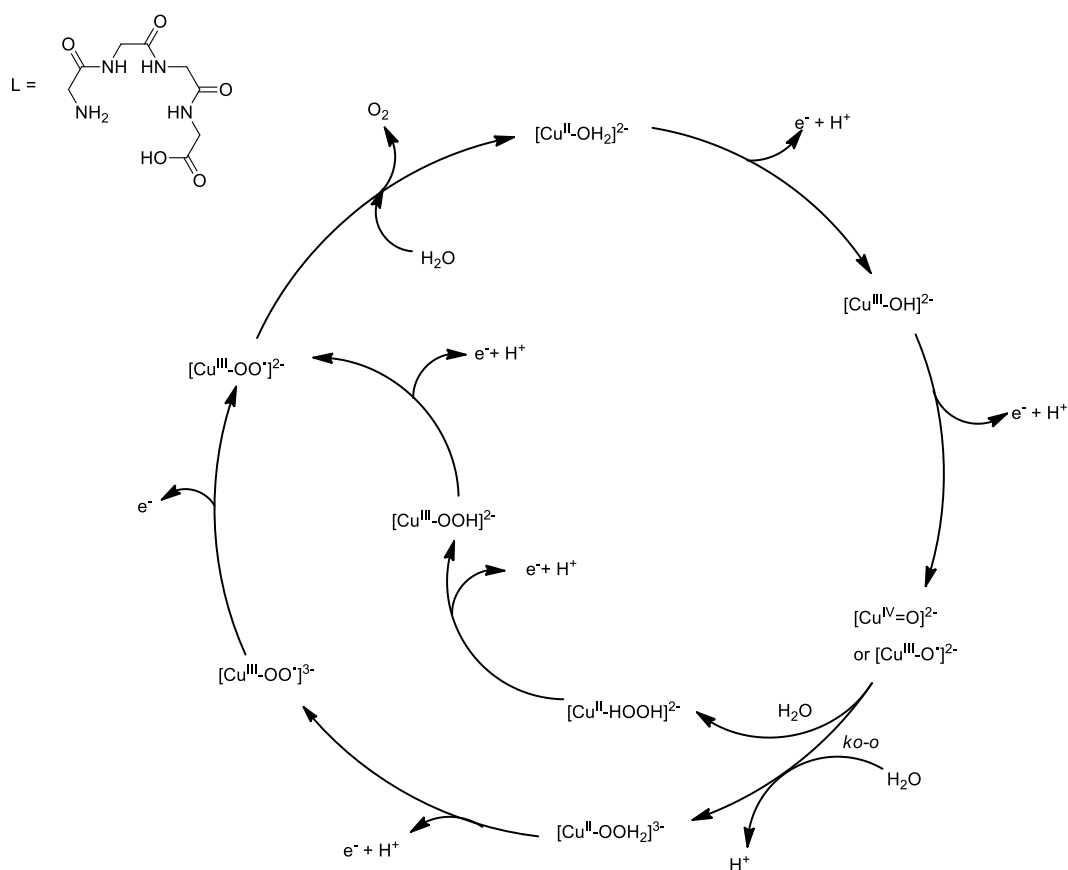


Figure 2.14: Copper complexes used in electrocatalytic water oxidation.

Copper (II) complexes have been extensively studied in electrocatalytic water oxidation.^{70, 84} Copper has been a metal of interest due to its low toxicity and low cost. Another attractive feature of copper in the development of water oxidation catalysis is its well-established biomimetic O_2 chemistry.⁸⁵⁻⁸⁶ Examples of copper(II) complexes that have been studied in electrocatalytic water oxidation catalysts are shown in Figure 2.14, while Table 2.4 summarises the activities of these complexes. The first reported copper-based molecular electrocatalyst for water oxidation was by Mayer *et al.*⁸⁷, who showed an application of a

simple Cu-bipyridine system (**39**). The electrocatalyst was very efficient with TOF of 100 s^{-1} in extremely basic solutions (pH range 11.8 to 13.3) and at a relatively high overpotential of 750 mV. Among the complexes studied at neutral pH, a tetranuclear complex $[\text{Cu}_4(\text{bpy})_4(\mu_2\text{-OH})_2(\mu_3\text{-OH})_2(\text{H}_2\text{O})_2]^{2+}$ (bpy = 2,2'-bipyridine) **40** was efficient in electrocatalytic water oxidation at an overpotential of 730 mV in comparison to mononuclear complexes **41** and **42**, which catalysed water oxidation at an overpotential of 880 mV. This indicates that the multinuclear sites in complex **40** contribute to the efficiency of water oxidation. A copper(II) polypeptide complex, $[(\text{TGG}^{4-})\text{Cu}^{\text{II}}\text{-OH}_2]^{2-}$ ligated by a triglycylglycine macrocyclic ligand (TGG) **43** was active in electrocatalytic water oxidation at a lower overpotential of 520 mV and a TOF of 33 s^{-1} in 0.25 M phosphate buffer at pH 11. The mechanistic pathway for water oxidation of a copper polypeptide complex **37** is illustrated in Scheme 2.13.



Scheme 2.13: Proposed electrocatalytic water oxidation by a negatively charged copper complex, $[(\text{TGG}^{4-})\text{Cu}^{\text{II}}\text{-OH}_2]^{2-}$.⁸⁸

In the mechanism, the initial catalyst, $[(\text{TGG}^{4-})\text{Cu}^{\text{II}}\text{-OH}_2]^{2-}$ is oxidised to $[(\text{TGG}^{4-})\text{Cu}^{\text{III}}\text{-OH}]^{2-}$. A second irreversible oxidation, which arises from further oxidation of $[(\text{TGG}^{4-})\text{Cu}^{\text{III}}\text{-OH}]^{2-}$ is observed at $E_{p,a} = 1.32\text{ V}$ vs NHE. The said oxidation peak is pH-dependent, suggesting additional proton loss. The product of the second oxidation would be the formally d^7

$[(TGG^{4-})Cu^{IV}(O)]^{2-}$, which is analogous to the reactive $d^3 Ru^V(O)$ form of Ru polypyridyl complexes. The $Cu^{IV}(O)$ species undergoes a rate-limiting O–O bond formation through the WNA mechanism which involves the reaction with a second water molecule. As found for $[Ru^V(tpy)(bpm)(O)]^{3+}$, oxo transfer may involve a second water molecule or added base (OH^- , HPO_4^{2-} , PO_4^{3-}), which serves as a proton acceptor and atom proton transfer (APT) to give a hydroperoxide intermediate ($Cu^{II}(OOH)$) directly. The irreversibility for the second oxidation, and the elevated current levels following oxidation to $[(TGG^{4-})Cu^{IV}(O)]^{2-}$, presumably come from further oxidation of the intermediate peroxide, release of O_2 , and re-entry into the catalytic cycle, followed by further oxidation of $[(TGG^{4-})Cu^{II}(OOH)]^{3-}$. This mechanism is analogous to the mechanism established for single-site Ru polypyridyl water oxidation catalysts.⁴¹

Table 2.4: A summary of copper(II) complexes used in electrocatalytic water oxidation.

Catalyst	Reaction conditions	Overpotential/mV	K_{cat}/s^{-1}	Reference
39	0.1 M electrolyte (NaOAc+NaOH) pH 11.8–13.3	750	100	87
40	0.1 M pH 7.0 PBS	730	-	89
41	0.2 M pH 7.0 PBS	880	-	90
42	0.2 M pH 7.0 PBS	880	-	90
43	0.25 M pH 11 PBS	520	33	88

2.6 Conclusions

Water splitting offers an environmentally friendly route to the production of hydrogen. Natural photosynthesis inspires the development of efficient water oxidation catalysts. Chemical water oxidation allows for the screening and optimisation of catalysts, whereas electrocatalytic water oxidation allows for the study of catalyst behaviour in a photo-electrochemical cell. There has been extensive research on water oxidation catalysts based on precious metals such as ruthenium and iridium complexes. The contribution made by studies of ruthenium-based water oxidation catalysis on the mechanistic pathways of water oxidation is commendable. Most of the reported mechanisms on water oxidation catalysis are analogous to the well-established ruthenium intermediates. There has been an increase in research focusing on water oxidation

catalysts based on earth-abundant, cheap, and environmentally friendly metals such as Mn, Fe, Ni, Cu, and Co. Among the earth-abundant and inexpensive metals, Mn and Fe complexes are mostly used towards chemical water oxidation, whereas Cu, Co, and Ni are mostly used towards electrocatalytic water oxidation. From this review, it is evident that abundant and cheap metals are capable of oxidising water to oxygen regardless of the route taken.

2.7 References

1. Andrews, J.; Shabani, B., *Procedia Eng.* 2012, 49, 15-25.
2. Koroneos, C.; Dompros, A.; Roumbas, G.; Moussiopoulos, N., *Resour Conserv Recycl.* 2005, 44 (2), 99-113.
3. Christopher, K.; Dimitrios, R., *Energy Environ. Sci.* 2012, 5 (5), 6640-6651.
4. Crabtree, G. W.; Dresselhaus, M. S.; Buchanan, M. V., *Phys. Today* 2004, 57 (12), 39-44.
5. Nowotny, J.; Sorrell, C. C.; Sheppard, L. R.; Bak, T., *Int. J. Hydrogen Energy* 2005, 30 (5), 521-544.
6. Crabtree, G. W.; Dresselhaus, M. S., *MRS Bull.* 2008, 33 (4), 421-428.
7. Dau, H.; Limberg, C.; Reier, T.; Risch, M.; Roggan, S.; Strasser, P., *The Mechanism of Water Oxidation: From Electrolysis via Homogeneous to Biological Catalysis.* 2010; Vol. 2, pp 724-761.
8. Que, L.; Tolman, W. B., *Nature* 2008, 455 (7211), 333-340.
9. Young, K. J.; Brennan, B. J.; Tagore, R.; Brudvig, G. W., *Acc. Chem. Res.* 2015, 48 (3), 567-574.
10. Ferreira, K. N.; Iverson, T. M.; Maghlaoui, K.; Barber, J.; Iwata, S., *Science* 2004, 303 (5665), 1831-1838.
11. Kamiya, N.; Shen, J.-R., *Proc. Natl. Acad. Sci. U.S.A.* 2003, 100 (1), 98-103.
12. Zouni, A.; Witt, H.-T.; Kern, J.; Fromme, P.; Krauss, N.; Saenger, W.; Orth, P., *Nature* 2001, 409 (6821), 739-743.
13. Blakemore, J. D.; Crabtree, R. H.; Brudvig, G. W., *Chem. Rev.* 2015, 115 (23), 12974-13005.
14. Barber, J.; Murray, J. W., *Philos.* 2008, 363 (1494), 1129-1138.
15. Nagashima, H.; Asada, M.; Mino, H., *Biophys. Physicobiol.* 2018, 15, 45-50.
16. Kärkäs, M. D.; Verho, O.; Johnston, E. V.; Åkermark, B., *Chem. Rev.* 2014, 114 (24), 11863-12001.
17. Loll, B.; Kern, J.; Saenger, W.; Zouni, A.; Biesiadka, J., *Nature* 2005, 438 (7070), 1040-1044.

18. Brudvig, G. W., *Philos. Trans. R. Soc. London, Ser. B: Biol. Sci.* 2008, 363 (1494), 1211-1219.
19. Haumann, M.; Liebisch, P.; Müller, C.; Barra, M.; Grabolle, M.; Dau, H., *Science* 2005, 310 (5750), 1019-1021.
20. Kok, B.; Forbush, B.; McGloin, M., *Photochem. Photobiol.* 1970, 11 (6), 457-475.
21. Vinyard, D. J.; Khan, S.; Brudvig, G. W., *Faraday Discuss.* 2015, 185 (0), 37-50.
22. Zhang, B.; Sun, L., *Dalton Trans.* 2018, 47 (41), 14381-14387.
23. Najafpour, M. M.; Moghaddam, A. N.; Allakhverdiev, S. I.; Govindjee, *Biochim Biophys Acta Biomembr.* 2012, 1817 (8), 1110-1121.
24. McConnell, I.; Li, G.; Brudvig, G. W., *Chem. Biol.* 2010, 17 (5), 434-447.
25. Inoue, H.; Shimada, T.; Kou, Y.; Nabetani, Y.; Masui, D.; Takagi, S.; Tachibana, H., *ChemSusChem* 2011, 4 (2), 173-179.
26. McCrory, C. C. L.; Jung, S.; Ferrer, I. M.; Chatman, S. M.; Peters, J. C.; Jaramillo, T. F., *J. Am. Chem. Soc.* 2015, 137 (13), 4347-4357.
27. McCrory, C. C. L.; Jung, S.; Peters, J. C.; Jaramillo, T. F., *J. Am. Chem. Soc.* 2013, 135 (45), 16977-16987.
28. Schley, N. D.; Blakemore, J. D.; Subbaiyan, N. K.; Incarvito, C. D.; D'Souza, F.; Crabtree, R. H.; Brudvig, G. W., *J. Am. Chem. Soc.* 2011, 133 (27), 10473-10481.
29. Fukuzumi, S.; Hong, D., *Eur. J. Inorg. Chem.* 2014, 2014 (4), 645-659.
30. Shaffer, D. W.; Xie, Y.; Concepcion, J. J., *Chem. Soc. Rev.* 2017, 46 (20), 6170-6193.
31. Bofill, R.; García-Antón, J.; Escriche, L.; Sala, X., *J. Photochem. Photobiol. B, Biol.* 2015, 152, 71-81.
32. Yagi, M.; Kaneko, M., *Chem. Rev.* 2001, 101 (1), 21-35.
33. Baffert, C.; Romain, S.; Richardot, A.; Lepretre, J. C.; Lefebvre, B.; Deronzier, A.; Collomb, M. N., *J. Am. Chem. Soc.* 2005, 127 (39), 13694-13704.
34. Limburg, B.; Bouwman, E.; Bonnet, S., *Coord. Chem. Rev.* 2012, 256 (15-16), 1451-1467.
35. Limburg, J.; Vrettos, J. S.; Chen, H.; De Paula, J. C.; Crabtree, R. H.; Brudvig, G. W., *J. Am. Chem. Soc.* 2001, 123 (3), 423-430.
36. Ottone, C.; Hernández, S.; Armandi, M.; Bonelli, B., *Sacrificial Oxidants as a Means to Study the Catalytic Activity of Water Oxidation Catalysts. In Testing Novel Water Oxidation Catalysts for Solar Fuels Production*, Springer: 2019; pp 29-47.
37. Parent, A. R.; Crabtree, R. H.; Brudvig, G. W., *Chem. Soc. Rev.* 2013, 42 (6), 2247-2252.
38. Chen; Tagore, R.; Olack, G.; Vrettos, J. S.; Weng, T.-C.; Penner-Hahn, J.; Crabtree, R. H.; Brudvig, G. W., *Inorg. Chem.* 2007, 46 (1), 34-43.
39. Gersten, S. W.; Samuels, G. J.; Meyer, T. J., *J. Am. Chem. Soc.* 1982.

40. Sens, C.; Romero, I.; Rodríguez, M.; Llobet, A.; Parella, T.; Benet-Buchholz, J., *J. Am. Chem. Soc.* 2004, 126 (25), 7798-7799.
41. Concepcion, J. J.; Jurss, J. W.; Templeton, J. L.; Meyer, T. J., *J. Am. Chem. Soc.* 2008, 130 (49), 16462-16463.
42. Concepcion, J. J.; Tsai, M.-K.; Muckerman, J. T.; Meyer, T. J., *J. Am. Chem. Soc.* 2010, 132 (5), 1545-1557.
43. Polyansky, D. E.; Muckerman, J. T.; Rochford, J.; Zong, R.; Thummel, R. P.; Fujita, E., *J. Am. Chem. Soc.* 2011, 133 (37), 14649-14665.
44. Zong, R.; Thummel, R. P., *J. Am. Chem. Soc.* 2005, 127 (37), 12802-12803.
45. Duan, L.; Bozoglian, F.; Mandal, S.; Stewart, B.; Privalov, T.; Llobet, A.; Sun, L., *Nat. Chem.* 2012, 4 (5), 418-423.
46. Abdel-Magied, A. F.; Arafa, W. A. A.; Laine, T. M.; Shatskiy, A.; Kärkäs, M. D.; Åkermark, B.; Johnston, E. V., *ChemCatChem* 2017, 9 (9), 1583-1587.
47. McDaniel, N. D.; Coughlin, F. J.; Tinker, L. L.; Bernhard, S., *J. Am. Chem. Soc.* 2008, 130 (1), 210-217.
48. Navarro, M.; Smith, C. A.; Li, M.; Bernhard, S.; Albrecht, M., *Chem. Eur. J.* 2018, 24 (24), 6386-6398.
49. Tagore, R.; Chen, H.; Zhang, H.; Crabtree, R. H.; Brudvig, G. W., *Inorg. Chim. Acta* 2007, 360 (9), 2983-2989.
50. Yagi, M.; Narita, K., *J. Am. Chem. Soc.* 2004, 126 (26), 8084-8085.
51. Yagi, M.; Narita, K.; Maruyama, S.; Sone, K.; Kuwabara, T.; Shimizu, K.-i., *Biochim. Biophys. Acta, Bioenerg.* 2007, 1767 (6), 660-665.
52. Limburg, J.; Vrettos, J. S.; Collomb, M.-N.; Liable-Sands, L. M.; Rheingold, A. L.; Crabtree, R. H.; Brudvig, G. W., A functional model for the oxygen-evolving complex of photosystem II. *Science* 1999, pp 1524-1527.
53. Liu, T.; Zhang, B.; Sun, L., *Chem. Asian J.* 2019, 14 (1), 31-43.
54. Okamura, M.; Kondo, M.; Kuga, R.; Kurashige, Y.; Yanai, T.; Hayami, S.; Praneeth, V. K.; Yoshida, M.; Yoneda, K.; Kawata, S., *Nature* 2016, 530 (7591), 465-468.
55. Roger, I.; Symes, M. D., *J. Mater. Chem. A* 2016, 4 (18), 6724-6741.
56. Fillol, J. L.; Codolà, Z.; Garcia-Bosch, I.; Gàmez, L.; Pla, J. J.; Costas, M., *Nat. Chem.* 2011, 3 (10), 807-813.
57. Panchbhai, G.; Singh, W. M.; Das, B.; Jane, R. T.; Thapper, A., *Eur. J. Inorg. Chem.* 2016, 2016 (20), 3262-3268.
58. Yu, W.-B.; He, Q.-Y.; Ma, X.-F.; Shi, H.-T.; Wei, X., *Dalton Trans.* 2015, 44 (1), 351-358.
59. Najafpour, M. M.; Ebrahimi, F.; Safdari, R.; Ghobadi, M. Z.; Tavahodi, M.; Rafighi, P., *Dalton Trans.* 2015, 44 (35), 15435-15440.
60. Nakazono, T.; Parent, A. R.; Sakai, K., *Chem. Commun.* 2013, 49 (56), 6325-6327.

61. Das, B.; Orthaber, A.; Ott, S.; Thapper, A., *Chem. Commun.* 2015, 51 (66), 13074-13077.
62. Appel, A. M.; Helm, M. L., *Determining the overpotential for a molecular electrocatalyst.* ACS Publications: 2014.
63. Bard, A. J.; Faulkner, L. R., *Electrochemical Methods* 2001, 2 (482), 580-632.
64. Savéant, J.-M., *Chem. Rev.* 2008, 108 (7), 2348-2378.
65. Zanello, P.; Nervi, C.; de Biani, F. F., *Practice and Application*, RSC, Cambridge, UK 2003.
66. Stracke, J. J.; Finke, R. G., *J. Am. Chem. Soc.* 2011, 133 (38), 14872-14875.
67. Aligholivand, M.; Shaghaghi, Z.; Bikas, R.; Kozakiewicz, A., *RSC Adv.* 2019, 9 (69), 40424-40436.
68. Woods, J. A.; Lalrempuia, R.; Petronilho, A.; McDaniel, N. D.; Müller-Bunz, H.; Albrecht, M.; Bernhard, S., *Energy Environ. Sci.* 2014, 7 (7), 2316-2328.
69. Zhu, G.; Glass, E. N.; Zhao, C.; Lv, H.; Vickers, J. W.; Geletii, Y. V.; Musaev, D. G.; Song, J.; Hill, C. L., *Dalton Trans.* 2012, 41 (42), 13043-13049.
70. Lee, H.; Wu, X.; Sun, L., *Nanoscale* 2020, 12 (7), 4187-4218.
71. Singh, A.; Spiccia, L., *Coord. Chem. Rev.* 2013, 257 (17-18), 2607-2622.
72. Sun, T.; Xia, N., *Int. J. Electrochem.* 2018, 13, 4601-4612.
73. Yamazaki, H.; Shouji, A.; Kajita, M.; Yagi, M., *Coord. Chem. Rev.* 2010, 254 (21-22), 2483-2491.
74. Naruta, Y.; Sasayama, M. a.; Sasaki, T., *Angew. Chem. Int. Ed.* 1994, 33 (18), 1839-1841.
75. Maayan, G.; Gluz, N.; Christou, G., *Nat. Catal.* 2018, 1 (1), 48-54.
76. Luo, G. Y.; Huang, H. H.; Wang, J. W.; Lu, T. B., *ChemSusChem* 2016, 9 (5), 485-491.
77. Wang, D.; Bruner, C. O., *Inorg. Chem.* 2017, 56 (22), 13638-13641.
78. Wang, J. W.; Zhang, X. Q.; Huang, H. H.; Lu, T. B., *ChemCatChem* 2016, 8 (20), 3287-3293.
79. Wang, L.; Duan, L.; Ambre, R. B.; Daniel, Q.; Chen, H.; Sun, J.; Das, B.; Thapper, A.; Uhlig, J.; Dinér, P., *J. Catal.* 2016, 335, 72-78.
80. Zhang, L.-H.; Yu, F.; Shi, Y.; Li, F.; Li, H., *Chem. Commun.* 2019, 55 (43), 6122-6125.
81. Wang, Z. Q.; Tang, L. Z.; Zhang, Y. X.; Zhan, S. Z.; Ye, J. S., *J. Power Sources* 2015, 287, 50-57.
82. Wang, D.; Groves, J. T., *Proc. Natl. Acad. Sci. U.S.A.* 2013, 110 (39), 15579-15584.
83. Shi, H. T.; Li, X. X.; Wu, F. H.; Yu, W. B., *Dalton Trans.* 2017, 46 (46), 16321-16326.
84. Lukács, D.; Szyrwił, Ł.; Pap, J. S., *Catalysts* 2019, 9 (1), 83.
85. Haack, P.; Limberg, C., *Angew. Chem. Int. Ed.* 2014, 53 (17), 4282-4293.
86. Mirica, L. M.; Ottenwaelder, X.; Stack, T. D. P., *Chem. Rev.* 2004, 104 (2), 1013-1046.

87. Barnett, S. M.; Goldberg, K. I.; Mayer, J. M., *Nat. Chem.* 2012, 4 (6), 498-502.
88. Zhang, M. T.; Chen, Z.; Kang, P.; Meyer, T. J., *J. Am. Chem. Soc.* 2013, 135 (6), 2048-2051.
89. Li, T.-T.; Zheng, Y.-Q., *Dalton Trans.* 2016, 45 (32), 12685-12690.
90. Prevedello, A.; Bazzan, I.; Dalle Carbonare, N.; Giuliani, A.; Bhardwaj, S.; Africh, C.; Cepek, C.; Argazzi, R.; Bonchio, M.; Caramori, S., *Chem. Asian J.* 2016, 11 (8), 1281-1287.

Chapter 3: Synthesis and characterization of bis(pyrazolyl)pyridine copper(II) complexes as catalysts in chemical and electrocatalytic water oxidation.

3.1 Introduction

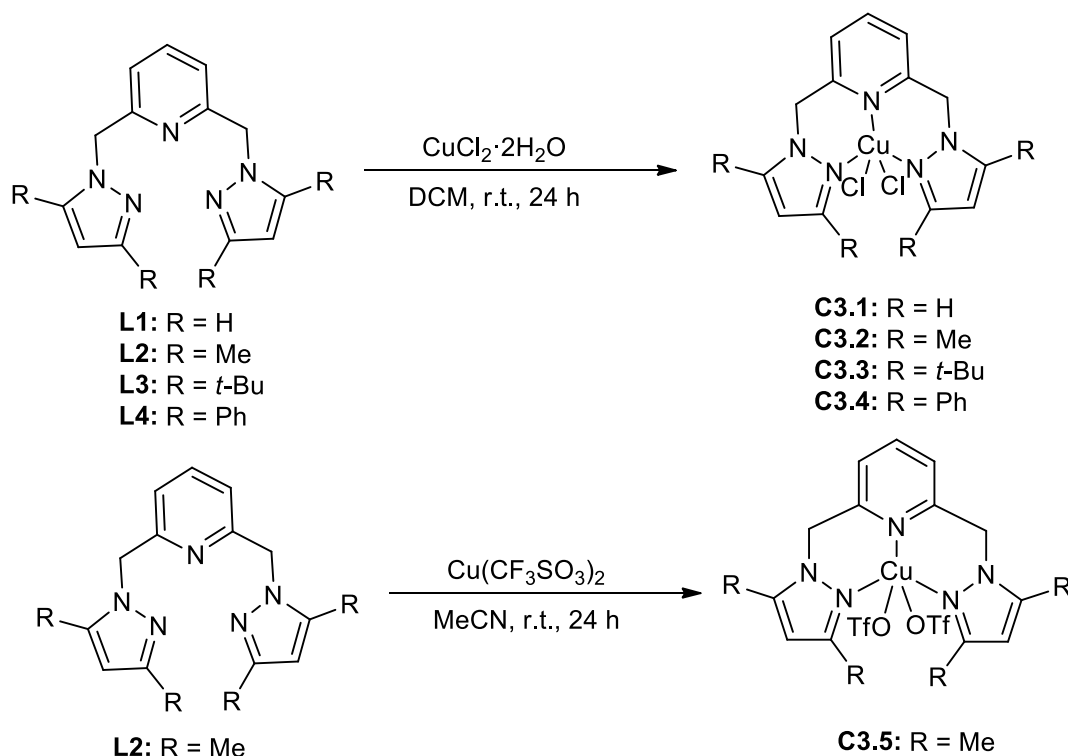
Hydrogen is a clean and renewable energy source, or rather an energy store used to generate power in fuel cells, which provides an attractive alternative to fossil fuels. An environmentally friendly method to produce molecular hydrogen is through the oxidation/splitting of water, an abundant natural resource.¹⁻³ Different approaches to water oxidation have been considered, which include chemically driven and electrocatalytic water oxidation. As water oxidation is a multi-electron process, with a multi-proton transfer, which is associated with an uphill energy transformation, the use of catalysts is therefore required.² The oxidation of water using chemical oxidants has been extensively studied over the years.³⁻⁷ To be effective, chemical oxidants, must be able to oxidise the pre-catalysts to form the active catalyst intermediates. CAN has been the sacrificial oxidant of choice amongst others, which include sodium peroxodisulfate, Ru(III) tris(bipyridine) cation, potassium peroxymonosulfate (oxone), and sodium *m*-periodate. The preference for CAN over other oxidants is due to its stability in aqueous solutions and its availability.⁸ Numerous Ru and Ir metal complexes have been reported as efficient homogeneous molecular catalysts for water oxidation.^{4, 7, 9} The major drawbacks associated with the development of catalysts derived from these metals are high cost, scarcity, and toxicity. It is therefore advantageous to develop water oxidation catalysts (WOCs) based on cost-effective, nontoxic, and abundant first-row transition metals. This holds great benefits towards a green and renewable energy environment. Over the years, there has been a growing number of reports on chemically-driven homogeneous water oxidation reactions employing first-row transition metals such as Fe, Co, Cu, and Mn as catalysts.¹⁰ Das *et al.*¹¹ explored the water oxidation activity of two Fe-complexes bearing a pentapyridyl ligand (pyridine-2,6-diylbis[di(pyridin-2-yl)methanol]) towards Ce^{IV}-induced water oxidation (TON of 16) under acidic condition (pH~1.5) and could identify high valent iron oxo intermediates as the active species. They also proposed two different mechanisms for water oxidation that are largely dependent on pH. Panchbhai *et al.*¹² evaluated tetrazadentate (N,N'-diisopropyl-N, N'-bis(2-pyridylmethyl)-1,2-diaminoethane and N-methyl-N-(2-pyridinylmethyl)-2,2'-bipyridine-6-methanamine) ligated iron complexes using CAN as the primary oxidant, obtaining a TON of 14. Reports on chemical water oxidation employing copper(I or II) complexes are scarce.¹³ Copper (II) complexes have been extensively studied in electrocatalytic water oxidation.¹⁴⁻²⁰ Electrocatalytic water splitting involves the production of oxygen and protons under applied potential difference. Water oxidation, i.e., OER, takes place

at the anode, while the HER, i.e., proton reduction, takes place at the cathode in an electrochemical cell setup. Most of the reports of electrocatalytic WOCs are on metal oxides rather than molecular complexes.²¹ Irrespective of the focus on metal oxides, the development of molecular electrocatalytic water oxidation catalysts based on abundant environmentally friendly metals such as nickel, iron, cobalt, and copper has been on the rise due to the possibility of structural and electronic tuning to obtain improved catalysts.²²⁻²⁵ The first copper homogeneous electrocatalyst was reported by Mayer *et al.*¹⁵ The copper(II) bipyridine complex operating at pH 11 to 13.3 was efficient in electrocatalytic water oxidation at an overpotential of 750 mV with a TOF of 100 s⁻¹. Han and co-workers¹⁶ reported a tetrakis(4-N-methylpyridyl)porphyrin ligated Cu(II) complex efficient towards electrocatalytic water oxidation at neutral pH. The complex catalysed water oxidation at a low overpotential of 310 mV and a TOF of 30 s⁻¹. The decomposition of the molecular complex followed by electrodeposition of nanoparticles on the working electrode is a controversial topic in the development of homogeneous water oxidation catalysts. In some cases, the molecular complex is a precursor of nanoparticle films that are active in water oxidation, which then suggests that the water oxidation is heterogeneous.²⁶⁻²⁹ There are only a few reports on chemically-driven Cu(II) complexes.

In this chapter, we report on the synthesis of bis(pyrazol-1-ylmethyl)pyridine Cu(II) complexes and their ability to catalyse chemical water oxidation under acidic conditions (pH 1). The complexes are also investigated for electrocatalytic water oxidation in a phosphate buffer at pH 7.

3.2 Results and discussion

3.2.1 Synthesis and characterisation of complexes, C3.1 to C3.5.



Scheme 3.1: Synthesis route for copper(II) complexes **C3.1** to **C3.5**.

Novel bis(pyrazol-1-ylmethyl)pyridine ligated copper(II) complexes **C3.1-C3.5** were synthesised from previously reported ligands³⁰⁻³¹. The preparation of these ligands involves a phase transfer catalysis reaction. The ligands were obtained in good yields with 94 % for **L1**, 95 % for **L2**, 46 % for **L3**, and 93 % for **L4**. Characterization of these ligands was done using Nuclear Magnetic Resonance spectroscopy, ¹H, and ¹³C{¹H} NMR spectroscopy. Figure 3.1 shows the proton NMR spectrum and the assignment of peaks for ligand **L2** as an example. The methyl groups on the pyrazole appear as a singlet upfield around 2.18 ppm. The linker proton appears as a singlet around 5.25 ppm whereas the pyrazolyl proton appears as a singlet around 5.85 ppm. Aromatic protons of the pyridine ring appear further downfield with a doublet around 6.69 ppm and a triplet around 7.54 ppm. The peak assignment on the ¹³C{¹H} NMR is shown in Figure 3.2. The carbons on the methyl groups on the pyrazolyl moiety are upfield at 11.39 to 13.9. The linker carbon appears at 54.74 ppm and the pyrazolyl carbon at 105.84 ppm. The aromatic carbons appear further downfield around 120.19-157.82 ppm. The ligands were further characterised by FTIR and the stretching frequency of interest was the C=N of the pyridine ring.

Chapter 3: Synthesis and characterization of bis(pyrazolyl)pyridine copper(II) complexes as catalysts in chemical and electrocatalytic water oxidation.

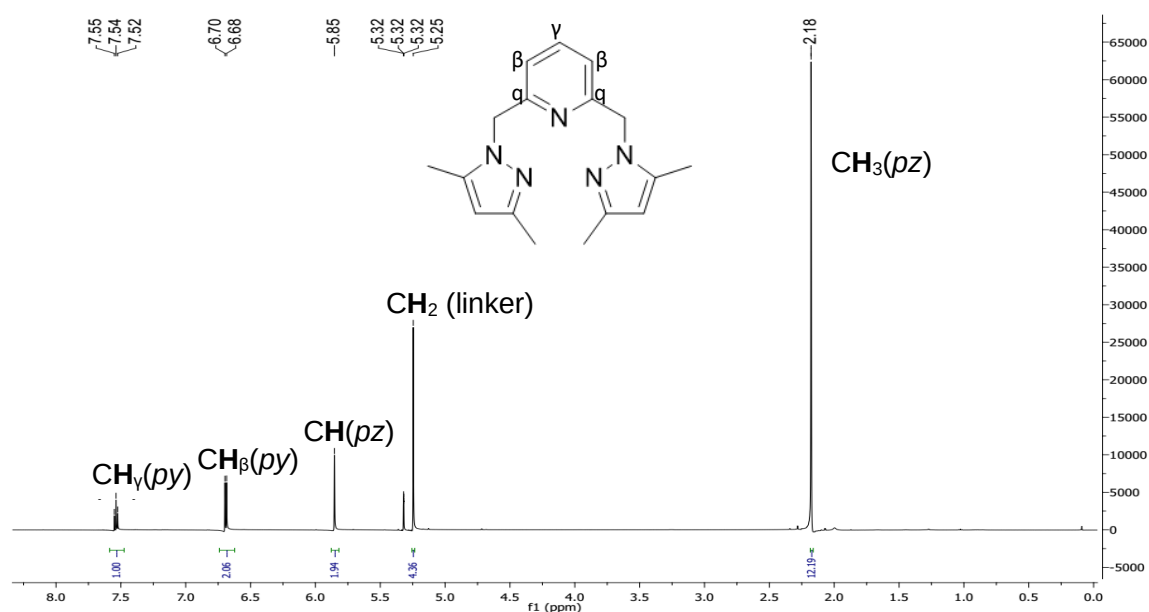


Figure 3.1 ^1H (Dichloromethane- d_2) NMR spectrum of ligand **L2**.

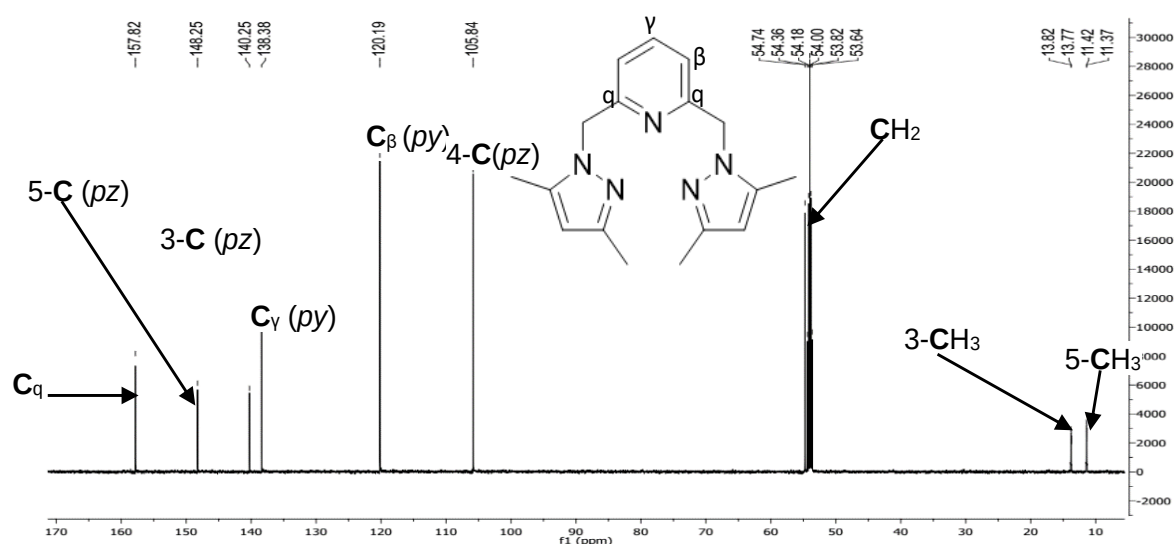


Figure 3.2: $^{13}\text{C}\{^1\text{H}\}$ (Dichloromethane- d_2) NMR of **L2**

L1-L4 and copper(II) chloride dihydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$). Complex **C3.5** was synthesised from **L2** and copper(II) triflate ($\text{Cu}(\text{CF}_3\text{SO}_3)_2$) as illustrated in Scheme 3.1. The complexes were obtained in low to excellent yields, **C3.1** (87%), **C3.2** (88%), **C3.3** (33%), **C3.4** (54%), and **C3.5** (46%). Complex characterization was carried out using characterisation techniques such as FTIR, magnetic susceptibility, mass spectrometry, and elemental analysis. The comparison of the stretching frequencies of the C=N of the pyridine ring in ligands **L1-L4** and stretching frequencies of complexes **C3.1** to **C3.5** confirmed the coordination of the metal through the C=N of the pyridine ring as shown in Table 3.1.

Table 3.1: FTIR stretching frequencies of (C=N) (py) in the ligands and complexes.

Ligand	(C=N) (py) ν cm^{-1}	Complex	(C=N) (py) ν cm^{-1}
L1	1596	C3.1	1605
L2	1579	C3.2	1601
L3	1593	C3.3	1603
L4	1575	C3.4	1602
L2	1579	C3.5	1610

The complexes are expected to be paramagnetic (d^9) with one unpaired electron. Magnetic susceptibility studies were done in dimethylformamide (DMF) for complexes **C3.1** to **C3.4** and in acetonitrile (MeCN) for complex **C3.5** at room temperature (22 to 25 °C). The magnetic moments (μ_{eff}) ranged from 1.83 to 2.22 BM, which confirms the +2 oxidation state of the metal centre and the d^9 electronic configuration with one unpaired electron. The electron donor ability of the complexes as well as the anions could possibly result in slightly different magnetic moment values although all the complexes have one unpaired electron. The magnetic moment values are within the range of similar reported Cu(II) complexes.³²⁻³⁵

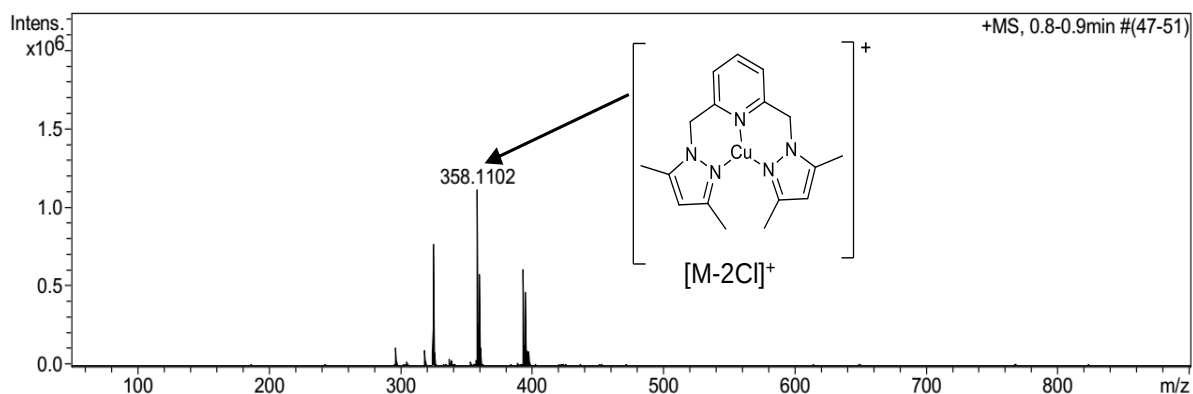
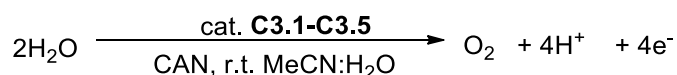


Figure 3.3: ESI-MS spectrum of complex **C3.2**.

A fragmentation pattern of the mass spectrum is shown for complex **C3.2** in Figure 3.3. In the mass spectrum, complexes **C3.1** and **C3.2** show the molecular ion peak with a loss of one chloride ion ($[M-Cl]^+$) with an m/z of 337.02 and 358.11, respectively. Complexes **C3.3** and **C3.4** show a loss of two chloride anions with m/z of 526.30 and 606.17, respectively, while complex **C3.5** shows the molecular ion peak with the loss of one triflate anion. Elemental analysis was conducted to confirm the purity of the isolated complexes. The complexes are hygroscopic and can easily absorb moisture from the environment. Water molecules were

present in complexes **C3.2** to **3.4**, while complex **C3.5** contained one molecule of acetonitrile that was used as the solvent during synthesis. All the above-mentioned techniques confirmed the successful synthesis of Cu(II) complexes.

3.2.2 Chemical water oxidation catalysed by complexes, **C3.1** to **C3.5**



Scheme 3.2: Chemical water oxidation catalysed by Cu(II) complexes **C3.1** to **C3.5**.

Given the solubility of Cu(II) complexes **C3.1** to **C3.5** in water, complex **C3.1** and **C3.2** were investigated for chemically-driven water oxidation using CAN as the primary oxidant (Scheme 3.2). Oxygen evolution reactions were performed using a standard Clark-type oxygraph electrode (Hansatech Instruments) placed in a thermostated cell (25 °C) for all measurements. The signal was recorded for the entire duration of the experiment at 1.0 s intervals using the Oxygraph+ software (Hansatech Instruments). The oxygen evolution curves are shown in Figure 3.4. The complexes had low activities with TONs of 1.81 and 2.07 and TOFs of 0.0068 s⁻¹ and 0.0078 s⁻¹ for complexes **C3.1** and **C3.2**, respectively. Complex **C3.2** containing the methyl-substituted pyrazole on the ligand scaffold was the more active in comparison to complex **C3.1** with the unsubstituted pyrazole moiety on the ligand framework. The presence of the electron-donating group enhances water oxidation by lowering the reduction potential of the metal. The low activities in solely aqueous media could be due to the de-coordination of the ligands from the metal, which is more prevalent in water due to the increased lability of the metal-ligand bond.³⁶

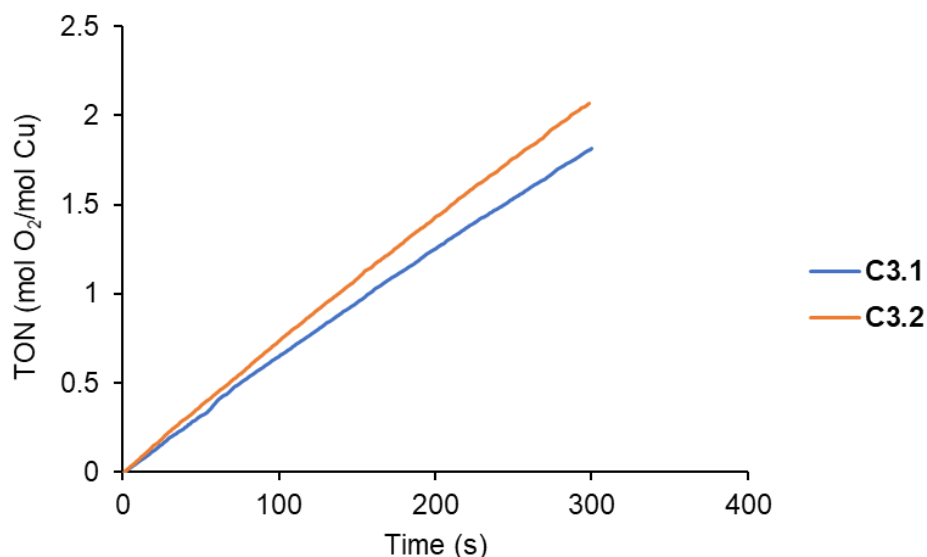


Figure 3.4: Oxygen evolution curves of complexes **C3.1** and **C3.2** with water as the solvent.

Complexes **C3.1** to **C3.5** were studied in chemically driven water oxidation in a mixture of MeCN and H₂O (1:1) instead of just water using CAN as the sacrificial oxidant. Figure 3.5a shows a drastic increase in O₂ concentration after the addition of the catalyst to CAN, which is indicated by the arrow. The TOF was calculated from the steepest region (5 seconds reaction time) on the TON curve. The oxygen evolution curves obtained after 5 minutes reaction time are shown in Figure 3.5b and the activities are summarised in Table 3.2. An enhancement in activity when the reaction is performed in MeCN and H₂O (1:1) was observed as compared to the reaction done in water only. The TON of complex **C3.2** increased from 2.07 to 4.22 and the TOF increased from 0.0078 s⁻¹ to 0.033 s⁻¹, which was a substantial improvement. Complex **C3.2** was the most active of the complexes containing the chloride anion (**C3.1-C3.4**). Replacing the chloride anion with triflate improved the TOF significantly from 0.033 s⁻¹ for complex **C3.2** to 0.115 s⁻¹ for complex **C3.5**. This can be attributed to the lability of triflate anions, which is greater than that of chloride anions. The triflate anions detach faster from the complex allowing for the rapid insertion of the substrate, water.³⁷ This observation contradicts a report by Fillol *et al.* wherein the Fe complexes containing chloride and triflate anions showed comparable results.² Complex **C3.5** deactivates faster over time in comparison to complex **C3.2**, regardless of having higher a TOF as observed in Figure 3.2b.

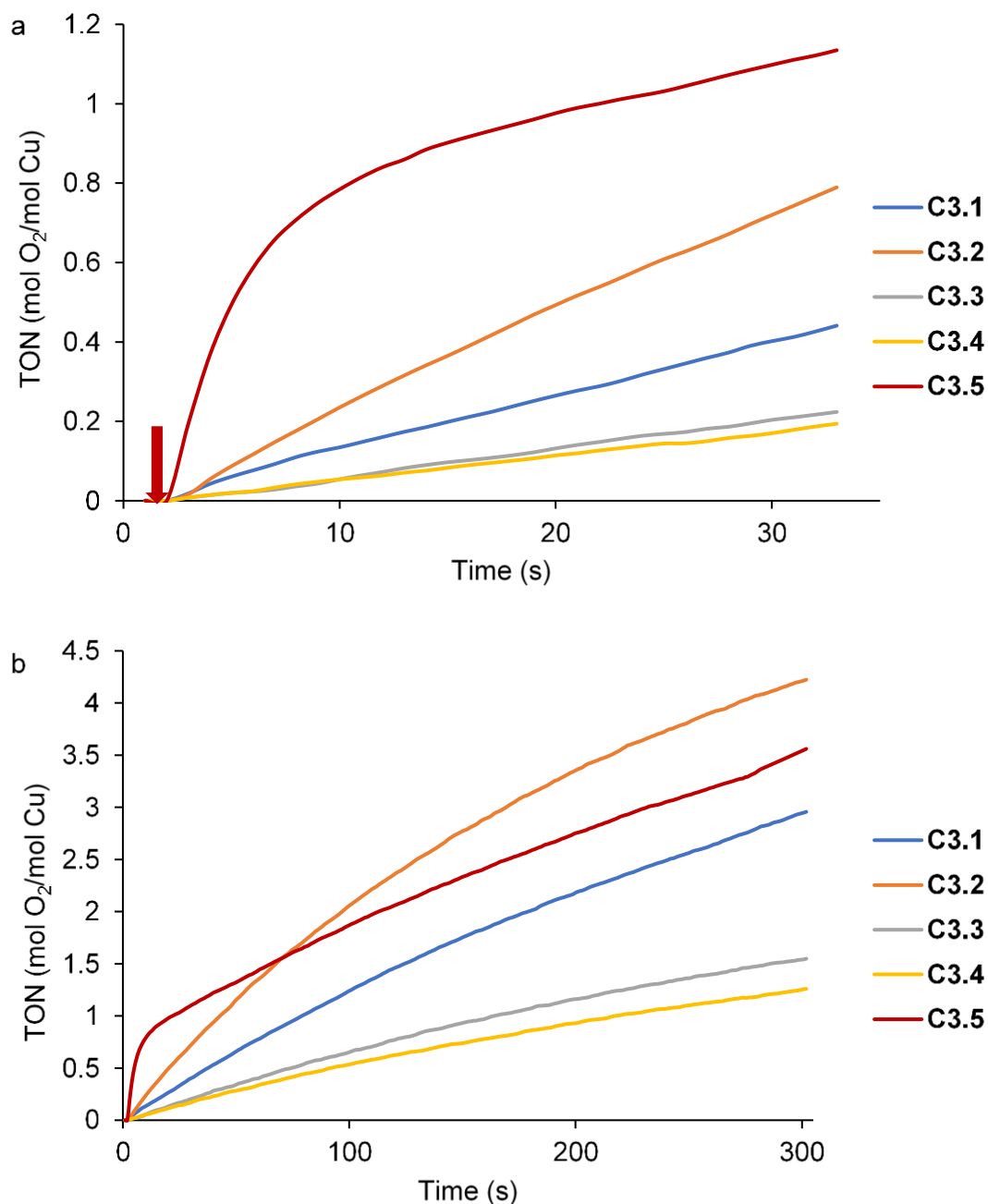


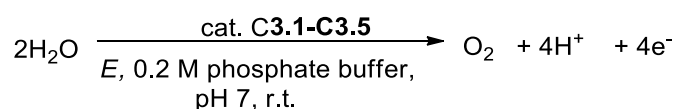
Figure 3.5a: Oxygen evolution curves showing the catalytic region after catalyst addition performed in a mixture of MeCN:H₂O (1:1); 3.5b: Oxygen evolution curves of complex **C3.1** to **C3.5** in chemical water oxidation after 5 minutes' reaction time.

