

Contents

1	Introduction	1
1.1	Natural Photosynthesis	2
1.2	Artificial Photosynthesis	5
1.2.1	Light Harvesting	7
1.2.2	The Acceptor Side: Fuel Production	8
1.2.3	The Donor Side: Water Oxidation	9
1.3	The Mechanism of Water Oxidation	10
1.3.1	Generation of Reactive Metal-Oxo Units by Proton Coupled Electron Transfer Steps	11
1.3.2	Oxygen-Oxygen Bond Formation	14
1.3.3	Release of Dioxygen	16
1.4	Water Oxidation at the <i>Oxygen Evolving Complex</i>	18
1.5	Catalysts for Water Oxidation	21
1.5.1	The Blue Dimer	22
1.5.2	The 3,5-Bis(2-pyridyl)pyrazolate Ligand System	24
1.5.3	Dinuclear Complexes with a Pyridazine Bridging Unit	27
1.5.4	The Mononuclear Complex $[\text{Ru}(\text{trpy})(\text{bpy})(\text{OH}_2)]^{2+}$	28
1.5.5	Mononuclear Complexes Based on the Dianionic 2,2'-Bipyridine-6,6'-dicarboxylic Acid Ligand	29
1.6	The Bis(bipyridyl)pyrazolate Ligand System	32
2	Outline	35
2.1	Complex Design	35
2.2	Project Challenges	37

3	A Synthetic Key Intermediate with an Unusual Binding Motif of Dimethyl Sulphoxide	39
3.1	Introduction	39
3.1.1	Binding Modes of Dimethyl Sulphoxide in Transition Metal Complexes	40
3.1.2	Dichlorotetrakis(dimethyl sulphoxide)ruthenium(II)	42
3.1.3	Monomeric Ruthenium Complexes Based on the Bis-(pyridyl)pyrazole Ligand	42
3.2	Synthesis and Reactivity of the Synthetic Key Intermediate	44
3.2.1	Synthesis	44
3.2.2	Reactivity	47
3.3	Structural and Spectroscopic Characterisation of a Complex with an <i>S,O</i> -Bridging DMSO Ligand	49
3.4	Conclusion	52
4	Complexes Based on the Bis(bipyridyl)pyrazolate Ligand System with Different Substituents on the Pyrazolate Core	55
4.1	Introduction	55
4.1.1	Effects of Subtle Ligand Variations in Literature Known Water Oxidation Catalysts	56
4.1.2	The Bis(bipyridyl)pyrazolate Ligand System	60
4.2	Synthesis	61
4.3	Complexes with a Chlorido-Aqua Coordination Motif in the <i>in, in</i> -Position	63
4.3.1	Structure in Solid State: X-Ray Crystallography	63
4.3.2	Structure in Solution: NMR Spectroscopy	65
4.3.3	Redox properties: Electrochemistry	67
4.4	Acetato Bridged Complexes	69
4.4.1	Structure in Solid State: X-Ray Crystallography	69
4.4.2	Structure in Solution: NMR-spectroscopy	72
4.4.3	Redox Properties: Electrochemistry	74
4.4.4	Water Oxidation Catalysis with Ce ^{IV} as Sacrificial Oxidant	77
4.5	Conclusion	89

5	Kinetic and Synthetic Control: Towards a Water-Soluble Diaqua Species	91
5.1	Introduction	91
5.2	Preparation of Water-Soluble Carbonato and Acetato Bridged Complexes	95
5.2.1	A Water-Soluble Complex with a Carbonato Bridge	95
5.2.2	A Water-Soluble Complex with an Acetato Bridge	99
5.3	Exchange Kinetics Towards the Diaqua Species	104
5.3.1	Replacement of the Acetato Bridge	104
5.3.2	Replacement of the Bicarbonato Bridge	117
5.4	Synthetic Control of the Ligands in the <i>in, in</i> -Position	129
5.4.1	Preparation of a Water-Soluble Diaqua Species	129
5.4.2	Characterisation of a Water-Insoluble Diaqua Species	133
5.4.3	Summary of Synthesis and Spectroscopic Properties	137
5.5	Conclusion	142
6	Benchmarking Spectroscopic Features of Complexes in Higher Oxidation States	145
6.1	Introduction	145
6.1.1	Classification of Mixed-Valent Compounds	146
6.1.2	Measuring Interaction Strength in Mixed-Valent Complexes	149
6.1.3	Examples of Mixed-Valent Ruthenium Complexes	151
6.2	Chlorido-Aqua Compounds	154
6.3	An Acetato Bridged Complex in Higher Oxidation States	159
6.3.1	Electrochemical Oxidation: Spectroelectrochemistry	159
6.3.2	Chemical Oxidation: Spectrophotometric Redox Titration	163
6.3.3	Synthetic Preparation of Higher Oxidation States	168
6.3.4	X-Ray Crystallography	170
6.3.5	Analysis of the Intervalence Charge Transfer Band	172
6.3.6	EPR Spectroscopy	178
6.3.7	X-ray Absorption Spectroscopy	180
6.4	Conclusion	184