Table 3.2: Copper(II) chemically driven water oxidation.

Complex	^a TON	^b TOF
C3.1	2.95	0.018
C3.2	4.22	0.033
C3.3	1.55	0.005
C3.4	1.26	0.006
C3.5	3.50	0.115

Reaction conditions: 25 μ M, [CAN]: 110 mM, Solvent: MeCN:H₂O (1:1, total volume: 2 mL). ^aTON after 5 minutes' reaction time. ^b, TOF was calculated from the steepest slope of the TON curve over a 5 second period.

3.2.3 Electrocatalytic water oxidation mediated by complexes **C3.1** to **C3.5**



Scheme 3.3: Electrocatalytic water oxidation catalysed by Cu(II) complexes **C3.1-C3.5** dissolved in 0.2 M phosphate buffer at pH 7.

Cu(II) complexes **C3.1** to **C3.5** were evaluated towards electrocatalytic water oxidation in a phosphate buffer using cyclic voltammetry (CV) (Scheme 3.3). The Cu(II) complexes are water-soluble and readily dissolve in phosphate buffer solutions. The solution of complexes dissolved in 0.2 M phosphate buffer was degassed with nitrogen for 15 minutes before each experiment. The CVs were obtained under air using a glassy carbon working electrode (GCE), Ag/AgCl reference electrode, and a platinum wire counter electrode. The rotating disk electrode (RDE) was set at 3000 rpm to avoid the build-up of oxygen bubbles on the surface of the GCE. Potentials were measured versus an Ag/AgCl electrode and are reported versus NHE by adding +0.199 V to the measured potential.

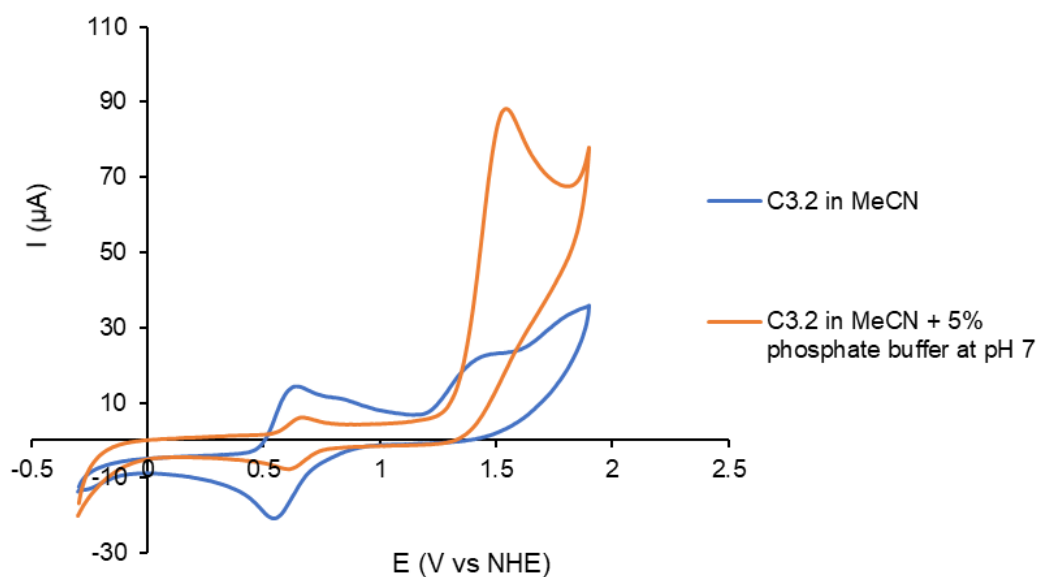


Figure 3.6: Cyclic voltammograms of complex **C3.2** (0.5 mM) in 0.1 M Bu₄NPF₆ in MeCN (blue) and **C3.2** in 0.1 M Bu₄NPF₆ in MeCN with added 5% (v/v) phosphate buffer at pH 7 (orange) recorded at a scan rate of 50 mV s⁻¹.

Scanning a solution of 0.5 mM **C3.2** dissolved in 0.1 M Bu₄NPF₆ in MeCN from -0.5 to +1.7 V, showed a reversible redox wave at $E_{1/2} = +0.57$ V; this wave is assigned to the oxidation of Cu(II) to Cu(III) (Figure 3.6).^{20, 38} The addition of 5% phosphate buffer (v/v) into the solution enhances the catalytic current with an irreversible wave responsible for water oxidation visible at an onset potential of +1.57 V.

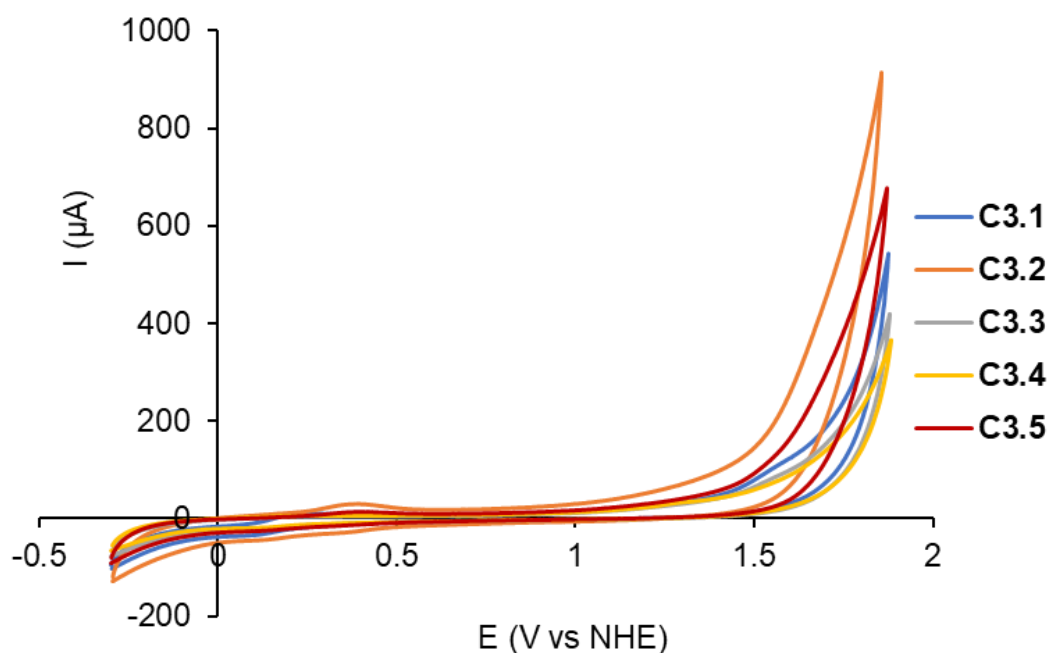


Figure 3.7: Cyclic voltammograms of 0.1 mM **C3.1** to **C3.5** in 0.2 M phosphate buffer pH 7 recorded at a scan rate of 100 mV s⁻¹.

Complexes **C3.1** to **C3.5** (0.1 mM) were investigated in electrocatalytic water oxidation in 0.2 M phosphate buffer at pH 7 (Figure 3.7). Scanning from -0.5 to +1.7, the Cu(III)/Cu(II) redox couple was shifted to lower potentials in a phosphate buffer as compared to when recorded in MeCN, which can be attributed to solvent effects. The irreversible peak was not as well defined in phosphate buffer, although in some cases the oxidation of Cu(II) to Cu(III) could be observed, the reduction of Cu(III) to Cu(II) was not visible. This could be a result of complex decomposition under electrochemical conditions.³⁹ The oxidation of Cu(II) to Cu(III) was followed by a large irreversible wave responsible for water oxidation with onset potentials ranging from + 1.50 to +1.64 V.

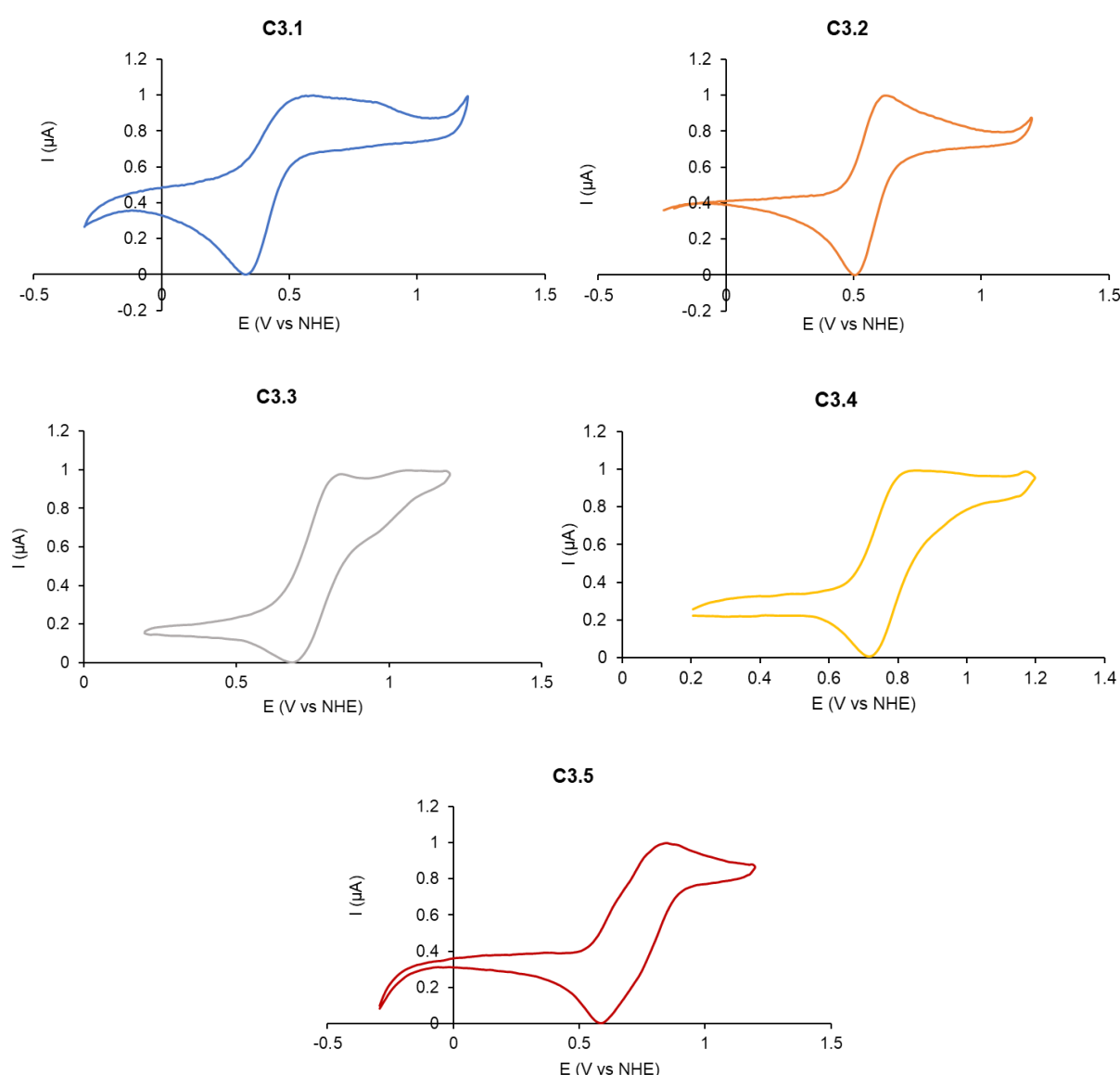


Figure 3.8: CVs of 0.5 mM **C3.1-C3.5** in 0.1 M Bu_4NPF_6 in MeCN showing the Cu(III)/Cu(II) redox couple recorded at a scan rate of 10 mV s^{-1} . The y axis shows the normalised current.

Complex **C3.2** efficiently catalysed water oxidation at the lowest overpotential of 683 mV (Table 3.3 entry 2). The second-lowest overpotential of 743 mV was obtained with complex **C3.5** (Table 3.3 entry 5), which has the same ligand scaffold as complex **C3.2** and triflate anions instead of chloride anions. The low overpotentials of these complexes can be attributed to the electron-donating ability of methyl groups on the pyrazolyl moiety of the ligand. Complexes **C3.3** (Table 3.3 entry 3) and **C3.4** (Table 3.3 entry 4) resulted in the highest overpotential of 823 mV. Complex **C3.3** bears the tertiary group on the pyrazole meanwhile **C3.4** contains the phenyl group on the pyrazole. The oxidation potentials of the Cu(III)/Cu(II) redox couples shown in the CVs in Figure 3.8 supported the trend observed in the activity of the complexes. Comparing complexes **C3.2** to **C3.4**, complex **C3.2** had the lowest oxidation potential of +0.57 V, and the lowest overpotential. Conversely, complexes **C3.3** and **C3.4** had the highest oxidation potential of 0.77 and 0.88 V, respectively, and the highest overpotentials. Although complex **C3.1** had the lowest oxidation potential of +0.45 V, the complex catalysed water oxidation at a higher overpotential of 783 mV as compared to complex **C3.5**, which had an oxidation potential of +0.72 V. This observation could suggest that complex **C3.1** containing the unsubstituted pyrazolyl moiety on the ligand is easily oxidised and therefore not stable.

Chapter 3: Synthesis and characterization of bis(pyrazolyl)pyridine copper(II) complexes as catalysts in chemical and electrocatalytic water oxidation.

Table 3.3: Copper (II) complexes as pre-catalysts in electrocatalytic water oxidation.

Entry	Complexes	Reaction conditions	^a Overpotential/mV	Reference
1	C3.1	0.2 M phosphate buffer pH 7	783	This work
2	C3.2	0.2 M phosphate buffer pH 7	683	This work
3	C3.3	0.2 M phosphate buffer pH 7	823	This work
4	C3.4	0.2 M phosphate buffer pH 7	823	This work
5	C3.5	0.2 M phosphate buffer pH 7	743	This work
6	[Cu(THAM)(H ₂ O) ₂] ₂ SO ₄	0.2 M phosphate buffer pH 12	390	40
7	[Cu(en) ₂ (OH ₂) ₂] ²⁺	0.2 M phosphate buffer pH 12	540	41
8	[Cu(TPA)(OH ₂)](ClO ₄) ₂	0.1 M borate buffer pH 9.2	749	42
9	[Cu(MeTPA)(OH ₂)]	0.1 M borate buffer pH 9-11	600	28

^a The overpotential was calculated as follows: Overpotential = $E_{\text{onset}} - (1.23 - (0.059\text{pH}))$. E_{onset} is extrapolated from the CV using the tangent method en = 1,2-ethylenediamine, THAM = tris(hydroxymethyl) aminomethane, TPA = tris(2-pyridylmethyl)amine)

3.2.3.1 Evidence of heterogeneous nanoparticles

Determining the nature of species which are active catalysts for water oxidation is a necessary exercise as there is a fine line between homogeneous and heterogeneous water oxidation catalysis. This is caused by the decomposition of the molecular catalyst that leads to the formation of nanomaterials, which are also active towards water oxidation.⁴³⁻⁴⁴ Indeed, the presence of heterogeneous species was confirmed by electrochemical methods. The first evidence of nanomaterial electrodeposition on the glassy carbon electrode surface was the gradual increase in current with each increasing cycle⁴⁵⁻⁴⁶ as observed in Figure 3.9. The glassy carbon electrode was analysed by SEM post-electrocatalysis; however, no CuO nanoparticles could be observed. The CuO nanomaterials could be present in very low concentrations below the SEM detection limits. The electrolyte was also analysed by DLS and no nanoparticles were observed in the solution.

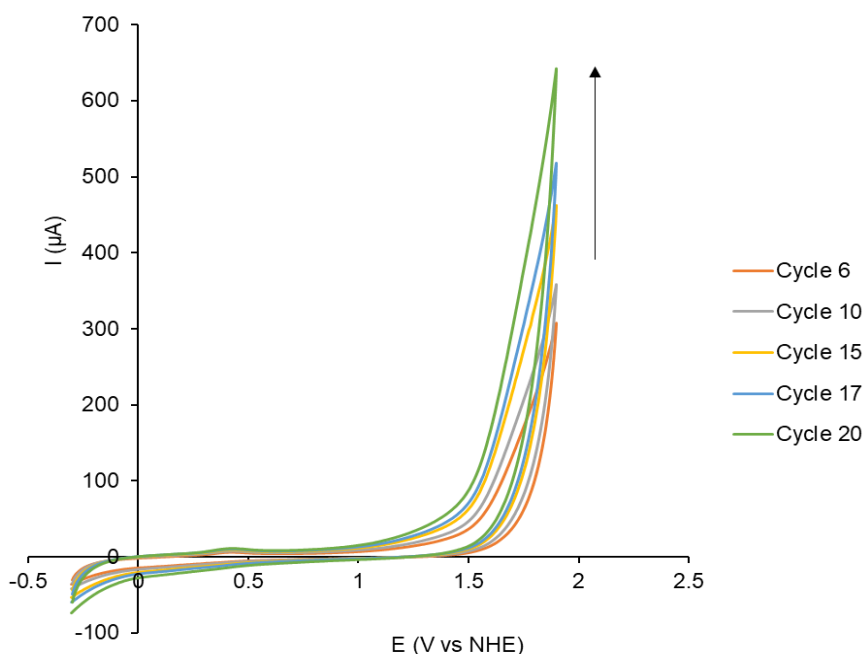


Figure 3.9: CVs showing 0.5 mM **C3.2** in phosphate buffer pH 7 cycled 20 times at 100 mV s⁻¹.

To further check for electrodeposition on the glassy carbon electrode, the electrode was rinsed post-electrolysis with the phosphate buffer and reanalysed in a blank buffer solution, which showed an increase in current (Figure 3.10). Decreasing the pH of the phosphate buffer to 6 did not improve the stability of the complex as observed in Figure 3.11 wherein the electrodeposition of nanomaterial was observed when the rinsed glassy carbon was analysed in a blank buffer. Electrocatalytic water oxidation mediated by copper(II) complexes **C3.1** to **C3.5** is not homogeneous and proceeds as a result of CuO nanomaterials formed *in situ*. In

comparison to other complexes that act as pre-catalysts in the electrodeposition of nanoparticles, complexes **C3.1** to **C3.5** have higher potentials as observed in Table 3.3.

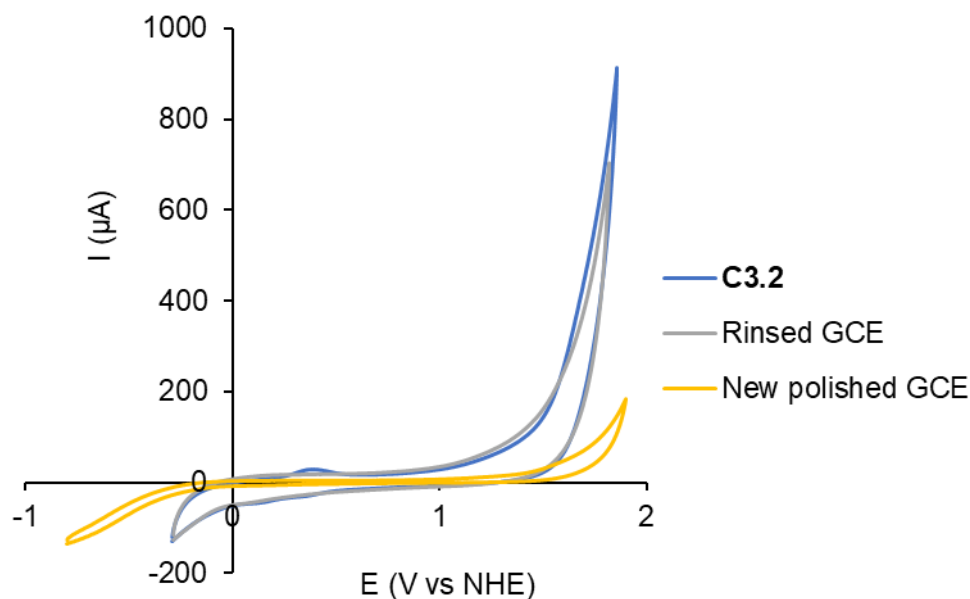


Figure 3.10: CVs of 0.1 mM **C3.2** in 0.2 M phosphate buffer at pH 7 after 6 cycles, the rinsed electrode in 0.2 M phosphate buffer (blank), and the polished electrode in the blank solution recorded at 100 mV s⁻¹.

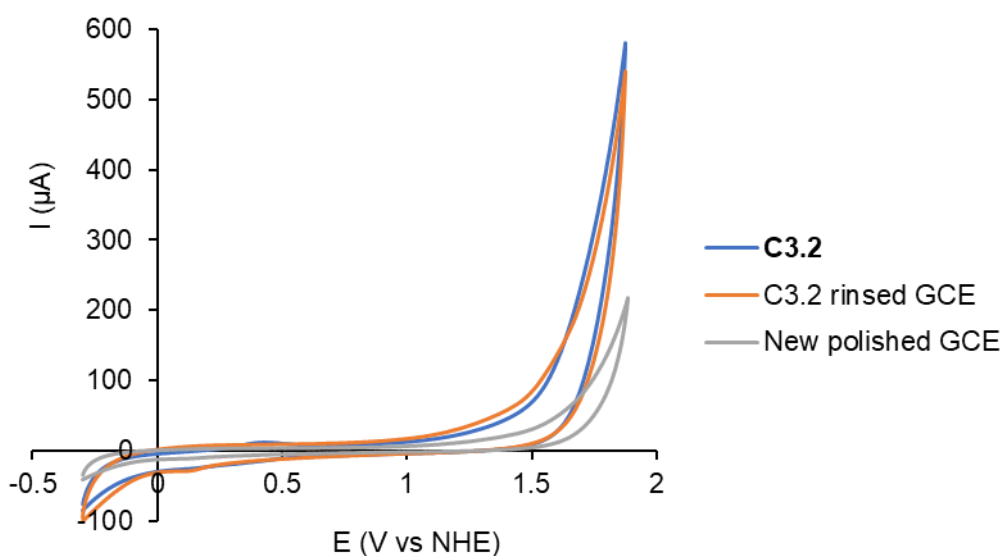


Figure 3.11: CVs of 0.1 mM **C3.2** in 0.2 M phosphate buffer at pH 6 after 6 cycles, the rinsed electrode in 0.2 M phosphate buffer (blank), and the polished electrode in the blank solution recorded at 100 mV s⁻¹.

3.3 Conclusions

Bis(pyrazol-1-ylmethyl)pyridine ligated copper(II)-chloride and triflate complexes, **C3.1- C3.5**, were successfully synthesised and characterised using analytical techniques. The copper(II) complexes showed activity in chemically-driven water oxidation in aqueous media using CAN as the primary oxidant; however, improved activities were observed when the reaction was carried out in a MeCN: H₂O(1:1) mixture. Complex **C3.2** was the most active of the copper chloride complexes (**C3.1-C3.4**) with a TON of 4.22 and TOF of 0.033 s⁻¹. Replacing the chloride anion with triflate improved the TOF to 0.115 s⁻¹ as observed with complex **C3.5**. The copper(II) complexes showed activity in electrocatalytic water oxidation at pH 7; however, the molecular complexes acted as pre-catalysts in the electrodeposition of CuO nanomaterials on the glassy carbon electrode. The structure of the catalyst influenced the activity as complex **C3.2** had the lowest overpotential (683 mV) and complex **C3.3** and **C3.4** had the highest overpotential (823 mV). This suggests that the ligand may play a role in the morphology of the formed CuO nanoparticles.

3.4 Experimental

3.4.1 General considerations

Reagents for the synthesis of ligands such as 3,5-dimethylpyrazole, 2,6-bis(chloromethyl)pyridine, 2-(chloromethyl)-pyridine hydrochloride, and hydrazine monohydrate were purchased from Sigma Aldrich and used as received. The pyrazolyl ligand precursors, 3,5-di-*tert*-butyl-1H-pyrazole and 3,5-diphenyl-1H-pyrazole, were synthesised following literature procedures.⁴⁷ (Pyrazol-1-ylmethyl)pyridine ligands were synthesised following literature procedures.³⁰⁻³¹ The metal precursors Cu(OTf)₂ (Sigma-Aldrich) and CuCl₂·2H₂O (Saarchem) were used as received. All moisture and oxygen-sensitive reactions were performed using Schlenk techniques. The solvents were distilled under a nitrogen atmosphere using Na metal for diethyl ether and CaH₂ for dichloromethane as drying agents. NMR (¹H and ¹³C) spectra were recorded on a Bruker Ultrashield Plus at 600 MHz and 151 MHz respectively. FTIR analysis was done on a BrukerAlpha-P range infrared instrument fitted with ATR in the range of 400 cm⁻¹ to 4000 cm⁻¹. Magnetic susceptibility studies were done using a Sherwood Scientific MK1 with 4mm diameter sample tubes containing 50 mM of the sample. Mass spectrometry was performed on Bricker microTOF-Q II mass spectrometer. Elemental analysis was performed on a Perkin Elmer 2400 Elemental Analyzer. Cyclic voltammetry studies were done on a BioLogic VSP potentiostat employing a water-jacketed electrochemical cell connected to a refrigerated temperature controller (Julabo F-12 ED). DLS analysis was performed on a Mastersizer 2000 Ver. 5.60 from Malvern instruments.

3.4.2 Synthesis of ligands and complexes

3.4.2.1 Synthesis of 2,6-bis((1H-pyrazol-1-yl)methyl)pyridine (**L1**)

A mixture of 2,6-bis(chloromethyl)pyridine (0.5 g, 2.84 mmol) and pyrazole (0.38 g, 5.68 mmol) was dissolved in toluene (20 mL). To the mixture, 12 mL of 40% NaOH was added followed by 10 drops of tetrabutylammonium hydroxide (TBAOH). The reaction mixture was stirred at 80-90 °C for 18 h. The reaction workup involved the separation of the organic layer from the aqueous layer. The organic layer was washed with water (2 x 20 mL) and dried over MgSO₄. The solvent was evaporated under reduced pressure resulting in an oily clear product. Yield: 0.64 g (94 %). ¹H NMR: (600 MHz, ppm, CDCl₃): δ 5.42 (s, 4H, CH₂), 6.29 (s, 2H, 4-H (pz)), 6.80 (d, 2H, H_β (py), ²J_{HH} = 6.0 Hz) 7.50-7.55 (m, 5H, H_γ (py), 5-H (pz), 3-H (pz)). ¹³C{¹H} NMR: (150 MHz, ppm, CDCl₃): δ 57.29 (CH₂), 106.22 (4-C (pz)), 120.47 (C_β (py)) 129.9 (5-C (pz)) 138.08 (C_γ (py)) 139.93 (3-C (pz)) 156.49 (C_q). FTIR (ATR) ν cm⁻¹: 1596 (C=N) (py).

3.4.2.2 Synthesis of 2,6-bis((3,5-dimethyl-1H-pyrazol-1-yl)methyl)pyridine (**L2**)

Following the same synthetic procedure as **L1**, **L2** was synthesised from 2,6-bis(chloromethyl)pyridine (0.5 g, 2.84 mmol) and 3,5-dimethyl-1H-pyrazole (0.55g, 5.68 mmol). The product was isolated as a white solid. Yield: 0.79 g (95 %). ¹H NMR: (600 MHz, ppm, CD₂Cl₂): δ 2.18 (s, 12H, CH₃ (pz)), 5.25 (s, 4H, CH₂), 5.85 (s, 2H, 4-H (pz)), 6.69 (d, 2H, H_β (py), ²J_{HH} = 12.0 Hz) 7.54 (t, 1H, H_γ (py), ³J_{HH} = 12 Hz). ¹³C{¹H} NMR: (150 MHz, ppm, CDCl₃): δ 11.39 (5-CH₃), 13.9 (3-CH₃), 54.74 (CH₂), 105.84 (4-C (pz)), 120.19 (C_β (py)) 138.38 (C_γ (py)), 140.25 (3-C (pz)), 148.05 (5-C (pz)) 157.82 (C_q). FTIR (ATR) ν cm⁻¹: 1579 (C=N) (py).

3.4.2.3 Synthesis of 2,6-bis((3,5-di-*tert*-butyl-1H-pyrazol-1-yl)methyl)pyridine (**L3**)

L3 was synthesised from 2,6-bis(chloromethyl)pyridine (0.25 g, 1.42 mmol) and 3,5-di-*tert*-butyl-1H-pyrazole (0.51 g, 2.84 mmol) in the same manner as the synthesis of **L1**. The product was isolated as a pale-yellow solid. Yield: 0.304 g (46 %). ¹H NMR: (600 MHz, ppm, CDCl₃): δ 1.24 (s, 18H, 5-(CH₃)₃ (pz)), 1.30 (s, 18H, (3-CH₃)₃ (pz)), 5.53 (s, 4H, CH₂), 5.91 (s, 2H, 4-H (pz)), 6.28 (d, 2H, H_β (py), ²J_{HH} = 6.0 Hz) 7.39 (t, 1H, H_γ (py), ³J_{HH} = 6.0 Hz). ¹³C{¹H} NMR: (150 MHz, ppm, CDCl₃): δ 30.2 (5-(CH₃)₃), 30.6 (3-(CH₃)₃), 31.32 (5-C(CH₃)₃), 31.95 (3-C(CH₃)₃), 56.31 (CH₂), 100.54 (4-C (pz)), 118.93 (C_β (py)) 137.82 (C_γ (py)), 152.04 (5-C (pz)), 157.02 (C_q), 160.77 (3-C (pz)). FTIR (ATR) ν cm⁻¹: 1593 (C=N) (py).

3.4.2.4 Synthesis of 2,6-bis((3,5-diphenyl-1H-pyrazol-1-yl)methyl)pyridine (**L4**)

L4 was prepared from 2,6-bis(chloromethyl)pyridine (0.5 g, 2.84 mmol) and 3,5-diphenyl-1H-pyrazole (1.25 g, 5.68 mmol) following the same procedure as the synthesis of **L1**. The product was isolated as a white solid. Yield: 1.44 g (93 %) ^1H NMR: (600 MHz, ppm, CDCl_3): δ 5.45 (s, 4H, CH_2), 6.67 (s, 2H, 4-H (pz)), 6.87(d, 2H, H_v , $^2\text{J}_{\text{HH}} = 6$ Hz), 7.30-7.35 (m, 16H, Ph) 7.47 (t, 1H, H_v , $^3\text{J}_{\text{HH}} = 6.0$ Hz) 7.84 (d, 4H, Ph, $\text{J}_{\text{HH}} = 12$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR: (150 MHz, ppm, CDCl_3): δ 54.74 (CH_2), 10C26(4-C (pz)), 119.91 (C_β (py)) 137.99(C_v (py)), 139.75 (3-C (pz)), 148.05 (5-C (pz)) 157.02 (C_q). FTIR (ATR) ν cm^{-1} : 1575 (C=N) (py).

3.4.2.5 Synthesis of complex **C3.1**

Complex **C3.1** was synthesised from 2,6-bis((1H-pyrazol-1-yl)methyl)pyridine (0.072 g, 0.30 mmol) dissolved in 2.5 mL of dichloromethane and copper chloride dihydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$) (0.051 g, 0.30 mmol) dissolved in 2.5 mL dichloromethane. The blue solution was stirred at room temperature for 24 h. The solution was reduced, and the addition of diethyl ether (3 x10 mL) resulted in the precipitation of the complex, which was dried under vacuum. The product was isolated as a blue solid. Yield: 0.0972 g (87 %). ESI-MS (m/z): 337.02 [M-Cl] Elemental Analysis: Calculated (found) for: $\text{C}_{13}\text{H}_{13}\text{Cl}_2\text{CuN}_5$ C, 41.78(41.52); H, 3.51(3.53); N, 18.74(19.5) FTIR (ATR) ν cm^{-1} : 1605 (C=N) (py). $\mu_{\text{eff}} = 1.88$ BM

3.4.2.6 Synthesis of complex **C3.2**

Complex **3.2** was synthesised from 2,6-bis((3,5-dimethyl-1H-pyrazol-1-yl)methyl)pyridine (0.089 g, 0.30 mmol) dissolved in 2.5 mL of dichloromethane and copper chloride dihydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$) (0.051 g, 0.30 mmol) dissolved in 2.5 mL dichloromethane. The green solution was stirred at room temperature for 24 h. The solution was reduced and the addition of diethyl ether (3 x10 mL) resulted in the precipitation of the complex, which was dried under vacuum. The product was isolated as a green solid. Yield: 0.1278 g (88 %). ESI-MS (m/z): 358.11 [M-2Cl] $^+$. Elemental Analysis: Calculated (found) for: $\text{C}_{17}\text{H}_{27}\text{Cl}_2\text{CuN}_5\text{O}_3$ C, 42.20(42.94); H, 5.62(4.72); N, 14.47(14.91). FTIR (ATR) ν cm^{-1} : 1601 (C=N) (py). $\mu_{\text{eff}} = 1.86$ BM

3.4.2.7 Synthesis of complex **C3.3**

Complex **C3.3** was synthesised from 2,6-bis((3,5-di-*tert*-butyl-1H-pyrazol-1-yl)methyl)pyridine (0.093 g, 0.20 mmol) dissolved in 2.5 mL of dichloromethane and copper chloride dihydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$) (0.034 g, 0.20 mmol) dissolved in 2.5 mL dichloromethane. The green solution was stirred at room temperature for 24 h. The solution was reduced and the addition of diethyl ether (3 x10 mL) resulted in the precipitation of the complex, which was dried under vacuum. The product was isolated as a green solid. Yield: 0.0420 g (33%). ESI-MS (m/z): 526.30 [M-

$2\text{Cl}]^+$ Elemental Analysis: Calculated (found) for: $\text{C}_{29}\text{H}_{49}\text{Cl}_2\text{CuN}_5\text{O}_2$ C, 54.92(54.78); H, 7.79(6.75); N, 11.04(11.26). FTIR (ATR) $\nu\text{ cm}^{-1}$: 1603 (C=N) (py). $\mu_{\text{eff}} = 1.89\text{ BM}$

3.4.2.8 Synthesis of complex **C3.4**

Complex **C3.4** was synthesised from 2,6-bis((3,5-diphenyl-1H-pyrazol-1-yl)methyl)pyridine (0.109 g, 0.20 mmol) dissolved in 2.5 mL of dichloromethane and copper chloride dihydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$) (0.034 g, 0.20 mmol) dissolved in 2.5 mL dichloromethane. The green solution was stirred at room temperature for 24 h. The solution was reduced and the addition of diethyl ether (3 x10 mL) resulted in the precipitation of the complex, which was dried under vacuum. The product was isolated as a green solid. Yield: 0.0804 g (54%). ESI-MS (m/z): 606.17 [$\text{M}-2\text{Cl}]^+$. Elemental Analysis: Calculated (found) for: $\text{C}_{37}\text{H}_{37}\text{Cl}_2\text{CuN}_5\text{O}_4$ C, 59.24(58.52); H, 4.97(3.56); N, 9.34(8.96). FTIR (ATR) $\nu\text{ cm}^{-1}$: 1602 (C=N) (py). $\mu_{\text{eff}} = 2.22\text{ BM}$

3.4.2.9 Synthesis of complex **C3.5**

Complex **C3.5** was synthesised from 2,6-bis((3,5-dimethyl-1H-pyrazol-1-yl)methyl)pyridine (0.089 g, 0.30 mmol) dissolved in 2.5 mL of acetonitrile and copper triflate ($\text{Cu}(\text{CF}_3\text{SO}_3)_2$) (0.108 g, 0.30 mmol) dissolved in 2.5 mL acetonitrile. The green solution was stirred at room temperature for 24 h. The solution was reduced and the addition of diethyl ether (3 x10 mL) resulted in the precipitation of the complex, which was dried under vacuum. The product was isolated as a green solid. Yield: 0.0955 g (46%). ESI-MS (m/z): 507.06 [$\text{M}-\text{OTf}]^+$ Elemental Analysis: Calculated (found) for: $\text{C}_{21}\text{H}_{24}\text{CuF}_6\text{N}_6\text{O}_6\text{S}_2$ C, 36.13(36.03); H, 3.47(3.40); N, 12.04(11.80) FTIR (ATR) $\nu\text{ cm}^{-1}$: 1610 (C=N) (py). $\mu_{\text{eff}} = 1.83\text{ BM}$

3.4.3 Electrocatalytic water oxidation

CV technique was carried out for electrochemical characterization of the electrocatalysts employing a conventional water-jacketed three-electrode electrochemical cell connected to a refrigerated temperature controller (Julabo F-12 ED). The counter electrode used was the platinum wire (Bio-Logic) and the reference electrode was a Ag/AgCl electrode (Bio-Logic). A glassy carbon electrode disc insert (Sigradur G, HTW Germany) with a geometrical area of 0.196 cm^2 was used as the working electrode. Before performing experiments, the glassy carbon was polished with $0.05\text{ }\mu\text{M}$ alumina suspension (Gamma Micropolish II, Buehler) and was subsequently washed with Milli-Q water, ethanol (Merck), and isopropanol (Merck). The working electrode was assembled into a rotating disc electrode setup. Current Potential curves of the samples were recorded using a VSP double-channel potentiostat from biologic science instruments. Current potential curves of the samples were recorded using a VSP double-channel potentiostat from BioLogic Science Instruments.

3.4.4 Chemical water oxidation

Oxygen evolution reactions were performed using a standard Clark-type oxygraph electrode (Hansatech Instruments) placed in a thermostated cell (25 °C) for all measurements. The signal was recorded for the entire duration of the experiment at 1.0 s intervals using the Oxygraph+ software (Hansatech Instruments). The signal was calibrated using a mixture (1:1) of acetonitrile and water ($[O_2] = 261 \mu\text{M}$, 25 °C).⁴⁸ Stock solutions of the catalysts were freshly prepared by dissolving the complex in acetonitrile. The stock solution was then degassed with argon to ensure an oxygen-free solution. Following the addition of the CAN (Sigma Aldrich), the cell was purged with argon before catalyst addition.

3.5 References

1. Crabtree, G. W.; Dresselhaus, M. S., *MRS Bull.* 2008, 33 (4), 421-428.
2. Fillol, J. L.; Codolà, Z.; Garcia-Bosch, I.; Gàmez, L.; Pla, J. J.; Costas, M., *Nat. Chem.* 2011, 3 (10), 807-813.
3. Baffert, C.; Romain, S.; Richardot, A.; Lepretre, J. C.; Lefebvre, B.; Deronzier, A.; Collomb, M. N., *J. Am. Chem. Soc.* 2005, 127 (39), 13694-13704.
4. Blakemore, J. D.; Crabtree, R. H.; Brudvig, G. W., *Chem. Rev.* 2015, 115 (23), 12974-13005.
5. Limburg, B.; Bouwman, E.; Bonnet, S., *Coord. Chem. Rev.* 2012, 256 (15-16), 1451-1467.
6. Limburg, J.; Vrettos, J. S.; Chen, H.; De Paula, J. C.; Crabtree, R. H.; Brudvig, G. W., *J. Am. Chem. Soc.* 2001, 123 (3), 423-430.
7. Yagi, M.; Kaneko, M., *Chem. Rev.* 2001, 101 (1), 21-35.
8. Parent, A. R.; Crabtree, R. H.; Brudvig, G. W., *Chem. Soc. Rev.* 2013, 42 (6), 2247-2252.
9. Shaffer, D. W.; Xie, Y.; Concepcion, J. J., *Chem. Soc. Rev.* 2017, 46 (20), 6170-6193.
10. Kärkäs, M. D.; Verho, O.; Johnston, E. V.; Åkermark, B., *Chem. Rev.* 2014, 114 (24), 11863-12001.
11. Das, B.; Orthaber, A.; Ott, S.; Thapper, A., *ChemSusChem* 2016, 9 (10), 1178-1186.
12. Panchbhai, G.; Singh, W. M.; Das, B.; Jane, R. T.; Thapper, A., *Eur. J. Inorg. Chem.* 2016, 2016 (20), 3262-3268.
13. Yu, W.-B.; He, Q.-Y.; Ma, X.-F.; Shi, H.-T.; Wei, X., *Dalton Trans.* 2015, 44 (1), 351-358.

14. Lee, H.; Wu, X.; Sun, L., *Nanoscale* 2020, 12 (7), 4187-4218.
15. Barnett, S. M.; Goldberg, K. I.; Mayer, J. M., *Nat. Chem.* 2012, 4 (6), 498-502.
16. Liu, Y.; Han, Y.; Zhang, Z.; Zhang, W.; Lai, W.; Wang, Y.; Cao, R., *Chem. Sci.* 2019, 10 (9), 2613-2622.
17. Lukács, D.; Szyrwił, Ł.; Pap, J. S., *Catalysts* 2019, 9 (1), 83.
18. Nestke, S.; Ronge, E.; Siewert, I., *Dalton Trans.* 2018, 47 (31), 10737-10741.
19. Praneeth, V. K. K.; Kondo, M.; Woi, P. M.; Okamura, M.; Masaoka, S., *ChemPlusChem* 2016, 81 (10), 1123-1128.
20. Zhang, M. T.; Chen, Z.; Kang, P.; Meyer, T. J., *J. Am. Chem. Soc.* 2013, 135 (6), 2048-2051.
21. McCrory, C. C. L.; Jung, S.; Ferrer, I. M.; Chatman, S. M.; Peters, J. C.; Jaramillo, T. F., *J. Am. Chem. Soc.* 2015, 137 (13), 4347-4357.
22. Singh, A.; Spiccia, L., *Coord. Chem. Rev.* 2013, 257 (17-18), 2607-2622.
23. Das, B.; Thapper, A.; Ott, S.; Colbran, S. B., *Sustain. Energy Fuels* 2019, 3 (9), 2159-2175.
24. Sun, T.; Xia, N., *Int. J. Electrochem.* 2018, 13, 4601-4612.
25. Yamazaki, H.; Shouji, A.; Kajita, M.; Yagi, M., *Coord. Chem. Rev.* 2010, 254 (21-22), 2483-2491.
26. Li, T.-T.; Zheng, Y.-Q., *Dalton Trans.* 2016, 45 (32), 12685-12690.
27. Liu, X.; Cui, S.; Qian, M.; Sun, Z.; Du, P., *Chem. Commun.* 2016, 52 (32), 5546-5549.
28. Liu, X.; Jia, H.; Sun, Z.; Chen, H.; Xu, P.; Du, P., *Electrochem. Commun.* 2014, 46, 1-4.
29. van der Ham, C. J.; Işık, F.; Verhoeven, T. W.; Niemantsverdriet, J. H.; Hetterscheid, D. G., *Catal. Today* 2017, 290, 33-38.
30. Ojwach, S. O.; Guzei, I. A.; Benade, L. L.; Mapolie, S. F.; Darkwa, J., *Organometallics* 2009, 28 (7), 2127-2133.
31. Watson, A. A.; House, D. A.; Steel, P. J., *Inorg. Chim. Acta* 1987, 130 (2), 167-176.
32. Chandra, S.; Sharma, A. K., *Spectrochim. Acta A Mol. Biomol. Spectrosc.* 2009, 72 (4), 851-857.
33. Kirkan, B.; Gup, R., *Turk. J. Chem.* 2008, 32 (1), 9-17.
34. Morrison, R. M.; Thompson, R. C., *Can. J. Chem.* 1978, 56 (7), 985-991.
35. Raman, N.; Ravichandran, S.; Thangaraja, C., *J. Chem. Sci.* 2004, 116 (4), 215-219.
36. Sala, X.; Maji, S.; Bofill, R.; García-Antón, J.; Escriche, L.; Llobet, A., *Acc. Chem. Res.* 2014, 47 (2), 504-516.
37. Dhakal, B.; Bohé, L.; Crich, D., *J. Org. Chem.* 2017, 82 (18), 9263-9269.
38. Bhattacharjee, A.; Dey, S.; Roy, P., *Inorg. Chim. Acta* 2019, 490, 93-103.

Chapter 3: Synthesis and characterization of bis(pyrazolyl)pyridine copper(II) complexes as catalysts in chemical and electrocatalytic water oxidation.

39. Lee, K. J.; McCarthy, B. D.; Dempsey, J. L., *Chem. Soc. Rev.* 2019, 48 (11), 2927-2945.
40. Chen, H.; Gao, Y.; Lu, Z.; Ye, L.; Sun, L., *Electrochim. Acta* 2017, 230, 501-507.
41. Lu, C.; Du, J.; Su, X.-J.; Zhang, M.-T.; Xu, X.; Meyer, T. J.; Chen, Z., *ACS Catal.* 2016, 6 (1), 77-83.
42. Liu, X.; Zheng, H.; Sun, Z.; Han, A.; Du, P., *ACS Catal.* 2015, 5 (3), 1530-1538.
43. Schley, N. D.; Blakemore, J. D.; Subbaiyan, N. K.; Incarvito, C. D.; D'Souza, F.; Crabtree, R. H.; Brudvig, G. W., *J. Am. Chem. Soc.* 2011, 133 (27), 10473-10481.
44. Stracke, J. J.; Finke, R. G., *J. Am. Chem. Soc.* 2011, 133 (38), 14872-14875.
45. Safdari, R.; Mohammadi, M. R.; Hołyńska, M.; Chernev, P.; Dau, H.; Najafpour, M. M., *Dalton Trans.* 2018, 47 (46), 16668-16673.
46. Wang, J.-W.; Sahoo, P.; Lu, T.-B., *ACS Catal.* 2016, 6 (8), 5062-5068.
47. Wyk, J. L. V.; Omondi, B.; Appavoo, D.; Guzei, I. A.; Darkwa, J., *J. Chem. Res.* 2012, 474-477.
48. Truesdale, G. A.; Downing, A. L., *Nature* 1954, 173 (4417), 1236-1236.

Chapter 4: Synthesis and characterisation of bis(pyrazol-1-ylmethyl)pyridine-ligated Cu(I) complexes as catalysts in chemical and electrochemical water oxidation.

4.1 Introduction

Copper complexes are attractive as WOCs due to their biomimetic chemistry with oxygen.¹⁻⁴ In redox metalloenzymes, copper coordinated to a variety of nitrogen donor ligands produce η^1 and η^2 as well as μ - $\eta^1 \eta^2$ peroxo complexes. Some of these copper peroxo complexes undergo facile and reversible O-O bond formation and cleavage under mild conditions, an important mechanistic step in water oxidation. Reports on chemical water oxidation employing copper(I or II) complexes are scarce.⁵ To date, most of the reports on copper(II) water oxidation have been studied relative to electrocatalytic water oxidation.⁶⁻¹¹ The initial study on copper-based molecular electrocatalysts for water oxidation was done by Mayer and coworkers¹² in an application of a very straightforward Cu-bipyridine system. The electrocatalyst was very efficient with a TOF of 100 s^{-1} in extremely basic solutions (pH range 11.8 to 13.3) and at a relatively high overpotential (750 mV). Electron paramagnetic resonance spectroscopy (EPR) was used to ascertain the nature of the species in solution, with (bpy)Cu(OH)₂ proposed as the active intermediate of the catalyst beyond pH 12. Praneeth *et al.*⁹ reported a multinuclear copper complex ligated by 1,3-bis(6-hydroxy-2-pyridyl)-1H-pyrazole active in electrocatalytic water oxidation at an overpotential of 500 mV at pH 12.5. UV-Vis spectroscopy and energy-dispersive X-ray (EDX) spectroscopy were used to demonstrate that the catalyst operates as a homogeneous molecular catalyst. Najafpour *et al.*¹³ reported a copper(II) complex [(L)Cu(NO₃)], (L = deprotonated (*E*)-3-(pyridin-2-yl)diazanyl)-naphthalen-2-ol) evaluated towards both electrocatalytic and chemical water oxidation. The complex was not active towards chemical water oxidation using CAN due to its instability in acidic solution. Electrocatalytic water oxidation at pH 11 led to the decomposition of the molecular complex to form CuO nanoparticles. Scanning electron microscopy (SEM) and EDX analysis confirmed that the copper complex is not a molecular homogeneous water oxidation catalyst. Li *et al.*¹⁴ evaluated a tetranuclear chair-like copper(II) complex [Cu₄(bpy)₄(μ_2 -OH)₂(μ_3 -OH)₂(H₂O)₂][C₈H₄O₄]₂ (bpy = 2,2'-bipyridine, C₈H₄O₄ = terephthalate dianion) containing aqua- and bridging μ -hydroxo ligands in electrocatalytic water oxidation at neutral pH. The complex oxidised water at an overpotential of 730 mV in a phosphate buffer at pH 7. Homogeneity of the catalyst during the electrocatalysis was confirmed. The working pH plays a vital role in the stability of homogeneous electrocatalytic water oxidation catalysts. Lu *et al.*¹⁵ observed an entirely homogeneous oxidation of water at pH 8; however, the formation of heterogeneous species was observed at pH 12 during electrocatalytic water

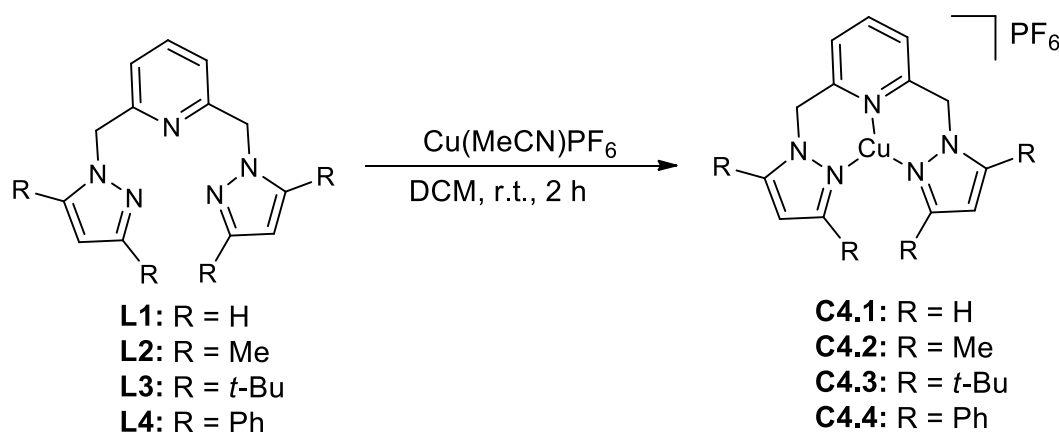
oxidation catalysed by diamine Cu(II) complexes. Copper, an inexpensive and abundant metal, has shown a great deal of potential in the development of efficient electrocatalytic water oxidation catalysts; however, there is still a lack of chemically-driven water oxidation processes that employ copper complexes.

In this chapter, we report the preparation of novel bis(pyrazol-1-ylmethyl)pyridine copper(I) complexes bearing different donating groups on the pyrazole ring, which are the first Cu(I) complexes that display activity for chemically-driven water oxidation under acidic conditions (pH 1) and electrocatalytic water oxidation under a neutral pH of 6.5.

4.2 Results and discussion

4.2.1 Ligand and complex synthesis

Bis(pyrazol-1-ylmethyl)pyridine Cu(I) complexes, **C4.1** to **C4.4**, were synthesised following previously reported procedures for bis(pyrazol-1-ylmethyl)pyridine ligands¹⁶⁻¹⁷ and $[\text{Cu}(\text{MeCN})_4\text{PF}_6]$ (Scheme 4.1). The synthesis resulted in the preparation of four complexes bearing different groups on the pyrazolyl moiety, namely H (**C4.1**), Me (**C4.2**), *t*-Bu (**C4.3**), and Ph (**C4.4**), which were isolated in moderate to good yields, **C4.1** (88%), **C4.2** (72%), **C4.3** (70%), **C4.4** (65%). The complexes were characterised by a variety of spectroscopic and analytical techniques, including Fourier-transform infrared (FTIR) spectroscopy, magnetic susceptibility, nuclear magnetic resonance (NMR) spectroscopy, electrospray ionisation mass spectrometry (ESI-MS), elemental analysis, and single-crystal X-ray diffraction (scXRD).



Scheme 4.1: Preparation of the bis(pyrazol-1-ylmethyl)pyridine Cu(I) complexes, **C4.1** to **C4.4**

Magnetic susceptibility studies were conducted in acetonitrile at room temperature. The μ_{eff} values for **C4.1** to **C4.4** were zero, which confirmed that these complexes are diamagnetic in

the +1 oxidation state.¹⁸⁻¹⁹ As such, they were further characterised by NMR (¹H and ¹³C) spectroscopy. Figure 4.1 and Figure 4.2 show examples of ¹H and ¹³C NMR spectrums of complex **C4.2**. In the ¹H NMR spectra of complexes **C4.1** to **C4.4**, the methylene and pyrazole protons were observed in the range of δ 5.21 to 5.71 and 6.02 to 7.09 ppm, respectively, coinciding with a downfield shift in comparison to the free ligands, which is characteristic of the coordination of the ligand to the metal centre.²⁰⁻²² Analogous shifts of the methylene and pyrazole carbon resonances were observed in the ¹³C NMR spectra of **C4.1** to **C4.4**. It should be noted that **C4.1** oxidised rapidly in solution, leading to NMR spectral data which is characteristic of a paramagnetic species shown in the appendix. This is attributed to the destabilising effect of the noncoordinating PF₆ anion. NMR spectral data of the chloro analogue of **C4.1** was consistent with a diamagnetic Cu(I) system.

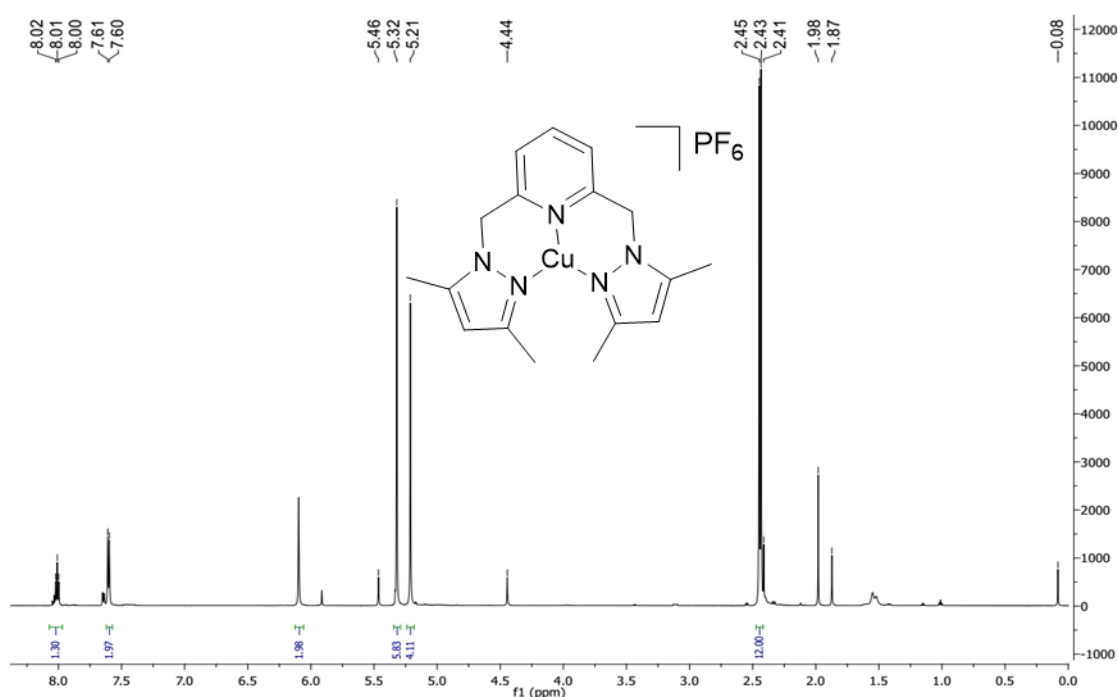


Figure 4.1: ¹H (Dichloromethane-d₂) NMR spectrum of ligand **C4.2**

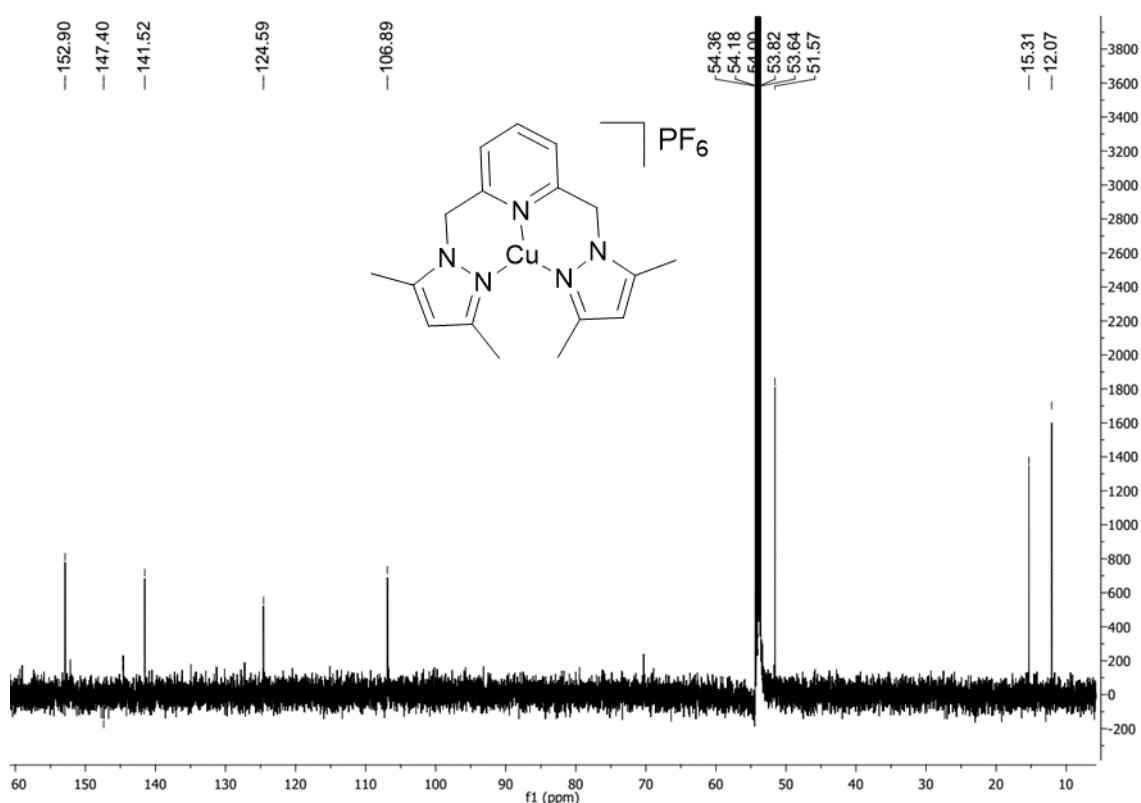


Figure 4.2: $^{13}\text{C}\{\text{H}\}$ (Dichloromethane- d_2) NMR of **C4.2**

Table 4.1: FTIR stretching frequencies of (C=N) (py) in the ligands and complexes

Ligand	(C=N) (py) $\nu \text{ cm}^{-1}$	Complex	(C=N) (py) $\nu \text{ cm}^{-1}$
L1	1596	C4.1	1600
L2	1579	C4.2	1600
L3	1593	C4.3	1604
L4	1575	C4.4	1597

FTIR analysis of **C4.1** to **C4.4** showed a slight shift in the $\nu_{\text{C=N}}$ absorption band to lower wavenumbers in the range 1597 to 1604 cm^{-1} as shown in Table 4.1, further confirming successful complexation.²³⁻²⁴ Complexes **C4.1** to **C4.4** were also characterised by ESI-MS operating in positive ion mode. The molecular ion peak was identified as the cationic species at m/z 302.05, 358.11, 526.30, 606.17 for complexes **C4.1** to **C4.4**, respectively. Figure 4.3 shows a fragmentation pattern of complex **C4.2**. Finally, elemental analysis of **C4.1** to **C4.4** established the bulk purity of the isolated complexes.

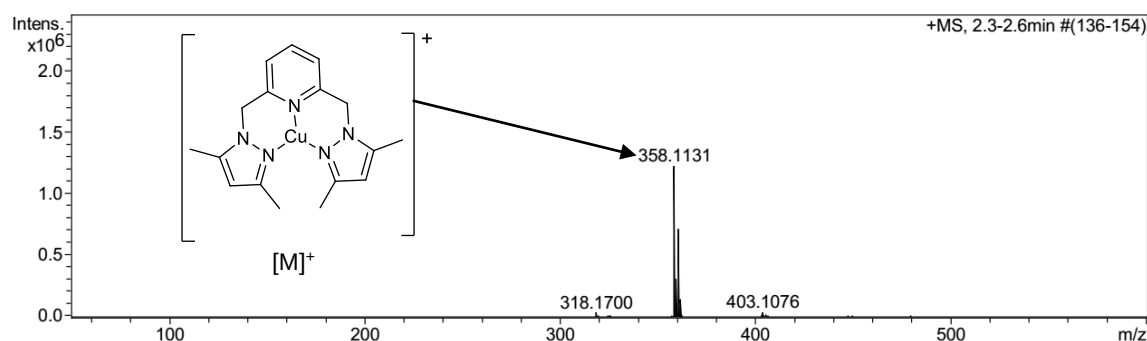


Figure 4.3: ESI-MS spectrum of complex **C4.2**

The molecular structures of complexes **C4.2**, **C4.3**, and **C4.4** were established with single-crystal XRD analysis. Diffraction quality crystals were obtained by slow diffusion of diethyl ether into saturated dichloromethane solutions of the complexes at 4 °C. Ellipsoid diagrams for **C4.2**, **C4.3**, and **C4.4** are provided in Figure 4.4, while crystallographic data and selected bond lengths and angles are provided in Table 4.2 and 4.3, respectively. The coordination geometry around the metal centre for **C4.2**, **C4.3**, and **C4.4** is a distorted T-shape, with N1-Cu1-N3 and N3-Cu1-N3' bond angles in the range 89 to 98° and 173°, respectively. The Cu1-N1 (pyridine) bond lengths were in the range of 2.075 to 2.110 Å. In the case of complex **C4.2**, the Cu1-N3/3' (pyrazole) bond lengths were in the range of 2.058 to 2.076 Å. In contrast, the Cu1-N3/3' (pyrazole) bond lengths were slightly shorter for **C4.3**, in the range of 1.924 to 1.940 Å. The shortest bond lengths for Cu1-N3/3' (pyrazole) in the range of 1.910 to 1.907 Å were observed for complex **C4.4**. The introduction of bulkier groups reduces the Cu1-N3/3' (pyrazole) bond length as a result of steric effects.²⁵ The observed bond lengths are within range for analogous Cu(I) complexes reported in the literature.²⁶⁻²⁸

Chapter 4: Synthesis and characterisation of bis(pyrazol-1-ylmethyl)pyridine-ligated Cu(I) complexes as catalysts in chemical and electrochemical water oxidation.

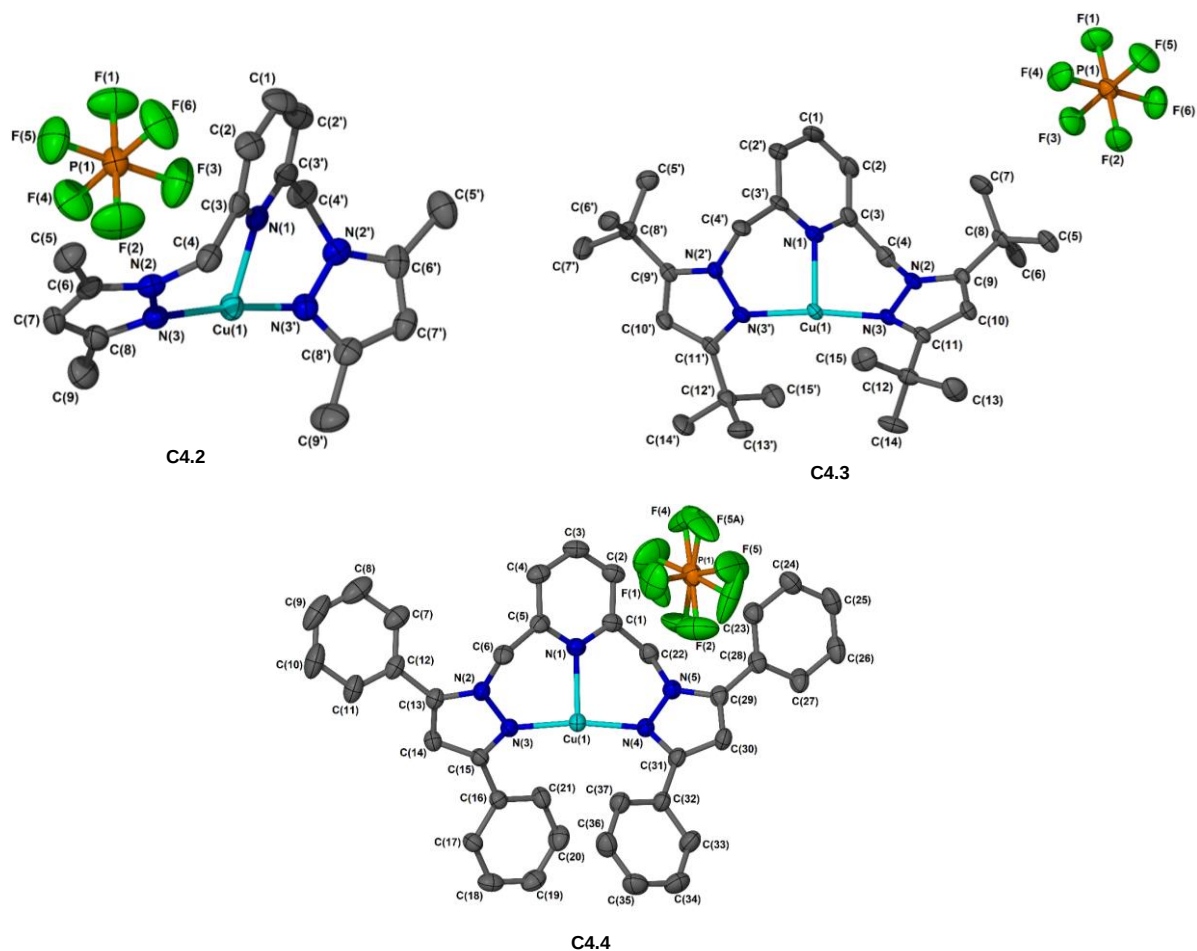


Figure 4.4: Ellipsoid diagrams of **C4.2**, **C4.3**, and **C4.4**, respectively, drawn at 50% probability. Hydrogen atoms were omitted for clarity.

Table 4.2: Crystal data and refinement for **C4.2**, **C4.3**, and **C4.4**

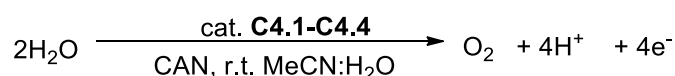
Parameter	C4.2	C4.3	C4.4
Chemical formula	C ₁₇ H ₂₁ CuF ₆ N ₅ P	C ₂₉ H ₄₅ CuF ₆ N ₅ P	C ₃₇ H ₂₉ CuF ₆ N ₆ P
Formula weight (g/mol)	503.90	670.21	753.15
Temperature (K)	293(2)	293(2)	273(2)
Wavelength (Å)	0.71076	0.71076	0.71076
Crystal size (mm)	0.200 x 0.200 x 0.200	0.200 x 0.200 x 0.200	0.097 x 0.111 x 0.279
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	P 1 21/n 1	P 21 21 21	P 1 21/c 1
a (Å)	8.2344(6)	11.3842(9)	a = 11.7594(5)
b (Å)	14.8317(10)	15.6425(10)	23.6227(11)
c (Å)	17.2444(12)	18.2628(13)	13.1379(6)
α (deg) (°)	90	90	90
β (deg)(°)	95.076(5)	90	112.115(2)
γ (deg)(°)	90	90	90
Volume (Å³)	2097.8(3)	3252.2(4)	3381.1(3)
Z	4	4	4
D_{calc} (g/cm³)	1.589	1.369	1.480
Absorption coefficient (mm⁻¹)	1.182	0.781	0.763
F(000)	1020	1404	1536
Goodness of Fit on F²	1.287	1.192	1.496
Final R₁ indices [I>2σ(I)]	0.0799	0.0507	0.664
wR₂ [I>2σ(I)]	0.1818	0.1369	0.1951

Table 4.3: Selected bond lengths and bond angles for **C4.2**, **C4.3**, and **C4.4**

Bond lengths (Å)	C4.2	C4.3	C4.4
Cu1-N1	2.075(4)	2.110(3)	2.101(3)
Cu1-N3	2.077(5)	1.924(4)	1.910(2)
Cu1-N3'	2.058(5)	1.940(4)	1.907(2)
Bond Angles (Deg) (°)			
N1-Cu1-N3'	89.2(2)	92.3(2)	95.41(1)
N1-Cu1-N3	97.6(2)	93.9(1)	93.41(1)
N3'-Cu1-N3	173.2(2)	173.2(2)	171.12(1)

4.2.2 Cu(I)-catalysed chemically-driven water oxidation

The copper(I) complexes **C4.1** to **C4.4** were investigated as pre-catalysts for chemically-driven water oxidation (Scheme 4.2). Oxygen evolution was recorded as a function of time on a Hansatech Oxygraph (Hansatech Instruments Ltd, Norfolk, England), with the oxygen evolution curves shown in Figure 4.5.



Scheme 4.2: Chemically driven water oxidation catalysed by **C4.1** to **C4.4**

The activity of **C4.1** to **C4.4** towards water oxidation was investigated in the presence of CAN at pH 1. The arrow indicates the point of addition of the catalyst to the reaction mixture. From the slope of the curves, it is evident that all of them are catalytically active. Complex **C4.2** was the most active followed by **C4.3** with TOF-values of 0.31 and 0.14 s⁻¹ respectively, whereas **C4.4** is the least active with a TOF of 0.0086 s⁻¹.

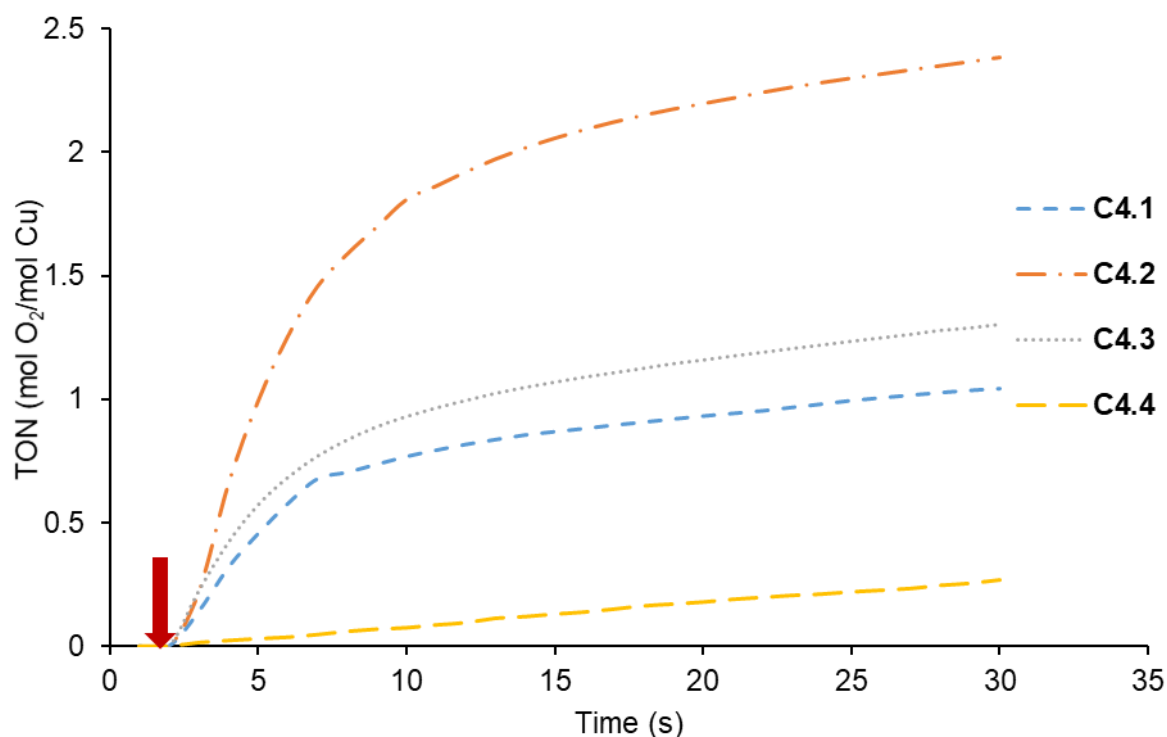


Figure 4.5: Oxygen evolution curves for Cu(I) complexes **C4.1** to **C4.4**

The results obtained in these reactions are summarised in Table 4.4. Copper(I) complexes having electron-donating substituents such as Me (**C4.2**) and *t*-Bu (**C4.3**) showed higher activity with a TON of 4.6 and 3.96, and TOF of 0.31 and 0.14 s⁻¹ respectively, while complexes containing unsubstituted pyrazole (**C4.1**) and the phenyl substituent (**C4.4**) resulted in lower activities with a TON of 2.67 and 2.30, and TOF of 0.13 s⁻¹ and 0.0086 s⁻¹, respectively. The comparatively higher activity of **C4.2** and **C4.3** can be attributed to the electron-donating ability of the substituents on the ligand framework. The presence of electron-donating groups in the ligand framework lowers the oxidation potential of the metal centre, which, in turn, increases the observed water oxidation efficiency.²⁹⁻³¹ Das *et al.*³² made a similar observation with their two structurally similar heteroleptic Ru-complexes having *t*-Bu and NO₂ groups on the terpyridine ligand as electron-donating and electron-withdrawing substituents.

Chapter 4: Synthesis and characterisation of bis(pyrazol-1-ylmethyl)pyridine-ligated Cu(I) complexes as catalysts in chemical and electrochemical water oxidation.

Table 4.4: Summary of results of different copper(I) complexes towards chemical water oxidation with CAN

Entry	Catalyst	^a TON	^b TOF
1	C4.1	2.67	0.13
2	C4.2	4.60	0.31
3	C4.3	3.96	0.14
4	C4.4	2.30	0.0086

Reaction conditions: 25 μ M, [CAN]: 110 mM, solvent: MeCN: H₂O (1:1, 2 mL); **a**) TON after 5 minutes reaction time; **b**) TOF was calculated from the steepest slope of the TON curve over a 5 second period.

The results from Figure 4.5 and Table 4.4 are also supported by cyclic voltammetry (CV) studies (Figure 4.6). Figure 4.3(Inset) shows an irreversible wave assigned to the first oxidation of complex **C4.2** from Cu(I) to Cu(II) at E_{pa} +0.224 V (vs normal hydrogen electrode (NHE)).¹⁴ Complexes **C4.1** to **C4.4** showed a reversible Cu(III)/Cu(II) couple with E_{1/2}-values in the range +0.56 to +0.83 V (vs NHE).³³ Complex **C4.2** had the lowest oxidation potential (E_{1/2} = +0.56 V) and was the most efficient pre-catalyst for chemically-driven water oxidation (TON and TOF of 4.6 and 0.31 s⁻¹ respectively). The most positive oxidation potential (E_{1/2} = +0.83 V) was observed for the least active phenyl (acting as an electron-withdrawing group) substituted complex **C4.4**. The oxidation potentials of the unsubstituted complex **C4.1** and the *t*-butyl substituted complex **C4.3** were E_{1/2} = +0.59 V and +0.82 V, respectively. Although **C4.3** had a more positive oxidation potential than **C4.1**, it was more stable under the highly acidic conditions, as it had a TON of 3.96. Steric effects can be a contributing factor to the stability of the metal-bound substrate intermediate during a catalytic cycle.³⁰ Therefore, the activity of these catalysts is influenced by both electronic and steric effects on the pyrazolyl moiety of the catalyst.

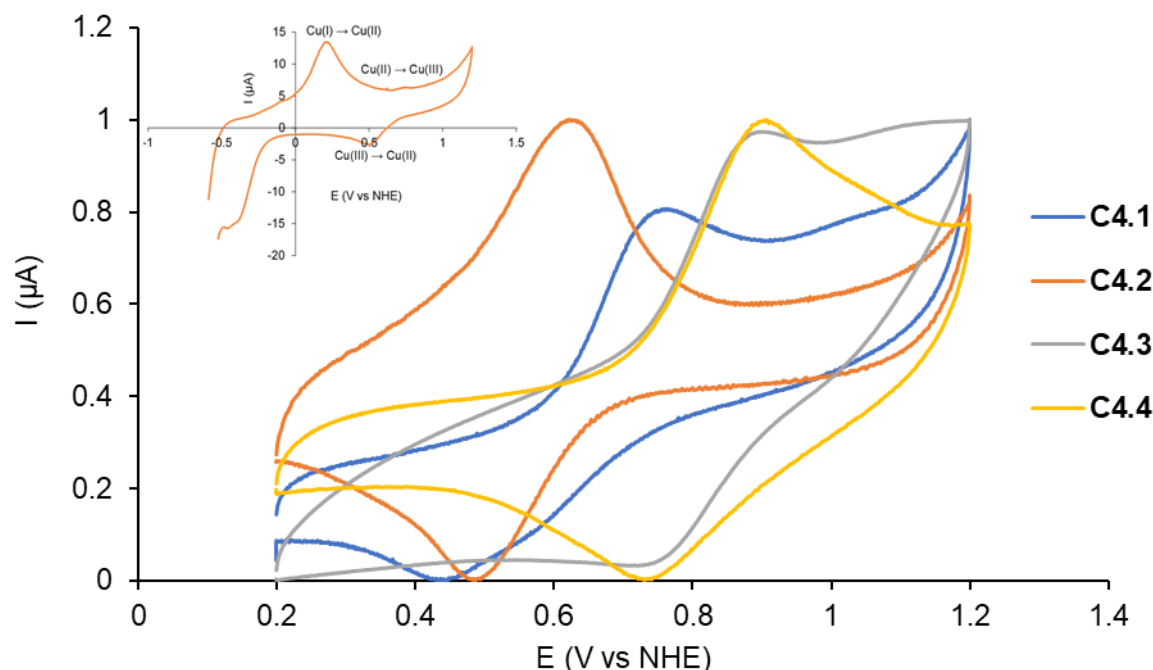


Figure 4.6: CVs of the Cu(I) complexes (0.5 mM) performed in 0.1 M Bu_4NPF_6 in acetonitrile with the glassy carbon as the working electrode, platinum wire as a counter electrode, and Ag/AgCl as the reference electrode. The scan rate was 10 mV s^{-1} . Inset: A cyclic voltammogram showing irreversible wave assigned to the first oxidation of Cu(I) to Cu(II) for complex **C4.2**. The reversible waves showing the reversible Cu(II)/Cu(I) couple of **C4.1 to C4.4**

Complex **C4.2** was chosen for further investigations towards water oxidation due to its high activity. The rate dependency on $[\text{Cu}]$ was studied and the data is illustrated in Figure 4.7. The initial rate was determined from the first 5 seconds of the reaction time after the addition of the catalyst. At low concentrations of 2.5–10 μM , a non-linear dependency between the catalyst concentration and the dioxygen evolution was observed, which is characteristic of a second-order reaction (Figure 4.7a). This suggests the formation of copper dimers at low catalyst concentration prior to catalyst activation.^{34–36} As the concentration increases, the initial reaction rate becomes first order as a function of $[\text{Cu}]$, which is indicative of only one Cu complex being involved in the O–O bond formation step, and therefore water oxidation proceeds via water nucleophilic attack (Figure 4.7b).^{36–38} The similar change in reaction order as the concentration increases was also observed by Shaffer *et al.*³⁹ where ruthenium bipyridine-dicarboxylate complexes were investigated in CAN-driven water oxidation.

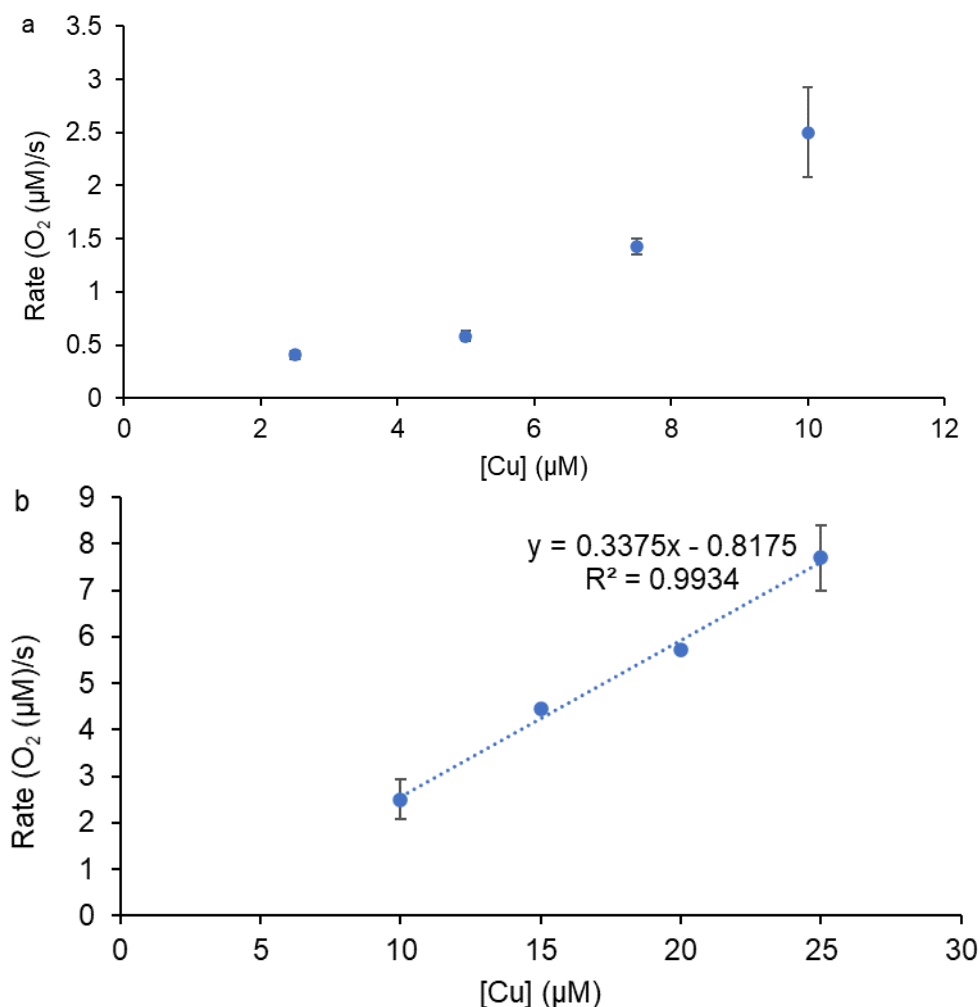


Figure 4.7: Initial rate data of the catalyst system studied using **C4.2** and 110 mM CAN as the primary oxidant showing a, second-order at low concentrations and b, first-order at higher concentrations

The effect of $[CAN]$ on the activity was studied at high $[Cu]$ associated with mononuclear Cu(I) species using **C4.2** (25 μM) as shown in Figure 4.8. At low $[CAN]$, the rate shows a linear dependency on the concentration of CAN, attributed to the formation of a Cu-CAN complex at low $[CAN]$.⁴⁰ At a higher $[CAN]$ (>10 mM), the reaction order is observed to be zero indicating saturation behaviour. Therefore, the rate-determining step at low Ce(IV) concentrations could be viewed as an interaction between the oxidant and the catalyst forming a Cu-CAN active complex. At high CAN concentrations, the Cu-CAN interaction is reversible and independent of $[CAN]$, and therefore a zero reaction order is observed.^{37, 40} The addition of excess amounts of CAN does not lead to an increase in the activity of the catalyst.³⁸ This could be due to catalyst decomposition caused by ligand oxidation or hydrolysis of the metal centre due to the highly acidic medium.

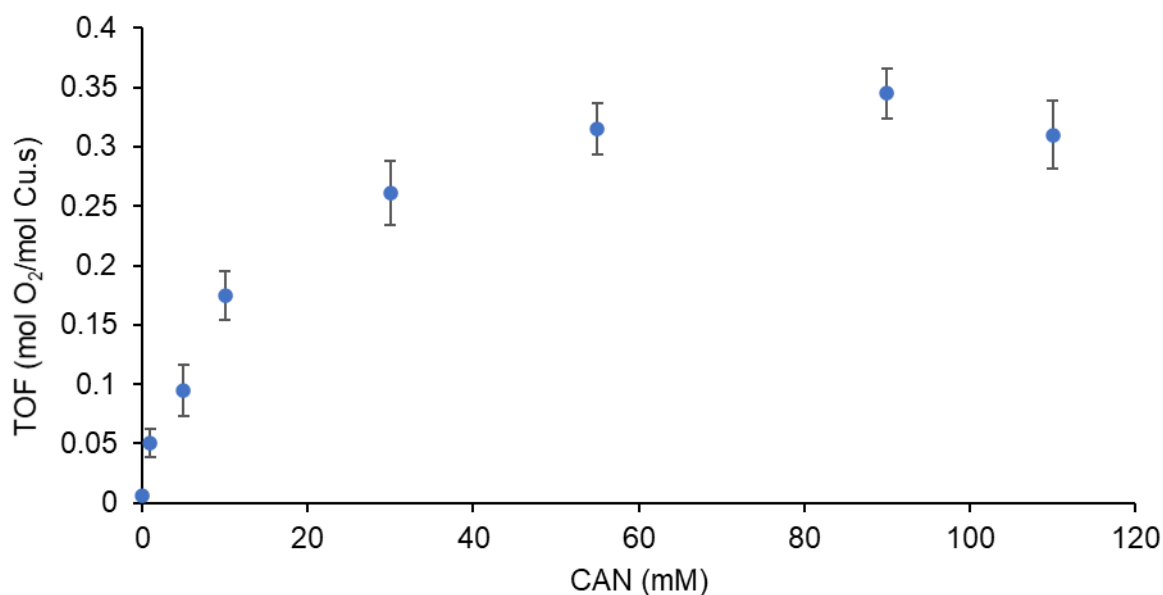


Figure 4.8: Effect of CAN on the activity of the catalyst studied using 25 μM **C4.2**.

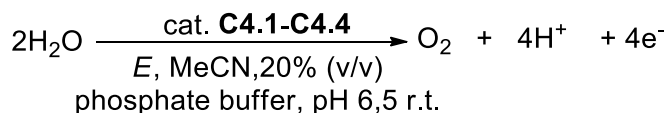
Other chemical oxidants such as sodium *m*-periodate (NaIO_4) and sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$) were studied in chemically-driven water oxidation using **C4.2**, as illustrated in Table 4.5. The initial pH of the solution was dependent on the oxidant used, with CAN having the lowest pH of 1, while the use of $\text{Na}_2\text{S}_2\text{O}_8$ exhibited a pH of 2.23 and NaIO_4 a pH of 4.50. CAN resulted in the highest activity with the highest TON (4.6) and TOF (0.31 s^{-1}) among the three investigated oxidants. Although $\text{Na}_2\text{S}_2\text{O}_8$ had the lowest TOF (0.044 s^{-1}), the catalyst is more stable exhibiting the second highest TON of 4.02. These results demonstrate that the catalyst is most active in highly acidic conditions with CAN as the primary oxidant and Cu-CAN is the active form of the catalyst, as was proposed by Codola *et al.*⁴⁰ with their highly active Fe-complex.

Table 4.5: The effect of a chemical oxidant on the TON and TOF of water oxidation

Oxidant	Concentration (mM)	TON ^a	TOF ^b
CAN	110	4.6	0.31
Sodium-m-periodate	110	3.77	0.14
Sodium persulfate	110	4.02	0.044

Reaction conditions: 25 μM , Solvent: MeCN:H₂O (1:1, 2 mL); **a**) TON after 5 minutes' reaction time; **b**) TOF was calculated from the slope of the first 5 seconds on the TON curve

4.2.3 Cu(I)-catalysed electrocatalytic water oxidation



Scheme 4.3: Electrocatalytic water oxidation using Cu(I) complexes **C4.1** to **C4.4**

4.2.3.1 The effect of catalyst structure on electrocatalytic water oxidation

Cu(I) complexes **C4.1** to **C4.4** were evaluated as pre-catalysts for electrocatalytic water oxidation in a phosphate buffer (Scheme 4.3) using CV (Figure 4.9). The Cu(I) complexes are insoluble in aqueous solutions; therefore, the complexes were first dissolved in a solution of acetonitrile and 0.1 M NBu₄PF₆ (supporting electrolyte) followed by the addition of 20% (v/v) 0.2 M phosphate buffer (pH 6.5). The solution was degassed with nitrogen for 15 minutes, prior to each experiment. The CVs were obtained under air using a glassy carbon working electrode (GCE), Ag/AgCl reference electrode, and a platinum wire counter electrode. Potentials were measured versus Ag/AgCl electrode and are reported versus NHE through the addition of +0.199 V to the measured potential.

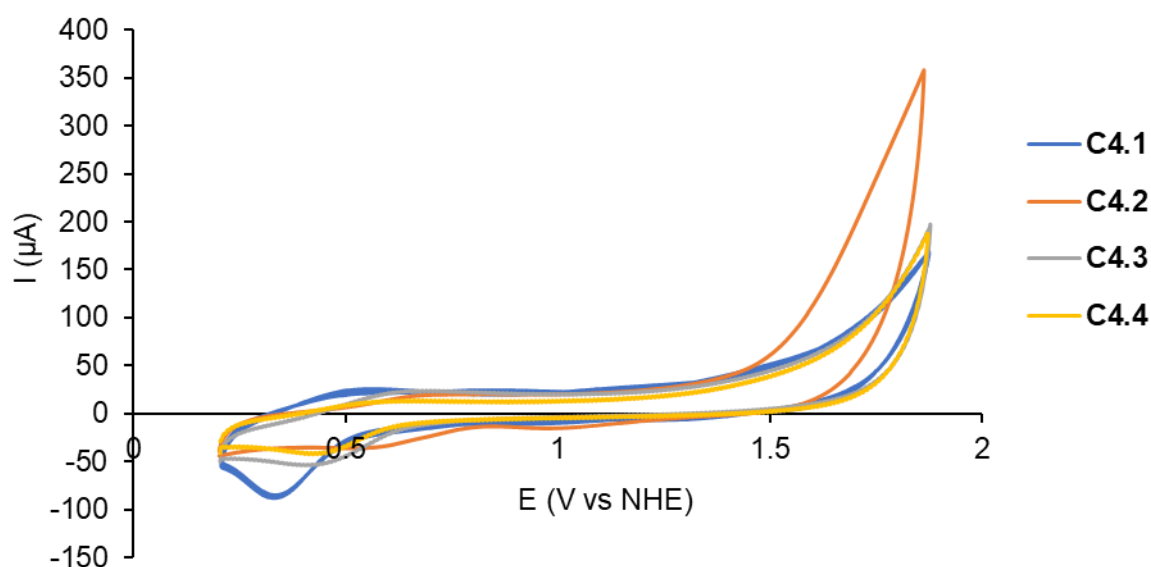


Figure 4.9: CVs of Cu(I) complexes **C4.1** to **C4.4** [0.42 mM] in a mixture of MeCN and 20% (v/v) phosphate buffer (0.2 M, pH 6.5) recorded at a scan rate of 100 mV s⁻¹.

On scanning at 100 mV s^{-1} from 0.0 to +1.7 V, solutions of 0.42 mM in MeCN and 0.2 M phosphate buffer at pH 6.5, all complexes **C4.1** to **C4.4** exhibited a reversible oxidation peak between $E_{1/2} = +0.56 \text{ V}$ and $+0.83 \text{ V}$ assigned to the Cu(III)/Cu(II) redox couple.³³ This was followed by a large irreversible pH-dependent oxidation wave with an onset potential from +1.52 V to +1.63 V attributed to the oxidation of water. This irreversible wave is absent on the CV of the complex in a solution of MeCN and 0.1 M NBu₄PF₆; however, the wave emerges upon the addition of 20% (v/v) 0.2 M phosphate buffer (pH 6.5) as illustrated for complex **C4.2** in Figure 4.10.

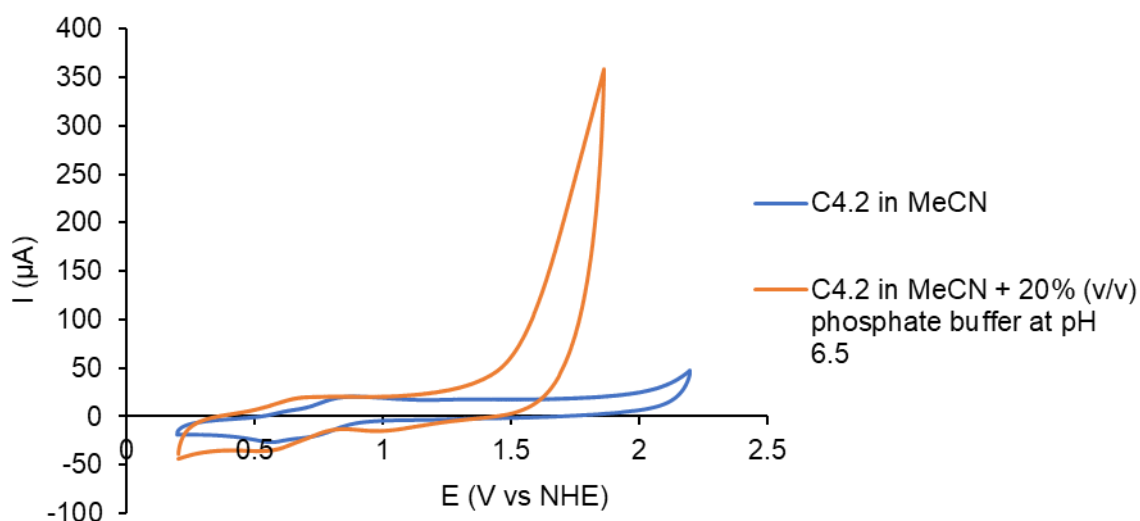


Figure 4.10: CVs of Cu(I) complex **C4.2** [0.5 mM] in a solution of MeCN and 0.1 M NBu₄PF₆ (blue) and **C4.2** [0.42 mM] in a mixture of MeCN and 20% (v/v) phosphate buffer (0.2 M, pH 6.5) (orange) recorded at a scan rate of 100 mV s^{-1} .

The activities of complexes **C4.1** to **C4.4** were compared based on the overpotential at pH 6.5 (Table 4.6). Complex **C4.2** had the lowest overpotential of 674 mV and a TOF of 9.77 s^{-1} making it the most active complex among the four catalysts used in this study. In comparison to literature, complex **C4.2** has a lower overpotential and higher TOF than most reported copper pre-catalysts (Table 4.6 entries 7-12). However, our most active pre-catalyst, **C4.2**, still falls short in comparison to the current state of the art in copper-catalysed electrocatalytic water oxidation (Table 4.6, entries 5-6 and 13). The most active copper electrocatalyst is the recently reported tetra-amidate macrocyclic ligated copper complex which efficiently catalysed water oxidation at a very low overpotential of 200 mV and the highest TOF of 140 s^{-1} in phosphate buffer at pH 7.⁴¹ Complex **C4.1** had the second-lowest overpotential of 744 mV followed by complex **C4.3** at 774 mV. The least active complex, with the highest overpotential of 784 mV, was complex **C4.4**. The overpotentials of the Cu(I) complexes are within the range of reported copper complexes studied at near-neutral pH (500-1000 mV).^{14, 42-43} The order of overpotentials from lowest to highest is dependent on the oxidation potentials (Cu^{III}/Cu^{II}) of the

complexes. Complex **C4.2** with the lowest oxidation potential of $E_{1/2} = +0.56$ V resulted in the lowest overpotential of 670 mV, whereas complex **C4.4** with the highest oxidation potential of $E_{1/2} = +0.83$ V resulted in the highest overpotential of 780 mV. The order of activity based on TOF for the electrocatalytic water oxidation was as follows: **C4.2** > **C4.4** > **C4.1** > **C4.3**, whereas in CAN-driven water oxidation the order of activity based on TOF was: **C4.2** > **C4.3** > **C4.1** > **C4.4**. Complex **C4.2** is the most active in both the CAN-driven chemical water oxidation and electrocatalytic water oxidation; however, the least active complex **C4.4** in CAN-driven water oxidation had the second-highest TOF of 1.47 s^{-1} for electrocatalytic water oxidation. The difference in activity trends between chemical water oxidation and electrocatalytic water oxidation was also observed by Olivares *et al.*⁴⁴ with iridium complexes containing C, N-bidentate chelating triazolylidene-pyridyl ligands as catalysts. They observed enhanced activity for CAN-driven water oxidation in the presence of electron-donating groups on the ligand scaffold, whereas in electrocatalytic water oxidation, the activity is highest when the triazolylidene ligand is unsubstituted. It indicates an I2M (binuclear) type mechanism where steric plays an important role, instead of a WNA mechanism in electrocatalytic water oxidation with these systems.⁴⁵ As observed in Table 4.6, there is no clear correlation between overpotential and TOF, since a catalyst can have a low overpotential and a low TOF. However, complex **C4.2**, which had the lowest overpotential in this study, also had the highest TOF among the four complexes.