7	Insight into the Water Oxidation Process	185
7.1	Introduction	185
7.2	Catalytic Water Oxidation	186
7.3	Towards a Mechanistic Proposal	189
7.3.1	Spectrophotometric Redox Titration	189
7.3.2	Spectroelectrochemistry	193
7.3.3	Stability of Different Redox States	195
7.3.4	Analysis of the Intervalence Charge Transfer Band in the Ru ^{II} /Ru ^{III} Oxidation State	199
7.3.5	<i>Pourbaix</i> Diagram	203
7.3.6	EPR Spectroscopy	215
7.3.7	X-ray Absorption Spectroscopy	221
7.3.8	Exchange Kinetics with Acetonitrile	225
7.3.9	Labelling Experiments	231
7.3.10	A Mechanistic Scenario	237
7.4	Evaluation and Preliminary Investigation of Parameters Controlling the Mechanism of O-O Bond Formation	244
7.4.1	Parameters Determining O-O Bond Formation	244
7.4.2	Solvent Effects on O-O Bond Formation	248
7.5	Pathways of Catalyst Deactivation	265
7.5.1	Deactivation by Anation: Coordination of Phosphate	265
7.5.2	Characterisation of the Species After Catalysis	282
7.5.3	In Conclusion: Improving the Stability of the Catalyst	285
7.6	Conclusion	288
8	Conclusion	291
8.1	Summary	291
8.2	Outlook	294
9	Experimental Section	295
9.1	Material and Methods	295
9.2	Ligand Synthesis	303
9.2.1	^H Diketone	303
9.2.2	^{Me} Diketone	305
9.2.3	^{Me} _{bbp} H	306

9.3	Complex Synthesis	307
9.3.1	$\text{MeA}(\text{Cl}, \text{H}_2\text{O})$ and $\text{MeA}(\text{dmsO})$	307
9.3.2	$\text{MeB}(\text{dmsO})$	310
9.3.3	$\text{MeB}(\text{CO}_3)$	312
9.3.4	$\text{MeC}(\text{O}_2\text{H}_3)$	314
9.3.5	$\text{Me}_1(\text{Cl}, \text{H}_2\text{O})$	315
9.3.6	$\text{Br}_1(\text{Cl}, \text{H}_2\text{O})$	318
9.3.7	$\text{Me}_1(\text{OAc})$	321
9.3.8	$\text{Br}_1(\text{OAc})$	323
9.3.9	$\text{Me}_1(\text{OH})_2$, $\text{Me}_1(\text{O}_2\text{H}_3)$ and $\text{Me}_1(\text{H}_2\text{O})_2$	325
9.3.10	$\text{Me}_1(\text{H}_2\text{PO}_4)$	327
9.3.11	$\text{Me}_3(\text{Cl}, \text{H}_2\text{O})$	329
9.3.12	$\text{Me}_3(\text{CO}_3)$	331
9.3.13	$\text{Me}_3(\text{OAc})$	335
9.3.14	$\text{Me}_3(\text{OH})_2$, $\text{Me}_3(\text{O}_2\text{H}_3)$, and $\text{Me}_3(\text{H}_2\text{O})_2$	337
Appendix		341
I	UV-vis-NIR Spectroscopy	343
I.1	Spectroelectrochemistry	343
I.1.1	$\text{Me}_1(\text{Cl}, \text{H}_2\text{O})$	343
I.1.2	$\text{Me}_1(\text{OAc})$	345
I.1.3	$\text{Me}_3(\text{H}_2\text{O})_2$	346
I.2	Spectrophotometric Redox Titrations	348
I.2.1	$\text{Me}_1(\text{OAc})$	348
I.2.2	$\text{Me}_3(\text{H}_2\text{O})_2$	351
I.2.3	$\text{Me}_1(\text{H}_2\text{O})_2$	352
I.3	Exchange Kinetics Towards the Diaqua Species	353
I.3.1	Replacement of the Acetato Bridge	353
I.3.2	Replacement of the Bicarbonato Bridge	354
I.3.3	Species After Catalysis	355
I.4	Stability of $\text{Me}_3(\text{H}_2\text{O})_2$ in Different Oxidation States	356
I.4.1	$\text{Ru}^{\text{II}}\text{Ru}^{\text{II}}$	356
I.4.2	$\text{Ru}^{\text{II}}\text{Ru}^{\text{III}}$	357
I.5	Exchange Kinetics with Acetonitrile	358