Chapter 4: Synthesis and characterisation of bis(pyrazol-1-ylmethyl)pyridine-ligated Cu(I) complexes as catalysts in chemical and electrochemical water oxidation.

Table 4.6: Calculated overpotentials of copper complexes **C4.1** to **C4.4** at pH 6.5

Entry	Catalyst	⁴⁶ (mM)	pH	Overpotential ^a /mV	TOF ^b / s ⁻¹	Reference
1	C4.1	0.42	6.5	744	0.33	This work
2	C4.2	0.42	6.5	674	9.77	This work
3	C4.3	0.42	6.5	774	0.30	This work
4	C4.4	0.42	6.5	784	1.47	This work
5	Cu porphyrin	1.0	7.0	300	30	46
6	[(Py ₃ P)Cu(OH)] ⁻	0.7	8.0	400	20	47
7	[Cu ₂ (BPMAN)(m-OH)] ³⁺	1.0	7.0	800	0.60	43
8	[Cu(en) ₂] ²⁺	1.0	8.0	540	0.40	15
9	[Cu ₄ (bpy) ₄ (μ ₂ -OH) ₂ (μ ₃ -OH) ₂ (H ₂ O) ₂] ²⁺	1.0	7.0	730	-	14
10	[Cu(TPA)(OH ₂)] ²⁺	1.0	7.0	970	0.10	48
11	Cucyclam	1.0	7.0	880	-	42
12	CuMe ₄ cyclam	1.0	7.0	880	-	42
13	CuTAML	1.0	7.0	200	140	41

^a The overpotential was calculated as follows: Overpotential = $E_{\text{onset}} - (1.23 - (0.059\text{pH}))$. E_{onset} is extrapolated from the CV using the tangent method. ^b TOF was calculated from the slope of i_{cat}/i_p vs $1/v^{1/2}$. Abbreviations used in this table: porphyrin = tetrakis(4-N-methyl-pyridyl)porphyrin, Py₃P = N,N-bis(2-(2-pyridyl)ethyl)pyridine-2,6-dicarboxamidate, bpmn = 2,7-[bis(2-pyridyl-methyl)aminomethyl]-1,8-naphthyridine, en = 1,2-ethylenediamine, bpy = 2,2'-bipyridine, TPA = tris-(pyridylmethyl) amine, cyclam = 1,4,8,11-tetraazacyclotetradecane, Me₄cyclam = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane

4.2.3.2 Kinetic studies

The effect of catalyst concentration on the catalytic current was studied using complex **C4.2** in 0.2 M phosphate buffer at pH 6.5 (Figure 4.11). The catalytic current at 1.7 V varies linearly with catalyst concentration at low concentrations (< 0.1 mM). This indicates that water oxidation occurs at a single site and that O-O bond formation proceeds via a water nucleophilic attack mechanism.^{47, 49-51} Although this is the most common O-O bond formation pathway in electrocatalytic water oxidation involving copper complexes, it is disputed by Koepke *et al.*⁷ who suggest that molecular copper-catalysed water oxidation O-O bond formation does not proceed through the WNA mechanism, instead, the I2M mechanism is thermodynamically more favourable. Intermolecular WNA and redox isomerisation of the dimer were concluded in energetically accessible pathways. It should be noted that their results were obtained at pH 12.5, significantly higher than the operating pH in this study. Kafentzi *et al.*⁵² studied electrocatalytic water oxidation using a copper(II) complex, [(RPY2)Cu(OTf)₂] (RPY2 = N-substituted bis[2-pyridyl(ethylamine)] ligands; R = indane; OTf = triflate). At neutral pH 6 to 8, the complex was suggested to catalyse water oxidation at a single site with O-O bond formation proceeding via the WNA mechanism. At higher pH, catalysis ceased and can be attributed to the formation of dinuclear copper(II) species. Changes in copper complex speciation induced by pH changes were also observed by Barnett *et al.*¹² where a copper bipyridine complex was studied in electrocatalytic water oxidation. EPR spectroscopic studies showed that at pH-values lower than 8, a monomeric aquo complex [(bpy)Cu(H₂O)₂]²⁺ is observed, whereas at pH-values 8 to 12, the dimeric form of the complex [(bpy)Cu(μ -OH)₂]²⁺ is dominant. At pH higher than 12, a monomeric bis-hydroxide (bpy)Cu(OH)₂ is observed. The literature reports suggest that at near-neutral pH, monomeric species are most likely to be responsible for water oxidation catalysis; therefore, O-O bond formation proceeds via the WNA mechanism.

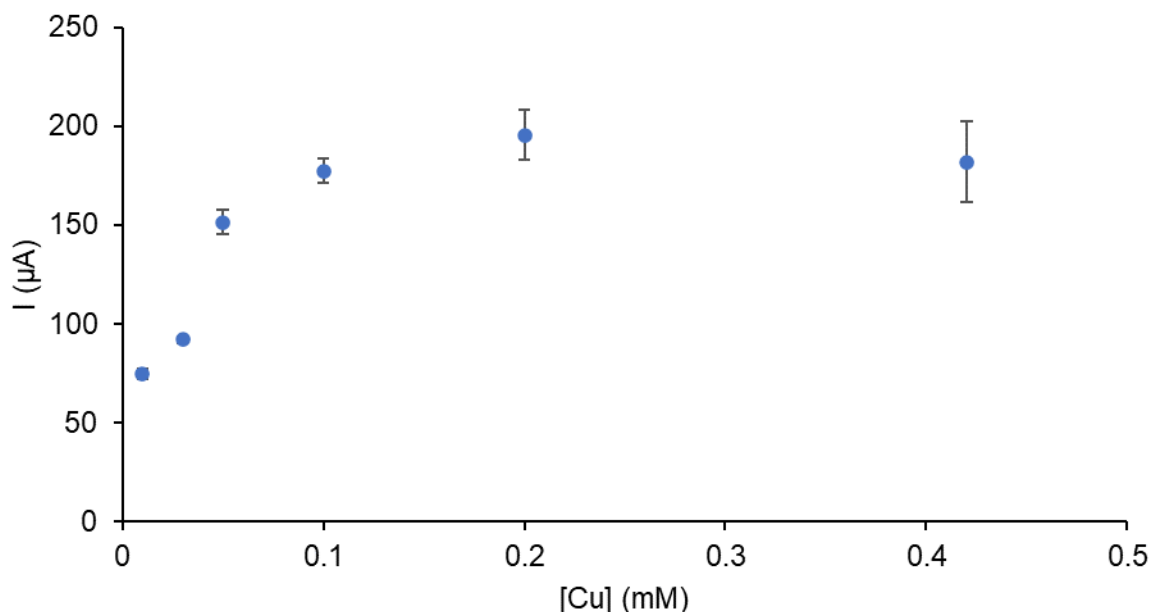


Figure 4.11: The effect of concentration of the catalytic current at 1.7 V studied using complex **C4.2** at pH 6.5.

The effect of scan rate on the catalytic current was evaluated for **C4.1** to **C4.4**. The catalytic oxidation wave at 1.7 V was scan rate dependent as shown for **C4.2** in Figure 4.12. The current at 1.7 V was linearly dependent on the square root of the scan rate, which is indicative of a diffusion-limited process, thereby indicating a homogeneous water oxidation.⁵³

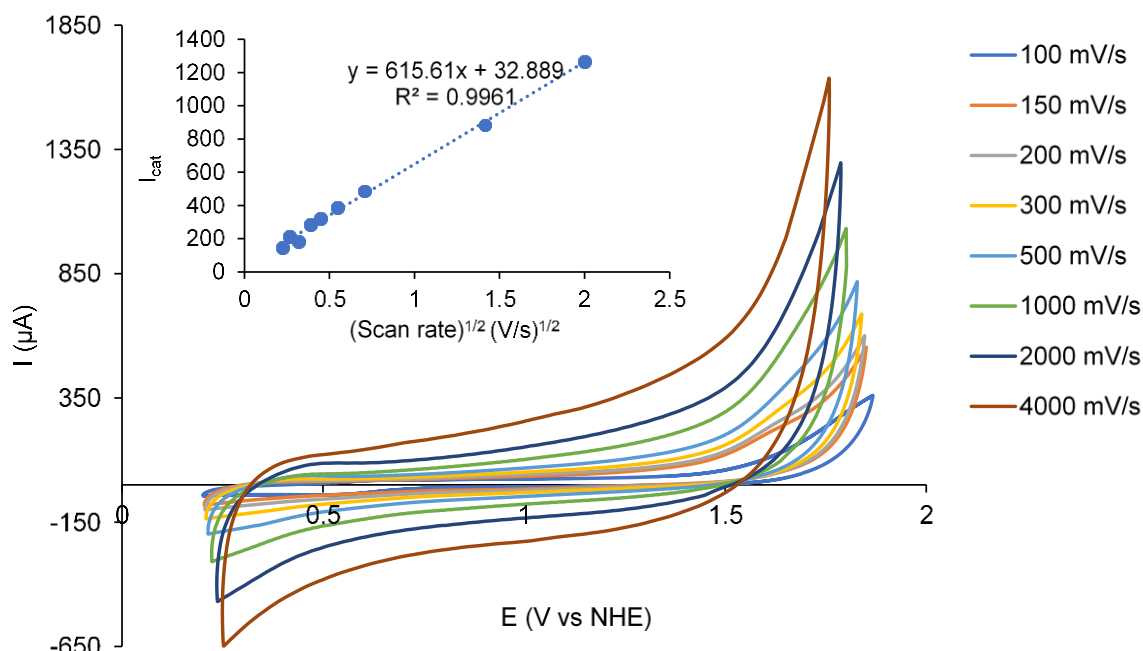


Figure 4.12: Scan rate dependence of 0.42 mM **C4.2** scanned at 100 to 4 000 mV/s. Inset: Linear scan rate dependence of the catalytic current at 1.7 V versus the square root of the scan rate

A graph of catalytic current/peak current as a function of $1/(\text{scan rate})^{1/2}$ was plotted as shown in Figure 4.13. From equations (4.1) to (4.4) k_{cat} , which is the catalytic TOF, was calculated from the slope of the graph.⁵³⁻⁵⁵

$$I_{\text{cat}} = n_{\text{cat}}FA[\text{Cu}](k_{\text{cat}}D_{\text{Cu}})^{1/2} \quad (4.1)$$

In equation 1 $n_{\text{cat}} = 4$, which is the number of electrons transferred during water oxidation, F is the Faraday constant, A is the electrode surface area in cm^2 , $[\text{Cu}]$ is the concentration of the catalyst (in mol/L), and D_{Cu} is the diffusion coefficient of the catalyst. The peak current for the non-catalytic redox couple Cu(III/II) at $E_{1/2} = +0.56$ vs NHE varies linearly with the square root of the scan rate. The result is consistent with the Randles-Sevcik equation.

$$i_p = 0.4633nFA[\text{Cu}](nFvD_{\text{Cu}}/RT)^{1/2} \quad (4.2)$$

At 25 °C equation (4.2) becomes (4.3):

$$i_p = 2.69 \times 10^5 n^{3/2} A D_{\text{Cu}}^{1/2} [\text{Cu}] v^{1/2} \quad (4.3)$$

The ratio of equation (1)/(2), i_{cat}/i_p results in equation (4.4)

$$i_{\text{cat}}/i_p = (0.359 n_c/n_p^{3/2} k_{\text{cat}}^{1/2}) 1/v^{1/2} \quad (4.4)$$

where n_c is the number of electrons transferred during water oxidation (4 electrons), n_p is the number of electrons transferred in a non-catalytic redox event for the Cu(III/II) couple (1 electron), and v is the scan rate. Catalytic turnover frequency, k_{cat} (TOF) is calculated from the slope of the plot i_{cat}/i_p vs $1/v^{1/2}$.

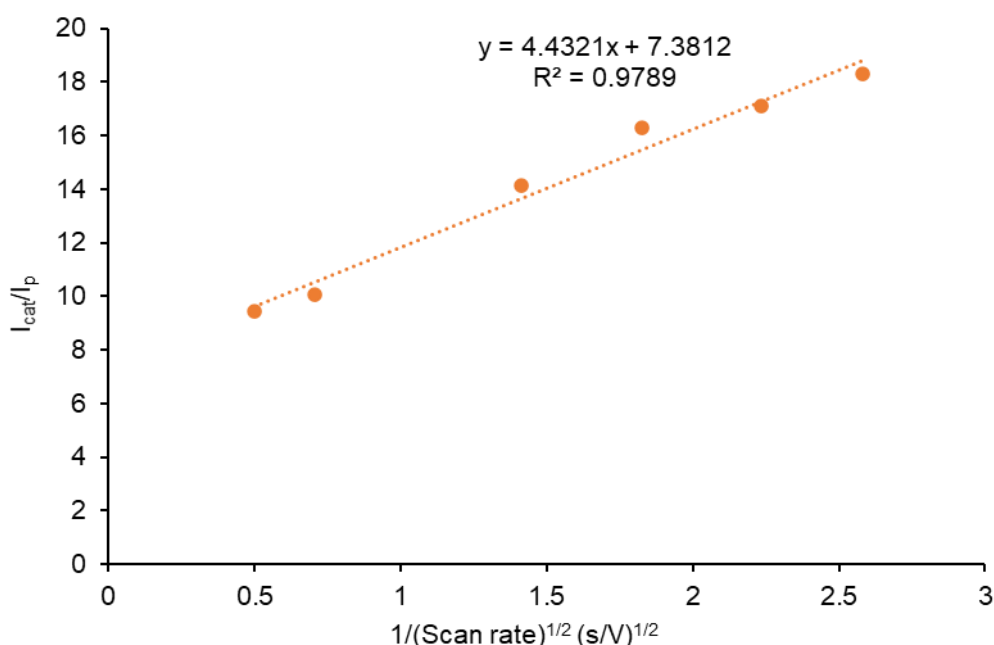


Figure 4.13: A graph of catalytic current/peak current (I_{cat}/I_p) as a function of $1/v^{1/2}$ studied using complex **C4.2**

4.2.3.3 pH dependence studies

The effect of pH on the Cu(I) catalysed electrocatalytic water oxidation was investigated using complex **C4.2** as shown in Figure 4.14. A decrease in the onset potential was observed upon increasing the pH from 4.0 to 6.5 consistent with a proton-coupled electron transfer (PCET) process.^{33, 50} The onset potential for water oxidation displays pH dependence with a slope of 44mV/pH (Figure 4.14 Inset).

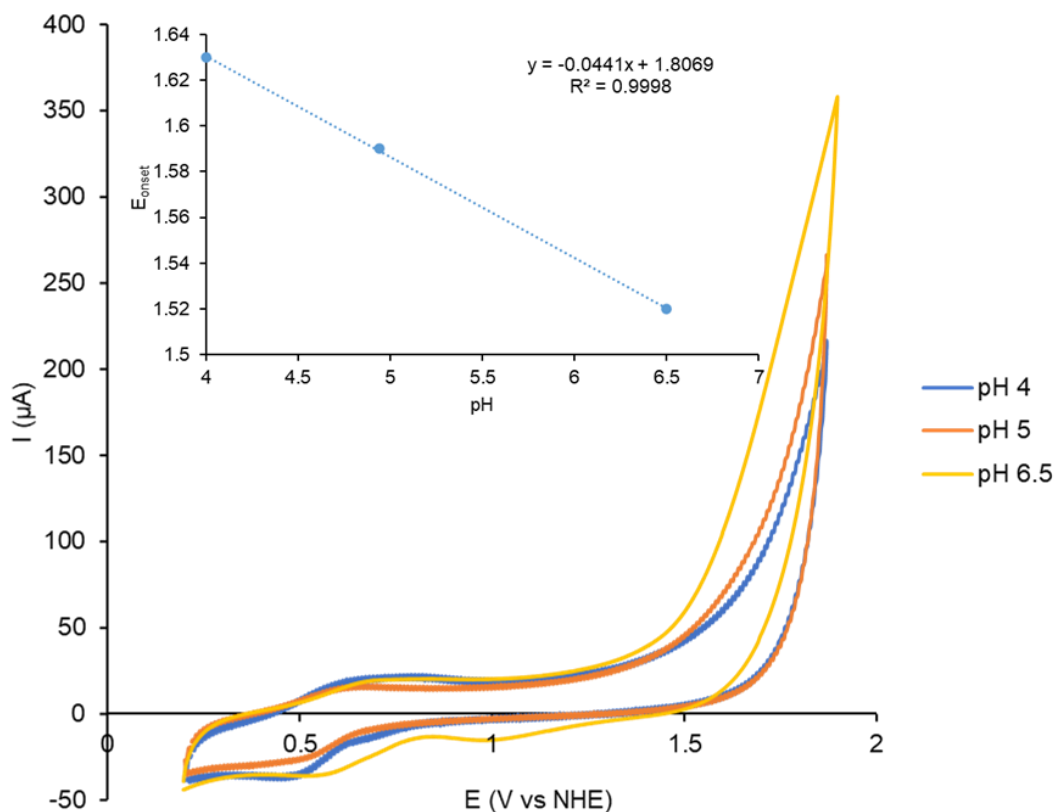


Figure 4.14: CVs showing the effect of pH on the activity of the catalyst studied by complex 0.42 mM **C4.2** in a mixture of MeCN and 20% (v/v) phosphate buffer (0.2 M) pH 4 to 6.5 recorded at a scan rate of 100 mV s⁻¹. Inset: The effect of pH on the onset potential studied in 0.42 mM **C4.2** a mixture of MeCN and 20% (v/v) phosphate buffer (0.2 M) pH. The onset potential was determined using the tangent method.

4.2.3.4 Evidence for homogeneous catalysis

Investigating the integrity of molecular WOCs is often necessary as there is a possibility of catalyst degradation and nanoparticle formation. In such cases, nanoparticles are the active species for water oxidation instead of the molecular catalyst.⁵⁶⁻⁵⁷ During electrocatalysis, no discolouration of the electrodes was observed and suggests that no electrodeposition of nanomaterials took place on the electrode. The absence of electrodeposition after six cycles was confirmed by using a rinsed electrode in a blank solution as shown in Figure 4.15. The current observed was the same as that of the new polished electrode, and therefore no

electrodeposition was observed after six cycles. The post-electrolysis solution of 0.42 mM **C4.2** in a mixture of MeCN and 20% (v/v) phosphate buffer (0.2 M, pH 6.5) was analysed by dynamic light scattering (DLS). The DLS results in Figure 4.16 show that there are no copper oxide nanoparticles generated in the solution. All the above-mentioned methods, which probed the true nature of the catalyst, proved that the catalyst is entirely homogeneous, and no heterogeneous species were observed.

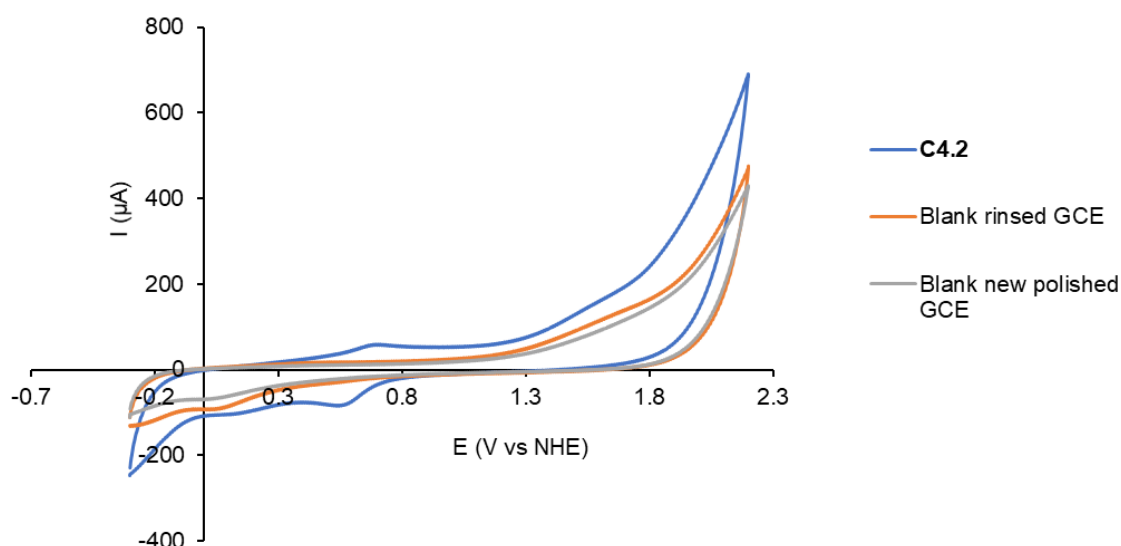
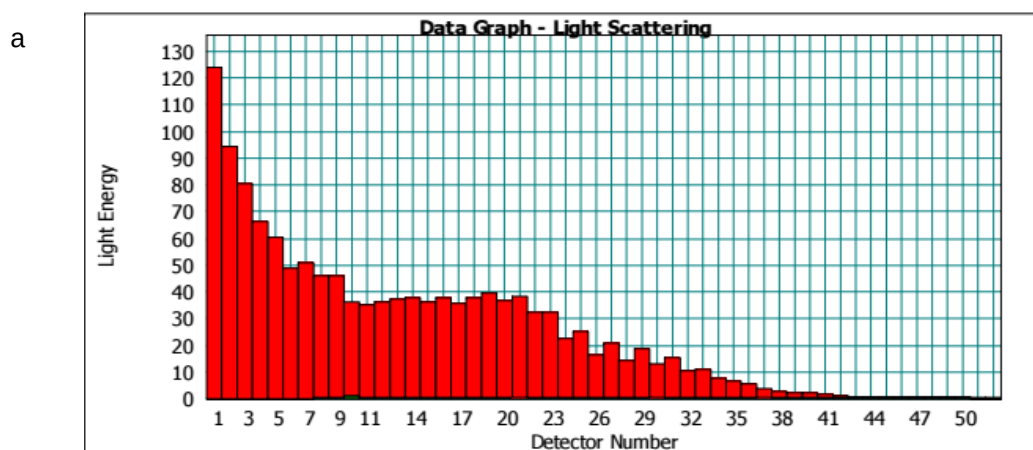


Figure 4.15: CVs in a mixture of MeCN and 20% (v/v) phosphate buffer (0.2 M, pH 6.5) of 0.42 mM **C4.2** (blue) after six cycles, followed by a rinsed electrode in a fresh blank solution (orange) and a new polished electrode in blank solution (grey), recorded at a scan rate of 100 mV s^{-1} .



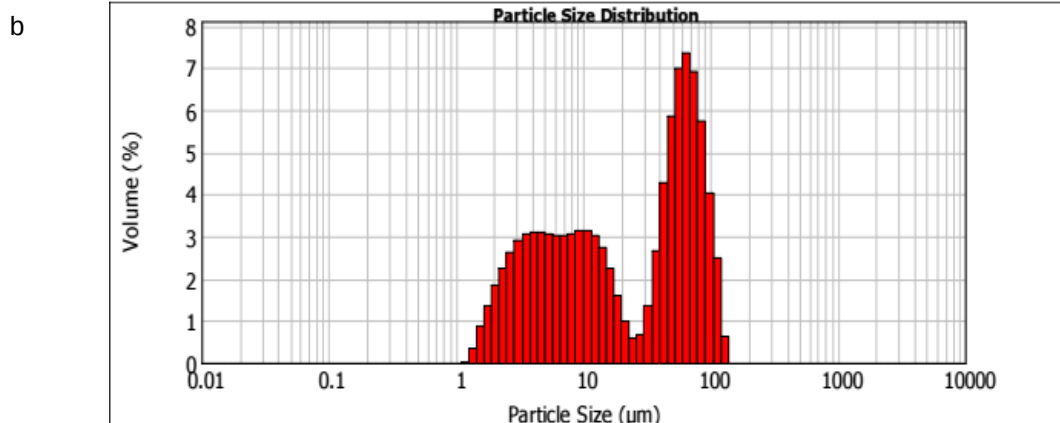


Figure 4.16: a Data graph of the background against a 0.42 mM **C4.2** in a mixture of MeCN and 20% (v/v) phosphate buffer (0.2 M, pH 6.5) in the absence of the electrolyte; b, particle distribution in the absence of the supporting electrolyte determined by DLS measurements post-electrolysis of 0.42 mM **C4.2** in a mixture of MeCN and 20% (v/v) phosphate buffer (0.2 M, pH 6.5)

4.2.3.5 Stability of the catalyst

The stability of the catalyst was investigated by scanning the electrolyte 150 times in the CV from -0.5 to +2V (Figure 4.17). The shape of the curve changed slightly as the number of cycles increased due to the formation of oxygen bubbles on the surface of the glassy carbon electrode, which interferes with the analysis. The current increased slightly after 33 cycles, which hinted at the formation of additional active species. Therefore, electrodeposition on the glassy carbon after 150 cycles was investigated by using a rinsed electrode in a fresh blank solution (Figure 4.18). A catalytic current was observed, which confirmed the electrodeposition of nanoparticles on the electrode surface, implying catalyst degradation over time and points to the catalyst not being stable over a long period.

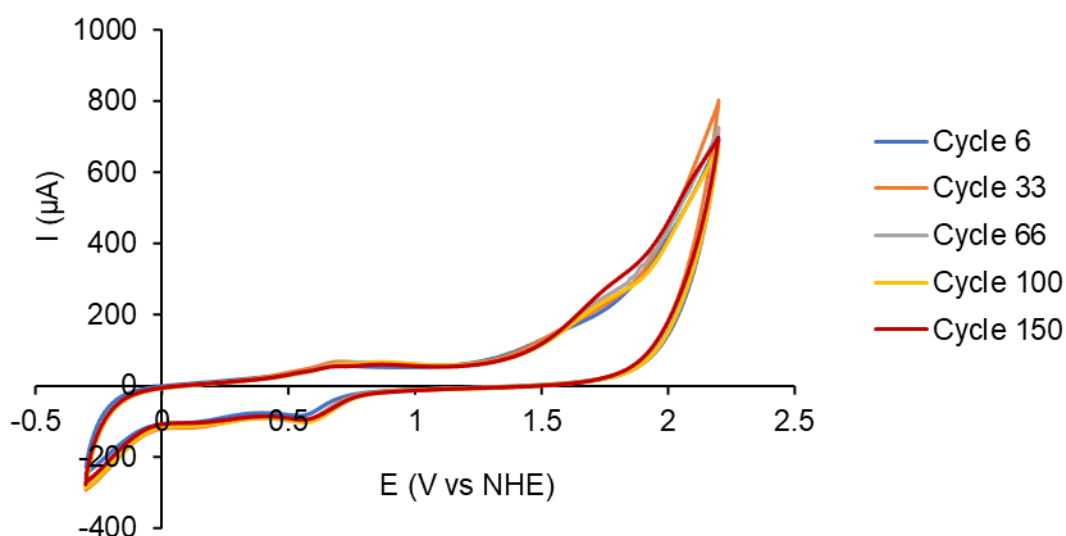


Figure 4.17: CVs in a mixture of MeCN and 20% (v/v) phosphate buffer (0.2 M, pH 6.5) of 0.42 mM **C4.2** scanned 150 times at a scan rate of 100 mV s⁻¹

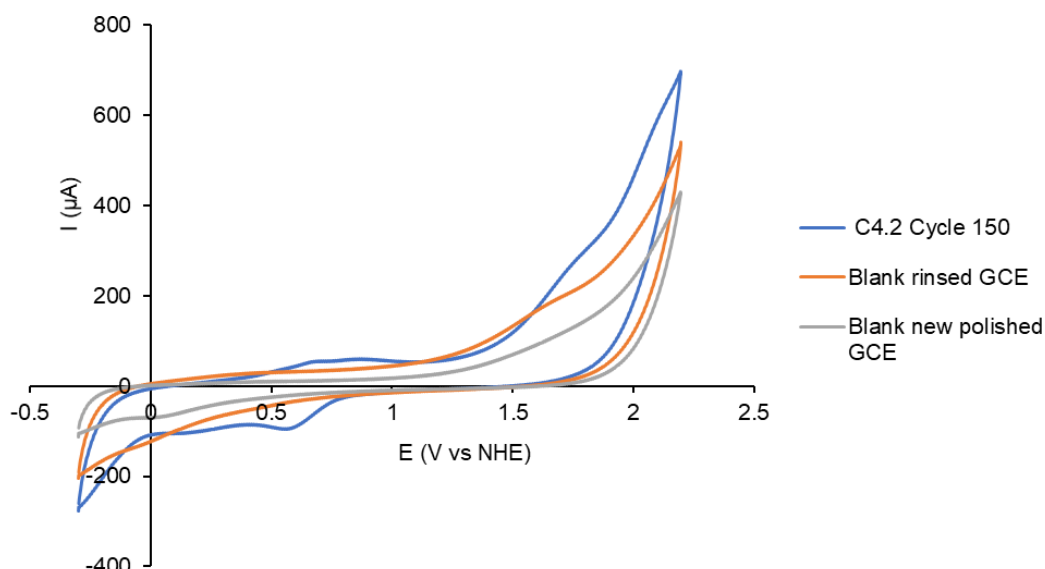


Figure 4.18: CVs in a mixture of MeCN and 20% (v/v) phosphate buffer (0.2 M, pH 6.5) of 0.42 mM **C4.2** (blue) after 150 cycles, followed by a rinsed electrode in a fresh blank solution (orange) and a new polished electrode in blank solution (grey), recorded at a scan rate of 100 mV s⁻¹.

4.3 Conclusions

Novel bis(pyrazol-1-ylmethyl)pyridine copper(I) complexes bearing different groups on the pyrazolyl moiety, **C4.1-C4.4**, were successfully synthesised and characterised. Complexes **C4.1-C4.4** show activity towards chemically driven water oxidation with CAN as the primary chemical oxidant. The complexes show stability under extremely acidic conditions of pH ~1. Complex **C4.2** bearing a methyl group on the pyrazole was the most active catalyst with a TON and TOF of 4.6 and 0.31 s⁻¹, respectively. The substituents on the pyrazolyl moiety had a significant influence on catalytic activity, with electron-donating groups resulting in higher activities. The initial rate order changes with catalyst concentration as the reaction is second-order at low [Cu], whereas at high [Cu] concentration the reaction is first order. Therefore, depending on [Cu], O-O bond formation proceeds via both the I2M and WNA mechanistic pathways. Complexes **C4.1-C4.4** were active for electrocatalytic water oxidation under applied potential differences in solutions of MeCN and phosphate buffer at near-neutral pH of 6.5. Complex **C4.2** resulted in the lowest overpotential of 674 mV and the highest TOF of 9.77 s⁻¹ among the four complexes, which, to the best of our knowledge, is better than most of the reported copper complexes that operate at neutral pH. The catalytic current at 1.7 V showed a linear dependence on the concentration of the catalyst, which suggests single-site water oxidation catalysis taking place via the WNA mechanism. A PCET process is involved in water oxidation since the onset potential decreased with increasing pH. The order of reactivity of the complexes between chemical and electrocatalytic water oxidation differed slightly due to different reaction conditions and corresponding different water oxidation mechanisms.

Regardless, complex **C4.2** was the most active among the catalysts evaluated in this study for both chemical and electrocatalytic water oxidation.

4.4 Experimental Section

4.4.1 General considerations

All moisture and oxygen-sensitive reactions were performed using Schlenk techniques. The solvents were distilled under a nitrogen atmosphere using Na metal for diethyl ether and CaH₂ for dichloromethane as drying agents. The metal precursor tetrakis(acetonitrile)copper(I) hexafluorophosphate (Cu(MeCN)₄PF₆) was purchased from Sigma Aldrich and used as received. The oxidants CAN (Sigma Aldrich), sodium-*m*-periodate (Sigma Aldrich), and sodium persulfate (Sigma Aldrich) were used as received. NMR (¹H and ¹³C) spectra were recorded on a Bruker Ultrashield Plus at 600 MHz and 151 MHz respectively. FTIR analysis was done on a Bruker Alpha-P range infrared instrument fitted with ATR in the range of 400 to 4000 cm⁻¹. Magnetic susceptibility studies were done using a Sherwood Scientific MK1 with 4mm diameter sample tubes containing 50 mM of the sample. Mass spectrometry was performed on Bruker microTOF-Q II mass spectrometer. Elemental analysis was performed on a Perkin Elmer 2400 Elemental Analyzer. CV studies were done on a BioLogic VSP potentiostat employing a water-jacketed electrochemical cell connected to a refrigerated temperature controller (Julabo F-12 ED). DLS studies were performed on a Mastersizer 2000 Ver. 5.60 from Malvern instruments.

4.4.2 Synthesis of complexes

4.4.2.1 Synthesis of complex **C4.1**

A solution of 2,6-bis(1H-pyrazol-1-yl)methylpyridine (**L1**, 0.060 g, 0.25 mmol) in 2.5 mL dichloromethane was added to a solution of tetrakis(acetonitrile)copper(I) hexafluorophosphate (Cu(MeCN)₄PF₆) (0.094 g, 0.25 mmol) in 2.5 mL dichloromethane. The resulting green solution was stirred under argon for 2 h at room temperature. The solution was reduced, and the addition of diethyl ether (3 x 10 mL) resulted in the precipitation of the complex, which was dried under vacuum. The complex was isolated as a green solid. Yield: 0.0978 g (88 %). FTIR (ATR) ν cm⁻¹: 1600 (C=N). ESI-MS (*m/z*): 302.05 [M]⁺. Analysis calc. (found) for C₁₃H₁₃CuF₆N₅P: C 34.87 (35.0); H 2.93 (3.21); N 15.64 (14.78).

4.4.2.2 Synthesis of complex **C4.2**

A solution of 2,6-bis((3,5-dimethyl-1H-pyrazol-1-yl)methyl)pyridine (**L2**, 0.074 g, 0.25 mmol) in 2.5 mL dichloromethane was added to a solution of tetrakis(acetonitrile)copper(I) hexafluorophosphate (Cu(MeCN)₄PF₆) (0.094 g, 0.25 mmol) in 2.5 mL dichloromethane. The resulting yellow solution was stirred under argon for 2 h at room temperature. The solution

was reduced, and the addition of diethyl ether (3 x 10 mL) resulted in the precipitation of the complex, which was dried under vacuum. The complex was isolated as a yellow solid. Yield: 0.0910 g (72 %). ^1H NMR (**C4.2**): (600 MHz, ppm, CD_2Cl_2): δ 2.43 (s, 6H, 5- CH_3 (pz)), 2.45 (s, 6H, 3- CH_3 (pz)), 5.21 (s, 4H, CH_2), 6.10 (s, 2H, 4-H (pz)), 7.61 (d, 2H, H_β (py)), $^2J_{\text{HH}} = 6.0$ Hz) 8.01 (t, 1H, H_γ (py), $^3J_{\text{HH}} = 6.0$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR: (150 MHz, ppm, CDCl_3): δ 12.07 (5- CH_3), 15.31 (3- CH_3), 51.57 (CH_2), 106.89 (4-C (pz)), 124.59 (C_β (py)) 138.38(C_γ (py)), 141.52 (3-C (pz)), 147.40 (5-C (pz)) 152.90 (C_q). ESI-MS (m/z): 358.11 $[\text{M}]^+$. FTIR (ATR) ν cm^{-1} : 1600 (C=N). Analysis calc. (found) for $\text{C}_{17}\text{H}_{21}\text{CuF}_6\text{N}_5\text{P}$: C 40.52 (40.16); H 4.20 (3.93); N 13.90 (13.24).

4.4.2.3 Synthesis of complex **C4.3**

A solution of 2,6-bis((3,5-di-*tert*-butyl-1H-pyrazol-1-yl)methyl)pyridine (**L3**, 0.116 g, 0.25 mmol) in 2.5 mL dichloromethane was added to a solution of tetrakis(acetonitrile)copper(I) hexafluorophosphate ($\text{Cu}(\text{MeCN})_4\text{PF}_6$) (0.094 g, 0.25 mmol) in 2.5 mL dichloromethane. The resulting yellow solution was stirred under argon for 2 h at room temperature. The solution was reduced, and the addition of diethyl ether (3 x 10 mL) resulted in the precipitation of the complex, which was dried under vacuum. The complex was isolated as a yellow solid. Yield: 0.1173 g (70%). ^1H NMR: (600 MHz, ppm, CDCl_3): δ 1.45 (s, 18H, 5-(CH_3)₃ (pz)), 1.54 (s, 18H, (3- CH_3)₃ (pz)), 5.53 (s, 4H, CH_2), 6.02 (s, 2H, 4-H (pz)), 7.68 (d, 2H, H_β (py), $^2J_{\text{HH}} = 6.0$ Hz) 7.97 (t, 1H, H_γ (py), $^3J_{\text{HH}} = 6.0$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR: (150 MHz, ppm, CDCl_3): δ 30.19 (5-(CH_3)₃), 31.35 (3-(CH_3)₃), 31.75 (5-C(CH_3)₃), 32.27 (3-C(CH_3)₃), 54.15(CH_2), 101.97 (4-C (pz)), 124.14 (C_β (py)) 141.05(C_γ (py)), 151.55 (5-C (pz)), 154.91(C_q), 162.45 (3-C (pz)). ESI-MS (m/z): 526.30 $[\text{M}]^+$. FTIR (ATR) ν cm^{-1} : 1604 (C=N). Analysis calc. (found) for $\text{C}_{29}\text{H}_{51}\text{CuF}_6\text{N}_5\text{O}_3\text{P}$: C 47.96 (47.45); H 7.08 (6.05); N, 9.64 (8.69).

4.4.2.4 Synthesis of complex **C4.4**

A solution of 2,6-(3,5-diphenyl-1H-pyrazol-1-yl)methyl)pyridine (**L4**, 0.136 g, 0.25 mmol) in 2.5 mL dichloromethane was added to a solution of tetrakis(acetonitrile)copper(I) hexafluorophosphate ($\text{Cu}(\text{MeCN})_4\text{PF}_6$) (0.094 g, 0.25 mmol) in 2.5 mL dichloromethane. The resulting yellow solution was stirred under argon for 2 h at room temperature. The solution was reduced, and the addition of diethyl ether (3 x 10 mL) resulted in the precipitation of the complex, which was dried under vacuum. The complex was isolated as a yellow solid. Yield: 0.1220 g (65 %) ^1H NMR: (600 MHz, ppm, Acetone- d_6): δ 5.71 (s, 4H, CH_2), 7.09 (s, 2H, 4-H (pz)), 7.35(d, 2H, H_γ , $^2J_{\text{HH}} = 6$ Hz), 7.63-7.68 (m, 16H, Ph(H)) 7.97 (t, 1H, H_γ , $^3J_{\text{HH}} = 6.0$ Hz) 8.11 (d, 4H, Ph(H), $J_{\text{HH}} = 12$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR: (150 MHz, ppm, Acetone- d_6): δ 53.12 (CH_2), 128.42(4-C (pz)), 129.64 (C_β (py)) 130.25(C_γ (py)), 130.39 (3-C (pz)), 131.12 (5-C (pz)) 132.39 (C_q) . ESI-MS (m/z): 606.17 $[\text{M}]^+$. FTIR (ATR) ν cm^{-1} : 1597 (C=N). Analysis calc. (found) for $\text{C}_{37}\text{H}_{31}\text{CuF}_6\text{N}_5\text{OP}$: C 57.70 (57.85); H 4.06 (4.34); N, 9.09 (8.45).

4.4.3 Crystallographic data collection

Single crystals of **C4.2**, **C4.3**, and **C4.4** were mounted on a nylon loop and centred in a stream of liquid nitrogen at 293(2) K. Crystal evaluation and data collection were performed on a Bruker D8 Quest Eco diffractometer with Mo K α radiation (λ = 0.71073 Å). Data collection, reduction, and refinement were performed using SAINT⁵⁸ and SADABS,⁵⁹ which form part of the APEX3 software package.⁶⁰ The structures were solved by direct methods and refined by full-matrix least-squares on F^2 using SHELX-2016⁶¹ within the X-seed graphic user interface.⁶²⁻
⁶³ All non-hydrogen atoms were refined anisotropically and all hydrogen atoms were placed using calculated positions and riding models. Crystal structure data for complexes **C4.2-C4.4**, with accession numbers CCDC 2034903-2034905, is available from the CCDC.

4.4.4 Chemical water oxidation

Oxygen evolution reactions were performed using a standard Clark-type oxygraph electrode (Hansatech Instruments) placed in a thermostated cell (25 °C) for all measurements. The signal was recorded for the entire duration of the experiment at 1.0 s intervals using the Oxygraph+ software (Hansatech Instruments). The signal was calibrated using a mixture (1:1) of acetonitrile and water ($[O_2]$ = 261 μ M, 25 °C).⁶⁴ Stock solutions of the catalysts were freshly prepared by dissolving the complex in acetonitrile. The stock solution was then degassed with argon to ensure an oxygen-free solution. Following the addition of the CAN, the cell was purged with argon before catalyst addition.

4.4.5 Electrocatalytic water oxidation

CV technique was carried out for electrochemical characterisation of the electrocatalysts employing a conventional water-jacketed three-electrode electrochemical cell connected to a refrigerated temperature controller (Julabo F-12 ED). The counter electrode used was the platinum wire (Bio-Logic) and the reference electrode was a Ag/AgCl electrode (Bio-Logic). A glassy carbon electrode disc insert (Sigradur G, HTW Germany) with a geometrical area of 0.196 cm² was used as the working electrode. Before performing experiments, the glassy carbon was polished with 0.05 μ M alumina suspension (Gamma Micropolish II, Buehler) and was subsequently washed with Milli-Q water, ethanol (Merck), and isopropanol (Merck). The working electrode was assembled into a rotating disc electrode setup. Current Potential curves of the samples were recorded using a VSP double-channel potentiostat from biologic science instruments. Current Potential curves of the samples were recorded using a VSP double-channel potentiostat from BioLogic Science Instruments.

4.5 References

1. Hayashi, H.; Fujinami, S.; Nagatomo, S.; Ogo, S.; Suzuki, M.; Uehara, A.; Watanabe, Y.; Kitagawa, T., *J. Am. Chem. Soc.* **2000**, *122* (9), 2124-2125.
2. Lewis, E. A.; Tolman, W. B., *Chem. Rev.* **2004**, *104* (2), 1047-1076.
3. Maiti, D.; Woertink, J. S.; Narducci Sarjeant, A. A.; Solomon, E. I.; Karlin, K. D., *Inorg. Chem.* **2008**, *47* (9), 3787-3800.
4. Mirica, L. M.; Ottenwaelder, X.; Stack, T. D. P., *Chem. Rev.* **2004**, *104* (2), 1013-1046.
5. Yu, W.-B.; He, Q.-Y.; Ma, X.-F.; Shi, H.-T.; Wei, X., *Dalton Trans.* **2015**, *44* (1), 351-358.
6. Fisher, K. J.; Materna, K. L.; Mercado, B. Q.; Crabtree, R. H.; Brudvig, G. W., *ACS Catal.* **2017**, *7* (5), 3384-3387.
7. Koepke, S. J.; Light, K. M.; Vannatta, P. E.; Wiley, K. M.; Kieber-Emmons, M. T., *J. Am. Chem. Soc.* **2017**, *139* (25), 8586-8600.
8. Lukács, D.; Szyrwił, Ł.; Pap, J. S., *Catalysts* **2019**, *9* (1), 83.
9. Praneeth, V. K. K.; Kondo, M.; Woi, P. M.; Okamura, M.; Masaoka, S., *ChemPlusChem* **2016**, *81* (10), 1123-1128.
10. Rudshiteyn, B.; Fisher, K. J.; Lant, H. M.; Yang, K. R.; Mercado, B. Q.; Brudvig, G. W.; Crabtree, R. H.; Batista, V. S., *ACS Catal.* **2018**, *8* (9), 7952-7960.
11. Shen, J.; Wang, M.; Zhang, P.; Jiang, J.; Sun, L., *Chem. Commun.* **2017**, *53* (31), 4374-4377.
12. Barnett, S. M.; Goldberg, K. I.; Mayer, J. M., *Nat. Chem.* **2012**, *4* (6), 498-502.
13. Najafpour, M. M.; Ebrahimi, F.; Safdari, R.; Ghobadi, M. Z.; Tavahodi, M.; Rafighi, P., *Dalton Trans.* **2015**, *44* (35), 15435-15440.
14. Li, T.-T.; Zheng, Y.-Q., *Dalton Trans.* **2016**, *45* (32), 12685-12690.
15. Lu, C.; Du, J.; Su, X.-J.; Zhang, M.-T.; Xu, X.; Meyer, T. J.; Chen, Z., *ACS Catal.* **2016**, *6* (1), 77-83.
16. Ojwach, S. O.; Guzei, I. A.; Benade, L. L.; Mapolie, S. F.; Darkwa, J., *Organometallics* **2009**, *28* (7), 2127-2133.
17. Watson, A. A.; House, D. A.; Steel, P. J., *Inorg. Chim. Acta* **1987**, *130* (2), 167-176.
18. Arayne, M. S.; Sultana, N.; Khan, M. A.; Malik, A., *Pak. J. Pharm. Sci.* **2002**, *15* (2), 69-79.
19. Jaramillo-Fierro, X.; Zambrano, C.; Fernández, F.; Saez-Puche, R.; Costa, C.; Guerrero, V.; González, S., *Univ. Sci.* **2018**, *23* (2), 241-266.
20. Hamann, J. N.; Herzigkeit, B.; Jurgeleit, R.; Tuczec, F., *Coord. Chem. Rev.* **2017**, *334*, 54-66.

21. Mobinkhaledi, A.; Foroughifar, N.; Hogabry, B.; Zamani, K., *J. Chem. Soc. Pak.* **2002**, 24 (2), 149-151.
22. Rolff, M.; Schottenheim, J.; Decker, H.; Tuczek, F., *Chem. Soc. Rev.* **2011**, 40 (7), 4077-4077.
23. Sánchez-Viveros, J. M.; Bucio-Ortega, J.; Ortiz-Pastrana, N.; Olguín, J., *New J. Chem.* **2019**, 43 (25), 9776-9783.
24. Wang, S.; Du, S.; Zhang, W.; Asuha, S.; Sun, W. H., *ChemistryOpen* **2015**, 4 (3), 328-334.
25. Halcrow, M. A., *Crystals* **2016**, 6 (5), 58.
26. Chen, Y.; Chen, J. S.; Gan, X.; Fu, W. F., *Inorg. Chim. Acta* **2009**, 362 (7), 2492-2498.
27. Lutz M. Engelhardt, C. P.; Allan, H. W., *J. Chem. Soc., Dalton Trans.* **1985**, 1, 117-123.
28. Uber, J. S.; Vogels, Y.; Van Den Helder, D.; Mutikainen, I.; Turpeinen, U.; Fu, W. T.; Roubeau, O.; Gamez, P.; Reedijk, J., *Eur. J. Inorg. Chem.* **2007**, (26), 4197-4206.
29. Abdel-Magied, A. F.; Arafa, W. A. A.; Laine, T. M.; Shatskiy, A.; Kärkäs, M. D.; Åkermark, B.; Johnston, E. V., *ChemCatChem* **2017**, 9 (9), 1583-1587.
30. Navarro, M.; Smith, C. A.; Li, M.; Bernhard, S.; Albrecht, M., *Chem. Eur. J.* **2018**, 24 (24), 6386-6398.
31. Wanniarachchi, D. C.; Heeg, M. J.; Verani, C. N., *Inorg. Chem.* **2014**, 53 (7), 3311-3319.
32. Das, B.; Ezzedinloo, L.; Bhadbhade, M.; Bucknall, M. P.; Colbran, S. B., *Chem. Commun.* **2017**, 53 (72), 10006-10009.
33. Zhang, M. T.; Chen, Z.; Kang, P.; Meyer, T. J., *J. Am. Chem. Soc.* **2013**, 135 (6), 2048-2051.
34. Blakemore, J. D.; Schley, N. D.; Balcells, D.; Hull, J. F.; Olack, G. W.; Incarvito, C. D.; Eisenstein, O.; Brudvig, G. W.; Crabtree, R. H., *J. Am. Chem. Soc.* **2010**, 132 (45), 16017-16029.
35. Duan, L.; Araujo, C. M.; Ahlquist, M. S.; Sun, L., *PNAS* **2012**, 109 (39), 15584-15588.
36. Shaffer, D. W.; Xie, Y.; Concepcion, J. J., *Chem. Soc. Rev.* **2017**, 46 (20), 6170-6193.
37. Fillol, J. L.; Codolà, Z.; Garcia-Bosch, I.; Gàmez, L.; Pla, J. J.; Costas, M., *Nat. Chem.* **2011**, 3 (10), 807-813.
38. Panchbhai, G.; Singh, W. M.; Das, B.; Jane, R. T.; Thapper, A., *Eur. J. Inorg. Chem.* **2016**, 2016 (20), 3262-3268.
39. Shaffer, D. W.; Xie, Y.; Szalda, D. J.; Concepcion, J. J., *Inorg. Chem.* **2016**, 55 (22), 12024-12035.
40. Codolà, Z.; Gómez, L.; Kleespies, S. T.; Que Jr, L.; Costas, M.; Lloret-Fillol, J., *Nat. Commun.* **2015**, 6 (1), 1-10.

41. Garrido-Barros, P.; Moonshiram, D.; Gil-Sepulcre, M.; Pelosin, P.; Gimbert-Suriñach, C.; Benet-Buchholz, J.; Llobet, A., *J. Am. Chem. Soc.* **2020**, *142* (41), 17434-17446.
42. Prevedello, A.; Bazzan, I.; Dalle Carbonare, N.; Giuliani, A.; Bhardwaj, S.; Africh, C.; Cepek, C.; Argazzi, R.; Bonchio, M.; Caramori, S., *Chem. Asian J.* **2016**, *11* (8), 1281-1287.
43. Su, X. J.; Gao, M.; Jiao, L.; Liao, R. Z.; Siegbahn, P. E.; Cheng, J. P.; Zhang, M. T., *Angew. Chem.* **2015**, *127* (16), 4991-4996.
44. Olivares, M.; van der Ham, C. J.; Mdluli, V.; Schmidtendorf, M.; Müller-Bunz, H.; Verhoeven, T. W.; Li, M.; Niemantsverdriet, H. J.; Hetterscheid, D. G.; Bernhard, S., *Eur. J. Inorg. Chem.* **2020**, *2020*, 801-812.
45. Das, B.; Thapper, A.; Ott, S.; Colbran, S. B., *Sustain. Energy Fuels* **2019**, *3* (9), 2159-2175.
46. Liu, Y.; Han, Y.; Zhang, Z.; Zhang, W.; Lai, W.; Wang, Y.; Cao, R., *Chem. Sci.* **2019**, *10* (9), 2613-2622.
47. Coggins, M. K.; Zhang, M. T.; Chen, Z.; Song, N.; Meyer, T. J., *Angew. Chem. Int. Ed.* **2014**, *53* (45), 12226-12230.
48. Su, X.-J.; Zheng, C.; Hu, Q.-Q.; Du, H.-Y.; Liao, R.-Z.; Zhang, M.-T., *Dalton Trans.* **2018**, *47* (26), 8670-8675.
49. Chen, F.; Wang, N.; Lei, H.; Guo, D.; Liu, H.; Zhang, Z.; Zhang, W.; Lai, W.; Cao, R., *Inorg. Chem.* **2017**, *56* (21), 13368-13375.
50. Nestke, S.; Ronge, E.; Siewert, I., *Dalton Trans.* **2018**, *47* (31), 10737-10741.
51. Wang, J.; Huang, H.; Lu, T., *Chin. J. Chem.* **2017**, *35* (5), 586-590.
52. Kafentzi, M. C.; Papadakis, R.; Gennarini, F.; Kocher, A.; Iranzo, O.; Le Mest, Y.; Le Poul, N.; Tron, T.; Faure, B.; Simaan, A. J., *Chem. Eur. J.* **2018**, *24* (20), 5213-5224.
53. Bard, A. J.; Faulkner, L. R., *Electrochemical Methods* **2001**, *2* (482), 580-632.
54. Savéant, J.-M., *Chem. Rev.* **2008**, *108* (7), 2348-2378.
55. Zanello, P.; Nervi, C.; de Biani, F. F., *Practice and Application*, RSC, Cambridge, UK **2003**.
56. Schley, N. D.; Blakemore, J. D.; Subbaiyan, N. K.; Incarvito, C. D.; D'Souza, F.; Crabtree, R. H.; Brudvig, G. W., *J. Am. Chem. Soc.* **2011**, *133* (27), 10473-10481.
57. Stracke, J. J.; Finke, R. G., *J. Am. Chem. Soc.* **2011**, *133* (38), 14872-14875.
58. *SAINT, Version 8.38A*; Bruker AXS Inc: 2017.
59. Sheldrick, G. *SADABS, Version 2012/1*; Bruker AXS Inc: 2012.
60. *APEX3, Version 2017.3*; Bruker AXS Inc: 2017.
61. Sheldrick, G., *Acta Crystallogr., Sect. C: Struct. Chem.* **2015**, *71* (1), 3-8.
62. Atwood, J. L.; Barbour, L. J., *Cryst. Growth Des.* **2003**, *3* (1), 3-8.
63. Barbour, L. J., *J. Supramol. Chem.* **2001**, *1* (4), 189-191.

64. Truesdale, G. A.; Downing, A. L., *Nature* **1954**, 173 (4417), 1236-1236.

.

Chapter 5: Synthesis, characterization, and catalytic evaluation of bis(pyrazol-1-ylmethyl)pyridine-ligated Co(II) complexes in water oxidation reactions.

5.1 Introduction

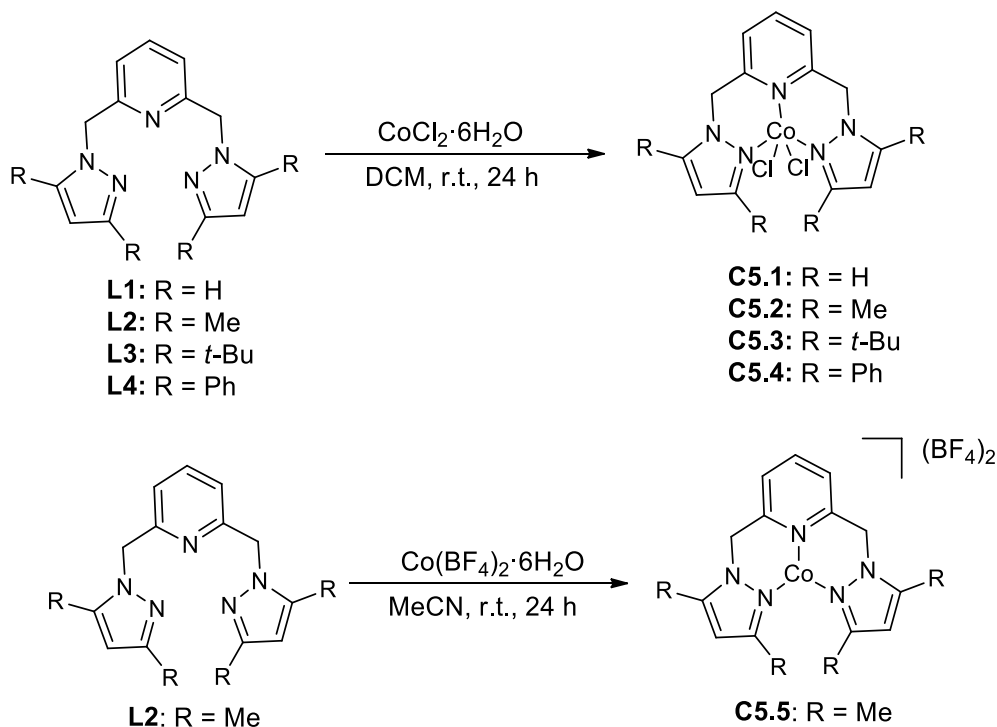
Cobalt is one of the transition metals of interest in the development of WOCs. Owing to its abundance and ability to readily change its oxidation state, which is an attractive feature for water oxidation. Cobalt oxides have been explored as water oxidation catalysts, however, they are not efficient.¹⁻³ Among the first-row transition metals, cobalt has the highest oxidation potential of 1.84 V vs NHE, which makes it unfavourable to oxidise Co(II) without a ligand to stabilise Co(III). Therefore, the ligand plays an important role in cobalt-mediated water oxidation. The interest in cobalt-based water oxidation catalysts has been on the rise with more cobalt electrocatalysts reported than chemical and photochemically-driven water oxidation catalysts. Wang and co-workers⁴ reported on a cobalt porphyrin complex that is efficient towards electrocatalytic water oxidation at an overpotential of 920 mV under mild conditions at neutral pH. The homogeneity of the catalyst was confirmed using various characterisation techniques. The critical role that the buffer plays, which is accepting protons during the O-O bond formation was established.⁴ Wang *et al.*⁵ reported the most active cobalt electrocatalyst, an N, N'-bis(2'-pyridinecarboxamide)-1,2-benzene ligated cobalt(II) complex with a TOF of 81.54 s⁻¹. The complex catalysed water oxidation at an overpotential of 560 mV at pH 8.6. Another homogeneous cobalt electrocatalyst ([L₂Co^{II}(CH₃OH)₄] L = (E)-4-((2-hydroxynaphthalen-1-yl)diazinyl)benzenesulfonate), which catalysed electrocatalytic water oxidation at an overpotential of 520 mV with a TOF of 5 s⁻¹ at pH 9 was reported by Shi *et al.*⁶ Investigations into the nature of the catalyst proved that the catalyst was entirely homogeneous. One of the drawbacks in the development of cobalt molecular water oxidation catalysts is the decomposition of the ligands under electrochemical conditions, which leads to the formation of oxides that are also active in water oxidation. There has been a considerable amount of cobalt complexes that have been previously reported as stable homogeneous water oxidation catalysts, which after further investigations, revealed that heterogeneous CoO_x species were involved in water oxidation.⁷⁻¹³ A dinuclear cobalt complex (TPA)Co-(μ-OH)(μ-O₂)Co(TPA)](ClO₄)₃ (TPA = tris(2-pyridylmethyl)amine) was reported as a homogeneous molecular catalyst in photochemical water oxidation.¹⁰ Investigations of the complex using several characterisation methods such as scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy-dispersive X-ray spectroscopy (EDX), and electrochemical methods revealed the possibility of CoO_x catalysing water oxidation. Safdari *et al.*⁸ studied a cobalt complex [Co^{III}(DPKOH)₂]Cl (DPK = di(2-pyridyl)ketone) previously

reported as a homogeneous photochemical water oxidation catalyst by Zhao *et al.*¹³ Characterisation techniques such as cyclic voltammetry (CV) and SEM-EDX confirmed the presence of cobalt-based species of the fluorine-doped tin oxide (FTO) electrode, which could be responsible for water oxidation. Investigating the stability of a molecular water oxidation catalyst is important as there is a possibility of ligand decomposition, resulting in the deposition of CoO_x film on the surface of the working electrode, which behaves as a heterogeneous water oxidation catalyst. Most of the reports on homogeneous cobalt complexes are on photochemical water oxidation.¹⁴ Das *et al.*¹⁵ reported a cobalt(II) complex, [Co^{II}(Py5OH)(Cl)](BF₄) (Py5 = 2,6-bis(methoxydi(pyridin-2-yl)methyl)pyridine) that showed activity towards photochemical water oxidation in the presence of Ru^{II}(bpy)₃²⁺ and Na₂S₂O₃ resulting in a TON of 51 and TOF of 1.3 s⁻¹. The catalytic activity of the complex was also studied in chemical water oxidation using Ru^{II}(bpy)₃²⁺ as the primary oxidant resulting in a TON of 15. To the best of our knowledge, there are no reports on chemically-driven water oxidation with Co(II) using the readily available and inexpensive CAN.

Herein we report the synthesis and characterisation of five cobalt complexes, **C5.1** to **C5.5**, and their ability to catalyse electrocatalytic water oxidation with the emphasis on their stability as homogeneous water oxidation catalysts. The complexes are also investigated in chemically-driven water oxidation with CAN as the primary oxidant

5.2 Results and discussion

5.2.1 Synthesis and characterisation of cobalt complexes C5.1 to C5.5



Scheme 5.1: Cobalt complexes investigated towards chemical and electrocatalytic water oxidation.

Cobalt complexes **C5.1** to **C5.4** were synthesised by reacting previously synthesised ligands (**L1-L4**) and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in dichloromethane. Complexes **C5.1-C5.4** have been reported before¹⁶, whereas complex **C5.5** is novel. Complex **C5.5** was synthesised from **L2** and $\text{Co}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ in acetonitrile (Scheme 5.1). The complexes were obtained in moderate to good yields; **C5.1** (83%), **C5.2** (71%), **C5.3** (62%), **C5.4** (48%), **C5.5** (87%). The complexes were successfully characterised using analytical techniques such as FTIR, elemental analysis, and magnetic susceptibility.

Table 5.1: FTIR stretching frequencies of (C=N) (py) in the ligands and complexes.

Ligand	(C=N) (py) ν cm^{-1}	Complex	(C=N) (py) ν cm^{-1}
L1	1596	5.1	1601
L2	1579	5.2	1605
L3	1593	5.3	1610
L4	1575	5.4	1607
L2	1579	5.5	1604

FTIR confirmed the coordination through the pyridine C=N wherein the stretching frequencies of C=N (pyridine) of the ligands were compared to that of the complexes as illustrated in Table 5.1. There was a shift from lower wavenumbers in the ligands (**L1-L4**) to higher wavenumbers in complexes **C5.1** to **C5.5**. Magnetic susceptibility studies for complexes **C5.1** to **C5.5** were done in solution at room temperature (22-25 °C). Complexes **C5.1**, **C5.2**, and **5.5** were dissolved in acetonitrile, while complexes **C5.3** and **C5.4** were dissolved in dichloromethane. The magnetic moments (μ_{eff}) of complexes **C5.2** to **C5.5** ranged from 4.61 to 5.68 BM and for complex **C5.1** the μ_{eff} was 1.93 BM, which occurs in less common situations. These values show that the complexes are paramagnetic with a +2 oxidation state of the metal (Co^{2+}) and a d^7 configuration with three unpaired electrons (high-spin complexes). Complex **C5.1** was an exception with a d^7 configuration with one unpaired electron (low-spin complex). The μ_{eff} values are in range with reported Co complexes with a +2 oxidation state.¹⁷⁻¹⁹

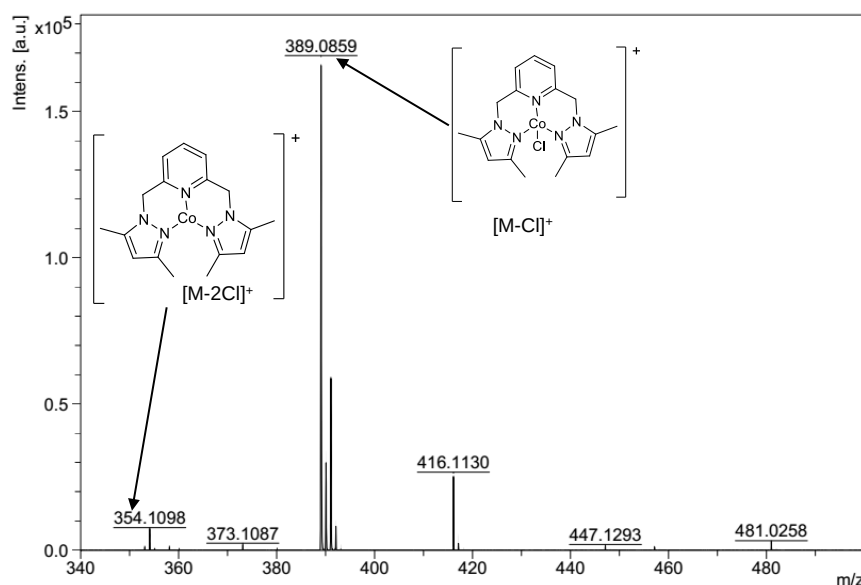
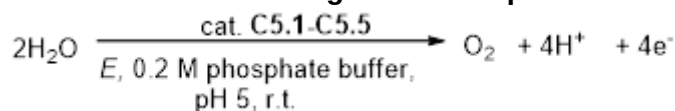


Figure 5.1: ESI-MS spectrum of complex **C5.2** showing the subsequent loss of chloride anions.

ESI-MS spectroscopy was also used to characterise the complexes with an example of a fragmentation pattern of **C5.2** shown in Figure 5.1. The pattern shows the subsequent loss of the chloride anions with $[M-Cl]^+$ having a m/z of 389.0859 and $[M-2Cl]^+$ with a m/z of 354.1098. Complex **C5.1**, **C5.3**, and **C5.4** showed a loss of a chloride ion with a m/z of 332.95, 557.42, and 637.15 respectively. Complex **C5.5** showed a bound water molecule $[(M+H)\cdot H_2O]^+$ with a m/z of 373.11. Elemental analysis confirmed the purity of the complexes and illustrate the hygroscopic nature of the complexes. Although the complexes were thoroughly dried and stored under argon in the glove box, almost all the complexes contained a few molecules of water. The complexes could easily absorb moisture from the environment during analysis. This is not unusual as the complexes were synthesised from hydrates and therefore have a high affinity for water molecules.

5.2.2 Electrocatalytic water oxidation using cobalt complexes C5.1-C5.5



Scheme 5.2: Electrocatalytic water oxidation of cobalt complexes **C5.1** to **C5.5** in phosphate buffer at pH 5

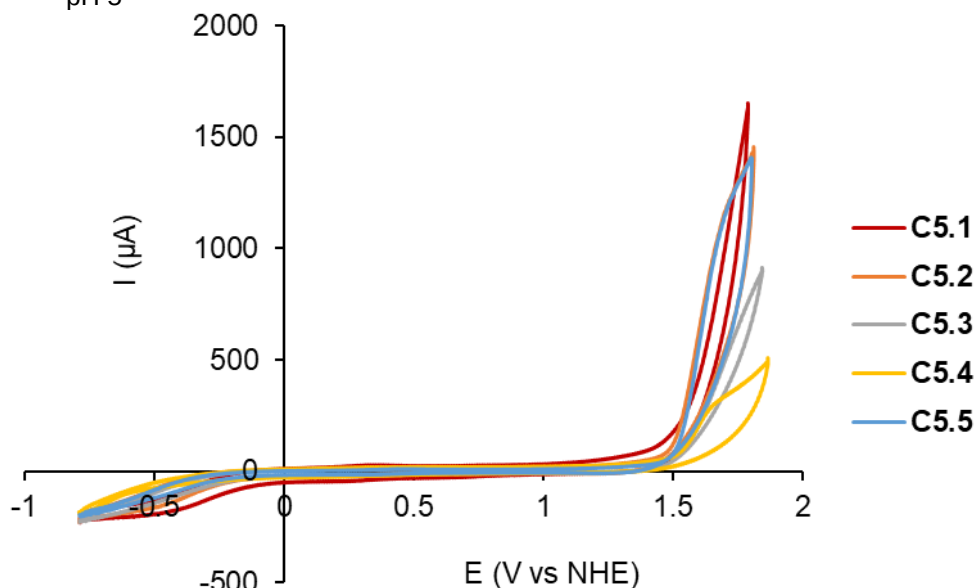


Figure 5.2: CVs of cobalt complexes **C5.1** to **C5.5** (0.1 mM) in 0.2 M phosphate buffer at pH 5 recorded at a scan rate of 100 mV s⁻¹.

The Co(II) complexes **C5.1** to **C5.5** were evaluated towards electrocatalytic water oxidation in phosphate buffer (Scheme 5.2) using CV (Figure 5.2). Co(II) complexes **C5.1-C5.5** are water-soluble and readily dissolve in phosphate buffer solutions. The solution of complexes dissolved in 0.2 M phosphate buffer was degassed with nitrogen for 15 minutes before each experiment. The CVs were obtained under air using a glassy carbon working electrode (GCE), Ag/AgCl reference electrode, and a platinum wire counter electrode. The RDE was rotated at 3 000 rpm to avoid the accumulation of oxygen bubbles on the GCE surface. Potentials were

measured versus Ag/AgCl electrode and are reported versus NHE through the addition of +0.199 V to the measured potential. Upon scanning solutions of 0.1 mM in 0.2 M phosphate buffer at pH 5 at 100 mV.s⁻¹ from -1.0 to +1.7 V, all complexes **C5.1** to **C5.5** exhibited a reversible oxidation peak between $E_{1/2} = +0.26$ V and +0.40 V assigned to the Co(III)/Co(II) redox couple.⁶ The reversible Co(III)/Co(II) redox couple was followed by a large irreversible wave with onset potentials ranging from +1.50 V to +1.57 V (vs NHE). The irreversible peak is due to the oxidation of Co(III) to Co(IV)²⁰⁻²¹ species and the wave is visible in a CV performed in a solution of 0.1 M NBu₄PF₆ and DMF (Figure 5.3). The addition of 5% (v/v) of 0.2 M phosphate buffer at pH 5 resulted in an increase in current and the well-defined Co(IV) irreversible peak disappears, which is as a result of the formation of a high valent cobalt oxo Co^{IV}(O) responsible for water oxidation.²²

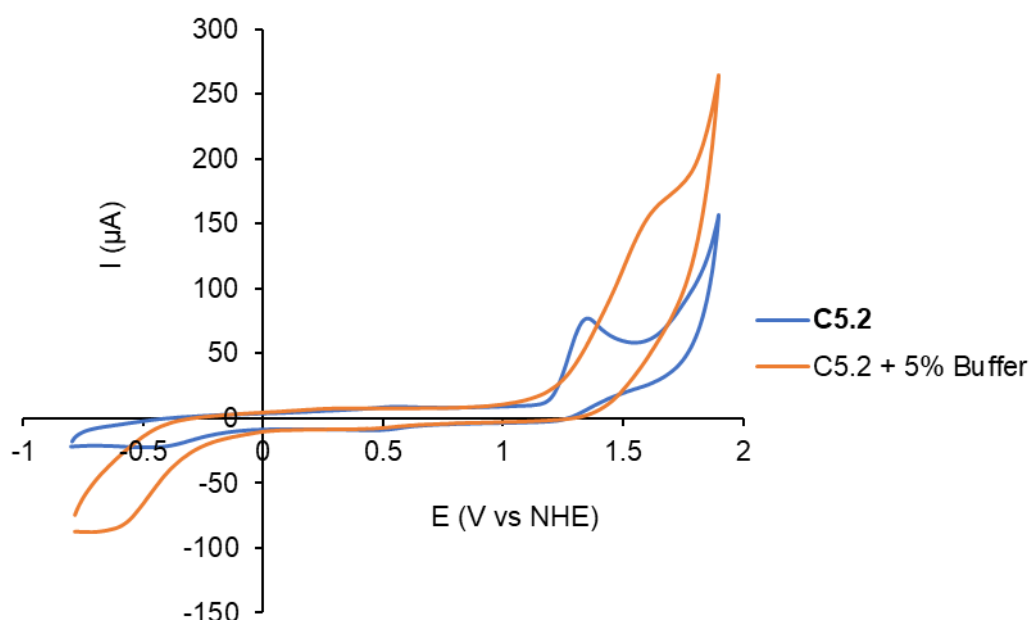


Figure 5.3: CVs of complex **C5.2** (0.5 mM) performed in 0.1 M Bu₄NPF₆ in DMF (Blue) and **C5.2** performed in 0.1 M Bu₄NPF₆ in DMF with added 5% (v/v) phosphate buffer at pH 5 recorded at a scan rate of 100 mV s⁻¹.

5.2.2.1 The effect of catalyst structure on electrocatalytic water oxidation

The activities of complexes **C5.1-C5.5** were compared to previous studies based on overpotential and TOF as summarised in Table 5.2. Complex **C5.2** and **C5.5** had the lowest overpotential of 565 mV. These complexes bear the methyl-substituted pyrazole on the ligand. The low overpotential is attributed to the electron-donating ability of the methyl groups in the complex. Complexes **C5.2** and **C5.5** have the same ligand but differ in the anionic species with chloride anion in complex **C5.2** and tetrafluoroborate in complex **C5.5**. Complex **C5.5** had the highest TOF of 855 s⁻¹, which suggests that the anion in the complex affected the efficiency of the catalyst. This TOF is the highest in comparison to the reported Co electrocatalysts,

either homogeneous or heterogeneous as observed in Table 5.2 (entries 5-7). Complex **C5.3** with bulky tertiary butyl on the pyrazole had resulted in the highest overpotential of 635 mV followed by complex **C5.4** containing electron-withdrawing phenyl substituted pyrazole on the ligand framework, which catalysed water oxidation at an overpotential of 625 mV. Although complex **C5.4** had slightly lower overpotential in comparison to **C5.3**, complex **C5.4** had the lowest TOF of 75 s⁻¹.

Table 5.2: A summary of activities of Co complexes **C5.1** to **C5.5** in comparison to previous studies

Entry	Complexes	PH	Overpotential ^a /mV	TOF /s ⁻¹	Reference
1	C5.1	5	585	119	This work
2	C5.2	5	565	326	This work
3	C5.3	5	635	152	This work
4	C5.4	5	625	75	This work
5	C5.5	5	565	855	This work
6	Co ₃ O ₄	5	325	0.035	23-24
7	Co(PO ₃) ₂	6.4	440	0.21	25
8	[(L)Co ^{II}]Cl ₂	8.6	688	81.54	5

^a The overpotential was calculated as follows: Overpotential = $E_{\text{onset}} - (1.23 - (0.059\text{pH}))$. E_{onset} is extrapolated from the CV using the tangent method. [(L)Co^{II}]Cl₂ (L= N, N'-bis(2'-pyridinecarboxamide)-1,2-benzene).

5.2.2.2 Kinetic studies

The effect of catalyst concentration on the catalytic current was studied using complex **C5.2** at pH 5. As the concentration increased from 0.03 mM to 0.1 mM the current also increased, as shown in Figure 5.4a. The relationship between the catalyst concentration and the catalytic current at 1.7 V was non-linear. The plot in Figure 5.4b is indicative of a second-order rate of reaction. This suggests that the electrocatalytic water oxidation does not take place at a single site and proceeds via the radical coupling of two oxos (I2M) mechanism.

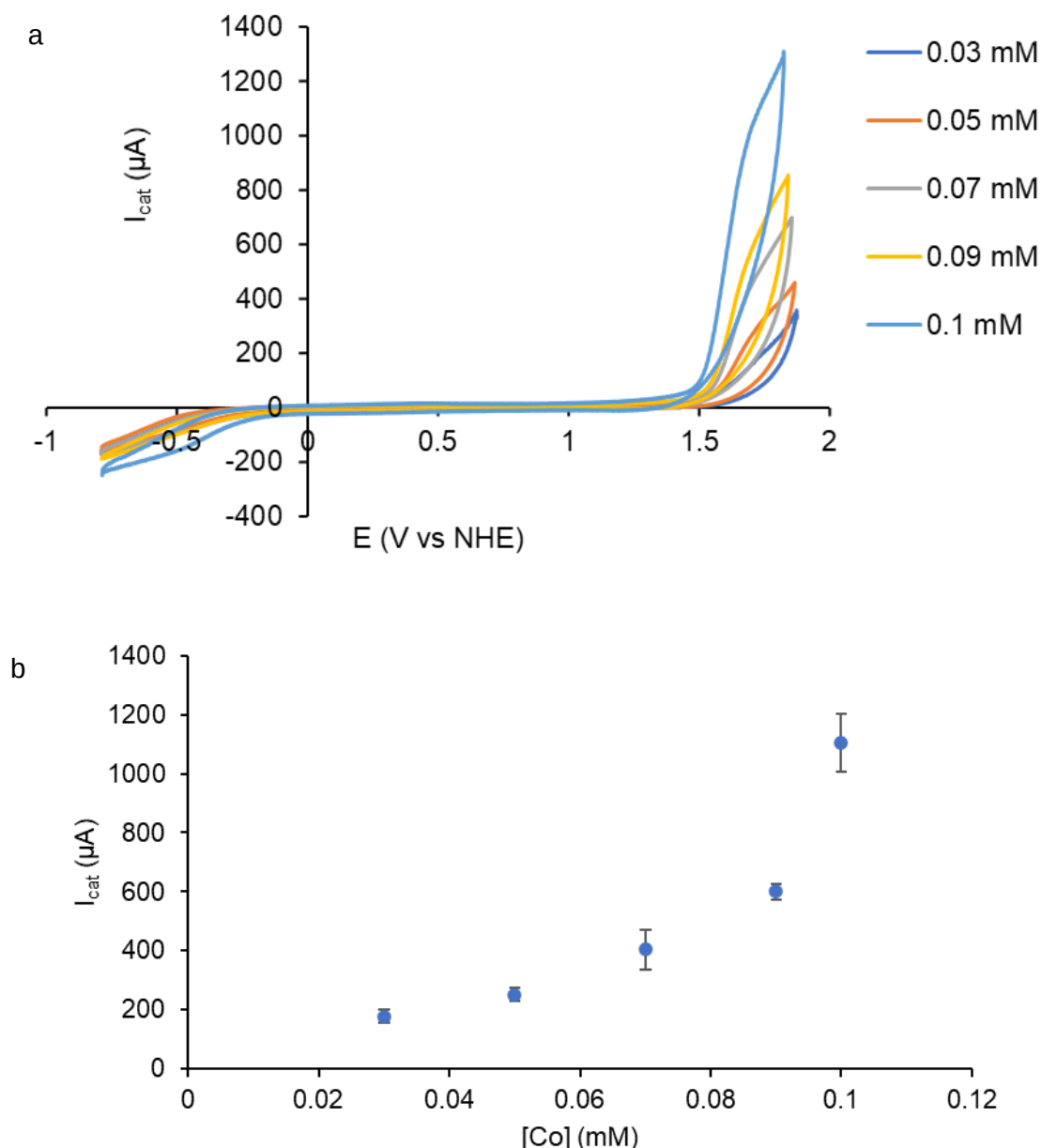


Figure 5.4 a:, CVs showing **C5.2** in 0.2 M phosphate buffer at varying concentrations (0.03 mM-0.1 mM) recorded at 100 mV s⁻¹ and 5.4b: the effect of concentration on the catalytic current at 1.7 V studied using complex **C5.2** in 0.2 M phosphate buffer at pH 5.

The CVs of 0.1 mM **C5.2** in 0.2 M phosphate buffer at pH 5 recorded at different scan rates are shown in Figure 5.5. An increase in catalytic current with increasing scan rates is observed. A graph of catalytic current/peak current as a function of $1/(\text{scan rate})^{1/2}$ was plotted as shown in Figure 5.6. From equations (5.1) to (5.4) k_{cat} , which is the TOF, was calculated from the slope of the graph.²⁶⁻²⁸

$$I_{cat} = n_{cat}FA[Co](k_{cat}D_{Co})^{1/2} \quad (5.1)$$

In equation 5.1 $n_{cat} = 4$, which is the number of electrons transferred during water oxidation, F is defined as the Faraday constant, whereas A is the electrode surface area in cm², $[Co]$ is the concentration of the catalyst (in mol/L), and D_{Co} is described as the diffusion coefficient of the

catalyst. The peak current for the non-catalytic redox couple Co(III/II) at $E_{1/2} = +0.37$ vs NHE for complex **C5.2** varies linearly with the square root of the scan rate. The result is consistent with the Randles-Sevcik equation.

$$i_p = 0.4633nFA[Co](nFvD_{Co}/RT)^{1/2} \quad (5.2)$$

At 25 °C equation (5.2) becomes (5.3):

$$i_p = 2.69 \times 10^5 n^{3/2} A D_{Co}^{1/2} [Co] v^{1/2} \quad (5.3)$$

The ratio of equation (1)/(2), i_{cat}/i_p results in equation (5.4)

$$i_{cat}/i_p = (0.359 n_c/n_p^{3/2} k_{cat}^{1/2}) 1/v^{1/2} \quad (5.4)$$

Where n_c is the number of electrons that are transferred in water oxidation (4 electrons), n_p is the number of electrons transferred in a non-catalytic redox event for the Co(III/II) couple (1 electron) ($E_{1/2} = +0.26$ V to $+0.40$ V), and v is the scan rate. Catalytic turnover frequency, k_{cat} (TOF) is calculated from the slope of the plot i_{cat}/i_p vs $1/v^{1/2}$.

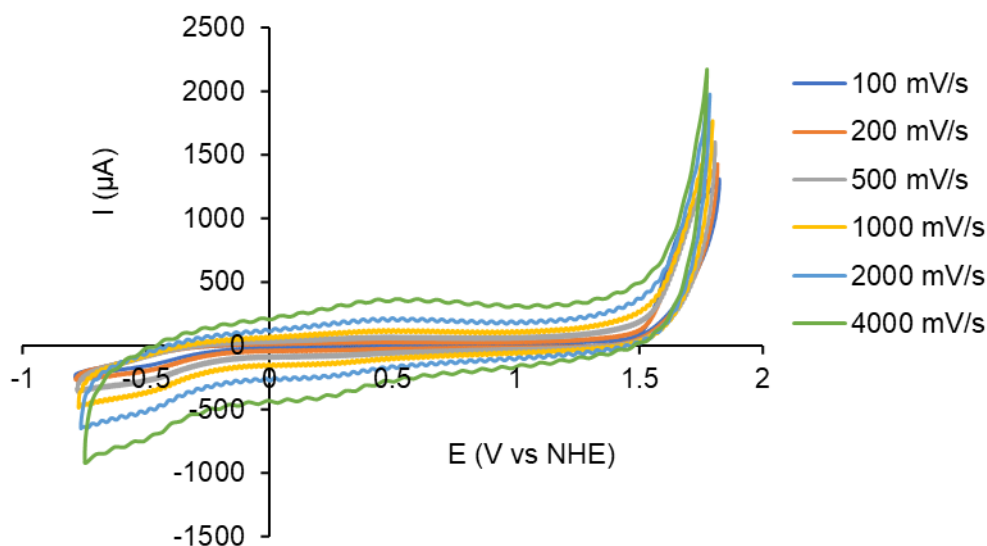


Figure 5.5: CVs showing the effect of scan rate on the catalytic current studied using 0.1 mM **C5.2**.

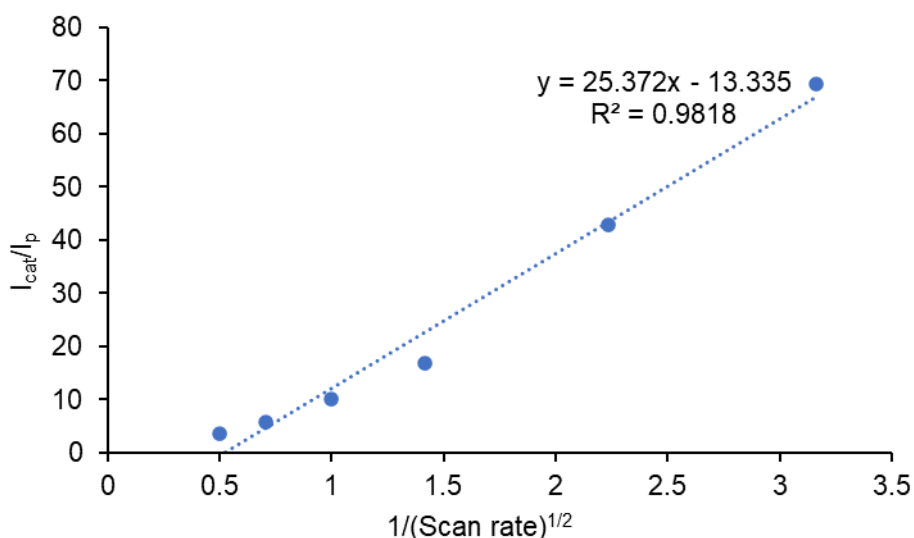


Figure 5.6: A plot of I_{cat}/I_p versus $1/(\text{Scan rate})^{1/2}$.

5.2.2.3 Investigating the integrity of the molecular catalyst

Complex **C5.1** was used to study the stability of cobalt complexes over a range of pH (5-7) as it contains a simple unsubstituted pyrazole ligand. Different methods were used to confirm the formation of CoO_x nanoparticles during electrocatalysis. At pH 7, the metal ion scavenger method was used to detect the presence of free Co^{2+} in the solution. A solution of 0.1 mM **C5.1** was cycled six times and at the end of the 6th cycle $\text{Ca}(\text{OH})_2$, a source of Ca^{2+} , was added into the reaction mixture for it to bind to any free Co^{2+} ions in solution. A decrease in the current was observed after the addition of $\text{Ca}(\text{OH})_2$, indicating the presence of nanoparticles in solution (Figure 5.7a). At pH 7, discolouration of the platinum wire was also observed, which is another indication of nanoparticle formation. Furthermore, to check for any electrodeposition on the glassy carbon electrode, the glassy carbon electrode was rinsed with the buffer and cycled again in a blank buffer solution. A considerable amount of current was observed, as shown in Figure 5.7b.

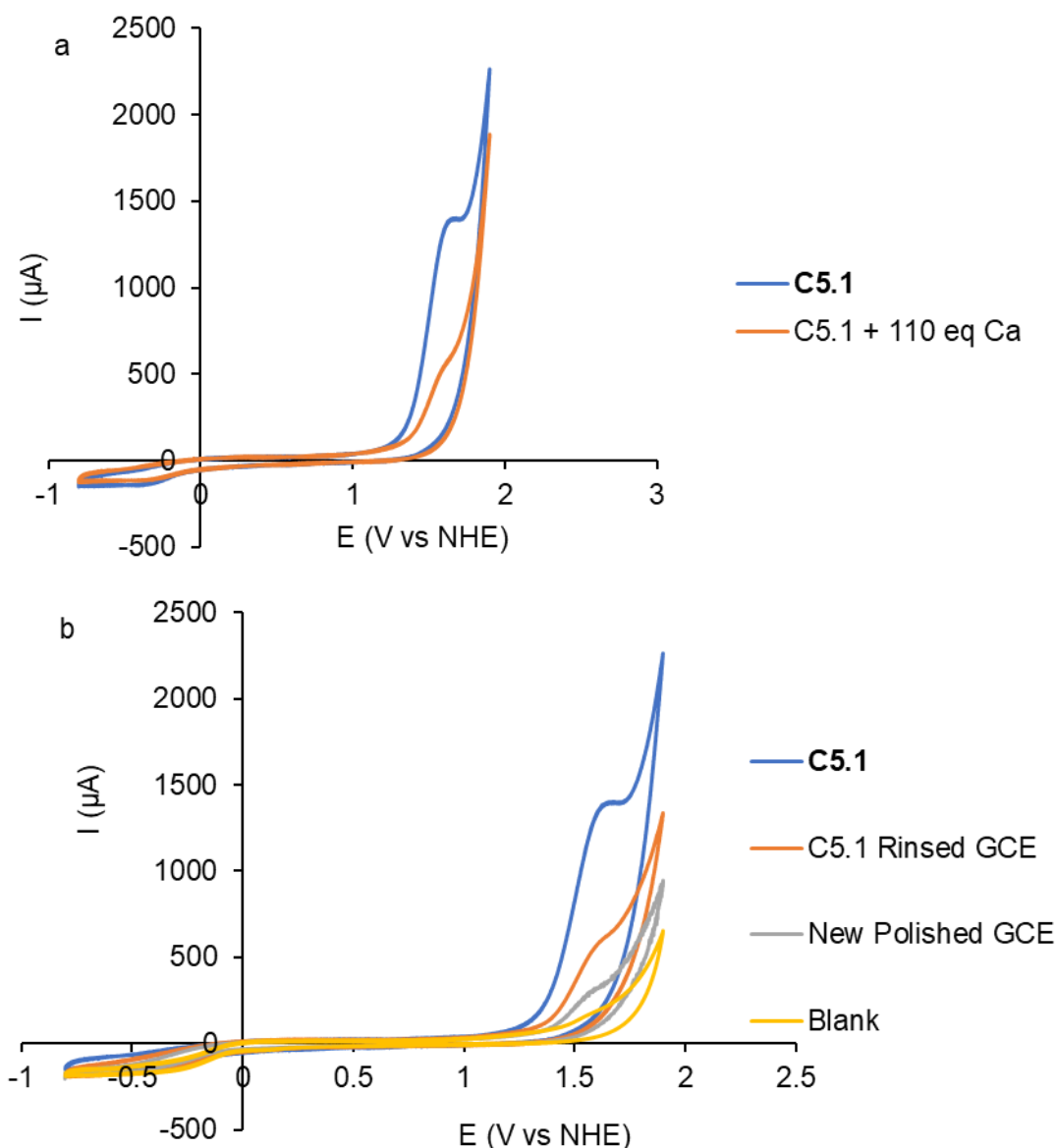


Figure 5.7: CVs of 0.1 mM **C5.1** in phosphate buffer at pH 7 at the end of the 6th cycle showing the presence of nanoparticles detected by a metal-ion scavenger method, b Checking for electrodeposited material on the GCE surface.

To establish the nature of the CoO_x nanoparticles formed, the electrodeposition was optimised by cycling 0.5 mM **C5.2** in 0.2 M phosphate buffer at pH 7 20 times at $100 \text{ mV}\cdot\text{s}^{-1}$. The first evidence of electrodeposition is the gradual increase in current with each cycle as can be seen in Figure 5.8. Thereafter, the glassy carbon electrode was analysed by SEM-EDX. The SEM images in Figure 5.9 show a layer of the electrodeposited nanoparticles on the glassy carbon electrode. The EDX pattern (Figure 5.10) confirmed the presence of cobalt species on the electrodeposited layer.

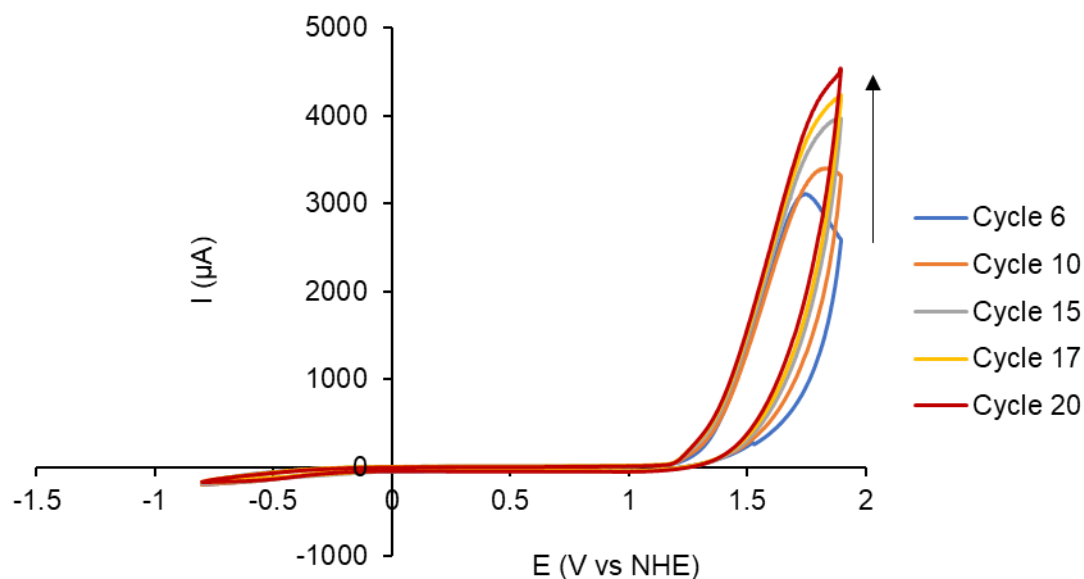


Figure 5.8: CVs of **C5.2** (0.5 mM) dissolved in 0.2 M phosphate buffer at pH 7 cycled 20 times at a scan rate of 100 mV.s^{-1}

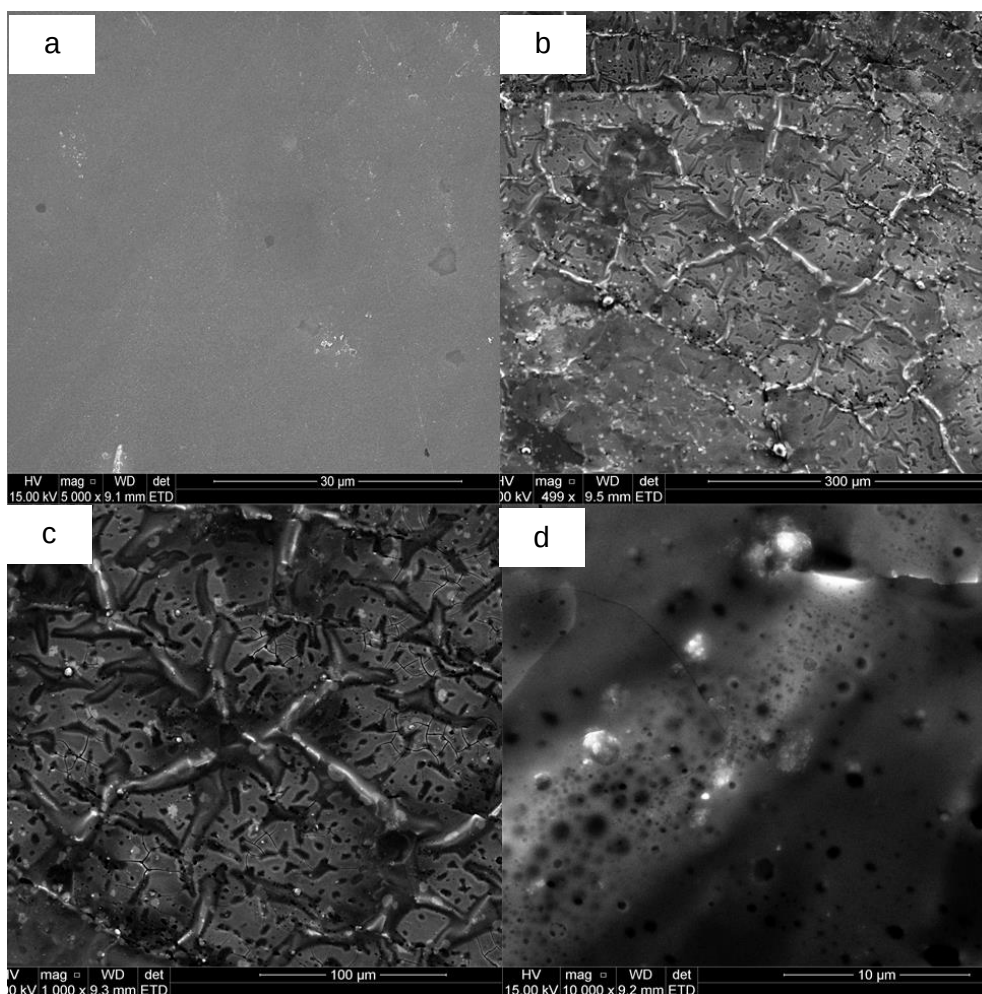


Figure 5.9: a, SEM image (scale $30 \mu\text{m}$) of the bare polished GCE. SEM images b, (scale $300 \mu\text{m}$), c, (scale $100 \mu\text{m}$), and d, (scale $10 \mu\text{m}$) showing the GCE post-electrocatalysis of 0.5 mM **C5.2** in phosphate buffer at pH 7 after 20 CV cycles.

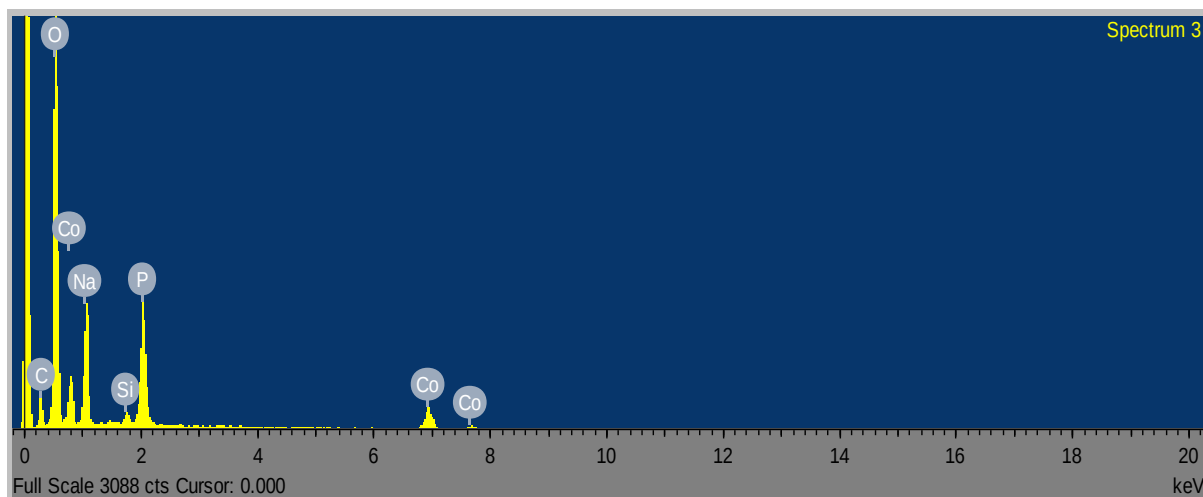


Figure 5.10: EDS pattern of the GCE post-electrocatalysis of 0.5 Mm **5.2** in phosphate buffer after 20 CV cycles.

Decreasing the pH to 6 resulted in a faint discoloration on the platinum wire and a decrease in current upon the addition of the $\text{Ca}(\text{OH})_2$. At pH 5.5, the addition of the $\text{Ca}(\text{OH})_2$ did not lead to a decrease in current; however, a very faint brown colour was observed on the platinum wire. At pH 5, there was no discoloration of the platinum wire and the addition of $\text{Ca}(\text{OH})_2$ did not lead to any decrease in current. To further ascertain the electrodeposition of the nanoparticles at the GCE surface, the GCE was rinsed with the buffer post-electrolysis. The rinsed GCE was cycled in a blank buffer solution without the catalyst. A significant current was observed, as shown in Figure 5.11, which is higher than that of the blank solution with a polished electrode, which confirmed electrodeposition of the CoO_x nanoparticles on the GCE, even though visual discoloration was not observed.