I.6	Spectrophotometric Acid-Base Titration	360
I.7	Exchange Kinetics with Phosphate	361
II	Mass Spectrometry	363
II.1	Complexes	363
II.2	Labelling Experiments	364
III	Electrochemistry	371
III.1	Complexes	371
III.1.1	$\text{Me}_1(\text{Cl}, \text{H}_2\text{O})$	371
III.1.2	$\text{Br}_1(\text{Cl}, \text{H}_2\text{O})$	372
III.1.3	$\text{Me}_1(\text{OAc})$	373
III.1.4	$\text{Me}_3(\text{HCO}_3)$	373
III.1.5	$\text{Me}_1(\text{O}_2\text{H}_3)$ and $\text{Me}_1(\text{H}_2\text{O})_2$	374
III.2	Exchange Kinetics Towards the Diaqua Species	378
III.2.1	Replacement of the Acetato Bridge	378
III.2.2	Replacement of the Bicarbonato Bridge	379
III.3	<i>Pourbaix</i> Diagram	380
III.3.1	Redox Processes of $\text{Me}_3(\text{H}_2\text{O})_2$ at Different pH Values	380
III.3.2	Determination of Redox Potentials	385
III.3.3	Electrochemistry of $\text{Me}_1(\text{H}_2\text{O})_2$ in a Phosphate Buffer	387
IV	Kinetic Data	389
IV.1	Exchange Kinetics Towards the Diaqua Species	390
IV.1.1	Replacement of the Bicarbonato Bridge	390
IV.1.2	Replacement of the Acetato Bridge	392
IV.2	Exchange Kinetics with Acetonitrile	393
IV.3	Exchange Kinetics with Phosphate	394
V	NMR Spectroscopy	395
V.1	Ligands	396
V.1.1	Me_{bbpH}	396
V.1.2	Br_{bbpH}	402
V.1.3	H_{bbpH}	406

V.2	Complexes	410
V.2.1	$\text{MeA}(\text{dmso})$	410
V.2.2	$\text{MeB}(\text{dmso})$	417
V.2.3	$\text{MeB}(\text{CO}_3)$	422
V.2.4	$\text{MeC}(\text{O}_2\text{H}_3)$	425
V.2.5	$\text{Me1}(\text{Cl}, \text{H}_2\text{O})$	431
V.2.6	$\text{Br1}(\text{Cl}, \text{H}_2\text{O})$	436
V.2.7	$\text{Me1}(\text{OAc})$	441
V.2.8	$\text{Br1}(\text{OAc})$	446
V.2.9	$\text{Me1}(\text{OH})_2$, $\text{Me1}(\text{O}_2\text{H}_3)$ and $\text{Me1}(\text{H}_2\text{O})_2$	451
V.2.10	$\text{Me1}(\text{H}_2\text{PO}_4)$	456
V.2.11	$\text{Me3}(\text{Cl}, \text{H}_2\text{O})$	462
V.2.12	$\text{Me3}(\text{CO}_3)$	463
V.2.13	$\text{Me3}(\text{OAc})$	468
V.2.14	$\text{Me3}(\text{OH})_2$, $\text{Me3}(\text{O}_2\text{H}_3)$ and $\text{Me3}(\text{H}_2\text{O})_2$	474
V.3	Exchange Kinetics Towards the Diaqua Species	479
V.3.1	Replacement of the Acetato Bridge	479
V.3.2	Replacement of the Bicarbonato Bridge	481
V.4	Synthetic Control of the Bridging Ligand	483
V.5	Species After Catalysis	484
VI	EPR Spectroscopy	485
VI.1	$\text{Me1}(\text{OAc})$	485
VI.2	$\text{Me3}(\text{H}_2\text{O})_2$	486
VI.3	EPR Parameter of the Blue Dimer	489
VII	X-ray Crystallography	491
VII.1	Additional Crystal Structures	491
VII.1.1	$\text{Me1}(\text{Cl}, \text{H}_2\text{O})$	491
VII.1.2	$\text{Me1}(\text{OAc})$	492
VII.1.3	$\{[\text{Ru}(\text{pySO}_3)_2(\text{MeCN})][\text{Ru}(\text{pySO}_3)(\text{MeCN})_2]$ $(\mu\text{-}^{\text{Me}}\text{bbp})\}$	492
VII.1.4	$\text{Me1}(\text{H}_2\text{PO}_4)$	493
VII.2	Selected Geometric Parameters	493

VII.3	Selected Bond Lengths and Angles	497
VII.3.1	MeB(dmso)	497
VII.3.2	Me1(Cl,H ₂ O)	499
VII.3.3	Br1(Cl,H ₂ O)	500
VII.3.4	Me1(OAc)	501
VII.3.5	Me1(OAc) (Ru ^{II} Ru ^{III})	502
VII.3.6	Br1(OAc)	503
VII.3.7	Me1(O ₂ H ₃)	504
VII.3.8	Me1(H ₂ PO ₄)	505
VII.3.9	Me3(CO ₃)	509
VII.3.10	Me3(OAc)	511
VII.4	Crystal Data and Refinement Details	512
VIII	X-ray Absorption Spectroscopy	517
VIII.1	X-ray Absorption Near Edge Structure	517
VIII.2	Extended X-ray Absorption Fine Structure	519
IX	Catalysis	523
IX.1	Setup	523
IX.2	Me1(OAc)	525
IX.3	Br1(OAc)	526
IX.4	Me3(H ₂ O) ₂	527
	Bibliography	529
	Structures of Ligands and Complexes	554
	List of Abbreviations	561
	Scientific Contributions	565
	Acknowledgement	567