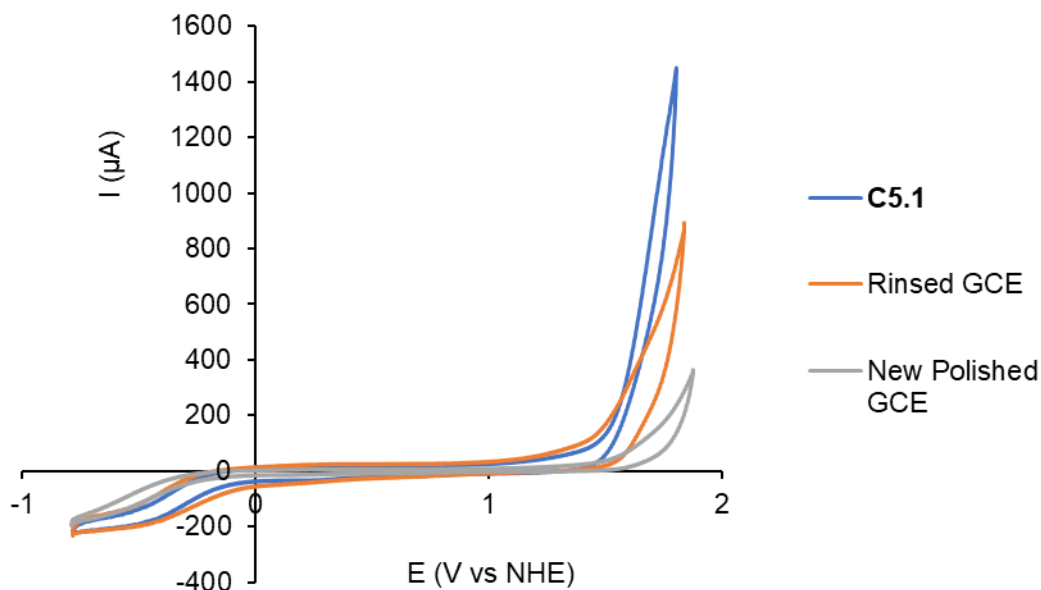
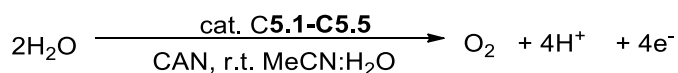


Figure 5.11: CV of 0.1 mM **5.1** in 0.2 M phosphate buffer pH 5, and CV of the rinsed GCE in phosphate buffer only (blank) and new polished GCE in the blank.

5.2.3 Chemical water oxidation catalysed by cobalt complexes **C5.1** to **C5.5**



Scheme 5.3: Chemical water oxidation catalysed by complexes **C5.1-C5.5** with CAN as the primary oxidant.

Cobalt complexes **C5.1** to **C5.5** were investigated towards chemical water oxidation with CAN as the primary oxidant in a 1:1 mixture of MeCN:H₂O (Scheme 5.3). Attempts to do the reaction solely in water were not successful as low activities were observed. All the complexes were active and the oxygen evolution curves as confirmed by an increase in [O₂] upon the addition of a catalyst shown in Figure 5.12a. Figure 5.12b shows the TON after 5 minutes' reaction time.

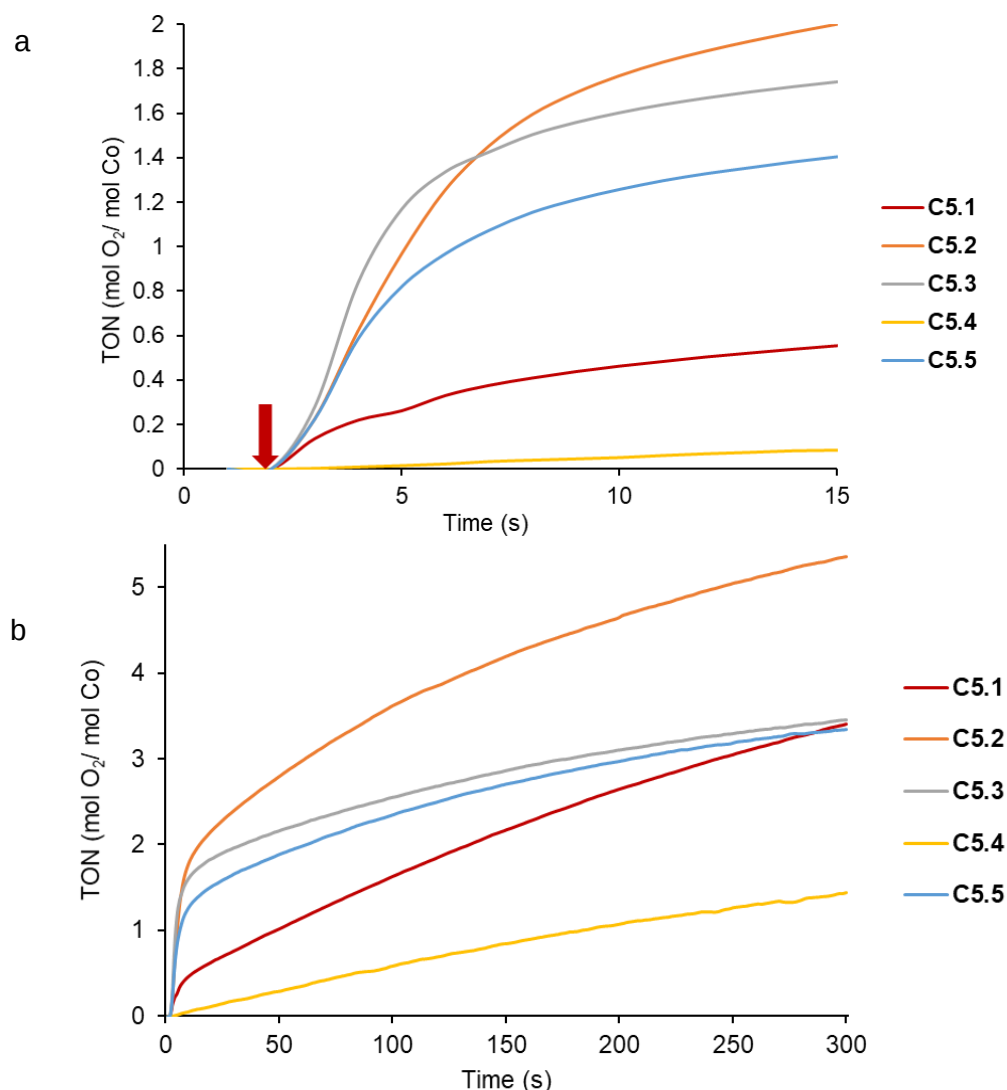


Figure 5.12a: The oxygen evolution curves showing how the reaction proceeds for the first 10 seconds, the arrow shows the catalyst addition to the reaction mixture. 5.12b: Oxygen evolution curves of cobalt(II) complexes **C5.1** to **C5.5** showing the TON for 5 minutes' reaction time.

A summary of the activity metrics of **C5.1-C5.5** towards chemical water oxidation is shown in Table 5.3. Among the complexes containing the chloride anions (**C5.1-C5.4**), complex **C5.2** was the most active with a TON of 5.37 and a TOF of 0.31 s^{-1} . Complex **C5.2** contains electron-donating methyl groups on the pyrazole in the ligand framework, which can be attributed to the efficiency of the catalyst in chemical water oxidation. Although complexes **C5.1** and **C5.3** had comparable TONs of 3.43 and 3.46 respectively, complex **C5.3** is more active with a TOF of 0.31 s^{-1} . This suggests that despite being more active, complex **C5.3** deactivates faster under highly acidic conditions during water oxidation. Deactivation of the molecular complex under highly acidic conditions is very common. This is due to the decomposition of the ligand framework of the catalyst, which can be caused by ligand oxidation, ligand de-coordination, or a combination of both.²⁹⁻³⁰ Complex **C5.4** containing electron-withdrawing phenyl substituents on the pyrazole moiety of the complex was the lowest-performing complex with a TON of 1.45

and a TOF of 0.0075 s^{-1} . Changing the anion did not influence the activity as complex **C5.5** containing a tetrafluoroborate (BF_4^-) anion (TON 3.35 and TOF, 0.21 s^{-1}) was less active as compared to chloride-containing complex **C5.2**.

Table 5.3: Summary of results of different Cobalt (II) complexes on chemical water oxidation with CAN

Entry	Complex	^a TON	^b TOF
1	C5.1	3.43	0.06
2	C5.2	5.37	0.31
3	C5.3	3.46	0.28
4	C5.4	1.45	0.0075
5	C5.5	3.35	0.21

Reaction conditions: [Co]: $25\text{ }\mu\text{M}$, [CAN]: 110 mM , Solvent: MeCN: H_2O (1:1, total volume: 2 mL). ^a, TON after 5 minutes' reaction time. ^b, TOF was calculated from the steepest slope of the TON curve over a 5-second period.

5.3 Conclusions

Bis(pyrazol-1-ylmethyl)pyridine-ligated Co(II)-chloride and -tetrafluoroborate complexes **C5.1-C5.5** were successfully synthesised and characterised. Complexes **C5.1-C5.5** showed activity towards electrocatalytic water oxidation at pH 5. Complex **C5.2** was the most active complex among the chloride-containing complexes (**C5.1-C5.4**), displaying efficient electrocatalytic water oxidation at an overpotential of 565 mV and a TOF of 326 s^{-1} . The least active chloride-containing complexes were **C5.3** and **C5.4**, mediating electrocatalytic water oxidation at an overpotential of 635 and 625 mV , and TOF of 152 s^{-1} and 75 s^{-1} , respectively. Replacing the chloride anion with the tetrafluoroborate anion did not influence the overpotential; however, complex **C5.5** had the highest TOF of 855 s^{-1} . The complexes were very active; however, the presence of heterogeneous cobalt species was confirmed using various techniques. This suggests that the complexes are not entirely homogeneous during the electrocatalytic water oxidation process. Cobalt complexes **C5.1** to **5.5** were active towards chemically-driven water oxidation. Complex **C5.2** was the most active with a TON of 5.37 and TOF of 0.31 s^{-1} ; meanwhile, complex **C5.4** was the least active complex with a TON of 1.45 and a TOF of 0.0075 s^{-1} . In the case of chemical water oxidation, replacing the chloride anion with tetrafluoroborate did not improve the activity.

5.4 Experimental

5.4.1 General considerations

All moisture and oxygen-sensitive reactions were performed using Schlenk techniques. The solvents were distilled under a nitrogen atmosphere using Na metal for diethyl ether and CaH₂ for dichloromethane as drying agents. NMR (¹H and ¹³C) spectra were recorded on a Bruker Ultrashield Plus at 600 MHz and 151 MHz respectively. FTIR analysis was done on a BrukerAlpha-P range infrared instrument fitted with ATR in the range of 400 cm⁻¹ to 4000cm⁻¹. Magnetic susceptibility studies were done using a Sherwood Scientific MK1 with 4mm diameter sample tubes containing 50 mM of the sample. Mass spectrometry was performed on BruckermicroTOF-Q II mass spectrometer. Elemental analysis was performed on a Perkin Elmer 2400 Elemental Analyzer. Cyclic voltammetry studies were done on a BioLogic VSP potentiostat employing a water-jacketed electrochemical cell connected to a refrigerated temperature controller (Julabo F-12 ED). DLS analysis was performed on a Mastersizer 2000 Ver. 5.60 from Malvern instruments. SEM analysis were done using SEM (FEI Quanta FEG 250) with an integrated XMax 20 EDX system (Oxford Instruments).

5.4.2 Synthesis of complexes

5.4.2.1 Synthesis of Complex **C5.1**

Complex **C5.1** was synthesised from 2,6-bis((1H-pyrazol-1-yl)methyl)pyridine (**C3.1**) (0.071 g, 0.30 mmol) dissolved in 2.5 mL of dichloromethane and cobalt(II) chloride hexahydrate (0.071 g, 0.30 mmol) dissolved in 2.5 mL of dichloromethane. The reaction mixture was stirred for 24 h. The solution was reduced, and the addition of diethyl ether (3 x10 mL) resulted in the precipitation of the complex, which was dried under vacuum. The product was isolated as a purple solid. Yield: 0.1019 g (83%). ESI-MS (m/z): 332.95 [M-Cl-H]⁺ Elemental Analysis: Calculated(found) for C₁₃H₁₇Cl₂CoN₅O₂: C, 38.54(38.39); H, 5.23(3.78); N, 17.29(16.72).FTIR: 1601(C=N), 2958 (H₂O). $\mu_{\text{eff}} = 1.95$ BM.

5.4.2.2 Synthesis of Complex **C5.2**

Complex **C5.2** was synthesised from 2,6-bis((3,5-dimethyl-1H-pyrazol-1-yl)methyl)pyridine (**C3.2**) (0.089 g, 0.30 mmol) dissolved in 2.5 mL of dichloromethane and cobalt(II) chloride hexahydrate (0.071 g, 0.30 mmol) dissolved in 2.5 mL of dichloromethane. The reaction mixture was stirred for 24 h. The solution was reduced, and the addition of diethyl ether (3 x10 mL) resulted in the precipitation of the complex, which was dried under vacuum. The product was isolated as a blue solid. Yield: 0.094 g (71%). ESI-MS (m/z): 389.08 [M-Cl]⁺. Elemental Analysis: Calculated (found) for C₁₇H₂₃Cl₂CoN₅O: C, 46.07(47.14); H, 5.23(5.51); N, 15.80(15.97). FTIR: 1605(C=N), 2958 (H₂O). $\mu_{\text{eff}} = 4.61$ BM.

5.4.2.3 Synthesis of complex **C5.3**

Complex **5.3** was synthesised from 2,6-bis((3,5-di-*tert*-butyl-1H-pyrazol-1-yl)methyl)pyridine (**3.3**) (0.139 g, 0.30 mmol) dissolved in 2.5 mL of dichloromethane and cobalt(II) chloride hexahydrate (0.071g, 0.30 mmol) dissolved in 2.5 mL dichloromethane. The reaction mixture was stirred for 24 h. The solution was reduced, and the addition of diethyl ether (3 x10 mL) resulted in the precipitation of the complex, which was dried under vacuum. The product was isolated as a blue solid. Yield: 0.111 g (62%). ESI-MS (*m/z*): 557.42 [M-Cl]⁺. Elemental analysis: Calculated (found) for C₂₉H₄₅Cl₂CoN₅: C, 58.68 (58.48); H, 7.64(7.9); N, 11.80(11.74); FTIR: 1610 (C=N), 2958 (H₂O). μ_{eff} = 5,68 BM.

5.4.2.4 Synthesis of complex **C5.4**

Complex **C5.4** was synthesised from 2,6-bis((3,5-diphenyl-1H-pyrazol-1-yl)methyl)pyridine (**C3.4**) (0.0967 g, 0.18 mmol) dissolved in 2.5 mL of dichloromethane and cobalt(II) chloride hexahydrate (0.043 g, 0.18 mmol) dissolved in 2.5 mL dichloromethane. The reaction mixture was stirred for 24 h. The solution was reduced, and the addition of diethyl ether (3 x10 mL) resulted in the precipitation of the complex, which was dried under vacuum. The product was isolated as a blue solid. Yield: 0.058 g (48%). ESI-MS (*m/z*): 637.15 [M-Cl]⁺ Elemental analysis: Calculated (found) for C₃₇H₃₉Cl₂CoN₅O₅: C, 58.20(58.30); H, 5.15(4.04); N, 9.16(8.24). FTIR: 1607 (C=N), 2958 (H₂O). μ_{eff} = 5,43 BM.

5.4.2.5 Synthesis of complex **C5.5**

Complex **C5.5** was synthesised from 2,6-bis((3,5-dimethyl-1H-pyrazol-1-yl)methyl)pyridine (**C3.2**) (0.089g, 0.30 mmol) dissolved in 2.5 mL of acetonitrile and cobalt(II) tetrafluoroborate hexahydrate Co(BF₄)₂·6H₂O (0.102 g, 0.30 mmol) dissolved in 2.5 mL of MeCN. The reaction mixture was stirred for 24 h. The solution was reduced, and the addition of diethyl ether (3 x10 mL) resulted in the precipitation of the complex, which was dried under vacuum. The product was isolated as a brown solid. Yield: 0.1374 g (87%). ESI-MS (*m/z*): 373.11 [(M+H)·H₂O]⁺ Elemental Analysis: Calculated (found) for C₁₇H₂₇B₂CoF₈N₅O₃: C, 35.08 (35.37); H, 4.68(4.23); N, 12.03(12.23) %. FTIR: 1604 (C=N), 2958 (H₂O). μ_{eff} = 4,49 BM.

5.4.3 Chemical water oxidation

Oxygen evolution reactions were performed using a standard Clark-type oxygraph electrode (Hansatech Instruments) placed in a thermostated cell (25 °C) for all measurements. The signal was recorded for the entire duration of the experiment at 1.0 s intervals using the Oxygraph+ software (Hansatech Instruments). The signal was calibrated using a mixture (1:1) of acetonitrile and water ([O₂] = 261μM, 25 °C).³¹ Stock solutions of the catalysts were freshly prepared by dissolving the complex in acetonitrile. The stock solution was then degassed with argon to ensure an oxygen-free solution. Following the addition of the CAN, the cell was purged with argon before catalyst addition.

5.4.4 Electrocatalytic water oxidation

CV technique was carried out for electrochemical characterisation of the electrocatalysts employing a conventional water-jacketed three-electrode electrochemical cell connected to a refrigerated temperature controller (Julabo F-12 ED). The counter electrode used was a platinum wire (Bio-Logic) and the reference electrode used was a Ag/AgCl electrode (Bio-Logic). A glassy carbon electrode disc insert (Sigradur G, HTW Germany) with a geometrical area of 0.196 cm² was used as the working electrode. Before performing experiments, the glassy carbon was polished with 0.05 µM alumina suspension (Gamma Micropolish II, Buehler) and was subsequently washed with Milli-Q water, ethanol (Merck), and isopropanol (Merck). The working electrode was assembled into a rotating disc electrode setup. Current Potential curves of the samples were recorded using a VSP double-channel potentiostat from biologic science instruments. Current Potential curves of the samples were recorded using a VSP double-channel potentiostat from BioLogic Science Instruments.

5.5 References

1. Tahir, M.; Mahmood, N.; Pan, L.; Huang, Z.-F.; Lv, Z.; Zhang, J.; Butt, F. K.; Shen, G.; Zhang, X.; Dou, S. X., *J. Mater. Chem. A*. 2016, 4 (33), 12940-12946.
2. Tahir, M.; Pan, L.; Idrees, F.; Zhang, X.; Wang, L.; Zou, J.-J.; Wang, Z. L., *Nano Energy* 2017, 37, 136-157.
3. Tahir, M.; Pan, L.; Zhang, R.; Wang, Y.-C.; Shen, G.; Aslam, I.; Qadeer, M.; Mahmood, N.; Xu, W.; Wang, L., *ACS Energy Lett.* 2017, 2 (9), 2177-2182.
4. Wang, D.; Groves, J. T., *Proc. Natl. Acad. Sci. U.S.A.* 2013, 110 (39), 15579-15584.
5. Wang, Z. Q.; Tang, L. Z.; Zhang, Y. X.; Zhan, S. Z.; Ye, J. S., *J. Power Sources* 2015, 287, 50-57.
6. Shi, H. T.; Li, X. X.; Wu, F. H.; Yu, W. B., *Dalton Trans.* 2017, 46 (46), 16321-16326.
7. Huang, Z.; Luo, Z.; Geletii, Y. V.; Vickers, J. W.; Yin, Q.; Wu, D.; Hou, Y.; Ding, Y.; Song, J.; Musaev, D. G., *J. Am. Chem. Soc.* 2011, 133 (7), 2068-2071.
8. Safdari, R.; Mohammadi, M. R.; Holyńska, M.; Chernev, P.; Dau, H.; Najafpour, M. M., *Dalton Trans.* 2018, 47 (46), 16668-16673.
9. Stracke, J. J.; Finke, R. G., *J. Am. Chem. Soc.* 2011, 133 (38), 14872-14875.
10. Wang, H. Y.; Mijangos, E.; Ott, S.; Thapper, A., *Angew. Chem. Int. Ed.* 2014, 53 (52), 14499-14502.
11. Wang, J.-W.; Sahoo, P.; Lu, T.-B., *ACS Catal.* 2016, 6 (8), 5062-5068.
12. Yin, Q.; Tan, J. M.; Besson, C.; Geletii, Y. V.; Musaev, D. G.; Kuznetsov, A. E.; Luo, Z.; Hardcastle, K. I.; Hill, C. L., *Science* 2010, 328 (5976), 342-345.

13. Zhao, Y.; Lin, J.; Liu, Y.; Ma, B.; Ding, Y.; Chen, M., *Chem. Commun.* 2015, 51 (97), 17309-17312.
14. Nakazono, T.; Parent, A. R.; Sakai, K., *Chem. Commun.* 2013, 49 (56), 6325-6327.
15. Das, B.; Orthaber, A.; Ott, S.; Thapper, A., *Chem. Commun.* 2015, 51 (66), 13074-13077.
16. Benade, L. L. (Pyrazolylpyridine)-Iron, Cobalt and Nickel Complexes as Carbon-carbon Bond Formation Catalysts. University of Johannesburg, 2010.
17. Morrison, R. M.; Thompson, R. C., *Can. J. Chem.* 1978, 56 (7), 985-991.
18. Shakir, M.; Varkey, S. P., *Polyhedron* 1994, 13 (5), 791-797.
19. Shalash, A. M.; Ali, H. I. A., *Chem. Cent. J.* 2017, 11 (1), 1-11.
20. Chen, D.; Dong, C.-L.; Zou, Y.; Su, D.; Huang, Y.-C.; Tao, L.; Dou, S.; Shen, S.; Wang, S., *Nanoscale* 2017, 9 (33), 11969-11975.
21. Wasylenko, D. J.; Palmer, R. D.; Schott, E.; Berlinguette, C. P., *Chem. Commun.* 2012, 48 (15), 2107-2109.
22. Das, D.; Pattanayak, S.; Singh, K. K.; Garai, B.; Gupta, S. S., *Chem. Commun.* 2016, 52 (79), 11787-11790.
23. Jiao, F.; Frei, H., *Energy Environ. Sci.* 2010, 3 (8), 1018-1027.
24. Harriman, A.; Pickering, I. J.; Thomas, J. M.; Christensen, P. A., *J. Chem. Soc. Faraday Trans.* 1988, 84 (8), 2795-2806.
25. Ahn, H. S.; Tilley, T. D., *Adv. Funct. Mater.* 2013, 23 (2), 227-233.
26. Bard, A. J.; Faulkner, L. R., *Electrochemical Methods* 2001, 2 (482), 580-632.
27. Savéant, J.-M., *Chem. Rev.* 2008, 108 (7), 2348-2378.
28. Zanello, P.; Nervi, C.; de Biani, F. F., *Practice and Application*, RSC, Cambridge, UK 2003.
29. Bairagya, M. D.; Bujol, R. J.; Elgrishi, N., *Chem. Eur. J.* 2020, 26 (18).
30. Sala, X.; Maji, S.; Bofill, R.; García-Antón, J.; Escriche, L.; Llobet, A., *Acc. Chem. Res.* 2014, 47 (2), 504-516.
31. Truesdale, G. A.; Downing, A. L., *Nature* 1954, 173 (4417), 1236-1236.

Chapter 6: Concluding remarks and future recommendations

6.1 Concluding remarks

Water oxidation offers a green route of producing hydrogen, which is a promising energy storage solution. The inspiration found in natural photosynthesis in the development of water oxidation catalysts is commendable. Research in the development of water oxidation catalysts based on earth-abundant, non-toxic, and cheap metals such as Cu, Fe, Ni Co has attracted a great deal of attention.

Bis(pyrazol-1-ylmethyl)pyridine ligated Cu(II) (**C3.1-C3.5**), Cu(I) (**C4.1-C4.4**), and Co(II) (**C5.1-C5.5**) complexes were successfully synthesised and characterised. The complexes showed activity towards chemical and electrocatalytic water oxidation. Cu(II) complexes, **C3.1-C3.5**, were the least active towards both chemical water oxidation and electrocatalytic water oxidation. Amongst these Cu(II) complexes containing the chloride anion, the highest TON (4.22) and TOF (0.033 s^{-1}) for chemical water oxidation in the presence of CAN were achieved using complex **C3.2**. Complex **C3.2** bears an electron-donating methyl group on the pyrazolyl moiety, which contributes to the high activities. The TOF improved by more than three-fold when the chloride anion was replaced by a triflate anion wherein complex **C3.5** achieved a TOF of 0.115 s^{-1} . In electrocatalytic water oxidation, Cu(II) complexes act as pre-catalysts in the *in situ* generated CuO nanoparticles, which are the actual active species catalysing water oxidation. Although the molecular catalyst decomposes, the effect of molecular structure could be easily established with the methyl-substituted **C3.2** having the lowest overpotential.

This study represents the first examples of the application of copper(I) complexes towards water oxidation. Complexes **C4.1-C4.4** showed activity towards chemically-driven water oxidation with CAN as the primary oxidant. Complex **C4.2** resulted in the highest TON of 4.60 and a TOF of 0.31 s^{-1} . The initial rate data indicated that at low [Cu], chemically-driven water oxidation involves two metal centres and proceeds through the I2M mechanism. At high [Cu], chemically-driven water oxidation takes place at a single site via the WNA mechanism. The lowest overpotential towards electrocatalytic water oxidation at 674 mV was achieved with complex **C4.2**. The catalyst was confirmed to be entirely homogeneous and no CuO nanomaterials were observed. The novel Cu(I) complexes show potential as the first efficient Cu(I)-based WOCs.

Cobalt(II) complexes, **C5.1-C5.5**, showed activity towards electrocatalytic water oxidation at pH 5 with very high TOFs ($75\text{ to }855\text{ s}^{-1}$). The TOFs observed for these complexes are much

higher than those of previously reported cobalt complexes. Despite the high activity, the complexes were not stable and the presence of CoOx nanomaterials was confirmed. The complexes also showed activity in chemically-driven water oxidation with a highest of TON 5.37 and the highest TOF of 0.31 s^{-1} achieved by complex **C5.2**.

Overall, the catalyst structure contributed immensely to the activity of chemical and electrocatalytic water oxidation. Complexes containing the methyl-substituted pyrazole were more efficient as compared to complexes containing the weakly donating phenyl substituents. This highlights the importance of ligand design principles during the development of molecular WOCs as they can be fine-tuned to enhance the activity.

6.2 Future recommendations

This study shows that water-soluble Cu(II) and Co(II) complexes have potential in electrocatalytic water oxidation. However, the main challenge is the decomposition of the molecular catalyst, which leads to the formation of nanomaterials. The decomposition of the molecular catalyst could be as a result of ligand oxidation, ligand de-coordination, or a combination of both. In complexes based on first-row transition metals, the metal-ligand bonds are much more labile in water, which results in de-coordination. The stability of the molecular catalyst under highly oxidising conditions can be improved in many ways, including ligand modification and stabilisation through immobilisation. The ligand can be modified by tuning the electronic and steric properties to avoid de-coordination and ligand oxidation. Immobilisation of the molecular catalyst on the surface of electrodes, in porous materials, and on the surface of other solids can also improve the stability of the molecular catalyst. Copper(II) and cobalt(II) complexes show potential as chemically-driven water oxidation catalysts. Optimisation of these catalyst systems in chemical water oxidation is recommended.

Appendix: Supplementary information

This section covers examples of spectral data such as NMR, FTIR and ESI-MS included in each chapter. Additional information on how TOF in chemical water oxidation was extrapolated is also included. The tangent method to determine the onset potential for the calculation of the overpotential is illustrated here.

Supporting information for Chapter 3: Synthesis and characterization of bis(pyrazolyl)pyridine copper(II) complexes as catalysts in chemical and electrocatalytic water oxidation. Supporting information

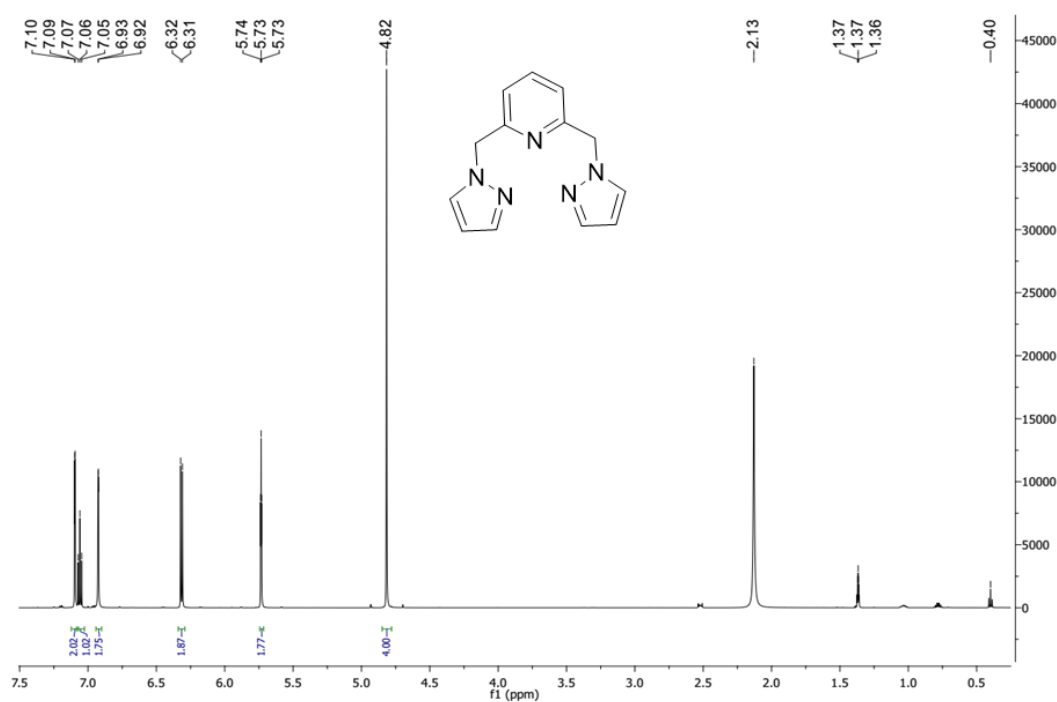


Figure S1: ^1H NMR spectrum for L1

Appendix: Supplementary information

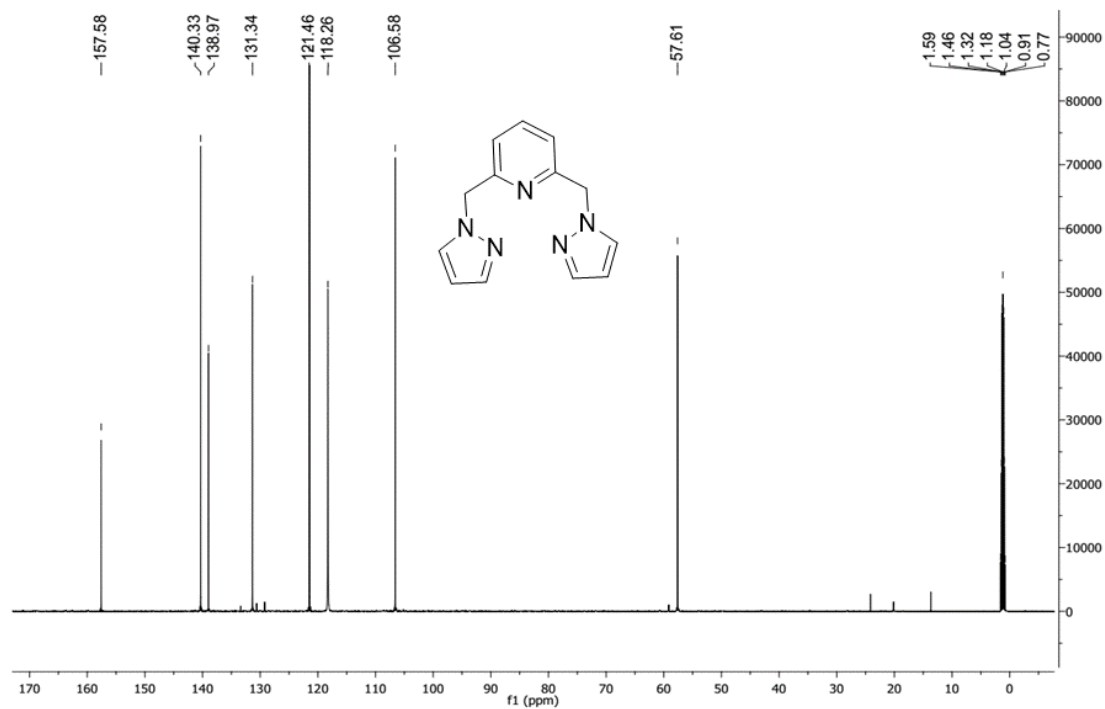


Figure S2: $^{13}\text{C}\{^1\text{H}\}$ NMR for ligand **L1**

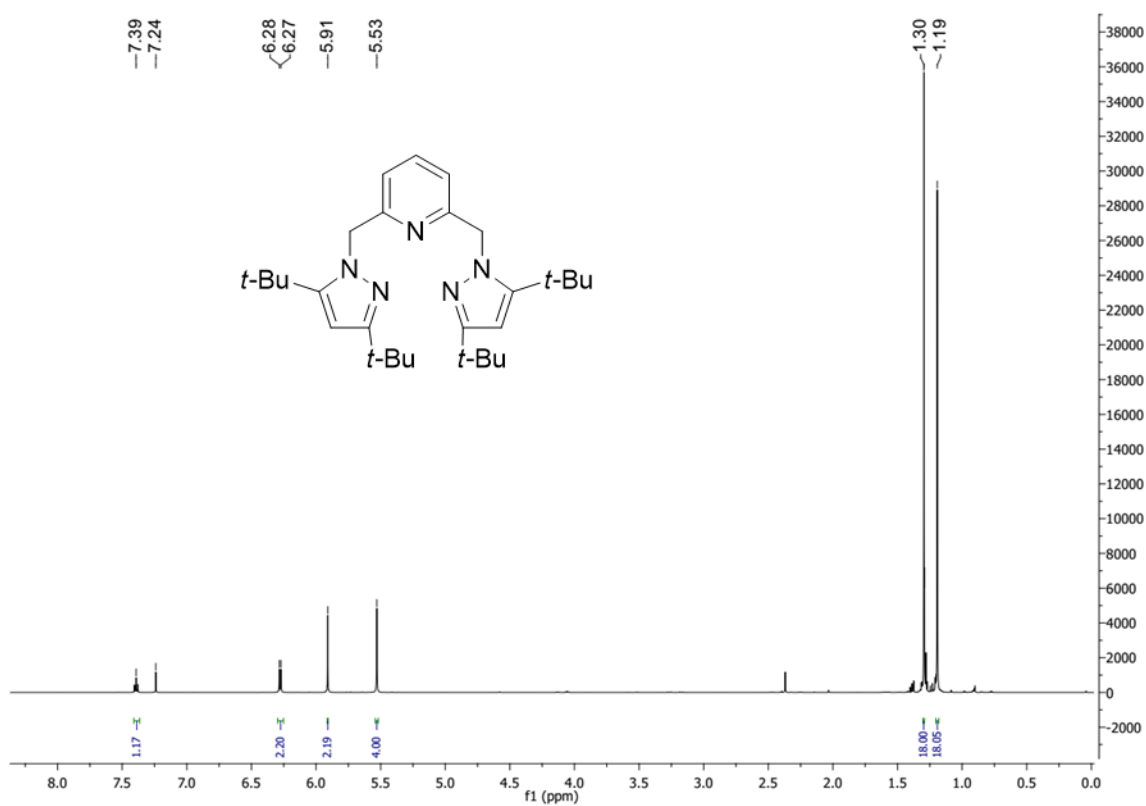


Figure S3: ^1H NMR spectrum for **L3**

Appendix: Supplementary information

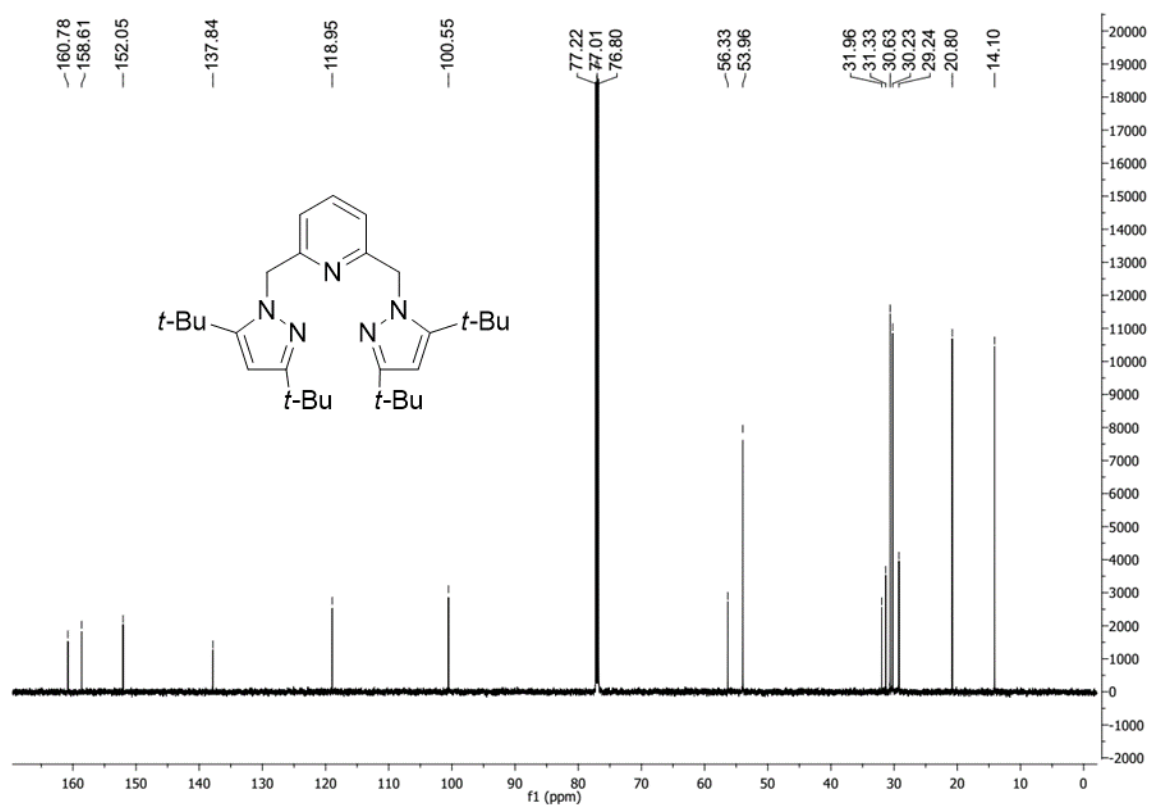


Figure S4: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum for **L3**

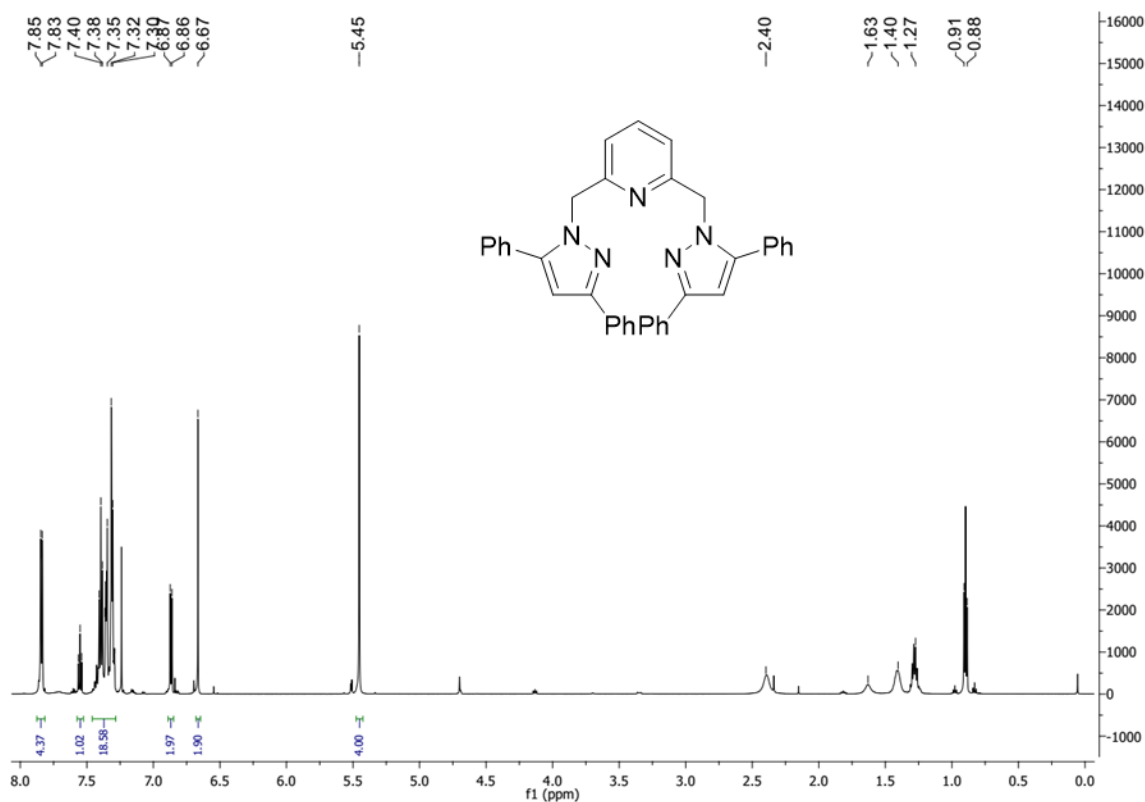
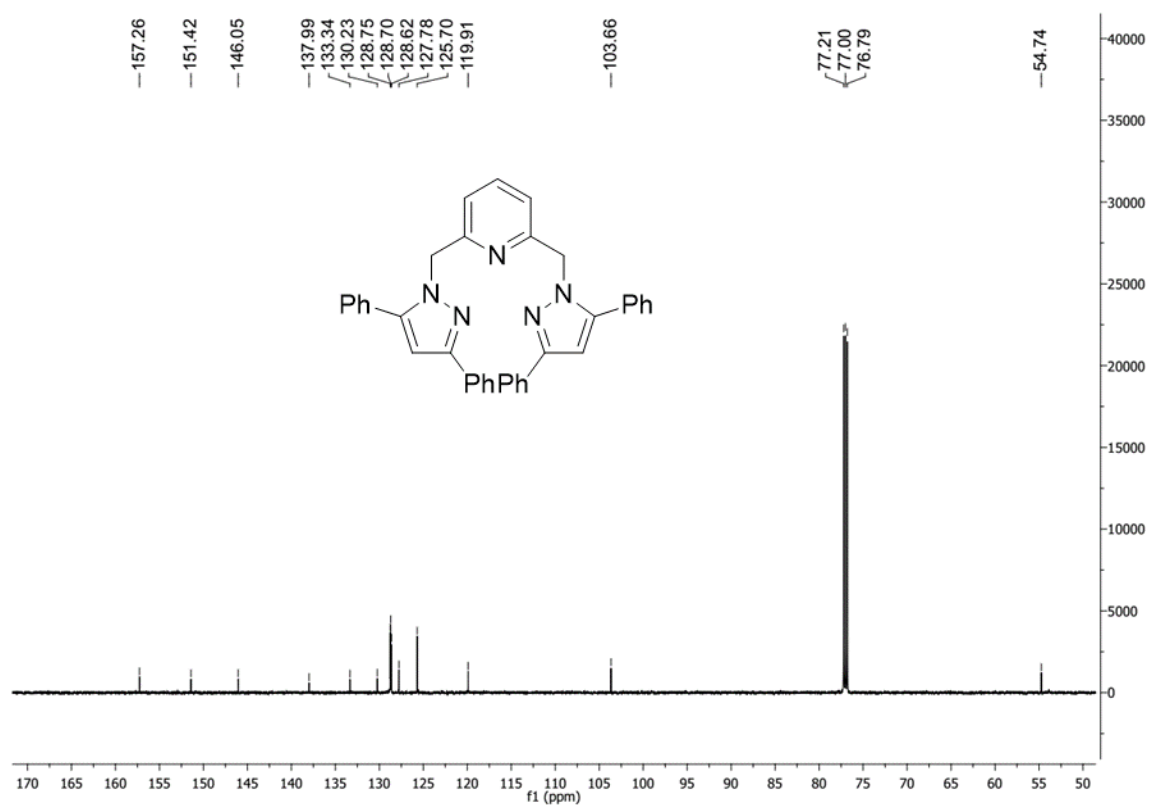


Figure S5: ^1H NMR spectrum for **L4**

Appendix: Supplementary information



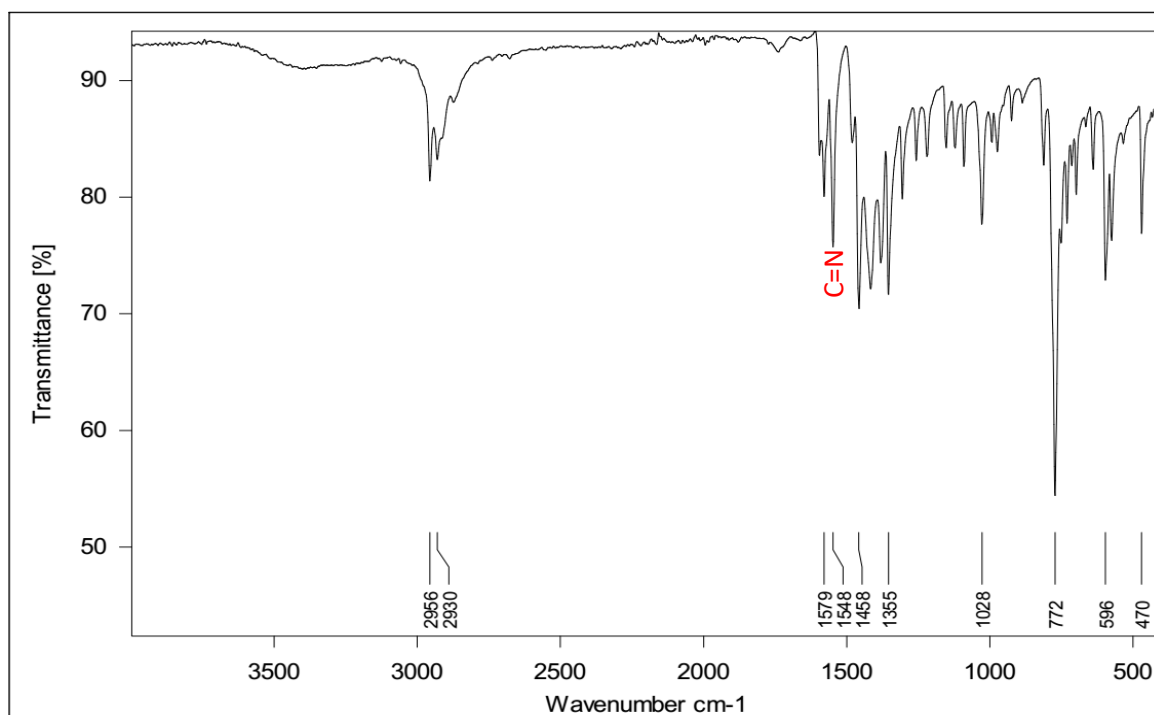


Figure S8: FTIR spectrum for **L2**

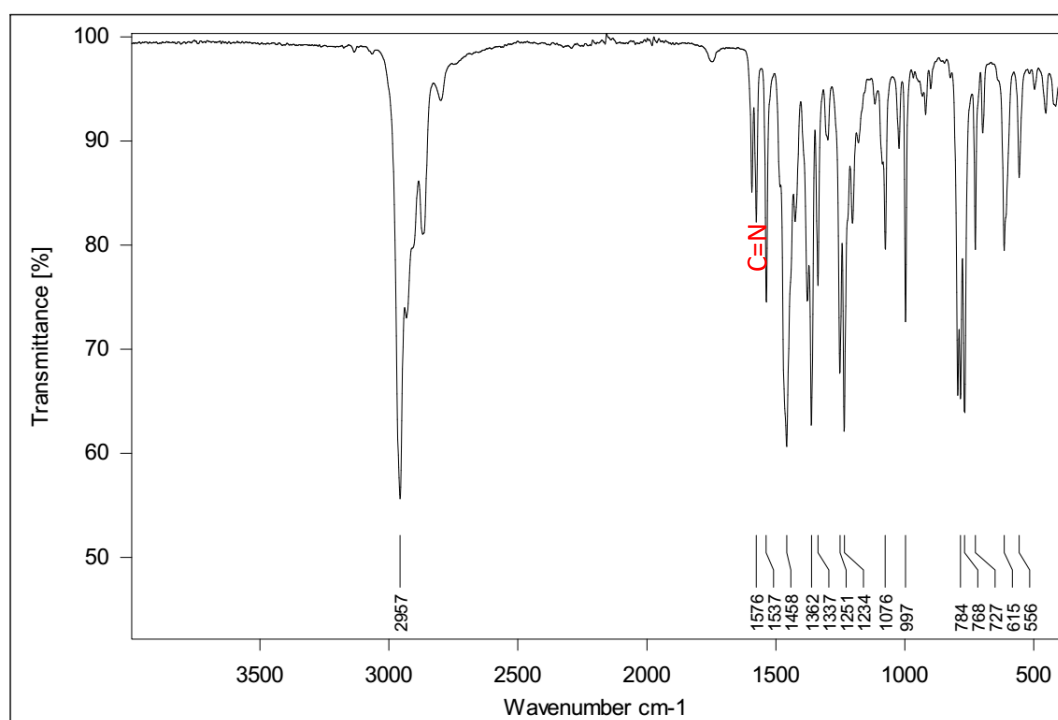


Figure S9: FTIR spectrum for **L3**

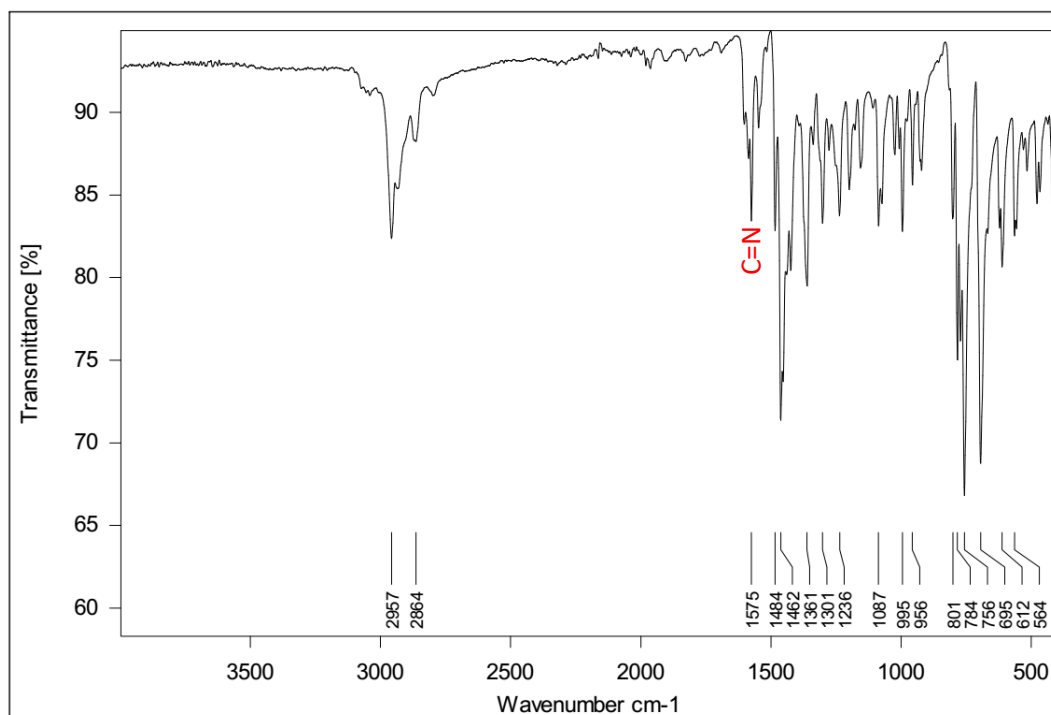


Figure S10: FTIR spectrum for **L4**

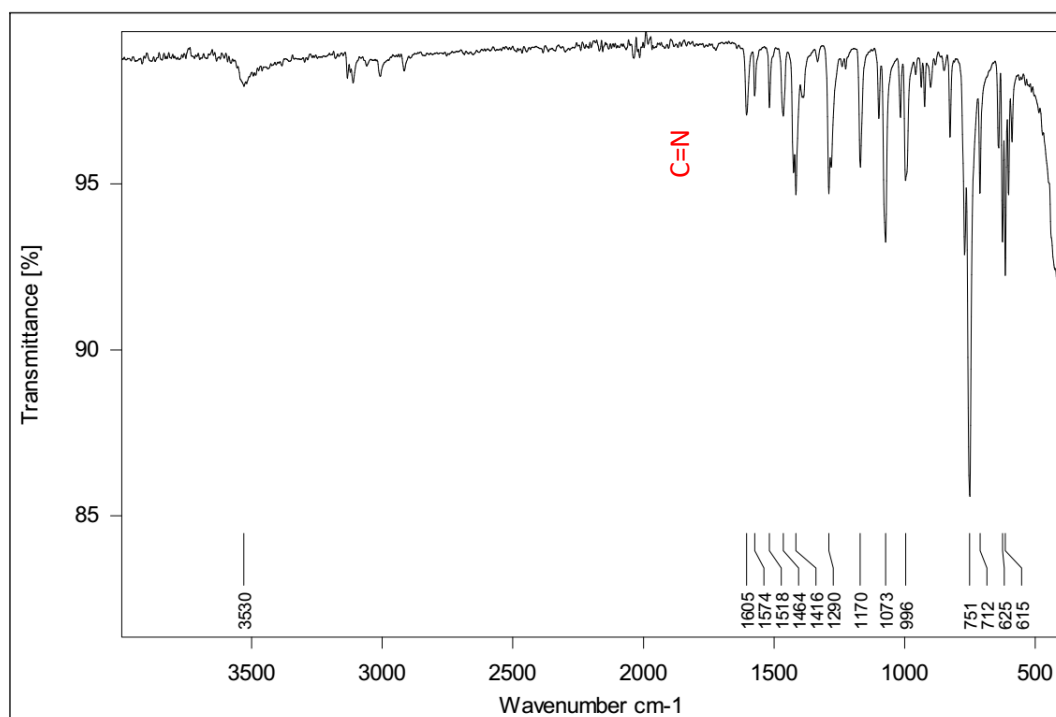


Figure S11: FTIR spectrum for **C3.1**

Appendix: Supplementary information

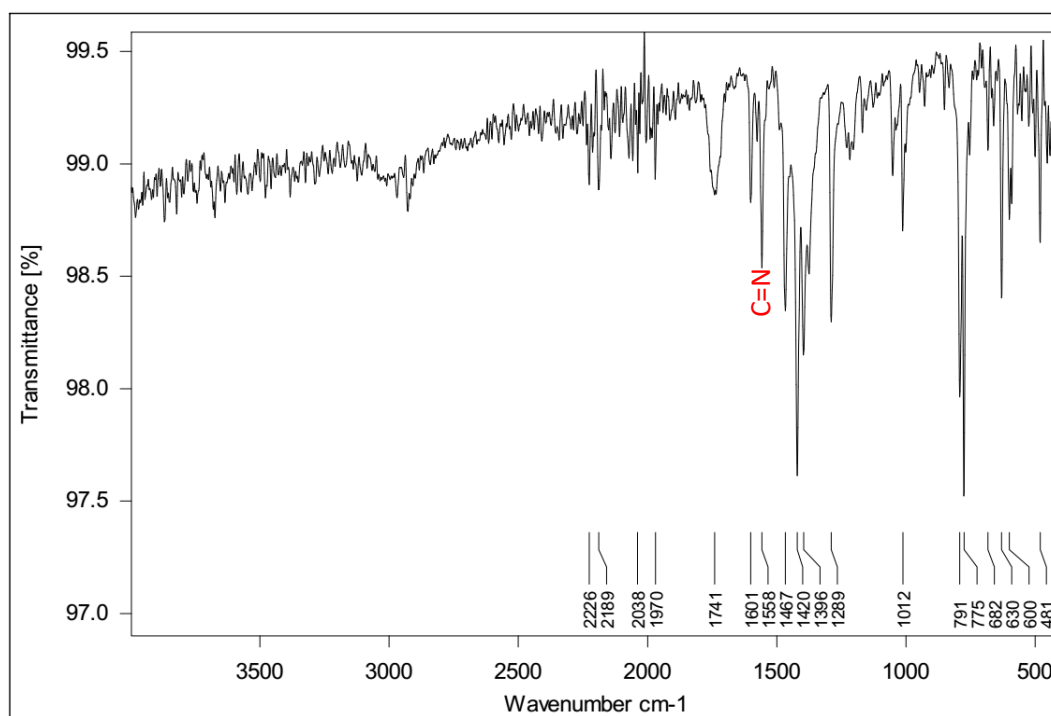


Figure S12: FTIR spectrum for **C3.2**

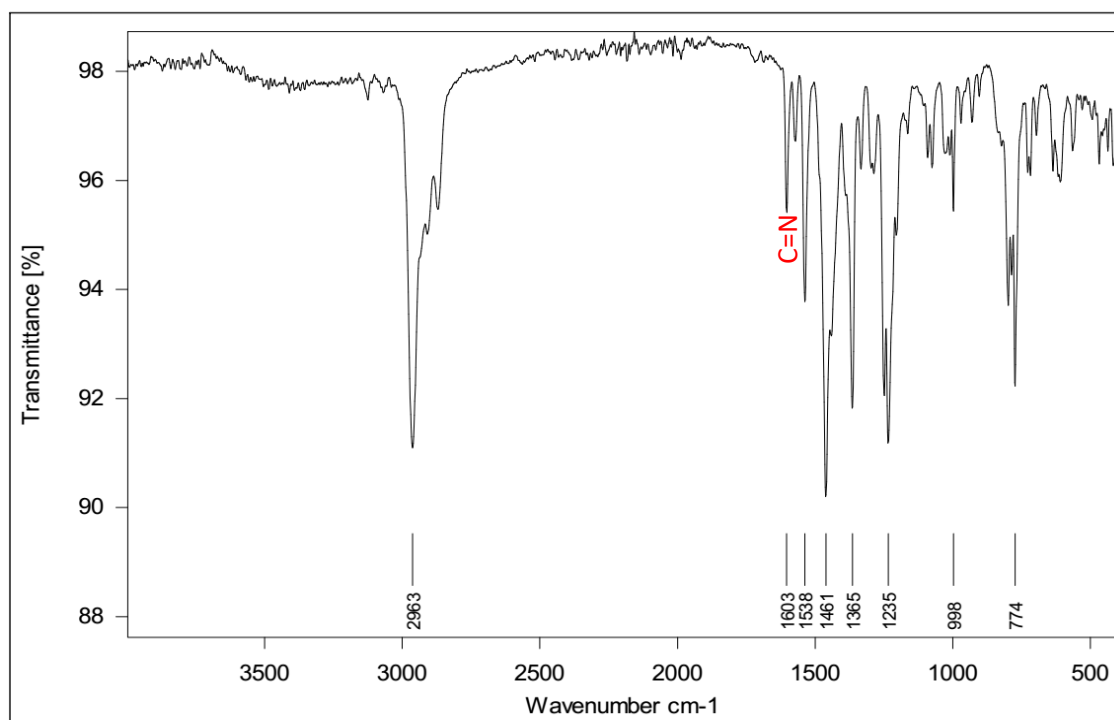


Figure S13: FTIR spectrum for **C3.3**

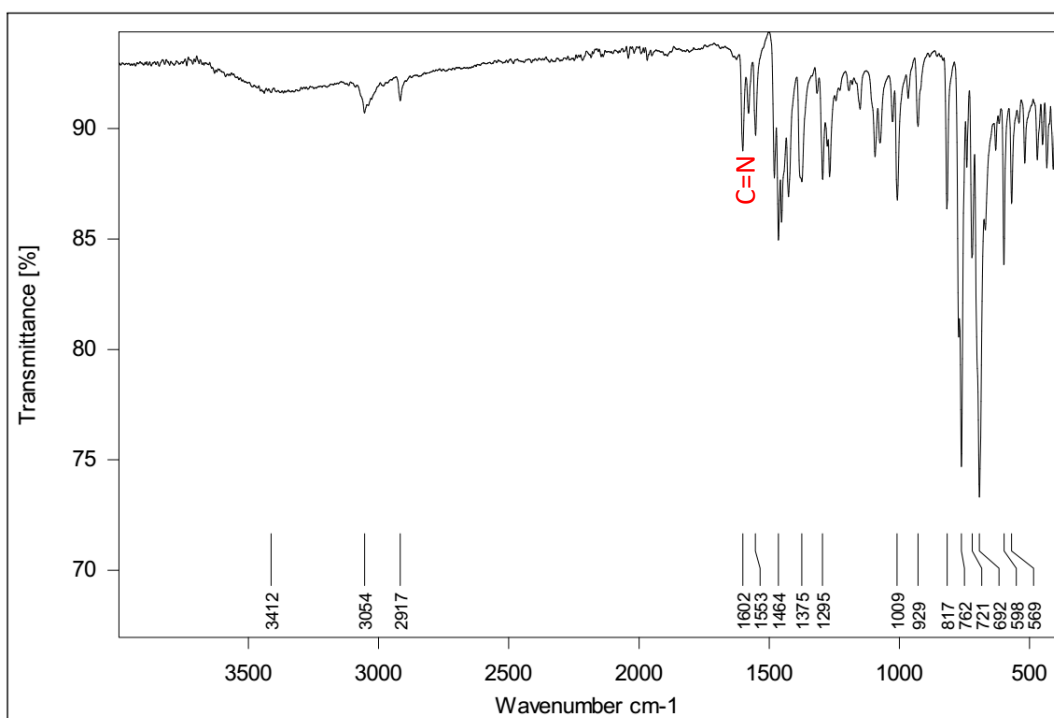


Figure S14: FTIR spectrum for **C3.4**

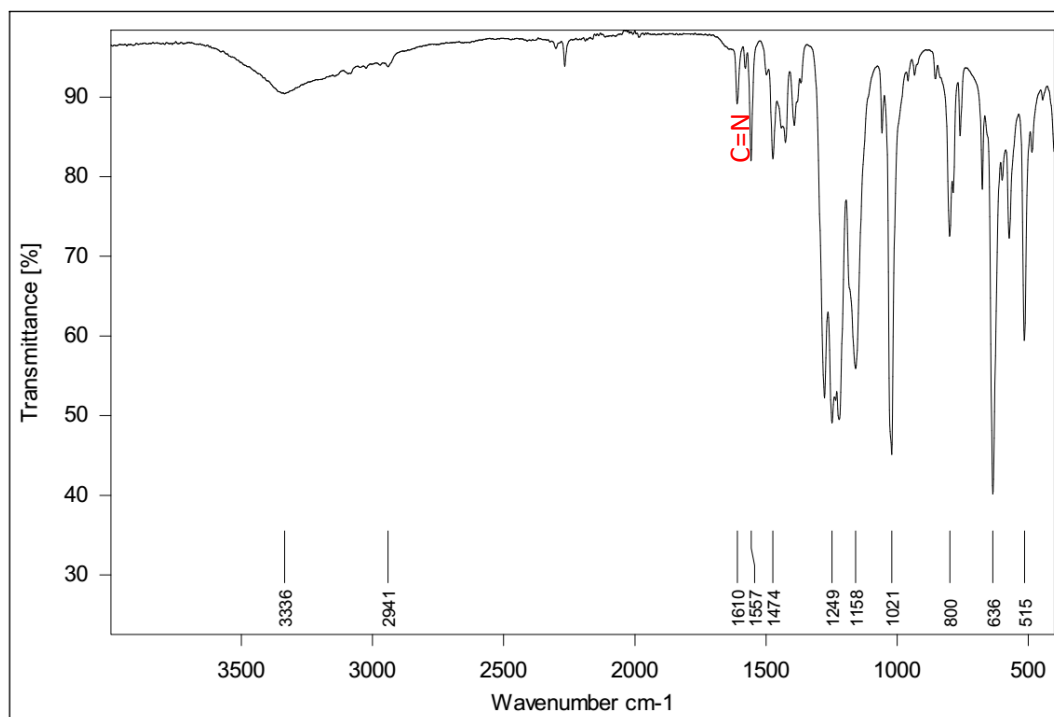


Figure S15: FTIR spectrum for **C3.5**

Appendix: Supplementary information

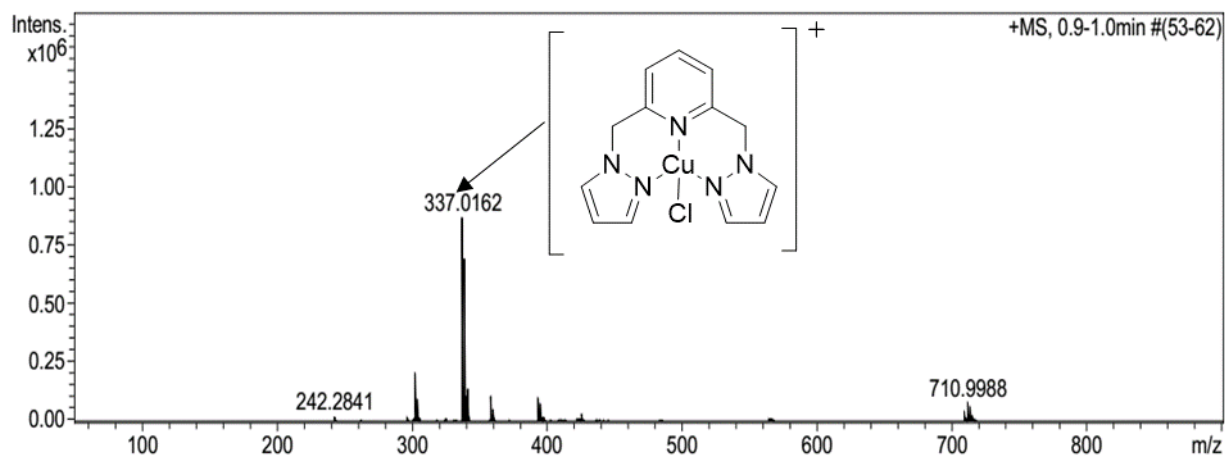


Figure S16: ESI-MS Spectrum for **C3.1**

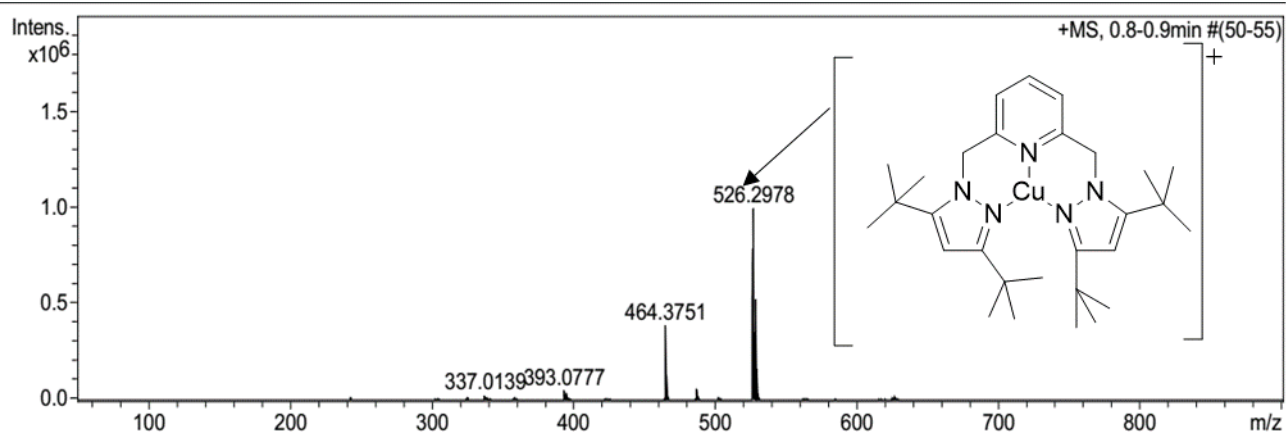


Figure S17: ESI-MS Spectrum for **C3.3**

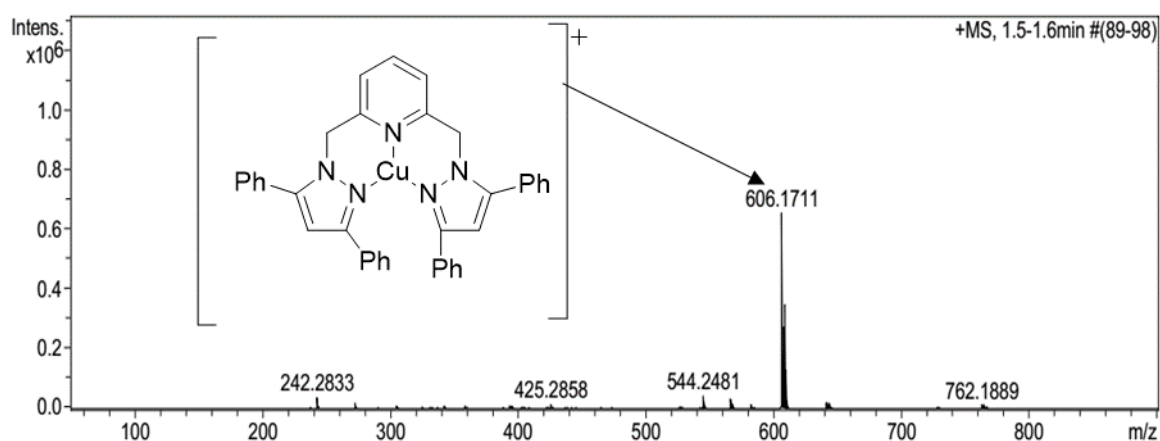


Figure S18: ESI-MS Spectrum for **C3.4**

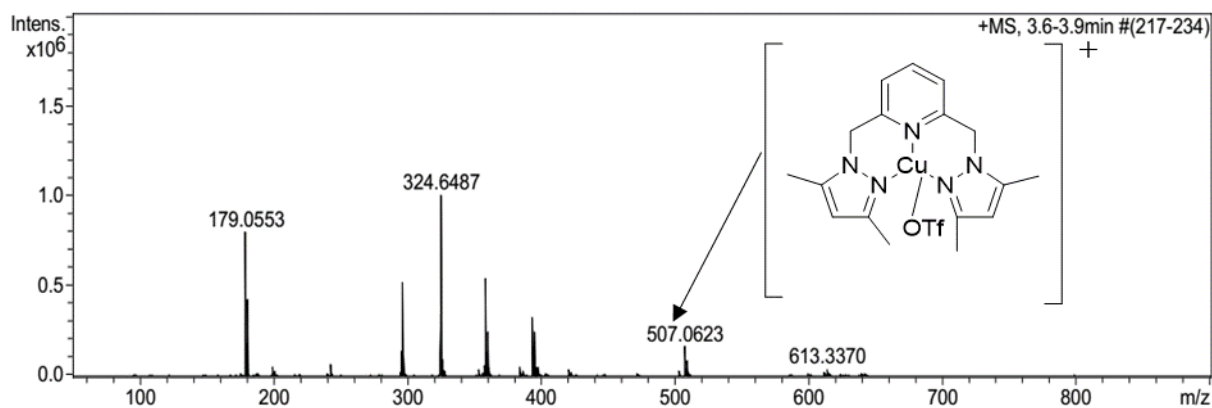


Figure S19: ESI-MS Spectrum for **C3.5**

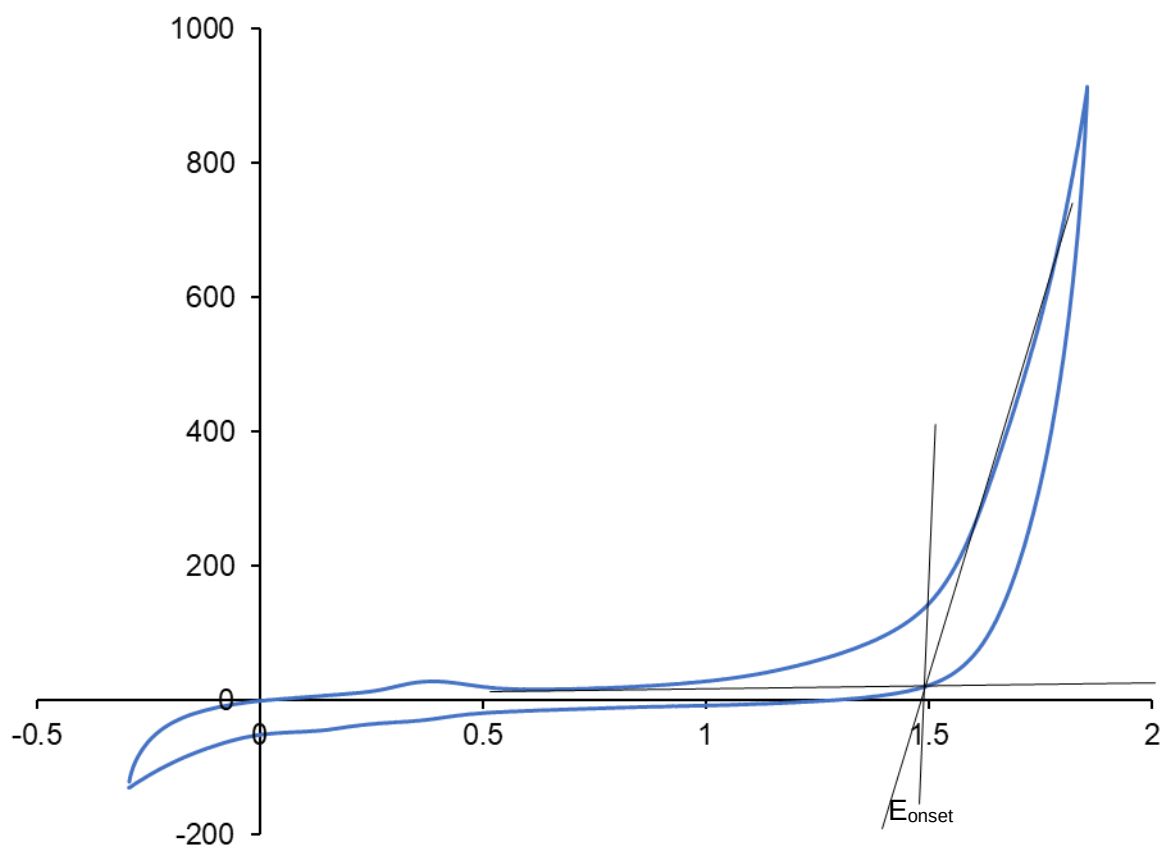


Figure S20: A tangent method for the determination of onset potential for complex **C3.2**.

Supporting information for Chapter 4: Synthesis and characterisation of bis(pyrazol-1-ylmethyl)pyridine-ligated Cu(I) complexes as catalysts in chemical and electrochemical water oxidation.

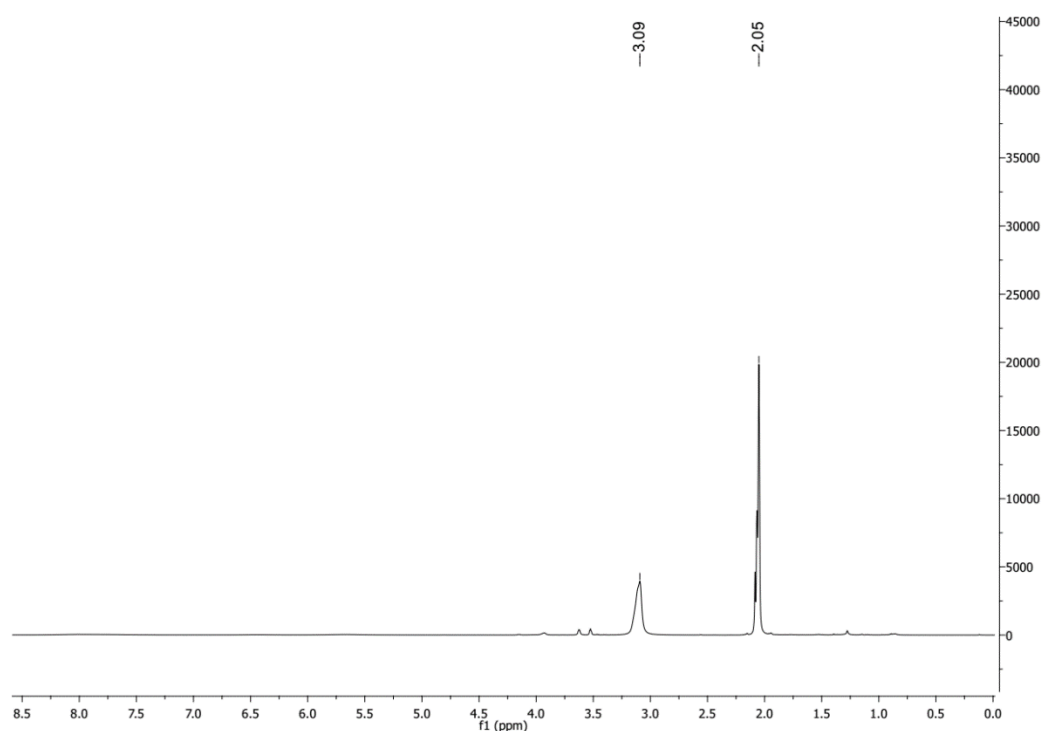


Figure S21: ¹H NMR spectrum of complex C1 in Acetone-d₆

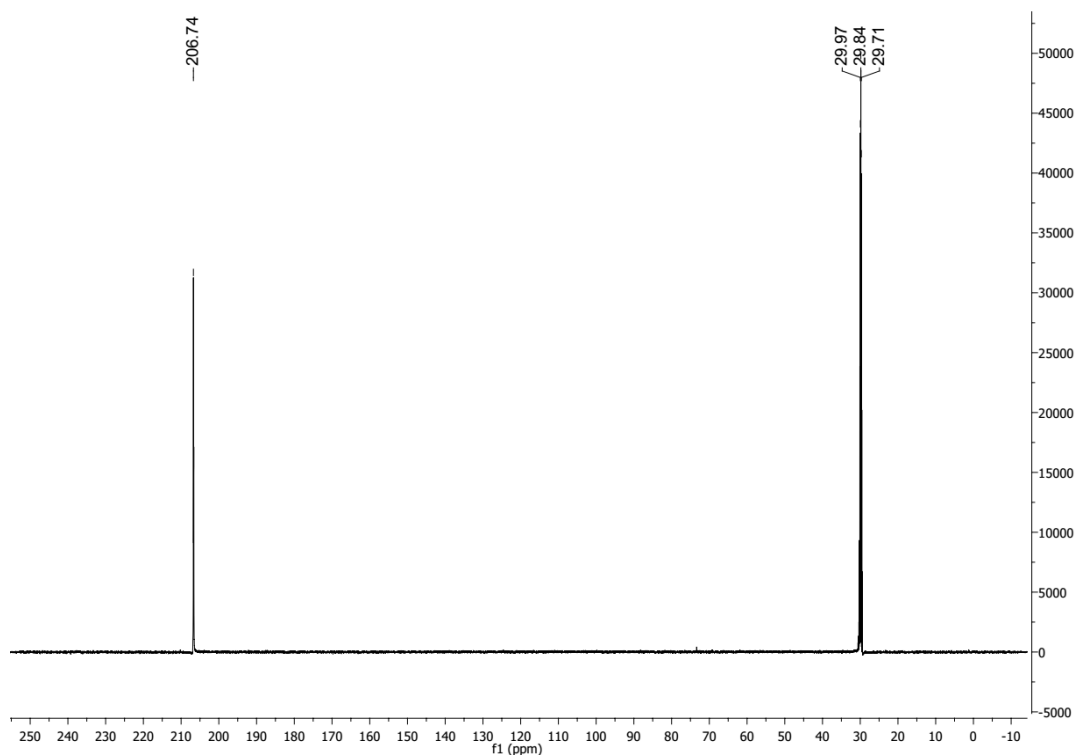


Figure S22: ¹³C{¹H} NMR spectrum of complex C1 in Acetone-d₆

Appendix: Supplementary information

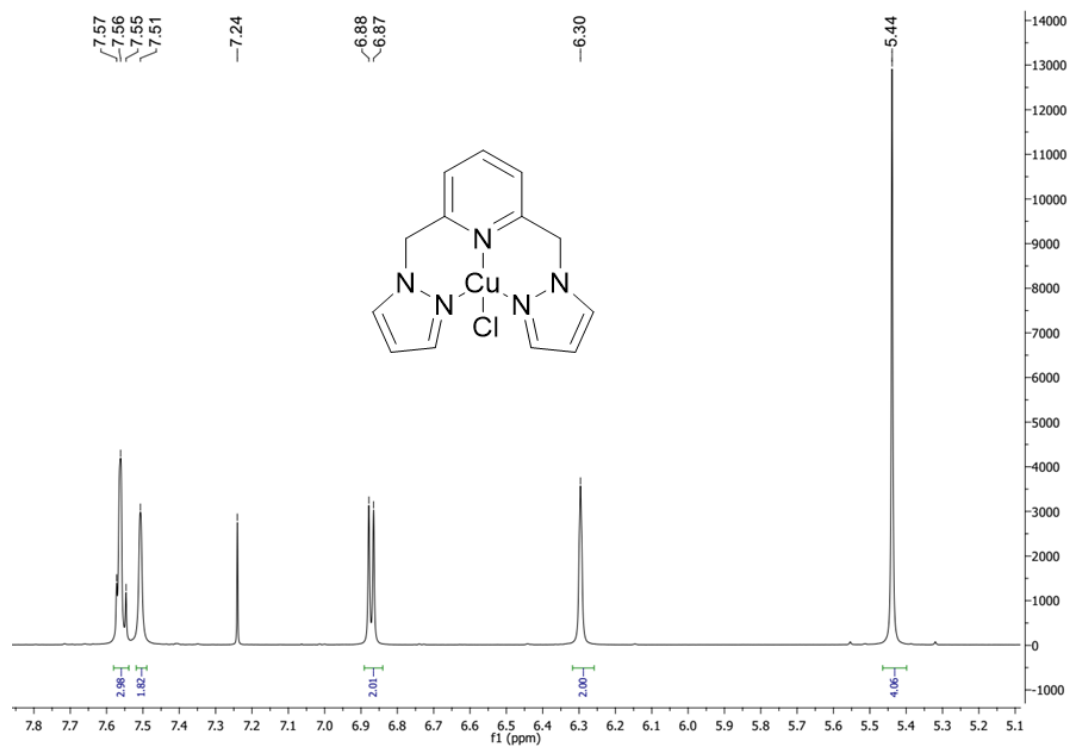


Figure S23: ^1H NMR spectrum of an *in situ* synthesised **L1** and CuCl complex in CDCl_3

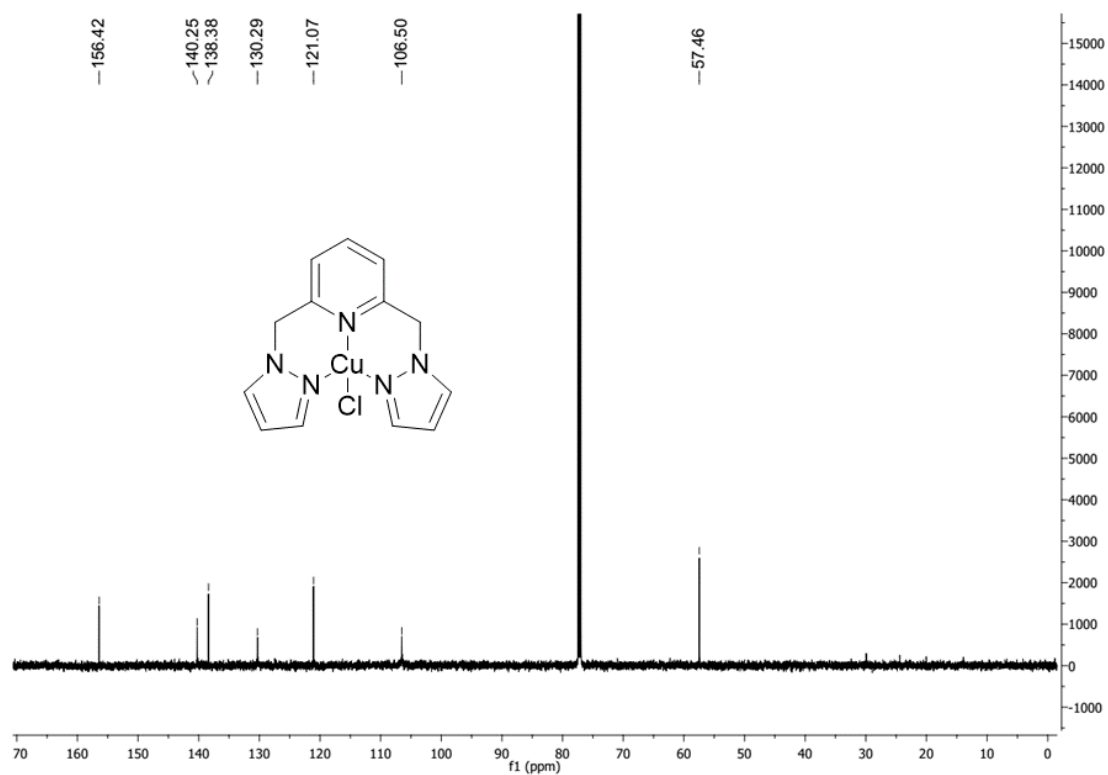


Figure S24: $^{13}\text{C}\{\text{H}\}$ NMR spectrum in situ synthesised **L1** and CuCl complex in CDCl_3

Appendix: Supplementary information

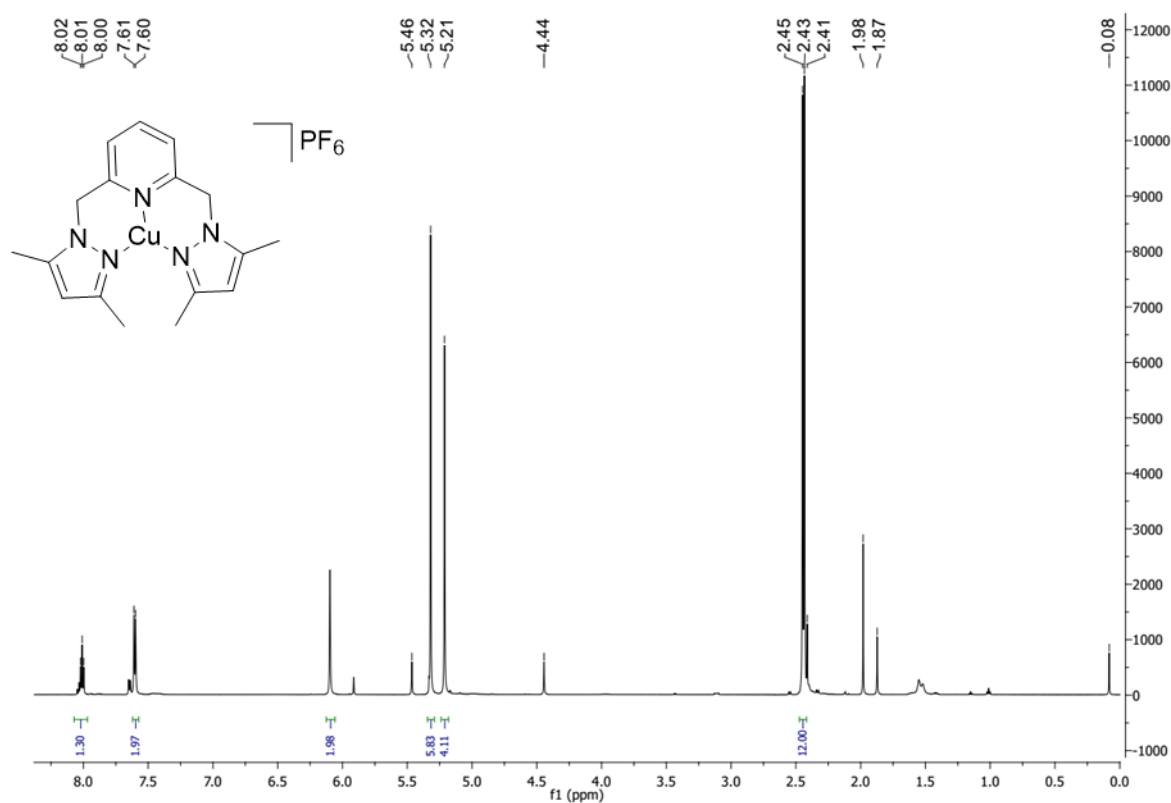


Figure S25: ¹H NMR spectrum for **C4.2**

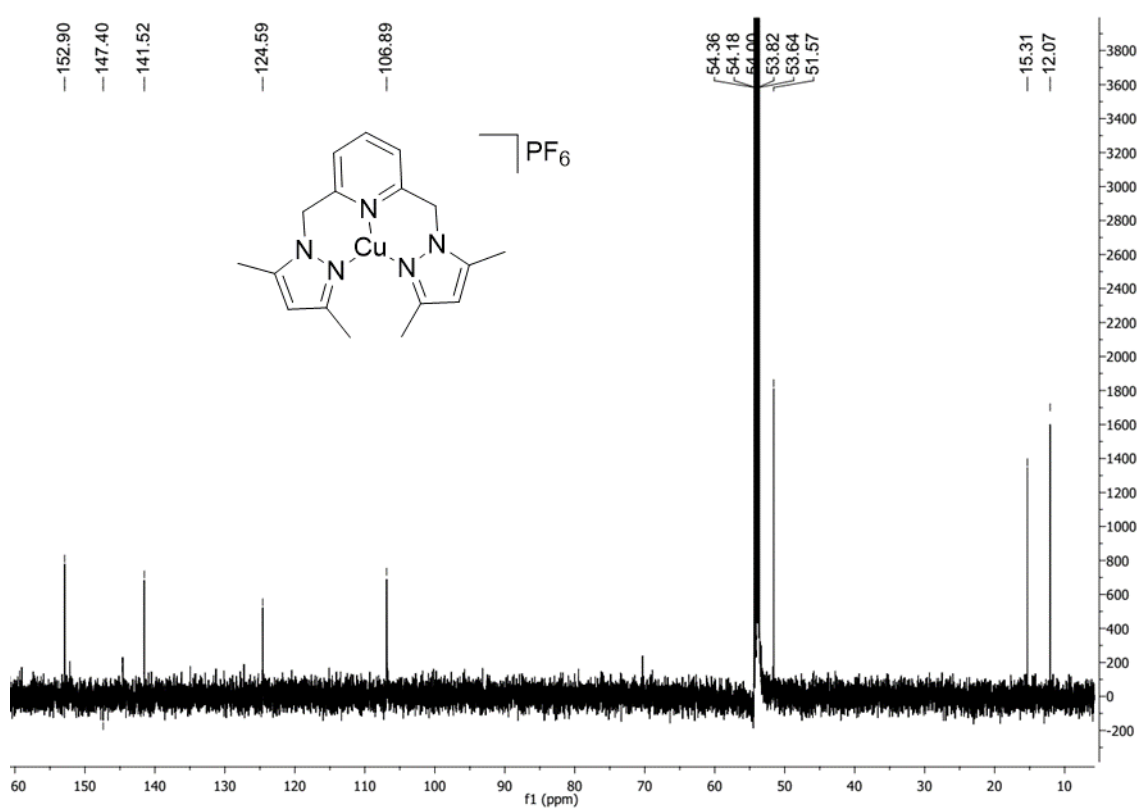


Figure S26: ¹³C{¹H} NMR spectrum for **C4.2**

Appendix: Supplementary information

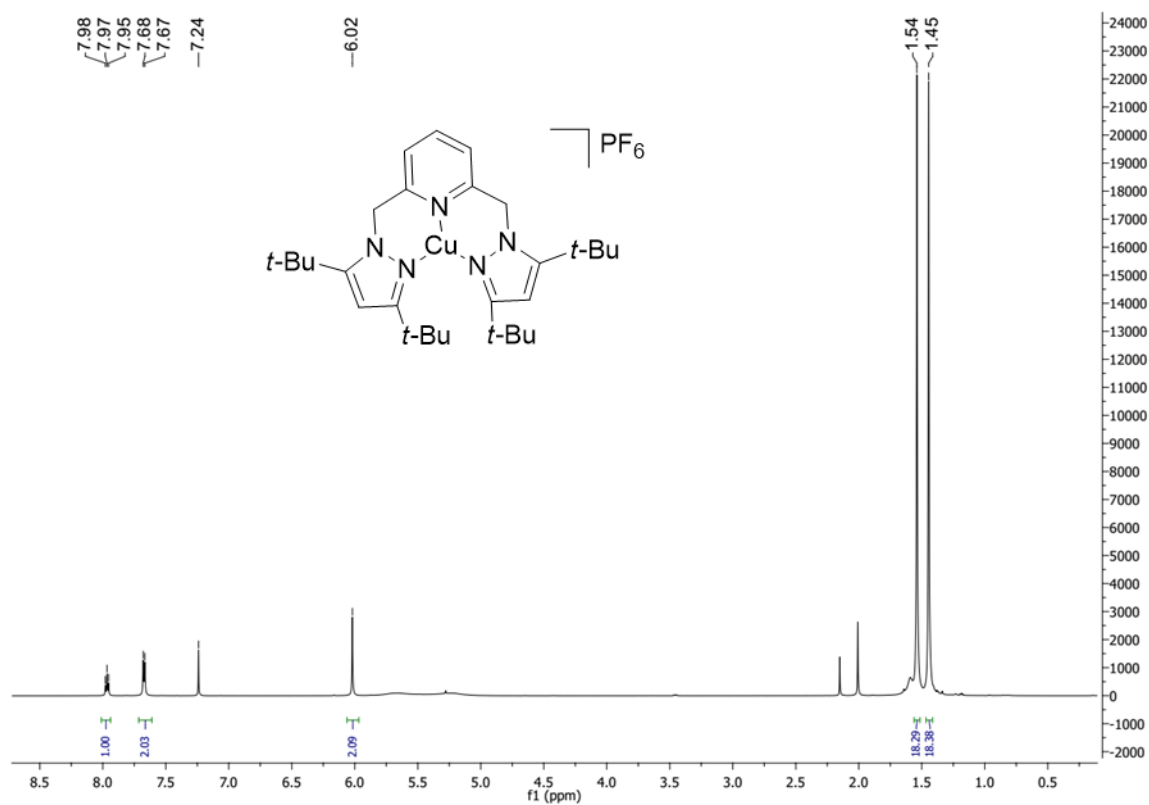


Figure S27: ¹H NMR spectrum for **C4.3**

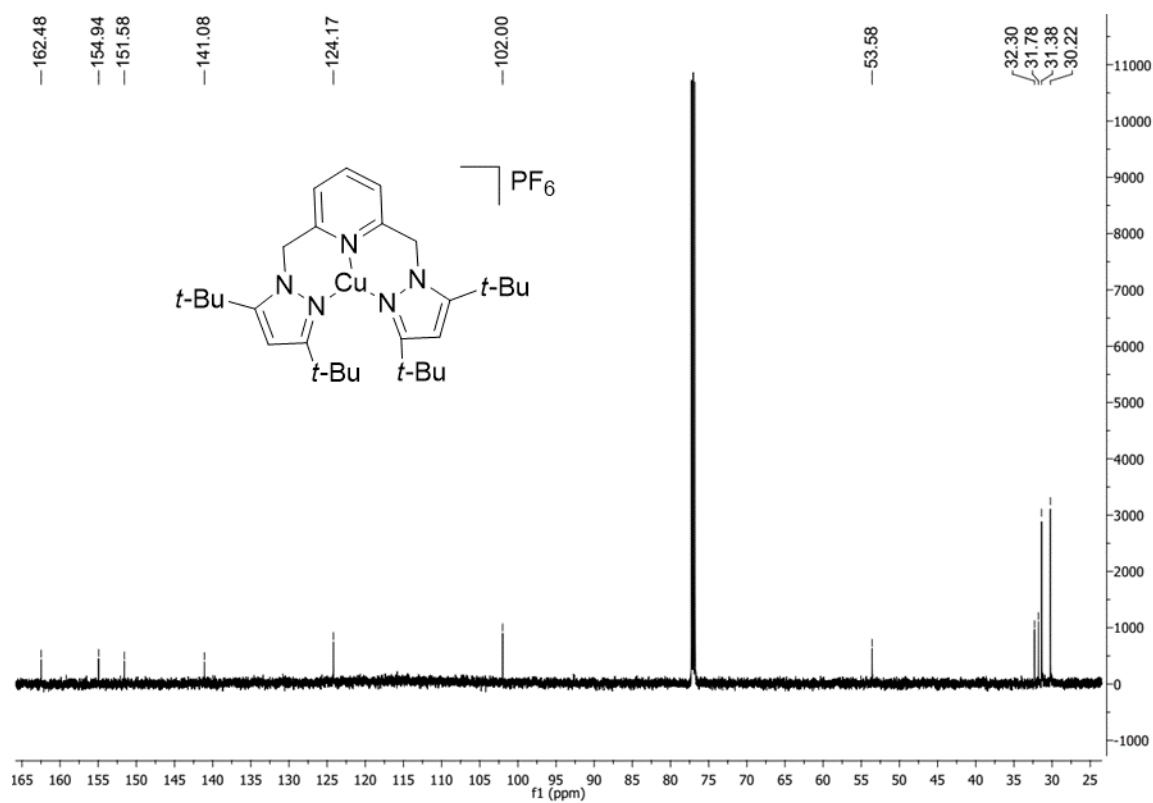


Figure S28: ¹³C{¹H} NMR spectrum for complex **C4.3**

Appendix: Supplementary information

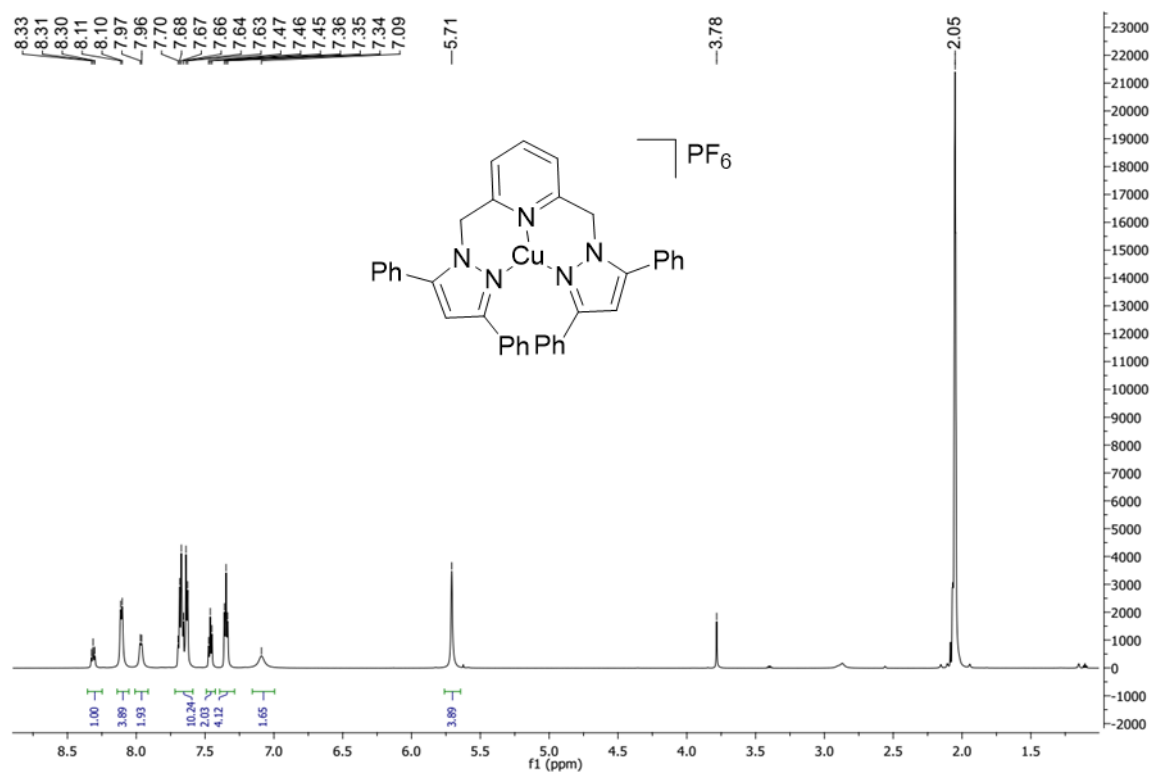


Figure S29: ^1H NMR spectrum for **C4.4**

Appendix: Supplementary information

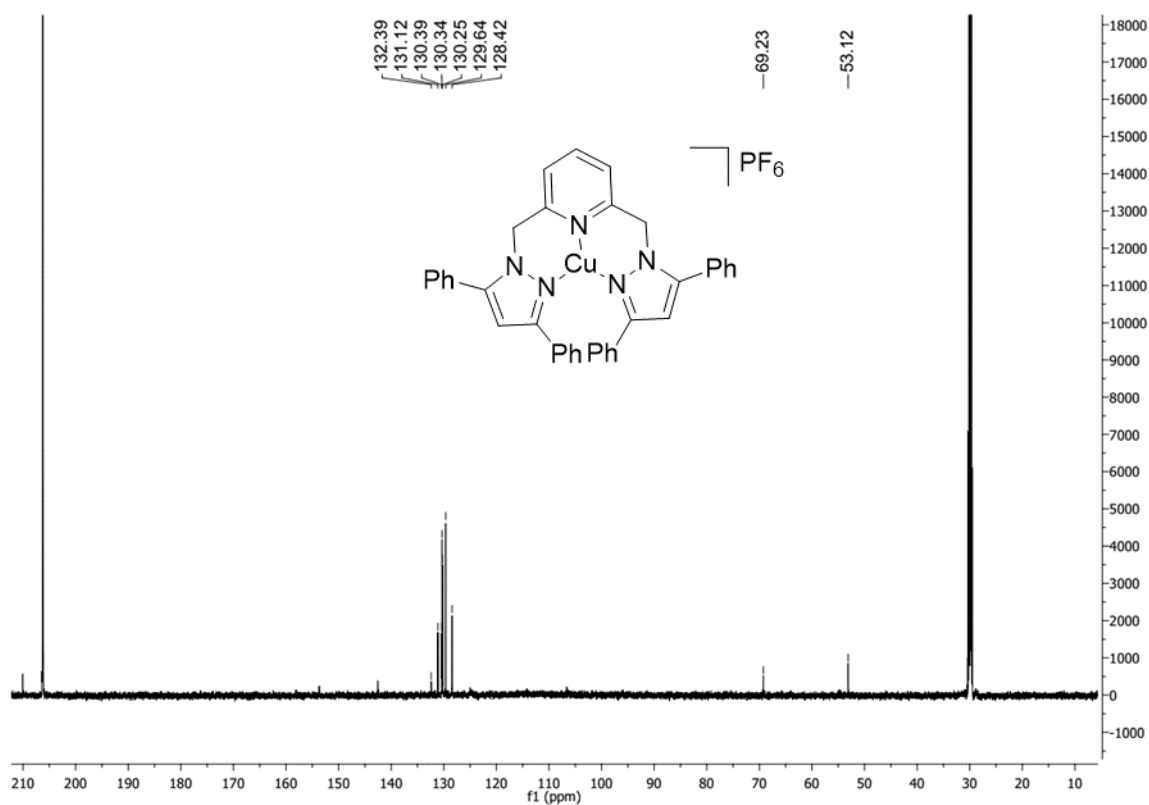


Figure S30: $^{13}\text{C}\{\text{H}\}$ NMR spectrum for **C4.4**

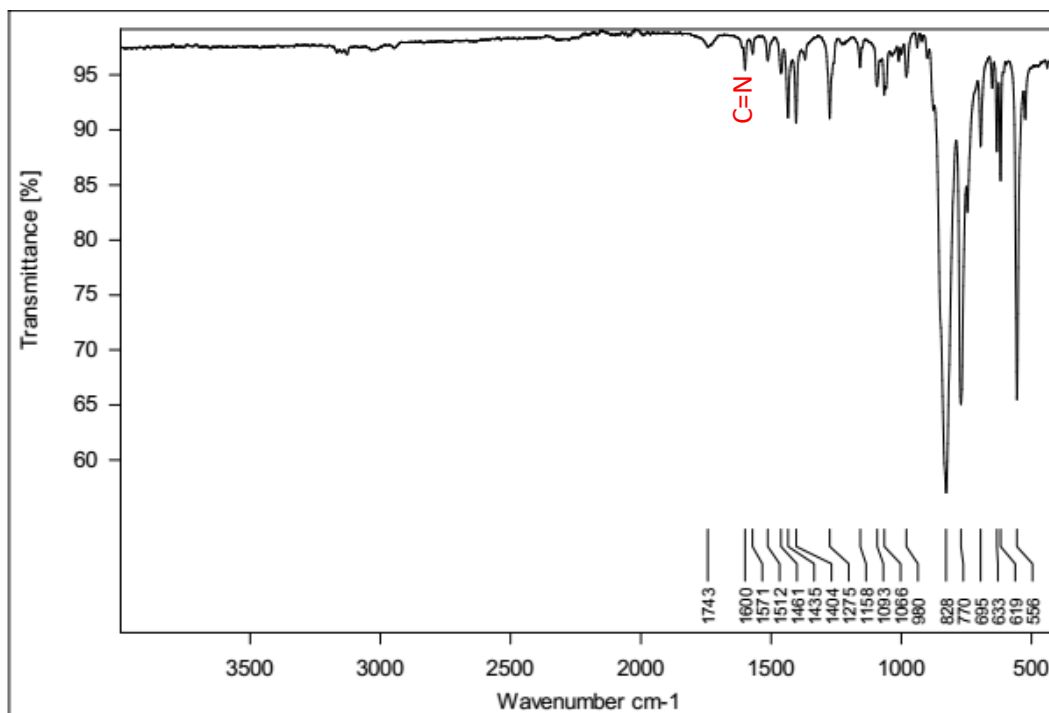


Figure S31: FTIR spectrum for **C4.1**

Appendix: Supplementary information

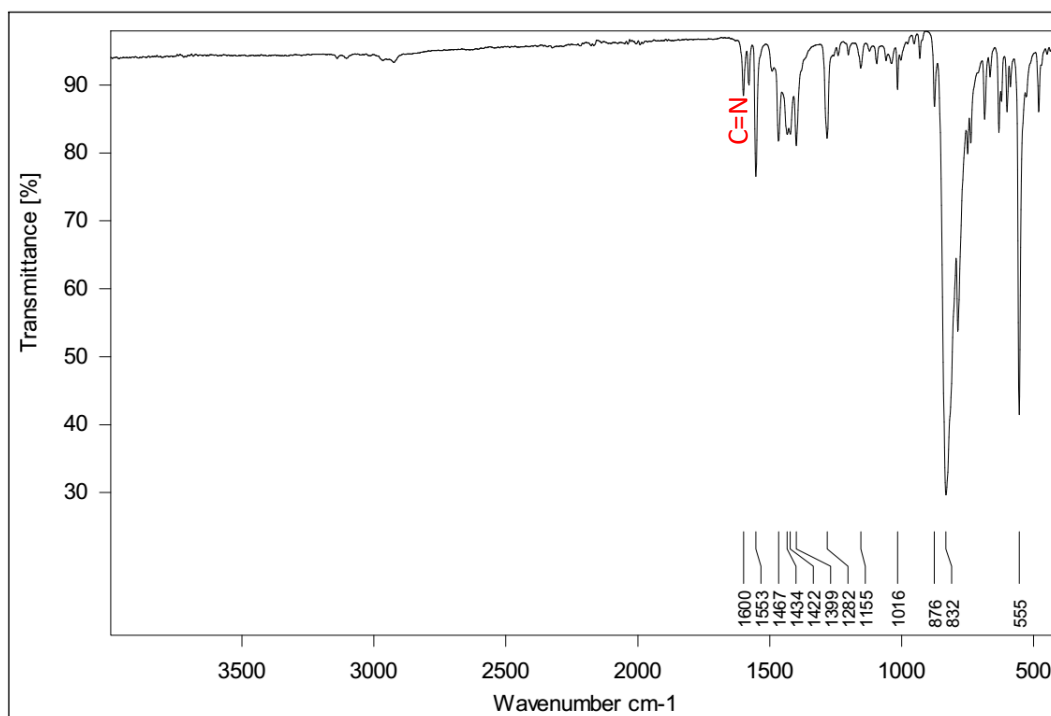


Figure S32: FTIR spectrum for **C4.2**

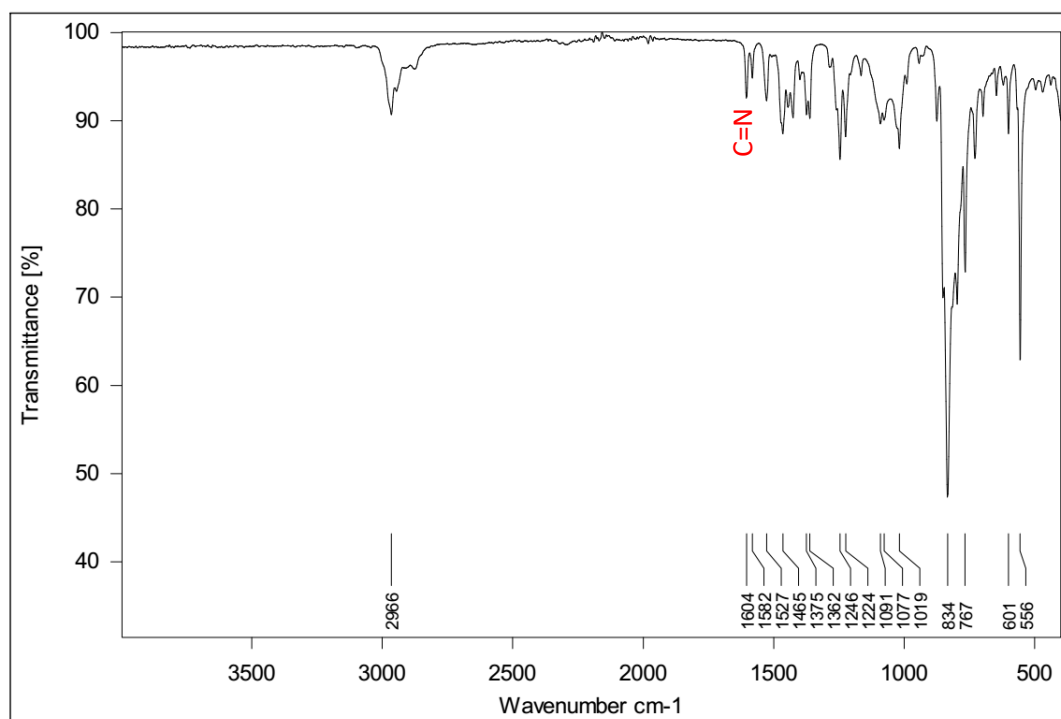


Figure S33: FTIR spectrum for **C4.3**

Appendix: Supplementary information

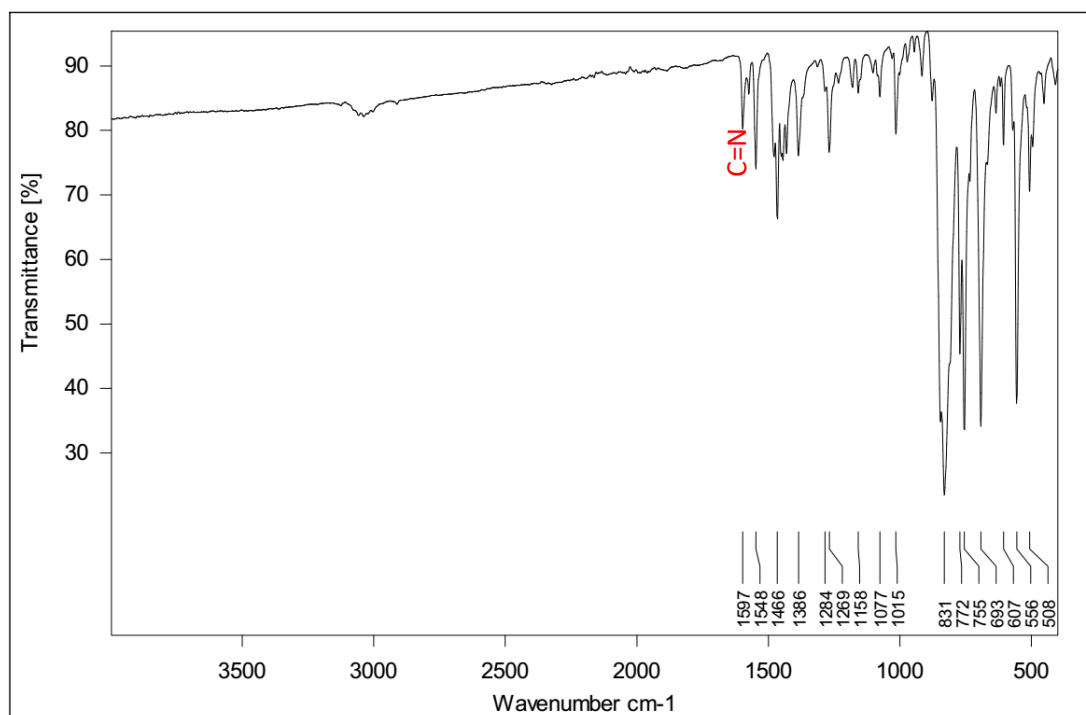


Figure S34: FTIR spectrum for **C4.4**

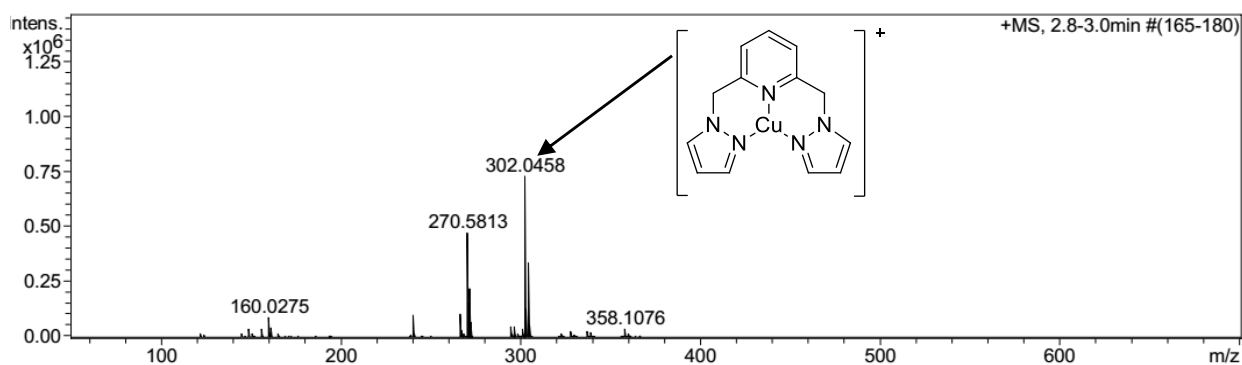


Figure S35: ESI-MS Spectrum for **C4.1**

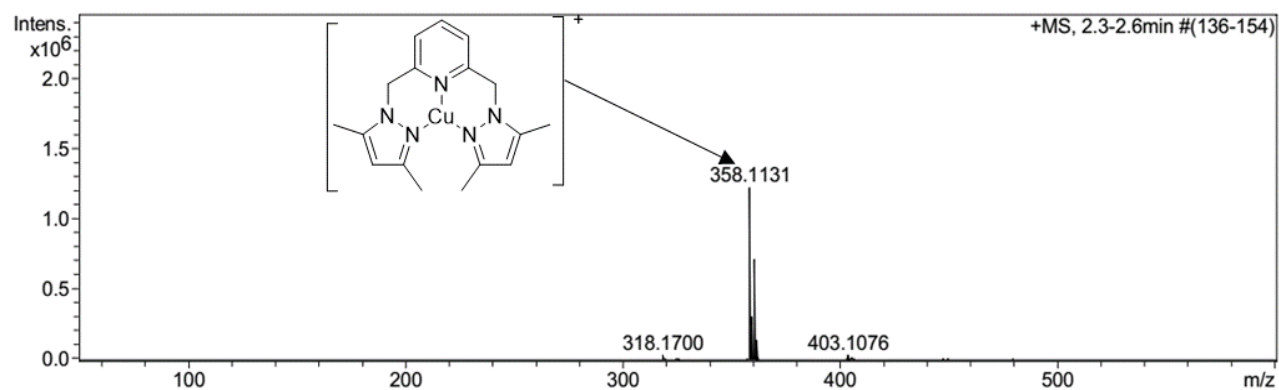


Figure S36: ESI-MS Spectrum for **C4.2**

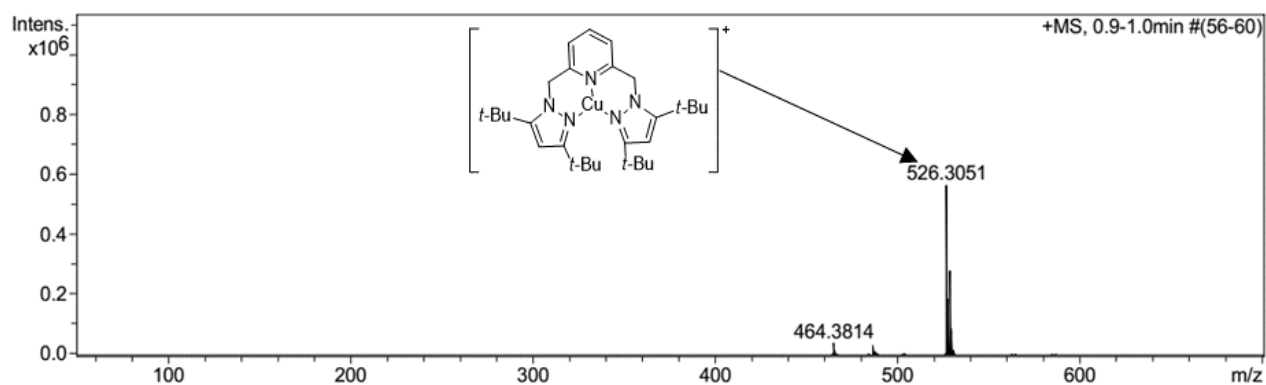


Figure S37: ESI-MS Spectrum for **C4.3**

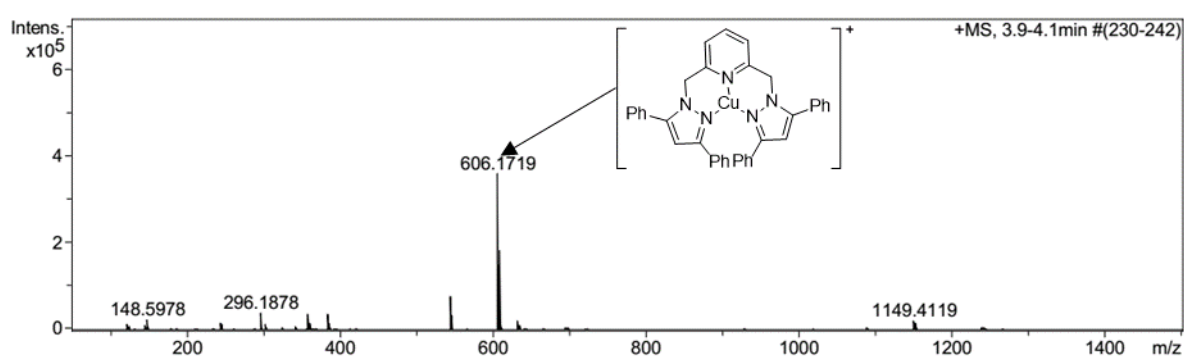


Figure S38: ESI-MS Spectrum for **C4.4**

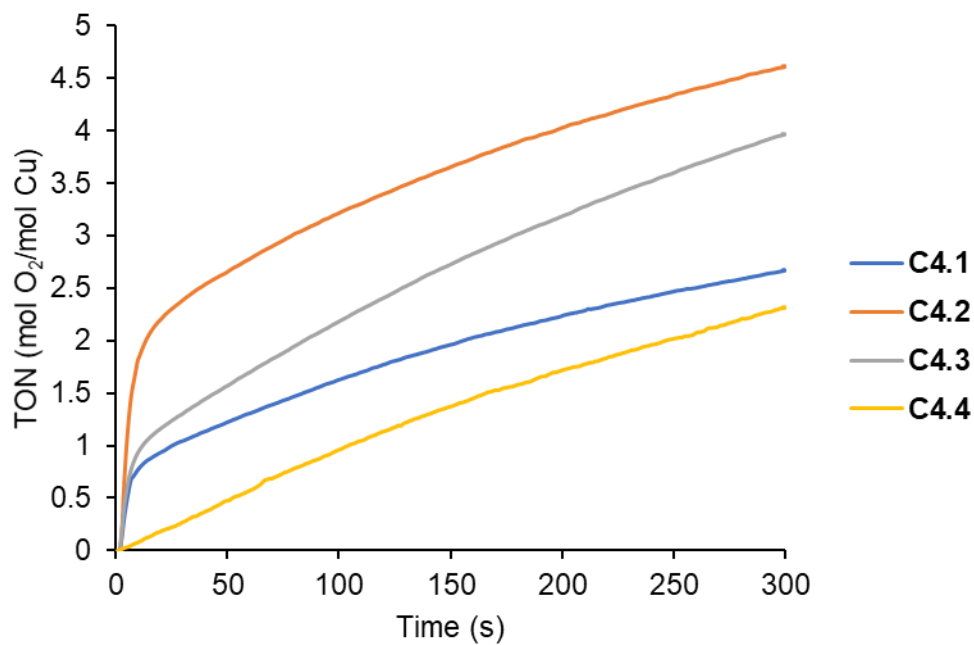


Figure S39: The oxygen evolution curves of Cu(I) complexes **C4.1** to **C4.4** after 5 minutes' reaction time.

Supporting information for Chapter 5: Synthesis, characterization, and catalytic evaluation of bis(pyrazol-1-ylmethyl)pyridine-ligated Co(II) complexes in water oxidation reactions.

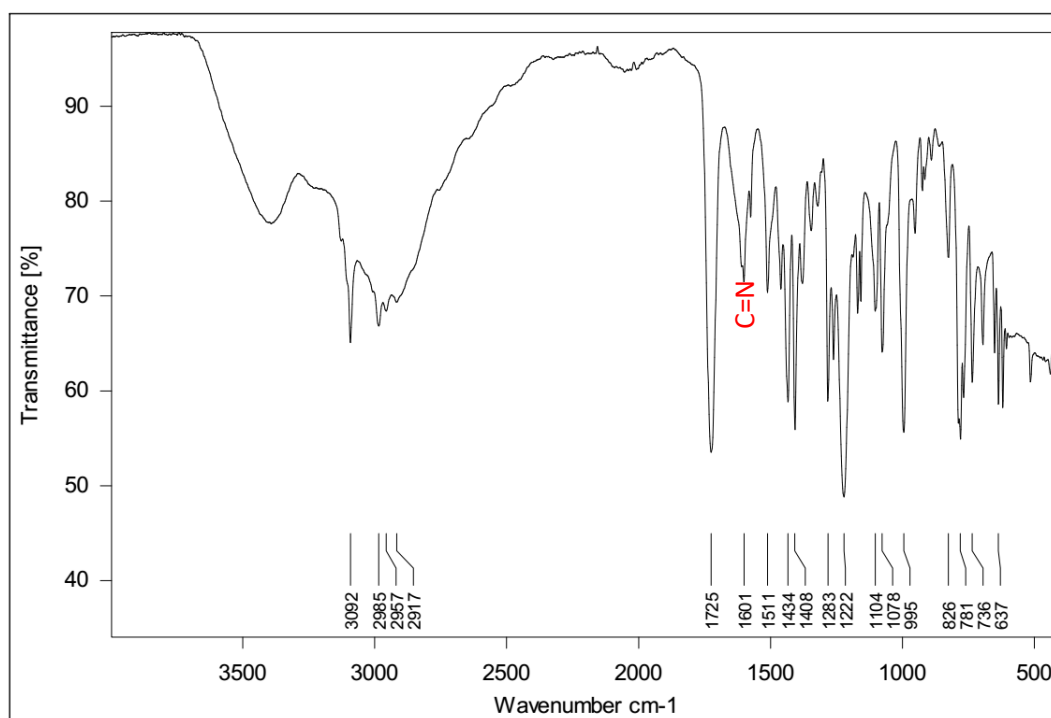


Figure S40: FTIR spectrum for **C5.1**

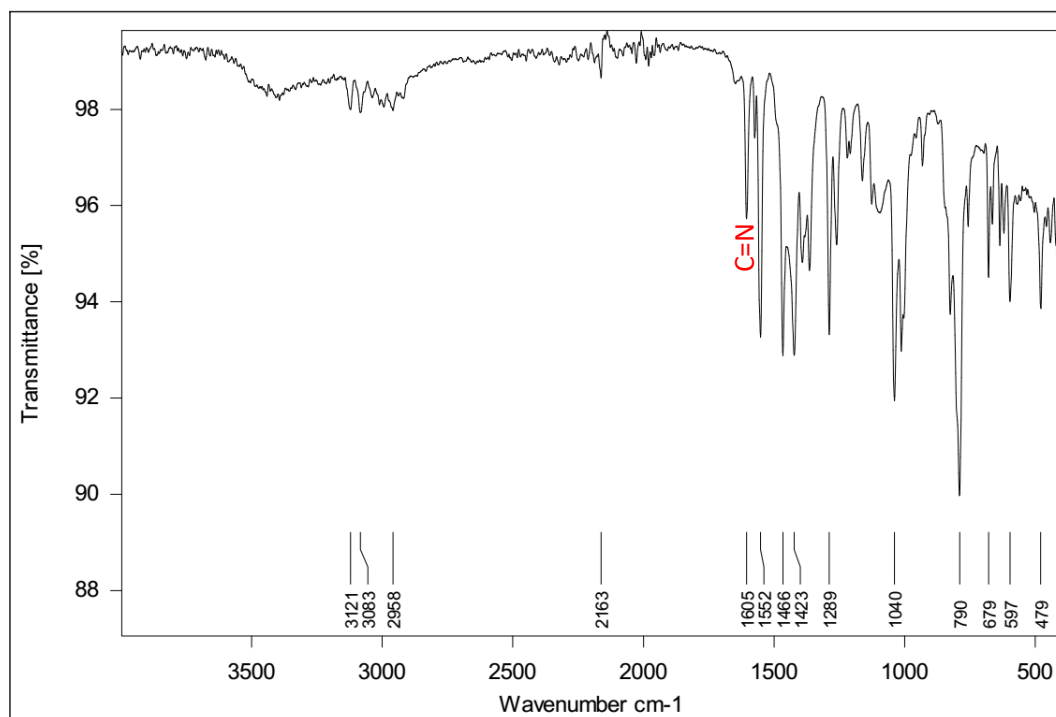


Figure S41: FTIR spectrum for **C5.2**

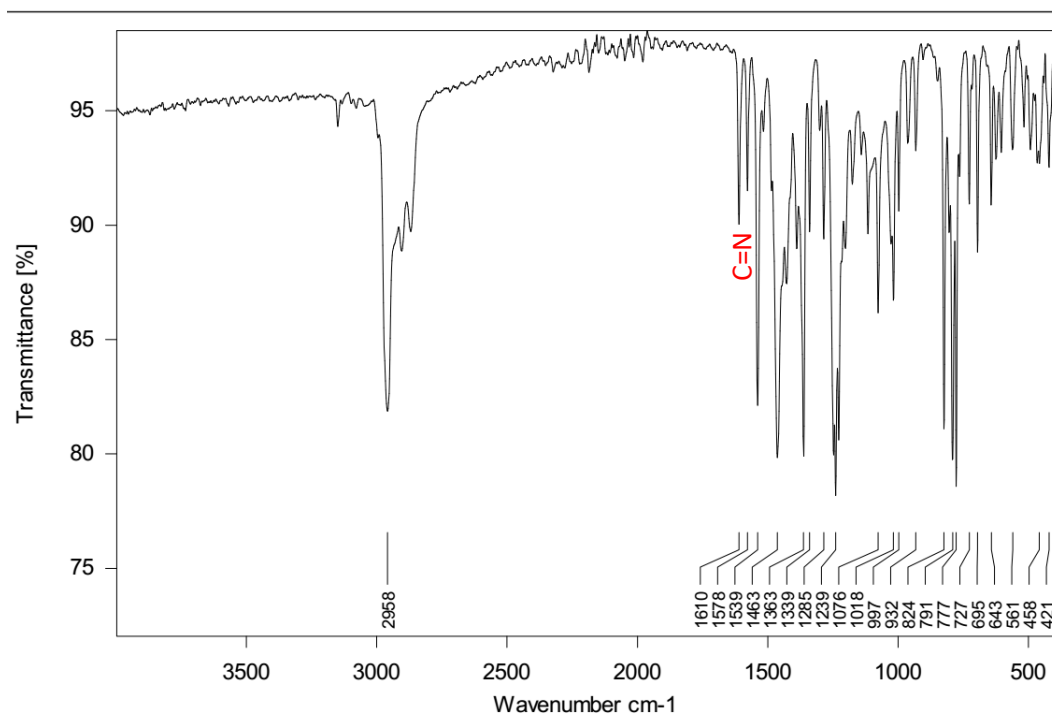


Figure S42: FTIR spectrum for **C5.3**

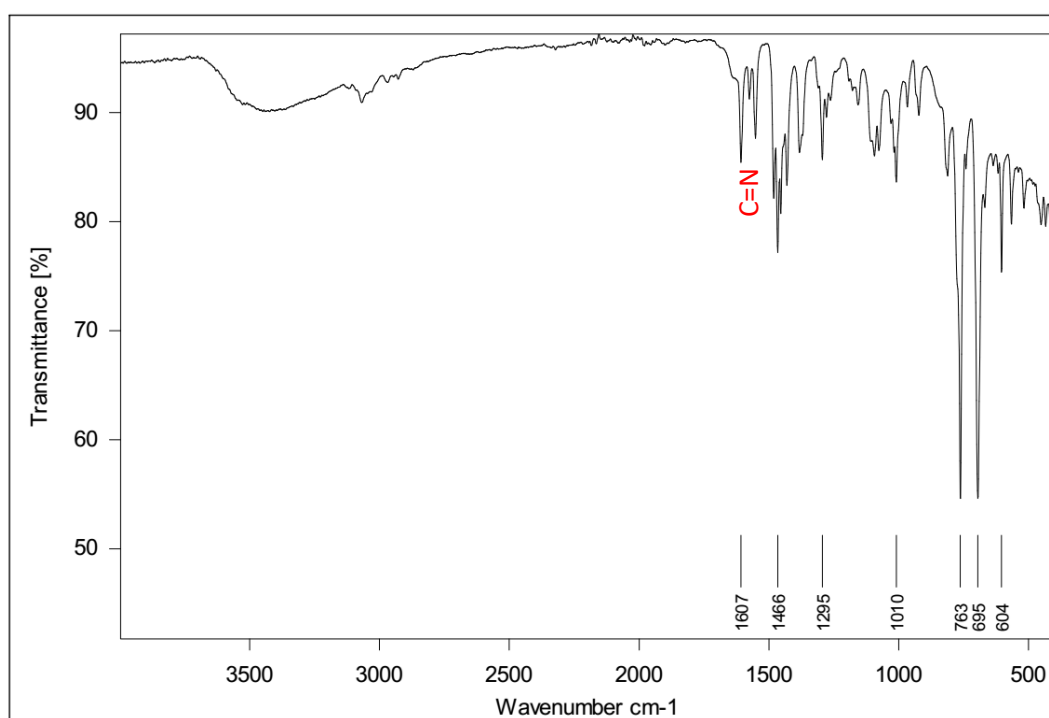


Figure S43: FTIR spectrum for **C5.4**

Appendix: Supplementary information

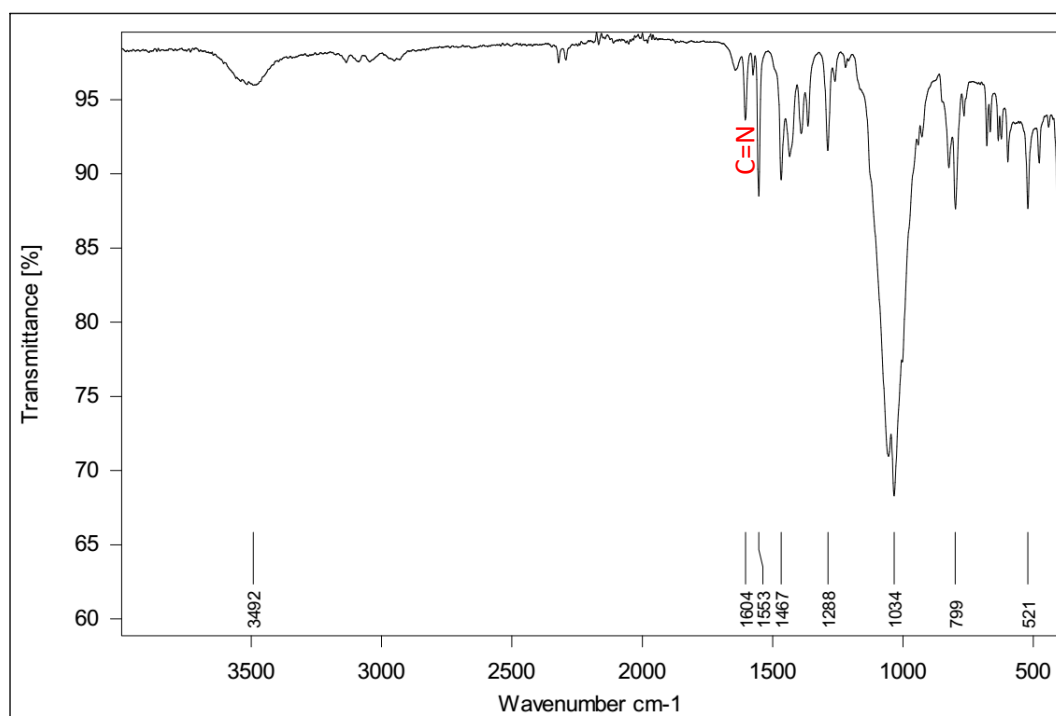


Figure S44: FTIR spectrum for **C5.5**

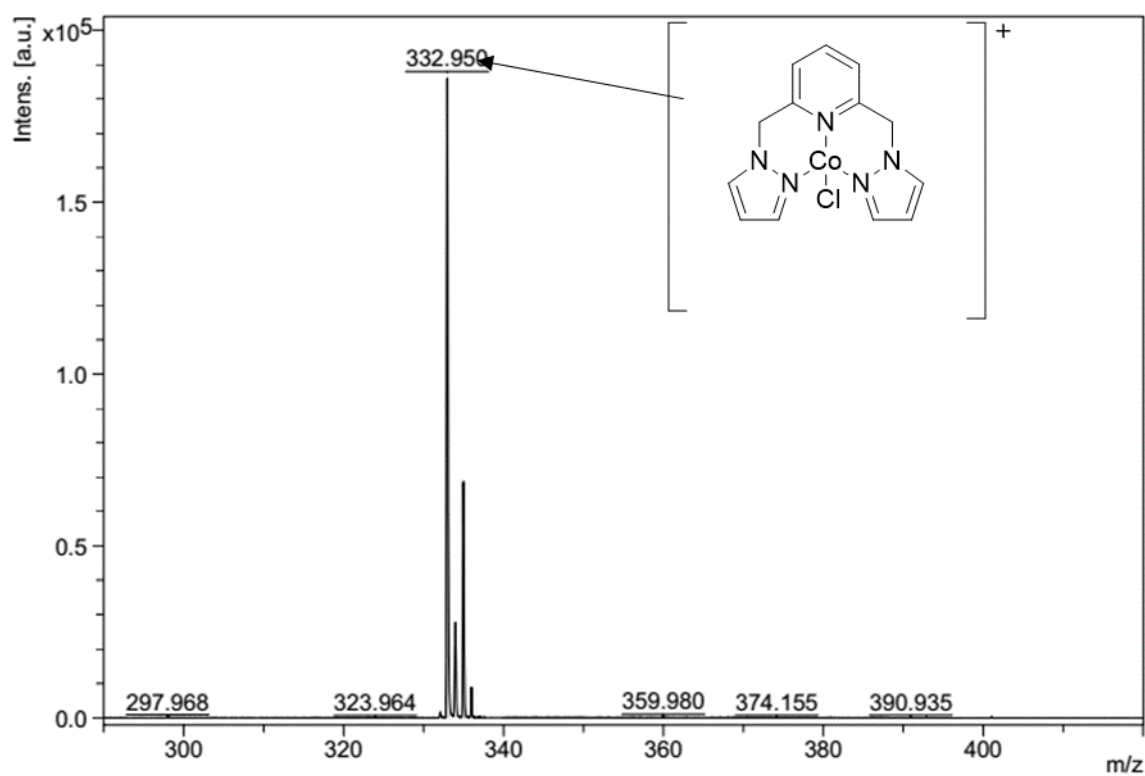


Figure S45: ESI-MS Spectrum for **C5.1**

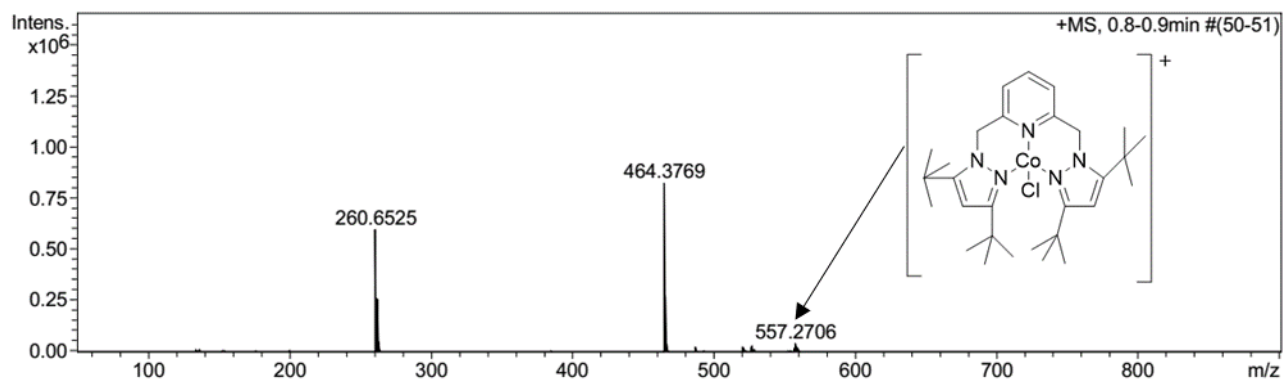


Figure S46: ESI-MS Spectrum for **C5.3**

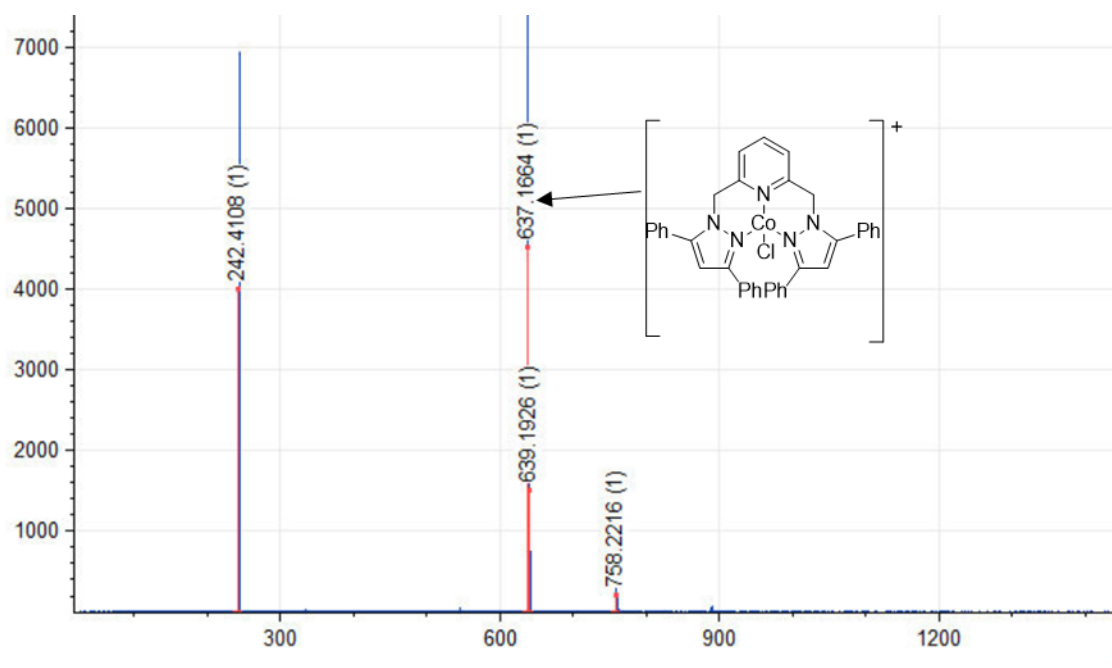


Figure S47: ESI-MS Spectrum for **C5.4**

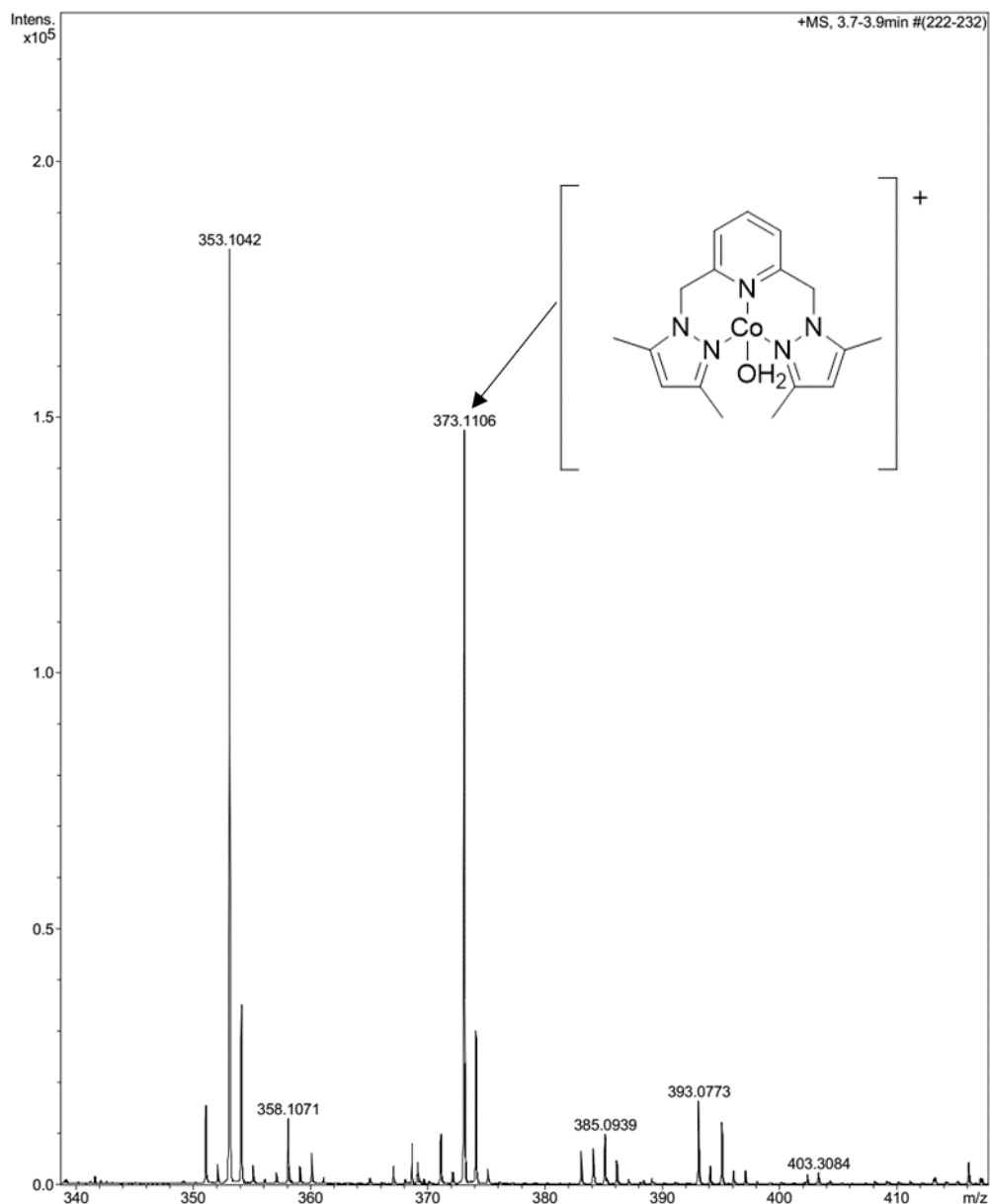


Figure S48: ESI-MS Spectrum for **C5.4**

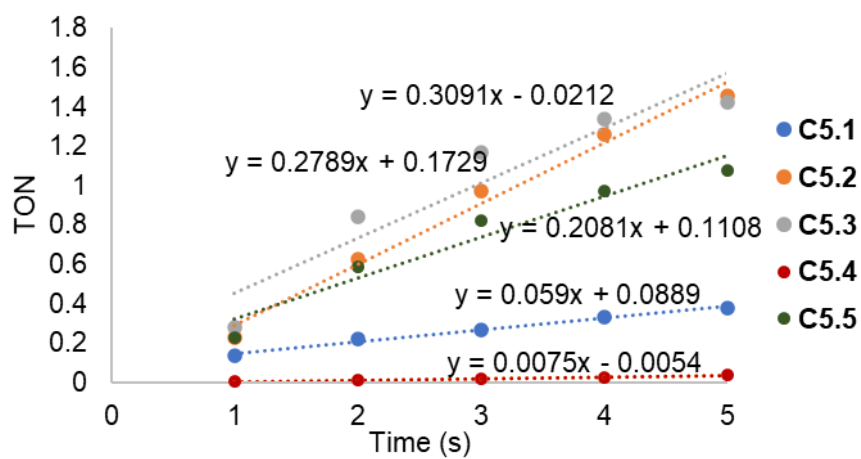


Figure S49: Linear graphs showing the slopes of the TON graph for complexes **C5.1-C5.5**